Handout 2: Derivation of the Molecular Integrals

In the following document, derivations of solutions to the molecular integrals are presented in guided exercise form. Key equations and solutions are boxed as *Essential Equations*. In order, the four following energy molecular integrals are presented:

1. **Overlap** $(A|B)$. In this section, the necessary specialized notation that will be used throughout all derivations is addressed. Additional details of how two centers ($\vec{A}$, $\vec{B}$) are reduced to one ($\vec{P}$) are provided. In addition to the radial components of both CGTOs ϕ_A and ϕ_B, which are treated by the Gaussian Product Theorem, the angular momentum components are derived through the use of standard binomial coefficients. Standard integral formulae, as are found in tables of integrals, are presented for use, allowing for the derivation of the final, code-able expression of $(A|B)$. The student/reader also derives the normalization constant N. Additional discussion of matrix structure, with respect to the atomic orbital basis, is included, and the discussion applies to $\mathbf{T}$ and $\mathbf{V}$ in addition to $\mathbf{S}$. This section ends with a discussion of the difference between minimal and extended basis sets.

2. **Kinetic energy** $(A|-\frac{1}{2}\nabla^2|B)$. This brief section leads the reader to the conclusion that the expression for a kinetic energy matrix element is simply a sum of overlap integrals, each term in the summation led by a constant.

3. **Electron-nuclear attraction** $(A|\frac{-Z_C}{\vec{r}_{iC}}|B)$. The presence of an inverse operator ($\vec{r}_{iC}$ being in the denominator) marks a radical departure from $(A|B)$ and $(A|-\frac{1}{2}\nabla^2|B)$. Its solution fundamentally depends on a Fourier transformation, which serves to draw $\vec{r}_{iC}$ out of the denominator. This section introduces the Boys Function, F_ν, which can only be solved numerically.

4. **Electron-electron repulsion** $(AB|CD)$. Characterized by another inverse operator ($\vec{r}_{ij}^{-1}$), these molecular integrals entail a solution similar to that of $(A|\frac{-Z_C}{\vec{r}_{iC}}|B)$. While the previous integrals are one-electron in nature, requiring one third center $\vec{P}$, the electron-electron repulsion treats two electrons through the use of two third centers, $\vec{P}$ and $\vec{Q}$. Hence, there is approximately twice as much manipulation as for the electron-nuclear attraction integrals. Additionally, these matrix elements make up a rank-4 tensor (or four-dimensional matrix) instead of a two-dimensional matrix; the structure of a rank-4 tensor is discussed.

As the student or reader works through the following material, they are encouraged to use a sheet to cover up exercise solutions, which immediately follow the questions and are marked by a thick black line. Most exercises are relatively straightforward, and shouldn't take more than 15 minutes each to complete.

2.1 Overlap integrals

A single matrix element for the overlap of two atomic orbitals ϕ_A and ϕ_B has the general form

$$(A|B) = \int \phi_A \phi_B \, \mathrm{d}\tau \,, \tag{1}$$

where $\mathrm{d}\tau$ is the differential volume element over three dimensions. We employ Cartesian coordinates,

$$\mathrm{d}\tau \implies \mathrm{d}V \equiv \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z \,.$$

As described in the main article, a single atomic orbital ϕ_A can be represented by a linear combination of Cartesian Gaussian primitives χ_a,

$$\phi_A = \sum_{a=1}^{K_a} \mathrm{d}_a N_a \chi_a = \sum_{a=1}^{K_a} \mathrm{d}_a N_a x^{l_A} y^{m_A} z^{n_A} \mathrm{e}^{-\alpha_a r_A^2} \,, \tag{2}$$

where $r_A^2 = x_A^2 + y_A^2 + z_A^2$.

In fact, the exact notation for any electron position r, including r_A, is $\vec{r}$ (which in this case would be $\vec{r}_A$). For notational clarity the vector symbol is sometimes only implied, as was the case in the main article and Handout 1. Because $\vec{r}$ is a vector quantity, then, $x_A \equiv \vec{r}_{A_x} = \vec{r}_x - \vec{A}_x$, the x-component of the distance between the electron and center A; the simpler notation x_A is used for notational clarity. See Fig. 1. Also, x^{l_A} implies $x_A^{l_A}$, as seen in Eq. 2.

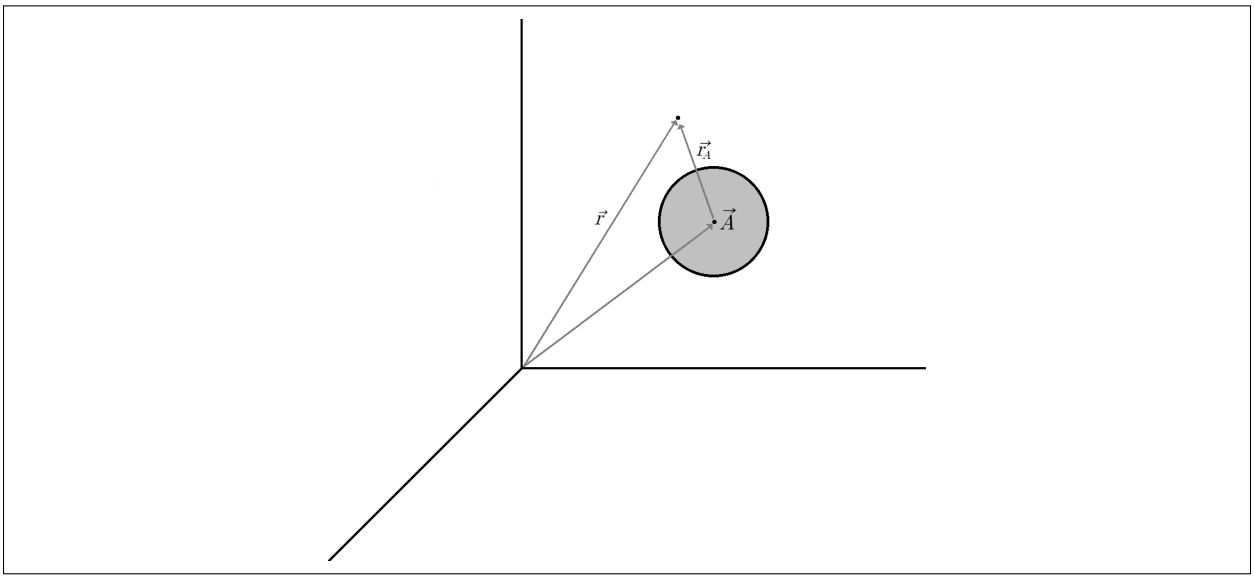

Figure 1: The molecular coordinate system. $\vec{r}$ defines the electron's coordinates with respect to the origin; $\vec{A}$ is the coordinates of atom A, or atom-centered orbital ϕ_A. $\vec{r}_A$ is the distance between the electron and the atom's center.

Thus, Eq. 1 becomes

$$(A|B) = \sum_{a=1}^{K_a} \sum_{b=1}^{K_b} \mathrm{d}_a \mathrm{d}_b N_a N_b \int \chi_a(\vec{A}, \alpha_a, l_A, m_A, n_A) \chi_b(\vec{B}, \alpha_b, l_B, m_B, n_B) \, \mathrm{d}V \,. \tag{3}$$

While this form allows us to see that each primitive is normalized and multiplied by its contraction coefficient, we still have a general integral expression that is not code-able. The notation adopted in Eq. 3 indicates the functional independence of each primitive on several parameters:

- $\vec{A}$ is a positon vector which describes the Cartesian coordinates of the atom on which the orbital is centered in terms of x, y, and z components (this gives rise to the term "atom-centered orbitals," which are indeed the basis of our molecular integrals);
- α_a is a constant (a basis set parameter, alongside contraction coefficient d_a) which appears as a factor in the exponent;
- l, m, and n are angular momentum components with respect to coordinates x, y, and z.

Expanding out the integral over the Gaussian primitives χ_a and χ_b, we have

$$\int \chi_A \chi_B \, dV = \int \underbrace{x^{l_A} y^{m_A} z^{n_A} \mathrm{e}^{-\alpha_a r_A^2}}_{\chi_a} \underbrace{x^{l_B} y^{m_B} z^{n_B} \mathrm{e}^{-\alpha_b r_B^2}}_{\chi_b} \, \mathrm{d}V \,. \tag{4}$$

Using $r^2 = x^2 + y^2 + z^2$, this becomes

$$\int_0^\infty \int_0^\infty \int_0^\infty x^{l_A} y^{m_A} z^{n_A} \mathrm{e}^{-\alpha_a (x_A^2 + y_A^2 + z_A^2)} x^{l_B} y^{m_B} z^{n_B} \mathrm{e}^{-\alpha_b (x_B^2 + y_B^2 + z_B^2)} \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z \,. \tag{5}$$

Eq. 5 can be rearranged on the basis of the separability of the Cartesian coordinates

$$\int_0^\infty x^{l_A} x^{l_B} \mathrm{e}^{-\gamma (x_A^2 + x_B^2)} \mathrm{d}x \int_0^\infty y^{m_A} y^{m_B} \mathrm{e}^{-\gamma (y_A^2 + y_B^2)} \mathrm{d}y \int_0^\infty z^{n_A} z^{n_B} \mathrm{e}^{-\gamma (z_A^2 + z_B^2)} \mathrm{d}z \,, \tag{6}$$

where

$$\gamma = \alpha_a + \alpha_b \,. \tag{7}$$

Each of these integrals are analogous, so we will focus on solving for one, the x-component.

$$\int_0^\infty x^{l_A} x^{l_B} \mathrm{e}^{-\gamma (x_A^2 + x_B^2)} \, \mathrm{d}x \,. \tag{8}$$

It is relatively straightforward to derive the expression for the overlap of s orbitals – that is, when l_A and l_B equal 0, neither having angular momentum.

Exercise.
Derive the analytical solution for the overlap of s orbitals ϕ_A and ϕ_B (non-normalized). First form the Gaussian product of centers $\vec{A}$ and $\vec{B}$, as discussed in Handout 1. Then, having formed $\widetilde{K}$ and the exponential function, $\exp\left(-\gamma r_P^2\right)$, where $\gamma = \alpha_a + \alpha_b$, integrate over the x-component of this function by using the following equation from a table of integrals.

Essential Equation

$$\int_0^\infty \mathrm{e}^{-k r^2} = \frac{1}{2} \sqrt{\frac{\pi}{k}} \tag{9}$$

Note that, upon going from coordinates over $\vec{r}_A$ and $\vec{r}_B$ to $\vec{r}_P$, the limits of integration will change from $\int_0^\infty$ to $\int_{-\infty}^\infty$. This is because, while the distance between an electron and the center of an atom ($\vec{r}_A$) can never be less than zero, this restriction no longer applies to a center *between* two nuclei. In such a case, the result of using Eq. 9 must be multipled by two.

