Structure of the exact wave function. IV. Excited states from exponential ansatz and comparative calculations by the iterative configuration interaction and extended coupled cluster theories

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In a previous paper of this series [Paper III: Nakatsuji, J. Chem. Phys. 105, 2465 (2001)], the author showed a high potentiality of the extended coupled cluster (ECC) method to calculate the exact wave function of the ground state. In this paper, we propose ECC-configuration interaction (CI) method, which is an accurate useful method to calculate the excited states from the ECC wave function of the ground state. In contrast to the ECC method, the standard ECC-CI method is approximate, but we can make it exact by generalizing its excitation operator (ECC-CI general). The ECC-CI method is applicable not only to the excited states having the same spin-space symmetry as the ground state, but also to those having different spin-space symmetries and to the ionized and electron-attached states. The theoretical framework of the ECC-CI method is similar to that of the symmetry-adapted-cluster (SAC)-CI method proposed in 1978 by the present author. Next in this paper, we examine the performance of the methods proposed in this series of papers for a simple one-dimensional harmonic oscillator. The iterative configuration interaction (ICI) and ECC methods are examined for the ground state and the ICI-CI and ECC-CI methods for the excited states. The ICI method converges well to the exact ground state and the excited states are calculated nicely by the ICI-CI method in both the standard and general active spaces. In contrast to the simplest (S)ECC examined in Paper III, the ECC2 method shows quite a rapid convergence to the exact ground state, which enables us to calculate the true exact wave function in the ECC form. The ECC-CI methods in both the standard and general active spaces also work well to calculate the excited states. Thus, we conclude that the ICI and ECC approaches have a potentiality to provide useful method to calculate accurate wave functions of the ground and excited states. A merit of ECC is that it provides the exact wave function in a simple explicit form. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Toward precise predictions and gigantic-scale systems are the two ways modern quantum chemistry must expand in this decade. The first aim is essentially realized if we can solve the Schrödinger equation with a realistic cost. The full-CI method, only one general method of solving the Schrödinger equation within a given basis set, is however very time consuming and highly demanding computationally and therefore cannot be applied to chemically interesting systems. Since the Hamiltonian operator has a very simple structure, involving only one and two particle operators, its eigenfunctions must also have some simple structure, reflecting the simplicity of the Hamiltonian. Though modern algorithms of the full-CI method[1,2] utilize this fact in the evaluation of the matrix elements, it does not presume such a simplicity in the structure of the wave function.

The Schrödinger equation is given by

$$(H-E)\psi=0, \tag{1.1}$$

where the Hamiltonian involves only one- and two-particle operators as

$$H=\sum_i^N v(i)+\sum_{i>j}^N w(i,j), \tag{1.2}$$

in a coordinate representation, or

$$H=\sum_{pr} v_p^r a_r^+ a_p+\sum_{pqrs} w_{pq}^{rs} a_r^+ a_s^+ a_q a_p, \tag{1.3}$$

in a second-quantized form. In Eq. (1.3) the indices p,q,r,s run over all m reference orbitals (both occupied and unoccupied). The number of terms in Eq. (1.3) is

$$M_{\text{GSD}}=m^2+\left[\frac{m}{2}(m-1)\right]^2, \tag{1.4}$$

where we did not assume the Hermiticity of the operators v and w, and GSD stands for general singles and doubles.

We have studied in this series of studies[3–5] the structure of the exact wave function using the equations that are equivalent to the Schrödinger equation in a necessary and

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sufficient sense. This equivalence is important, since these equations have the same determinative power as the Schrödinger equation. The variational principle,

$$\langle \psi | H - E | \delta \psi \rangle = 0, \tag{1.5}$$

is well-known to be equivalent to the Schrödinger equation. The energy of the system, E, is defined by

$$\langle \psi | H - E | \psi \rangle = 0. \tag{1.6}$$

The variational principle is used to search for the best possible wave function within the functional form of the given ψ. If ψ can become exact in its functional form, this principle gives the exact wave function as an extreme.

Another useful set of equations that is equivalent to the Schrödinger equation is H-square or H-nijou ("nijou" is Japanese meaning square) equations. The equation,

$$\langle \psi | (H - E)^2 | \psi \rangle = 0, \tag{1.7}$$

and each of the following equations

$$\langle \psi | (H - E) H | \psi \rangle = 0, \tag{1.8}$$

and

$$\langle \psi | H^2 - E^2 | \psi \rangle = 0, \tag{1.9}$$

together with Eq. (1.6) are equivalent to the Schrödinger equation. Further, based on these equations, we have shown in Paper II a useful set of equations that is equivalent to the Schrödinger equation. We define a division of the Hamiltonian operator into N_D parts by

$$H = \sum_{I=1}^{N_D} H_I. \tag{1.10}$$

Then, the wave function ψ that satisfies

$$\langle \psi | (H - E) H_I | \psi \rangle = 0, \quad (I = 1, \ldots, N_D), \tag{1.11}$$

and Eq. (1.6) is exact in the necessary and sufficient sense. Similarly, the wave function ψ that satisfies

$$\langle \psi | (H - E)(H_I - E_I) | \psi \rangle = 0, \quad (I = 1, \ldots, N_D), \tag{1.12}$$

is also exact in the necessary and sufficient sense. In Eq. (1.12), the partial energy E_I corresponding to H_I is defined by

$$\langle \psi | H_I - E_I | \psi \rangle = 0, \tag{1.13}$$

and satisfies

$$E = \sum_{I=1}^{N_D} E_I. \tag{1.14}$$

We refer to Eqs. (1.11) and (1.12) also as H-square or H-nijou equations. Equation (1.8) is a special case of Eq. (1.11) for $N_D = 1$. Likewise, Eq. (1.7) is a special case of Eq. (1.12). It is easily seen from Eq. (1.7) that the H-nijou equation is valid *only* to the exact wave function: when we define

$$f(\psi) = \langle \psi | (H - E)^2 | \psi \rangle, \tag{1.15}$$

this quantity is always positive or zero, and $f(\psi) = 0$ is realized only when ψ is exact.

An underlying principle in this series of papers[3–5] is that we can find the structure of the exact wave function by the following criterion. When we apply the variational principle to some candidate function ψ, and if the variational equation actually gives one set of the H-nijou equations, then that ψ has the structure of the exact wave function. This is realized, for example, when

$$\delta_I \psi = H_I \psi, \tag{1.16}$$

or

$$\delta_I \psi = (H_I - E_I) \psi, \tag{1.17}$$

where δ_I represents a variation with respect to the variable associated to H_I included in ψ, since then we have Eq. (1.11) or (1.12) as a result of the variational equation (1.5). In other words, when this holds, the variational best is the exact wave function: that ψ has a freedom to be able to become the exact wave function. Note however that the condition given by Eq. (1.16) or (1.17) is a bit too strong: it is enough if we could obtain Eq. (1.11) or (1.12) from Eq. (1.5), as we argued in Paper III. In other words, Eq. (1.16) or (1.17) is a sufficient condition for ψ to have an exact structure, but not necessary. Theorem II-2 of Paper I[3] is a special case of the above theorem.

This fact further implies that the exact wave function can be described with only N_D variables, N_D being defined by Eq. (1.10). The equivalence of a set of the N_D equations (1.11) or (1.12) to the Schrödinger equation means that we can describe the exact wave function with only N_D variables, because these equations have the same determinative power as the Schrödinger equation. This actually implies that the exact wave function can be described with the number of variables from unity to, say, M_{GSD}. The latter corresponds to the division of the Hamiltonian defined by Eq. (1.3). These numbers are much smaller than the number of variables in full-CI, so that this line of research may lead us to a new simpler method of solving the Schrödinger equation.

