





Solving the Schrödinger equation of atoms and molecules using one- and two-electron integrals only

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A variational theory called free-complement (FC) s_{ij} theory for solving the Schrödinger equation of atoms and molecules using only one- and two-electron integrals over Slater or Gaussian functions is proposed. It is derived from the scaled Schrödinger equation [Phys Rev. Lett. **93**, 030403 (2004)] by replacing the two-electron part r_{ij} of the scaling g operator with $s_{ij} = r_{ij}^2$, both of which solve the divergence difficulty inherent to the original Schrödinger equation by avoiding the interelectron collisions. The s_{ij} function can be rewritten with only one-electron functions so that when the initial wave function of the FC theory is composed of only one-electron functions, the FC wave function including s_{ij} can be rewritten with only one-electron functions. Therefore, the variational calculations of the FC s_{ij} theory can be performed with only one- and two-electron integrals. However, in comparison with the r_{ij} function, the s_{ij} function behaves less efficiently when two electrons come close to each other: the electron-electron cusp condition is not satisfied with the FC s_{ij} theory, though the wave function has explicit r_{ij} dependence. On the other hand, the electron-nuclear cusp condition is satisfied, even with the Gaussian functions, for the presence of the electron-nuclear function r_{iA} in the g operator. Test applications of the FC s_{ij} theory were done to He, Li, and the $^5S^o$ sp^3 state of carbon atom and to hydrogen molecule using the local-molecular orbital (MO)- and valence bond (VB)-type initial functions. We examined both Slater and Gaussian functions. As the order of the FC theory increased, the wave functions were improved and the energies approached from a few kcal/mol to less than 1 kcal/mol accuracies relative to the known exact values. Thus, with the FC s_{ij} theory, the Schrödinger equation was solved to less than 1 kcal/mol accuracy for all the systems examined. The costs for the s_{ij} calculations were much smaller than those of the r_{ij} theory. However, for the $^5S^o$ sp^3 state of the carbon atom, we observed that the convergence rate became slow when the calculation came close to ~ 1 kcal/mol accuracy. This suggests that for the FC s_{ij} theory, the calculations would become easier if the required accuracy is within a few kcal/mol for the absolute energy. Actually, what we need in chemical studies are mostly related to the difference energy, whose accuracy could be better than that of the absolute energy with the robust variational method. Two lines of future studies were suggested.

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I. INTRODUCTION

Since the Schrödinger equation (SE) given by

$$(H - E)\psi = 0, \quad (1)$$

$$H = -\sum_i \frac{1}{2} \Delta_i - \sum_A \frac{1}{2} \Delta_A - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}}, \quad (2)$$

is a governing principle of chemical science [1], a goal or a starting point of quantum chemistry is to establish a general method of solving the SE. With this aim, starting from the study of the structure of the exact wave function [2], our research has been focused on finding the method of solving the SE as accurately and as easily as possible [3–9]. A reason why the SE was left unsolved for about 80 years since its discovery lay in the divergence difficulty of the integrals of

the Hamiltonian of Eq. (2) in the variational calculations [3]. To overcome this difficulty, one of the authors introduced in 2004 the scaled SE (SSE) [3] given by

$$g(H - E)\psi = 0, \quad (3)$$

where the scaling operator g was defined by

$$g = \sum_{i,A} r_{iA} + \sum_{i<j} r_{ij}. \quad (4)$$

This operator is always positive except for the colliding points r_0 , and even at r_0 , this operator does not eliminate the information of the Hamiltonian since

$$\lim_{r \rightarrow r_0} gV \neq 0, \quad (5)$$

where V is the electron-nuclear attraction and electron-electron repulsion potentials in the Hamiltonian given by Eq. (2); we assume here Born-Oppenheimer (BO) approximation, though our theory is applicable also to the non-BO case [10]. For these natures of the g operator, the SE and the SSE has the same set of solutions: we can divide SSE by g without affecting the solutions. So, we solve the SSE instead of the SE. Then, we do not meet the divergence difficulty of

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the integrals. The general method of solving the SE and SSE was formulated in several variants [4]. Among them, a simple way of solving the SSE is to use the simplest ICI (iterative complement interaction) formula [3,4,6] given by

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n, \quad (6)$$

which leads to the exact solutions of the SE (or SSE) at convergence.

A more efficient method, originally called free ICI [3] and renamed later as the free-complement (FC) method [6], was formulated from Eq. (6). Starting from some initial function ψ_0 , we apply the simplest ICI method as given by Eq. (6) to the order $n + 1$. Then, from the right-hand side of Eq. (6), we select all the independent analytical functions, throw out all the diverging functions, collect the rest that are referred to as complement functions (cf's) $\{\phi_I\}$, give independent coefficients $\{c_I\}$ to all of them, and we obtain the expression of the FC wave function written as

$$\psi_{n+1} = \sum_{I=0}^M c_I \phi_I. \quad (7)$$

The cf ϕ_I is the function of r_{iA} and r_{ij} and is written by

$$\phi_I = f_I(r_{iA}, r_{ij})\phi_0, \quad (8)$$

with $\phi_0 = \psi_0$ and $f_0 = 1$. This FC wave function becomes potentially exact as n increases, and the structure of the FC wave function is related to the theory published in 1985 [11]. Thus, when we calculate the coefficients $\{c_I\}$ using the variational principle, we can get the essentially exact solutions of the SE. For example, for the helium atom, we could obtain the energy that was accurate to over 40 digits [12] and the essentially exact nature of the solutions was demonstrated from the flatness of the local energy plane $H\psi(r)/\psi(r)$ [13]. For the hydrogen molecule, the FC theory gave highly accurate results [3,14]. Recently, we have reported essentially exact potential curves for the ground and many excited states of different symmetries and reported the vibrational levels of many different electronic states [15]. Recently, we could obtain highly accurate wave functions for the ground and many excited states of Li and Be atoms [16].

However, in the variational calculations of larger molecules, the integral evaluations become difficult for the cf's including r_{ij} functions: they cause three-, four-, and even more-electron integrals. When we use the local Schrödinger equation (LSE) method [5], instead of the variational principle, we become free from the integral evaluations and we could obtain highly accurate solutions of the SE using the sampling-type methodology for the first-row atoms and small molecules [5–7,9]. It was also shown that the effect of the Pauli principle decays exponentially as the distance of the electron pair increases and using this fact, the interexchange (*i*Exg) theory was proposed [7]. Combined with the *i*Exg theory, the FC theory for solving the SE was applied to large systems like He fullerene [7], and further simplifications were formulated for the FC theory to be applied to large and even giant molecular systems [8].

