

Exponentially generated configuration interaction (EGCI) method applied to high-spin multiplicity

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The exponentially generated configuration interaction (EGCI) method is extended to high-spin multiplicity. This method, in which excited, ionized, and electron attached states are calculated on the basis of the correlated wave function of the ground state, is applicable to quasidegenerate states of various spin multiplicity and various number of excitation processes. The accuracy and efficiency of the EGCI method is examined for the high-spin quasidegenerate states with multiple excitation nature. Test calculations are performed for several high-spin states of C_2 , C_2^+ , N_2 , N_2^+ , and *m*-phenylenebis(methylene) (*m*-PBM) molecules. The EGCI method reproduces well the full-CI results in total energy, spectroscopic constants, and spin density distributions. The EGCI method is confirmed to be accurate and useful not only for investigating the energetics involved in the study of dynamics and reactions but also for studying spin density distributions of various spin multiplet states.

I. INTRODUCTION

High-spin states have received much attention in many fields of science.¹⁻²⁰ They play an important role in reaction dynamics and energy relaxation processes, and in the design of ferromagnetic materials. They appear in the ground and excited states of molecules with degenerate or near degenerate orbital structure, such as diatomics, metal complexes and clusters, and well-designed organic high-spin compounds, *etc.* For example, the ground state of C_2^+ is identified as quartet state $X^4\Sigma_g^+$.¹⁻⁸ Furthermore, these high-spin molecules often have quasidegenerate characters with various spin multiplet states owing to their highly degenerate open-shell structure. Therefore, theoretical method for investigating the properties and dynamics of these high-spin molecules should be able to deal with not only one high-spin state but also all of the related high-spin states in a same accuracy.

Recently, we have extended our SAC(symmetry adapted cluster)-CI method to high-spin multiplicity.²¹ The SAC-CI method²² describes excited, ionized, and electron attached states using the functional space for such states generated by the SAC calculation²³ for the ground state. This method has been shown to be very accurate and useful.²⁴ We applied the method to the high-spin states of N_2 , N_2^+ , OH, and *m*-PBM systems and confirmed that it is again accurate and efficient.²¹ The remarkable advantage of the SAC-CI method is as follows. (1) It is applicable to a large number of excited states at the same time. (2) It is applicable to a various spin multiplicities in the same manner. (3) The effect of higher order excitations are included in the nonlinear unlinked terms. (4) If such effect is essential, it can also be included in the linked term.²⁵ However, the SAC-CI method critically depends on the validity of the SAC theory, which is the single reference cluster expansion theory. There should exist at least one such state for solving SAC method. For cases in which such state does not exist, we have proposed exponentially generated

wave function (EG-WF) method²⁶ to which the MR(multireference)-SAC,²⁷ MEG(mixed exponentially generated),²⁸ and EGCI methods²⁹ belong.

The EGCI method has been designed to overcome the defect of the single-reference cluster expansion method, and nevertheless, to have desirable properties of the cluster expansion method.^{26,29} The expansion operator in the EGCI method is generated along the exponential expansion and yet free variables are given for each operator. Therefore, it is essentially one of the CI methods and therefore variational. However, it satisfies size-consistency and self-consistency to the order of truncations of the higher terms.²⁶ The EGCI method was extended to excited, ionized, electron attached states with the use of the excitator method,²⁹ which is common to the SAC-CI method.

In this paper, we apply the EGCI method to the high-spin states with quartet to septet multiplicities, and investigate its accuracy and efficiency. We apply the EGCI method to the ground and excited states of the quasidegenerate high spin states of C_2 , C_2^+ , N_2 , N_2^+ , and *m*-phenylenebis(methylene) (*m*-PBM) molecules. The accuracy of the EGCI method is examined for the energy and spin density by comparing with the full-CI results calculated at the same time for these molecules.

II. EGCI METHOD FOR HIGH-SPIN MULTIPLICITY

In this series of papers,²⁶⁻²⁹ we have introduced a new basic expansion operator defined by

$$\begin{aligned} \mathcal{E} \mathcal{L} \mathcal{P} \left(\sum_K a_K A_K^\dagger \right) \\ = Q \left(a_0 + \sum_K a_K A_K^\dagger + \frac{1}{2} \sum_{K,L} a_{KL} A_K^\dagger A_L^\dagger + \dots \right), \end{aligned}$$

where the excitation operator A_K^\dagger runs over all the space and spin symmetries and Q is a symmetry projector. Single and double excitation operators are usually adopted for the

A_K^\dagger operators. The constructions of the higher order excitation operators are made in the spirit of the cluster expansion theory: the higher order operators are generated as the products of lower-order operators as in the cluster expansion. In order to include all possible highly connected terms such as simultaneous double excitations, all independent spin and space functions are included for the product operators $\{A_K^\dagger A_L^\dagger\}$, and the redundant terms are deleted. The coefficients of the product operators a_{KL} are made free from those of the lower operators a_K , which is important for quasi-degenerate states.

The EGCI method normally starts from the totally symmetric singlet state and the wave function is defined with the $\mathcal{E}\mathcal{L}\mathcal{P}$ operator as^{26,29}

$$\begin{aligned}\Psi_g^{\text{EGCI}} &= \mathcal{E}\mathcal{L}\mathcal{P} \left(\sum_K a_K A_K^\dagger \right) |0\rangle \\ &= Q \left(a_0 + \sum_K a_K A_K^\dagger + \frac{1}{2} \sum_{K,L} a_{KL} A_K^\dagger A_L^\dagger + \dots \right) |0\rangle,\end{aligned}$$

where $|0\rangle$ is the Hartree-Fock determinant. The wave functions for the excited, ionized, and electron attached states are constructed by applying the excitation operator, \mathfrak{R} as,

$$\Psi_e^{\text{EGCI}} = \mathfrak{R} \Psi_g^{\text{EGCI}}.$$

The operator \mathfrak{R} , which is a kind of reaction operators, is called excitator in order to distinguish it from the more elemental excitation operators A_K^\dagger . This operator describes excitation, ionization, and electron attachment, and at the same time the reorganizations of orbitals and electron correlations. The excitator \mathfrak{R} is expanded by a linear combination of the excitation operators $\{B_K^\dagger\}$ as

$$\mathfrak{R} = \sum_K b_K B_K^\dagger$$

and the resultant EGCI wave function of various spin multiplicity is expressed as

$$\begin{aligned}\Psi_e^{\text{EGCI}} &= Q \left(\sum_K b_K B_K^\dagger + \frac{1}{2} \sum_{K,L} b_{KL} A_K^\dagger B_L^\dagger \right. \\ &\quad \left. + \frac{1}{3!} \sum_{K,L,M} b_{KLM} A_K^\dagger A_L^\dagger B_M^\dagger + \dots \right) |0\rangle.\end{aligned}$$

