This document introduces members of the lab to numerical quadrature and the related software within our group library. A greater emphasis is placed on understanding the concepts required for its practical application than providing a generic overview. The discussion of one-dimensional integration primarily focuses on Gauss-Laguerre quadrature and its usage in computing the integral of a three-dimensional spherical function. This particular example is chosen due to the natural transition to angular quadrature and extension to the integration of arbitrary three-dimensional functions; however, the concepts discussed with the Gauss-Laguerre example are easily applied to Gauss-Hermite quadrature, for example, and its application to anharmonic oscillator problems. Multicenter molecular quadrature is discussed with emphasis on understanding the conceptual problem of double counting integrands and the associated requirement of spatial partition functions.

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I. GAUSSIAN QUADRATURE

A. Overview

In Sec. I E it will be shown that an arbitrary function \( f(x) \), that is smooth and free of singularities, can be integrated by (a) projecting the function into a linear combination of orthogonal polynomials which can be integrated exactly and then (b) integrating over the orthogonal polynomials.

Sec. ID describes how a set of orthogonal polynomials can be integrated exactly. The integration over a continuous variable is transformed into a sum of discrete points, which occur at the roots of a high-order polynomial.

Sec. IC briefly describes how the roots of a polynomial can be determined by eigen-decomposition.

Sec. IB reviews the definition of orthogonal polynomials.
Sec. IF explains how to perform numerical quadrature using YorkLib.

B. Orthogonal polynomials

A polynomial of degree \( n \), written here as \( p_n(x) \), has the form

\[
p_n(x) = a_0 x^0 + a_1 x^1 + a_2 x^2 + \cdots + a_{n-1} x^{n-1} + a_n x^n
\]

(1)

A set of orthogonal polynomials obey the identity

\[
\int_a^b w(x) p_i(x) p_j(x) dx = \delta_{ij} \int_a^b w(x) p_i(x)^2 dx,
\]

(2)

where \( w(x) \) is referred to as a “weight function”. Note that the polynomials only have to be orthogonal over the range \([a, b]\), to classify being orthogonal.

An example of a set of orthogonal polynomials are the associated Laguerre functions \( L_n^\alpha(x) \), which are orthogonal over the weight function \( x^\alpha e^{-x} \) in the range \([0, \infty)\).

The first few associated Laguerre polynomials are

\[
L_0^\alpha(x) = 1
\]

(3)

\[
L_1^\alpha(x) = \alpha - x + 1
\]

(4)

\[
L_2^\alpha(x) = \frac{1}{2} \left( x^2 - 2(\alpha + 2)x + (\alpha + 1)(\alpha + 2) \right)
\]

(5)

and are displayed in Fig. 1.

By showing the few lowest Laguerre polynomials, it is stressed that there is nothing “mysterious” about orthogonal polynomials - they’re just polynomials which happen to have the property of being orthogonal when integrated over a specific weight function.

C. Finding the roots of a polynomial

The roots of a polynomial are the values of \( x \) for which \( p_n(x) = 0 \). They can be determined by diagonalizing the ma-

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The resulting eigenvalues are the roots of its characteristic equation, which is, by construction, the polynomial \( p_n(x) \).

As an example, consider the 2-point Gauss-Laguerre quadrature roots.

\[
L_2(x) = 1 - 2x + \frac{1}{2}x^2
\]

\[
a_0 = 1 \\
a_1 = -2 \\
a_2 = \frac{1}{2}
\]

The companion matrix is

\[
\begin{pmatrix}
0 & -a_0/a_2 & & \\
1 & -a_1/a_2 & & \\
0 & 0 & & \\
& & & \ddots & \\
0 & 0 & & & 1
\end{pmatrix}
\]

The eigenvalues of a \( 2 \times 2 \) matrix \( \begin{pmatrix} a & b \\ c & d \end{pmatrix} \) are given by

\[
\lambda = \frac{a + d}{2} \pm \frac{\sqrt{(a - d)^2 + 4bc}}{2},
\]

which yield

\[
x_1 = \frac{4}{2} - \frac{\sqrt{8 + 16}}{2} = 2 - \sqrt{2} \\
x_2 = \frac{4}{2} + \frac{\sqrt{8 + 16}}{2} = 2 + \sqrt{2}
\]

Note that the roots of orthogonal polynomials have the special property of being real and fall within the same range of orthogonality.

**D. Exact integration of orthogonal polynomials**

In this section, it is shown that all low-order orthogonal polynomials can be integrated by summing a unique set of quadrature weights.