The solution for the y and the z components will be entirely analogous to the solution for the x component. The results can be easily combined into a single solution over the three Cartesian coordinates. Include the results for the y and z, in addition to x, components in your answer for a solution over all space in all dimensions.

Solution.
Letting $l = m = n = 0$,

$$\phi_A = x^0 y^0 z^0 \mathrm{e}^{-\alpha_a r_A^2} = \mathrm{e}^{-\alpha_a r_A^2} ,$$
$$\phi_B = x^0 y^0 z^0 \mathrm{e}^{-\alpha_b r_B^2} = \mathrm{e}^{-\alpha_b r_B^2} .$$

Forming the Gaussian product of these two orbitals, centered on $\vec{P}$:

$$\begin{aligned}\phi_A \phi_B &= \mathrm{e}^{-\alpha_a r_A^2} \mathrm{e}^{-\alpha_b r_B^2} \\ &= \exp\left(-\frac{\alpha_a \alpha_b}{\gamma} |\vec{AB}|^2\right) \exp\left(-\gamma r_P^2\right) \\ &= \widetilde{K}_P \exp\left(-\gamma r_P^2\right) ,\end{aligned}$$

where

$$\vec{AB} = \vec{A} - \vec{B} .$$

$|\vec{AB}|^2$ was introduced in the main article, and is simply the distance formula.

$$|\vec{AB}|^2 = (\vec{A}_x - \vec{B}_x)^2 + (\vec{A}_y - \vec{B}_y)^2 + (\vec{A}_z - \vec{B}_z)^2 . \tag{10}$$

Because $\widetilde{K}_P$ is a constant, it can be pulled outside the integral:

$$\begin{aligned}\int_{-\infty}^{\infty} \widetilde{K}_P \exp\left(-\gamma r_P^2\right) \mathrm{d}V &= \widetilde{K}_P \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[-\gamma(x_P^2 + y_P^2 + z_P^2)\right] \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \\ &= \widetilde{K}_P \int_{-\infty}^{\infty} \mathrm{e}^{-\gamma x_P^2} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{e}^{-\gamma y_P^2} \mathrm{d}y \int_{-\infty}^{\infty} \mathrm{e}^{-\gamma z^2} \mathrm{d}z .\end{aligned}$$

First solving for the x-component, we use the standard solution from a table of integrals, shown in Eq. 9. Since we are integrating not over $[0, \infty)$, but rather $(-\infty, \infty)$, we must multiply the solution by two. Thus,

$$\int_{-\infty}^{\infty} \mathrm{e}^{-\gamma x^2} = \sqrt{\frac{\pi}{\gamma}} \tag{11}$$

The result will be identical for the y and the z components. Thus,

$$\int \phi_A \phi_B \,\mathrm{d}V = \widetilde{K}_P \int_{-\infty}^{\infty} \mathrm{e}^{-\gamma x_P^2} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{e}^{-\gamma y_P^2} \mathrm{d}y \int_{-\infty}^{\infty} \mathrm{e}^{-\gamma z_P^2} \mathrm{d}z = \widetilde{K}_P \left(\frac{\pi}{\gamma}\right)^{3/2} . \tag{12}$$

[end of solution]

The overlap integral is more complicated when one or both orbitals have orbital angular momentum, because this requires taking the product of polynomials (e.g., $x^{l_A} x^{l_B}$) in addition to the Gaussian functions.

We will consider the polynomial part of the integral first. Recall that $x_A \equiv (\vec{r}_x - \vec{A}_x)^{l_A}$. We have been and will continue to use x as shorthand notation for $\vec{r}_x$. Thus, our product of polynomials can be written as

$$x^{l_A} x^{l_B} \equiv (x - \vec{A}_x)^{l_A} (x - \vec{B}_x)^{l_B} . \tag{13}$$

Our objective is to extract the x (i.e., $\vec{r}_x$) from each polynomial, because this is the coordinate being integrated over. By employing the Gaussian product theorem and forming a third center $\vec{P}$ between centers $\vec{A}$ and $\vec{B}$ (see Fig. 2),

$$\vec{P} = \frac{\alpha_a \vec{A} + \alpha_b \vec{B}}{\alpha_a + \alpha_b} , \tag{14}$$

$$(x - \vec{A}_x)^{l_A} = \{(x - \vec{P}_x) + (\vec{P}_x - \vec{A}_x)\}^{l_A} = (x_P - \vec{PA}_x)^{l_A} \,. \tag{15}$$

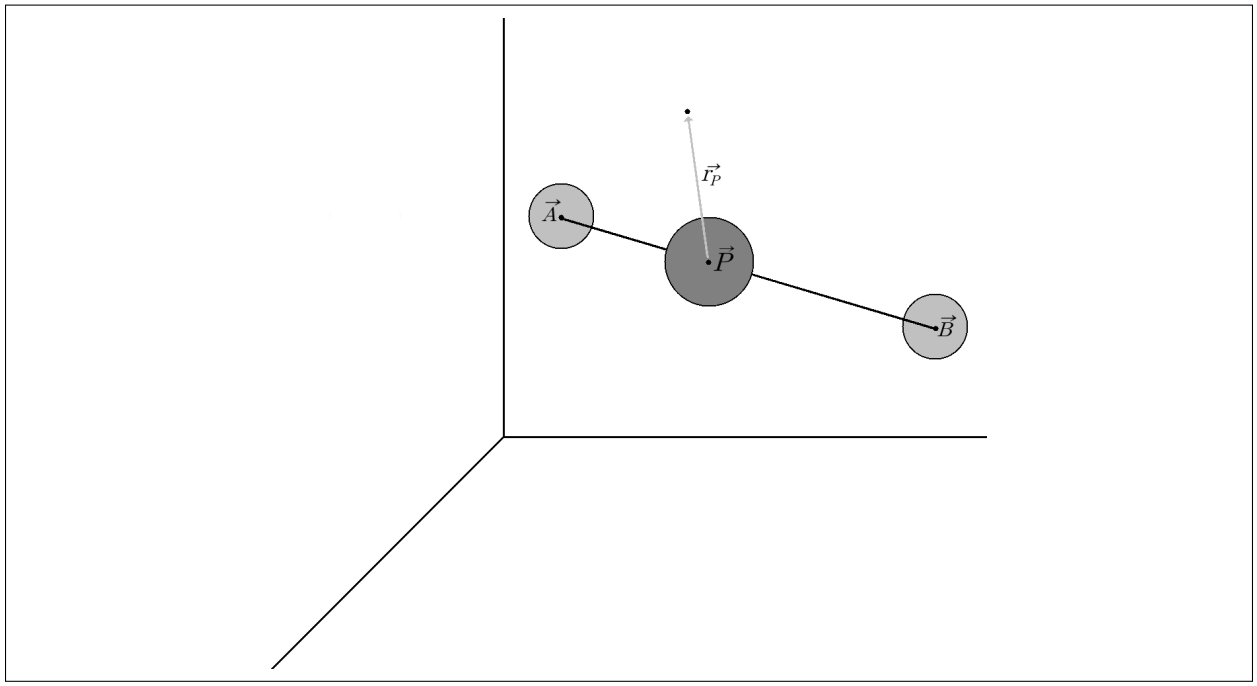

Figure 2: $\vec{r}_P$ is the distance between the electron and the newly formed third center $\vec{r}_P$, which is formed as the Gaussian product of centers $\vec{A}$ and $\vec{B}$.

We have employed the x-component of the vector quantity $\vec{P}$, which is the third Gaussian center located between centers $\vec{A}$ and $\vec{B}$. Using the standard binomial expansion,

$$(a+b)^n = \sum_{k=0}^{n} \binom{n}{k} a^{n-k} b^k \,, \tag{16}$$

where $\binom{n}{k}$ is the binomial coefficient meaning "n choose k" or

$$\binom{n}{k} = \frac{n!}{k!(n-k)!} \,, \tag{17}$$

we can recast Eq. 15.

Exercise.
Express the right-most side of Eq. 15 as a binomial expansion, with a binomial coefficient "l_A choose i."

Solution.

$$(x_P - \vec{PA}_x)^{l_A} = \sum_{i=0}^{l_A} \binom{l_A}{i} (\vec{PA}_x)^{l_A - i} (x_P)^i \tag{18}$$

[end of solution]

By taking the product of the binomial expansions of each polynomial, we have

$$\begin{aligned}(x_P - \vec{PA}_x)^{l_A}(x_P - \vec{PB}_x)^{l_B} &= \sum_{i=0}^{l_A}\binom{l_A}{i}(\vec{PA}_x)^{l_A-i}(x_P)^i \sum_{j=0}^{l_B}\binom{l_B}{j}(\vec{PB}_x)^{l_B-j}(x_P)^j \\ &= \sum_{i=0}^{l_A}\sum_{j=0}^{l_B}\binom{l_A}{i}\binom{l_B}{j}(\vec{PA}_x)^{l_A-i}(\vec{PB}_x)^{l_B-j}(x_P)^i(x_P)^j \\ &= \sum_{i=0}^{l_A}\sum_{j=0}^{l_B}\binom{l_A}{i}\binom{l_B}{j}(\vec{PA}_x)^{l_A-i}(\vec{PB}_x)^{l_B-j}x_P^{i+j}\end{aligned} \tag{19}$$

Having collected terms x^i and x^j, and by introducing a coefficient c_k, we can reduce two sums to one:

$$(x_P - \vec{PA}_x)^{l_A}(x_P - \vec{PB}_x)^{l_B} = \sum_{k=0}^{l_A+l_B} c_k(l_A, l_B, \vec{PA}_x, \vec{PB}_x)x_P^k \tag{20}$$

Now we define the coefficient c_k with some generalized variables.

Essential Equation

$$c_k(l, m, a, b) = \sum_{i=0}^{l}\sum_{j=0}^{m}\binom{l}{i}\binom{m}{j}a^{l-i}b^{m-j}\,; \quad i + j \stackrel{!}{=} k \tag{21}$$

In Eq. 21 the variables for c_k are generalized because we will be using this coefficient again later with different arguments. The notation featuring an equals sign with an exclamation over it is the directive that the coefficient formula is only evaluated when the sum of i and j is equal to k. In the parent function to which c_k belongs, Eq. 20, the single summation constrains the sum of i and j in the coefficient to being *equal* to k. For example, if $l_A + l_B = 2 + 3 = 5$, and we are in the state of summation when $k = 1$, then when evaluating c_k, *either* summation variable i (which has an upper bound of 2) *or* summation variable j (which has an upper bound of 3) must be equal to one, and the other to zero. If this condition is not met, the formula is bypassed until the next combination of summations in c_k is equal to k.

