Ab initio LCAO MO SCF CI Calculations on the Electronic Structure of the Cyclopropenyl Cation

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(Received July 14, 1978)

Ab initio LCAO MO SCF and limited CI calculations are carried out on the electronic structure of the $C_3H_3^+$ ion. Two kinds of basis sets are used, namely the minimal STO's and the minimal STO's plus 3d orbitals on each carbon atom. With the latter basis, the equilibrium C–C distance is calculated to be 1.389 Å. It is predicted that the C–C bond distance of $C_3H_3^+$ is shorter than that of C_6H_6. The calculated C–C stretching force constant is 7.92 mdyn/Å and is close to the experimental value 6.59 mdyn/Å. Contour diagrams of the charge distribution of valence electrons are drawn and it is revealed that the calculated C–C bonds are bent and have two maxima in charge density. In terms of population analysis of localized MO's, it is shown that the C–H bond in this molecule has a higher s-character than the C–H bonds in C_2H_4 and C_6H_6 and is close to an sp hybrid. This is in accord with a very large NMR coupling constant $J_{^{13}C-H}$. From CI calculations of low lying excited states, singlet σ-π^* states ($^1A_1''$, $^1E''$, $^1A_2''$) are calculated to be lower than the singlet π-π^* state ($^1E'$).

The cyclopropenyl cations are the smallest ring systems which have two π-electrons and satisfy the Hückel $4n+2$ rule. Their electronic structures are of great interest since the molecules are highly strained. The simplest one, $C_3H_3^+$, has been synthesized by Breslow and Groves.[1] The D_{3h} configuration of the ion is indicated on the basis of the IR and NMR spectra.[1] One might think that the C–C bonds in this system would be weaker than the usual C–C bonds such as those in C_6H_6 and thus the equilibrium C–C bond distance would be longer and the C–C stretching force constant smaller. Apparently, this is not the case. X-Ray diffraction shows that trisdimethylaminocyclopropenyl cation has a regular triangle cyclopropenyl ring with a C–C bond length of 1.363 Å[2] and that the C–C bond length of triphenylcyclopropenyl cation is 1.373 Å.[3] These values are significantly smaller than the C–C bond distance of 1.397 Å[4] in C_6H_6. From IR spectra, the Urey-Bradley force constant of the ring C–C stretching of $C_3H_3^+$ has been estimated to be 6.590 mdyn/Å,**,[5] which is larger than the C_6H_6 value of 5.78 mdyn/Å.[6]

In spite of these immense theoretical interest, there have been only three *ab initio* all-electron calculations on $C_3H_3^+$ as far as the authors are aware. Clark carried out *ab initio* LCAO SCF MO calculations on both $C_3H_3^+$ and $C_3H_3^-$ and discussed the aromaticity and antiaromaticity.[7] Ha, Graf and Günthard reported an extensive *ab initio* LCAO SCF MO investigation on $C_3H_3^+$, C_3H_3, and $C_3H_3^-$ and discussed the geometry and stability of these species.[8] Their basis set consists of Gaussian lobe functions and is approximately of the double zeta quality. Radom, Hariharan, Pople, and Schleyer also carried out *ab initio* LCAO SCF MO calculation on $C_3H_3^+$ using STO-3G and 6-31G and obtained the equilibrium structure of the ion.[9]

In this paper, the results of *ab initio* LCAO MO SCF CI calculations on $C_3H_3^+$ are reported. The C–C bond distance is varied and the equilibrium C–C distance and the C–C stretching force constant are calculated and are compared with experiment. The occupied MO's are transformed into localized MO's and the nature of the C–C and C–H bonds is discussed in terms of the contour diagrams of the charge distribution and the population analysis of these localized MO's. CI calculations of the low lying excited states are carried out for the first time and the character of these states is discussed.

