

Exponentially generated configuration interaction theory. Descriptions of excited, ionized, and electron attached states

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A method of calculating wave functions of excited, ionized, and electron attached states on the basis of the correlated wave function for the ground state is given. This method, called *excitator* method, is a generalization of the SAC-CI (symmetry adapted cluster–configuration interaction) method. The excitator method is applied to the exponentially generated configuration interaction (EGCI) method previously proposed. The computational algorithm is described and test applications are performed for several lower states of the singlet, triplet, ionized, and anion states of CO and C₂ at different internuclear distances. The accuracy of the proposed EGCI method is shown to be good relative to the full-CI energies for various states with different multiplicities, different numbers of electrons, different single and multi-electron processes, and different internuclear distances. Although the sizes of the present test calculations are small, these properties are important for studying dynamics and reactions involving different electronic states.

I. INTRODUCTION

Two methods are popularly used for calculating electron correlations in atoms and molecules. They are the CI method^{1,2} and cluster expansion method.³⁻⁹ The CI method is written as

$$\Psi^{\text{CI}} = \left(d_0 + \sum_K d_K R_K^\dagger \right) \Phi_0^{\text{CI}}, \quad (1)$$

and the cluster expansion method as

$$\Psi^{\text{SAC}} = \exp\left(\sum_K C_K S_K^\dagger\right) |0\rangle, \quad (2)$$

where

$$\begin{aligned} \exp\left(\sum_K C_K S_K^\dagger\right) &= 1 + \sum_K C_K S_K^\dagger + \frac{1}{2} \sum_{K,L} C_K C_L S_K^\dagger S_L^\dagger \\ &+ \frac{1}{3!} \sum_{K,L,M} C_K C_L C_M S_K^\dagger S_L^\dagger S_M^\dagger + \dots \end{aligned} \quad (3)$$

We consider here, for simplicity, only totally symmetric states and define excitation operators S_K^\dagger and R_K^\dagger to be symmetry adapted. Φ_0^{CI} is a reference function in the CI expansion and $|0\rangle$ a single determinant defined by

$$|0\rangle = \|\varphi_1 \alpha \varphi_1 \beta \cdots \varphi_i \alpha \varphi_i \beta \cdots \varphi_n \alpha \varphi_n \beta\|, \quad (4)$$

for which we usually use Hartree–Fock (HF) determinant. The expansion given by Eq. (2) is symmetry-adapted-cluster (SAC) expansion,⁷ since the operators involved are symmetry adapted. Otherwise, the expansion represents a mixed symmetry.

Both CI and cluster expansion methods are in principle exact, but when approximated, they have different merits and demerits. The CI method has an upper bound nature but the cluster expansion method does not, because only the nonvariational method of solution is practical for the cluster expansion method. The cluster expansion method is usually

more rapidly convergent than CI, since it takes into accounts the effect of simultaneous occurrences of pair collisions. The CI method is applicable to quasi-degenerate states but the cluster expansion method is not since it is a single-reference theory. The cluster expansion method satisfies size consistency¹⁰ (or size extensivity)¹¹ and self-consistency,¹² but the CI method does not.

In the previous papers of this series,¹³⁻¹⁵ we have considered a method of removing the drawbacks of the cluster expansion theory by generalizing the exponential operator given by Eq. (3). We have introduced a new expansion operator defined by

$$\begin{aligned} &\text{EXP}\left(\sum_K a_K A_K^\dagger\right) \\ &\equiv Q\left(a_0 + \sum_K a_K A_K^\dagger + \frac{1}{2} \sum_{K,L} a_{KL} A_K^\dagger A_L^\dagger\right. \\ &\quad \left. + \frac{1}{3!} \sum_{K,L,M} a_{KLM} A_K^\dagger A_L^\dagger A_M^\dagger + \dots\right), \end{aligned} \quad (5)$$

where we add here a symmetry projector Q in order to permit the symmetry adapted operators A_K^\dagger to run all the symmetries. The EXP operator is more general than the exp operator since the coefficients of the product operators (say a_{KL}) are free from those of the lower order terms (say a_K and a_L). We have defined exponentially generated (EG) CI wave function by¹⁴

$$\Psi^{\text{EGCI}} = \text{EXP}\left(\sum_K a_K A_K^\dagger\right) |0\rangle. \quad (6)$$

The excitation operators involved in this expansion are essentially the same as those in the cluster expansion, but all the terms have independent variables. Therefore, this expansion is a linear CI expansion. The constructions of higher excitation configurations are done in the spirit of the cluster expansion theory, and only linearly independent terms are

included. It satisfies an upper-bound nature and is applicable to quasi-degenerate case as shown below. Furthermore, since this expansion is just a generalization of the cluster expansion, it satisfies size consistency and self-consistency, when all the higher excitation terms are involved without an approximation. When some higher excitation terms are neglected, these properties are satisfied to the order of such approximation.

The unknown problem of the EGCI method is the convergence property. It should be examined by applying to a number of molecules, which is a purpose of this study. Intuitively, this method assumes that when some excitations are important, excitations from such excited configurations, which are product terms, should also be important, and the coefficients of the latter ones are reoptimized independent of those of the first one. As expected from the analysis of the breakdown of the cluster expansion method for an elongated CO molecule,¹³ this method should be useful for the processes in which the nature of electron correlations changes from separable to nonseparable one. Homolytic bond dissociation process is a typical example.

Accurate descriptions of excited and ionized states are very important for studying dynamics of molecular excited states. When the ground state is HF dominant, the SAC theory works well and the SAC-CI theory¹⁶ describes well the excited, ionized, and electron attached states.^{9,15} This is based on an approximate transferability of electron correlations among these states. Another purpose of this paper is to propose a general method of describing excited, ionized, and electron attached states on the basis of the correlated wave function for the ground state. Particularly, we here develop such method combining with the EGCI wave function for the ground state. The resultant method, called EGCI method in a wider sense, is applicable even for the quasi-degenerate case. We summarize the algorithms of calculations of the newly coded EGCI program.

The proposed EGCI method is applied to the ground, excited, ionized, and anion states of CO and C₂ in equilibrium and elongated distances. We want to examine the accuracy of the proposed method by comparing with the full CI calculations for all of these states. Though benchmark full CI calculations of about 10⁷ configurations are reported in the literature,¹⁷ the calculated states are too limited. So, we carry out here independent full CI calculations solving 5–10 solutions for each of the singlet, triplet, ionized, and anion states at different geometries, though the size of the calculations are much smaller. The CO molecule is chosen because the weight of the HF configuration in the ground state approaches zero as the bond distance is elongated. The C₂ molecule is interesting because it has many singly and doubly excited states in a lower energy region.¹⁸ This molecule is also unique since it has the excited states of anion in a stable energy region.¹⁸ In the present sizes of the calculations, quantitative comparisons of the calculated results are possible only with the full CI results, but not with the experimental values.

In the following, we mean by “excitation” not only an excitation alone, but also an ionization and an electron attachment, when we are not strict.

II. DESCRIPTION OF EXCITED, IONIZED, AND ELECTRON ATTACHED STATES

Let a correlated wave function for the ground state be Ψ_g , and assume that the excited states Ψ_e are generated from this by applying the excitation operator, \mathcal{R} , as

$$\Psi_e = \mathcal{R}\Psi_g. \quad (7)$$

The excitation operator \mathcal{R} , which is a kind of a reaction operator, is called *excitator*, in order to distinguish it from more elementary excitation operators such as S_K^\dagger and A_K^\dagger in Eqs. (1)–(6). More explicitly, we call it *excitator*, *ionizer*, or *anionizer*. It describes an excitation, ionization, or electron attachment, respectively, and at the same time, the changes in orbitals and electron correlations after the excitation. This method is called excitator method.

The idea of the excitator is very old. It was used in the Green's function method¹⁹ and the equation of motion method.²⁰ In the formulation of the SAC-CI theory,¹⁶ the excitator method was naturally introduced as a result of the variational principle applied to the SAC wave function.⁷ The nonvariational formulation was given later.²¹ Since the SAC theory is formally exact, the SAC-CI theory is also formally exact. Therefore, the excitator method is formally exact.

The physical basis of the excitator method is as follows. Electronic excitations usually involve only one or two electrons of a molecule. Other electrons are reorganized by this excitation, but their environments have some similarity to those in the ground state. The excitator method is considered to be efficient for describing electron correlations in excited states since it starts from the electron correlations of the ground state. It describes the excitation itself and the reorganizations in electron correlations induced by this excitation. This method should be easier than the method calculating all the correlations in the excited state from the beginning, independently from those of the ground state, though such calculations are usually done in an ordinary CI method. The same should also be true for ionizations and electron attachments.

