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The Doublet Instabilities of the Hartree–Fock Solutions for the Cation and Anion Radicals of Fulvalene Systems

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The doublet instabilities of the restricted Hartree–Fock (RHF) solutions for the ion radicals of fulvalene systems, some of which have been known to show the lattice instabilities, are examined in the framework of the semi-empirical SCF MO approximation. The RHF solutions for the anion radical of heptafulvalene and the cation radical of pentafulvalene are found to be doublet unstable at the conventional D_{2h} nuclear arrangement. We calculate the broken-symmetry charge-density-wave (CDW) solutions lower in energy than the usual symmetry-adapted RHF solutions and examine their properties. It is shown that the energy lowerings due to the CDW solutions are very small in both the ion radicals, but their density matrix elements are remarkably different from those for the symmetry-adapted RHF solutions. It is also shown that the proton hyperfine splittings for the anion radical of heptafulvalene calculated assuming the CDW solution are in good agreement with the experimental values. Finally, we refer to the relationship between the doublet instability of the RHF solution and the lattice instability.

Key words: Ion radicals of fulvalene systems – Doublet instabilities of the HF solutions.

1. Introduction

The ESR spectra of the cation and anion radicals of heptafulvalene have been reported by Sevilla et al. [1]. It was found that in the cation radical the unpaired spin density is delocalized throughout the molecule, while in the anion radical the spin density is localized essentially on a single seven-membered ring. This means that when one extra electron is added to the neutral molecule, the lattice instability, that is, the molecular symmetry reduction from D_{2h} to C_{2v} occurs.

Toyota and Nakajima [2, 3] have investigated the origin of the sharp contrast in spin-density distribution between the cation and the anion radical of heptafulvalene, by examining the energetically most favorable ground-state nuclear arrangements of each radical in the framework of the semiempirical open-shell SCF MO procedure.

On the other hand, it has been shown that the lattice instability is closely related with the instability of the restricted Hartree–Fock (RHF) solution for the most symmetrical nuclear arrangement [9]. For open-shell systems the relevant instability is the doublet instability.

The doublet stability conditions of the RHF solutions for open-shell systems were formulated by Paldus and Čižek [4–6]. When the usual RHF solutions are doublet unstable, there appear new HF solutions lower in energy than the conventional symmetry-adapted RHF solutions. They are characterized by the charge-density waves (CDW), and the symmetries of them are in general lower than those of the nuclear arrangement used. In this sense, the doublet instability is analogous to the singlet instability in closed-shell systems [7–9].

Paldus and Čižek [10] examined the doublet instabilities of the usual RHF solutions for the odd polyenic radicals in the framework of the semiempirical MO approximation. In particular, the doublet instability of the RHF solution for the allyl radical has been reinvestigated at the *ab initio* level of calculations by Mckelvey and Hehre [11], Mckelvey and Berthier [12], and Paldus and Veillard [13].

In this paper we examine the doublet instabilities of the usual RHF solutions for the ion radicals of fulvalene systems, some of which have been known to show the lattice instabilities [2, 3, 14], in the framework of the semiempirical SCF MO approximation. When the conventional RHF solutions are doublet unstable, we calculate the broken-symmetry CDW solutions and examine their properties. It will be shown that in these ion radicals the energy lowerings due to the CDW solutions are very small, but their density matrix elements are remarkably different from those for the symmetry-adapted RHF solutions. Finally, we refer to the relationship between the doublet instability of the conventional RHF solution and the lattice instability.

2. The Doublet Stability Conditions

The doublet stability conditions of the RHF solutions for the open-shell case were formulated by Paldus and Čižek [4, 5], which require that all the eigenvalues of the following eigenvalue problem are to be positive:

$$\begin{pmatrix} \mathbf{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \boldsymbol{D} \\ \boldsymbol{D}^* \end{pmatrix} = \lambda \begin{pmatrix} \boldsymbol{D} \\ \boldsymbol{D}^* \end{pmatrix} \tag{1}$$

where elements of the square matrices, $\boldsymbol{A}$ and $\boldsymbol{B}$, represent the configuration interactions between spin unflip singly excited configurations and those between the RHF ground state and spin unflip bi-excited configurations, respectively. The elements of the column matrix $\boldsymbol{D}$ are the mixing coefficients which give the weights with which the virtual RHF molecular orbitals are admixed to the occupied ones, and the asterisk superscript denotes the complex conjugate.

