Analytical energy gradient of the symmetry-adapted-cluster configuration-interaction general-*R* method for singlet to septet ground and excited states

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A method of calculating analytical energy gradients of the singlet and triplet excited states, ionized states, electron-attached states, and high-spin states from quartet to septet states by the symmetry-adapted-cluster configuration-interaction general-*R* method is developed and implemented. This method is a powerful tool in the studies of geometries, dynamics, and properties of the states of molecules in which not only one-electron processes but also two- and multielectron processes are involved. The performance of the present method was confirmed by calculating the geometries and the spectroscopic constants of the diatomic and polyatomic molecules in various electronic states involving the ground state and the one- to three-electron excited states. The accurate descriptions were obtained for the equilibrium geometries, vibrational frequencies, and adiabatic excitation energies, which show the potential usefulness of the present method. The particularly interesting applications were to the $C'\,^1A_g$ state of acetylene, the $A\,^2\Delta_u$ and $B\,^2\Sigma_u^+$ states of CNC and the $^4B_1$ and $a\,^4\Pi_u$ states of N_3 radical. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1637033]

I. INTRODUCTION

The derivatives of the adiabatic potential energy surface of a molecule with respect to the nuclear coordinate (i.e., the forces acting on the nuclei) are key fundamental quantities for investigating the geometries, vibrations, chemical reactions, energy relaxation processes, and dynamics of molecules and molecular systems.[1] This is so not only for the ground state of molecular systems, but also for their excited and ionized states, in particular, because for the latter it is generally rather difficult to obtain this information by experimental techniques alone. Furthermore, the derivatives of the energy with respect to the external electric and magnetic fields provide the electric and magnetic properties of molecules in the ground, excited, and ionized states of molecules.

Usually, molecular excited and ionized states are described by one-electron excitations and ionizations from the ground state and they have been most extensively investigated by both experimental and theoretical methods. On the other hand, there also exist a lot of excited and ionized states that are characterized by the (two and more) multielectron processes. These electronic states often appear in high-energy chemistry and play an important role in spectroscopy, relaxation processes, etc., though they have been less focused in comparison with the one-electron processes, because these states are usually less visible by the selection rule involving photon. The satellite peaks observed in the ionization spectrum are typical examples of the states arising from the multielectron processes, i.e., one electron ionization accompanied by excitations. There also exist such multielectron excited states in the excitation spectrum of polyenes and in the high-spin multiplet states of transition metal complexes and clusters. In order to investigate the geometries, chemical reactions, etc., of the electronic states involving multielectron processes, information on the derivatives of the adiabatic potential energy surface is very important. We, therefore, formulate in this paper the analytical energy gradient method for these states, implement the result, and apply it to the excited and ionized states of several molecular systems.

The SAC (symmetry-adapted-cluster)[2]/SAC-CI (configuration interaction)[3] method was published in 1978 for studying the ground, excited, ionized, and electron-attached

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(anion) states of molecules and has been successfully applied to various chemistries and physics involving many different kinds of electronic states.[4] The analytical gradients of the SAC/SAC-CI energy were formulated and implemented in this laboratory at the SD (single double)-R level,[5,6] and applied to the calculations of equilibrium geometries, dipole moments, and vibrational frequencies of molecules in various electronic states of molecules. However, as the SAC-CI SD-R method is quantitatively applicable only to the electronic states generated by the one-electron process from the ground state, we cannot expect reliable results from this method when it is applied to the multielectron processes that sometimes appear in the excited and ionized states and in the course of chemical reaction and relaxation dynamics. Furthermore, when we study the excited states of open-shell systems by the SAC-CI method, they are often described by the two-electron processes from the closed-shell SAC state. Therefore, it was anticipated to develop the analytical energy gradient method that can be applicable to such electronic states of molecules.

There are two standards in the choice of the linked operators, R, in the SAC-CI method. In the SD-R method, only single- and double-excitation operators are adopted for the R operators, while in the general-R method,[7,8] triple-, quadruple-, and higher-excitation operators are further included. The SAC-CI SD-R method is reliable for ordinary single electron excitation and ionization processes, while the general-R method is designed to describe multiple-electron processes with high accuracy and has been applied successfully, for example, in the calculations of ionization spectra involving shake-up satellite peaks.[9–13] Details of the SAC-CI general-R method can be found in Ref. 7 and in a review article recently summarized.[9]

In the present study, the analytical energy gradients of the SAC-CI general-R method were developed and implemented. Since the SAC-CI method has also been applied to high-spin states from quartet to septet spin multiplicities,[14] we developed further the analytical energy gradients of the SAC-CI method to include high-spin multiplet states. As shown in the exponentially generated CI (EGCI) study[15] of the high-spin states, quasidegenerate orbital structure often appears in the high-spin states of molecules. It is therefore important to extend the SAC-CI general-R method to the high-spin states. The targets of the present method are therefore singlet and triplet excited states, doublet ionized and electron-attached states, and quartet-to-septet high-spin states of molecules that are described by general multielectron processes. Brief communications of the present method have been reported recently.[16,17] The SAC-CI general-R energy gradient code has been based on the SAC-CI 96 program system,[18] which has further been incorporated and implemented in the development version of the GAUSSIAN[19] suite of programs that have recently been distributed as GAUSSIAN 03.[20] To the best of our knowledge, this is the first work in which an analytical derivative method for the excited states involving the multielectron process has been implemented.

In Sec. II, we summarize the analytical energy gradient formula for the SAC and SAC-CI methods, explain the implementation of the SAC-CI general-R energy gradient method, and then describe the computational algorithm. In Sec. III, we give the numerical results of the spectroscopic constants of diatomic molecules using the present method. In Sec. IV, the results for the various electronic states of several molecules are given and discussed. Finally, Sec. V summarizes the conclusions.

II. THEORY

A. Analytical gradient for the SAC method

The analytical gradient for the SAC method[5,6] was formulated and implemented previously in the SAC/SAC-CI program system.[19,20] Here we briefly summarize some results pertinent to the present study.

The SAC wave function[3,4] is described as the cluster expansion around the reference function $|0\rangle$,

$$\Psi_{\text{SAC}} = \exp(S)|0\rangle, \tag{1}$$

where $|0\rangle$ is usually the closed-shell Hartree–Fock (HF) single determinant and

$$S = \sum_I C_I S_I^+. \tag{2}$$

S_I^+ is the symmetry-adapted excitation operator and C_I is the SAC coefficient.

The nonvariational solution of the SAC wave function is obtained by left-projecting the Schrödinger equation for the SAC wave function onto the reference and linked excited configurations,

$$\langle 0|H - E_{\text{SAC}}|\Psi_{\text{SAC}}\rangle = 0, \tag{3}$$

and

$$\langle 0|S_K(H - E_{\text{SAC}})|\Psi_{\text{SAC}}\rangle = 0, \tag{4}$$

where H is the Hamiltonian and E_{SAC} is the SAC energy. The SAC method gives not only the SAC wave function for the ground state, but also the complementary functional space that spans the space for the excited states.[3,4] The SAC equations (3) and (4) may be rewritten as

$$\Delta E_{\text{SAC}} = \sum_I C_I H_{0I} \tag{5}$$

and

$$H_{K0} + \sum_I C_I(H_{KI} - \Delta E_{\text{SAC}} S_{KI}) + \frac{1}{2}\sum_I \sum_J C_I C_J H_{K,IJ} = 0, \tag{6}$$

where $\Delta E_{\text{SAC}} = E_{\text{SAC}} - E_{\text{HF}}$ and S_{IJ} represents the overlap matrix, $\langle 0|S_I S_J^+|0\rangle$. H_{0I}, H_{IJ}, and $H_{I,JK}$ are the Hamiltonian matrices defined by $\langle 0|HS_I^+|0\rangle$, $\langle 0|S_I H S_J^+|0\rangle$, and $\langle 0|S_I H S_J^+ S_K^+|0\rangle$, respectively. In the programming, we adopted the approximations that the linked terms include all single- (S_1) and selected double- (S_2) excitation operators, and the unlinked terms include quadruple-excitation operators as products of further selected double-excitation operators ($S_2 S_2$).[9]

