RESEARCH ARTICLE | JULY 10 2023

## Gaussian functions with odd power of r produced by the free complement theory **FREE**

Yusaku I. Kurokawa 💿 ; Hiroshi Nakatsuji 💌 💿

Check for updates

J. Chem. Phys. 159, 024103 (2023) https://doi.org/10.1063/5.0155105





**The Journal of Chemical Physics** 



11 July 2023 00:56:12

AIP Publishing **Submit Today!** 



# Gaussian functions with odd power of *r* produced by the free complement theory

Cite as: J. Chem. Phys. 159, 024103 (2023); doi: 10.1063/5.0155105 Submitted: 18 April 2023 • Accepted: 19 June 2023 • Published Online: 10 July 2023



Yusaku I. Kurokawa ២ and Hiroshi Nakatsuji® ២

### **AFFILIATIONS**

Quantum Chemistry Research Institute, Kyoto Technoscience Center 16, 14 Yoshida Kawara-machi, Sakyo-Ku, Kyoto 606-8305, Japan

<sup>a)</sup>Author to whom correspondence should be addressed: h.nakatsuji@qcri.or.jp

### ABSTRACT

We investigate, in this paper, the Gaussian (G) function with odd powers of r,  $rx^ay^bz^c \exp(-\alpha r^2)$ , called the r-Gaussian or simply the rG function. The reason we investigate this function here is that it is generated as the elements of the complement functions (cf's) when we apply the free complement (FC) theory for solving the Schrödinger equation to the initial functions composed of the Gaussian functions. This means that without the rG functions, the Gaussian set of functions cannot produce the exact solutions of the Schrödinger equation, showing the absolute importance of the rG functions in quantum chemistry. Actually, the rG functions drastically improve the wave function near the cusp region. This was shown by the applications of the present theory to the hydrogen and helium atoms. When we use the FC- $s_{ij}$  theory, in which the inter-electron function  $r_{ij}$  is replaced with its square  $s_{ij} = r_{ij}^2$  that is integrable, we need only one- and two-electron integrals for the G and rG functions. The one-center one- and two-electron integrals of the rG-NG expansion method, in which an rG function is expanded by a linear combination of the G functions. The optimal exponents and coefficients of this expansion were given for N = 2, 3, 4, 5, 6, and 9. To show the accuracy and the usefulness of the rG-NG method, we applied the FC- $s_{ij}$  theory to the hydrogen molecule.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0155105

### I. INTRODUCTION

The exact solutions of the Schrödinger equation of a hydrogenlike atom in the ground and excited states are represented by the Slater functions,

$$\chi_{STO} = r_A^n x_A^a y_A^b z_A^c \exp\left(-\alpha r_A\right), \tag{1}$$

where A denotes the center of the function. For this reason, Slater functions are thought to be better to represent the wave functions of atoms and molecules than Gaussian functions

$$\chi_{GTO} = x_A^a y_A^b z_A^c \exp\left(-\alpha r_A^2\right). \tag{2}$$

However, in the modern quantum chemistry, Gaussian functions are widely used to represent the wave functions of molecules.<sup>1–3</sup> This is because one- and two-electron integrals over the Gaussian functions can be evaluated in closed forms, while those over the Slater functions are not always possible.<sup>1–7</sup> Although some other functions such

as the Bessel functions<sup>8</sup> and the hyperbolic functions<sup>9</sup> were also proposed to represent the wave functions, we will not focus on them in this paper. For the details about the Gaussian functions, many review articles are helpful.<sup>1,6,7,10,11</sup>

The Gaussian functions are much different from the Slater functions, especially at the short (near cusp) and long-range regions.<sup>12,13</sup> To improve the behaviors of the Gaussian functions, a linear combination of the Gaussian functions has been used, such as the STO-NG expansion method<sup>14</sup> and the contracted Gaussian-type orbital (CGTO) method.<sup>15–17</sup> With such methods, the intermediate and long-range regions would be improved. However, unfortunately, any linear combination of Gaussian orbitals cannot describe the cusp correctly.<sup>18</sup> The cusp region is important, because much stabilization is expected when an electron comes very close to the nucleus. Actually, the cusp originates from the singularity of the Coulombic potential.

Based on the studies of 2000–2004, one of the authors proposed the free complete-elements (FC) theory, which is a general theory for solving the Schrödinger equation.<sup>19–29</sup> When we apply this theory to

the initial wave functions composed of the Gaussian functions with the choice<sup>27</sup> of the scaling function *g* to be *r*, we obtain the functions of the form

$$\chi_{\rm rG} = r_A^n x_A^a y_A^b z_A^c \, \exp\left(-\alpha r_A^2\right) \quad (n \neq 0). \tag{3}$$

We referred to this function with odd *n* as the *r*-Gaussian function or simply rG function: the even n function can be transformed to the sum of the conventional Gaussian functions given by Eq. (2). The rG function belongs to the class of the Gaussian functions but has an odd power term in the front. If we perform the calculations without the rG function, the converging speed of the FC method to the exact wave function becomes very slow, and the cusp condition is not satisfied, as shown below in this paper. This means that the rG functions are necessary to represent the exact, or at least accurate, wave functions. Unlike the conventional Gaussian functions given by Eq. (2), the rG functions given by Eq. (3) can describe the cusp at the origin because the first derivative of the rG function with *n* being odd is non-zero at the origin. Thus, the inclusion of the rG functions in quantum chemistry calculations is necessary for obtaining the reasonably accurate wave functions; therefore, we study in this paper the role of the rG functions in quantum chemistry and the methods of introducing the rG functions, like integral evaluations, in the quantum-chemical calculations.

This paper is organized as follows: in Sec. II, we introduce the rG function and discuss its importance for energy and properties. In Sec. III, we derive the closed formula for the one-center one- and two-electron integrals including the rG function. In Sec. IV, we use these closed formulas to calculate the hydrogen and helium atoms with the FC theory. We will compare the converging speed of the calculated energy to the exact one for the cases with and without the rG functions. In Sec. V, the multi-center integrals, including the rG function, are classified into the ones which are expressed in a closed form. In Sec. VI, we propose the rG-NG expansion method to calculate the integrals that are not expressed in a closed form. In Sec. VII, we apply the rG-NG expansion method to the hydrogen molecule with the FC theory. The summary will be given in Sec. VIII.

### **II. IMPORTANCE OF THE RG FUNCTION**

In this section, we explain how the rG function is generated from the FC theory. Then, we define the form of the rG function used in this paper. We study the behaviors of the rG function near the cusp and in the long-range region of the wave function. Then, we study the role of the rG function in satisfying the cusp condition with the Gaussian functions alone.

### A. Generation of the rG function

The rG function is necessary for producing the exact wave function within the ground of the Gaussian functions. This is clear from the fact that it is generated automatically with the FC theory, which produces the exact wave function from any approximate wave function. In the FC theory,<sup>19–29</sup> the exact wave function is expressed by a linear combination of the complement functions (cf's)  $\phi_I$  as

$$\psi = \sum_{I} c_{I} \phi_{I}. \tag{4}$$

The cf's are generated from an initial function  $\psi_0$ , according to the simplest ICI [iterative configuration (or complement) interaction] scheme of the FC formalism

$$\Psi_{n+1} = [1 + C_n g (H - E_n)] \Psi_n, \tag{5}$$

where *H* is the Hamiltonian of the system,  $E_n$  is the energy of  $\psi_n$ ,  $C_n$  is a variational parameter, *n* is called *order*, and *g* has the general form of  $g = \sum_{i,A} g_{iA} + \sum_{i,j} g_{ij}$ . The cf's are produced as the linearly independent and non-diverging analytical functions included in the right-hand side of Eq. (5).

We produce the appropriate cf's starting from the initial function  $\psi_{0}$ , which is composed of the normal Gaussian functions. With the Gaussian functions, integrability is the main concern; therefore, the appropriate choice of the scaling function is necessary. For the one-electron electron-nuclear part of the wave function, which is the main topic of this paper, we choose the scaling function as  $g_{iA} = r_{iA}$ . This choice is a "reasonable" choice, as discussed in the previous paper.<sup>27</sup> Although the choice like  $g_{iA} = 1$  $-\exp(-\gamma r_{iA})$  from the correct set of the g functions<sup>27</sup> is a good choice, it gives a mixed Slater-Gauss description and so is not appropriate here. The "approximate" choice,  $g_{iA} = 1 - \exp(-\gamma r_{iA}^2)$ may also be a good choice, but this choice is not good because then the electron-nuclear cusp-condition is not satisfied. As mentioned above, the satisfaction of the electron-nuclear cusp condition is expected to be important not only for the cusp condition itself but also from the energetic point of view for the strongly attractive electron nuclear interaction near the cusp region. Thus, we decided on the above choice of  $g_{iA} = r_{iA}$  in the present paper. The two-electron part of the *g* function,  $g_{ij}$  is not the main

subject of this paper, but some general considerations would be helpful. The first choice,  $g_{ij} = r_{ij}$  is not good for integrability. From the integrability and the Gaussian environment, the approximate function in the previous paper<sup>27</sup>  $g_{ij} = 1 - \exp(-\gamma r_{ij}^2)$  would be a good compromise: we have to abandon the electron-electron cusp condition, but in contrast to the electron-nuclear case, this condition would be less important in this case because, energetically, the electron pair is strongly repulsive; therefore a strong collision is not realistic. Another choice is  $g_{ij} = r_{ij}^2$ . With this choice, the FC theory is called FC- $s_{ij}$  theory,<sup>26</sup> in which,  $s_{ij} = r_{ij}^2$ . With this choice, the calculations can be performed using only one and two electron integrals, like in the conventional quantum chemistry theories. This is trivial because  $s_{ij} = r_{ij}^2 = (x_i - x_j)^2 + (y_i - y_j)^2$  $(z_i - z_j)^2 = r_i^2 + r_j^2 - 2x_i x_j - 2y_i y_j - 2z_i z_j$ . At least with these two choices, the FC theory with Gaussian functions can be performed by the integral method. Within the two choices described above, the first choice would be better in quality, but the second choice is easier.

### **B.** Spherical harmonic Gaussian orbital

Here, let us discuss shortly the real-valued spherical harmonic Gaussian orbital defined by

$$\chi_{SH} = S_{l,m} \exp\left(-\alpha r^2\right),\tag{6}$$

where  $S_{l,m}$  (l = 0, 1, 2, ..., m = -l, ..., l) is the spherical harmonic function defined by

11 July 2023 00:56:12

$$S_{l,m} = r^{l} P_{l}^{m} (\cos \theta) \cos m\phi,$$
  

$$S_{l,-m} = r^{l} P_{l}^{m} (\cos \theta) \sin m\phi,$$
  

$$S_{l,0} = r^{l} p_{l} (\cos \theta),$$
(7)

where,  $P_l^m$  is the associated Legendre polynomial, and  $p_l$  is the Legendre polynomial. With this orbital, the *r* term seems to exist outside the exp () term if *l* is larger than unity. However, the *r* term disappears if the spherical harmonic function is rewritten with the *x*, *y*, and *z* coordinates using the relation,

$$S_{l,m} = \sum_{i,j,k} a_{i,j,k}^{l,m} x^i y^j z^k,$$
 (8)

where the coefficient *a* is a constant depending on *l*, *m*, *i*, *j*, and k.<sup>6</sup> Thus, the spherical harmonic Gaussian is actually a sum of Gaussian functions, not including the rG function. In this paper, we do not explicitly deal with the spherical harmonic Gaussian functions.