The radial portion of the orbital product $\phi_A \times \phi_B$ is analyzed just as it was in an earlier exercise. Over x, y, and z components,

$$\begin{aligned}(\mathrm{e}^{-\alpha_a r_A^2}) \times (\mathrm{e}^{-\alpha_b r_B^2}) &= \exp\left(-\frac{\alpha_a\alpha_b}{\gamma}|\vec{AB}|^2\right)\exp\left(-\gamma r_P^2\right) \\ &= \widetilde{K}_P \exp\left(-\gamma r_P^2\right).\end{aligned} \tag{22}$$

We now couple the results of this analysis of the radial portion of $\phi_A\phi_B$ with our analysis of the angular portion, seen in final form in Eqs. 20 and 21 for the x-component (with analogous expression for y and z). Looking at just the x-component of their product – with $\widetilde{K}_P$ set aside until the end of the derivation, because it is just a constant requiring no further manipulation – they make up an equation we call S_x. It can be seen that the general equation for the overlap of the x-component of Gaussian primitives (Eq. 8) now has the following form:

$$S_x = \sum_{k=0}^{l_A+l_B} c_k(l_A, l_B, \vec{PA}_x, \vec{PB}_x)\int_{-\infty}^{\infty} x_P^k \exp\left(-\gamma x_P^2\right)\mathrm{d}x \tag{23}$$

We have succeeded in recasting an integral that initially had been over the two centers $\vec{A}$ and $\vec{B}$ (see Eq. 8) to one over the single intermediate center $\vec{P}$. It remains to evaluate the "integral" portion of Eq. 23. Because it is a Gaussian integral over a single center, it is actually a standard integral with a known solution that can easily be found in a table of integrals. Several such closely related integrals are shown below.

Essential Equation

$$\int_0^\infty x^{2k} e^{-ax^2} \mathrm{d}x = \sqrt{\frac{\pi}{a}} \frac{(2k-1)!!}{2^{k+1} a^k} \quad (k \in \mathbb{Z},\, a > 0, !! \text{ is the double factorial}) \tag{24}$$

$$\int_{-\infty}^\infty x^{2k} e^{-ax^2} \mathrm{d}x = 2 \int_0^\infty x^{2k} e^{-ax^2} \mathrm{d}x \tag{25}$$

$$\int_{-\infty}^\infty x^{k} e^{-ax^2} \mathrm{d}x = \sqrt{\frac{\pi}{a}} \frac{(2k-1)!!}{(2a)^k} \quad (k \in \mathbb{Z},\, a > 0, !! \text{ is the double factorial}) \tag{26}$$

A double factorial is defined as follows:

$$(2n-1)!! = \begin{cases} 1 \cdot 3 \cdot 5 \cdots (n-2) \cdot n & \text{if } n \text{ is odd} \\ 2 \cdot 4 \cdot 6 \cdots (n-2) \cdot n & \text{if } n \text{ is even} \end{cases}$$

$$(-1)!! = 0!! = 1$$

Exercise.
Insert the tabulated solution in Eq. 26 to solve the integral portion of S_x (Eq. 23).

Solution.
Inserting the tabulated solution gives

$$\int_{-\infty}^\infty x_P^k \exp\left(-\gamma x_P^2\right) \mathrm{d}x = \sqrt{\frac{\pi}{\gamma}} \frac{(2k-1)!!}{(2\gamma)^k}. \tag{27}$$

[end of solution]

Thus, we have a code-able equation for S_x.

Essential Equation

$$S_x = \sum_{k=0}^{\lfloor (l_A + l_B)/2 \rfloor} c_{2k}(l_A, l_B, \vec{PA}_x, \vec{PB}_x) \sqrt{\frac{\pi}{\gamma}} \frac{(2k-1)!!}{(2\gamma)^k} \tag{28}$$

Exercise.
The upper bound of summation and the argument for the c_k function changed in Eq. 28 from 23. This has the effect of passing in to the general c_k function only *even* integers of k. Why should only even integers be evaluated? (Hint: In the integral of Eq. 23, we are integrating not over $[0, \infty)$, but $(-\infty, \infty)$. Consider this with respect to the parity of the integrand – that is, whether the power function x^k is even or odd, as defined by whether k is even or odd.)

Solution.
If the exponent k in the integral of S_x (Eq. 27) is an odd number, then integration over it returns zero. If k is an even function, then the integral will be non-zero. Hence, it is only worthwhile evaluating even values of k.

Strictly speaking, we *could* leave the summation and arguments to the c_k function as they were in Eq. 23, but this would mean spending precious computational power on terms that we know mathematically will be zero.
[end of solution]

With a solution for S_x (Eq. 28), analogous expressions for S_y and S_z, and by re-including $\vec{K}_P$, we have a code-able equation for the overlap integral $(A|B)$.

Essential Equation

$$(A|B) = \sum_{a=1}^{K_a}\sum_{b=1}^{K_b} \mathrm{d}_a \mathrm{d}_b N_a N_b \times \underbrace{\exp\left(-\frac{\alpha_a\alpha_b}{\gamma}|\vec{AB}|^2\right)}_{\vec{K}_P} \times S_x \times S_y \times S_z \tag{29}$$

The formula for $|\vec{AB}|^2$ is found in Eq. 10. Recalling that the contraction coefficients (d_a, d_b) and exponential factors (α_a, α_b) are tabulated basis set values, then the only remaining factor of Eq. 29 to calculate is the normalization constant, N. The following formula is used.

Essential Equation

$$N(\alpha, l, m, n) = \left[\left(\frac{2\alpha}{\pi}\right)^{3/2} \frac{(4\alpha)^{l+m+n}}{(2l-1)!!(2m-1)!!(2n-1)!!}\right]^{1/2} \tag{30}$$

Exercise.
Derive the normalization constant N. Begin by considering the overlap integral of primitive χ_a,

$$\chi_a = N x^l y^m z^n e^{-\alpha r^2}$$

with itself, where N is what we must solve for after integration. That is, for

$$\int \chi_a \chi_a \,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 1,$$

which is expanded as

$$N^2 \int_0^\infty \int_0^\infty \int_0^\infty (x^l y^m z^n e^{-\alpha r^2})(x^l y^m z^n e^{-\alpha r^2})\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,,$$

solve for N. (Hint: Use Eq. 24 once per coordinate.)

Solution.
Before we present the solution to this problem, recall that typically several Gaussian primitives are summed ("contracted") to represent one orbital ϕ_A, but integrals must be evaluated with respect to individual primitives. Hence, the results of each of these integral evaluations are then summed.

Now,

$$\int \chi_a \chi_a \,\mathrm{d}V = 1 \tag{31}$$

Thus,

$$\begin{aligned}\int \chi_a \chi_a \, \mathrm{d}V &= \int_0^\infty (N x^l y^m z^n e^{-\alpha r^2})(N x^l y^m z^n e^{-\alpha r^2}) \, \mathrm{d}V \\ &= N^2 \int_0^\infty x^{2l} y^{2m} z^{2n} e^{-2\alpha r^2} \, \mathrm{d}V.\end{aligned} \tag{32}$$

Recalling that

$$r^2 = x^2 + y^2 + z^2 \,, \tag{33}$$

then

$$\begin{aligned}N^2 \int_0^\infty x^{2l} y^{2m} z^{2n} e^{-2\alpha r^2} \, \mathrm{d}V &= N^2 \int_0^\infty \int_0^\infty \int_0^\infty x^{2l} y^{2m} z^{2n} e^{-2\alpha(x^2+y^2+z^2)} \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z \\ &= N^2 \int_0^\infty x^{2l} e^{-2\alpha x^2} \, \mathrm{d}x \int_0^\infty y^{2m} e^{-2\alpha y^2} \, \mathrm{d}y \int_0^\infty z^{2n} e^{-2\alpha z^2} \mathrm{d}z \,.\end{aligned} \tag{34}$$

(Here the integration limits are 0 to infinity, because the coordinates are with respect to atomic centers, not third, Gaussian product centers.) By employing Eq. 24

$$\int_0^\infty x^{2l} e^{-2\alpha x^2} \, \mathrm{d}x = \frac{(2l-1)!!\sqrt{\pi}}{(4\alpha)^l \sqrt{2\alpha}} \,. \tag{35}$$

By analogy for the remaining terms, we have

$$\begin{aligned}N^2 \int_0^\infty x^{2l} e^{-2\alpha x^2} \, \mathrm{d}x \int_0^\infty y^{2m} e^{-2\alpha y^2} \, \mathrm{d}y \int_0^\infty z^{2n} e^{-2\alpha z^2} \, \mathrm{d}x &= N^2 \times \frac{(2l-1)!!\sqrt{\pi}}{(4\alpha)^l \sqrt{2\alpha}} \times \frac{(2m-1)!!\sqrt{\pi}}{(4\alpha)^m \sqrt{2\alpha}} \times \frac{(2n-1)!!\sqrt{\pi}}{(4\alpha)^n \sqrt{2\alpha}} \\ &= N^2 \times \left[\left(\frac{\pi}{2\alpha} \right)^{3/2} \frac{(2l-1)!!(2m-1)!!(2n-1)!!}{(4\alpha)^{l+m+n}} \right] = 1 \,.\end{aligned} \tag{36}$$

Rearranging the last line of Eq. 36 to solve for N simply requires multiplying both sides by the inverse of the expression in square brackets, and then taking the square root of both sides. This gives us our normalization constant N.

$$N = \left[\left(\frac{2\alpha}{\pi} \right)^{3/2} \frac{(4\alpha)^{l+m+n}}{(2l-1)!!(2m-1)!!(2n-1)!!} \right]^{1/2} \tag{37}$$

[end of solution]

Eq. 29 corresponds to one matrix element – one "box" of the 7×7 overlap matrix for H_2O shown in Fig. 3, where $\phi_A = |A) = |\mathrm{O1s})$, or $|\mathrm{O2s})$, or $|\mathrm{O2p}_x)$, *etc.*, and $\phi_B = |\mathrm{O1s})$, or $|\mathrm{O2s})$, or $|\mathrm{O2p}_x)$, *etc.* Among the $7 \times 7 = 49$ elements, one element features, by way of example, the overlap of oxygen's $2s$ orbital with hydrogen's $1s$ orbital. In another element we have the other hydrogen's $1s$ orbital overlapping with oxygen's $2p_x$ orbital; in another still, there is the oxygen's $2p_y$ orbital overlapping with its $1s$ orbital – and so on. Each of these possible overlaps constitute a single element of the overlap integral matrix, which we term **S**; individual overlaps in $(A|B)$ are shown in Fig. 4. It is worth pointing out that an orbital's overlap with itself will, when normalized, be exactly equal to 1. In addition to factors of symmetry (s vs. p, *etc.*) and differences in orbital energy, the overlap integrals of atomic orbitals that are separated by greater distance will have smaller values. This is demonstrated in Fig. 5.

