METHODS FOR ACCURATE CALCULATIONS OF
MULTI-CENTER INTEGRALS OF THE SQUARED COULOMB
POTENTIAL FOR LOWER BOUNDS TO ENERGY LEVELS OF
MOLECULAR SYSTEMS

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Abstract. In this paper methods for calculations of multi-center integrals of
squared Coulomb potentials and Slater-type orbitals (STO) are derived. These
integrals are necessary for accurate lower bounds to energy levels of molecular
systems. All multi-center integrals are reduced to fundamental integrals using
the Gaunt coefficients and translation of STO. When the potential is the usual
Coulomb potential, using the Laplace expansion or the Neumann expansion
of the potential the integrals can be calculated. However, for the squared
Coulomb potentials such expansions are not known. For the fundamental one-
center and two-center integrals with squared Coulomb potentials, by methods
free from such expansions exact analytic expressions and expressions by one-
dimensional integrals of analytic functions are derived. The methods mainly
rely on the integration in ellipsoidal coordinates, the Fourier transform, Hob-
son’s theorem and expansion of differential operators by simple ones suitable
for the calculation. Numerical results by these expressions are given and com-
pared.

1. Introduction

As is well known, under the Born-Oppenheimer approximation properties of
molecules such as molecular structures and rates of chemical reactions are under-
stood from the dependence of electronic energy levels (i.e. eigenvalues of elec-
tronic Hamiltonians) on nuclear positions. Thus estimates for the eigenvalues of
the Hamiltonian are central to studies of molecules. However, unless the eigenvalue
problem is solved exactly, it is very difficult to evaluate the difference between the
true eigenvalue and the estimates.

A method to obtain error estimates is to give both upper and lower bounds of
the eigenvalues. In this method the true eigenvalue evidently lies between the two
values. Upper bounds can be obtained by the variational method. Compared to
upper bounds accurate lower bounds are much more difficult to achieve in many
respects. Therefore, most of the results obtained so far are concerned with vari-
ational upper bound, some perturbation theory or expansion theory whose error
estimate is hopeless, or some approximation for bulk from a macroscopic viewpoint
which is irrelevant to usual molecules.

However, only by the variational method reliable evaluation is impossible. Conver-
gence itself is obvious if we use a complete system in a certain appropriate Hilbert
space as a basis set, but it is the rate of the convergence that is important in practi-
cal calculations. One should note that seeming convergence of the value as the basis
set increases does not necessarily imply the convergence to the true energy level,
since addition of functions that does not contribute to the true eigenfunction to
the basis set does not improve the value. In particular, there is no mathematically
rigorous evidence that accurate upper bounds are obtained effectively using some
basis set such as the Slater or Gaussian type orbitals ordered in a natural way or
their linear combination obtained in some way, and increasing the basis set.

Unfortunately, comparison of the upper bounds with experimental energy levels
is also impossible except for equilibrium positions of the nuclei, because energy levels
for unstable nuclear positions are difficult to determine experimentally accurately.
In fact one of the most common purposes of calculations of energy levels is to predict
the equilibrium geometry of molecules which is the minimum point of the sum of
the energy level and the nuclear repulsion potential as a function of nuclear positions.
For such a purpose we need a method which guarantees accuracy of the evaluation
without resort to experimental data. Thus there should be a method of eigenvalue
evaluation for which it is confirmed that the error from the true eigenvalue is very
small in a mathematically rigorous way at least for small molecules. Therefore,
methods for lower bounds are desirable.

In lower bound methods, Temple’s inequality\(^1,2\) is known to have high accuracy
at least for simple systems. However, in order to apply Temple’s inequality we need
a lower bound of the eigenvalue next to the evaluated one. Thus we need to seek
rough lower bounds by other methods in order to apply Temple’s inequality. The
most promising method for such lower bounds would be the Weinstein-Aronszajn
intermediate problem method\(^3,4\) in which the Coulomb repulsion potentials between electrons are regarded as pertur-
bation by a positive operator.

In these methods (including the method by Temple’s inequality), one needs to
calculate the integral \(\langle \Psi | H^2 | \Psi \rangle\), where \(\Psi\) is the wave function for \(N\) electrons and
\(H\) is the Hamiltonian of all the electrons written in atomic units as

\[
H = \frac{-1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|r_i - R_A|} + \sum_{1 \leq i < j \leq N} \frac{1}{|r_i - r_j|}.
\]

Here \(M\) is the number of nuclei, \(r_i\) and \(R_A\) are positions of electron \(i\) and nucleus \(A\)
respectively, and \(Z_A\) is the atomic number of nucleus \(A\). The problem of evaluation
of such integrals has been one of the main difficulties in lower bound estimates\(^7,8\)
and has not been solved essentially so far.

As the function \(\Psi\) some approximate eigenfunction of the Hamiltonian is used.
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. Kato\(^9\) proved that a true eigenfunction \(\Psi(\mathbf{r}, \tilde{\mathbf{r}})\) satisfies
\(\frac{\partial \Psi^A}{\partial r_A} |_{r_A=0} = -Z_A \Psi(R_A, \tilde{\mathbf{r}})\) except at some points \(\tilde{\mathbf{r}}\) of a set of lower dimension. Here \(r_A = |\mathbf{r} - R_A|\) and \(\Psi^A\) is the average value of \(\Psi\) taken over the sphere \(r_A = \text{const}\) for a
fixed value of \(\tilde{\mathbf{r}}\). This well-known result called Kato’s cusp condition implies that
the true eigenfunction has cusps at the positions of nuclei like the eigenfunction of
the hydrogen atom. Hence, for accurate evaluation of the energy level the Slater-
type orbital (STO) which has a factor as \(e^{-\zeta r}\) is suitable. Nevertheless, in practical
calculations Gaussian-type orbitals (GTO) which has a factor as \(e^{-\zeta r^2}\) are often
used because the calculation of integrals for GTO is easier than that for STO.

In order to approximate the expectation value of squared Hamiltonian \(H^2\) with
respect to a Slater determinant of STO \(\psi\) by that of a linear combination \(\sum_i \phi_i\) of
where \( \| u \| = \sqrt{\langle u, u \rangle} \) and \( \mathcal{F} \) is the Fourier transform. However, the Fourier transform of STO is a rational function (cf. Eq. (3.13)) in contrast to that of the integrals encountered in the calculations of variational upper bounds of molecular integrals. The results in this paper are concerned with the evaluation of \( \langle \Psi | H^2 | \Psi \rangle \) where \( \Psi \) is a linear combination of the Slater determinants \( \langle N! \rangle^{-1/2} \det | \psi_1 \psi_2 \cdots \psi_N | \) of STO. Here each \( \psi_i \) is STO centered at one of the positions \( \mathbf{R}_A, \ A = 1, \ldots, M \) of the nuclei. One of the most difficult integrals in the terms of \( \langle \Psi | H^2 | \Psi \rangle \) would be the integral of the following form:

\[
\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi_1^*(\mathbf{r}_A) \psi_2(\mathbf{r}_B) \frac{1}{| \mathbf{r} - \mathbf{r}' |^2} \psi_3^*(\mathbf{r}'_C) \psi_4(\mathbf{r}'_D) d\mathbf{r} d\mathbf{r}',
\]

where \( \mathbf{r}_A := \mathbf{r} - \mathbf{R}_A \) and \( \mathbf{r}'_C := \mathbf{r}' - \mathbf{R}_C \). If the squared Coulomb potential \( \frac{1}{| \mathbf{r} - \mathbf{r}' |} \) is replaced by the usual Coulomb potential \( \frac{1}{| \mathbf{r} - \mathbf{r}' |^3} \), this integral is the multi-center integral encountered in the calculations of variational upper bounds of molecular energy levels and is a central subject in the variational method. A product of two STOs centered at the same point can be expressed as a finite sum of STOs using Gaunt coefficients[10] and STO centered at \( \mathbf{R}_A \) can be expanded by STOs centered at different point \( \mathbf{R}_B \). Thus the calculation of integral Eq. (1.1) is reduced to that of the integrals of the following form:

\[
\int_{\mathbb{R}^3} \psi_1^*(\mathbf{r}_A) \psi_2(\mathbf{r}_B) \frac{1}{| \mathbf{r} - \mathbf{r}' |^2} \psi_2(\mathbf{r}'_B) d\mathbf{r} d\mathbf{r}'.
\]