### C. Behavior of rG at r = 0 and $r = \infty$

Here, we investigate the simplest rG function,  $\chi_{rG} = r \exp(-\alpha r^2)$ , and the simplest Gaussian function,  $\gamma_G = \exp(-\alpha r^2)$ . Their Maclaurin expansions are written as

$$\chi_{rG} = \sum_{n=0}^{\infty} \frac{(-\alpha)^n}{n!} r^{2n+1} = r - \alpha r^3 + \frac{1}{2} \alpha^2 r^5 - \cdots,$$
(9)

and

$$\mathcal{Y}_G = \sum_{n=0}^{\infty} \frac{(-\alpha)^n}{n!} r^{2n} = 1 - \alpha r^2 + \frac{1}{2} \alpha^2 r^4 - \cdots,$$
(10)

respectively. From Eq. (9), the rG function is expressed as a linear combination of r including odd powers only, and from Eq. (10), the Gaussian function is a linear combination of r with even powers only. This is in contrast to the Slater function

$$\Psi_S = \exp\left(-r\right),\tag{11}$$

whose Maclaurin expansion is

$$\Psi_S = \sum_{n=0}^{\infty} \frac{\left(-r\right)^n}{n!} = 1 - r + \frac{1}{2}r^2 - \frac{1}{6}r^3 + \cdots,$$
(12)

that includes terms with both odd and even powers of r.

The first derivative of the rG function is

$$\frac{d\chi_{rG}}{dr} = \exp\left(-\alpha r^2\right) - 2\alpha r^2 \exp\left(-\alpha r^2\right), \tag{13}$$

and the value of the first derivative at the origin is

$$\left. \frac{d\chi_{rG}}{dr} \right|_{r=0} = 1. \tag{14}$$

On the other hand, the first derivative of the Gaussian function is

$$\frac{d\gamma_G}{dr} = -2\alpha r \exp\left(-\alpha r^2\right),\tag{15}$$

and its value at the origin is

J. Chem. Phys. **159**, 024103 (2023); doi: 10.1063/5.0155105 Published under an exclusive license by AIP Publishing

$$\left. \frac{d\gamma_G}{dr} \right|_{r=0} = 0. \tag{16}$$

This is the reason why the Gaussian functions do not satisfy the electron-nucleus (e-n) cusp condition,<sup>18</sup>

$$\left. \frac{\partial \hat{\psi}}{\partial r} \right|_{r=0} = -Z\psi(r=0), \tag{17}$$

where *Z* is the charge of the nucleus. The value of the rG function at the origin is zero,  $\chi_{rG}(\mathbf{r} = 0) = 0$ , which also implies that the rG function alone does not satisfy the e-n cusp condition.<sup>18</sup> We will show in Sec. II D how the rG function satisfies the cusp condition.

At the limit of  $r \to \infty$ , both the rG and Gaussian functions converge to zero,  $\chi_{rG} \to 0$  and  $\gamma_G \to 0$ , respectively. The converging speed of the rG function is slower (i.e., expanding) than the Gaussian function since  $\chi_{rG}/\gamma_G = r > 0$ , but is more rapid than the Slater function.

### D. Gaussian functions that satisfy cusp condition

Let us take a linear combination of the Gaussian and rG functions as

$$\chi = \exp\left(-\alpha_1 r^2\right) - Cr \, \exp\left(-\alpha_2 r^2\right). \tag{18}$$

Its Maclaurin expansion,

$$\chi = 1 - Cr - \alpha_1 r^2 + C \alpha_2 r^3 + \cdots,$$
 (19)

includes the terms with both odd and even powers of *r*. Since  $\frac{d}{dr}\chi|_{r=0} = -C$  and  $\chi(r=0) = 1$ , Eq. (18) satisfies the n-e cusp condition if C = Z. Note that this holds true with the arbitrary exponents  $\alpha_1$  and  $\alpha_2$ . If either of the simple Gaussian or rG functions does not exist, the cusp condition is never satisfied. In Fig. 1, the Gaussian, Slater, and the function  $\chi$  given by Eq. (18) with C = 1,  $\alpha_1 = 1$ , and  $\alpha_2 = 2$  are plotted.



**FIG. 1.** Plots of the Gaussian function  $\chi_1 = \exp(-r^2)$ , the linear combination of the Gaussian and rG functions  $\chi_2 = \exp(-\alpha_1 r^2) - Cr \exp(-\alpha_2 r^2)$  [Eq. (18) with  $\alpha_1 = 1, \alpha_2 = 2, C = 1$ ], and the Slater function  $\chi_3 = \exp(-r)$ .

If we express the Slater function [Eq. (11)] by a linear combination of the rG functions (n = 0, 1, 2, 3, ...) with  $\alpha = 1$ , it becomes

$$\Psi_S \simeq \sum_{n=0}^{\infty} c_n r^n \exp\left(-r^2\right),\tag{20}$$

where the coefficients are  $c_0 = 1, c_1 = -1, c_2 = 3/2, c_3 = -7/6$ , and  $c_4 = 25/24, \ldots$  Since  $\Psi_S(r=0) = c_0 = 1$  and  $\frac{d}{dr}\Psi_S|_{r=0} = c_1$ = -1 = -Z, Eq. (20) satisfies the cusp condition. Note that the function whose first derivative at the origin is nonzero among the functions of  $r^n \exp(-r^2)$  (n = 0, 1, 2, 3, ...) is only when n = 1; therefore, the rG function (n = 1) is necessary to form the cusp. Only the first two terms (n = 0 and 1) are necessary to satisfy the relation as expected by the cusp value. The other terms would have different values to represent the exact wave function, keeping the relations as expected by the higher order cusp conditions, as we studied before.<sup>30,31</sup> For general atoms, this would be true.

### **III. MOLECULAR INTEGRALS**

Some wave functions that behave correctly at the cusp region have been proposed: for instance, the Jastrow factor multiplied by the Gaussian function in the quantum Monte Carlo (QMC) studies,<sup>32</sup> improvement of molecular Gaussian functions over small regions,<sup>33</sup> and the explicitly correlated Gaussian (ECG) functions with an odd power of r.<sup>34</sup> Unfortunately, the closed form integral formulas for these wave functions are not known except for some limited cases. Harris derived the recurrence relations for the explicitly correlated Gaussian functions with odd powers of r.<sup>35</sup> However, as noted in his paper that "odd powers cause great difficulty in integral evaluation," the integration over the rG function for a general molecule is still difficult.3

Thus, the integrals over the rG functions are the key point that makes them useful for variational calculations. Among the molecular integrals, including the rG function, the most important integrals, i.e., the one-center one- and two-electron integrations, are always possible and expressed in a closed form, which will be shown in this section. We do not discuss the integrals, including only Gaussian functions, since they are already known.<sup>1-</sup>

#### A. One-center one-electron integral

The one-center one-electron integral over the rG functions,  $\chi = r^n x^a y^b z^c \exp\left(-\alpha r^2\right)$   $(n = 0, 1, 2, \ldots)$ , is written as

$$\begin{aligned} \langle \chi | \hat{O} | \chi' \rangle &= \int r^n x^a y^b z^c \exp\left(-\alpha r^2\right) \hat{O} r^{n'} x^{a'} y^{b'} z^{c'} \\ &\times \exp\left(-\alpha' r^2\right) dx dy dz, \end{aligned}$$
(21)

where the operator  $\hat{O}$  is  $\hat{O} = 1$ , 1/r, or  $-\frac{1}{2}\Delta$  for the overlap, nuclear attraction, and kinetic integrals, respectively. For the overlap integral, the right-hand side (rhs) of Eq. (21) can be written as

$$I(n, a, b, c, \alpha) = \int r^n x^a y^b z^c \exp\left(-\alpha r^2\right) dx dy dz, \qquad (22)$$

where n, a, b, c, and  $\alpha$  of Eq. (22) are n + n', a + a', b + b', c + c', and  $\alpha + \alpha'$  of Eq. (21), respectively. For the nuclear attraction integral, Eq. (21) is written again as Eq. (22) where *n*, *a*, *b*, *c*, and  $\alpha$  in Eq. (22) are n + n' - 1, a + a', b + b', c + c', and  $\alpha + \alpha'$  in Eq. (21), respectively. When we operate  $\Delta$  on  $\chi$  for the kinetic integral, we get

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\chi = \left[\frac{n(n-2)}{r^2} + \frac{nk}{r^2} + \frac{a(a-1)}{x^2} + \frac{b(b-1)}{y^2} + \frac{c(c-1)}{z^2} - 4\alpha n - 2\alpha k + 4\alpha^2 r^2\right]\chi \quad (23)$$

where k = 2(a + b + c) + 3. Equation (23) implies that the kinetic integral is written as a linear combination of Eq. (22) with n, a, b, and c changed. Thus, all the one-center one-electron integrals are written as the linear combination of Eq. (22). The detailed derivation to evaluate Eq. (22) is written in Appendix A, and the result is as follows:

(i) when *n* is odd,

$$I(n, a, b, c, \alpha) = I(-1, a, b, c, \alpha) \times \frac{1}{\alpha^m} \times d(d+1)(d+2)\cdots(d+m-1), \qquad (24)$$

where  $I(-1, a, b, c, \alpha)$  is

$$I(-1, a, b, c, \alpha) = \frac{C}{8\alpha^d} \frac{\Gamma(d)}{\Gamma(12+d)} \Gamma\left(\frac{1}{2}(a+1)\right) \\ \times \Gamma\left(\frac{1}{2}(b+1)\right) \Gamma\left(\frac{1}{2}(c+1)\right),$$
(25)

 $C = \left[1 + (-1)^{a} + (-1)^{b} + (-1)^{c} + (-1)^{a+b} + (-1)^{a+c} + (-1)^{b+c}\right]$  $+(-1)^{a+b+c}$ , m=(1+n)/2, and  $d=1+\frac{1}{2}(a+b+c)$ , where C is eight when all of a, b, and c are even, and is zero otherwise.

when *n* is even, (ii)

$$I(n, a, b, c, \alpha) = I(0, a, b, c, \alpha) \times \frac{1}{\alpha^m} \times d(d+1)(d+2)\cdots(d+m-1),$$
(26)

where  $I(0, a, b, c, \alpha)$  is

$$I(0, a, b, c, \alpha) = \frac{C}{8\alpha^d} \Gamma\left(\frac{1}{2}(a+1)\right) \Gamma\left(\frac{1}{2}(b+1)\right) \Gamma\left(\frac{1}{2}(c+1)\right)$$
(27)  
with  $d \equiv \frac{3}{2} + \frac{1}{2}(a+b+c)$ .

