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The Unrestricted Hartree-Fock Theory of Chemical Reactions. II

——*Dissociation Reaction of Asymmetric Two-Center Two-Electron System*——

Hideo FUKUTOME

Department of Physics, Kyoto University, Kyoto

The mechanism of the change of reaction character from radical to ionic ones is studied in the scope of the unrestricted Hartree-Fock theory for the simplest example of dissociation reaction of asymmetric two-center two-electron system. It is shown that the spin density wave ground state, which corresponds to the ground state of radical nature, disappears when the asymmetry of two atoms exceeds a certain limit and a closed shell state of ionic character becomes the ground one. It is shown that the transition of the ground state character by introduction of asymmetry of atoms is easier at a small interatomic distance than at large distances. All time reversal invariant solutions of the UHF equation for the asymmetric two-center two-electron system are obtained. It is shown that the UHF theory provides satisfactory approximations to exact eigenstates except for a failure to approximate the singly excited singlet state. As an additional remark, instability of the symmetric closed shell ground state electronic configuration of ortho-benzyne is indicated.

§ 1. Introduction

In a previous paper[1] of this series (hereafter we cite it as I) we showed that in many kinds of chemical reactions the conventional closed shell ground state electronic cofiguration becomes unstable and indicated for the case of the homopolar two-center two-electron system that a new stable ground state of spin density wave (SDW) type appears accompanying the instability. We interpreted the appearance of the SDW ground state as a theoretical indication of radical nature of the reaction. Under this theoretical characterization of radical reactions, a question arises how to describe ionic reactions in the scope of the unrestricted Hartree-Fock (UHF) theory. It is a general situation of ionic reactions that heterologous atoms of different electronegativities are involved. We study, in this paper, the dissociation reaction of an asymmetric two-center two-electron system as the simplest system to be able to see how the nature of the reaction changes by introduction of heterologous atoms. We shall show that if the asymmetry of the atoms exceeds a certain limit, the SDW ground state disappears and a closed shell state of ionic character becomes the ground state. Besides this principal result, we shall obtain all time reversal invariant solutions of the UHF equation for asymmetric two-center two-electron system. We shall finally

add a remark about the instability of the symmetric electronic configuration of benzyne.

The notation used in this paper is the same as that in I unless explicitly stated.

§ 2. The UHF equation for two-center two-electron system

The occupied orbitals of an UHF state of a two-center two-electron system is expanded by the orthogonalized atomic orbitals χ_1 and χ_2 of the two centers as

$$\phi_1^\pm = \cos\frac{\lambda^\pm}{2}\chi_1 + \sin\frac{\lambda^\pm}{2}\chi_2 . \qquad (2\cdot1)$$

We consider only the real orbitals satisfying the requirement of time reversal invariance. The Hartree-Fock (HF) energy of the UHF state is given by (I·5·2). Substituting (2·1) into (I·5·2), we obtain

$$E_H = \varepsilon + 2(a\sin\varphi + b\cos\varphi)\cos\sigma$$
$$+ \frac{1}{2}(c-d)\cos 2\varphi + \frac{1}{2}(c+d)\cos 2\sigma + \frac{f}{2}\sin 2\varphi, \qquad (2\cdot2)$$

where φ and σ are the parameters defined by

$$\left.\begin{array}{l} \varphi = \frac{1}{2}(\lambda^+ + \lambda^-), \\ \sigma = \frac{1}{2}(\lambda^+ - \lambda^-) \end{array}\right\} \qquad (2\cdot3)$$

and

$$\left.\begin{array}{l} \varepsilon = K_{11} + K_{22} + \frac{1}{2}(\gamma_{11} + \gamma_{22} + 2\gamma_{12}), \\ a = K_{12} + \frac{1}{2}\langle\chi_1\chi_2|\chi_1\chi_1 + \chi_2\chi_2\rangle, \\ b = \frac{1}{2}\{K_{11} - K_{22} + \frac{1}{2}(\gamma_{11} - \gamma_{22})\}. \\ c = \frac{1}{4}(\gamma_{11} + \gamma_{22} - 2\gamma_{12}), \\ d = \langle\chi_1\chi_2|\chi_1\chi_2\rangle, \\ f = \langle\chi_1\chi_2|\chi_1\chi_1 - \chi_2\chi_2\rangle. \end{array}\right\} \qquad (2\cdot4)$$

From the variation of (2·2) with respect to σ and φ, we obtain the equations to determine them:

$$\{a\sin\varphi + b\cos\varphi + (c+d)\cos\sigma\}\sin\sigma = 0, \qquad (2\cdot5)$$

$$(a\cos\varphi - b\sin\varphi)\cos\sigma - \frac{1}{2}(c-d)\sin 2\varphi + \frac{f}{2}\cos 2\varphi = 0. \qquad (2\cdot6)$$

We may solve Eqs. (2·5) and (2·6) without any approximation, but in order to avoid unnecessary complications, we use the neglect of differential overlap (NDO) approximation in the following discussions. In the case of dissociation reaction, no essential feature is lost by the NDO approximation. In the NDO approximation,

$$a = K_{12},$$
$$d = 0, \quad f = 0. \tag{2.7}$$

We introduce the following quantities:

$$e = \tfrac{1}{2} + (E_H - \varepsilon)/2c,$$
$$p = b/c, \tag{2.8}$$
$$q = -a/c,$$

then Eqs. (2·2), (2·5) and (2·6) become

$$e = \tfrac{1}{2} + (p \cos\varphi - q \sin\varphi)\cos\sigma + \tfrac{1}{4}(\cos 2\varphi + \cos 2\sigma), \tag{2.9}$$

$$(p \cos\varphi - q \sin\varphi + \cos\sigma)\sin\sigma = 0, \tag{2.10}$$

$$(p \sin\varphi + q \cos\varphi)\cos\sigma + \sin\varphi \cos\varphi = 0. \tag{2.11}$$