This concludes our discussion of how one matrix element of the overlap integral matrix **S** is evaluated.

	$\|\mathrm{O}1s)$	$\|\mathrm{O}2s)$	$\|\mathrm{O}2p_x)$	$\|\mathrm{O}2p_y)$	$\|\mathrm{O}2p_z)$	$\|\mathrm{H}_a1s)$	$\|\mathrm{H}_b1s)$
$(\mathrm{O}1s\|$							
$(\mathrm{O}2s\|$							
$(\mathrm{O}2p_x\|$							
$(\mathrm{O}2p_y\|$							
$(\mathrm{O}2p_z\|$							
$(\mathrm{H}_a1s\|$							
$(\mathrm{H}_b1s\|$							

Figure 3: The 7×7 overlap integral matrix $\mathbf{S}$ for water in the STO-3G orbital basis.

	$\|\mathrm{O}1s)$	$\|\mathrm{O}2s)$	$\|\mathrm{O}2p_x)$	$\|\mathrm{O}2p_y)$	$\|\mathrm{O}2p_z)$	$\|\mathrm{H}_a1s)$	$\|\mathrm{H}_b1s)$
$(\mathrm{O}1s\|$	$(\mathrm{O}1s\|\mathrm{O}1s)$	$(\mathrm{O}1s\|\mathrm{O}2s)$	$(\mathrm{O}1s\|\mathrm{O}2p_x)$	$(\mathrm{O}1s\|\mathrm{O}2p_y)$	$(\mathrm{O}1s\|\mathrm{O}2p_z)$	$(\mathrm{O}1s\|\mathrm{H}_a1s)$	$(\mathrm{O}1s\|\mathrm{H}_b1s)$
$(\mathrm{O}2s\|$	$(\mathrm{O}2s\|\mathrm{O}1s)$	$(\mathrm{O}2s\|\mathrm{O}2s)$	$(\mathrm{O}2s\|\mathrm{O}2p_x)$	$(\mathrm{O}2s\|\mathrm{O}2p_y)$	$(\mathrm{O}2s\|\mathrm{O}2p_z)$	$(\mathrm{O}2s\|\mathrm{H}_a1s)$	$(\mathrm{O}2s\|\mathrm{H}_b1s)$
$(\mathrm{O}2p_x\|$	$(\mathrm{O}2p_x\|\mathrm{O}1s)$	$(\mathrm{O}2p_x\|\mathrm{O}2s)$	$(\mathrm{O}2p_x\|\mathrm{O}2p_x)$	$(\mathrm{O}2p_x\|\mathrm{O}2p_y)$	$(\mathrm{O}2p_x\|\mathrm{O}2p_z)$	$(\mathrm{O}2p_x\|\mathrm{H}_a1s)$	$(\mathrm{O}2p_x\|\mathrm{H}_b1s)$
$(\mathrm{O}2p_y\|$	$(\mathrm{O}2p_y\|\mathrm{O}1s)$	$(\mathrm{O}2p_y\|\mathrm{O}2s)$	$(\mathrm{O}2p_y\|\mathrm{O}2p_x)$	$(\mathrm{O}2p_y\|\mathrm{O}2p_y)$	$(\mathrm{O}2p_y\|\mathrm{O}2p_z)$	$(\mathrm{O}2p_y\|\mathrm{H}_a1s)$	$(\mathrm{O}2p_y\|\mathrm{H}_b1s)$
$(\mathrm{O}2p_z\|$	$(\mathrm{O}2p_z\|\mathrm{O}1s)$	$(\mathrm{O}2p_z\|\mathrm{O}2s)$	$(\mathrm{O}2p_z\|\mathrm{O}2p_x)$	$(\mathrm{O}2p_z\|\mathrm{O}2p_y)$	$(\mathrm{O}2p_z\|\mathrm{O}2p_z)$	$(\mathrm{O}2p_z\|\mathrm{H}_a1s)$	$(\mathrm{O}2p_z\|\mathrm{H}_b1s)$
$(\mathrm{H}_a1s\|$	$(\mathrm{H}_a1s\|\mathrm{O}1s)$	$(\mathrm{H}_a1s\|\mathrm{O}2s)$	$(\mathrm{H}_a1s\|\mathrm{O}2p_x)$	$(\mathrm{H}_a1s\|\mathrm{O}2p_y)$	$(\mathrm{H}_a1s\|\mathrm{O}2p_z)$	$(\mathrm{H}_a1s\|\mathrm{H}_a1s)$	$(\mathrm{H}_a1s\|\mathrm{H}_b1s)$
$(\mathrm{H}_b1s\|$	$(\mathrm{H}_b1s\|\mathrm{O}1s)$	$(\mathrm{H}_b1s\|\mathrm{O}2s)$	$(\mathrm{H}_b1s\|\mathrm{O}2p_x)$	$(\mathrm{H}_b1s\|\mathrm{O}2p_y)$	$(\mathrm{H}_b1s\|\mathrm{O}2p_z)$	$(\mathrm{H}_b1s\|\mathrm{H}_a1s)$	$(\mathrm{H}_b1s\|\mathrm{H}_b1s)$

Figure 4: The overlap integral matrix $\mathbf{S}$ for water showing explicitly every integral $(A|B)$ that must be evaluated.

An Aside on Minimal vs. Extended Basis Sets

This is a good time to mention the idea of a minimal basis set versus other kinds of basis sets. The *minimal basis set* corresponds most closely to the electron configurations we learn about in freshman chemistry. For example, while the electron configuration of a carbon atom is

$$1s^2\, 2s^2\, 2p^2\,, \tag{38}$$

our minimal basis configuration would consist of the set of all $1s$, $2s$ and $2p$ spatial orbitals making up carbon's shells:

$$1\mathrm{s}\, 2\mathrm{s}\, 2\mathrm{p}_x\, 2\mathrm{p}_y\, 2\mathrm{p}_z\,. \tag{39}$$

In other words we provide functions for *every* orbital of a shell that is occupied in the electron configuration. This means that the atomic orbital configuration of boron looks the same as it does for carbon (1s 2s $2\mathrm{p}_x$ $2\mathrm{p}_y$ $2\mathrm{p}_z$), in spite of having a different *electron* configuration. Even lithium has this orbital configuration, in spite of not having any $2p$ orbitals occupied in the ground state. Early investigators found that including terms for the complete shell, instead of just the occupied orbitals, gave more accurate results. Note that it is the basis set parameters d_p and α_p that differ between atoms, even though all second-row atoms have the same minimal basis *configuration* shown in Eq. 39.

	$\|\mathrm{O}1s)$	$\|\mathrm{O}2s)$	$\|\mathrm{O}2p_x)$	$\|\mathrm{O}2p_y)$	$\|\mathrm{O}2p_z)$	$\|\mathrm{H}_a1s)$	$\|\mathrm{H}_b1s)$
$(\mathrm{O}1s\|$	1.00000	0.23670	0.00000	0.00000	0.00000	0.05695	0.05695
$(\mathrm{O}2s\|$	0.23670	1.00000	0.00000	0.00000	0.00000	0.48979	0.48979
$(\mathrm{O}2p_x\|$	0.00000	0.00000	1.00000	0.00000	1.00000	0.00000	0.00000
$(\mathrm{O}2p_y\|$	0.00000	0.00000	0.00000	1.00000	0.00000	0.30738	-0.30738
$(\mathrm{O}2p_z\|$	0.00000	0.00000	0.00000	0.00000	1.00000	-0.25785	-0.25785
$(\mathrm{H}_a1s\|$	0.05695	0.48979	0.00000	0.30738	-0.25785	1.00000	0.28279
$(\mathrm{H}_b1s\|$	0.05695	0.48979	0.00000	-0.30738	-0.25785	0.28279	1.00000

```
3

O       0.00000     0.00000     0.22700
H       0.00000     1.35300    -0.90800
H       0.00000    -1.35300    -0.90800
```

Figure 5: The outcome of evaluating every element of the overlap integral matrix **S** in the minimal STO-3G basis, using Eq. 29 for each element, and the `.xyz` coordinates (units Bohr) shown below it.

Exercise.
Write the electron configurations and minimal basis sets of:

1. Lithium
2. Nitrogen
3. Oxygen
4. Chlorine
5. Vanadium
6. Krypton

Solution.

1. $1s^2 2s$; $1s\,2s\,2p_x\,2p_y\,2p_z$
2. $1s^2 2s^2 2p^3$; $1s\,2s\,2p_x\,2p_y\,2p_z$
3. $1s^2 2s^2 2p^4$; $1s\,2s\,2p_x\,2p_y\,2p_z$
4. $1s^2 2s^2 2p^6 3s^2 3p^5$; $1s\,2s\,2p_x\,2p_y\,2p_z\,3s\,3p_x\,3p_y\,3p_z$
5. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$; $1s\,2s\,2p_x\,2p_y\,2p_z\,3s\,3p_x\,3p_y\,3p_z\,4s\,3d_{z^2}\,3d_{xz}\,3d_{yz}\,3d_{xy}\,3d_{x^2-y^2}$
6. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$; $1s\,2s\,2p_x\,2p_y\,2p_z\,3s\,3p_x\,3p_y\,3p_z\,4s\,3d_{z^2}\,3d_{xz}\,3d_{yz}\,3d_{xy}\,3d_{x^2-y^2}\,4p_x 4p_y 4p_z$

[end of solution]

The other kind of basis set is the broadly defined *extended basis set*, which is any kind of basis set other than minimal. This includes *split-valence basis sets* like 3-21G. "Split valence" implies that core orbitals (closer to the nucleus) are treated with one contracted Gaussian-type function (CGTF), while valence orbitals are treated with more than one. The notation is telling: Core orbitals are represented by one CGTF that is a contraction of *three* primitives, while valence orbitals are represented by two CGTFs: one is a contraction of *two* primitives, and the other has just *one* primitive.

Unfortunately, when we discuss extended basis sets, we can no longer equate the term "orbital" with CGTF (though be warned that some writers do!). With the 3-21G basis set, the actual $2p_x$ orbital of the carbon atom, which is a valence orbital, is now described in terms of *two* CGTFs. Throughout this paper, however, and the programming project, we will be using a minimal basis set, so it *is* appropriate to use the

terms interchangeably – i.e., a CGTF is our direct mathematical representation of an orbital (see Eq. 2). During the early stages of coming to grips with molecular integrals it provides useful physical intuition to think of it this way. Nevertheless, it is important that the reader be aware that, for extended basis sets, it's no longer appropriate or meaningful to refer to CGTFs as orbitals.