### B. One-center two-electron integral

Using the rG functions,  $\chi_i \equiv r^{n_i} x^{a_i} y^{b_i} z^{c_i} \exp(-\alpha_i r^2)$ , the onecenter two-electron integral,  $I_{ijkl} \equiv \langle \chi_i(1)\chi_j(2)|\frac{1}{r_{12}}|\chi_k(1)\chi_l(2)\rangle$ , is written explicitly as

$$I_{a_{1}b_{1}c_{1}n_{1},a_{2}b_{2}c_{2}n_{2},\alpha\beta} \equiv \int r_{1}^{n_{1}}x_{1}^{a_{1}}y_{1}^{b_{1}}z_{1}^{c_{1}} \\ \times \exp\left(-\alpha r_{1}^{2}\right)\frac{1}{r_{12}}r_{2}^{n_{2}}x_{2}^{a_{2}}y_{2}^{b_{2}}z_{2}^{c_{2}} \\ \times \exp\left(-\beta r_{2}^{2}\right)dx_{1}dy_{1}dz_{1}dx_{2}dy_{2}dz_{2}, \quad (28)$$

where  $n_1 = n_i + n_k$ ,  $a_1 = a_i + a_k$ ,  $b_1 = b_i + b_k$ ,  $c_1 = c_i + c_k$ , and  $\alpha = \alpha_i + \alpha_k$ , and similarly for  $n_2$ ,  $a_2$ ,  $b_2$ ,  $c_2$ , and  $\beta$ . The derivation to

ARTICLE

calculate Eq. (28) is written in Appendix B, and the results are as follows:

$$I_{a_1b_1c_1n_1,a_2b_2c_2n_2,\alpha\beta} = \lim_{L \to \infty} \sum_{l=0}^{L} A(l, a_1b_1c_1, a_2b_2c_2) \\ \times R(l, a_1b_1c_1n_1, a_2b_2c_2n_2, \alpha, \beta),$$
(29)

where the angular part A is

$$A(l, a_{1}b_{1}c_{1}, a_{2}b_{2}c_{2})$$

$$= \frac{1}{2^{l}}\sum_{k=0}^{\lfloor l/2 \rfloor} (-1)^{k} \frac{(2l-2k)!}{k!(l-k)!(l-2k)!} \sum_{n_{a}=0}^{l-2k} \sum_{n_{b}=0}^{l-2k-n_{a}} \frac{(l-2k)!}{n_{a}!n_{b}!n_{c}!}$$

$$\times T(a_{1}+b_{1}+n_{a}+n_{b}+1, c_{1}+n_{c})P(b_{1}+n_{b}, a_{1}+n_{a})$$

$$\times T(a_{2}+b_{2}+n_{a}+n_{b}+1, c_{2}+n_{c})P(b_{2}+n_{b}, a_{2}+n_{a})$$
(30)

with

$$T(m,n) \equiv \int_0^{\pi} \sin^m \theta \cos^n \theta d\theta = \frac{1 + (-1)^n}{2} \frac{\Gamma((m+1)/2)\Gamma((n+1)/2)}{\Gamma((m+n+2)/2)}$$
(31)

and

$$P(m,n) \equiv \int_{0}^{2\pi} \sin^{m} \phi \cos^{n} \phi d\phi$$
  
=  $\frac{\left[1 + (-1)^{n}\right] \left[1 + (-1)^{m}\right]}{2} \frac{\Gamma((m+1)/2)\Gamma((n+1)/2)}{\Gamma((m+n+2)/2)},$   
(32)

and the radial part R is

 $R(l, a_1b_1c_1n_1, a_2b_2c_2n_2, \alpha, \beta) = R'(l, a_1b_1c_1n_1, a_2b_2c_2n_2, \alpha, \beta)$  $+ R'(l, a_2b_2c_2n_2, a_1b_1c_1n_1, \beta, \alpha).$ (33)

Here we define  $d_i \equiv a_i + b_i + c_i + n_i + 2$  (i = 1, 2). The value of R' can be calculated differently when  $d_1 + l$  is odd or even, as follows:

- (i) When  $d_1 + l$  is odd, let us define  $m_1 \equiv (d_1 + l - 1)/2$ .
- (i-1) when  $d_1 + d_2$  is even In this case,  $d_2$ -*l* is always odd, and *R'* can be calculated as

$$R'(l, a_{1}b_{1}c_{1}n_{1}, a_{2}b_{2}c_{2}n_{2}, \alpha\beta) = -\frac{1}{2}\sum_{k=0}^{m_{1}} \frac{m_{1}!}{(m_{1}-k)!\alpha^{k+1}} \frac{(2m_{2}-1)!!}{2^{m_{2}+1}} \frac{\sqrt{\pi}}{\sqrt{(\alpha+\beta)^{2m_{2}+1}}} + \frac{m_{1}!}{2\alpha^{m_{1}+1}} \frac{(2m_{3}-1)!!}{2^{m_{3}+1}} \frac{\sqrt{\pi}}{\beta^{2m_{3}-1}}$$
(34)

with  $m_2 = (d_1 + d_2 - 2 - 2k)/2$  and  $m_3 = (d_2 - l - 1)/2$ . (i-2) when  $d_1 + d_2$  is odd

In this case, R' can be calculated as

$$R'(l, a_1b_1c_1n_1, a_2b_2c_2n_2, \alpha, \beta) = -\frac{1}{4}\sum_{k=0}^{m_1} \frac{m_1!}{(m_1 - k)!\alpha^{k+1}} \frac{m_2!}{(\alpha + \beta)^{m_2 + 1}} + \frac{m_1!}{2\alpha^{m_1 + 1}} \frac{m_3!}{2\beta^{m_3 + 1}}$$
(35)

with 
$$m_2 = (d_1 + d_2 - 3 - 2k)/2$$
 and  $m_3 = (d_2 - l - 2)/2$ .

- (ii) When  $d_1 + l$  is even, let us define  $m_1 \equiv (d_1 + l)/2$ .
- (ii-1) when  $d_1 + d_2$  is even In this case, R' can be calculated as

 $R'(l,a_1b_1c_1n_1,a_2b_2c_2n_2,\alpha,\beta)$ 

$$= -\sum_{k=0}^{m_1-1} \frac{(d_1+l-1)!!}{2^{k+1}\alpha^{k+1}(2m_1-2k-1)!!} \frac{(2m_2-1)!!\sqrt{\pi}}{2^{m_2+1}(\alpha+\beta)^{(2m_2+1)/2}} + \frac{(2m_1-1)!!\sqrt{\pi}}{2^{m_1+1}\alpha^{m_1}\sqrt{\alpha}} E(d_2-l-1,\alpha,\beta)$$
(36)

with  $m_2 \equiv (d_1 + d_2 - 2 - 2k)/2$ , where the function *E* is defined as

$$E(n,\alpha,\beta) \equiv \int_{r=0}^{\infty} r^n er f(\sqrt{\alpha}r) \exp\left(-\beta r^2\right) dr.$$
(37)

See Appendix C for the evaluation of the function E in Eq. (37).

(ii-2) when  $d_1 + d_2$  is odd

In this case, R' can be calculated as

 $R'(l, a_{1}b_{1}c_{1}n_{1}, a_{2}b_{2}c_{2}n_{2}, \alpha, \beta) = -\sum_{k=0}^{m_{1}-1} \frac{(d_{1}+l-1)!!}{2^{k+1}\alpha^{k+1}(2m_{1}-2k-1)!!} \frac{m_{2}!}{2(\alpha+\beta)^{m_{2}+1}} + \frac{(2m_{1}-1)!!\sqrt{\pi}}{2^{m_{1}+1}\alpha^{m_{1}}\sqrt{\alpha}} E(d_{2}-l-1, \alpha, \beta)$ (38)

with  $m_2 = (d_1 + d_2 - 3 - 2k)/2$ . See Appendix C for the evaluation of the function *E*.

### IV. APPLICATION TO THE HYDROGEN AND HELIUM ATOMS

In this section, we use the normal Gaussian function as the initial wave function of the FC theory and apply the variational principle. The target system here is the hydrogen and helium atoms because all the integrals required are expressed in a closed form. The details of the FC theory were explained elsewhere.<sup>19–29</sup>

### A. Application to the hydrogen atom 1. Calculation with rG functions

The initial wave functions we employed here were simple Gaussian functions,  $\phi_0^1 = \exp(-\alpha r_1^2)$  and  $\phi_0^2 = r_1^2 \exp(-\alpha r_1^2)$ , where the latter function is generated when the  $\phi_0^1$  is differentiated by the exponent  $\alpha$ . It can decrease the  $\alpha$  dependence on the initial function. The g function was set as the inverse of the Coulombic potential,  $g = r_1$ . The complement functions (cf's) generated by the FC theory were  $\{r^0, r^1, r^2, r^3, r^5\} \times \exp(-\alpha r_1^2)$  (M = 5) at order n = 1,  $\{r^0, r^1, r^2, r^3, r^4, r^5, r^6, r^8\} \times \exp(-\alpha r_1^2)$  (M = 8) at order n = 2, and  $\{r^0, \ldots, r^{3n}, r^{3n+2}\} \times \exp(-\alpha r_1^2)$  at order  $n (n = 1, 2, 3, \ldots)$ , where the number of the cf's M was M = 3n + 2. From order n = 1, the rG function  $r^1 \exp(-\alpha r_1^2)$  was generated by the FC theory.

| Order <i>n</i> | $M^{a}$ | Optimal $\alpha^{b}$ | Total energy (au)    | $\Delta E (\text{kcal/mol})^{c}$ | Cusp value |
|----------------|---------|----------------------|----------------------|----------------------------------|------------|
|                |         |                      | With rG functions    |                                  |            |
| 0              | 2       | 0.282 942            | -0.42441318157839    | 47.431                           | 0.0        |
| 1              | 5       | 0.215723             | -0.49958629341505    | 0.260                            | -0.836678  |
| 2              | 8       | 0.136 482            | -0.49999216922977    | $4.913 \times 10^{-3}$           | -0.971019  |
| 3              | 11      | 0.115731             | -0.49999998478251    | $9.538 \times 10^{-6}$           | -0.997 952 |
| 4              | 14      | 0.088 564 3          | -0.49999999974948    | $1.883 \times 10^{-7}$           | -0.999702  |
| 5              | 17      | 0.0841721            | -0.49999999999941    | $3.702 	imes 10^{-10}$           | -0.999694  |
|                |         |                      | Without rG functions |                                  |            |
| 0              | 2       | 0.282 942            | -0.42441318157839    | 47.431                           | 0.0        |
| 1              | 2       | 0.282 942            | -0.42441318157839    | 47.431                           | 0.0        |
| 2              | 5       | 0.487 134            | -0.48660767061344    | 8.404                            | 0.0        |
| 3              | 5       | 0.487 134            | -0.48660767061344    | 8.404                            | 0.0        |
| 4              | 8       | 0.559 442            | -0.49229141570777    | 4.837                            | 0.0        |
| 5              | 8       | 0.559 442            | -0.49229141570777    | 4.837                            | 0.0        |
| 6              | 11      | 0.685074             | -0.49664613044047    | 2.105                            | 0.0        |
| 7              | 11      | 0.685074             | -0.49664613044047    | 2.105                            | 0.0        |
| 8              | 14      | 0.742 184            | -0.49759013133312    | 1.512                            | 0.0        |
| 9              | 14      | 0.742 184            | -0.49759013133312    | 1.512                            | 0.0        |
| 10             | 17      | 0.849087             | -0.49861405213097    | 0.870                            | 0.0        |
| Exact          |         |                      | -0.50000000000000    |                                  | -1.0       |

TABLE I. The energy of the hydrogen atom calculated with and without the cf's including the rG functions generated by the FC theory.