The UHF equation in the form of (2·10) and (2·11) contains the two parameters p and q. The parameter q is proportional to the resonance integral K_{12} and a monotonely descreasing function of interatomic distance R. It is the parameter to determine dominantly R dependency of the solution. The parameter p becomes zero for the homopolar system, and the larger the asymmetry of the system is, the larger is the value of p. Noting that $K_{ii} = -I_i$ at $R = \infty$ and using the the semi-empirical evaluation $\gamma_{ii} = I_i - E_i$ of the one-center Coulomb repulsion integrals, where I_i and E_i are the ionization potential and the electron affinity of the i-th atom, we obtain the semi-empirical value of p at $R = \infty$:
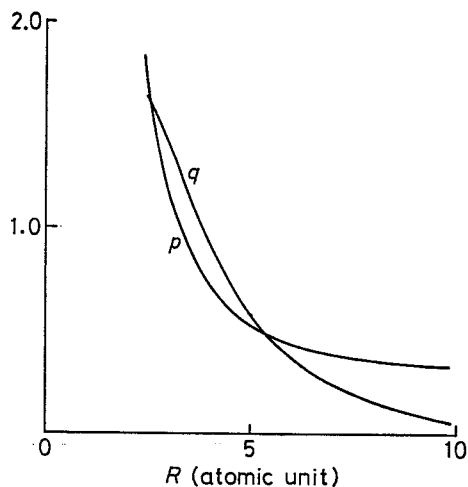

Fig. 1. R dependencies of the parameters q and p for LiH evaluated with non-empirical parametrization are shown. LiH is treated as a two-center two-electron system consisted of the $2s$ orbital of Li and the $1s$ orbital of H.
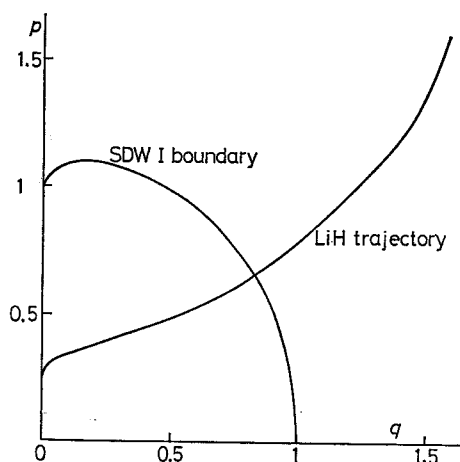
Fig. 2. The existence domain (3·7) of the SDW I solution is shown. It is inside of the boundary. The trajectory of LiH in the q, p space with varying R is also shown. R decreases on going from left to right of the trajectory.

$$p(\infty) = \{\tfrac{1}{2}(I_2 + E_2) - \tfrac{1}{2}(I_1 + E_1)\} / \{I_1 - E_1 + I_2 - E_2\}$$

Therefore, the semi-empirical value of $p(\infty)$ is proportional to the difference of Mulliken's electronegativity of the two atoms. Thus, p is the parameter to represent the asymmetry of the system. We show in Fig. 1, as an illustration of R dependencies of p and q, those for LiH evaluated with non-empirical parametrization. We also show in Fig. 2 the trajectory of LiH with varying R in the q, p space. It is to be noted that the asymmetry parameter p is a monotonely decreasing function of R and its value becomes larger for smaller R.

Equation (2·10) leads to the two classes of solutions:

$$p \cos \varphi - q \sin \varphi + \cos \sigma = 0 \,, \qquad (2\cdot12)$$

$$\sin \sigma = 0 \,. \qquad (2\cdot13)$$

In the solutions satisfying (2·12), $\lambda^+ \neq \lambda^-$ and they are of SDW type, while, in the solutions satisfying (2·13) $\lambda^+ = \lambda^-$ and they are of closed shell type.

§ 3.   The SDW solutions of the UHF equation

We consider in this section the solutions satisfying (2·12) and (2·11). From (2·12) we have

$$\cos \sigma = q \sin \varphi - p \cos \varphi \,. \qquad (3\cdot1)$$

Substituting (3·1) into (2·11), we have

$$(1 + q^2 - p^2) \sin 2\varphi - 2pq \cos 2\varphi = 0 \,. \qquad (3\cdot2)$$

From (3·2) the parameter φ is determined as

$$\sin 2\varphi = \pm 2pq / \{(1 + q^2 - p^2)^2 + 4p^2 q^2\}^{1/2},$$
$$\cos 2\varphi = \pm (1 + q^2 - p^2) / \{(1 + q^2 - p^2)^2 + 4p^2 q^2\}^{1/2}, \qquad (3\cdot3)$$

where the double signs in (3·3) must be taken in the same order. The solutions with the plus and the minus signs of (3·3) respectively lead to different solutions of SDW type. We call the solution with the minus sign in (3·3) the SDW I and that with the plus sign the SDW II.