The eigenvector $\boldsymbol{d}_{\min}$ of Eq. (1), corresponding to the lowest eigenvalue $\lambda_{\min}$, gives the direction of the steepest descent when $\lambda_{\min} < 0$, or the slowest ascent when $\lambda_{\min} > 0$, of the energy hypersurface of the energy functional at the point of the symmetry-adapted RHF solution.

When the elements of the matrices, $\boldsymbol{A}$ and $\boldsymbol{B}$, are real, the eigenvalue problem Eq. (1) can be reduced into the following two eigenvalue problems [10]:

$$\begin{aligned}(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{D}_{+} &= \lambda_{+}\boldsymbol{D}_{+}\\ (\boldsymbol{A}-\boldsymbol{B})\boldsymbol{D}_{-} &= \lambda_{-}\boldsymbol{D}_{-}\end{aligned} \tag{2}$$

If $\lambda_{+} < 0$ or $\lambda_{-} < 0$, a doublet instability occurs and a new HF solution is a real CDW solution or a complex CDW solution lower in energy than the conventional symmetry-adapted RHF solution, respectively.

3. Results and Discussion

3.1. *Doublet Instabilities of the* RHF *Solutions*

The optimum nuclear arrangements with the D_{2h} symmetry of the ion radicals of fulvalene systems (Fig. 1) [2, 3] were calculated previously by using Longuet–Higgins and Pople's SCF MO method [15] in conjunction with the

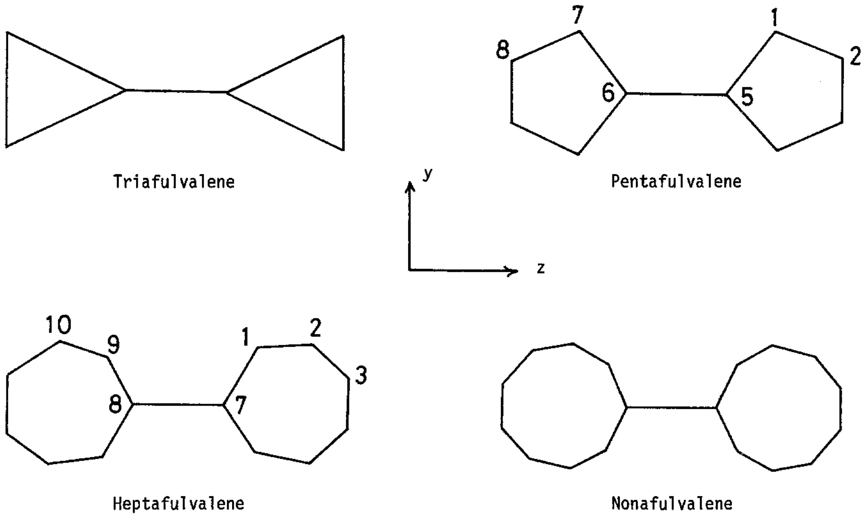

Fig. 1. The carbon skeletons of the fulvalene systems, the choice of molecular axes, and the numberings of atomic positions

variable bond length technique [16]. The RHF solutions to which the stability conditions will be applied are those corresponding to the molecular geometries thus optimized with respect to C–C bond length.

The calculated lowest-lying eigenvalues λ_{min} and the symmetries of the corresponding eigenvectors $\boldsymbol{d}_{\text{min}}$ are listed in Table 1. It is noted that all of these eigenvalues are obtained from the λ_+ subproblem of Eq. (2) and that the eigenvalues for the anion radicals of triafulvalene and heptafulvalene and the cation radicals of pentafulvalene and nonafulvalene are negative. Since for these ion radicals the directions of the steepest descent in the variational space of the energy functional are of b_{1u} symmetry, there appear broken-symmetry CDW solutions having the C_{2v} spatial symmetry. In what follows, we examine the CDW solutions for the anion radical of heptafulvalene and the cation radical of pentafulvalene.

