Free iterative-complement-interaction calculations of the hydrogen molecule

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The free iterative-complement-interaction (ICI) method based on the scaled Schrödinger equation proposed previously has been applied to the calculations of very accurate wave functions of the hydrogen molecule in an analytical expansion form. All the variables were determined with the variational principle by calculating the necessary integrals analytically. The initial wave function and the scaling function were changes to see the effects on the convergence speed of the ICI calculations. The free ICI wave functions that were generated automatically were different from the existing wave functions, and this difference was shown to be physically important. The best wave function reported in this paper seems to be the best worldwide in the literature from the variational point of view. The quality of the wave function was examined by calculating the nuclear and electron cusps.

I. INTRODUCTION

When the quantum chemical methodology came out, the first molecular application was done to hydrogen molecule. In 1927, Heitler and London [1] applied newly born quantum mechanics to this molecule, which was a birth of quantum chemistry. After a pioneering study of helium atom by Hylleraas [2], James and Coolidge [3] applied their explicitly correlated functions to hydrogen molecule and obtained very accurate results. Since then, Kolos, Roothaan, Wolniewitz, Komasa, Cencek, Rychlewski, Kutzelnigg, and others [4–12] have reported very accurate wave functions of this molecule. Recently, Rychlewski and Komasa gave an extensive review [13] including the explicitly correlated functions of hydrogen molecule. We have recently developed a methodology for exactly solving the Schrödinger equation in an analytical expansion form [14–16]. So, in this paper, we apply our methodology to the hydrogen molecule in order to examine the efficiency of the proposed method and the quality of the calculated energy and wave function.

The methodology is based on the study on the structure of the exact wave function [14–16]. When the structure of the exact wave function is clarified, we construct such functions and make the variables included to be optimal by using the variational principle. However, when we formulate such a theory based on the regular Schrödinger equation for atoms and molecules, we encounter a difficulty called the singularity problem [15,16]. The formulation includes the integrals of higher powers of the Hamiltonian, but such integrals diverge owing to the singularity of the Coulomb potential included in the Hamiltonian. We showed that this difficulty could be avoided by introducing the scaled Schrödinger equation [15,16]: when we reformulate our theory based on the scaled Schrödinger equation, our theory for constructing the exact wave function becomes free from the singularity problem. Further, the free iterative-complement-interaction (ICI) method provides a very flexible way of constructing the exact wave function in both of the choices of the initial function ψ_0 and of the scaling g function.

We explain in the next section our methodology applied to the calculations of the exact wave function of the hydrogen molecule. Detailed computational aspects are then described and the results are summarized. We compare the present free ICI wave functions with the existing accurate wave functions in the field of explicitly correlated wave functions and examine the importance of the terms newly generated by the present free ICI method. The quality of the present wave function is examined by calculating the nuclear and electron cusp values [17]. The conclusion of this study is given in the last section. The Appendix summarizes briefly the mathematics necessary for the present study.

II. FREE ICI METHOD APPLIED TO THE HYDROGEN MOLECULE

We want to solve the Schrödinger equation of the hydrogen molecule,

$$(H - E)\psi = 0, \tag{1}$$

with the Hamiltonian given by

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_{1a} - 1/r_{1b} - 1/r_{2a} - 1/r_{2b} + 1/r_{12} + 1/R, \tag{2}$$

where 1 and 2 denote electrons, a and b two protons, and R the internuclear distance. When we introduce the elliptic coordinates

$$\lambda_i = (r_{ia} + r_{ib})/R, \quad \mu_i = (r_{ia} - r_{ib})/R, \quad \rho = 2r_{12}/R, \tag{3}$$

with i being 1 or 2, the kinetic operator and the potential operator are written as

$$\nabla_i^2 = \frac{4}{R^2(\lambda_i^2 - \mu_i^2)}\left[\frac{\partial}{\partial \lambda_i}(\lambda_i^2 - 1)\frac{\partial}{\partial \lambda_i} + \frac{\partial}{\partial \mu_i}(1 - \mu_i^2)\frac{\partial}{\partial \mu_i}\right.$$
$$\left. + \left\{\frac{1}{\lambda_i^2 - 1} + \frac{1}{1 - \mu_i^2}\right\}\frac{\partial^2}{\partial \phi_i^2}\right] \tag{4}$$

and

$$V_{ne} + V_{ee} = \frac{2}{R}\left(-\frac{\lambda_1}{\lambda_1^2 - \mu_1^2} - \frac{\lambda_2}{\lambda_2^2 - \mu_2^2} + \frac{1}{\rho}\right), \quad (5)$$

respectively, where V_{ne} and V_{ee} represent the nuclear attraction and electron repulsion operators, respectively.

One can see that the Hamiltonian includes the Coulombic potential that becomes plus or minus infinity when two particles meet together. Higher powers of such a potential become strongly diverging like a well potential so that the integrals of ψ^2 over such higher powers of the potential diverge. Therefore, the ICI calculations based on the ordinary Hamiltonian become impossible since it involves such diverging integrals. However, this singularity problem can be avoided by introducing the scaled Schrödinger equation

$$g(H - E)\psi = 0, \quad (6)$$

where g is a scaling function that is positive and nonzero everywhere except at the singular points r_0 and even there it satisfies

$$\lim_{r \to r_0} gV = a, \quad (7)$$

with a being a nonzero constant. The condition given by Eq. (7) is necessary for not to eliminate the information of the Hamiltonian at the singular points: the singularity is also an important physics of the system.

Based on the scaled Schrödinger equation, we can formulate the ICI method that is free from the singularity problem. The simplest ICI (SICI) wave function is defined by the recursion formula as

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n, \quad (8)$$

which is guaranteed to become exact at convergence and we do not have the singularity difficulty in the course of the iteration process starting from the initial function ψ_0 because of the existence of the scaling function g. In the present calculation of the hydrogen molecule, we use actually the free ICI method that is formulated from the SICI wave function as follows. We examine the right-hand side of Eq. (8), collect all the independent functions, and arrange them as $\{\phi_k\}^{(n)}$, $k = 1, \ldots, M_n$. Here M_n is the number of independent functions included in $\{\phi_k\}^{(n)}$. With this set of functions $\{\phi_k\}^{(n)}$, we expand our ψ_{n+1} as

$$\psi_{n+1} = \sum_{k=1}^{M_n} c_{k,n}\phi_k. \quad (9)$$

The coefficients $\{c_{k,n}\}$, $k = 1, \ldots, M_n$, are calculated with the variational principle (the ordinary Ritz variational principle is easier to use than the variational principle for the scaled Schrödinger equation).

