

Symmetry-adapted cluster–configuration interaction method applied to high-spin multiplicity

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The SAC–CI (symmetry-adapted cluster–configuration interaction) method is extended to high-spin multiplicity and applied to the quartet, quintet, sextet, and septet states of N_2 , N_2^+ , OH, and *m*-phenylenebis(methylene) (*m*-PBM) molecules. The results show good agreement with those of the full-CI reference calculations, though the dimensions of the calculations are much smaller than those of the full-CI method. The smallness of the calculational efforts and the excellent agreement with the full-CI results assure that the SAC–CI method is useful and accurate not only for singlet, doublet, and triplet states but also for high-spin multiplet states.

I. INTRODUCTION

High-spin states sometimes occur for molecules with degenerate or near-degenerate orbital structures. Some transition metal complexes and clusters have high-spin states in their ground and excited states. For linear molecules, high-spin states often play a significant role in predissociation and recombination processes.^{1–5} For example, $1^5\Sigma_g^+$ state of N_2 is known to be responsible for the predissociation of $a^1\Pi_g$ and $B^3\Pi_g$ states and for the recombination of the two $N(^4S)$ atoms.² The predissociation observed for the $A^2\Sigma^+(v=2)$ state of the OH radical is attributed to the existence of the repulsive $1^4\Sigma^-$ state.^{3–5} Other interesting examples of high-spin states are organic ferromagnetic molecules:^{6–14} several organic π -conjugated molecules composed of methylene and phenylene fragments show ferromagnetism in their ground state due to “topological degeneracy.” Molecules of high-spin ground states up to tridecet ($S=6$) state have been synthesized.¹¹ For some ferromagnetic molecules, several different spin states lie closely together,¹² so that accurate theoretical information on the relative stability is very important for definite identifications. However, these molecules are sometimes so large that the calculations including spin and electron correlations with large basis sets are difficult. In this sense, we need a theory that is useful and yet accurate for all the low- and high-spin multiplicities.

The SAC (symmetry-adapted cluster)/SAC–CI theories are based on the cluster expansion method and are designed to describe electron correlations efficiently.^{15–18} The method has been applied successfully to various systems of excited, ionized, and electron-attached states and has been confirmed to be simple and accurate enough to be useful.¹⁸ The SAC–CI theory was originally formulated for arbitrary spin multiplicity,¹⁶ though the implementation has been limited so far up to triplet-spin multiplicity.¹⁹ The method has been extended to arbitrary multireference cases.^{20,21} In the present article, we apply the SAC–CI method to the calculations of several high-spin multiplet states, namely, quartet, quintet, sextet, and septet states.

Benchmark calculations have been performed for the high-spin states of N_2 , N_2^+ , OH, and *m*-phenylenebis(methylene) molecules. The accuracy of the SAC–CI results is examined by comparing with the full-CI results.

II. METHOD AND CALCULATIONS

The SAC wave function is expressed as¹⁵

$$\Psi_g^{\text{SAC}} = Q \exp\left(\sum_I C_I S_I^\dagger\right) |0\rangle,$$

where $|0\rangle$ is a single determinant (usually Hartree–Fock), S_I^\dagger a symmetry-adapted excitation operator, and Q a symmetry projector. The SAC–CI wave function is constructed by applying the reaction operator \mathfrak{R} to the SAC wave function as¹⁶

$$\Psi_e^{\text{SAC-CI}} = \mathfrak{R} \Psi_g^{\text{SAC}},$$

where the excitator \mathfrak{R} generates excited, ionized, and electron-attached states. The excitator \mathfrak{R} is expanded by a linear combination of the excitation operators as

$$\mathfrak{R} = \sum_K d_K P R_K^\dagger,$$

where P is the projector that projects out the space of the SAC wave function, and R_K^\dagger is the excitation, ionization, or electron attachment operator.¹⁶ In the present SAC–CI method for high-spin multiplicity, the R_K^\dagger operator is defined to generate the corresponding high-spin multiplicity.

In the program SAC85,¹⁹ the R_K^\dagger operators represent single and double excitations. Recently, we reported that the inclusion of higher excitation operators is effective for improving the accuracy for multiple-electron excitation processes.²² In the present calculation, we follow the spirit of the program SAC85: we include two- and three-electron excitation operators, $R(2)$ and $R(3)$, for R_K^\dagger of the quartet and quintet states. Namely, as shown in Table I, the symmetry-adapted $2h-1p$, $3h-2p$ and $2h-2p$, $3h-3p$ operators are included for quartet and quintet states, respectively.