In this paper analytic expressions and expressions by one-dimensional integrals of analytic functions are derived for this fundamental integral for both the cases of \( \mathbf{R}_A = \mathbf{R}_B \) and \( \mathbf{R}_A \neq \mathbf{R}_B \) (In this paper, the term “analytic expression” means an expression by functions for which efficient accurate evaluation have been well-established). If the factor \( \frac{1}{| \mathbf{r} - \mathbf{r}' |} \) is replaced by the usual Coulomb potential \( \frac{1}{| \mathbf{r} - \mathbf{r}' |^3} \), integral Eq. (1.2) with \( \mathbf{R}_A = \mathbf{R}_B \) can be calculated using the Laplace expansion[13]

\[
\frac{1}{| \mathbf{r} - \mathbf{r}' |^3} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l + 1} \frac{r_<^{2l}}{r_>^{2l+1}} Y_{lm}^* (\theta', \phi') Y_{lm} (\theta, \phi),
\]

where \( (r, \theta, \varphi) \) and \( (r', \theta', \varphi') \) 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. Moreover, in this case for \( \mathbf{R}_A = \mathbf{R}_C, \ \mathbf{R}_B = \mathbf{R}_D \) and \( \mathbf{R}_A \neq \mathbf{R}_B \), integral Eq. (1.2) can be calculated using the Neumann expansion[13][15]

\[
\frac{1}{| \mathbf{r} - \mathbf{r}' |} = \frac{2}{R} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-1)^m (2l + 1) \left( \frac{(l - |m|)!}{(l + |m|)!} \right)^2 P_{l}^{(|m|)} (\xi_<) Q_{l}^{(|m|)} (\xi_>) P_{l}^{(|m|)} (\eta_<) P_{l}^{(|m|)} (\eta_>) e^{i m \varphi} e^{-i m \varphi'},
\]

where \( (\xi, \eta, \varphi) \) and \( (\xi', \eta', \varphi') \) 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 Legendre functions, and \( R = | \mathbf{R}_A - \mathbf{R}_B | \). However, for the squared
Coulomb potential such expansions have not been known. There has not been any substantial progress for the method to evaluate integral Eq. (1.1) so far as far as the author knows. In fact it seems that such a study has long been abandoned due to its difficulty. In this paper we derive expressions for integral Eq. (1.2) by methods free from such expansions.

For both \(R_A = R_B\) (one-center integral) and \(R_A \neq R_B\) (two-center integrals) analytic expressions (for special cases of STO in the case of \(R_A = R_B\)) and expressions by one-dimensional integrals are derived. For both one-center and two-center integrals the analytic expressions are applicable only if the scaling parameters \(\zeta\) of \(\psi_1\) and \(\psi_2\) are different. For the derivation of the expressions wide range of techniques are needed. In particular, we need integration in ellipsoidal coordinates, techniques concerning the Fourier transform, Hobson’s theorem and expansion of differential operators by simple ones suitable for the calculation.

Numerical results by the analytic expression and the expression by one-dimensional integrals are compared. Accuracy of the expressions by one-dimensional integrals is much better than the analytic expressions because of cancellation of significant digits in the analytic expressions. The accuracy would be reasonable for application to lower bound calculations of energy levels of small molecules.

2. Definitions and basic formulas

We consider the functions known as Slater type orbitals (STO). Let us denote the Cartesian coordinates of \(r \in \mathbb{R}^3\) by \(x, y, z\). We also denote the polar coordinates of \(r\) by \(r, \theta, \varphi\). An unnormalized STO considered in this paper is defined by

\[
\chi_{lm}^n(r, \zeta) = Z_l^m(r) r^{n-1} e^{-\zeta r},
\]

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

\[
Z_l^m(r) = e^{im\theta} P_l^{|m|}(\cos \theta) e^{im\varphi},
\]

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

\[
Y_{lm}(\theta, \varphi) = r^{m+|m|} \left( \frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right)^{1/2} P_l^{|m|}(\cos \theta) e^{im\varphi} = \left( \frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right)^{1/2} r^{-l} Z_l^m(r).
\]

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

\[
\int_0^\pi \int_0^{2\pi} Y_{lm}^*(\theta, \varphi) Y_{l'm'}(\theta, \varphi) \sin \theta d\theta d\varphi = \delta_{ll'} \delta_{mm'}.
\]

3. Fundamental one-center integrals

The fundamental one-center integral \(\chi_{lm}^n | \chi_{l'm'}^n\) is defined by

\[
\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|r - r'|^2} \chi_{lm}^n(r, \zeta) \chi_{l'm'}^n(r', \zeta') i drdr'.
\]
where $\chi^*_{lm}$ is the complex conjugate of $\chi^n_{lm}$. As we will see in Sect. 3.2 this integral is not zero only if $l = l'$ and $m = m'$.

### 3.1. Method 1: analytic expression for $l = m = 0$

For the fundamental one-center integrals with $l = m = 0$ we have the following analytic expression.

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

The formula Eq. (3.1) is derived as follows. Since $\chi^n_{00} = \left( -\frac{\partial}{\partial \zeta} \right)^n \chi^0_{00}$ we have only to prove

$$
[x^n_{00}]^0 = 16\pi^2 \frac{\log \zeta - \log \zeta'}{\zeta^2 - \zeta'^2}.
$$

By the change of variables $\tilde{r} = -r$, $\tilde{r}' = r' - r$, we have

$$
[x^0_{00}]^0 = \int_{\mathbb{R}^2} \int_{\mathbb{R}^2} \frac{1}{|r - r'|^2} |r| |r'|^{n'} \, d\tilde{r} d\tilde{r}'.
$$

In order to calculate $\tilde{r}$ integral, we introduce the ellipsoidal coordinates. Let $q, q' \in \mathbb{R}^2$ be points such that $q \neq q'$ and set $D = |q - q'|$, $\tilde{r}_q = |r - q|$, $\tilde{r}_q' = |r - q'|$. When we choose the direction of $q - q'$ as the direction of the third axis in $\mathbb{R}^3$ and $\tilde{r}_q$, $\tilde{r}_q'$ as the origin, ellipsoidal coordinates $(\xi, \eta, \varphi)$ of $\tilde{r}$ with foci $q, q'$ is defined by $\xi = \frac{\tilde{r}_q + \tilde{r}_q'}{2}$, $\eta = \frac{\tilde{r}_q - \tilde{r}_q'}{2}$, $\varphi = \arccos \left( \tilde{x}/\sqrt{\tilde{x}^2 + \tilde{y}^2} \right)$, where $\tilde{r} = (\tilde{x}, \tilde{y}, \tilde{z})$. Then the integration of a function $f(\tilde{r})$ is written as

$$
\int_{\mathbb{R}^3} f(\tilde{r}) \, d\tilde{r} = \frac{D^3}{8} \int_{\xi}^{1} \left\{ \int_{-1}^{1} \left\{ \int_{0}^{2\pi} (\xi^2 - \eta^2) f(\xi, \eta, \varphi) \, d\varphi \right\} \, d\eta \right\} \, d\xi.
$$

Thus setting $q = 0$, $q' = r'$ we obtain

$$
\int_{\mathbb{R}^3} \frac{e^{-\zeta |\tilde{r}|}}{|\tilde{r}|} \frac{e^{-\zeta' |\tilde{r}'|}}{|\tilde{r}' - \tilde{r}|} \, d\tilde{r} = \frac{2\pi}{|\tilde{r}'| \left( \zeta^2 - \zeta'^2 \right)} \int_{0}^{1} \int_{0}^{\infty} e^{-\frac{\zeta + \zeta'}{|\tilde{r}'|} \left( \zeta - \zeta' \right) \tilde{r} \, d\tilde{r}} \, d\xi.
$$

Thus by the change of variables to the polar coordinates we have

$$
\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|\tilde{r}'|^2} \frac{1}{|\tilde{r}' - \tilde{r}|} \, d\tilde{r} d\tilde{r}' = \frac{4\pi}{\zeta + \zeta'} \int_{0}^{1} \int_{0}^{\infty} e^{-\left( \zeta |\tilde{r}'| + (\zeta' - \zeta) |\tilde{r}'| \right) \tilde{t}} \, d\tilde{t} \, d\xi.
$$

which completes the proof.

