Mixed-exponentially generated wave function method for ground, excited, ionized, and electron attached states of a molecule

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Wave functions of excited, ionized, and electron attached states are produced by applying the excitator method to the mixed-exponentially generated (MEG) wave function for a ground state. This method is called excited-(EX-)MEG method and the computational algorithm is summarized. The MEG/EX-MEG method is a generalization of the SAC(symmetry adapted cluster)/SAC-CI method. Test applications are given for singlet, triplet, ionized, and anion states of hydrogen fluoride at different internuclear distances (R = Re, 2.1815 Re, and 3.2722 Re). Full-CI calculations are also done for all of these states in order to examine the accuracy of the MEG/EX-MEG method. It is good and reasonably constant among the various states with different energies, different multiplicities, different numbers of electrons, and different internuclear distances, though the sizes of the calculations are smaller than those of the conventional CI.

I. INTRODUCTION

A purpose of this series of studies[1-5] is to establish practically useful theories and computational methods for calculating potential energy surfaces of molecules in ground, excited, ionized, and electron attached states, and the transitions among them. The SAC (symmetry adapted cluster)[6]/SAC-CI method[5,7] is well established[8] and able to describe these states in considerable accuracy.[9,10] However, a limitation of this method is that the SAC theory is a single reference theory and therefore inapplicable when no state is well approximated by the Hartree–Fock (HF) model.[1] For chemical processes involving homolytic fissions of chemical bonds, quasidegenerate situations sometimes occur near dissociation limits. Since the SAC/SAC-CI method is so useful for calculating ground, excited, ionized, and electron attached states,[10] its generalization to quasidegenerate cases is really anticipated. The purpose of this paper is to generalize the SAC/SAC-CI method to such cases. We aim to get reliable potential curves of ground, excited, ionized, and electron attached states by smaller-size calculations than ordinary CI methods.

Electron correlations in atoms and molecules may be divided into "*separable*" and "*nonseparable*" (or "*coupled*") ones.[2,11,12] For separable correlations, cluster expansion of the wave function is most suitable.[10] It is written as

$$\Psi^{\mathrm{SAC}} = \exp\Big(\sum_K C_K S_K^\dagger\Big)|0\rangle, \tag{1}$$

where the exp operator is defined by

$$\exp\Big(\sum_K C_K S_K^\dagger\Big) = 1 + \sum_K C_K S_K^\dagger + \frac{1}{2}\sum_{K,L} C_K C_L S_K^\dagger S_L^\dagger + \frac{1}{3!}\sum_{K,L,M} C_K C_L C_M S_K^\dagger S_L^\dagger S_M^\dagger + \cdots, \tag{2}$$

and $|0\rangle$ is a single determinant,

$$|0\rangle = \|\varphi_1\alpha\varphi_1\beta\cdots\varphi_i\alpha\varphi_i\beta\cdots\varphi_n\alpha\varphi_n\beta\|. \tag{3}$$

This is the SAC expansion since the excitation operator $S_K^\dagger$ is chosen to be symmetry adapted. It belongs to the coupled cluster approach which was developed and used by Cizek,[13] Paldus,[14] Bartlett,[15] Mukherjee,[16] and others.[17] We have introduced the SAC expansion,[6] since the symmetry adaptation of the operators is necessary, because otherwise the wave function represents a mixed symmetry.[18] This expansion satisfies size consistency[19] or size extensivity,[20] and self-consistency.[21]

When the SAC theory well described a given state, the excited, ionized, and electron attached states produced therefrom are calculated by the SAC-CI method. This combination of the methods, SAC/SAC-CI method, has been applied successfully to a variety of molecular spectroscopic properties, as recently summarized in review articles.[9,10]

On the other hand, nonseparable correlations are not written by the exponential operator given by Eq. (1).[1] A typical example is the so-called quasidegenerate correlation, which appears in bond-breaking processes, open shells, and excited states. In the previous paper, we have proposed a new exponential-type operator[1,2]

$$\mathscr{E}\mathscr{L}\mathscr{P}\Big(\sum_K a_K A_K^\dagger\Big) \equiv Q\Big(a_0 + \sum_K a_K A_K^\dagger + \frac{1}{2}\sum_{K,L} a_{KL} A_K^\dagger A_L^\dagger + \frac{1}{3!}\sum_{K,L,M} a_{KLM} A_K^\dagger A_L^\dagger A_M^\dagger + \cdots\Big), \tag{4}$$

as being suitable for such correlations. We add here a symmetry projector Q in order to permit symmetry adapted operators $A_K^\dagger$ to run all the symmetries. In comparison with the ordinary exponential operator, the operator $\mathscr{E}\mathscr{L}\mathscr{P}$ has free variables even for the product operator terms. This makes the $\mathscr{E}\mathscr{L}\mathscr{P}$ expansion free from the breakdown of the cluster expansion in a quasidegenerate situation,[1] though the number of the variables is much larger in the $\mathscr{E}\mathscr{L}\mathscr{P}$ expansion than in the exp expansion. We have defined the wave function

$$\Psi^{\mathrm{EGCI}} = \mathscr{E}\mathscr{L}\mathscr{P}\Big(\sum_K a_K A_K^\dagger\Big)|0\rangle, \tag{5}$$

which is called exponentially generated configuration interaction (EGCI) wave function. It describes both separable

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and nonseparable correlations.

In a previous paper,[4] we have used the idea of reaction operator for constructing the wave functions of excited, ionized, and electron attached states, Ψ_e from a given correlated wave function of say, a ground state Ψ_g, as

$$\Psi_e = \mathscr{R}\Psi_g. \tag{6}$$

The reaction operator $\mathscr{R}$ describes the excitation itself and the reorganizations in electron correlations induced by this excitation. The basic idea of this method is that the electron correlations in the excited states would be more easily calculated by modifying the ground state correlations rather than calculating them from the beginning without referring to the ground state ones. This idea has also been used in the Green function method[22] and the equation of motion method.[23] We call the operator $\mathscr{R}$ as excitator in order to distinguish it from more elementary excitation operators such as $S_K^\dagger$ and $A_K^\dagger$.