In the free ICI method summarized above, we have two freedoms: one is the choice of the g function and the other is the choice of the initial function ψ_0. First, we explain the choice of the g function. Referring to the potential of the hydrogen molecule given by Eq. (5), we examined two different g functions

$$g_1 = \frac{\lambda_1^2 - \mu_1^2}{\lambda_1}\frac{\lambda_2^2 - \mu_2^2}{\lambda_2}\rho \quad (10)$$

and

$$g_2 = -\frac{\lambda_1^2 - \mu_1^2}{\lambda_1} - \frac{\lambda_2^2 - \mu_2^2}{\lambda_2} + \rho. \quad (11)$$

The function g_1 is a product of the inverse of the Coulomb potentials, $g_1 = 1/V_{ne}(1)V_{ne}(2)V_{ee}$, and g_2 is a sum of the inverse of each Coulomb potential, $g_2 = 1/V_{ne}(1) + 1/V_{ne}(2) + 1/V_{ee}$. In the free ICI calculation, the g_2 function is more preferable than the g_1 function for the following two reasons. First, when one of the three terms in the g_1 function becomes zero, the other terms can be arbitrary, so that the restriction may not be complete. Second, the function g_1 is more complex than the function g_2, so that the choice of g_1 makes the ICI wave function more complex than the choice of g_2. The g_2 function produces more plain and flexible complements functions than the function g_1. However, the function g_1 also produces functions that are singular, so that we have to eliminate such functions from our expansion bases of the exact wave function: the wave function must be integrably finite by its definition.

The initial functions ψ_0 that were adopted in the present calculations are of two kinds. One is the simplest possible function given by

$$\psi_0^{(1)} = \exp[-\alpha(r_{1a} + r_{2a} + r_{1b} + r_{2b})] = \exp[-\alpha(\lambda_1 + \lambda_2)]. \quad (12)$$

The spin part is singlet and antisymmetric, so that the spatial part is symmetric. This is a product of the $1s$ orbitals centered on the two protons. The other initial function we used in this study is given by

$$\psi_0^{(L)} = \sum_{l=1}^{L} \exp[-\alpha(\lambda_1 + \lambda_2)]\rho^{l-1}. \quad (13)$$

When $L = 1$, the initial function given by Eq. (13) is identical with that given by Eq. (12). This choice was based on the suggestion due to Kolos and Wolniewicz [5] that an inclusion of the functions of higher power in ρ accelerates the convergence of the expansion of the wave function. Kolos and Wolniewicz [5] also noted that the inclusion of the functions higher powers in λ and μ did not accelerate the convergence. The orbital exponent α in Eqs. (12) and (13) is a nonlinear parameter and may be optimized variationally at each iteration n, but the ICI theory claims that we can get the exact wave function with only linear expansions and so we fixed α to 1.1. The internuclear distance R was also fixed to the experimental value $R = 1.4011$ a.u., which is also used in other calculations to be compared with the present one. The calculations at $R = 1.4$ a.u. were also carried out for comparison with the previous results in the literature.

The initial functions ψ_0 given above are analytical functions, and by inserting these initial functions into Eq. (8), one gets analytical functions that are necessary for constructing the first iteration function ψ_1: the kinetic operator in the Hamiltonian is essentially a differentiation operator, and the

TABLE I. Ground-state energy of the hydrogen molecule calculated with the g function given by Eq. (10).

Initial function (L)[a]	Number of iterations (n)	Number of basis functions (M_n)	Total energy (a.u.)
1	0	1	−0.999 780 120 198 08
	1	11	−1.169 313 411 900 71
	2	186	−1.174 470 133 104 04
	3	1156	−1.174 475 901 628 54
Best value			−1.174 475 931 397 74

[a]L is defined in Eq. (13).

potential function and the g function are multiplicative functions. These operations are automatically done by using symbolic operation programs like MAPLE [18]. Then, one gets ψ_1 of the SICI in an analytical form. In the free ICI, one extracts from this ψ_1 all independent analytical functions, selects only such functions that do not give divergence in the calculations of Hamiltonian and overlap integrals, and collects them as $\{\phi_k\}^{(1)}$, $k=1,\ldots,M_1$. Then, one gives an independent variable $c_{k,1}$ to each ϕ_k and expands one's ψ_1 of free ICI as $\psi_1 = \sum_{k=1}^{M_1} c_{k,1}\phi_k$. The variables $\{c_{k,1}\}$ are determined by the variational principle by solving the secular equation. The Hamiltonian and overlap matrices are calculated without the singularity problem for the existence of the g function. After the diagonalization one gets the free ICI functions of the first iteration, ψ_1. The lowest solution is an approximation to the ground state and the second lowest solution is an approximation to the first excited state, etc. Putting this ψ_1 into Eq. (8) and doing the same procedure as above, one obtains ψ_2. One repeats this iteration cycle until one gets the convergence in one's desired accuracy. Since the secular equation at each iteration cycle is due to the variational principle, the energy approaches from above the true energies, for both ground and excited states. Note that in the free ICI method, the next iteration cycle does not require the variables $\{c_{k,n}\}$ of the former cycles, so that one can get the nth iteration free ICI functions $\{\phi_k\}^{(n)}$ directly from ψ_0 by applying n times the operator part of Eq. (8) to ψ_0. This means that the accumulation of errors during the iteration process does not occur in the free ICI calculations.

The Hamiltonian and overlap integrals over the basis functions $\{\phi_k\}^{(n)}$ were calculated analytically by applying and extending the method reported by James and Coolidge [3]. We reduced the basic integrals into the forms that can be handled with MAPLE. The details were summarized briefly in the Appendix for convenience. As we proceed with iterations, the number of the independent functions $\{\phi_k\}^{(n)}$ increases and they may involve the functions whose overlap integrals are rather close to unity. This means that the calculations must be performed in high accuracy, and we kept 60-decimal-figure accuracy throughout the calculations. The secular equation was also solved in high precision using the GMP (GNU multiple precision arithmetic) library [19].

III. RESULTS

A. Energy and wave function

We first performed the free ICI calculations of the hydrogen molecule using the scaling function g_1 given by Eq. (10)

and the simple initial function $\psi_0^{(1)}$ given by Eq. (12). We summarize in Table I the calculated energies at different iteration cycles. At the bottom of the table, we gave the best value obtained in the present free ICI calculations. One can see that as the iteration proceeds, the energy approaches the best value from above. Already at the second iteration with dimension 186, the energy is correct to five decimal figures, which is by far beyond the chemical accuracy. At the third iteration, we obtain the energy correct to seven decimal figures. We will show later that our wave function is different from those existing in the literature.

We next performed the free ICI calculations using the scaling function g_2 given by Eq. (11) and a set of initial functions $\psi_0^{(L)}$ $(L=1-6)$ given by Eq. (13). The results are given in Table II. When L is unity, the initial function is the same as that used in Table I, so that the difference is due only to the difference in the g function. In Table II the number of the complement functions at the fifth iteration is 832 and the energy is −1.174 475 917 a.u., which is lower than the energy of Table I at the third iteration, −1.174 475 901 a.u. with 1156 independent functions. This means that the g_2 function given by Eq. (11) is more efficient than the g_1 function given by Eq. (10). Actually, a multiplication of the g_1 function increases the orders of all variables λ_1, λ_2, and ρ by unity or minus unity, but the g_2 function increases the order of only one of the variables λ_1, λ_2, or ρ by unity, so that the g_2 function can produce more flexible basis functions than the g_1 function, leading to more efficient basis functions.