3.2. Broken-Symmetry CDW *Solutions*

3.2.1. Heptafulvalene Anion Radical

From the stability calculations, it is revealed that the electronic configurations which contribute dominantly to the doublet instability of the RHF solution are those including the orbital jumps from the highest doubly occupied orbital ϕ_7 to the next lowest vacant one ϕ_{10} and from the half-filled orbital ϕ_8 to the lowest vacant one ϕ_9. In order to simplify the procedure for obtaining the CDW solution, we take into account only the above two orbital jumps and solve the eigenvalue problems Eq. (2). This approximate procedure is justified, for the lowest eigenvalue thus obtained reproduces well that obtained by including all the excited configurations (see Table 1). Then, the new occupied

Table 1. The lowest-lying eigenvalues λ_{min} and the symmetries of the corresponding eigenvectors $\boldsymbol{d}_{\text{min}}$

Molecule (point group and symmetry)[a]	λ_{min} (eV)	Symmetry of $\boldsymbol{d}_{\text{min}}$
Triafulvalene$^+$ (D_{2h}; B_{3u})[c]	2.42	b_{2u}
Triafulvalene$^-$ (D_{2h}; A_u)	−1.17	b_{1u}
Pentafulvalene$^+$ (D_{2h}; B_{1g})	−1.25 (−1.15)[b]	b_{1u}
Pentafulvalene$^-$ (D_{2h}; B_{2g})	1.67	b_{3g}
Heptafulvalene$^+$ (D_{2h}; B_{3u})	1.25	b_{1u}
Heptafulvalene$^-$ (D_{2h}; A_u)	−1.20 (−1.14)[b]	b_{1u}
Nonafulvalene$^+$ (D_{2h}; B_{1g})	−1.11	b_{1u}
Nonafulvalene$^-$ (D_{2h}; B_{2g})	0.99	b_{1u}
Heptafulvalene$^-$ (C_{2v}; A_2)	0.72	b_2
Pentafulvalene$^+$ (C_{2v}; A_2)	0.88	b_2

[a] The point group and symmetry of the RHF ground state.

[b] The eigenvalue obtained by including the two most important electronic excited configurations in the stability problem.

[c] The + or − sign refers to the cation or the anion radical, respectively.

molecular orbitals are formed as:

$$\begin{aligned}
&\psi_i = \phi_i \qquad (i = 1-6)\\
&\psi_7 = \mu_1\phi_7 + \mu_2\phi_{10} \\
&\psi_8 = \lambda_1\phi_8 + \lambda_2\phi_9
\end{aligned} \tag{3}$$

and

$$\begin{aligned}
&\mu_1 = \{1-(0.366\kappa)^2\}^{1/2}, \qquad \mu_2 = -0.336_{\kappa}\\
&\lambda_1 = \{1-(0.942\kappa)^2\}^{1/2}, \qquad \lambda_2 = 0.942_{\kappa}
\end{aligned} \tag{4}$$

where κ is the dimensionless mixing parameter, which indicates the degree of deformation of the CDW solution from the symmetry-adapted RHF solution. Using the above orbitals, we can write the CDW solution as:

$$\begin{aligned}
{}^2\Psi_{\mathrm{CSW}}(\kappa) = {}&\mu_1^2\lambda_1\,{}^2\Psi_{\mathrm{RHF}}(A_u) + \mu_1^2\lambda_2\,{}^2\Psi_1(B_{1g}, 8 \rightarrow 9)\\
&+\sqrt{2}\mu_1\mu_2\lambda_1\,{}^2\Psi_1(B_{1g}, 7 \rightarrow 10)\\
&+\sqrt{2}\mu_1\mu_2\lambda_2\,{}^2\Psi_2(A_u, 7, 8 \rightarrow 9, 10)\\
&+\mu_2^2\lambda_1\,{}^2\Psi_2(A_u, 7, 7 \rightarrow 10, 10)\\
&+\mu_2^2\lambda_2\,{}^2\Psi_3(B_{1g}, 7, 7, 8 \rightarrow 10, 10, 9)
\end{aligned} \tag{5}$$

where the superscript and the subscript attached to the wavefunction Ψ denote respectively the multiplicity of the configuration and the number of electron jump. The orbital jumps involved are specified in the parentheses after Ψ.

The CDW solution thus obtained comprises the configurations of A_u and B_{1g} symmetries. In order to obtain the symmetry-restored solution, one in general projects away the symmetry-breaking components out of the broken-symmetry CDW solution [17–19]. In usual cases, the above projection procedure brings about further energy lowering. The symmetry–breaking components are the configurations of B_{1g} symmetry, for the RHF ground state is of A_u symmetry. The unnormalized symmetry–restored A_u solution is obtained by the simple deletion of the configurations of B_{1g} symmetry from the broken-symmetry CDW solution. On the other hand, the unnormalized symmetry-restored B_{1g} solution is obtained by deleting the configurations of A_u symmetry.

