

Full configuration-interaction calculations with the simplest iterative complement method: Merit of the inverse Hamiltonian

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The simplest iterative complement (SIC) calculations starting from Hartree-Fock and giving full configuration interaction (CI) at convergence were performed using regular and inverse Hamiltonians. Each iteration step is variational and involves only one variable. The convergence was slow when we used the regular Hamiltonian, but became very fast when we used the inverse Hamiltonian. This difference is due to the Coulomb singularity problem inherent in the regular Hamiltonian; the inverse Hamiltonian does not have such a problem. For this reason, the merit of the inverse Hamiltonian over the regular one becomes even more dramatic when we use a better-quality basis set. This was seen by comparing the calculations due to the minimal and double- ζ basis sets. Similar problematic situations exist in the Krylov sequence and in the Lanczos and Arnoldi methods.

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I. INTRODUCTION

The Schrödinger equation (SE) is the most important governing principle in atomic and molecular physics and chemistry:

$$H\psi = E\psi, \quad (1)$$

where the Hamiltonian is written as

$$H = \sum_i -\frac{1}{2}\Delta_i - \sum_i \sum_A Z_A/r_{Ai} + \sum_{i>j} 1/r_{ij} \quad (2)$$

in an ordinary notation. Within a given set of complete orthonormal functions $\{\phi_i\}$, the solution of the Schrödinger equation (SE) is called a full configuration interaction (CI) where the wave function ψ is expressed as $\psi = \sum_i c_i \phi_i$. When we introduce the Hamiltonian matrix \mathbf{H} whose element is $H_{ij} = \langle \phi_i | H | \phi_j \rangle$, the full CI equation is written as

$$\mathbf{H}\mathbf{C} = E\mathbf{C}, \quad (3)$$

where \mathbf{C} is a vector composed of $\{c_i\}$. In the second-quantized form the Hamiltonian is written as

$$H = \sum_{ps} v_p^s a_s^\dagger a_p + \sum_{pqrs} w_{pq}^{st} a_s^\dagger a_r^\dagger a_q a_p, \quad (4)$$

where $p, q, s,$ and t are elements of a given orthonormal orbital like Hartree-Fock, and v_p^s and w_{pq}^{st} are their one- and two-electron integrals.

Usually, a full CI solution involves a diagonalization of a very large Hamiltonian matrix \mathbf{H} . Previously, we have shown [1] that with only two-dimensional diagonalization, we can obtain a full-CI solution, when we use the simplest iterative complement (SIC) method [2],

$$\psi_{n+1}^r = (1 + C_n^r H) \psi_n^r = \psi_{n,0}^r + C_n^r \psi_{n,1}^r, \quad (5)$$

for solving the SE. In the above equation, n is the iteration number and C_n^r is a single variable in each iteration. The superscript

r means that we use the *regular* Hamiltonian introduced above instead of the *inverse* Hamiltonian introduced below. The second equality is to define $\psi_{n,0}^r = \psi_n^r$ and $\psi_{n,1}^r = H\psi_n^r$, which will be used later. The IC method was originally called the iterative configuration interaction (ICI) method. Later, it was renamed as the IC (iterative complement) method to generalize it to an analytical case. The SIC method is the simplest one among the members of the IC method [2]. The SIC wave function was proven to become exact at convergence, namely to become equivalent to the full CI in the present case. This was demonstrated previously starting from the Hartree-Fock but the convergence was slow. In the SIC two-dimensional secular equation, the Hamiltonian matrix involves the integral of the H^3 operator even at the beginning ($n = 0$), which was calculated by the three-times products of the Hamiltonian matrix \mathbf{H} . Similar calculations of full CI were reported with the use of a different member of the IC method [3].

We know, on the other hand, that the analytical integrals including more-than-third powers of Hamiltonian diverge plus or minus infinity [4–6], namely,

$$\langle \tilde{\psi} | H^m | \tilde{\psi} \rangle = \pm\infty, \quad m \geq 3, \quad (6)$$

where $\tilde{\psi}$ is any approximate wave function and H is the analytical Hamiltonian given by Eq. (2). This problem is called the singularity problem. Finite size of the nucleus [7] does not solve this problem. However, when we use the second-quantized Hamiltonian, the singularity problem is not obvious. Actually, when the basis set is crude, we can multiply its Hamiltonian matrix many times, as in the SIC calculations reported previously [1]. However, this was simply due to the crudeness of the basis set. With the analytic Hamiltonian this is, in principle, impossible. So, the SIC calculation with the regular Hamiltonian is problematic.

