Methods for accurate calculations of multi-center integrals of the squared Coulomb potential for lower bounds to energy levels of molecular systems

Sohei Ashida
Department of Mathematics
Gakushuin University

1 Introduction

Electronic energy levels (eigenvalues of electronic Hamiltonians) govern the properties of molecules such as stable structures and dynamics and are central to quantum chemistry. The electronic Hamiltonian for N electrons acting on $L^2(\mathbb{R}^{3N})$ is written as

$$H(\mathbf{R}_1,\dots,\mathbf{R}_M) := -\frac{1}{2}\sum_{i=1}^{N}\Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{1\le i<j\le N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|},$$

$$V(\mathbf{r}) := -\sum_{A=1}^{M}\frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|},$$

where $\mathbf{R}_1,\dots,\mathbf{R}_M \in \mathbb{R}^3$ are positions of M nuclei, $Z_1,\dots,Z_M \in \mathbb{N}$ atomic numbers of M nuclei, $\mathbf{r}_1,\dots,\mathbf{r}_N \in \mathbb{R}^3$ positions of N electrons and $\Delta_{\mathbf{r}_i}$ is the Laplacian for $\mathbf{r}_i$. Let $E(\mathbf{R}_1,\dots,\mathbf{R}_M)$ be an eigenvalue of $H(\mathbf{R}_1,\dots,\mathbf{R}_M)$. The equilibrium structures of the molecule are minimum points of the function

$$F(\mathbf{R}_1,\dots,\mathbf{R}_M) := E(\mathbf{R}_1,\dots,\mathbf{R}_M) + \sum_{1\le A<B\le M}\frac{Z_A Z_B}{|\mathbf{R}_A-\mathbf{R}_B|},$$

of the nuclear positions $\mathbf{R}_1,\dots,\mathbf{R}_M$. The rate of chemical reactions are also determined by the graphs of $F(\mathbf{R}_1,\dots,\mathbf{R}_M)$ over curves connecting two equilibrium positions. (The whole system may split into subsystems, in which case the equilibrium position is at infinity.)

Enormous time and effort are spent on the evaluation of the eigenvalues. However, most of the results are concerned with upper bounds by the variational method (Rayleigh-Ritz method based on the min-max principle) or some perturbation or expansion theory. As for the perturbation or expansion theory,

it would be hopeless to give practical error estimates between the values calculated by the method and the true eigenvalues. As for the variational method, only upper bounds are obtained and it is obviously impossible to obtain error estimates by the variational method only.

A method to obtain error estimates is to obtain both upper and lower bounds. If we obtain an upper bound E_{ub} and a lower bound E_{lb} of an eigenvalue E, we obviously have $|E - E_{ub}|, |E - E_{lb}| \leq E_{ub} - E_{lb}$. Thus E_{ub} and E_{lb} are approximations to E with an error estimate $E_{ub} - E_{lb}$. This is the reason why we seek lower bounds. Despite the obvious motivation there has not been significant progress for lower bounds. There is no general method for lower bounds without strong additional restriction or information about the operator, known methods often do not have enough accuracy, and quantities needed in the estimates are usually very difficult (impossible at present) to evaluate.

The most successful method for lower bounds would be the method by Temple's inequality (cf. [8, 15]). The lower bound by Temple's inequality is known to have high accuracy at least for simple systems, but in the inequality we need a lower bound to the eigenvalue next to the evaluated one. Therefore, it is impossible to obtain lower bounds by Temple's inequality only, and we need to find rough lower bounds by other methods. The most promising method for that purpose would be the Weinstein-Aronszajn intermediate method (cf. [17, 2]) or rather methods derived from that method (cf. [16, 4]). However, in the application of the Weinstein-Aronszajn method, we confront integrals for which no method of accurate evaluation have been known. The integral has the form

$$\begin{aligned}&[\psi_1(\mathbf{r}_A)\psi_2(\mathbf{r}_B)|\psi_3(\mathbf{r}'_C)\psi_4(\mathbf{r}'_D)]\\ &\quad := \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \psi_1^*(\mathbf{r}_A)\psi_2(\mathbf{r}_B)\frac{1}{|\mathbf{r}-\mathbf{r}'|^2}\psi_3^*(\mathbf{r}'_C)\psi_4(\mathbf{r}'_D)d\mathbf{r}d\mathbf{r}',\end{aligned} \tag{1.1}$$

where $\mathbf{r}_A = \mathbf{r} - \mathbf{R}_A \in \mathbb{R}^3$ and $\psi_i,\ i = 1, \ldots, 4$ are the Slater type orbitals (STO).

If the factor $\frac{1}{|\mathbf{r}-\mathbf{r}'|^2}$ is replaced by the usual Coulomb potential $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$, the integral is the multi-center integral whose evaluation is the central subject of the calculation of the variational upper bounds of electronic Hamiltonians. In the variational method when all STOs are centered at the same point (i.e. $\mathbf{R}_A = \mathbf{R}_B = \mathbf{R}_C = \mathbf{R}_D$), we can calculate the integral using the Laplace expansion (see e.g. [18, 7])

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{2l+1}\frac{r_<^l}{r_>^{l+1}}Y_{lm}^*(\theta',\varphi')Y_{lm}(\theta,\varphi),$$

where (r, θ, φ) and (r', θ', φ') are polar coordinates of $\mathbf{r}$ and $\mathbf{r}'$ respectively, $r_< = \min\{r, r'\}$, $r_> = \max\{r, r'\}$, and Y_{lm} is the spherical harmonics.

The case of $\mathbf{R}_A = \mathbf{R}_B \neq \mathbf{R}_C = \mathbf{R}_D$ can also be evaluated using the Laplace expansion. When $\mathbf{R}_A = \mathbf{R}_C \neq \mathbf{R}_B = \mathbf{R}_D$, the integral for the usual Coulomb

potential can be calculated using the Neumann expansion (cf. [11, 14])

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{2}{R}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-1)^m(2l+1)\left(\frac{(l-|m|)!}{(l+|m|)!}\right)^2 \times P_l^{|m|}(\xi_<)Q_l^{|m|}(\xi_>)P_l^{|m|}(\eta)P_l^{|m|}(\eta')e^{im\varphi}e^{-im\varphi'},$$

where (ξ,η,φ) and (ξ',η',φ') are ellipsoidal coordinates of $\mathbf{r}$ and $\mathbf{r}'$ respectively with foci $\mathbf{R}_A$ and $\mathbf{R}_B$, $\xi_< = \min\{\xi,\xi'\}$, $\xi_> = \max\{\xi,\xi'\}$, $P_l^{|m|}$ and $Q_l^{|m|}$ are the associated Legeandre functions, and $R = |\mathbf{R}_A - \mathbf{R}_B|$. For the other cases we use the translation of STO (cf. [13]). We expand $\psi(\mathbf{r}_B)$ by STOs φ_j centered at $\mathbf{R}_A$ as

$$\psi(\mathbf{r}_B) = \sum_{j=1}^{\infty} c_j\varphi_j(\mathbf{r}_A).$$

In the case of multi-center integrals for lower bounds of the eigenvalues we need to deal with $\frac{1}{|\mathbf{r}-\mathbf{r}'|^2}$ instead of $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$. Therefore, we can not use either the Laplace and Neumann expansions, and similar expansions are not known for the squared Coulomb potential. By methods free from such expansions analytic expressions and expressions by one-dimensional integrals have been derived for fundamental one-center and two-center integrals by the author (cf. [3]). A reduction scheme of three and four-center integrals to the fundamental one and two-center integrals with error estimates have also been derived. Numerical calculations of the fundamental one and two-center integrals have been performed by these expressions. Fundamental hybrid two-center integrals were also evaluated using the results for the fundamental one and two-center integrals. The results obtained using the expressions by one-dimensional integrals were found to have high accuracy and would be reasonable for the calculations of lower bounds for energy levels of small molecules.