Recall that orthogonal polynomials obey the identity

\[
\int_a^b w(x)p_i(x)p_j(x)dx = \delta_{ij}\int_a^b w(x)p_i(x)^2dx,
\]

Notice that \( p_0(x) \) is a polynomial of degree zero, therefore, it must be a constant. This allows us to write

\[
\int_a^b w(x)p_i(x)p_0(x)dx = \delta_{i0}\int_a^b w(x)p_i(x)^2dx = 0
\]

\[
\text{const.} \times \int_a^b w(x)p_i(x)dx = 0
\]

Consider the set of roots \( x_1, \ldots, x_n \) of the polynomial \( p_n(x) \). It is trivial to show that

\[
\int_a^b w(x)p_n(x)dx = \sum_{j=1}^n w_jp_n(x_j) = 0
\]

for any set of \( w_j \)'s, because \( p_n(x_j) = 0 \) for all \( x_j \); however, it is possible to show that there exists a unique set of \( w_j \)'s, for which all polynomials of order \( 1 \leq i \leq n \) simultaneously obey the relation

\[
\int_a^b w(x)p_i(x)dx = \sum_{j=1}^n w_jp_i(x_j) = 0.
\]

This is done by solving the simultaneous set of equations.
It can be shown that the determinant of this square matrix is nonzero, therefore, it is invertible, i.e., a unique solution exists.

**E. Integration by projecting an integrand into orthogonal polynomials**

We now have a method for exactly integrating over known polynomials and we turn our attention to using this method to solve the integral

\[
\int_a^b f(x)dx,
\]

where \( f(x) \) is a smooth function free of singularities. It will now be shown that

\[
\int_a^b f(x)dx = \sum_{i=1}^n \frac{w_i}{u(x_i)} f(x_i)
\]

To show this, we begin by projecting \( f(x) \) into the set of orthogonal polynomials \([p_0(x), \ldots , p_n(x)]\)

\[
f(x) = w(x) \sum_j p_j(x) \int f(x') p_j(x')dx' = \sum_j w(x)p_j(x)c_j.
\]

where

\[
c_j = \int f(x')p_j(x')dx'
\]

is an expansion coefficient. The representation of \( f(x) \) by the basis expansion is made more accurate by increasing the order of expansion. This is emphasized in Fig. 2.

The projected representation of \( f(x) \) is inserted and integrated exactly via quadrature.

\[
\int_a^b f(x)dx = \int_a^b \sum_j w(x) p_j(x) c_j dx = \sum_j c_j \int_a^b w(x) p_j(x) dx = \sum_j c_j \sum_{i=1}^n w_i p_j(x_i)
\]

As written, this result is of little use because the expansion coefficients \( c_j \) involve solving integrals [Eq. (20)] that are more complicated than our initial problem! If one had a mechanism for solving the integrals appearing in Eq. (20), then why didn’t they just use that same mechanism to solve the integral in Eq. (17)? Fortunately, explicit evaluation of the expansion coefficients can be avoided by inserting unity and contracting the expansion back into the original function, i.e.,

\[
\int_a^b f(x)dx = \sum_j c_j \sum_{i=1}^n w_i p_j(x_i) = \sum_{i=1}^n w_i \left( \sum_j p_j(x_i) c_j \right) = \sum_{i=1}^n \frac{w_i}{u(x_i)} \left( \sum_j w(x_i) p_j(x_i) c_j \right) = \sum_{i=1}^n \frac{w_i}{u(x_i)} f(x_i).
\]

In this way, the projection into a basis occurs implicitly.

**F. Gaussian quadrature using YorkLib**

YorkLib/GaussianQuadratureMod provides routines for various quadrature types and are listed in Table I. The choice of quadrature type is often guided by the limits of integration.

<table>
<thead>
<tr>
<th>Type</th>
<th>( u(x) )</th>
<th>( p(x) )</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gauss-Hermite</td>
<td>( e^{-x^2} )</td>
<td>( H_n(x) )</td>
<td>((-\infty, \infty))</td>
</tr>
<tr>
<td>Gauss-Laguerre</td>
<td>( x^n e^{-x} )</td>
<td>( L_n^{\alpha}(x) )</td>
<td>((0, \infty))</td>
</tr>
<tr>
<td>Gauss-Legendre</td>
<td>( 1 )</td>
<td>( P_n^{\alpha}(x) )</td>
<td>((-1, 1))</td>
</tr>
<tr>
<td>Gauss-Jacobi</td>
<td>( (1-x)^{\alpha}(1+x)^{\beta} )</td>
<td>( P_n^{\alpha,\beta}(x) )</td>
<td>((-1, 1))</td>
</tr>
</tbody>
</table>

The interface to these routines are all very similar and we will focus exclusively on Gauss-Laguerre quadrature because the limits of integration are most often used in the calculation of integrals found in quantum chemistry. For example, consider the integral of a radial function \( f(r) \) over all-space.

\[
\int f(r)d^3r = \int \int_0^{\infty} f(r)r^2 drd\Omega = 4\pi \int_0^{\infty} f(r)r^2 dr.
\]
The function $f(x) = e^{-\frac{1}{2}x^2}$ and the representation of $f(x)$ in an expansion of Laguerre polynomials of order $n$. The quadrature evaluation of this integral is

$$4\pi \int_0^\infty f(r)r^2dr = 4\pi \sum_{i=1}^n w_i x_i^2 f(x_i)$$

(24)

Define, for convenience,

$$\omega_i = \frac{w_i}{x_i^2 e^{-x_i}} x_i^2,$$

(25)

then the integral can be expressed as

$$\int f(r)d^3r = 4\pi \sum_{i=1}^n \omega_i f(x_i)$$

(26)