In the framework of the excitator method, the SAC-CI method¹⁶ is written as

$$\Psi^{\text{SAC-CI}} = \mathcal{R}\Psi^{\text{SAC}}, \quad (8)$$

with the excitator \mathcal{R} being expanded by a linear combination of the excitation operators $\{R_K^\dagger\}$,

$$\mathcal{R} = \sum_K d_K R_K^\dagger. \quad (9)$$

A rapid convergence of the SAC-CI method has been confirmed from many applications to various kinds of excited and ionized states.⁹ This is basically due to and a proof of an approximate transferability of electron correlations between ground and excited states.

The excitator \mathcal{R} is determined by requiring the Schrödinger equation within the space $\{\Phi_K\}$ in which the ground and excited states are defined,

$$\langle \Phi_K | (H - E) \mathcal{R} | \Psi_g \rangle = 0. \quad (10)$$

The excited states should be orthogonal and Hamiltonian orthogonal to the ground state,

$$\langle \Psi_g | \mathcal{R} \Psi_g \rangle = 0, \quad \langle \Psi_g | H \mathcal{R} | \Psi_g \rangle = 0. \quad (11)$$

When \mathcal{R}_a and \mathcal{R}_b are the operators which generate different excited states Ψ_e^a and Ψ_e^b , i.e.,

$$\begin{aligned} \Psi_e^a &= \mathcal{R}_a \Psi_g, \\ \Psi_e^b &= \mathcal{R}_b \Psi_g, \end{aligned} \quad (12)$$

then, the following conditions should also be satisfied.

$$\langle \Psi_g | \mathcal{R}_a^\dagger \mathcal{R}_b | \Psi_g \rangle = \delta_{ab}, \quad \langle \Psi_g | \mathcal{R}_a^\dagger H \mathcal{R}_b | \Psi_g \rangle = E_a \delta_{ab}. \quad (13)$$

III. EGCI METHOD FOR EXCITED, IONIZED, AND ELECTRON ATTACHED STATES

In this section, we formulate the excitator method, adopting the ground-state EGCI wave function as Ψ_g . The EGCI wave function for totally symmetric states, including the ground state, is given by Eqs. (5) and (6). When we define the operators $\{Q(A_K^\dagger, A_K^\dagger A_L^\dagger, A_K^\dagger A_L^\dagger A_M^\dagger, \dots)\}$ as $\{G_K^\dagger\}$, it is written as

$$\Psi^{\text{EGCI}} = \sum_K g_K G_K^\dagger |0\rangle. \quad (14)$$

The solution is obtained by the secular equation

$$\begin{aligned} \langle 0 | H - E | \Psi^{\text{EGCI}} \rangle &= 0, \\ \langle 0 | G_K (H - E) | \Psi^{\text{EGCI}} \rangle &= 0. \end{aligned} \quad (15)$$

The wave functions for the excited, ionized, and anion states are generated by the excitator method as

$$\begin{aligned} \Psi^{\text{EX-EGCI}} &= \mathcal{R} \Psi^{\text{EGCI}} \\ &= \mathcal{R} \text{EXP} \left(\sum_K a_K A_K^\dagger \right) |0\rangle, \end{aligned} \quad (16)$$

where EX-EGCI stands for the excitator method applied to the EGCI wave function. We now expand the excitator \mathcal{R} by a linear combination of a set of excitation operators $\{B_K^\dagger\}$,

$$\mathcal{R} = \sum_K \iota_K B_K^\dagger, \quad (17)$$

with ι_K being *not* a coefficient but *an operator* which makes free the products as

$$\begin{aligned} \iota_K a_0 &= b_K, \\ \iota_K a_L &= \frac{1}{2} b_{KL}, \\ \iota_K a_{LM} &= \frac{1}{3} b_{KLM}, \end{aligned} \quad (18)$$

etc. Then, the EX-EGCI wave function is rewritten as

$$\begin{aligned} \Psi^{\text{EX-EGCI}} &= Q \left(\sum_K b_K B_K^\dagger + \frac{1}{2} \sum_{K,L} b_{KL} B_K^\dagger A_L^\dagger \right. \\ &\quad \left. + \frac{1}{3!} \sum_{K,L,M} b_{KLM} B_K^\dagger A_L^\dagger A_M^\dagger + \dots \right) |0\rangle. \end{aligned} \quad (19)$$

We here attach the symmetry projector Q , for convenience, but this is not essential since the EX-EGCI wave function is a linear expansion.

The basic idea of EX-EGCI may be seen from a comparison of Eqs. (5), (6), and (19). The correlations $\{A_L^\dagger\}$ important in the ground state should also be important in the

excited states, so that we consider in the excited state the excitations B_K^\dagger from such correlated configurations, $A_L^\dagger |0\rangle$, resulting in the configurations, $B_K^\dagger A_L^\dagger |0\rangle$. In contrast to the SAC-CI method described by Eqs. (8) and (9), we here give free coefficients b_{KL} , instead of the products $b_K a_L$. This is the spirit of the *ex/2* operator, in contrast to the *exp* operator.

When we define the operators $\{Q(B_K^\dagger, B_K^\dagger A_L^\dagger, B_K^\dagger A_L^\dagger A_M^\dagger, \dots)\}$ in Eq. (19) as $\{E_K^\dagger\}$, the EX-EGCI wave function is rewritten in a compact form as

$$\Psi^{\text{EX-EGCI}} = \sum_K e_K E_K^\dagger |0\rangle. \quad (20)$$

For totally symmetric states, $\{B_K^\dagger\}$ may be equal to $\{A_K^\dagger\}$ and $B_0^\dagger = 1$ (identity operator), so that Eq. (19) becomes equal to Eq. (6). For other states, the operators $\{B_K^\dagger\}$ are the symmetry adapted excitation operators for the corresponding excitations, ionizations, or electron attachments.

The solution for the EX-EGCI wave function is straightforward. Applying the variational principle to Eq. (20), we obtain

$$\langle 0 | E_K (H - E) | \Psi^{\text{EX-EGCI}} \rangle = 0, \quad (21)$$

which is an ordinary secular equation. The solution satisfies

$$\langle \Psi^{\text{EGCI}} | \Psi^{\text{EX-EGCI}} \rangle = 0, \quad \langle \Psi^{\text{EGCI}} | H | \Psi^{\text{EX-EGCI}} \rangle = 0, \quad (22)$$

and

$$\begin{aligned} \langle \Psi_a^{\text{EX-EGCI}} | \Psi_b^{\text{EX-EGCI}} \rangle &= \delta_{ab}, \\ \langle \Psi_a^{\text{EX-EGCI}} | H | \Psi_b^{\text{EX-EGCI}} \rangle &= E_a \delta_{ab}. \end{aligned} \quad (23)$$

In Eq. (22) we have assumed that a common set of the operators $\{A_K^\dagger\}$ is used for totally symmetric ground and excited states.

Because of the similarity between the EGCI and EX-EGCI wave functions given by Eqs. (6) and (19), it is convenient to call the EGCI/EX-EGCI method as just the EGCI method.

The EGCI method is a CI method with special configuration generation and selection (see below) schemes. It is different from other CI schemes like due to Shavitt¹ and Buenker and Peyerimhoff.² Up to the linear operator terms, these methods are similar, but for higher terms, the present method generates configurations as products of lower excitation operators in the spirit of the SAC and SAC-CI theories. Namely, the excitations from already important excited configurations should be important [see Eq. (5)] and the correlation operators which are important in the ground state should also be important in the excited and ionized states [see Eqs. (16) and (19)]. The method is rather automatic and unambiguous.

IV. COMPUTATIONAL ALGORITHM

For totally symmetric singlet states, we calculate both ground and excited states, simultaneously. The linear operator term of Eq. (5) consists of totally symmetric single and double excitation operators selected by the perturbation selection method with the threshold λ_A .²² The selection is done for all the states under consideration. We also perform

similar selections for different symmetries and store the results into $\{A_k^\dagger\}$. We perform CIs with these $\{A_k^\dagger\}$ operators. The product operators $\{A_k^\dagger A_L^\dagger\}$ are made of the A_k^\dagger operators whose coefficients in these SDCIs are larger than a given threshold λ_{AA} which is of the order of $\sqrt{\lambda_A}$. We include in Eq. (5) only such product operators that are totally symmetric and linearly independent of all the other $\{A_k^\dagger, A_k^\dagger A_L^\dagger\}$ operators. The same procedure is done for the higher product operators $\{A_k^\dagger A_L^\dagger A_M^\dagger\}$, $\{A_k^\dagger A_L^\dagger A_M^\dagger A_N^\dagger\}$ etc. In the present version of the program²³ we can include up to the four-product operators of up to eight-electron excitations. The accuracy of the calculation is shown by the set of the thresholds, $(\lambda_A, \lambda_{AA}, \lambda_{AAA}, \lambda_{AAAA})$. When all the operators in the expansion are selected, the EGCI is just a CI and we solve the secular equation [Eq. (15)] by a direct procedure or by an iterative method,²⁴ depending on the size of the matrices under consideration.