2 Lower bound methods

2.1 Temple's inequality

Let us denote isolated eigenvalues of a lower semibounded operator H in ascending order as

$$\mu_1 \le \mu_2 \le \cdots \le \mu_\infty,$$

where μ_∞ is the infimum of the essential spectrum of H. When μ_i is the lowest isolated eigenvalue, we interpret μ_j for $j > i$ as $\mu_j = \mu_\infty$. The following Temple's inequality gives highly accurate lower bounds at least for simple systems (see [8, 4]).

Theorem 2.1 (Temple's inequality)**.** *If $\psi \in D(H)$, $\|\psi\| = 1$ and $\mu_{(k+1)lb}$ satisfy $\langle\psi, H\psi\rangle < \mu_{(k+1)lb} \le \mu_{k+1}$, we have the following Temple's inequality:*

$$\mu_k \ge \langle\psi, H\psi\rangle - \frac{\langle\psi, H^2\psi\rangle - \langle\psi, H\psi\rangle^2}{\mu_{(k+1)lb} - \langle\psi, H\psi\rangle}.$$

Here $\mu_{(k+1)lb}$ must be a lower bound to μ_{k+1}. A variational upper bound to μ_{k+1} is not allowed. Since $\langle\psi, H^2\psi\rangle - \langle\psi, H\psi\rangle^2 = \langle\psi, (H - \langle\psi, H\psi\rangle)^2\psi\rangle \geq 0$, the second term in the right-hand side is negative. Thus it is predicted that for accurate lower bounds we need $\langle\psi, H\psi\rangle \geq \mu_k$ (This inequality always holds for $k = 1$). Therefore, we need $\mu_{(k+1)lb} > \mu_k$, that is, $\mu_{(k+1)lb}$ separates μ_k and μ_{k+1}. Moreover, the larger $\mu_{(k+1)lb}$ is, the larger the right-hand side is. In order to apply Temple's inequality we need to obtain lower bounds $\mu_{(k+1)lb}$ by other methods.

2.2 Weinstein-Aronszajn intermediate problem method

Actually, we do not have many methods for lower bounds. A method which seems to have a possibility to give a value $\mu_{(k+1)lb}$ which satisfies $\mu_{(k+1)lb} > \mu_k$ is the Weinstein-Aronszajn intermediate problem method and methods derived from that method (although this speculation is groundless). The idea of these methods is summarized as follows (see [16, 4]).

- If operators A and B satisfy $A \leq B$, then $\mu_k^A \leq \mu_k^B$.
- If C is a finite-dimensional operator, μ is an eigenvalue of $A + C$ if and only if μ is a zero of $\det W(\mu)$, where $W(\mu)$ is a finite-dimensional matrix expressed using A, μ and a basis of $\operatorname{Ran} C$.

If $A \leq A + C \leq B$, we have $\mu_k^A \leq \mu_k^{A+C} \leq \mu_k^B$. Moreover, in some cases the calculation of the zeros of $\det W(\mu)$ can be executed. Thus we can calculate a lower bound μ_k^{A+C} of μ_k^B which improves a trivial lower bound μ_k^A in such a case. In all methods derived from the Weinstein-Aronszajn method, B must be an operator represented as a sum $A + G$ of A whose eigenvalue problem is solvable and a positive operator G.

In the case of the electronic Hamiltonian we regard H as a sum $A + G$ of

$$A := -\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} V(\mathbf{r}_i),$$

and a positive operator

$$G := \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Although the eigenvalue problem of A is not solvable, it is a sum of one-body operators, and it would be better to handle such a one-body operators first than handling the eigenvalue problem of H directly. When we apply the Weinstein-Aronszajn method in the next step, we need to calculate the integral $\langle\Psi, G^2\Psi\rangle$ where Ψ is an approximation of the eigenfunction of H. In fact, the same kind of integral is needed in all lower bound methods including the method by Temple's inequality

3 Structure of the eigenfunction

3.1 Exponential decay

A well-known property of the eigenfunction of the electronic Hamiltonian is the exponential decay (cf. Agmon [1]). Let us introduce a few notations to express the decay rate.

For $I \subsetneq \{1, \cdots, N\}$ we define a subset X_I of $\mathbb{R}^{3N}$ by

$$X_I := \{(\mathbf{r}_1, \ldots, \mathbf{r}_N) \in \mathbb{R}^{3N} : \mathbf{r}_i = 0 \text{ if } i \notin I\}.$$

We also define an operator H_I on $L^2(X_I)$ by

$$H_I := -\sum_{i \in I} \Delta_{\mathbf{r}_i} + \sum_{i \in I} V(\mathbf{r}_i) + \sum_{\substack{1 \le i < j \le N \\ i,j \in I}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Set $\Lambda_I := \inf \sigma(H_I)$ for $I \neq \emptyset$ and $\Lambda_I := 0$ for $I = \emptyset$. For any $(\mathbf{r}_1, \ldots, \mathbf{r}_N) \in \mathbb{R}^{3N} \setminus \{0\}$ denote by $I(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ the subset of integers $i \in \{1, \cdots, N\}$ such that $\mathbf{r}_i = 0$. For $E < \inf \sigma_{ess}(H)$ let us denote by $\rho(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ the geodesic distance from 0 to $(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ with respect to the Riemannian metric

$$ds^2 = (\Lambda_{I(\mathbf{r}_1, \ldots, \mathbf{r}_N)} - E) \sum_{i=1}^{N} |d\mathbf{r}_i|^2.$$

Here $|d\mathbf{r}_i|^2 := (dx_i)^2 + (dy_i)^2 + (dz_i)^2$, where (x_i, y_i, z_i) is the Cartesian coordinates of $\mathbf{r}_i \in \mathbb{R}^3$. Using the distance the exponential decay is expressed as follows.

Theorem 3.1 ([1, Theorem 4.12])**.** *Let Ψ be an eigenfunction associated with an eigenvalue $E < \inf \sigma_{ess}(H)$. Then for any $\epsilon > 0$ there exists a constant $C_\epsilon > 0$ such that*

$$|\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)| \le C_\epsilon e^{-(1-\epsilon)\rho(\mathbf{r}_1, \ldots, \mathbf{r}_N)}$$

a.e. on $\mathbb{R}^{3N}$.

3.2 Kato's cusp condition

Another important property of the eigenfunction is the cusp condition (cf. Kato [9]).