The subroutine Gauss_Laguerre takes 2 arrays of length $n$ and the scalar parameter $\alpha$ of the associated Laguerre polynomial (if $\alpha = 0$, then it is a regular Laguerre polynomial). The length of the arrays determine the order of projection, and hence, the number of quadrature points to be used in computing the integral. The values of the $i^{th}$ element of each array are exactly the $w_i$'s and $x_i$'s appearing in the above formula’s. Therefore, the procedure for computing the integral is:

1. Choose the order, $n$.
2. Call Gauss_Laguerre to get the values of the quadrature weights, $w_i$, and roots, $x_i$.
3. Form the re-factored weights $\omega_i$ using Eq. (25).
4. Evaluate the function $f(r)$ at each of the quadrature roots and perform the summation in Eq. (26)

Following this procedure as described above works; however, it is not ideal. Often times, the roots of the orthogonal polynomials are not concentrated where the integrand is large; instead, it is more efficient to have the quadrature roots concentrated where the integrand is large. From a more pragmatic perspective, if the integrand is zero at a particular quadrature point, then it does not contribute anything to the sum in Eq. (26). As an example, Fig. 3 displays the integrand $\pi^{3/2}e^{-x^2}x^2$ (solid line) and the locations of the quadrature roots using a 15-point rule (circles). Notice that the integrand is negligibly small beyond $x > 5$, however, the majority of quadrature roots are beyond $x > 5$.

Of course, using a larger rule increases the number of points in the region where the integrand is large; however,
even more points are placed in the region where the integrand is negligible (see Fig. 4). Therefore, increasing the quadrature-rule is still not ideal.

This problem can be overcome by scaling the quadrature roots (so that they are concentrated where the integrand is large) via \textit{u-substitution}. Scaling the quadrature roots is equivalent to “smearing the function out” across the unscaled quadrature roots. To “smear a function out” is to evaluate \( f(x_i) \), where \( x_i > 1 \), instead of \( f(x_i) \) while making a change of integration variable. A \textit{u-substitution} has the general form

\[
\int_{a}^{b} f(u(x)) \frac{du}{dx} \, dx = \int_{u(a)}^{u(b)} f(u) \, du \tag{27}
\]

or alternatively written as

\[
\int_{a}^{b} f(u(x)) \, dx = \int_{a}^{b} \frac{f(u(x))}{\frac{du}{dx}} \, dx = \int_{u(a)}^{u(b)} f(u) \, du \tag{28}
\]

Consider the transformation

\[
u(x) = x \lambda \tag{29}\]
\[
\frac{du}{dx} = \lambda, \tag{30}\]

it then follows

\[
\int_{a}^{b} f(x) \, dx = \int_{a}^{b} f(u(x)/\lambda) \, du
= \int_{a}^{b} \frac{f(u/\lambda)}{\lambda} \, du
= \frac{1}{\lambda} \int_{a}^{b} f(u/\lambda) \, du, \tag{31}\]

where the first equality used the relation \( x = u(x)/\lambda \) (by definition of the transformation) and the second equality changed the integration variable from \( x \) to \( u \) using Eq. (28).

In essence, this transformation divides all quadrature roots by \( \lambda \) and divides all quadrature weights by \( \lambda \). The scaling of the quadrature roots is emphasized in Fig. 5.

Returning to our example, one can rewrite the integral as

\[
4\pi \int_{0}^{\infty} f(r)^2 \, dr = 4\pi \frac{1}{\lambda} \int_{0}^{\infty} f(u(\lambda)/\lambda^2) \, du
= 4\pi \sum_{i=1}^{n} \frac{u_i}{\lambda^2} e^{-u_i^2} \left( \frac{u_i}{\lambda} \right)^2 f \left( \frac{u_i}{\lambda} \right), \tag{32}\]

For convenience, define

\[
\omega'_i = \frac{u_i}{\lambda} e^{-u_i^2} \left( \frac{u_i}{\lambda} \right)^2, \tag{33}\]
\[
x'_i = u_i/\lambda, \tag{34}\]

then

\[
\int f(r) \, d^3r = 4\pi \sum_{i=1}^{n} \omega'_i f(x'_i). \tag{35}\]

The \textit{ideal} procedure for computing the integral is:

1. Choose the order, \( n \).
2. Call Gauss-Laguerre to get the values of the quadrature weights, \( w_i \), and roots, \( u_i \).
3. Form the re-factored, scaled weights \( \omega'_i \) using Eq. (33).
4. Form the scaled roots \( x'_i \) using Eq. (34).
5. Evaluate the function \( f(r) \) at each of the scaled quadrature roots and perform the summation in Eq. (35)

An example FORTRAN program is provided below following this procedure. It evaluates

\[
\int \pi^{-3/2} e^{-r^2} \, d^3r \tag{36}\]

using a 15-point Gauss-Laguerre rule (\( \alpha = 0 \), with a scaling of \( \lambda = 10 \). The analytic result is 1.0.
FIG. 5. The function $\pi^{3/2} e^{-x^2} x^2$ (solid) and locations of the Gauss-Laguerre quadrature roots using a 15-point rule scaled by $\lambda = 10$. Note that all of the quadrature roots are located where the integrand is large.