<sup>a</sup>The number cf's.

<sup>b</sup>The exponent used in the cf's.

<sup>c</sup>The difference from the exact energy.

Table I shows the total energy of the hydrogen atom calculated with these cf's, where the exponents  $\alpha s$  in the cf's were common and optimized at each order, and  $\Delta E$  is the difference from the exact energy.

At order n = 1, a very accurate energy of  $\Delta E = 0.260$  kcal/mol, which satisfies the chemical accuracy ( $\Delta E < 1$  kcal/mol), with only five cf's. As the order increases, the total energy and the cusp value converge to the exact values and the optimal exponent becomes smaller. This can be understood that as the order increases, the cusp region is described better and better by the rG function, while the long-distance regions are described better and better by the small exponents because both rG and Gaussian functions with small exponents can describe the long regions. Here, the exponent  $\alpha$  was optimized commonly for all functions, but it may be optimized succeeding for the functions generated at each order. Finally, we note that these improvements are not only due to the rG functions but also due to all the cf's generated by the FC theory.

### 2. Calculation without rG functions

Here, we removed the rG functions such as  $r^n \exp(-\alpha r^2)$ (*n*: odd) from the cf's generated above. Then the cf's at order one became identical to those at order zero, as  $\{r^0, r^2\} \times \exp(-\alpha r_1^2)$ (*M* = 2). Similarly, the cf's at order *n* and *n* + 1 (*n*: even) became identical. Using these cf's without  $r^n \exp(-\alpha r^2)$  (*n*: odd), we calculated the energy of the hydrogen atom, as shown in Table I.

Without the rG functions, the converging speed was extremely slow: at order ten (twice of five of the result with the rG functions),  $\Delta E$  became 0.870 (<1) kcal/mol with 17 functions, including up tor<sup>32</sup> exp ( $-\alpha r^2$ ). The cusp values were zero since Gaussian functions alone cannot express the cusp. The optimized exponent became much larger as the order increased, in contrast to the results with the rG functions, where rG functions were included in the calculation. This implies that the cf's without rG functions try to describe the cusp region by using large exponents. The long-distance regions were described by the large power of *r*, even though without odd powers. These results clearly show the importance of the rG functions to describe the exact wave function of the hydrogen atom. The FC theory naturally generates such functions and leads us to the exact wave function.

### B. Application to the helium atom

### 1. Calculation with rG functions

We next applied the FC theory to the helium atom. The initial wave function was taken as  $\phi_0^1 = \exp(-\alpha r_1^2 - \alpha r_2^2)$  and  $\phi_0^2 = (r_1^2 + r_2^2) \exp(-\alpha r_1^2 - \alpha r_2^2)$ , similarly to the hydrogen atom case: the latter function was generated by differentiating  $\phi_0^1$  by  $\alpha$ . The *g* function was a linear combination of the inverse of the Coulombic potential,  $g = r_1 + r_2 + r_{12}$ . Generating the cf's according to the FC scheme, we obtained the cf's that have the form of  $\phi = \hat{A}r_1^a r_2^b r_{12}^c \exp(-\alpha r_1^2 - \alpha r_2^2)$ , where  $\hat{A}$  is the anti-symmetrizer, and *a*, *b*, and *c* are nonnegative integers. We calculated the energy of the helium atom with these cf's, as shown in Table II.

At order zero, the total energy is very high ( $\Delta E = 378.223$  kcal/mol), but as the order increased, the energy rapidly improved

| Order <i>n</i> | $M^{a}$ | Optimal $\alpha^{b}$ | Total energy (au)    | $\Delta E (\text{kcal/mol})^{c}$ | Cusp value |
|----------------|---------|----------------------|----------------------|----------------------------------|------------|
|                |         |                      | With rG functions    |                                  |            |
| 0              | 2       | 0.3836               | -2.300 987           | 378.223                          | 0.0        |
| 1              | 14      | 0.3094               | -2.892648            | 6.950                            | -1.584     |
| 2              | 46      | 0.2114               | -2.903384            | 0.214                            | -1.920     |
| 3              | 108     | 0.1748               | -2.903714            | $6.51 \times 10^{-3}$            | -1.989     |
|                |         |                      | Without rG functions |                                  |            |
| 0              | 2       | 0.3836               | -2.300987            | 378.223                          | 0.0        |
| 1              | 6       | 0.5777               | -2.593 150           | 194.888                          | 0.0        |
| 2              | 19      | 0.6486               | -2.767 562           | 85.443                           | 0.0        |
| 3              | 36      | 0.7126               | -2.795 921           | 67.648                           | 0.0        |
| 4              | 69      | 0.7636               | -2.832854            | 44.472                           | 0.0        |
| Exact          |         |                      | -2.903724            |                                  | -2.0       |

TABLE II. The energy of the helium atom calculated with and without the cf's including the rG functions generated by the FC theory.

ârri 1 (?

<sup>a</sup>The number cf's.

<sup>b</sup>The exponent used in the cf's.

<sup>c</sup>The difference from the exact energy.

and became converging to the exact energy variationally. Actually, at order two, we got a chemical accuracy of  $\Delta E = 0.214$  (<1) kcal/mol with 46 cf's including the rG functions. The optimized exponent became smaller as the order increased, which implies that the long-range regions were improved at higher order: the cusp region was already improved with the rG functions.

### 2. Calculation without rG functions

Next, we removed the rG functions such as  $\phi = \hat{A}r_1^a r_2^b r_{12}^c \exp(-\alpha r_1^2 - \alpha r_2^2)$  with *a* or/and *b* being odd from the cf's generated above, i.e., cf's with both *a* and *b* are even are used. However, the cf's with *c* being odd were not removed. The energy calculated with these cf's is shown in Table II.

As the order increased, the total energy became lower, but the speed was very slow: even at order four, the energy was still as high as  $\Delta E = 44.472$  kcal/mol with the remaining 69 functions and without the rG functions. This is in sharp contrast to the calculations where the rG functions were included in the manner of the FC theory. Similarly to the hydrogen-atom case, the optimal exponent became larger and larger as the order increased, which implies that the cf's without the rG functions are very poor to describe the cusp region. Actually, the cusp values were all zeros. Thus, we understand

that the rG function is very important to describe the exact wave function.

### 3. Comparison with Full CI

For comparison, we carried out the Full CI calculations of the helium atom with the well-optimized Gaussian basis set series, augccpVXZ (X = D, T, Q, and 5), which include CGTOs with various values of exponents but do not include the rG functions and the  $r_{12}$  terms. As shown in Table III, a full CI energy of 1842 configurations with the aug-cc-pV5Z gives  $\Delta E = 0.259$  kcal/mol, which is worse than an FC energy of  $\Delta E = 0.214$  kcal/mol at order two with only 46 cf's. These results imply that the rG functions that are produced by the FC theory are of critical importance to describe the exact wave function, rather than using the CGTOs with various exponents.

### V. MULTI-CENTER ONE- AND TWO- ELECTRON INTEGRALS

The multi-center integrals over the rG functions are not known in the closed form, unlike the popular Gaussian functions. Here, the "closed form" means that the integral is written by a finite number of elementary functions (including the exponential and error functions).

| TABLE III Full CLenergy   | of the helium ator | n with the well-ontimized | Gaussian basis functions |
|---------------------------|--------------------|---------------------------|--------------------------|
| TABLE III. Full OF energy |                    | i wiui uie weii-opuinizeu | Gaussian basis iuncuons. |

| Basis set   | Number of basis functions | Number of configurations $M$ | Energy (au) | $\Delta E$ (kcal/mol) | Cusp value |
|-------------|---------------------------|------------------------------|-------------|-----------------------|------------|
| aug-cc-pVDZ | 9                         | 24                           | -2.889 548  | 8.896                 | 0.0        |
| aug-cc-pVTZ | 23                        | 144                          | -2.900836   | 1.812                 | 0.0        |
| aug-cc-pVQZ | 55                        | 554                          | -2.902720   | 0.630                 | 0.0        |
| aug-cc-pV5Z | 105                       | 1842                         | -2.903 312  | 0.259                 | 0.0        |
| Exact       |                           |                              | -2.903 724  |                       | -2.0       |

#### TABLE IV. Integrals including rG functions which are expressed in a closed form.

| Туре                               | Integrals <sup>a</sup>   |
|------------------------------------|--|
| One-center one-electron integral   | $\langle \eta_A   \hat{O}   \eta_A' \rangle$ ( $\hat{O} = 1, \frac{1}{r_A}, -\frac{1}{2}\Delta$ )  |
| One-center two-electron integral   | $\left\langle \eta_A \eta_A'  ight _{	au_{12}}^1 \left  \eta_A'' \eta_A'''  ight angle$  |
| Two-center one-electron integral   | $\langle \chi_A    \gamma_B  angle, \langle \chi_A   \Delta   \gamma_B  angle,  \langle \chi_A   rac{1}{r_A}   \eta_B  angle,  \langle \chi_A   rac{1}{r_B}   \chi_A  angle$   |
| Two-center two-electron integral   | $\left\langle \chi_A \chi_B \right  \tfrac{1}{r_{12}} \left  \chi_A' \chi_B' \right\rangle, \left\langle \chi_A \gamma_C \right  \tfrac{1}{r_{12}} \left  \chi_A' \gamma_D \right\rangle \left( (\text{C, D}) = (\text{A, B}), (\text{B, B}), (\text{B, A}) \right)$ |
| Three-center two-electron integral | $\langle \chi_A \gamma_B   \frac{1}{r_{12}}   \chi_A' \gamma_C \rangle$ (C $\neq$ A, B)  |

<sup>a</sup> The  $\chi$  and  $\gamma$  represent the rG and Gaussian functions, respectively. The  $\eta$  is either  $\chi$  or  $\gamma$ . The subscripts A, B, C, and D of  $\chi$  and  $\gamma$  represent the center of the orbital.

| TABLE V | <ol> <li>Integrals, in</li> </ol> | ncluding the r | G function, | that are not | t expressed | in a c | losed | form. |
|---------|-----------------------------------|----------------|-------------|--------------|-------------|--------|-------|-------|
|---------|-----------------------------------|----------------|-------------|--------------|-------------|--------|-------|-------|

| Туре  | Integrals <sup>a</sup>  |
|---|---|
| Two-center one-electron integral            | $\langle \chi_A   \chi_B  angle, \langle \chi_A   \Delta   \chi_B  angle, \langle \chi_A   \frac{1}{r_B}   \gamma_A  angle, \langle \chi_A   \frac{1}{r_B}   \gamma_B  angle$   |
| Three-center one-electron integral          | $\langle \chi_A   rac{1}{r_C}   \chi_B  angle, \langle \chi_A   rac{1}{r_C}   arphi_B  angle$   |
| Two-center two-electron integral            | $\left\langle \chi_A \eta_C \big  \frac{1}{r_{12}} \big  \gamma_A \eta_D \right\rangle ((C, D) = (A, B), (B, B), (B, A)), \left\langle \chi_A \eta_C \big  \frac{1}{r_{12}} \big  \gamma_B \eta_D \right\rangle (C, D = A \text{ or } B)$ |
| Three- or four-center two-electron integral | $\left\langle \chi_A \eta_B \right  \frac{1}{r_{12}} \left  \eta_C \eta_D \right\rangle \left( (\text{C},\text{D}) \neq (\text{A},\text{A}), (\text{A},\text{B}), (\text{B},\text{B}), (\text{B},\text{A}) \right)$                       |

<sup>a</sup>The  $\chi$  and  $\gamma$  represent the rG and Gaussian functions, respectively. The  $\eta$  is either  $\chi$  or  $\gamma$ . The subscripts A, B, C, and D of  $\chi$  and  $\gamma$  represent the center of the orbital.