Theorem 3.2 (Kato's cusp condition [9])**.** *Let $\mathbf{r} \in \mathbb{R}^3$ be a position of an electron and $\tilde{\mathbf{r}} \in \mathbb{R}^{3(N-1)}$ be the position of the other electrons. Then an eigenfunction $\Psi(\mathbf{r}, \tilde{\mathbf{r}})$ satisfies $\frac{\partial \hat{\Psi}^A}{\partial r_A}\Big|_{r_A=0} = -Z_A \Psi(\mathbf{R}_A, \tilde{\mathbf{r}})$ except at some points $\tilde{\mathbf{r}}$ of a set of lower dimension, where $r_A = |\mathbf{r} - \mathbf{R}_A|$, and $\hat{\Psi}^A$ is the average value of Ψ taken over the sphere $r_A = \text{const}$ for a fixed value of $\tilde{\mathbf{r}}$.*

An approximation to the eigenfunction is constructed as a linear combination of Slater determinants

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) := (N!)^{-1/2} \sum_{\tau \in \mathbf{S}_N} (\operatorname{sgn} \tau) \psi_1(\mathbf{r}_{\tau(1)}) \cdots \psi_N(\mathbf{r}_{\tau(N)}).$$

According to Kato's cusp condition we can expect that $\psi_i(\mathbf{r})$ with a radial factor $e^{-\zeta r},\ \zeta > 0,\ r := |\mathbf{r}|$ is suitable for the approximation. Such a function is in general called a Slater type orbital (STO).

4 Slator type orbital (STO)

Let us denote the Cartesian coordinates and the polar coordinates of $\mathbf{r} \in \mathbb{R}^3$ by x, y, z and r, θ, φ respectively. Here we consider the following unnormalized STO:

$$\chi^n_{lm}(\mathbf{r}, \zeta) := Z^m_l(\mathbf{r}) r^{n-1} e^{-\zeta r},$$

where $n, l \in \mathbb{N},\ m \in \mathbb{Z},\ -l \le m \le l,\ \zeta > 0$ is a parameter, and $Z^m_l(\mathbf{r})$ is the spherical function defined by

$$Z^m_l(\mathbf{r}) := i^{m+|m|} r^l P^{|m|}_l(\cos\theta) e^{im\varphi},$$

that are actually homogeneous polynomials of x, y, z of degree l. Here $P^m_l(t)$ is the associated Legendre function defined by $P^m_l(t) = (1-t^2)^{m/2} \frac{d^m}{dt^m} P_l(t)$, where $P_l(t)$ is the Legendre polynomial. It is well known that Z^m_l satisfies the Laplace equation $\nabla^2 Z^m_l = 0$. We also define $Y_{lm}(\theta, \varphi)$ by

$$\begin{aligned} Y_{lm}(\theta, \varphi) &:= i^{m+|m|} \left(\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right)^{1/2} P^{|m|}_l(\cos\theta) e^{im\varphi} \\ &= \left(\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right)^{1/2} r^{-l} Z^m_l(\mathbf{r}). \end{aligned}$$

Then Y_{lm} are spherical harmonics, and they are orthogonal to each other in $L^2(\mathbb{S}^2)$, i.e.

$$\int_0^\pi \int_0^{2\pi} Y^*_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi) \sin\theta d\theta d\varphi = \delta_{ll'} \delta_{mm'}. \tag{4.1}$$

5 Fundamental one and two-center integrals

5.1 fundamental one-center integral

When all functions in (1.1) are centered at the same point (i.e. $\mathbf{R}_A = \mathbf{R}_B = \mathbf{R}_C = \mathbf{R}_D$) and each function is STO, the integral (1.1) is reduced to the following fundamental one-center integral.

$$[\chi^n_{lm} | \chi^{n'}_{l'm'}] := \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{r}'|^2} \overline{\chi^n_{lm}}(\mathbf{r}, \zeta) \chi^{n'}_{l'm'}(\mathbf{r}', \zeta') d\mathbf{r} d\mathbf{r}'.$$

5.1.1 analytic expression

We can prove that $[\chi^n_{lm}|\chi^{n'}_{l'm'}] = 0$ unless $l = l'$ and $m = m'$ (cf. Subsection 5.2). Moreover, when $l = m = 0$, we have the following analytic expression for $[\chi^n_{00}|\chi^{n'}_{00}]$.

$$[\chi^n_{00}|\chi^{n'}_{00}] = 16\pi^2 \left(-\frac{\partial}{\partial\zeta}\right)^n \left(-\frac{\partial}{\partial\zeta'}\right)^{n'} \frac{\log\zeta - \log\zeta'}{\zeta^2 - \zeta'^2}. \tag{5.1}$$

For the calculation of the derivatives in the right-hand side of (5.1) we need the formula ([12, (A.3)])

$$\left(\frac{\partial}{\partial\zeta}\right)^\nu = \sum_{k=\left[\frac{\nu+1}{2}\right]}^{\nu} \zeta^{2k-\nu}\beta^\nu_k \left(\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^k, \tag{5.2}$$

which can be easily confirmed by induction with respect to ν, where $\beta^\nu_k = \frac{2^{k-\nu}\nu!}{(\nu-k)!(2k-\nu)!}$ and $[t]$ is the greatest integer less than or equal to t. Using this equation and for derivatives equation of the form

$$\frac{1}{r}\frac{d}{dr}\frac{1}{(s+r^2)^k} = -\frac{2k}{(s+r^2)^{k+1}}, \tag{5.3}$$

we obtain

$$\begin{aligned}\frac{\partial^\nu}{\partial\zeta^\nu}\frac{\partial^{\nu'}}{\partial\zeta'^{\nu'}}\frac{1}{\zeta^2-\zeta'^2} = &\sum_{k=\left[\frac{\nu+1}{2}\right]}^{\nu} (-1)^k 2^k \zeta^{2k-\nu}\beta^\nu_k \sum_{k'=\left[\frac{\nu'+1}{2}\right]}^{\nu'} 2^{k'}\zeta^{2k'-\nu'}\beta^{\nu'}_{k'} \\ &\times (k+k')!\frac{1}{(\zeta^2-\zeta'^2)^{k+k'+1}}.\end{aligned}$$

The right-hand side of (5.1) is easily calculated using this formula.

5.1.2 expression by one-dimensional integrals

If we allow one-dimensional integrals to remain in an expression of $[\chi^n_{lm}|\chi^{n'}_{l'm'}]$, we have the following expression which is valid even if $l \neq 0$ and $m \neq 0$.

$$\begin{aligned}[\chi^n_{lm}|\chi^{n'}_{l'm'}] =&(-1)^{n+n'}\delta_{ll'}\delta_{mm'}\alpha_{lm} \sum_{p=\left[\frac{n+1}{2}\right]}^{n} \zeta^{2p-n}\beta^n_p \\ &\times \sum_{q=\left[\frac{n'+1}{2}\right]}^{n'} \zeta'^{2q-n'}\beta^{n'}_q \gamma^l_{pq} I^l_{pq},\end{aligned} \tag{5.4}$$

where

$$\alpha_{lm} := \frac{2^{2l+3}(l!)^2(l+|m|)!\pi^2}{(2l+1)(l-|m|)!},$$

$$\gamma_{pq}^{l} := (-2)^{p+q}\frac{(l+p+q)!}{l!},$$

and

$$I_{pq}^{l} := \int_0^1 \frac{u^{l+p}(1-u)^{l+q}}{(\zeta^2 u + \zeta'^2(1-u))^{l+p+q+1}}du. \tag{5.5}$$