Table II gives a comparison of the usage of different initial functions, all with the same g_2 function. As L increases, the initial function already includes explicitly the interelectron distance ρ. If ρ is essential, it is better to include it from the beginning of the calculations and this is the case as seen from the table: the energy with $L=1$ and $n=6$ is −1.174 475 930 732 a.u. with 1788 functions, which is higher in energy than the case of $L=4$ and $n=4$ with 1667 functions, −1.174 475 931 331 a.u. By using better-quality initial function, we can get better energy with smaller number of basis functions. However, probably more important implication of Table II is that we can always get very accurate results as we perform iterations, independent of the quality of the initial functions. When the number of the basis functions is similar, the calculated energy is more-or-less similar.

Between the differences in the g function and in the initial function, the difference in the g function causes a larger dif-

TABLE II. Ground-state energy of the hydrogen molecule calculated with the g function given by Eq. (11).

L[a]	n[b]	M_n[c]	Energy (a.u.)	L[a]	n[b]	M_n[c]	Energy (a.u.)
1	0	1	−0.999 780 120 198 080	2	0	2	−1.138 078 114 832 792
1	1	5	−1.164 409 776 802 471	2	1	9	−1.169 819 224 009 141
1	2	30	−1.172 712 604 472 602	2	2	57	−1.174 397 294 989 745
1	3	114	−1.174 434 056 534 598	2	3	215	−1.174 474 888 511 114
1	4	343	−1.174 475 391 331 891	2	4	624	−1.174 475 918 013 359
1	5	832	−1.174 475 917 716 333	2	5	1459	−1.174 475 930 608 043
1	6	1788	−1.174 475 930 732 940				
3	0	3	−1.142 973 092 050 475	4	0	4	−1.143 082 324 090 173
3	1	17	−1.173 036 862 957 403	4	1	25	−1.173 448 296 529 433
3	2	114	−1.174 471 341 851 610	4	2	174	−1.174 475 069 845 826
3	3	414	−1.174 475 901 329 452	4	3	630	−1.174 475 928 234 319
3	4	1119	−1.174 475 930 609 382	4	4	1667	−1.174 475 931 331 490
5	0	5	−1.143 084 264 123 815	6	0	6	−1.143 084 849 985 530
5	1	33	−1.173 489 787 488 802	6	1	41	−1.173 497 602 544 993
5	2	260	−1.174 475 797 933 379	6	2	346	−1.174 475 872 960 003
5	3	951	−1.174 475 931 085 682	6	3	1276	−1.174 475 931 318 436
5	4	2441	−1.174 475 931 391 155	6	4	3246	−1.174 475 931 397 736

[a]L of Eq. (13).
[b]Iteration number.
[c]M_n of Eq. (9): number of basis functions at the nth iteration.

ference of the calculated results. We see from the comparison of Tables I and II that the energy calculated with 1156 functions produced with the g_1 function, −1.174 475 901 a.u. is higher than the one calculated with only 624 functions (about half) produced with the g_2 function, −1.174 475 918 a.u. This example emphasizes again the importance of the choice of the g function.

In the literature, many earlier calculations were done for the bond length of 1.4 a.u. So we also performed the free ICI calculations with $R=1.4$ a.u. and the results are given in Table III. The g function was due to Eq. (11) and the initial function was due to Eq. (13) with $L=6$. Comparing the energies for $R=1.4$ and 1.4011, the latter is lower, showing that the minimum-energy bond length should be closer to the latter. The experimental bond length is 1.401 12 a.u. [20].

Many important studies have been reported using the explicitly correlated wave functions of the hydrogen molecule [13]. We summarize in Table IV some of the representative

studies. As the present result, we gave our best results shown in Tables II and III for $R=1.4011$ and 1.4 a.u., respectively. First, we notice that our best results are certainly the best worldwide in the literature for both cases of $R=1.4$ and 1.4011 a.u. The second best energies were reported by Cencek and Kutzelnigg [9] for $R=1.4$ a.u. and by Cencek and Rychlewski [10] for $R=1.4011$ a.u. They used Gaussian functions.

Our free ICI wave functions are composed of the Slater-type functions and are written as

$$\psi = \sum_i c_i (1+p_{12}) \exp[-\alpha(\lambda_1+\lambda_2)]\lambda_1^{m_i}\lambda_2^{n_i}\mu_1^{j_i}\mu_2^{k_i}\rho^{l_i},$$

(14)

where p_{12} is an electron exchange operator. This wave function is very simple and similar to the original wave function due to James and Coolidge [3]. Our wave function and

TABLE III. Ground-state energy of hydrogen molecule at $R=1.4$ a.u. calculated with the g function given by Eq. (10).

Initial function (L)[a]	Number of iterations (n)	Number of basis functions (M_n)	Energy (a.u.)
6	0	6	−1.143 006 074 717
6	1	41	−1.173 494 068 035
6	2	346	−1.174 475 655 534
6	3	1276	−1.174 475 714 138

[a]L of Eq. (13).

TABLE IV. History of accurate calculations of the hydrogen molecule.

Type of wave function	Reference	H-H distance (au)	Total energy (au)
Hartree-Fock	Sundholm[a]	1.4	−1.133 629 573
Full CI ($33\sigma27\pi18\delta16\phi$)	Liu-Hagstrom[b]	1.4	−1.1743 304 3
Hylleraas type	James-Coolidge[c]	1.4	−1.173 539[d]
Gaussian functions	Cencek-Kutzelnigg[e]	1.4	−1.174 475 714 037
Free ICI (extended Hylleraas type)	Present	1.4	−1.174 475 714 138
Hylleraas type	Wolniewicz[f]	1.4011	−1.174 475 930 742
Gaussian functions	Cencek-Rychlewski[g]	1.4011	−1.174 475 931 39
Free ICI (extended Hylleraas type)	Present	1.4011	−1.174 475 931 397 74

[a]Reference [21].
[b]Reference [11].
[c]Reference [3].
[d]The energy and the wave function were recalculated as shown in Table VIII.
[e]Reference [9].
[f]Reference [7].
[g]Reference [10].

James-Coolidge wave function differ only in the powers m and n of the variables λ_1 and λ_2: m and n are always non-negative in the James-Coolidge wave function, but they can be even negative in the present free ICI wave function. In other words, our ICI theory starting from the initial functions given by Eqs. (12) and (13) generates not only non-negative power terms of λ_1 and λ_2, but also negative power terms of them. Such functions are theoretically more relevant for describing the exact wave function of the hydrogen molecule than the original James-Coolidge functions. We show later in this paper some of the important roles of these negative-power functions in our wave function. The high quality of the present free ICI wave function would be attributed to the existence of these negative m and n terms.

