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Theory of the Unrestricted Hartree-Fock Equation and Its Solutions. III

——*Classification of Instabilities and Interconnection Relation between the Eight Classes of UHF Solutions*——

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A general theory on classification of instability and interconnection relation between UHF solutions is developed. It is shown that instability of a UHF solution is splitted into subinstabilities irreducible to the invariance group of the UHF solution. All types of instability for the eight classes of UHF solutions are listed up and explicit conditions for the instabilities are derived. It is shown that the type of a UHF solution emerging from an instability is determined by the type of the instability. The invariance groups of the UHF solutions emerging from instability of a UHF solution are the subgroups of the invariance group of the initial UHF solution. From this, the interconnection relation between the eight classes of UHF solutions is determined. Expressions for HF energy for the eight classes of UHF solutions are derived.

§ 1. Introduction

Since the work of Overhauser[1] indicating that the helical spin density wave solution of the Hartree-Fock (HF) equation emerges from instability of the closed shell solution, importance of instability phenomenon in an HF solution has been recognized. Instability of an HF ground state solution is a signal for appearance of new ground state solution and represents a change in "electronic phase" of the system. A general condition for instability of an HF solution was firstly formulated by Thouless.[2] Through many works[3] on instability and unrestricted Hartree-Fock (UHF) solutions in particular systems, it has been recognized that instability of an HF solution involves various different types of instability and UHF solutions of different structures emerge from them. Paldus and Cizek,[4] the author[5] and Ostlund[6] have shown that the instability of a closed shell solution invariant for time reversal involves four different subtypes of instability. The author[7] has recently formulated instability condition for DODS (different orbitals for different spins) configuration and shown that its instability is also splitted into four subtypes but two of them are degenerate. However, the reason for the presence of subtypes in instability of an HF solution and the connection between the type of instability and the type of a UHF solution emerging from it have not been clearly understood on a general footing.

In the present paper, we develop a theory on classification of instability and interconnection relation between UHF solutions based upon the group theoretical classification and characterization of UHF solutions developed in the preceding paper[8] and the density matrix formulation developed in the first paper[9] of this series (hereafter we cite them as II and I). In the present theory, the invariance groups of UHF solutions, which are the subgroups of the group of spin rotation and time reversal to characterize the eight classes of UHF solutions, play a central role. We shall show that instability of a UHF solution is splitted into subtypes irreducible to the invariance group of the solution. We list up all types of instability for the eight classes of UHF solutions and give the explicit conditions for the instabilities to occur. We shall show also that the type of a UHF solution emerging from an instability is determined by the group theoretical symmetry type of the instability. From this, we can determine instability mediated interconnection relation between the eight classes of UHF solutions. We also show that the interconnection relation derived from the group theoretical method is verified from inspection on the structure of HF energy for the eight classes of UHF solutions.

The notation used in this paper is the same as those used in I and II.

§ 2. Instability and interconnection of UHF solutions

Let Ψ_α, $\alpha=1\cdots n$, and Ψ_μ, $\mu=n+1\cdots 2M$, be the occupied and unoccupied orbitals of a UHF solution. We denote the row vectors of the occupied and unoccupied orbitals by $\Psi=(\Psi_\alpha)$ and $\Psi'=(\Psi_\mu)$, respectively. Let $\varphi=(\varphi_\alpha)$ and $\varphi'=(\varphi_\mu)$ be another set of orbitals. From (I, 2·41), φ and φ' can be represented in the following form:

$$\left.\begin{aligned}\varphi&=\Psi C\left(\frac{\Lambda}{2}\right)+\Psi' S\left(\frac{\Lambda}{2}\right),\\ \varphi'&=\Psi'\tilde{C}\left(\frac{\Lambda}{2}\right)-\Psi S^+\left(\frac{\Lambda}{2}\right),\end{aligned}\right\}\tag{2·1}$$

in terms of a matrix $\Lambda=(\Lambda_{\mu\alpha})$ after carrying out a unitary transformation which does not mix φ and φ'. $C(\Lambda)$, $\tilde{C}(\Lambda)$ and $S(\Lambda)$ are the matrix functions defined by (I, 2·27). Let P and Q be the projection operators $P=\Psi\Psi^+$ and $Q=\varphi\varphi^+$. From (I, 2·31) and (I, 2·4), we have

$$\left.\begin{aligned}&Q-P=\tfrac{1}{2}D=\tfrac{1}{2}(X+X^++\tilde{Z}-Z),\\ &X=S(\Lambda),\ Z=P-C(\Lambda),\ \tilde{Z}=1-P-\tilde{C}(\Lambda).\end{aligned}\right\}\tag{2·2}$$

From (I, 6·7), the difference between the HF energies of φ and Ψ is given as

$$\begin{aligned}\Delta E_H&=E_H(Q)-E_H(P)\\ &=\tfrac{1}{2}\sum_{\zeta\eta}H_{\zeta\eta}D_{\eta\zeta}+\tfrac{1}{8}\sum_{\zeta\eta\iota\kappa}[\zeta\eta|\iota\kappa]D_{\eta\zeta}D_{\kappa\iota},\end{aligned}\tag{2·3}$$

where $H_{\zeta\eta}$ is the HF operator of Ψ. From (I, 2·32), X, Z and $\tilde{Z}$ satisfy the relations

$$\left.\begin{aligned} X^+X+Z^2&=2Z\,,\\ XX^++\tilde{Z}^2&=2\tilde{Z}\,,\end{aligned}\right\} \tag{2·4}$$

and we have

$$\left.\begin{aligned} D_{\alpha\beta}&=-\tfrac{1}{2}\sum_{\zeta}D_{\alpha\zeta}D_{\zeta\beta}\,,\\ D_{\mu\nu}&=\tfrac{1}{2}\sum_{\zeta}D_{\mu\zeta}D_{\zeta\nu}\,.\end{aligned}\right\} \tag{2·5}$$

Since Ψ is a UHF solution, $H_{\mu\alpha}=0$, and, by using (2·5), Eq. (2·3) may be rewritten as

$$\left.\begin{aligned} \Delta E_H&=\tfrac{1}{8}\sum_{\zeta\eta\iota\kappa}\langle\zeta\eta|I|\kappa\iota\rangle D^*_{\zeta\eta}D_{\kappa\iota}\,,\\ \langle\zeta\eta|I|\kappa\iota\rangle&=H'_{\zeta\kappa}\delta_{\eta\iota}+H'_{\iota\eta}\delta_{\zeta\kappa}+[\zeta\eta|\iota\kappa]\,,\end{aligned}\right\} \tag{2·6}$$

where $H'_{\zeta\eta}$ is defined by

$$H'_{\alpha\beta}=-H_{\alpha\beta}\,,\ \ H'_{\mu\nu}=H_{\mu\nu}\,,\ \ H'_{\mu\alpha}=H'_{\alpha\mu}=0\,. \tag{2·7}$$

By the use of (I, 2·27), D is expanded into a power series of Λ as

$$D=\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)!}\{\Lambda(\Lambda^+\Lambda)^n+(\Lambda^+\Lambda)^n\Lambda^+\}+\sum_{n=1}^{\infty}\frac{(-1)^n}{(2n)!}\{(\Lambda^+\Lambda)^n-(\Lambda\Lambda^+)^n\}\cdots. \tag{2·8}$$

Substituting (2·8) into (2·6), we may easily obtain the variation of E_H to any desired order of Λ.