In the previous calculation for singlet, doublet and triplet states,²⁹ we included one- and two- electron operators for the B_K^\dagger operators. For higher-spin multiplicity, higher order excitation operators are necessarily included in the B_K^\dagger operators. In the present calculation, the B_K^\dagger operators are taken to be identical with the operators defined as R_K^\dagger operators in Table I of Ref. 21. For example, two- and three-electron operators, $B(2)$ and $B(3)$, are necessary for quartet and quintet states; namely, symmetry adapted $2h1p$, $3h2p$ and $2h2p$, $3h3p$ operators are adopted for quartet and quintet, respectively. The SAC-CI calculations with these operators are referred to as SAC-CI(R-DT) in the present paper.

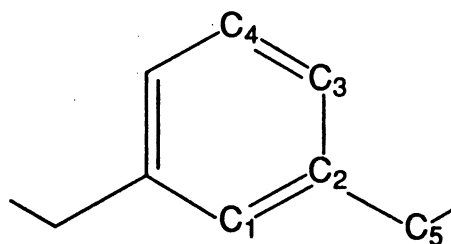


FIG. 1. Molecular structure of *m*-phenylenebis(methylene).

The physical basis of the excitator method is as follows. Electronic excitations usually involve only one or two electrons and the other electrons lie in the environments more or less similar to those of the ground state. Therefore, the correlations in the excited states are more easily described by starting from those of the ground state than by starting from the beginning. In the EGCI method, we utilize the knowledge of the ground-state correlations through the operators A_K^\dagger .

In actual applications, we adopt the configuration selection method, especially for the higher order terms. The detailed algorithm of the configuration selection in the EGCI method was reported in the preceding paper.²⁶ We adopt the same configuration selection algorithm and use the set of the thresholds $(\lambda_A, \lambda_{AA}, \lambda_{AAA})$ in the following discussions and in the tables.

III. CALCULATIONAL DETAILS

The present method is applied to several high-spin states of C_2 , C_2^+ , N_2 , N_2^+ , and *m*-phenylenebis (methylene) (*m*-PBM) molecules. In the previous report,²⁹ we have applied the EGCI method to the singlet to triplet states of C_2 , C_2^+ , and C_2^- . The potential curves of the quartet states of C_2^+ and the quintet states of C_2 are calculated at appropriate 13 points. The hyperfine splitting constant (hfsc) is calculated for the $X^4\Sigma_g^+$ state of C_2^+ with the C-C distance of 1.41 Å as in the previous theoretical studies.^{1,2} For N_2 and N_2^+ we perform calculations at the internuclear distance of 2.0 Å (1.82 r_e), because we are interested in the quasidegenerate states of these molecules. The high-spin states of N_2 at the equilibrium geometry have successfully been calculated by the SAC-CI method.²¹ The molecular structure of *m*-PBM and the numbering of the carbon atoms are depicted in Fig. 1. The molecular geometry is constructed from those of free benzene and methylene: the C-C and C-H lengths in benzene ring are set to 1.397 and 1.084 Å, respectively, and the C-C-H angle and the C-H length of the methylene group to 140° and 1.08 Å, respectively.

The basis set for carbon is the [4s2p] set of Huzinaga-Dunning³⁰ plus Rydberg *s* function with $\zeta_s = 0.023$ for the calculation of the potential curves of C_2 and C_2^+ . The minimal STO-6G set is used for the calculation of the hfsc of C_2^+ , because the complete full-CI calculations are difficult for the [4s2p] basis. The basis set for nitrogen is the [4s2p]

TABLE I. Full-CI and EGCI results for the quartet and quintet states of C_2 and C_2^+ at $R=1.2425 \text{ \AA}$.^a

State	Excitation level	Main configuration ^b	EGCI ^c		Full-CI		Difference (mhartree)
			Size	Energy	Size	Energy	
Quartet states (ion) ^d							
$1^4\Sigma_g^-$	2	0.92(221111)	239	-75.035 90	1220	-75.036 67	0.77
$1^4\Pi_g$	2	0.93(21121)	234	-75.033 22	1160	-75.034 08	0.86
$1^4\Sigma_u^-$	3	0.89(21112)	281	-74.948 60	1220	-74.949 14	0.54
$2^4\Pi_g$	2+4	0.86(2211001)+0.37(2011201)	234	-74.759 26	1160	-74.760 20	0.94
$1^4\Pi_u$	3	0.67(211111)+0.55(2120101)	296	-74.730 55	1160	-74.731 08	0.53
$1^4\Sigma_g^+$	2	0.67(211201)+0.67(2121001)	206	-74.719 48	1080	-74.720 86	1.38
$2^4\Pi_u$	3	0.55(211111)+0.48(2102101) -0.48(2120101)	296	-74.690 38	1160	-74.690 72	0.34
$1^4\Delta_g$	2	0.67(211201)-0.67(2121001)	206	-74.683 19	1220	-74.684 24	1.05
$1^4\Sigma_u^+$	3	0.57(221011)-0.57(2201101) +0.32(201211)+0.32(2021101)	252	-74.681 01	1080	-74.681 53	0.52
$1^4\Delta_u$	3	0.63(220111)+0.63(2210101)	252	-74.677 74	1220	-74.678 11	0.37
$2^4\Sigma_g^-$	2	0.67(212101)-0.67(2112001)	239	-74.649 88	1220	-74.651 03	1.15
$2^4\Sigma_u^-$	3	0.51(220111)-0.51(2210101) +0.37(21112)	281	-74.549 56	1220	-74.551 65	2.09
Average discrepancy							0.88
Quintet states ^e							
$1^5\Sigma_g^+$	2	0.66(2121101)+0.66(211211)	281	-75.315 90	950	-75.316 29	0.39
$1^5\Pi_g$	2	0.94(2211101)	216	-75.276 14	1090	-75.277 37	1.31
$1^5\Delta_g$	2	0.68(2121101)-0.68(211211)	281	-75.266 53	950	-75.266 77	0.24
$1^5\Pi_u$	3	0.91(211121)	280	-75.200 33	1030	-75.200 70	0.37
$1^5\Sigma_u^-$	2	0.89(221110001)	291	-75.121 26	1090	-75.122 78	1.52
$2^5\Sigma_g^+$	2+4	0.85(2211011)+0.40(2011211)	281	-75.026 21	950	-75.026 77	0.56
Average discrepancy							0.73

^aEquilibrium distance of the ground state of the C_2 molecule.