The one-center one- and two-electron integrals are expressed in a closed form, as shown in Secs. III A, and III B. The two-center (namely A and B) one-electron integral cannot be expressed in a closed form if the integrant has both  $r_A^n$  and  $r_B^m$  terms (*n* and *m* are odd including -1) outside the exp functions. Only when the  $1/r_A$ term of the nuclear attraction potential cancels the  $r_A^n$  term (*n* is odd), the one-electron integral can be expressed in a closed form. The three-center one-electron integral, including the rG function, cannot be expressed in a closed form.

The two-, three-, and four-center (namely *A*, *B*, *C*, and *D*) twoelectron integral with the rG functions cannot be expressed in a closed form generally because the integrant includes more than two kinds of odd powers of  $r_A$ ,  $r_B$ ,  $r_C$ ,  $r_D$ , or  $r_{12}$ . Only when the bra and ket functions have the rG functions with the same center and the same electron number, the two-electron integral can be done in a closed form because the two rG functions with the same center give the normal Gaussian function (even power of r). In such case, the integral is three-centered or two-centered one. In Table IV, the Hamiltonian integrals that can be expressed in a closed form are listed, where the  $\chi$  and  $\gamma$  represent the rG and Gaussian functions, respectively, and  $\eta$  is either  $\chi$  or  $\gamma$ . In Table V, the Hamiltonian integrals that cannot be expressed in a closed form, to the authors' best knowledge, are listed.

### VI. rG-NG EXPANSION

As explained in Sec. V, the integral including the rG function is not always written in a closed form. A possible way to do such integrations is to use the expansion method of the rG functions with ordinary Gaussian functions. We call this method the rG-NG expansion method, like the STO-NG expansion method of O-ohata, Taketa, and Huzinaga.<sup>14</sup> By expanding the rG function(s) in the integrand by Gaussian functions, the integrand is expressed as a linear combination of normal Gaussian functions, and then we can always perform the integration.

We calculate the integrals analytically when it is possible and by the expansion method when the complete analytical method is not known. Even in the latter case, the integral values are accurate when we use the expansion number *N*, which is not too small, as will be shown later. We can calculate the cusp values from our original wave function composed of the G and rG functions, giving the nonzero cusp values corresponding to the qualities of the wave functions used.

Note that we replace the rG part in the integrand with the NGexpanded Gaussian functions only when we calculate the integrals shown in Table V. We do not replace the rG wave function itself by the expanded functions. Thus, the wave function, including the rG function, does not lose the cusp. Even though the rG part in the integrant is replaced with the Gaussian functions, the integral value does not change so much, as shown in this section, since the volume around the cusp is very small.

### A. Least square fitting of the rG function

First, let us express the simplest rG function,  $r \exp(-r^2)$ , by a linear combination of *N* Gaussian functions (*N* = 2, 3, 4...),

11 July 2023 00:56:12

| Coefficient             | α                     | Norm                | Coefficient/norm   |
|-------------------------|-----------------------|---------------------|--------------------|
|                         | Ν                     | <i>V</i> = 2        |                    |
| -0.821 947 686 546      | 2.430 284 026 359     | 1.387 244 036 443   | -0.592 504 033 143 |
| 1.012758684238          | 0.822 936 412 214     | 0.615 793 075 984   | 1.644 641 233 778  |
|                         | Ν                     | <i>V</i> = 3        |                    |
| -0.231 132 200 153      | 9.229 168 980 590     | 3.773 827 462 243   | -0.061 246 096 295 |
| -0.966448306287         | 1.763421030872        | 1.090629157540      | -0.886138335479    |
| 1.293 743 956 365       | 0.885 896 274 098     | 0.650 799 556 906   | 1.987 929 989 561  |
|                         | Ν                     | V = 4               |                    |
| -0.119243215058         | 27.563 055 577 560    | 8.573 449 870 085   | -0.013908428563    |
| -0.244873137144         | 5.083 450 943 806     | 2.412843033044      | -0.101487388028    |
| -1.103916603413         | 1.524 507 977 161     | 0.977 816 515 108   | -1.128960890266    |
| 1.523 453 984 094       | 0.916 041 042 601     | 0.667 338 670 069   | 2.282 879 821 631  |
|                         | Ν                     | <i>I</i> = 5        |                    |
| -0.071 639 108 816      | 71.360 386 041 332    | 17.498 587 170 477  | -0.004093993882    |
| -0.124760345054         | 13.106 575 211 939    | 4.909 384 083 415   | -0.025412626703    |
| -0.263663687751         | 3.709 883 799 726     | 1.905 155 033 169   | -0.138394872418    |
| -1.229197644878         | 1.399 772 323 043     | 0.917 176 975 615   | -1.340196796865    |
| 1.723 661 292 096       | 0.933 711 384 771     | 0.676970248746      | 2.546 140 388 427  |
|                         | Ν                     | <i>N</i> = 6        |                    |
| -0.046184298897         | 167.605 582 607 617   | 33.199 110 835 111  | -0.001 391 130 598 |
| -0.076079502014         | 30.758 767 497 376    | 9.308 651 882 563   | -0.008172988202    |
| -0.132266574507         | 8.634 462 363 825     | 3.589 934 856 262   | -0.036843725528    |
| -0.282425421559         | 3.025 219 115 124     | 1.634849275304      | -0.172753186379    |
| -1.344390627075         | 1.322 883 808 029     | 0.879 126 492 650   | -1.529234573541    |
| 1.903 782 666 123       | 0.945 306 333 949     | 0.683 265 540 271   | 2.786 299 840 861  |
|                         | Ν                     | <i>V</i> = 9        |                    |
| -0.015344717018         | 1 494.545 145 214 440 | 171.313 611 581 681 | -0.000 089 570 915 |
| -0.024395272860         | 274.171 594 067 078   | 48.020 528 453 792  | -0.000508017584    |
| -0.037762088092         | 76.805 211 387 704    | 18.490 689 624 785  | -0.002042221727    |
| $-0.057\ 577\ 491\ 339$ | 26.478053817384       | 8.319 067 299 029   | -0.006921147440    |
| -0.089786550011         | 10.404 697 107 366    | 4.128 879 170 601   | -0.021745986332    |
| -0.153404904990         | 4.505 653 563 474     | 2.204 085 509 135   | -0.069600251149    |
| -0.334422988781         | 2.148 628 918 050     | 1.264827078083      | -0.264402142061    |
| -1.646466633260         | 1.204 367 638 394     | 0.819 368 757 478   | -2.009433015640    |
| 2.366 671 815 831       | 0.964 258 756 895     | 0.693514085114      | 3.412 579 306 795  |

**TABLE VI.** Optimal coefficients and exponents in the rG-NG expansion (N = 2, 3, 4, 5, 6, 9).

$$r \exp\left(-r^{2}\right) \approx \sum_{i=1}^{N} C_{i} \exp\left(-\alpha_{i}r^{2}\right),$$
 (39)

where  $\{\alpha_i\}$  and  $\{C_i\}$  are the exponents and the linear expansion coefficients, respectively. We determine these parameters by using the least square fitting techniques: they are determined by minimizing the error  $\varepsilon$  given by

$$\varepsilon \equiv \int_{r=0}^{\infty} \left[ r \, \exp\left(-r^2\right) - \sum_{i=1}^{N} C_i \, \exp\left(-\alpha_i r^2\right) \right]^2 r^2 dr.$$
 (40)

When the  $\varepsilon$  value takes the minimum, the first derivatives with respect to  $\{\alpha_i\}$  and  $\{C_i\}$  are zero,

$$\forall i, \ \frac{\partial \varepsilon}{\partial C_i} = 0 \text{ and } \forall i, \ \frac{\partial \varepsilon}{\partial \alpha_i} = 0.$$
 (41)

We determined the { $\alpha_i$ } and { $C_i$ } to satisfy  $\sum_{i=1}^N |\partial \varepsilon / \partial C_i| + |\partial \varepsilon / \partial \alpha_i| < 10^{-15}$  by using the Newton's method and confirmed that all the eigenvalues of the Hessian matrix were positive.



**FIG. 2.** (a) Plots of the rG function (red) and rG-NG functions (blue: N = 2, green: N = 3), and (b) their radial distribution functions, where  $r^2$  is multiplied by each function. As N increases further, the rG-NG functions overlap almost completely with the rG function, supporting the high accuracy of this expansion.

**TABLE VII.** Least-square-fitting error  $\varepsilon$  of the rG-NG expansion [Eq. (40)] for N = 2, 3, 4, 5, 6, 9, and the value at the origin of the rG-NG expanded function [ $\psi(0)$ ] that must converge to zero.

| Ν                                       | 2   | 3  | 4  | 5  | 6  | 9   | $\psi_0^{\ a}$ |
|---|---|--|--|--|--|---|----------------|
| $rac{arepsilon}{\psi(0)^{\mathrm{b}}}$ | $\begin{array}{c} 4.2872 \times 10^{-5} \\ 1.9081 \times 10^{-1} \end{array}$ | $1.8445 \times 10^{-6}$<br>$9.6163 \times 10^{-2}$ | $1.3821 \times 10^{-7}$<br>$5.5421 \times 10^{-2}$ | $1.4335 \times 10^{-8}$<br>$3.4401 \times 10^{-2}$ | $1.8574 \times 10^{-9}$<br>$2.2436 \times 10^{-2}$ | $9.5642 \times 10^{-12}$<br>$7.5112 \times 10^{-3}$ | 0.0<br>0.0     |

<sup>a</sup> $\psi_0$  is the rG function,  $r \exp(-r^2)$ .

 ${}^{b}\psi$  is the rG-NG expanded function.