TABLE I. Linked and unlinked operators included in the present calculation.

Spin multiplicity	Linked operator ^{a,b}		Unlinked operator ^c
Quartet	$R(2) = R_{ij}^a$ $= a_{aa}^\dagger a_{ib} a_{j\beta}$	$R(3) = S_i^a R_{jk}^b$	$S(2) R_{ij}^a$
Quintet	$R(2) = R_{ij}^{ab}$ $= a_{aa}^\dagger a_{ib} a_{j\beta} a_{\alpha\beta}$	$R(3) = S_i^a R_{jk}^{bc}$	$S(2) R_{ij}^{ab}$
Sixtet	$R(3) = R_{ijk}^{ab}$ $= a_{aa}^\dagger a_{ib} a_{j\beta} a_{\alpha\beta} a_{k\gamma}$	$R(4) = S_i^a R_{jkl}^{bc}$	$S(2) R_{ijk}^{ab}$
Septet	$R(3) = R_{ijk}^{abc}$ $= a_{aa}^\dagger a_{ib} a_{j\beta} a_{\alpha\beta} a_{k\gamma} a_{\delta\epsilon}$	$R(4) = S_i^a R_{jkl}^{bcd}$	$S(2) R_{ijk}^{abc}$

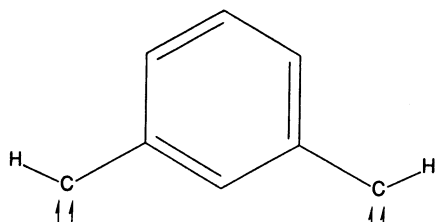
^aThe operator S_i^a denotes singlet-type single excitation operator; $S_i^a = (a_{aa}^\dagger a_{ia} + a_{ab}^\dagger a_{ib})/\sqrt{2}$.

^bValues in parentheses denote excitation levels relative to the closed-shell Hartree-Fock configuration.

^cThe operator $S(2)$ denotes double-excitation operators like $S_i^a S_j^b$ of Ψ_g^{SAC} .

Three- and four-electron excitation operators, $R(3)$ and $R(4)$, are used for sextet and septet states. We include all independent spin functions, except for the case stated later. The explicit forms of these linked operators are given in Table I. For the unlinked operators, we include the products of the double-excitation operators S_j^\dagger of Ψ_g^{SAC} and the lower-excitation operators of R_K^\dagger , which are $R(2)$ for quartet and quintet states and $R(3)$ for sextet and septet states; for quartet, for example, $\{S_i^a S_j^b \times R_{kl}^c\}$ operators are included, but $\{S_i^a S_j^b \times R_{klm}^{cd}\}$ operators are not included except for the calculations of the quartet states of OH radical. The unlinked operators included in the present calculation are also summarized in Table I.

The present method is applied to the several lower states of the singlet to septet states of N_2 , N_2^+ , OH, and *m*-phenylenebis(methylene) (*m*-PBM) molecules. The internuclear distances of N_2 and N_2^+ are taken to be 1.097 68 Å for all the states, which is the equilibrium distance of the ground state of the N_2 molecule. The OH distance of 0.969 66 Å, which is again the equilibrium distance for the ground state, is used for all the states of OH. The molecular structure of *m*-PBM is depicted in Fig. 1. The phenylene and methylene geometries are borrowed from those of the free benzene and methylene: the C-C and C-H lengths in the benzene ring are set to 1.397 Å and 1.084 Å, respectively, and the C-C-H angle and the C-H length of the methylene group are 140° and 1.08 Å, respectively. The basis set of N is the [4s2p] set of Huzinaga and

FIG. 1. *m*-phenylenebis(methylene) molecule.

Dunning²³ plus the Rydberg *s* function with $\zeta_s = 0.028$. The basis set for OH is the [4s2p/2s] set.²³ For the *m*-PBM molecule, the STO-6G basis is used. The resultant SCF dimensions are 22, 12, and 46 for N_2 , OH, and *m*-PBM, respectively.