Method of Calculations

The wave functions of $C_3H_3^+$ are obtained by *ab initio* LCAO MO SCF and CI calculations. Two kinds of basis sets are used. One is the minimal STO's. The other is the minimal STO's plus 3d orbitals on each carbon atom. One reason for adding the 3d orbitals is to hope for a better description of the bent C–C bonds. The former basis is called Min. and the latter Min.+C3d, hereafter. The orbital exponents adopted are shown in Table 1. The values of H1s and C1s, 2s and 2p orbitals are optimized for C_6H_6 by Hehre, *et al.*[10] The exponents of C3d orbitals are optimized for CO by Nesbet.[11] In the evaluation of molecular integrals, these STO's are expanded in terms of GTO's; the H1s and C1s, 2s and 2p orbitals are expanded by five GTO's and the C3d orbitals by three GTO's, respectively. The expansion coefficients are those given by Stewart.[12]

TABLE 1. ORBITAL EXPONENTS

H1s	1.21
C1s	5.67
2s, $2p_v$,[a] $2p_h$,[b] $2p_z$	1.71
$3d_{z^2}$, $3d_{h^2-v^2}$, $3d_{hv}$	1.895
$3d_{hz}$, $3d_{vz}$	1.429

a) The v axis is pointing towards the partner H atom.
b) The h axis is in the molecular plane and perpendicular to the v axis.

In the CI calculations, configuration state functions are constructed as follows. All single and double excitations are considered from $2a_1'$, $2e'$, $3a_1'$, $3e'$, and $1a_2''$ to $1e''$, $1a_2'$, $4e'$, $4a_1'$, $2e''$, $2a_2''$, $5e'$, $5a_1'$, and $3e''$ orbitals (These orbitals are indicated by * in Table 2 in Section 3.). Other molecular orbitals are excluded, that

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** This value is obtained by assuming that the C–C bond distance of $C_3H_3^+$ is equal to that of triphenylcyclopropenyl cation.

is, $1a_1'$ and $1e'$ as core and the orbitals whose energies are greater than 1.0 a.u. This is called occupation Scheme I. In another choice, occupation Scheme II, only single and double excitations from the four highest occupied MO's $3a_1'$, $3e'$, and $1a_2''$ to the six lowest unoccupied MO's $1e''$, $1a_2'$, $4e'$, and $4a_1'$ are taken into account. The method of the first order interacting space proposed by McLean and Liu[13] is employed in order to reduce the number of configuration state functions without sacrificing the accuracy too much.

The D_{3h} configuration is assumed in the present calculations. This configuration is indicated on the basis of the IR and NMR spectra[1] and is supported theoretically by Ha and others.[8] The C–H internuclear distance is fixed at 1.09 Å which is the observed C–H distance in C_6H_6.[14] The calculation is repeated for the following six C–C distances, 1.300, 1.350, 1.375, 1.400, 1.425, and 1.500 Å. The calculated energy curve is expressed as a fifth degree polynominal of the C–C distance and the minimum energy, the equilibrium C–C distance and the C–C stretching force constant are determined.

In order to investigate the nature of C–C and C–H bonds of the system, the resulting MO's are transformed into localized MO's by a unitary transformation. The measure of localization proposed by Hall[15] and applied extensively by Edmiston and Ruedenberg[16] is adopted. This is to maximize the total self-energy of the orbitals. The unitary transformation is applied only to the valence MO's. Namely the three lowest MO's, $1a_1'$ and $1e'$, are omitted since, in our opinion, the distinction between valence electrons and inner-shell electrons is more fundamental than the requirement of "localization."

Results and Discussion

The calculated potential curves are illustrated in Fig. 1. In the ground state CI calculations, the occupation Scheme I is used. The orbital energies are given in Table 2. The values in the parentheses are those

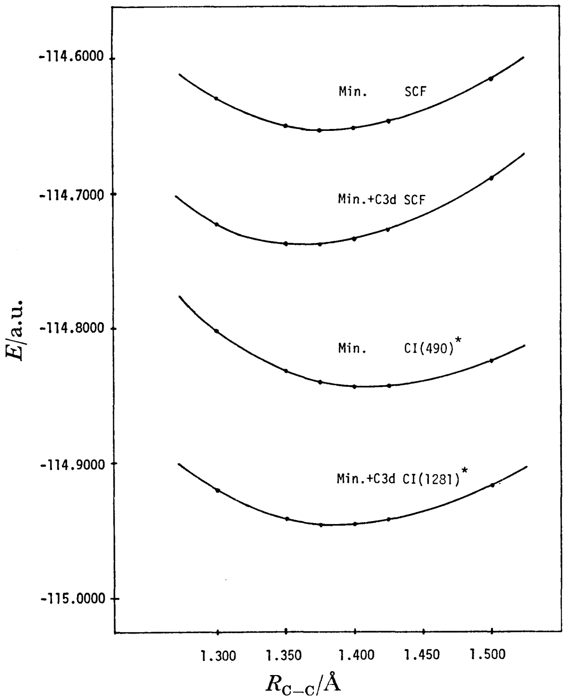

Fig. 1. Potential curves of $C_3H_3^+$.
* Dimension of CI solved in C_{2v} symmetry.

