

An approximate atomic two-electron kinetic integral using B -splines

Shiro L. Saito

Abstract

An approximate atomic two-electron kinetic integral formula and its numerical check are presented. The approximation is carried out using the incomplete resolution of identity constructed from B -spline sets. The resulting formula is sums of products of one-electron kinetic and two-electron integrals. The numerical accuracy of the approximation depends on parameters of the B -spline sets. Consequently, the optimal parameters of a B -spline set which can give highly accurate integral values are determined.

1. INTRODUCTION

The Hylleraas-type method¹ is a powerful quantum mechanical computational method and is able to provide highly accurate atomic energies and properties. A feature of Hylleraas-type wave functions is to explicitly include inter-electronic coordinates. For example, a Hylleraas-type wave function for a two-electron atom of S -state is written as

$$\Psi = \sum_{n_1, n_2, n_{12}} C_{n_1, n_2, n_{12}} \mathcal{A} r_{12}^{n_{12}} (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \Theta \quad (1)$$

where r_{12} is the inter-electronic coordinate, Θ is a spin function, \mathcal{A} is the antisymmetrizer, and $(n, \zeta)_i$ is an s -type Slater-type function (STF):

$$(n, \zeta)_i \equiv r_i^n e^{-\zeta r_i} Y_0^0(\theta, \varphi) \quad (2)$$

Unfortunately, it is difficult to apply the Hylleraas-type method to many-electron systems because many-electron integrals are required. Many-electron integrals have very complicated formulas, and their numerical computational load is quite heavy. In particular, the kinetic integral formula is very complicated.

The formula for a two-electron kinetic integral is also complicated. Calculations of the wave function (1) require the following two-electron kinetic integral:

$$\begin{aligned}
& \left\langle r_{12}^{n_{12}} (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \left| -\frac{1}{2} \nabla_1^2 \right| r_{12}^{n'_{12}} (n'_1, \zeta'_1)_1 (n'_2, \zeta'_2)_2 \right\rangle \\
&= \frac{1}{2} \left(n_1 n'_1 + \frac{1}{2} n_1 n'_{12} + \frac{1}{2} n'_1 n_{12} \right) \left\langle (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \left| r_1^{-2} r_{12}^{n_{12}+n'_{12}} \right| (n'_1, \zeta'_1)_1 (n'_2, \zeta'_2)_2 \right\rangle \\
&\quad - \frac{1}{2} \left(n_1 \zeta'_1 + n'_1 \zeta_1 + \frac{1}{2} n'_{12} \zeta_1 + \frac{1}{2} n_{12} \zeta'_1 \right) \left\langle (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \left| r_1^{-1} r_1^{n_{12}+n'_{12}} \right| (n'_1, \zeta'_1)_1 (n'_2, \zeta'_2)_2 \right\rangle \\
&\quad + \frac{1}{2} \zeta_1 \zeta'_1 \left\langle (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \left| r_{12}^{n_{12}+n'_{12}} \right| (n'_1, \zeta'_1)_1 (n'_2, \zeta'_2)_2 \right\rangle \\
&\quad + \frac{1}{2} \left(n_{12} n'_{12} + \frac{1}{2} n_1 n'_{12} + \frac{1}{2} n'_1 n_{12} \right) \left\langle (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \left| r_{12}^{n_{12}+n'_{12}-2} \right| (n'_1, \zeta'_1)_1 (n'_2, \zeta'_2)_2 \right\rangle \\
&\quad - \frac{1}{2} (n_1 n'_{12} + n'_1 n_{12}) \left\langle (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \left| r_1^{-2} r_2^2 r_{12}^{n_{12}+n'_{12}-2} \right| (n'_1, \zeta'_1)_1 (n'_2, \zeta'_2)_2 \right\rangle \\
&\quad - \frac{1}{2} (n_{12} \zeta'_1 + n'_{12} \zeta_1) \left\langle (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \left| r_1 r_{12}^{n_{12}+n'_{12}-2} \right| (n'_1, \zeta'_1)_1 (n'_2, \zeta'_2)_2 \right\rangle \\
&\quad + \frac{1}{2} (n_{12} \zeta'_1 + n'_{12} \zeta_1) \left\langle (n_1, \zeta_1)_1 (n_2, \zeta_2)_2 \left| r_1^{-1} r_{12}^{n_{12}+n'_{12}-2} \right| (n'_1, \zeta'_1)_1 (n'_2, \zeta'_2)_2 \right\rangle. \tag{3}
\end{aligned}$$