The SAC/SAC-CI calculations are performed without configuration selection. The high-spin calculations are carried out by modifying the SAC85 program.¹⁹ The RHF MOs are calculated by the program HONDO7²⁴ and are used as the reference orbitals. The full-CI calculations are performed for examining the accuracy of the present method. In order to keep the size of the full-CI calculation to be practical, the active space is limited to be very small: five occupied and five unoccupied MOs are adopted for N_2 ; $(2s\sigma_g)^2(2s\sigma_u)^2(p\pi_u)^4(p\sigma_g)^2$ (Rydberg *s*, σ_g) (Rydberg *s*, σ_u) $(p\pi_g)(p\sigma_u)$, and four occupied and seven unoccupied MOs for *m*-PBM. For the OH radical, all 12 MOs are included in the active space. The full-CI calculation of the OH radical is performed by using the Slater-determinant-based algorithm of Knowles *et al.*²⁵ coded by Momose.²⁶ Other full-CI calculations are done using the program HONDO7.²⁴

III. RESULTS

A. N_2 and N_2^+

First, we investigate the accuracy of the present method for N_2 and N_2^+ . They have a number of excited states of various spin multiplicity. The valence MO of N_2 is $(p\sigma_g)^2(p\pi_u)^4(p\pi_g)(p\sigma_u)$ in its ground state. Six or five electrons distribute among these orbitals, and therefore high-spin states up to septet state exist for N_2 and those up to sextet state for N_2^+ . Some of these high-spin states are important in the predissociation and recombination processes. Potential curves of these high-spin states cross those of the low-spin states and lead to predissociations. For example, $1^5\Sigma_g^+$ state is a predissociation path of a $1^1\Pi_g$ and $B^3\Pi_g$ states, and $1^7\Sigma_u^+$ state dissociates into $N(^4S^0) + N(^4S^0)$ which is the same atomic limit as the $X^1\Sigma_g^+$ state.

We carry out full-CI and SAC/SAC-CI calculations of N_2 and N_2^+ at the equilibrium geometry ($R = 1.097$ 68 Å) of the ground state of N_2 . The results are summarized in Tables II and III, which show the leading configurations, total energies, and the size of calculations. "Excitation level" denotes the number of electrons involved in the excitation from the HF closed-shell configuration. The present choice of the linked operators corresponds to that of the SAC-CI (SD) method,²² and therefore the present calculations give reliable energies for the states whose main configurations are generated by the lower-level excitation operators of the linked term; i.e., single excitations for the states up to triplet-spin multiplicity, double excitations for quartet and quintet states, and triple excitations for sextet and septet states. Tables II and III include only such states. In order to describe the states generated by many-electron processes, higher multiple-excitation operators should be included in the R_K^\dagger operators.²²

The results for the ground and low-lying excited states

TABLE II. Full-CI and SAC-CI results for singlet, doublet, and triplet states of N_2 and N_2^+ .

State	Excitation level	Main configuration ^a	Size	SAC-CI		Excitation energy (Δ^c)		Full-CI		Expt. (eV)	
				Total energy (Δ^b) (a.u.)		(eV)		Total energy (a.u.)	Excitation energy (eV)		
Singlet states											
$X^1\Sigma_g^+$	0	0.97(22222)	72	-108.963 14	(1.78)	0.0		2640	-108.964 92	0.0	
$a^1\Pi_g$	1	0.95(222211)	34	-108.614 13	(3.90)	9.50	(0.07)	2408	-108.618 03	9.43	9.39 ^d
$a'^1\Sigma_u^-$	1	0.70(222121) +0.70(2212201)	26	-108.570 18	(6.96)	10.69	(0.14)	2296	-108.577 14	10.55	10.15-10.45 ^d
Average discrepancy					(4.21)		(0.11)				
Doublet states (ionized)											
$X^2\Sigma_g^+$	1	0.95(22221)	21	-108.388 66	(-0.49)	15.63	(-0.06)	3596	-108.388 17	15.69	15.60 ^e
$A^2\Pi_u$	1	0.97(22122)	13	-108.318 27	(5.47)	17.55	(0.10)	3460	-108.323 74	17.45	16.98 ^e
$B^2\Sigma_u^+$	1	0.91(21222)	27	-108.261 69	(7.38)	19.09	(0.15)	3596	-108.269 07	18.94	18.78 ^e
Average discrepancy					(4.45)		(0.07)				
Triplet states											
$A^3\Sigma_u^+$	1	0.70(221221) +0.70(2221201)	63	-108.659 43	(2.98)	8.26	(0.03)	3788	-108.662 41	8.23	7.86 ^d
$B^3\Pi_g$	1	0.96(22211)	50	-108.660 70	(2.96)	8.23	(0.03)	3720	-108.663 66	8.20	8.12 ^d
$W^3\Delta_u$	1	0.70(222121) -0.70(2212201)	63	-108.612 70	(5.65)	9.54	(0.11)	3788	-108.618 35	9.43	9.15-9.3 ^d
$C^3\Pi_u$	1	0.93(2122201)	58	-108.539 63	(5.09)	11.52	(0.09)	3720	-108.544 72	11.43	11.25 ^d
$E^3\Sigma_g^+$	1	0.94(222210001)	62	-108.513 27	(-0.44)	12.24	(0.06)	3688	-108.512 83	12.30	(11.95-12.0) ^{d,f}
Average discrepancy					(3.42)		(0.05)				