In Table VI, the optimal exponents  $\{\alpha_i\}$  and coefficients  $\{C_i\}$  are listed for N = 2, 3, 4, 5, 6, and 9, respectively. The normalization factors and the coefficients divided by the normalization factor are also given (they would be useful when one uses them in quantum chemical packages). For each N, the minimum exponent was a little smaller than 1.0 (0.822... 0.964, etc.), while the positive coefficients and the other exponents were larger than 1.0 with negative coefficients. This is understood as follows: in the region of very large *r*, the  $r \exp(-r^2)$ is well expressed by one exp  $(-r^2)$  because the  $r \exp(-r^2)$  asymptotically approaches  $\exp(-r^2)$  as  $r \to \infty$ . Therefore, their signs should be identical. In the region of small r, the Gaussian functions with the larger exponents are necessary to mimic  $r \exp(-r^2)$ . The value at the origin (r = 0) of the first Gaussian function (with  $\alpha < 1$ ) is unity, but that of  $r \exp(-r^2)$  is zero. To compensate for this gap, the signs of the rest of the Gaussian functions should be opposite.

For example of the rG-*N*G functions, we showed in Fig. 2(a) the plots of the rG-*N*G functions (N = 2 and 3) to compare with the rG function. In the region of small *r*, there is a large gap between the rG-*N*G function and the rG function. The values of the rG-*N*G functions at the origin,  $\psi(0)$ , are 0.19 and 0.096 for N = 2 and 3, respectively, while that of the rG function is zero. However, as *N* (number of expansions) increases, the value at the origin converges to zero (see Table VII for N = 4, 5, 6, and 9). These gaps are not so important when we consider the radial distribution function ( $\psi \times r^2$ ) because the volume around the origin is very small. Comparing the radial distribution function of the rG-2G function with the rG

function, they are almost overlapping [see Fig. 2(b)] except in the region of large *r*. However, the gap between the rG-NG and rG functions becomes smaller as *N* increases. Even for N = 3, the gap is invisible in the original scale in Fig. 2(b). The amount of the gap is measured by the least square error  $\varepsilon$  [Eq. (40)], and it is listed in Table VII for N = 2, 3, 4, 5, 6, and 9.

For N = 4 and N = 6, the error is  $\varepsilon = 1.3821 \times 10^{-7}$  and  $1.8574 \times 10^{-9}$ , respectively. These errors are smaller than those for the STO-NG expansion:  $\varepsilon = 6.8803 \times 10^{-5}$  and  $4.0069 \times 10^{-6}$  for N = 4 and N = 6, respectively.<sup>14</sup> Thus, the efficiency of the least square fitting for the rG-NG expansion is better than that for the STO-NG expansion.

Using the rG-*N*G functions, we calculated expectation values for operators  $\hat{O} = 1$ , d/dr,  $d^2/dr^2$ , 1/r,  $-\frac{1}{2}\Delta$ , and *r*. The errors in the calculated expectation values are listed in Table VIII. It is observed that the error of the expectation value decreases roughly by one digit as *N* increases by unity, except for  $\langle \psi | d^2 / dr^2 | \psi \rangle$ . In this case, the error of the expansion near the nuclei is expanded by the second differentiation, leading to a slow convergence. Contrary to this, the  $\langle \psi | r | \psi \rangle$  value converges faster because the error of the expansion near the nuclei is diminished by the *r* term.

### B. rG-NG expansion for the arbitrary exponent

If we substitute *r* in Eq. (39) for  $\sqrt{ar}$  (*a* > 0) and divide both sides by  $\sqrt{a}$ , we get

| $\hat{O} \setminus N$ | 2                        | 3                        | 4                        | 5                        | 6                        | 9                        | $\psi_0^{b}$            |
|-----------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|
| 1                     | $3.6487\times 10^{-4}$   | $1.5698 \times 10^{-5}$  | $1.1763\times 10^{-6}$   | $1.2200 \times 10^{-7}$  | $1.5808\times 10^{-8}$   | $8.1399 	imes 10^{-11}$  | $1.1750 \times 10^{-1}$ |
| d/dr                  | $-1.6737 \times 10^{-3}$ | $-1.1111 \times 10^{-4}$ | $-1.2357 \times 10^{-5}$ | $-1.8398 \times 10^{-6}$ | $-3.3334 \times 10^{-7}$ | $-4.1923 \times 10^{-9}$ | $-1.2500 	imes 10^{-1}$ |
| $d^2/dr^2$            | $7.0201 \times 10^{-2}$  | $9.2629 \times 10^{-3}$  | $1.7870 \times 10^{-3}$  | $4.2847\times10^{-4}$    | $1.1899 \times 10^{-4}$  | $4.4676 \times 10^{-6}$  | $-1.1750 	imes 10^{-1}$ |
| 1/r                   | $-1.6737 \times 10^{-3}$ | $-1.1111 \times 10^{-4}$ | $-1.2357 \times 10^{-5}$ | $-1.8398 \times 10^{-6}$ | $-3.3334 \times 10^{-7}$ | $-4.1923 \times 10^{-9}$ | $1.2500 	imes 10^{-1}$  |
| $-\frac{1}{2}\Delta$  | $1.0341 \times 10^{-2}$  | $1.3367 \times 10^{-3}$  | $2.5630 	imes 10^{-4}$   | $6.1314 \times 10^{-5}$  | $1.7012 \times 10^{-5}$  | $6.3829 \times 10^{-7}$  | $1.3708 	imes 10^{-1}$  |
| r                     | $3.1376 \times 10^{-4}$  | $9.2535 \times 10^{-6}$  | $5.2628 \times 10^{-7}$  | $4.3495 \times 10^{-8}$  | $4.6201 \times 10^{-9}$  | $1.4281 \times 10^{-11}$ | $1.2500 	imes 10^{-1}$  |

**TABLE VIII.** The error of the rG-NG expanded functions (N = 2, 3, 4, 5, 6, 9) in the expectation value for the operator  $\hat{O}$ .<sup>a</sup>

<sup>a</sup> The value  $1 - \langle \psi | \hat{O} | \psi \rangle / \langle \Psi_0 | \hat{O} | \Psi_0 \rangle$  is shown, where  $\psi_0$  is the rG function,  $r \exp(-r^2)$ , and  $\psi$  is the rG-NG expanded function.

<sup>b</sup>The expectation values of  $\langle \Psi_0 | \hat{O} | \Psi_0 \rangle$  is shown.

$$r \exp\left(-ar^2\right) \approx \sum_{i=1}^N \frac{C_i}{\sqrt{a}} \exp\left(-(\alpha_i a)r^2\right).$$
 (42)

Thus, the rG function with arbitrary exponent *a* can be expanded with  $\{\alpha_i a\}$  and  $\{C_i/\sqrt{a}\}$ , where  $\{\alpha_i\}$  and  $\{C_i\}$  are the same values as those for a = 1.

### C. Two-center integral with the rG-NG expansion

In this section, we check the accuracy of the two-center integral with the rG-NG expansion. The target integral is

$$F = \int r_A \, \exp\left(-\alpha r_A^2\right) \, r_B \, \exp\left(-\alpha r_B^2\right) d\mathbf{r},\tag{43}$$

where A and B are separated by *R*. This integral cannot be expressed in a closed form because it includes two rG functions in the integrand. To calculate this integral value, we expand the  $r_B \exp(-\alpha r_B^2)$ term by *N* Gaussian functions, i.e., we approximate it by

$$F_{NG} = \int r_A \exp\left(-\alpha r_A^2\right) \sum_{i=1}^N C_i \exp\left(-\alpha_i r_B^2\right) d\mathbf{r}, \qquad (44)$$

and we further expand the  $r_A \exp(-\alpha r_A^2)$  term and approximate by

$$F_{NG,NG} = \int \sum_{i=1}^{N} C_i \exp\left(-\alpha_i r_A^2\right) \sum_{j=1}^{N} C_j \exp\left(-\alpha_j r_B^2\right) d\mathbf{r}.$$
 (45)

In a practical calculation, we do not need to expand the  $r_A \exp(-\alpha r_A^2)$  term in Eq. (44) to evaluate the integral because Eq. (44) can be expressed in a closed form. However when we calculate the three- or four-center integral which are listed in Table V, we need to use the rG-*N*G expansion more than once. In such cases, we need to check the accuracy of the two-folded use of the rG-*N*G expansion. The calculated values of Eqs. (44) and (45) with  $\alpha = 0.27095$  and R = 1.4011 and R = 2.0 are shown in Table IX. Note that the exponent  $\alpha = 0.27095$  is the optimal STO-1G exponent for  $\exp(-r)$  and R = 1.4011 is the equilibrium distance of the hydrogen molecule.

In Table IX, the  $F_{NG}$  and  $F_{NG,NG}$  converge to the exact value as the number of expansion N increases. When N = 9, the F values have more than 8- digit accuracies in all cases. The accuracy of  $F_{NG}$  was almost the same as  $F_{NG,NG}$  for all of N, which implies that multiple use of rG-NG expansion little loss the accuracy of integration. Note that, in general, the use of rG-NG expansion m times appears in  $N^m$  expanded terms, and the computation time increases proportional to  $N^m$ .

### VII. APPLICATION TO HYDROGEN MOLECULE

We next applied the rG-NG method to the hydrogen molecule at the equilibrium geometry. The calculations were performed using the FC-*s*<sub>ij</sub> method,<sup>26</sup> which is an approximate FC theory in which the two-electron *g*<sub>ij</sub> function is approximated by *r*<sub>ij</sub><sup>2</sup> and further *r*<sub>ij</sub><sup>2</sup> is rewritten using the one-electron functions alone, as explained in Sec. II A. Therefore, we cannot expect the highly accurate result as obtained above for the He atom. The initial wave function was the Valence Bond (VB) type function,  $\Psi_0 = \hat{A} \sum_{i=1}^{N_{AO}} \sum_{j=1}^{N_{AO}} c_{i,j} \phi_0^{(i,j)}$ , where  $\phi_0^{(i,j)} = \varphi_{A,i}(1)\varphi_{B,i}(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2))$ , and  $\varphi_{A,i}(1)$ 

where  $\phi_0^{(i,j)} = \varphi_{A,i}(1)\varphi_{B,j}(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2))$ , and  $\varphi_{A,i}(1)$ and  $\varphi_{B,j}(2)$  (*i*, *j* = 1...  $N_{AO}$ ) are the Dunning-Hay's DZP (double-zeta polarization) basis functions<sup>16</sup> centered on nuclei *A* and *B* and occupied by electrons 1 and 2, respectively. The  $\pi$  orbitals were not included in the initial wave function. Therefore, the number of the initial basis functions used was  $N_{AO} = 3$ , and the total number of the initial cf's was  $M_0 = 9$ . Applying the FC- $s_{ij}$  method, the cf's including the rG functions were generated. We used the rG-9G expansion method for the integrals of rG functions for which the integrals cannot be expressed in the closed form, and for others we used the closed integral forms summarized also above.