For large $n$ and $n'$ the calculation of the right-hand side of Eq. (3.1) is not so easy. We are going to derive one efficient method now. Since Eq. (3.1) is symmetric...
with respect to $\zeta$ and $\zeta'$, we have only to calculate $\frac{\partial^{\nu}}{\partial \zeta^{\nu}} \frac{\partial^{\nu'}}{\partial \zeta'^{\nu'}} \log \zeta$. Using binomial coefficients we have

$$\frac{\partial^{n}}{\partial \zeta^{n}} \frac{\partial^{n'}}{\partial \zeta'^{n'}} \frac{\partial^{\nu}}{\partial \zeta^{\nu}} \frac{\partial^{\nu'}}{\partial \zeta'^{\nu'}} \log \zeta = \log \zeta \frac{\partial^{n}}{\partial \zeta^{n}} \frac{\partial^{n'}}{\partial \zeta'^{n'}} \frac{1}{\zeta^2 - \zeta'^2} + \sum_{\nu=0}^{n-1} \binom{n}{\nu} (-1)^{n-\nu-1} (n-\nu-1)! \zeta^{n-\nu} \frac{1}{\partial \zeta^{\nu}} \frac{\partial^{\nu'}}{\partial \zeta'^{\nu'}} \frac{1}{\zeta^2 - \zeta'^2}.$$ 

In order to calculate $\frac{\partial^{\nu}}{\partial \zeta^{\nu}} \frac{\partial^{\nu'}}{\partial \zeta'^{\nu'}} \frac{1}{\zeta^2 - \zeta'^2}$ we need the following formula for differential operator\[15\] which can be confirmed easily by induction with respect to $n$:

$$(3.3) \quad \left( \frac{\partial}{\partial \zeta} \right)^n = \sum_{k=\left[\frac{n}{2}\right]}^{n} \zeta^{2k-n} \beta_k \left( \frac{1}{\zeta} \frac{\partial}{\partial \zeta} \right)^k,$$ 

where $\beta_k = \frac{2^{n-k}n!}{(n-k)!}!$ and $[t]$ is the greatest integer less than or equal to $t$. Using Eq. (5.3) we can calculate as

$$\frac{\partial^{\nu}}{\partial \zeta^{\nu}} \frac{\partial^{n'}}{\partial \zeta'^{n'}} \frac{1}{\zeta^2 - \zeta'^2} = \sum_{k=\left[\frac{n}{2}\right]}^{\nu} (-1)^{k} 2^k \zeta^{2k-\nu} \beta_k \sum_{k'=\left[\frac{n'}{2}\right]}^{n'} 2^{k'} \zeta^{2k'-n'} \beta_{k'} \times (k + k')! \frac{1}{(\zeta^2 - \zeta'^2)^{k+k'+1}}.$$ 

3.2. Method 2: reduction to one-dimensional integrals on a bounded interval. Even for $l = m = 0$ the expression (3.1) can not be used when $\zeta = \zeta'$, because the denominator is zero and it is difficult to determine the limit as $\zeta \to \zeta'$ in particular for large $n$ and $n'$. However, if we allow existence of one-dimensional integrals of analytic functions on a bounded interval, an expression for arbitrary $l, m$ and $\zeta, \zeta'$ can be derived.

Let us denote the Fourier transform of $f$ by $\mathcal{F}f$:

$$\mathcal{F}f(r) = \int_{\mathbb{R}^3} e^{-ik \cdot r} f(r) dr.$$

We regard $\int_{\mathbb{R}^3} \frac{1}{|r|^2} \chi_{lm}^{(n)}(r, \zeta) dr$ as a convolution $\frac{1}{|r|^2} \ast \chi_{lm}^{(n)}$ whose Fourier transform is given by $\mathcal{F}\left(\frac{1}{|r|^2} \ast \chi_{lm}^{(n)}\right) = (\mathcal{F}\frac{1}{|r|^2})(\mathcal{F}\chi_{lm}^{(n)})$. Since we have\[16\]

$$(3.4) \quad \left(\frac{\mathcal{F}}{|r|^2}\right)(k) = \frac{2\pi^2}{|k|},$$

by Perseval’s formula we can rewrite the integral as

$$(3.5) \quad \chi_{lm}^{n} \chi_{lm'}^{n'} = 2^{-2} \pi^{-1} \int_{\mathbb{R}^3} |k|^{-1} \mathcal{F}\chi_{lm}^{n}(k) \mathcal{F}\chi_{lm'}^{n'}(k) dk.$$ 

Now we need an expression of $\mathcal{F}\chi_{lm}^{n}$. We shall first calculate $\mathcal{F}(e^{-r})(k)$. In the polar coordinates the Fourier transform is written as

$$\mathcal{F}(e^{-r})(k) = 2\pi \int_{0}^{\infty} \int_{0}^{\pi} e^{-ir k \cos \theta} e^{-r \sin \theta} d\theta dr,$$ 

where

$$e^{-ir k \cos \theta} = \cos(k \cos \theta, r) - i \sin(k \cos \theta, r).$$
where \( k = |k| \) and we choose the direction of \( k \) as the direction of the axis of the polar coordinates on which \( \theta = 0 \). Integration with respect to \( r \) can be performed by integration by parts, and we obtain

\[
\mathcal{F}(e^{-\zeta r})(k) = 2\pi \int_0^\pi \frac{2 \sin \theta}{(ik \cos \theta + 1)^3} d\theta = \frac{8\pi}{(1 + k^2)^2}.
\]

By the change of coordinates \( r \to \zeta^{-1} r \) we have

\[
\mathcal{F}(e^{-\zeta r})(k) = \zeta^{-3} \mathcal{F}(e^{-\zeta^{-1} r})(\zeta^{-1} k) = \frac{8\pi \zeta}{(\zeta^2 + k^2)^2}.
\]

Noting that \( r^{-1} e^{-\zeta r} = \int_0^\infty e^{-\zeta t} dt \) and changing the order of integration we obtain

\[
\mathcal{F}(\chi^0_{lm}(r, \zeta))(k) = \mathcal{F}(r^{-1} e^{-\zeta r})(k) = \int_0^\infty \mathcal{F}(e^{-\zeta t})(k) dt = \int_0^\infty e^{-\zeta t} dt = \frac{4\pi}{\zeta^2 + k^2}.
\]

Here we note that

\[
\chi^n_{lm} = \left(-\frac{\partial}{\partial \zeta}\right)^n \chi^0_{lm}.
\]

By Eq. (3.7) we have only to consider \( \chi^0_{lm} \). Using the formula for the Fourier transforms of functions multiplied by variables, we can see that the Fourier transform of \( \chi^0_{lm} \) is written as

\[
\mathcal{F}(\chi^0_{lm}(r, \zeta))(k) = Z^m_l((\nabla_k) \mathcal{F}(r^{-1} e^{-\zeta r}) = i^l Z^m_l(\nabla_k) \mathcal{F}(r^{-1} e^{-\zeta r}),
\]

where \( \nabla_k = \left(\frac{\partial}{\partial k_x}, \frac{\partial}{\partial k_y}, \frac{\partial}{\partial k_z}\right) \).

Now we need to calculate \( Z^m_l(\nabla_k) \mathcal{F}(r^{-1} e^{-\zeta r}) \). For this purpose we use the following Hobson’s theorem. Let \( f(x, y, z) \) be a homogeneous polynomial of degree \( l \in \mathbb{N} \) in the variables \( x, y, z \) and \( F \in C^\infty(\mathbb{R}) \). Then we have

\[
f(\nabla) F(r) = \sum_{\nu=0}^{l+1} \frac{1}{2^{\nu} \nu!} \left[ \frac{1}{r} \frac{d}{dr} \right]^{l-\nu} F(r) \nabla^{2\nu} f(x, y, z).
\]

If \( f \) is a solution to the Laplace equation \( \nabla^2 f = 0 \), only the power \( \nabla^{2\nu} \) with \( \nu = 0 \) produces a nonzero result:

\[
f(\nabla) F(r) = \left[ \frac{1}{r} \frac{d}{dr} \right]^l F(r) f(x, y, z).
\]

We note here that

\[
\frac{1}{r} \frac{d}{dr} \frac{1}{r} = \frac{2}{(s + r^2)^{k+1}}.
\]

Since \( Z^m_l \) satisfies the Laplace equation, using Eqs. (3.6), (3.10) and (3.11) we obtain

\[
Z^m_l(\nabla_k) \mathcal{F}(r^{-1} e^{-\zeta r}) = (-1)^l 2^{l+2} l! \pi \frac{Z^m_l(k)}{(\zeta^2 + k^2)^{l+1}}.
\]

It follows from Eqs. (3.10), (3.8) and (3.12) that

\[
\mathcal{F}(\chi^n_{lm}) = (-i)^l 2^{l+2} l! \pi \left(-\frac{\partial}{\partial \zeta}\right)^n \frac{Z^m_l(k)}{(\zeta^2 + k^2)^{l+1}}.
\]
By the change of the variables

\[ \chi^{n'}_{lm} = i^l (-i)^{m+n+1} \chi^{n'}_{lm} \]

where \( m = m' \) and \( n = n' \).