We next determine $\cos \sigma$. We obtain from (3·1)

$$\cos^2 \sigma = \tfrac{1}{2} \{p^2 + q^2 + (p^2 - q^2) \cos 2\varphi - 2pq \sin 2\varphi\} \,. \qquad (3\cdot4)$$

Substituting (3·3) into (3·4), we have

$$\cos^2 \sigma = \tfrac{1}{2} [p^2 + q^2 \pm \{(1 + q^2 - p^2)(p^2 - q^2) - 4p^2 q^2\} / \{(1 + q^2 - p^2)^2 + 4p^2 q^2\}^{1/2}] \,. \tag{3\cdot5}$$

In order for the SDW solutions to exist, the condition

$$\cos^2 \sigma \leqq 1 \qquad (3\cdot6)$$

must hold. For the SDW II solution, it can be shown that the condition (3·6) is satisfied for all values of p and q. However, for the SDW I solution, (3·6) is satisfied only in a limited region of p and q. From (3·5) and (3·6) the condition for the SDW I solution to exist is given as

$$p^2+q^2-1 \leqq p^2q^2/\{(1+q^2-p^2)^2+4p^2q^2\}. \tag{3·7}$$

We show in Fig. 2 the existence domain (3·7) of the SDW I solution.

By substituting (3·1) into (2·9) and using (3·3) the normalized HF energy e of the SDW solutions are obtained as

$$e=\tfrac{1}{4}[1-p^2-q^2 \pm \{(1+q^2-p^2)^2+4p^2q^2\}^{1/2}]. \tag{3·8}$$

where the minus and the plus signs in (3·8) respectively correspond to the SDW I and II.

In order to clarify the nature of the SDW solutions, we consider the special cases of $p=0$ and $q=0$.

The case $p=0$ is nothing but the case of homopolar system. The SDW I solution for $p=0$ is given from (3·3) and (3·1) as

$$\left.\begin{array}{ll}\sin 2\varphi=0, & \cos 2\varphi=-1,\\ \cos \sigma=q.\end{array}\right\} \tag{3·9}$$

The orbitals of the SDW I are obtained from (3·9) and (2·1) as

$$\phi_1{}^{\pm}=[\tfrac{1}{2}(1\pm\sqrt{1-q^2})]^{1/2}\chi_1+[\tfrac{1}{2}(1\mp\sqrt{1-q^2})]^{1/2}\chi_2$$

and

$$\phi_1{}^{\pm}=[\tfrac{1}{2}(1\mp\sqrt{1-q^2})]^{1/2}\chi_1+[\tfrac{1}{2}(1\pm\sqrt{1-q^2})]^{1/2}\chi_2. \tag{3·10}$$

The SDW I orbitals (3·10) are identical with the SDW orbitals (I·5·25) of homopolar system in the NDO approximation.

The SDW II for $p=0$ is given by

$$\left.\begin{array}{ll}\sin 2\varphi=0, & \cos 2\varphi=1,\\ \cos \sigma=0.\end{array}\right\} \tag{3·11}$$

Hence, the orbitals of the SDW II at $p=0$ become

$$\phi_1{}^{\pm}=\frac{1}{\sqrt{2}}(\chi_1\pm\chi_2)$$

and

$$\phi_1{}^{\pm}=\frac{1}{\sqrt{2}}(\chi_1\mp\chi_2). \tag{3·12}$$

Thus, the SDW II in the homopolar system is the conventional singly excited cofiguration $(\phi_1)(\phi_2)$.

The case $q=0$ is the case of an infinite interatomic distance. Then, the SDW I is given by

$$\left.\begin{array}{ll} \sin 2\varphi = 0\,, & \cos 2\varphi = -1\,, \\ \cos \sigma = 0\,. \end{array}\right\} \tag{3.13}$$

It exists only in the range $p \leqq 1$. Hence, the orbitals of the SDW I at $q=0$ are

$$\left.\begin{array}{ll} \phi_1{}^+ = \chi_1\,, & \phi_1{}^- = \chi_2 \\ & \\ \phi_1{}^+ = \chi_2\,, & \phi_1{}^- = \chi_1\,. \end{array}\right\} \tag{3.14}$$

and

Thus, the SDW I at $q=0$ corresponds to the state of isolated neutral atoms. The SDW II for $q=0$ is given by

$$\left.\begin{array}{ll} \sin 2\varphi = 0\,, & \\ \cos 2\varphi = 1\,, & \cos \sigma = -p;\ (|p|<1) \\ \quad\quad\ = -1\,, & \quad\quad\ = 0.\ (|p|>1) \end{array}\right\} \tag{3.15}$$

Note that in this solution the values of φ and σ change discontinuously at $|p|=1$. Hence, the orbitals of the SDW II at $q=0$ are for $|p|<1$

$$\left.\begin{array}{l} \phi_1{}^\pm = [\tfrac{1}{2}(1-p)]^{1/2}\chi_1 \pm [\tfrac{1}{2}(1+p)]^{1/2}\chi_2 \\ \\ \phi_1{}^\pm = [\tfrac{1}{2}(1-p)]^{1/2}\chi_1 \mp [\tfrac{1}{2}(1+p)]^{1/2}\chi_2 \end{array}\right\} \tag{3.16}$$

and

and for $|p|>1$ they are identical with (3.14). It is to be noted that the orbitals of the SDW II for $|p|<1$ are delocalized even at infinite interatomic distance, while those for $|p|>1$ become localized.