Exercise.
In the 3-21G basis set, the hydrogen $1s$ orbital is considered a valence orbital, so it is treated with two CGTFs; the oxygen $1s$, by contrast, is treated with just one CGTF. What would be the dimensions of an overlap matrix for H_2O, represented by a 3-21G basis set? Note that the hydrogen $1s$ orbital is considered to be a valence orbital.

Solution.

- Two CGTFs for each hydrogen $1s$ orbital (considered a valence orbital)
- One CGTF for the oxygen $1s$ core orbital
- Two CGTFs for each $2s$, $2p_x$, $2p_y$, and $2p_z$ orbital

Thus, $2 + 2 + 1 + (2 \times 4) = 13$, producing a 13×13 matrix. See Fig. 6.
[end of solution]

	$\lvert O1s)$	$\lvert O2s')$	$\lvert O2p'_x)$	$\lvert O2p'_y)$	$\lvert O2p'_z)$	$\lvert O2s'')$	$\lvert O2p''_x)$	$\lvert O2p''_y)$	$\lvert O2p''_z)$	$\lvert H_a1s)$	$\lvert H_a1s')$	$\lvert H_b1s)$	$\lvert H_b1s')$
$(O1s\rvert$													
$(O2s'\rvert$													
$(O2p'_x\rvert$													
$(O2p'_y\rvert$													
$(O2p'_z\rvert$													
$(O2s''\rvert$													
$(O2p''_x\rvert$													
$(O2p''_y\rvert$													
$(O2p''_z\rvert$													
$(H_a1s\rvert$													
$(H_a1s'\rvert$													
$(H_b1s\rvert$													
$(H_b1s'\rvert$													

Figure 6: The basic structure of the water overlap integral matrix $\mathbf{S}$ in the 3-21G basis is a 13×13 matrix instead of 7×7 as in STO-3G. Valence orbitals are split into two distinct contracted Gaussian-type functions (CGTFs), each having their own set of matrix elements. Clearly, many more terms must be evaluated than for the matrix in the STO-3G basis, and so computation with a 3-21G basis set will take longer than those a STO-3G basis set.

2.2 Kinetic energy integrals

The general form of a kinetic energy matrix element is $(A|-\frac{1}{2}\nabla^2|B)$,

$$\sum_{a=1}^{K_a}\sum_{b=1}^{K_b} \mathrm{d}_a \mathrm{d}_b N_a N_b \int\int\int \chi_a(\vec{A},\alpha_a,l_A,m_A,n_A)\left[-\frac{1}{2}\nabla^2\chi_b(\vec{B},\alpha_b,l_B,m_B,n_B)\right]\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \tag{40}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \tag{41}$$

Exercise.
Show the effect of the x-component of ∇^2 acting on the primitive Gaussian χ_b, where

$$\chi_b = x^{l_B}y^{m_B}z^{n_B}e^{-\alpha_b r_B^2} = x^{l_B}y^{m_B}z^{n_B}e^{-\alpha_b(x_B^2+y_B^2+z_B^2)},$$

For now, disregard N, the normalization constant.

Solution.

$$\begin{aligned}
\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x}\chi_b\right) =& \frac{\partial}{\partial x}\left(l_B x^{(l_B-1)}y^{m_B}z^{n_B}e^{-\alpha_b r_B^2} - 2\alpha_b x^{(l_B+1)}y^{m_B}z^{n_B}e^{-\alpha_b r_B^2}\right)\\
=& \Big[(l_B-1)l_B x^{(l_B-2)}y^{m_B}z^{n_B} - x^{l_B}y^{m_B}z^{n_B}2\alpha_b\left(2l_B-2\alpha_b x^2+1\right)\Big]\mathrm{e}^{-\alpha_b r_B^2}\\
=& l_B(l_B-1)\chi_b(\vec{B},\alpha_b,l_B-2,m_B,n_B) - (4\alpha_b l_B+1)\chi_b(\vec{B},\alpha_b,l_B,m_B,n_B)\\
&+4\alpha_b^2\chi_b(\vec{B},\alpha_b,l_B+2,m_B,n_B)
\end{aligned} \tag{42}$$

[end of solution]

Exercise.
Multiply the result of Eq. 42 on the left by χ_a and integrate over $\mathrm{d}x$. Multiply the three integrations that are formed by $-\frac{1}{2}$. Do not attempt to solve the integrals.

Solution.

$$\begin{aligned}
\int \chi_a\left(-\frac{1}{2}\nabla^2\right)\chi_b\,\mathrm{d}x =& \alpha_b(2l_B+1)\int \chi_a(\vec{A},\alpha_a,l_A,m_A,n_A)\chi_b(\vec{B},\alpha_b,l_B,m_B,n_B)\,\mathrm{d}x\\
&-2\alpha_b^2\int \chi_a(\vec{A},\alpha_a,l_A,m_A,n_A)\chi_b(\vec{B},\alpha_b,l_B+2,m_B,n_B)\,\mathrm{d}x\\
&-\frac{1}{2}l_B(l_B-1)\int \chi_a(\vec{A},\alpha_a,l_A,m_A,n_A)\chi_b(\vec{B},\alpha_b,l_B-2,m_B,n_B)\,\mathrm{d}x
\end{aligned} \tag{43}$$

[end of solution]

Exercise.
Repeat the previous exercise for dimensions y and z. Add together the results (over dimensions x, y, and z) and collect terms by the three common coefficients

$$\left[2(l_B + m_B + n_B) + 3\right], \quad -2\alpha_b^2, \quad -\frac{1}{2}$$

Finally, lead this multiple integral (over dimensions x, y, and z) expression by the primitive "contraction"

$$\sum_{a=1}^{K_a}\sum_{b=1}^{K_b} \mathrm{d}_a \mathrm{d}_b N_a N_b$$

What do you notice about the result?

Solution.

Essential Equation

$$(A|-\frac{1}{2}\nabla^2|B) = \sum_{a=1}^{K_a}\sum_{b=1}^{K_b} \mathrm{d}_a \mathrm{d}_b N_a N_b \int\int\int \chi_a(\vec{A},\alpha_a,l_A,m_A,n_A)\Big\{\alpha_b\left[2(l_B+m_B+n_B)+3\right]\chi_b(\vec{B},\alpha_b,l_B,m_B,n_B) - 2\alpha_b^2\Big[\chi_b(\vec{B},\alpha_b,l_B+2,m_B,n_B)+\chi_b(\vec{B},\alpha_b,l_B,m_B+2,n_B)+\chi_b(\vec{B},\alpha_b,l_B,m_B,n_B+2)\Big] - \frac{1}{2}\Big[l_B(l_B-1)\chi_b(\vec{B},\alpha_b,l_B-2,m_B,n_B)+m_B(m_B-1)\chi_b(\vec{B},\alpha_b,l_B,m_B-2,n_B)+n_B(n_B-1)\chi_b(\vec{B},\alpha_b,l_B,m_B,n_B-2)\Big]\Big\} \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \tag{44}$$

The entire matrix element for kinetic energy, Eq. 44, is effectively just *a sum of seven different overlap integrals*, with coefficients. By coupling Eq. 44 with Eq. 29, you have a fully code-able expression for the kinetic energy integral matrix element!
[end of solution]

2.3 Electron-nuclear attraction integrals

The electron-nuclear attraction integral is our first of two potential energy integrals. But like the overlap and kinetic energy integrals we've already dealt with, the electron-nuclear attraction integrals are also two-center integrals (center of ϕ_A and center of ϕ_B). As the name implies, here we are dealing with the potential energy associated with the attraction of an electron to nuclei. The operator is $(\vec{r}_{iC})^{-1}$ where $\vec{r}_{iC} = \vec{r}_i - \vec{C}$, the distance between electron i and nucleus C. While we are only dealing with two centers, and hence form two-dimensional matrices, we must form n two-dimensional integrals, one for each nucleus (i.e., atom). Once each matrix is computed, we simply add up these matrices into one two-dimensional matrix $\mathbf{V}$:

$$\mathbf{V} = \sum_{C}^{n} \mathbf{V}_C = \mathbf{V}_1 + \mathbf{V}_2 + ...\mathbf{V}_n \tag{45}$$

The general form of a matrix element belonging to a matrix $\mathbf{V}_C$ is

$$\begin{aligned}(A|\frac{-Z_C}{\vec{r}_{iC}}|B) &= \int\int\int \phi_A \left(\frac{-Z_C}{\vec{r}_{iC}}\right) \phi_B \,\mathrm{d}V_i \\ &= \sum_{a=1}^{K_a}\sum_{b=1}^{K_b} \mathrm{d}_a \mathrm{d}_b N_a N_b \underbrace{\int\int\int \chi_a(\vec{A}, \alpha_a, l_A, m_A, n_A) \left(\frac{-Z_C}{\vec{r}_{iC}}\right) \chi_b(\vec{B}, \alpha_b, l_B, m_B, n_B) \,\mathrm{d}V_i}_{V}\end{aligned} \tag{46}$$

where we now contend with a third index, C. Z_C is a constant, the atomic number of atom C. The part of Eq. 46 needing to be solved is V, a multiple integral over Gaussian primitives χ_a and χ_b with the potential energy operator $(-Z_C/\vec{r}_{iC})$.

Spelling out V more explicitly,

$$V = \int_0^\infty \int_0^\infty \int_0^\infty x^{l_A} y^{m_A} z^{n_A} e^{-\alpha_a r_A^2} \left(\frac{-Z_C}{\vec{r}_{iC}}\right) x^{l_B} y^{m_B} z^{n_B} e^{-\alpha_b r_B^2} \mathrm{d}V_i \,, \tag{47}$$

$$\mathrm{d}V_i = \mathrm{d}x \,\mathrm{d}y \,\mathrm{d}z \,.$$

Rearranging by Cartesian coordinates,

$$V = \int_0^\infty \int_0^\infty \int_0^\infty x^{l_A} x^{l_B} y^{m_A} y^{m_B} z^{n_A} z^{n_B} e^{-\alpha_a r_A^2} e^{-\alpha_b r_B^2} \left(\frac{-Z_C}{\vec{r}_{iC}}\right) \mathrm{d}V_i \tag{48}$$

The Gaussian product theorem will now serve to reduce the number of centers in our problem from two ($\vec{A}$, $\vec{B}$) to one ($\vec{P}$), greatly simplifying the mathematics. We begin with the radial part.