The SAC-CI wave function is written in the excitator formalism as

$$\Psi^{\text{SAC-CI}} = \mathscr{R}^{\text{SAC-CI}}\Psi^{\text{SAC}}, \tag{7}$$

$$\mathscr{R}^{\text{SAC-CI}} = \sum_K d_K R_K^\dagger, \tag{8}$$

where $R_K^\dagger$ is a symmetry-adapted excitation, ionization, or electron attachment operator. In the original formulation of the SAC-CI theory,[7] the excitator method was naturally introduced as a result of the variational principle applied to the SAC wave function. The nonvariational formulation was given later.[24] Previously, we have defined EX-(excited-) EGCI method by[4]

$$\Psi^{\text{EX-EGCI}} = \mathscr{R}^{\text{EX-EGCI}}\Psi^{\text{EGCI}}, \tag{9}$$

$$\mathscr{R}^{\text{EX-EGCI}} = \sum_K \mathscr{b}_K B_K^\dagger, \tag{10}$$

where $\mathscr{b}_K$ is not a coefficient like d_K in Eq. (8), but an operator which makes free the products as

$$\begin{aligned} \mathscr{b}_K a_0 &= b_K, \\ \mathscr{b}_K a_L &= \tfrac{1}{2} b_{KL}, \\ \mathscr{b}_K a_{LM} &= \frac{1}{3!} b_{KLM}, \end{aligned} \tag{11}$$

etc. We have given in some detail the method, the algorithm of calculations, and the results of test calculations.[4]

In bond dissociation processes, we sometimes observe that near equilibrium geometry all the correlations are essentially separable, but as the bond is elongated, some of the correlations are transformed into nonseparable ones, though the rest remains separable throughout the reaction. For example, the correlations associated with the breaking bond sometimes transform like this, though the correlations associated to the other parts remain essentially separable. When we describe the former by the $\mathscr{E}\mathscr{L}\mathscr{P}$ operator and the latter by exp, we obtain,

$$\Psi^{\text{MEG4}} = \exp\left(\sum_I C_I S_I^\dagger\right)\mathscr{E}\mathscr{L}\mathscr{P}\left(\sum_K a_K A_K^\dagger\right)|0\rangle, \tag{12}$$

which are the fourth of the five mixed-exponentially generated (MEG) wave functions previously proposed.[2] It is therefore called MEG4 method. It is identical with the multireference (MR) SAC method proposed earlier.[1] The basic idea is an optimal use of the $\mathscr{E}\mathscr{L}\mathscr{P}$ and exp operators for nonseparable and separable correlations, respectively.

The MEG4 method is applicable not only to the ground state, but also to excited states. It has been applied successfully to the totally symmetric ground and excited states of F_2, LiF, CO, and H_2O at different nuclear separations.[3,25] We have demonstrated complex behaviors of electron correlations in the lower four $^1\Sigma$ states of the CO molecule during the bond elongation process.[3,25] However, its application to different symmetries was somewhat difficult.[1]

In this paper, we propose a method of calculating excited, ionized, and electron attached states, applying the excitator method to the MEG4 wave function for a ground state. Since the MEG4 method is a multireference-type generalization of the SAC method, the resultant method called EX-(excited-)MEG4 method is a generalization of the SAC-CI method. It includes the SAC-CI method as a special case. Since the MEG4 method is applicable to both separable and nonseparable correlations, the MEG4/EX-MEG4 method is expected to be useful for calculating potential energy curves of ground, excited, ionized, and anion states of a reacting molecule. We give here, in some detail, the formulation of the method and the algorithm of calculations. Test applications are given for hydrogen fluoride (HF) at equilibrium and elongated internuclear distances. The results are compared with those of the full CI calculations carried out separately for all of the ground, excited, ionized, and anion states. Concluding remarks are given in the last section.

II. MEG4/EX-MEG4 METHOD

In the MEG4 wave function given by Eq. (12), the $\mathscr{E}\mathscr{L}\mathscr{P}$ part represents the nonseparable correlation. The exp part then represents cluster expansion around this nonseparable reference configurations. The $\mathscr{E}\mathscr{L}\mathscr{P}$ part may then be called multireference (MR) part. When we write the MR part of Eq. (12) as Φ_0, i.e.,

$$\Phi_0 = \mathscr{E}\mathscr{L}\mathscr{P}\left(\sum_K a_K A_K^\dagger\right)|0\rangle = \sum_K g_K G_K^\dagger|0\rangle, \tag{13}$$

the MEG4 method is written as

$$\begin{aligned} \Psi^{\text{MEG4}} &= \exp\left(\sum_I C_I S_I^\dagger\right)\Phi_0 \\ &= \exp\left(\sum_I C_I S_I^\dagger\right)\left(\sum_K g_K G_K^\dagger\right)|0\rangle. \end{aligned} \tag{14}$$

In the solution of the MEG4 method, two choices of the algorithms are possible.[3] One is to take the two sets of the excitation operators $\{S_I^\dagger\}$ and $\{G_K^\dagger\}$ to be exclusive, and calculate the coefficients $\{C_I\}$ and $\{g_K\}$, iteratively. The other is to calculate the MR part beforehand by a small EGCI calculation, and then consider the cluster expansion around that function. The operators $\{S_I^\dagger\}$ and $\{G_K^\dagger\}$ need not be exclusive. In the previous paper,[3] we have taken the first choice and given the algorithm and the calculated results. Here we adopt the second choice, so that the operators $S_I^\dagger$ and $G_K^\dagger$ need not be exclusive.

The present method of solution is as follows. The MR

part defined by Eq. (13) is generated by the EGCI algorithm[4] and calculated by

$$\langle 0|G_K(H-E_0)|\Phi_0\rangle = 0. \tag{15}$$

The exp part is solved by the nonvariational method by requiring the Schrödinger equation in the space of $|\Phi_0\rangle$ and $S_l^\dagger|\Phi_0\rangle$,

$$\langle \Phi_0|H-E|\Psi^{\text{MEG4}}\rangle = 0,$$
$$\langle \Phi_0|S_l(H-E)|\Psi^{\text{MEG4}}\rangle = 0, \tag{16}$$

where E is the energy of the system. We note that the generalized Brillouin theorem similar to that in the SAC method[7] is obtained by applying the variational principle.

$$\langle \Psi^{\text{MEG4}}|(H-E)S_K^\dagger|\Psi^{\text{MEG4}}\rangle = 0. \tag{17}$$

We produce the excited, ionized, and electron attached states from the MEG4 wave function for the ground state by the excitator method as

$$\Psi^{\text{EX-MEG4}} = \mathscr{R}\Psi^{\text{MEG4}}$$
$$= \mathscr{R}\exp\left(\sum_l C_l S_l^\dagger\right)\mathscr{E}\mathscr{L}\mathscr{P}\left(\sum_K a_K A_K^\dagger\right)|0\rangle, \tag{18}$$

where the excitator $\mathscr{R}$ describes excitations, ionizations, and electron attachments and EX-MEG4 stands for excited-(EX-)MEG4. As in the SAC-CI method, the exp part describes transferable correlations between ground and excited states, and we apply the operator $\mathscr{R}$ only to the MR part

$$\Psi^{\text{EX-MEG4}} = \exp\left(\sum_l C_l S_l^\dagger\right)\mathscr{R}\ \ \mathscr{E}\mathscr{L}\mathscr{P}\left(\sum_K a_K A_K^\dagger\right)|0\rangle. \tag{19}$$