^aThe MO ordering is (σ_g) (σ_u) ($p_x\pi_u$) ($p_y\pi_u$) ($p\sigma_g$) ($p_x\pi_g$) ($p_y\pi_g$) ($p\sigma_u$) (Rydberg s,σ_g) (Rydberg s,σ_u).

^bDeviation from the full-CI results (in mhartree).

^cDeviation from the full-CI results (in eV).

^dReferences 28-30.

^eReference 31.

^fUncertainty in the experimental value is 0.2 eV (Ref. 29); the T_0 value is 11.89 eV (Ref. 28).

of low-spin multiplet states of N_2 and N_2^+ molecules, namely singlet, doublet (ionized), and triplet states are summarized in Table II: the SAC-CI and full-CI results are compared to each other. Three singlet and doublet states and five triplet states are calculated. The SAC-CI method reproduces the correct ordering of these states calculated by the full-CI method. The deviations of the SAC-CI results from the full-CI ones are within 7.5 mhartree in the total energy and within 0.15 eV in the excitation energy. The average discrepancies in the total energy and the excitation energy are 3.92 mhartree and 0.08 eV, respectively. The sizes of the SAC-CI calculation are quite small, less than 100, and two orders of magnitude smaller than the full-CI ones. Thus the SAC-CI method is very effective for these low-spin states, as already confirmed by many calculations.^{16,18,27}

The excitation energies for the low-spin states are also compared with the experimental values.²⁸⁻³¹ Because of the insufficiency in the basis set and the active space, the present results do not necessarily reproduce the experimental values. However, the ordering of the excited states is properly reproduced except for the $A^3\Sigma_u^+$ state and the excitation characters are the same as those reported in the previous calculations using extend basis set.³⁰ The deviations from the experimental values are to within 0.3 eV. Further, the ionization potentials are calculated as 15.63, 17.55, and 19.09 eV for the $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ states, respectively, which are compared with the experimental values, 15.69, 16.98, and 18.78 eV, respectively.³¹

Next, we examine the results for the high-spin multiplicities. Eight quartet states of N_2^+ are calculated. These quartet states dissociate into $N(^4S^0) + N(^3P)$ and $N(^4S^0) + N(^1D)$ in their atomic limits. $2^4\Pi_u$ and $2^4\Pi_g$ states whose main configurations are described by three-electron excitation operators are omitted. These eight quartet states exist in a narrow energy region (within 0.18 a.u.); nevertheless, the present SAC-CI calculation gives the same correct ordering as the full-CI one. The average deviations from the full-CI results are 3.46 mhartree for total energy and 0.06 eV for the ionization energy. These deviations are very small, though the dimensions of the SAC-CI calculations are only 85-89, very small in comparison with the full-CI ones, 2400-2500. This shows the efficiency of the SAC-CI method for the quartet states. Among these states, some quartet states are lower than the shake-up states like $C^2\Sigma_u^+$ and $D^2\Pi_g$ states.

We calculate ten quintet spin states and they dissociate into $N(^4S^0) + N(^4S^0)$, $N(^4S^0) + N(^2D^0)$, and $N(^4S^0) + N(^2P^0)$ in the atomic limits. These high-spin states of the N_2 molecule lie in a higher-energy region than the first ionized state ($X^2\Sigma_g^+$): a reason is that the present calculation gives the vertical excitation energy. The lowest four states, $1^5\Pi_u$ to $1^5\Pi_g$, have valence excitation nature, while the following six states have the Rydberg components at the present geometry. Again, the SAC-CI calculation gives a correct ordering for all of these ten quintet states. The average discrepancy of the SAC-CI results from the full-CI ones is only 2.27 mhartree, though the dimensions

TABLE III. Full-CI and SAC-CI results for quartet, quintet, sextet, and septet states of N_2 and N_2^+ .