II. 3-DIMENSIONAL NUMERICAL QUADRATURE

A. Angular integration

This section briefly discusses the evaluation of the angular integral

$$\int f(\Omega) d\Omega = \int_0^{2\pi} \int_0^\pi f(\theta, \phi) \sin(\theta) d\theta d\phi$$  

using Lebedev quadrature. Note that most functions are conveniently programmed using Cartesian coordinates, therefore, it is worthwhile to briefly discuss notation. The angular coordinate $\Omega$ is related to Cartesian coordinates $r \equiv \{x, y, z\}$, via

$$\Omega = \rho = \frac{r}{|r|} = \hat{r}.$$  

In other words, $\Omega$ represents the Cartesian coordinates of a vector pointing to the surface of a unit sphere. Angular integration, therefore, is the integration of a function living on the surface of a sphere.

The orthogonal polynomials living on the surface of a unit sphere are special functions called spherical harmonics. The corresponding weight function is unity in the angular coordinate $\Omega$. Different normalization conventions of spherical harmonics are used in the literature and the convention used here satisfy the orthonormality condition,

$$\int Y_{lm}(\Omega) Y_{l'm'}(\Omega) d\Omega = \int_0^{2\pi} \int_0^\pi Y_{lm}(\theta, \phi)$$

$$\times Y_{l'm'}(\theta, \phi) \sin(\theta) d\theta d\phi = \delta_{ll'} \delta_{mm'}$$  

One could follow a procedure similar to that described in Secs. 1B-IE to produce a set of quadrature weights and roots

PROGRAM QuadExample
USE DataTypes, ONLY : SP,I4B
USE ConstantsMod, ONLY : SQRT_PI,FOUR_PI
USE GaussianQuadratureMod, ONLY : Gauss_Laguerre
IMPLICIT NONE
!------------------------------------------------
INTEGER(I4B),PARAMETER :: Npt = 15_I4B
REAL(SP),PARAMETER :: Alpha=0.0_SP,Lambda=10.0_SP
REAL(SP) :: RadPts(Npt),RadWts(Npt),integral,x,w
REAL(SP) :: Norm,f
INTEGER(I4B) :: i
!------------------------------------------------
!GET THE N-POINT GAUSS-LAGUERRE QUADRATURE
! POINTS AND WEIGHTS
CALL Gauss_Laguerre(RadPts,RadWts,Alpha)
! REMOVE THE LAGUERRE WEIGHT FUNCTION
DO i=1,Npt
x = RadPts(i)
w = x**Alpha * EXP(-x)
RadWts(i) = RadWts(i) / w
END DO
! SCALE THE ROOTS AND WEIGHTS BY 1/LAMBDA
RadPts = RadPts / Lambda
RadWts = RadWts / Lambda
! ABSORB x**2 INTO THE DEFINITION OF THE WEIGHTS
! SO WE CAN INTEGRATE THE RADIAL INTEGRAL IN
! SPHERICAL COORDINATES (CONVENIENT)
DO i=1,Npt
RadWts(i) = RadWts(i) * RadPts(i)**2
END DO
! COMPUTE THE RADIAL INTEGRAL OF THE FUNCTION
integral = integral + w * f
DO i=1,Npt
x = RadPts(i)
w = RadWts(i)
END DO
WRITE(6,'(F20.10)')integral*FOUR_PI
END PROGRAM QuadExample
for spherical harmonics; however, Lebedev and Laikov\textsuperscript{1–7} developed a highly efficient set of quadrature points based on special properties of the octahedral symmetry point-group. The resulting sets of weights and points are referred to as Lebedev angular quadrature grids and are generally regarded as being superior (number of points vs. accuracy) to other angular quadrature schemes. The mathematical arguments and development of the Lebedev angular quadrature grids are beyond the purpose of this text (many of their papers are written in Russian journals that I don’t have access to and probably couldn’t read anyway) and it will suffice to note that these grids allow integration of spherical harmonics (to within an accuracy of $1 \times 10^{-14}$) while using a minimum number of quadrature points. Lebedev quadrature is written here as

$$\int f(\Omega)d\Omega = \sum_{j=1}^{N_\Omega} w_{\Omega,j} f(\hat{r}_j)$$

(40)

where it is understood that the weight function $w(\Omega) = 1$, and thus “disappears” from the quadrature formula.

Lebedev points and weights can be retrieved from York-Lib using the routine AngularQuad in AngularQuadrature-Mod. An example using this routine is

\begin{verbatim}
CALL AngularQuad(0,350,AngPts, &
& AngWts,ALLOC=.TRUE.)
\end{verbatim}

The first argument asks for Lebedev points and weights (Gaussian product rules are not considered in this text). The second argument asks for a quadrature using a 350 point rule. The next 2 arguments are pointer arrays with dimensionality AngPts(:,:) and AngWts(:,), which will be filled with the coordinates of the quadrature points and weights, respectively. The final (optional) argument tells the routine to allocate (or reallocate if already allocated) the pointer arrays to the sizes AngPts(1:3,1:350) and AngWts(1:350).