Thus the EGCI part of the EX-MEG4 wave function takes the form of the EX-EGCI wave function given by Eqs. (9) and (10). As in the EX-EGCI method [Eq. (10)],[4] the operator $\mathscr{R}$ is expanded by the excitation, ionization, or electron attachment operators $\{B_K^\dagger\}$ as

$$\mathscr{R} = \sum_K \mathscr{L}_K B_K^\dagger, \tag{20}$$

where $\{\mathscr{L}_K\}$ are not simple coefficients but the free-coefficient operators defined by Eq. (11). Thus the EX-MEG4 wave function is written as

$$\Psi^{\text{EX-MEG4}} = \exp\left(\sum_l C_l S_l^\dagger\right)\mathscr{Q}$$
$$\times\left(\sum_K b_K B_K^\dagger + \frac{1}{2}\sum_{K,L} b_{KL}B_K^\dagger A_L^\dagger + \frac{1}{3!}\sum_{K,L,M} b_{KLM}B_K^\dagger A_L^\dagger A_M^\dagger + \cdots\right)|0\rangle$$
$$= \exp\left(\sum_l C_l S_l^\dagger\right)\left(\sum_K e_K E_K^\dagger\right)|0\rangle. \tag{21}$$

In Eq. (21), the part, $\Sigma_K e_K E_K^\dagger|0\rangle$, represents the principal correlations in the excited state and the operators $\{E_K^\dagger\}$ are constructed by the EX-EGCI algorithm reported previously.[4] The exp part represents the transferable correlations and so the operators $\{S_l^\dagger\}$ and the coefficients $\{C_l\}$ are transferred from the MEG4 wave function of the ground state. The unknown coefficients $\{e_K\}$ are determined with the equation

$$\langle \Phi_0|E_K(H-E)|\Psi^{\text{EX-MEG4}}\rangle = 0. \tag{22}$$

Note that in Eq. (22) the coefficients $\{e_K\}$ are determined totally for the EX-MEG4 wave function and not only for the EX-EGCI part. The diagonalization is therefore due to the nonsymmetric method.[26]

We note a similarity of Eq. (22) to Eq. (16) of the MEG4 method. In particular, the bra is not $\langle 0|$, but $\langle \Phi_0|$. However, this similarity does not mean here a strict holdness of the orthogonality and H orthogonality between the ground and excited states,[24] because the EX-EGCI part of the EX-MEG4 wave function largely differs from the EGCI part of the MEG4 wave function. For the lowest singlet A_1 state, the MR part of the MEG4 wave function is reoptimized in the EX-MEG4 calculation, so that the EX-MEG4 solution for this state may become better than the MEG4 solution. From Eq. (22) we see that different EX-MEG4 solutions satisfy

$$\langle \Psi_a^{\text{EX-MEG4}}|\Psi_b^{\text{EX-MEG4}}\rangle = \delta_{ab},$$
$$\langle \Psi_a^{\text{EX-MEG4}}|H|\Psi_b^{\text{EX-MEG4}}\rangle = E_a\delta_{ab}, \tag{23}$$

within the space $\{E_K^\dagger|\Phi_0\rangle\}$. Thus when we use the EX-MEG4 solution even for the lowest singlet A_1 state, we have the correct relations [Eq. (23)] for all the states under consideration. This is important for studying phenomena involving different states.

III. COMPUTATIONAL ALGORITHM OF THE MEG4/EX-MEG4 METHOD

The present algorithm of the MEG4 method is different from the previous one[3] in that the $\{S_l^\dagger\}$ and $\{A_K^\dagger\}$ operators in Eq. (12) are not necessarily exclusive.

The MR part Φ_0 given by Eq. (13) is calculated by the EGCI method.[4] The threshold λ_A^g for the MR part can not be chosen as good as that in the standard EGCI method, since by this threshold, the size of the multireference configurations is determined. However, the threshold for the higher order terms, λ_{AA}^g, should be chosen to be much smaller than $\sqrt{\lambda_A^g}$,[4] or practically should be equal to λ_A^g, since the higher-order terms are very important here. The same is true for the thresholds, λ_{AAA}^g and λ_{AAAA}^g; namely we should include as higher terms as possible in the expansion of the $\mathscr{E}\mathscr{L}\mathscr{P}$ operator in Φ_0.

The operators $\{S_l^\dagger\}$ are totally symmetric and chosen to be single and double excitation operators. Since calculations of the unlinked terms are time consuming, they are calculated only for those $S_l^\dagger$ operators whose coefficients in the ground state SDCI are larger than a given threshold C_λ and for those $G_K^\dagger$ operators [Eq. (13)] whose coefficients g_K are larger than g_λ. This algorithm is similar to that of SAC-CI in SAC85.[8,27] The coefficients $\{C_l\}$ are obtained by iteratively solving Eq. (16).

We next explain the algorithm of the EX-MEG4 calculations for excited, ionized, and anion states. The $\{S_l^\dagger\}$ operators and their coefficients $\{C_l\}$ are transferred from the MEG4 wave function for the ground state. The EX-EGCI part of the EX-MEG4 wave function given by Eq. (21) is constructed by the following EX-EGCI algorithm.[4] In comparison with the EGCI part in MEG4, that in EX-MEG4

should be selected more precisely; namely the threshold λ^e_A in EX-MEG4, with e standing for excited states, should be smaller than λ^g_A in MEG4 for both $\{A^\dagger_K\}$ and $\{B^\dagger_K\}$ operators. The threshold λ^e_{AA} for the product operators is about $\sqrt{\lambda^e_A}$, and the same for the higher thresholds, λ^e_{AAA}, etc. The reason of the relation, $\lambda^e_A < \lambda^g_A$ is found from a comparison with the SAC/SAC-CI algorithm. In SAC, the operator $\mathscr{C}\mathscr{R}\mathscr{P}(\Sigma_K a_K A^\dagger_K)$ is just a unit operator, but in SAC-CI, the EX-EGCI part is usually a sum of single and double excitations, one excitation level higher than real excitations[5] since we mostly study single-electron excitation or ionization processes. In EX-MEG4, we calculate not only single but also multiple excitation processes, so that we include in this term single, double, and higher excitation operators; in the present program[28] we can include up to eight-electron excitations. The unlinked terms are calculated only for those $S^\dagger_I$ operators whose MEG4 coefficients are larger than C_λ and for those $E^\dagger_K$ operators [Eq. (21)] whose coefficients in their CI are larger than e_λ. The coefficients $\{e_K\}$ are obtained by solving the secular equation for a nonsymmetric matrix, Eq. (22). An iterative diagonalization procedure[23] for nonsymmetric matrices has already been prepared.