The second order variation $\delta^2E_H(\Lambda)$ is given by

$$\delta^2E_H(\Lambda)=\tfrac{1}{8}\tilde{\Lambda}^+\Omega\tilde{\Lambda}\,, \tag{2·9}$$

where Ω and $\tilde{\Lambda}$ are the matrix and the column vector of $2n(2M-n)$ dimension given respectively by

$$\left.\begin{aligned} \Omega&=\begin{bmatrix}(\langle\mu\alpha|I|\nu\beta\rangle), & (\langle\mu\alpha|I|\beta\nu\rangle)\\ (\langle\mu\alpha|I|\beta\nu\rangle^*), & (\langle\mu\alpha|I|\nu\beta\rangle^*)\end{bmatrix},\\ \tilde{\Lambda}&=\begin{bmatrix}(\Lambda_{\mu\alpha})\\ (\Lambda^*_{\mu\alpha})\end{bmatrix},\\ \langle\mu\alpha|I|\nu\beta\rangle&=H_{\mu\nu}\delta_{\alpha\beta}-H_{\beta\alpha}\delta_{\mu\nu}+[\mu\alpha|\beta\nu],\\ \langle\mu\alpha|I|\beta\nu\rangle&=[\mu\alpha|\nu\beta].\end{aligned}\right\} \tag{2·10}$$

The matrix Ω is called the instability matrix of a UHF solution Ψ. The eigenvectors $\tilde{\Lambda}_p$ of Ω,

$$\Omega\tilde{\Lambda}_p=\omega_p\tilde{\Lambda}_p,\quad p=1\cdots 2n(2M-n), \tag{2·11}$$

have always the form of $\tilde{\Lambda}$ given in (2·10) since Ω satisfies the relation

$$\begin{bmatrix}0&1\\1&0\end{bmatrix}\Omega^*\begin{bmatrix}0&1\\1&0\end{bmatrix}=\Omega\,. \tag{2·12}$$

The matrix Λ can be expanded in terms of the eigenvectors of Ω as

$$\Lambda = \sum_p x_p \Lambda_p \, . \tag{2·13}$$

A UHF solution Ψ is stable for the variation in the direction of Λ_p if ω_p is positive but is unstable if ω_p is negative. The point where ω_p becomes zero is called the instability threshold.

As we shall show in a succeeding paper of this series, new UHF solution φ emerges from an instability threshold of Ψ, if the third or fourth order variation $\delta^3 E_H(\Lambda)$ or $\delta^4 E_H(\Lambda)$ as a polynomial of x_p has finite coefficients in the directions of x_i, where $\tilde{\Lambda}_i$ are the eigenvectors of Ω with zero eigenvalue at the instability threshold. The solution φ in the vicinity of the instability threshold is related to Ψ by Eq. (2·1) with Λ in the form

$$\Lambda = \sum_i x_i \Lambda_i \, , \tag{2·14}$$

where x_i are small parameters. Conversely, if a UHF solution φ interconnects and coalesces to another UHF solution Ψ at a point, then the point should be an instability threshold of Ψ. If there is only an eigenvector $\tilde{\Lambda}_0$ of Ω with zero eigenvalue at the instability threshold, i.e., the instability is non-degenerate, then the Λ matrix connecting the emerging solution φ to Ψ is proportional to Λ_0 in the vicinity of the instability threshold:

$$\Lambda = x_0 \Lambda_0 \, . \tag{2·15}$$

Although all interconnecting points of UHF solutions correspond to instability thresholds, the converse is not true. Sometimes, an instability threshold may represent a crossing point of two UHF solutions as we have illustrated for the system of internal rotation of ethylene[7] (it should be noted also that not all of crossing points of UHF solutions correspond to instability thresholds). Therefore, we may subdivide instabilities into the two categories; the interconnecting (IC) instabilities and the crossing (CR) instabilities. In this paper, we do not enter into detailed discussion on the condition to discriminate IC and CR instabilities and the behavior of UHF solutions in the vicinity of an IC instability threshold. The problems will be discussed in succeeding papers of this series. In the present paper, we discuss on the group theoretical aspect of instability and interconnection of UHF solutions based upon the above-mentioned relation between them and the group theoretical characterization of UHF solutions discussed in II.

§ 3. Group theoretical classification of instability and interconnection relation between the eight classes of UHF solutions

The eight subgroups of the group G of spin rotation (SR) and time reversal (TR) listed in (II, 2·10) are the groups characterizing UHF solutions and we call them the invariance groups of UHF solutions. Let F be the invariance group of a UHF solution Ψ. For any element g in F, there are n-dimensional and $2M-n$-dimensional unitary matrices V_g and V_g' such that

$$g\Psi=\Psi V_g\,,\ g\Psi'=\Psi' V_g'. \tag{3·1}$$

By operating g, the orbital φ defined by (2·1) transforms as

$$g\varphi=\{\Psi C(\Lambda_g/2)+\Psi' S(\Lambda_g/2)\}V_g\,, \tag{3·2}$$

where Λ_g is

$$\left.\begin{aligned}\Lambda_g&=V_g'\Lambda V_g^+, && \text{(for unitary } g),\\ &=V_g'\Lambda^* V_g^+, && \text{(for antiunitary } g),\end{aligned}\right\} \tag{3·3}$$

(the elements of G involving TR are antiunitary). Hence, the matrix Λ is a second order tensor of F with transformation property (3·3).