In Paper I of this series,[3] we have investigated the possibility of the general singles and doubles (GSD) description of the exact wave function based on Theorem II-1 of Paper I, which is also a kind of H-nijou equation, and proposed iterative CI (ICI) method including GSD number of variables. In Paper II,[4] we have presented the H-nijou equations, Eqs. (1.11) and (1.12), and shown that the number of variables necessary to solve the Schrödinger equation is defined by the number of division of the Hamiltonian operator, and therefore ranges from unity to the GSD number. Based on this finding, we have extended the concept of the ICI method and proposed the ICIND method, which is the ICI including N_D variables. We have also considered the methods of calculating the excited states from the ICI theory. The simplest (S)ICI method that includes only one variable is similar to the surplus function approach proposed recently by Huang et al.[6] It is also related to the Lanczos method[7] in eigenvalue problems.[8] In Paper III,[5] we have examined the exponential ansatz and shown that it can also be exact if the operator is defined using the divided Hamiltonian. We have proposed extended coupled cluster (ECC) method, and two interesting cases were considered: one is the S(simplest)ECC that includes only one variable and the other is the general ECCND ($N_D \geq 2$). SECC is exact in spite of its simple structure, but is

rather inflexible. ECCND is also able to describe the exact wave function rather efficiently through its flexible nonlinear structure. Test calculations were given for harmonic oscillator, showing different behaviors of the SECC and ECCND methods: when truncated, the SECC was rather slowly converging, but the ECCND converged quite nicely.[5]

One purpose of this paper is to formulate a method to calculate the excited states from the ECCND method. We refer to the proposed method as the ECC-CI method, since the theoretical framework of the theory is similar to that of the SAC(symmetry adapted cluster)-CI theory.[9,10] Though the ECC method is exact, the ECC-CI method is not, but it can be improved up to the exact limit by expanding the operator space. Another purpose of this paper is to examine the ICI and ECC methods in the calculations of the ground and excited states of harmonic oscillator. We examine the convergence behaviors of both methods and the qualities of the calculated ground and excited states. The harmonic oscillator is probably the simplest possible system, but the analytical application of the ICI and ECC methods may clarify their behaviors, some of which would be common to those for more general many-electron systems, which is a goal of the present theory.

II. ECC

We summarize here briefly the extended coupled cluster (ECC) theory.[5] We first define the division of the Hamiltonian into N_D parts

$$H = \sum_{I=1}^{N_D} H_I, \tag{2.1}$$

and correspondingly, we define the variable operator,

$$S = \sum_{I=1}^{N_D} C_I H_I, \tag{2.2}$$

which includes N_D variables $\{C_I\}$. Using this variable operator, we define the coupled cluster expansion by

$$\psi = \exp(S)\,\psi_0 \tag{2.3a}$$

$$= \left[1 + S + \frac{1}{2}S^2 + \frac{1}{3!}S^3 + \cdots \right] \psi_0, \tag{2.3b}$$

where ψ_0 is some reference function, which may be Hartree–Fock $|0\rangle$, or some other function. Since this is a small extension of the coupled cluster theory,[11–13] we called it extended coupled cluster (ECC) theory:[14] since this ECC involves N_D variables, we refer to the ECC given by Eq. (2.3) as ECCND method.

When we divide the Hamiltonian into all singles and doubles parts as given by Eq. (1.3), we have ECCGSD,

$$\psi_{\text{ECCGSD}} = \exp(T)\,\psi_0, \tag{2.4}$$

$$T = \sum_{pr} C_p^r a_r^+ a_p + \sum_{pqrs} C_{pq}^{rs} a_r^+ a_s^+ a_q a_p. \tag{2.5}$$

On the other hand, the conventional coupled cluster within singles and doubles (CCSD) is written as

$$\psi_{\text{CCSD}} = \exp(T_c)\,\psi_0, \tag{2.6}$$

$$T_c = \sum_{ia} C_i^a a_a^+ a_i + \sum_{ijab} C_{ij}^{ab} a_a^+ a_b^+ a_j a_i, \tag{2.7}$$

where the indices i, j run over occupied orbitals and a, b over unoccupied orbitals. Since the operator T_c does not correspond to a division of the Hamiltonian operator, the conventional CCSD does not have a freedom of the exact wave function, while since the ECCGSD operator T corresponds to a division of the Hamiltonian as defined by Eq. (1.3), the ECCGSD is capable of representing the exact wave function, as discussed in Paper III.[5] Nooijen[15] also proposed independently that the generalized CCSD that is equivalent to the above ECCGSD might be exact. Van Voorhis and Head-Gordon[16] recently confirmed numerically that the ECCGSD certainly gives the exact wave function for neon and N_2.

It was also shown in Paper III that the SECC including only one variable,

$$\psi = \exp(CH)\,\psi_0, \tag{2.8}$$

is exact in the necessary and sufficient sense: the variational determination of the variable C gives the H-nijou equation, Eq. (1.8). As shown by Kozloff and Tal-Ezer,[17] this SECC becomes exact with a large negative value (negative infinite) of C. Therefore, a truncation of the expansion of the exponential operator at some order is not a good approximation: it is desirable to treat it in the exponential form, not in its approximate finite-order truncated form. This implies that the convergence of the SECC may not be fast, though actually its rate is dependent on the quality of the reference function ψ_0. A simple example was given in Paper III. The SECC is also related to the t expansion of Horn and Weinstein[18] and connected-moments expansion of Cioslowski.[19]

Since even the simplest ECC (SECC) is exact, the ECCND should also be exact: it includes SECC as a special case. Therefore, we impose variational and H-nijou equations to the ECCND and obtain,

$$G^I(\{C_I\}) = \langle \psi | (H-E) \left[H_I + \frac{1}{2}(H_I S + S H_I) + \frac{1}{3!}(H_I S^2 \right.$$

$$\left. + S H_I S + S^2 H_I) + \cdots \right] | \psi_0 \rangle = 0, \tag{2.9}$$

and

$$F^I(\{C_I\}) = \langle \psi | (H-E) H_I | \psi \rangle$$

$$= \langle \psi | (H-E) \left[H_I + H_I S \right.$$

$$\left. + \frac{1}{2} H_I S^2 + \cdots \right] | \psi_0 \rangle = 0, \tag{2.10}$$

respectively, for all $I (1 \leq I \leq N_D)$ The exact wave function should satisfy both of them. Subtracting Eq. (2.9) from Eq. (2.10), we obtain

$$\Delta^I(\{C_I\}) = \langle\psi|(H-E)\left[\frac{1}{2}(H_I S - SH_I) + \frac{1}{3!}(2H_I S^2 - SH_I S\right.$$

$$\left. - S^2 H_I) + \cdots\right]|\psi_0\rangle$$

$$= \langle\psi|(H-E)\left\{\frac{1}{2}[H_I,S] + \frac{1}{3!}(2[H_I,S]S\right.$$

$$\left. + S[H_I,S]) + \cdots\right\}|\psi_0\rangle = 0 \tag{2.11}$$

for all I. If all H_I and S commute, $[H_I,S]=0$, Eq. (2.11) holds and Eq. (2.9) reduces to Eq. (2.10), but in general, such commutation relation can not be assumed. If two of the three equations, Eqs. (2.9)–(2.11), hold, this ψ satisfies both variational and H-nijou equations, and therefore, it is exact. Since Eqs. (2.9)–(2.11) are all non-linear for the variables $\{C_I\}$, they can be satisfied not only in the SECC case, where all C_I are equal (Case A), but also in a more general case where C_I takes different optimal values (Case B).[5] We have shown in Paper III that a quick convergence of the ECC expansion is realized in Case B. This is natural since the standard CCSD, an approximation of ECCGSD as explained above, is already a good approximation of the exact wave function for many molecular systems.[5]

The ECC method describes the ground state of each symmetry. Since the S operator is totally symmetric, the ECC exponential operator is also totally symmetric, and therefore, the symmetry of the calculated state is that of the reference function ψ_0. In the next section, we consider how to calculate the excited states from the ECC theory of the ground state.

III. ECC-CI

We now formulate the theory for the excited states from the ECC theory of the ground state. Though the ECC theory for the ground state is exact, the theory presented in this section for the excited state is not exact. We start from the H-nijou equation for the ground state,

$$\langle\psi_g|(H-E)H_K|\psi_g\rangle = 0 \quad (K=1,\ldots,N_D), \tag{3.1}$$

where the subscript g on ψ_g denotes the ground state. Now, we define the (excited) functions Φ_K by

$$\Phi_K = H_K \psi_g, \tag{3.2}$$

then this set of functions $\{\Phi_K\}$, $(K=1,\ldots,N_D)$ satisfies the Brillouin-orthogonality with the exact ground state ψ_g,

$$\langle\psi_g|(H-E)|\Phi_K\rangle = 0, \tag{3.3}$$

as easily seen from Eq. (3.1). This relation implies that the functions $\{\Phi_K\}$ are good basis for the excited states of ψ_g, so that we approximate our excited states by a linear combination of these excited functions as

$$\psi_e = \sum_{K=0}^{N_D} d_K \Phi_K = \left(\sum_{K=0}^{N_D} d_K H_K\right)\psi_g, \tag{3.4}$$

where we have included ψ_g $(=\Phi_0, H_0=1)$ to ensure the orthogonality of ψ_e to ψ_g. If we introduce the operator R by

$$R = \sum_{K=0}^{N_D} d_K H_K, \tag{3.5a}$$

then this operator is a generator of the excited state from the ground state as

$$\psi_e = R\psi_g. \tag{3.6}$$

Note a similarity of the R operator defined by Eq. (3.5a) to the S operator defined by Eq. (2.2). For convenience, we denote the set of operators $\{H_K\}$ included in Eq. (3.5a) as $\mathcal{R}_S$,

$$\mathcal{R}_S = \{1, H_K\} = \{R_S\}, \tag{3.7}$$

where the subscript S implies "standard," in contrast to "general" introduced in the next section. With the use of Eq. (3.7), the excitation operator R is written as

$$R = \sum_{S=0}^{N_D} d_S R_S. \tag{3.5b}$$

We refer to this method of calculating the excited states as the ECC-CI method, since Eq. (3.4) is CI-like. This naming is also due to the similarity of the present theory to the SAC (symmetry adapted cluster)-CI theory for excited states.[9,10] The SAC theory[20] is a kind of coupled cluster theory[11,13] for the ground state, like ECC is for the ground state, and the SAC-CI theory is for the excited state and was formulated similarly to Eqs. (3.4)–(3.6) using the SAC ground state ψ_g^{SAC} instead of the ECC ground state ψ_g. The CCLRT (coupled cluster linear response theory)[21–23] and the EOMCC (equation-of-motion coupled cluster) theory[24–26] developed later are equivalent to the SAC-CI theory.[27]