5.2 fundamental two-center integral

When the condition $\mathbf{R}_A = \mathbf{R}_B \neq \mathbf{R}_C = \mathbf{R}_D$ is satisfied in (1.1) and each function is STO, the integral is reduced to the following fundamental two-center integral.

$$\begin{aligned}[\chi_{lm}^{n}|\chi_{l'm'}^{n'}]_R &:= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{1}{|\mathbf{r}-\mathbf{r}'|^2}\overline{\chi_{lm}^{n}}(\mathbf{r}_A)\chi_{l'm'}^{n'}(\mathbf{r}'_B)d\mathbf{r}d\mathbf{r}' \\ &= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{1}{|\mathbf{r}-\mathbf{r}'-\mathbf{R}|^2}\overline{\chi_{lm}^{n}}(\mathbf{r})\chi_{l'm'}^{n'}(\mathbf{r}')d\mathbf{r}d\mathbf{r}',\end{aligned}$$

where $\mathbf{R} := \mathbf{R}_B - \mathbf{R}_A$. If we choose the direction of $\mathbf{R}$ as the direction of the axis of the polar coordinates of χ_{lm}^{n} and $\chi_{l'm'}^{n'}$, the integral depends only on $R = |\mathbf{R}|$. Thus using the parameter R we have denoted the integral by $[\chi_{lm}^{n}|\chi_{l'm'}^{n'}]_R$. For the two-center integrals we can prove

$$[\chi_{lm}^{n}|\chi_{l'm'}^{n'}]_R = 0,\ m \neq m'.$$

We need the following formula for products of Y_{lm}:

$$Y_{lm}Y_{l'm'} = \sum_{\tilde{l}=l_{\min}}^{l_{\max}} G_{\tilde{l}}^{lml'm'}Y_{\tilde{l}\ m+m'}, \tag{5.6}$$

where $G_{\tilde{l}}^{lml'm'}$ is called the Gaunt coefficient (cf. [18, Appendix C]). Here the summation limits in (5.6) are given by

$$\begin{aligned} l_{\max} &= l + l', \\ l_{\min} &= \begin{cases} \mu_{\min}, & \text{if } l_{\max}+\mu_{\min} \text{ is even}, \\ \mu_{\min}+1, & \text{if } l_{\max}+\mu_{\min} \text{ is odd}, \end{cases} \\ \mu_{\min} &= \max\{|l-l'|, |m+m'|\}. \end{aligned} \tag{5.7}$$

5.2.1 analytic expression

We have the following analytic expression of $[\chi_{lm}^{n}|\chi_{l'm}^{n'}]_R$

$$\begin{aligned}[\chi_{lm}^{n}|\chi_{l'm}^{n'}]_R = (-1)^{n+n'+l'+m+1}8\pi^2 &\sum_{\tilde{l}=l_{\min}}^{l_{\max}} D_{\tilde{l}}^{l(-m)l'm}G_{\tilde{l}}^{l(-m)l'm} \\ &\times \sum_{p=0}^{\Delta l} E_p^{\tilde{l}\Delta l}R^{2\Delta l-2p}Z_{\tilde{l}}^{0}(\mathbf{R}) \\ &\times (U_{l+l'-p}^{nln'l'}(R,\zeta,\zeta') + U_{l+l'-p}^{n'l'nl}(R,\zeta',\zeta)),\end{aligned}$$

where

$$D_{\tilde{l}}^{lml'm'} := \left(\frac{4\pi(2\tilde{l}+1)(l+|m|)!(l'+|m'|)!(\tilde{l}-|m+m'|)!}{(2l+1)(2l'+1)(l-|m|)!(l'-|m'|)!(\tilde{l}+|m+m'|)!} \right)^{1/2},$$

$$E_p^{\tilde{l}\Delta l} := \frac{2^p \Delta l! \Gamma(\Delta l + \tilde{l} + 3/2)}{p!(\Delta l - p)! \Gamma(\Delta l + \tilde{l} - p + 3/2)},$$

and

$$U_q^{nln'l'}(R,\zeta,\zeta') := \sum_{\mu=0}^{n} \binom{n}{\mu} \sum_{\nu=0}^{l} \binom{l}{\nu} v_{n'l'}^{n-\mu\ l-\nu}(\zeta,\zeta') w_q^{\mu\nu}(R,\zeta),$$

with

$$v_{n_2 l_2}^{n_1 l_1}(\zeta,\zeta') := \left(\frac{\partial}{\partial\zeta}\right)^{n_1} \left(\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{l_1} \left(\frac{\partial}{\partial\zeta'}\right)^{n_2} \left(\frac{1}{\zeta'}\frac{\partial}{\partial\zeta'}\right)^{l_2} \frac{1}{\zeta^2 - \zeta'^2},$$
$$w_q^{\mu\nu}(R,\zeta) := \left(\frac{\partial}{\partial\zeta}\right)^{\mu} \left(\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{\nu} \left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{q} \frac{g(\zeta R)}{\zeta R}.$$

Here

$$g(t) := e^{-t}\mathrm{Ei}(t) - e^{t}\mathrm{Ei}(-t),$$

where $\mathrm{Ei}(t)$ is the exponential integral defined by

$$\mathrm{Ei}(t) := -\mathrm{p.v.} \int_{-t}^{\infty} \frac{e^{-s}}{s} ds.$$

It remains to calculate $v_{n_2 l_2}^{n_1 l_1}(\zeta,\zeta')$ and $w_q^{\mu\nu}(R,\zeta)$. With the help of (5.2) and (5.3) we obtain

$$v_{n_2 l_2}^{n_1 l_1}(\zeta,\zeta') = (-1)^{l_1} \sum_{\lambda_1=\left[\frac{n_1+1}{2}\right]}^{n_1} (-1)^{\lambda_1} 2^{\lambda_1+l_1} \beta_{\lambda_1}^{n_1} \zeta^{2\lambda_1-n_1}$$
$$\times \sum_{\lambda_2=\left[\frac{n_2+1}{2}\right]}^{n_2} 2^{\lambda_2+l_2} \beta_{\lambda_2}^{n_2} \zeta^{2\lambda_2-n_2} \frac{(\lambda_1+l_1+\lambda_2+l_2)!}{(\zeta^2-\zeta'^2)^{\lambda_1+l_1+\lambda_2+l_2+1}}.$$

As for $w_q^{\mu\nu}(R,\zeta)$ using (5.2) one finds

$$w_q^{\mu\nu}(R,\zeta) = \sum_{\sigma=\left[\frac{\mu+1}{2}\right]}^{\mu} \beta_\sigma^\mu \zeta^{2\sigma-\mu} \tilde{w}_q^{\nu+\sigma}(R,\zeta),$$

where

$$\tilde{w}_q^s(R,\zeta) := \left(\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{s} \left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{q} \frac{g(\zeta R)}{\zeta R}.$$