The matrices V_g and V_g' are generated by the following matrices. In the case of an S_e-axial solution, there are matrices $A(\boldsymbol{e})$ and $A'(\boldsymbol{e})$ such that

$$(\boldsymbol{e}\cdot\boldsymbol{\sigma})\Psi=\Psi A(\boldsymbol{e}),\ (\boldsymbol{e}\cdot\boldsymbol{\sigma})\Psi'=\Psi' A'(\boldsymbol{e}). \tag{3·4}$$

By operating $(\boldsymbol{e}\cdot\boldsymbol{\sigma})$ on φ, Λ is transformed into

$$\Lambda_a(\boldsymbol{e})=A'(\boldsymbol{e})\Lambda A^+(\boldsymbol{e}). \tag{3·5}$$

In the case of a T-invariant solution, there are matrices T and T' such that

$$\Psi^t=\Psi T\,,\ \Psi'^t=\Psi' T'. \tag{3·6}$$

By operating TR on φ, Λ is transformed into

$$\Lambda_t=T'\Lambda^* T^+. \tag{3·7}$$

In the case of an M_e-invariant solution, there are matrices $M(\boldsymbol{e})$ and $M'(\boldsymbol{e})$ such that

$$(\boldsymbol{e}\cdot\boldsymbol{\sigma})\Psi^t=\Psi M(\boldsymbol{e}),\ (\boldsymbol{e}\cdot\boldsymbol{\sigma})\Psi'^t=\Psi' M'(\boldsymbol{e}). \tag{3·8}$$

By the magnetic transformation $(\boldsymbol{e}\cdot\boldsymbol{\sigma})\varphi^t, \Lambda$ is transformed into

$$\Lambda_m(\boldsymbol{e})=M'(\boldsymbol{e})\Lambda^* M^+(\boldsymbol{e}). \tag{3·9}$$

The matrices A, T and M satisfy

$$\left.\begin{aligned}&A^2(\boldsymbol{e})=1\,,\ A^+(\boldsymbol{e})=A(\boldsymbol{e}),\\ &TT^*=-1\,,\ T^T=-T\,,\\ &M(\boldsymbol{e})M^*(\boldsymbol{e})=1\,,\ M^T(\boldsymbol{e})=M(\boldsymbol{e}),\end{aligned}\right\} \tag{3·10}$$

because of the relations $(\boldsymbol{e}\cdot\boldsymbol{\sigma})^2=1$, $(\Psi^t)^t=-\Psi$ and $(\boldsymbol{e}\cdot\boldsymbol{\sigma})((\boldsymbol{e}\cdot\boldsymbol{\sigma})\Psi^t)^t=\Psi$. That is, they are Hermitian, antisymmetric and symmetric unitary, respectively. The following relations also hold among them. In the case of an S-invariant solution, there are three A matrices $A(\boldsymbol{e}_i), i=1, 2, 3$, with $(\boldsymbol{e}_i\cdot\boldsymbol{e}_j)=\delta_{ij}$. Because of the relation $(e_i\cdot\sigma)(e_j\cdot\sigma)=-(e_j\cdot\sigma)(e_i\cdot\sigma)=i[e_i\times e_j]\cdot\sigma$, they satisfy

$$A(e_i)A(e_j)=-A(e_j)A(e_i)=iA(e_i\times e_j). \tag{3·11}$$

In the case of S_e-axial and T-invariant ASCW solutions, an M matrix can be obtained as

$$M(e)=A(e)T=-TA^*(e). \tag{3·12}$$

The latter part of (3·12) is obtained from the relation $(e\cdot\sigma)\Psi^t=-((e\cdot\sigma)\Psi)^t$. In the case of S_{e1}-axial and M_{e2}-invariant ASDW solutions, besides the matrices $A(e_1)$ and $A(e_2)$, another M matrix can be obtained as

$$M(e_3)=-iA(e_1)M(e_2)=-iM(e_2)A^*(e_1), \tag{3·13}$$

where we have used $i(e_3\cdot\sigma)\Psi^t=(e_1\cdot\sigma)(e_2\cdot\sigma)\Psi^t=(e_2\cdot\sigma)((e_1\cdot\sigma)\Psi)^t$. We have also the relation

$$M(e_2)M^*(e_3)=-M(e_3)M^*(e_2)=iA(e_1), \tag{3·14}$$

from $i(e_1\cdot\sigma)\Psi=(e_2\cdot\sigma)((e_3\cdot\sigma)\Psi^t)^t=-(e_3\cdot\sigma)((e_2\cdot\sigma)\Psi^t)^t$. Summarizing the above, we have the symmetry operations for the eight classes of UHF solutions derived from the invariance groups as listed in Table I.

From (3·10), we obtain

$$(\Lambda_a)_a=\Lambda,\ (\Lambda_t)_t=\Lambda,\ (\Lambda_m)_m=\Lambda. \tag{3·15}$$

Therefore, any of the symmetry operations listed in Table I is a twofold operation for Λ, and the matrix Λ satisfying

$$\Lambda_a=\pm\Lambda,\ \Lambda_t=\pm\Lambda,\ \Lambda_m=\pm\Lambda, \tag{3·16}$$

is an irreducible tensor of F. The combination of the signs in (3·16) should be consistent with the constraints from (3·11) to (3·14). If Λ is an irreducible tensor of F, then $S(\Lambda)$ is also an irreducible tensor with the same symmetry type as Λ but $C(\Lambda)$ and $\tilde{C}(\Lambda)$ are irreducible identity tensors of F, i.e., invariant to all symmetry operations of F. Therefore, if Λ is an identity tensor of F, then φ has the same invariance group as Ψ, but, if Λ is an irreducible non-identity tensor of F, then φ is of broken F symmetry.

Since the instability matrix Ω is a fourth order tensor of F, it can be splitted into a direct sum of submatrices irreducible to F. Therefore, the eigenvectors $\tilde{\Lambda}_p$ of Ω should be irreducible second order tensors of F. Therefore, instabilities of an F-invariant UHF solution can be classified into subtypes according to the symmetry type of the eigenvector $\tilde{\Lambda}_p$.

Since the UHF solution φ emerging from and interconnecting to Ψ at a non-degenerate instability threshold of Ψ has the Λ matrix proportional to an eigenvector of Ω as given in (2·15) in the vicinity of the instability threshold, its symmetry type is determined by the symmetry type of the instability from which it emerges. The symmetry operations of Ψ leaving the Λ matrix invariant are preserved as the symmetry operations of φ, but those changing the sign of Λ are not.

Table I. Invariance operations for the eight classes of UHF solutions.

TICS	$A(e_1)$, $A(e_2)$, $A(e_3)$, T $M(e_1)$, $M(e_2)$, $M(e_3)$
CCW	$A(e_1)$, $A(e_2)$, $A(e_3)$
ASCW	$A(e)$, T, $M(e)$
ASDW	$A(e_1)$, $M(e_2)$, $M(e_3)$
ASW	$A(e)$
TSCW	T
TSDW	$M(e)$
TSW	None

We list up in Table II all possible symmetry types of instability for the eight classes of UHF solutions. Listed in the first row are the symmetry operations of the solution Ψ given in Table I. The sign in the column under each symmetry operation represents the symmetry type of the Λ matrix for the symmetry operation. Given in the first column are the proposed symbols of the instabilities. The combination of the signs in each row is chosen so as to be consistent with the constraints from (3·11) to (3·14). The symmetry type of the UHF solution φ emerging from the instability is given in the last column. Since the set of the symmetry operations of φ is the set of the plus signed symmetry operations of the instability, the symmetry type of φ is determined by seeking in Table I the class of a UHF solution having the set of symmetry operations which is isomorphic to the set of the plus signed symmetry operations of the instability.