Table 2. Molecular orbital energies of $C_3H_3^+$ (a.u.)

	Occupation		Present study $R_{C-C}=1.375$Å ($R_{C-C}=1.400$ Å)		Ha $R_{C-C}=1.400$Å
	I	II	Min.	Min.+C3d	
occ. $1a_1'$	2	2	−11.6167(−11.6113)	−11.5898(−11.5878)	−11.8156
$1e_1'$	2	2	−11.6154(−11.6102)	−11.5886(−11.5869)	−11.8137
$2a_1'$	*	2	−1.5260 (−1.5017)	−1.4983 (−1.4755)	−1.6192
$2e'$	*	2	−1.0651 (−1.0614)	−1.0602 (−1.0573)	−1.1359
$3a_1'$	*	*	−0.9813 (−0.9754)	−0.9711 (−0.9659)	−1.0588
$3e'$	*	*	−0.7956 (−0.7874)	−0.7799 (−0.7728)	−0.8770
$1a_2''$	*	*	−0.7735 (−0.7571)	−0.7574 (−0.7430)	−0.8385
unocc. $1e''$	*	*	−0.0612	−0.0905	
$1a_2'$	*	*	0.2160	0.1912	
$4e'$	*	*	0.2411	0.2245	
$4a_1'$	*	*	0.2951	0.2269	
$2e''$	*	0	—	0.5249	
$2a_2''$	*	0	—	0.5755	
$5e'$	*	0	0.6826	0.6306	
$5a_1'$	*	0	—	0.6639	
$3e''$	*	0	—	0.6921	
$6a_1'$	0	0	—	1.0808	
$1a_1''$	0	0	—	1.1593	
$6e'$	0	0	—	1.2783	
$7e'$	0	0	—	1.5378	
$2a_2'$	0	0	—	1.7914	
$8e'$	0	0	—	2.0630	

TABLE 3. C–C EQUILIBRIUM BOND DISTANCE AND C–C STRETCHING FORCE CONSTANT OF $C_3H_3^+$

	SCF				CI		Obsd
	This work				This work		
	Min.	Min.+C3d	Ha[a)]	Radom[b)]	Min.	Min.+C3d	
Total energy(a.u.)	−114.6549	−114.7388	−114.7442	−115.00369	−114.8444	−114.9466	—
C–C eq. bond dis. (Å) R^e_{C-C}	1.383	1.365	1.40	1.377	1.413	1.389	1.373[c)],1.363[d)]
Force constant (mdyn/Å) k_{C-C}	9.56	9.19	—	—	8.07	7.92	6.59[e)]

a) See Ref. 8. b) See Ref. 9. c) See Ref. 3. d) See Ref. 2. e) See Ref. 5.

for the C–C bond distance of 1.400 Å, which is used by Ha and others.[8)] Although their absolute values are larger than our values by 0.08—0.23 a.u., the order is the same and the relative positions are very similar between the two calculations.

Equilibrium C–C Bond Distance and the C–C Stretching Force Constant. By using the results shown in Fig. 1, the equilibrium C–C bond distance R^e_{C-C} and the stretching force constant k_{C-C} are determined. First, R^e_{C-C} and $k_{A_1'}$ (stretching force constant of totally symmetric vibrational mode) are calculated by expanding the potential curves in terms of a polynominal of fifth degree. Next, if we neglect the cross terms such as $\Delta r_1 \Delta r_2$ in the expansion, k_{C-C} is one third of $k_{A_1'}$. By using this relation, k_{C-C} is estimated. The R^e_{C-C} and k_{C-C} are given in Table 3 with the results of the previous calculations. It is noted that the C–C bond distance becomes larger and the C–C stretching force constant smaller by the CI calculation in comparison with the SCF results. The calculated C–C distance by CI with the Min.+C3d basis is close to the observed values at the substituted cyclopropenyl cations.[2,3)] The equilibrium C–C distance of C_6H_6 is calculated to be 1.39 Å in the SCF calculation by Newton and others.[17)] Since the calculated value of R^e_{C-C} of $C_3H_3^+$ at the SCF level is smaller than this value, the equilibrium C–C distance of $C_3H_3^+$ is expected to be smaller than that of C_6H_6. The C–C bond distance of $C_3H_3^+$ has not been determined experimentally so far.

