

SAC-CI GENERAL-R METHOD: THEORY AND APPLICATIONS TO THE MULTI-ELECTRON PROCESSES

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1. Introduction

Accurate descriptions of excited and ionized states of molecules have long been a challenging subject in quantum chemistry. Chemistry involving these states has shown a rich variety of phenomena that were quite appealing but could not be fully understood without knowledge of their electronic structure underlying the observed phenomena. Many of the excited and ionized states are described as one-electron processes from the ground state. However, there exist a lot of excited and ionized states that are characterized by two- or more-electron excitations from the ground state. Since these states are usually not observed by optical measurements, these multi-electron processes have been less focused, both experimentally and theoretically.

In 1982, one of the authors calculated the ionization spectra of H₂O, CO₂, COS, and CS₂ by the SAC-CI method¹⁻³ and was deeply impressed by the existence of so many two-electron excitation-ionization states in the inner-valence region of the spectra. Most of these states were not observed, because the transitions to these states from the ground state were *optically* forbidden: only few were observed as shake-up satellite peaks when mixing with single-electron processes could occur. However, since so many states exist, they must play an important role in rather high-energy chemistry, for example, in energy-relaxation processes, high-energy reaction processes, etc. These states are interesting theoretically, since they usually involve much information on the electron correlations of molecules, as it is in the satellite peaks in the valence ionization spectra. This means also that accurate description of these multi-electron processes is more difficult than that of the single-electron processes. Thus, accurate descriptions of multi-electron processes are theoretically challenging subject.

The SAC/SAC-CI(symmetry-adapted-cluster configuration-interaction) method⁴⁻⁹ has been successfully applied to the various kinds of molecular spectroscopy.^{1-3,10-23} For ordinary single-electron processes, the SD-*R* method was enough and gave qualitatively satisfactory results.^{8,9} However, this was not so for the two-, three-electron processes, like ionization-excitation processes involved in satellite peaks of ionization spectra. The SAC-CI general-*R* method²⁴ was designed to give quantitative descriptions for not only one-electron processes but also multi-electron processes appearing in the excited, ionized, and electron-attached states in rather higher-energy region. In the original paper published in 1991, the potential usefulness and applicability of the general-*R* method were demonstrated by the applications

to the various electronic states of CO and C₂.²⁴ It was also shown that the exponential generation algorithm²⁵⁻²⁷ was useful in the performance of the SAC-CI general-*R* method. The method was also shown to be useful for the excited states of open-shell systems, since they are often described by the two-electron processes from the closed-shell SAC state.

There are many two-electron states in the inner-valence region of even small molecules, as mentioned above. This causes a problem in the iterative diagonalization of large dimension matrices. The SAC-CI general-*R* method has a merit at this point, since its computational dimension is much smaller than that of ordinary CI approaches. We have calculated a variety of satellite peaks appearing in the valence ionization spectra.²⁸⁻³⁴ We have confirmed the accuracy of the SAC-CI general-*R* method for the main and satellite peaks of the ionization spectra by comparing it with the full-CI spectra of N₂ and CO.²⁸ More recently, we have performed a series of SAC-CI general-*R* studies on the ionization spectra of various molecules, for example, HCl,³⁰ C₂H₄,²⁹ CO₂,³¹ H₂X (X=O, S, Se),³⁴ cyclopentadiene,³² pyridine,³³ etc., and obtained quite accurate results that agree well with the experimental spectra, giving accurate assignment of the spectra.

It should be noted that the development of the experimental techniques, such as high-resolution synchrotron radiation photoelectron spectroscopy (SRPES), X-ray PES, electron momentum spectroscopy (EMS), and Penning ionization spectroscopy (PIES) have enabled the detailed analysis of the satellite peaks not only about the peak positions and intensity, but also about their ionization characters that reflect their electronic structures. Theoretical information is, therefore, very important in the assignment and interpretation of these spectroscopic results.

The analytical energy gradient of the SAC/SAC-CI method has been formulated and implemented,^{35,36} and recently, this method has been extended to the SAC-CI general-*R* method.³⁷ This general-*R* gradient method has provided important quantitative descriptions of the spectroscopic properties such as molecular geometry, vibrational frequency, and adiabatic excitation energy of the multi-electron states in the excitation, ionization, and electron-attachment processes. This method is also useful to study similar properties of the excited states of open-shell systems. We can also study chemical reaction dynamics and energy relaxation processes, in which multi-electron processes often play an important role as mentioned above.

In 1985, the SAC/SAC-CI computer program system (SAC85)^{38,39} has been published. It was also this year that the program system of the

MEG(multi-exponential generation)/EX(excited)-MEG method was completed.⁴⁰ This MEG/EX-MEG program is a very general code that can deal with not only multi-reference quasi-degenerate states²⁵⁻²⁷ but also completely general SAC/SAC-CI calculations including higher excitation operators R without any neglect of unlinked terms. The recent version⁴¹ was made more efficient in integral evaluation and diagonalization.

As a theory of the excited states, coupled cluster linear response theory (CC-LRT) were formulated in time-dependent manner by Monkhorst and Dalgaard^{42,43} and time-independent manner by Mukherjee.⁴⁴ After a decade, CC-LRT^{45,46} were reformulated and the equation-of-motion coupled-cluster (EOM-CC) method^{47,48} were published. It has been theoretically pointed out that they are identical to the SAC-CI method.⁴⁻⁹ However, this fact has not been properly described in the papers of EOM-CC and CC-LRT. The IP-EOM-CC⁴⁹ and EA-EOM-CC⁵⁰ are just equivalent to the SAC-CI method for ionization and electron attachment processes: in SAC-CI, all of the singlet and triplet excitations, ionizations and electron attachments were calculated at the same time since the original program coded in 1978 to 1979. The extension to include higher-order terms, namely, SAC-CI general- R method²⁴ is closely related with EOM-CCSDT^{51,52} and response theory of CC3⁵³ published much later. We will show some numerical result confirming the equivalence of EOM-CC and CC-LRT to SAC-CI.

In this review article, we first explain the SAC/SAC-CI methods briefly in Sec.2. In Sec.3, the results of C_2 are reviewed from the original work of the general- R method.²⁴ In Sec.4, we show more recent applications of the general- R method to the valence ionization spectra of molecules, such as N_2 , CO , H_2O , H_2S and $XONO_2$ ($X=F, Cl, Br, I$) molecules. In Sec.5, we show SAC-CI general- R analytical energy gradient calculations. In Sec.6, we will numerically confirm the equivalence of EOM-CC and CC-LRT to SAC-CI. We also show that some approximations adopted in current SAC-CI are accurate and useful. Sec.7 gives a summary of this article.

2. Theory

2.1. SAC/SAC-CI method

For totally symmetric ground state, we define the SAC expansion as,

$$\Psi_g^{SAC} = \exp(S)|0\rangle \quad (1)$$

where $|0\rangle$ is Hartree-Fock and

$$S = \sum_I C_I S_I^\dagger \quad (2)$$

S_I^\dagger being symmetry-adapted excitation operator. Note that the SAC expansion can also be defined for higher-symmetries.⁴

In the SAC expansion the unknown variables C_I are associated to the S_I^\dagger , so that we require the Schrödinger equation is satisfied within the space of the linked configurations as

$$\langle 0 | H - E_g | \Psi_g^{\text{SAC}} \rangle = 0 \quad (3a)$$

$$\langle 0 | S_I (H - E_g) | \Psi_g^{\text{SAC}} \rangle = 0. \quad (3b)$$

This solution is called non-variational.

The variational solution is obtained by applying the variational principle to the SAC wave function and we obtain,

$$\langle \Psi_g^{\text{SAC}} | H - E_g | \Psi_g^{\text{SAC}} \rangle = 0 \quad (4a)$$

$$\langle \Psi_g^{\text{SAC}} | (H - E_g) S_I^\dagger | \Psi_g^{\text{SAC}} \rangle = 0. \quad (4b)$$

The variational solution is more difficult than the non-variational one, because it includes the integrals between unlinked terms. Recently, variational CCD⁵⁴ solution has been obtained by Voorhis and Head-Gordon and shown to behave properly even up to the dissociation limit.