The formulation for the ECCGSD case is interesting, where the division of the Hamiltonian is defined by Eq. (1.3). In this case, we start from the H-nijou equations,

$$\langle\psi_g|(H-E)a_r^+ a_p|\psi_g\rangle = 0,$$

$$\langle\psi_g|(H-E)a_r^+ a_s^+ a_q a_p|\psi_g\rangle = 0, \tag{3.8}$$

which were given in Paper I as Theorem II-1. Note, in these equations, we have omitted the constant integral factors, v_p^r and w_{pq}^{rs} of Eq. (1.3). Now, we define the excited functions $\{\Phi_K\}$ of the ECCGSD-CI method by

$$\Phi_{p,r} = a_r^+ a_p \psi_g,$$

$$\Phi_{pq,rs} = a_r^+ a_s^+ a_q a_p \psi_g, \tag{3.9}$$

and approximate our excited state by a linear combination of these functions as,

$$\psi_e = R\psi_g = \left(d_0 + \sum_{p,r} d_{p,r} a_r^+ a_p + \sum_{pq,rs} d_{pq,rs} a_r^+ a_s^+ a_q a_p\right)\psi_g, \tag{3.10}$$

where the ground state is included to ensure the orthogonality of ψ_e to ψ_g. This is ECCGSD-CI, and this expression would be familiar since it is similar to the standard singles and doubles SAC-CI.

Now, we come back again to the ECCND-CI case. The expansion coefficients d_K are determined variationally by the secular equation,

$$\langle \Phi_K | H - E | \psi_e \rangle = 0 \quad (K = 0, 1, \ldots, N_D), \tag{3.11a}$$

which is equivalent to

$$\sum_{L=0}^{N_D} \langle \Phi_K | (H - E) | \Phi_L \rangle d_L = 0 \quad (K = 0, 1, \ldots, N_D). \tag{3.11b}$$

The solutions of this secular equation satisfy orthogonality and Hamiltonian-orthogonality to the ground-state ψ_g and to each other, namely,

$$\langle \psi_e | \psi_g \rangle = 0, \quad \langle \psi_e | H | \psi_g \rangle = 0, \tag{3.12}$$

and

$$\langle \psi_{e'} | \psi_e \rangle = \delta_{ee'}, \quad \langle \psi_{e'} | H | \psi_e \rangle = E_e \delta_{ee'}, \tag{3.13}$$

respectively.

Though the ECC wave function for the ground state is exact, the ECC-CI wave function defined in this section for the excited state is approximate, since the space spanned by $\{\Phi_K\}$ is not complete. The nature of the excited states described by this method is characterized and restricted by the nature of the $\{\Phi_K\}$ space. To explicitly express the quality of the calculated excited states, we may refer to the above ECC-CI method as ECCND-CIND method, where the first ND stands for the size of the ECC calculations and the second ND stands for the size of the $\{\Phi_K\}$ space considered in the ECC-CI calculations. This is in some sense similar to the SAC-CI SD-R method in which the dimensions of both SAC and SAC-CI are singles and doubles (R stands for the SAC-CI excitation operator).

We note that when ψ_g strictly satisfies the ECC equation, Eq. (3.1), then it is exact and not modified by the ECC-CI method, but when ψ_g is an approximate solution of the ECC equation, it may be improved at the ECC-CI step: the ground state solution obtained from the ECC-CI secular equation, Eq. (3.11), may become lower than that of the input approximate ψ_g. The improved ψ_g satisfies the relation similar to Eq. (3.12).

Like in the SAC-CI method, we can also consider the nonvariational method of solution. Though the quality of the solution would become worse, the computational labor is diminished. In the nonvariational method, the bra-functions of Eq. (3.11a) are replaced by the set $\{\psi_0, H_K \psi_0\}$, where ψ_0 is the reference function and we obtain

$$\langle \psi_0 | H - E | \psi_e \rangle = 0, \tag{3.14a}$$

$$\langle \psi_0 | H_K^* (H - E) | \psi_e \rangle = 0 \quad (K = 1, \ldots, N_D). \tag{3.14b}$$

The nonvariational method is acceptable when the set of bras in Eq. (3.14), $\{\psi_0, H_K \psi_0\}$ is a good approximation of the set $\{\Phi_K\}$. We note that when ψ_0 is Hartree–Fock and when some H_K operators are composed only of purely $^X t$ type operators,[28] which include either a_i^+ or a_a, where the subscripts i and a denote occupied and unoccupied orbitals, respectively,[3] then Eq. (3.14b) would vanish identically and therefore, this nonvariational method would be inappropriate, because the number of the equations would be smaller than that of the variables.

The above ECC-CI method produces the excited states belonging to the same symmetry as the ground state. How-

ever, like in the SAC-CI method, we can extend the ECC-CI method so that it also gives the excited states of different spin-space symmetries, ionized states, and electron-attached states. Since the operators of the ECC-CIGSD are composed of a set of the products of the creation and annihilation operators a_r^+ and a_p where the suffices r and p denote spin-space orbitals, it is easy to introduce similar set of substitution operators that belong to different spin-space symmetry. Examples are seen from the SAC-CI operators given in Refs. 9 and 10. Denoting such set of operators again by $\mathcal{R}_S = \{R_S\}$, and using Eqs. (3.5b) and (3.6), we can calculate the excited states belonging to the different symmetry.

Similarly, we can calculate the ionized and electron-attached states. In the above case, the substitution operators were made of the products of the same number of creation and annihilation operators. But, if the number of the creation operators is smaller by n than the number of the annihilation operators, it is the n-electron ionization operator, and if the number of the creation operators is larger by n than the number of the annihilation operators, it is the n-electron-attachment operator. If we denote such set of operators again by $\mathcal{R}_S = \{R_S\}$, we can calculate n-electron ionized and n-electron-attached states by applying the operator R defined by Eq. (3.5b) to the ground state as in Eq. (3.6).

IV. ECC-CI general

Since the ECC-CI method in the standard active space described above may be insufficient to obtain sufficient accuracy, we need a theory that can reach up to the exact limit along the same line of the formalism. We give here as such theory ECC-CI general theory. In this theory, we can describe the excited, ionized, and electron-attached states in a sufficient accuracy even up to the exact limit by expanding the size of the R operator. This method is similar to the SAC-CI general-R method.[27,29–31]

We expand the ECC-CI space defined by $\mathcal{R}_S$ of Eq. (3.7) by including the operators that are linearly independent from them. Such linearly independent operators may be made of the products of the lower operators as

$$\mathcal{R}_A = \{H_I H_J, \ H_I H_J H_K, \ H_I H_J H_K H_L, \ \ldots\} = \{R_A\}, \tag{4.1}$$

where the subscript A implies "additional." Here, we note in general, $H_I H_J \neq H_J H_I$, etc. Using these higher operators, we expand the ECC-CI operator as

$$\mathcal{R}_{\mathcal{G}} = \mathcal{R}_S + \mathcal{R}_A, \tag{4.2}$$

and calculate the excited state by

$$\psi_e = R \psi_g, \tag{4.3}$$

where

$$R = \sum_{S=0}^{N_D} d_S R_S + \sum_A d_A R_A. \tag{4.4}$$

We refer to this expansion of ECC-CI as ECC-CI general, from the similarity to the SAC-CI general-R theory.[29] Note that for the SECC ($N_D = 1$), the space $\mathcal{R}_{\mathcal{G}}$ defined by Eq. (4.2) is just the same as the Krilov space.[32]

When our ECC is ECCGSD, the standard operator space $\mathcal{R}_S$ is defined by singles and doubles $\{1, a_r^+ a_p, a_r^+ a_s^+ a_q a_p\}$, and the additional operators for the ECC-CI general are composed of the product operators like triples, quadruples, and highers as,

$$\mathcal{R}_A = \{a_s^+ a_t^+ a_u^+ a_r a_q a_p, \; a_t^+ a_u^+ a_v^+ a_w^+ a_s a_r a_q a_p, \ldots\},$$
(4.5)

and therefore, it is easily understood that this ECC-CI general can formally become up to exact.