The calculated C–C stretching force constants are improved by CI and the CI results are in fair agreement with experiment. However, it is difficult to say whether the C–C stretching force constant of $C_3H_3^+$ would be greater than that of C_6H_6, or not. One will have to calculate the stretching force constant of C_6H_6 in the same manner and to compare the result with that of $C_3H_3^+$.

Charge Distribution and Localized Molecular Orbitals. The σ-bonds of three membered ring molecules would have the maxima of charge distribution outside the ring, that is, the bonds are bent. X-Ray diffraction showed that cyclopropane has such bent bonds.[18)] In order to examine whether the calculated C–C bonds of $C_3H_3^+$ are bent or not, the contour diagrams of the charge distribution of the valence electrons are drawn, using the ground state wave functions obtained by the Min. and Min.+C3d SCF calculations and are shown in Figs. 2 and 3, respectively. The contributions of the three lowest molecular orbitals, $1a_1'$ and $1e'$, are excluded since they consist of mainly carbon core orbitals. According to these figures, the C–C bonds of

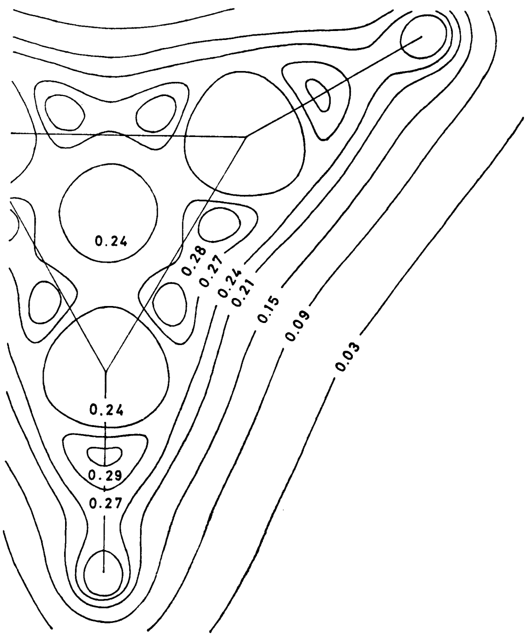

Fig. 2. Valence electron density (e/a.u.^{3}) in $C_3H_3^+$ obtained from Min. SCF.

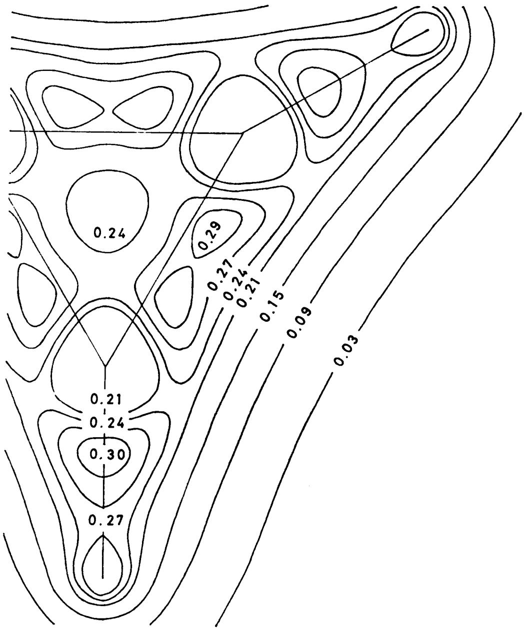

Fig. 3. Valence electron density (e/a.u.^{3}) in $C_3H_3^+$ obtained from Min.+C3d SCF.

$C_3H_3^+$ are bent having the two maxima of charge density. Ha and others also reported a similar diagram of $C_3H_3^+$.[8] However, because of the existence of the inner-shell electrons, the positions of the maxima of C–C and C–H bonds and the degree of the bending were not so clear. It is interesting to note that the charge density in the C–C and C–H bond regions increases by the addition of 3d orbitals, as is clear from Figs. 2 and 3.