Although this formula is very complicated, it is possible to simplify it. The resolution of identity (RI) reduces the two-electron kinetic integral to sums of products of one-electron kinetic and two-electron integrals. This procedure was applied to many-electron integrals by Kutzelnigg.² The final formula of the two-electron kinetic integral has infinite summations. For actual numerical calculations, the RI has to be approximated using an incomplete set. The use of an incomplete RI constructed from any flexible function may provide highly accurate numerical results. A B -spline set is suitable for the construction of an incomplete RI.

The B -splines of order K $\{B_{i,K}\}$ are piecewise polynomials of degree $K - 1$ on a knot sequence in a cavity of radius R . The knot sequence $\{t_i\}$ is a set of points defined on an interval $[0, R]$.^{3,4} $B_{i,K}(r)$ is nonzero in the interval $[t_i, t_{i+K})$. The advantage of B -splines is that they are very flexible and are relatively free from computational linear dependence. It has been shown that atomic calculations with B -splines provide highly accurate energies and properties.⁶⁻⁸ Therefore, it is expected that an incomplete RI constructed from a B -spline set may give highly accurate two-electron kinetic integral values. The purpose in this study is to formulate the approximate two-electron kinetic integral using the incomplete RI and to check its numerical accuracy.

Section 2 presents formulas of the two-electron kinetic integral using the complete RI and its approximation. In Section 3, computational details are presented. Section 4 summarizes the relative errors of the approximate two-electron kinetic integrals and discusses the accuracy of the approximation. Optimal parameters of the B -spline set are also determined.

2. THEORY

In this section, we reduce the two-electron kinetic integral using an incomplete RI. Hereafter, A, B, C, \dots express the atomic orbitals: $A = a(r)Y_{l_A}^{m_A}(\theta, \varphi)$. In particular, I, J, K, \dots express complete orbitals. The RI is written as

$$P = \sum_{IJ} |IJ\rangle \langle IJ|. \quad (4)$$

Eq.(4) employs a simple notation:

$$\sum_I \equiv \sum_{i=1}^{\infty} \sum_{l_i=0}^{\infty} \sum_{m_i=-l_i}^{l_i}. \quad (5)$$

Using the RI, the two-electron kinetic integral is written as follows:

$$\langle r_{12}^m AB | T_1 | r_{12}^n CD \rangle = \langle r_{12}^m AB | P T_1 P | r_{12}^n CD \rangle \quad (6)$$

$$= \sum_{IJKL} \langle AB | r_{12}^m | IJ \rangle \langle IJ | T_1 | KL \rangle \langle KL | r_{12}^n | CD \rangle$$

$$= \sum_{IJKL} \langle AB | r_{12}^m | IJ \rangle \langle I | T_1 | K \rangle \langle KJ | r_{12}^n | CD \rangle$$

$$= \sum_{k_1=0}^{k_1^{\max}} \sum_{k_2=0}^{k_2^{\max}} \sum_{l=0}^{\infty} \sum_{l'=0}^{\infty} A_{l,l'}^{k_1,k_2} \sum_{ijk} (ai, bj)_{k_1}^m (i | T_1 | j)_l (ck, dj)_{k_2}^n \quad (7)$$

with

$$(i | T_1 | j)_l = \int dr_1 i(r_1) \left[-\frac{1}{2} \frac{d^2}{dr_1^2} + \frac{l(l+1)}{2r_1^2} \right] j(r_1), \quad (8)$$

$$(ab, cd)_k^n = \sum_{s=0}^{s_{\max}} D_{k,s}^n \int dr_1 \int dr_2 a(r_1) b(r_1) \frac{r_1^{k+2s}}{r_>} c(r_2) d(r_2), \quad (9)$$

and

$$A_{l,l'}^{k_1,k_2} = \sum_{m=-l}^l c^{k_1}(l_A, m_A, lm) c^{k_2}(lm, l_C, m_C) \sum_{m'=-l'}^{l'} c^{k_1}(l', m', l_B, m_B) c^{k_2}(l_D, m_D, l' m'), \quad (10)$$