The first derivative of the SAC correlation energy with respect to the external parameter a is given in the Hamiltonian matrix form as,[5,6]

$$\frac{\partial \Delta E_{SAC}}{\partial a} = \sum_I \left[\left\{ 1 + \left(\sum_K \sum_J Z_K^{SAC} C_J S_{KJ} \right) \right\} C_I - Z_I^{SAC} \right] \frac{\partial H_{0I}}{\partial a}$$
$$- \sum_K \sum_I Z_K^{SAC} C_I \frac{\partial H_{KI}}{\partial a}$$
$$- \frac{1}{2} \sum_K \sum_I \sum_J Z_K^{SAC} C_I C_J \frac{\partial H_{K,IJ}}{\partial a}, \tag{7}$$

where Z_K^{SAC} is a component of the SAC Z-vector and is calculated from the following simultaneous linear equation:[6]

$$\sum_K \left\{ H_{KI} - \left(\sum_J C_J S_{KJ} \right) H_{0I} - \Delta E_{SAC} S_{KI} \right.$$
$$\left. + \sum_J C_J H_{K,IJ} \right\} Z_K^{SAC} = H_{0I}. \tag{8}$$

Explicit calculation of the first derivatives of the SAC coefficients $\partial C_I / \partial a$ is circumvented by using the interchange technique[21] or the so-called Z-vector method.[22]

In Eq. (7), the first derivatives of the Hamiltonian matrix element are generally expressed in terms of one- and two-electron coupling constants as

$$\frac{\partial H_{XY}}{\partial a} = \sum_{ij}^{MO} \gamma_{ij}^{XY} \frac{\partial f_{ij}}{\partial a} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{XY} \frac{\partial (ij|kl)}{\partial a}, \tag{9}$$

where the subscripts i, j, k, l refer to the spatial orbitals, and f_{ij} and $(ij|kl)$ denote fock matrix element and two-electron molecular orbital (MO) integral, respectively. The matrix elements γ_{ij}^{XY} and Γ_{ijkl}^{XY} are the one- and two-electron coupling constants between configuration functions Φ_X and Φ_Y and are independent of the parameter a, where X and Y correspond to I, J, K, L for the SAC wave function and to M, N for the SAC-CI wave function in this paper. In the SAC energy gradient calculation, γ_{ij}^{XY} and Γ_{ijkl}^{XY} for the SAC wave function are evaluated using our own formalism[23] based on the table-CI type idea.[24]

Using Eq. (9), we can rewrite Eq. (7) in MO representation in terms of effective density matrices (EDMs) for the SAC wave function as

$$\frac{\partial \Delta E_{SAC}}{\partial a} = \sum_{ij}^{MO} \gamma_{ij}^{SAC} \frac{\partial f_{ij}}{\partial a} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{SAC} \frac{\partial (ij|kl)}{\partial a}. \tag{10}$$

The matrix elements γ_{ij}^{SAC} and Γ_{ijkl}^{SAC} of the EDMs are given by

$$\gamma_{ij}^{SAC} \equiv \sum_I \left[\left\{ 1 + \left(\sum_K \sum_J Z_K^{SAC} C_J S_{KJ} \right) \right\} C_I - Z_I^{SAC} \right] \gamma_{ij}^{0I}$$
$$- \sum_K \sum_I Z_K^{SAC} C_I \gamma_{ij}^{KI}$$
$$- \frac{1}{2} \sum_K \sum_I \sum_J Z_K^{SAC} C_I C_J \gamma_{ij}^{K,IJ} \tag{11}$$

and

$$\Gamma_{ijkl}^{SAC} \equiv \sum_I \left[\left\{ 1 + \left(\sum_K \sum_J Z_K^{SAC} C_J S_{KJ} \right) \right\} C_I - Z_I^{SAC} \right] \Gamma_{ijkl}^{0I}$$
$$- \sum_K \sum_I Z_K^{SAC} C_I \Gamma_{ijkl}^{KI}$$
$$- \frac{1}{2} \sum_K \sum_I \sum_J Z_K^{SAC} C_I C_J \Gamma_{ijkl}^{K,IJ}, \tag{12}$$

respectively.[5,6] Thus, the first derivative of the SAC energy is evaluated from Eqs. (8), (10)–(12).

B. Analytical energy gradient for the SAC-CI method

Next, we summarize the analytical energy gradient formula for the SAC-CI method, which was formulated and implemented previously at the SD-R level.[5,6]

The SAC-CI wave function is generated from the correlated SAC ground state as[3,4]

$$\Psi_{SAC-CI}^p = \sum_K d_K^p R_K^\dagger \Psi_{SAC}, \tag{13}$$

where $\{R_K^+\}$ represents a set of excitation, ionization, and/or electron-attachment operators, and $\{d_K^p\}$ is its coefficients for the pth excited state.

The nonvariational (NV) SAC-CI equation is obtained by projecting the Schrödinger equation for the SAC-CI wave function onto the space of the linked excited configurations as

$$\langle 0 | R_K (H - E_{SAC-CI}^p) | \Psi_{SAC-CI}^p \rangle = 0, \tag{14}$$

where E_{SAC-CI}^p is the SAC-CI energy of pth excited state. Neglecting some less important unlinked integrals, the SAC-CI energy relative to the HF energy, ΔE_{SAC-CI}^p, is derived as

$$\Delta E_{SAC-CI}^p = \sum_M \sum_N d_M^{L(p)} d_N^{R(p)} \left(H_{MN} + \sum_I C_I H_{M,NI} \right), \tag{15}$$

where $\Delta E_{SAC-CI}^p = E_{SAC-CI}^p - E_{HF}$, H_{MN}, and $H_{M,NI}$ are the Hamiltonian matrices defined by $\langle 0 | R_M H R_N^+ | 0 \rangle$ and $\langle 0 | R_M H R_N^+ S_I^+ | 0 \rangle$, respectively, d_M^L and d_N^R are the SAC-CI left- and right-vectors.

The first derivative of the SAC-CI correlation energy is given in the Hamiltonian matrix form as[6]

$$\frac{\partial \Delta E_{SAC-CI}}{\partial a} = \sum_I \left\{ \sum_K Z_K^{SAC-CI} \left(\sum_J C_J S_{KJ} \right) C_I \right.$$
$$\left. - Z_I^{SAC-CI} \right\} \frac{\partial H_{0I}}{\partial a} + \sum_M \sum_N d_M^L d_N^R \frac{\partial H_{MN}}{\partial a}$$
$$- \sum_K \sum_I Z_K^{SAC-CI} C_I \frac{\partial H_{KI}}{a}$$
$$+ \sum_M \sum_N \sum_I d_M^L d_N^R C_I \frac{\partial H_{M,NI}}{\partial a}$$
$$- \frac{1}{2} \sum_K \sum_I \sum_J Z_K^{SAC-CI} C_I C_J \frac{\partial H_{K,IJ}}{a}, \tag{16}$$

TABLE I. R operator for each spin multiplicity in the present SAC-CI program system (Refs. 19 and 22). Subscripts i, j, k, l, m, n and a, b, c, d, e, f denote occupied and unoccupied orbitals, respectively, in the reference configuration $|0\rangle$.