The dependence of the energy expectation values of the broken–symmetry CDW solution and the symmetry-restored A_u and B_{1g} solutions on the mixing parameter κ is shown in Fig. 2. It is seen that the three energy curves cross one another at the κ values of ca. 0.65 and ca. 0.80. The stable broken–symmetry CDW solution is found at the κ value of ca. 0.69 and the associated energy lowering from the symmetry–adapted RHF solution is calculated to be 0.286 eV. The energy minimum points for the symmetry-restored A_u and B_{1g} solutions are found at the κ values of ca. 0.70 and ca. 0.50 and the associated energy depressions from the symmetry-adapted RHF solution are calculated to be 0.293 eV and 0.291 eV, respectively. Consequently, in the framework of the approximation used the symmetry-restored A_u solution becomes the ground

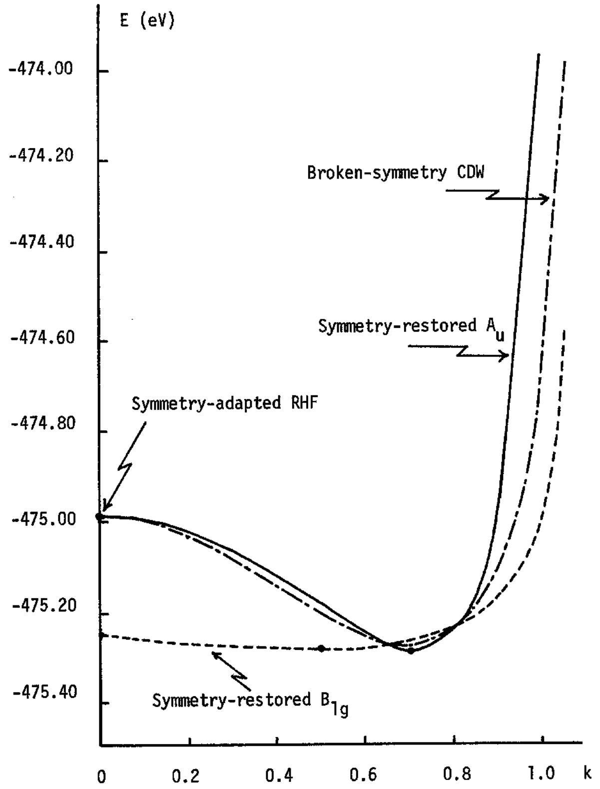

Fig. 2. The dependence of the energy expectation values of the broken-symmetry CDW solution and the symmetry-restored A_u and B_{1g} solutions on the mixing parameter κ for the heptafulvalene anion radical at the D_{2h} nuclear arrangement

state, which is lower than the symmetry-restored B_{1g} solution corresponding to the lowest doublet excited state only by 0.002 eV. It should be noted that only in the region of interest the symmetry-restored A_u solution is lower in energy than the broken-symmetry CDW solution.

In Fig. 3 is shown the distribution of density matrix elements of the stable broken-symmetry CDW solution, together with that of the symmetry-adapted (D_{2h}) RHF solution. It should be remarked that there is a notable difference in bond-order distribution between the CDW solution and the symmetry-adapted RHF solution: in the CDW solution the double-bond fixation is considerably enhanced on a single seven-membered ring, while it is relaxed on the other seven-membered ring. Further, if we take the values of electron density for the RHF solution as the reference values, the charge-density alternation can be seen along the long molecular (z) axis in the distribution of electron density for the CDW solution. It is also seen that the distribution of density matrix elements of the CDW solution is very similar to that of the symmetry-adapted RHF solution, obtained previously [2, 3], corresponding to the reduced C_{2v} nuclear arrangement. This will be discussed later in connection with the lattice instability.