Since $\tilde{w}_q^s(R,\zeta)$ is symmetric with respect to the exchange of the pairs (ζ,s) and (R,q), it remains to derive an expression for $\tilde{w}_q^s(R,\zeta)$ with $s \geq q$. Here we need the following formulas for operators:

$$\left(\frac{1}{R}\frac{\partial}{\partial R}\right)^q \frac{1}{R} = \sum_{j=0}^{q} C_j^q R^{2j-2q-1} \left(\frac{1}{R}\frac{\partial}{\partial R}\right)^j, \tag{5.8}$$

with

$$C_j^q = \frac{2^j q! \prod_{i=0}^{q}(2j-2i+1)}{(q-j)!(2j+1)!},$$

and

$$\left(\frac{1}{\zeta}\frac{\partial}{\partial \zeta}\right)^\tau = \sum_{\kappa=1}^{\tau} (-1)^{\tau-\kappa} B_\kappa^\tau \zeta^{\kappa-2\tau} \left(\frac{\partial}{\partial \zeta}\right)^\kappa,$$

with

$$B_\kappa^\tau := \frac{(2\tau-\kappa-1)!}{2^{\tau-\kappa}(\tau-\kappa)!(\kappa-1)!},$$

which can easily be confirmed by induction with respect to q and τ respectively. Note that $\frac{1}{R}$ in (5.8) is a multiplication operator, and that the left hand side does not mean application of $\left(\frac{1}{R}\frac{\partial}{\partial R}\right)^q$ to $\frac{1}{R}$. Combining these equations and

$$\frac{1}{\zeta}\frac{\partial}{\partial \zeta}\frac{1}{R}\frac{\partial}{\partial R}\frac{g^{(M)}(\zeta R)}{\zeta} = \frac{g^{(M+2)}(\zeta R)}{\zeta},$$

one has

$$\begin{aligned}
&\tilde{w}_q^s(R,\zeta) \\
&\quad = \sum_{j=0}^{q} C_j^q \sum_{\kappa=1}^{s-j+1} (-1)^{s-j+1-\kappa} B_\kappa^{s-j+1} \zeta^{\kappa-2(s-j+1)} R^{2j-2q+\kappa-2} g^{(2j+\kappa-1)}(\zeta R).
\end{aligned} \tag{5.9}$$

The derivatives of g in the last expression is expressed by direct calculations as

$$\begin{aligned}
g^{(2M)}(t) &= -\sum_{i=1}^{M} \frac{2(2i-2)!}{t^{2i-1}} + g(t), \\
g^{(2M+1)}(t) &= \sum_{j=1}^{M} \frac{2(2i-1)!}{t^{2i}} - e^t \mathrm{Ei}(-t) - e^{-t}\mathrm{Ei}(t).
\end{aligned}$$

5.2.2 expression by one-dimensional integrals

Also for two-center integrals if we allow one-dimensional integrals to remain in an expression, we have the following expression:

$$[\chi_{lm}^n | \chi_{l'm}^{n'}]_R = A_m^{ll'} \sum_{\tilde{l}=l_{\min}}^{l_{\max}} (2\tilde{l}+1)^{1/2} G_{\tilde{l}}^{l-ml'm} M_{ll'\tilde{l}}^{nn'}, \tag{5.10}$$

where

$$A_m^{ll'} = (-1)^{l'+m} i^{l+l'} 2^{l+l'+3} l! l'! \pi \left(\frac{\pi (l+|m|)!(l'+|m|)!}{(2l+1)(2l'+1)(l-|m|)!(l'-|m|)!} \right)^{1/2},$$

$$\begin{aligned} M_{ll'\tilde{l}}^{nn'} &= (-1)^{n+n'} \sum_{p=\left[\frac{n+1}{2}\right]}^{n} \beta_p^n \zeta^{2p-n} (-2)^p \frac{(l+p)!}{l!} \\ &\times \sum_{p'=\left[\frac{n'+1}{2}\right]}^{n'} \beta_{p'}^{n'} \zeta'^{2p'-n'} (-2)^{p'} \frac{(l'+p')!}{l'!} L_{\tilde{l}\,\Delta l}^{l+p\ l'+p'}, \end{aligned} \tag{5.11}$$

and

$$\begin{aligned} L_{\tilde{l}\,\Delta l}^{l+p\ l'+p'} =& (2\pi)^{3/2} (-i)^{\tilde{l}} R^{l+l'+2p+2p'+2} \\ &\times \int_0^\infty \frac{k^{l+l'+1/2} J_{\tilde{l}+1/2}(k)}{((\zeta R)^2+k^2)^{l+p+1} ((\zeta' R)^2+k^2)^{l'+p'+1}} dk. \end{aligned} \tag{5.12}$$

Here $J_{\tilde{l}+1/2}$ is the Bessel function.

6 Three and four-center integrals

For three and four-center integrals we expand STO by a complete orthogonal system of STO. A complete orthogonal system of STO is given by

$$P_l^m(\cos\theta) e^{im\varphi} r^l e^{-r} L_p^{2l+2}(2r),$$

where $p, l \in \mathbb{N},\ m \in \mathbb{Z},\ l \geq |m|$ and $L_p^{2l+2}(s)$ is the associated Laguerre polynomial [5]. Using this system we can expand STO centered at $\mathbf{R}_B$ by those centered at 0 as

$$P_L^M(\cos\Theta) R^{N-1} e^{-R} = \sum_{l=M}^{\infty} P_l^M(\cos\theta) (2\mu r)^l e^{-\mu r} \sum_{p=0}^{\infty} C_{lp}^{NLM} L_p^{2l+2}(2\mu r), \tag{6.1}$$

where $R := |\mathbf{r} - \mathbf{R}_B|$, Θ is the angle between the z axis and $\mathbf{r} - \mathbf{R}_B$ and $\mu > 0$. Recurrence relations for the calculation of C_{lp}^{NLM} have been obtained by Rico and López [13],

In the following arguments we consider expansions by a complete orthonormal system φ_i of STO generally. We expand $\psi_2(\mathbf{r}_B)$ and $\psi_4(\mathbf{r}'_D)$ of $[\psi_1(\mathbf{r}_A)\psi_2(\mathbf{r}_B)|\psi_3(\mathbf{r}'_C)\psi_4(\mathbf{r}'_D)]$ in (1.1) by STOs φ_j centered at $\mathbf{R}_A$ and $\mathbf{R}_C$ respectively:

$$\psi_2(\mathbf{r}_B) = \sum_{j=1}^{\infty} c_j \varphi_j(\mathbf{r}_A),$$

$$\psi_4(\mathbf{r}'_D) = \sum_{k=1}^{\infty} \tilde{c}_k \varphi_k(\mathbf{r}'_C).$$

The equation (6.1) is an example of such an expansion. Let us assume that φ_i can be written as a linear combination of χ^n_{lm}. Then with the help of the Gaunt coefficients each $[\psi_1(\mathbf{r}_A)\varphi_j(\mathbf{r}_A)|\psi_3(\mathbf{r}'_C)\varphi_k(\mathbf{r}'_C)]$ can be written as a finite sum of fundamental one or two-center integrals. Since in practical calculations we need to truncate the expansions up to a finite sum $\Phi_J(\mathbf{r}_A) = \sum_{j=1}^J c_j\varphi_j(\mathbf{r}_A)$ and $\tilde{\Phi}_K(\mathbf{r}'_C) = \sum_{k=1}^K \tilde{c}_k\varphi_k(\mathbf{r}'_C)$, we have to estimate the error by the truncation written as follows:

$$\begin{aligned}
&[\psi_1(\mathbf{r}_A)\psi_2(\mathbf{r}_B)|\psi_3(\mathbf{r}'_C)\psi_4(\mathbf{r}'_D)] - [\psi_1(\mathbf{r}_A)\Phi_J(\mathbf{r}_A)|\psi_3(\mathbf{r}'_C)\tilde{\Phi}_K(\mathbf{r}'_C)] \\
&\quad = [\psi_1(\mathbf{r}_A)(\psi_2(\mathbf{r}_B) - \Phi_J(\mathbf{r}_A))|\psi_3(\mathbf{r}'_C)\psi_4(\mathbf{r}'_D)] \\
&\qquad + [\psi_1(\mathbf{r}_A)\Phi_J(\mathbf{r}_A)|\psi_3(\mathbf{r}'_C)(\psi_4(\mathbf{r}'_D) - \tilde{\Phi}_K(\mathbf{r}'_C))].
\end{aligned}$$