The SAC theory defines not only the SAC wave function for the ground state, but also the excited functions that span the basis for excited states.⁵⁻⁷ Starting from Eq. (4b), we define the excited functions $\{\Phi_K\}$ by

$$\Phi_K = P S_K^\dagger | \Psi_g^{\text{SAC}} \rangle \quad (5)$$

where P is an operator which projects out the ground state,

$$P = 1 - | \Psi_g^{\text{SAC}} \rangle \langle \Psi_g^{\text{SAC}} |. \quad (6)$$

Then, it is easily shown that the functions $\{\Phi_K\}$ satisfy

$$\langle \Phi_K | \Psi_g^{\text{SAC}} \rangle = 0, \quad \langle \Phi_K | H | \Psi_g^{\text{SAC}} \rangle = 0, \quad (7)$$

which means that the functions $\{\Phi_K\}$ form a basis for excited state. We therefore describe the excited state by a linear combination of these functions,

$$\Psi_e^{\text{SAC-CI}} = \sum_K d_K \Phi_K \quad (8)$$

which is the SAC-CI theory.

Applying the variational principle for solving the unknown variables $\{d_K\}$, we obtain

$$\langle \Phi_K | H - E_c | \Psi_e^{\text{SAC-CI}} \rangle = 0. \quad (9)$$

The SAC-CI wave function automatically satisfies the orthogonality and Hamiltonian orthogonality with the ground state and also with different excited states.

The SAC-CI wave function is also defined for the excited states having different symmetries, and for ionized and electron attached states. We generalize Eq. (5) as

$$\Phi_K = PR_K^\dagger | \Psi_g^{\text{SAC}} \rangle \quad (10)$$

where $\{R_K^\dagger\}$ represents a set of excitation, ionization, and/or electron attachment operators.

The non-variational SAC-CI solution is obtained by projecting the Schrödinger equation onto the space of the linked configurations,

$$\langle 0 | R_K (H - E_c) | \Psi_e^{\text{SAC-CI}} \rangle = 0. \quad (11)$$

In the case of totally symmetric singlet excited states, the non-variational SAC-CI formulation giving SAC solution for the ground state¹¹ is written as

$$\begin{pmatrix} \langle 0 | (H - E_c) e^S | 0 \rangle & \langle 0 | (H - E_c) R_K^\dagger e^S | 0 \rangle \\ \langle 0 | R_K (H - E_c) e^S | 0 \rangle & \langle 0 | R_K (H - E_c) R_K^\dagger e^S | 0 \rangle \end{pmatrix} = 0. \quad (12)$$

This is equivalent to the formulation based on Eq.(5) that uses the projector P .

The SAC-CI theory is based on the transferability of correlations between ground and excited states. This would be clearly understood by writing the SAC-CI wave function as,

$$\Psi_e^{\text{SAC-CI}} = \mathfrak{R} \Psi_g^{\text{SAC}} \quad (13)$$

where the excitation operator \mathfrak{R} is defined as,

$$\mathfrak{R} = \sum_K d_K R_K^\dagger. \quad (14)$$

For totally symmetric states, we may include identity operator within $\{R_K^\dagger\}$ to ensure the orthogonality of the excited states to the ground state. The electron correlation of the ground state is well described by the SAC wave function and the excitation operator describes a modification of the electron correlation by excitation: this is much easier than calculating all the correlations of the excited states from the beginning. Further, a balanced

description of electron correlations between ground and excited states is rather difficult actually. In physics community, this concept is often called renormalization.

2.2. SAC-CI general-*R* method

For implementing the SAC-CI method, there are two standards in the choice of the *R*-operators.^{8,24} First choice is to include single and double excitation operators within the *R*-operators. This choice gives accurate results when the excitations or ionizations involve only one-electron processes, as have been confirmed by many applications. The second choice is to include not only single and double excitation operators, but also triple-, quadruple- and higher-excitation operators within the *R*-operators. This choice is necessary when we study two-or-more electron processes in the excitation and ionization phenomena. We call the former method as the SD-*R* method and the latter as the general-*R* method.

The SAC-CI general-*R* method has the following features.

(1) It is applicable to various electronic states, singlet and triplet excited states, ionized states, electron-attached states and high-spin states from quartet to septet states including multi-electron processes in the same manner as the SAC-CI SD-*R* method.

(2) It is applicable to a large number of excited and ionized states at the same time.

(3) It is also useful to calculate the excited states of open-shell systems, since their excited states are often described by the two-electron processes from the closed-shell SAC state.

(4) It is useful to study the chemical reaction dynamics and energy relaxation processes, in which the multi-electron processes often play an important role.

For generating the triple-, quadruple-, and higher-excitation operators in the SAC-CI general-*R* method, the exponential generation algorithm²⁵⁻²⁷ is useful, which is explained in Sec. 2.3. This method combined with the perturbation selection has also been shown to be accurate and efficient. For small molecules, one can also generate all the triple and quadruple operators followed by the perturbation selection.

The method of calculating the analytical energy gradient for the SAC-CI general-*R* method has recently be developed and implemented.³⁷ For the details of the method, we refer to the original paper.³⁷ The method has

provided a powerful tool for investigating the geometries and vibrational frequencies of the excited states in which two- and multi-electron processes are involved.

2.3. Exponential generation algorithm

In the SAC-CI SD-*R* method, all the double excitation operators are generated and the perturbation selection is performed. However, this algorithm for triple, quadruple, and higher-excitation operators can be quite time-consuming even for the medium-sized molecules. This is circumvented effectively by introducing the exponential generation (EG) algorithm²⁵⁻²⁷ of the higher operators from the lower ones.

In the series of studies on the quasi-degenerate system, we introduced a new exponential-type operator defined by

$$\mathcal{E}\mathcal{D}\mathcal{P}\left(\sum_K a_K A_K^\dagger\right) = \mathcal{Q}\left(a_0 + \sum_K a_K A_K^\dagger + \frac{1}{2}\sum_{K,L} a_{KL} A_K^\dagger A_L^\dagger + \dots\right) \quad (15)$$

where the excitation operator A_K^\dagger runs over all the space and spin symmetries and \mathcal{Q} is a symmetry projector. Single and double excitation operators are usually adopted for 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, but the coefficients of the product operators a_{KL} are made free from those of the lower operators a_K . In order to include all possible highly connected terms such as simultaneous double excitations, all independent spin and space functions are included in $\{A_K^\dagger\}$ to produce the product operators $\{A_K^\dagger A_L^\dagger\}$.

For better understanding of the above method for constructing higher excitation operators in various spin symmetries, we explain the EGCI (exponentially generated CI) method. The EGCI method normally starts from the totally symmetric singlet ground states using $\mathcal{E}\mathcal{D}\mathcal{P}$ operator as

$$\Psi_g^{\text{EGCI}} = \mathcal{E}\mathcal{D}\mathcal{P}\left(\sum_K a_K A_K^\dagger\right)0. \quad (16)$$

In Eq. (16) we include only those single and double excitation operators A_K^\dagger that are important for the description of the ground state. In the expansion of the $\mathcal{E}\mathcal{D}\mathcal{P}$ operator, we successively generate higher product operators from

the lower ones using its importance as a criterion. The wave functions for the excited, ionized, and electron attached states are constructed by applying the excicator to the ground state as

$$\Psi_e^{\text{EGCI}} = \mathfrak{R} \Psi_g^{\text{EGCI}}. \quad (17)$$

\mathfrak{R} is expanded by a linear combination of the excitation operators $\{B_K^\dagger\}$ as

$$\mathfrak{R} = \sum_K b_K B_K^\dagger \quad (18)$$

where $\{B_K^\dagger\}$ is usually the single and double operators which describe the excitation, ionization, and electron attachment, and usually we choose only some important ones. Note that $\{b_K\}$ is not a simple coefficient but an operator that gives the independent coefficients for the product operators $\{A_K^\dagger B_L^\dagger\}$ and $\{A_K^\dagger A_L^\dagger B_M^\dagger\}$, etc. The resultant EGCI wave function of various spin multiplicity is thus expressed as

$$\Psi_e^{\text{EGCI}} = Q \left(\sum_K b_K B_K^\dagger + \frac{1}{2} \sum_{K,L} b_{KL} A_K^\dagger B_L^\dagger + \frac{1}{3!} \sum_{K,L,M} b_{KLM} A_K^\dagger A_L^\dagger B_M^\dagger + \dots \right) |0\rangle. \quad (19)$$

Again in Eq. (19), we generate higher product operators only from important lower operators A_K^\dagger and B_K^\dagger . In the SAC-CI general- R method, the higher-excitation operators $\{A_K^\dagger B_L^\dagger\}$ and $\{A_K^\dagger A_L^\dagger B_M^\dagger\}$ are generated in the same way. For more details, we refer to refs. 25 – 27.