By this method, the quality of the calculated excited states is improved, and furthermore, we can calculate higher excitation processes that may be rather poorly described by the standard ECC-CI method. For example, three electron excitation processes from the ground state would not be described within the ECCGSD-CIGSD method, but would be described when we include higher operators defined by Eq. (4.5).

The formation of the higher operators by Eq. (4.1) is an example of the exponential generation (EG) idea presented in 1985.[33] When lower operators R_I and R_J are of some importance, the product $R_I R_J$ should also be important in the description of the states. If it is difficult to include all of these higher operators, because the size of the product operators easily becomes formidably large, we may include only such products $R_I R_J$ in which both R_I and R_J are important by some given threshold. By such a criterion, we can produce only the important higher excitation operators.

The modifications of the ECC-CI general method to include the excited states of different symmetries, ionized states and the electron-attached states are rather simple. We can improve the quality and expand the nature of these states by expanding the active space by the ECC-CI general method. Many examples have actually been reported by the SAC-CI general-R methods[27,30,31] for the calculations of the ionization spectra including shake-up satellite peaks.

V. PERFORMANCE OF ICI AND ECC METHODS FOR HARMONIC OSCILLATOR

We here examine the performance of the ICI and ECC methods by applying them to the ground and excited states of a one-dimensional harmonic oscillator. This is probably the simplest possible system. Some behavior would be specific to this simple system, but some would be common to more complex electronic systems. We want to see the quality of the results calculated by the ICI and ICI-CI methods and the ECC and ECC-CI methods for the ground and excited states. In Paper III, we have applied the S(simplest)ECC, which is ECC1, and ECC2 to this model system and obtained much insight on the performance of these methods. Though both are exact, the performance of the *truncated* ECC is much different: the SECC is rather slowly converging, but ECC2 shows quite a rapid convergence. This shows a different behavior of ECCND for $N_D = 1$ and $N_D \geqslant 2$, and is due to a nonlinear nature of the ECCND method.

The Schrödinger equation for the one-dimensional harmonic oscillator is

TABLE I. SICI for the ground states of harmonic oscillator.

n	ε	C
Gerade		
0	1.0167	
1	1.000 203	−0.1961
2	1.000 004 46	−0.1093
3	1.000 001 04	−0.091 58
4	1.000 000 318	−0.1142
5	1.000 000 109	−0.075 76
6	1.000 000 0459	−0.0895
7	1.000 000 0206	−0.0654
8	1.000 000 0103	−0.0739
9	1.000 000 005 41	−0.0571
Ungerade		
0	3.05	
1	3.001 00	−0.139 55
2	3.000 0340	−0.0894
3	3.000 008 41	−0.0790
4	3.000 002 69	−0.0887
5	3.000 000 975	−0.0666
6	3.000 000 419	−0.0731
7	3.000 000 193	−0.0581
8	3.000 000 0984	−0.0621
9	3.000 000 0526	−0.0514

$$\left(-\frac{d^2}{dx^2} + x^2\right)\psi = \varepsilon\psi,$$
(5.1)

and the Hamiltonian is the sum of the kinetic and potential operators as

$$H = -\frac{d^2}{dx^2} + x^2.$$
(5.2)

Two lowest solutions of this equation are

$$\psi_g = \pi^{-1/4}\exp\left(-\frac{1}{2}x^2\right),$$

$$\varepsilon_g = 1,$$
(5.3)

and

$$\psi_e = \sqrt{2}\,\pi^{-1/4}x\exp\left(-\frac{1}{2}x^2\right),$$

$$\varepsilon_e = 3,$$
(5.4)

which are the ground states of the gerade and ungerade symmetries, respectively. The eigenvalues of the gerade states are 1.0, 5.0, 9.0, 13.0, 17.0, 21.0,..., and the ungerade eigenvalues are 3.0, 7.0, 11.0, 15.0, 19.0, 23.0, ... We take

$$\psi_0 = \exp(-\alpha x^2),$$
(5.5)

and

$$\psi_0 = x\exp(-\alpha x^2),$$
(5.6)

with $\alpha = 0.60$ as our reference functions ψ_0 for the gerade and ungerade states, respectively. $\alpha = 0.5$ is the exact solution.

The S operator for SICI and SECC is

TABLE II. ICI2 and ICI2-CI2 for gerade ground and excited states of harmonic oscillator.

n	ε	C_0	C_K	C_P
Ground state				
0	1.0167	...	...	...
1[a]	1.000 203	1.0	−.196 086 246	...
2	1.000 002 10	1.0	−.108 505 5618	−.107 506 5766
3	1.000 000 0406	1.0	−.075 653 4009	−.075 632 6339
4	1.000 000 004 85	1.0	−.068 844 6171	−.068 844 1948
5	1.000 000 000 804	1.0	−.072 965 4691	−.072 965 4621
6	1.000 000 000 160	1.0	−.058 936 1691	−.058 936 1679
Excited state				
0	...	...	...	...
1[a]	5.0998	1.0	−.999 799 67	...
2	5.002 94	−.232 577	−.531 423 50	1.0
3	5.000 0663	−.197 249	−.605 446 65	1.0
4	5.000 001 97	−.212 814	−.574 3707	1.0
5	5.000 000 0705	−.363 227	−.273 564	1.0
6	5.000 000 0226	−.413 158	−.173 683	1.0

[a]For $n=1$, the rank of the matrix is 2 and therefore identical with SICI.

$$S = C\left(-\frac{d^2}{dx^2} + x^2\right), \tag{5.7}$$

which includes only one variable, and that for ICI2 and ECC2 is

$$S = -C_K\frac{d^2}{dx^2} + C_P x^2, \tag{5.8}$$

which includes two variables C_K and C_P that are associated to the kinetic and potential operators, respectively.

A. ICI method

The ICI method is defined by the recursion,

$$\psi_n = (1 + S_n)\psi_{n-1}, \tag{5.9}$$

and the variables in each iteration are solved by the variational principle. As an initial function ψ_0, we take the functions given by Eqs. (5.5) and (5.6) for the gerade and ungerade ground states, respectively. We also calculate the excited

states by Methods B and C of Paper II. In the terminology of this paper, method B is called ICIND-CIND method, and method C is called ICIND-CI general. The latter naming is useful because it makes the active space involved in each method clear.

Table I gives the result of SICI for the gerade and ungerade ground states. The SICI shows a good convergence for both states. The energy converges nicely to the exact energy, 1.0 and 3.0, both from above. The coefficients initially vibrate to some extent and would converge to zero finally. But, it would take some more iterations before convergence. The energy converges faster than the wave function itself. Tables II and III are the results of ICI2 for the gerade and ungerade ground states, respectively. The excited state calculated from the same secular equation (namely by ICI2-CI2) is also given in these tables. Note for $n=1$ (first iteration), the rank of the matrix is 2, and therefore the result becomes identical with that of SICI. For higher iterations, the ICI2 gives faster convergence than SICI because of an increase in the number of the variational parameters. It is in-

TABLE III. ICI2 and ICI2-CI2 for ungerade ground and excited states of harmonic oscillator.

n	ε	C_0	C_K	C_P
Ground state				
0	3.05	...	...	...
1[a]	3.001 00	1.0	−.139 55	...
2	3.000 0145	1.0	−.088 643 9874	−.087 285 2785
3	3.000 000 371	1.0	−.065 561 1301	−.065 519 9553
4	3.000 000 0463	1.0	−.060 767 7653	−.060 766 6567
5	3.000 000 008 02	1.0	−.062 131 7043	−.062 131 6816
6	3.000 000 001 67	1.0	−.055 270 6686	−.052 706 6821
Excited state				
2	7.006 69	−.826 3355	−.443 8106	1.0
3	7.000 196	−.672 6282	−.551 4566	1.0
4	7.000 007 51	−.740 2273	−.506 5120	1.0
5	7.000 000 294	1.0	.175 0141	−.841 6808
6	7.000 000 0938	1.0	.102 194 12	−.768 860 799

[a]For $n=1$, the rank of the matrix is 2 and therefore identical with SICI.