	Single	Double	Triple	Quadruple	Quintuple	Sextuple
Singlet	$^1R_i^a = a_{a\alpha}^+ a_{i\alpha} + a_{a\beta}^+ a_{i\beta}/\sqrt{2}$	$^1R_{ij}^{ab}$	$^1R_{ijk}^{abc}$	$^1R_{ijkl}^{abcd}$	$(^1R_{ijklm}^{abcde})^a$	$(^1R_{ijklmn}^{abcdef})^a$
Doublet (ionized)	$^2R_i = a_{i\beta}$	$^2R_{ij}^b$	$^2R_{ijk}^{ab}$	$^2R_{ijkl}^{abc}$	$(^2R_{ijklm}^{abcd})^a$	$(^2R_{ijklmn}^{abcde})^a$
Doublet (anionized)	$^2R^a = a_{a\alpha}^+$	$^2R_j^{ab}$	$^2R_{ij}^{abc}$	$^2R_{ijk}^{abcd}$	$(^2R_{ijkl}^{abcde})^a$	$(^2R_{ijklm}^{abcdef})^a$
Triplet	$^3R_i^a = a_{a\alpha}^+ a_{i\beta}$	$^3R_{ij}^{ab}$	$^3R_{ijk}^{abc}$	$^3R_{ijkl}^{abcd}$	$(^3R_{ijklm}^{abcde})^a$	$(^3R_{ijklmn}^{abcdef})^a$
Quartet (ionized)		$^4R_{ij}^a = a_{a\alpha}^\dagger a_{i\beta} a_{j\beta}$	$^4R_{ijk}^{ab}$	$^4R_{ijkl}^{abc}$	$(^4R_{ijklm}^{abcd})^a$	$(^4R_{ijklmn}^{abcde})^a$
Quintet		$^5R_{ij}^{ab} = a_{a\alpha}^\dagger a_{b\alpha}^\dagger a_{i\beta} a_{j\beta}$	$^5R_{ijk}^{abc}$	$^5R_{ijkl}^{abcd}$	$(^5R_{ijklm}^{abcde})^a$	$(^5R_{ijklmn}^{abcdef})^a$
Sextet (ionized)			$^6R_{ijk}^{ab} = a_{a\alpha}^\dagger a_{b\alpha}^\dagger a_{i\beta} a_{j\beta} a_{k\beta}$	$^6R_{ijkl}^{abc}$	$(^6R_{ijklm}^{abcd})^a$	$(^6R_{ijklmn}^{abcde})^a$
Septet			$^7R_{ijk}^{abc} = a_{a\alpha}^\dagger a_{b\alpha}^\dagger a_{c\alpha}^\dagger a_{i\beta} a_{j\beta} a_{k\beta}$	$^7R_{ijkl}^{abcd}$	$(^7R_{ijklm}^{abcde})^a$	$(^7R_{ijklmn}^{abcdef})^a$

[a] The wave functions adopting operators in the parentheses are not available for the present SAC-CI energy gradient program system.

where Z_K^{SAC-CI} is a component of the SAC-CI Z-vector and is calculated from the SAC-CI Z-vector equation,[6]

$$\sum_K \left\{ H_{KI} - \left(\sum_J C_J S_{KJ} \right) H_{0I} - \Delta E_{SAC} S_{KI} \right.$$
$$\left. + \sum_J C_J H_{K,IJ} \right\} Z_K^{SAC-CI} = \sum_M \sum_N d_M^L d_N^R H_{M,NI}. \qquad (17)$$

By using Eq. (9), Eq. (16) is rewritten in MO representation in term of EDMs for the SAC-CI wave function,

$$\frac{\partial \Delta E_{SAC-CI}}{\partial a} = \sum_{ij}^{MO} \gamma_{ij}^{SAC-CI} \frac{\partial f_{ij}}{a} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{SAC-CI} \frac{\partial (ij|kl)}{\partial a}. \qquad (18)$$

The matrix elements of the EDMs γ_{ij}^{SAC-CI} and Γ_{ijkl}^{SAC-CI} are represented as

$$\gamma_{ij}^{SAC-CI} \equiv \sum_I \left\{ \sum_K Z_K^{SAC-CI} \left(\sum_J C_J S_{KJ} \right) C_I - Z_I^{SAC-CI} \right\} \gamma_{ij}^{0I}$$
$$+ \sum_M \sum_N d_M^L d_N^R \gamma_{ij}^{MN} - \sum_K \sum_I Z_K^{SAC-CI} C_I \gamma_{ij}^{KI}$$
$$+ \sum_M \sum_N \sum_I d_M^L d_N^R C_I \gamma_{ij}^{M,NI}$$
$$- \frac{1}{2} \sum_K \sum_I \sum_J Z_K^{SAC-CI} C_I C_J \gamma_{ij}^{K,IJ}, \qquad (19)$$

and

$$\Gamma_{ijkl}^{SAC-CI} \equiv \sum_I \left\{ \sum_K Z_K^{SAC-CI} \left(\sum_J C_J S_{KJ} \right) C_I - Z_I^{SAC-CI} \right\} \Gamma_{ijkl}^{0I}$$
$$+ \sum_M \sum_N d_M^L d_N^R \Gamma_{ijkl}^{MN} - \sum_K \sum_I Z_K^{SAC-CI} C_I \Gamma_{ijkl}^{KI}$$
$$+ \sum_M \sum_N \sum_I d_M^L d_N^R C_I \Gamma_{ijkl}^{M,NI}$$
$$- \frac{1}{2} \sum_K \sum_I \sum_J Z_K^{SAC-CI} C_I C_J \Gamma_{ijkl}^{K,IJ}, \qquad (20)$$

respectively.[5,6] Consequently, the analytical derivatives of the SAC-CI energy are evaluated from Eqs. (17), (19), and (20).

In the SAC-CI calculations, there are two standards in the choice of the R operators.[4,9] The first choice is to include

only single- and double-excitation operators within the R operators (SD-R method). The implementation of the energy gradient in the SD-R level was done previously by using the coupling constants for the SAC-CI wave function, γ_{ij}^{MN}, $\gamma_{ij}^{M,NI}$, Γ_{ijkl}^{MN}, and $\Gamma_{ijkl}^{M,NI}$ that were evaluated using our own formalism.[23] This method is useful for ordinary one-electron excitation and ionization processes.

The second choice is to include in the R operators not only single- and double-excitation operators, but also triple-, quadruple-, quintuple-, and sextuple-excitation operators (general-R method). The general-R method applies to various electronic states, singlet and triplet excited states, doublet ionized and electron-attached states, and high-spin states from quartet to septet states by choosing the R operators, as shown in Table I. For example, the SAC-CI general-R wave function for the singlet state is express as

$$^1\Psi_{SAC-CI} = \left(\sum_{(ia)} d_i^a \, ^1R_i^a + \sum_{(ijab)} d_{ij}^{ab} \, ^1R_{ij}^{ab} \right.$$
$$+ \sum_{(ijkabc)} d_{ijk}^{abc} \, ^1R_{ijk}^{abc}$$
$$\left. + \sum_{(ijklabcd)} d_{ijkl}^{abcd} \, ^1R_{ijkl}^{abcd} + \cdots \right) \Psi_{SAC}, \qquad (21)$$

where i, j, k, l and a, b, c, d denote occupied and unoccupied MOs, respectively, and the parentheses mean that the summation is limited to the nonredundant excitation operators.

The above-given analytical energy gradient formalism is valid for both SAC-CI SD-R and general-R methods. It is written by Eq. (18) and is evaluated using the SAC-CI Z-vector equation [Eq. (17)] and the EDMs of Eqs. (19) and (20) for the SAC-CI general-R wave function. The implementation of the analytical energy gradient for the SAC-CI general-R method over the already existing SD-R gradient code may be summarized as follows:

(1) The one- and two-coupling constants for the general-R wave function, γ_{ij}^{MN}, $\gamma_{ij}^{M,NI}$, Γ_{ijkl}^{MN}, and $\Gamma_{ijkl}^{M,NI}$ of Eqs. (19) and (20) are evaluated for triple-, quadruple-, and higher-excitation operators using the algorithm of the projective reduction formalism for bonded functions developed by Reeves and others.[25–27]

(2) In the SAC-CI Z-vector equation of Eq. (17), the summations on M and N run over the excitation operators including the higher-excitation operators summarized in Table I.

In Eqs. (17), (19), and (20), the unlinked terms that are redundant with the linked terms are neglected.

The algorithm for the SAC-CI general-R energy gradient code adopted in the GAUSSIAN 03[20] suite of programs may be summarized as follows.

(1) The self-consistent field calculation is performed and the derivatives of the one- and two-electron atomic orbital integrals are calculated.

(2) The SAC and SAC-CI general-R calculations are carried out, and the information on the selected operators and the SAC/SAC-CI coefficients are stored to be used in a later step.