In 2002, this author introduced the inverse Schrödinger equation (ISE):

$$H^{-1}\psi = E^{-1}\psi, \quad (7)$$

to avoid the singularity problem [4]. The inverse Hamiltonian H^{-1} is defined by $H^{-1}H = HH^{-1} = 1$. The ISE is equivalent to the original SE: The exact wave function is a common

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eigenfunction of both the regular and inverse Hamiltonians. We assume without loss of generality that our Hamiltonian is positive: If not, this is easily done by adding some positive constant ε_p to the original Hamiltonian. It was shown previously [4] that the ISE has the same determinative power as the SE. The variation principles and the H -square equations also exist in the inverse sides of the Hamiltonian. Furthermore, the cross- H -square equation and its family give a bridge connecting the two worlds of the Hamiltonians.

The equation corresponding to Eq. (3) for full CI is

$$\mathbf{H}^{-1}\mathbf{C} = E^{-1}\mathbf{C}, \quad (8)$$

where \mathbf{H}^{-1} is the inverse matrix of \mathbf{H} . Its element is written as $(\mathbf{H}^{-1})_{ij} = \langle \phi_i | H^{-1} | \phi_j \rangle$ because of the completeness of $\{\phi_i\}$: \mathbf{H}^{-1} is the matrix of the inverse Hamiltonian in our space.

It is possible to formulate the SIC method using the inverse Hamiltonian H^{-1} [4],

$$\psi_{n+1}^i = (1 + C_n^i H^{-1}) \psi_n^i = \psi_{n,0}^i + C_n^i \psi_{n,1}^i, \quad (9)$$

similarly to the regular case given by Eq. (5). The superscript i means that we use the inverse Hamiltonian instead of the regular one. With the inverse SIC method, we do not encounter the singularity problem and we are guaranteed to have the exact wave function at convergence [4]. We want to see in this paper what happens when we use the inverse Hamiltonian instead of the regular Hamiltonian in the SIC calculations.

II. KRYLOV SEQUENCE DESCRIBED BY REGULAR AND INVERSE HAMILTONIANS

The Krylov sequence plays an important role in the eigenvalue problem [8,9] and is related to the Arnoldi method [10] and the Lanczos method [11]. In my earlier paper, the Krylov sequence was extended to the inverse space [4]. We refer to it here because of its close relationship to the SIC method used here. From the similarity between an operator and its matrix in a complete space, the Krylov sequence can be written in an operator form, which is adopted here. The Hamiltonian Krylov sequence

$$\{\psi_0, H\psi_0, H^2\psi_0, H^3\psi_0, \dots\} \quad (10)$$

is used to solve the SE as a basis set to expand the exact wave function. Referring to the SIC method for solving the SE given by Eq. (5), we notice that in the SIC method the exact wave function is calculated in a stepwise manner considering the two contiguous elements of the Krylov sequence. After the introduction of the inverse Hamiltonian, we can introduce the inverse Hamiltonian Krylov sequence by

$$\{\psi_0, H^{-1}\psi_0, H^{-2}\psi_0, H^{-3}\psi_0, \dots\}. \quad (11)$$

The relation of this sequence to the inverse SIC method given by Eq. (9) is clear. Previously, we have proposed to introduce the *complete* Krylov sequence by [4]

$$\{\dots, H^{-3}\psi_0, H^{-2}\psi_0, H^{-1}\psi_0, \psi_0, H\psi_0, H^2\psi_0, H^3\psi_0, \dots\}, \quad (12)$$

which covers both positive and negative powers of H . The complete Krylov sequence gives wider space than the regular

and inverse ones: It always includes a complete set but its half may become useless as seen below.

A problem in the Krylov sequence is the singularity problem. When H includes a singular potential like the Coulomb potential, the elements of the regular Krylov sequence do not satisfy, except for ψ_0 , the necessary condition that the correct wave function must satisfy, namely the integratable finite condition. Therefore, the regular Krylov sequence is not adequate as a basis to expand the exact wave function of atoms and molecules. In such cases, we may use the inverse Krylov sequence, because this sequence is appropriate as a basis to expand the exact wave function. When we use the analytical Hamiltonian given by Eq. (2), the above statement is very clear. But, when we use the Hamiltonian matrix \mathbf{H} based on the second-quantized Hamiltonian given by Eq. (4), the singularity problem becomes unclear: One may think that one can multiply the Hamiltonian matrix many times. A similar situation may also occur in the usages of the Arnoldi method and the Lanczos method. This paper will show that we have to be careful on this problem.