3. Accuracy of the SAC-CI general- R method: C_2

The SAC-CI general- R method was proposed in 1991 and first applied to the excited, ionized and electron attached states of CO and C_2 to investigate its accuracy and efficiency for describing multi-electron processes.²⁴ Table 1 shows a comparison of the full-CI and SAC-CI results for C_2 at its equilibrium bond length. The basis set was the [4s2p] GTOs of Huginaga-Dunning.^{55,56} The active MOs were limited to four occupied and five unoccupied MOs. ‘Excitation level’ denotes the number of electrons involved in the excitation, ionization, or electron attachment. ‘Main configuration’ shows the most important configuration in the full-CI, ‘size’ denotes the SAC/SAC-CI dimensions, and Δ shows the difference in the total energy between SAC-CI and full-CI.

Since the $p\sigma$ -bonding MO is left unfilled in the low-lying region, the C_2 molecule has many doubly excited states in a relatively low-energy region.

Table 1. SAC-CI and full-CI results in hartree for C₂ at R=1.24253Å (equilibrium distance)

State	Exc. level	Main configuration ^a (C>0.35)	Full-CI		SAC-CI general-R ^b		
			size	energy	size	energy	Δ ^c *10 ³
Singlet							
¹ Σ _g ⁺	0	0.85(2222)-0.35(20222)	748	-75.52629	46	-75.51985	6.44
					112	-75.52378	2.51
¹ Π _u	1	0.96(22121)	654	-75.45297	86	-75.45147	1.50
¹ Σ _g ⁺	2	0.63(22202 + 22022)	748	-75.42469	112	-75.42195	2.74
¹ Δ _g	2	0.68(22202 - 22022)	748	-75.42356	112	-75.42130	2.26
¹ Π _g	2	0.90(21212)+0.36(2211101)	654	-75.32914	69	-75.32437	4.77
¹ Σ _u ⁺	1	0.86(21221)	688	-75.30272	111	-75.30186	0.86
¹ Σ _g ⁺	2	0.60(20222)+0.39(2222)	748	-75.25369	112	-75.24821	5.48
¹ Σ _u ⁺	1	0.62(221201 - 2221001)	620	-75.22000	79	-75.21597	4.03
¹ Δ _u	1	0.63(221201)+0.62(2221001)	620	-75.20743	111	-75.20551	1.92
						(2.90 ± 1.46) ^d	
Triplet							
³ Π _u	1	0.94(22121)	950	-75.50716	158	-75.50437	2.79
³ Σ _u ⁺	1	0.91(21221)	960	-75.48006	152	-75.47606	4.00
³ Σ _g ⁺	2	0.96(22112)	940	-75.45908	95	-75.45324	5.84
³ Π _g	2	0.90(21212)	960	-75.42354	124	-75.41957	3.97
³ Σ _u ⁺	1	0.57(222101 - 2212001)	960	-75.28156	152	-75.27305	8.51
³ Δ _u	1	0.62(2221001 + 2212001)	940	-75.25573	152	-75.24966	6.07
³ Π _g	2	0.80(2211101)+0.48(222011)	960	-75.23213	124	-75.22675	5.38
³ Σ _u ⁺	1	0.62(2221001+221201)	940	-75.23070	115	-75.22491	5.79
³ Π _g	2	0.59(2211101)+0.48(222011 - 220211)	960	-75.19460	124	-75.18999	4.61
³ Σ _g ⁺	2	0.50(212111 - 2112101)	920	-75.19404	124	-75.18586	8.18
		-0.42(212111 - 2112101)				(5.51 ± 1.72) ^d	
Cation							
² Π _u	1	0.84(2212)-0.39(20122)	756	-75.06396	145	-75.05952	4.44
² Δ _g	2	0.66(22201 - 22021)	784	-74.99347	141	-74.99174	1.73
² Σ _g ⁺	2	0.61(22201 + 22021)-0.37(20221)	784	-74.99019	141	-74.98752	2.67
² Σ _g ⁺	2	0.82(22111)-0.48(22111)	728	-74.97066	109	-74.96650	4.16
² Π _g	2	0.85(21211)	756	-74.96718	139	-74.96376	3.42
² Σ _u ⁺	1	0.90(2122)	784	-74.96041	149	-74.95513	5.28
² Π _u	3	0.89(22102)	756	-74.95202	145	-74.94621	5.81
² Δ _u	3	0.64(21202 - 21022)	728	-74.89972	123	-74.89819	1.53
² Σ _u ⁺	3	0.61(21202 + 21022)	784	-74.86227	149	-74.86018	2.09
² Σ _g ⁺	2	0.81(20221)	784	-74.84186	141	-74.83864	3.22
² Σ _u ⁺	3	0.78(21112)+0.45(21112)	728	-74.83681	123	-74.83394	2.87
						(3.38 ± 1.34) ^d	
Anion							
² Σ _g ⁺	1	0.93(22221)	1164	-75.57950	133	-75.57263	6.87
² Π _u	2	0.96(22122)	1100	-75.54346	142	-75.54102	2.44
² Σ _u ⁺	2	0.87(21222)	1144	-75.48444	121	-75.48003	4.41

Continue

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${}^3\Pi_g$	1	0.88(222201)	1100	-75.35620	125	-75.35020	6.00
${}^2\Sigma_g^+$	2	0.64(222111 - 2212101)	1144	-75.32372	121	-75.31868	5.04
${}^2\Sigma_g^-$	2	0.66(2221101)-0.50(221211)+0.45(221211)	1056	-75.32053	125	-75.31667	3.86
${}^3\Pi_g$	3	0.78(2211201)+0.56(222021)	1100	-75.31882	125	-75.31391	4.91
${}^2\Delta_g$	2	0.59(221211)+0.57(2221101)+0.35(2221101)	1056	-75.31794	121	-75.31379	4.15
${}^2\Delta_g$	2	0.60(221211)-0.58(2221101)+0.36(2221101)	1056	-75.30293	125	-75.29987	3.06
${}^2\Sigma_g^-$	2	0.65(2221101)-0.49(221211)+0.47(221211)	1056	-75.28780	125	-75.28073	7.07
						(4.78 ± 1.45) ^d	

^a The MO ordering is (2s)(2s σ^*)(p π)(p π)(p σ)(p π^*)(p π^*)(p σ^*)(p σ^*).

^b The first row is the SAC value and all the others are the SAC-CI values.

^c Δ shows the difference from the full CI result.

^d (x ± y) where x means the average discrepancy from the full-CI value and y means the standard deviation, both in millihartree.

As seen from the excitation level, there are many two- and even three-electron processes. The errors of the general-*R* method are consistently small, independent of the excitation levels; this is clearly seen from the average discrepancies and the standard deviations given in the parentheses. The sizes of the matrices involved are much smaller than those of the full-CI.

The average discrepancy in the excitation energy, ionization energy, and electron affinity was calculated from the results shown in Table 1, and it was 0.054 eV for the general-*R* method. From the results of CO and C₂, it was confirmed that the SAC-CI general-*R* method describes many-electron processes very accurately. *In general, the SAC-CI SD-R method is reliable for single electron processes. For two- and many-electron processes, we should use the general-R method.*

4. Valence and inner-valence ionization spectra of molecules

4.1. Comparison with the full-CI spectra: N₂ and CO

First we show the accuracy and efficiency of the SAC-CI general-*R* method for describing the main and satellite peaks in the ionization spectra. We investigated the outer- and inner-valence ionization spectra of N₂ and CO using full-CI and SAC-CI general-*R* method.²⁸ Though the molecules are small, many shake-up states exist in the inner-valence region.^{28,57-61} The basis sets were [4s2p1d] GTOs^{55,56} with one Rydberg *s* function. Since full-CI calculations were limited for solving many roots, the active spaces were restricted to five occupied and five unoccupied MOs. In the general-*R* calculations, higher-excitation operators were generated by the exponential

generation algorithm and were included up to 6-plex excitations. For comparison, SAC-CI SD-*R* calculations without perturbation selection were also performed.