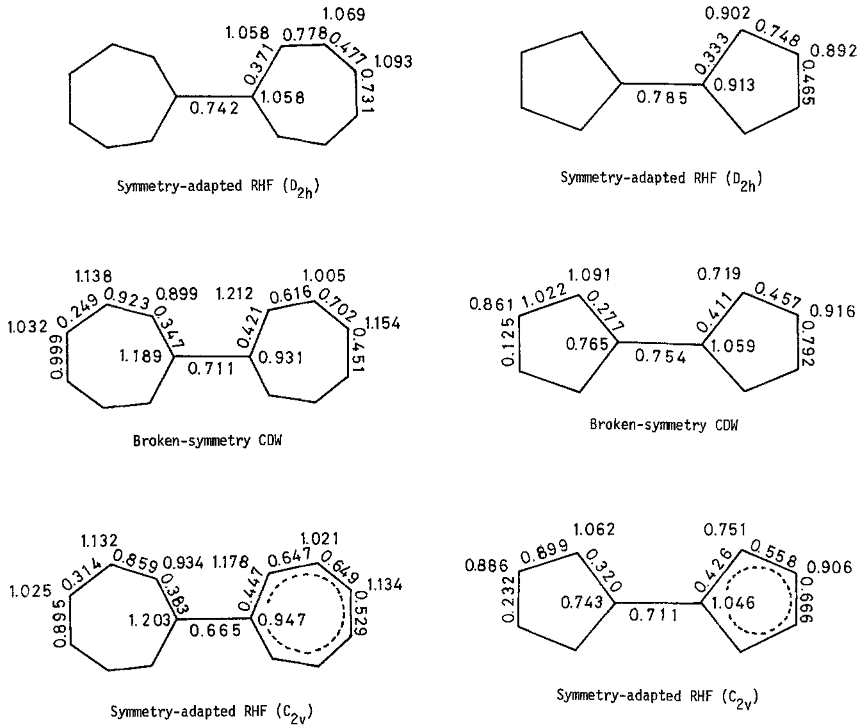

Fig. 3. The distribution of density matrix elements of the various solutions for the D_{2h} and C_{2v} nuclear arrangements of the heptafulvalene anion and pentafulvalene cation radicals

In Fig. 4 is shown the dependence of the unpaired spin densities of the broken-symmetry CDW solution on the mixing parameter κ. From this figure we can see how the spin-density distribution changes in each seven-membered ring as the mixing parameter κ increases. The detailed spin densities and the proton hyperfine splittings calculated assuming the stable broken-symmetry CDW solution are listed in Table 2, together with the previous results [2] obtained by assuming the symmetry-adapted RHF solution corresponding to the C_{2v} nuclear arrangement and the experimental values [1]. It is found that the unpaired spin-density distribution of the CDW solution is essentially localized on a single seven-membered ring, which is in good agreement with the previously calculated results and the experimental fact. It should be noted that without invoking the lattice instability of the ground-state nuclear arrangement, the observed proton hyperfine splittings can be accounted for by examining the broken-symmetry CDW solution.

3.2.2. Pentafulvalene Cation Radical

The CDW solution of the pentafulvalene cation radical is treated according to the same procedure as used in the preceding section. The electronic configurations which play an important role in the doublet instability of the RHF solution are those including the orbital jumps from the next highest doubly occupied orbital ϕ_3 to the lowest vacant one ϕ_6 and from the highest doubly

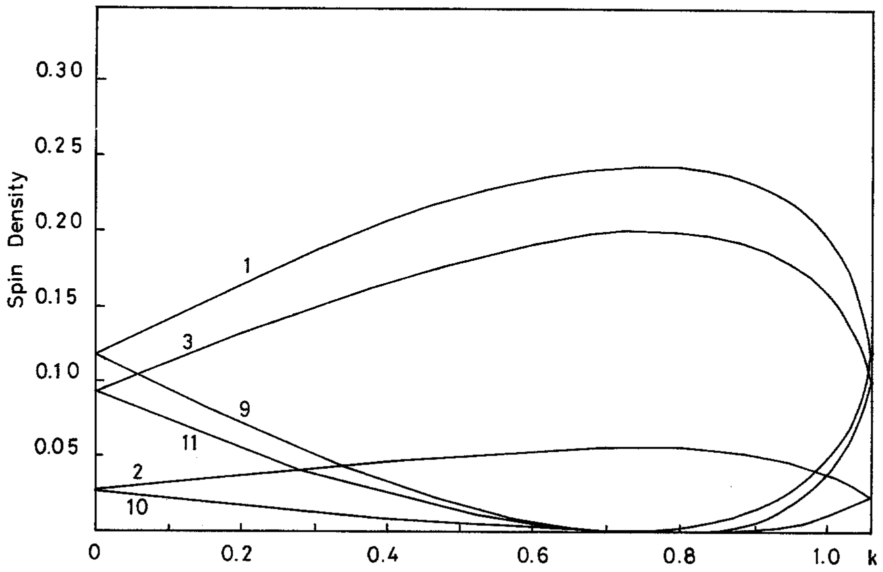

Fig. 4. The dependence of the unpaired spin densities of the broken-symmetry CDW solution of the heptafulvalene anion radical on the mixing parameter κ at the D_{2h} nuclear arrangement. The spin densities on the carbon atoms 7 and 8 are zero