(3) The CPSAC Z-vector equations [Eqs. (8) or (17)] are solved using Pulay's direct inversion in the iterative subspace (DIIS) method.[28] In the SAC-CI general-R calculations, the right term of Eq. (9) is evaluated not only for the single and double R operators but also for the triple, quadruple, and higher R operators.

(4) The MO EDMs for the SAC-CI general-R wave function given by Eqs. (19) and (20) are constructed and stored. As mentioned earlier, one- and two-electron coupling constants between configuration functions for triple-, quadruple-, and higher-excitation operators are evaluated using the projective reduction algorithm by Reeves and others,[25–27] while those for single and double excitations are evaluated using our own formalism[23] based on the table-CI type procedure.[24]

(5) The first derivatives of energy are evaluated by summing up the products between the AO integral derivatives and the corresponding coefficients which are obtained via backtransformation of the EDMs[6] and solving linear equations for CPHF, as usual.[1,29–33] In addition, the CPMOD equations are solved in GAUSSIAN 03 if the MOD method is used for calculation.[34,35] In evaluation of the forces on N atoms, explicit determination of the $3N$ sets of the first derivatives of MO coefficients is circumvented by the interchange technique,[21,22] as well as the SAC coefficient derivatives.

The numerical check was done by confirming that the calculated analytical energy gradient is equal to the numerical differentiation of the energy within computational accuracy.

III. NUMERICAL RESULTS: APPLICATION TO DIATOMIC MOLECULES

In the following, we study the spectroscopic constants of the ground and excited states of the diatomic molecules, CH^+, NH^+, C_2, CO^+, NO, N_2^+, and N_2, by applying the present SAC-CI general-R energy gradient method. Experimental measurements of the equilibrium internuclear distance (r_e), harmonic frequency (ω_e), and the adiabatic excitation energy (T_e) of these molecules were reported for various electronic states[36] and some of them are described by the two-electron processes. Actually, Herzberg gave experi-

mental adiabatic excitation enegy T_e for these molecules. They are therefore good benchmark molecules for the present examination. In the present calculations, we used the approximately variational SAC-CI (SAC-CI-V) method,[3] including all the MOs in the active space.

A. Singlet and triplet states of CH^+ and doublet states of NH^+

First, we study the spectroscopic properties of the singlet and triplet excited states of CH^+ and those of the doublet states of NH^+ without doing perturbation selection.[37] Both the SD-R and general-R methods were performed for these systems using the correlation-consistent polarized valence triple-zeta set (cc-pVTZ) without f function for C and N and without d function for H, $(10s5p2d/5s2p)/[4s3p2d/3s2p]$.[38] In the SAC-CI general-R calculations, systematic calculations were performed using SDT and SDTQ R operators in order to examine the effect of the R operators in different orders. The doublet states of NH^+ were obtained by the electron attachment to the closed-shell SAC state, NH^{2+}. Table II shows the results of r_e, ω_e, and T_e, compared with the experiments.[36] The excitation level denotes the number of electrons involved in the excitation process and the excitation character is shown by the SAC-CI coefficients of the main configurations. The values of ω_e were numerically calculated using the analytical first derivatives.

The low-lying $A\,^1\Pi$ state of CH^+ is described essentially by the one-electron excitation from the ground state, while the $b\,^3\Sigma^-$ and $B\,^1\Delta$ states are described by the two-electron excitations from the ground state. For the ground $X\,^1\Sigma^+$ state of CH^+, the experimental r_e was well reproduced by the SAC method. For the one-electron process, the SD-R and general-R methods gave very similar results in agreement with experiments, but for the two-electron processes, the general-R method gave considerably better results than the SD-R method, especially for T_e; the average deviations of the general-R (SDTQ) result from the experimental values were 0.004 Å, 53 cm^{-1}, and 0.08 eV for r_e, ω_e, and T_e, respectively. The effect of including up to quadruples amounts up to ~ 1.2 eV for T_e. Thus, for the two-electron processes, we should use the general-R method for obtaining quantitatively reliable results.

The ground $X\,^2\Pi$ state of NH^+ is described by the one-electron process, while the other excited states, $A\,^2\Sigma^-$, $B\,^2\Delta$, and $C\,^2\Sigma^+$, are represented by the two-electron processes. For the ground state, both SD-R and general-R methods gave good bond distance and the ω_e was improved by 93 cm^{-1} with the general-R method. For the other states, the general-R method drastically improves the results of the SD-R method, especially for T_e. The effects of including triples in the R operators are as large as 0.06–0.11 Å, 500–760 cm^{-1}, and 2.1–3.6 eV for r_e, ω_e, and T_e, respectively. The effect of including up to quadruples is prominent for the $A\,^2\Sigma^-$ state and the results are improved by 0.03 Å (r_e), 180 cm^{-1} (ω_e), and 0.20 eV (T_e). This is because the three-electron processes such as ($3\sigma^{-3}1\pi^2$) considerably mix to this state. The agreements of the general-R results

TABLE II. Excitation levels, equilibrium internuclear distances (r_e), harmonic frequency (ω_e), adiabatic excitation energies (T_e), and main configurations for the singlet and triplet states of CH$^+$ and the doublet states of NH$^+$.

Molecule	State	Method	Excitation level	r_e (Å)	ω_e (cm^{-1})	T_e (eV)	Main configurations[a,b] ($|C|>0.3$)
CH$^+$							
	$X\,^1\Sigma^+$	SAC	0	1.128	2848	$\cdots$	
		Expt.[c]		1.131	2740	$\cdots$	
	$A\,^1\Pi$	SD-R	1	1.238	1818	3.101	$0.96(3\sigma^{-1}1\pi)$
		General-R(SDT)	1	1.249	1729	2.998	$0.95(3\sigma^{-1}1\pi)$
		General-R(SDTQ)		1.251	1715	2.988	$0.95(3\sigma^{-1}1\pi)$
		Expt.[c]		1.234	1865	2.989	
	$b\,^3\Sigma^-$	SD-R	2	1.211	2273	5.952	$0.93(3\sigma^{-2}1\pi^2)$
		General-R(SDT)	2	1.246	2034	4.754	$0.91(3\sigma^{-2}1\pi^2)$
		General-R(SDTQ)		1.250	2013	4.696	$0.91(3\sigma^{-2}1\pi^2)$
		Expt.[c]		1.245	1939	4.736	
	$B\,^1\Delta$	SD-R	2	1.210	2224	7.780	$0.68(3\sigma^{-2}1\pi^2)-0.68(3\sigma^{-2}1\pi^2)$
		General-R(SDT)	2	1.232	2070	6.700	$0.67(3\sigma^{-2}1\pi^2)-0.67(3\sigma^{-2}1\pi^2)$
		General-R(SDTQ)		1.236	2044	6.641	$0.67(3\sigma^{-2}1\pi^2)-0.67(3\sigma^{-2}1\pi^2)$
		Expt.[c]		1.233	2076	6.513	
NH$^+$							
	$X\,^2\Pi$	SD-R	1	1.064	3122	$\cdots$	$0.97(1\pi)$
		General-R(SDT)	1	1.070	3041	$\cdots$	$0.95(1\pi)$
		General-R(SDTQ)	1	1.070	3029	$\cdots$	$0.95(1\pi)$
		Expt.[c]		1.070	2922	$\cdots$	
	$A\,^2\Sigma^-$	SD-R	2	1.123	2574	6.564	$0.57(3\sigma^{-1}1\pi^2)-0.57(3\sigma^{-1}1\pi^2)$
		General-R(SDT)	2	1.232	1811	2.948	$0.55(3\sigma^{-1}1\pi^2)-0.55(3\sigma^{-1}1\pi^2)$
		General-R(SDTQ)	2	1.261	1627	2.746	$0.54(3\sigma^{-1}1\pi^2)-0.54(3\sigma^{-1}1\pi^2)$ $+0.25(3\sigma^{-2}1\pi^3)$
		Expt.[c]		1.251	1585	2.752	
	$B\,^2\Delta$	SD-R	2	1.073	2921	5.673	$0.70(3\sigma^{-1}1\pi^2)-0.70(3\sigma^{-1}1\pi^2)$
		General-R(SDT)	2	1.128	2422	3.053	$0.69(3\sigma^{-1}1\pi^2)-0.69(3\sigma^{-1}1\pi^2)$
		General-R(SDTQ)	2	1.136	2331	3.004	$0.68(3\sigma^{-1}1\pi^2)-0.68(3\sigma^{-1}1\pi^2)$
		Expt.[c]		(1.152)	2280	2.889	
	$C\,^2\Sigma^+$	SD-R	2	1.092	2743	6.623	$0.70(3\sigma^{-1}1\pi^2)+0.70(3\sigma^{-1}1\pi^2)$
		General-R(SDT)	2	1.148	2285	4.555	$0.69(3\sigma^{-1}1\pi^2)+0.69(3\sigma^{-1}1\pi^2)$
		General-R(SDTQ)	2	1.152	2239	4.506	$0.68(3\sigma^{-1}1\pi^2)+0.68(3\sigma^{-1}1\pi^2)$
		Expt.[c]		1.163	2151	4.339	