The EX-EGCI method for nontotally symmetric excited states (e.g., singlet B_1 excited states, triplet excited states, etc.) and ionized and anion states is carried out similarly. We select symmetry adapted single and double excitation operators $\{B_k^\dagger\}$ to be included in Eq. (19) using the threshold λ_A . We perform an SDCI with these $\{B_k^\dagger\}$ operators. The product operators $\{B_k^\dagger A_L^\dagger\}$ are generated from the $\{B_k^\dagger\}$ operators, whose coefficients in this SDCI are larger than the threshold λ_{AA} , and the $\{A_L^\dagger\}$ operators already selected above for generating the products, $\{A_k^\dagger A_L^\dagger\}$. The higher operators $\{B_k^\dagger A_L^\dagger A_M^\dagger\}$ and $\{B_k^\dagger A_L^\dagger A_M^\dagger A_N^\dagger\}$ are similarly constructed with the use of the thresholds, λ_{AAA} (and) λ_{AAAA} . The solutions are obtained by diagonalizing the secular equation given by Eq. (21).

V. APPLICATIONS OF THE EGCI METHOD

A. CO molecule

The nature of the electron correlations involved in the CO molecule varies as a function of the internuclear distance.^{15,25-30} We have investigated the main configurations in the full-CI wave functions of the lower $^1\Sigma^+$ states as a function of the internuclear distance.^{15,29} Near the equilibrium geometry, the HF configuration is dominant in the ground state so that the correlations involved are essentially separable. As the CO distance is elongated, the weight of the HF configuration decreases and at the dissociation limit it vanishes identically, since the ground state dissociates into $C(^3P)$ and $O(^3P)$. The electron correlations in the intermediate length are typically quasi-degenerate, and the HF configuration distributes into several lower $^1\Sigma^+$ states. At the dissociation limit, the HF configuration is dominant in the higher (third or fourth depending on the basis set and the active space²⁵⁻³⁰) $^1\Sigma^+$ state. We have chosen this molecule for explaining the reason of the breakdown of the single-reference cluster expansion theory.¹³ The multireference (MR) SAC method has been applied to the calculations of the potential energy curves of the lower three $^1\Sigma^+$ states of CO.^{15,29} The results were satisfactory showing the reliability of the MR-SAC method for quasi-degenerate ground and excited states.

We here apply the EGCI method to the ground, excited, ionized, and anion states of the CO molecule at the length of 2.132 a.u. (equilibrium), 3.75 a.u., and 5.5 a.u. The basis is [4s2p] set of Huzinaga³¹ and Dunning.³² The HF energies are $-112.685\ 05$, $-112.348\ 90$, and $-112.286\ 63$ a.u. for $R = 2.132$ (R_{eq}), 3.75, and 5.5 a.u., respectively. In order to perform comparative full-CI calculations, the active MOs are limited to four occupied and four unoccupied HF MOs; $(2s_C)^2(p\pi)^4(p\sigma)^2(p\pi^*)(p\sigma^*)(p\sigma')$. The EGCI calculations are performed by setting the thresholds $(\lambda_A, \lambda_{AA}, \lambda_{AAA}, \lambda_{AAAA})$ as (0.0, 0.04, 0.2, 0.2) and (0.0, 0.04, ∞ , ∞), with the latter set being for comparison to see the effects of the excitations higher than the five-electron excitations.

Tables I–IV show the results for $R = R_{eq}$, 3.75 and 5.5 a.u. These tables involve eight singlet, five triplet, six ionized, and five anion states. The excitation level denotes the number of electrons involved in the excitation relative to the HF configuration. We first examine the results for $R = R_{eq}$ shown in Table I. The EGCI method gives the energies of the ground, excited, ionized, and anion states in fairly good agreement with the full-CI results. The average errors are 0.79, 0.95, 0.41, and 1.51 mhartrees, respectively, and the standard deviations are remarkably small. The dimensions of the present EGCI calculations are about one third of those of the full CI. In comparison with the EGCI results without including 5 to 8 electron excitations, the full EGCI results are only slightly better. This shows an unimportance of the triple and quadruple product terms, $\{A_k^\dagger A_L^\dagger A_M^\dagger\}$ and $\{A_k^\dagger A_L^\dagger A_M^\dagger A_N^\dagger\}$ at the equilibrium geometry. Since the EGCI method is variational, all the errors are positive.

Table II shows the excitation energies, ionization potentials, and electron affinities of CO at $R = R_{eq}$. The results of the EGCI method agree quite well with the full CI results. The average error is only 0.016, 0.018, 0.004, and -0.033 eV for the singlet, triplet, ionized, and anion states, respectively.

At $R = 3.75$ a.u., the coefficient of the HF configuration in the ground state is only 0.58 as seen from Table III. It distributes among the lower three $^1\Sigma^+$ states almost equally. The ground state is a mixture of the HF configuration with the singly excited $\pi \rightarrow \pi^*$ configuration, and the second $^1\Sigma^+$ state with the triply excited configuration, and the third one with the triply and doubly excited configurations. The energy of the EGCI method agrees well with the full CI energy for all of these states. The EGCI method is also useful for calculating other singlet, triplet, ionized, and anion states. The average discrepancies are 1.75, 1.37, 2.25, and 2.33 mhartrees, respectively, which are larger by about 1 mhartree than those for $R = R_{eq}$, because of the quasi-degenerate nature of the electronic configurations. The sizes of the EGCI calculations are also larger here by the same reason. It is interesting to note that the contributions of the 5 to 8 electron excitations are larger in this quasi-degenerate case, particularly for the ionic and anion states.

At $R = 5.5$ a.u., the ground state essentially consists of the two-electron excited configuration. The HF configuration is dominant in the third $^1\Sigma^+$ state. The excitation levels of most of the states shown in Table IV are higher than two,

TABLE I. Full-CI and EGCI results in hartree for CO at $R = 2.132$ a.u. (equilibrium distance)

State	Excitation level	Main configuration ^a	EGCI							
			Full-CI		General			Without 5–8 ex		
			Size	Energy	Size	Energy	$\Delta^b \times 10^3$	Size	Energy	$\Delta^b \times 10^3$
Singlet										
¹ Σ^+	0	0.98(2222)	492	-112.743 74	191	-112.743 47	0.27	178	-112.743 47	0.27
¹ Π	1	0.95(22211)	432	-112.414 98	151	-112.414 33	0.65	144	-112.414 31	0.67
¹ Σ^-	1	0.69(21210 - 212201)	408	-112.356 12	135	-112.355 09	1.03	124	-112.355 09	1.03
¹ Δ	1	0.68(212210 + 221201)	492	-112.355 38	191	-112.354 64	0.74	178	-112.354 64	0.74
¹ Π	1	0.89(12221)	432	-112.214 58	151	-112.213 57	1.01	144	-112.213 54	1.04
¹ Σ^+	1	0.92(2221001)	492	-112.201 40	191	-112.200 30	1.10	178	-112.199 85	1.55
¹ Σ^+	1	0.61(212210 - 221201)	492	-112.114 98	191	-112.113 95	1.03	178	-112.113 93	1.05
¹ Π	2	0.64(221111) -0.49(21212 + 212102)	432	-112.088 57	151	-112.088 11	0.46	144	-112.088 11	0.46
						(0.79 ± 0.29) ^c				(0.85 ± 0.38) ^c
Triplet										
³ Π	1	0.96(22211)	392	-112.497 03	187	-112.496 62	0.41	171	-112.496 56	0.47
³ Σ^+	1	0.69(21221 - 221201)	584	-112.400 58	156	-112.399 39	1.19	137	-112.399 36	1.22
³ Δ	1	0.69(21221 + 221201)	584	-112.377 71	156	-112.376 62	1.09	137	-112.376 61	1.10
³ Σ^-	1	0.68(22121 - 212201)	584	-112.363 76	180	-112.362 73	1.03	158	-112.362 73	1.03
³ Π	1	0.93(12221)	592	-112.261 51	187	-112.260 50	1.01	171	-112.260 47	1.04
						(0.95 ± 0.28) ^c				(0.97 ± 0.26) ^c
Ion										
² Σ^+	1	0.95(2221)	616	-112.227 48	261	-112.227 19	0.29	208	-112.226 71	0.77
² Π	1	0.96(2122)	588	-112.112 20	251	-112.111 82	0.38	185	-112.111 73	0.47
² Σ^+	1	0.93(1222)	616	-112.008 29	261	-112.007 83	0.46	208	-112.007 45	0.84
² Σ^-	2	0.68(22111) - 0.63(212101)	560	-111.826 83	218	-111.826 30	0.53	172	-111.826 25	0.58
² Δ	2	0.57(21211 + 221101)	616	-111.825 00	218	-111.824 47	0.53	172	-111.824 54	0.46
² Π	2	0.78(22201) - 0.53(12211)	588	-111.819 91	251	-111.819 62	0.29	185	-111.818 27	1.64
						(0.41 ± 0.10) ^c				(0.79 ± 0.40) ^c
Anion										
² Π	1	0.97(22221)	588	-112.615 20	174	-112.614 60	0.60	144	-112.614 36	0.84
² Σ^+	1	0.97(2222001)	616	-112.445 02	172	-112.441 78	3.24	139	-112.441 36	3.66
² Δ	2	0.68(222120 - 222102)	616	-112.350 09	157	-112.349 04	1.05	125	-112.348 98	1.11
² Σ^+	2	0.67(22212 + 222102)	616	-112.328 70	172	-112.327 19	1.51	139	-112.327 13	1.57
² Σ^-	2	0.81(222111)	560	-112.305 04	157	-112.303 91	1.13	125	-112.303 67	1.37
						(1.51 ± 0.91) ^c				(1.71 ± 1.01) ^c