Note that Lebedev quadrature comes in a set of specific sizes, called rules (our example above asked for the 350 point rule), each of which can integrate a spherical harmonic (to within an accuracy of $10^{-14}$) with a maximum angular momentum $L_{\text{max}}$. Similarly, each rule can integrate the square of spherical harmonic with angular momentum $L_{2,\text{max}}$. The rules and values of $L_{\text{max}}$ and $L_{2,\text{max}}$ are listed in Table II.

### B. Single-center integration

In this section, we seek to solve the integral

$$\int f(\mathbf{r})d^3\mathbf{r} = \int f(\mathbf{r},\Omega)d^3\mathbf{r}$$

$$= \int \int_0^\infty f(\mathbf{r},\Omega)r^2 dr d\Omega$$

$$= \int_0^{2\pi} \int_0^\pi \int_0^\infty f(\mathbf{r},\theta,\phi) \times r^2 \sin(\theta)dr d\theta d\phi$$

(41)

Suppose, for a moment, that the function $f(\mathbf{r})$ was separable into radial and angular components, e.g.,

$$f(\mathbf{r}) = f_r(\mathbf{r})f_\Omega(\Omega),$$

then the integral can be evaluated by

$$\int f(\mathbf{r})d^3\mathbf{r} = \int \int_0^\infty f_r(\mathbf{r})r^2 dr \int f_\Omega(\Omega)d\Omega$$

$$= \left( \sum_{j=1}^{N_\Omega} w_{\Omega,j} f_\Omega(\hat{r}_j) \right) \left( \sum_{k=1}^{N_r} w_r w_{\Omega,k} f_r(\hat{r}_k) \right).$$

(43)

where the radial weights $w_{r,j}$ and roots $r_j$ are assumed to have been properly re-factorized and scaled (including the absorption of the $r^2$-volume-related element). This particular case can be qualitatively be described as performing a radial integral over a “spoke” and a separate integral over the surface of a unit sphere.

In practice, functions are rarely separable into angular and radial components. The more general case can be written as

$$\int f(\mathbf{r})d^3\mathbf{r} = \sum_{j=1}^{N_\Omega} \sum_{k=1}^{N_r} w_{r,j} w_{\Omega,k} f_r(\hat{r}_k).$$

(44)

Note that $r_j\hat{r}_k$ is just “some point in space” whose distance from the origin is $r_j$ and whose direction is specified by $\hat{r}_k$. If we define

$$\mathbf{r}_i = r_i\hat{r}_k$$

and

$$w_i = w_{r,j} w_{\Omega,k}$$

(46)

then the integral can be written as

$$\int f(\mathbf{r})d^3\mathbf{r} = \sum_{i=1}^{N_r N_\Omega} w_i f(\mathbf{r}_i).$$

(47)
However, by applying Eqs. (45)-(46) and letting

\[ N = \sum_{j=1}^{N_{\alpha}} N_{\alpha}(j), \]

the integral can again be written simply as

\[ \int f(r) d^3r = \sum_{i=1}^{N} w_i f(r_i). \] (50)

An example quadrature grid is displayed in Fig. 6 and can be described as integrating over many angular quadrature spheres, each with a radius corresponding to a root of the radial quadrature.

Although Eq. (44) is more general than the previous cases where the 3-d integral was separable into angular and radial components, it is not the most general formulation nor does it necessarily form an ideal grid. Each “sphere” of the 3-d grid used the same angular quadrature, therefore, as the radius of the sphere gets bigger, the grid quickly becomes more sparse (the density of points in space becomes smaller). There is, however, no reason why each sphere needs the same number of quadrature points. Therefore, we can choose to use a larger number angular quadrature points for spheres of larger and larger radii (and fewer number of points for spheres with very small radii). In this way, one can choose to more evenly distribute the points in space. Notationally, this is expressed by making \( N_{\alpha} \) a function of \( j \), i.e.,

\[ \int f(r) d^3r = \sum_{j=1}^{N} \sum_{k=1}^{N_{\alpha}(j)} w_{r,j}w_{\alpha,k} f(r_j,r_k) \] (48)

However, by applying Eqs. (45)-(46) and letting

\[ N = \sum_{j=1}^{N_{\alpha}} N_{\alpha}(j), \] (49)

the integral can again be written simply as

\[ \int f(r) d^3r = \sum_{i=1}^{N} w_i f(r_i). \] (50)

1. The all-space normalization problem

Consider, for demonstration purposes, the integral over the sum of 2 L1-normalized Slater functions

\[ \int s_1(r) + s_2(r - R_c) d^3r = \int \left( \frac{1}{8\pi} \right) e^{-r^2} \]
\[ + \frac{1}{8\pi} e^{-|r - R_c|^2} d^3r. \] (51)

Suppose \( R_c = \{0,0,R\} \), i.e., the second Slater function is centered at a point along the \( z \)-axis. We can do this integral analytically (the answer is exactly 2); however, this is good because we will compare different quadrature schemes with this analytic result.