In this paper, we consider a different method of solving the SE, using the variational principle: the robust nature of the variational method is very attractive. The above method

includes the two-electron r_{ij} terms in the wave function. This is an origin of the high accuracy of the theory, but at the same time, it caused a difficulty in the variational method in the evaluation and handling of the three-, four-, etc., electron integrals. In contrast, popular quantum-chemical programs handle usually only one- and two-electron integrals, though they usually do not handle highly accurate wave functions close to the Schrödinger accuracy. In this paper, we propose a variational theory for solving the SE accurately by using one- and two-electron integrals only. Test applications of the proposed method will be performed for the He and Li atoms, the 5S (sp^3) state of the carbon atom, and the hydrogen molecule. Then, some concluding remarks will be given.

II. FREE-COMPLEMENT s_{ij} THEORY

When we use the variational method for solving the FC theory explained above, we have to evaluate the integrals originating from the g operator given by Eq. (4). The first r_{iA} term caused no problem since it is a one-electron function, but the second r_{ij} term did, as explained above, because it is a two-electron function. To relax this problem, we here consider the possibility of using the g operator given by

$$g = \sum_{i,A} r_{iA} + \sum_{i<j} s_{ij}, \quad s_{ij} = r_{ij}^2. \quad (9)$$

The first one-electron term is the same, but the second two-electron term is different. Like the r_{ij} function, the s_{ij} function can eliminate the divergence difficulty caused by the electron-electron repulsion potential in the Hamiltonian. However, the s_{ij} function would be less efficient than the r_{ij} function, since s_{ij} is smaller than r_{ij} when two electrons i and j are in the “colliding” region less than ~ 1 au. Further, the product of the s_{ij} term and the potential $1/r_{ij}$ becomes zero at the colliding position $r_{ij} = 0$, destroying the relation given by Eq. (5). Nevertheless, the reason of introducing the s_{ij} function instead of r_{ij} lies in a valuable merit that s_{ij} is transformed into the one-electron functions alone as

$$\begin{aligned} s_{ij} &= r_{ij}^2 = x_{ij}^2 + y_{ij}^2 + z_{ij}^2 \\ &= (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \\ &= r_i^2 + r_j^2 - 2x_i x_j - 2y_i y_j - 2z_i z_j, \end{aligned} \quad (10)$$

where the last two lines include only one-electron functions. Our initial function ψ_0 is composed of only one-electron functions. So, when we use the s_{ij} function, instead of the r_{ij} function, all the cf's $\{\phi_I\}$ of the FC theory are composed of only one-electron functions. Then, the Hamiltonian and overlap integrals between the cf's necessary for the variational calculations are all written within the one- and two-electron integrals [the two-electron integrals come from the interelectron potential $1/r_{ij}$ in the Hamiltonian given by Eq. (2)]. We refer to this theory as the FC s_{ij} theory and the original one as the FC r_{ij} theory. Like Eq. (8), the cf's of the FC s_{ij} theory are written as

$$\phi_I = f_I(r_{iA}, s_{ij})\phi_0. \quad (11)$$

Now, let us examine the FC s_{ij} theory from a general theoretical standpoint of solving the SE. As explained above, the s_{ij} operator is expected to be less efficient than the r_{ij}

operator. In particular, it does not satisfy Eq. (5) for the interelectron repulsion potential V_{e-e} , so that the s_{ij} operator erases the information of the SE at $r_{e-e} = 0$. This means that the electron-electron cusp condition given by

$$\left. \frac{\partial \bar{\psi}}{\partial r_{ij}} \right|_{r_{ij}=0} = \lambda \psi(r_{ij} = 0), \quad (12)$$

where $\bar{\psi}$ on the left-hand side is the spherically averaged wave function around $r_{ij} = 0$, is not satisfied for the wave function calculated by the FC s_{ij} theory. The value of λ should be 1/2 and 1/4, respectively, for the singlet and triplet electron-electron pairs, but it is calculated to be 0 with the FC s_{ij} theory. However, we note that the wave function of the FC s_{ij} theory includes the explicit dependence of r_{ij} in the form of s_{ij} , so that the value of $\partial\psi/\partial r_{ij}$ is not necessarily zero except at the electron-electron collisional points. On the other hand, when the wave function does not include the explicit r_{ij} function, the value of $\partial\psi/\partial r_{ij}$ is zero everywhere.

The FC s_{ij} theory satisfies the electron-nuclear cusp condition which is important since the electron-nuclear attraction potential becomes attractively infinite at the cusp region. The r_{iA} function in the g operator of Eq. (9) helps to satisfy the electron-nuclear cusp condition even when we use the Gaussian functions.

On the other hand, the electron-electron cusp condition should be less important than the electron-nuclear cusp condition since at the cusp region, the electron-electron repulsion energy becomes infinitely large so that the probability of the occurrence of the electron-electron collision must be small. Particularly, for the same spin pair, the probability should be zero from the Pauli principle. Nevertheless, the $e-e$ cusp condition should be important for the theory close to the exact level.

Different from the r_{ij} function, the s_{ij} function is written in some different expressions of the one-electron functions like Eq. (10). In the variational s_{ij} calculations, we can utilize this fact by relaxing the different elements. For example, we may handle the $r_i^2 + r_j^2$ part and the $x_i x_j + y_i y_j + z_i z_j$ part independently, and in molecules, we may handle the x , y , and z parts independently. With such relaxations, we can get a lower energy than otherwise. In the applications below, we adopted this relaxation method.

Since the computational merit of the FC s_{ij} theory that only one- and two-electron integrals are necessary in the variational calculations is so attractive over the demerit, we will examine in this paper how well this theory solves the SE for some small systems.

III. FC s_{ij} CALCULATIONS WITH SLATER AND GAUSSIAN FUNCTIONS

We perform the FC s_{ij} calculations using both Slater and Gaussian functions. Efficient integral evaluation methods for these functions are available in the literature [17–19]. For atoms, we used our own program for integral evaluations [20] and for the hydrogen molecules, we used the SMILES program [21] for Slater functions and our own program [22] for Gaussian functions.