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

^cThe threshold of the EGCI operator is $(\lambda_A,\lambda_{AA},\lambda_{AAA})=(0,0.04,0.2)$.

^dQuartet states which dissociate to $C(^3P_g)+C(^3P_u)$.

^eQuintet states which dissociate to $C(^3P)+C(^3P)$.

set³⁰ augmented with the Rydberg s function of $\zeta_s=0.025$. For the m -PBM molecule, the STO-6G set is used for both C and H atoms.

The EGCI calculations are performed with the thresholds $(\lambda_A,\lambda_{AA},\lambda_{AAA})=(0.0,0.04,0.2)$. The EGCI program³¹ is extended for high-spin multiplicity. The RHF MOs are calculated by the program HONDO7³² and are used as the reference orbitals. The full-CI and SD-CI calculations are performed and compared with the present method. The active space is limited to be small in order to keep the size of the full-CI calculations to be practical. Ten MOs adopted for the active spaces of C_2 and N_2 system are $(2s\sigma_g)(2s\sigma_u)(p\pi_u)(p\sigma_g)$ (Rydberg s,σ_g) (Rydberg s,σ_u) $(p\pi_g)(p\sigma_u)$, and four occupied and seven unoccupied MOs are used for m -PBM. Full-CI calculations of the hfsc and the spin density are performed by using the Slater-determinant-based algorithm of Knowles *et al.*³³ coded by Momose.³⁴ Other full-CI calculations are carried out with the use of the program HONDO7.³²

IV. RESULTS

A. C_2 and C_2^+ molecules

The electronic structures of C_2 and C_2^+ are very interesting. The valence shell of C_2 molecule is described as $(2s\sigma_g)^2(2s\sigma_u)^2(p\pi_u)^4(p\sigma_g)(p\pi_g)(p\sigma_u)$ in its ground state: the bonding $p\sigma$ MO is in the unoccupied region. This

causes the existence of many quasi-degenerate states and the states of multiple excitation natures. Therefore, a number of high-spin states exist in a relatively low energy region. Actually, the ground state of C_2^+ is identified to be the quartet state $X^4\Sigma_g^+$.¹⁻⁸

Here we investigate the accuracy of the present EGCI method, applying to the high spin states of C_2 and C_2^+ and comparing the results with the full-CI ones. For the low spin states of these molecules, we have already confirmed good performance of the EGCI method in the previous paper.²⁹ We note that the basis set and the active space used here are slightly different from those in the previous case. We calculate the quartet states of C_2^+ and the quintet states of C_2 at appropriate 13 geometries. The energies and the dimensions of the EGCI and full-CI calculations are compared in Tables I and II for the two representative distances, $R=1.24253 \text{ \AA}$ (equilibrium distance r_e of the ground state of C_2) and $R=2.0 \text{ \AA}$, respectively. Excitation level characterizes the main configuration by the number of electrons involved in the excitation from the closed-shell HF configuration. Many electronic states of C_2 and C_2^+ molecules are characterized by the multiple excitations with the excitation levels two, three, and four even at the equilibrium distance, as shown in Table I.

Low-lying 12 quartet states of C_2^+ are calculated. They dissociate to $C(^3P_g)+C(^2P_u)$ in their atomic limit.² The excitation natures of these states obtained in the present

TABLE II. Full-CI and EGCI results for the quartet and quintet states of C_2 and C_2^+ at $R=2.0 \text{ \AA}$.

State	Excitation level	Main configuration ^a	EGCI ^b		Full-CI		Difference (mhartree)
			Size	Energy	Size	Energy	
Quartet states (ion) ^c							
$1^4\Sigma_g^-$	2	0.89(22111)	415	-75.043 65	1220	-75.046 05	2.40
$1^4\Delta_u$	3	0.67(220111)-0.67(2210101)	382	-74.991 92	1220	-74.992 85	0.93
$1^4\Sigma_u^+$	3	0.67(221011)+0.67(2201101)	382	-74.989 66	1080	-74.990 60	0.94
$1^4\Pi_g$	2	0.93(2211001)	406	-74.954 19	1160	-74.955 28	1.09
$1^4\Sigma_u^-$	3	0.52(220111)+0.52(2210101) -0.45(21112)	419	-74.916 81	1220	-74.919 81	3.00
$1^4\Pi_u$	3	0.85(2210011)-0.32(211111)	433	-74.877 24	1160	-74.878 55	1.31
$2^4\Sigma_g^-$	4	0.75(2200111)+0.31(210121) -0.31(2110201)	415	-74.861 56	1220	-74.867 78	6.22
$2^4\Pi_g$	2	0.75(21121)-0.31(2110102)	406	-74.843 29	1160	-74.849 50	6.21
$2^4\Sigma_u$	3	0.61(21112)+0.57(22110001)	419	-74.834 24	1220	-74.837 47	3.23
$2^4\Pi_u$	3	0.50(2120101)+0.39(12211) -0.35(211111)-0.33(211111)	433	-74.810 97	1160	-74.814 37	3.40
$1^4\Sigma_g^+$	4	0.47(211021)+0.47(2101201) +0.35(22100101)+0.35(22010011)	379	-74.781 04	1080	-74.785 35	4.31
$1^4\Delta_g$	4	0.52(211021)-0.52(2101201) +0.38(22100101)+0.38(22010011)	379	-74.780 58	1220	-74.784 18	3.60
Average discrepancy							3.05
Quintet states ^d							
$1^5\Pi_g$	2	0.93(2211101)	353	-75.400 83	1090	-75.402 98	2.15
$1^5\Sigma_g^+$	2	0.93(2211011)	412	-75.335 48	950	-75.338 37	2.89
$1^5\Pi_u$	3	0.86(2210111)-0.33(211121)	372	-75.326 00	1030	-75.326 64	0.64
$1^5\Sigma_u^-$	2	0.80(22111001)-0.40(221111)	361	-75.261 28	1090	-75.263 39	2.11
$2^5\Sigma_g^+$	2	0.54(2121101)-0.54(211211)	412	-75.258 46	950	-75.262 02	3.56
$1^5\Delta_g$	2	0.56(2121101)+0.56(211211)	412	-75.221 17	950	-75.221 88	0.71
Average discrepancy							2.01

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

^bThe threshold of the EGCI operator is $(\lambda_A,\lambda_{AA},\lambda_{AAA})=(0,0.04,0.2)$.