Combining Eqs. (3.14), (3.15), (3.3) and (3.11) with (3.15)

Finally obtain

\[ \int_0^\infty \frac{2^{2l+1}}{(\zeta^2 + k^2)^{(2l+1) + 1}} dk = \int_0^1 \frac{u^l (1-u)^l}{(\zeta^2 u + \zeta^2 (1-u)^2)^{(2l+1) + 1}} du. \]

Combining Eqs. (3.14), (3.15), (3.3) and (3.11) with \( r \) replaced by \( \zeta \) and \( \zeta' \), we finally obtain

\[ \langle \chi^{n'}_{lm} | \chi_{l'm'} \rangle = (-1)^{n+n'} \delta_{ll'} \delta_{mm'} \alpha_{lm} \sum_{p=-\infty}^{n+1} \zeta^{2p-n} \beta_p \sum_{q=\infty}^{n'} \zeta'^{q-n'} \beta_q^{p} l_p^{l'} , \]

where

\[ \gamma_{pq}^l = (-2)^{p+q}(l+p+q)! \frac{l!}{l+p+q} \]

and

\[ l_{pq}^l = \int_0^1 \frac{u^{l+p}(1-u)^{l+q}}{(\zeta^2 u + \zeta^2 (1-u)^2)^{l+p+q+1}} du. \]

4. Fundamental Two-Center Integrals

In this section we consider the following fundamental two-center integrals for \( \chi_{lm}^{n'} \) and \( \chi_{l'm'}^{n'} \) centered at \( \mathbf{R}_A, \mathbf{R}_B \in \mathbb{R}^3, \mathbf{R}_A \neq \mathbf{R}_B: \)

\[ \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{r}'|^2} \chi_{lm}^{n'}(\mathbf{r}_A) \chi_{l'm'}^{n'}(\mathbf{r}_B) d\mathbf{r} d\mathbf{r}'. \]

By a translational change of variables we can rewrite the integral as

\[ \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{r}' + \mathbf{R}_A - \mathbf{R}_B|^2} \chi_{lm}^{n'}(\mathbf{r}) \chi_{l'm'}^{n'}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \]

If we choose the direction of \( \mathbf{R}_B - \mathbf{R}_A \) as the direction of the axis of the polar coordinates of \( \chi_{lm}^{n'} \) and \( \chi_{l'm'}^{n'} \), the integral depends only on the distance \( R = |\mathbf{R}_B - \mathbf{R}_A| \). Thus let us denote the integral by \( [\chi_{lm}^{n'} | \chi_{l'm'}^{n'}]_R \), i.e.

\[ [\chi_{lm}^{n'} | \chi_{l'm'}^{n'}]_R = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}_B|^2} \chi_{lm}^{n'}(\mathbf{r}) \chi_{l'm'}^{n'}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \]

(4.1)

\[ = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}_A|^2} \chi_{lm}^{n'}(\mathbf{r} + \mathbf{R}) \chi_{l'm'}^{n'}(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \]
where \( R = R_B - R_A \). Here we note

\[
[x^n_m|y^n_{m'}]_R = 0, \quad m \neq m'.
\]

Although this is proved by Parseval’s formula and the form Eq. (3.13) of the Fourier transform of \( x^n_m \), we shall give an elementary proof here. Recall that \( x^n_m \) depends on the angular coordinates \((\theta', \varphi')\) of \( r' \) through the factor \( Y_{l'm'}(\theta', \varphi') \). In the \( r' \)-integral in Eq. (4.1), we can choose the direction of \( r' \) as a new axis of the polar coordinates of \( r' \). Then the new polar coordinates of \( r' \) can be written as \((r', \gamma, \psi)\), where \( \gamma \) is the angle between \( r' \) and \( r \). Then \( Y_{l'm'}(\theta', \varphi') \) can be expanded by the spherical harmonics \( Y_{l'm}(\gamma, \psi) \) with respect to the new coordinates as

\[
Y_{l'm'}(\theta', \varphi') = \sum_{m=-l'}^{l'} C_m Y_{l'm}(\gamma, \psi).
\]

Setting \( \gamma = 0 \) and noting \( Y_{l'm}(0, \psi) = 0, \quad m \neq 0, \quad Y_{l'0}(0, \psi) = \left(\frac{2l'+1}{4\pi}\right)^{1/2} \), we can see that \( C_0 = \left(\frac{4\pi}{2l'+1}\right)^{1/2} Y_{l'm'}(\theta, \varphi) \), where \((\theta, \varphi)\) is the angular coordinates of \( r \).

Using \(|r - r'|^2 = r^2 - 2rr' \cos \gamma + r'^2\) we can calculate the \( r' \)-integral as

\[
(4.2) \quad \int_{\mathbb{R}^3} \frac{1}{|r - r'|^2} x^n_m(r')dr' = f(r) Y_{l'm'}(\theta, \varphi),
\]

where

\[
f(r) = 4\pi \frac{2l'+1}{2l'+1} \left(\frac{l' + |m'|}{l' - |m'|}\right)! \left(\frac{(l' + |m'|)!}{(l' - |m'|)!}\right)^{1/2} \times \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \frac{e^{-\beta r' \frac{r}{r'^2}} Y_{l'm'}(\gamma, \psi)}{r'^2 - 2rr' \cos \gamma + r'^2} d\gamma d\psi.
\]

Here we used that \( \psi \)-integral of \( Y_{l'm}(\gamma, \psi) \), \( m \neq 0 \) vanishes. The result \([x^n_m|y^n_{m')]_R = 0, \quad m \neq m'\) can be seen performing \( \varphi \)-integral in Eq. (4.1) with the help of Eq. (1.12). Therefore, hereafter we consider \([x^n_m|y^n_{m}]_R \) only.

For expressions of \([x^n_m|y^n_{m}]_R \) one needs to deal with products of spherical harmonics. For products of \( Y_{l'm} \) we have the following formula

\[
Y_{l'm} Y_{l'm'} = \sum_{l'=l_{\min}}^{l_{\max}} G_{l'}^{lm} m' Y_{l'm+m'},
\]

where \( G_{l'}^{lm} m' \) is called Gaunt coefficient for which analytic expressions and an efficient method of computation by recurrence formula are known. The summation limits are given by

\[
l_{\max} = l + l',
\]

\[
l_{\min} = \begin{cases} \mu_{\min}, & \text{if } l_{\max} + \mu_{\min} \text{ is even}, \\ \mu_{\min} + 1, & \text{if } l_{\max} + \mu_{\min} \text{ is odd}, \\ \end{cases}
\]

\[
\mu_{\min} = \max\{|l - l'|, |m + m'|\}.
\]
The formula corresponding to Eq. (4.3) for $Z_i^m$ is

\begin{equation}
Z_i^m Z_i^{m'} = \sum_{l=\max(l,m')}^{\min(l,m)} D_{ll}^m Z_i^{m'} \sigma_{l} \zeta l Z_i^{m+m'},
\end{equation}

where $\Delta l = (l + l' - \tilde{l})/2$ and

\begin{equation}
D_{ll}^m = \left( \frac{4\pi (2\tilde{l} + 1)(l + |m|)(l' + |m'|)(\tilde{l} - |m + m'|)!}{(2\tilde{l} + 1)(2l' + 1)(l - |m|)(l' - |m'|)(\tilde{l} + |m + m'|)!} \right)^{1/2}.
\end{equation}

Here note that considering the parity of functions one has $G_{ll}^{m,m'} \neq 0$ only if $l + l' - \tilde{l}$ is even, and thus $\Delta l$ is a natural number.