III. SIC METHOD WITH REGULAR OR INVERSE HAMILTONIAN

Now we formulate the SIC method with regular or inverse Hamiltonian. The SIC iterative calculations consist of two steps. First, we calculate the SIC wave function using Eq. (5) of the regular Hamiltonian or Eq. (9) of the inverse Hamiltonian. Second, we calculate the variables C_n^r or C_n^i using variation principle. When we use the regular variation principle $\langle \psi | H - E | \delta\psi \rangle = 0$ (so, the superscript v below is r), the secular equation for the regular ($a = r$) or inverse ($a = i$) SIC wave function is written as

$$({}^v\mathbf{h}_n^a - E_n^a \cdot {}^v\mathbf{s}_n^a)\mathbf{c}_n^a = 0, \quad (13)$$

where the two-dimensional Hamiltonian and overlap matrices are given by

$$\begin{aligned} {}^v\mathbf{h}_n^a &= \begin{pmatrix} \langle \psi_{n,0}^a | {}^vH | \psi_{n,0}^a \rangle, & \langle \psi_{n,0}^a | {}^vH | \psi_{n,1}^a \rangle \\ \langle \psi_{n,1}^a | {}^vH | \psi_{n,0}^a \rangle, & \langle \psi_{n,1}^a | {}^vH | \psi_{n,1}^a \rangle \end{pmatrix}, \\ {}^v\mathbf{s}_n^a &= \begin{pmatrix} \langle \psi_{n,0}^a | \psi_{n,0}^a \rangle, & \langle \psi_{n,0}^a | \psi_{n,1}^a \rangle \\ \langle \psi_{n,1}^a | \psi_{n,0}^a \rangle, & \langle \psi_{n,1}^a | \psi_{n,1}^a \rangle \end{pmatrix}, \\ {}^v\mathbf{c}_n^a &= \begin{pmatrix} 1 \\ C_n^a \end{pmatrix}, \end{aligned} \quad (14)$$

where vH denotes the Hamiltonian used in the variational step and then ${}^vH = H$ in the present case of using the regular Hamiltonian. $\psi_{n,0}^a$ and $\psi_{n,1}^a$ ($a = r$ or i) are defined in Eqs. (5) and (9). The n th-order SIC wave function $\psi_{n,0}^a$ is transformed into the form of $\psi_{n,0}^a = \sum_i d_{n,i}^a \phi_i$, where ϕ_i is an element of the full-CI configurations described by the various excitations from the Hartree-Fock configuration. The Hamiltonian matrix ${}^v\mathbf{h}_n^a$ of the regular variation problem for the regular SIC wave function involves the integral of H^3 at the (2,2) position that suffers the singularity problem even at the first iteration ($n = 0$). By continuing the 2×2 diagonalization at each order n , we obtain the converged solution ψ . Since each step is variational, the energy approaches the exact energy from above. When the SIC method is done with the regular Hamiltonian, Eq. (5), we

call it the R-R method and when the SIC method is done with the inverse Hamiltonian, Eq. (9), we call it the I-R method. The former “R” or “I” refer to the regular or inverse SIC method used to construct the wave function, and the latter “R” denotes the regular variational method used thereafter.

We can use the inverse variation principle [4] $\langle \psi | H^{-1} - E^i | \delta \psi \rangle = 0$, instead of the regular one, in the second step of calculating the single variable C_n^r or C_n^i . Then, the secular equation and the Hamiltonian and overlap matrices are given by Eqs. (13) and (14), respectively, with the superscript v being i which indicates that it is derived from the inverse variation principle. Then, ${}^v H$ in Eq. (14) is H^{-1} . The superscript a is either r or i depending on whether the regular or inverse SIC method was used. So, again, we have these combinations, the R-I and I-I methods. The first letter, “R” or “I,” distinguishes the Hamiltonian used in the SIC step and the latter “I” means that the inverse variation method is used in the variational step. Since each step is variational, the inverse energy approaches the exact full-CI value E^{-1} from below [4].

Thus, we have four distinct SIC calculations, R-R, R-I, I-R, and I-I methods. In the R-R method, the singularity problem occurs at any order. In the R-I method, the singularity problem is circumvented only at the first iteration ($n = 0$). In the I-R and I-I methods, the singularity problem is circumvented at any order. So, these two methods are the recommended procedures.

IV. SIC CALCULATIONS OF FULL CI WITH MINIMAL BASIS

We apply the method summarized above to the molecules H_2O , HCN , C_2H_2 , HCHO , and O_3 using the STO-6G basis [12]. The geometrical parameters are summarized in [13]. These molecules were studied previously using the R-R method described above [1]. We compare here with the results obtained using the inverse Hamiltonian. The Hamiltonian matrix was calculated by modifying the GAMESS program [14]. The full-CI calculations were due to the GUGA algorithm [15] in the GAMESS program. The initial wave function of the SIC calculation was Hartree-Fock.