The normalized HF energies of the SDW solutions at $p=0$ and $q=0$ are respectively given by

$$\left.\begin{array}{ll} e = -\tfrac{1}{2}q^2\,, & \text{(SDW I)} \\ \ = \tfrac{1}{2}\,, & \text{(SDW II)} \end{array}\right\} \tag{3.17}$$

$$\left.\begin{array}{ll} e = 0\,, & \text{(SDW I, } |p|<1 \text{ and SDW II, } |p|>1) \\ \ = \tfrac{1}{2}(1-p^2)\,. & \text{(SDW II, } |p|<1) \end{array}\right\} \tag{3.18}$$

Equation (3.17) is identical with (I.5.36) in the NDO approximation.

§ 4. The closed shell solutions of the UHF equation

For the closed shell solutions, $\lambda^+ = \lambda^- = \lambda$ and Eq. (2.11) becomes

$$p \sin \lambda + q \cos \lambda + \sin \lambda \cos \lambda = 0\,. \tag{4.1}$$

The normalized HF energy (2.9) becomes

$$e = 1 + p \cos \lambda - q \sin \lambda - \tfrac{1}{2}\sin^2\lambda\,. \tag{4.2}$$

Making use of (4.1) we may eliminate q or p from (4.2) and obtain

$$e = \frac{3}{2} - \frac{1}{2}\cos^2\lambda + \frac{p}{\cos\lambda} = \frac{1}{2}\sin^2\lambda - \frac{q}{\sin\lambda} \, . \qquad (4\cdot3)$$

By putting

$$x = p/\cos\lambda \, , \qquad y = q/\sin\lambda \, , \qquad (4\cdot4)$$

Eqs. (4·1) and (4·3) may be transformed into the following equations:

$$\left.\begin{array}{l} x+y+1=0 \, , \\[1mm] \dfrac{p^2}{x^2} + \dfrac{q^2}{y^2} = 1 \, , \end{array}\right\} \qquad (4\cdot5)$$

$$e = \frac{3}{2} - \frac{p^2}{2x^2} + x = \frac{q^2}{2y^2} - y \, . \qquad (4\cdot6)$$

Equation (4·5) may be rewritten in the following forms:

$$\left.\begin{array}{l} q = \pm (x+1)\sqrt{1-p^2/x^2} \, , \\[1mm] p = \pm (y+1)\sqrt{1-q^2/y^2} \, . \end{array}\right\} \qquad (4\cdot7)$$

Equation (4·7) gives the functional relationship between q and x for fixed p and one between p and y for fixed q. We show in Fig. 3 the graph of the function (4·7) for various values of the fixed parameter p or q. The function (4·7) has extrema at $x = -p^{2/3}$ or $y = -q^{2/3}$ when $|p|, |q| < 1$. The values of q or p at the extrema are $\pm (1-p^{2/3})^{3/2}$ or $\pm (1-q^{2/3})^{3/2}$. Therefore, if the value of q or p is within the range between the extremum values, that is, if the inequality

$$p^{2/3} + q^{2/3} \leqq 1 \qquad (4\cdot8)$$

is satisfied, then there are four solutions of x or y for given p and q, as seen in Fig. 3. We denote these four solutions as A, B, C and D according to the order of their energy (from lower to higher) at the positive values of p and q.

At the boundary of the domain (4·8) two of these solutions coalesce and at the outside of (4·8) only two solutions exist. The parameter ranges for these solutions to exist are
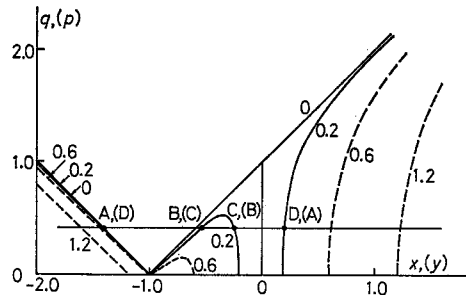

Fig. 3. Function (4·7), q vs. x with fixed p or p vs. y with fixed q, is indicated for the values 0, 0.2, 0.6 and 1.2 of the fixed parameter. The entities referring to p vs. y curve are indicated in parentheses. The closed shell solutions for $p=0.2$ and $q=0.4$ are indicated by the black dots on q vs. x curve of $p=0.2$ and named A, B, C and D according to the order of their energy (from lower to higher). The solutions for $p=0.4$ and $q=0.2$ are also given by the same dots on p vs. y curve of $q=0.2$ as those on q vs. x curve of $p=0.2$. Note that solutions represented by the same point on q vs. x and p vs. y curves respectively correspond to different solutions.

$$
\left.
\begin{aligned}
A:& \quad q>0, \quad 0>q>-(1-p^{2/3})^{3/2}, \\
B:& \quad q<0, \quad 0<q<(1-p^{2/3})^{3/2}, \\
C:& \quad p<0, \quad 0<p<(1-q^{2/3})^{3/2}, \\
D:& \quad p>0, \quad 0>p>-(1-q^{2/3})^{3/2}.
\end{aligned}
\right\} \tag{4.9}
$$

Regarding x or y as the varying parameter, we may easily plot from (4·6) and (4·7) the graphs of q and p dependencies of e for fixed values of p and q respectively. We show in Figs. 4 and 5 the q and p dependencies of the HF energy e for the closed shell solutions as well as those for the SDW solutions.

Now, we consider the closed shell solutions for the special cases of $p=0$ and $q=0$.