Kolos and Wolniewicz [5–7] extended the James-Coolidge wave function to a more general form like

$$\psi = \sum C(1 + p_{12})\exp[-\alpha\lambda_1 - \bar{\alpha}\lambda_2]\lambda_1^m\lambda_2^n\mu_1^j\mu_2^k\rho^l$$
$$\times [\exp(\beta\mu_1 + \bar{\beta}\mu_2) + (-1)^{j+k}\exp(-\beta\mu_1 - \bar{\beta}\mu_2)],$$
(15)

but they always used non-negative m and n in their wave functions. A reason for extending the James-Coolidge wave function was that the original James-Coolidge wave function did not have a proper asymmetric form as the interproton distance increases up to infinity. On the other hand, Cencek and co-workers [8–10] obtained very accurate wave functions using the Gaussian-type functions

$$\Psi = \sum C(1 + p_{12})\exp[-\alpha r_{1C}^2 - \bar{\alpha}r_{2C'}^2 - \beta r_{12}^2]. \quad (16)$$

They performed optimizations of a large number of nonlinear parameters. Primitive questions about this type of wave function are that how well the cusp conditions [17] are described and how important these properties are in the actual wave functions. Nevertheless, the easiness in the integral evaluations with the Gaussian bases is very important in actual calculations of atoms and molecules.

Table IV shows also the full CI energy [11] and the Hartree-Fock energy [21]. These calculations were performed at $R = 1.40$ a.u., like the original James-Coolidge calculations, while the other calculations were done at $R = 1.4011$ a.u. The full CI energy is the "exact" energy within a given space of the basis set. For the $(33\sigma27\pi18\delta16\phi)$ Gaussian-type basis, the full CI energy is −1.174 304 3 a.u. Referring to Table II, this energy is worse than that of the calculation, $L=2$ and $n=2$, −1.174 397 a.u., so that we estimate that this energy would be obtained with the functions less than 57, if we use the present free ICI method.

TABLE V. First iteration nine-term wave function of the free ICI calculation shown in Table II ($L=2$, $n=1$)[a]. The energy is −1.169 819 224 a.u.

No	$[m,n,j,k,p]$	Coefficient	No	$[m,n,j,k,p]$	Coefficient
1	[0, 0, 0, 0, 0]	1.000 000 000	6	[−1,0,0,0,0]	−0.169 894 927
2	[0, 0, 0, 0, 1]	−0.478 943 233	7	[−1,0,0,0,1]	0.310 672 513
3	[0, 0, 0, 0, 2]	−0.205 371 707	8	[−1,0,2,0,0]	0.064 715 165
4	[0, 1, 0, 0, 0]	0.558 786 404	9	[−1,0,2,0,1]	0.234 383 618
5	[0, 1, 0, 0, 1]	1.537 900 860			

[a]Each basis function is normalized to unity.

TABLE VI. Best five-term[a] extended James-Coolidge-type wave function of the hydrogen molecule within $-1 \leqslant m_i$, $n_i \leqslant 1$, $|m_i - n_i| \leqslant 1$, $0 \leqslant j_i$, $k_i \leqslant 2$, and $0 \leqslant l_i \leqslant 1$. $R = 1.4$ a.u. and $\alpha = 0.95$. The calculated energy was $-1.172\ 276\ 534$ a.u.

No	$[m, n, j, k, l]$	Coefficient	No	$[m, n, j, k, l]$	Coefficient
1	[0, 0, 0, 0, 0]	1.000 000 000	4	[0, 0, 1, 1, 0]	−0.055 207 501
2	[0, 0, 0, 0, 1]	0.718 124 997	5	[0, −1, 0, 2, 1]	0.081 476 902
3	[0, 0, 0, 2, 0]	0.198 062 046			

[a]Each basis function is normalized to unity.

B. Importance of the terms with negative powers of λ_i

The free ICI method produces automatically the analytical basis functions that are necessary to expand the exact wave function under a choice of initial function ψ_0 and the g function. In the present choice of the initial function, the ICI method always produced terms of λ_i that have positive, zero, and negative powers. Since these terms were produced theoretically by the ICI method, they are considered to be necessary for constructing the exact wave function. However, such terms were not included in the previous calculations by James and Coolidge and Kolos and Wolniewitz. So we examine here the importance of such terms in constructing the accurate wave functions of the hydrogen molecule. Note that for the helium atom the importance of similar terms with negative powers has been pointed out by Kinoshita [22].

First, the importance of the terms with negative powers of λ_i is understood from the high performance of the present free ICI calculations as presented in the preceding section. In Table V, we show the expansion coefficients of the nine basis functions obtained at the first iteration of the free ICI calculation shown in Table II ($L = 2$ and $n = 1$). This calculation is based on the g_2 function given by Eq. (11) and the initial function $\psi_0^{(2)}$ given by Eq. (13). The coefficients given in Table V are those for the terms of Eq. (14) designated by $[m, n, j, k, l]$, which are normalized to unity, and the first-iteration free ICI wave function $\psi_1^{(2)}$ was normalized such that the coefficient of the initial function, [0,0,0,0,0], is unity. One can see from Table V that the first five terms, Nos. 1–5, are conventional ones, but the other four terms are terms whose m are negative. You see that terms 6, 7, and 9 have large coefficients, showing the importance of the negative-power terms of λ_i.

Kolos and Roothaan [4] calculated five-term James-Coolidge wave functions using only positive powers and obtained an energy of $-1.171\ 619$ a.u. We have examined the best possible five-term extended James-Coolidge-type wave

function allowing the powers in Eq. (14) to change within $-1 \leqslant m_i$, $n_i \leqslant 1$, $|m_i - n_i| \leqslant 1$, $0 \leqslant j_i$, $k_i \leqslant 2$, and $0 \leqslant l_i \leqslant 1$. The bond length R and the orbital exponent α are the same as those used by Kolos and Roothaan [4], $R = 1.4$ a.u. and $\alpha = 0.95$. Table VI shows the calculated best wave function. It includes one term that has negative n and its coefficient is the second smallest. The calculated energy was $-1.172\ 276\ 534$ a.u. We also performed a similar calculation within the positive range of $0 \leqslant m_i$, $n_i \leqslant 1$, $0 \leqslant j_i$, $k_i \leqslant 2$, and $0 \leqslant l_i \leqslant 1$ and obtained the best wave function as shown in Table VII. The calculated energy was $-1.171\ 998\ 568$ a.u. The last term [1,1,0,0,0] was not included in the original 5-term Kolos-Roothaan wave function, though it was included in their 12-term wave function. They included instead the term [0,1,0,0,0]. The other four terms were common in all of these three wave functions. It is concluded that within 5-term James-Coolidge wave functions of hydrogen molecule, the best result is obtained by allowing negative-power terms of λ_i.