The symbols of instabilities refer to their symmetry type. ^1S and ^3S represent spin singlet and spin triplet, respectively. The transitions to cause ^1S and ^3S type instabilities are the spin singlet and spin triplet transitions of a closed shell configuration. The former preserves S-invariance but the latter violates it. Each of ^3S type instabilities involves three instabilities. Because of the constraint (3·11), the three S-axial symmetries in an S-invariant solution cannot be simultaneously violated and an S-axial symmetry should be conserved. There are three possible choices for the axis of the preserved S-axial symmetry. However, due to the isotropy of an S-invariant solution for SR, there is no preferred direction among the three axes. Therefore, the three instabilities have an identical instability submatrix. The S-axial solutions emerging from them have different axes of S-axial symmetry but can be transformed into each other by SR. $A_\pm$ represents conservation (+) or violation (−) of S-axial symmetry. The transitions to cause A_+ and A_- type instabilities are respectively the spin unflipping and spin flipping transitions of a DODS configuration and we may use the symbols SU and SF instead of A_+ and A_-. $T_\pm$ and $M_\pm$ represent conservation (+) or violation (−) of T-invariance and M-invariance, respectively. A_-M instability of an ASDW solution involves two instabilities. An ASDW solution has two axes of M-invariance which are orthogonal to each other and to a common axis of S-axial symmetry as shown in (3·13). In the case of A_- instability, the two M-invariances of an ASDW solution cannot be simultaneously conserved

Table II. Symmetry types of instability and the type of emerging UHF solution.

a) TICS:

	A_1	A_2	A_3	T	M_1	M_2	M_3	
$^1ST_+$	+	+	+	+	+	+	+	TICS
$^1ST_-$	+	+	+	−	−	−	−	CCW
	+	−	−	+	+	−	−	
$^3ST_+$	−	+	−	+	−	+	−	ASCW
	−	−	+	+	−	−	+	
	+	−	−	−	−	+	+	
$^3ST_-$	−	+	−	−	+	−	+	ASDW
	−	−	+	−	+	+	−	

b) CCW:

	A_1	A_2	A_3	
^1S	+	+	+	CCW
	+	−	−	
^3S	−	+	−	ASW
	−	−	+	

c) ASCW:

	$A(e)$	T	$M(e)$	
A_+T_+	+	+	+	ASCW
A_+T_-	+	−	−	ASW
A_-T_+	−	+	−	TSCW
A_-T_-	−	−	+	TSDW

d) ASDW:

	$A(e_1)$	$M(e_2)$	$M(e_3)$	
A_+M_+	+	+	+	ASDW
A_+M_-	+	−	−	ASW
A_-M	−	+	−	TSDW
	−	−	+	

e) ASW:

	$A(e)$	
A_+	+	ASW
A_-	−	TSW

f) TSCW:

	T	
T_+	+	TSCW
T_-	−	TSW

g) TSDW:

	$M(e)$	
M_+	+	TSDW
M_-	−	TSW

or violated because of the constraints (3·13) and (3·14). Either one of them should be violated but the other should be conserved. Due to the axial symmetry of ASDW solutions for SR around the axis of S-axial symmetry, there is no preferred direction among the two axes of M-invariance. Therefore, the two instabilities have an identical instability submatrix. The TSDW solutions emerg-

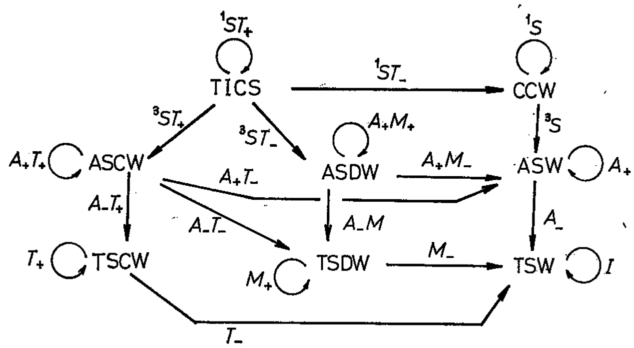

Fig. 1. Interconnection relation between the eight classes of UHF solutions mediated by non-degenerate instability is indicated by arrows. The starting point of an arrow is the type of initial UHF solution Ψ and the final point is that of the emerging solution φ. The type of instability to mediate the interconnection relation is indicated beside the arrow.

ing from them have different axes of M-invariance but can be transformed into each other by SR around the axis of S-axial symmetry of the initial ASDW solution. On account of the above reason, no designation of plus or minus sign is done for the M symbol in A_-M instability. About the above remarks, confer also the results in § 4.

$^1ST_\pm$, $^3ST_\pm$, $A_+M_\pm$ and A_-M instabilities in the present notation were denoted respectively as $S^\pm$, $T^\mp$, $ST^\pm$ and SF in our previous papers.[5),7)] The signs in our old notation referred to conservation or violation of the invariance of spatial orbitals to complex conjugation without change in spin direction. Such a symmetry operation corresponds to M_y-invariance operation. Our old statement to correspond it to T-invariance operation was misleading.

Summarizing the results in Table II, we show in Fig. 1 the interconnection relation between the eight classes of UHF solutions mediated by non-degenerate instabilities. It should be noted that the interconnection relation shown in Fig. 1 is isomorphic to the inclusion relation between the invariance groups of UHF solutions. The invariance groups of the UHF solutions emerging from a UHF solution should be the subgroups of the invariance group of the initial solution.

In the case of the degenerate instabilities, the other types of interconnection relation not indicated in Fig. 1 may arise. ^3S type and A_-M instabilities have respectively three and two subinstabilities with the same instability submatrices and are always degenerate. However, their degeneracy has its origin in the symmetry properties of S-invariant and ASDW solutions and is of intrinsic nature. Such an intrinsic degeneracy leads to an arbitrariness in the direction of the axis of symmetry in the S-axial and TSDW solutions emerging from the instabilities. Except this, the interconnection relation mediated by the intrinsically degenerate instabilities can be treated on the same footing as those mediated by the non-degenerate ones as we have done. Therefore, we use the term degeneracy in the sense to represent non-intrinsic one.