State	Excitation level	Main configuration ^a	SAC-CI		Full-CI		Difference (mhartree)
			Size	Energy	Size	Energy	
Quartet states (ion) ^b							
$1^4\Sigma_u^+$	2	0.68(222110001) + 0.68(22121001)	89	-108.076 06	2416	-108.075 61	-0.45
$1^4\Delta_u$	2	0.68(22211 001) + 0.68(221210001)	87	-108.027 87	2524	-108.030 24	2.37
$1^4\Pi_u$	2	0.96(212210001)	87	-108.005 66	2480	-108.011 84	6.18
$1^4\Sigma_u^-$	2	0.68(22211001) - 0.68(221210001)	87	-108.002 57	2524	-108.007 87	5.30
$1^4\Pi_g$	2	0.98(221120001)	89	-107.975 44	2480	-107.977 92	2.48
$1^4\Sigma_g^+$	2	0.66(21122001) + 0.66(212120001)	85	-107.965 63	2524	-107.966 68	1.05
$1^4\Delta_g$	2	0.66(21122001) - 0.66(212120001)	87	-107.916 63	2416	-107.919 95	3.32
$1^4\Sigma_g^-$	2	0.66(21212001) - 0.66(211220001)	85	-107.893 88	2524	-107.900 43	6.55
Average discrepancy							
Quintet states ^c							
$1^5\Pi_u$	2	0.98(221210011)	128	-108.377 14	1540	-108.377 56	0.42
$1^5\Sigma_g^+$	2	1.00(221120011)	124	-108.358 19	1540	-108.358 38	0.19
$1^5\Sigma_u^-$	2	0.98(212210011)	128	-108.340 24	1580	-108.346 65	6.41
$1^5\Pi_g$	2	0.95(212120011)	120	-108.269 21	1540	-108.269 99	0.78
$1^5\Sigma_u^+$	2	0.68(22121101) + 0.68(222111001)	116	-108.203 47	1515	-108.206 11	2.64
$2^5\Sigma_g^+$	2	0.65(222110101) + 0.65(22121011)	124	-108.167 90	1540	-108.170 82	2.92
$1^5\Delta_u$	2	0.68(22211101) + 0.68(221211001)	116	-108.160 48	1515	-108.160 45	-0.03
$2^5\Pi_u$	2	0.96(212211001)	128	-108.132 64	1540	-108.138 90	6.26
$1^5\Delta_g$	2	0.65(222110101) - 0.65(22121011)	124	-108.124 78	1540	-108.124 85	0.07
$2^5\Pi_g$	2	0.90(221121001) - 0.38(21221011)	120	-108.105 37	1540	-108.108 31	2.94
Average discrepancy							
Sextet states (ion) ^d							
$1^6\Pi_g$	3	0.99(212110011)	98	-107.760 82	615	-107.761 20	0.38
$1^6\Sigma_g^+$	3	0.97(221110011)	98	-107.743 08	629	-107.743 22	0.14
$1^6\Sigma_u^+$	3	0.99(211120011)	96	-107.629 94	629	-107.629 88	-0.06
Average discrepancy							
Septet state ^e							
$1^7\Sigma_u^+$	3	0.91(221110111)	80	-107.844 80	287	-107.844 98	0.18

^aThe MO ordering is $(\sigma_g)(\sigma_u)(p_x, p_y, p_z)(p_x, p_y, p_z)(p_x, p_y, p_z)(p_x, p_y, p_z)(p_x, p_y, p_z)(p_x, p_y, p_z)(p_x, p_y, p_z)(p_x, p_y, p_z)$.

^bQuartet states which dissociate to $N(^4S^0) + N(^3P)$ and $N(^4S^0) + N(^1D)$.

^cQuintet states which dissociate to $N(^4S^0) + N(^4S^0)$, $N(^4S^0) + N(^2D^0)$, and $N(^4S^0) + N(^2P^0)$.

^dSextet states which dissociate to $N(^4S^0) + N(^3P)$.

^eSeptet state which dissociates to $N(^4S^0) + N(^4S^0)$.

of the SAC-CI calculation are very small in comparison with the full-CI ones.