Using the Fourier transform and the Hardy inequality we can obtain the following estimate:

$$\begin{aligned}
&\left|[\psi_1(\mathbf{r}_A)\psi_2(\mathbf{r}_B)|\psi_3(\mathbf{r}'_C)\psi_4(\mathbf{r}'_D)] - [\psi_1(\mathbf{r}_A)\Phi_J(\mathbf{r}_A)|\psi_3(\mathbf{r}'_C)\tilde{\Phi}_K(\mathbf{r}'_C)]\right| \\
&\quad \le 4\pi^2\|\psi_1\|_{L^\infty}\|r'\psi_3(\mathbf{r}')\|_{L^\infty} \\
&\qquad \times \left(\|\psi_2(\mathbf{r}_B) - \Phi_J(\mathbf{r}_A)\|\|\psi_4\| + \|\Phi_J\|\|\psi_4(\mathbf{r}'_D) - \tilde{\Phi}_K(\mathbf{r}'_C)\|\right),
\end{aligned}$$

where $\|\cdot\|$ is the L^2-norm and $\|\cdot\|_{L^\infty}$ is the L^∞-norm. Note here that since φ_j is an orthonormal system, the L^2-norms of Φ_J and $\psi_2(\mathbf{r}_B) - \Phi_J(\mathbf{r}_A)$ are evaluated as

$$\|\Phi_J\|^2 = \sum_{j=1}^J |c_j|^2,$$

$$\|\psi_2(\mathbf{r}_B) - \Phi_J(\mathbf{r}_A)\|^2 = \|\psi_2\|^2 - \sum_{j=1}^J |c_j|^2.$$

The other norms are evaluated from the explicit form of STO.

7 Fundamental hybrid two-center integral

Fundamental hybrid two-center integrals are defined by

$$\begin{aligned}
&[\chi^{n_1}_{l_1m_1}|\chi^{n_2}_{l_2m_2}\chi^{n_3}_{l_3m_3}]_R \\
&\quad := \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \overline{\chi^{n_1}_{l_1m_1}}(\mathbf{r}_A,\zeta_1)\frac{1}{|\mathbf{r}-\mathbf{r}'|^2}\chi^{n_2}_{l_2m_2}(\mathbf{r}'_A,\zeta_2)\chi^{n_3}_{l_3m_3}(\mathbf{r}'_B,\zeta_3)d\mathbf{r}d\mathbf{r}' \\
&\quad = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \overline{\chi^{n_1}_{l_1m_1}}(\mathbf{r},\zeta_1)\frac{1}{|\mathbf{r}-\mathbf{r}'|^2}\chi^{n_2}_{l_2m_2}(\mathbf{r}',\zeta_2)\chi^{n_3}_{l_3m_3}(\mathbf{r}'_{AB},\zeta_3)d\mathbf{r}d\mathbf{r}',
\end{aligned}$$

where $\mathbf{R}_A \neq \mathbf{R}_B$ and $r'_{AB} = \mathbf{r}' - \mathbf{R}_B + \mathbf{R}_A$. The integral (1.1) with $\mathbf{R}_A = \mathbf{R}_B = \mathbf{R}_C \neq \mathbf{R}_D$ is reduced to integrals of this form using the Gaunt coefficient. We

apply the method in Section 6. For the expansion of $\chi_{l_3m_3}^{n_3}(\mathbf{r}'_{AB},\zeta_3)$ we use the following formula [13] which is identical to (6.1):

$$P_L^M(\cos\Theta)r_{AB}^{N-1}e^{-r_{AB}} = \sum_{k=M}^{\infty}\sum_{p=0}^{\infty} C_{kp}^{NLM}\omega_{kM}^{p}(\mathbf{r},\mu), \tag{7.1}$$

for $N, L, M \in \mathbb{N},\ L \geq M,\ \mu > 0$, where $r_{AB} = |\mathbf{r}_{AB}|$ and

$$\omega_{kM}^{p}(\mathbf{r},\mu) = P_k^M(\cos\theta)(2\mu r)^k e^{-\mu r} L_p^{2k+2}(2\mu r).$$

The coefficients C_{kp}^{NLM} can be calculated by recurrence relations depending on μ and $R = |\mathbf{R}_B - \mathbf{R}_A|$. Since the functions $\omega_{kM}^{p}(\mathbf{r},\mu),\ k = M, M+1, \ldots,\ p = 0, 1, \ldots$ form a complete orthogonal system, we can apply the arguments in Section 6.

The formula (7.1) and the expression of the Laguerre polynomial yield the expansion

$$\chi_{l_3m_3}^{n_3}(\mathbf{r}_{AB},\zeta_3) = \zeta_3^{-n_3-l_3+1}\sum_{k=M}^{\infty}\sum_{p=0}^{\infty}\sum_{q=0}^{p} T_{kpq}^{n_3l_3m_3}\chi_{km_3}^{q+1}(\mathbf{r},\zeta_3), \tag{7.2}$$

where $T_{kpq}^{n_3l_3m_3} = C_{kp}^{(n_3+l_3)l_3|m_3|}(-1)^q\binom{2k+p+2}{p-q}\frac{1}{q!}(2\zeta_3)^{k+q}$, and $C_{kp}^{(n_3+l_3)l_3|m_3|}$ depends on $\zeta_3 R$. Using this expansion we obtain

$$[\chi_{l_1m_1}^{n_1}|\chi_{l_2m_2}^{n_2}\chi_{l_3m_3}^{n_3}]_R = \zeta_3^{-n_3-l_3+1}\sum_{k=|m_3|}^{\infty}\sum_{p=0}^{\infty}\sum_{q=0}^{p} T_{kpq}^{n_3l_3m_3}[\chi_{l_1m_1}^{n_1}|\chi_{l_2m_2}^{n_2}\chi_{km_3}^{q+1}],$$

where

$$[\chi_{l_1m_1}^{n_1}|\chi_{l_2m_2}^{n_2}\chi_{km_3}^{q+1}] := \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\overline{\chi_{l_1m_1}^{n_1}}(\mathbf{r},\zeta_1)\frac{1}{|\mathbf{r}-\mathbf{r}'|^2}\chi_{l_2m_2}^{n_2}(\mathbf{r}',\zeta_2)\chi_{km_3}^{q+1}(\mathbf{r}',\zeta_3)d\mathbf{r}d\mathbf{r}'.$$