^aThe MO ordering is $2s\ p\pi\ p\pi\ p\sigma\ p\pi^*\ p\pi^*\ 2p\ \sigma^*\ 2p\ \sigma'$.^b Δ shows the difference from the full CI result.^c($x \pm y$) where x means the average discrepancy from the full-CI value and y means the standard deviation, both in mhartree.TABLE II. Excitation energies, ionization potentials and electron affinities in eV calculated by the full-CI and EGCI methods for CO at $R = 2.132$ a.u. (equilibrium distance).

State	Excitation level	Main configuration ^a	Full-CI		EGCI		Δ^b
			Size	Energy	Size	Energy	
Singlet							
¹ Σ^+	0	Hartree-Fock	492	0.0	191	0.0	0.0
¹ Π	1	$n \rightarrow \pi^*$	432	8.946	151	8.956	0.010
¹ Σ^-	1	$\pi \rightarrow \pi^*$	408	10.548	135	10.568	0.020
¹ Δ	1	$\pi \rightarrow \pi^*$	492	10.568	191	10.581	0.013
¹ Π	1	$2s \rightarrow \pi^*$	432	14.399	151	14.419	0.020
¹ Σ^+	1	$n \rightarrow 2p\sigma^*$	492	14.758	191	14.780	0.022
¹ Σ^+	1	$\pi \rightarrow \pi^*$	492	17.109	191	17.130	0.021
¹ Π	2	$n \rightarrow \pi^*, \pi \rightarrow \pi^*$	432	17.828	151	17.833	0.005
							(0.016) ^c
Triplet							
³ Π	1	$n \rightarrow \pi^*$	392	6.713	187	6.717	0.004
³ Σ^+	1	$\pi \rightarrow \pi^*$	584	9.338	156	9.363	0.025
³ Δ	1	$\pi \rightarrow \pi^*$	584	9.960	156	9.982	0.022
³ Σ^-	1	$\pi \rightarrow \pi^*$	584	10.340	180	10.360	0.020
³ Π	1	$2s \rightarrow \pi^*$	592	13.122	187	13.142	0.020
							(0.018) ^c

TABLE II. (continued).

State	Excitation level	Main configuration ^a	Full-CI		EGCI		Δ^b
			Size	Energy	Size	Energy	
Ion							
$^2\Sigma^+$	1	$n \rightarrow \infty$	616	14.048	261	14.049	0.001
$^2\Pi$	1	$\pi \rightarrow \infty$	588	17.185	251	17.188	0.003
$^2\Sigma^+$	1	$2s \rightarrow \infty$	616	20.013	261	20.018	0.005
$^2\Sigma^-$	2	$n, \pi \rightarrow \pi^*, \infty$	560	24.950	218	24.957	0.007
$^2\Delta$	2	$n, \pi \rightarrow \pi^*, \infty$	616	25.000	218	25.007	0.007
$^2\Pi$	2	$n, n \rightarrow \pi^*, \infty$	588	25.139	251	25.139	0.000
							(0.004) ^c
Anion							
$^2\Pi$	1	$\infty \rightarrow \pi^*$	588	-3.498	174	-3.507	-0.009
$^2\Sigma^+$	1	$\infty \rightarrow 2p\sigma^*$	616	-8.129	172	-8.209	-0.080
$^2\Delta$	2	$\infty, n \rightarrow \pi^*, \pi^*$	616	-10.712	157	-10.733	-0.021
$^2\Sigma^+$	2	$\infty, n \rightarrow \pi^*, \pi^*$	616	-11.294	172	-11.328	-0.034
$^2\Sigma^-$	2	$\infty, n \rightarrow \pi^*, \pi^*$	560	-11.938	157	-11.961	-0.023
							(-0.033) ^c

^a The MO ordering is $(2s)^2 (\pi)^2 (n)^2 (\pi^*) (p\sigma^*) (p\sigma')$.^b Difference from the full CI result.^c Average discrepancy.TABLE III. Full-CI and EGCI results in hartree for CO at $R = 3.75$ a.u.

State	Excitation level	Main configuration ^a	EGCI								
			Full-CI			General			Without 5-8 ex		
			Size	Energy	Size	Energy	$\Delta^b \times 10^3$	Size	Energy	$\Delta^b \times 10^3$	
Singlet											
$^1\Sigma^+$	0	$0.58(2222) + 0.36(21221 - 221201)$	492	-112.514 73	271	-112.513 78	0.95	247	-112.512 04	2.69	
$^1\Delta$	1	$0.53(21221 + 221201)$	492	-112.458 33	271	-112.457 16	1.17	247	-112.456 71	1.62	
$^1\Sigma^-$	1	$0.53(22121 - 212201)$	408	-112.458 09	225	-112.456 78	1.31	204	-112.456 35	1.74	
$^1\Pi$	1	$0.61(22211) + 0.45(2210111)$	432	-112.401 65	245	-112.399 78	1.87	222	-112.399 13	2.52	
$^1\Sigma^+$	0	$0.58(2222) + 0.35(2111111) + 0.33(2110112)$	492	-112.387 11	271	-112.384 22	2.89	247	-112.378 54	8.57	
$^1\Pi$	1	$0.67(2122001)$	432	-112.363 61	245	-112.361 82	1.79	222	-112.358 25	5.36	
$^1\Sigma^+$	0	$0.47(2222) - 0.33(2111111) - 0.32(211211)$	492	-112.338 18	271	-112.335 64	2.54	247	-112.332 11	6.07	
$^1\Pi$	1	$0.67(22211) - 0.45(2210111)$	432	-112.331 62	245	-112.330 15	1.47	222	-112.329 56	2.06	
						$(1.75 \pm 0.63)^c$				$(3.83 \pm 2.38)^c$	
Triplet											
$^3\Sigma^+$	1	$0.50(21221 - 221201) + 0.36(2121101 - 2211011)$	584	-112.470 87	294	-112.469 68	1.19	269	-112.468 60	2.27	
$^3\Delta$	1	$0.52(22121 + 212201)$	584	-112.460 32	294	-112.459 34	0.98	269	-112.458 76	1.56	
$^3\Sigma^-$	1	$0.53(22121 - 212201)$	584	-112.455 80	307	-112.454 87	0.93	280	-112.454 26	1.54	
$^3\Pi$	1	$0.75(22211)$	592	-112.422 38	302	-112.420 37	2.01	276	-112.419 42	2.96	
$^3\Pi$	1	$0.83(2122001)$	592	-112.388 82	302	-112.387 10	1.72	276	-112.385 22	3.60	
						$(1.37 \pm 0.43)^c$				$(2.39 \pm 0.80)^c$	
Ion											
$^2\Pi$	1	$0.78(2122)$	588	-112.078 47	403	-112.077 09	1.38	241	-112.074 14	4.33	
$^2\Sigma^+$	1	$0.76(2221)$	616	-112.015 83	420	-112.013 48	2.35	244	-112.009 99	5.84	
$^2\Pi$	3	$0.47(2111011) - 0.43(211201)$	588	-111.973 55	403	-111.969 18	4.37	241	-111.958 66	14.89	
$^2\Sigma^-$	3	$0.57(2111002) + 0.55(2112001)$	560	-111.972 55	384	-111.969 81	2.74	224	-111.959 14	13.41	
$^2\Delta$	2	$0.49(21211 + 221101) - 0.36(2120101 + 2210011)$	616	-111.963 20	384	-111.959 66	3.54	224	-111.954 56	8.64	
$^2\Sigma^-$	2	$0.48(212101) + 0.36(2210101 + 2120011)$	560	-111.961 30	384	-111.957 73	3.57	224	-111.952 36	8.94	
						$(2.25 \pm 1.12)^c$				$(9.34 \pm 3.77)^c$	
Anion											
$^2\Pi$	1	$0.59(22221) - 0.40(221211)$	588	-112.544 23	260	-112.541 80	2.43	200	-112.540 30	3.93	
$^2\Pi$	2	$0.46(221211) + 0.32(22221) - 0.32(21222)$	588	-112.479 79	260	-112.477 12	2.67	200	-112.474 86	4.93	
$^2\Pi$	2	$0.40(221211) + 0.33(21222 + 212202)$	588	-112.457 80	260	-112.455 24	2.56	200	-112.454 49	3.31	
$^2\Sigma^+$	1	$0.52(2222001) + 0.46(2122101 - 2212011)$	616	-112.455 52	268	-112.452 43	3.09	206	-112.445 43	10.09	
$^2\Sigma^-$	2	$0.72(222111) - 0.42(2220111) + 0.42(222111)$	560	-112.443 68	242	-112.441 98	1.70	187	-112.441 21	2.47	
						$(2.33 \pm 0.97)^c$				$(4.95 \pm 2.69)^c$	