[a]Hartree–Fock configuration for the ground state of CH$^+$ is given by $(\text{core})^2(2\sigma)^2(3\sigma)^2$.
[b]The electronic configuration and the excitation level relative to the closed-shell NH^{2+}, $(\text{core})^2(2\sigma)^2(3\sigma)^2$.
[c]Reference 36.

with the experimental values were satisfactory regardless of the excitation levels of the states.

B. Singlet and triplet states of C$_2$ and doublet states of CO$^+$ and NO

Next, we examine the performance of the present SAC-CI general-R energy gradient method for the singlet and triplet states of C$_2$ and the doublet states of CO$^+$ and NO using, in this case, the perturbation selection technique.[37] Both SD-R and general-R calculations were performed with the cc-pVTZ[38] without f functions. For NO, s- and p-type Rydberg functions ($\zeta_s=0.028$, $\zeta_p=0.025$ for N and $\zeta_s=0.032$, $\zeta_p=0.028$ for O) were also augmented, since the Rydberg states are expected to interact with the valence excited states. In the SAC-CI general-R, the R operators were limited up to triples. The doublet states of NO were obtained by the electron attachment of the closed-shell NO$^+$. The

perturbation selection was due to the state-selection scheme.[39] For the ground state of these diatomics, the energy threshold for the linked operator was 1×10^{-7} a.u. and the unlinked terms were written as the products of the important linked terms whose SDCI coefficients are larger than 0.005. For the excited and doublet states, the thresholds for double excitation operators were 1×10^{-7} a.u., and that for triples was $\lambda_e=1\times10^{-7}$ a.u., and the thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.005 and 0.0 for R and S operators, respectively. During the geometry optimization, we used the common set of R and S excitation operators, which were determined by the selection at the initial geometry. We used the experimental geometry as the initial one. When experimental geometry is not available, the optimized geometry at the SD-CI/SDT-CI level is used as the initial one. We confirmed that the dependence of the results on the initial geometry was

TABLE III. Excitation levels, equilibrium internuclear distances (r_e), adiabatic excitation energies (T_e), and main configurations for the singlet and triplet states of C_2.

State	Method	Excitation level	r_e (Å)	T_e (eV)	Main configurations[a] ($|C|>0.3$)
$X\,^1\Sigma_g^+$	General-R	0	1.268	⋯	
	CCSD(T)[b]		1.245	⋯	
	MRCI[c]		1.248	⋯	
	Expt.[d]		*1.243*	⋯	
$a\,^3\Pi_u$	General-R	1	1.307	0.094	$0.93(1\pi_u^{-1}3\sigma_g)$
	CCSD(T)[b]		1.311	0.104	
	MRCI[c]		1.318	0.081	
	Expt.[d]		*1.312*	*0.089*	
$b\,^3\Sigma_g^-$	General-R	2	1.366	0.842	$0.95(1\pi_u^{-2}3\sigma_g^2)$
	CCSD(T)[b]		1.370	0.809	
	MRCI[c]		1.374	0.911	
	Expt.[d]		*1.369*	*0.798*	
$A\,^1\Pi_u$	General-R	1	1.317	0.993	$0.97(1\pi_u^{-1}3\sigma_g)$
	Expt.[d]		*1.318*	*1.040*	
$c\,^3\Sigma_u^+$	General-R	1	1.200	1.637	$0.92(2\sigma_u^{-1}3\sigma_g)$
	Expt.[d]		*1.23*	*1.650*	
$d\,^3\Pi_g$	General-R	2	1.262	2.362	$0.89(1\pi_u^{-1}2\sigma_u^{-1}3\sigma_g^2)$
	Expt.[d]		*1.266*	*2.482*	
$C\,^1\Pi_g$	General-R	2	1.250	4.181	$0.90(1\pi_u^{-1}2\sigma_u^{-1}3\sigma_g^2)$
	Expt.[d]		*1.255*	*4.248*	
$e\,^3\Pi_g$	General-R	2	1.543	4.997	$0.83(1\pi_u^{-2}1\pi_g3\sigma_g)-0.42(1\pi_u^{-1}2\sigma_u^{-1}3\sigma_g^2)$ $+0.39(1\pi_u^{-2}1\pi_g3\sigma_g)$
	Expt.[d]		*1.535*	*5.058*	
$D\,^1\Sigma_u^+$	General-R	1	1.243	5.342	$0.84(2\sigma_u^{-1}3\sigma_g)$
	Expt.[d]		*1.238*	*5.361*	
$g\,^3\Delta_g$	General-R	2	1.355	9.130	$0.64(1\pi_u^{-1}2\sigma_u^{-1}1\pi_g3\sigma_g)$ $-0.63(1\pi_u^{-1}2\sigma_u^{-1}1\pi_g3\sigma_g)+0.31(1\pi_u^{-2}1\pi_g^2)$
	Expt.[d]		*1.358*	*9.073*	
rms[e]			0.009	0.058	

[a]Hartree–Fock configuration for the ground state is $(core)^4(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$.
[b]Reference 40.
[c]Reference 41.
[d]Reference 36.
[e]Root mean square (rms) is the difference between experimental and theoretical values.

negligibly small as far as proper geometries were used. We also confirmed the convergence of the optimized geometry: optimization was successively performed using the operators determined by the selection at the optimized geometry.

The spectroscopic constants in the various excited states of C_2 have been determined by experiment[36] and some of them are described by the two-electron processes. Note that the various electronic states of C_2 were studied by the SAC-CI general-R method in Ref. 7. Table III summarizes r_e and T_e for nine singlet and triplet excited states of C_2, calculated by the general-R method in comparison with the experimental[36] and other theoretical values.[40,41] Since the ground state of C_2 has quasidegenerate character, the general-R method was used for the calculation of the ground state. The $C\,^1\Pi_g$, $b\,^3\Sigma_g^-$, $d\,^3\Pi_g$, $e\,^3\Pi_g$, and $g\,^3\Delta_g$ states are described by the two-electron excitations from the ground state, while other states are described by the one-electron excitations. The agreements of the general-R results

with the experimental values were satisfactory regardless of the excitation level of each state: the discrepancies of the general-R results from the experimental values were 0.009 Å and 0.058 eV for r_e and T_e, respectively. The $a\,^3\Pi_u$ and $b\,^3\Sigma_g^-$ states were also calculated by the multireference (MR)-CI[41] and CCSD(T) methods[40] and their results have also provided good agreement with experiment. The T_e of the $c\,^3\Sigma_u^+$ state was underestimated by ~0.6 eV in comparison with the experiment.

Table IV summarizes r_e and T_e for the doublet states of CO^+ and NO calculated by the SD-R and general-R methods in comparison with the experiments.[36,42] For the $D\,^2\Pi$ and $3\,^2\Sigma^+$ states of CO^+, there are no experimental values of r_e. The $X\,^2\Sigma^+$, $A\,^2\Pi$, and $B\,^2\Sigma^+$ states of CO^+ are characterized by the one-electron process, while the $C\,^2\Delta$, $D\,^2\Pi$, and $3\,^2\Sigma^+$ states are represented by the two-electron processes, which correspond to the satellite states observed in the valence ionization spectrum of CO. For the $C\,^2\Delta$ and

TABLE IV. Excitation levels, equilibrium internuclear distances (r_e), adiabatic excitation energies (T_e), and main configurations for the doublet states of CO^+ and NO.