When only a single configuration is considered in the MR part, the MEG4/EX-MEG4 method reduces to the SAC/SAC-CI method. However, the present program[28] is more general than SAC85,[8] since we can expand the $\mathscr{R}$ operator of Eq. (20) with single to octaple excitation operators. We have shown[5] that such extension of the SAC-CI method is very useful for investigating multielectron processes such as those involved in the satellite peaks of ionization spectra. We call the SAC-CI methods whose $R^\dagger$ operators are singles and doubles, or include also higher excitations as SAC-CI with SD-R or general-R, respectively.[5]

IV. APPLICATIONS

We choose hydrogen fluoride as a test molecule of the MEG4/EX-MEG4 method. We calculate its ground state, singlet and triplet excited states, and doublet ionized and anion states, summing up to 21 states, at three different geometries $R = 0.916\,808$ (Req), 2.0 (2.1815 Req), and 3.0 Å (3.2722 Req). Full CI calculations are also carried out, for comparison, for all of these states. We also examine the reliability of the SAC-CI method with general-R for multielectron processes. The basis set is [3s2p/2s] CGTOs of Huzinaga and Dunning–Hay[29] plus one GTO with $\alpha = 0.036$ for 3s Rydberg orbital.[29] We have included all of the MOs into active orbitals (five occupied and seven unoccupied MOs). The results are shown in Tables I, II, and III for three different geometries, $R = 0.916\,808$ (R_{eq}), 2.0, and 3.0 Å, respectively.

Benchmark full-CI calculations for hydrogen fluoride are reported in the literature[30,31] using Huzinaga–Dunning [4s2p] set[32] plus polarization functions for three different geometries, R = Re (0.9165 Å), 1.5 Re (1.3748 Å), and 2.0 Re (1.8331 Å). The results were utilized previously for examining the accuracy of the SAC[33] and other coupled cluster methods.[34–36] However, these calculations were *only* for the ground state and the examined range of the internuclear distance was narrow. Therefore we have done independent full-CI calculations adding one Rydberg orbital instead of the polarization functions, and the solutions were obtained not only for the ground state, but also for several singlet and triplet excited states, ionized states, and electron attached states at three different geometries, R = Re, 2.1815 Re, and 3.2722 Re. These results are compared with the present results of the MEG4/EX-MEG4 calculations.

The Hartree–Fock orbitals are used as reference orbitals for all the calculations. Standard MO ordering is defined as $(1s)^2(2s)^2(\sigma_1)^2(\pi_1)^4(\sigma_2)(\sigma_3)(\sigma_4)(\pi_2)(\sigma_5)(\sigma_6)$. The canonical MO ordering is a bit different; at $R = R_{eq}$, the second and third unoccupied MOs are interchanged and at $R = 2.0$ and 3.0 Å, the occupied σ_1 and π_1 MOs are inverted. The main configurations are shown for each state by means of the occupation numbers of these MOs. The weight of the Hartree–Fock configuration in the ground state full CI is 0.96, 0.74, and 0.42 for $R = R_{eq}$, 2.0 and 3.0 Å, respectively, and so the quasidegenerate situation is realized at $R = 3.0$ Å. The HF energy is $-100.017\,34$, $-99.784\,98$, and $-99.671\,00$ a.u., respectively.

We carry out three different calculations; namely, in MEG4, the $A^\dagger_K$ operators in Eq. (13) is selected from single and double excitation operators by the three different thresholds, 0.15, 0.32, and 0.7 for the coefficients in the ground state SDCI. At $R = 2.0$ and 3.0 Å, the threshold 0.15 gives three references, $|0\rangle$, $|\sigma_1 \to \sigma_2\rangle$, and $|\sigma_1 \to \sigma_2, \sigma_1 \to \sigma_2\rangle$, the threshold 0.32 gives two references, $|0\rangle$ and $|\sigma_1 \to \sigma_2, \sigma_1 \to \sigma_2\rangle$, and the threshold 0.7 gives the single reference, $|0\rangle$. At $R = R_{eq}$, all the thresholds lead to the single reference $|0\rangle$. The single reference MEG4 is identical with SAC. The S operators in Eq. (14) include all single and double excitations. In the unlinked terms we have included only such $S^\dagger_I$ operators whose coefficients in the ground state SDCI are larger than 0.01.

In the EX-MEG4 calculations, the $S^\dagger_I$ operators and their coefficients $\{C_I\}$ in Eq. (21) are transferred from the ground state MEG4 result. In the unlinked term, we include only such $S^\dagger_I$ operators whose coefficients C_I are larger than 0.001. The $A^\dagger_K$ and $B^\dagger_K$ operators in Eq. (21) represent all single and double excitations. The product operators $Q\{B^\dagger_K A^\dagger_L,\ B^\dagger_K A^\dagger_L A^\dagger_M,\ B^\dagger_K A^\dagger_L A^\dagger_M A^\dagger_N\}$ are constructed from those $A^\dagger_K$ and $B^\dagger_K$ operators whose SDCI coefficients for the states under consideration are larger than the thresholds $(\lambda_A, \lambda^s_{AA}, \lambda^d_{AA}, \lambda_{AAA}, \lambda_{AAAA})$ which are actually (0.0, 0.01, 0.03, 0.07, 0.1) for all the states, where the superscripts s and d stand for single and double excitations, respectively. The single excitation operators are found to be very important in the product operators, so that the threshold for them, λ^s_{AA} is made as small as 0.01. For calculations of anion states, we use different thresholds (0.0, 0.01, 0.01, 0.07, 1.0), since multiple excitation terms are thought to be more important.

Tables I–III show the results for $R = R_{eq}$, 2.0 and 3.0 Å, respectively. The energies calculated by the MEG4/EX-MEG4 and SAC/SAC-CI methods are compared with the full-CI energies, and the differences denoted by Δ are given in millihartree, a unit which is convenient for chemical accuracy (1 mhartree = 0.63 kcal/mol). The SAC/SAC-CI re-

sults are given for $R = 2.0$ Å. At $R = R_{eq}$, MEG4/EX-MEG4 coincides with SAC/SAC-CI in the present calculational scheme, and at $R = 3.0$ Å, we could not get a convergence in the SAC solution, a typical behavior of the SAC method in a quasidegenerate situation.

We first discuss the results for $R = 2.0$ Å summarized in Table II, because at this distance we have both MEG4/EX-MEG4 and SAC/SAC-CI solutions for comparison. The first row shows the MEG4 and SAC energies for the ground state. The three-reference MEG4 result is almost equal to the two-reference one, and they are higher by about 6 mhartree than the full-CI result. The single-reference SAC result is about 1.2 mhartree higher than the two- and three-reference MEG4 results. The sizes of the matrices involved in the calculations are 44 388 for full CI, but only 235 for MEG4 and SAC, which is the dimension of all singles and doubles.

The rest of the results for the singlet, triplet, ion, and anion states are all due to the EX-MEG4 and SAC-CI methods. In particular, the second row shows the EX-MEG4 and SAC-CI results for the ground state. They are better than the MEG4 and SAC results since the general-R operators are used instead of the SD-R operators, and since they satisfy some necessary conditions [Eq. (23)] with the excited states. Though the sizes of full CI are from 42 336 to 87 408, those of EX-MEG4 and SAC-CI methods are much smaller, from 571 to 1240.