We consider in the following the case of doubly degenerate instability. Let $\tilde{\Lambda}_1$ and $\tilde{\Lambda}_2$ be the eigenvectors of Ω with zero eigenvalue at a doubly degenerate instability threshold. In order for non-intrinsic degeneracy of instability to occur, it is necessary that Λ_1 and Λ_2 are of different symmetries for F if Ψ has no spatial symmetry group to which it is invariant but may be of the same symmetry type for F if Ψ has a spatial invariance group and they are of different symmetries for it. As we shall show in a succeeding paper, if Λ_1 and Λ_2 are

Table III. The types of doubly degenerate instability leading to different interconnection relation from that of the non-degenerate case.

a) TICS:

	A_1	A_2	A_3	T	M_1	M_2	M_3	
$^3ST_+$	+	−	−	+	+	−	−	TSCW[1]
〃	−	+	−	+	−	+	−	
$^3ST_-$	+	−	−	−	−	+	+	TSDW[2]
〃	−	+	−	−	+	−	+	
$^3ST_+$	+	−	−	+	+	−	−	TSDW[2]
$^3ST_-$	−	+	−	−	+	−	+	
$^3ST_+$	+	−	−	+	+	−	−	ASW[3]
$^3ST_-$	+	−	−	−	−	+	+	
$^1ST_-$	+	+	+	−	−	−	−	ASW[3]
$^3ST_+$	+	−	−	+	+	−	−	
$^1ST_-$	+	+	+	−	−	−	−	ASW[3]
$^3ST_-$	+	−	−	−	−	+	+	

b) CCW:

	A_1	A_2	A_3	
^3S	+	−	−	TSW[4]
〃	−	+	−	

c) ASCW:

	$A(e)$	T	$M(e)$	
A_-T_+	−	+	−	TSW[5]
A_-T_-	−	−	+	
A_+T_-	+	−	−	TSW[5]
A_-T_+	−	+	−	
A_+T_-	+	−	−	TSW[5]
A_-T_-	−	−	+	

d) ASDW:

	$A(e_1)$	$M(e_2)$	$M(e_3)$	
A_-M	−	+	−	TSW[6]
〃	−	−	+	
A_-M	−	+	−	TSW[6]
A_+M_-	+	−	−	

of non-identity symmetries for F or for the spatial invariance group of Ψ, then new solutions φ_1, φ_2 and φ_{12} whose Λ matrices in the vicinity of the instability threshold are respectively of the forms

$$\left.\begin{aligned} &\Lambda^{(1)}=x_1\Lambda_1\,,\ \Lambda^{(2)}=x_2\Lambda_2\,,\\ &\Lambda^{(12)}=x_1'\Lambda_1+x_2'\Lambda_2\,, \end{aligned}\right\} \tag{3·17}$$

emerge from the degenerate instability threshold. The symmetry types of φ_1 and φ_2 are determined by those of Λ_1 and Λ_2 respectively in the same way as the case of non-degenerate instability. φ_{12} is the solution characteristic to the degenerate instability and its symmetry type is dependent on both of Λ_1 and Λ_2. If Λ_1 is of identity symmetry for F, then the symmetry type (for SR and TR) of φ_{12} is determined by that of Λ_2. The interconnection relation of φ_{12} to Ψ in this case is therefore the same as that given in Fig. 1. If Λ_1 and Λ_2 are of completely the same symmetry for F up to subtypes of ${}^3S$ and A_M, then, in this case too, the interconnection relation of φ_{12} to Ψ is the same as that given in Fig. 1. If Λ_1 and Λ_2 are of different non-identity symmetries for F, then the interconnection relation of φ_{12} to Ψ becomes different from that given in Fig. 1. We list up in Table III the combinations of Λ_1 and Λ_2 leading to different interconnection relation from that in Fig. 1.

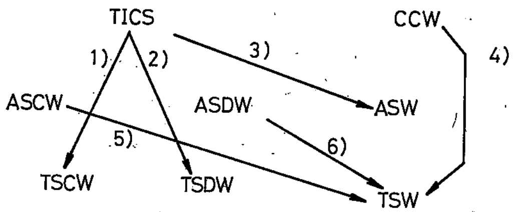

Fig. 2. Interconnection relation between the eight classes of UHF solutions which is realized only through doubly degenerate instability is indicated by arrows. The reference number beside arrow shows the type of degenerate instability to mediate the interconnection relation and corresponds to the reference number in the last column of Table III.

Given in the first column of Table III are the types of instabilities to be degenerated. The symmetry types of Λ_1 and Λ_2 to the symmetry operations listed in the first row are indicated by the plus and minus signs in the same way as Table II. The type of the emerging solution φ_{12} is indicated in the last column. It is determined by seeing the symmetry operations to which both of Λ_1 and Λ_2 have plus sign.

We show in Fig. 2, the interconnection relations listed in Table III which are possible only through the degenerate instabilities. The reference number beside the arrows are those given in the last column of Table III and indicates the types of degenerate instability leading to the interconnection relation. It is to be noted that the interconnection relation given in Fig. 2 is also consistent with the set theoretical inclusion relation between the invariance groups of UHF solutions. The invariance groups F_1, F_2 and F_{12} of φ_1, φ_2 and φ_{12} are the subgroups of the invariance group F of Ψ and F_{12} is the common intersection subgroup of F_1 and F_2; $F_{12}=F_1\cap F_2$. It should be noted also that two solutions in the form of φ_{12} but with different symmetries emerge from a degenerate instability consisted of two instabilities of ^{s}S types or two A_M instabilities. In these cases, two different combinations in the signs of A operations or M operations of component instabilities are possible as an example seen in Table III a) for the degenerate instability consisted of $^{s}ST_{+}$ and $^{s}ST_{-}$. Therefore, four different solutions emerge simultaneously from such a degenerate instability threshold.

§ 4. Expressions for the irreducible instability matrices

We derive in this section the explicit expressions for the irreducible instability matrices.

The Λ matrix for $T_{\pm}$ instability of a T-invariant solution satisfies $\Lambda^{*}=\pm T'^{*}\Lambda T^{T}$. From this and the relation

$$\langle\mu\alpha|I|\beta T,\nu T'\rangle=\langle\mu\alpha|I|\beta^{t}\nu^{t}\rangle=\langle\mu\alpha|\beta\nu\rangle+\langle\mu\beta^{t}|\alpha^{t}\nu\rangle\,, \tag{4·1}$$

we obtain the $T_{\pm}$ instability matrix as

$$\begin{aligned}(T_{\pm})=(\langle\mu\alpha|I|\nu\beta\rangle\pm\langle\mu\alpha|I|\beta^{t}\nu^{t}\rangle)=(&H_{\mu\nu}\delta_{\alpha\beta}-H_{\beta\alpha}\delta_{\mu\nu}\\&-\langle\mu\nu|\beta\alpha\rangle+(1\pm1)\langle\mu\alpha|\beta\nu\rangle\pm\langle\mu\beta^{t}|\alpha^{t}\nu\rangle),\end{aligned} \tag{4·2}$$

where $\alpha^{t}=\alpha T$ denotes the orbital $\Psi_{\alpha}{}^{t}=(\Psi T)_{\alpha}$.