Table 2. Spin densities and proton hyperfine splittings of the heptafulvalene anion radical

Atom	Symmetry-breaking CDW (D_{2h} nuclear configuration)		Symmetry-adapted RHF (C_{2v} nuclear configuration)		Observed
	Spin density	Hyperfine splitting (G)[a]	Spin density	Hyperfine splitting (G)[a]	Splitting const. (G)
1	0.244	6.36	0.275	7.15	8.22
2	0.054	1.40	0.040	1.04	
3	0.199	5.18	0.189	4.91	5.02
7	0.0	0.0	0.0	0.0	
8	0.0	0.0	0.0	0.0	
9	0.001	0.03	0.000	0.000	
10	0.001	0.03	0.000	0.000	
11	0.001	0.03	0.000	0.000	

[a] The hyperfine splittings a^H were calculated by using McConnell's relationship with $|Q| = 26G$.

occupied orbital ϕ_4 to the half-filled one ϕ_5. By using the mixing coefficients of the eigenvector corresponding to the eigenvalue obtained by taking into account the above two types of electron jump, the new occupied molecular orbitals are formed as:

$$\begin{aligned} \psi_i &= \phi_i \quad (i = 1, 2) \\ \psi_3 &= \mu_1\phi_3 + \mu_2\phi_6 \\ \psi_4 &= \lambda_1\phi_4 + \lambda_2\phi_5 \\ \psi_5 &= \lambda_1\phi_5 - \lambda_2\phi_4 \end{aligned} \tag{6}$$

and

$$\begin{aligned} \mu_1 &= \{1-(0.306\kappa)^2\}^{1/2}, & \mu_2 &= 0.306\kappa \\ \lambda_1 &= \{1-(0.952\kappa)^2\}^{1/2}, & \lambda_2 &= 0.952\kappa \end{aligned} \tag{7}$$

where κ is the dimensionless mixing parameter. Using the above orbitals, we can write the CDW solution as:

$$\begin{aligned} {}^2\Psi_{\mathrm{CDW}}(\kappa) = {} & \mu_1^2\lambda_1\,{}^2\Psi_{\mathrm{RHF}}(B_{1g}) + \mu_1^2\lambda_2\,{}^2\Psi_1(A_u, 4\rightarrow 5) \\ & + \sqrt{2}\mu_1\mu_2\lambda_1\,{}^2\Psi_1(A_u, 3\rightarrow 6) \\ & + \sqrt{2}\mu_1\mu_2\lambda_2\,{}^2\Psi_2(B_{1g}, 3, 4\rightarrow 5, 6) \\ & + \mu_2^2\lambda_1\,{}^2\Psi_2(B_{1g}, 3, 3\rightarrow 6, 6) \\ & + \mu_2^2\lambda_2\,{}^2\Psi_3(A_u, 3, 3, 4\rightarrow 6, 6, 5) \end{aligned} \tag{8}$$

The CDW solution thus obtained comprises the configurations of B_{1g} symmetry and those of A_u symmetry. In this case, the symmetry–breaking components are the configurations of A_u symmetry, for the RHF ground state is of B_{1g} symmetry.

The dependence of the energy expectation values of the broken–symmetry CDW solution and the symmetry–restored B_{1g} and A_u solutions on the mixing parameter κ is shown in Fig. 5. The energy lowering due to the stable broken–symmetry CDW solution is 0.227 eV, the value being comparable to that obtained in case of the anion radical of heptafulvalene. In the framework of the approximation used, the symmetry–restored B_{1g} solution becomes the ground state, which is lower than the symmetry–restored A_u solution corresponding to the lowest doublet excited state only by 0.019 eV.

In Fig. 3 is shown also the distribution of density matrix elements of the stable broken-symmetry CDW solution as well as that of the symmetry–adapted (D_{2h}) RHF solution. The bond-order distribution of the CDW solution is remarkably different from that of the symmetry–adapted RHF solution: on a single five-membered ring the double-bond fixation is greatly enhanced as compared with that in the symmetry–adapted RHF solution, while it is considerably relaxed on the other five-membered ring.

The unpaired spin densities calculated by assuming the stable broken-symmetry CDW solution are listed in Table 3, together with the previous results [2] obtained by assuming the symmetry–adapted RHF solution corresponding to the reduced C_{2v} nuclear arrangement. It should be remarked that the unpaired spin density is essentially localized on a single five-membered ring, and this behavior is quite similar to that seen in the anion radical of heptafulvalene.