It is convenient to classify the excited, ionized, and anion states by means of "excitation level," which is the number of elementary excitations necessary for producing the main configuration from the Hartree–Fock configuration. For ionized states, Koopmans-type ionizations correspond to the excitation level one, and excitation-ionization processes appearing in satellite peaks correspond to the levels higher than two. Electron attached states are also similarly classified.

We see in Table II that the differences in energy between the full-CI results and the EX-MEG4 and SAC-CI (general R) results are small (few millihartree) and relatively constant, though the sizes of the calculations of the latter two methods are 2 orders of magnitude smaller than those of full CI. The average values and the standard deviations for the Δ values are given in parentheses. For singlet states, they are

TABLE I. Full-CI and MEG4/EX-MEG4 (SAC/SAC-CI) results in hartree for hydrogen fluoride at $R = 0.916\,808$ Å (equilibrium distance).[a]

						MEG4/EX-MEG4 = SAC/SAC-CI[c]					
				Full CI		General R			SDR		
State		Main configuration[b] ($C>0.30$)	Excitation level	Size	Energy	Size	Energy	Δ×10³	Size	Energy	Δ×10³
Singlet											
$^1\Sigma$	1	0.98(22222)	0	443 88	−100.142 41	245	−100.140 88	1.53	245	−100.140 88	1.53
					−100.142 41	775	−100.140 51	1.90	245	−100.136 75	5.66
	2	0.89(221221) + 0.37(2212201)	1	443 88	−99.601 82	775	−99.600 10	1.72	245	−99.607 51	−5.69
	3	0.88(2212201) − 0.38(221221)	1	443 88	−99.457 18	775	−99.454 39	2.79	245	−99.459 78	−2.60
$^1\Pi$	1	0.82(222121) + 0.51(2221201)	1	423 36	−99.760 94	768	−99.759 96	0.98	144	−99.766 53	−5.59
	2	0.81(2221201) − 0.51(222121)	1	423 36	−99.635 14	768	−99.634 04	1.10	144	−99.639 62	−4.48
	3	0.94(22212001)	1	423 36	−99.139 90	768	−99.138 05	1.85	144	−99.140 21	−0.31
								(1.72 ± 0.65)[d]			
Triplet											
$^3\Sigma$	1	0.71(221221) + 0.65(2212201)	1	710 20	−99.651 76	993	−99.649 74	2.02	271	−99.651 42	0.34
	2	0.69(2212201) − 0.66(221221)	1	710 20	−99.514 70	993	−99.512 29	2.41	271	−99.515 38	−0.68
$^3\Pi$	1	0.78(222121) − 0.56(2221201)	1	708 80	−99.779 82	960	−99.778 38	1.44	213	−99.782 68	−2.86
	2	0.77(2221201) + 0.56(222121)	1	708 80	−99.643 50	960	−99.641 83	1.67	213	−99.647 31	−3.81
	3	0.93(22212001)	1	708 80	−99.154 36	960	−99.152 17	2.19	213	−99.154 89	−0.53
								(1.95 ± 0.39)[d]			
Ion											
$^2\Sigma$	1	0.97(22122)	1	485 60	−99.423 09	1162	−99.422 52	0.57	70	−99.432 05	−8.96
	2	0.51(2222001) − 0.51(2220201) + 0.36(222201) − 0.36(222021)	2	485 60	−98.897 22	1162	−98.895 67	1.55	...	...	...
	3	0.48(2220201) + 0.48(2222001) + 0.34(222021) + 0.34(222201)	2	485 60	−98.855 28	1162	−98.848 37	6.91	...	...	...
$^2\Pi$	1	0.96(22212)	1	471 40	−99.567 32	1043	−99.566 73	0.59	44	−99.579 02	−11.70
	2	0.61(2211201) + 0.42(221121) − 0.37(2211201) − 0.34(221121)	2	471 40	−98.847 53	1043	−98.845 04	2.49	44	−98.649 84	197.69
	3	0.53(221121) + 0.52(2211201) + 0.43(2211201)	2	471 40	−98.777 74	1043	−98.776 23	1.51	...	...	...
								(2.27 ± 2.38)[d]			
Anion											
$^2\Sigma$	1	0.98(222221)	1	874 08	−100.067 55	984	−100.062 15	5.40	105	−100.064 95	2.60
	2	0.98(2222201)	1	874 08	−99.924 58	984	−99.919 06	5.52	105	−99.920 78	3.80
$^2\Pi$	1	0.86(222122) − 0.42(2221211)	2	848 52	−99.740 15	1171	−99.734 54	5.61	60	−99.652 05	88.10
	2	0.96(2221211)	2	848 52	−99.653 06	1171	−99.646 50	6.56	60	−99.565 66	87.40
								(5.77 ± 0.53)[d]			

[a] The MEG4/EX-MEG4 method coincides with the SAC/SAC-CI method at this distance in the present choice of the thresholds (see the text).

[b] The MO ordering is $1s$, $2s$, σ_1, π_1, π_1, σ_2, σ_3, σ_4, π_2, π_2, σ_5, σ_6.

[c] The first row is the MEG4 (SAC) results and all the others are the EX-MEG4 (SAC-CI) results.

TABLE II. Full-CI, MEG4/EX-MEG4, and SAC/SAC-CI results in hartree for hydrogen fluoride at $R = 2.0$ (2.181 48 Re).