Exercise.
Calculate the Gaussian product for the radial portion of primitives χ_a and χ_b (each contributing to ϕ_A and ϕ_B, respectively) where the radial portion of χ_a is

$$\exp\left(-\alpha_a r_A^2\right) ,$$

and the radial portion of χ_b has the same form by analogy. Substitute $\alpha_a + \alpha_b$ with γ.

Solution.

$$\begin{aligned}\exp\bigl(-\alpha_a r_A^2\bigr)\exp\bigl(-\alpha_b r_B^2\bigr) &= \exp\left(-\frac{\alpha_a\alpha_b}{\gamma}|\vec{AB}|^2\right)\exp\bigl(-\gamma r_P^2\bigr)\\ &= \widetilde{K}_P\exp\bigl(-\gamma r_P^2\bigr)\end{aligned} \tag{49}$$

$$\gamma = \alpha_a + \alpha_b, \quad \vec{AB} = \vec{A} - \vec{B}$$

$$\vec{P} = \frac{\alpha_a\vec{A} + \alpha_b\vec{B}}{\gamma}, \quad \vec{r}_P = \vec{r}_i - \vec{P}, \quad x_P = x_i - \vec{P}_x$$

Note that x_P is the x-component of $\vec{r}_P$, and that x_i is the x-component of $\vec{r}_i$. In most equations $\vec{r}_P$ is shown simply as r_P to reduce notational clutter.
[end of solution]

Now we subject the angular part of the integral to the Gaussian product theorem.

Exercise.
Calculate the x-component of the product of angular components of primitives χ_a and χ_b,

$$x^{l_A}x^{l_B}\,.$$

Do the same for the y and z components. Name the coefficients c_l, c_m, and c_n, respectively.

Solution. Following the example of Eqs. 13, 15, and 20,

$$\begin{aligned}x^{l_A}x^{l_B} &= \sum_{l=0}^{l_A+l_B} c_l(l_A,l_B,\vec{PA}_x,\vec{PB}_x)x_P^l\\ y^{m_A}y^{m_B} &= \sum_{m=0}^{m_A+m_B} c_m(m_A,m_B,\vec{PA}_y,\vec{PB}_y)y_P^n\\ z^{n_A}z^{n_B} &= \sum_{n=0}^{n_A+n_B} c_n(n_A,n_B,\vec{PA}_z,\vec{PB}_z)z_P^m.\end{aligned}$$

[end of solution]

Up to this point, then,

$$\begin{aligned}V = &-Z_C\cdot\widetilde{K}_P\\ &\times\sum_{l=0}^{l_A+l_B}\sum_{m=0}^{m_A+m_B}\sum_{n=0}^{n_A+n_B} c_l(l_A,l_B,\vec{PA}_x,\vec{PB}_x)c_m(m_A,m_B,\vec{PA}_y,\vec{PB}_y)c_n(n_A,n_B,\vec{PA}_z,\vec{PB}z)\\ &\times\underbrace{\int x_P^l y_P^m z_P^n\exp\bigl(-\gamma r_P^2\bigr)\left(\frac{1}{\vec{r}_{iC}}\right)\mathrm{d}V}_{V_{RI}}\end{aligned} \tag{50}$$

Z_C and $\tilde{K}_P$ have been pulled out front of the integral because they are numerical constants. The final term, the "remaining integral" we've termed V_{RI}, is the yet-unsolved piece, and it takes some work to resolve. The first step of resolving the operator has already been treated: the numerator, $-Z_C$, is the atomic number of atom C, and hence a constant that can be pulled out of the integral, as we have done.

The difficulty lies in the inverse character of the operator: How do we deal with an operator that is in the denominator? The answer is that we must transform the integral so that there is no longer a denominator

term. We begin by recasting $\vec{r}_{iC}$, which is the notation for distance between electron i and nucleus of atom C, in terms of a third center $\vec{P}$:

$$\vec{r}_{iC} = \vec{r}_i - \vec{C} = (\vec{r}_i - \vec{P}) + (\vec{P} - \vec{C}) = \vec{r}_P + \vec{PC}, \tag{51}$$

where $\vec{PC} = \vec{P} - \vec{C}$, the distance between atom C and the third center $\vec{P}$.

We will perform this integral transformation with a Fourier transform. For an inverse vector (such as our operator) this Fourier transform has the following general form.

Essential Equation

$$\frac{1}{\vec{r}} = \frac{1}{2\pi^2} \int \frac{1}{\vec{k}^2} \exp\Big(\mathrm{i}\vec{k} \cdot \vec{r}\Big) \mathrm{d}\vec{k} \tag{52}$$

The study of Fourier transforms is a deep one, but we focus on its essential purpose, which as employed here is clear: The transform serves to draw the distance vector out of the denominator, and make the expression more mathematically tractable by passing it into the numerator as part of an exponential function. Unfortunately, we must do so at the price of a *new* integral and with the introduction of the variable coordinates $\vec{k}$.

$\vec{r}_{iC}$, in the argument of an exponential function, must now be integrated over the "transformation" variable $\vec{k} = \vec{k}_x + \vec{k}_y + \vec{k}_z$. The vector $\vec{k}$ is a vector with Cartesian components, so that the differential volume element of the vector is $\mathrm{d}\vec{k} = \mathrm{d}\vec{k}_x\, \mathrm{d}\vec{k}_y\, \mathrm{d}\vec{k}_z$. Take note: the imaginary number i is *not* the same thing as the letter i, which has been used up to this point to represent an electron (and will also be used separately later as an index in summations, because there aren't enough indices to go around!).

Exercise.
Use the Fourier transform of Eq. 52 to transform the electron-nuclear attraction operator of Eq. 51.

Solution.

$$\begin{aligned}
\frac{1}{\vec{r}_{iC}} &= \frac{1}{2\pi^2} \int \frac{1}{\vec{k}^2} \exp\Big[\mathrm{i}\vec{k} \cdot (\vec{r}_{iC})\Big] \mathrm{d}\vec{k} \\
&= \frac{1}{2\pi^2} \int \frac{1}{\vec{k}^2} \exp\Big[\mathrm{i}\vec{k} \cdot (\vec{PC} + \vec{r}_P)\Big] \mathrm{d}\vec{k} \\
&= \frac{1}{2\pi^2} \int \frac{1}{\vec{k}^2} \exp\Big(\mathrm{i}\vec{k} \cdot \vec{PC}\Big) \exp\Big(\mathrm{i}\vec{k} \cdot \vec{r}_P\Big) \mathrm{d}\vec{k}
\end{aligned} \tag{53}$$

[end of solution]

Exercise.
Substitute the result of Eq. 53 into V_{RI}, the last line of Eq. 50. In turn, decompose the terms $\exp\Big(\mathrm{i}\vec{k} \cdot \vec{r}_P\Big)$ and $\exp\big(-\gamma r_P^2\big)$ into their Cartesian coordinates, i.e.,

$$\exp\Big(\mathrm{i}\vec{k} \cdot \vec{r}_P\Big) = \exp\Big(\mathrm{i}\vec{k}_x \cdot x_P\Big) \exp\Big(\mathrm{i}\vec{k}_x \cdot y_P\Big) \exp\Big(\mathrm{i}\vec{k}_x \cdot z_P\Big)$$

$$\exp\big(-\gamma r_P^2\big) = \exp\big(-\gamma x_P^2\big) \exp\big(-\gamma y_P^2\big) \exp\big(-\gamma z_P^2\big)$$

Leave $\exp\Big(\mathrm{i}\vec{k} \cdot \vec{PC}\Big)$ unchanged.

Finally, rearrange the expression for V_{RI} by Cartesian coordinates, and collect exponential functions containing the same Cartesian coordinate into one exponential function, while still leaving $\exp\Big(\mathrm{i}\vec{k}\cdot\vec{PC}\Big)$ as an independent term. For example,

$$\exp\big(-ax^2\big)\exp(bx) = \exp\big(-ax^2+bx\big)\,.$$

Solution.

$$\begin{aligned}
V_{RI} =& \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot\vec{PC}\Big)\exp\Big(\mathrm{i}\vec{k}\cdot\vec{r}_P\Big)\mathrm{d}\vec{k}\int x_P^l y_P^m z_P^n \exp\big(-\gamma r_P^2\big)\,\mathrm{d}V \\
=& \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot\vec{PC}\Big)\exp\Big(\mathrm{i}\vec{k}_x\cdot x_P\Big)\exp\Big(\mathrm{i}\vec{k}_x\cdot y_P\Big)\exp\Big(\mathrm{i}\vec{k}_x\cdot z_P\Big)\mathrm{d}\vec{k} \\
&\times\int x_P^l y_P^m z_P^n \exp\big(-\gamma x_P^2\big)\exp\big(-\gamma y_P^2\big)\exp\big(-\gamma z_P^2\big)\,\mathrm{d}V \\
=& \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot\vec{PC}\Big) \\
&\times\int x_P^l y_P^m z_P^n \exp\Big(-\gamma x_P^2+\mathrm{i}\vec{k}_x x_P\Big)\exp\Big(-\gamma y_P^2+\mathrm{i}\vec{k}_y y_P\Big)\exp\Big(-\gamma z_P^2+\mathrm{i}\vec{k}_z z_P\Big)\,\mathrm{d}V \\
=& \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot\vec{PC}\Big)\,\mathrm{d}\vec{k} \\
&\times \underbrace{\int x_P^l \exp\Big(-\gamma x_P^2+\mathrm{i}\vec{k}_x x_P\Big)\mathrm{d}x_P}_{V_l^x}\underbrace{\int y_P^m \exp\Big(-\gamma y_P^2+\mathrm{i}\vec{k}_y y_P\Big)\mathrm{d}y_P}_{V_m^y}\underbrace{\int z_P^n \exp\Big(-\gamma z_P^2+\mathrm{i}\vec{k}_z z_P\Big)\,\mathrm{d}z_P}_{V_n^z}
\end{aligned} \tag{54}$$

[end of solution]

We now have four integrals to solve: The terms V_l^x, V_m^y, and V_n^z are identical in form, distinguished by variable and coordinate. To solve these integrals, of the form

$$V_l^x = \int_{-\infty}^{\infty} x_P^l \exp\Big(-\gamma x_P^2 + i\vec{k}_x x_P\Big)\mathrm{d}x_P\,, \tag{55}$$

we once again look to a table of integrals.

Essential Equation

$$\int_{-\infty}^{\infty} t^n \exp\big(-at^2+\mathrm{i}bt\big)\,\mathrm{d}t = \mathrm{i}^n n!\left(\frac{\pi}{a}\right)^{1/2}\left(\frac{1}{2\sqrt{a}}\right)^n \exp\big(-c^2\big)\times\sum_{j=0}^{\lfloor n/2\rfloor}\frac{(-1)^j}{j!}\frac{(2c)^{n-2j}}{(n-2j)!} \tag{56}$$

$$c = \frac{b}{2\sqrt{a}}$$

Exercise.
Let $\epsilon = (4\gamma)^{-1}$, let r be the summation index (not to be confused with the distance vector), and find the solution to Eq. 55 by using Eq. 56.