The cf's $\{\phi_I\}$ of the FC wave function are produced from the simplest ICI wave function given by Eq. (6) by the procedure written under Eq. (6). The change caused by the replacement of r_{ij} with s_{ij} is only that when we have r_{ij} with this procedure, we have to replace it with s_{ij} . As shown before in the applications of the FC theory to the hydrogen atom using both Slater and Gaussian functions [23], the Gaussian functions produce a larger number of cf's than the Slater functions, mainly through the kinetic operator in the Hamiltonian. For the hydrogen atom, the number of the cf's was three times larger with the Gaussians than with the Slaters, but the results were similar when compared in the same order; the results were slightly better with the Gaussians than with the Slaters [23].

When we use the initial function composed of the Gaussian function, $x_i^l y_i^m z_i^n \exp(-\beta r_i^2)$, the FC theory introduces the unusual one-electron Gaussian functions $r_i x_i^l y_i^m z_i^n \exp(-\beta r_i^2)$, which we call the r -Gauss function, including the r_i function originating from the g operator: we need to consider only r_i instead of r_i^k since in the cases of $k = 2n + 1$, the usage of $r_i^2 = x_i^2 + y_i^2 + z_i^2$ transforms them into the above simple r -Gauss formula. In the FC formulation, the presence of the r -Gauss function is essential to realize the results of the Schrödinger accuracy: for example, the electron-nuclear cusp condition is satisfied due to the presence of the r -Gauss function as shown previously [23]. The one-center integrals including r -Gauss functions are easily calculated, but most of the multicenter integrals are not known. Therefore, for the multicenter integrals including the r -Gauss function, we used the Gaussian-expansion method [24] due originally to Oohata, Taketa, and Huzinaga [25]. Since the electron-nuclear cusp condition is mostly related to the one-center atomic integrals, the values of the electron-nuclear cusps in molecules are scarcely affected by the accuracy of this Gaussian expansion method.

From the expression of the s_{ij} operator given by Eq. (10), we understand that the FC s_{ij} calculations will require the cf's with higher angular momentum functions. For the calculations of atoms, this does not cause any problem. However, for molecules, this causes a problem since most molecular quantum-chemical programs available have limits on the highest angular quantum numbers. This is true for both Gaussian and Slater programs. Therefore, for the present FC s_{ij} calculations, we have to improve the codes so as to adapt to higher angular momentum integrals [22]. The theoretical efforts on this subject are found in the literature for both Slater [26] and Gaussian [27] functions.

Now, let us apply the FC s_{ij} theory to the helium atom. We used both Slater and Gaussian functions. As the initial functions, we used two doubly occupied $1s$ orbitals of different exponents: $1s^{(k)} = \exp(-\alpha_{1s,k} r)$ and $1s^{(k)} = \exp(-\alpha_{1s,k} r^2)$ ($k = 1, 2$) for Slaters and Gaussians, respectively. We generated the cf's of the FC theory using the procedure described below of Eq. (6). At each order of the FC theory, we optimized only the two exponents $\alpha_{1s,1}$ and $\alpha_{1s,2}$ included in ϕ_0 commonly to all the cf's involved, which we referred to as “double-zeta” optimization. The results are summarized in Table I. Initially at $n = 0$, the Gaussian functions were much worse than the Slater functions, since it was composed of only two primitive Gaussian functions. As the order n increased,

TABLE I. Free-complement s_{ij} theory applied to He atom using optimized double-zeta Slater and Gaussian functions.^a

Slater function				Gaussian function			
n	M	Energy (a.u.)	$\Delta E = E_{\text{FC}} - E_{\text{exact}}$ (kcal/mol)	n	M	Energy (a.u.)	$\Delta E = E_{\text{FC}} - E_{\text{exact}}$ (kcal/mol)
0	2	-2.847 656	35.183	0	2	-2.473 516	269.959
1	6	-2.886 147	11.030	1	14	-2.886 477	10.823
2	14	-2.901 524	1.381	2	64	-2.902 432	0.811
3	26	-2.902 698	0.644	3	164	-2.903 234	0.307
4	44	-2.903 167	0.349			(cf selection)	
		(cf selection)		3	23	-2.899 100	2.901 (<3)
4	8	-2.899 141	2.876 (<3)	27	-2.900 712	1.890 (<2)	
	9	-2.900 571	1.979 (<2)	38	-2.902 148	0.989 (<1)	
	15	-2.902 342	0.867 (<1)	42	-2.902 311	0.887 (<0.9)	
	17	-2.902 568	0.725 (<0.8)	45	-2.902 451	0.799 (<0.8)	
	18	-2.902 626	0.689 (<0.7)	47	-2.902 655	0.671 (<0.7)	
	21	-2.902 802	0.578 (<0.6)	52	-2.902 795	0.583 (<0.6)	
	23	-2.902 950	0.486 (<0.5)	60	-2.902 951	0.485 (<0.5)	
	28	-2.903 088	0.399 (<0.4)	73	-2.903 096	0.394 (<0.4)	
Exact		-2.903 724 ^b				-2.903 724 ^b	

^aInitial functions with the double-zeta $1s$ orbitals: $\phi_0^{(k)} = (1s^{(k)})^2 \alpha \beta$ ($k = 1, 2$). The Slater orbitals used were $1s^{(k)} = \exp(-\alpha_{1s,k} r)$ with the optimized sets of $(\alpha_{1s,1}, \alpha_{1s,2}) = (1.688, 1.688), (1.947, 3.365), (1.818, 3.546), (2.203, 4.262), (2.508, 5.012)$ for $n = 0$ to 4: at $n = 0$, the optimized values of $\alpha_{1s,1}$ and $\alpha_{1s,2}$ became equal to the value of α_{1s} of the single-zeta case. The Gaussian orbitals used were $1s^{(k)} = \exp(-\alpha_{1s,k} r^2)$ using the optimized sets of $(\alpha_{1s,1}, \alpha_{1s,2}) = (0.552, 2.087), (0.417, 0.904), (0.328, 2.713), (0.326, 3.779)$ for $n = 0 - 3$.

^bExact energy from Ref. [12].

the number of the cf's, M increases, and the energies for both Slater and Gaussian functions were improved and quickly approached the exact value [12]. The differences from the exact energy ΔE became smaller than 1 kcal/mol at $n = 3$ and $n = 2$ with the Slater and Gaussian functions, respectively. Note that at this accurate level, the Gaussian functions worked better than the Slater functions when compared in the order of the FC calculations.