For the case of $p=0$, they are given by

$$
\left.
\begin{aligned}
y=q; & \quad A,\ q>-1 \quad \text{and} \quad D,\ q<-1, \\
=-q; & \quad B,\ q<1 \quad \text{and} \quad D,\ q>1, \\
=-1; & \quad C \quad \text{and} \quad D,\ |q|<1.
\end{aligned}
\right\} \tag{4.10}
$$

From (4·10), the explicit forms of the orbital are given by

$$
\left.
\begin{aligned}
\phi_1{}^{\pm}=&\frac{1}{\sqrt{2}}(\chi_1+\chi_2);\ A,\ q>-1 \quad \text{and} \quad D,\ q<-1, \\
=&\frac{1}{\sqrt{2}}(\chi_1-\chi_2);\ B,\ q<1 \quad \text{and} \quad D,\ q>1, \\
=&\left[\frac{1}{2}(1+\sqrt{1-q^2})\right]^{1/2}\chi_1-\left[\frac{1}{2}(1-\sqrt{1-q^2})\right]^{1/2}\chi_2 \\
& \hspace{5cm} ;\ C \quad \text{and} \quad D,\ |q|<1
\end{aligned}
\right\}
$$

and
$$
\left[\frac{1}{2}(1-\sqrt{1-q^2})\right]^{1/2}\chi_1-\left[\frac{1}{2}(1+\sqrt{1-q^2})\right]^{1/2}\chi_2 . \tag{4.11}
$$

Thus, in the homopolar system, the solutions A for $q>-1$ and D for $q<-1$ are the conventional symmetric ground state configuration $(\phi_1)^2$, the solutions C and D for $|q|<1$ are degenerated and correspond to the CDW solutions and the solution B for $q<1$ and D for $q>1$ correspond to the conventional antisymmetric doubly excited configuration $(\phi_2)^2$.

For the case of $q=0$, the closed shell solutions are given by

$$
\left.
\begin{aligned}
x=-1; & \quad A \quad \text{and} \quad B,\ |p|<1, \\
=-p; & \quad A,\ p>1 \quad \text{and} \quad C,\ p<1, \\
=p; & \quad A,\ p<-1 \quad \text{and} \quad D,\ p>-1.
\end{aligned}
\right\} \tag{4.12}
$$

From (4·12) the explicit forms of the orbital are given by

and

$$\phi_1^\pm = \left[\frac{1-p}{2}\right]^{1/2}\chi_1 + \left[\frac{1+p}{2}\right]^{1/2}\chi_2$$

$$\left[\frac{1+p}{2}\right]^{1/2}\chi_1 + \left[\frac{1-p}{2}\right]^{1/2}\chi_2 \quad ; \ A \ \text{and} \ B, \ |p|<1$$

$$= \chi_2; \ A, \ p>1 \ \text{and} \ C, \ p<1,$$

$$= \chi_1; \ A, \ p<-1 \ \text{and} \ D, \ p>-1.$$
$$(4\cdot13)$$

The solutions A and B for $|p|<1$ are delocalized even at infinite interatomic distance. The solutions A for $p>1$ and C for $p<1$ correspond to the ionic state of isolated atoms in which the two electrons are bound to the atom 2. The solutions A for $p<-1$ and D for $p>-1$ correspond to another ionic state, the two electrons bound to the other atom 1.

The HF energies of the closed shell solutions for $p=0$ and $q=0$ are respectively

$$e=\tfrac{1}{2}-q; \ A, \ q>-1 \ \text{and} \ D, \ q<-1,$$

$$= \tfrac{1}{2}+q; \ B, \ q<1 \ \text{and} \ D, \ q>1,$$

$$= 1+\tfrac{1}{2}q^2; \ C \ \text{and} \ D, \ |q|<1,$$
$$(4\cdot14)$$

$$e=\tfrac{1}{2}(1-p^2); \ A \ \text{and} \ B, \ |p|<1,$$

$$= 1-p; \ A, \ p>1 \ \text{and} \ C, \ p<1,$$

$$= 1+p; \ A, \ p<-1 \ \text{and} \ D, \ p>-1.$$
$$(4\cdot15)$$

§ 5. The exact eigenstates and the projected UHF states

The exact Hamiltonian of two-center two-electron system is given in the following form:

$$H=\varepsilon+\begin{bmatrix} c+2b, & d, & a+f/2, & a+f/2 \\ d, & c-2b, & a-f/2, & a-f/2 \\ a+f/2, & a-f/2, & -c, & d \\ a+f/2, & a-f/2, & d, & -c \end{bmatrix}\begin{matrix} (\chi_1{}^+)(\chi_1{}^-) \\ (\chi_2{}^+)(\chi_2{}^-) \\ (\chi_1{}^+)(\chi_2{}^-) \\ (\chi_1{}^-)(\chi_2{}^+), \end{matrix}$$
$$(5\cdot1)$$

when the expansion bases are chosen to be the Slater determinants of the atomic orbitals. The upper signs of χ_i represent the spin state of the atomic orbital. In the NDO approximation, $(5\cdot1)$ becomes

$$H=\varepsilon+c\begin{bmatrix} 1+2p, & 0, & -q, & -q \\ 0, & 1-2p, & -q, & -q \\ -q, & -q, & -1, & 0 \\ -q, & -q, & 0, & -1 \end{bmatrix}.$$
$$(5\cdot2)$$

From $(5\cdot2)$ the normalized exact energy e_E defined as before by

$$e_E = \tfrac{1}{2} + (E - \varepsilon)/2c \tag{5.3}$$

is determined by the following equation for the singlet states

$$e_E^3 - 2e_E^2 + (p^2 + q^2 - 1)e_E + q^2 = 0 \tag{5.4}$$

and for the triplet state

$$e_E = 0. \tag{5.5}$$

Equation (5.4) may be rewritten in the following forms:

$$\left. \begin{array}{l} q = \pm \left[e_E \left(e_E - 1 - \dfrac{p^2}{e_E - 1} \right) \right]^{1/2}, \\[4mm] p = \pm \left[(e_E - 1) \left(e_E - 1 - \dfrac{q^2}{e_E} \right) \right]^{1/2}. \end{array} \right\} \tag{5.6}$$