TABLE IV. ICI2-CI general for the gerade and ungerade states of harmonic oscillator.

	$n=2$	$n=4$	$n=6$
Variational			
E_0 (g)	1.000 000 000 001 59	1.000 000 000 000 172	1.000 000 000 000 157
E_1 (u)	3.000 000 000 0238	3.000 000 000 002 50	3.000 000 000 002 08
E_2 (g)	5.000 000 004 07	5.000 000 000 750	5.000 000 000 432
E_3 (u)	7.000 000 0208	7.000 000 003 55	7.000 000 001 79
E_4 (g)	9.000 000 756	9.000 000 0573	9.000 000 0107
E_5 (u)	11.000 002 37	11.000 000 180	11.000 000 0257
E_6 (g)	13.000 007 75	13.000 002 83	13.000 000 161
E_7 (u)	15.000 0205	15.000 005 38	15.000 000 314
E_8 (g)	17.000 693	17.000 0484	17.000 001 52
E_9 (u)	19.001 13	19.000 0817	19.000 002 38
E_{10} (g)	21.0246	21.000 428	21.000 0105
E_{11} (u)	23.0321	23.000 669	23.000 0139
Nonvariational			
E_0 (g)	0.999 999 999 9393	1.000 000 000 178	0.999 999 999 9751
E_1 (u)	2.999 999 999 435	2.999 999 999 791	2.999 999 999 775
E_2 (g)	5.000 662	4.999 992 01	5.000 000 0284
E_3 (u)	7.000 006 88	7.000 0487	7.000 000 0587
E_4 (g)	8.999 641	8.999 996 29	9.000 004 36
E_5 (u)	10.999 895	10.999 9281	11.000 005 64
E_6 (g)	13.000 853	13.000 220	12.999 669
E_7 (u)	14.997 20	15.001 97	14.999 777
E_8 (g)	17.0332	17.002 46	17.004 98
E_9 (u)	19.414	19.003 59	19.003 18
E_{10} (g)	21.124	21.005 10	20.9883
E_{11} (u)	23.224	22.9789	22.9861

teresting to note that the variational parameters C_K and C_P become closer as the iteration proceeds for both the gerade and ungerade ground states: they would converge to the same value and would converge to zero. This behavior shows that the ICI2 converges to the same solution as the SICI given in Table I. This is due to the linear nature of the ICI method. Even though the variables C_K and C_P become closer as the iteration proceeds, using two independent variables makes the convergence faster than just using one variable. Already at 5th iteration, the energy is correct by 9 zeros and 8 zeros after the decimal point for the gerade and ungerade ground states, respectively. Nevertheless, though the energy essentially converges, it would take some more iterations before true convergence of the wave function, where C_K and C_P become zero.

The excited states calculated by method B of Paper II, ICI2-CI2 in the present notation, also show a good convergence to the exact solution again from above, though the convergence is slower than that for the ground state. The results for the gerade excited states given in Table II and the ungerade excited state given in Table III are similar.

Table IV shows the result of method C, ICI2-CI general in the present notation. We have extended the variable space of the ICI-CI method, following Eqs. (4.1) and (4.2), by including not only the kinetic (k) and potential (p) operators, but also the higher products of the potential operators, pp, ppp, $pppp$, $ppppp$ in the active space, giving independent variable to each of the operators, following the spirit of the EGCI method.[33] Namely, the operator space used for defining the S operator in this calculation is written as

ICI2-CI2 (method B):   1, k, p,   (5.10)

ICI2 - CI general (method C):

1, k, p, pp, ppp, $pppp$, $ppppp$.   (5.11)

The dimension of the secular equation is 7 in the ICI2-CI general method in comparison with 3 of the original ICI2-CI2 method. As the (input) ICI2 solution for the ground state, we used the results of the 2nd, 4th, and 6th iterations given in Tables II and III. We have performed both variational and nonvariational calculations.

The results for the ground and excited states obtained by the variational ICI2-CI general method are certainly much improved, as expected, in comparison with those obtained by the ICI2-CI2 method. The numbers of zeros for the lower four states of Table IV are much larger than those of the corresponding states shown in Tables II and III. Note that the ground state is also much improved, since the results of the 2nd, 4th, and 6th iterations are not yet the true ICI solution. Further, by the ICI2-CI general method, we could calculate higher excited states not calculated by the ICI2-CI2 method. This merit of the ICI-CI general method is very important for investigations of higher excited and ionized states in atomic and molecular systems.

The nonvariational results are almost always worse than the variational results. Many results show overshooting of the exact energy. The accuracy of the nonvariational result depends rather critically on the accuracy of the ICI2 ground state. As the number of iterations n of the ICI2 calculation increases, the accuracy of the nonvariational calculations is improved. The higher excited states calculated by the nonvariational method are rather miserable particularly for $n=2$.

B. ECC2 method

We have already applied the SECC to the present harmonic oscillator in Paper III. The convergence of the truncated SECC was slow: even at $n=30$, we had only three and two zeros after the decimal point for the gerade and ungerade ground states, respectively, in contrast to the SICI result given in Table I. Though the truncated SECC certainly converges to the exact solution, the rate was much slower than the SICI given in this paper. The difference is that though the SICI has one fresh variable at each iteration step, the SECC has only one variable at any truncation level.

We apply here the ECC2 to the same harmonic oscillator. Some results were already given in Paper III. The S operator is given by Eq. (5.8) with two variables C_K and C_P. It is easily seen that the present ECC2 has at least three different solutions that give the exact wave function: one is the solution which is the same as the SECC with C_K and C_P both equal to C of SECC, the second is $C_K=0.0$ and $C_P=0.1$, a self-evident solution, and the third is the nontrivial solution that was already given in Paper III for the truncated ECC2 in 2nd and 3rd orders. This fact means that the solution of the ECC method is generally not unique, though all gives, of course, the same unique exact wave function. Since the first solution is already given in Paper III as the result of SECC, we discuss here the second self-evident solution and the third nontrivial solution of ECC2.

First, we consider the self-evident solution of ECC2: $C_K=0.0$ and $C_P=0.1$. In this case, the ECC2 becomes

$$\psi^{\text{ECC2}}=\exp(0.0k+0.1p)\exp(-0.6x^2)$$
$$=\exp(0.1x^2)\exp(-0.6x^2)$$
$$=\exp(-0.5x^2)$$
$$=\psi_{\text{exact}}, \tag{5.12}$$

for the gerade ground state, and

$$\psi^{\text{ECC2}}=\exp(0.0k+0.1p)x\exp(-0.6x^2)$$
$$=\exp(0.1x^2)x\exp(-0.6x^2)$$
$$=x\exp(-0.5x^2)$$
$$=\psi_{\text{exact}}, \tag{5.13}$$

for the ungerade ground state, so that they are exact. The values of C_K and C_P are common to both gerade and ungerade states. Since the values of C_K and C_P are different, this solution is different from the solution of SECC given in Paper III. Note that this self-evident exact solution is possible only for ECC2: other SICI, ICI2, and SECC do not have such a straightforward solution.

We apply ECC2-CI2 using this exact solution: the active space is given by Eq. (5.10). The result is given in Table V. The solutions for the excited states are also exact in both variational and nonvariational methods. We further applied ECC2-CI general using the exact solution for the ground state: the active space is given by Eq. (5.11). The result is summarized in Table V. Again, we get the exact solution for the lowest 12 states, not only by the variational method but also by the nonvariational method.

TABLE V. ECC2-CI2 and ECC2-CI general from the exact ground states of the gerade and ungerade states of harmonic oscillator.

	ECC2-CI2	ECC2-CI general
Variational		
E_0 (g)	1.0	1.0
E_1 (u)	3.0	3.0
E_2 (g)	5.0	5.0
E_3 (u)	7.0	7.0
E_4 (g)		9.0
E_5 (u)		11.0
E_6 (g)		13.0
E_7 (u)		15.0
E_8 (g)		17.0
E_9 (u)		19.0
E_{10} (g)		21.0
E_{11} (u)		23.0
Nonvariational		
E_0 (g)	1.0	1.0
E_1 (u)	3.0	3.0
E_2 (g)	5.0	5.0
E_3 (u)	7.0	7.0
E_4 (g)		9.0
E_5 (u)		11.0
E_6 (g)		13.0
E_7 (u)		15.0
E_8 (g)		17.0
E_9 (u)		19.0
E_{10} (g)		21.0
E_{11} (u)		23.0

Next, we discuss the nontrivial solution of ECC2, which is more important than the self-evident solution, since such self-evident solution would never occur in actual complex electronic systems. Tables VI and VII show the nontrivial solutions for the gerade and ungerade ground states, respectively, of the harmonic oscillator calculated by the ECC2 truncated at $n=2$, 3, 4, and 5, where n denotes the order of the truncation of the exponential operator, namely,

$$\psi_n=\left(1+S+\frac{1}{2}S^2+\frac{1}{3!}S^3+\cdots+\frac{1}{n!}S^n\right)\psi_0. \tag{5.14}$$

The results of these tables were calculated by the variational method given in Paper III. Note that the first-order ($n=1$) truncated ECC is identical to the first iteration of the ICI method and therefore omitted here. The values of the variables C_K and C_P were optimized only up to five decimal figures.