Fig. 1 compares the ionization spectra of N_2 calculated by the full-CI, SAC-CI general-*R* and SD-*R* methods. Three main peaks were well reproduced by both the general-*R* and SD-*R* methods. The satellite peaks in the inner-valence region were reproduced quite accurately by the general-*R* method, while the SD-*R* method was not as satisfactory for these peaks. Note that the SAC-CI general-*R* spectrum almost completely superposes the full-CI spectrum. The SAC-CI general-*R* method gave quite accurate peak positions and intensities for both main peaks and satellite peaks. The intensities were mainly due to the final-state interaction with $(3\sigma_g)^{-1}$ and $(2\sigma_u)^{-1}$, which were precisely described by explicit inclusion of interactions between dominant doubles and higher triples and quadruples.

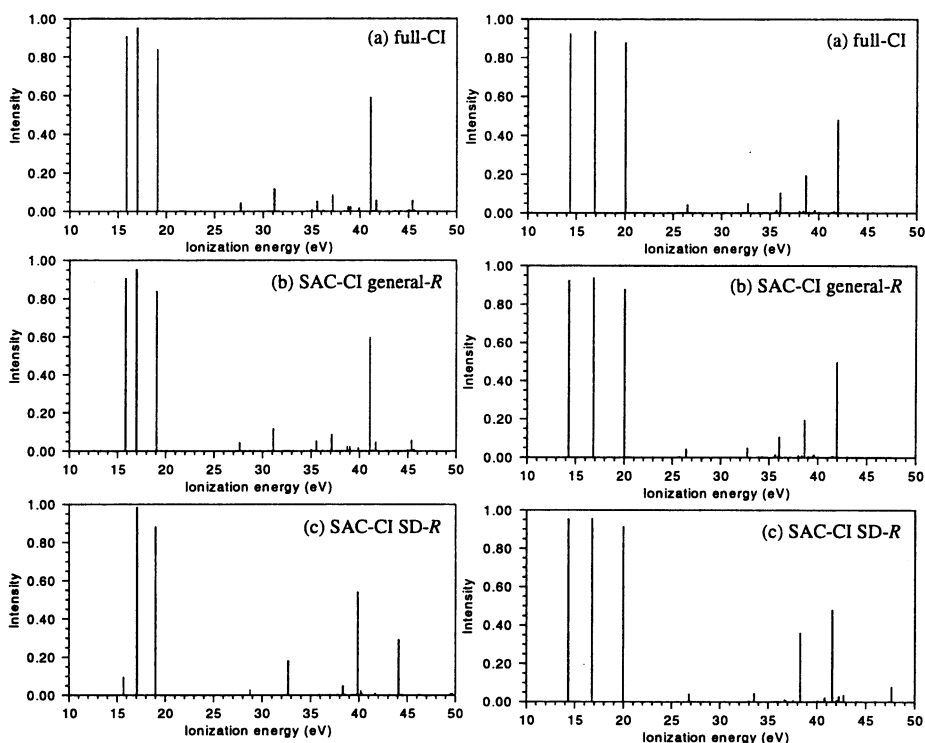


Fig. 1. Ionization spectrum of N_2

Fig. 2. Ionization spectrum of CO

Examination of the method was also performed for the ionization spectrum of CO as shown in Fig. 2. Many shake-up states appear in the 25 – 42 eV region as observed in the experimental spectrum. Again, the SAC-CI general-*R* method gave accurate spectrum for both position and intensity. It is interesting that the SD-*R* method gave better descriptions for CO than for N₂: two small peaks at ~26.5 and ~32.7 eV and prominent peak at ~42 eV were reproduced. But, the twinning of the peaks at c.a. 36.0 eV was only reproduced by the general-*R* method.

These results show that the SAC-CI general-*R* method is an accurate and reliable method and enables a quantitative analysis of the ionization spectra in both outer- and inner-valence regions.

4.2. Inner-valence ionization spectra of H₂O and H₂S

The Group VI hydrides show interesting characteristic ionization peaks in the inner-valence region of the ionization spectrum. In particular, the satellite peaks of H₂O and H₂S have been intensively studied by the SRPES,⁶² XPS,⁶³ and EMS spectroscopies.^{64,65} Since the inner-valence spectra are very complicated, the detailed assignments of the peaks have long been difficult. In this section, we show the SAC-CI general-*R* results of the inner-valence ionization spectra of H₂O and H₂S.³⁴ We compare our SAC-CI spectra directly with the experimental spectra and characterize in detail the nature of the satellite peaks. We calculated the vertical ionization energies at the experimental geometry.⁶⁶ Since two-electron processes involving the excitations to the Rydberg orbitals were known to be important, we used cc-pVTZ^{67,68} augmented with three s-, p-, and d-type Rydberg functions⁶⁹ for O and S.

The main peaks of these molecules were accurately calculated by both the general-*R* and SD-*R* methods, and so we here present only the results of the inner-valence spectra. Fig. 3 shows the inner-valence ionization spectrum of H₂O observed with the EMS⁶⁴ experiment compared with the spectrum calculated by the SAC-CI general-*R* method. The EMS experiment observed three satellite bands numbered 1-3, which were shown by a dashed line. Our calculation gave many satellite peaks in this region of the spectrum and these peaks makes up as a whole the bands observed experimentally.

For the prominent band 1 centered at 32.2 eV, we assigned three split ²A₁ states. The total pole strength of these states was calculated to be 0.612 in good agreement with the experimental intensity of 0.580.⁶⁴ For band 2 of

the medium pole strength at 35.0 eV, three shake-up states were calculated. These states were characterized as the shake-up states including the excitation to the Rydberg orbitals. We also found the medium band at around 37 eV, which was shown by arrow in Fig. 3. This band was composed by five shake-up states. The total intensity of the satellite peaks in the region of 34-38 eV was 0.168, which agreed well with the experimental value of 0.180.⁶⁴ The weak broad band 3 at 38.90 eV was assigned to the five shake-up states, which were mainly described as the ionizations accompanied by the excitations to the valence orbitals.

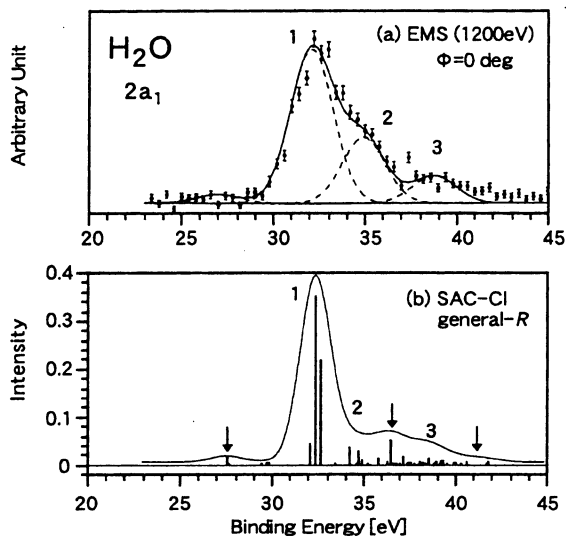


Fig. 3. Inner-valence ionization spectrum of H₂O by (a) EMS⁶⁴ and SAC-CI general-R method.³⁴

In the inner-valence region, we found two peaks that were not reported in the EMS study. In the lower energy region below the strong band 1, we calculated a weak peak at 27.56 eV. The EMS spectrum also seems to have a peak in this energy region ~27.0 eV. A very weak band seems to exist at around ~41 eV in EMS. Two shake-up states with low intensity were assigned to this band.