^cQuartet states which dissociate to $C(^3P_g)+C(^3P_u)$.

^dQuintet states which dissociate to $C(^3P)+C(^3P)$.

calculation are the same as those of the previous MRD-CI calculation with the extended basis set.² Most of these states, except for the $1^4\Sigma_g^-$, $1^4\Delta_g$, and $1^4\Sigma_u^+$ states, change their excitation natures as the change in the C-C distance. A remarkable avoided crossing occurs between the potential curves of the $4^4\Pi_g$ symmetry. $1^4\Pi_g$ state has the main electronic configuration, $(\sigma_g)^2(\sigma_u)^1(\pi_u)^3(\sigma_g)^1$ at $R=r_e$, while it is $(\sigma_g)^2(\sigma_u)^2(\pi_u)^2(\sigma_g)^1$ at $R=2.0 \text{ \AA}$. The dominant configuration of the $2^4\Pi_g$ state is just reverse as seen from Tables I and II and further changes occur at larger distance. Though many quartet states shown in Tables II and III have multiple excitation nature, the present EGCI method reproduces the full-CI results in high accuracy. The errors of the EGCI method is always positive, since it is variational. The average discrepancy for the quartet states is 0.88 and 3.05 mhartree for $R=r_e$ and $R=2.0 \text{ \AA}$, respectively. The EGCI dimension increases as the internuclear distance increases because of the quasidegenerate character of the states. Since the higher order terms are included explicitly, the efficiency of the EGCI method is inferior to that of the SAC-CI method.²¹ The calculational dimensions are 200-300 at $R=r_e$ and 380-430 at $R=2.0 \text{ \AA}$ in comparison with 1080-1220 of the full-CI method.

Six quintet states of C_2 , which dissociate to $C(^3P_g)+C(^3P_g)$ in the atomic limit, are examined in Tables I and

II. The avoided crossing occurs between the first and second $5^5\Sigma_g^+$ states: the dominant configuration of the $1^5\Sigma_g^+$ state is $(\sigma_g)^2(\sigma_u)^1(\pi_u)^3(\sigma_g)^1(\pi_g)^1$ at $R=r_e$, while that is $(\sigma_g)^2(\sigma_u)^2(\pi_u)^2(\pi_g)^2$ at $R=2.0 \text{ \AA}$. The $2^5\Sigma_g^+$ state has the complementary electronic configuration. The $1^5\Pi_u$ state also changes its electronic configuration from $(\sigma_g)^2(\sigma_u)^1(\pi_u)^2(\sigma_g)^2(\pi_g)^1$ at $R=r_e$ to $(\sigma_g)^2(\sigma_u)^2(\pi_u)^1(\sigma_g)^1(\pi_g)^2$ at $R=2.0 \text{ \AA}$. This state has three-electron excitation nature and is rather difficult to be described well. Again the results of the EGCI method is satisfactory for all the quintet states. The average discrepancy is 0.73 and 2.01 mhartree for $R=r_e$ and $R=2.0 \text{ \AA}$, respectively. The dimensions of the EGCI calculations are 200-300 at $R=r_e$ and 350-400 at $R=2.0 \text{ \AA}$, whereby those of the full-CI one are 950-1090.

The potential curves of the low-lying 12 quartet states of C_2^+ and 6 quintet states of C_2 are shown in Figs. 2 and 3, respectively. Though the active space and the basis set are small, the present calculation reproduces the overall behaviors of the potential curves reported in the previous studies.^{2,8} The total energies of the EGCI method agree with the full-CI ones with the errors less than 10 mhartree in all the nuclear distances. Therefore, the potential curves calculated by the two methods almost overlap to each other.

The spectroscopic constants for the bound quartet and

TABLE III. Spectroscopic constants for the bound quartet and quintet states of C_2 and C_2^+ .

State	Method	T_e (eV)	r_e (Å)	$\omega_e(\Delta^a)$ (cm^{-1})	$\omega_e\chi_e(\Delta^a)$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_{hump} (Å)
Quartet states (ion)								
$1^4\Sigma_g^-$	EGCI	0.0	1.48	1168 (15)	18.25 (-0.94)	1.28	0.0219	
	Full-CI	0.0	1.48	1153	19.19	1.28	0.0231	
$1^4\Pi_g$	EGCI	1.51	1.29	1863 (-11)	21.96 (-1.95)	1.68	0.0042	
	Full-CI	1.50	1.30	1874	23.91	1.67	0.0043	
$1^4\Sigma_u^-$	EGCI	2.97	1.41	1406 (13)	16.99 (-0.53)	1.40	0.0184	
	Full-CI	2.97	1.42	1393	17.52	1.40	0.0190	
$1^4\Delta_u$	EGCI	2.67	2.14	522 (5)	4.77 (-0.11)	0.62	0.0074	
	Full-CI	2.66	2.14	527	4.88	0.62	0.0072	
$1^4\Sigma_u^+$	EGCI	2.72	2.13	572 (0)	9.49 (0.50)	0.62	0.0061	
	Full-CI	2.71	2.14	572	8.99	0.62	0.0058	
$2^4\Pi_g$	EGCI	5.10	1.60	1559 (37)	16.67 (-0.17)	1.10	0.0050	2.03
	Full-CI	5.08	1.60	1522	16.70	1.10	0.0055	2.03
$1^4\Sigma_g^+$	EGCI	7.97	1.55	1103 (34)	23.01 (-1.71)	1.17	0.0178	1.92
	Full-CI	7.94	1.55	1069	24.72	1.17	0.0197	1.91
Average discrepancy				(16.43)	(0.84)			
Quintet states								
$1^5\Pi_g$	EGCI	2.98	1.70	744 (24)	12.78 (5.41)	0.97	0.0203	
	Full-CI	2.99	1.71	720	7.37	0.96	0.0163	
$1^5\Sigma_g^+$	EGCI	4.39	1.45	1298 (0)	27.78 (0.66)	1.34	0.0220	1.89
	Full-CI	4.39	1.45	1298	27.12	1.33	0.0207	1.87
$1^5\Delta_g$	EGCI	6.12	1.42	1480 (13)	6.97 (0.41)	1.40	0.0038	1.92
	Full-CI	6.11	1.42	1467	6.56	1.40	0.0037	1.93
Average discrepancy				(15.20)	(2.16)			