Another piece of evidence was obtained by performing calculations similar to the original James-Coolidge one. We recalculated the James-Coolidge 13-term wave function and show the result in Table VIII. The calculated energy was $-1.173\ 539\ 685$ a.u., which was slightly different from the original one, $E = 1.173\ 501$ a.u., reported by James and Coolidge later [3]. (For the 5- and 11-term wave functions, the present recalculations gave the same energies as those given in the original paper [3].) Then, we replaced the smallest two terms, term Nos. 5 and 7, of the original 13 terms with the two terms from $-1 \leqslant m$, $n \leqslant 1$, $|m - n| \leqslant 1$, $0 \leqslant j$, $k \leqslant 2$, and $0 \leqslant l \leqslant 1$. The lowest-energy result is given in Table IX that has the energy $-1.173\ 962\ 233$ a.u., which is substantially lower than the original James-Coolidge energy given in Table VIII. In Table IX, term Nos. 12 and 13 are the replaced ones and term No. 12 has positive m and n, but term No. 13 has negative m and n. Again, this shows the importance of the negative-power terms in the calculations of the hydrogen molecule.

TABLE VII. Best five-term[a] James-Coolidge-type wave function of the hydrogen molecule within the positive range of $0 \leqslant m_i$, $n_i \leqslant 1$, $0 \leqslant j_i$, $k_i \leqslant 2$, and $0 \leqslant l_i \leqslant 1$. $R = 1.4$ a.u. and $\alpha = 0.95$. The calculated energy was $-1.171\ 998\ 568$ a.u.

No	$[m, n, j, k, l]$	Coefficient	No	$[m, n, j, k, l]$	Coefficient
1	[0, 0, 0, 0, 0]	1.000 000 000	4	[0, 0, 1, 1, 0]	−0.067 134 733
2	[0, 0, 0, 0, 1]	0.802 238 155	5	[1, 1, 0, 0, 0]	−0.087 098 459
3	[0, 0, 0, 2, 0]	0.282 362 668			

[a]Each basis function is normalized to unity.

TABLE VIII. Recalculated 13-term[a] wave function of James and Coolidge with $R = 1.4$ a.u. and $\alpha = 3/4$. The calculated energy was $-1.173\,539\,685$ a.u.

No.	$[m,n,j,k,l]$	Coefficient	No.	$[m,n,j,k,l]$	Coefficient
1	$[0, 0, 0, 0, 0]$	1.000 000 000	8	$[1, 0, 0, 0, 0]$	−0.933 408 702
2	$[0, 0, 0, 0, 1]$	0.553 586 789	9	$[1, 0, 0, 2, 0]$	−0.052 106 263
3	$[0, 0, 0, 0, 2]$	−0.099 140 955	10	$[1, 0, 1, 1, 0]$	0.044 627 723
4	$[0, 0, 0, 2, 0]$	0.195 335 087	11	$[1, 0, 2, 0, 0]$	−0.074 756 346
5	$[0, 0, 0, 2, 1]$	0.044 417 387	12	$[2, 0, 0, 0, 0]$	0.315 198 529
6	$[0, 0, 1, 1, 0]$	−0.062 129 657	13	$[1, 0, 0, 0, 1]$	−0.188 359 478
7	$[0, 0, 1, 1, 1]$	−0.006 994 087			

[a]Basis functions are normalized to unity.

We also have some intuitive explanations about the importance of the negative-power terms of λ_i. Figure 1 shows the illustrations of the functions $\phi = \exp(-\lambda)\lambda^m\mu^2$ with positive and negative m. Figure 1(a) is for $m = 1, 2, 3$ and Fig. 1(b) for $m = 0, -1, -2$, and the two protons were assumed to be at $z = 0$ and 1. Note that the variables λ_i and μ_i describe the wave function outside and inside, respectively, of the two nuclei. We see that the functions with positive m do not show a nice cusplike behavior near the positions of the nuclei, but those with negative m show reasonable cusplike behaviors at the nuclear positions. This also explains the importance of the functions with negative powers of λ_i.

C. Cusp properties

The exact wave function must satisfy some necessary conditions like the variational condition, virial theorem, cusp condition, etc. In the free ICI wave function given by Eq. (14), the coefficients $\{c_i\}$ were calculated with the variational principle. We did not optimize the exponent α, since the theorem of ICI guarantees that we can approach the exact result with only linear variables. The cusp property is known to be a rather sensitive property, reflecting the quality of the calculated wave functions. Below, we examine how well the present ICI wave functions satisfy the cusp conditions.

Kato [17] presented two cusp conditions for the exact many-electron wave functions: the nuclear cusp condition and electron cusp condition. The nuclear cusp condition is expressed for the hydrogen molecule as [4]

$$F_N(\lambda_2, \mu_2) = \left[\frac{-1}{R\lambda_1\Psi}\left(\lambda_1\frac{\partial\Psi}{\partial\lambda_1} - \mu_1\frac{\partial\Psi}{\partial\mu_1}\right)\right]_{\lambda_1=1,\mu_1=-1} = Z_A = 1,$$
(17)

which is the condition when electron 1 is at proton a. The left-hand side (LHS) of Eq. (17) is a function of the electron coordinate 2, so that Eq. (17) must be satisfied at any coordinate of electron 2, except at the additional singular point $\lambda_2 = 1$ and $\mu_2 = -1$, where electron 2 also collides with proton a. The electron cusp condition is given by

$$F_e(\lambda_i, \mu_i) = \left[\frac{1}{\Psi}\frac{\partial\Psi}{\partial r_{12}}\right]_{r_{12}=0} = \frac{1}{2},$$
(18)

which is the condition when two electrons meet together. The LHS is also the function of the variables other than $\rho = r_{12}$ and so it must be $1/2$ everywhere except for the additional singular points.

Figure 2 shows the plots of the function F_N along the iteration process of the free ICI calculations using the g_2 function and the initial function $\psi_0^{(6)}$: at the fourth iteration of this calculation we have obtained the worldwide best value of the energy of the hydrogen molecule shown in Tables II and IV. Figure 2(a) is along the z coordinate that connects

TABLE IX. The wave function constructed from the 11 terms of James and Coolidge 13 terms plus 2 terms from $-1 \leqslant m, n \leqslant 1, |m-n| \leqslant 1, 0 \leqslant j,$ and $k \leqslant 2,$ and $0 \leqslant l \leqslant 1$ for the H_2 molecule with $R = 1.4$ a.u. and $\alpha = 3/4$.[a,b] The calculated energy was $-1.173\,962\,233$ a.u.