Next, we show the results of the inner-valence spectrum of H₂S, which has more complicated structure than that of H₂O as shown in Fig. 4. It shows the theoretical ionization spectrum in the entire inner-valence region along with the EMS experimental spectrum. In order to elucidate this spectrum,

many experimental techniques have been applied: the SRPES⁶² observed 13 peaks and gave fine analysis especially in the region of 22-24 eV. The XPS⁶³ experiment determined the relative cross sections of the satellite peaks. The present SAC-CI general-*R* method calculated more than 35 states with considerable intensities up to double ionization threshold, and gave detailed theoretical assignments for all of these peaks.

As seen in Fig. 4, the SAC-CI general-*R* method reproduced the shape of the EMS spectrum. A weak band 1 was observed below the strong peak; the present method calculated “shake-down” state assigned as $(2b_1^{-2}na_1)$, which was consistent with the experimental analysis. For the strong band 2 observed at 22.37 eV, a prominent peak was calculated at 22.21 eV, which was characterized as a linear combination of $(4a_1^{-1})$ and $(2b_1^{-2}na_1)$. The intensity of this peak was calculated to be 0.241 in agreement with the XPS intensity of 0.210. Two split peaks were calculated at 23.20 and 23.62 eV, and constitute band 3 centered at 24.07 eV of EMS. For the bands 4–7 observed in the EMS, many satellite peaks were continuously calculated. As shown in Fig. 4, the convoluted theoretical spectrum agreed well with the shape of EMS spectrum in this region. An arrow in the theoretical spectrum shows a cluster of small satellite peaks: this was observed by the SRPES and XPS,^{62,63} but was missing in the EMS, though a small structure was also observed by EMS.

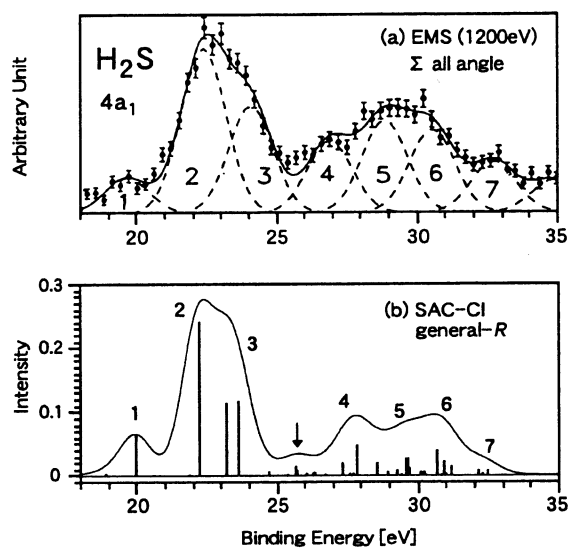


Fig. 4. Inner-valence ionization spectrum of H₂S by (a) EMS⁶⁵ and SAC-CI general-*R* method.³⁴

In the series of studies for Group V and VI hydrides,^{34,70} the SAC-CI general-*R* method has reproduced fine details of the experimental ionization spectra for not only the peak positions but also the intensities as shown in the present examples. It could successfully give quantitative assignments for the peaks in both the outer- and inner-valence regions.

4.3. Outer-valence ionization spectra of XONO₂ (X=F, Cl, Br, I)

In conjugated molecules, multi-electron processes appear in lower energy region of the ionization spectra than in non-conjugated molecules. The valence ionization spectra of XONO₂ (X=F, Cl, Br, I) are of interest, since their He I PES have been recently observed except for X=I.⁷¹⁻⁷³ XONO₂ is known to be an important molecular species in the ozone depletion catalytic cycle in the atmosphere.⁷⁴⁻⁷⁷ In particular, ClO, which appears in the ozone depletion cycle, reacts with NO₂ to produce ClONO₂, and therefore, ClONO₂ is considered to be one of the important temporary reservoir species of Cl atom.

We have investigated the outer-valence ionization spectra of these compounds by the SAC-CI SD-*R* method.²¹ The calculated spectra agreed very well with the experimental ones and some new assignments were proposed. Here, we apply the SAC-CI general-*R* method to these molecules to see the effects of the two-electron processes interacting with the one-electron processes that constitute the main peaks. The geometries and the basis sets were the same as those used in the SD-*R* study.²¹ The basis sets are [5s3p1d] GTOs⁵⁶ for N, O, and F, [6s5p1d] GTOs⁷⁸ for Cl. For Br and I, the relativistic effective core potential^{79,80} was used with [2s2p1d] GTO basis.

We show the SAC-CI general-*R* spectra of ClONO₂ and BrONO₂ in Figs. 5 and 6, respectively, in comparison with the spectra observed by the He I PES. For the main peaks that are due to the one-electron processes, the present general-*R* calculations gave the same assignments as those of the previous SD-*R* calculations.²¹ However, in the present calculations, many shake-up states appeared in the low-energy region and the Koopmans' picture broke down. Correlation diagram of the valence ionized states of XONO₂ is shown in Fig. 7 for X = F, Cl, Br, and I. From Fig. 7, we see that the character of HOMO is different between FONO₂ and other molecules. The valence ionized states shift to smaller energy as X is replaced from Cl to I, reflecting the I.P. of the halogen atoms.

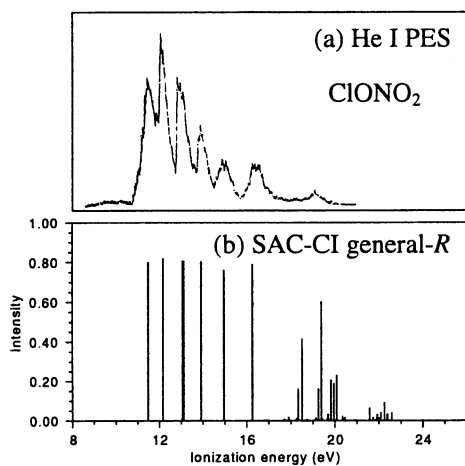


Fig. 5. Outer-valence ionization spectrum of ClONO_2 by (a) He I PES⁷¹ and (b) SAC-CI general-R

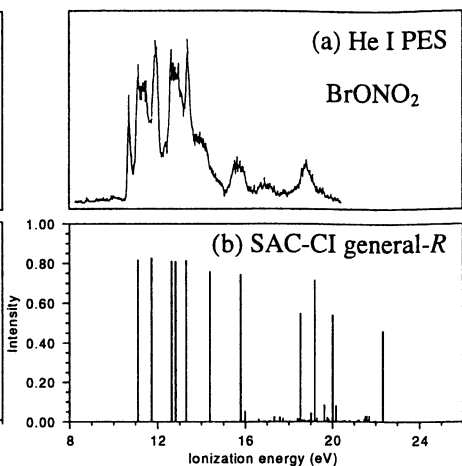


Fig. 6. Outer-valence ionization spectrum of BrONO_2 by (a) He I PES⁷³ and (b) SAC-CI general-R

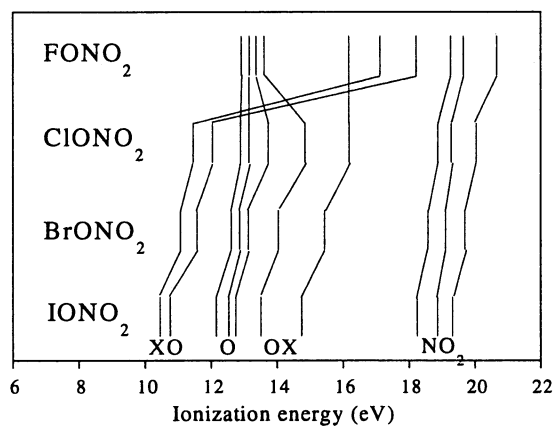


Fig. 7. Correlation diagram of outer-valence ionized states of XONO_2 ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$) calculated by the SAC-CI method

For ClONO_2 , the first and second ionized states were characterized as the ionizations from the orbitals localized on ClO unit. The third band was reported to be an overlapping band since different two vibrational structures

were observed. Actually, in our calculation, two ionized states were closely calculated for this band. Up to 16 eV, all the states are mainly described by the one-electron processes. Many satellite peaks appeared below from the band around 18 eV as shown in Fig. 5. The intensities of these peaks originate from the MOs localized on NO₂ unit. For BrONO₂, the IPs of the shake-up states were calculated in the energy of 16-18 eV. Correspondingly, in the He I PES, a weak continuous band was observed in this region.