Molecule	State	Method	Excitation level	r_e (Å)	T_e (eV)	Main configurations[a,b] ($|C|>0.3$)
CO^+	$X\,^2\Sigma^+$	SD-*R*	1	1.115	⋯	$0.97(5\sigma^{-1})$
		General-*R*	1	1.115	⋯	$0.95(5\sigma^{-1})$
		Expt.[b]		*1.115*	⋯	
	$A\,^2\Pi$	SD-*R*	1	1.249	2.382	$0.96(1\pi^{-1})$
		General-*R*	1	1.237	2.557	$0.93(1\pi^{-1})$
		Expt.[b]		*1.244*	*2.571*	
	$B\,^2\Sigma^+$	SD-*R*	1	1.155	5.594	$0.93(4\sigma^{-1})$
		General-*R*	1	1.162	5.646	$0.86(4\sigma^{-1})$
		Expt.[b]		*1.169*	*5.688*	
	$C\,^2\Delta$	SD-*R*	2	1.300	11.22	$0.71(1\pi^{-1}2\pi5\sigma^{-1})-0.71(1\pi^{-1}2\pi5\sigma^{-1})$
		General-*R*	2	1.333	8.004	$0.71(1\pi^{-1}2\pi5\sigma^{-1})-0.71(1\pi^{-1}2\pi5\sigma^{-1})$
		Expt.[b]		*1.340*	*7.812*	
	$D\,^2\Pi$	SD-*R*	2	1.248	12.28	$0.84(5\sigma^{-2}2\pi)-0.35(4\sigma^{-1}2\pi1\pi^{-1})$
		General-*R*	2	1.249	8.885	$0.82(5\sigma^{-2}2\pi)-0.37(4\sigma^{-1}2\pi1\pi^{-1})$ $-0.30(5\sigma^{-2}3\pi)$
		Expt.[b]		⋯	*8.087*	
		Expt.[c]		⋯	*8.407*	
	$3\,^2\Sigma^+$	SD-*R*	2	1.270	11.88	$0.24(4\sigma^{-1})-0.70(5\sigma^{-1}2\pi1\pi^{-1})$ $-0.70(5\sigma^{-1}2\pi1\pi^{-1})$
		General-*R*	2	1.270	9.140	$0.41(4\sigma^{-1})-0.65(5\sigma^{-1}2\pi1\pi^{-1})$ $-0.65(5\sigma^{-1}2\pi1\pi^{-1})$
		Expt.[b]		⋯	*9.074*	
		Expt.[c]		⋯	*9.011*	
NO	$X\,^2\Pi$	SD-*R*	1	1.150	⋯	$0.98(2\pi)$
		General-*R*	1	1.153	⋯	$0.94(2\pi)$
		Expt.[b]		*1.151*	⋯	
	$B\,^2\Pi$	SD-*R*	2	1.416	10.44	$0.82(1\pi^{-1}2\pi^2)+0.63(1\pi^{-1}2\pi^2)$
		General-*R*	2	1.398	5.536	$0.83(1\pi^{-1}2\pi^2)+0.55(1\pi^{-1}2\pi^2)$
		Expt.[b]		*1.416*	*5.693*	
	$B'\,^2\Delta$	SD-*R*	2	1.275	12.13	$0.69(4\sigma^{-1}2\pi^2)-0.69(4\sigma^{-1}2\pi^2)$
		General-*R*	2	1.296	7.544	$0.68(4\sigma^{-1}2\pi^2)-0.68(4\sigma^{-1}2\pi^2)$
		Expt.[b]		*1.302*	*7.484*	
	$G\,^2\Sigma^-$	SD-*R*	2	1.299	13.59	$0.57(4\sigma^{-1}2\pi^2)-0.57(4\sigma^{-1}2\pi^2)$
		General-*R*	2	1.320	7.990	$0.55(4\sigma^{-1}2\pi^2)-0.55(4\sigma^{-1}2\pi^2)$
		Expt.[b]		*1.343*	*7.8*	

[a]The electronic configuration and the excitation level relative to the closed-shell CO, $(core)^4(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$ and to the closed-shell NO^+, namely, $(core)^4(3\sigma)^2(\sigma)^2(1\pi)^4$.
[b]Reference 36.
[c]Reference 42.

$3\,^2\Sigma^+$ states, the general-*R* methods gave good results for both r_e and T_e in comparison with experiment: the deviations from the experimental values were to within 0.007 Å and 0.19 eV for r_e and T_e, respectively. The T_e of the $A\,^2\Pi$ and $B\,^2\Sigma^+$ states were slightly underestimated, but, in excellent agreement with the experimental values; the deviations were to within 0.04 eV. Potential energy curve of the $D\,^2\Pi$ state has double minima[43,44] and we presented r_e and T_e for the inner well. Our results gave similar values to the recent MRCI calculation[43] for r_e, but T_e was overestimated in comparison with the experiment.

In the present paper, we study the $B\,^2\Pi$, $B'\,^2\Delta$ and $G\,^2\Sigma^-$ excited states of NO involving two-electron process,

since the SD-*R* method has already been applied to the excited states of one-electron process like Rydberg-excitations in the previous paper.[6] For these three excited states, the general-*R* method gave considerably better results than the SD-*R* method, especially for T_e; the deviations from the experimental values were within 0.19 eV for these states. These excited states are mainly characterized as $(1\pi^{-1}2\pi^2)$ or $(4\sigma^{-1}2\pi^2)$, which involve the excitation to π^*-orbital. Therefore, the NO bond of these states is elongated by excitation and the present calculation reproduces this feature. Since the $B\,^2\Pi$ state is just below the Rydberg $C\,^2\Pi$ state, Rydberg functions were important to describe the interaction between these states.

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TABLE V. Excitation levels, equilibrium internuclear distances (r_e), adiabatic excitation energies (T_e), and main configurations for the quartet states of N_2^+.

State	Method	Excitation level	r_e (Å)	T_e[a] (eV)	Main configurations[b] ($|C|>0.3$)
$a\ ^4\Sigma_u^+$	SAC-CI DT-R	2	1.341	⋯	$0.65(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)+0.65(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)$
	SAC-CI DTQ-R	2	1.350	⋯	$0.63(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)+0.61(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)$
	MRCI[c]		1.353	⋯	
	CI[d]		1.42	⋯	
$b\ ^4\Pi_g$	SAC-CI DT-R	2	1.415	1.088	$0.94(1\pi_u^{-2}1\pi_g)$
	SAC-CI DTQ-R	2	1.445	0.818	$0.91(1\pi_u^{-2}1\pi_g)$
	MRCI[c]		1.457	0.872	
	CI[d]		1.52	1.7	
$c\ ^4\Delta_u$	SAC-CI DT-R	2	1.321	1.701	$0.65(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)-0.65(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)$
	SAC-CI DTQ-R	2	1.341	1.517	$0.64(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)-0.62(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)$
	MRCI[c]		1.339	1.480	
	CI[d]		1.39	2.2	
$d\ ^4\Sigma_u^-$	SAC-CI DT-R	2	1.318	2.759	$0.65(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)-0.65(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)$
	SAC-CI DTQ-R	2	1.338	2.533	$0.65(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)-0.61(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g)$
	MRCI[c]		1.335	2.390	
	CI[d]		1.38	3.1	
$e\ ^4\Sigma_g^+$	SAC-CI DT-R	2+3	1.254	4.229	$0.63(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g)+0.62(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g)$ $+0.31(3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2)$
	SAC-CI DTQ-R	2+3	1.285	4.021	$0.57(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g)+0.56(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g)$ $+0.42(3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2)$
	MRCI[c]		1.281	3.995	
$f\ ^4\Pi_u$	SAC-CI DT-R	2	1.158	5.050	$0.93(2\sigma_u^{-1}3\sigma_g^{-1}1\pi_g)$
	SAC-CI DTQ-R	2	1.167	5.057	$0.89(2\sigma_u^{-1}3\sigma_g^{-1}1\pi_g)$
	MRCI[c]		1.154	4.640	
	CI[d]		1.19	5.7	

[a]Energy difference from the lowest $a\ ^4\Sigma_u^+$ state.
[b]The electronic configuration and the excitation level relative to the closed-shell N_2, $(core)^4(2\sigma_g)^2(2\sigma_u)^2$ $(3\sigma_g)^2(1\pi_u)^4$.
[c]Reference 46.
[d]Reference 47.