The calculated energies of the hydrogen molecule are shown in Table X. At order n = 0, the error of the energy  $\Delta E$  was 14.88 kcal/mol. As the order increased, the errors became smaller. At order n = 2, the error  $\Delta E$  became 0.62 (<1) kcal/mol and then we could get the chemical accuracy. However, the results are much less satisfactory because, in the FC- $s_{ij}$  method, the two-electron  $g_{ij}$  function was approximated using the one-electron functions.<sup>26</sup>

We also calculated the energy by removing the rG functions from the cf's generated above, and the results were shown in Table X. At order n = 2, the error was 0.72 (<1) kcal/mol, which was worse than but not much different from the results of including the rG functions. For the helium case, the errors of the energies calculated without the rG functions were much worse than those calculated with the rG functions (see Table II). This difference is understood as follows: in the hydrogen molecule, the generated cf's improve 11 July 2023 00:56:12

|       |                       | $F_{NG}$ [Eq. (44)]        | $F_{NG,NG}$ [Eq. (45)] |                            |  |
|-------|-----------------------|----------------------------|------------------------|----------------------------|--|
| Ν     | Value <sup>a</sup>    | Total number of expansions | Value <sup>a</sup>     | Total number of expansions |  |
|       |                       | <i>R</i> = 1.401 1         | au                     |                            |  |
| 2     | <b>31.8</b> 33 852 31 | 2                          | <b>31</b> .798 442 96  | 4                          |  |
| 3     | <b>31.86</b> 7 585 14 | 3                          | <b>31.86</b> 5 422 17  | 9                          |  |
| 4     | <b>31.869</b> 511 73  | 4                          | <b>31.869</b> 252 50   | 16                         |  |
| 5     | <b>31.869 736</b> 37  | 5                          | <b>31.869 701</b> 06   | 25                         |  |
| 6     | <b>31.869 765</b> 98  | 6                          | <b>31.869 760</b> 04   | 36                         |  |
| 9     | <b>31.869 771</b> 67  | 9                          | <b>31.869</b> 77166    | 81                         |  |
| Exact | 31.869 771 82         |                            | 31.869 771 82          |                            |  |
|       |                       | <i>R</i> = 2.0 a           | u                      |                            |  |
| 2     | <b>26.5</b> 01 822 21 | 2                          | <b>26</b> .483 328 13  | 4                          |  |
| 3     | <b>26.519</b> 914 50  | 3                          | <b>26.51</b> 9 169 01  | 9                          |  |
| 4     | <b>26.520 691</b> 49  | 4                          | <b>26.520</b> 702 11   | 16                         |  |
| 5     | <b>26.520 691</b> 20  | 5                          | <b>26.520</b> 700 17   | 25                         |  |
| 6     | <b>26.520 684</b> 28  | 6                          | <b>26.520 686</b> 29   | 36                         |  |
| 9     | <b>26.520 682 3</b> 6 | 9                          | <b>26.520 682</b> 19   | 81                         |  |
| Exact | 26.520 682 30         |                            | 26.520 682 30          |                            |  |

**TABLE IX.** Convergence of the integral value of Eq. (43) by the rG-NG expansion. (R = 1.4011 au and 2.0 au,  $\alpha = 0.270$  95).

<sup>a</sup>Boldface denotes the converged figure.

**TABLE X.** The energy of the hydrogen molecule calculated by the FC- $s_{ij}$  method with and without the cf's including the rG functions.

| Order <i>n</i> | М   | Total energy (au)    | $\Delta E  (\text{kcal/mol})^{\text{a}}$ |
|----------------|-----|----------------------|--|
|                |     | With rG functions    |  |
| 0              | 9   | -1.150 771           | 14.88                                    |
| 1              | 162 | -1.170226            | 2.67                                     |
| 2              | 999 | -1.173490            | 0.62                                     |
|                |     | Without rG functions |  |
| 0              | 9   | -1.150 771           | 14.88                                    |
| 1              | 108 | -1.169730            | 2.98                                     |
| 2              | 639 | -1.173325            | 0.72                                     |
| Exact          |     | -1.174 476           |  |

<sup>a</sup>The difference from the exact energy.

both the bonding region and the atomic region. Since the bonding region is distant from the nuclei, the wave function calculated with the rG functions has little difference from those calculated without the rG functions. The wave function in the atomic region was well described without the rG functions by the contracted primitive Gaussian functions in the DZP basis.

Thus, in these test calculations, we could confirm that the rG-NG expansion worked well in a molecular calculation.

### VIII. SUMMARY

In this paper, we introduced the rG function defined by Eq. (3). This function is a product of the ordinary Gaussian function and the

term  $r^n$ . The rG, Gaussian, and Slater functions were compared, and were focused on the cusp regions. By introducing the rG function, the cusp condition can be satisfied.

It is important to note that the rG function is generated automatically when we apply the FC theory to the initial function composed of the Gaussian function. This means that the rG function is necessary to construct the exact wave function starting from the Gaussian function. In Tables I and II, we showed that the FC theory applied to the hydrogen and helium atoms certainly leads to their exact wave function with the complement functions, including the rG functions. We then showed the important effects of the rG functions leading to the exact wave function by taking them off of the expansion. For the hydrogen atom, an accurate energy of  $\Delta E = 0.260$  kcal/mol ( $\Delta E$  is the difference from the exact energy) was obtained with only five functions, including the rG functions, while  $\Delta E = 0.870$  kcal/mol was obtained with ten normal Gaussian functions. For the helium atom,  $\Delta E = 0.214$ kcal/mol was obtained with 46 functions including the rG function, while still  $\Delta E = 44.47$  kcal/mol remained with 69 normal Gaussian functions. We also noted that the rG functions are important for improving the cusp regions, as well as the regions distant from the nucleus. These results clearly show the importance of the rG functions.

For the multi-center rG integrals, no closed forms are available. So, we proposed the rG-NG expansion method, where the rG function is expressed as a linear combination of the ordinary Gaussian functions. The optimal coefficients and exponents of the individual Gaussian functions were determined by the least-mean-square fitting method. The errors  $\varepsilon$  of the fitting method in the rG-NG expansion were smaller than those of the STO-NG expansion. Using the rG-NG expansion, we calculated a two-center overlap integral

and showed that the multiple use of the rG-NG expansion little affects the accuracy of the integrals. Finally, we applied the rG-NG expansion to calculate the hydrogen molecule with the FC- $s_{ij}$  method. At order n = 2, the error of the energy  $\Delta E$  from the exact energy was 0.62 kcal/mol, which was smaller than the chemical accuracy. This calculation showed the usefulness of the rG-NG expansion method in molecular calculations. Consequently, it is recommended to include the rG functions in any Gaussian based calculations.

In this paper, we took and introduced the rG functions produced by the FC theory for solving the Schrödinger equation on the Gaussian group of functions. We investigated the basic problems of utilizing the rG functions in quantum chemistry calculations and applied the results to very small systems. General applications to the normal size of molecules on the Gaussian ground will be done in future works.

### ACKNOWLEDGMENTS

The computations were performed using the computers at the Research Center for Computational Science, Okazaki, Japan (Project No. 22-IMS-C012). We also partly used the computational resources of supercomputer Fugaku provided by the RIKEN Center for Computational Science and SQUID at the Cybermedia Center, Osaka University, Japan, through the HPCI System Research Project (Project IDs: hp210157 and hp220091). This research was funded by the JSPS KAKENHI (Grant No. 22H02045).

### AUTHOR DECLARATIONS

### **Conflict of Interest**

The authors have no conflicts to disclose.

### **Author Contributions**

**Yusaku I. Kurokawa**: Investigation (equal); Writing – original draft (equal). **Hiroshi Nakatsuji**: Conceptualization (equal); Funding acquisition (equal); Methodology (equal).

### DATA AVAILABILITY

The data that support the findings of this study are available within the article.

### APPENDIX A: ONE-CENTER ONE-ELECTRON INTEGRAL WITH rG FUNCTION

The one-center one-electron integral with the rG function can be written as a linear combination of the following integral:

$$I(n, a, b, c, \alpha) \equiv \int r^n x^a y^b z^c \exp\left(-\alpha r^2\right) dx dy dz \qquad (A1)$$

where *n*, *a*, *b*, and *c* are non-negative integers, and  $\alpha$  is positive.

When n is odd, (A1) can be calculated by

$$I(n, a, b, c, \alpha) = (-1)^m \frac{\partial^m}{\partial \alpha^m} I(-1, a, b, c, \alpha),$$
(A2)

where  $m \equiv (1 + n)/2$ , and when *n* is even, (A1) can be calculated by

$$I(n, a, b, c, \alpha) = (-1)^m \frac{\partial^m}{\partial \alpha^m} I(0, a, b, c, \alpha),$$
(A3)

where  $m \equiv n/2$ . Thus,  $I(n, a, b, c, \alpha)$  can be calculated from  $I(-1, a, b, c, \alpha)$  or  $I(0, a, b, c, \alpha)$  according to the *n* value. They can be easily calculated if we use the polar coordinates, and the results are written in Eqs. (25) and (27) in the main text.

### APPENDIX B: ONE-CENTER TWO-ELECTRON INTEGRAL WITH rG FUNCTION

The one-center two-electron integral with the rG function can be generally written as

$$I_{a_{1}b_{1}c_{1}n_{1},a_{2}b_{2}c_{2}n_{2},\alpha\beta} \equiv \int r_{1}^{n_{1}}x_{1}^{a_{1}}y_{1}^{b_{1}}z_{1}^{c_{1}}$$

$$\times \exp\left(-\alpha r_{1}^{2}\right)\frac{1}{r_{12}}r_{2}^{n_{2}}x_{2}^{a_{2}}y_{2}^{b_{2}}z_{2}^{c_{2}}$$

$$\times \exp\left(-\beta r_{2}^{2}\right)dx_{1}dy_{1}dz_{1}dx_{2}dy_{2}dz_{2}.$$
 (B1)

The  $1/r_{12}$  can be expressed by the Laplace expansion as

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{1}{r_{>}} \left(\frac{r_{<}}{r_{>}}\right)^{l} P_{l}(\cos\theta_{12}), \tag{B2}$$

where  $r_{>} \equiv \max(r_{1}, r_{2})$ ,  $r_{<} \equiv \min(r_{1}, r_{2})$ . The  $\theta_{12}$  is the angle between  $\mathbf{r}_{1}$  and  $\mathbf{r}_{2}$ , and  $\cos \theta_{12}$  can be expressed using the polar coordinates of  $\mathbf{r}_{1}$  and  $\mathbf{r}_{2}$  as

$$\cos \theta_{12} = \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1 r_2} = \frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{r_1 r_2}$$
$$= \sin \theta_1 \cos \phi_1 \sin \theta_2 \cos \phi_2 + \sin \theta_1 \sin \phi_1 \sin \theta_2 \sin \phi_2$$
$$+ \cos \theta_1 \cos \theta_2. \tag{B3}$$

Since the Legendre polynomial is defined by

$$P_n(x) = \frac{1}{2^2} \sum_{k=0}^{\lfloor n/2 \rfloor} (-1)^k \frac{(2n-2k)!}{k!(n-k)!(n-2k)!} x^{n-2k}, \qquad (B4)$$

the  $P_l(\cos \theta_{12})$  in Eq. (B2) is expressed, using Eq. (B3), as

$$P_{l}(\cos\theta_{12}) = \frac{1}{2^{l}} \sum_{k=0}^{\lfloor l/2 \rfloor} (-1)^{k} \frac{(2l-2k)!}{k!(l-k)!(l-2k)!} \\ \times \sum_{n_{a}=0}^{l-2k} \sum_{n_{b}=0}^{l-2k-n_{a}} \frac{(l-2k)!}{n_{a}!n_{b}!n_{c}!} (\sin\theta_{1}\,\cos\phi_{1}\,\sin\theta_{2}\,\cos\phi_{2})^{n_{a}} \\ \times (\sin\theta_{1}\,\sin\phi_{1}\,\sin\theta_{2}\,\sin\phi_{2})^{n_{b}} (\cos\theta_{1}\,\cos\theta_{2})^{n_{c}}.$$
(B5)