Using (5.6) we can see that

$$\begin{aligned}&[\chi_{l_1m_1}^{n_1}|\chi_{l_2m_2}^{n_2}\chi_{km_3}^{q+1}]\\ &\quad = \delta_{m_1(m_2+m_3)}D_{l_1}^{l_2m_2km_3}G_{l_1}^{l_2m_2km_3}[\chi_{l_1m_1}^{n_1}|\chi_{l_1m_1}^{n_2+q+l_2+k-l_1}(\zeta_2+\zeta_3)],\end{aligned} \tag{7.3}$$

for $l_2+l_3 \geq l_1 \geq l_{\min}$ and it vanishes in the other cases. Here $[\chi_{l_1m_1}^{n_1}|\chi_{l_1m_1}^{n_2+q+l_2+k-l_1}(\zeta_2+\zeta_3)]$ is the fundamental one-center integral with the index $\zeta_2+\zeta_3$ of the second STO, and $l_{\min}$ is the natural number defined by (5.7) with l, l', m, m' replaced by l_2, k, m_2, m_3. From (7.3) we can see that $[\chi_{l_1m_1}^{n_1}|\chi_{l_2m_2}^{n_2}\chi_{l_3m_3}^{n_3}]_R = 0$ unless $m_1 = m_2 + m_3$. In practical calculations we truncate the expansion of $\chi_{l_3m_3}^{n_3}(\mathbf{r}_{AB})$ in (7.2) up to finite terms. We denote the finite sum by $\Phi_J(\mathbf{r})$ as in Section 6, that is, if we use the terms up to $k = k_{\max}$ and $p = p_{\max}$,

$$\Phi_J(\mathbf{r}) := i^{m_3+|m_3|}e^{im\varphi}\zeta_3^{-n_3-l_3+1}\sum_{k=|m_3|}^{k_{\max}}\sum_{p=0}^{p_{\max}} C_{kp}^{(n_3+l_3)l_3|m_3|}\omega_{k|m_3|}^{p}(\mathbf{r},\zeta_3).$$

Following the arguments in Section 6 we have the error bound of the truncation

$$
\begin{aligned}
&|[\chi^{n_1}_{l_1m_1}|\chi^{n_2}_{l_2m_2}\chi^{n_3}_{l_3m_3}]_R - [\chi^{n_1}_{l_1m_1}|\chi^{n_2}_{l_2m_2}\Phi_J]| \\
&\quad \le 4\pi^2 \|r\chi^{n_1}_{l_1m_1}(\mathbf{r})\| \|\chi^{n_2}_{l_2m_2}\|_{L^\infty} \|\chi^{n_3}_{l_3m_3}(\mathbf{r}_{AB}) - \Phi_J(\mathbf{r})\| \\
&\quad \le 8\pi^2 \sqrt{\frac{\pi(2n_1+2l_1+2)!(l_1+|m_1|)!}{(2\zeta_1)^{2n_1+2l_1+3}(2l_1+1)(l_1-|m_1|)!}} \left(\frac{n_2+l_2-1}{\zeta_2}\right)^{n_2+l_2-1} \frac{(l_2+|m_2|)!}{l_2!} \\
&\qquad \times e^{-n_2-l_2+1} \|\chi^{n_3}_{l_3m_3}(\mathbf{r}_{AB}) - \Phi_J(\mathbf{r})\|,
\end{aligned}
\tag{7.4}
$$

where

$$
[\chi^{n_1}_{l_1m_1}|\chi^{n_2}_{l_2m_2}\Phi_J] := \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \overline{\chi^{n_1}_{l_1m_1}}(\mathbf{r},\zeta_1)\frac{1}{|\mathbf{r}-\mathbf{r}'|^2}\chi^{n_2}_{l_2m_2}(\mathbf{r}',\zeta_2)\Phi_J(\mathbf{r}')d\mathbf{r}d\mathbf{r}'.
$$

8 Numerical results

8.1 fundamental one and two-center integrals

The accurate significant figures of the one-center integral $[\chi^n_{lm}|\chi^{n'}_{lm}]$ for $\zeta = 1$, $\zeta' = 0.5$ were determined by the expression (5.4) and numerical one-dimensional integration. Examples are given in Table 1. The one-dimensional integral I^l_{pq} in

Table 1: The accurate significant figures of $[\chi^n_{lm}|\chi^{n'}_{lm}]$

n	n'	l	m	$[\chi^n_{lm}\|\chi^{n'}_{lm}]$	N_{ae}
2	3	0	0	1.56939270526650(4)	14
2	3	5	4	3.425716931848(16)	
2	3	10	9	1.0469905487775(39)	
4	4	0	0	1.953591848090(6)	13
4	4	5	4	5.8161756391883(19)	
4	4	10	9	6.7706640231478(42)	
6	5	0	0	6.77033700568(8)	11
6	5	5	4	1.5712472039294(23)	
6	5	10	9	5.9442801255419(46)	
8	8	0	0	8.8795833287(13)	9
8	8	5	4	2.22546915631(29)	
8	8	10	9	4.332795650516(53)	
11	10	0	0	5.5789551(19)	7
11	10	5	4	7.1529791758(35)	
11	10	10	9	5.881306549(60)	
14	14	0	0	2.5509(28)	4
14	14	5	4	3.91588207(45)	
14	14	10	9	1.642355950(71)	

The notation (ν) signifies $\times 10^\nu$.

(5.5) was evaluated approximating the integrand by the Chebyshev interpolation with typical order 1000 and integrating the polynomial. The accurate significant figures were obtained by determining invariant figures by varying the order of

the Chebyshev interpolation. For $l = m = 0$ the evaluation by the analytic expression was also executed. The number of the accurate figures N_{ae} of the value by the analytic expression are also shown in Table 1. The number N_{ae} was determined comparing the value obtained by using the expression (5.1) and the value by the one-dimensional integrals obtained above as a reliable reference.

The accurate significant figures of the two-center integral $[\chi^n_{lm}|\chi^{n'}_{l'm}]_R$ for $R = 4$, $\zeta = 1$, $\zeta' = 0.5$ were determined by the expression (5.10) and numerical one-dimensional integration. Examples are given in Table 2. The integral $L^{l+p\ l'+p'}_{\tilde{l}\,\Delta l}$ in (5.12) was evaluated using the Chebyshev interpolation with typical order 1000 as in the case of one-center integral. Typically integration on the interval $[0, 100]$ is enough, because that on $[100, \infty)$ is relatively very small and negligible owing to the decay of the integrands. The accurate significant figures of $[\chi^n_{lm}|\chi^{n'}_{l'm}]_R$ were obtained by determining invariant figures varying the order of the Chebyshev interpolation and the interval of the integration of $L^{l+p\ l'+p'}_{\tilde{l}\,\Delta l}$. The evaluation by analytic expression was also executed as in the case of one-center integrals and the number of the accurate figures N_{ae} of the value by the analytic expression are given.

Table 2: The accurate significant figures of $[\chi^n_{lm}|\chi^{n'}_{l'm}]_R$

n	l	n'	l'	m	$[\chi^n_{lm}\|\chi^{n'}_{l'm}]_R$	N_{ae}
3	2	3	2	1	2.2243751772625(7)	10
3	2	3	3	1	−2.7566722179287(8)	10
2	4	4	5	4	−1.3610327905104(16)	6
2	4	4	6	4	2.0420467016732(17)	4
2	5	2	6	4	−5.4090782928132(16)	3
2	6	2	6	4	4.986742283667(17)	1
2	7	2	6	5	2.73141199999476(20)	1
2	7	2	7	5	8.0955544928731(21)	0
5	9	5	10	3	−1.0629407232265(33)	0
5	10	5	10	3	9.83626880416(33)	0
10	5	10	4	2	3.8326037195(29)	0
10	5	10	5	2	6.9193761122(31)	0

The notation (ν) signifies $\times 10^{\nu}$.