After obtaining the chemical accuracy, we performed the cf-selection method: we examined the energetic contribution of each cf included in the wave function, and ordered them in the energetic contribution. With this method, we can find the smallest set of the cf's necessary for the desired accuracy. Then, we can reproduce the chemical accuracy with the smaller number of the cf's. This cf-selection method is explained in the Appendix.

We applied the cf-selection method to the $n = 4$ Slater results and to the $n = 3$ Gaussian results. It was shown that for obtaining the accuracy of 3 kcal/mol relative to the exact energy, 8 Slater and 23 Gaussian cf's were necessary, for the 2 kcal/mol accuracy, 9 Slater, and 27 Gaussian cf's, for the 1 kcal/mol accuracy (chemical accuracy), 15 Slater, and 38 Gaussian cf's, for the 0.8 kcal/mol accuracy, 17 Slater, and 45 Gaussian cf's, and so forth. Generally, the Gaussians requires two to three times more cf's than the Slaters. We can compare the present results of the s_{ij} theory to those of the r_{ij} theory [12] and we find that the s_{ij} theory is less efficient than the r_{ij} theory, though the calculations are easier with the s_{ij} theory.

We next applied the FC s_{ij} theory to the Li atom using both Slater and Gaussian functions and the results were summarized in Table II. We used two sets of $(1s)^2(2s)^1$ functions with $1s = \exp(-\alpha_{1s} r)$ and $2s = r \exp(-\alpha_{2s} r) - d \exp(-\alpha_{2s} r)$ for the Slater case having different sets of exponents and coeffi-

cient d as given in the footnote of the table. For Gaussians, the functions were of the type $\exp(-\alpha r^2)$ but others were essentially the same. As seen from Table II, the difference from the exact energy ΔE approaches rapidly from a few kcal/mol to less than 1 kcal/mol; the chemical accuracy was obtained at $n = 4$ with the Slater functions and at $n = 3$ with the Gaussian functions. Again, the order n necessary to obtain the chemical accuracy was smaller with the Gaussians than with the Slaters. When we apply the cf-selection method after obtaining the chemical accuracy, we see that the chemical accuracy was realized with the selected 37 cf's for the Slater case and with the selected 164 cf's for the Gaussian case, which are much smaller than the total numbers of the cf's at the orders 4 and 3, respectively, for the Slater and Gaussian cases, respectively.

Thus, with the FC s_{ij} theory, we could obtain chemical accuracy for both Slater and Gaussian cases. From the order n , Gaussian was more efficient than Slater as we observed earlier for the hydrogen atom [23]. However, the number of the cf's is larger with the Gaussians than with the Slaters, since with the former, the cf's are generated not only from the potential operators in the Hamiltonian, but also from the kinetic operators, in the procedures described from Eqs. (6) and (7). When we compare the results of the FC s_{ij} theory with those of the FC r_{ij} theory, we see that the former is less efficient than the latter: the result of the r_{ij} method can be seen for Li from our recent paper [16] from the ground-state line of Table VIII. The FC r_{ij} theory gave more compact descriptions than the FC s_{ij} theory.

We next apply the FC s_{ij} theory to solving the SE of the $5S^0(sp^3)$ state of the carbon atom. This state is not only the most important state of the carbon atom, which is the most important element in chemistry and biology, but also a hot subject in the variational computational quantum chemistry.

TABLE II. Free-complement s_{ij} theory applied to Li atom using optimized double-zeta Slater and Gaussian functions.^a

Slater function				Gaussian function			
n^b	M	Energy (a.u.)	$\Delta E = E_{\text{FC}} - E_{\text{exact}}$ (kcal/mol)	n	M	Energy (a.u.)	$\Delta E = E_{\text{FC}} - E_{\text{exact}}$ (kcal/mol)
0	2	-7.419 190	36.941	0	2	-6.586 026	559.760
1	10	-7.458 890	12.029	1	34	-7.444 839	20.846
2	36	-7.474 094	2.489	2	322	-7.475 776	1.433
3	100	-7.476 270	1.123	3	1666	-7.477 270	0.496
4	222	-7.476 932	0.707			(cf selection)	
	(cf selection)			3	73	-7.473 416	2.914 (<3)
4	17	-7.473 381	2.936 (<3)	102		-7.474 909	1.977 (<2)
	22	-7.475 025	1.904 (<2)	164		-7.476 472	0.997 (<1)
	37	-7.476 489	0.986 (<1)	181		-7.476 627	0.899 (<0.9)
	43	-7.476 628	0.898 (<0.9)	202		-7.476 786	0.799 (<0.8)
	64	-7.476 791	0.797 (<0.8)	231		-7.476 949	0.697 (<0.7)
				312		-7.477 105	0.599 (<0.6)
				872		-7.477 264	0.499 (<0.5)
Exact		-7.478 060 ^b				-7.478 060 ^b	

^aInitial functions using double-zeta $1s$ and $2s$ orbitals: $\phi_0^{(k)} = (1s^{(k)})^2 \alpha \beta (2s^{(k)}) \alpha$ ($k = 1, 2$). The Slater orbitals used were $1s^{(k)} = \exp(-\alpha_{1s,k} r)$, $2s^{(k)} = r \exp(-\alpha_{2s,k} r) - d_k \exp(-\alpha_{2s,k} r)$ with the optimized sets $(\alpha_{1s,1}, \alpha_{2s,1}, d_1, \alpha_{1s,2}, \alpha_{2s,2}, d_2) = (2.689, 0.677, 0.4605, 2.700, 0.865, 0.2730), (3.038, 0.696, 0.5011, 5.179, 0.690, 0.4211), (2.897, 0.746, 0.4747, 5.541, 0.671, 0.2266), (3.023, 0.843, -6.8742, 6.330, 0.681, 0.2842), (3.390, 0.895, -5.4772, 7.656, 0.686, 0.4515)$ for $n = 0 - 4$. The Gaussian orbitals used were $1s^{(1)} = \exp(-\alpha_{1s,1} r^2)$, $2s^{(1)} = r \exp(-\alpha_{2s,1} r^2) - d_1 \exp(-\alpha_{2s,1} r^2)$, $1s^{(2)} = \exp(-\alpha_{1s,2} r^2)$, $2s^{(2)} = r \exp(-\alpha_{2s,2} r^2) - d_2 \exp(-\alpha_{2s,2} r^2)$ with the optimized sets $(\alpha_{1s,1}, \alpha_{2s,1}, d_1, \alpha_{1s,2}, \alpha_{2s,2}, d_2) = (1.445, 0.0628, -4.9078, 5.457, 0.0654, -0.3614), (1.072, 0.0643, -3.7342, 2.536, 0.0677, -0.4632), (0.826, 0.0633, -10.768, 3.967, 0.0798, 0.04690), (0.802, 0.0635, -13.2310, 5.123, 0.0590, -1.1715)$ for $n = 0 - 3$.