4.1. **Method 1: analytic expression.** In order to obtain an analytic expression of $[\chi_{lm}^n | \chi_{lm'}^{n'}]_R$ we apply the shift-operator approach\[^2\] We define a differential operator $\Omega_{lm}^n (\nabla, \zeta)$ by

\begin{equation}
\Omega_{lm}^n (\nabla, \zeta) = Z_i^m (\nabla) \left( -\frac{1}{r} \frac{\partial}{\partial r} \right)^n \left( -\frac{1}{\zeta} \frac{\partial}{\partial \zeta} \right)^l,
\end{equation}

where $\nabla = (\frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z})$ with the Cartesian coordinates $(X, Y, Z)$ of $R$. Then by Hobson’s theorem Eq. (4.10) and

\begin{equation}
\frac{1}{r} \frac{\partial}{\partial r} \left( -\frac{1}{\zeta} \frac{\partial}{\partial \zeta} \right) (r^{-1} e^{-\zeta r}) = r^{-1} e^{-\zeta r},
\end{equation}

we can see that

\begin{equation}
\chi_{lm}^n (r, \zeta) = \Omega_{lm}^n (\nabla, \zeta) (r_A^{-1} e^{-\zeta r_A}),
\end{equation}

where $r_A = |r_A| = |r - R_A|$. Thus we can rewrite $[\chi_{lm}^n | \chi_{lm'}^{n'}]_R$ as

\begin{equation}
[\chi_{lm}^n | \chi_{lm'}^{n'}]_R = \Omega_{lm}^m (\nabla, \zeta) \Omega_{lm'}^n (\nabla, \zeta') \int_{R^3} \int_{R^3} \frac{e^{-\zeta |r - R_A|} e^{-\zeta' |r' - R_B|}}{|r - r'|^2} \frac{dr dr'}{|r - R_A| |r' - R_B|},
\end{equation}

where

\begin{equation}
\Omega_{lm}^m (\nabla, \zeta) = Z_i^m (\nabla) \left( -\frac{1}{\zeta} \frac{\partial}{\partial \zeta} \right)^l.
\end{equation}

For $[\chi_{00}^0 | \chi_{00}^0]_R$ we have the following expression whose proof is given in the appendix:

\begin{equation}
[\chi_{00}^0 | \chi_{00}^0]_R = \frac{8\pi^2}{\zeta^2 - \zeta'^2} \left( g(\zeta' R) - g(\zeta R) \right).
\end{equation}

Here

\[g(t) = e^{-t} \text{Ei}(t) - e^t \text{Ei}(-t),\]

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

\[\text{Ei}(t) = -\text{p.v.} \int_{-t}^\infty \frac{e^{-s}}{s} ds.\]
With the help of Eq. (4.5) and the equation $Z_l^m = (-1)^m Z_l^m$ the differential operator $Z_l^m(\nabla_A)Z_l^m(\nabla_B)$ in Eq. (4.6) applied to a function $f(R)$ of $R$ is written as

$$Z_l^m(\nabla_A)Z_l^m(\nabla_B)f(R) = (-1)^{l+m} \sum_{l=\text{min}}^{\text{max}} D_l^{t_m} G_l^{t_m} \nabla_B^{2\Delta l} Z_l^0(\nabla_B)f(R),$$

Using Hobson's theorem Eq. (5.9) and

$$\nabla_R^2 (R^{2\Delta l} Z_l^0(R)) = 2\Delta l (2\Delta l + 2\tilde{l} + 1) R^{2\Delta l - 2} Z_l^0(R),$$

The last expression is rewritten as

$$Z_l^m(\nabla_A)Z_l^m(\nabla_B)f(R) = (-1)^{l+m} \sum_{l=\text{min}}^{\text{max}} D_l^{t_m} G_l^{t_m} \sum_{p=0}^{\Delta l} E_p^{l\Delta l} R^{2\Delta l - 2p} Z_l^0(R) \times \left( \frac{1}{R} \right)^{l+l'-p} f(R),$$

where

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

Combining Eqs. (4.6)-(4.8) one obtains

$$[\chi_l^m | \chi_l^m]_R = (-1)^{n + n' + l' + m + 1} n^2 \sum_{l=\text{min}}^{\text{max}} D_l^{t_m} G_l^{t_m} \sum_{p=0}^{\Delta l} E_p^{l\Delta l} R^{2\Delta l - 2p} Z_l^0(R) \times (U_{l+l'-p}^{rlm} R, \zeta, \zeta') + U_{l+l'-p}^{nlm} R, \zeta, \zeta'),$$

where

$$U_{l+l'-p}^{nlm} (R, \zeta, \zeta') = \left( \frac{\partial}{\partial \zeta} \right)^n \left( \frac{1}{\zeta} \right) \left( \frac{\partial}{\partial \zeta'} \right)^{l'} \left( \frac{1}{\zeta'} \right) \left( \frac{1}{\zeta} \right)^{l} \left( \frac{1}{\zeta'} \right)^{l'} \left( \frac{1}{\zeta} \right)^{l} \zeta^R \zeta'^R.$$

With the help of Eqs. (3.3) and (3.11) we obtain

$$v_{n_1 l_1}^{n_2 l_2} (\zeta, \zeta') = (-1)^{l_1} \left( \frac{\partial}{\partial \zeta} \right)^{n_1} \left( \frac{1}{\zeta} \right)^{l_1} \left( \frac{\partial}{\partial \zeta'} \right)^{n_2} \left( \frac{1}{\zeta'} \right)^{l_2} \frac{1}{\zeta^2 - \zeta'^2},$$

$$v_{n_1 l_1}^{n_2 l_2} (R, \zeta) = \left( \frac{\partial}{\partial \zeta} \right)^{n_1} \left( \frac{1}{\zeta} \right)^{n_2} \left( \frac{1}{\zeta} \right)^{l_1} \frac{g(\zeta R)}{\zeta R}.$$

With the help of Eqs. (3.3) and (3.11) we obtain

$$v_{n_1 l_1}^{n_2 l_2} (\zeta, \zeta') = (-1)^{l_1} \sum_{l_2=\frac{l_1+l_1+1}{2}}^{l_1} (-1)^{\lambda_1 + \lambda_1 + 1} \beta_{n_1}^{n_2} \zeta_1^{\lambda_1 - n_1} \times \sum_{l_2=\frac{l_2+1}{2}}^{l_2} 2^{\lambda_1 + \lambda_1} \beta_{n_2}^{\lambda_2} \zeta_2^{\lambda_2 - n_2} \frac{(\lambda_1 + l_1 + \lambda_2 + l_2)!}{(\zeta^2 - \zeta'^2)\lambda_1 + l_1 + \lambda_2 + l_2 + 1}.$$
Using Eq. (3.3) one finds

\[ w_{\mu \nu}^{\sigma}(R, \zeta) = \sum_{\sigma = 0}^{\infty} \beta_{\sigma \mu} \zeta^{2\sigma - \mu} \tilde{w}_{q}^{\nu \sigma}(R, \zeta), \]

where

\[ \tilde{w}_{q}^{\sigma}(R, \zeta) = \left( \frac{1}{\zeta} \frac{\partial}{\partial \zeta} \right)^{s} \left( \frac{1}{R} \frac{\partial}{\partial R} \right)^{q} g(\zeta R) \]

Since \( \tilde{w}_{q}^{\sigma}(R, \zeta) \) is symmetric with respect to the exchange of the pairs \((\zeta, s)\) 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 formula for operators:

\[ C_{j}^{q} = \frac{2^{j}q! \prod_{i=0}^{q}(2j - 2i + 1)}{(q - j)!(2j + 1)!}. \]

which can easily be confirmed by induction with respect to \( q \) and \( \tau \) respectively. Note that \( \frac{1}{R} \) in Eq. (4.10) 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 Eq. (4.10), the equation

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

and Eq. (4.11) one has

\[ \tilde{w}_{q}^{s}(R, \zeta) = \sum_{j=0}^{q} C_{j}^{q} R^{2j - 2q - 1} \left( \frac{1}{\zeta} \frac{\partial}{\partial \zeta} \right)^{s-j+1} \left( \frac{1}{R} \frac{\partial}{\partial R} \right)^{j} \]

\[ = \sum_{j=0}^{q} C_{j}^{q} \sum_{\kappa=1}^{s-j+1} (-1)^{s-j+1-\kappa} B_{\kappa}^{s-j+1} \zeta^{\kappa - 2(s-j+1)} R^{2j - 2q + \kappa - 2} g^{(2j + \kappa - 1)}(\zeta R). \]