C. Quartet states of N_2^+ and Quintet states of N_2

Next, the present SAC-CI general-R energy gradient method is applied to the high-spin states. We calculated the spectroscopic constants of the quartet states of N_2^+ and the quintet states of N_2. The SAC-CI-V high-spin calculations were performed using the double-zeta plus polarization (DZP) basis sets of Huzinaga-Dunning $(9s5p1d)/[4s2p1d]^{45}$ and cc-pVTZ basis sets for N_2^+ and N_2, respectively. Two types of SAC-CI calculations were performed: DT-R included double and triple R-operators and DTQ-R further included quadruples. Perturbation selection was performed using the state-selection scheme. For the quartet and quintet states, the thresholds for double, triple, and quadruple R operators were 1×10^{-7} a.u. and the thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.005 and 0.0 for R and S operators, respectively.

Table V show the calculated r_e and T_e for the quartet states of N_2^+, compared with other theoretical results.[46,47] The quartet states of N_2^+ were obtained by the ionizations of the neutral closed-shell state. Though there are no experimental data for these quartet states, they were theoretically

studied by the MRCI[46] and CI methods[47] and seven quartet states were found to be bound. All quartet states were described by the two-electron processes from the closed-shell state, but the mixing of three-electron process was found for the $e\ ^4\Sigma_g^+$ state. The average discrepancies between SAC-CI DT-R and DTQ-R results were 0.02 Å and 0.15 eV for r_e and T_e, respectively. The effects of including quadruples were large especially for T_e values. The DTQ-R results for these states gave similar results to those of the MRCI method. The T_e values calculated by the early CI method were overestimated by $\sim$1 eV relative to both SAC-CI and MRCI results.

In Table VI, the results of r_e and T_e for the quintet states of N_2 are presented in comparison with the experimental values.[36] For the $A''\ ^5\Sigma_g^+$ and $C''\ ^5\Pi_u$ states, the spectroscopic constants have been reported in Ref. 36. These states are described by two-electron process, and therefore both SAC-CI DT-R and DTQ-R methods gave similar results: the deviations between these methods were 0.02 Å and 0.08 eV for r_e and T_e, respectively. The T_e were underestimated by 0.6–0.7 eV relative to the experimental values. Note that the experimental values for the $A''\ ^5\Sigma_g^+$ state were determined along with the early theoretical calculation.[48]

TABLE VI. Excitation levels, equilibrium internuclear distances (r_e), adiabatic excitation energies (T_e), and main configurations for the quintet states of N_2.

State	Method	Excitation level	r_e (Å)	T_e (eV)	Main configurations[a] ($|C| > 0.3$)
$A'' \, ^5\Sigma_g^+$	SAC-CI DT-*R*	2	1.587	9.374	$0.95(1\pi_u^{-2}1\pi_g^2)$
	SAC-CI DTQ-*R*	2	1.596	9.263	$0.93(1\pi_u^{-2}1\pi_g^2)$
	Expt.[b]		(1.55)	(9.77)	
$C'' \, ^5\Pi_u$	SAC-CI DT-*R*	2	1.472	10.921	$0.95(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^2)$
	SAC-CI DTQ-*R*	2	1.502	10.872	$0.93(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^2)$
	Expt.[b]		⋯	11.593	

[a]Hartree–Fock configuration for the ground state of N_2 is given by $(core)^4(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$.
[b]Reference 36: values in parentheses were determined along with theoretical calculation (Ref. 48).

IV. APPLICATION TO POLYATOMIC MOLECULES

In this section, the present method is applied to the equilibrium geometries and adiabatic excitation energies of polyatomic molecules, acetylene, CNC, and N_3 radical, which have some electronic states characterized by the multielectron processes. In the present calculations, both SAC-CI-V SD-*R* and general-*R* (SDT) calculations were performed for these systems, including all the MOs in the active space. For the quartet states of N_3, SAC-CI-V DT-*R* and DTQ-*R* high-spin calculations were carried out. The DZP basis sets[45] were used for acetylene and N_3, and the DZP basis sets augmented with *s*- and *p*-type Rydberg functions ($\zeta_s = 0.023$, $\zeta_p = 0.021$ for C and $\zeta_s = 0.028$, $\zeta_p = 0.025$ for N) were used for CNC. Configuration selection was performed using the state-selection scheme.[39] For the ground state, energy threshold for the linked operator was 1×10^{-7} a.u. and the unlinked terms were written as the products of the important linked terms whose SDCI coefficients are larger than 0.005. For the singlet excited, doublet and quartet states, the thresholds for double- and triple-excitation operators were 1×10^{-7} a.u. and the thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.005 and 0.0 for *R* and *S* operators, respectively.

A. *Trans*-bent structures in the $A \, ^1A_u$ and $C' \, ^1A_g$ states of acetylene

The ground and lowest singlet excited ($A \, ^1A_u$) states of acetylene have been extensively studied both experimentally and theoretically. Recent theoretical calculation[49] has investigated the *trans*-bent structure in the $A \, ^1A_u$ state using the equation-of-motion coupled cluster (EOM-CCSD) method with DZP and VZ2P basis sets and well reproduced the experimental structure. The EOM-CCSD method is essentially identical with the SAC-CI SD-*R* method.[9] In 1992, the *trans*-bent structure in the $C' \, ^1A_g$ state of C_2H_2 was spectroscopically measured by Lundberg *et al.*[50] The $A \, ^1A_u$ state is described by the one-electron process, while the $C' \, ^1A_g$ state is described by the two-electron process. Therefore, we are interested in the spectroscopic constants of these excited states especially for the $C' \, ^1A_g$ state. Table VII summarizes the SAC-CI SD-*R* and general-*R* results for the singlet ground and excited states of C_2H_2, in comparison with the experiments.[50–52] The SAC method was performed for the ground state and well reproduced the experimental

geometries.[51] For the $A \, ^1A_u$ state, both SD-*R* and general-*R* methods gave the results of the same quality. For the $C' \, ^1A_g$ state, the general-*R* method drastically improves the results of the SD-*R* method, especially for T_e. The optimized geometries are in excellent agreement with experimental values; the deviations are within 0.02 Å and 0.03°. The $A \, ^1A_u$ and $C' \, ^1A_g$ states are described as $(1a_u^{-1}4a_g)$ and $(1a_u^{-2}4a_g^2)$, respectively, in which $1a_u$ orbital corresponds to valence $1\pi_u$ orbital for the liner structure. Thus, *trans*-bent structures become stable in these excited states by the single or double excitation from $1\pi_u$ orbital.

B. Ground and excited states of the open-shell molecule CNC

Next, we show the results for the open-shell molecule CNC, whose excited states are described by the two-electron processes from the closed-shell SAC state. We first calculate the closed-shell CNC^+ by the SAC method, and then calculate various electronic states of CNC radical by the electron-attachment of the SAC-CI method. In Table VIII, the SAC-CI SD-*R* and general-*R* results of r_e and T_e are compared with the experiment[53] and with CASPT2 results.[54]

The ground state, $X \, ^2\Pi_g$, is described by the one-electron process, while the other two excited states, $A \, ^2\Delta_u$ and $B \, ^2\Sigma_u^+$, are represented by the two-electron process. For r_e, both SD-*R* and general-*R* gave excellent results for the ground and excited states: the deviations from the experiment were within 0.009 Å. For T_e, the general-*R* method drastically improves the results of the SD-*R* method. The effect of including triples in the *R* operators is as large as 3.4–3.5 eV. The adiabatic excitation energies calculated by the general-*R* method agree well with the experiment; T_e were slightly underestimated by 0.086 and 0.017 eV for $A \, ^2\Delta_u$ and $B \, ^2\Sigma_u^+$, respectively. The CASPT2 method underestimated these values by 0.34 and 0.31 eV,[54] though the basis sets were different from the present ones.