No.	$[m,n,j,k,l]$	Coefficient	No.	$[m,n,j,k,l]$	Coefficient
1	$[0, 0, 0, 0, 0]$	1.000 000 000	8	$[1, 0, 1, 1, 0]$	0.015 613 455
2	$[0, 0, 0, 0, 1]$	0.650 858 318	9	$[1, 0, 2, 0, 0]$	−0.033 975 753
3	$[0, 0, 0, 0, 2]$	−0.059 439 543	10	$[1, 0, 0, 0, 1]$	−0.404 443 002
4	$[0, 0, 0, 2, 0]$	0.138 956 703	11	$[2, 0, 0, 0, 0]$	0.337 386 255
5	$[0, 0, 1, 1, 0]$	−0.041 545 078	12	$[1, 1, 0, 0, 1]$	0.071 193 197
6	$[1, 0, 0, 0, 0]$	−0.933 425 960	13	$[-1, -1, 0, 2, 1]$	0.031 686 115
7	$[1, 0, 0, 2, 0]$	−0.018 305 773			

[a]Basis functions are normalized to unity.
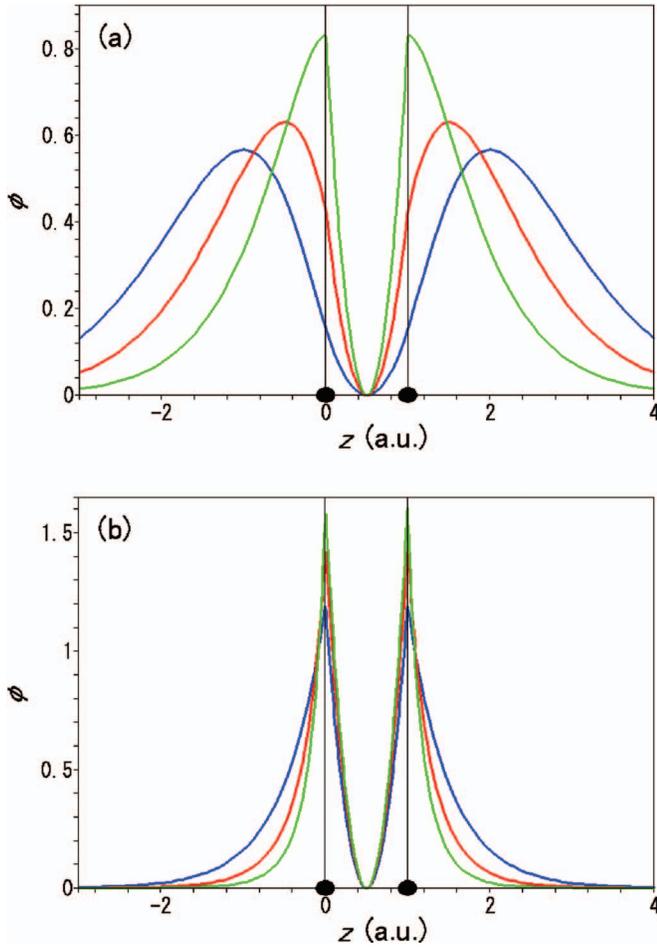[b]The last two terms, Nos. 12 and 13, are the selected terms.

FIG. 1. (Color) (a) Plot of the function $\phi = \exp(-\lambda)\lambda^m\mu^2$ with $m=1$ (green), $m=2$ (red), and $m=3$ (blue). The two protons are at $z=0$ and $z=1$ a.u. (b) Plot of the function $\phi = \exp(-\lambda)\lambda^m\mu^2$ with $m=-2$ (green), $m=-1$ (red), and $m=0$ (blue). The two protons are at $z=0$ and $z=1$ a.u.

two protons lying at $z=0$ and $z=1.4011$ a.u., and Fig. 2(b) is along an axis lying parallel to the z coordinate and distant from it by 1 a.u. The figures show the local values of the cusp function F_N when electron 2 moves along these axes. Though the cusp value of the free ICI wave function is very different from unity at the first iteration ($n=1$), it becomes closer and closer to unity as the iteration proceeds. At $n=4$, the cusp values are unity everywhere except at the position of nucleus a [the origin of Fig. 2(a)], where an additional singularity occurs. There, not only does nucleus a collide with the two electrons, but also the two electrons collide with each other: this is a new singularity point not expressed by Eq. (15). It is remarkable that at $z=1.4011$ a.u. of Fig. 2(a), the value of F_N becomes unity at $n=4$: there, the two cusp conditions for the two pairs—electron 1, nucleus a, and electron 2, nucleus b—are satisfied independently.

Figure 3 shows plots of the function F_e along the iteration process of the same free ICI wave functions given in Fig. 2 above. Figure 3(a) shows the value of the cusp function F_e when the colliding two electrons move along the z axis and Fig. 3(b) along the axis separated by 1 a.u. from the z axis. Again, the cusp value is improved as the iteration proceeds:
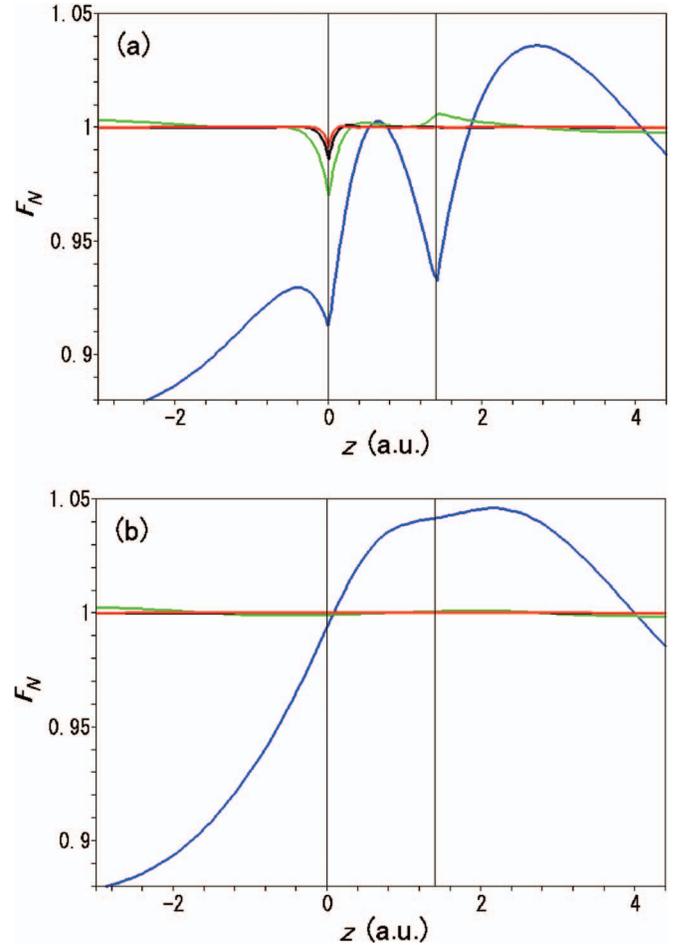

FIG. 2. (Color) (a) Plots of the nuclear-electron cusp function F_N along the z coordinate that connects two protons lying at $z=0$ and $z=1.4011$ a.u. at different iteration processes of the free ICI calculations using the g_2 function and the initial function $\psi_0^{(6)}$: iteration number $n=1$ (blue), $n=2$ (green), $n=3$ (violet), and $n=4$ (red). The wave function at $n=4$ is our best wave function reported in this paper. (b) Plots of the nuclear-electron cusp function F_N along the axis lying parallel to the z coordinate that connects two protons lying at $z=0$ and $z=1.4011$ a.u. at different iteration processes of the free ICI calculations using the g_2 function and the initial function $\psi_0^{(6)}$: iteration number $n=1$ (blue), $n=2$ (green), $n=3$ (violet), and $n=4$ (red). The wave function at $n=4$ is our best wave function reported in this paper.

the cusp value of the wave function at $n=1$ is far from one-half, but it comes closer and closer to one-half as n increases. At the nuclear positions a and b along the z axis, the cusp value is different from one half even for the best wave function since there an additional singularity occurs: there, two colliding electrons collide farther with the nucleus. Except at these two points, the cusp function F_e of our best free ICI wave function ($n=4$) is flat and takes one-half everywhere along the z axis and along the axis apart 1 a.u. from the z axis.