State		Main configuration[a] ($C>0.30$)	Excitation level	Full CI		MEG4/EX-MEG4[b] Three reference			MEG4/EX-MEG4[b] Two reference			SAC/SAC-CI[c] General R			SAC/SAC-CI[c] SDR		
				Size	Energy	Size	Energy	$\Delta\times10^3$	Size	Energy	$\Delta\times10^3$	Size	Energy	$\Delta\times10^3$	Size	Energy	$\Delta\times10^3$
Singlet																	
$^1\Sigma$	1	0.86(22222) − 0.41(220222)	0	44 388	− 99.994 87	235	− 99.988 61	6.26	235	− 99.988 60	6.27	235	− 99.987 44	7.43	235	− 99.987 44	7.43
					− 99.994 87	869	− 99.993 60	1.27	819	− 99.993 21	1.66	789	− 99.993 13	1.74	235	− 99.985 61	9.26
	2	0.77(221221) + 0.43(220222) + 0.40(22222)	1	44 388	− 99.756 03	869	− 99.753 23	2.80	819	− 99.752 50	3.53	789	− 99.753 29	2.74	235	− 99.746 35	9.68
	3	0.92(2212201)	1	44 388	− 99.545 61	869	− 99.543 25	2.36	819	− 99.544 04	1.57	789	− 99.544 09	1.52	235	− 99.540 22	5.39
$^1\Pi$	1	0.86(222121) − 0.45(221122)	1	42 336	− 99.960 34	621	− 99.958 09	2.25	590	− 99.958 60	1.74	571	− 99.958 68	1.66	144	− 99.949 20	11.14
	2	0.91(2221201) − 0.33(222121)	1	42 336	− 99.588 51	621	− 99.585 25	3.26	590	− 99.587 61	0.90	571	− 99.587 17	1.34	144	− 99.591 98	− 3.47
	3	0.64(221122) − 0.59(2211211) + 0.33(222121)	2	42 336	− 99.462 42	621	− 99.460 06	2.36	590	− 99.459 30	3.12	571	− 99.459 43	2.99	144	− 99.383 24	79.18
							(2.38 ± 0.66)[d]			(2.09 ± 1.01)[d]			(2.00 ± 0.69)[d]				
Triplet																	
$^3\Sigma$	1	0.98(221221)	1	71 020	− 99.959 77	937	− 99.958 08	1.69	904	− 99.958 19	1.58	895	− 99.958 38	1.39	271	− 99.954 63	5.14
	2	0.92(2212201) − 0.31(2202211)	1	71 020	− 99.551 60	937	− 99.549 57	2.03	904	− 99.550 34	1.26	895	− 99.550 39	1.21	271	− 99.547 25	4.35
$^3\Pi$	1	0.88(222121) − 0.43(221122)	1	70 880	− 99.963 69	959	− 99.961 76	1.93	930	− 99.962 13	1.56	914	− 99.962 18	1.51	213	− 99.951 94	11.75
	2	0.85(2221201)	1	70 880	− 99.600 40	959	− 99.597 44	2.96	930	− 99.599 15	1.25	914	− 99.598 61	1.79	213	− 99.600 90	− 0.50
	3	0.71(221122) − 0.31(222121) + 0.30(2221201)	2	70 880	− 99.553 62	959	− 99.550 62	3.00	930	− 99.550 24	3.38	914	− 99.550 42	3.20	213	− 99.471 03	82.59
							(2.32 ± 0.61)[d]			(1.81 ± 0.89)[d]			(1.82 ± 0.80)[d]				
Ion																	
$^2\Sigma$	1	0.91(22122) + 0.36(220221)	1	48 560	− 99.468 54	914	− 99.466 29	2.25	883	− 99.467 15	1.39	879	− 99.467 20	1.34	70	− 99.466 00	2.54
	2	0.57(222021) − 0.57(222201) + 0.33(221202) − 0.33(221022)	2	48 560	− 99.237 34	914	− 99.236 07	1.27	883	− 99.236 43	0.91	879	− 99.236 45	0.89	...	...	...
	3	0.70(220221) − 0.36(222021) − 0.36(222201)	2	48 560	− 99.228 28	914	− 99.227 26	1.02	883	− 99.226 99	1.29	879	− 99.227 17	1.11	70	− 99.124 25	10.43
$^2\Pi$	1	0.88(22212) − 0.41(221121)	1	47 140	− 99.501 47	838	− 99.499 67	1.80	811	− 99.500 59	0.88	801	− 99.500 56	0.91	44	− 99.493 08	8.39
	2	0.57(221121) − 0.52(221121) + 0.51(220122)	2	47 140	− 99.313 59	838	− 99.310 45	3.14	811	− 99.309 84	3.75	801	− 99.309 28	4.31	...	...	...
	3	0.75(221121) − 0.38(220122) + 0.36(221121)	2	47 140	− 99.229 21	838	− 99.227 23	1.98	811	− 99.226 74	2.47	801	− 99.226 39	2.82	44	− 99.138 25	90.96
							(1.91 ± 0.75)[d]			(1.78 ± 1.12)[d]			(1.89 ± 1.38)[d]				
Anion																	
$^2\Sigma$	1	0.95(222221)	1	87 408	− 100.049 38	1248	− 100.043 70	5.68	1235	− 100.043 88	5.50	1232	− 100.043 83	5.55	102	− 100.029 83	19.55
	2	0.77(221222) − 0.33(2222201) − 0.33(2212211)	2	87 408	− 99.923 84	1248	− 99.920 23	3.61	1235	− 99.919 90	3.94	1232	− 99.919 34	4.50	102	− 99.899 25	24.59
$^2\Pi$	1	0.83(222122) + 0.45(2221211)	2	84 852	− 99.929 16	1240	− 99.925 29	3.87	1224	− 99.925 68	3.48	1222	− 99.925 69	3.47	59	− 99.850 04	79.12
	2	0.88(2221211) + 0.44(2211221)	2	84 852	− 99.865 18	1240	− 99.860 07	5.11	1224	− 99.861 47	3.71	1222	− 99.861 44	3.74	...	...	...
							(4.57 ± 0.99)[d]			(4.57 ± 0.91)[d]			(4.32 ± 0.93)[d]				

[a] The MO ordering is $1s$, $2s$, σ_1, π_1, π_1, σ_2, σ_3, σ_4, π_2, π_2, σ_5, σ_6.

[b] The first row is the MEG4 results and all the others are the EX-MEG4 results.

[c] The first row is the SAC results and all the others are the SAC-CI results.

[d] $(x \pm y)$ where x means the average discrepancy from the full-CI value and y means the standard deviation, both in millihartree.

TABLE III. Full-CI and MEG4/EX-MEG4 results in hartree for hydrogen fluoride at $R = 3.0$ Å (3.272 22 Re).