^aValues in parentheses show the deviations from the full-CI results (in cm^{-1}).

quintet states are calculated by the Dunham method.³⁵ The EGCI and full-CI results are compared in Table III. The term energy T_e of the quartet states of C_2^+ are calculated relative to the ground state $X^4\Sigma_g^+$. The EGCI calculation

reproduces well the full-CI results for the T_e and r_e values. The errors lie within 0.03 eV for T_e and within 0.01 Å for r_e . The present T_e and r_e values are slightly larger than those due to Petrongolo *et al.*² The EGCI results are also

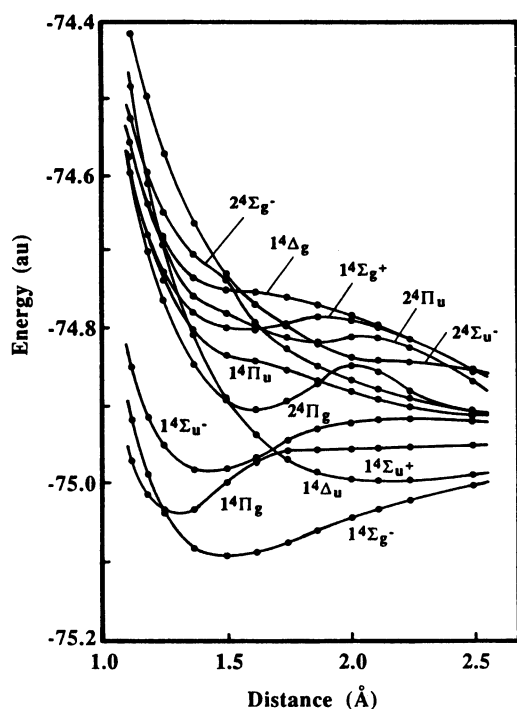


FIG. 2. Potential curves for the quartet states of C_2^+ molecule calculated by the full-CI and SAC-CI methods. Basis set is [4s2p] of Huzinaga-Dunning plus Rydberg s function with $\zeta=0.023$ and the active space is limited to four occupied and six unoccupied MOs.

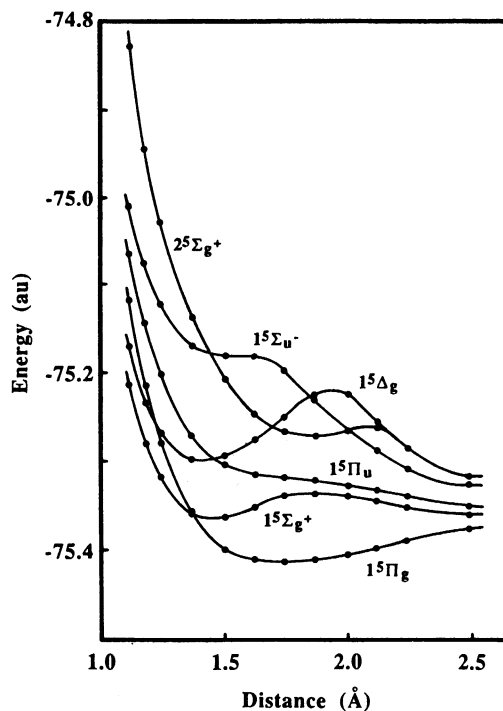


FIG. 3. Potential curves for the quintet states of C_2 molecule calculated by the full-CI and SAC-CI methods. Basis set is [4s2p] of Huzinaga-Dunning plus Rydberg s function with $\zeta=0.023$ and the active space is limited to four occupied and six unoccupied MOs.

TABLE IV. Total energy and hyperfine splitting constant (hfsc) for the $X^4\Sigma_g^-$ state of C_2^+ calculated by the EGCI, full-CI, and SD-CI method with the use of the STO-6G basis.

Method	Dimension	Total energy		Hfsc ^b		
		(a.u.)	Δ^a (mhartree)	(G)	Δ^a (G)	Δ^a (%)
full-CI ^c	3176	-75.076 86		56.37		
EGCI	223	-75.075 73	1.13	56.73	0.36	0.6
SD-CI ^d	97	-74.982 76	94.10	84.65	28.28	50.2

^aDeviation from the full-CI results.

^bExperimental hfsc is 34.5 (G).

^cReference calculation is performed using the Slater-determinant-based full-CI algorithm.

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

encouraging for the vibrational constant ω_e : the average discrepancy of ω_e is 16.43 cm^{-1} for the quartet states and 15.2 cm^{-1} for the quintet states. The vibrational anharmonicity constant $\omega_e\chi_e$ sensitively reflects the shape of the potential curve. This value is also well reproduced by the EGCI method. The average discrepancies of $\omega_e\chi_e$ are 0.82 and 2.16 cm^{-1} for the quartet and quintet states, respectively. The accuracy of the EGCI results is excellent even for the higher order terms, B_e , α_e : the errors are within 0.01 and 0.004 cm^{-1} , respectively. The shape of the repulsive potential curves is also well reproduced by the EGCI method as seen from Figs. 2 and 3.

The $2^4\Pi_g$ and $1^4\Sigma_g^+$ states of C_2^+ and the $1^5\Sigma_g^+$ and $1^5\Delta_g$ states of C_2 have characteristic humps in their potential curves. The r_{hump} in Table III gives the internuclear distance where the potential curve has the maximum in energy at the avoided crossing region. Again the EGCI method gives the excellent results for r_{hump} with the error of only $\pm 0.01 \text{ \AA}$.

Thus the EGCI method describes well the potential curves of the several quartet states of C_2^+ and the several quintet states of C_2 . These results show that the EGCI method is useful for investigating the reaction dynamics involving high spin-multiplicity.