By using (5.6), we may easily draw the graphs of q and p dependencies of e_E for fixed values of p and q as shown in Figs. 4 and 5.
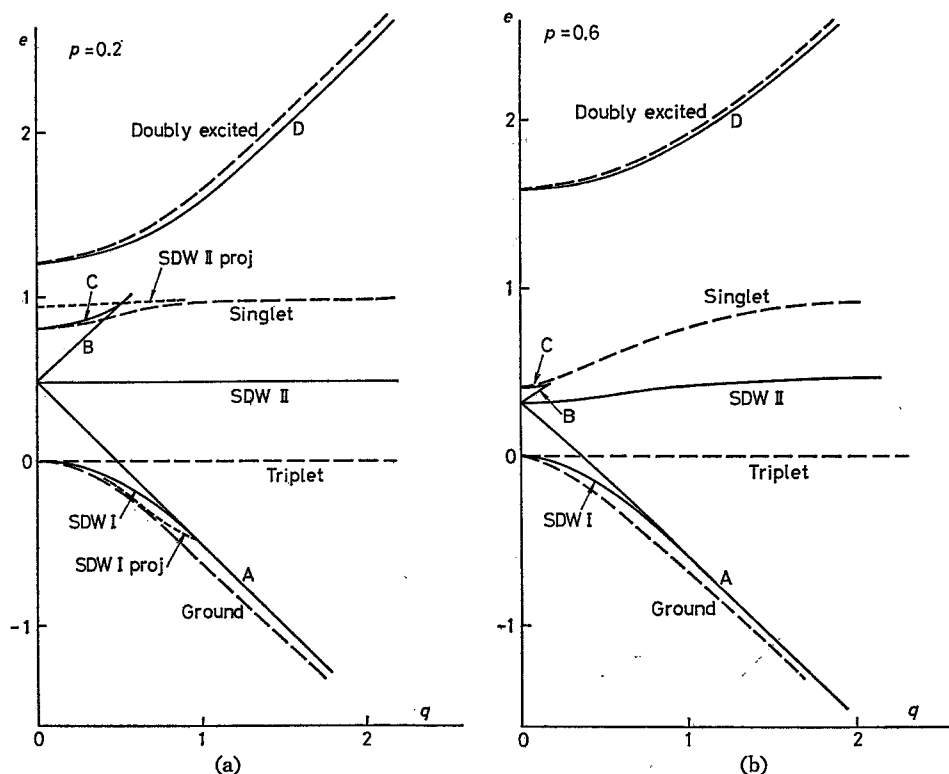

Fig. 4. q dependencies of the normalized energy e for the solutions of UHF equation (the real line) and for the exact eigenstates (the dashed line) are indicated for the fixed values 0.2 (a) and 0.6 (b) of p. The corresponding graph for $p=0$ was given in Fig. 11(a) of I. In the case of $p=0.2$, q dependencies of e for the singlet projected SDW solutions are also indicated (the dotted line).
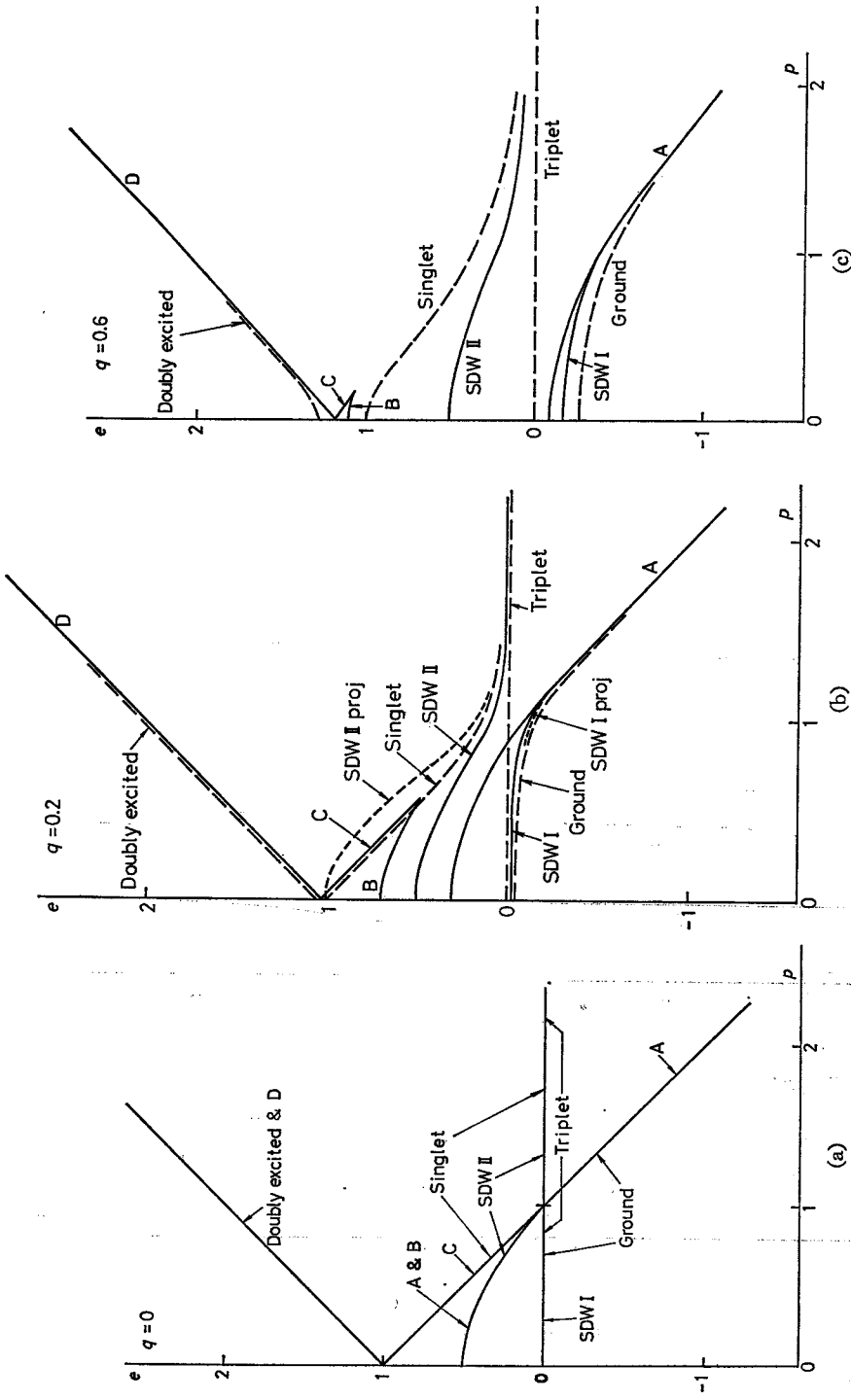
Fig. 5. p dependencies of the normalized energy e for the solutions of UHF equation (the real line) and for the exact eigenstates (the dashed line) are indicated for the fixed values 0 (a), 0.2 (b) and 0.6 (c) of q. In the case of $q=0.2$, the p dependencies of e for the singlet projected SDW solutions are also indicated (the dotted line).