Table I shows the summary of the results. The positive shift energy is included in the caption. Since the $1s$ orbitals were frozen to the initial Hartree-Fock ones, the energy in

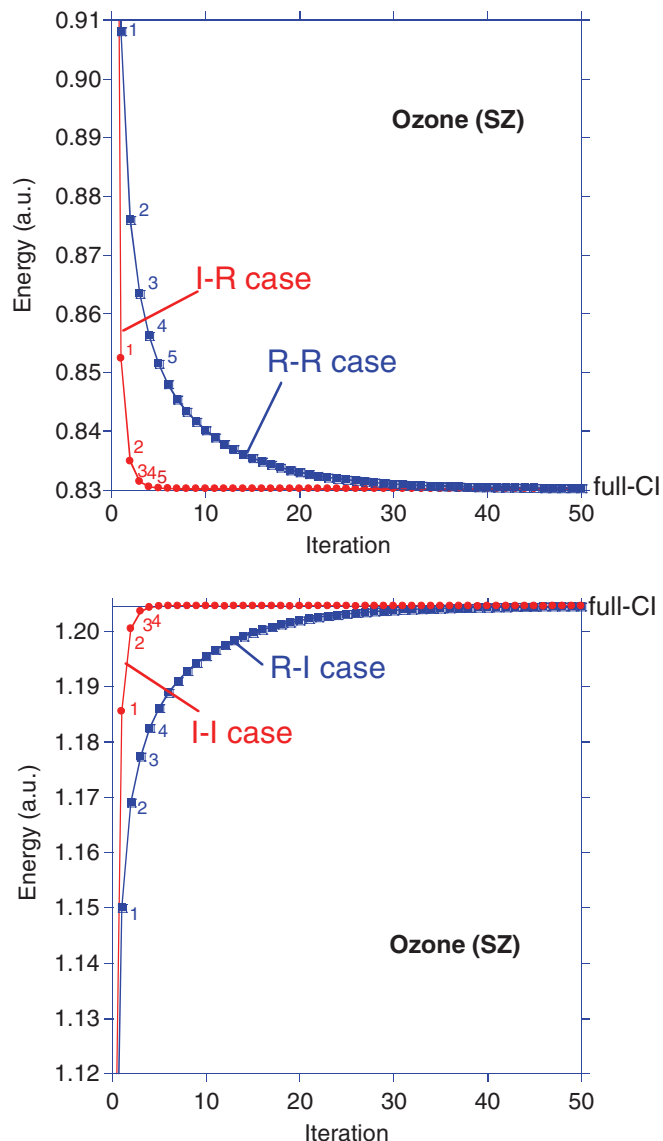


FIG. 1. (Color online) Convergence process of the R-R and I-R cases (above) and the R-I and I-I cases (below) of the SIC calculations of the full CI for O_3 with the minimal basis.

TABLE I. SIC calculations with minimal basis. Positive shift energy ε_p is 24.0, 29.0, 26.0, 41.0, and 86.0 a.u., respectively for H_2O , HCN , C_2H_2 , HCHO , and O_3 . $E_p - \varepsilon_p$ is valence electron energy. The $1s$ orbitals of the second-row atoms were frozen as cores. The frozen-core energy and the nuclear repulsion energy are -61.24327 and 9.00935 for H_2O ; -88.58359 and 23.87882 for HCN ; -76.39699 and 24.79128 for C_2H_2 ; -104.93835 and 31.36441 for HCHO ; and -207.33247 and 68.82230 for O_3 , all in a.u.

Molecule	Active space Occ. \times unocc.	Full CI				SIC							
		Dimension	Energy		Dimension	R-R case		R-I case		I-R case		I-I case	
			E_p	$1/E_p$		Iter.	Energy	Iter.	Energy	Iter.	Energy	Iter.	Energy
H_2O	4×2	37	0.50601	1.97625	2	11	0.50601	12	1.97625	3	0.50601	3	1.97625
HCN	5×4	1436	0.96356	1.03782	2	32	0.96356	29	1.03782	3	0.96356	4	1.03782
C_2H_2	5×5	2640	0.82984	1.20505	2	33	0.82984	31	1.20504	5	0.82984	4	1.20504
HCHO	6×4	3644	0.98942	1.01070	2	38	0.98942	33	1.01070	4	0.98942	4	1.01070
O_3	9×3	4067	0.83019	1.20454	2	74	0.83019	73	1.20454	8	0.83019	7	1.20454
	SDCI initial				2	55	0.83019	55	1.20454	6	0.83019	6	1.20454

TABLE II. SIC calculations with double- ζ basis. Positive shift energy ε_p is 35.0, 129.0, 10.0, 8.0, and 41.0 a.u. for Ne[3s2p]FC, Ne[3s2p]LiH, CH⁺ FC, and CH⁺, respectively, where FC denotes frozen core. The frozen-core energy in a.u. is -93.84625 for NeFC and -33.29414 for CH⁺. The nuclear repulsion energy in a.u. is 0.99488 for LiH and 2.80755 for CH⁺.