At the end, make the substitution

$$\left(\frac{4\pi}{\epsilon}\right)^{1/2} \to \left(\frac{\pi}{\gamma}\right)^{1/2},$$

while leaving the other ϵ terms unchanged. This will prove useful later.

Solution.

$$V_l^x = \mathrm{i}^l l! \left(\frac{\pi}{\gamma}\right)^{1/2} \epsilon^{l/2} \exp\left(-\epsilon \vec{k}_x^2\right) \times \sum_{r=0}^{\lfloor l/2 \rfloor} \frac{(-1)^r (2\sqrt{\epsilon}\vec{k}_x)^{l-2r}}{r!(l-2r)!} \tag{57}$$

[end of solution]

Exercise.
Calculate the product $V_l^x \times V_m^y \times V_n^z$, and collect terms with powers of l, m, and n as much as possible. Then, collect the spatially decomposed exponential functions into one $\exp\left(-\epsilon\vec{k}^2\right)$ term.

Solution.

$$\begin{aligned} V_l^x \times V_m^y \times V_n^z =& \mathrm{i}^{(l+m+n)} \left(\frac{\pi}{\gamma}\right)^{3/2} l!m!n!\epsilon^{\left(\frac{l+m+n}{2}\right)} \\ & \times \sum_{r=0}^{\lfloor l/2 \rfloor} \sum_{s=0}^{\lfloor m/2 \rfloor} \sum_{t=0}^{\lfloor n/2 \rfloor} \frac{(-1)^{(r+s+t)} (2\sqrt{\epsilon})^{(l+m+n)-2(r+s+t)}}{r!s!t!(l-2r)!(m-2s)!(n-2t)!} \\ & \times \exp\left(-\epsilon\vec{k}^2\right) \vec{k}_x^{l-2r} \vec{k}_y^{m-2s} \vec{k}_z^{n-2t} \end{aligned} \tag{58}$$

The form of your solution may differ. Ensure that, with proper algebraic manipulation, your form and that presented here are equivalent.
[end of solution]

We have succeeded in resolving the three integrals of Eq. 54 (V_l^x, V_m^y, V_n^z) over spatial coordinates $\mathrm{d}x_P\,\mathrm{d}y_P\,\mathrm{d}z_P$, as seen by the first two lines of Eq. 58. We collect these sums of constants into their own terms C_{RI}, to separate it from the last line of Eq. 58, which is an integral we must still resolve.

Exercise.
If

$$\begin{aligned} C_{RI} =& C_{RI_x} C_{RI_y} C_{RI_z} \\ =& \mathrm{i}^{(l+m+n)} \left(\frac{\pi}{\gamma}\right)^{3/2} l!m!n!\epsilon^{\left(\frac{l+m+n}{2}\right)} \\ & \times \sum_{r=0}^{\lfloor l/2 \rfloor} \sum_{s=0}^{\lfloor m/2 \rfloor} \sum_{t=0}^{\lfloor n/2 \rfloor} \frac{(-1)^{(r+s+t)} (2\sqrt{\epsilon})^{(l+m+n)-2(r+s+t)}}{r!s!t!(l-2r)!(m-2s)!(n-2t)!}\,, \end{aligned} \tag{59}$$

which are the first two lines of Eq. 58, use Eq. 58 to convince yourself that

$$V_l^x \times V_m^y \times V_n^z = C_{RI} \times \exp\left(-\epsilon\vec{k}^2\right) \vec{k}_x^{l-2r} \vec{k}_y^{m-2s} \vec{k}_z^{n-2t}\,.$$

.

Solution.

$$\begin{aligned} V_l^x \times V_m^y \times V_n^z =& \mathrm{i}^{(l+m+n)} \left(\frac{\pi}{\gamma}\right)^{3/2} l!m!n!\epsilon^{\left(\frac{l+m+n}{2}\right)} \\ & \times \sum_{r=0}^{\lfloor l/2 \rfloor} \sum_{s=0}^{\lfloor m/2 \rfloor} \sum_{t=0}^{\lfloor n/2 \rfloor} \frac{(-1)^{(r+s+t)} (2\sqrt{\epsilon})^{(l+m+n)-2(r+s+t)}}{r!s!t!(l-2r)!(m-2s)!(n-2t)!} \\ & \times \exp\left(-\epsilon \vec{k}^2\right) \vec{k}_x^{l-2r} \vec{k}_y^{m-2s} \vec{k}_z^{n-2t} \\ =& C_{RI} \times \exp\left(-\epsilon \vec{k}^2\right) \vec{k}_x^{l-2r} \vec{k}_y^{m-2s} \vec{k}_z^{n-2t} \end{aligned} \tag{60}$$

[end of solution]

By inserting Eq. 60 (i.e., $V_l^x \times V_m^y \times V_n^z$) into the last line of Eq. 54, we have

$$\begin{aligned} V_{RI} =& \frac{1}{2\pi^2} \cdot C_{RI} \int \frac{1}{\vec{k}^2} \exp\left(i\vec{k} \times \vec{PC}\right) \left[\exp\left(-\epsilon \vec{k}^2\right) \vec{k}_x^{l-2r} \vec{k}_y^{m-2s} \vec{k}_z^{n-2t}\right] \mathrm{d}\vec{k} \\ =& \frac{C_{RI}}{2\pi^2} \cdot V'_{RI} \,, \end{aligned} \tag{61}$$

where we have given the name V'_{RI} to the integral over the transformation variable $\vec{k}$ still to be resolved.

In V'_{RI} of Eq. 61, we must address the problematic $\vec{k}^{-2}$ term, which when expanded is

$$\frac{1}{\vec{k}^2} = \frac{1}{\vec{k}_x^2 + \vec{k}_y^2 + \vec{k}_z^2} \,. \tag{62}$$

To treat $\vec{k}^{-2}$ we will take advantage of yet another identity, though in doing so must we must once again introduce another integral.

Essential Equation

$$\exp\left(-\epsilon \vec{k}^2\right) = 2\epsilon \vec{k}^2 \int_0^1 \frac{\mathrm{d}u}{u^3} \exp\left(-\epsilon \vec{k}^2 u^{-2}\right) \tag{63}$$

We refrained from decomposing $\exp\left(-\epsilon \vec{k}^2\right)$ in earlier steps in order to use this identity.

Exercise.
Substitute this identity (Eq. 63) into V'_{RI} (Eq. 61), and express the result in terms of four integrals: three integrals dedicated to each of the x, y, and z components of $\vec{k}$ (for *all* $\vec{k}$ terms, inside and outside of exponential functions), and one integral to the variable u. Then collect exponential functions with respect to each coordinate.

Solution.

$$\begin{aligned} V'_{RI} &= \int \frac{1}{\vec{k}^2} \exp\left(i\vec{k} \times \vec{PC}\right) \left[\exp\left(-\epsilon \vec{k}^2\right) \vec{k}_x^{l-2r} \vec{k}_y^{m-2s} \vec{k}_z^{n-2t}\right] \mathrm{d}\vec{k} \\ &= \int \frac{1}{\vec{k}^2} \exp\left(i\vec{k} \times \vec{PC}\right) \left\{ \left[2\epsilon \vec{k}^2 \int_0^1 \frac{\mathrm{d}u}{u^3} \exp\left(-\epsilon \vec{k}^2 u^{-2}\right)\right] \vec{k}_x^{l-2r} \vec{k}_y^{m-2s} \vec{k}_z^{n-2t} \right\} \mathrm{d}\vec{k} \end{aligned} \tag{64}$$

The $\vec{k}^2$ term in the denominator is cancelled by the $\vec{k}^2$ in the identity. In turn, decomposing all $\vec{k}$ terms into components, and then collecting terms by these components, gives

$$\begin{aligned} V'_{RI} = 2\epsilon &\int_0^1 \frac{\mathrm{d}u}{u^3} \\ &\times \int_{-\infty}^{\infty} k_x^{l-2r} \exp\Big(-\epsilon u^{-2}\vec{k}_x^2 + \mathrm{i}\vec{PC}_x\vec{k}_x\Big)\,\mathrm{d}\vec{k}_x \\ &\times \int_{-\infty}^{\infty} k_y^{m-2s} \exp\Big(-\epsilon u^{-2}\vec{k}_y^2 + \mathrm{i}\vec{PC}_y\vec{k}_y\Big)\,\mathrm{d}\vec{k}_y \\ &\times \int_{-\infty}^{\infty} k_z^{n-2t} \exp\Big(-\epsilon u^{-2}\vec{k}_z^2 + \mathrm{i}\vec{PC}_z\vec{k}_z\Big)\,\mathrm{d}\vec{k}_z\,. \end{aligned} \tag{65}$$

[end of solution]

Let us define I_{k_x} as one of the three integrals over $\mathrm{d}\vec{k}$ in Eq. 65, such that

$$I_{k_x} = \int_{-\infty}^{\infty} k_x^{l-2r} \exp\Big(-\epsilon u^{-2}\vec{k}_x^2 + \mathrm{i}\vec{PC}_x\vec{k}_x\Big)\,\mathrm{d}\vec{k}_x \tag{66}$$

$$\tag{67}$$

and

$$V'_{RI} = 2\epsilon \int_0^1 \frac{\mathrm{d}u}{u^3} \times I_{k_x} I_{k_y} I_{k_z}\,. \tag{68}$$

You should be able to see that I_{k_x} is of the same standard form that was used to evaluate the original "spatial" Cartesian factors (e.g., the integral over $\mathrm{d}x_P$ for V_l^x).

Exercise.
Show that, by applying Eq. 56 to I_{k_x} as expressed in Eq. 65, the solution to I_{k_x} is

$$\begin{aligned} I_{k_x} = &\mathrm{i}^{l-2r} \left(\frac{\pi}{\epsilon}\right)^{1/2} \left(\frac{1}{2}\right)^{l-2r} \left(\frac{1}{\sqrt{\epsilon}}\right)^{l-2r} \\ &\times \sum_{i=0}^{\lfloor (l-2r)/2 \rfloor} \epsilon^{(2r+2i-l)/2} \cdot \vec{PC}_x^{\,l-2r-2i} \frac{(-1)^i (l-2r)!}{i!(l-2r-2i)!} \\ &\times u \cdot u^{(l-2r)} \cdot u^{(l-2r-2i)} \exp\Big(-\gamma \vec{PC}_x^{\,2} \cdot u^2\Big) \end{aligned} \tag{69}$$

Note the distinction between the imaginary number i and the index i.