^a The MO ordering is $2s, p\pi, p\pi, p\sigma, p\pi^*, p\pi^*, p\sigma^*, p\sigma'$.^b Δ shows the difference from the full CI result.^c $(x \pm y)$ where x means the average discrepancy from the full-CI value and y means the standard deviation, both in hartree.

TABLE IV. Full-CI and EGCI results in hartree for CO at $R = 5.5$ a.u.

State	Excitation level	Main configuration ^a	EGCI							
			Full-CI		General			Without 5–8 ex		
			Size	Energy	Size	Energy	$\Delta^b \times 10^3$	Size	Energy	$\Delta^b \times 10^3$
Singlet										
$^1\Sigma^+$	2	0.57(2211011 – 2121101)	492	– 112.424 90	161	– 112.424 09	0.81	140	– 112.423 76	1.14
$^1\Delta$	2	0.57(2121101 + 2211011)	492	– 112.422 81	131	– 112.422 01	0.80	112	– 112.421 67	1.14
$^1\Sigma^-$	2	0.58(2211101) – 0.58(2121011)	408	– 112.422 34	131	– 112.421 54	0.80	112	– 112.421 19	1.15
$^1\Pi$	3	0.83(2111012)	432	– 112.389 36	133	– 112.388 04	1.32	117	– 112.378 79	10.57
$^1\Pi$	3	0.83(2210111)	432	– 112.381 54	133	– 112.378 09	3.45	117	– 112.377 35	4.19
$^1\Sigma^+$	4	0.93(2110112)	492	– 112.357 62	161	– 112.352 44	5.18	140	– 112.352 15	5.47
$^1\Sigma^+$	0	0.91(2222)	492	– 112.335 71	161	– 112.335 56	0.15	140	– 112.335 45	0.26
$^1\Pi$	1	0.95(21220010)	432	– 112.317 62	133	– 112.316 69	0.93	117	– 112.315 93	1.69
						(1.68 ± 1.61) ^c			(3.20 ± 3.24) ^c	
Triplet										
$^3\Sigma^+$	2	0.46(2121101 – 2211011) – 0.40(2121101 – 2211011)	584	– 112.423 14	164	– 112.422 47	0.67	144	– 112.422 23	0.91
$^3\Delta$	2	0.46(2121101 + 2211011) – 0.41(2121101 + 2211011)	584	– 112.421 73	164	– 112.421 07	0.66	144	– 112.420 83	0.90
$^3\Sigma^-$	2	0.50(2211101) + 0.47(2121011)	584	– 112.421 21	173	– 112.420 55	0.66	152	– 112.420 31	0.90
$^3\Pi$	3	0.64(2111012)	592	– 112.390 23	167	– 112.388 27	1.96	147	– 112.384 56	5.67
$^3\Pi$	1	0.90(2122001)	592	– 112.385 05	167	– 112.383 87	1.18	147	– 112.378 85	6.20
						(1.03 ± 0.51) ^c			(2.92 ± 2.47) ^c	
Ion										
$^2\Pi$	2	0.79(2121001)	588	– 112.051 32	252	– 112.050 09	1.23	164	– 112.047 94	3.38
$^2\Sigma^-$	3	0.82(2111002)	560	– 112.025 36	224	– 112.023 49	1.87	132	– 112.006 23	19.13
$^2\Sigma^+$	1	0.89(2221)	616	– 111.986 15	241	– 111.985 60	0.55	147	– 111.983 02	3.13
$^2\Pi$	2	0.86(2121001)	588	– 111.979 19	241	– 111.978 56	0.63	164	– 111.976 88	2.31
$^2\Sigma^+$	3	0.57(2210011 – 2120101)	616	– 111.950 06	241	– 111.945 05	5.01	147	– 111.937 46	12.60
$^2\Delta$	3	0.57(2210011 + 2120101)	616	– 111.948 92	241	– 111.944 96	3.96	147	– 111.936 36	12.56
						(2.21 ± 1.69) ^c			(8.85 ± 6.31) ^c	
Anion										
$^2\Pi$	3	0.63(2211111)	588	– 112.451 69	211	– 112.449 51	2.18	152	– 112.449 26	2.43
$^2\Sigma^+$	4	0.49(2111112) + 0.42(2121102 – 2211012)	616	– 112.413 94	185	– 112.409 97	3.97	139	– 112.404 10	9.84
$^2\Delta$	3	0.50(2121102 + 2211012)	616	– 112.400 29	185	– 112.396 59	3.70	139	– 112.389 59	10.70
$^2\Sigma^-$	3	0.53(2211102)	560	– 112.399 98	170	– 112.396 27	3.71	124	– 112.389 29	10.69
$^2\Pi$	3	0.47(2211111) + 0.47(2121201)	588	– 112.395 22	211	– 112.392 76	2.46	152	– 112.391 88	3.34
						(3.20 ± 0.73) ^c			(7.40 ± 3.71) ^c	

^aThe MO ordering is $2s, p\pi, p\pi, p\sigma, p\pi^*, p\pi^*, p\sigma^*, p\sigma'$.

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

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

but the errors of the EGCI results are again small. The average errors are 1.68, 1.03, 2.21, and 3.20 mhartrees for the singlet, triplet, ionized, and anion states, and are close to those for $R = 3.75$ a.u. For anion, the average error is relatively large because the excitation levels are three or even four. We see there are two results for which the error is about 5 mhartree (3 kcal/mol). One is the second $^1\Sigma^+$ state which is four electron excited state relative to the HF configuration. The other is the second $^2\Sigma^+$ ionized state which is simultaneous ionization–two electron excitation state relative to the HF configuration. The EGCI calculations without 5–8 excitations indicate the importance of the higher excitations for several states; the states whose Δ values are larger than 10 mhartree are all triply excited state relative to the HF configuration.

B. C₂ molecule

The electronic structure of the C₂ molecule is very interesting.^{17,18,33–35} The valence MO configuration at the equi-

librium geometry is $(2s\sigma)^2(2s\sigma^*)^2(p\pi)^4(p\sigma) \times (p\pi^*)(p\sigma^*)(p\sigma')$. Eight valence electrons occupy $2s\sigma$, $2s\sigma^*$ and $p\pi$ MOs, and the $p\sigma$ MO is left unoccupied in the low-lying region. Because of the existence of this orbital, C₂ has very low lying singly and doubly excited states. Furthermore, the anion C₂[–] is more stable than the neutral molecule and has discrete excited states.