The Λ matrix for $M_{\pm}$ instability of an M-invariant solution satisfies $\Lambda^{*}=\pm M'^{*}\Lambda M^{T}$. From this and the relation

$$\langle\mu\alpha|I|\beta M,\nu M'\rangle=\langle\mu\alpha|I|\beta^{m},\nu^{m}\rangle=\langle\mu\alpha|\beta\nu\rangle-\langle\mu\beta^{m}|\alpha^{m}\nu\rangle\,, \tag{4·3}$$

we obtain the $M_{\pm}$ instability matrix as

$$\begin{aligned}(M_{\pm})=(\langle\mu\alpha|I|\nu\beta\rangle\pm\langle\mu\alpha|I|\beta^{m}\nu^{m}\rangle)=(&H_{\mu\nu}\delta_{\alpha\beta}-H_{\beta\alpha}\delta_{\mu\nu}\\&-\langle\mu\nu|\beta\alpha\rangle+(1\pm1)\langle\mu\alpha|\beta\nu\rangle\mp\langle\mu\beta^{m}|\alpha^{m}\nu\rangle),\end{aligned} \tag{4·4}$$

where $\alpha^{m}=\alpha M$ denotes the orbital $\Psi_{\alpha}{}^{m}=(\Psi M)_{\alpha}=(\boldsymbol{e}\cdot\boldsymbol{\sigma})\Psi_{\alpha}{}^{t}$. For M_{y}-invariant case, orbitals are real and we have $\Psi^{m}=i\Psi$ and $\langle\mu\beta^{m}|\alpha^{m}\nu\rangle=\langle\mu\beta|\alpha\nu\rangle$.

As we have shown in II, an S-axial solution is a DODS configuration and its orbitals may be put as

$$\left.\begin{aligned}\Psi_{\alpha}&=\Psi_{a1}\eta_{1},\quad a_{1}=1\cdots n_{1}\,,\\&=\widetilde{\Psi}_{a2}\eta_{2},\quad a_{2}=1\cdots n_{2}\,.\end{aligned}\right\} \tag{4·5}$$

The Λ matrix for $A_{\pm}$ instability of an S_{z}-axial solution (4·5) is of the form

$$\left.\begin{aligned}A_{+}&:\ \Lambda_{mr,as}=\delta_{rs}\Gamma_{mr,as}\,,\\A_{-}&:\ \Lambda_{mr,as}=(1-\delta_{rs})\Gamma_{mr,as}\,.\end{aligned}\right\} \tag{4·6}$$

Equation (4·6) shows that A_{+} instability is related only to spin unflipping transitions and A_{-} to spin flipping transitions in a DODS configuration. For the DODS solution (4·5), we obtain

$$\left.\begin{aligned}\langle m_r a_s|I|n_u b_v\rangle &= \delta_{ru}\delta_{sv}(H_{mr,nr}\delta_{as,bs} - H_{bs,as}\delta_{mr,nr} \\ &\quad - \langle m_r n_r|b_s a_s\rangle) + \delta_{rs}\delta_{uv}\langle m_r a_r|b_u n_u\rangle,\\ \langle m_r a_s|I|b_v n_u\rangle &= \delta_{rs}\delta_{uv}\langle m_r a_r|n_u b_u\rangle \\ &\quad - \delta_{rv}\delta_{su}\langle m_r b_r|n_s a_s\rangle,\end{aligned}\right\} \tag{4·7}$$

where $a_r, r=1, 2$, denotes the orbital Ψ_{a1} or $\tilde{\Psi}_{a2}$.

From (4·6) and (4·7), the A_+ instability matrix is obtained as

$$(A_+) = \begin{bmatrix} (\langle m_r a_r|I|n_s b_s\rangle), & (\langle m_r a_r|I|b_s n_s\rangle) \\ (\langle m_r a_r|I|b_s n_s\rangle^*), & (\langle m_r a_r|I|n_s b_s\rangle^*) \end{bmatrix}. \tag{4·8}$$

Because of the relation

$$\langle m_r a_s|I|n_s b_r\rangle = \langle m_r a_s|I|b_s n_r\rangle = 0 \quad (r\neq s), \tag{4·9}$$

the A_- instability matrix decomposes into a direct sum of two matrices (A_-) and (A_-'), and (A_-) is given by

$$(A_-) = \begin{bmatrix} (\langle m_1 a_2|I|n_1 b_2\rangle), & (\langle m_1 a_2|I|b_1 n_2\rangle) \\ (\langle m_2 a_1|I|b_2 n_1\rangle^*), & (\langle m_2 a_1|I|n_2 b_1\rangle^*) \end{bmatrix}. \tag{4·10}$$

(A_-') is obtained by interchanging the spin indeces 1 and 2 in (4·10) but has the same set of eigenvalues as (A_-) since

$$(A_-') = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} (A_-)^* \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}. \tag{4·11}$$

In the case of an ASDW solution, the spatial orbitals Ψ_{f1} and $\tilde{\Psi}_{f2}$ are real. Substituting (4·5) into (4·4) and using (4·6), we have $A_+M_\pm$ instability matrix as

$$(A_+M_\pm) = (\langle m_r a_r|I|n_s b_s\rangle \pm \langle m_r a_r|I|b_s n_s\rangle). \tag{4·12}$$

Because of Eq. (4·9), A_-M_+ and A_-M_- instability matrices become identical in conformity with the result in the preceding section, and the A_-M instability matrix is a real matrix with the same form as (4·10).

In the case of an ASCW solution,

$$\Psi_{a1} = \tilde{\Psi}^*_{a2} = \Psi_a,\ n_1 = n_2. \tag{4·13}$$

Substituting (4·5) with (4·13) into (4·2) and using (4·6) and (4·9), we obtain $A_+T_\pm$ and $A_-T_\pm$ instability matrices as

$$\left.\begin{aligned}&(A_+T_\pm) = (\langle m_r a_r|T_\pm|n_s b_s\rangle),\\ &\langle m_1 a_1|T_\pm|n_1 b_1\rangle = \langle m_2 a_2|T_\pm|n_2 b_2\rangle^* = \langle ma|S_\pm|nb\rangle \\ &\quad = H_{mn}\delta_{ab} - H_{ba}\delta_{mn} - \langle mn|ba\rangle + (1\pm 1)\langle ma|bn\rangle,\\ &\langle m_1 a_1|T_\pm|n_2 b_2\rangle = \langle m_2 a_2|T_\pm|n_1 b_1\rangle^* = \langle ma|S_\pm|bn\rangle \\ &\quad = (1\pm 1)\langle ma|nb\rangle \mp \langle mb|na\rangle,\end{aligned}\right\} \tag{4·14}$$

$$\left.\begin{aligned} &(A_-T_\pm) = (\langle m_1a_2|T_\pm|n_1b_2\rangle), \\ &\langle m_1a_2|T_\pm|n_1b_2\rangle = \langle m_2a_1|T_\pm|n_2b_1\rangle^* \\ &\qquad = H_{mn}\delta_{ab} - H_{ab}\delta_{mn} - \langle mn|ab\rangle \pm \langle mb|an\rangle , \end{aligned}\right\} \tag{4·15}$$

where the index a denotes the spatial orbital Ψ_a.