where $T_1 = -\frac{1}{2} \nabla_1^2$. Thus, the two-electron kinetic integral is reduced to sums of products of one-

electron kinetic integrals $(i|T_1|j)_l$ and two-electron integrals $(ai, bj)_k^n$. In Eq.(9), $D_{k,s}^n$ is a coefficient given by:

$$D_{k,s}^n = \frac{\left[-\frac{n}{2} \right]_k \left[k - \frac{n}{2} \right]_s \left[-\frac{n+1}{2} \right]_s}{\left[-\frac{1}{2} \right]_k \left[k + \frac{3}{2} \right]_s s!} \quad (11)$$

where $[a]_n$ is Pochhammer's symbol. For n odd we have $s_{\max} = \frac{n+1}{2}$, whereas for n even, $s_{\max} = \frac{n}{2} - k$. In Eq.(10), $c^k(lm, l' m')$ is a Condon-Shortley coefficient⁵ defined by:

$$c^k(lm, l' m') = \left(\frac{4\pi}{2k+1} \right)^{\frac{1}{2}} \int Y_l^{m*}(\theta, \varphi) Y_k^{m-m'}(\theta, \varphi) Y_{l'}^{m'}(\theta, \varphi) \sin^2\theta d\theta d\varphi. \quad (12)$$

The values of $k_{1\max}$ and $k_{2\max}$ in Eq.(7) are

$$k_{1\max} = \begin{cases} \frac{m}{2}, & (m: \text{even}) \\ \infty, & (m: \text{odd}) \end{cases}, \quad k_{2\max} = \begin{cases} \frac{n}{2}, & (n: \text{even}) \\ \infty, & (n: \text{odd}) \end{cases}. \quad (13)$$

Let us construct an incomplete RI from a B -spline set. The radial functions $i(r)$ can take any orthonormal set. In this work, the radial functions $i(r)$ are expanded using a unitary matrix U which diagonalizes the overlap matrix and eigenvalues s_i of the overlap matrix of the N -term B -spline set:

$$i(r) = \sum_{j=1}^N U_{ij} s_j^{-\frac{1}{2}} B_{j+1,K}(r), \quad (i=1, \dots, N). \quad (14)$$

Thus, the summations for i, j , and k in Eq.(7) become finite, and hence numerical calculations become feasible.

3. COMPUTATIONAL ASPECTS

This section presents computational details of the approximate two-electron kinetic integrals. We examine the two-electron kinetic integrals over 1s-type STFs as:

$$I(m, n) \equiv \langle r_{12}^m AA | T_1 | r_{12}^n AA \rangle, \quad (15)$$

where $A = a(r) Y_0^0(\theta, \varphi)$ and $a(r) = e^{-\zeta r}$. In this case, Eq.(7) becomes

$$\langle r_{12}^m AA | T_1 | r_{12}^n AA \rangle = \sum_{l=0}^{l_{\max}} (2l+1)^{-2} \sum_{ijk} (ai, aj)_l^m (i|T_1|k)_l (ak, aj)_l^n. \quad (16)$$

The value of l_{\max} depends on the parity of m and n , the values of which are listed in TABLE 1.

TABLE 1. Values of l_{\max} of Eq.(16).

m	n	l_{\max}
even	even	$\min\left(\frac{m}{2}, \frac{n}{2}\right)$
even	odd	$\frac{m}{2}$
odd	even	$\frac{n}{2}$
odd	odd	∞

The radial function $re^{-\zeta r}$ is expanded with an N -term B -spline set, namely,

$$re^{-\zeta r} \approx \sum_{i=1}^N C_i B_{i+1,K}(r). \quad (17)$$

where C_i are the linear expansion coefficients. This B -spline expansion of STF is highly accurate.⁹ We determine C_i by solving the system of linear equations as:

$$\sum_{j=1}^N \left[\int_0^R dr B_{i+1,K}(r) B_{j+1,K}(r) \right] C_j = \int_0^R dr B_{i+1,K}(r) re^{-\zeta r}, \quad (i=1, \dots, N). \quad (18)$$

These integrals are evaluated by the Gauss integration procedure.