3.3. The Relationship Between the Doublet and Lattice Instabilities

In the anion radical of heptafulvalene and the cation radical of pentafulvalene, it is found that the bond-order and electron density distributions due to the broken-symmetry CDW solutions are quite similar to those due to the RHF

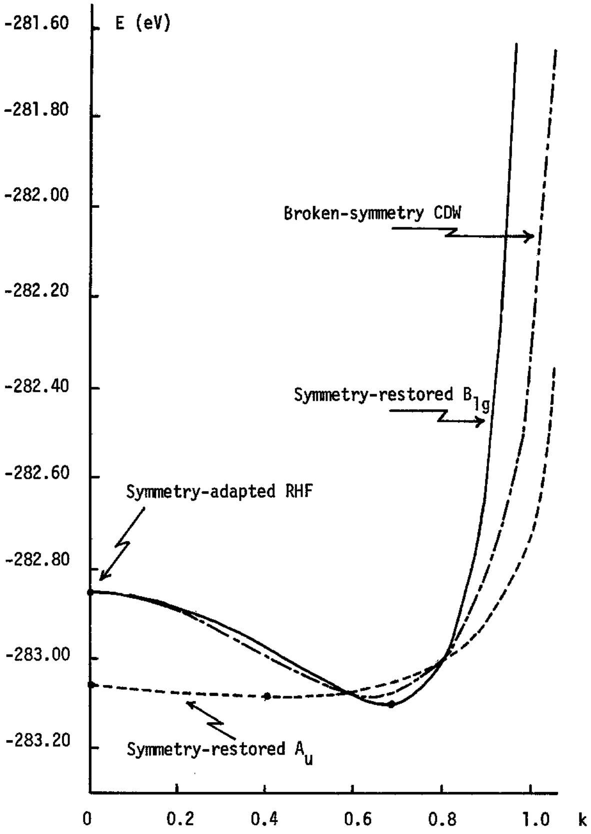

Fig. 5. The dependence of the energy expectation values of the broken-symmetry CDW solution and the symmetry-restored B_{1g} and A_u solutions on the mixing parameter κ for the pentafulvalene cation radical at the D_{2h} nuclear arrangement

Table 3. Spin densities and proton hyperfine splittings of the pentafulvalene cation radical

Atom	Symmetry-breaking CDW solution (D_{2h} nuclear configuration)		Symmetry-adapted RHF solution (C_{2v} nuclear configuration)	
	Spin density	Hyperfine splitting (G)[a]	Spin density	Hyperfine splitting (G)[a]
1	0.351	9.12	0.379	9.85
2	0.142	3.70	0.120	3.12
5	0.0	0.0	0.0	0.0
6	0.0	0.0	0.0	0.0
7	0.005	0.12	0.000	0.00
8	0.002	0.06	0.000	0.00

[a] The hyperfine splittings a^H were calculated by using McConnell's relationship with $|Q| = 26G$.

solutions for the distorted nuclear arrangement brought about by the lattice instability. The reason for this is explained as follows.

In the heptafulvalene anion radical, the most important excited configuration which contributes to the doublet instability is that corresponding to the orbital jump from the half-filled molecular orbital to the lowest vacant one (see Eqs. (3) and (4)). The admixture of the above configuration to the RHF ground state leads to the broken–symmetry CDW solution which exhibits the C_{2v} symmetry with respect to the distribution of density matrix elements.

On the other hand, we have derived in a previous paper [3] the condition for the lattice instability for the open-shell conjugated hydrocarbons, which is stated as follows: the ground-state nuclear arrangement is unstable if the energy gap between the lowest doublet excited state and the ground state is smaller than a certain critical value, ca. 0.6 eV. If the energy gap is smaller than the critical value, the molecule under consideration would be distorted into a new nuclear arrangement with a lower symmetry. The type of nuclear displacement effective for the lattice instability is predicted from the distribution of two-center components of the transition density between the ground state and the lowest excited state [20, 21]. In the heptafulvalene anion radical at the D_{2h} nuclear arrangement, the lowest excited state (B_{1g}) corresponds to the same type of the orbital jump as that responsible for the doublet instability and is higher than the ground state (A_u) only by 0.033 eV in the approximation of the single determinant description. On the basis of the criterion stated above, the symmetrical nuclear arrangement is unstable under the nuclear deformation of b_{1u} symmetry, resulting in the molecular symmetry reduction from D_{2h} to C_{2v}.