Atom or molecule	Basis set	Active space Occ. \times unocc.	Full CI				SIC													
			Energy		Dimension	1/ E_p	R-R case		R-I case		I-R case		I-I case							
			E_p	$1/E_p$			Iter.	Energy	Iter.	Energy	Iter.	Energy	Iter.	Energy	Iter.					
Ne	[3s2p]FC	4 \times 4	1764	0.22172	4.51026	2	14	0.22172	14	4.51026	2	2	0.22172	2	4.51026	2	2	0.22172	2	4.51026
	[3s2p]	SD-CI initial	5292	0.37497	2.66686	2	7	0.22172	8	4.51026	1	1	0.22172	1	4.51026	1	1	0.22172	1	4.51026
	[4s2p/2s]	SD-CI initial	620	0.99644	1.00358	2	62	0.37497	58	2.66686	2	27	0.37497	24	2.66686	1	1	0.37497	1	2.66686
	[5s2p/3s]	SD-CI initial	1257	0.98864	1.01149	2	3	0.99644	2	1.00358	12	103	0.99644	103	1.00358	12	12	0.99644	12	1.00358
CH ⁺	[3s2p/2s]FC	2 \times 12	2389	0.98434	1.01591	2	309	0.98864	304	1.01149	2	309	0.98864	304	1.01149	12	12	0.98864	12	1.01149
	[4s2p/2s]FC	2 \times 8	273	0.54481	1.83549	2	667	0.54481	711	1.83549	2	667	0.54481	711	1.83549	8	8	0.54481	8	1.83549
	[5s2p/2s]FC	2 \times 9	418	0.53098	1.88330	2	266	0.53098	282	1.88330	2	266	0.53098	282	1.88330	5	5	0.53098	5	1.88330
	[3s2p/2s]	SD-CI initial	620	0.53057	1.88477	2	102	0.53098	123	1.88330	2	102	0.53098	123	1.88330	2	2	0.53098	2	1.88330
CH ⁺	[4s2p/2s]	2 \times 10	2575	0.23773	4.20637	2	1450	0.53057	1619	1.88477	2	1450	0.53057	1619	1.88477	5	5	0.53057	5	1.88477
	[5s2p/2s]	3 \times 8	4582	0.22305	4.48332	2	802	0.23773	955	4.20637	2	802	0.23773	955	4.20637	6	6	0.23773	6	4.20637
	[3s2p/2s]	SD-CI initial	7818	0.22189	4.50666	2	318	0.22305	386	4.48332	2	318	0.22305	386	4.48332	3	3	0.22305	3	4.48332
	[5s2p/2s]	SD-CI initial	7818	0.22189	4.50666	2	148	0.22305	250	4.48332	2	148	0.22305	250	4.48332	2	2	0.22305	2	4.48332
	[3s2p/2s]	SD-CI initial	7818	0.22189	4.50666	2	1576	0.22189	1987	4.50666	2	1576	0.22189	1987	4.50666	3	3	0.22189	3	4.50666
	[4s2p/2s]	SD-CI initial	7818	0.22189	4.50666	2	710	0.22189	1138	4.50666	2	710	0.22189	1138	4.50666	2	2	0.22189	2	4.50666

Table I is the valence electron energy relative to the frozen-core energy defined by $E_{\text{FC}} = 2 \sum_i^{n_c} h_{ii} + \sum_{ij}^{n_c} (2J_{ij} - K_{ij})$ using the Hartree-Fock quantities, where i, j run only the core orbitals. The frozen-core energy and the nuclear repulsion energy of each molecule are given in the caption of the table. The sum of the valence electron energy, the frozen-core energy, and the nuclear repulsion energy is the total energy in an ordinary sense.

The dimension of the full-CI calculation was 4067 for O_3 and the calculated valence electron energy and its inverse were 0.830 19 and 1.204 54 a.u., respectively. The SIC calculations gave the same energies after the iterations of the two-dimensional calculations: 74 and 73 iterations in the R-R and R-I cases and only eight and seven iterations in the I-R and I-I cases. (These iteration numbers are those when the SIC energy becomes equal to the full-CI one to within $\pm 0.5 \times 10^{-5}$ a.u. This criterion is different from the previous one [1] where the threshold was $\pm 1.0 \times 10^{-5}$ a.u.) For other molecules, the I-R and I-I cases always converged much faster than the R-R and R-I cases.