In the case of an S-invariant solution,

$$\Psi_{a1} = \tilde{\Psi}_{a2} = \Psi_a , \quad n_1 = n_2 . \tag{4·16}$$

The A matrix for ${}^1S$ and ${}^3S$ instabilities are spin scalar and spin vector, respectively:

$$\left.\begin{aligned} &{}^1S, \ A_{mr,as} = \delta_{rs}\Gamma_{ma} , \\ &{}^3S, \ A^i_{mr,as} = (\sigma_i)_{rs}\Gamma_{ma} , \quad i = 1, 2, 3 . \end{aligned}\right\} \tag{4·17}$$

From (4·17), ${}^1S$ and ${}^3S$ instability matrices are obtained as

$$({}^{2\mp1}S) = \begin{bmatrix} (\langle ma|S_\pm|nb\rangle), & \pm(\langle ma|S_\pm|bn\rangle) \\ \pm(\langle ma|S_\pm|bn\rangle^*), & (\langle ma|S_\pm|nb\rangle^*) \end{bmatrix}, \tag{4·18}$$

where $\langle ma|S_\pm|nb\rangle$ and $\langle ma|S_\pm|bn\rangle$ are the quantities with the same forms as those defined in (4·14). Equation (4·16) shows that if Ψ_a's in (4·13) and (4·16) are the same,

$$({}^1S) = (A_+T_+), \ ({}^3S) = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} (A_+T_-) \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{4·19}$$

In the case of a TICS solution, the spatial orbital Ψ_a is real, and ${}^1ST_\pm$ and ${}^3ST_\pm$ instability matrices are given by

$$\left.\begin{aligned} &({}^1ST_\pm) = (\langle ma|S_+|nb\rangle \pm \langle ma|S_+|bn\rangle), \\ &({}^3ST_\pm) = (\langle ma|S_-|nb\rangle \pm \langle ma|S_-|bn\rangle). \end{aligned}\right\} \tag{4·20}$$

Equation (4·20) for the irreducible instability matrices of a TICS solution has been obtained previously.[4)~6)] Equation (4·20) shows

$$({}^1ST_-) = ({}^3ST_+). \tag{4·21}$$

As we shall see in the next section, an ASCW solution (4·13) and a CCW solution (4·16) with the same Ψ_a always coexist as a degenerate pair and an ASW solution is degenerate with respect to complex conjugation of up and down spin orbitals respectively. Equations (4·21) and (4·19) are the consequences of the degeneracies. Equation (4·21) implies that degenerate CCW and ASCW solutions emerge simultaneously from a TICS solution. Equation (4·19) implies that new degenerate CCW and ASCW solutions emerge simultaneously from ${}^1S$ and A_+T_+ instabilities and degenerate ASW solutions from ${}^3S$ and A_+T_- instabilities of degenerate CCW and ASCW solutions.

§ 5. Standard expressions for HF energy

In practical applications of UHF theory, it is important to study UHF solutions and their interconnection relation from energetic point of view. Therefore, we derive finally the expressions of HF energy for the eight classes of UHF solutions referring to the standard forms of UHF orbital given in II. We start from the general standard form (II, 3·4) of the UHF density matrix.

We split the density matrix (II, 3·4) into the two parts as

$$\left.\begin{aligned} &Q=P+\tfrac{1}{2}D\,,\quad P=\begin{bmatrix}\sum_A^+ \Psi_A\Psi_A^\dagger, & 0\\ 0, & \sum_A^- \tilde{\Psi}_A\tilde{\Psi}_A^\dagger\end{bmatrix},\\ &D=\sum_{A=1}^{K}\begin{bmatrix}(\cos\lambda_A-\varepsilon_A)\Psi_A\Psi_A^\dagger, & \sin\lambda_A\Psi_A\tilde{\Psi}_A^\dagger\\ \sin\lambda_A\tilde{\Psi}_A\Psi_A^\dagger, & (\varepsilon_A-\cos\lambda_A)\tilde{\Psi}_A\tilde{\Psi}_A^\dagger\end{bmatrix},\end{aligned}\right\}\tag{5·1}$$

where ε_A is a sign function over the index $A=1\cdots K$ with either of $\varepsilon_A=1$ or -1 assigned arbitrarily to each A and $\Sigma^\pm$ is the summation over the A's with $\varepsilon_A=\pm1$ and $A=K+1\cdots M$ if there are overcrowded arbitals. Substituting (5·1) into (2·3), which holds for arbitrary Ψ, we obtain the general standard expression of HF energy:

$$\begin{aligned} E_H(Q)=&E_H(P)+\tfrac{1}{2}\sum_{A=1}^{K}k_A(\varepsilon_A-\cos\lambda_A)\\ &+\tfrac{1}{8}\sum_{A,B=1}^{K}\{L_{AB}(\varepsilon_A-\cos\lambda_A)(\varepsilon_B-\cos\lambda_B)-M_{AB}\sin\lambda_A\sin\lambda_B\},\end{aligned}\tag{5·2}$$

$$\left.\begin{aligned} &k_A=K_{\tilde{A}\tilde{A}}-K_{AA}+\langle\tilde{A}\tilde{A}-AA|\sum_B^+BB+\sum_B^-\tilde{B}\tilde{B}\rangle\\ &\quad+\sum_B^+\langle AB|BA\rangle-\sum_B^-\langle\tilde{A}\tilde{B}|\tilde{B}\tilde{A}\rangle,\\ &L_{AB}\doteq L(AB\tilde{A}\tilde{B})=\langle\tilde{A}\tilde{A}-AA|\tilde{B}\tilde{B}-BB\rangle-\langle AB|BA\rangle-\langle\tilde{A}\tilde{B}|\tilde{B}\tilde{A}\rangle,\\ &M_{AB}=M(AB\tilde{A}\tilde{B})=\langle AB|\tilde{B}\tilde{A}\rangle+\langle BA|\tilde{A}\tilde{B}\rangle,\\ &E_H(P)=\sum_A^+K_{AA}+\sum_A^-K_{\tilde{A}\tilde{A}}+\tfrac{1}{2}\sum_{A,B}^+[AA|BB]\\ &\quad+\tfrac{1}{2}\sum_{A,B}^-[\tilde{A}\tilde{A}|\tilde{B}\tilde{B}]+\sum_A^+\sum_B^-\langle AA|\tilde{B}\tilde{B}\rangle,\end{aligned}\right\}\tag{5·3}$$

where the indeces A and $\tilde{A}$ denote the functions Ψ_A and $\tilde{\Psi}_A$.

We can easily see that

$$\sin\lambda_A=0\,,\ \cos\lambda_A=\varepsilon_A\,,\tag{5·4}$$

is always an extremum of (5·2) for variation of λ_A. (5·4) corresponds to S_z-axial configuration with the density matrix P. There are 2^K different choices of ε_A, and there are 2^K points in the variation space of λ_A which correspond to S_z-axial configurations with different electron occupations.