^bExact energy from Ref. [16].

To the best of our knowledge, Noga *et al.* [28] used the CCSD(T)-F12 method and Brown *et al.* [29] used the quantum Monte Carlo method for the 3P ground state and we used the FC-LSE method for the 3P and $^5S^o$ states of the carbon atom [9], all methods being nonvariational. Recently, Strasburger [30] performed the variational calculations for the 3P and $^5S^o$ states with the symmetry-projected, explicitly correlated Gaussian lobe method and reported for the $^5S^o$ state the energy lower by 0.751 mH than the value estimated from the experimental value [9].

We performed the FC s_{ij} calculations for the carbon $^5S^o sp^3$ configuration $(1s)^2(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1$ using the Slater functions only and the results were summarized in Table III. The calculations here are basically similar to those shown in Tables I and II: we optimized two sets of the parameters $(\alpha_{1s}, \alpha_{2s}, d, \alpha_{2p})$ commonly to all the cf's involved. After step 5, since the numbers of the cf's to be handled are larger than those of the above two cases, we used the cf-selection step before increasing the order n of the calculations to keep the size of the calculations feasible. We note that we have two reference exact energies, one estimated from the NIST experimental values [31,32] and the other the lowest variational energy reported by Strasburger [30], which are referred to as $eE-a$ and $eE-b$, respectively, where “ eE ” denotes the exact energy.

From step 0 to step 5, we performed the FC calculations increasing both r_i and s_{ij} operators or only r_i operators, optimizing the two sets of the parameters $(\alpha_{1s}, \alpha_{2s}, d, \alpha_{2p})$. We obtained the result of 2.60 kcal/mol accuracy relative to $eE-a$ or of 3.07 kcal/mol relative to $eE-b$. Then, we applied the cf-selection method to make the size of the wave function

smaller and then increased the order n . With the cf-selection method, we reduced the size from 3930 cf's of step 5 to the important 615 cf's at the energy of 3.00 kcal/mol above the $eE-a$. Then, we applied r_i and s_{ij} operators and obtained $M = 4452$ cf's whose ΔE was 1.45 kcal/mol above the $eE-a$. Next, we reduced the cf size by the cf-selection method to $M = 1133$ and then relaxed the radial and angular elements of the s_{ij} operators obtaining 5059 cf's whose ΔE was 1.248 kcal/mol above the $eE-a$. Then, we selected 1490 important cf's and applied the r_i and relaxed $s_{1s,1s}$ operators since the intra- $1s$ correlations seemed to be important and obtained 9387 cf's whose ΔE was 0.740 kcal/mol above the $eE-a$ and 1.211 kcal/mol above $eE-b$. Then, we reduced the number of the cf's to 2102 by the cf-selection method and applied r_i and relaxed $s_{1s,1s}$ operators and obtained the energy $-37.690 224$ au which is 0.487 kcal/mol above $eE-a$ and 0.958 kcal/mol above the $eE-b$. We repeated the same selection and the application of the r_i and relaxed $s_{1s,1s}$ operators and obtained the energy $-37.690 418$ a.u. which is 0.365 kcal/mol above $eE-a$ and 0.837 kcal/mol above the $eE-b$. The energies obtained in the eighth and ninth steps were within the chemical accuracy from both estimates of the exact energy: this result supports strongly the variational result obtained by Strasburger as being the best variational energy of the $^5S^o(sp^3)$ state of the carbon atom so far obtained. The difference of the two energies, -37.691 au from experimental values and $-37.691 751$ from the nonrelativistic variational calculation by Strasburger, would be attributed to the relativistic and other effects [16]. We note that the costs for the FC s_{ij} calculations were much smaller than that of the r_{ij} calculations, even though the calculational process of Table III was far from smart.

TABLE III. Free-complement s_{ij} theory applied to the $^5S^o$ sp^3 state of carbon atom using optimized double-zeta Slater functions.^a

Step	Operation	M	Energy (a.u.)	$\Delta E = E_{FC} - E_{\text{exact}}$ (kcal/mol) ^b
0		2	-37.531 477	100.102 (100.573)
1	r_i, s_{ij}	18	-37.625 807	40.909 (41.380)
2	r_i, s_{ij}	124	-37.672 690	11.489 (11.961)
3	r_i	500	-37.681 544	5.934 (6.405)
4	r_i	1540	-37.685 353	3.543 (4.015)
5	r_i	3930	-37.686 851	2.603 (3.075)
	cf selection	615	-37.686 220	3.000 (3.471)
6	r_i, s_{ij}	4452	-37.688 684	1.453 (1.925)
	cf selection	1133	-37.688 207	1.753 (2.224)
	s_{ij} relax	5059	-37.689 012	1.248 (1.719)
	cf selection	1490	-37.688 845	1.352 (1.824)
7	r_i , relaxed $s_{1s,1s}$	9387	-37.689 821	0.740 (1.211)
	cf selection	2102	-37.689 599	0.879 (1.350)
8	r_i , relaxed $s_{1s,1s}$	13019	-37.690 224	0.487 (0.958)
	cf selection	2154	-37.689 864	0.713 (1.184)
9	r_i , relaxed $s_{1s,1s}$	13814	-37.690 418	0.365 (0.837)
9	cf selection	2942	-37.690 162	0.526 (0.997)
		3091	-37.690189	0.509 (0.980)
		3442	-37.690220	0.489 (0.960)
Exact			-37.691 ^c (-37.691 751) ^d	