The SDW solutions given in § 3 are not the eigenstates of the total spin. The projection of SDW solution to spin eigenstates, singlet and triplet states leads to wave functions

$$
\begin{aligned}
^1\Psi &= \{\phi_1^+(1)\,\phi_1^-(2) + \phi_1^+(2)\,\phi_1^-(1)\} / \{2(1 + \langle\phi_1^+|\phi_1^-\rangle^2)\}^{1/2}, \\
^3\Psi &= \{\phi_1^+(1)\,\phi_1^-(2) - \phi_1^+(2)\,\phi_1^-(1)\} / \{2(1 - \langle\phi_1^+|\phi_1^-\rangle^2)\}^{1/2}.
\end{aligned} \tag{5.7}
$$

The energy expectation values of these states are

$$
\langle H\rangle = \{\langle\phi_1^+|K|\phi_1^+\rangle + \langle\phi_1^-|K|\phi_1^-\rangle \pm 2\langle\phi_1^+|\phi_1^-\rangle\langle\phi_1^+|K|\phi_1^-\rangle
$$
$$
+ \langle\phi_1^+\phi_1^+|\phi_1^-\phi_1^-\rangle \pm \langle\phi_1^+\phi_1^-|\phi_1^-\phi_1^+\rangle\} \{1 \pm \langle\phi_1^+|\phi_1^-\rangle^2\}^{-1}, \tag{5.8}
$$

where the plus and the minus signs in (5.8) respectively correspond to the singlet and the triplet states. By substituting (2.1) and using (2.2), (5.8) becomes

$$
\begin{aligned}
^1\langle H\rangle &= \varepsilon + \{2(E_H - \varepsilon) + (c+d)\sin^2\sigma\} / (1 + \cos^2\sigma), \\
^3\langle H\rangle &= \varepsilon - (c+d).
\end{aligned} \tag{5.9}
$$

By defining e_{proj} in the same way as for (5.3) and using the NDO approximation, (5.9) becomes

$$
\begin{aligned}
^1e_{\text{proj}} &= 2e / (1 + \cos^2\sigma), \\
^3e_{\text{proj}} &= 0 .
\end{aligned} \tag{5.10}
$$

Thus, the triplet projected SDW gives the energy identical with that of the exact triplet state, while the energy of the singlet projected SDW is higher or lower than that of the SDW according to $e > 0$ or $e < 0$ as seen from (5.10). Therefore, the singlet projected SDW I leads to a better approximation to the ground state as was noted for the homopolar system.[2] The energies of the projected SDW are also shown in Figs. 4 and 5.

§ 6. Conclusions and discussion

As seen from Figs. 4 and 5, the SDW I in the domain (3.7) and the closed shell solution $A(q>0)$ or $B(q<0)$ at the outside of (3.7) are a good approximation to the exact ground state. Salotto and Burnelle[3] have already shown that the UHF theory provides satisfactory ground state adiabatic potentials for the dissociation reactions of H_2 and LiH. The present analysis indicated this for the general two-center two-electron system. The closed shell solution $D(p>0)$ or $C(p<0)$ is also a good approximation to the exact doubly excited state. The triplet projected SDW coincides with the exact triplet state. However, on the contrary to these cases, there is no state that covers the whole range of p and q in the UHF approximation appropriate as the approximation to the exact singlet singly excited state. For small values of p and q, the solution C is a good approximation to the exact singlet singly excited state and, for large values of p and q, the singlet

projected SDW II becomes a good approximation. However, these approximate states are not continuously connected to each other and no good approximation exists for intermediate values of p and q. This indicates that the UHF theory fails to approximate the singly excited singlet state over whole ranges of q and p.