First, we are rather surprised by a marvelous converging behavior of the ECC2 method. Only with the two variables, the $n=5$ results are accurate by ten zeros and nine zeros for the gerade and ungerade ground states, respectively. In comparison with the truncated SECC result given in Paper III, the convergence of the truncated ECC2 is *much* faster. In comparison with the ICI2 result, the ECC2 energy is better by one order of magnitude than the ICI2 one, if we compare the order n result of ECC2 to the nth iteration result of ICI2. This is marvelous considering the fact that in the ECC2 method, the two variables are optimized only once, but in the ICI2 method, the two variables are reoptimized at each iteration step. Within the present accuracy of C_K and C_P, the smallness of G_n^I and $\partial E_n/\partial C_I$ implies that the solution is essentially at the variational minimum, and the smallness of

TABLE VI. Truncated ECC2 for the gerade ground state of harmonic oscillator.

		$n=2$	$n=3$	$n=4$	$n=5$
Optimal	C_K	−0.036 41	−0.036 62	−0.036 62	−0.036 62
	C_P	+0.056 50	+0.055 80	+0.055 79	+0.055 78
E_n		1.000 002 10	1.000 000 0313	1.000 000 000 438	1.000 000 000 0271
G_n^I	$I=K$	-1.1605×10^{-5}	1.2517×10^{-5}	-1.4802×10^{-5}	1.1979×10^{-5}
	$I=P$	1.3959×10^{-5}	1.0381×10^{-5}	1.2320×10^{-5}	0.9969×10^{-5}
Δ_n^I	$I=K$	-0.2290×10^{-5}	0.1253×10^{-5}	0.1500×10^{-5}	-0.1213×10^{-5}
	$I=P$	-0.1475×10^{-5}	0.2094×10^{-5}	-0.0277×10^{-5}	-0.1000×10^{-5}
$\partial E_n/\partial C_I$	$I=K$	1.4179×10^{-5}	1.5306×10^{-5}	-1.8099×10^{-5}	1.4648×10^{-5}
	$I=P$	0.4837×10^{-5}	1.2694×10^{-5}	1.5065×10^{-5}	-1.2190×10^{-5}
Virial coefficient		1.999 871	2.000 011	2.000 016	1.999 987

Δ_n^I implies that both of the variational and H-nijou equations are essentially satisfied. The virial relation is also well-satisfied.

Another important fact is that the optimal values of C_K and C_P are different, showing that the present ECC2 result is different from the SECC results given in Tables I–III of Paper III. The value of C_P is larger (in absolute magnitude) than that of C_K. This is in sharp contrast from the SICI and ICI2 results given in Tables II and III, where the values of C_K and C_P become close as the iteration proceeds and finally converge to the same solution as the SICI one. This behavior of ECC2 is due to the nonlinear nature of the ECC method. Furthermore, at $n=4$ and 5, the values of the variables of the gerade and ungerade ground states are the same, within the present accuracy of calculations. This means that the quality of the initial function ψ_0 is the same for both states.

Probably the most impressive and important result from Tables VI and VII is that the convergence of the variables C_K and C_P is quite rapid in the truncated ECC2 method. (It may be noted that the converged values of C_K and C_P of the present solution of ECC2 are not zero, in contrast to the ICI case.) The values of these variables converge up to five decimal figures already at the truncation of order 5. This fact

implies that we can easily calculate *the exact wave function* simply by using the converged coefficients in the ECC2 wave function as

$$\psi_{\text{exact}}\cong N\exp(-0.036\,62k+0.055\,78p)\psi_0, \tag{5.15}$$

which is valid for both the gerade and ungerade ground states. Here, k and p represent kinetic and potential operators, respectively, in the Hamiltonian given by Eq. (5.2). The energy calculated from the right-hand side of Eq. (5.15) is above the exact energy only by 0.208×10^{-10} and 0.623×10^{-10} for the gerade and ungerade states, respectively, being essentially in the same order of accuracy as the $n=5$ result given in Tables VI and VII, reflecting the accuracy of the variables C_K and C_P of the present optimization. This reflects also the Eckert theorem. The correctness of Eq. (5.15) for the wave function is more clearly checked by comparing numerically the both sides. ψ_{exact} is given by Eqs. (5.3) and (5.4) for the gerade and ungerade states, respectively, and ψ_0 is given by Eqs. (5.5) and (5.6), respectively, with $\alpha=0.60$. Therefore, we can directly compare both sides of Eq. (5.15) numerically by expanding them into

TABLE VII. Truncated ECC2 for the ungerade ground state of harmonic oscillator.

		$n=2$	$n=3$	$n=4$	$n=5$
Optimal	C_K	−0.036 39	−0.036 62	−0.036 62	−0.036 62
	C_P	+0.056 91	+0.055 81	+0.055 79	+0.055 78
E_n		3.000 0146	3.000 000 307	3.000 000 004 94	3.000 000 000 152
G_n^I	$I=K$	-2.2053×10^{-5}	1.9039×10^{-5}	-0.3047×10^{-5}	1.6060×10^{-5}
	$I=P$	-1.3409×10^{-5}	-1.6156×10^{-5}	0.2544×10^{-5}	-1.3365×10^{-5}
Δ_n^I	$I=K$	-1.2299×10^{-5}	-0.2076×10^{-5}	0.0310×10^{-5}	-0.1626×10^{-5}
	$I=P$	-0.7864×10^{-5}	0.5616×10^{-5}	-0.5860×10^{-5}	-0.1519×10^{-5}
$\partial E_n/\partial C_I$	$I=K$	6.3107×10^{-5}	5.4681×10^{-5}	-0.8750×10^{-5}	4.6127×10^{-5}
	$I=P$	-3.8371×10^{-5}	-4.6400×10^{-5}	0.7308×10^{-5}	3.8386×10^{-5}
Virial coefficient		1.999 683	2.000 048	2.000 002	1.999 986

TABLE VIII. Exact wave function estimated from the ECC2 wave function at $n=5$.[a]

i	ECC2 at $n=5$	Estimated	Exact
Gerade ground			
0	$0.751\,13\times10^{-0}$	$0.751\,13\times10^{-0}$	$0.751\,13\times10^{-0}$
1	$0.375\,56\times10^{-0}$	$0.375\,57\times10^{-0}$	$0.375\,56\times10^{-0}$
2	$0.938\,86\times10^{-1}$	$0.938\,92\times10^{-1}$	$0.938\,91\times10^{-1}$
3	$0.156\,44\times10^{-1}$	$0.156\,49\times10^{-1}$	$0.156\,48\times10^{-1}$
4	$0.195\,37\times10^{-2}$	$0.195\,61\times10^{-2}$	$0.195\,61\times10^{-2}$
5	$0.194\,82\times10^{-3}$	$0.195\,61\times10^{-3}$	$0.195\,61\times10^{-3}$
6	$0.161\,13\times10^{-4}$	$0.163\,01\times10^{-4}$	$0.163\,00\times10^{-4}$
7	$0.112\,97\times10^{-5}$	$0.116\,44\times10^{-5}$	$0.116\,43\times10^{-5}$
8	$0.676\,22\times10^{-7}$	$0.727\,74\times10^{-7}$	$0.727\,70\times10^{-7}$
9	$0.340\,81\times10^{-8}$	$0.404\,30\times10^{-8}$	$0.404\,28\times10^{-8}$
Ungerade ground			
0	$1.062\,25\times10^{-0}$	$1.062\,26\times10^{-0}$	$1.062\,25\times10^{-0}$
1	$0.531\,11\times10^{-0}$	$0.531\,13\times10^{-0}$	$0.531\,13\times10^{-0}$
2	$0.132\,76\times10^{-0}$	$0.132\,78\times10^{-0}$	$0.132\,78\times10^{-0}$
3	$0.221\,13\times10^{-1}$	$0.221\,31\times10^{-1}$	$0.221\,30\times10^{-1}$
4	$0.275\,89\times10^{-2}$	$0.276\,64\times10^{-2}$	$0.276\,63\times10^{-2}$
5	$0.274\,47\times10^{-3}$	$0.276\,64\times10^{-3}$	$0.276\,63\times10^{-3}$
6	$0.225\,77\times10^{-4}$	$0.230\,53\times10^{-4}$	$0.230\,52\times10^{-4}$
7	$0.156\,45\times10^{-5}$	$0.164\,67\times10^{-5}$	$0.164\,66\times10^{-5}$
8	$0.913\,44\times10^{-6}$	$0.102\,92\times10^{-6}$	$0.102\,91\times10^{-6}$
9	$0.435\,00\times10^{-8}$	$0.571\,77\times10^{-8}$	$0.571\,73\times10^{-8}$