In this work, all radial functions are expanded with a common B -spline set. In this case, necessary integrals are as follows:

$$(B_{i,K}, B_{j,K}), \quad (B_{i,K} | T_1 | B_{j,K})_{\lambda}, \quad (B_{i,K} B_{j,K}, B_{k,K} B_{l,K})_{\lambda}^m, \quad (19)$$

where $(B_{i,K}, B_{j,K})$ is the one-electron overlap integral. We use 100-term B -spline sets with $R = 60$ constructed on the exponential knot sequences, with endpoints of K -fold multiplicity. The parameters K and R_1 of the B -spline sets take all combinations of

$$K = 9, 11, 13, 15, \quad (20)$$

$$R_1 = 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, \quad (21)$$

where R_1 is the initial interval of the knot sequence.

We examine $I(1, 0), I(2, 0), I(1, 1), I(2, 1)$, and $I(2, 2)$ with $\zeta=0.5, 1, 5$, and 10. Here, $I(1, 1)$ has an infinite summation. We calculate $I(1, 1)$ using $l_{\max}=20$. As a measure of accuracy of the integral, we use the relative error

$$\left| \frac{I(m, n) - I_{\text{STF}}(m, n)}{I_{\text{STF}}(m, n)} \right|, \quad (22)$$

where $I_{\text{STF}}(m, n)$ is an exact integral value calculated using Eq.(3). All the calculations are performed at double precision.

4. RESULTS AND DISCUSSION

We calculated the approximate two-electron kinetic integrals $I(1, 0)$, $I(2, 0)$, $I(1, 1)$, $I(2, 1)$, and $I(2, 2)$ using Eqs.(15) and (16). In this section, we discuss the dependence of the accuracy of $I(m, n)$ on parameters m and n and on the B-spline sets.

TABLEs 2 and 3 summarize the relative errors for $I(1, 0)$, $I(2, 0)$, $I(2, 1)$, and $I(2, 2)$. First, we discuss the dependence of the accuracy of $I(m, n)$ with each ζ on m and n . These integrals have almost the same accuracy regardless of m and n , except for $I(m, n)$ with $\zeta = 10$. For $I(m, n)$ with $\zeta = 10$, the relative error of only $I(1, 0)$ is smaller than that of the other $I(m, n)$. The incomplete RI may similarly act on $I(m, n)$ with small ζ , regardless of m and n .

Next, we discuss the accuracy of the B-spline sets for $I(m, n)$ with each ζ . For $I(m, n)$ with $\zeta=0.5$, the B-spline sets with $R_1=10^{-2}$ and 10^{-3} yield accurate integral values. The B-spline sets with $R_1=10^{-4}$, except at $K=15$, also give accurate integral values. Hence, these B-spline sets well approximate the RI for $I(m, n)$ with $\zeta=0.5$. However, the B-spline sets with $R_1=10^{-5}$ are unsuitable for the incomplete RI because they give larger relative errors. In addition, $I(m, n)$ with $\zeta=1$ have almost the same accuracy as $I(m, n)$ with $\zeta=0.5$. The B-spline sets that are suitable for $I(m, n)$ with $\zeta=0.5$ can be used for the calculations of $I(m, n)$ with $\zeta=1$.

The use of large ζ changes the dependence of the accuracy of $I(m, n)$ on the B-spline sets. The relative errors for $I(m, n)$ with $\zeta=5$ and 10 are slightly larger than those for $I(m, n)$ with $\zeta=0.5$ and 1. The dependence of the relative errors on K increases with decreasing R_1 . The B-spline sets with $R_1=10^{-5}$ yield larger relative errors than those with $R_1 \geq 10^{-4}$. In particular, this is conspicuous for $I(2, 2)$ with $\zeta=5$ and 10. From the above discussion, we conclude that the B-spline set with $K=11$ and $R_1=10^{-3}$ gives accurate values of $I(m, n)$ with $\zeta=0.5 - 10$. This B-spline set may be suitable for the construction of the incomplete RI for the two-electron kinetic integrals.