The localized MO's have certain advantages over cannonical MO's in describing a bond. The occupied MO's are thus transformed into the localized MO's by the Edmiston and Ruedenberg procedure.[16] This is carried through with the Min. basis. The contour diagrams of charge distribution of the localized MO's corresponding to the C–C and C–H bonds are illustrated in Figs. 4 and 5, respectively.

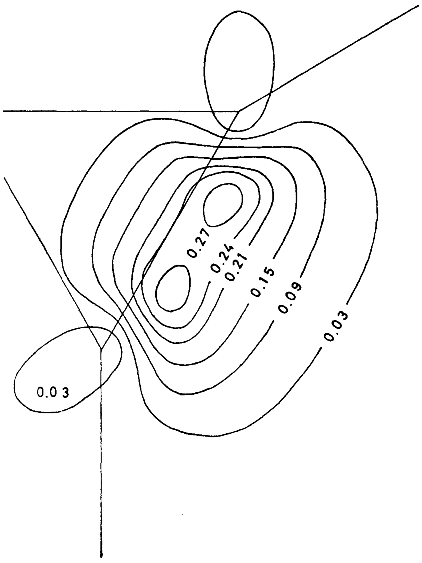

Fig. 4. Electron density (*e*/a.u.^{3}) of two electrons in a localized C–C orbital in $C_3H_3^+$.

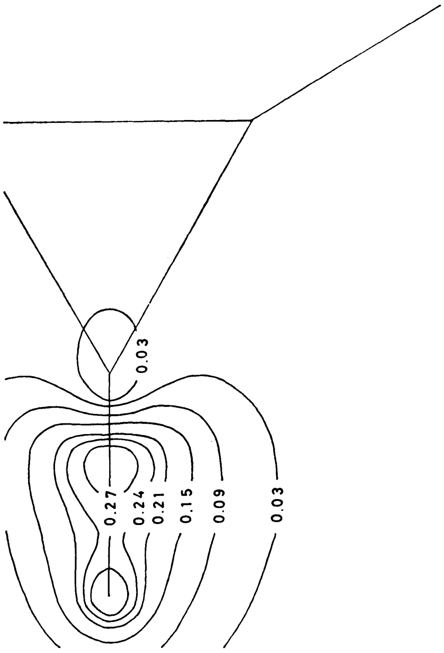

Fig. 5. Electron density (*e*/a.u.^{3}) of two electrons in a localized C–H orbital in $C_3H_3^+$.

Table 4. Ratios of the hybrid orbitals and $J_{^{13}C-H}$

	sp^x		$J_{^{13}C-H}$(Hz)
	C–C	C–H	
C_2H_4	1.74	1.85[a]	157[b]
C_6H_6	1.73	1.87[a]	159[b]
$C_3H_3^+$	2.28	0.99	265[c]

a) See Ref. 20. b) See Ref. 21. c) See Ref. 1.

The ratio of 2s and 2p orbitals in a hybrid sp^x is estimated by the coefficients of these localized MO's. The values of x are given by $(C_{2ph}^2+C_{2pv}^2)/C_{2s}^2$, where C_{2s}, C_{2ph}, and C_{2pv} are the coefficients of STO's in the localized MO's. Newton and others reported the ratio for several molecules determined by the same procedure.[19,20] The ratio for $C_3H_3^+$ is compared with their results of C_2H_4 and C_6H_6 in Table 4. It is seen that the localized MO's of C_2H_4 and C_6H_6 are rather similar to the sp^2 hybrid orbitals in the region around the carbon nuclei. In the same region, the C–H bond orbital of $C_3H_3^+$ has a higher s-character than C_2H_4 and C_6H_6 and is closer to an sp hybrid. Breslow pointed out that the ^{13}C–H coupling constant $J_{^{13}C-H}$ of NMR spectra of $C_3H_3^+$ is quite large.[1] The values of coupling constant of C_2H_4, C_6H_6,[21] and $C_3H_3^+$ are also included in Table 4. As was shown by Ramsey,[22] the Fermi contact term which gives a dominant contribution to the constant, is proportional to the density of s-electrons at the two nuclei. In Table 4, this relation is seen to hold approximately, namely, $1/3 : 1/2 \simeq 159 : 265$.