5. Analytical energy gradient of the SAC-CI general-*R* method

Recently, the SAC-CI analytical energy gradient method has been extended to the general-*R* method, and the performance of the method has been examined for the excited states of BH and CH,³⁷ for which some experimental information for the two-electron processes is available.⁸¹ As noted in Sec. 2.2, the method is useful for studying the physical properties of the multi-electron processes and the excited states of open-shell systems. Here, we show the results of the excited states of BH and CNC.

5.1. BH

First, we show the spectroscopic properties of BH. In the SAC-CI general-*R* method, the *R*-operators were limited up to triples. The results of r_e , ω_e , and T_e are summarized in Table 2 comparing with the experimental values.⁸¹

As shown by ‘excitation level’, low-lying A¹Π and a³Π states of BH are described essentially by one-electron excitations from the ground state, while C¹Δ, C¹Σ⁺ and b³Σ⁻ states are described by two-electron excitations. For the one-electron excitation processes, the SAC-CI SD-*R* and general-*R* methods give very similar results in good agreement with experiments: the effects of the triples are negligibly small and within 0.005 Å, 0.03 eV, and 50 cm⁻¹ for r_e , T_e , and ω_e , respectively. For the other three states generated by the two-electron excitation processes, the general-*R* method gives considerably better results than the SD-*R* method, especially for T_e . The effect of including triples amounts up to c.a. 0.8 eV for T_e of b³Σ⁻ and C¹Δ states. The calculated r_e agreed excellently with experiments for these states; the deviations were within 0.002 Å. Thus, for the two-electron processes, we should use the SAC-CI general-*R* method for obtaining quantitatively reliable results.

Table 2. Excitation level, equilibrium internuclear distance (r_e), adiabatic excitation energy (T_e), and harmonic vibrational frequency (ω_e), for the singlet and triplet states of BH.

State	Method	Exc. level	r_e (Å)	T_e (eV)	ω_e (cm ⁻¹)	Main configuration ^a
$X^1\Sigma_g^+$	SAC	0	1.243	---	2362	
	Exptl. ^b		1.232	---	2356	
$a^3\Pi$	SD- <i>R</i>	1	1.194	1.190	2664	$0.94(3\sigma^{-1}1\pi)+0.32(3\sigma^{-1}2\pi)$
	general- <i>R</i>	1	1.195	1.163	2653	$0.93(3\sigma^{-1}1\pi)+0.32(3\sigma^{-1}2\pi)$
	Exptl. ^b		1.201	---	---	
$A^1\Pi$	SD- <i>R</i>	1	1.236	3.074	2227	$0.94(3\sigma^{-1}1\pi)$
	general- <i>R</i>	1	1.241	3.018	2171	$0.93(3\sigma^{-1}1\pi)$
	Exptl. ^b		1.219	2.868	2251	
$b^3\Sigma^-$	SD- <i>R</i>	2	1.206	5.470	2629	$0.86(3\sigma^{-2}1\pi^2)+0.30(3\sigma^{-2}1\pi 2\pi)$ $-0.30(3\sigma^{-2}1\pi 2\pi)$
	general- <i>R</i>	2	1.228	4.616	2405	$0.84(3\sigma^{-2}1\pi^2)+0.30(3\sigma^{-2}1\pi 2\pi)$ $-0.30(3\sigma^{-2}1\pi 2\pi)$
	Exptl. ^b		1.227	---	---	
$C^1\Delta$	SD- <i>R</i>	2	1.190	6.815	2776	$0.90(3\sigma^{-2}1\pi^2)$
	general- <i>R</i>	2	1.198	6.092	2673	$0.89(3\sigma^{-2}1\pi^2)$
	Exptl. ^b		1.196	5.701	2610	
$C^1\Sigma^+$	SD- <i>R</i>	2	1.191	7.550	2762	$0.63(3\sigma^{-2}1\pi^2)+0.63(3\sigma^{-2}1\pi^2)$
	general- <i>R</i>	2	1.200	7.014	2657	$0.63(3\sigma^{-2}1\pi^2)+0.63(3\sigma^{-2}1\pi^2)$
	Exptl. ^b		1.213	6.854	2475	

^a The Hartee-Fock electronic configuration for the ground state is $(1\sigma)^2(2\sigma)^2(3\sigma)^2$.

^b Ref. 81

5.2. CNC

Next, we show the result for the open-shell molecule CNC, whose excited states are described by the two-electron processes from the closed-shell SAC (cation) state. We first calculate closed-shell CNC⁺ by the SAC method, and

then calculate various electronic states of CNC radical by the SAC-CI electron-attachment method. In Table 3, the SAC-CI general-*R* and SD-*R* results of r_e and T_e are compared with the experiment and with the CASPT2 calculation.⁸² The *R*-operators up to triples were included in the general-*R* calculation.

Table 3. Excitation level, equilibrium internuclear distance (R_{CN}), adiabatic excitation energy (T_e) for the doublet ground and excited states of CNC.

State	Method	Exc. level	R_{CN} (Å)	T_e (eV)	Main configuration ^a
$X^2\Pi_g$	SD- <i>R</i>	1	1.257	---	$0.97(1\pi_g)+0.13(1\pi_u^{-1}1\pi_g2\pi_u)$
	general- <i>R</i>	1	1.253	---	$0.91(1\pi_g)+0.16(1\pi_u^{-1}1\pi_g2\pi_u)$
	CASPT2 ^b		1.253	---	
	Exptl. ^c		1.245	---	
$A^2\Delta_u$	SD- <i>R</i>	2	1.257	7.205	$0.92(3\sigma_u^{-1}1\pi_g^2)+0.92(3\sigma_u^{-1}1\pi_g^2)$
	general- <i>R</i>	2	1.256	3.934	$0.92(3\sigma_u^{-1}1\pi_g^2)+0.91(3\sigma_u^{-1}1\pi_g^2)$
	CASPT2 ^b		1.257	3.425	
	Exptl. ^c		1.249	3.761	
$B^2\Sigma_u^+$	SD- <i>R</i>	2	1.260	7.644	$0.65(3\sigma_u^{-1}1\pi_g^2)+0.65(3\sigma_u^{-1}1\pi_g^2)$
	general- <i>R</i>	2	1.259	4.545	$0.65(3\sigma_u^{-1}1\pi_g^2)+0.65(3\sigma_u^{-1}1\pi_g^2)$
	CASPT2 ^b		1.259	4.001	
	Exptl. ^c		1.259	4.315	

^a The electronic configuration and the excitation level are given relative to the closed-shell CNC⁺, namely, (core)⁶(3 σ_g)²(2 σ_u)²(1 π_u)⁴(4 σ_g)²(3 σ_u)²

^b Ref. 82

^c Ref. 81

The ground state, $X^2\Pi_g$ is described by the one-electron process, while the other two doublet excited states, $A^2\Delta_u$ and $B^2\Sigma_u^+$, are represented by the two-electron process. For r_e , both general-*R* and SD-*R* gave excellent results for the ground and excited states: the deviations from the experiment are within 0.008 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 3.1-3.3 eV. The adiabatic excitation energies calculated by the general-*R* method agree well with the experiment, while the CASPT2 method underestimates these values.

6. Equivalence of EOM-CC and CC-LRT to SAC-CI

The EOM-CC and CC-LRT methods are equivalent to the SAC-CI method. This was obvious theoretically from the beginning, however, this fact has not been properly understood by some investigators. In this section, we give some numerical proofs that show the equivalence of EOM-CC and CC-LRT to SAC-CI both in the SD level. We performed SAC-CI SD-*R* calculations for CH₂ and CH⁺ for which the EOM-CCSD⁵² and CCSD-LRT⁴⁶ calculations were reported. We also would like to take this opportunity to show that the approximation of neglecting the unimportant unlinked terms and the perturbation selection of the linked operators are both accurate and useful. As noted in the introduction, the program system MEG/EX-MEG⁴⁰ coded in 1985 can perform both SAC-CI SD-*R* and general-*R* calculations as special cases of more general MEG/EX-MEG calculations without introducing any approximations. Such calculations are also possible with the SAC-CI96 program system.⁴¹

The excitation energies of the singlet and triplet excited states of CH₂ and singlet excited states of CH⁺ are compared in Tables 4 and 5, respectively. The basis sets and geometries are identical to those used in the EOM-CCSD and CCSD-LRT calculations. The SAC-CI SD-*R* results obtained without any selections are given in the column under 'full'. From Table 4 we see that the SAC-CI SD-*R* and EOM-CCSD give identical results, and from Table 5 that the SAC-CI SD-*R* and CCSD-LRT give identical results: This is a numerical proof of the equivalence of the three methods.