The rest part of the integrand in Eq. (B1) is written as

J. Chem. Phys. **159**, 024103 (2023); doi: 10.1063/5.0155105 Published under an exclusive license by AIP Publishing

$$\begin{aligned} x_{1}^{a_{1}}y_{1}^{b_{1}}z_{1}^{c_{1}}r_{1}^{n_{1}} \exp\left(-\alpha r_{1}^{2}\right)x_{2}^{a_{2}}y_{2}^{b_{2}}z_{2}^{c_{2}}r_{2}^{n_{2}} \\ &\times \exp\left(-\beta r_{2}^{2}\right)dx_{1}dy_{1}dz_{1}dx_{2}dy_{2}dz_{2} \\ &= dr_{1}dr_{2}d\theta_{1}d\theta_{2}d\phi_{1}d\phi_{2} \ r_{1}^{a_{1}+b_{1}+c_{1}+n_{1}+2}r_{2}^{a_{2}+b_{2}+c_{2}+n_{2}+2} \\ &\times \exp\left(-\alpha r_{1}^{2}\right)\exp\left(-\beta r_{2}^{2}\right)(\sin\theta_{1})^{a_{1}+b_{1}+1}(\cos\theta_{1})^{c_{1}}(\sin\phi_{1})^{b_{1}} \\ &\times (\cos\phi_{1})^{a_{1}}(\sin\theta_{2})^{a_{2}+b_{2}+1}(\cos\theta_{2})^{c_{2}}(\sin\phi_{2})^{b_{2}}(\cos\phi_{2})^{a_{2}}, \end{aligned}$$
(B6)

where the Jacobian,  $J = r_1^2 r_2^2 \sin \theta_1 \sin \theta_2$ , is considered.

Using Eqs. (B2), (B5), and (B6), the two-electron integral can be written as a linear combination of a product of angular and radial parts as

$$I_{a_{1}b_{1}c_{1}n_{1},a_{2}b_{2}c_{2}n_{2},\alpha\beta} = \lim_{L \to \infty} \sum_{l=0}^{L} A(l,a_{1}b_{1}c_{1},a_{2}b_{2}c_{2}) \times R(l,a_{1}b_{1}c_{1}n_{1},a_{2}b_{2}c_{2}n_{2},\alpha,\beta), \quad (B7)$$

where  $L = \min(a_1 + b_1 + c_1, a_2 + b_2 + c_2)$ , and A is fined in Eq. (30). The upper bound *L* of the summation in Eq. (B7) can be truncated at  $L = \min(a_1 + b_1 + c_1, a_2 + b_2 + c_2)$  because  $A(l, a_1b_1c_1, a_2b_2c_2)$ = 0 for all  $l > \min(a_1 + b_1 + c_1, a_2 + b_2 + c_2)$ . See the main text for the evaluation of *A*. The radial part *R* is defined by

$$R(l, a_{1}b_{1}c_{1}n_{1}, a_{2}b_{2}c_{2}n_{2}, \alpha, \beta)$$

$$\equiv \int_{r_{1}=0}^{\infty} \int_{r_{2}=0}^{\infty} \frac{r_{<}^{l}}{r_{>}^{l+1}} r_{1}^{a_{1}+b_{1}+c_{1}+n_{1}+2} r_{2}^{a_{2}+b_{2}+c_{2}+n_{2}+2}$$

$$\times \exp\left(-\alpha r_{1}^{2}\right) \exp\left(-\beta r_{2}^{2}\right) dr_{1} dr_{2}.$$
(B8)

The  $r_>$  and  $r_<$  in Eq. (B8) disappear by separating the integration range as

$$R(l, a_1b_1c_1n_1, a_2b_2c_2n_2, \alpha, \beta) = R'(l, a_1b_1c_1n_1, a_2b_2c_2n_2, \alpha, \beta) + R'(l, a_2b_2c_2n_2, a_1b_1c_1n_1, \beta, \alpha)$$
(B9)

where

$$R'(l, a_1b_1c_1n_1, a_2b_2c_2n_2, \alpha, \beta) \equiv \int_{r_2=0}^{\infty} r_2^{d_2-l-1} \exp\left(-\beta r_2^2\right) \\ \times \int_{r_1=0}^{r_2} r_1^{d_1+l} \exp\left(-\alpha r_1^2\right) dr_1 dr_2.$$
(B10)

See the main text for the evaluation of R'.

### **APPENDIX C: EVALUATION OF Eq. (37)**

For n = 0 and 1, Eq. (37) is evaluated as

$$E(0,\alpha,\beta) = \frac{\arctan\left(\sqrt{\alpha/\beta}\right)}{\sqrt{\pi}\sqrt{\beta}}$$
(C1)

and

$$E(1,\alpha,\beta) = \frac{1}{2} \frac{\sqrt{\alpha}}{\beta \sqrt{\alpha + \beta}},$$
 (C2)

respectively. For n > 1, integrating Eq. (37) by parts yields a relation between  $E(n, \alpha, \beta)$  and  $E(n - 2, \alpha, \beta)$  as follows:

(i) when *n* is odd

$$E(n,\alpha,\beta) = \frac{n-1}{2\beta}E(n-2,\alpha,\beta) + \frac{\sqrt{\alpha}}{\beta\sqrt{\pi}}\frac{(n-2)!!}{2^{(n+1)/2}}\frac{\sqrt{\pi}}{(\alpha+\beta)^{n/2}};$$
(C3)

(ii) when *n* is even

$$E(n,\alpha,\beta) = \frac{n-1}{2\beta}E(n-2,\alpha,\beta) + \frac{\sqrt{\alpha}}{\beta\sqrt{\pi}}\frac{[(n-2)/2]!}{2(\alpha+\beta)^{n/2}}.$$
 (C4)

Starting from Eq. (C1) when n is even or Eq. (C2) when n is odd,  $E(n, \alpha, \beta)$  for arbitrary integer *n* can be calculated using Eqs. (C3) or (C4).

#### REFERENCES

<sup>1</sup>I. Shavitt, "The Gaussian functions in calculations of statistical mechanics and quantum mechanics," in Methods in Computational Physics, Advances in Research and Applications, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press, New York, London, 1963), Vol. 2, Chap. 1.

<sup>2</sup>F. E. Harris, Rev. Mod. Phys. 35, 558 (1963).

<sup>3</sup>S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).

<sup>4</sup>K. O-ohata, H. Taketa, and S. Huzinaga, J. Phys. Soc. Jpn. 21, 2313 (1966).

<sup>5</sup>S. Huzinaga, Suppl. Prog. Theor. Phys. 40, 52 (1967).

<sup>6</sup>V. R. Saunders, "Molecular integrals over Gaussian-type functions," in Handbook of Molecular Physics and Quantum Chemistry, Molecular Electronic Structure, edited by S. Wilson (John Wiley & Sons, Ltd., 2003), Vol. 2, Chap. 29.

<sup>7</sup>S. Reine, T. Helgaker, and R. Lindh, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2, 290 (2012).

<sup>8</sup>H. P. Trivedi and E. O. Steinborn, Rhys. Rev. A. 25, 113 (1982).

<sup>9</sup>T. Koga, J. Mol. Struct.: THEOCHEM **451**, 1 (1998).

<sup>10</sup>E. R. Davidson and D. Feller, Chem. Rev. **86**, 681–696 (1986).

<sup>11</sup>I. Shavitt, Isr. J. Chem. 33, 357 (1993).

<sup>12</sup>W. Kutzelnigg, Int. J. Quant. Chem. 113, 203 (2012).

<sup>13</sup>L. K. McKemmish and P. M. W. Gill, J. Chem. Theory Comput. 8, 4891 (2012).

<sup>14</sup>K. O-ohata, H. Taketa, and S. Huzinaga, J. Phys. Soc. Jpn. 21, 2306 (1966).

<sup>15</sup>B. J. Rosenberg and I. Shavitt, J.Chem. Phys. **63**, 2162 (1975).

<sup>16</sup>T. H. Dunning and P. J. Hay, "Gaussian basis sets for molecular calculations," in Modern Theoretical Chemistry: Methods of Electronic Structure Theory, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, Chap. 1.

<sup>17</sup>S. Huzinaga, Gaussian Basis Sets for Molecular Calculations, Physical Sciences

Data, edited by S. Huzinaga (Elsevier, Amsterdam, 1984), Vol. 16.

<sup>18</sup>T. Kato, Commun. Pure Appl. Math. 10, 151 (1957).

<sup>19</sup>H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000).

<sup>20</sup>H. Nakatsuji, Phys. Rev. Lett. **93**, 030403 (2004).

<sup>21</sup>H. Nakatsuji, Phys. Rev. A 72, 062110 (2005). <sup>22</sup>H. Nakatsuji, Acc. Chem. Res. 45, 1480 (2012).

<sup>23</sup>H. Nakatsuji, H. Nakashima, and Y. I. Kurokawa, J. Chem. Phys. 149, 114105 (2018).

<sup>24</sup>H. Nakatsuji, H. Nakashima, and Y. I. Kurokawa, J. Chem. Phys. 149, 114106 (2018).

<sup>25</sup>Y. I. Kurokawa, H. Nakashima, and H. Nakatsuji, Phys. Chem. Chem. Phys. 21, 6327-6340 (2019).

<sup>26</sup>H. Nakatsuji, H. Nakashima, and Y. I. Kurokawa, Phys. Rev. A 101, 062508 (2020).

<sup>27</sup>H. Nakatsuji, H. Nakashima, and Y. I. Kurokawa, J. Chem. Phys. 156, 014113 (2022).

<sup>28</sup>H. Nakatsuji and H. Nakashima, Chem. Phys. Lett. 806, 140002 (2022).

<sup>29</sup>H. Nakatsuji and H. Nakashima, J. Chem. Phys. 157, 094109 (2022).

<sup>30</sup>Y. I. Kurokawa, H. Nakashima, and H. Nakatsuji, J. Chem. Phys. **139**, 044114 (2013). <sup>31</sup>Y. I. Kurokawa, H. Nakashima, and H. Nakatsuji, J. Chem. Phys. **140**, 214103

(2014).

- <sup>32</sup>B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
- <sup>33</sup>D. M. Bishop, J. Chem. Phys. 48, 1322 (1964); 48, 291 (1968).
- <sup>34</sup>K. Pachucki and J. Komasa, Chem. Phys. Lett. **389**, 209 (2004).
- <sup>35</sup>F. E. Harris and H. J. Monkhorst, Int. J. Quant. Chem. **106**, 3186–3189 (2006).