^aInitial functions with double-zeta $1s$, $2s$, and $2p$ orbitals were used: $\phi_0^{(k)} = (1s^{(k)})^2 \alpha \beta (2s^{(k)} 2p_x^{(k)} 2p_y^{(k)} 2p_z^{(k)}) \alpha \alpha \alpha \alpha$ ($k = 1, 2$). The Slater orbitals used were $1s^{(k)} = \exp(-\alpha_{1s,1} r)$, $2s^{(k)} = r \exp(-\alpha_{2s,k} r) - d_k \exp(-\alpha_{2s,k} r)$, $2p_{x,y,z}^{(k)} = (x, y, z) \exp(-\alpha_{2p,k} r)$ with the optimized sets $(\alpha_{1s,1}, \alpha_{2s,1}, \alpha_{2p,1}, d_1, \alpha_{1s,2}, \alpha_{2s,2}, \alpha_{2p,2}, d_2) = (5.684, 1.748, 1.586, 0.03104, 6.218, 4.868, 1.844, 0.1861)$, $(5.482, 1.670, 2.029, 0.3312, 6.561, 2.123, 1.480, 0.2145)$, $(5.556, 1.728, 1.654, 0.2217, 10.759, 1.7634, 1.531, 0.1298)$, $(5.610, 1.953, 1.888, 0.1248, 10.983, 1.940, 1.495, 0.2677)$, $(5.523, 2.185, 2.001, -0.4849, 10.943, 1.986, 1.626, 0.2623)$, $(5.905, 2.337, 2.141, -0.8030, 11.709, 2.125, 1.740, 0.1630)$ at step = 0 – 5. For step = 6 – 9, the same set as step = 5 was used.

^b ΔE without parentheses is from footnote c and ΔE with parentheses is from footnote d.

^cExact energy estimated from the absolute ground-state energy given in Ref. [31] and the NIST experimental excitation energies of Ref. [32].

^dLowest variational energy so far obtained from Ref. [30].

We applied the cf-selection method to the result of the ninth step and the results were shown at the bottom of Table III. We obtained the chemical accuracy result against eE - b as $\Delta E = 0.997$ kcal/mol with 2941 cf's, which was much smaller than the total number of the cf's, 13 814 of step 9. Continuing further the cf-selection method, we obtained $\Delta E = 0.980$ kcal/mol with 3091 cf's and $\Delta E = 0.960$ kcal/mol with 3442 cf's. These results of the cf-selection method are useful since with the FC s_{ij} method, the results can be handled only with the one- and two-electron integrals.

Thus, we could obtain a highly accurate result close to the Schrödinger limit by using only one- and two-electron integrals with the FC s_{ij} theory. However, in comparison with the results obtained for the smaller atoms shown in Tables I and II, the convergence rate for the carbon atom became slow after step 5 reaching about 3 kcal/mol accuracy. The method of calculations after step 5 was far from smart, though it was partly due to the limitations of the computers we used. Also, the wave functions obtained at the chemical accuracy at steps 8 and 9 were not compact enough as the reference accurate atomic wave function, though the cf-selected wave functions obtained therefrom would have some value, since they are relatively compact and can be handled with one- and two-electron integrals only. However, if we can permit the required accuracy to be within a few kcal/mol for the absolute energy, the calculations of the FC s_{ij} theory would become

much easier: for the present case, we can use the result of step 5. In chemistry, what we need in most studies is the accuracy of the difference energy, not the absolute energy. For example, the heat of formation of a molecule is the difference of the absolute energy of a molecule relative to the sum of the absolute energies of the constituent atoms. So, if each absolute energy is calculated in some constant accuracy with the variational method, the accuracy of the difference energy would become better. The robust nature of the variational method is important for this type of calculations.

Now, as a last test calculation, we apply the present FC s_{ij} theory to the hydrogen molecule in the equilibrium geometry of $R = 1.4011$ au using both Slater and Gaussian functions. For the H_2 molecule, some two-center integrals including r -Gauss functions must be calculated by the Gaussian-expansion method [24] with the six-term expansion in the present case. First, we show the calculations starting from the local-molecular orbital (MO) initial wave function composed of the three local-MO functions given by

$$\begin{aligned}
 \phi_0^1 &= (1s_A + 1s_B)^2 \alpha \beta, \\
 \phi_0^2 &= (1s_A - 1s_B)^2 \alpha \beta, \\
 \phi_0^3 &= (1s_A + 1s_B)(x_A 1s_A - x_B 1s_B)(\alpha \beta - \beta \alpha),
 \end{aligned} \tag{13}$$

where $1s_{A \text{ or } B} = \exp(-\alpha r_{A \text{ or } B})$ for the Slater function and $1s_{A \text{ or } B} = \exp(-\alpha r_{A \text{ or } B}^2)$ for the Gaussian function. The first

TABLE IV. Free-complement s_{ij} theory applied to H_2 molecule starting from the MO-type initial functions using optimized double-zeta Slater and Gaussian functions.

Slater function ^a				Gaussian function ^b			
n	M	Energy (a.u.)	$\Delta E = E_{FC} - E_{\text{exact}}$ (kcal/mol)	n	M	Energy (a.u.)	$\Delta E = E_{FC} - E_{\text{exact}}$ (kcal/mol)
0	6	-1.151 301	14.543	0	6	-1.045 981	80.632
1	28	-1.169 851	2.902	1	116	-1.169 399	3.186
2	94	-1.172 934	0.968	2	710	-1.173 771	0.442
3	234	-1.1732 932	0.742				
	(cf selection)				(cf selection)		
3	14	-1.169 928	2.854 (<3)	2	53	-1.169 852	2.902 (<3)
	19	-1.171 424	1.915 (<2)		67	-1.171 347	1.963 (<2)
	33	-1.172 889	0.996 (<1)		114	-1.172 894	0.993 (<1)
	39	-1.173 045	0.898 (<0.9)		124	-1.173 046	0.897 (<0.9)
	64	-1.173 223	0.786 (<0.8)		139	-1.173 203	0.799 (<0.8)
		-1.174 476 ^c				-1.174 476 ^c	

^aThe Slater orbitals used are $1s^{(k)} = \exp(-\alpha_k r)$ ($k = 1, 2$) with the optimized exponents of $(\alpha_1, \alpha_2) = (1.272, 1.654), (1.470, 2.270), (1.344, 2.330), (1.650, 2.521)$ at $n = 0 - 3$.

^bThe Gaussian orbitals used are $1s^{(k)} = \exp(-\alpha_k r^2)$ ($k = 1, 2$) with the optimized exponents of $(\alpha_1, \alpha_2) = (0.3014, 1.1453), (0.1922, 0.6970), (0.2117, 1.4347)$ at $n = 0 - 2$.