It has been shown that the anion radical of triafulvalene and the cation radicals of pentafulvalene and nonafulvalene suffer the same type of lattice instability [2, 3]. It can be shown that in these radicals also the excited configuration effective for the doublet instability is the same as that effective for the lattice instability. It is thus indicated that the symmetry of nuclear deformation in the lattice instability is identical with that of the direction of the steepest descent in the variational space of energy functional in the doublet instability. This is the reason for the appearance of a similar distribution of density matrix elements in both the instabilities.

Next we show in Fig. 6 the relative total energy of various solutions for the D_{2h} and C_{2v} nuclear arrangements of the heptafulvalene anion radical. The total energy has been assumed to be expressed as the sum of the three parts: the π-electron energy, the core repulsion energy and the σ-bond energy [8, 22]. In the pentafulvalene cation radical, we can also obtain qualitatively the same energy diagram as that shown in Fig. 6.

In the anion radical of heptafulvalene, it is expected that the broken–symmetry CDW solution would be stabilized by the electrostatic interaction through the nuclear deformation of b_{1u} symmetry. This will be performed by distorting the

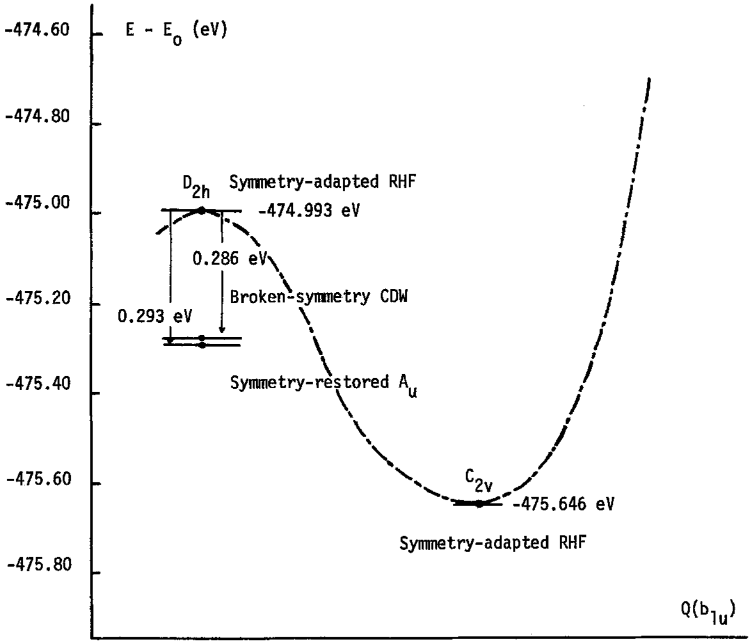

Fig. 6. The relative total energies of various solutions for the D_{2h} and C_{2v} nuclear arrangements of the heptafulvalene anion radical. E_0 is the sum of the σ-bond and core repulsion energies at the D_{2h} nuclear arrangement

nuclear arrangement so that it may match up with the distribution of bond-order matrix elements of the stable broken–symmetry CDW solution [8]. In the distorted structure (C_{2v}) thus obtained, it is expected that the broken-symmetry CDW solution becomes to be symmetry adapted. Actually the symmetry–adapted RHF solution at the C_{2v} nuclear arrangement is doublet stable (see Table 1). As seen in Fig. 4, the symmetry–adapted RHF solution corresponding to the C_{2v} nuclear arrangement is lower in energy than the symmetry-restored A_u solution corresponding to the D_{2h} nuclear arrangement. We can thus confirm that the ground-state nuclear arrangement of the heptafulvalene anion radical is of C_{2v} symmetry.

4. Conclusion

The doublet instabilities of the RHF solutions for the anion radicals of triafulvalene and heptafulvalene and the cation radicals of pentafulvalene and nonafulvalene suggest that for these systems the symmetrical (D_{2h}) nuclear arrangement does not represent a minimum of the potential energy surface and a nuclear configuration with a lower symmetry (C_{2v}) is more stable. All the molecules that exhibit the doublet instabilities suffer actually the lattice instabilities [2, 3]. The doublet instability is intimately related with the lattice instability in the sense that the occurrence of both instabilities is associated with the existence of a sufficiently low-lying doublet excited state and the direction of the steepest descent in the variational space of energy functional is the same as that of the nuclear displacement effective for the lattice instability. This situation is quite similar to the relationship between the singlet and the lattice instability for the closed-shell systems [8].

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