TABLE 2. Relative errors of approximate two-electron kinetic integrals $I(m, n)$ for $\zeta=0.5$ and 1. $A(B)$ implies $A \times 10^B$.

m, n	$\zeta=0.5$				$\zeta=1$				
	$K=9$	$K=11$	$K=13$	$K=15$	$K=9$	$K=11$	$K=13$	$K=15$	
$R_1=10^{-2}$	1 0	6.4(-15)	1.9(-14)	1.9(-14)	6.4(-14)	1.0(-14)	6.1(-15)	2.9(-14)	2.0(-15)
	2 0	3.2(-14)	6.7(-15)	2.5(-14)	8.2(-14)	1.3(-14)	4.3(-14)	5.0(-14)	1.1(-14)
	2 1	0.0	0.0	3.2(-14)	8.5(-14)	8.8(-15)	8.8(-15)	5.8(-15)	1.2(-13)
	2 2	1.3(-14)	6.4(-15)	6.4(-15)	2.4(-13)	8.2(-15)	1.6(-14)	8.2(-15)	5.7(-13)
$R_1=10^{-3}$	1 0	0.0	6.4(-15)	2.6(-14)	9.0(-14)	6.1(-14)	1.2(-14)	4.1(-15)	8.4(-14)
	2 0	5.0(-15)	1.3(-14)	1.7(-14)	9.7(-14)	3.5(-14)	4.3(-14)	3.4(-14)	3.6(-14)
	2 1	2.3(-15)	1.8(-14)	2.3(-15)	1.1(-13)	5.0(-14)	5.8(-15)	2.9(-14)	2.4(-13)
	2 2	2.2(-14)	3.3(-15)	1.6(-14)	3.1(-13)	5.7(-14)	1.6(-14)	4.1(-14)	3.2(-12)
$R_1=10^{-4}$	1 0	1.9(-14)	3.6(-13)	2.2(-13)	2.7(-11)	2.3(-14)	1.2(-13)	1.2(-12)	3.4(-13)
	2 0	3.2(-14)	6.9(-13)	1.3(-13)	4.3(-11)	4.1(-14)	5.2(-14)	9.8(-13)	7.7(-13)
	2 1	1.8(-14)	6.0(-13)	2.9(-13)	3.8(-11)	2.9(-15)	8.2(-14)	7.7(-13)	9.4(-12)
	2 2	1.9(-14)	7.9(-13)	5.1(-13)	6.2(-11)	0.0	9.0(-14)	8.5(-13)	7.1(-11)
$R_1=10^{-5}$	1 0	1.2(-10)	2.5(-12)	4.3(-10)	1.1(-8)	2.1(-11)	4.3(-11)	1.2(-10)	2.5(-9)
	2 0	1.9(-10)	1.3(-11)	2.4(-10)	1.5(-8)	2.7(-11)	4.5(-11)	1.8(-10)	3.4(-9)
	2 1	1.4(-10)	3.7(-10)	5.4(-10)	1.1(-8)	2.0(-11)	6.7(-11)	1.9(-10)	2.2(-9)
	2 2	1.4(-10)	7.8(-10)	8.6(-10)	1.0(-8)	1.8(-11)	7.2(-11)	2.1(-10)	4.4(-9)

TABLE 3. Relative errors of approximate two-electron kinetic integrals $I(m, n)$ for $\zeta=5$ and 10. $A(B)$ implies $A \times 10^B$.