We have performed full-CI and EGCI calculations of C₂ at $R = 1.24253 \text{ \AA}$ (R_{eq}) and at $R = 2.0 \text{ \AA}$. The basis set is again the $[4s2p]$ set³² and the HF energy is -75.35648 and -75.16715 a.u., respectively. The $1s$ orbitals are kept fixed. Table V shows the results for the singlet, triplet, ionized, and anion states of C₂ at $R = R_{\text{eq}}$. The singlet and triplet excitation energies, ionization energies, and electron affinities are calculated from this table and shown in Table VI, together with the pictorial assignment of the main configurations. Table VII gives the results for $R = 2.0 \text{ \AA}$.

We first examine the results for the singlet state at $R = R_{\text{eq}}$. The ground state of C₂ is a closed-shell $^1\Sigma_g^+$ state,

TABLE V. Full-CI and EGCI results in hartree for C_2 at $R = 1.242\ 53\ \text{\AA}$ (equilibrium distance):

State	Excitation level	Main configuration ^a ($C > 0.3$)	Full-CI		EGCI		$\Delta^b \times 10^3$
			Size	Energy	Size	Energy	
Singlet							
$^1\Sigma_g^+$	0	0.85(2222) - 0.35(20222)	748	- 75.526 29	287	- 75.524 72	1.57
$^1\Pi_u$	1	0.96(22121)	654	- 75.452 97	239	- 75.451 00	1.97
$^1\Sigma_g^+$	2	0.63(22202 + 22022) - 0.32(20222)	748	- 75.424 69	287	- 75.423 36	1.33
$^1\Delta_g$	2	0.68(22202 - 22022)	748	- 75.423 56	241	- 75.422 97	0.59
$^1\Pi_g$	2	0.90(21212) + 0.36(2211101)	654	- 75.329 14	254	- 75.327 17	1.97
$^1\Sigma_u^+$	1	0.86(21221)	688	- 75.302 72	252	- 75.299 98	2.74
$^1\Sigma_g^+$	2	0.60(20222) + 0.39(2222) - 0.30(21211 - 2112101)	748	- 75.253 69	287	- 75.251 31	2.38
$^1\Sigma_u^-$	1	0.62(221201 - 2221001)	620	- 75.220 00	231	- 75.218 45	1.55
$^1\Delta_u$	1	0.63(221201) + 0.62(2221001)	620	- 75.207 43	231	- 75.205 42	2.01
							(1.79 ± 0.59) ^c
Triplet							
$^3\Pi_u$	1	0.94(22121)	950	- 75.507 16	324	- 75.505 04	2.12
$^3\Sigma_u^+$	1	0.91(21221)	960	- 75.480 06	328	- 75.478 23	1.83
$^3\Sigma_g^-$	2	0.96(22112)	940	- 75.459 08	340	- 75.457 04	2.04
$^3\Pi_g$	2	0.90(21212)	960	- 75.423 54	346	- 75.422 26	1.28
$^3\Sigma_u^+$	1	0.57(222101 - 2212001) + 0.31(21221)	960	- 75.281 56	328	- 75.279 03	2.53
$^3\Delta_u$	1	0.62(2221001 + 2212001)	940	- 75.255 73	296	- 75.253 82	1.91
$^3\Pi_g$	2	0.80(2211101) + 0.48(222011)	960	- 75.232 13	346	- 75.231 36	0.77
$^3\Sigma_u^-$	1	0.62(2221001 + 221201)	940	- 75.230 70	296	- 75.228 25	2.45
$^3\Pi_g$	2	0.59(2211101) + 0.48(222011 - 220211) - 0.34(2211101)	960	- 75.194 60	346	- 75.194 02	0.58
$^3\Sigma_g^+$	2	0.50(212111 - 2112101) - 0.42(212111 - 2112101)	920	- 75.194 04	345	- 75.192 53	1.51
							(1.70 ± 0.63) ^c
Cation							
$^2\Pi_u$	1	0.84(2212) - 0.39(20122)	756	- 75.063 96	288	- 75.062 54	1.42
$^2\Delta_g$	2	0.66(22201 - 22021)	784	- 74.993 47	320	- 74.991 46	2.01
$^2\Sigma_g^+$	2	0.61(22201 + 22021) - 0.37(20221)	784	- 74.990 19	326	- 74.988 08	2.11
$^2\Sigma_g^-$	2	0.82(22111) - 0.48(22111)	728	- 74.970 66	326	- 74.969 48	1.18
$^2\Pi_g$	2	0.85(21211)	756	- 74.967 18	324	- 74.966 04	1.14
$^2\Sigma_u^+$	1	0.90(2122)	784	- 74.960 41	328	- 74.957 49	2.92
$^2\Pi_u$	3	0.89(22102)	756	- 74.952 02	288	- 74.951 41	0.61
$^2\Delta_u$	3	0.64(21202 - 21022)	728	- 74.899 72	299	- 74.899 10	0.62
$^2\Sigma_u^+$	3	0.61(21202 + 21022)	784	- 74.862 27	328	- 74.861 13	1.14
$^2\Sigma_g^+$	2	0.81(20221)	784	- 74.841 86	326	- 74.839 10	2.76
$^2\Sigma_u^-$	3	0.78(21112) + 0.45(21112)	728	- 74.836 81	299	- 74.836 02	0.79
							(1.52 ± 0.78) ^c
Anion							
$^2\Sigma_g^+$	1	0.93(22221)	1164	- 75.579 50	435	- 75.576 68	2.82
$^2\Pi_u$	2	0.96(22122)	1100	- 75.543 46	406	- 75.542 69	0.77
$^2\Sigma_u^+$	2	0.87(21222)	1144	- 75.484 44	427	- 75.483 28	1.16
$^2\Pi_u$	1	0.88(222201)	1100	- 75.356 20	419	- 75.353 10	3.10
$^2\Sigma_u^+$	2	0.64(222111 - 2212101)	1144	- 75.323 72	427	- 75.322 34	1.38
$^2\Sigma_u^-$	2	0.66(2221101) - 0.50(221211) + 0.45(221211)	1056	- 75.320 53	404	- 75.320 04	0.49
$^2\Pi_g$	3	0.78(2211201) + 0.56(222021)	1100	- 75.318 82	419	- 75.318 06	0.76
$^2\Delta_u$	2	0.59(221211) + 0.57(2221101)	1056	- 75.317 94	404	- 75.317 34	0.60
$^2\Delta_u$	2	+ 0.35(2221101) + 0.32(221211)					
$^2\Delta_u$	2	0.60(221211) - 0.58(2221101)	1056	- 75.302 93	404	- 75.301 88	1.05
$^2\Sigma_u^-$	2	+ 0.36(2221101) - 0.33(221211)					
$^2\Sigma_u^-$	2	0.65(2221101) - 0.49(221211) + 0.47(221211)	1056	- 75.287 80	404	- 75.286 53	1.27
							(1.34 ± 0.86) ^c

^a The MO ordering is $2s\sigma$, $2s\sigma^*$, $p\pi$, $p\pi$, $p\sigma$, $p\pi^*$, $p\pi^*$, $p\sigma^*$, $p\sigma^*$.

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

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

for which the weight of the HF configuration is only 0.72. Within the singlet manifold, there are three lower excited states. The lowest one is $p\pi \rightarrow p\sigma$ singly excited $^1\Pi_u$ state and the second and third ones are $p\pi \rightarrow p\sigma$ doubly excited $^1\Sigma_g^+$

and $^1\Delta_g$ states. Table VI shows many other singly and doubly excited states. The EGCI method well reproduces the full-CI results, though the sizes of the calculations are considerably smaller than those of the full CI. The average dis-

TABLE VI. Excitation energies, ionization potentials and electron affinities in eV calculated by the full-CI and EGCI methods for C_2 at $R = 1.24253 \text{ \AA}$ (equilibrium distance).