State		Main configuration[a] ($C>0.30$)	Excitation level	Full-CI		MEG4/EX-MEG4[b]					
						Three reference			Two reference		
				Size	Energy	Size	Energy	$\Delta\times10^3$	Size	Energy	$\Delta\times10^3$
Singlet											
$^1\Sigma$	1	0.68(22222) − 0.60(220222) + 0.37(221221)	0	44 388	−99.972 69	230	−99.964 95	7.74	230	−99.961 32	11.37
					−99.972 69	933	−99.971 50	1.19	871	−99.970 06	2.63
	2	0.65(221221) − 0.64(22222) − 0.33(220222)	1	44 388	−99.716 12	933	−99.712 92	3.20	871	−99.712 55	3.57
	3	0.85(2212201) − 0.48(2202211)	1	44 388	−99.526 01	933	−99.520 93	5.08	871	−99.522 43	3.58
$^1\Pi$	1	0.83(222121) + 0.52(221122)	1	42 336	−99.971 53	661	−99.968 68	2.85	626	−99.969 86	1.67
	2	0.85(2221201) + 0.46(2211211)	1	42 336	−99.536 75	661	−99.531 18	5.57	626	−99.540 70	−3.95
	3	0.67(2211211) + 0.59(2201221)	2	42 336	−99.499 49	661	−99.496 23	3.26	626	−99.494 63	4.86
								(3.53 ± 1.59)[c]			(2.06 ± 3.13)[c]
Triplet											
$^3\Sigma$	1	0.98(221221)	1	71 020	−99.971 53	880	−99.969 33	2.20	838	−99.969 22	2.31
	2	0.85(2212201) − 0.48(2202211)	1	71 020	−99.533 94	880	−99.530 74	3.20	838	−99.532 71	1.23
$^3\Pi$	1	0.83(222121) − 0.52(221122)	1	70 880	−99.971 72	923	−99.969 21	2.51	891	−99.970 00	1.72
	2	0.70(2221201) + 0.43(2221201) + 0.38(221122)	1	70 880	−99.550 76	923	−99.546 02	4.74	891	−99.551 14	−0.38
	3	0.60(2211211) − 0.47(2221201) + 0.38(221122)	2	70 880	−99.537 66	923	−99.532 60	5.06	891	−99.536 17	1.49
								(3.54 ± 1.30)[c]			(1.27 ± 1.01)[c]
Ion											
$^2\Sigma$	1	0.84(22122) − 0.51(220221)	1	48 560	−99.469 72	881	−99.466 88	2.84	850	−99.468 54	1.18
	2	0.56(222021) − 0.56(222201) + 0.36(221022) − 0.36(221202)	2	48 560	−99.249 89	881	−99.248 66	1.23	850	−99.248 69	1.20
	3	0.67(220221) + 0.40(22122) − 0.32(222021) − 0.32(222201)	2	48 560	−99.249 52	881	−99.248 27	1.25	850	−99.247 95	1.57
$^2\Pi$	1	0.75(22212) + 0.59(221121)	1	47 140	−99.476 22	859	−99.473 06	3.16	830	−99.476 73	−0.51
	2	0.56(220122) − 0.48(221121) − 0.45(22212) + 0.40(221121)	3	47 140	−99.354 59	859	−99.351 94	2.65	830	−99.350 06	4.53
	3	0.82(221121) + 0.32(220122)	2	47 140	−99.249 63	859	−99.247 67	1.96	830	−99.246 75	2.88
								(2.18 ± 0.83)[c]			(1.81 ± 1.72)[c]
Anion											
$^2\Sigma$	1	0.88(222221) − 0.40(221222)	1	87 408	−100.041 50	1319	−100.035 46	6.04	1301	−100.035 58	5.92
	2	0.80(221222) + 0.37(222221)	2	87 408	−99.947 25	1319	−99.942 94	4.31	1301	−99.941 84	5.41
$^2\Pi$	1	0.87(222122) + 0.38(2221211)	2	84 852	−99.944 41	1289	−99.939 72	4.69	1262	−99.939 84	4.57
	2	0.82(2221211) − 0.51(2211221)	2	84 852	−99.877 35	1289	−99.872 36	4.99	1262	−99.874 89	2.46
								(5.01 ± 0.74)[c]			(4.59 ± 1.53)[c]

[a] The MO ordering is $1s, 2s, \sigma_1, \pi_1, \pi_1, \sigma_2, \sigma_3, \sigma_4, \pi_2, \pi_2, \sigma_5, \sigma_6$.

[b] The first row is the MEG4 results and all the others are the EX-MEG4 results.

[c] $(x \pm y)$ where x means the average discrepancy from the full-CI value and y means the standard deviation, both in millihartree.

calculated for the EX-MEG4 results. We see that the errors are roughly constant among the singlet, triplet, and ionized states, independent of the excitation levels. The errors for the anion states are relatively large. A reason is that we did not include anion basis so that the present anion results are less physical than the other results. The smallness of the standard deviation is remarkable, which shows the constancy in errors. This constancy in errors is important for studying electronic processes involving different electronic states. We will show later the accuracy of the MEG4/EX-MEG4 method for excitation, ionization and electron attachment energies.

Table II also shows the results of the SAC-CI method with SD-R. As examined before,[5,10,37] they compare well with the full-CI results for one-electron excitation processes. However, for higher excitation processes, the SD-R SAC-CI results largely differ from the full-CI ones, though this is not the case for the other methods shown in Table II. In comparison with the general-R SAC-CI results, it is clear that the main reason lies in the size and the nature of the $R^\dagger$ operators. When they are restricted to singles and doubles, the errors in describing two-electron processes become large, though the errors for the single-electron processes are reasonably small. This result suggests a guideline in constructing the $\{R_K^\dagger\}$ operators in SAC-CI and EX-MEG4. That is, the $\{R_K^\dagger\}$ operators should be chosen from the space of the operators whose maximum excitation level is higher by unity, at least, than the physical process under consideration.[5] For example, for studying singly excited states and Koopmans-type ionizations, singles and doubles are enough for $\{R_K^\dagger\}$, but for doubly excited states and shake-up ionizations and electron attachments, the $\{R_K^\dagger\}$ operators should be chosen at least from the space of singles, doubles, and triples. This is automatically done in the present EX-EGWF program.[28]

The differences among the three-reference, two-reference, and single-reference EX-MEG4 results (the last ones are actually the SAC-CI general-R results) are small. Prob-

ably, at $R = 2.0$ Å, the single and double $\sigma \rightarrow \sigma^*$ excitations represent mainly the dynamic correlations which are most compactly expressed by the exp operator. The differences from the full-CI energies are all positive, except for the SD-R SAC-CI results for the 2 $^1\Pi$ and 2 $^3\Pi$ states, which slightly overshoot the full-CI energies.

Table III shows the results for $R = 3.0$ Å. In the ground state, the weights of the Hartree–Fock and doubly excited $\sigma \rightarrow \sigma^*$ configurations are 0.46 and 0.36, respectively, as seen from the full-CI main configurations. Thus the quasidegenerate situation is realized at this geometry. We have performed three-, two-, and single-reference MEG4 calculations, but the last one, which is the SAC calculation, did not converge. So, we can not give the SAC/SAC-CI results in this table. The first row shows the MEG4 results. The error is large and this shows the importance of higher excitations in the linked term. These MEG4 wave functions include only up to double excitations in the linked term. The EX-MEG4 solutions for the ground state is, however, much superior to the MEG4 results, since they include higher excitations in the linked term. We recommend to use this solution for the ground state since it satisfies Eq. (23) with the excited states. The three-reference results are improved by 3.6 mhartree over the two-reference MEG4 results.

The differences of the EX-MEG4 energies from the full-CI ones are again rather constant among the various different states. This constancy holds better for the three-reference case than does for the two-reference case, though the average error is larger for the former. This trend is seen from the average discrepancy and the standard deviation shown in the parentheses. (The standard deviation for the triplet states is an exception.) We note that the ionic 2 $^2\Pi$ state is the result of the three-electron process relative to the Hartree-Fock configuration. In the two-reference calculations, the Δ values are negative for the 2 $^1\Pi$, 2 $^3\Pi$, and ionic 1 $^2\Pi$ states. However, no such state exists in the three-reference case. Other trends in Table III are similar to those in Table II.