Next, three states of the sextet spin multiplicity are calculated: they dissociate into $N(^4S^0) + N(^3P)$. The errors for these sextet states are within 0.4 mhartree and the average error is only 0.19 mhartree. Finally, only one septet state $1^7\Sigma_g^+$ is calculated. This state is described by a three-electron operator and has a Rydberg nature at this geometry. Since the excitation level increases as the spin multiplicity increases, the number of independent spin functions, and therefore the dimensions of the SAC-CI calculation, increase relative to that of the full-CI method: the ratio is ~ 0.04 for quartet and 0.28 for septet. However, when we introduce the configuration selection method³² or the method described below, we can much reduce the size of the SAC-CI calculation.

We thus conclude that the SAC-CI method gives accurate and efficient descriptions of not only the low-spin multiplicities, singlet, doublet, and triplet, but also the high-spin ones, quartet, quintet, sextet, and septet of the N_2 and N_2^+ molecules.

B. OH radical

Next, we investigate the low-lying electronic states of the OH radical at the equilibrium geometry ($R=0.969 66$

Å) of the ground state. We summarize the result in Table IV. The ground state $X^2\Pi$ and the first excited state $A^2\Sigma^+$ of OH are well described by the one-electron excitation operators, so that these states are properly described by the present SAC-CI (SD) method. The errors of the SAC-CI results are within 2 mhartree. The smallness of the SAC-CI calculation is remarkable: the SAC-CI dimensions are only 44 and 77 in comparison with the full-CI dimensions of 98044 and 97616, respectively.

Two quartet states, $1^4\Sigma^-$ and $1^4\Pi$, exist in a low-energy region and have the electronic configurations, $(p\sigma)^2(p\pi)^2(\sigma^*)^1$ and $(p\sigma)^1(p\pi)^3(\sigma^*)^1$, respectively. The total energy of the $1^4\Sigma^-$ state calculated by the SAC-CI method is somewhat worse (the error is 13.9 mhartree) than the preceding results. This SAC-CI calculation is the same as before and includes only $S(2)R_{ij}^a$ type unlinked operators as shown in Table I. We denote this calculation as "without H35" in Table IV. Examining the calculated result, we find that the $1^4\Sigma^-$ state has some nature of three-electron excitation at this geometry. Therefore we examine the effect of the unlinked terms of the form $\{S_i^a S_j^b \times R_{klm}^{cd}\}$. For saving computer time, we include only such unlinked terms of the R_{klm}^{cd} operators whose CI coefficients in the $\{R_K^\dagger|0\rangle\}$ space is larger than 0.1. The result is given in the column under "with H35": the deviation

TABLE IV. Full-CI and SAC-CI results for doublet and quartet states of the OH radical.

State	Excitation level	Main config. ^a	SAC-CI				Full-CI				Expt. (eV)
			Without H35 ^b		With H35 ^b		Total energy (a.u.)	Excitation energy (eV)	Size	Excitation energy (eV)	
			Total energy (a.u.)	Excitation energy (Δ^c) (eV)	Total energy (a.u.)	Excitation energy (Δ^c) (eV)					
Doublet states											
$X^2\Pi$	1	0.96(2221)	44	-75.492 96	(1.67)	98044	-75.494 63	4.22	4.05 ^e		
$A^2\Sigma^+$	1	0.96(2122)	77	-75.337 80	(1.73)	97616	-75.339 53				
Quartet states											
$1^4\Sigma^-$	2	0.90(22111)	328	-75.178 13	(13.93)	66351	-75.192 06	8.23	8.23		
$1^4\Pi$	2	0.92(21121)	356	-75.070 75	(5.82)	50904	-75.076 57	11.31(-0.07)	11.38		

^aThe MO ordering is $(2s)(p\sigma)(p_x, p_y)(p_z, \pi^*)(\sigma^*)$.

^bH35 means the unlinked integrals of the form $\langle 0 | R(3)HS(2)R(3) | 0 \rangle$.

^cDeviation from the full-CI results (in mhartree).

^dDeviation from the full-CI results (in eV).

^eExperimental value is term energy; Reference 33.

TABLE V. Full-CI and SAC-CI results of 1^5A_1 state for *m*-phenylenebis(methylene).

Method	Main configuration ^a	Size	Energy (a.u.)	Difference (mhartree)
Full-CI	0.68(221111) +0.41(2211101) -0.38(22110101) -0.23(22110011)	5462	-305.527 29	0.0
SD-CI ^b		354	-305.479 48	47.81
SAC-CI (Full)		354	-305.520 56	6.73
SAC-CI (1-ref) ^c		122	-305.519 20	8.09
SAC-CI (4-ref) ^d		216	-305.520 50	6.79

^aThe MO ordering is

(core)(a_2)(b_1)(a_1)(b_2)(a_2)(b_1)(b_1)(a_2)(b_1)(a_1)(a_1).