m, n	$\zeta=5$				$\zeta=10$				
	$K=9$	$K=11$	$K=13$	$K=15$	$K=9$	$K=11$	$K=13$	$K=15$	
$R_1=10^{-2}$	1 0	1.3(-14)	4.5(-14)	3.2(-14)	1.9(-13)	3.7(-14)	2.2(-13)	2.0(-13)	4.1(-12)
	2 0	7.0(-13)	2.1(-12)	2.3(-14)	7.1(-12)	1.1(-11)	7.2(-11)	1.6(-11)	1.3(-10)
	2 1	2.6(-13)	4.4(-13)	2.7(-14)	4.5(-12)	1.0(-11)	1.6(-11)	1.2(-11)	6.0(-11)
	2 2	1.7(-13)	9.8(-13)	5.7(-13)	1.7(-10)	9.8(-12)	1.1(-11)	1.4(-11)	1.2(-9)
$R_1=10^{-3}$	1 0	3.8(-14)	1.5(-13)	9.0(-14)	3.8(-14)	1.4(-14)	1.8(-13)	5.3(-14)	9.0(-14)
	2 0	1.0(-12)	2.6(-12)	2.6(-12)	1.6(-12)	8.9(-12)	7.4(-11)	2.0(-11)	2.3(-11)
	2 1	1.2(-12)	4.1(-14)	5.9(-13)	1.5(-11)	1.2(-11)	1.9(-11)	1.0(-11)	8.8(-11)
	2 2	1.1(-12)	7.0(-13)	4.5(-12)	6.0(-10)	1.6(-11)	2.1(-11)	1.3(-11)	1.1(-8)
$R_1=10^{-4}$	1 0	1.6(-13)	2.6(-13)	1.6(-13)	1.3(-14)	3.2(-13)	1.1(-13)	1.4(-13)	3.5(-14)
	2 0	1.0(-12)	7.4(-12)	1.5(-12)	2.9(-12)	4.4(-11)	3.7(-11)	8.5(-11)	1.9(-11)
	2 1	1.8(-13)	4.9(-12)	2.0(-12)	3.2(-10)	4.4(-12)	9.1(-12)	2.1(-11)	1.8(-9)
	2 2	1.0(-12)	5.7(-12)	1.0(-10)	4.0(-8)	4.4(-12)	2.9(-11)	1.2(-9)	5.5(-7)
$R_1=10^{-5}$	1 0	3.8(-14)	2.3(-13)	1.9(-11)	4.0(-11)	1.1(-13)	5.8(-13)	1.5(-12)	1.1(-12)
	2 0	1.1(-12)	2.9(-12)	9.8(-12)	5.7(-11)	1.2(-10)	3.2(-11)	1.1(-10)	1.9(-10)
	2 1	1.2(-12)	1.3(-12)	5.9(-12)	8.3(-10)	3.1(-11)	1.2(-11)	2.2(-12)	2.5(-8)
	2 2	1.8(-12)	3.4(-12)	8.1(-10)	1.3(-7)	1.6(-11)	1.8(-11)	5.3(-9)	7.8(-6)

We attempted to use another knot sequence:

$$0, R_1, R_1(1 + \beta), R_1(1 + \beta + \beta^2), \dots, R, \quad (23)$$

where β is the parameter characterizing the distribution of the knots. Here β is chosen to satisfy the following condition:

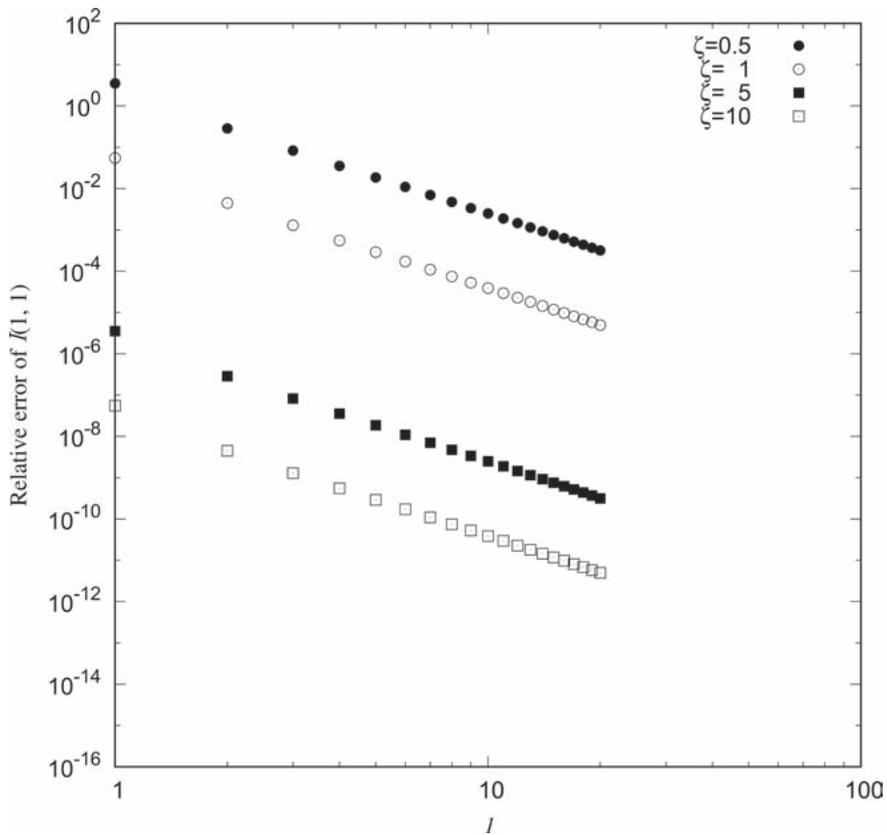
$$R = R_1(1 + \beta + \beta^2 + \dots + \beta^{N-K+2}), \quad (\beta \geq 1). \quad (24)$$