A policy of the SAC/SAC-CI program is we calculate only important terms, and we neglect terms if they are certainly negligibly small. By doing so, we can make programs more efficient, so that we can calculate larger and more complex systems, and the physics and chemistry of the calculated results becomes clearer than otherwise we can. It is by this virtue that we could have been able to apply our SAC-CI method to the porphyrin systems¹⁸⁻²⁰ and to the reaction center of photosynthesis of *Rhodospseudomonas viridis*.^{22,23} For this purpose, we may introduce the following approximations.

(1) Some classes of unimportant unlinked terms are neglected from the

beginning.

(2) The perturbation selection of the linked operators and further the selection among the unlinked terms composed of the selected linked terms are performed.

The accuracy of these approximations is also shown in Tables 4 and 5. App.(1) means that we adopt the approximation (1) given above, and App.(2) means that the approximation (2) is further done together with the approximation (1). It is seen that both approximations give reliable results within chemical accuracy. The results of SAC-CI-V method^{6,7} are also given for CH⁺, and we can see the reliability of this method.

Table 4. Excitation energy (in eV) of singlet and triplet excited states for CH₂ with 6-31G*

State	SAC-CI-NV			EOM-CCSD ^d	Full-CI ^d
	Full ^a	App.(1) ^b	App.(2) ^c		
Singlet					
A ₁	5.844	5.871	5.796	5.844	4.517
	9.120	9.109	9.111	9.120	9.053
A ₂	6.101	6.105	6.105	6.101	6.093
B ₁	1.668	1.669	1.692	1.668	1.679
B ₂	9.692	9.660	9.637	9.692	8.254
Triplet					
A ₁	8.389	8.376	8.406	8.389	8.327
A ₂	5.300	5.305	5.325	5.300	5.315
B ₁	-0.344	-0.344	-0.328	-0.344	-0.310
B ₂	8.382	8.370	8.342	8.382	6.904
	9.304	9.299	9.304	9.304	9.150

^a SAC-CI-NV with all terms and without any selection

^b Unlinked terms of R₁*S₂ and R₂*S₂ are included and others are neglected.

^c Unlinked terms are same as b) and further selection is performed

with $\lambda_g=10^{-6}$, $\lambda_e=10^{-7}$, $\tau_g=0.005$, $\tau_s=\tau_d=0.05$, $\tau=10^{-3}$.

^d Ref. 52

Table 5. Excitation energy (in eV) of singlet excited states for CH⁺ with [5s3p1d/3s1p].

State	SAC-CI-NV			SAC-CI-V		CC-LRT ^d
	Full ^a	App.(1) ^b	App.(2) ^c	App.(1) ^b	App.(2) ^c	
¹ Σ ⁺	9.109	9.098	9.082	9.114	9.080	9.109
	13.580	13.577	13.591	13.574	13.587	13.580
¹ Π	3.261	3.272	3.283	3.262	3.280	3.261
	14.454	14.468	14.460	14.444	14.455	14.454

^a SAC-CI-NV with all terms and without any selection

^b Unlinked terms of R₁*S₂ and R₂*S₂ are included and others are neglected.

^c Unlinked terms are same as b) and further selection is performed

with $\lambda_g=10^{-6}$, $\lambda_e=10^{-7}$, $\tau_g=0.005$, $\tau_s=\tau_d=0.05$, $\tau=10^{-3}$.

^d Ref. 46

When we want to apply the SAC-CI method to multi-electron processes as discussed in this review, the improvement within the SD-*R* approximation is meaningless: we have to extend the *R*-space to include higher excitation operators such as triple, quadruple, etc., excitations, as clearly shown in 1991.²⁴ Again, the number of triples, quadruple, etc. operators are huge even for molecules of moderate size, so that we adopt the EG algorithm combined with the perturbation selection. This makes us possible to calculate chemically interesting systems with considerable accuracy. We have performed such calculations of general-*R* method for many molecules.^{28-34,70} In recent papers of the EOM-CC and CC-LRT, similar extensions of the *R*-operator are also done, but they do not adopt the approximations (1) and (2) explained above.⁵¹⁻⁵³

7. Summary

In this review article, we have explained the SAC-CI general-*R* method in comparison with the SD-*R* method and showed some applications to the valence ionization spectra of molecules. The SAC-CI general-*R* method is applicable not only to ordinary one-electron processes, but also to multi-electron processes accompanied by the excitation (from singlet to septet), ionization, and electron-attachment processes. It is also applicable to

the excited states of open-shell systems. It can deal with a large number of different states at the same time: this merit is important for calculations of ionization spectra, because so many different states of different multi-electron processes are involved up to deep inner valence region. For this reason, these multi-electron processes should be important for the study of high-energy chemical reaction dynamics and energy relaxation processes.

In this review, we first explained the underlying theoretical background of the SAC-CI general-*R* method and the algorithms currently adopted in the program. We next showed the accuracy and the efficiency of the method in the test calculations of the excited, ionized, and electron attached states of CO and C₂ in comparison with the full-CI results.²⁴ We also compared the valence ionization spectra of N₂ and CO with the full-CI spectra.²⁸ More recently, the method has been extensively applied to a variety of the systems for which interesting valence ionization spectra have been observed.^{29-34,70} Here, the applications to H₂O, H₂S, and XONO₂ (X=F, Cl, Br, I) have been reviewed. The spectra of these molecules were quantitatively reproduced so that the present method gave the detailed assignments for the band observed by the experiments.

The analytical energy gradients of the SAC-CI general-*R* method have been recently developed and implemented. This is a very powerful tool for studying the geometrical and vibrational properties of the molecular states that are produced by multi-electron processes from the ground state: experimental investigations are rather difficult, though some pioneering studies certainly exist,⁸¹ and so, reliable theoretical calculations are very valuable. The results of BH and CNC for which some of the excited states are described by the multi-electron processes have been presented. The method was confirmed to be quite accurate providing reliable results for the properties of the systems including multi-electron processes.

We presented the numerical results for the excited states of CH₂ and CH⁺ that show the EOM-CC and CC-LRT methods are the same as the SAC-CI method. We also showed that some of the unlinked terms can be safely neglected and that the perturbation selection of linked operators is an accurate and useful approximation. This makes the SAC-CI SD-*R* and general-*R* method to be chemically useful method.