State	Excitation		Full-CI		EGCI		Δ^b
	level	Main configuration ^a	Size	Energy	Size	Energy	
Singlet							
$^1\Sigma_g^+$	0	Hartree-Fock	748	0.0	287	0.0	0.0
$^1\Pi_u$	1	$p\pi \rightarrow p\sigma$	654	1.995	239	2.006	0.011
$^1\Sigma_g^+$	2	$p\pi, p\pi \rightarrow p\sigma, p\sigma$	748	2.765	287	2.758	-0.007
$^1\Delta_g$	2	$p\pi, p\pi \rightarrow p\sigma, p\sigma$	748	2.795	241	2.769	-0.027
$^1\Pi_g$	2	$2s\sigma^*, p\pi \rightarrow p\sigma, p\sigma$	654	5.365	254	5.376	0.011
$^1\Sigma_u^+$	1	$2s\sigma^* \rightarrow p\sigma$	688	6.084	252	6.116	0.032
$^1\Sigma_g^+$	2	$2s\sigma^*, 2s\sigma^* \rightarrow p\sigma, p\sigma$	748	7.418	287	7.440	0.022
$^1\Sigma_u^-$	1	$p\pi \rightarrow p\pi^*$	620	8.335	231	8.334	-0.001
$^1\Delta_u$	1	$p\pi \rightarrow p\pi^*$	620	8.677	231	8.689	0.012
							(0.015) ^c
Triplet							
$^3\Pi_u$	1	$p\pi \rightarrow p\sigma$	950	0.520	324	0.536	0.015
$^3\Sigma_u^+$	1	$2s\sigma^* \rightarrow p\sigma$	960	1.258	328	1.265	0.007
$^3\Sigma_g^-$	2	$p\pi, p\pi \rightarrow p\sigma, p\sigma$	940	1.829	340	1.842	0.013
$^3\Pi_g$	2	$2s\sigma^*, p\pi \rightarrow p\sigma, p\sigma$	960	2.796	346	2.788	-0.008
$^3\Sigma_u^+$	1	$p\pi \rightarrow p\pi^*$	960	6.659	328	6.686	0.026
$^3\Delta_u$	1	$p\pi \rightarrow p\pi^*$	940	7.362	296	7.372	0.009
$^3\Pi_g$	2	$p\pi, p\pi \rightarrow p\sigma, p\pi^*$	960	8.005	346	7.983	-0.022
$^3\Sigma_u^-$	1	$p\pi \rightarrow p\pi^*$	940	8.043	296	8.067	0.024
$^3\Pi_g$	2	$p\pi, p\pi \rightarrow p\sigma, p\pi^*$	960	9.026	346	8.999	-0.027
$^3\Sigma_g^+$	2	$2s\sigma^*, p\pi \rightarrow p\sigma, p\pi^*$	920	9.041	345	9.039	-0.002
							(0.015) ^c
Cation							
$^2\Pi_u$	1	$p\pi \rightarrow \infty$	756	12.581	288	12.577	-0.004
$^2\Delta_g$	2	$p\pi, p\pi \rightarrow p\sigma, \infty$	784	14.499	320	14.511	0.012
$^2\Sigma_g^+$	2	$p\pi, p\pi \rightarrow p\sigma, \infty$	784	14.588	326	14.603	0.015
$^2\Sigma_g^-$	2	$p\pi, p\pi \rightarrow p\sigma, \infty$	728	15.120	326	15.109	-0.011
$^2\Pi_g$	2	$2s\sigma^*, p\pi \rightarrow p\sigma, \infty$	756	15.214	324	15.203	-0.012
$^2\Sigma_u^+$	1	$2s\sigma^* \rightarrow \infty$	784	15.399	328	15.435	0.037
$^2\Pi_u$	3	$p\pi, p\pi, p\pi \rightarrow p\sigma, p\sigma, \infty$	756	15.627	288	15.601	-0.026
$^2\Delta_u$	3	$2s\sigma^*, p\pi, p\pi \rightarrow p\sigma, p\sigma, \infty$	728	17.050	299	17.024	-0.026
$^2\Sigma_u^+$	3	$2s\sigma^*, p\pi, p\pi \rightarrow p\sigma, p\sigma, \infty$	784	18.069	328	18.057	-0.012
$^2\Sigma_g^+$	2	$2s\sigma^*, 2s\sigma^* \rightarrow p\sigma, \infty$	784	18.624	326	18.657	0.032
$^2\Sigma_u^-$	3	$2s\sigma^*, p\pi, p\pi \rightarrow p\sigma, p\sigma, \infty$	728	18.762	299	18.741	-0.021
							(0.019) ^c
Anion							
$^2\Sigma_g^+$	1	$\infty \rightarrow p\sigma$	1164	1.448	435	1.414	-0.034
$^2\Pi_u$	2	$p\pi, \infty \rightarrow p\sigma, p\sigma$	1100	0.467	406	0.489	-0.022
$^2\Sigma_u^+$	2	$2s\sigma^*, \infty \rightarrow p\sigma, p\sigma$	1144	-1.138	427	-1.128	0.011
$^2\Pi_g$	1	$\infty \rightarrow p\pi^*$	1100	-4.628	419	-4.670	-0.042
$^2\Sigma_u^+$	2	$p\pi, \infty \rightarrow p\sigma, p\pi^*$	1144	-5.512	427	-5.507	0.005
$^2\Sigma_u^-$	2	$p\pi, \infty \rightarrow p\sigma, p\pi^*$	1056	-5.599	404	-5.570	0.029
$^2\Pi_g$	3	$p\pi, p\pi, \infty \rightarrow p\sigma, p\sigma, p\pi^*$	1100	-5.646	419	-5.624	0.022
$^2\Delta_u$	2	$p\pi, \infty \rightarrow p\sigma, p\pi^*$	1056	-5.670	404	-5.643	0.026
$^2\Delta_u$	2	$p\pi, \infty \rightarrow p\sigma, p\pi^*$	1056	-6.078	404	-6.064	0.014
$^2\Sigma_u^-$	2	$p\pi, \infty \rightarrow p\sigma, p\pi^*$	1056	-6.490	404	-6.482	0.008
							(0.021) ^c

^aThe Hartree-Fock MO ordering is $2s\sigma, 2s\sigma^*, p\pi, p\pi, p\sigma, p\pi^*, p\pi^*, p\sigma^*, p\sigma'$.

^bDifference from the full CI result.

^cAverage discrepancy.

crepancy is 1.79 mhartree. The discrepancy in the excitation energy shown in Table VI is 0.015 eV. Considering the complexities of the excitations, this accuracy of the EGCI method is satisfactory.

We next examine the results for the triplet state. The

lowest triplet state is $p\pi \rightarrow p\sigma$ singly excited $^3\Pi_u$ state, which is only 0.5 eV higher than the ground state. The experimental adiabatic excitation energy is only 0.09 eV.¹⁸ (The C-C distance of the $^3\Pi_u$ state is elongated by 0.05 Å.) The second and third states are $2s\sigma^* \rightarrow p\sigma$ singly excited state and

TABLE VII. Full CI and EGCI results in hartree for C_2 at $R = 2.0 \text{ \AA}$.