The most straight-forward way to evaluate this integral is by separating the integrand and solving 2 integrals, i.e.,

\[ \int s_1(r) + s_2(r - R_c) d^3r = \int s_1(r) d^3r \]
\[ + \int s_2(r - R_c) d^3r. \] (52)

Each of these integrals can be represented by single-center integration grids and integrated quite well, but what would you do if your integral was

\[ \int s_1(r)s_2(r - R_c) d^3r? \] (53)

C. Multi-center integration

Integrand often encountered in quantum chemistry are large at significantly different areas of space, i.e., they are not well-confined to a particular region of space. For example, molecular orbitals can span large areas of a molecule, especially in conjugated systems. Molecular orbitals are very well described by a linear combination of atomic orbitals, however, and it would therefore make sense to place a quadrature grid on each atom (since the atomic orbitals are largest near its atom). But if we include more than 1 quadrature center, and each quadrature grid integrates over all-space (as described in the previous section), then how many times are we integrating over all-space? If we want to integrate over all-space once, then what modification to the single-center quadrature scheme must we make? This is the main topic of this section and we begin by illustrating the problem in more detail. After a significant discussion of this “all-space normalization problem” is made, the approach for overcoming this problem will be explained. The approach which will eventually be discussed is the use of partition functions, i.e., functions which partition space (these are not thermodynamic partition functions) such that space is integrated exactly once.
FIG. 7. The location of the 3-d quadrature grids (projected onto the x-y plane) using uniform (left) and nonuniform (right) angular quadrature rules as a function of radius.

You would no longer be able to separate the integral!

$$\int s_1(r) s_2(r - R_c) d^3r \neq \int s_1(r) d^3r \times \int s_2(r - R_c) d^3r.$$  \hspace{1cm} (54)

Furthermore, unlike Gaussian overlaps, the integrand is largest at either of the centers and one will yield suboptimal results using a single quadrature grid in its evaluation.

We will return to the overlap of 2 Slater functions later in this text; however, we will focus on our original problem of integrating the sum of 2 Slater functions. This serves as a much more useful example in describing the nuances of multi-center quadrature because the main issue that arises is the normalization of all-space.

As a first attempt at solving the integral, we will use a single quadrature center located on the origin and we evaluate

$$\int s_1(r) + s_2(r - R_c) d^3r = \sum_{i=1}^{N_1} w_i [s_1(r_i) + s_2(r_i - R_c)].$$  \hspace{1cm} (55)

This is nothing more than what was introduced in the previous section and we will see that it performs extremely poorly.

As a second approach, we will integrate using 2 quadrature grids, each centered coincident with one of the Slater functions.

$$\int s_1(r) + s_2(r - R_c) d^3r = \sum_{\alpha=1}^{N_1} \sum_{i=1}^{N_\alpha} w_{i,\alpha} [s_1(r_{i,\alpha}) + s_2(r_{i,\alpha} - R_c)],$$  \hspace{1cm} (56)

where $\alpha$ is an index denoting the quadrature grid, i.e., the first quadrature grid contributes $N_1$ points and the second quadrature grid contributes $N_2$ points. Similarly, the first quadrature grid contributes the points and weights $r_{i,\alpha}$ and $w_{i,\alpha}$ and the second contributes $r_{i,\alpha}$ and $w_{i,\alpha}$. An example of 2-such grids are displayed in Fig. 8 as a visual aid.

How well do each of these 2 methods perform? Fig. 9 displays the result of the integral using each of these 2 methods and compares it against the analytic result. In the single-center case, a total of 880 points were used (80 spheres each containing 110 points). The 2-center case used 2 such grids (a total of 1760 points). In both cases, Gauss-Laguerre quadrature is used for the radial integration, the roots of which are scaled by $\lambda = 10$.

As seen in Fig. 9, the single-center integration performs much better than the 2-center method at small distances, but performs extremely poorly as the Slaters are separated by a very large distance. In fact, it is exactly correct in the limit infinite separation. Neither of these 2 approaches, however, work well everywhere. Additionally, there are artifacts in both curves occurring at intermediate distances. Understanding these 2 plots is vital for the understanding of spatial-partitioning. Therefore, let us examine why neither of these 2 approaches perform well. We begin by focusing on the explanation of the behaviour of the single-center approach.