B. Hyperfine splitting constant of the $X^4\Sigma_g^-$ state of C_2^+

Next we investigate the accuracy of the high-spin EGCI wave function in terms of hyperfine splitting constants (hfsc). Since hfsc is a local property, proportional to the spin density at the nucleus, theoretical estimation sensitively depends on the quality of the wave function used. It is important to include adequately the electron correlation and spin correlation effects.^{36,37} In particular, multiple excitation configurations are important for quantitative estimations of this property. The SAC-CI method, in which higher order terms are included in the unlinked terms, has been successfully applied to the calculations of the hfsc's of various radicals.³⁸⁻⁴³ The EGCI method, which includes higher order terms more explicitly, would also be a reliable method for calculating the hfsc's.

The ground state of the C_2^+ molecule is $X^4\Sigma_g^-$ and it has some multiple excitation nature and therefore would give a good example for the present examination. Since inner core polarization is quite important for theoretical

estimation of hfsc's, CI calculations should include all the core and valence orbitals in the active space. Because of this requirement, full-CI calculations using the extended basis are impossible, and therefore, we use the minimal STO-6G basis for the present calculation. The total energy and the hfsc of the $X^4\Sigma_g^-$ state calculated by the EGCI, full-CI, and SD-CI methods are summarized in Table IV. The full-CI method gives the hfsc of 56.37 (G) in comparison with the observed value, 34.5 (G).⁷ The SD-CI method gives the hfsc of 84.65 (G); the deviation is as large as 28.28 (G), which corresponds to 50.2% of the exact value. This indicates the importance of multiple excitations. On the other hand, the EGCI method reproduces the full-CI result quantitatively with the error of only 0.35 (G) (0.6% of the exact value). The dimension of the EGCI calculation is 223 , while that of the full-CI is 3176 .

The EGCI method for high spin multiplicity thus reproduces the full-CI results not only for the total energy but also for the hfsc. Though the examinations are only for small systems, the EGCI method, which includes the effect of multiple excitations, would give an accurate and useful method for calculating the energy and the hfsc of high-spin states.

C. N_2 and N_2^+ molecules

N_2 molecule has three higher occupied and three lower unoccupied valence MO's, and therefore, N_2 and N_2^+ molecules have a number of various high-spin states; high-spin states up to septet states exists for N_2 and up to sextet states for N_2^+ . Some of the high-spin states play an important role in the predissociation and recombination processes. However, most of these states have multiple-excitation nature at large internuclear distances, and therefore, quantitative descriptions of these states are difficult. Previously, the SAC-CI method is applied to these molecules at $R=1.09768 \text{ \AA}$, which is the equilibrium distance of N_2 in the ground state, and shown to be quite accurate for the states from singlet to septet multiplicities.²¹ Here we apply the EGCI method to the quartet to septet states of N_2 and N_2^+ at the elongated internuclear distance, $R=2.0 \text{ \AA}$. The results are summarized in Table V.

Ten quartet states of N_2 and eleven quintet states of N_2^+ are calculated. These quartet states dissociate to $N(^4S^0) + N^+(^3P)$ and $N(^4S^0) + N^+(^1D)$, and these quin-

TABLE V. Full-CI and EGCI results for the quartet, quintet, sextet, and septet states of N_2 and N_2^+ at $R=2.0$ Å.

State	Excitation level	Main configuration ^a	EGCI ^b		Full-CI		Difference (mhartree)
			Size	Energy	Size	Energy	
Quartet states (ion) ^c							
$1^4\Sigma_u^+$	2+4	0.57(222110001–22121001) +0.36(221010012–220110021)	384	–108.227 15	2416	–108.232 46	5.31
$1^4\Pi_g$	2	0.88(221120001)	417	–108.223 59	2480	–108.226 06	2.47
$1^4\Pi_u$	3	0.84(221020011)	368	–108.175 41	2480	–108.178 58	3.17
$1^4\Delta_u$	2+4	0.60(222110001+22121001) –0.31(221010012+220110021)	381	–108.164 24	2524	–108.168 26	4.23
$1^4\Sigma_g^+$	3	0.90(221110011)	378	–108.153 90	2524	–108.157 02	3.12
$1^4\Delta_g$	2	(0.69+0.55+0.39)(221110011)	378	–108.146 28	2416	–108.149 11	2.83
$1^4\Sigma_u^-$	2	0.53(22211001+221210001) –0.44(2211201)	381	–108.144 76	2524	–108.147 67	2.91
$2^4\Pi_g$	2+4	0.76(2212101)–0.38(221010102)	417	–108.120 77	2480	–108.124 70	3.93
$1^4\Sigma_g^-$	3	0.47(22111002+221110002) –0.46(222010011+220210011)	390	–108.116 26	2524	–108.119 61	3.35
$2^4\Pi_u$	3	0.54(222010101)+0.48(22111011) –0.44(22111011)	368	–108.090 26	2480	–108.093 83	3.57
Average discrepancy							3.49
Quintet states ^d							
$1^5\Sigma_g^+$	2	0.80(221120011)	306	–108.729 49	1540	–108.730 43	0.94
$1^5\Pi_u$	2+4	0.87(221210011)+0.35(221100112)	289	–108.646 25	1540	–108.647 18	1.15
$2^5\Sigma_g^+$	2+4	0.48(222110101–22121011–221120011) –0.33(221010112+220110121)	306	–108.640 91	1540	–108.641 62	0.71
$1^5\Pi_g$	3	0.78(221110021)–0.49(222100111)	273	–108.606 19	1540	–108.606 70	0.51
$1^5\Delta_g$	2+4	0.56(222110101+22121011) +0.37(221010112–220110121)	306	–108.600 38	1540	–108.600 94	0.56
$2^5\Pi_u$	2+4	0.84(22112011)–0.34(221010211)	289	–108.596 03	1540	–108.597 01	0.98
$1^5\Delta_u$	3	0.48(222010111–220210111) +0.47(221110102–221110102)	283	–108.586 59	1515	–108.587 06	0.47
$1^5\Sigma_u^+$	3	(0.60–0.58+0.34)(221110111)	283	–108.581 08	1515	–108.581 54	0.46
$1^5\Sigma_g^-$	2	0.56(22211011+221210101) +0.35(221010121+220110112)	308	–108.571 15	1540	–108.571 81	0.66
$2^5\Pi_g$	3	0.76(220120111)–0.45(221110201)	273	–108.556 44	1540	–108.557 19	0.75
$1^5\Sigma_u^-$	3	0.47(222010111+220210111) –0.46(221110102+221110102)	297	–108.555 52	1580	–108.556 05	0.53
Average discrepancy							0.70
Sextet states (ion) ^e							
$1^6\Sigma_g^+$	3	0.97(221110011)	190	–108.230 46	629	–108.230 66	0.20
$1^6\Pi_u$	3	0.92(22111011)–0.33(2211100101)	180	–108.154 96	615	–108.155 15	0.19
$1^6\Pi_g$	4	0.91(220110111)–0.32(2201100111)	198	–108.096 62	615	–108.097 57	0.95
$1^6\Sigma_u^+$	4	0.79(221100111)+0.45(211120011)	201	–108.057 95	629	–108.059 19	1.24
Average discrepancy							0.65
Septet state ^f							
$1^7\Sigma_u^+$	3	0.95(221110111)+0.31(2211100111)	120	–108.687 11	287	–108.687 28	0.17