Equation (5·2) without any constraint on $\Psi_A, \tilde{\Psi}_A$ and λ_A represents HF energy of TSW configuration. HF energy of M_y-invariant TSDW configuration with orbitals (II, 4·21) is obtained by letting Ψ_A and $\tilde{\Psi}_A$ real. Without loss of generality we may assume

$$\left.\begin{aligned} &\varepsilon_A=1, \quad A=1\cdots p, \\ &\varepsilon_{A'}=-1, \quad A'=p+1\cdots 2p, \\ &\varepsilon_{A''}=1, \quad A''=2p+1\cdots K. \end{aligned}\right\} \tag{5·5}$$

HF energies for TSCW, M_z-invariant TSDW and S_x-axial ASW configurations with orbitals (II, 4·13), (II, 4·14) and (II, 5·3) respectively are obtained by imposing on (5·2) the constraints

$$\left.\begin{aligned} &\text{TSCW}, \ \tilde{\Psi}_A=\Psi_{A'}^*, \ \tilde{\Psi}_{A'}=-\Psi_A^*, \ 2p=K, \\ &\text{TSDW}, \ \tilde{\Psi}_A=\Psi_{A'}^*, \ \tilde{\Psi}_{A'}=\Psi_A^*, \ \tilde{\Psi}_{A''}=\Psi_{A''}^*, \\ &\text{ASW}, \ \ \tilde{\Psi}_A=\Psi_{A'}, \ \tilde{\Psi}_{A'}=\Psi_A, \ \tilde{\Psi}_{A''}=\Psi_{A''}, \end{aligned}\right\} \tag{5·6}$$

$$\sin\lambda_{A'}=\sin\lambda_A, \ \cos\lambda_{A'}=-\cos\lambda_A, \ \sin\lambda_{A''}=1. \tag{5·7}$$

The constraint (5·6) leads to

$$\left.\begin{aligned} &L_{AB}=L_{A'B'}, \ L_{AB'}=L_{A'B}, \ \ L_{AB''}=L_{A'B''}, \\ &M_{AB}=M_{A'B'}, \ M_{AB'}=M_{A'B}, \ M_{AB''}=M_{A'B''}, \\ &k_A+\tfrac{1}{2}\sum_{B''}L_{AB''}=-(k_{A'}+\tfrac{1}{2}\sum_{B''}L_{A'B''})=h_{A'}-h_A, \\ &k_{A''}+\tfrac{1}{2}\sum_{B''}L_{A''B''}=0, \\ &h_A=K_{AA}+\langle AA|2\sum_B{}' BB+\sum_{B''}B''B''\rangle \\ &\qquad -\sum_B{}'\langle AB|BA\rangle-\tfrac{1}{2}\sum_{B''}\langle AB''|B''A\rangle, \end{aligned}\right\} \tag{5·8}$$

where $\sum_B'$ is the summation over $B=1\cdots p$ and $K+1\cdots M$ if there are overcrowded orbitals. We can show that (5·7) is an extremum of (5·2) with the constraint (5·8) for variation of $\lambda_{A'}$ and $\lambda_{A''}$. The constraints (5·6) and (5·7) lead to the following expression for HF energy:

$$\begin{aligned} E_H(Q)=E_H(P)&-\tfrac{1}{8}\sum_{A'',B''}(L_{A''B''}+M_{A''B''}) \\ &+\sum_{A=1}^{p}\{(h_{A'}-h_A)(1-\cos\lambda_A)-\tfrac{1}{2}\sum_{B''}M_{AB''}\sin\lambda_A\} \\ &+\tfrac{1}{4}\sum_{A,B=1}^{p}\{(L_{AB}-L_{AB'})(1-\cos\lambda_A)(1-\cos\lambda_B) \\ &\qquad -(M_{AB}+M_{AB'})\sin\lambda_A\sin\lambda_B\}, \end{aligned} \tag{5·9}$$

where

$$\left.\begin{aligned}
&L_{AB}-L_{AB'}=L(ABA'B')-L(AB'A'B), && \\
&M_{AB}+M_{AB'}=M(ABB'A')\mp M(AB'BA'), && \binom{-\text{ TSCW}}{+\text{ TSDW}}, \\
&\qquad\qquad\quad =M(ABA'B')+M(AB'A'B), && (\text{ASW}), \\
&M_{AB''}=0\,, && (\text{TSCW}), \\
&\qquad =M(AB''B''A'), && (\text{TSDW}), \\
&\qquad =M(AB''A'B''), && (\text{ASW}), \\
&L_{A''B''}+M_{A''B''}=0\,, && (\text{TSCW, ASW}), \\
&\qquad\qquad\quad =\langle A''B''|A''B''-B''A''\rangle\,, && (\text{TSDW}),
\end{aligned}\right\} \tag{5·10}$$

In the case $K=2p$ where there is no unpaired orbital $\Psi_{A''}$, $M_{AB''}\equiv 0$. Then, 2^p points

$$\sin\lambda_A=0\,,\ A=1\cdots p \tag{5·11}$$

are extrema of (5·9) for variation of λ_A. At the points (5·11), TSCW and TSDW configurations reduce to ASCW configuration and ASW to CCW. In the cases of TSDW and ASW configurations with unpaired orbitals, (5·11) cannot in general be extrema of (5·9) for variation of λ_A unless the condition $M_{AB''}=0$ is satisfied. In ASW configuration with unpaired orbitals, P is of the form of an open shell restricted HF (RHF) configuration. Hence, open shell RHF configuration cannot be a solution of the UHF equation unless the condition $M_{AB''}=0$ is satisfied by spatial symmetry of orbitals.

ASCW and CCW configurations are obtained from TSCW and ASW configurations respectively by putting $K=2p$, Ψ_A real and $\Psi_{A'}$ pure imaginary. Thus obtained HF energies of ASCW and CCW configurations are identical. ASDW configuration is obtained from TSDW configuration by putting all of Ψ functions real. At the points (5·11), ASCW, CCW and ASDW configurations without unpaired orbitals reduce to TICS configuration.

The expression of $E_H(P)$ in (5·3) shows that $E_H(P)$ is invariant to complex conjugations $\Psi_A\to\Psi_A{}^*$ and $\tilde{\Psi}_A\to\tilde{\Psi}_A{}^*$ of up and down spin orbitals respectively. Therefore, if there is a DODS solution with orbitals $\{\Psi_A\eta_1, \tilde{\Psi}_A\eta_2\}$, then $\{\Psi_A\eta_1, \tilde{\Psi}_A{}^*\eta_2\}$, $\{\Psi_A{}^*\eta_1, \tilde{\Psi}_A\eta_2\}$ and $\{\Psi_A{}^*\eta_1, \tilde{\Psi}_A{}^*\eta_2\}$ are also solutions of the UHF equation and they are degenerate. As a corollary of this theorem, we see that if there is a CCW solution with orbitals $\{\Psi_A\eta_1, \Psi_A\eta_2\}$ then there is always an ASCW solution with orbitals $\{\Psi_A\eta_1, \Psi_A{}^*\eta_2\}$ and vice versa.

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