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

\[ g^{(2M)}(t) = - \sum_{i=1}^{M} \frac{2(2i - 2)!}{t^{2i-1}} + g(t), \]

\[ g^{(2M+1)}(t) = \sum_{j=1}^{M} \frac{2(2i - 1)!}{t^{2i}} - e^{t} \text{Ei}(-t) - e^{-t} \text{Ei}(t). \]
4.2. Method 2: Reduction to one-dimensional integrals. Using Parseval’s formula, Eqs. (3.13), (4.15) and $F(\chi_{lm}(x)) = e^{-iR_k \cdot k} F(\chi_{lm}(x))$ we obtain

$$[\chi_{lm}|\chi'_{lm}]_R = A''_{lm} \sum_{l'=l_{\min}}^{l_{\max}} (2l + 1)^{1/2} G_{l'}^{l-m} m M_{l''l}'',$$

where

$$A''_{lm} = (-1)^{l'+m+l'+t'} 2^{l'+t'+3} 4! \pi \left( \frac{\pi (l+|m|)! (l'+|m|)!}{(2l+1)(2l'+1)(l-|m|)! (l'-|m|)!} \right)^{1/2},$$

and

$$M_{l''l}'' = (-1)^{n+n'} \sum_{p=|n+1|}^{n} \beta_p^\prime \zeta^{2p-n} (-2)^p \frac{(l+p)!}{l!} \times \sum_{p'=|n'+1|}^{n'} \beta_p^\prime \zeta^{2p'-n'} (-2)^{p'} \frac{(l'+p')!}{p'!} J_{l''l}^{l+p+l'+p'},$$

with

$$L_{l''l}^{l+p+l'+p'} = \int_{\mathbb{R}^3} e^{-iR \cdot k} \frac{k^{2l'-1} Z_{l'}(k)}{(\zeta^2 + k^2)^{l+p+1} (\zeta^{2l'} + k^2)^{l'+p'+1}} dk.$$ 

This integral is again a Fourier transform. For the evaluation of this Fourier transform we use the Rayleigh expansion of a plane wave in terms of spherical Bessel functions and spherical harmonics

$$e^{-iR \cdot k} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-i)^l j_l(Rk) Y_{lm}^*(\theta_k, \varphi_k) Y_{lm}(\theta_R, \varphi_R),$$

where $j_l$ is the spherical Bessel function. With the help of this expansion we obtain

$$L_{l''l}^{l+p+l'+p'} = (2\pi)^{3/2} (-i)^l R^l + l'+2p+2p'+2$$

$$\times \int_0^{\infty} \frac{k^{l+l'+1/2} J_{l+1/2}(k)}{((\zeta R)^2 + k^2)^{l+p+1} ((\zeta^{l'} R)^2 + k^2)^{l'+p'+1}} dk,$$

where $J_{l+1/2}$ is the Bessel function.

5. Method for three and four-center integrals

Three and four-center integrals are reduced to one or two-center integrals with quantitative error bounds. We consider general integral $[\psi_1(r_A)\psi_2(r_B)|\psi_3(r'_C)|\psi_4(r'_D)]$, where each $\psi_i$ has the form of $\chi_{lm}^n$. In $[\psi_1(r_A)\psi_2(r_B)|\psi_3(r'_C)|\psi_4(r'_D)]$ we expand $\psi_2(r_B)$ and $\psi_4(r'_D)$ by STOs $\varphi_j$ centered at $R_A$ and $R_C$, respectively:

$$\psi_2(r_B) = \sum_{j=1}^{\infty} c_j \varphi_j(r_A),$$

$$\psi_4(r'_D) = \sum_{k=1}^{\infty} \xi_k \varphi_k(r'_C).$$
As \( \varphi_j \) we can choose a complete orthonormal system. Each \( \varphi_j \) can be written as a linear combination of \( \chi_{lm}^n \). Thus with the help of the Gaunt coefficients each \( [\psi_1(r_A) \varphi_j(r_A)]\psi_3(r'_C) \varphi_k(r'_C) \) can be written as a finite sum of fundamental one or two-center integrals. Since in the practical calculation we need to truncate the expansions up to a finite sum \( \Phi_J(r_A) = \sum_{j=1}^J c_j \varphi_j(r_A) \) and \( \Phi_K(r'_C) = \sum_{k=1}^K c_k \varphi_k(r'_C) \), we have to estimate the error by the truncation written as follows:

\[
[\psi_1(r_A)\psi_2(r_B)|\psi_3(r'_C)\psi_4(r'_D)] - [\psi_1(r_A)\Phi_J(r_A)|\psi_3(r'_C)\Phi_K(r'_C)]
\]

(5.1)

\[
= [\psi_1(r_A)\psi_2(r_B) - \Phi_J(r_A))|\psi_3(r'_C)\psi_4(r'_D)]
\]

\[
+ [\psi_1(r_A)\Phi_J(r_A)|\psi_3(r'_C)(\psi_4(r'_D) - \Phi_K(r'_C)]).
\]

For the estimate we use the \( L^\infty \)-norm defined by \( \| \psi \|_{L^\infty} = \sup_{r \in \Sigma} |\psi(r)| \), in addition to the usual \( L^2 \)-norm. The norm \( \| \chi_{lm}^n \|_{L^\infty} \) of \( \chi_{lm}^n \) can be evaluated easily. Since \( \varphi_j \) is an orthonormal system, the \( L^2 \)-norms of \( \Phi_J \) and \( \psi_2(r_B) - \Phi_J(r_A) \) are also evaluated as

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

\[
\| \psi_2(r_B) - \Phi_J(r_A) \|^2 = \| \psi_2 \|^2 - \sum_{j=1}^J |c_j|^2.
\]

By the Schwarz inequality the first term in the right-hand side of Eq. (5.1) is estimated as

\[
\| [\psi_1(r_A)\psi_2(r_B) - \Phi_J(r_A))|\psi_3(r'_C)\psi_4(r'_D)] \|
\]

\[
\leq \| \psi_1(r_A)\psi_2(r_B) - \Phi_J(r_A)) \| \left\| \frac{1}{r^2} \ast (\psi_3(r'_C)\psi_4(r'_D)) \right\|
\]

\[
\leq \| \psi_1 \|_{L^\infty} \| \psi_2(r_B) - \Phi_J(r_A) \| \left\| \frac{1}{r^2} \ast (\psi_3(r'_C)\psi_4(r'_D)) \right\|.
\]

Using Eq. (3.4) and the Hardy inequality the last factor is estimated as

\[
\left\| \frac{1}{r^2} \ast (\psi_3(r'_C)\psi_4(r'_D)) \right\| = \left\| \frac{1}{r^2} \ast (\psi_3(r)\psi_4(r'_C)) \right\|
\]

\[
= 2^{-1/2}\pi^{1/2} \left\| \frac{1}{r} \mathcal{F}(\psi_3(r)\psi_4(r'_C)) \right\|(k)
\]

\[
\leq (2\pi)^{1/2} \| \nabla_k \mathcal{F}(\psi_3(r)\psi_4(r'_C)) \| (k)
\]

\[
= 4\pi^2 \| r\psi_3(r)\psi_4(r'_C) \|
\]

\[
\leq 4\pi^2 \| r\psi_3(r) \|_{L^\infty} \| \psi_4 \|,
\]

where \( r_{CD} = r - R_D + R_C \). Thus we obtain

\[
\| [\psi_1(r_A)\psi_2(r_B) - \Phi_J(r_A))|\psi_3(r'_C)\psi_4(r'_D)] \|
\]

\[
\leq 4\pi^2 \| \psi_1 \|_{L^\infty} \| \psi_2(r_B) - \Phi_J(r_A) \| \| r\psi_3(r) \|_{L^\infty} \| \psi_4 \|.
\]
Thus we have the error estimate for the truncation as
\[ (6.1) \]
\[
\left| \psi_1(r_A) \Phi_J(r_A) \psi_3(r_C^{'}) (\psi_4(r_D') - \tilde{\Phi}_K(r_C^{'}) ) \right| \\
\leq 4 \pi^2 \| \psi_1 \|_{L^\infty} \| \Phi_J \| \| r \psi_3(r) \|_{L^\infty} \| \psi_4(r_D) - \tilde{\Phi}_K(r_C) \| .
\]

In practical calculations we need to choose \( J \) and \( K \) large enough so that the last factor will be small enough.