State	Excitation level	Main configuration ^a ($C > 0.3$)	Full CI		EGCI		$\Delta^b \times 10^3$
			Size	Energy	Size	Energy	
Singlet							
$^1\Delta_g$	2	0.63(22022 - 22202)	748	-75.405 96	246	-75.403 60	2.36
$^1\Sigma_g^+$	2	0.51(22202 + 22022) - 0.45(2222)	748	-75.405 48	296	-75.403 50	1.98
$^1\Sigma_g^+$	0	0.61(2222) + 0.34(22202 + 22022)	748	-75.393 01	296	-75.391 11	1.90
$^1\Pi_u$	1	0.87(22121) - 0.30(221012)	654	-75.392 52	251	-75.390 08	2.44
$^1\Sigma_u^-$	3	0.67(2201201 + 221021)	620	-75.369 11	234	-75.365 79	3.32
$^1\Pi_g$	2	0.59(222011) - 0.52(2211101) - 0.46(2211101)	654	-75.340 56	250	-75.338 23	2.33
$^1\Pi_g$	2	0.67(2211101) + 0.48(222011 - 220211)	654	-75.299 40	250	-75.297 60	1.80
$^1\Pi_g$	2	0.80(220211) + 0.35(222011) + 0.32(2211101)	654	-75.281 20	250	-75.278 84	2.36
$^1\Sigma_u^-$	1	0.65(2221001 + 221201)	620	-75.269 06	234	-75.265 97	3.09
$^1\Sigma_g^+$	2	0.67(2211011) - 0.41(2222) - 0.37(2211011)	748	-75.260 80	296	-75.258 95	1.85
							(2.34 ± 0.49) ^c
Triplet							
$^3\Pi_u$	1	0.86(22121)	950	-75.425 77	427	-75.424 64	1.13
$^3\Sigma_g^-$	2	0.91(22112)	940	-75.419 31	370	-75.417 14	2.17
$^3\Sigma_u^+$	1	0.56(222101 + 2212001)	960	-75.373 85	415	-75.370 87	2.98
$^3\Pi_g$	2	0.64(2211101) - 0.58(222011)	950	-75.373 26	416	-75.371 88	1.38
$^3\Sigma_u^-$	3	0.67(221021 + 2201201)	940	-75.365 20	382	-75.362 71	2.49
$^3\Sigma_u^+$	3	0.67(220121 + 2210201)	960	-75.365 20	415	-75.362 89	2.31
$^3\Sigma_u^+$	3	0.64(220121 - 2210201)	960	-75.361 35	415	-75.357 80	3.55
$^3\Pi_g$	2	0.91(2211101)	950	-75.345 75	416	-75.344 22	1.53
$^3\Pi_g$	2	0.58(2211101) + 0.48(220211 - 222011) - 0.34(2211101)	950	-75.330 72	416	-75.329 47	1.25
$^3\Sigma_u^-$	1	0.62(2221001 + 221201)	940	-75.315 49	382	-75.310 55	4.94
							(2.09 ± 0.79) ^c
Cation							
$^2\Delta_g$	2	0.61(22021 - 22201)	784	-75.034 06	336	-75.032 70	1.36
$^2\Pi_u$	3	0.92(22102)	756	-75.033 45	354	-75.029 86	3.59
$^2\Sigma_g^+$	2	0.60(22201 + 22021)	784	-75.029 16	356	-75.027 51	1.65
$^2\Sigma_g^-$	2	0.77(22111) - 0.45(22111) + 0.31(2200111)	728	-75.013 18	336	-75.011 10	2.08
$^2\Sigma_u^-$	3	0.58(221011 + 2201101) + 0.33(221011 + 2201101)	728	-75.000 52	314	-74.997 17	3.35
$^2\Pi_u$	1	0.84(2212) - 0.32(221002)	756	-74.990 16	354	-74.985 60	4.56
$^2\Delta_u$	3	0.57(221011 - 2201101) + 0.34(2201101 - 221011)	728	-74.965 84	314	-74.961 78	4.06
$^2\Sigma_u^+$	3	0.57(220111 - 2210101) - 0.34(220111 - 2210101)	784	-74.963 65	343	-74.959 50	4.15
$^2\Pi_g$	4	0.80(220021)	756	-74.948 87	328	-74.945 68	3.19
$^2\Pi_g$	2	0.59(2211001) - 0.50(222001) - 0.37(220021)	756	-74.939 74	328	-74.936 97	2.77
							(3.08 ± 1.04) ^c
Anion							
$^2\Sigma_g^+$	1	0.78(22221)	1164	-75.479 19	445	-75.476 21	2.98
$^2\Pi_u$	2	0.87(22122)	1100	-75.465 59	429	-75.461 63	3.96
$^2\Sigma_u^+$	2	0.59(222111 + 2212101)	1144	-75.428 42	457	-75.425 25	3.17
$^2\Pi_g$	3	0.68(221201) - 0.59(222021)	1100	-75.408 70	402	-75.404 26	4.44
$^2\Pi_g$	3	0.58(221201) + 0.47(220221 - 222021) - 0.33(221201)	1100	-75.370 49	402	-75.367 72	2.77
$^2\Sigma_u^-$	2	0.63(2221101) - 0.55(221211) + 0.31(221211)	1056	-75.369 66	437	-75.367 14	2.52
$^2\Sigma_u^+$	2	0.63(2212101 - 222111)	1144	-75.369 66	457	-75.367 13	2.53
$^2\Pi_g$	3	0.69(220221) - 0.45(222201)	1100	-75.358 22	402	-75.354 54	3.68
$^2\Sigma_u^-$	2	0.65(2221101) + 0.54(221211) + 0.37(221211)	1056	-75.353 21	437	-75.350 64	2.57
$^2\Sigma_u^-$	2	0.63(2221101) + 0.52(221211) - 0.36(221211)	1056	-75.348 80	437	-75.345 78	3.02
$^2\Pi_g$	1	0.74(222201) + 0.40(220221)	1100	-75.345 00	402	-75.340 12	4.88
							(3.22 ± 0.77) ^c

^aThe MO ordering is $1s, 2s\sigma, 2s\sigma^*, p\pi, p\pi, p\sigma, p\pi^*, p\pi^*, p\sigma^*, p\sigma'$.

^bDifference from the full CI result.

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

$p\pi \rightarrow p\sigma$ doubly excited state, respectively. The EGCI method reproduces the full-CI energies to within 1.70 mhartree on average. For triplet excitation energies, the average error is 0.015 eV.

The ionic states of C_2 at $R = R_{eq}$ are very interesting in that the shake-up states appear in very low-energy region. The lowest state corresponds to the Koopmans ionization from the $p\pi$ MO, though the mixing of the doubly excited

configuration is remarkable. We note that this mixing originates from that in the ground state; namely, as seen from Table V, the $1^2\Pi_u$ state is generated just by annihilating one of the $p\pi$ electrons of the ground state without affecting the coefficients of the configurations. The experimental ionization energy is 12.15 eV¹⁸ and the present EGCI value is 12.58 eV. Another Koopmans state shown in this table is the first $^2\Sigma_u^+$ state which is generated by losing $2s\sigma$ electron. The other states are all shake-up states with the excitation levels two and three. The lowest shake-up state is only 0.07 a.u. (1.9 eV) higher than the lowest Koopmans state. The agreement between the full-CI and EGCI results are excellent for all of the ionic states shown in Tables V and VI.

Because of the existence of the vacant $p\sigma$ MO, the lowest $^2\Sigma_g^+$ and the second lowest $^2\Pi_u$ states of the anion C_2^- are lower than the neutral ground state. The electron affinity shown in Table VI is positive for these two states. Experimentally, at least three lowest anion states seem to be lower than the neutral ground state, though this is for the adiabatic states.¹⁸ The lack of the anion basis in the present calculation would also have caused this discrepancy. The lowest anion state is produced by an electron attachment on the $p\sigma$ MO. The second and third states correspond to the $p\pi \rightarrow p\sigma$ and $2s\sigma^* \rightarrow p\sigma$ excitations, respectively, from the ground state of the anion. These states are produced by the two electron processes from the singlet ground state of C_2^- . The anion of C_2^- has many other singly and doubly excited states relative to the anion ground state in a relatively low-energy region. The present EGCI method reproduces the full-CI energies to within 1.34 mhartree on average. The accuracies are almost constant among the singlet, triplet, cation, and anion states.

Table VII shows the results for C_2 at $R = 2.0 \text{ \AA}$. In this elongated geometry, none of the lower singlet $^1\Sigma_g^+$ states are represented by the HF configuration. The HF configuration is almost equally distributed into the lower three $^1\Sigma_g^+$ states. The lowest singlet state is $^1\Delta_g$ in which the main configuration is produced by the two electron excitation from the $p\pi$ MO to the $p\sigma$ MO. This configuration is also the main configuration of the second lowest state $^1\Sigma_g^+$. The excitation levels of the singlet states shown in Table VII distribute from zero to three, but the errors of the EGCI results relative to the full-CI ones are 2.34 mhartree on average, a bit larger than that obtained for the equilibrium distance. The smallness of the standard deviation is also remarkable.

Table VII also gives the results for the triplet, ionized, and anion states of C_2 at the elongated distance, $R = 2.0 \text{ \AA}$. The excitation levels of the main configurations distribute from one to three and even to four for the cation $^2\Pi_g$ state, though the physical meaning of the main configuration is somewhat vague here because the HF configuration and the $p\pi \rightarrow p\sigma$ doubly excited configuration are quasi-degenerate as shown above. The average errors of the EGCI results relative to the full-CI ones are $2 \sim 3$ mhartree, a bit larger than those at the equilibrium distance.

VI. CONCLUDING REMARKS

In this paper, we have proposed the excitator method for describing excited, ionized, and anion states on the basis

of the correlated wave function for the ground state. We have given a formulation of this method using the EGCI wave function for the ground state. The resultant method is called again as EGCI method in a wider sense. We have given the algorithms of calculations used in the newly coded program.²³ Test calculations are performed for several lower states of the singlet, triplet, ionized, and electron attached states of CO and C_2 at equilibrium and elongated distances. The results are compared with the full CI results and their accuracies are examined. We have observed the following points. (1) The EGCI method is applicable to the ground state, singlet and triplet excited states, and doublet ionized and anion states of different excitation levels with errors small relative to the full-CI energies. This property is important for studying electronic processes involving different electronic states. (2) The accuracies in these states are relatively constant for the changes in the internuclear distance. Though more extensive applications are certainly necessary for final conclusions, we expect that the EGCI method would be useful for investigating dynamics and reactions involving molecular ground, excited, ionized, and/or anion states.

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