The convergence behavior of the SIC calculations are shown in Fig. 1 for O_3 . The upper figure is for the R-R and I-R cases and the lower one is for the R-I and I-I cases. Since every step of the SIC calculation is variational, the energy always decreases in the R-R and I-R cases, and increases in the R-I and I-I cases. In the accuracy of Fig. 1, four, five iterations were enough for the I-R and I-I cases, but more than 40 iterations were necessary for the R-R and R-I cases: The rapid convergence is due to the usage of the inverse Hamiltonian in the SIC method. The regular Hamiltonian was not good because it caused the singularity problem. The Krylov sequence given by Eq. (10) suffered the singularity problem. A similar advantage of the usage of the inverse Hamiltonian over the regular one was observed previously for the hydrogen atom [4] in the IC (called ICI before) calculations of the exact wave function.

In the last row of Table I, we gave the result when the singles and doubles (SD) CI wave function was used as an initial function. (Other data are due to the Hartree-Fock initial guess.) The convergence was accelerated: 74 and 73 for the R-R and R-I cases were reduced to 55 for both cases and eight and seven for the I-R and I-I cases were reduced to six for both cases. A better-quality initial function is useful for getting faster convergence. However, even this improvement was much less effective than using the inverse Hamiltonian in the SIC step.

V. SIC CALCULATIONS OF FULL CI WITH DOUBLE- ζ BASIS

We know already that the analytical integral including H^n of the regular Hamiltonian diverges for n larger than 3. In the preceding section, we could perform the SIC calculations even with the regular Hamiltonian, multiplying the \mathbf{H} matrix even up to 70–80 times, which is just impossible with the analytical Hamiltonian. We could do so because the second-quantized Hamiltonian constructed by the STO-6G basis is very crude. In this section we will see what happens when the basis set is improved to the double- ζ quality and so the second-quantized Hamiltonian is improved toward the analytical Hamiltonian.

How much difference can we see between the regular and inverse Hamiltonians?

We calculate here Ne atom, LiH, and CH^+ using different-quality basis sets higher than the double- ζ quality [16]. Table II is a summary of the results. “FC” below the basis set means frozen core. The positive shift energy, the frozen-core energy, and the nuclear repulsion energy are given in the caption. The full-CI dimension is 273–7818, while the SIC dimension is always only 2. The convergence rate is different from atom to molecules and among different quality bases. But, the I-R and I-I methods always give much faster convergence than the R-R and R-I methods. The iteration times of the R-R and R-I calculations starting from the Hartree-Fock initial guess are 14–62 for atoms and 103–1987 for molecules, while those

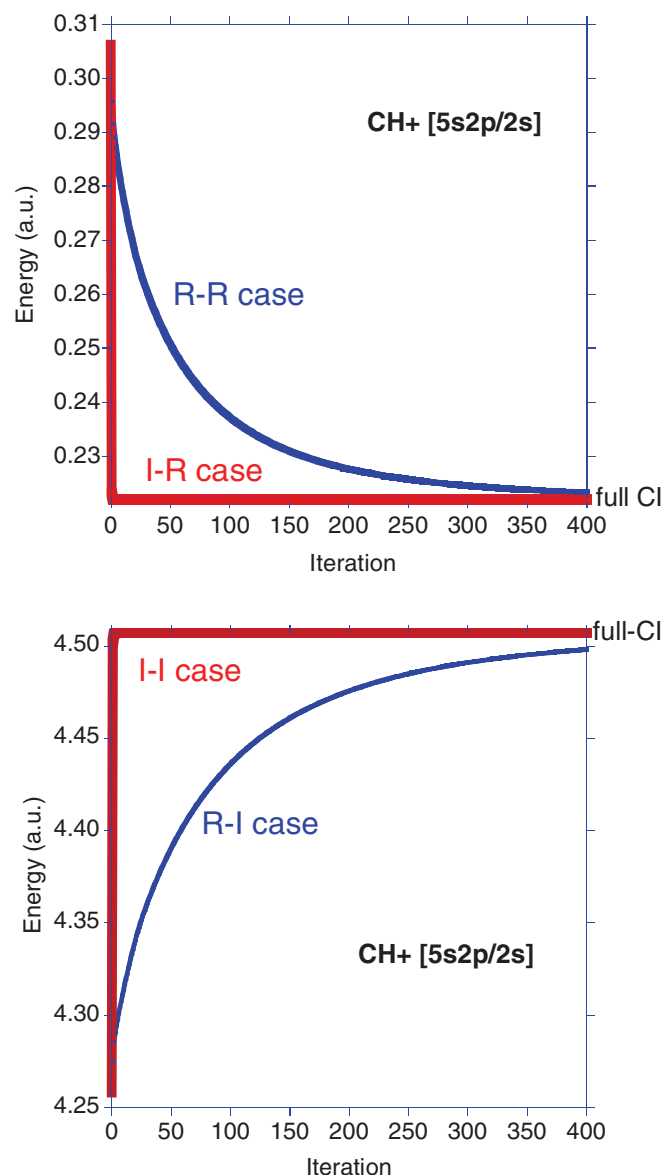


FIG. 2. (Color online) Overall convergence process of the R-R and I-R cases (above) and the R-I and I-I cases (below) of the SIC calculations of the full CI for CH^+ with the [5s2p/2s] basis.