In contrast to the high accuracy of the method by one-dimensional integrals, the accuracy of the analytic expression deteriorates rapidly as l, l', n and n' increase, and the results are completely meaningless for the parameters greater than moderate values. It was observed that in the calculation of $\tilde{w}^s_q$ in (5.9) enormous cancellations of significant digits happened.

8.2 fundamental hybrid two-center integral

The fundamental hybrid two-center integrals were evaluated by the method in Section 7. For the evaluation of the one-center integrals in the right-hand side of (7.3) the expression by one-dimensional integrals was used. Here recall that $[\chi^{n_1}_{l_1m_1}|\chi^{n_2}_{l_2m_2}\chi^{n_3}_{l_3m_3}]_R = 0$ unless $m_1 = m_2 + m_3$. Examples for $\zeta_1 = 1.0, \zeta_2 =$

$0.5, \zeta_3 = 1.0,\ R = 0.5$ are presented in Table 3. Terms in (7.1) corresponding to $k \leq 15$ and $p \leq 15$ were used for the calculation. The error bounds of the errors by this truncation given after $\pm$ in Table 3 were calculated from (7.4).

Table 3: The accurate significant figures of $[\chi^{n_1}_{l_1(m_2+m_3)}|\chi^{n_2}_{l_2m_2}\chi^{n_3}_{l_3m_3}]_R$

n_1	l_1	n_2	l_2	m_2	n_3	l_3	m_3	$[\chi^{n_1}_{l_1(m_2+m_3)}\|\chi^{n_2}_{l_2m_2}\chi^{n_3}_{l_3m_3}]_R$
1	1	1	1	0	3	2	1	$2.00918 \pm 0.00042(3)$
1	1	1	1	0	4	2	1	$8.49388 \pm 0.00039(3)$
1	2	1	1	1	3	2	1	$-5.6044 \pm 0.0084(3)$
1	2	1	2	1	4	2	1	$5.77148 \pm 0.00035(5)$
3	2	1	1	0	4	2	1	$-1.8072 \pm 0.0054(4)$
3	2	1	2	1	4	2	1	$1.573420 \pm 0.000095(7)$

The notation (ν) signifies $\times 10^{\nu}$.

9 Multiple precision calculation

In order to evaluate three and four-center integrals by the method in Section 6 we need more accuracy for one and two-center integrals. The main reason of the loss of accuracy in the evaluation of the fundamental one and two-center integrals is the cancellation of significant digits in the summations in expressions (5.4), (5.10) and (5.11). Since a double precision number has only 53 bits in its significand, it can keep at most only 15 digits as a decimal number. Therefore, even if we calculate the one-dimensional integrals numerically with the best accuracy in double precision, the cancellation of significant digits in the summations causes low accuracy. The only solution of this problem would be the calculation by higher precision.

Because currently no commercial CPU supports arbitrary precision calculations at the level of computer architecture, we need to use a module of programs which supports arbitrary precision calculations at the level of software. A famous module (library) of C programming language for arbitrary precision calculations is GNU MP (GMP) (see e.g. [10]). For floating point numbers a library called MPFR which is based on GMP is available. In order to use C++ libraries and write readable codes using the four basic arithmetic operations we also use the MPFR C++ wrapper by Holoborodko (cf. [6]). Using these libraries we can easily evaluate the integrals numerically with very high accuracy. Even several hundreds of accurate significant digits can be obtained easily. For example the first 200 accurate significant figures of the integral I^2_{32} in (5.5) is

given as follows.

$$I_{32}^2 = 0.076640949428932818283977491196142448985766303891258402522149415914026951207585817558339758721247143374374291248115193609879247647496568853336960895244638907164243887106890840656861891448433169594302624$$

For the evaluation we used the Chebychev interpolation with typical order 1000 and integration of the polynomial as in Section 8. The accurate significant figures were obtained by determining invariant figures by varying the order of the Chebyshev interpolation.

When we evaluate each integrals with such high accuracy and subsequent summations in (5.4), (5.10) and (5.11) by multiple precision calculation, even if cancellation of dozens of significant figures happens, we will have more than a hundred of accurate significant digits for the fundamental one and two-center integrals. Thus we can also evaluate three and four-center integrals with very high accuracy.

Acknowledgement
This work was supported by the Research Institute for Mathematical Sciences, an international Joint Usage/Research center located in Kyoto University.

References

[1] S. Agmon, Lectures on exponential decay of solutions of second-order elliptic equations: Bounds on eigenfunctions of N-body Schrödinger operators, Princeton University Press, (1982)

[2] N. Aronszajn, Approximation methods for eigenvalues of completely continuous symmetric operators, Proc. of the Symposium on Spectral Theory and Differential Problems, pp. 179–202. (1951)

[3] S. Ashida, Methods for accurate calculations of multi-center integrals of the squared Coulomb potential for lower bounds to energy levels of molecular systems, Preprint https://arxiv.org/pdf/2109.02086.pdf

[4] C. Beattie and F. Goerisch, Methods for computing lower bounds to eigenvalues of self-adjoint operators, *Numer. Math.* **72** (1995), 143–172.

[5] I. S. Gradsteyn, and I. M. Ryzhik, Table of Integrals, Series and Products, Academic Press, (2007)

[6] P. Holoborodko, MPFR C++, http://www.holoborodko.com/pavel/mpfr/

[7] J. D. Jackson, Classical Electrodynamics 2nd ed., Wiley, (1975)

[8] T. Kato, On the upper and lower bounds of eigenvalues, *J. Phys. Soc. Jpn.* **4** (1949), 334–339.

[9] T. Kato, On the eigenfunctions of many-particle systems in quantum mechanics, *Commun. Pure Appl. Math.* **10** (1957), 151–177.

[10] T. Kouya, Multiple precision numerical calculation, (Japanese) Morikita Shuppan, (2019)

[11] F. E. Neumann, Vorlesungen über die Theorie des Potentials und der Kugelfunktionen, B. G. Teubner, (1878)

[12] T. A. Niehaus, R. López and J. F. Rico, Efficient evaluation of the Fourier transform over products of Slater-type orbitals on different centers, *J. Phys. A* **41** (2008), 485205

[13] J. F. Rico and R. López, Recurrence relations for the expansion of Slater-type orbitals about displaced centers, *J. Chem. Phys.* **85** (1986), 5890–5894.

[14] K. Rüdenberg, A study of two-center integrals useful in calculations on molecular structure. II. the two-center exchange integrals, *J. Chem. Phys.* **19** (1951), 1459–1477.

[15] G. Temple, The theory of Rayleigh's principle as applied to continuous systems, *Proc. Roy. Soc.* **119** (1928), 276–293.

[16] H. F. Weinberger, Variational methods for eigenvalue approximation, SIAM, (1974)

[17] A. Weinstein and W. Stenger, Methods of Intermediate problems for eigenvalues, Academic Press, (1972)

[18] E. J. Weniger, The spherical tensor gradient operator, Collect. Czech. Chem. Commun. **70**, 1225 (2005).