The SDW I solution which corresponds to the ground state of radical nature exists only in the limited region (3·7). It ceases to exist not only for the region of large q which corresponds to the region of small interatomic distance but also for the region of large p which corresponds to the system of large asymmetry. Physical meaning of the disappearance of the SDW I solution at large p is seen most clearly at $R=\infty$. At $R=\infty$, the condition $|p|>1$ of non-existence of the SDW I ground state may be rewritten as

$$K_{11}+K_{22}>2K_{11}+\gamma_{11} \quad \text{or} \quad 2K_{22}+\gamma_{22}.$$

This is nothing but the condition that the radical state of two isolated neutral atoms is of energy higher than either of the states of the pair of isolated ions 1⁻ and 2⁺ or 1⁺ and 2⁻. Therefore, when the asymmetry of the system exceeds the limit (3·7), the character of the ground state changes from radical to ionic one.

It is interesting to see that the asymmetry parameter p becomes larger for smaller R as indicated in Fig. 2 in the example of LiH. This property of the parameter p and the shape of the domain (3·7), i.e., the critical value of p becomes smaller for R approaching the value of $q=1$, make the transition of the ground state character from radical to ionic one by an increment of intrinsic asymmetry of the system much easier at finite R near $q=1$. This result seems to offer a basis for theoretical explanation of ionic character observed for some elimination and addition reactions. It was known that olefin forming elimination reactions of hydrogen bromide from brominated alkyls exhibit ionic characters and are considered to proceed via an ionic four-center transition state[4] as indicated in Fig. 6(a). The non-concerted 2+2 cycloaddition reactions of substituted ethylenes are considered to proceed via the U shaped transition state[5] as indicated in Fig. 6(b). The transition state for the 2+2 cycloaddition of tetracyanoethylene to substituted styrenes was shown to be ionic as shown for the upper route of Fig. 6(b), while that for the 2+2 cycloaddition of fluorinated ethylenes to dienes was shown to be bi-radical as shown for
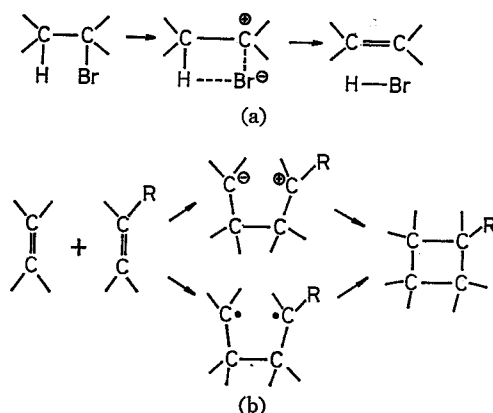

Fig. 6. Transition states of olefine forming elimination reactions of hydrogen bromide from brominated alkyls (a) and non-concerted 2+2 cycloaddition reactions of substituted ethylenes (b).
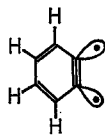
Fig. 7. Ortho-benzyne and the atomic orbitals of the extra triple bond.

the lower route of Fig. 6(b).[5] The present result for simple two-center two-electron system does not directly apply to these complex systems, but it predicts that at finite distances between leaving or approaching atoms corresponding to the transition states of these reactions a change of the ground state from radical to ionic one may be induced by introduction of small increment of asymmetry between the atoms. Thus, the UHF theory seems to provide a promising theoretical basis to understand the mechanism to determine radical vs. ionic character of the reactions.

We add a remark related to the results in I. It concerns with the electronic state of ortho-benzyne. The peripheral two electrons in benzyne, Fig. 7, may be treated as an homopolar two-center two-electron system. Because the atomic orbitals of these two electrons extend toward opposite directions, the resonance integral between them is small and the parameter q is also small. Under the CNDO approximation,[6] the value of q is evaluated to be 0.695 for the same geometry as benzene. Thus. the symmetric closed shell electronic configuration of the two peripheral electrons in benzyne falls into the instability region $|q| < 1$ and the broken symmetry SDW state becomes the ground state. Instability of the symmetric closed shell electronic configuration of benzyne may also be concluded from the ab initio calculation of Wilhite and Whitten.[7] They showed that the ground state of ortho-benzyne is triplet for the SCF approximation, but becomes singlet when CI is performed. In a homopolar two-center two-electron system such an unusual situation may occur if the parameter q is in the range

$$(r+r^2)^{1/2} < q < \tfrac{1}{2}+r$$

as can be seen from Fig. 11(b) of I. The value of q in the above range is in the instability region.

The conclusion of electronic instability of benzyne raises an interesting question about the limit of applicability of Woodward and Hoffmann's (W-H) selection rule.[8] The W-H rule is based on concept of orbital symmetry. In the case of benzyne, the symmetrical orbital is unstable and the SDW orbital of broken symmetry becomes the orbital of ground state configuration. Thus, the concept of orbital symmetry itself does not hold for benzyne. This breakdown of orbital symmetry was indicated also from the CI point of view. Wilhite and Whitten showed that the mixing ratio of the antisymmetric configuration to the symmetric one is -0.46 which is a too large value that makes the concept of orbital symmetry meaningless. It has been known that cycloaddition reactions of benzyne exhibit the behavior violating the W-H rule.[9] This abnormal behavior of benzyne might be closely related to the electronic instability arising in it.

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