IV. CONCLUSION

The free ICI method developed in earlier papers has been applied to the hydrogen molecule to calculate its very accu-
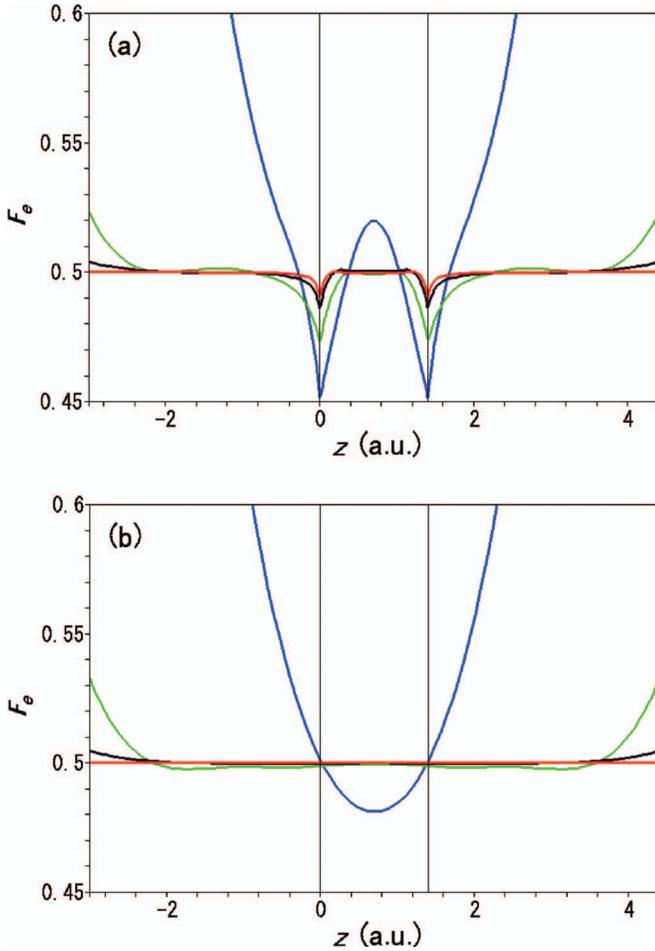
FIG. 3. (Color) (a) Plots of the electron-electron cusp function F_e along the z coordinate that connects two protons lying at $z=0$ and $z=1.4011$ a.u. at different iteration processes of the free ICI calculations using the g_2 function and the initial function $\psi_0^{(6)}$: iteration number $n=1$ (blue), $n=2$ (green), $n=3$ (violet), and $n=4$ (red). The wave function at $n=4$ is our best wave function reported in this paper. (b) Plots of the electron-electron cusp function F_e along the axis lying parallel to the z coordinate that connects two protons lying at $z=0$ and $z=1.4011$ a.u. at different iteration processes of the free ICI calculations using the g_2 function and the initial function $\psi_0^{(6)}$: iteration number $n=1$ (blue), $n=2$ (green), $n=3$ (violet), and $n=4$ (red). The wave function at $n=4$ is our best wave function reported in this paper.

rate wave functions. We could obtain the best variational wave functions in the literature for both $R=1.4011$ and 1.4 a.u. with a rather simple Hylleraas-James-Coolidge form. The difference of the present free ICI wave function from the previous James-Coolidge ones was the existence of the negative-power terms of λ_i. These terms were generated automatically by the free ICI formalism, so that these functions are believed to be essential for effective descriptions of the exact wave function of the hydrogen molecule. We have shown some results showing the importance of these negative-power terms.

We have examined two different g functions and several initial functions. A clever choice of the g function was more important than the different choices of the initial function.

However, it was also true that any initial functions have given the converging series of energies to the same best value. This was also true for the two g functions examined here. We have also shown that the cusp values, rather sensitive properties of the wave function, were substantially improved as the iteration proceeds. Recently, we have extended the present methodology to the relativistic case [23]. Accurate and systematic descriptions of the relativistic electronic structures of many-electron systems are a very important subject that must be explored in the near future.

APPENDIX

We briefly summarize here the method of analytical calculations of the integrals that appear in the variational calculations of the free ICI wave function given in the form of Eq. (14). The formulation is a small generalization of the one presented by James and Cooligde in their original paper [3]. Ruedenberg [24] also gave formulas related to the present case.

The integrals we have to calculate are the Hamiltonian and overlap integrals

$$H_{ij} = \int \int \phi_i H \, \phi_j d\tau_1 d\tau_2,$$

$$S_{ij} = \int \int \phi_i \phi_j d\tau_1 d\tau_2, \tag{A1}$$

where the functions ϕ_i have the form

$$\phi_i = (1 + p_{12})\exp[-\alpha(\lambda_1 + \lambda_2)]\lambda_1^{m_i}\lambda_2^{n_i}\mu_1^{j_i}\mu_2^{k_i}\rho^{l_i}, \tag{A2}$$

where m and n are positive and negative integers and zero and j, k, and l are non-negative integers. Applying the Hamiltonian on ϕ_i, we obtain

$$H\phi_i = \sum_j d_j(1 + p_{12})\exp[-\alpha(\lambda_1 + \lambda_2)]\lambda_1^{m_j}\lambda_2^{n_j}\mu_1^{j_j}\mu_2^{k_j}\rho^{l_j}, \tag{A3}$$

which are similar in form to Eq. (14), and this process can be easily done with the use of MAPLE or other similar program. The Jacobian for the elliptic coordinate is given by

$$d\tau_1 d\tau_2 = \frac{R^6}{64}(\lambda_1^2 - \mu_1^2)(\lambda_2^2 - \mu_2^2)d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2. \tag{A4}$$

Then, all the integrals reduce to the sums of the integrals

$$I = \int \exp[-2\alpha(\lambda_1 + \lambda_2)]\lambda_1^m\lambda_2^n\mu_1^j\mu_2^k\rho^l d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2. \tag{A5}$$