[a]The coefficients c_i of $\psi=\Sigma_i(-)^i c_i x^{2i}$ for gerade ground state and of $\psi=\Sigma_i(-)^i c_i x^{2i+1}$ for ungerade ground state are given.

$$\psi=\sum_i (-)^i c_i x^{2i} \tag{5.16}$$

for the gerade state, and

$$\psi=\sum_i (-)^i c_i x^{2i+1} \tag{5.17}$$

for the ungerade state. We compare in Table VIII the coefficients c_i of both sides of Eq. (5.15). The column below ECC2 at $n=5$ shows c_i for the truncated wave function, the column below "estimated" shows c_i for the right-hand side of Eq. (5.15) and the column below "exact" shows c_i for the exact wave function. We again note that the present optimization is valid only up to five decimal figures for the variables. In Table VIII, c_i for the truncated ECC2 becomes depart from the exact one for higher i, but c_i of the right-hand side of Eq. (5.15) is always close to the exact one to five decimal figures: such closeness of c_i actually continues to higher i than shown here. Therefore, we can conclude that the estimation of the exact wave function by Eq. (5.15) is very accurate. This is a very encouraging result: we can calculate *the exact wave function* simply by using the explicit ECC function, when the convergence of the variables is rapid with respect to the truncation. We can do this since we know the explicit structure of the exact wave function as ECCND given by Eq. (2.3a). This is in sharp contrast to the ICI case. This is valuable especially when we calculate accurate properties of molecules. In comparison with the ICI result, the rapid convergence of the ECC2 seems to reflect the fact that the ECC gives a compact accurate expression of the structure of the exact wave function.

We have already shown in Paper III that this rapid converging behavior of the truncated ECC2 is in sharp contrast to the slow convergence of the truncated SECC. We have written the reasons in some details in Paper III.

Using the solutions of the truncated ECC2 given in Tables VI and VII for the ground states of gerade and ungerade symmetries, respectively, we have performed ECC2-CI2 calculations for the excited states by both of the variational and nonvariational methods, and the results are given in Table IX. Though the ECC-CI method is essentially the method to calculate excited states, it also gives the ground state as a lowest solution, since we include ψ_g in Eq. (3.4) to ensure the orthogonality between the ground and excited states. When the ground state is approximate, as in the present truncated approximation, the ground state is improved also at the (variational) ECC-CI level. Comparing the gerade and ungerade ground states of Table IX obtained by the variational method to those of Tables VI and VII, we see that the ground state is improved by one to two orders of magnitude by the ECC-CI method. We could calculate by the ECC2-CI2 method one excited state for each symmetry, and Table IX shows the four lower states of the harmonic oscillator. The quality of the calculated result becomes worse as the energy of the excited state becomes higher, but all of the states are much improved as the order of the truncation for the ground state ECC2 increases. At $n=5$, even the second ungerade state, the worst state in this calculation, is correct by eight zeros to the exact energy. Further, we can use the estimated exact ground state given in Table VIII and the result is shown in the last column of Table IX. The quality of the calculated result is much improved.

We have also carried out the nonvariational calculations at the ECC2-CI2 level, and the result is given in Table IX. As expected, the nonvariational result is almost always worse than the corresponding variational result. Further, though the

TABLE IX. Truncated ECC2-CI2 for the gerade and ungerade states of harmonic oscillator.[a]

	$n=2$	$n=3$	$n=4$	$n=5$	Estimated exact
Variational					
E_0 (g)	1.000 000 0360	1.000 000 003 11	1.000 000 000 0343	1.000 000 000 000 460	1.0
E_1 (u)	3.000 000 313	3.000 000 0348	3.000 000 000 448	3.000 000 000 007 69	3.0
E_2 (g)	5.000 0664	5.000 001 69	5.000 000 0331	5.000 000 000 815	5.000 000 000 125
E_3 (u)	7.000 197	7.000 006 73	7.000 000 162	7.000 000 004 06	7.000 000 000 208
Nonvariational					
E_0 (g)	1.000 002 05	1.000 006 38	1.000 000 0305	1.000 000 0150	1.000 000 000 000 257
E_1 (u)	3.000 000 797	3.000 004 47	2.999 999 147	3.000 000 395	3.000 000 000 001 29
E_2 (g)	5.001 01	5.000 0698	5.000 0141	5.000 335	5.000 003 51
E_3 (u)	7.002 39	6.996 81	7.000 0358	6.999 992 86	7.000 005 86

[a]1.0 and 3.0 means that the number has more than 15 zeros after the decimal point.

variational energy is always above the true exact energy, the nonvariational one sometimes overshoots the exact energy: this is seen for E_3 of $n=3$, E_1 of $n=4$, and E_3 of $n=5$. When we use the estimated exact ground state given in Table VIII, the nonvariational solution is also much improved.

Table X shows the result obtained by the ECC2-CI general calculations, extending the variable operator space as given by Eq. (5.11). By this calculation, we can not only improve the accuracies of all the states, but also calculate a larger number of excited states. Table X shows the twelve lower states of the harmonic oscillator in comparison with four of the ECC2-CI2 method shown in Table IX. Furthermore, in comparison with the ECC2-CI2 results given in Table IX, the results of ECC2-CI general are very much improved in quality. The number of zeros below the decimal

point increases much in this table. The accuracy of the results is improved very much as the order of the truncation n for the ground state ECC2 increases. This is especially so when we use the estimated exact ground state given in Table VIII. The solution obtained at this level is essentially exact, like those shown in Table V. Thus, the ECC2-CI general method is very promising for calculating accurate ground and excited states.

Table X also gives the nonvariational results of ECC2-CI general. The accuracy of the nonvariational method is rather capricious, and is almost always worse than that of the variational method. But, even so, the accuracy becomes steadily better as the order n increases. In contrast to the variational case, we see a lot of overshooting in the nonvariational case. However, the nonvariational solution obtained from the esti-

TABLE X. Truncated ECC2-CI general for the gerade and ungerade states of harmonic oscillator.[a]

	$n=2$	$n=3$	$n=4$	$n=5$	Estimated exact
Variational					
E_0 (g)	1.000 000 000 001 69	1.000 000 000 000 221	1.000 000 000 000 0673	1.000 000 000 000 0107	1.0
E_1 (u)	3.000 000 000 0267	3.000 000 000 002 94	3.000 000 000 000 951	3.000 000 000 000 153	3.0
E_2 (g)	5.000 000 004 25	5.000 000 000 954	5.000 000 000 418	5.000 000 000 0764	5.0
E_3 (u)	7.000 000 0226	7.000 000 004 31	7.000 000 001 91	7.000 000 000 316	7.0
E_4 (g)	9.000 000 781	9.000 000 153	9.000 000 0167	9.000 000 0116	9.0
E_5 (u)	11.000 002 52	11.000 000 444	11.000 000 0507	11.000 000 0314	11.0
E_6 (g)	13.000 008 13	13.000 002 96	13.000 003 16	13.000 000 567	13.0
E_7 (u)	15.000 0224	15.000 007 19	15.000 006 23	15.000 001 25	15.0
E_8 (g)	17.000 686	17.000 420	17.000 091 38	17.000 0103	17.0
E_9 (u)	19.001 11	19.000 666	19.000 154	19.000 0193	19.0
E_{10} (g)	21.0244	21.005 64	21.000 84	21.000 0833	21.000 000 001 37
E_{11} (u)	23.0317	23.007 82	23.001 26	23.000 138	23.000 000 001 62
Nonvariational					
E_0 (g)	0.999 999 999 9605	0.999 999 999 9438	0.999 999 999 9710	1.000 000 000 000 262	1.0
E_1 (u)	2.999 999 999 509	3.000 000 003 37	3.000 000 000 125	2.999 999 999 9485	3.0
E_2 (g)	5.000 000 180	4.999 999 9391	5.000 001 01	4.999 999 99549	5.0
E_3 (u)	6.999 9659	7.000 002 09	6.999 9895	6.999 999 9534	7.0
E_4 (g)	8.999 995 36	9.000 000 219	8.999 993 43	9.000 000 403	9.0
E_5 (u)	11.000 475	11.000 0487	11.000 0297	11.000 002 78	11.0
E_6 (g)	13.000 393	13.000 199	13.000 192	13.000 0231	13.0
E_7 (u)	15.000 708	15.000 411	15.000 413	14.999 999 9719	15.0
E_8 (g)	17.0269	17.0121	17.001 89	17.000 517	17.000 000 000 127
E_9 (u)	19.0106	19.004 42	18.996 81	19.001 48	19.000 000 000 184
E_{10} (g)	21.154	21.0280	21.0155	21.002 78	21.000 0387
E_{11} (u)	23.441	23.143	23.0698	22.999 101	23.000 0457

[a]1.0, 3.0, etc., means that the number has more than 15 zeros after the decimal point.

mated exact ground state is again almost exact.