At large separation ($\approx 37$ units), the single-center approach produces an answer of 1 instead of 2. This is easily understood by examining the locations of the quadrature points relative to where the integrand is large. Fig. 10 displays the integrand for several separations, the largest separa-
Just as the origin-centered grid integrates the origin-centered Slater function (which integrates to unity). In contrast, in the limit that the 2 Slater functions are coincident, Slater function well. Therefore, the quadrature is only integrating the origin-centered units away from the origin; however, the contribution of the second Slater function to the integrand is negligible below 31 extrema should all lie within the range of the 2 asymptotic limits: 2 (when they are close together) and 1 when they are far apart), but why would the integral ever be greater than 2? First of all, the angular integration becomes less accurate as the separation increases (see the discussion in the previous section). Secondly, recall that we aren’t actually integrating the integrand; we are actually integrating the projection of the integrand in a basis of orthogonal polynomials. More precisely, the radial integral is the Laguerre-polynomial projection of the approximate integrand resulting from the Lebedev quadrature over Ω. To emphasize this point, let us examine the radial integrand and the basis-representation of the radial integrand. The radial function of our integrand is

\[ f(r) = r^2 \int s_1(r) + s_2(r - R_c) d\Omega, \]  

which can be computed analytically. The radial integrand upon angular quadrature integration is

\[ f(r) = r^2 \sum_{i=1}^{110} w_i (s_1(r \hat{r}_i) + s_2(|r - R_c| \hat{r}_i)) \]

and the basis representation is

\[ \hat{f}(r) = e^{-r} \sum_{j=0}^{80} L_j(r) \int f(r') L_j(r') dr' \]

\[ = e^{-r} \sum_{j=0}^{80} L_j(r) \sum_k w_k f(r_k) L_j(r_k), \]

where we have determined the expansion coefficients via quadrature.

Fig. 11 shows \( f(r) \) (both exact and angular quadrature result) and \( \hat{f}(r) \) (resulting from angular quadrature integration)
The sum of 2 Slater functions separated by various distances.

FIG. 10. The $z$-component of the integrand $s_1(r) + s_2(r-R_c)$ for various separations along the $z$-axis. The points are the locations of the quadrature grid centered about the origin. The lower plot is a zoomed version of the upper plot.

for various separations. As expected from our previous discussion, the numerical results are very accurate when the 2 Slater functions are coincident (or nearly coincident) because the implicit basis-representation of the integrand and angular integration are both excellent. In the limit that the 2 Slaters are separated by a large distance (such that the second Slater is negligibly represented on the grid), then the single-center grid integrates the origin-centered Slater function very well. Looking at the curves for $R = 50$, we see that the basis represents this half of the integrand precisely (and totally ignores the other half of the integrand). At intermediate distances, however, where the second Slater is inadequately sampled, the basis representation of the integrand and the result of the angular integration are both extremely poor. Although it is not shown, one finds a similar basis-representation of the integrand upon analytic evaluation of the angular coordinate. Representing a peak in the integrand far from the origin requires the use of high-order polynomials which, due to the limited size of the basis, propagate into areas of the integrand near the origin.

Thusfar, the explanations for the behaviour observed in Fig. 10 has been limited to the case of single-center integration; however, having completed this, the explanation of the 2-center integration results in Fig. 10 become trivial. The system studied here has been constructed with high symmetry, both in the integrand and in the integration grids. By construction, the 2-center results are exactly twice the 1-center results, always; however, if the 2 quadrature grids were not identical, the 2 limits (integral approaches 4 as $R \to 0$ and approaches 2 as $R \to \infty$) would still be retained. 2-center integration is far superior to single-center integration, because it correctly integrates in the limit that the 2 centers are well-separated. Single-center integration cannot possibly achieve this limit. The discussion will now focus on the modifications to the 2-center scheme are necessary to achieve good accuracy when the grids are not well-separated.

2. Spatial-partition functions

The case studied in the previous section served as a useful demonstration of the all-space normalization problem and it was noted that it was possible to solve the integral if we had separated the integral into 2 integrals (one integral over the first Slater function and the other over the second Slater). We also noted that a simple separation of the integrand wasn’t possible for an overlap integral. In this section, it is shown how one can separate an arbitrary integrand into many integrals, each of which can be accurately integrated via separate quadrature grids.

Consider the decomposition of the function $f(r)$

$$f(r) = \sum_{\alpha=1}^{N} \frac{L_{\alpha}(r)f(r)}{\sum_{\beta=1}^{N} l_{\beta}(r)} = \sum_{\alpha=1}^{N} L_{\alpha}(r)f(r),$$  \hspace{1cm} (61)

where

$$L_{\alpha}(r) = \frac{l_{\alpha}(r)}{\sum_{\beta=1}^{N} l_{\beta}(r)}$$  \hspace{1cm} (62)

and $L_{\alpha}(r)$ holds the property (by construction)

$$\sum_{\alpha=1}^{N} L_{\alpha}(r) = 1.$$  \hspace{1cm} (63)

$l_{\alpha}(r)$ is any arbitrary function that we choose to be very large in the region of the $\alpha^{th}$ quadrature center and small everywhere else. $L_{\alpha}$, therefore, is a function that is $\approx 1$ in the region about the $\alpha^{th}$ quadrature center and is $\approx 0$ everywhere else. Using this partitioning of space, we can rewrite an integral over all-space as a sum of integrals, each over all-space, but whose integrand is only non-negligable in the region about the $\alpha^{th}$ quadrature center.

$$\int f(r)d^3r = \sum_{\alpha=1}^{N} \int L_{\alpha}(r)f(r)d^3r$$  \hspace{1cm} (64)