Now, we summarize the necessary formulas to calculate these integrals. First, the variables of ρ are transformed by using the relation

$$\rho^2 = \lambda_1^2 + \lambda_2^2 + \mu_1^2 + \mu_2^2 - 2 - 2\lambda_1\lambda_2\mu_1\mu_2$$
$$- 2[(\lambda_1^2 - 1)(\lambda_2^2 - 1)(1 - \mu_1^2)(1 - \mu_2^2)]^{1/2}\cos(\varphi_1 - \varphi_2),$$
$$(A6)$$

which is obtained from the second cosine formula and the expansion

$$\rho^{-1} = \sum_{\tau=0}^{\infty} \sum_{N=0}^{\infty} D_\tau^N P_\tau^N\left(\frac{\lambda_1}{\lambda_2}\right)Q_\tau^N\left(\frac{\lambda_2}{\lambda_1}\right)P_\tau^N(\mu_1)P_\tau^N(\mu_2)$$
$$\times \cos N(\varphi_1 - \varphi_2), \qquad (A7)$$

which is Von Neuman's expansion, where

$$D_\tau^0 = 2\tau + 1, \qquad (A8)$$

$$D_\tau^N = 2(2\tau+1)\left[\frac{(\tau-N)!}{(\tau+N)!}\right]^2 \quad (N>0).$$

P and Q are the unnormalized complex associated Legendre functions of the first and second kinds, and we take upper variable when $\lambda_2 \geq \lambda_1$ and lower variable otherwise.

We introduce the function Z defined by

$$Z(\nu,m,n,j,k,l) = \int \exp[-2\alpha(\lambda_1 + \lambda_2)]$$
$$\times \lambda_1^m\lambda_2^n\mu_1^j\mu_2^k\rho^l M^\nu d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$
$$(A9)$$

where

$$M = [(\lambda_1^2 - 1)(\lambda_2^2 - 1)(1 - \mu_1^2)(1 - \mu_2^2)]^{1/2}\cos(\varphi_1 - \varphi_2).$$
$$(A10)$$

Then, the integral I defined by Eq. (A5) is written with this Z function as

$$I = Z(0,m,n,j,k,l). \qquad (A11)$$

From Eq. (A6), we obtain the recursion formula

$$Z(\nu,m,n,j,k,l) = Z(\nu,m+2,n,j,k,l-2) + Z(\nu,m,n+2,j,k,l-2) + Z(\nu,m,n,j+2,k,l-2) + Z(\nu,m,n,j,k+2,l-2)$$
$$- 2Z(\nu,m,n,j,k,l-2) - 2Z(\nu,m+1,n+1,j+1,k+1,l-2) - 2Z(\nu+1,m,n,j,k,l-2), \qquad (A12)$$

which implies that the value of the function Z reduces finally to the sum of the following terms, depending on the parity of the integer l:

$$\text{case } (a): \quad Z(\nu,m,n,j,k,0) \quad (l,\text{even}),$$
$$\text{case } (b): \quad Z(\nu,m,n,j,k,-1) \quad (l,\text{odd}). \qquad (A13)$$

For case (a), the Z value is written as

$$Z(\nu,m,n,j,k,0) = L(\nu,m,\alpha)L(\nu,n,\alpha)U(\nu,j)U(\nu,k)f_0(\nu),$$
$$(A14)$$

where

$$L(\nu,m,\alpha) = \int_1^\infty \exp(-2\alpha\lambda)(\lambda^2 - 1)^{\nu/2}\lambda^m d\lambda,$$

$$U(\nu,j) = \int_{-1}^1 (1 - \mu^2)^{\nu/2}\mu^j d\mu, \qquad (A15)$$

$$f_0(\nu) = \int_{-\pi}^\pi \int_{-\pi}^\pi \cos^\nu(\varphi_1 - \varphi_2)d\varphi_1 d\varphi_2.$$

When ν is odd, $f_0(\nu)$ is zero, so that $Z(\nu,m,n,j,k,0)=0$.

For case (b), we substitute Eq. (A7) into Eq. (A9) and obtain the Z value written in the form

$$Z(\nu,m,n,j,k,-1) = \sum_{\tau=0}^{\infty} \sum_{N=0}^{\infty} D(\tau,N)R(\tau,\nu,N,j)R(\tau,\nu,N,k)$$
$$\times H(\tau,\nu,N,m,n,\alpha)f(\nu,N), \qquad (A16)$$

where

$$D(\tau,N) = D_\tau^N,$$

$$R(\tau,\nu,N,j) = \int_{-1}^1 (1 - \mu^2)^{\nu/2}P_\tau^N(\mu)\mu^j d\mu,$$

$$H(\tau,\nu,N,m,n,\alpha) = \int_1^\infty \int_1^\infty \exp[-2\alpha(\lambda_1 + \lambda_2)]$$
$$\times \lambda_1^m\lambda_2^n[(\lambda_1^2 - 1)(\lambda_2^2 - 1)]^{\nu/2}$$
$$\times P_\tau^N\left(\frac{\lambda_1}{\lambda_2}\right)Q_\tau^N\left(\frac{\lambda_2}{\lambda_1}\right)d\lambda_1 d\lambda_2$$
$$= \int_1^\infty d\lambda_1 \int_1^{\lambda_1} d\lambda_2 \exp[-2\alpha(\lambda_1 + \lambda_2)]$$
$$\times (\lambda_1^m\lambda_2^n + \lambda_1^n\lambda_2^m)[(\lambda_1^2 - 1)(\lambda_2^2 - 1)]^{\nu/2}$$
$$\times P_\tau^N(\lambda_2)Q_\tau^N(\lambda_1)$$

$$f(\nu,N) = \int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\cos^{\nu}(\varphi_1 - \varphi_2)\cos N(\varphi_1 - \varphi_2)d\varphi_1 d\varphi_2,$$

$$\text{(A17)}$$

and D_{τ}^{N} is given by Eq. (A8). In Eq. (A16), we have two infinite summations, but they actually reduce to finite sums because of the following reasons. It is nonzero only when (1) $\tau \geq N$, from the properties of the Legendre P functions, (2) $N \leq \nu$ from the property of the function $f(\nu,N)$, and (3) $\tau \leq j+\nu$ from the property of $R(\tau,\nu,N,j)$. Further since these variables are all non-negative integers, Eq. (A16) is rewritten as

$$Z(\nu,m,n,j,k,-1) = \sum_{N=0}^{\nu}\sum_{\tau=N}^{\min(j,k)+\nu} D(\tau,N)R(\tau,\nu,N,j)R(\tau,\nu,N,k)$$

$$\times H(\tau,\nu,N,m,n,\alpha)f(\nu,N), \quad \text{(A18)}$$

where $\min(j,k)$ means the smaller value of j and k.

The functions appearing in Eqs. (A14) and (A18) are all calculated with the MAPLE program [18], for example, so that the Hamiltonian integral H_{ij} and the overlap integral S_{ij} are expressed by a linear combination of $Z(0,m,n,j,k,l)$. Thus, after the diagonalization of the secular equation, $\mathbf{HC}=E\mathbf{SC}$, one obtains the energy E and the coefficient vector $\mathbf{C}$.

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