It is true that the one-dimensional harmonic oscillator is probably the simplest possible system, so that we cannot generalize the present result to more complex electronic systems. Nevertheless, it is thought that the present results would already show some of the general aspects of the ICI and ECC methods and their solutions. We may safely say that the ICI and ECC methods are worth studying in more details as methods of giving exact solution of the Schrödinger equation.

VI. CONCLUSION

In this paper, we have first presented the method of describing the excited states, ionized states, and the electron-attached states from the ECCND method. Since the ECCND method is very promising as a method of calculating the ground state, it is important to prepare the method of calculating the excited states of the same system. The proposed method is called the ECC-CI method, because the theoretical framework is very similar to that of the SAC-CI method proposed in 1978 by the author, which was also formulated by the variational principle. Standard ECC-CI method that is ECCND-CIND is approximate, but by expanding the CI space, we obtain the ECC-CI general method that can even become exact. We are able not only to improve the quality of the calculated states, but also to expand the nature of the excited states up to higher multiple-excitation processes.

Second, we have applied the ICI and ECC methods to the calculations of the ground and excited states of the harmonic oscillator. The ICI method gave good convergence: the ICI2 gave a faster convergence than the SICI, and converged to the same solution as the SICI. The convergence of the wave function takes more iterations than the convergence of energy. The excited states were successfully calculated by the standard ICI-CI method. The ICI-CI general method gives better quality and a larger number of excited states than the standard ICIND-CIND method.

The ECC2 method gave at least three different solutions of the unique exact ground state of the harmonic oscillator: the solution that is the same as the SECC solution, the self-evident and nontrivial solutions. The nontrivial solution, which is most important as a general solution of ECC2, shows quite a rapid convergence to the exact wave function. This is in sharp contrast to the slow convergence of the SECC shown in Paper III. Using this fact, we could estimate *the exact wave function* simply by using the explicit ECC form. Further, in contrast to the ICI case, the self-evident and nontrivial solutions of ECC2 are different from that of the SECC. Because of the flexibility of the ECC2 due to its nonlinear nature, the truncated ECC2 gives much better result than the SECC. This is a very valuable feature of the ECC method. The ECC-CI method gave also a very promising result. Similarly to the ICI-CI results, the ECC-CI method gave very good results for both the ground and excited states. In particular, very good results for the ground and excited states were obtained by the ECC-CI general method. When the ground state is exact, the ECC-CI methods, both CI2 and CI general, gave the exact excited states by both variational and non-variational methods.

Though one-dimensional harmonic oscillator is the simplest possible system, some of the present results should be in common to those of the more general complex electronic systems.

The results of the present series of papers may lead to a new wave in the studies of exact and very accurate wave functions of the ground and excited states of molecular systems, making precise predictions possible in the theoretical studies of chemistry and physics.

ACKNOWLEDGMENTS

[1] P. J. Knowles and N. C. Handy, Chem. Phys. Lett. **111**, 315 (1984).

[2] G. L. Bendazzoli and S. Evangelisti, J. Chem. Phys. **98**, 3141 (1993).

[3] H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000).

[4] H. Nakatsuji and E. R. Davidson, J. Chem. Phys. **115**, 2000 (2001).

[5] H. Nakatsuji, J. Chem. Phys. **115**, 2465 (2001).

[6] H. Huang, Q. Xie, Z. Cao, Z. Li, Z. Yue, and L. Ming, J. Chem. Phys. **110**, 3703 (1999); H. Huang, X. Zeng, and L. Ming, *ibid.* **112**, 5257 (2000); M. G. Marmorino, *ibid.* **114**, 2513 (2001).

[7] C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950).

[8] E. R. Davidson, Comput. Phys. Commun. **53**, 1 (1989); W. A. Berger, H. G. Miller, and R. M. Dreizler, J. Phys. A **10**, 1089 (1977); J. H. van Lenthe and P. Pulay, J. Comput. Chem. **11**, 1164 (1990).

[9] H. Nakatsuji, Chem. Phys. Lett. **59**, 362 (1978); *ibid.* **67**, 329, (1979).

[10] H. Nakatsuji, in *Computational Chemistry, Reviews of Current Trends*, Vol. 2 edited by J. Leszczynski (World Scientific, Singapore, 1997), p. 62–124 and the references cited therein.

[11] F. Coster, Nucl. Phys. **7**, 421 (1958); F. Coster and H. Kümmel, *ibid.* **17**, 477 (1960).

[12] O. Sinanoglu, J. Chem. Phys. **36**, 706 (1962); Adv. Chem. Phys. **6**, 315 (1964).

[13] J. Cízek, J. Chem. Phys. **45**, 4256 (1966); Adv. Chem. Phys. **14**, 35 (1969).

[14] The naming "Extended Coupled Cluster (ECC)" happened to be identical to that already used by Arponen [Ann. Phys. (N.Y.) **151**, 311 (1983)], but the present ECC is different from that of Arponen.

[15] M. Nooijen, Phys. Rev. Lett. **84**, 2108 (2000).

[16] T. Van Voorhis and M. Head-Gordon, J. Chem. Phys., **115**, 5033 (2001). The author thanks the authors of this paper for giving him this preprint prior to publication. See also, T. Van Voorhis and M. Head-Gordon, J. Chem. Phys. **113**, 8873 (2000).

[17] R. Kosloff and H. Tal-Ezer, Chem. Phys. Lett. **127**, 223 (1986); see also T. J. Park and J. C. Light, J. Chem. Phys. **85**, 5870 (1986).

[18] D. Horn and M. Weinstein, Phys. Rev. D **30**, 1256 (1984).

[19] J. Cioslowski, Phys. Rev. Lett. **58**, 83 (1987).

[20] H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053 (1978).

[21] D. Mukherjee and P. K. Mukherjee, Chem. Phys. **39**, 325 (1979).

[22] E. Dalgaard and H. Monkhorst, Phys. Rev. A **28**, 1217 (1983); See also, H. Monkhorst, Int. J. Quantum Chem., Quantum Chem. Symp. **11**, 421 (1977).

[23] H. Koch and P. Jorgensen, J. Chem. Phys. **93**, 3333 (1990); H. Koch, H. J. Aa. Jensen, T. Helgaker, and P. Jorgensen, J. Chem. Phys. **93**, 3345 (1990).

[24] J. Geertsen, M. Rittby, and R. J. Bartlett, Chem. Phys. Lett. **164**, 57 (1989).

[25] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993); D. J. Wadt and R. J. Bartlett, *ibid.* **101**, 3073 (1994).

[26] J. F. Stanton and J. Gauss, J. Chem. Phys. **101**, 8938 (1994); J. F. Stanton and R. J. Bartlett, *ibid.* **102**, 3629 (1995).

[27] M. Ehara, M. Ishida, K. Toyota, and H. Nakatsuji, *Reviews in Modern*

Quantum Chemistry, A Tribute to Professor Robert G. Parr, edited by K. D. Sen (World Scientific, Singapore, in press).

[28] See Tables I and II of Paper I.

[29] H. Nakatsuji, Chem. Phys. Lett. **177**, 331 (1991).

[30] M. Ehara, P. Tomasello, J. Hasegawa, and H. Nakatsuji, Theor. Chem. Acc. **102**, 161 (1999).

[31] M. Ehara, M. Ishida, and H. Nakatsuji, J. Chem. Phys. **114**, 8990 (2001); and the references cited therein.

[32] J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Oxford University Press, Oxford, 1965).

[33] H. Nakatsuji, J. Chem. Phys. **83**, 5743 (1985); *ibid.* **94**, 6716 (1991).