Each of these integrals can then be determined from a sum of
FIG. 11. The radial integrand defined by Eq. (58) for various separations of the Slater functions. Shown are the exact integrand (green), the integrand resulting from 110-point angular quadrature (black), and the Laguerre-basis representation (red) of the quadrature approximate, i.e., black curve, which is what the quadrature formula actually integrates.

single center quadrature integrations.  

\[ \int f(r) \, d^3r = \sum_{i=1}^{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} w_{i,\alpha} L_{\alpha}(r_{i,\alpha}) f(r_{i,\alpha}) \]

(65)

where we have again used the combined, double-index notation \( i, \alpha \) to denote the \( i^{th} \) point of the \( \alpha^{th} \) quadrature grid [see Eq. (56) and the discussion immediately following] and we have introduced the notation \( L_{\alpha}(r_{i,\alpha}) = L_{\alpha,\alpha} \) for convenience.

In order to compare the accuracy of this spatial-partitioning scheme with single-center integration (presented in the preceding section), we must introduce forms for \( L_{\alpha}(r) \). For the time being, we will again focus our attention on computing the integral of the sum of 2 L1-normalized Slater functions separated by a distance, \( R \).

The first form of \( L_{\alpha}(r) \) considered is a modification to Hirshfeld partitioning. Formally, Hirshfeld partitioning is

\[ L_{\alpha}(r) = \frac{\rho_{\alpha}^0(r)}{\sum_{\beta=1}^{N_{\alpha}} \rho_{\beta}^0(r)} \]

(66)

where \( \rho_{\alpha}^0(r) \) is the isolated, unperturbed, spherical atomic density of atom \( \alpha \). In the present case, \( \rho_{\alpha}^0(r) = s_{\alpha}(r) \). Hirshfeld partitioning can be useful for analyzing properties of the density; however, it typically doesn’t yield a function \( L_{\alpha}(r) \) that localizes the partitions of space enough. The modification to Hirshfeld partitioning considered here is

\[ L_{\alpha}(r) = \frac{1}{r_{\alpha}} \left( \frac{\rho_{\alpha}^0(r)}{\sum_{\beta=1}^{N_{\alpha}} \rho_{\beta}^0(r)} \right)^6 \]

(67)

This form of \( L_{\alpha}(r) \) becomes very large at its corresponding quadrature center and quickly decays to zero.

The second form which is considered is Becke’s “fuzzy Voronoi”, described in Ref. 8:

\[ s(\mu_{\alpha\beta}) = \prod_{\beta \neq \alpha} s(\mu_{\alpha\beta}) \]

(68)

where

\[ s(\mu_{\alpha\beta}) = \frac{1}{2} \left[ 1 - p(p(\mu_{\alpha\beta})) \right] \]

(69)
Comparison of numerical errors between different partitioning schemes

![Graph showing comparison of numerical errors](image)

**FIG. 12.** Numerical errors in the calculation of the integral appearing in Eq. (51) using the modified Hirshfeld partitioning (black) and Becke’s fuzzy Voronoi (3x recursion) (red).

\[
p(x) = \frac{3}{2}x^2 - \frac{1}{2}x^3
\]

(70)

\[
\mu_{\alpha\beta} = \frac{|r - R_{\alpha}| - |r - R_{\beta}|}{|R_{\alpha} - R_{\beta}|}.
\]

(71)

\(R_{\alpha}\) denotes the location of the \(\alpha^{th}\) quadrature center in space. The \(\alpha^{th}\) spatial-partition function, \(L_{\alpha}(r)\), is then given by Eq. (62).

Fig. 12 displays the absolute error \(I(R) - \tilde{I}(R)\) (where \(I(R) = 2\), i.e., the analytic result of the integral as a function of \(R\), and \(\tilde{I}(R)\) is the numerical result) using the modified-Hirschfeld and Becke-partitioning schemes. Both methods perform very well (which is why only the errors are shown). When the error is positive, it means that the analytic result is greater than the numerical result and, conversely, negative values indicate that the numerical result is larger than the analytic result. In the range \(0 < R < 25\), Becke’s partitioning scheme yields errors which are both smoother and significantly smaller in magnitude than the modified-Hirschfeld partitioning. (Note to self: This is due to Becke’s use of elliptical coordinates in the construction of the partition function - modified Hirschfeld produces small dimples in the outer-regions along the ray joining 2 centers.)

Fig. 13 compares the errors resulting from Becke’s fuzzy Voronoi for various recursion levels (Becke recommends recursion level 3). The recursion level effectively acts as a measure of sharpness of the switching region, i.e., as the recursion level is increased to infinity, the switching region becomes a step function. At very large separations, steeper switching is more accurate because, as the 2 centers separate, the switch-

Comparison of numerical errors between different Becke partitioning schemes

![Graph showing comparison of numerical errors](image)

**FIG. 13.** Numerical errors in the calculation of the integral appearing in Eq. (51) using Becke’s fuzzy Voronoi for various levels of recursion in the calculation of \(s(\mu)\).

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