6. FUNDAMENTAL HYBRID TWO-CENTER INTEGRALS

Fundamental hybrid two-center integrals are defined by
\[
\left[ \chi_{l_1m_1}^{n_1} \chi_{l_2m_2}^{n_2} \chi_{l_3m_3}^{n_3} \right]_R = \\
\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_{l_1m_1}^{n_1} (r_A, \zeta_1)}{|r-r'|^2} \frac{\chi_{l_2m_2}^{n_2} (r_A', \zeta_2)}{|r-r'|^2} \frac{\chi_{l_3m_3}^{n_3} (r_B', \zeta_3)}{|r-r'|^2} dr dr',
\]
where \( R_A \neq R_B \) and \( r_A' = r' - R_B + R_A \). The integral Eq. (6.1) with \( R_A = R_B = R_C \neq R_D \) is reduced to integrals of this form using the Gaunt coefficient.

We can evaluate this integral expanding \( \chi_{l_3m_3}^{n_3} (r_{AB}', \zeta_3) \) by STOs centered at 0 by the method in Section 5 and evaluating the resulting one-center integrals by the method in Section 3. For the expansion of \( \chi_{l_3m_3}^{n_3} (r_{AB}', \zeta_3) \) we use the following formulæ (6.2)
\[
P_L^M (\cos \Theta) r_A^{N-1} e^{-r_{AB}} = \\
\sum_{k=M}^{\infty} \sum_{p=0}^{\infty} C_{kp}^{NLM} \omega_{kM}^p (r, \mu),
\]
for \( N, L, M \in \mathbb{N}, \ L \geq M, \mu > 0 \), where \( r_{AB} = |r_{AB}| \) and
\[
\omega_{kM}^p (r, \mu) = P_k^M (\cos \theta) (2 \mu)^k e^{-\mu r} L_p^k (2 \mu r).
\]
Here \( L_p^{2k+2} (2 \mu r) \) is the associated Laguerre polynomial. The coefficients \( C_{kp}^{NLM} \) can be calculated by recurrence relations depending on \( \mu \) and \( R = |R_B - R_A| \).

Since the functions \( \omega_{kM}^p (r, \mu), k = M, M+1, \ldots, p = 0, 1, \ldots, \) form a complete orthogonal system, we can apply the arguments in Section 3. The formula Eq. (6.1) and the expression of the Laguerre polynomial yield the expansion
\[
\chi_{l_3m_3}^{n_3} (r_{AB}', \zeta_3) = i^{m_3+|m_3|} e^{i m_3 \varphi} \zeta_3^{-n_3-l_3+1} \\
\sum_{k=|m_3|}^{\infty} \sum_{p=0}^{\infty} C_{kp}^{n_3+l_3} 5|m_3| \zeta_3^{-p} \omega_{kM}^p (r, \zeta_3)
\]
\[
= \zeta_3^{-n_3-l_3+1} \sum_{k=M}^{\infty} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} T_{kpq}^{m_3l_3} \chi_{km_3}^{n_3+1} (r, \zeta_3),
\]
where $T_{k_{pq}}^{n_1, n_2, m_3} = C_{k_{pq}}^{(n_1 + l_1)l_3|m_3}((-1)^q \frac{(2k_{pq} + 1)!}{p!} (2\zeta_3)^{k_{pq} + q})$, and $C_{k_{pq}}^{(n_1 + l_1)l_3|m_3}$ depends on $\zeta_3 R$. Using this expansion we obtain

$$[\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2} \chi_{l_3 m_3}^{n_3}]_R = \zeta_3^{-n_3 - l_3 + 1} \sum_{k = |m_3|} \sum_{p = 0} \sum_{q = 0} T_{k_{pq}}^{n_1, n_2, m_3} [\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2} \chi_{k m_3}^{q+1}],$$

where

$$[\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2} \chi_{k m_3}^{q+1}] = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \chi_{l_1 m_1}^{n_1} (r, \zeta_1) \frac{1}{|r - r'|^2} \chi_{l_2 m_2}^{n_2} (r', \zeta_2) \chi_{k m_3}^{q+1} (r', \zeta_3) dr dr'.$$

Using Eq. (6.3) we can see that

$$[\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2} \chi_{3|k m_3}^{q+1}] = \delta_{m_1 (m_2 + m_3)} D_{l_1}^{l_2 m_2 k m_3} G_{l_1}^{l_2 m_2 k m_3} [\chi_{l_1 m_1}^{n_1} | \chi_{l_1 m_1}^{n_2 + l_2 + k + l_1} (\zeta_2 + \zeta_3)],$$

for $l_2 + l_3 \geq l_1 \geq l_{\text{min}}$ and it vanishes in the other cases. Here $[\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2 + l_2 + k + l_1} (\zeta_2 + \zeta_3)]$ is the fundamental one-center integral with the index $\zeta_2 + \zeta_3$ of the second STO, and $l_{\text{min}}$ is the natural number defined by Eq. (4.3) with $l, l', m, m'$ replaced by $l_2, k, m_2, m_3$. From Eq. (6.3) we can see that $[\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2} \chi_{l_3 m_3}^{n_3}]_R = 0$ unless $m_1 = m_2 + m_3$. In practical calculations we truncate the expansion of $\chi_{l_1 m_1}^{n_1} (r_{AB})$ in Eq. (6.2) up to finite terms. Let us denote the finite sum by $\Phi_J (r)$ as in Section 5 that is, if we use the terms up to $k = k_{\text{max}}$ and $p = p_{\text{max}},$

$$\Phi_J (r) = i^{m_3 + |m_3|} e^{i m_2 \zeta_3} \sum_{k = |m_3|}^{k_{\text{max}}} \sum_{p = 0}^{p_{\text{max}}} C_{k_{pq}}^{(n_1 + l_1)l_3|m_3} \omega_{k|m_3} (r, \zeta_3).$$

Following the arguments in Section 5 we have the error bound of the truncation

$$||[\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2} \Phi_J] - [\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2} \Phi_J]|_R || \leq 4 \pi^2 ||r_{l_1 m_1}^{n_1} (r)|| ||r_{l_2 m_2}^{n_2} || L_\infty ||\chi_{l_3 m_3}^{n_3} (r_{AB}) - \Phi_J (r)||$$

$$\leq 8 \pi^2 \sqrt{\pi (2n_1 + 2l_1 + 1)! (l_1 + |m_1|)!} \left( \frac{n_2 + l_2 - 1}{\zeta_2} \right)^{n_2 + l_2 - 1} \left( \frac{l_2 + |m_2|}{l_1 - |m_1|} \right)! \times e^{-n_2 - l_2 + 1} ||\chi_{l_3 m_3}^{n_3} (r_{AB}) - \Phi_J (r)||,$$

where

$$[\chi_{l_1 m_1}^{n_1} | \chi_{l_2 m_2}^{n_2} \Phi_J] = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \chi_{l_1 m_1}^{n_1} (r, \zeta_1) \frac{1}{|r - r'|^2} \chi_{l_2 m_2}^{n_2} (r', \zeta_2) \Phi_J (r') dr dr'.$$

Here for the estimate of $||\chi_{l_2 m_2}^{n_2} || L_\infty$ we used the following formula

$$P^m_l (z) = \frac{(-1)^m (l + m)!}{l! \pi} \int_0^\pi \left( z + \sqrt{z^2 - 1} \cos \varphi \right) l \cos m \varphi d \varphi, $$

(note that the coefficient of our definition of $P^m_l (z)$ and that in the reference are different by the factor $(-1)^m$) and estimated the associated Legendre function as

$$|P^m_l (\cos \theta)| \leq \frac{(l + m)!}{l! \pi} \int_0^\pi d \varphi = \frac{(l + m)!}{l!}.$$
7. Numerical results

The fundamental one-center integrals were evaluated for $\zeta = 1$, $\zeta' = 0.5$ by the analytic expression and the expression by one-dimensional integrals. As for the one-dimensional integrals the integral $I_{pq}$ in Eq. (3.16) was evaluated approximating the integrand by the Chebyshev interpolation with typical order 1000 and integrating the polynomial. Calculations with high orders by this method are extremely easy because the zeros of the Chebyshev polynomials have easy analytic expressions. This method is slightly different from the Chebyshev-Gauss quadrature and gives much better results for simple analytic integrands than the Chebyshev-Gauss quadrature. This method would be an ordinary way, but specific name for the method could not be found. Accurate significant figures were obtained by determining invariant figures by varying the order of the Chebyshev interpolation. All calculations were performed with double precision. For $l = m = 0$ the number of the accurate figures $F_{ae}$ of the value by the analytic expression are also shown in Table 1. The number $F_{ae}$ was determined comparing the value obtained by using the expression Eq. (3.1) and the value by the one dimensional integrals obtained above as a reliable reference. Examples are presented in Table 1.