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

^bThe threshold of the EGCI operator is $(\lambda_A, \lambda_{AA}, \lambda_{AAA}) = (0, 0.04, 0.2)$.

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

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

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

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

tet states to $N(^4S^0) + N(^4S^0)$, $N(^4S^0) + N(^2D^0)$, and $N(^4S^0) + N(^2P^0)$ in their atomic limits. At $R=1.098$ Å, most of these states are described by two electron excitations from the closed-shell configuration, so that the SAC-CI (R-DT) method gave an excellent result.²¹ However, at 2.0 Å, three- and four-electron excitations become important, as seen from Table V, and therefore, multiple excitations are essentially important for the descriptions of these states. However, as seen from Table V, the EGCI method gives very accurate descriptions for all the states. The average discrepancies in the total energy are 3.49 and

0.70 mhartree for the quartet and quintet states, respectively. The dimensions of the EGCI calculations are about one-sixth of those of the full CI for the quartet states and one-fifth for the quintet states.

Four sextet states of N_2^+ are examined and they dissociate to $N(^4S^0) + N(^3P)$ in the atomic limit. The dominant configurations of the $1^6\Pi_g$ and $1^6\Sigma_u^+$ states are described by the four-electron excitation operators, so that they are difficult to be described by the previous SAC-CI(R-TQ) method: we have to use SAC-CI(R-general) method.²¹ The errors of the present EGCI method for

TABLE VI. EGCI, full-CI, and SD-CI results for the 1^5A_1 , 1^3B_2 , and 1^1A_1 states of *m*-phenylenebis(methylene).

State	Main configuration ^a	SD-CI ^b			EGCI				Full-CI			Exptl.	
		Size	Energy		Excitation energy (cm ⁻¹)	Size	Energy		Excitation energy (cm ⁻¹)	Size	Energy (a.u.)	Excitation energy (cm ⁻¹)	Excitation energy (cm ⁻¹)
			(a.u.)	Δ ^c			(a.u.)	Δ ^c					
1^5A_1	0.68(221111) +0.41(2211101) -0.38(22110101) -0.23(22110011)	354	-305.479 48	47.81	7270	400 ^d	-305.520 94	6.35	1790	5462	-305.527 29		
1^3B_2	0.39(222011) -0.39(220211) -0.25(22112) +0.23(2220101) -0.23(2220101)	135	-305.446 37	72.36	7270	1012 ^e	-305.512 80	5.93	1790	12730	-305.518 73	1880	> 300 ^f
1^1A_1	0.38(221111) +0.28(22021001) -22201001) +0.26(22022) -22202) 0.25(2220011) +0.25(222002) -220202)	120	-305.444 23	68.37	7740	754 ^e	-305.507 44	5.16	2960	8300	-305.512 60	3220	

^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.

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

^dEGCI calculation using the threshold of $(\lambda_A, \lambda_{AA}, \lambda_{AAA}) = (10^{-5}, 0.1, 10.0)$.

^eEGCI calculation using the threshold of $(\lambda_A, \lambda_{AA}, \lambda_{AAA}) = (0, 0.04, 0.2)$.

^fReferences 16 and 17: ENDOR experiment

these sextet states are within 1.24 mhartree and the average error is only 0.65 mhartree.

Finally, only one septet state $1^7\Sigma_g^+$ is calculated. Since the excitation level increases as the spin multiplicity increases, the number of independent spin functions and therefore the dimension of the EGCI calculation increases relative to that of the full-CI method. The discrepancy is 0.17 mhartree.

We thus conclude that the EGCI method describes well the quasidegenerate states and the states of multiple excitation natures in the high-spin multiplet states of the N_2 and N_2^+ molecules.

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

Here, we investigate the ground and excited states of *m*-phenylenebis(methylene) (*m*-PBM), which is the smallest unit of a series of the organic high-spin molecules.¹⁴⁻²⁰ The quintet ground state of this molecule was examined by the SAC-CI method in the previous paper.²¹ Here we consider the ground state 1^5A_1 and the low-lying two excited states, 1^3B_2 and 1^1A_1 states. The results of the EGCI, full-CI and SD-CI methods are summarized in Tables VI.

The relative stability of these three states is calculated as $1^5A_1 < 1^3B_2 < 1^1A_1$, which is consistent with the calculations of Teki *et al.*¹⁷ using the Heizenberg Hamiltonian, though the space symmetries of these states were not given in their report. Though the energy separations of these three states are overestimated in comparison with the experimental evidence, the ordering of these states is correctly reproduced both by the SD-CI and EGCI methods.

However, the absolute values of the total energies of the SD-CI method deviate by 48, 72, and 68 mhartree from those of the full-CI for the 1^5A_1 , 1^3B_2 , and 1^1A_1 states, respectively. Since the two excited states, 1^3B_2 and 1^1A_1 , have two-electron excitation nature as seen from the main configurations, multiple excitation operators are necessary for quantitative descriptions of these states. The EGCI method includes such multiple excitation operators, so that the errors in the total energy are small, ~ 6 mhartree: these three states having different spin-multiplicity are quantitatively described in a good balance by the EGCI method. The calculational dimensions of the EGCI method are less than one-tenth of those of the full CI. These results indicate that the excitation operators in the EGCI method are selected appropriately and efficiently for all the spin multiplicities. We note that in the previous SAC-CI(R-DT) method,²¹ the ground 1^5A_1 state is described with the error of 6.73 mhartree.