^bWith $2h-2p$ and $3h-3p$ configurations from closed-shell HF.

^cReference configuration is (221111).

^dFour main configurations shown for full-CI are adopted as reference configurations.

from the full-CI is reduced to 4.72 mhartree. We are sure that a better improvement will be obtained if we adopt the SAC-CI(*R*-general) method reported previously.²²

The vertical excitation energy of the $A^2\Sigma^+$ state is calculated to be 4.22 eV, which is compared with the experimental term energy, 4.05 eV.³³ Two quartet states are calculated at 8.23 and 11.38 eV, which are lower in energy than the first ionization potential, 12.9 eV, though they are unstable states. The deviations from the full-CI results in the excitation energy are within 0.08 eV.

C. *m*-phenylenebis(methylene) (*m*-PBM)

Last, we investigate the ground state of *m*-phenylenebis(methylene) (*m*-PBM). This molecule is the smallest unit of a series of the organic high-spin molecules synthesized in Itoh's⁶⁻¹² and Iwamura's^{13,14} laboratories. The ground state of *m*-PBM is calculated to be 1^5A_1 state, the same result as that obtained by Teki *et al.* using the Heizenberg Hamiltonian.⁹ The total energy of this 1^5A_1 state is calculated by different methods and shown in Table V. The SD-CI calculation with the same excitation operators as in the SAC-CI calculation gives a deviation from the full-CI energy by 47.81 mhartree, very large. On the other hand, the SAC-CI result, denoted as "full" in Table V, deviates only 6.73 mhartree. The 1^5A_1 state of *m*-PBM is properly described by the two-electron excitation operators of the quintet spin multiplicity, so that the present SAC-CI calculation gives a good description.

Here, we consider a convenient method of reducing the number of linked operators in the SAC-CI calculation. The choice of the excitation operators described in Sec. II has an advantage of giving a large configuration space including various kinds of excitation nature, and therefore, is suitable for solving many roots in a wide energy region. However, the calculation of high-spin multiplicity involves many independent spin functions, and therefore, the resultant number of excitation operators becomes large. It is impossible to handle all triple- and quadruple-excitation operators when the active space is large. One possible method is to limit the excitation operators to those that

interact with the leading configurations of the reference states, namely single- and double-excitation operators relative to the reference configurations within the symmetry-adapted $2p-2h$ and $3p-3h$ operators. This procedure is also performed automatically by the configuration selection method.³² However, this method makes it possible to omit the generation of a large number of unimportant excitation operators prior to the configuration selection step.

We test this procedure for the 1^5A_1 state of m -PBM. First, we adopt only one main configuration of the 1^5A_1 state as a reference [denoted as SAC-CI (1-ref)]. The dimension is reduced to 122, in comparison with that of the SAC-CI (full) calculation, 354. The energy error is 8.09 mhartree compared with 6.73 mhartree. Next, we adopt four configurations given in Table V as reference configurations: this SAC-CI (4-ref) calculation describes most of the electron correlations obtained by the SAC-CI (full) method. The energy error of the former is 6.79 mhartree in comparison with that of the latter 6.73 mhartree. The usefulness of this method would become more remarkable as the active space becomes larger.

IV. CONCLUSION

The SAC-CI method is extended to high-spin multiplicity and the calculation is carried out for the quartet, quintet, sextet, and septet states. The present results for the several high-spin states of N_2 , N_2^+ , OH, and m -phenylenebis(methylene) (m -PBM) show good agreements with the full-CI results, though the calculational dimensions of the SAC-CI method are much smaller than those of the full-CI method. We have confirmed that the SAC-CI method is simple enough to be useful and accurate enough to be useful not only for the singlet, doublet, and triplet states,¹⁸ but also for the high-spin quartet, quintet, sextet, and septet states. We have introduced a convenient procedure to omit the generation of a large number of unimportant excitation operators before the configuration selection step. This method is useful for high-spin states.

Higher multiple-electron processes sometimes become important for high-spin states of quasidegenerate systems. We are now examining the EGCI and MR-SAC methods^{20,21,34,35} for describing the quasidegeneracy in high-spin states.

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