^cExact energy from Refs. [14,15].

one of Eq. (13) is the bonding local MO, the second one is the two-electron excited configuration to the antibonding local MO, and the third one is the polarization function pair. We performed double-zeta calculations for the $1s_A$ and $1s_B$ orbitals: at each level of the calculations, two exponents α_1 and α_2 were optimized commonly to all the cf's. Since the molecule is not spherically symmetric, we relaxed the $x_i x_j$ part from the $y_i y_j + z_i z_j$ part of the expression given by the third line of Eq. (10) with x being parallel to the molecular axis. The results of the FC s_{ij} calculations starting from the local-MO initial functions are summarized in Table IV: the left-hand side is for the Slater function and the right-hand side is for the Gaussian function.

We discuss first the results for the Slater functions. Starting from the initial set of functions that was higher by 14.54 kcal/mol from the exact energy, we got at first order ($n = 1$) the accuracy of 2.90 kcal/mol, at second order 0.97 kcal/mol, and at $n = 3$, 0.74 kcal/mol accuracy, the last two being less than 1 kcal/mol accuracy (chemical accuracy). By performing the cf selection for the $n = 3$ wave function, we found that the chemical accuracy was achieved with 33 cf's in contrast to 94 cf's of the second-order wave function.

We next discuss the results of the Gaussian functions. The first impression of the results was that the energy of the initial function was very poor: the ΔE value was 80.6 kcal/mol above the exact value. This is because they are the results of two primitive Gaussian functions. However, even from such a crude initial wave function, when we apply the FC s_{ij} theory, the accuracy was improved at $n = 1$ to $\Delta E = 3.19$ kcal/mol, which was close to the result of the Slater function, and at $n = 2$, the result reached already the chemical accuracy of $\Delta E = 0.44$ kcal/mol. In comparison with the Slater functions, the results of the Gaussian functions were good if we compare at the same order, however the number of the cf's were much larger with the Gaussians than with the Slaters. When we applied the cf-selection method to the second-order result, the chemical accuracy was obtained with the 114 cf's; though this

number is much smaller than 710 of $n = 2$, it is still about three times larger than the Slater-function case. Thus, as far as the compactness is concerned, the Slater functions are much better than the Gaussian functions. This is the general trend that could be seen also from Tables I and II for He and Li atoms, respectively.

Next, we applied the present FC s_{ij} theory to the valence bond (VB)-type initial functions of the H_2 molecule given by

$$\begin{aligned}
 \phi_0^1 &= 1s_A 1s_B (\alpha\beta - \beta\alpha), \\
 \phi_0^2 &= [(1s_A)^2 + (1s_B)^2] \alpha\beta, \\
 \phi_0^3 &= (x_A 1s_A 1s_B - 1s_A x_B 1s_B) (\alpha\beta - \beta\alpha), \\
 \phi_0^4 &= x_A 1s_A x_B 1s_B (\alpha\beta - \beta\alpha),
 \end{aligned} \tag{14}$$

where $1s_{A \text{ or } B} = \exp(-\alpha r_{A \text{ or } B})$ for the Slater function and $1s_{A \text{ or } B} = \exp(-\alpha r_{A \text{ or } B}^2)$ for the Gaussian function. ϕ_0^1 represents the covalent function, ϕ_0^2 the ionic function, ϕ_0^3 the polarization function, and ϕ_0^4 the double polarization function. Table V shows the results. In this calculation, we handled ϕ_0^1 as being the zeroth-order function and the other three functions as first-order functions: the cf's at order n of Table V is the sum of the order n cf's produced from ϕ_0^1 and the order $(n - 1)$ cf's produced from ϕ_0^2, ϕ_0^3 , and ϕ_0^4 .

When we use the Slater-type functions, we could get accuracy of less than 2 kcal/mol at order 2 with 34 cf's and the chemical accuracy at $n = 3$ as $\Delta E = 0.74$ kcal/mol. By applying the cf-selection method to the order 3 result, we found that actually only 30 cf's were necessary for getting the chemical accuracy. We also showed the results for the higher accuracies. The right-hand side of Table V gives the results for the Gaussian functions. Though the energy of the covalent double-zeta Gaussian functions were very crude ($\Delta E = 89.7$ kcal/mol), the FC theory improved the energy to $\Delta E = 1.62$ kcal/mol at $n = 1$ and we could get the chemical accuracy already at $n = 2$. Probably, this is due to the fact that we had a much larger number of functions with the Gaussians than with the Slaters as we have seen similar trends in Tables I and II.

TABLE V. Free-complement s_{ij} theory applied to H_2 molecule starting from the VB-type initial functions using optimized double-zeta Slater and Gaussian functions.

Slater function ^a				Gaussian function ^b			
n	M	Energy (a.u.)	$\Delta E = E_{FC} - E_{\text{exact}}$ (kcal/mol)	n	M	Energy (a.u.)	$\Delta E = E_{FC} - E_{\text{exact}}$ (kcal/mol)
0	2	-1.141 658	20.593	0	2	-1.031 520	89.706
1	12	-1.161 817	7.944	1	32	-1.171 887	1.624
2	34	-1.171 340	1.968	2	286	-1.173 088	0.871
3	72	-1.173 289	0.745	3	1597	-1.173 939	0.337
	(cf selection)				(cf selection)		
3	14	-1.170 109	2.740 (<3)	3	43	-1.169 774	2.951 (<3)
	15	-1.171 647	1.775 (<2)		61	-1.171 325	1.977 (<2)
	30	-1.172 890	0.995 (<1)		97	-1.172 884	0.999 (<1)
	39	-1.173 043	0.899 (<0.9)		103	-1.173 047	0.897 (<0.9)
	52	-1.173 203	0.799 (<0.8)		114	-1.173 205	0.797 (<0.8)
		-1.174 476 ^c				-1.174 476 ^c	

^aThe Slater orbitals used are $1s^{(k)} = \exp(-\alpha_k r)$ ($k = 1, 2$) with the optimized exponents of $(\alpha_1, \alpha_2) = (1.3056, 1.5452)$, $(1.4465, 1.7124)$, $(1.3282, 2.0011)$, $(1.6589, 2.7933)$ at $n = 0 - 3$.