E. Spin density distribution in *m*-PBM

Spin density distribution is one of the most important and characteristic properties of ferromagnetic molecules. We investigate the spin density distributions in the ground 1^5A_1 state and the first excited 1^3B_2 state of *m*-PBM. The hfsc's are experimentally determined and the comparison of the hfsc's is a good examination of the quality of the wave function. However, the estimation of the hfsc's without including inner core polarizations is meaningless, and for including them the present system requires the active space of 46 MO's even if the minimal set is adopted, so that the full-CI calculation is impossible for this system. We

TABLE VII. Spin density distribution on each carbon of *m*-phenylenebis(methylene) for the 1^5A_1 and 1^3B_2 states calculated by the EGCI, full-CI, and SD-CI methods.

Atom: <i>x</i>	SD-CI			EGCI			Full-CI $\langle x \rho^{\alpha-\beta} x \rangle^a$
	$\langle x \rho^{\alpha-\beta} x \rangle^a$	$\Delta^b \times 10^3$	Δ^b (%)	$\langle x \rho^{\alpha-\beta} x \rangle^a$	$\Delta^b \times 10^3$	Δ^b (%)	
1^5A_1 state							
C1: <i>pπ</i>	0.287 20	-23.79	(7.6)	0.316 22	+5.23	(1.7)	0.310 99
C2: <i>pπ</i>	-0.120 73	+32.97	(21.5)	-0.148 43	+5.27	(3.4)	-0.153 70
C3: <i>pπ</i>	0.262 77	-14.96	(5.4)	0.275 42	-2.31	(0.8)	0.277 73
C4: <i>pπ</i>	-0.095 70	+36.55	(27.6)	-0.130 92	+1.33	(1.0)	-0.132 25
C5: <i>pπ</i>	0.791 15	-23.29	(2.9)	0.808 18	-6.26	(0.8)	0.814 44
C5: <i>pn</i>	0.702 56	+1.28	(0.2)	0.703 51	+2.23	(0.3)	0.701 28
1^3B_2 state							
C1: <i>pπ</i>	0.072 56	-140.07	(65.8)	0.202 70	-9.93	(4.7)	0.212 63
C2: <i>pπ</i>	0.001 56	+102.62	(101.5)	-0.095 16	+5.90	(5.8)	-0.101 06
C3: <i>pπ</i>	0.054 55	-133.52	(71.0)	0.181 85	-6.22	(3.3)	0.188 07
C4: <i>pπ</i>	0.000 23	+88.63	(100.3)	-0.083 62	+4.78	(5.4)	-0.088 40
C5: <i>pπ</i>	0.476 18	-36.65	(7.1)	0.514 82	+1.99	(3.9)	0.512 83
C5: <i>pn</i>	0.320 97	+72.17	(29.0)	0.253 30	+4.50	(1.8)	0.248 80

^aThe total spin density is normalized to $2S$, the number of unpaired α spins.

^bDeviation from the full-CI results.

therefore compare the spin density distributions on the valence *pπ* and *pn* orbitals of each carbon atom of *m*-PBM calculated from the wavefunctions obtained in the previous section by the EGCI, full-CI, and SD-CI method. The results for the 1^5A_1 and 1^3B_2 states are summarized in Table VII. Total spin densities are normalized to $2S$. The numbering of the carbon atoms is shown in Fig. 1.

In the 1^5A_1 state, the unpaired π electrons are distributed alternately in accordance with the ENDOR experiment¹⁶ and this feature was also obtained from the Heisenberg Hamiltonian.¹⁷ The SD-CI method also reproduces this feature, but, it underestimates the amplitude of the π -spin densities by 0.015–0.037 in comparison with the full-CI results: the errors are 3%–28% of the exact values and they are attributed to the lack of the multiple excitation configurations. On the other hand, the errors of the EGCI method for the π - and *n*-spin densities are only 1.33 – 6.26×10^{-3} (1%–3% of the exact values).

The effect of the multiple excitations is more remarkable for the spin densities of the 1^3B_2 state than those for the 1^5A_1 state. The π -spin densities of 1^3B_2 state also change their signs alternately, though the amplitudes are rather small. The SD-CI calculation gives positive π -spin densities for all the carbon sites. On the other hand, the EGCI calculation, which includes up-to-six-electron excitation operators, reproduces this alternate nature of the π -spin densities. Again the errors of the EGCI method are in the order of 10^{-3} , which correspond to 2%–6% of the exact values.

We thus conclude that the EGCI method is accurate not only for the energetics but also for spin density distributions.

V. SUMMARY

The EGCI method is extended to high-spin multiplicity and test calculations are performed for quartet, quintet, sextet, and septet states. This method, in which excited,

ionized, and electron attached states are calculated using the information on the correlated wave function of the ground state, is applicable to quasidegenerate states of various spin multiplicities and various numbers of excitation processes. The examinations of the EGCI method are performed for several high-spin states of C_2 , C_2^+ , N_2 , N_2^+ , and *m*-PBM, especially for the states whose main configurations are described by multiple excitation operators. The EGCI method reproduces well the full-CI results for the potential curves and the spectroscopic constants of the quartet states of C_2^+ and the quintet states of C_2 . The quasidegenerate high-spin states of N_2 and N_2^+ at $R=2.0$ Å and the various spin-multiplet states of *m*-PBM are also described well by the EGCI method.

The accuracy of the EGCI method is also investigated in terms of the hfsc's and the spin density distributions. The results of the EGCI method show good agreements with those of the full-CI. For the hfsc of the $X^4\Sigma_g^-$ state of C_2^+ , the deviation from the full-CI value is only 0.6% of the exact value. The *pπ*- and *pn*-spin densities are examined for the 1^5A_1 and 1^3B_2 states of *m*-PBM. The errors of the EGCI method is 0.8%–3.4% and 1.8%–5.8% of the exact values for the 1^5A_1 and 1^3B_2 states, respectively.

In conclusion, the EGCI method is confirmed to be accurate and useful not only for investigating the energetics appearing in the studies dynamics and reactions, but also for studying the spin density distributions of various spin multiplet states.

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