C. The lowest doublet and quartet states of the N_3 radical

The azide free radical N_3 has been extensively studied experimentally as well as theoretically. The ground state of N_3 has been recognized as the doublet state, $X \, ^2\Pi_g$, in the linear structure which has been spectroscopically determined by Douglas and Jones.[55] Though there are no experimental

TABLE VII. Excitation levels, optimized geometries, adiabatic excitation energies (T_e), and main configurations for the singlet ground and excited states of acetylene.

State	Method	Excitation level	R_{CH} (Å)	R_{CC} (Å)	θ_{CCH} (deg)	T_e (eV)	Main configurations[a] ($|C|>0.3$)
$X\,^1A_g$	SAC	0	1.068	1.219	180	⋯	
(Linear)	Expt.[b]		1.063	1.203	180	⋯	
$A\,^1A_u$	SD-R	1	1.098	1.377	122.6	5.485	$0.97(1a_u^{-1}4a_g)$
(Trans)	General-R	1	1.097	1.385	121.7	5.329	$0.94(1a_u^{-1}4a_g)$
	Expt.[c]		1.097	1.375	122.5	5.232	
$C'\,^1A_g$	SD-R	2	1.105	1.634	103.8	10.098	$0.94(1a_u^{-2}4a_g^2)$
(Trans)	General-R	2	1.111	1.643	103.0	7.844	$0.93(1a_u^{-2}4a_g^2)$
	Expt.[d]		1.14	1.65	103	7.723	

[a]The HF electronic configurations are $(core)^4(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$ for the linear structure and $(core)^4(2a_g)^2(2b_u)^2(3a_g)^2(3b_u)^2(1a_u)^2$ for the trans-bent structure, respectively.
[b]Reference 51.
[c]Reference 52.
[d]Reference 50.

data for the quartet states, the lowest quartet state has been theoretically studied using the CASCI,[56] UMP2,[56] and MRD-CI[57] methods: the former work predicted that the bent $^4B_1$ state is more stable than linear $a\,^4\Pi_u$ state. We calculated these doublet and quartet states of N_3 by the SAC-CI general-R energy gradient method. For the quartet state, both linear and bent structures were examined. The doublet and quartet states of N_3 were obtained by the ionization from the closed-shell N_3^-. Table IX summarizes the optimized geometries, adiabatic excitation energies for the lowest doublet and quartet states of N_3, compared with experimental[55] and other theoretical results.[56]

The ground state, $X\,^2\Pi_g$, is described by the one-electron process from the closed-shell state. Both SD-R and general-R (SDT) methods gave excellent results in comparison with the experiment within 0.008 Å for R_{NN}. For the lowest quartet state, the SAC-CI results are close to those of the CASCI method and show that the bent $^4B_1$ state is ener-

getically stable relative to the linear $a\,^4\Pi_u$ state. For T_e, the DTQ-R method improves the values by including quadruple R operators: the difference between the DT-R and DTQ-R results are 0.004 Å, 0.3°, and 0.33 eV for R_{NN}, θ, and T_e, respectively.

V. CONCLUSION

Analytical energy gradients of the SAC-CI general-R method for the singlet and triplet states, doublet ionized and electron-attached states, and high-spin states from quartet to septet states were developed and implemented in the GAUSSIAN 03[20] suite of programs. The reliability and usefulness of the present method were confirmed from the applications to various molecules. The advantages of the SAC-CI general-R analytical energy gradients are summarized as follows:

(1) The present method is quantitatively applicable to the singlet and triplet excited states, doublet ionized and

TABLE VIII. Excitation levels, equilibrium internuclear distances (R_{CN}), adiabatic excitation energies (T_e), and main configurations for the doublet ground and excited states of CNC.

State	Method	Excitation level	R_{CN} (Å)	T_e (eV)	Main configurations[a] ($|C|>0.3$)
$X\,^2\Pi_g$	SD-R	1	1.256	⋯	$0.97(1\pi_u)$
	General-R	1	1.251	⋯	$0.92(1\pi_u)$
	CASPT2[b]		1.253	⋯	
	Expt.[c]		1.245	⋯	
$A\,^2\Delta_u$	SD-R	2	1.257	7.197	$0.65(3\sigma_u^{-1}1\pi_g^2)+0.65(3\sigma_u^{-1}1\pi_g^2)$
	General-R	2	1.255	3.675	$0.65(3\sigma_u^{-1}1\pi_g^2)+0.65(3\sigma_u^{-1}1\pi_g^2)$
	CASPT2[b]		1.257	3.425	
	Expt.[c]		1.249	3.761	
$B\,^2\Sigma_u^+$	SD-R	2	1.262	7.694	$0.65(3\sigma_u^{-1}1\pi_g^2)+0.65(3\sigma_u^{-1}1\pi_g^2)$
	General-R	2	1.260	4.298	$0.65(3\sigma_u^{-1}1\pi_g^2)+0.65(3\sigma_u^{-1}1\pi_g^2)$
	CASPT2[b]		1.259	4.001	
	Expt.[c]		1.259	4.315	

[a]The electronic configuration and the excitation level relative to the closed shell CNC^+, namely, $(core)^6(3\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(4\sigma_g)^2(3\sigma_u)^2$.
[b]Molecular geometries are optimized by CASSCF/6s4p2d2f (Ref. 54).
[c]Reference 53.

TABLE IX. Excitation levels, optimized geometries, adiabatic excitation energies (T_e), and main configurations for the doublet and quartet states of N_3.

State	Method	Excitation level	R_{NN} (Å)	θ (deg)	T_e (eV)	Main configurations[a] ($|C| > 0.3$)
$X\,^2\Pi_g$	SD-*R*	1	1.191	180	$\cdots$	$0.96(1\pi_g^{-1})$
$(D_{\infty h})$	General-*R*	1	1.188	180	$\cdots$	$0.91(1\pi_g^{-1})$
	CASCI[c]		1.170	180	$\cdots$	
	UMP2[c]		1.185	180	$\cdots$	
	Expt.[b]		*1.182*	*180*	$\cdots$	
$^4B_1$	SAC-CI DT-*R*	2	1.273	118.3	2.108	$0.93(1a_2^{-1}4b_2^{-1}6a_1)$
(C_{2v})	SAC-CI DTQ-*R*	2	1.275	118.0	1.754	$0.88(1a_2^{-1}4b_2^{-1}6a_1)$
	CASCI[c]		1.265	118.9	1.76	
	UMP2[c]		1.258	118.5	2.45	
$a\,^4\Pi_u$	SAC-CI DT-*R*	2	1.271	180	4.013	$0.93(1\pi_g^{-2}2\pi_u)$
$(D_{\infty h})$	SAC-CI DTQ-*R*	2	1.275	180	3.705	$0.88(1\pi_g^{-2}2\pi_u)$
	CASCI[c]		1.259	180	3.85	
	UMP2[c]		1.257	180	4.58	

[a]The electronic configurations and the excitation levels relative to the closed-shell linear and bent N_3^- of $(\text{core})^6(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^4$ and $(\text{core})^6(3a_1)^2(2b_2)^2(4a_1)^2(5a_1)^2(1b_1)^2(3b_2)^2(1a_2)^2(4b_2)^2$, respectively.
[b]Reference 55.
[c]Reference 56.

electron-attached states, and high-spin states from quartet to septet states including the multielectron processes.

(2) It is useful for investigating the excited states of open-shell systems, since they are often described by the two-electron process from the closed-shell SAC state.

(3) It is useful for studying the satellite peaks in the valence-ionization spectrum of molecules. We will apply this method to investigate the vibrational progressions of the satellites peaks in the forthcoming paper.[44]

(4) Detailed description would be obtained for the chemical reaction and energy relaxation processes by using this method, since multielectron processes sometimes play an important role.

We think that the present method should be a powerful tool for investigating the dynamics and property in the excited, ionized, electron-attached, and high-spin states involving the multielectron processes.

ACKNOWLEDGMENT

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