Table 1. The accurate significant figures of $|\chi_{lm}|^n|\chi_{lm}'|^{n'}$

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

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

Examining each step of the calculation, it was observed that the loss of accuracy in the expression by one-dimensional integrals was due to the cancellation of significant digits in the summations in Eq. (3.16). The cancellation was less and the result was more accurate often for large $l$ than for small $l$.

The fundamental two-center integrals were also evaluated by the two expressions for $R = 4$, $\zeta = 1$, $\zeta' = 0.5$. As for the one-dimensional integrals the integral
$L^{l+p} l' p'$ in Eq. (4.12) was evaluated using the Chebyshev interpolation with typical order 1000 as in the case of one-center integral. Typically integration on the interval $[0, 100]$ was enough, because that on $[100, \infty)$ was relatively very small and negligible owing to the decay of the integrands. All calculations were performed with double precision. The accurate significant figures of $[\chi_{lm}^n | \chi_{l'm'}^{n'}]_R$ were obtained by determining invariant figures varying the order of the Chebyshev interpolation and the interval of the integration of $L^{l+p} l' p'$. The number of the accurate figures $F_{ac}$ of the value by the analytic expression was determined comparing the value obtained by using the expression Eq. (4.9) and the value obtained above as a reliable reference. Examples are presented in Table 2.

| $n$ | $l$ | $l'$ | $m$ | $[\chi_{lm}^n | \chi_{l'm'}^{n'}]_R$ | $F_{ac}$ |
|-----|-----|-----|-----|-----------------|-------|
| 3   | 2   | 3   | 2   | 1               | 2.2243751772625(7) | 10    |
| 3   | 2   | 3   | 3   | 1               | -2.7566722179287(8) | 10    |
| 2   | 4   | 4   | 5   | 4               | -1.3610327950104(16) | 6     |
| 2   | 4   | 4   | 6   | 4               | 2.0420467016732(17)  | 4     |
| 2   | 5   | 2   | 6   | 4               | -5.409078298132(16)  | 3     |
| 2   | 6   | 2   | 6   | 4               | 4.98674283667(17)    | 1     |
| 2   | 7   | 2   | 6   | 5               | 2.7314119999476(20)  | 1     |
| 2   | 7   | 2   | 7   | 5               | 8.095554498731(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 $(\nu)$ 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 $\tilde{w}_q$ in Eq. (4.12) enormous cancellations of significant digits happen.

Finally the fundamental hybrid two-center integrals were evaluated by the method in Subsection 6. For the evaluation of one-center integrals in the right hand side of Eq. (6.3) we used the expression by one-dimensional integrals as above. Here recall that $[\chi_{l_1m_1}^{n_1} \chi_{l_2m_2}^{n_2} \chi_{l_3m_3}^{n_3}]_R = 0$ unless $m_1 = m_2 + m_3$. Examples for $\zeta_1 = 1.0, \zeta_2 = 0.5, \zeta_3 = 1.0, R = 0.5$ are presented in Table 3. Terms in Eq. (6.2) 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 the Table 3 were calculated from Eq. (6.4). It was confirmed that the number of significant figures of the finite sum in the expansion of $[\chi_{l_1m_1}^{n_1} \chi_{l_2m_2}^{n_2} \chi_{l_3m_3}^{n_3}]_R$ which were determined changing the order of the one-dimensional integrals is greater than the number of meaningful figures from the viewpoint of the error bound by Eq. (6.4).
In this appendix we prove Eq. (4.7). First the change of the variable \( \tilde{\mathbf{r}} = \mathbf{r} - \mathbf{r}' \) in Eq. (4.1) with \( n = l = m = 0 \) yields

\[
(A.1) \quad [\chi_0^0, \chi_0^0]_R = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|\tilde{\mathbf{r}} - \mathbf{R}|^2} \frac{e^{-\zeta|\tilde{\mathbf{r}}|} e^{-\zeta'|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} d\tilde{\mathbf{r}} d\mathbf{r}.
\]

The \( \mathbf{r} \) integral can be performed in the same way as in Eq. (3.2) and yields

\[
(A.2) \quad \int_{\mathbb{R}^3} \frac{e^{-\zeta|\mathbf{r}|} e^{-\zeta'|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} = \frac{4\pi}{|\mathbf{R}|(\zeta^2 - \zeta'^2)} (e^{-\zeta|\mathbf{r}'|} - e^{-\zeta'|\mathbf{r}|}).
\]

Hence it remains to calculate the \( \tilde{\mathbf{r}} \) integral. Changing the variable to the ellipsoidal coordinates with foci 0 and \( \mathbf{R} \), we have

\[
\int_{\mathbb{R}^3} \frac{1}{|\tilde{\mathbf{r}} - \mathbf{R}|^2} \frac{e^{-\zeta|\tilde{\mathbf{r}}|}}{|\tilde{\mathbf{r}}|} d\tilde{\mathbf{r}} = 2\pi \int_{-\infty}^{\infty} \int_{-1}^{1} \frac{e^{-\zeta \xi + \eta}}{\xi - \eta} d\xi d\eta.
\]

Next we change the variable as \( t = \xi + \eta, \quad s = \xi - \eta \) and obtain

\[
(A.3) \quad \int_{\mathbb{R}^3} \frac{1}{|\tilde{\mathbf{r}} - \mathbf{R}|^2} \frac{e^{-\zeta|\tilde{\mathbf{r}}|}}{|\tilde{\mathbf{r}}|} d\tilde{\mathbf{r}} = \pi \left( \int_0^1 \int_{2-t}^{2+t} \frac{e^{-\zeta \frac{4t}{s}}}{s} ds dt + \int_1^{\infty} \int_{1-t}^{1+t} \frac{e^{-\zeta \frac{4t}{s}}}{s} ds dt \right)
\]

\[
\quad \quad = \pi \left( \int_0^1 e^{-\zeta \frac{4t}{s}} (\log(2 + t) - \log(2 - t)) dt 
\quad \quad + \int_1^{\infty} e^{-\zeta \frac{4t}{s}} (\log(t + 2) - \log(t - 2)) dt \right).
\]

The integral for the integrands including the factor \( \log(t + 2) \) is easily calculated by integration by parts as

\[
(A.4) \quad \pi \int_0^\infty e^{-\zeta \frac{4t}{s}} \log(t + 2) dt = \frac{2\pi \log 2}{\zeta R} + \frac{2\pi}{\zeta R} \int_0^\infty e^{-\zeta \frac{4t}{s}} \frac{t + 2}{s} dt
\]

\[
\quad \quad = \frac{2\pi \log 2}{\zeta R} - \frac{2\pi}{\zeta R} e^{\zeta R} Ei(-\zeta R).
\]
The integrals for the factors \( \log(2 - t) \) and \( \log(t - 2) \) are improper integrals and require attention. They are expressed as a limit and calculated as

\[
- \pi \lim_{\epsilon \to +0} \left( \int_0^{2-\epsilon} e^{-\zeta R t} \log(2 - t) \, dt + \int_{2+\epsilon}^{\infty} e^{-\zeta R t} \log(t - 2) \, dt \right)
\]

\[
= -\pi \lim_{\epsilon \to +0} \left( -\frac{2 \log \epsilon}{\zeta R} e^{-\frac{2(2-\epsilon)}{2-t}} + \frac{2 \log 2}{\zeta R} \right) \int_0^{2-\epsilon} e^{-\frac{2t}{2-t}} dt
\]

\[
+ \frac{2 \log \epsilon}{\zeta R} e^{-\frac{2(2+\epsilon)}{2-t}} + \frac{2}{\zeta R} \int_{2+\epsilon}^{\infty} e^{-\frac{2t}{2-t}} dt
\]

\[
= -\frac{2 \pi \log 2}{\zeta R} + \frac{2 \pi}{\zeta R} e^{-\zeta R Ei(\zeta R)}. \tag{A.5}
\]

Combining Eqs. (A.3)-(A.5) we obtain

\[
\int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{R}|^2} \, d\mathbf{r} = \frac{2 \pi}{\zeta R} e^{-\zeta R Ei(\zeta R)} - \frac{2 \pi}{\zeta R} e^{\zeta R Ei(-\zeta R)}. \tag{A.6}
\]

Equation (4.7) immediately follows from Eqs. (A.1), (A.2) and (A.6).

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