Low Lying Excited States. The electronic structure

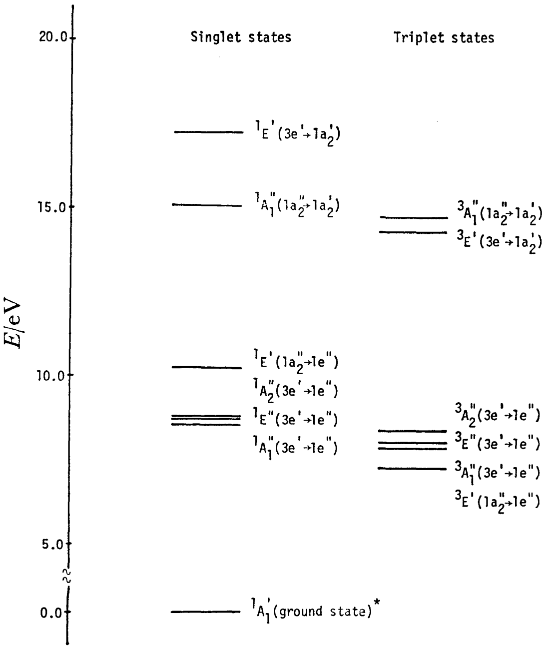

Fig. 6. Excitation energies of $C_3H_3^+$.
* −114.8003 a.u. obtained by CI calculation with occupation II basis. Dimension of CI is 140 in C_{2v} symmetry.

of excited states in highly strained molecules is of considerable experimental and theoretical interest. The excitation energies of $C_3H_3^+$ has never been measured, probably because of its instability. CI calculations of the low lying excited states of $C_3H_3^+$ are carried out for the geometry with the C–C bond distance of 1.400 Å and the results are given in Fig. 6. In these calculations, the occupation Scheme II is used. The values in Fig. 6. are the excitation energies of the π-π^*($1a_2''\rightarrow 1e''$), π-σ^*($1a_2''\rightarrow 1a_2'$), σ-π^*($3e'\rightarrow 1e''$), and σ-σ^*($3e'\rightarrow 1a_2'$) states. It should be noted that the singlet σ-π^* states ($^1A_1''$, $^1E''$, $^1A_2''$) are lower than the singlet π-π^* state ($^1E'$). All excited states are represented well by a single configuration except for the singlet σ-σ^* state ($^1E'$) and in these states the weights of the leading configurations are as big as 82—96%. In the singlet σ-σ^* state ($^1E'$), the weight of leading configuration is 47% and that of $(3a_1')^2(3e')^3(1a_2'')^2(4e')^1$ is 36%.

Conclusions

The LCAO MO SCF and CI calculations are carried out on the electronic structure of $C_3H_3^+$ and the following conclusions are obtained.

1. The calculated C–C bond distance of $C_3H_3^+$ is 1.389 Å. This is close to the experimental values of the substituted cyclopropenyl cations. The C–C distance of $C_3H_3^+$ is expected to be shorter than that of C_6H_6. The C–C stretching force constant is calculated to be 7.92 mdyn/Å, and is close to the experimental value of 6.59 mdyn/Å.
2. The contour diagram of the charge distribution of valence electrons indicates that the σ-bonds of $C_3H_3^+$ are bent outwardly.
3. The ratio, x of a hybrid orbital sp^x to be found in $C_3H_3^+$ is estimated by the coefficients in the localized MO's. The value x of the C–H bond is 0.99 reflecting that the bond has a larger s-character, compared with the C–H bonds in C_2H_4 and C_6H_6. This is in accord with the very large NMR coupling constant $J_{^{13}C-H}$ of the ion.
4. The low lying excited states of $C_3H_3^+$ are calculated by the CI calculations. The singlet σ-π^* state ($^1A_1''$, $^1E''$, $^1A_2''$) are lower than the singlet π-π^* state ($^1E'$).

We wish to thank Professor Fukashi Sasaki, Professor Hiroshi Kashiwagi, Dr. Kiyoshi Tanaka, and Dr. Hiroshi Tatewaki for helpful suggestions and discussions. Thanks are also due to Dr. Kiyoshi Tanaka, Dr. Hiroshi Tatewaki, Mr. Tsutomu Nomura, and Dr. Takeshi Noro for making their CI program package COMICAL available. The calculations reported in this paper were carried out on the FACOM 230-75 computer at the Hokkaido University Computing Center.

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