We call this knot sequence a “geometric series knot sequence”.⁶ Although the first point of this knot sequence is R_1 , the knot distribution at large R is similar to the exponential knot sequence distribution with the first interval $10R_1$. Hence, the geometric series knot sequence is suitable for calculating diffuse atomic orbitals. For calculations of $I(m, n)$, the results when using the geometric series knot sequence are almost the same as those using the exponential knot sequence. Both knot sequences have the same quality for the incomplete RI. To improve the accuracy of the incomplete RI, the number of terms of the B -spline set has to be increased.

Finally, we discuss the convergence of $I(1, 1)$ against the l value. TABLE 4 lists $I(1, 1)$ values that are given by the B -spline set with $K=13$ and $R_1=10^{-3}$, along with the exact values. All the relative errors are very large, namely, 7×10^{-6} . FIG. 1 plots the convergence of $I(1, 1)$ against the value of l . As shown in Fig.1, the convergence of all the integral values is very slow. Hence, $l_{\max}=20$ is too small. The value of l_{\max} has to be very large number. However, the use of a very large l_{\max} value is impractical. To obtain converged values using a small l_{\max} value, any convergence acceleration method has to be applied, e.g., the Aitken's Δ^2 method¹¹, the Levin u transformation method¹², an asymptotic-expansion method¹³, etc. Improvements in the convergence of $I(1, 1)$ are being carried out.

TABLE 4. Exact and approximate values and relative errors of $I(1, 1)$. $A(B)$ implies $A \times 10^B$.

ζ	Exact value	Approximate value	relative error
0.5	0.8000 0000 0000 0000(1)	0.7999 9472 7299 5467(1)	6.6(-6)
1	0.1250 0000 0000 0000(0)	0.1249 9912 5358 7063(0)	7.0(-6)
5	0.8000 0000 0000 0000(-5)	0.7999 9440 7717 9909(-5)	7.0(-6)
10	0.1250 0000 0000 0000(-6)	0.1249 9912 7658 9780(-6)	7.0(-6)

FIG. 1. Convergence of $I(1, 1)$ against the value of l .

REFERENCES

- ¹E.A. Hylleraas, Z. Phys. 54, 347 (1929).
- ²W. Kutzelnigg and W. Klopper, J. Chem. Phys. 94, 1985 (1991).
- ³C. de Boor, A Practical Guide to Splines (Springer-Verlag, New York, Berlin, Heidelberg, 2001).
- ⁴J. Sapirstein and W.R. Johnson, J. Phys. B 29, 5213 (1996).
- ⁵E.U. Condon and G.H. Shortley, The Theory of Atomic Spectra (Cambridge U.P., Cambridge, England, 1963).
- ⁶S.L. Saito, Theor. Chem. Acc. 109, 326 (2003).
- ⁷S.L. Saito, At. Data Nucl. Data Tables, 95, 836 (2009).
- ⁸S.L. Saito, J. Chem. Phys., 130, 074306 (2009).
- ⁹S.L. Saito, Chukyo Univ. Bulletin of the School of International Liberal Studies 9, 23 (2016)
- ¹⁰T. L. Gilbert and P. J. Bertoncini, J. Chem. Phys. 61, 3026 (1974).
- ¹¹A.C. Aitken, Proc. Royal. Soc. 46, 289 (1926).
- ¹²I. Porras and F.W. King, Phys. Rev. A49, 1637 (1994).
- ¹³G.W.F. Drake and Zong-Chao Yan, Phys. Rev. A52, 3681 (1995).