We next discuss the results shown in Table I, which is for $R = R_{eq}$ (0.916 808 Å). In the present choice of the

TABLE IV. Excitation energies, ionization potentials, and electron affinites in eV calculated by the full-CI and MEG4/EX-MEG4 (SAC/SAC-CI with general R) methods for hydrogen fluoride at $R = 0.916\ 808$ Å (equilibrium distance).[a]

				Full-CI		MEG4/EX-MEG4[b]		
State	Main configuration[a]		Excitation level	Size	Excitation energy	Size	Excitation energy	Δ[c]
Singlet								
$^1\Sigma^+$	1	Hartree–Fock	0	44 388	0.0	377	0.0	0.000
	2	$\sigma_1 \rightarrow 3s$	1	44 388	14.710	377	14.705	−0.005
	3	$\sigma_1 \rightarrow \sigma_1^*$	1	44 388	18.646	377	18.670	0.024
$^1\Pi$	1	$p\pi \rightarrow 3s$	1	42 336	10.380	272	10.355	−0.025
	2	$p\pi \rightarrow \sigma_1^*$	1	42 336	13.804	272	13.782	−0.022
	3	$p\pi \rightarrow \sigma_2$	1	42 336	27.280	272	27.278	−0.002
								(−0.006)[d]
Triplet								
$^3\Sigma^+$	1	$\sigma_1 \rightarrow 3s$	1	71 020	13.351	436	13.355	0.004
	2	$\sigma_1 \rightarrow \sigma_1^*$	1	71 020	17.081	436	17.095	0.014
$^3\Pi$	1	$p\pi \rightarrow 3s$	1	70 880	9.867	421	9.854	−0.013
	2	$p\pi \rightarrow \sigma_1^*$	1	70 880	13.576	421	13.570	−0.006
	3	$p\pi \rightarrow \sigma_2$	1	70 880	26.886	421	26.894	0.008
								(−0.001)[d]
Ion								
$^2\Sigma^+$	1	$\sigma_1 \rightarrow \infty$	1	48 560	19.574	607	19.537(20.0)[e]	−0.037
	2	$p\pi, p\pi \rightarrow \sigma_1^*, \infty$	2	48 560	33.884	607	33.874	−0.010
	3	$p\pi, p\pi \rightarrow \sigma_1^*, \infty$	2	48 560	35.025	607	35.161	0.136
$^2\Pi$	1	$p\pi \rightarrow \infty$	1	47 140	15.649	596	15.613(16.05)[e]	−0.036
	2	$\sigma_1, p\pi \rightarrow \sigma_1^*, \infty$	2	47 140	35.236	596	35.251	0.015
	3	$\sigma_1, p\pi \rightarrow 3s, \infty$	2	47 140	37.135	596	37.124	−0.011
								(−0.009)[d]
Anion								
$^2\Sigma^+$	1	$\infty \rightarrow 3s$	1	87 408	−2.037	703	−2.132	−0.095
	2	$\infty \rightarrow \sigma^*$	1	87 408	−5.928	703	−6.026	−0.098
$^2\Pi$	1	$p\pi, \infty \rightarrow 3s, 3s$	2	84 852	−10.946	710	−11.047	−0.101
	2	$p\pi, \infty \rightarrow 3s, \sigma^*$	2	84 852	−13.316	710	−13.443	−0.127
								(−0.105)[d]

[a] Hartree–Fock MO ordering at equilibrium geometry is $(1s)^2(2s)^2(\sigma_1)^2(\pi)^4(3s)(\sigma_1^*)(\sigma_2)(p\pi^*)(\sigma_3)(\sigma_4)$.

[b] The MEG4/EX-MEG4 method coincides with the SAC/SAC-CI method with R † general at this distance in the present choice of the thresholds (see the text).

[c] Difference from the full-CI value.

[d] Average discrepancy.

[e] Values in parentheses are experimental values.

thresholds, MEG4 becomes identical with SAC and EX-MEG4 with SAC-CI with general R. Table I also shows the SD-R SAC-CI results. As in Table II, they compare well with full-CI for one-electron processes, but unsatisfactorily for two-electron ionization and electron attachment processes. However, when we use general-R operators, the accuracy of the results is much improved and becomes rather constant, independent of the excitation levels, as the smallness of the standard deviation clearly shows. This result implies that the automatic generation of higher operators by the EGCI algorithm is successful.

Another interesting point in Table I is that many SD-R SAC-CI energies overshoot the exact energies. Note further that such cases are seen only for the states whose excitation levels are single relative to the ground state. The same was the case in Tables II and III. Though the origin of the overshooting lies in the nonvariational solution, it is interesting to clarify why it occurs only for the single electron processes.

From the results of Table I, we can calculate (vertical) transition energies for hydrogen fluoride. Table IV shows the excitation energy, ionization potential, and electron affinity calculated in eV. Here, the MEG4/EX-MEG4 method is the same as the SAC/SAC-CI method with general-R. The average deviation in excitation energy from the full-CI results is only -0.004 eV. This shows the usefulness of the MEG4/EX-MEG4 method for calculating transition energies of various states including singlet, triplet, ionized, and anion states with different excitation levels. Though meaningful comparisons with experiments are difficult because of the insufficiency in the basis set, we refer to the experimental ionization potentials from the $p\pi$ and σ_1 orbitals to be 16.05 and 20.0 eV,[38] respectively, in comparison with the present results of 15.61 and 19.54 eV, respectively.

Finally, we compare the results of Tables I–III for $R = R_{eq}$, 2.0 and 3.0 Å. We see that the average error deviates from 1.27–3.54 mhartree for singlet, triplet, and ionized states. For anion states, it deviates within 4.15–5.77 mhartree. We therefore conclude that the accuracy of the MEG4/EX-MEG4 method is rather constant, independent of the internuclear distance. This method would be useful for calculating potential energy surfaces of the ground, excited, ionized and anion states in chemical accuracy.

V. CONCLUDING REMARKS

In this paper, we have proposed the EX-MEG4 method, which is derived by applying the excitator method to the MEG4 wave function. The MEG4/EX-MEG4 method describes ground, excited, ionized, and electron attached states, and is a standard generalization of the SAC/SAC-CI method to multireference cases. We have described the computational algorithms currently used in our program. Test calculations are performed for the several lower states of each of the singlet, triplet, ionized, and anion states of hydrogen fluoride at R = Re, 2.18 Re, and 3.27 Re, and the results are compared with full CI. We have observed that the differences from the full-CI energies are small and rather constant among the various states with different multiplicities, different numbers of electrons, different excitation levels, and different internuclear distances. We emphasize that the dimensions of the present calculations are small. Though many applications are necessary before deducing final conclusions, the present method may be useful for studying reactions and dynamics involving various states among the ground, excited, ionized, and anion states.

We have also observed that the SAC/SAC-CI method with general $R^\dagger$ operators is reliable and useful, when the Hartree–Fock configuration is dominant in one of the singlet states (usually the ground state). By extending the $R^\dagger$ operators to be general, rather than restricting them to singles and doubles, the reliability of the SAC-CI method is much improved for multielectron processes.

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