for the I-R and I-I cases are only 2 for atoms and 3–12 for molecules. When we use the SD CI wave function as ψ_0 , the iteration numbers drop down by about 1/2 in all the cases. Thus the use of the SD CI ψ_0 has some merit, but the most remarkable result is a marvelous convergence speed of the SIC method when the inverse Hamiltonian is used in the wave function generation step (the I-R and I-I cases). The difference between the R-R and R-I methods was small, as expected from the theoretical consideration.

The merit of the inverse Hamiltonian over the regular one is more clearly seen from Figs. 2 and 3, which show the convergence processes of the four different cases of the SIC calculations for the $[5s2p/2s]$ basis of CH^+ , which were the largest calculations in Table II: The full-CI dimension was 7818. The convergence speeds of the R-R and R-I cases

were very slow: There was still some error even at 400 times iterations, but the convergence of the I-R and I-I cases was quite fast. In Fig. 2 the profile is like the vertical-horizontal axis, but in Fig. 3 which was enlarged only up to 30 iterations, we see a rapid convergence of the I-R and I-I cases, in contrast to the very slow convergence in the R-R and R-I cases. In the I-R and I-I cases, even two iterations gave an accurate enough result in the scale of Fig. 3. Actually, when we start from the SD CI initial guess, the second iteration result was already accurate up to five decimal figures, as shown in Table II. This is a rather surprising result.

Comparing Fig. 1 for the minimal basis with Figs. 2 and 3 for the double- ζ basis, we see that the advantage of the inverse Hamiltonian is more enhanced for the double- ζ basis than for the minimal basis. We think the reason is as follows. As the basis is improved, the freedom of the wave function near the nuclear and electron cusps increases, and hence the nuclear and electron singularity problems become severe in the R-R and R-I cases even in the matrix formalism, while in the I-R and I-I cases, the use of the inverse Hamiltonian resolves this difficulty, and moreover a larger freedom in the wave function gives a faster adjustment of the wave function, leading to a faster convergence. Thus, the results shown in this section demonstrate a prominent merit of using the inverse Hamiltonian in the SIC calculations of the full-CI wave function.

VI. CONCLUDING REMARKS

The full-CI description of the exact wave function requires a large number of variables. On the other hand, the IC theory requires only a small number of variables [2]; in particular, the SIC method requires only one variable per iteration. When we apply the SIC theory to the full-CI solution, the regular and inverse Hamiltonians work quite differently. Between the two steps involved in the SIC calculations, the first wave function generation step using Eq. (5) of the regular Hamiltonian or Eq. (9) of the inverse Hamiltonian is more important than the second variation step to calculate the single variables C_n^r or C_n^i . Among the four distinct SIC methods, the R-R, R-I, I-R, and I-I methods, the singularity problem does not occur at any order in the I-R and I-I methods, but it does occur at any order in the R-R method, and in the R-I method, the singularity problem is circumvented only at the first order ($n = 0$). Actually, when only the regular Hamiltonian was used, namely in the R-R case, the calculations required a lot of iterations. But, when the inverse Hamiltonian was used in the first wave function generation step, namely in the I-R and I-I methods, quite a rapid convergence was obtained. Though some improvement was seen in the R-I calculations, it was not so impressive. These results are understood from the singularity problem that the regular Hamiltonian has but the inverse Hamiltonian does not have. Thus, the I-R and I-I methods are the recommended procedures among the four distinct SIC methods.