^bThe Gaussian orbitals used are $1s^{(k)} = \exp(-\alpha_k r^2)$ ($k = 1, 2$) with the optimized exponents of $(\alpha_1, \alpha_2) = (0.2981, 1.0334)$, $(0.2201, 0.8791)$, $(0.2337, 1.3185)$ at $n = 0 - 2$. At $n = 3$, $(\alpha_1, \alpha_2) = (0.2337, 1.3185)$ which is the same as that of $n = 2$ is used.

^cExact energy, Refs. [14,15].

At $n = 3$, we could get a highly accurate result of $\Delta E = 0.34$ kcal/mol. When we apply the cf-selection method to this result, we see that only 97 functions were necessary for obtaining the chemical accuracy.

In comparison with the MO-type calculations shown in Table IV, the present VB-type results seem to be better than the MO-type ones for both Slater and Gaussian functions, even though the order-counting of the initial functions was favorable for the local-MO calculations.

Finally, we compare the results of the H_2 molecule with those of the He atom, both two-electron systems. From the order that is necessary to get the chemical accuracy, both calculations were roughly similar, but when we compare from the necessary numbers of the cf's for getting the chemical accuracy, the H_2 calculations were less efficient than the He calculations: for getting the similar accuracy, about a twice larger number of cf's was necessary for the H_2 calculations than for the He calculations, for both the MO-type and VB-type calculations.

IV. CONCLUSION

Based on the scaled Schrödinger equation [3], we have proposed the FC s_{ij} theory with s_{ij} being r_{ij}^2 as a variational theory that requires only one- and two-electron integrals for solving the SE in some accuracy, in contrast to the original theory referred to as the FC r_{ij} theory that requires us to evaluate three- and more-electron integrals. The s_{ij} operator can prevent the divergence difficulty of the integrals, likewise the r_{ij} operator, though s_{ij} is less efficient than r_{ij} because s_{ij} behaves less satisfactorily than r_{ij} in particular near the electron-electron cusp region. An important merit associated to s_{ij} is that it can be rewritten only with the one-electron functions as shown by Eq. (10), so that the wave function produced by the FC s_{ij} theory is composed of only one-electron functions. Therefore, the variational calculations of the FC s_{ij} theory can be performed within one- and two-

electron integrals: the two-electron integrals come from the integrals of the $1/r_{ij}$ operator included in the Hamiltonian.

Because this merit is attractive, we have examined in this paper how accurately the FC s_{ij} theory can solve the SE. By applying to the He, Li, ${}^5S^0(sp^3)$ state of the C atom and H_2 molecule using Slater and Gaussian functions, we found that as the order of the theory was increased, the variational FC s_{ij} theory improved the solutions from a few kcal/mol accuracy to the chemical accuracy of less than 1 kcal/mol error from the reference exact energy by using only one- and two-electron integrals. The convergence rates to the exact limits were slow in comparison with the FC r_{ij} calculations performed before, but the computational costs were much smaller. Judging from the order n of the FC theory, the Gaussian functions converged faster than the Slater functions, but from the number of the cf's necessary, the Slater functions were more compact than the Gaussian functions. For the ${}^5S^0(sp^3)$ state of the C atom, we could get the result that supports the recent calculations performed by Strasburger [30]: the nonrelativistic variational energy of the ${}^5S^0(sp^3)$ state of the C atom is lower than -37.691 a.u. but above -37.691751 a.u. Though the present calculation was performed as a test calculation of the FC s_{ij} theory, the result was already at a state-of-the-art level. The local-MO- and VB-type calculations of the H_2 molecule with the Slater and Gaussian functions showed similar behaviors to those performed for atoms. However, the convergence rate to the chemical accuracy was about twice slower than that for the He atom, the same two-electron system, when counted from the numbers of the necessary cf's. Thus, with the FC s_{ij} theory, we could obtain the chemical accuracy of less than 1 kcal/mol for all the systems examined here.

However, we have also observed for the ${}^5S^0(sp^3)$ state of the C atom that the convergence rate became slow when the calculation came close to ~ 1 kcal/mol accuracy: up to a few kcal/mol accuracy, the calculations were straightforward, but thereafter, the calculations were not smart. However, if we can permit the required accuracy of the FC s_{ij} calculations

to be within a few kcal/mol for the absolute energy, the calculations would become much easier. Actually, most chemical phenomena are governed by the difference energy, not the absolute energy, involved in the phenomena. Therefore, it is necessary to examine the accuracy of the difference energy in the variational calculations of the FC s_{ij} theory. If the above relaxation in the necessary accuracy of the theory is permitted, the practical calculations would become easier. The robust nature of the variational method would be helpful in doing such computational research.

Thus, we would like to suggest two lines of future studies. First, it is still very important to investigate how to improve the theory itself to obtain easily the chemical accuracy solutions of the SE for the absolute energy. Second, we must investigate how much is the accuracy of the difference energy obtained with the variational calculations of the FC s_{ij} theory applied to real chemical phenomena.

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APPENDIX: SELECTION OF IMPORTANT COMPLEMENT FUNCTIONS

After a set of the FC s_{ij} calculations, it is useful to have an efficient method of selecting the important complement functions (cf's) in the orders of their energy contributions. This is necessary for obtaining a compact set of cf's that gives some energy accuracy and for continuing the series of the FC s_{ij} calculations without making the dimensions too large for handling.

The cf-selection method is designed to produce a compact set from a diffuse one by choosing the important cf's, one by one, from the diffuse set without much loss of accuracy. As we did in the present calculations, we obtain the result of the desired accuracy, chemical accuracy for example, by increasing the order n of the FC theory with a diffuse dimension M . Then, we try to produce a compact set by the systematic selections of the cf's involved in the diffuse set. The algorithm is as follows. (i) First, we choose the initial function(s) ϕ_0 as the most important cf (set). (ii) Add i th cf ($i \neq 0$) chosen from the diffuse set to ϕ_0 , solve the eigenvalue problem of the dimension 2, and obtain the energy E_i ($i < M$). Repeat it for all the $M - 1$ candidates of the diffuse set. (iii) Select the cf ϕ_{select} that gives the largest energy lowering using the energy set $\{E_m\}$ and replace ϕ_0 by $\phi_0 + \phi_{\text{select}}$. (iv) Repeat (ii) and (iii) until we get the desired accuracy for the system. (v) When we get the desired accuracy at the k th iteration, the first $k + 1$ cf's are the compact set we want to obtain.

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