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References

1. H. Nakatsuji and T. Yonezawa, *Chem. Phys. Lett.* **87**, 426 (1982).
2. H. Nakatsuji, *Chem. Phys.* **75**, 425 (1983).
3. H. Nakatsuji, *Chem. Phys.* **76**, 283 (1983).
4. H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053 (1978).
5. H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978).
6. H. Nakatsuji, *Chem. Phys. Lett.* **67**, 329 (1979).
7. H. Nakatsuji, *Chem. Phys. Lett.* **67**, 334 (1979).
8. H. Nakatsuji, *SAC-CI method: Theoretical Aspects and Some Recent Topics*, Computational Chemistry - Review of Current Trends, Vol. 2, (World Scientific Singapore, 1997).
9. H. Nakatsuji, *Acta Chim. Hungarica* **129**, 719 (1992).
10. H. Nakatsuji, O. Kitao and T. Yonezawa, *J. Chem. Phys.* **83**, 723 (1985).
11. O. Kitao and H. Nakatsuji, *Proc. Indian Acad. Sci.* **96**, 155 (1986).
12. O. Kitao and H. Nakatsuji, *J. Chem. Phys.* **87**, 1169 (1987).
13. H. Nakatsuji, M. Ehara, M. H. Palmer and M. F. Guest, *J. Chem. Phys.* **97**, 2561 (1992).
14. H. Nakatsuji and M. Ehara, *J. Chem. Phys.* **98**, 7179 (1993).
15. H. Nakatsuji, M. Ehara and T. Momose, *J. Chem. Phys.* **100**, 5821 (1994).
16. H. Nakatsuji and M. Ehara, *J. Chem. Phys.* **101**, 7658 (1994).
17. M. Ehara and H. Nakatsuji, *J. Chem. Phys.* **102**, 6822 (1995).
18. H. Nakatsuji, J. Hasegawa, and M. Hada, *J. Chem. Phys.* **104**, 2321 (1996).
19. K. Toyota, J. Hasegawa and H. Nakatsuji, *Chem. Phys. Lett.* **250**, 437 (1996).
20. K. Toyota, J. Hasegawa and H. Nakatsuji, *J. Phys. Chem.* **101**, 446 (1997).
21. M. Ehara, Y. Ohtsuka and H. Nakatsuji, *Chem. Phys.* **226**, 113 (1998).
22. H. Nakatsuji, J. Hasegawa, K. Ohkawa, *Chem. Phys. Lett.* **296**, 499 (1998).
23. J. Hasegawa, K. Ohkawa, H. Nakatsuji, *J. Phys. Chem.* **B102**, 6205 (1989).
24. H. Nakatsuji, *Chem. Phys. Lett.* **177**, 331 (1991).
25. H. Nakatsuji, *J. Chem. Phys.* **83**, 731 (1985).
26. H. Nakatsuji, *J. Chem. Phys.* **83**, 5743 (1985).
27. H. Nakatsuji, *J. Chem. Phys.* **94**, 6716 (1991).
28. M. Ehara and H. Nakatsuji, *Chem. Phys. Lett.* **282**, 347 (1998).
29. J. Hasegawa, M. Ehara and H. Nakatsuji, *Chem. Phys.* **230**, 23 (1998).
30. M. Ehara, P. Tomasello, J. Hasegawa and H. Nakatsuji, *Theor. Chem. Acc.* **102**, 161 (1999).

31. M. Ehara and H. Nakatsuji, *Spectrochim. Acta.* **A55**, 487 (1998).
32. J. Wan, M. Ehara, M. Hada and H. Nakatsuji, *J. Chem. Phys.* **113**, 5245 (2000).
33. J. Wan, M. Hada, M. Ehara and H. Nakatsuji, *J. Chem. Phys.* **114**, 5117 (2001).
34. M. Ehara, M. Ishida and H. Nakatsuji, *J. Chem. Phys.* **114**, 8990 (2001).
35. H. Nakajima and H. Nakatsuji, *Chem. Phys. Lett.* **280**, 79 (1997).
36. H. Nakajima and H. Nakatsuji, *Chem. Phys.* **242**, 177 (1998).
37. M. Ishida, K. Toyota, M. Ehara and H. Nakatsuji, *Chem. Phys. Lett.* in press.
38. H. Nakatsuji, *Program System for SAC and SAC-CI Calculations*, Program Library No. 146(Y4/SAC) Data Processing Center of Kyoto University, 1985.
39. H. Nakatsuji, *Program Library SAC85 (No. 1396)* Computer Center of the Institute for Molecular Science, Okazaki, Japan, 1986.
40. H. Nakatsuji, *Program system for the MEG/EX-MEG methods applied to molecular ground, excited, ionized, and electron attached states*, 1985.
41. H. Nakatsuji, M. Hada, M. Ehara, J. Hasegawa, T. Nakajima, H. Nakai, O. Kitao and K. Toyota, *SAC/SAC-CI program system (SAC-CI96) for calculating ground, excited, ionized, and electron-attached states having singlet to septet spin multiplicities*, 1996.
42. H. Monkhorst, *Int. J. Quantum Chem. Sympos.* **11**, 421 (1977).
43. E. Dalgaard and H. Monkhorst, *Phys. Rev.* **A28**, 1217 (1983).
44. D. Mukherjee and P. K. Mukherjee, *Chem. Phys.* **39**, 325 (1979).
45. H. Koch and P. Jorgensen, *J. Chem. Phys.* **93**, 3333 (1990).
46. H. Koch, H. J. Aa. Jensen, T. Helgaker, and P. Jorgensen, *J. Chem. Phys.* **93**, 3345 (1990).
47. J. Geertsen, M. Rittby and R. J. Bartlett, *Chem. Phys. Lett.* **164**, 57 (1989).
48. J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993).
49. J. F. Stanton and J. Gauss, *J. Chem. Phys.* **101**, 8938 (1994).
50. J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **102**, 3629 (1995).
51. D. J. Wadt and R. J. Bartlett, *J. Chem. Phys.* **101**, 3073 (1994).
52. S. Hirata, M. Nooijen and R.J. Bartlett, *Chem. Phys. Lett.* **326**, 255 (2000).
53. O. Christiansen, H. Koch, P. Jorgensen, *Chem. Phys. Lett.* **243**, 409 (1995).
54. T. V. Voorhis and M. Head-Gordon, *J. Chem. Phys.* **113**, 8873 (2000).
55. S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
56. T. H. Dunning Jr., *J. Chem. Phys.* **53**, 2823 (1970).
57. N. Kosugi, H. Kuroda and S. Iwata, *Chem. Phys.* **39**, 337 (1979).
58. W. C. Ermler, A. D. McLean, *J. Chem. Phys.* **73**, 2297 (1980).
59. P. W. Langhoff, S. R. Langhoff, T. N. Rescigno, J. Schirmer, L. S. Cederbaum, W. Domcke, W. von Niessen, *Chem. Phys.* **58**, 71 (1981).
60. J. Schirmer and O. Walter, *Chem. Phys.* **78** 201 (1983).
61. S. Ten-no, S. Iwata, S. Pal and D. Mukherjee, *Theor. Chem. Acc.* **102** 252 (1999).
62. M. Y. Adam, C. Cauletti and M. N. Plancastelli, *J. Electron Spectrosc. Relat. Phenom.* **42**, 1 (1987).

63. M. Y. Adam, A. Naves de Brito, M. P. Keane, S. Svensson, L. Karlsson, E. Kalline and N. Correia, *J. Electron Spectrosc. Relat. Phenom.* **56**, 241 (1991).
64. A. O. Bawagan, L. Y. Lee, K. T. Leung and C. E. Brion, *Chem. Phys.* **99**, 367 (1985).
65. C. L. French, C. E. Brion and E. R. Davidson, *Chem. Phys.* **122**, 247 (1988).
66. G. Herzberg, *Molecular Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).
67. T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
68. D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).
69. H. Dunning, Jr. and P. J. Hay, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer, III (Plenum, New York, 1977).
70. M. Ishida, M. Ehara and H. Nakatsuji, submitted for publication.
71. D. Wang, Y. Li, P. Jiang, X. Wang and B. Chen, *Chem. Phys. Lett.* **260**, 99 (1996).
72. D. Wang, Y. Li, P. Jiang, X. Wang and B. Chen, *Chem. Phys. Lett.* **262**, 771 (1996).
73. D. Wang and J. Peng, *J. Phys. Chem.* **100**, 4362 (1996).
74. F. S. Rowland, J. E. Spencer and M. J. Molina, *J. Phys. Chem.* **80**, 2711 (1976).
75. F. S. Rowland, *Ann. Rev. Phys. Chem.* **42**, 731 (1991).
76. M. J. Prather, *Nature* **355**, 534 (1992).
77. D. R. Hanson and A. R. Ravishankara, *J. Phys. Chem.* **96**, 7674 (1992).
78. A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72**, 5639 (1980).
79. L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, W. C. Ermler, *J. Chem. Phys.* **87**, 2812 (1987).
80. R. B. Ross, J. M. Powers, T. Atashroo, W. C. Ermler, L. A. LaJohn, P. A. Christiansen, *J. Chem. Phys.* **93**, 6654 (1990).
81. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, (Van Nostrand, New York, 1979).
82. R. Pd. and P. Chandra, *J. Chem. Phys.* **114**, 1589 (2001).