This is understood also from the Krylov sequence that is related theoretically to the SIC method. When the regular Hamiltonian is used, the elements of the Krylov sequence given by Eq. (10) have singularity and therefore they are not appropriate as a basis set to expand the wave function because

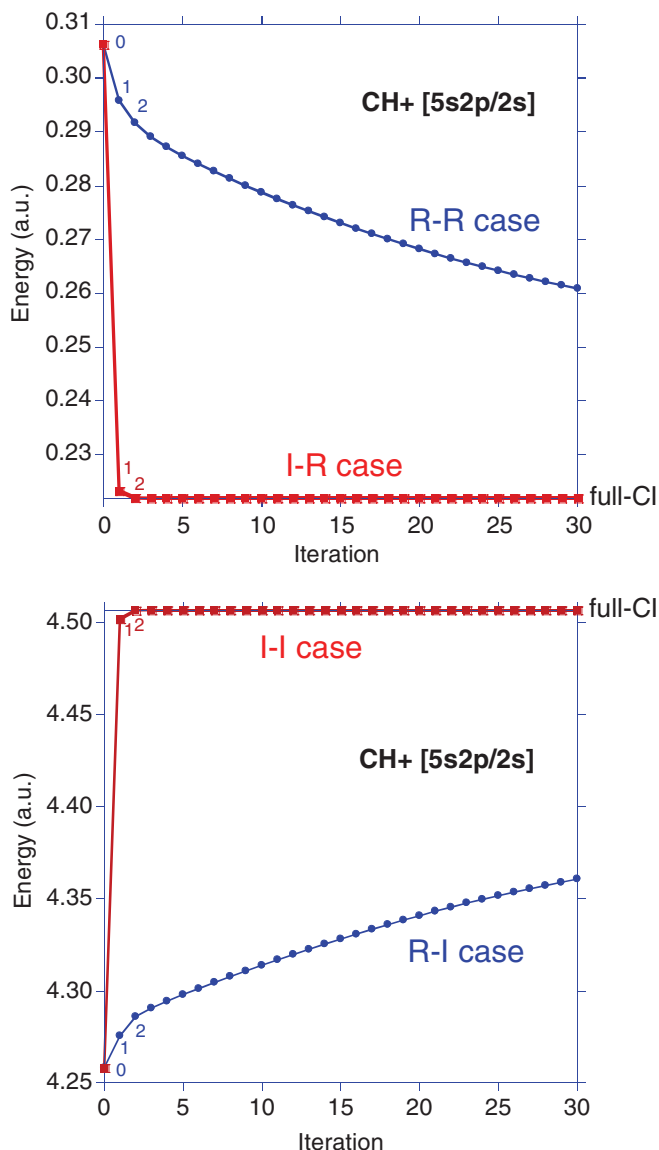


FIG. 3. (Color online) Detailed convergence process of the R-R and I-R cases (above) and the R-I and I-I cases (below) of the SIC calculations of the full CI for CH^+ with the $[5s2p/2s]$ basis.

they do not satisfy the condition of integrability that the correct wave function must satisfy. Actually, the Hamiltonian integrals calculated from the elements of the Krylov sequence given by Eq. (10) all diverge for the singularity problem when the analytical Hamiltonian given by Eq. (2) is used. Though such divergence may not occur when we use the second-quantized Hamiltonian based on some incomplete basis set, the obtained finite values of the integrals are simply due to the incompleteness of the used basis set and therefore their values are essentially unreliable. On the other hand, when we use the inverse Hamiltonian, we do not have the singularity problem and the Krylov sequence given by Eq. (11) is well defined and can be used as a basis set to expand the full-CI wave function and the exact wave function. A similar argument should also hold in the usage of the Arnoldi method and the Lanczos method.

Overall, the inverse Hamiltonian gives a stable and efficient ground for the descriptions of the full-CI and exact wave functions of atoms and molecules. In the inverse side of the world, there are no dangerous pitfalls on the playground of electrons and therefore things are much more stable there. Therefore, the inverse world should be explored more extensively. In the present study, the inverse matrix was calculated by using a conventional subroutine library. However, this is not realistic for most practical studies. It is necessary to efficiently describe the inverse matrix even approximately with high accuracy. Such study is in progress.

A note may be useful, that is, on the positive energy dependence of the total iteration number. Though the regular Hamiltonian method does not depend on the amount of the

positive energy ε_p , the inverse Hamiltonian method does. So, by changing ε_p , one can modify the convergence speed. This is well known, for example, in the inverse iteration method [8], so we performed several calculations using different positive energies for the two steps of the SIC method and observed some variations in the iteration numbers. However, these variations were much smaller than those caused by the change of the regular Hamiltonian into the inverse one.

Another note is that we have shown previously [3] that the general singles and doubles (GSD) case of the IC theory, which was proposed in 2000 [2], can be formulated in such a way that is free from the singularity problem without introducing the inverse Hamiltonian. Actually, the IC-GSD method in such a formalism has given a very fast convergence to the full CI.

For analytical cases, this author introduced the scaled Schrödinger equation (SSE) [5] that is equivalent to the original SE. The SSE has led to several general ways of solving the SE, among which we have used the free complement (FC) method [5,6] most frequently [17] to solve the SE of atoms and molecules.

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