Solution.

$$
\begin{aligned}
I_{k_x} =& \int_{-\infty}^{\infty} k_x^{l-2r} \exp\Big(-\epsilon u^{-2}\vec{k}_x^2 + \mathrm{i}\vec{PC}_x\vec{k}_x\Big)\,\mathrm{d}\vec{k}_x \\
=& \mathrm{i}^{l-2r}(l-2r)!\left(\frac{\pi}{\epsilon u^{-2}}\right)^{1/2}\left(\frac{1}{2\sqrt{\epsilon u^{-2}}}\right)^{l-2r}\exp\left[-\left(\frac{\vec{PC}_x}{2\sqrt{\epsilon u^{-2}}}\right)^2\right] \\
& \times \sum_{i=0}^{\lfloor (l-2r)-2i\rfloor}\frac{(-1)^i}{i!}\left[\frac{\vec{PC}_x}{\sqrt{\epsilon u^{-2}}}\right]^{(l-2r)-2i} \times \frac{1}{[(l-2r)-2i]!} \\
=& \mathrm{i}^{l-2r}\cdot\left(\frac{\pi}{\epsilon}\right)^{1/2}\left(\frac{1}{2}\right)^{l-2r}\left(\frac{1}{\epsilon}\right)^{(l-2r)/2} \\
& \times \sum_{i=0}^{\lfloor (l-2r)/2\rfloor}\frac{(-1)^i}{i!}\left[\frac{\vec{PC}_x\cdot u}{\sqrt{\epsilon}}\right]^{l-2r-2i}\cdot\frac{(l-2r)!}{(l-2r-2i)!} \\
& \times u\cdot u^{l-2r}\cdot\exp\left[-\left(\frac{\vec{PC}_x\cdot u}{\sqrt{4\epsilon}}\right)^2\right] \\
=& \mathrm{i}^{l-2r}\left(\frac{\pi}{\epsilon}\right)^{1/2}\left(\frac{1}{2}\right)^{l-2r}\left(\frac{1}{\sqrt{\epsilon}}\right)^{l-2r} \\
& \times \sum_{i=0}^{\lfloor (l-2r)/2\rfloor}\overbrace{\epsilon^{(2r+2i-l)/2}}^{\epsilon^{-(l-2r-2i)/2}}\vec{PC}_x^{\,l-2r-2i}\frac{(-1)^i(l-2r)!}{i!(l-2r-2i)!} \\
& \times u\cdot u^{(l-2r)}\cdot u^{(l-2r-2i)}\exp\Big(-\gamma\vec{PC}_x^{\,2}\cdot u^2\Big)
\end{aligned}
$$

[end of solution]

The solutions to I_{k_y} and I_{k_z} hold by analogy to Eq. 69, with summation indices of j and k, respectively. It is noteworthy that in *each* I_k expression, there are a distinct set of terms that include u.

Exercise.
Extract all factors that include u from I_{k_x}, I_{k_y}, and I_{k_z}, and let I'_{k_x}, I'_{k_y}, and I'_{k_z} be the equations for I_{k_x}, I_{k_y}, and I_{k_z} without the u terms. For example,

$$
\begin{aligned}
I'_{k_x} =& \mathrm{i}^{l-2r}\left(\frac{\pi}{\epsilon}\right)^{1/2}\left(\frac{1}{2}\right)^{l-2r}\left(\frac{1}{\sqrt{\epsilon}}\right)^{l-2r} \\
& \times \sum_{i=0}^{\lfloor (l-2r)/2\rfloor}\epsilon^{(2r+2i-l)/2}\cdot\vec{PC}_x^{\,l-2r-2i}\frac{(-1)^i(l-2r)!}{i!(l-2r-2i)!}\,.
\end{aligned}
\tag{70}
$$

Include the u terms removed from I_k as further integrand to the integral

$$\int_0^1 \frac{\mathrm{d}u}{u^3},$$

which appears in V'_{RI} (Eq. 65). That is, fill in the bracketed part of

$$\int_0^1 u^{-3} \cdot [\text{additional } u \text{ terms}] \cdot \mathrm{d}u\,,$$

with the u terms that are removed from I_k. Simplify the resulting integral, but don't attempt to solve. Let ν equal the collection of powers outside of the exponential factors.

Solution.

$$\begin{aligned}\int_0^1 \frac{\mathrm{d}u}{u^3} \Big[& u \cdot u^{(l-2r)} \cdot u^{(l-2r-2i)} \exp\Big(-\gamma \vec{PC}_x^{\,2} \cdot u^2\Big) \\ & \times u \cdot u^{(m-2s)} \cdot u^{(m-2s-2j)} \exp\Big(-\gamma \vec{PC}_y^{\,2} \cdot u^2\Big) \\ & \times u \cdot u^{(n-2t)} \cdot u^{(n-2t-2k)} \exp\Big(-\gamma \vec{PC}_z^{\,2} \cdot u^2\Big)\Big] = \\ \int_0^1 \frac{\mathrm{d}u}{u^3} \cdot u^3 \cdot u^{2\nu} \cdot \exp\Big[-\gamma(\vec{PC}_x^{\,2} & + \vec{PC}_y^{\,2} + \vec{PC}_z^{\,2}) u^2\Big]\end{aligned}$$

Simplifying, this is

$$\int_0^1 u^{2\nu} \exp\Big(-\gamma |\vec{PC}|^2 \cdot u^2\Big) \mathrm{d}u\,, \tag{71}$$

where

$$\nu = l + m + n - 2(r + s + t) - (i + j + k)\,.$$

[end of solution]

At this point it is worth taking a step back and seeing where our considerable amount of work has taken us. Let us update our expression for V_{RI}, which you should remind yourself makes up part of V (Eq. 50). V_{RI} was last expressed in full in Eq. 61.

$$\begin{aligned} V_{RI} =& \frac{C_{RI}}{2\pi^2} \cdot V'_{RI} \\ =& \frac{C_{RI}}{2\pi^2} \cdot 2\epsilon \cdot I'_{k_x} I'_{k_y} I'_{k_z} \int_0^1 u^{2\nu} \exp\Big(-\gamma |\vec{PC}|^2 \cdot u^2\Big) \mathrm{d}u \\ =& \frac{\epsilon}{\pi^2} \cdot C_{RI_x} C_{RI_y} C_{RI_z} \cdot I'_{k_x} I'_{k_y} I'_{k_z} \int_0^1 u^{2\nu} \exp\Big(-\gamma |\vec{PC}|^2 \cdot u^2\Big) \mathrm{d}u \end{aligned} \tag{72}$$

We will address the integral over $\mathrm{d}u$ momentarily. First, recall that C_{RI} and I'_k are simply collections of constants, without any variables, so it would be useful to simplify these constants as much as possible by combining them.

Exercise.
It can be seen from Eq. 59 that

$$C_{RI} = C_{RI_x} C_{RI_y} C_{RI_z} \tag{73}$$

such that

$$C_{RI_x} = \mathrm{i}^l \left(\frac{\pi}{\gamma}\right)^{1/2} \epsilon^{l/2} \sum_{r=0}^{l/2} \frac{(-1)^r (2\sqrt{\epsilon})^{l-2r}}{r!(l-2r!)} \,. \tag{74}$$

Using Eqs. 70 and 74, show that

$$C_{RI_x} \times I'_{k_x} = \left(\frac{\pi}{\gamma}\right)^{1/2} \left(\frac{\pi}{\epsilon}\right)^{1/2} \sum_{r=0}^{l/2} \sum_{i=0}^{\lfloor (l-2r)/2 \rfloor} \mathrm{i}^{2(l-r)} (-1)^r \frac{l!(-1)^i \vec{PC}_x^{\,l-2r-2i}}{i!(l-2r-2i)!} \,. \tag{75}$$

Solution.

$$\begin{aligned}
C_{RI_x} \times I'_{k_x} =& \mathrm{i}^l \left(\frac{\pi}{\gamma}\right)^{1/2} \epsilon^{l/2} \sum_{r=0}^{l/2} \frac{(-1)^r (2\sqrt{\epsilon})^{l-2r}}{r!(l-2r!)} \\
&\times \mathrm{i}^{l-2r} \left(\frac{\pi}{\epsilon}\right)^{1/2} \left(\frac{1}{2}\right)^{l-2r} \left(\frac{1}{\sqrt{\epsilon}}\right)^{l-2r} \\
&\times \sum_{i=0}^{\lfloor (l-2r)/2 \rfloor} \epsilon^{(2r+2i-l)/2} \cdot \vec{PC}_x^{\,l-2r-2i} \frac{(-1)^i (l-2r)!}{i!(l-2r-2i)!} \\
=& \left(\frac{\pi}{\gamma}\right)^{1/2} \left(\frac{\pi}{\epsilon}\right)^{1/2} \sum_{r=0}^{l/2} \sum_{i=0}^{\lfloor (l-2r)/2 \rfloor} \mathrm{i}^l \mathrm{i}^{l-2r} (-1)^r \\
&\times \sqrt{\epsilon}^{l-2r} \times \left(\frac{1}{\sqrt{\epsilon}}\right)^{l-2r} 2^{l-2r} \left(\frac{1}{2}\right)^{l-2r} \\
&\times \epsilon^{l/2} \epsilon^{(2r+2i-l)/2} \frac{(-1)^i \vec{PC}_x^{\,l-2r-2i} (l-2r)!}{i!(l-2r-2i)!(l-2r)!} \\
=& \left(\frac{\pi}{\gamma}\right)^{1/2} \left(\frac{\pi}{\epsilon}\right)^{1/2} \sum_{r=0}^{l/2} \sum_{i=0}^{\lfloor (l-2r)/2 \rfloor} \mathrm{i}^{2(l-r)} (-1)^r \frac{l!(-1)^i \vec{PC}_x^{\,l-2r-2i}}{i!(l-2r-2i)!}
\end{aligned}$$

[end of solution]

Exercise.
Construct the analogous y- and z-component products of C_{RI} and I'_k. Then, show that to resolve all but the integral over du in Eq. 72, we take the product $(\epsilon/\pi^2) \times C_{RI} \times I'_k$, as follows:

$$\begin{aligned}
\frac{\epsilon}{\pi^2} \times C_{RI_x} C_{RI_y} C_{RI_z} \times I'_{k_x} I'_{k_y} I'_{k_z} =& \frac{2\pi}{\gamma} \sum_{r=0}^{\lfloor l/2 \rfloor} \sum_{i=0}^{\lfloor (l-2r)/2 \rfloor} \frac{(-1)^l (-1)^i l! \vec{PC}_x^{\,l-2r-2i}}{i!(l-2r-2i)!} \\
&\times \sum_{s=0}^{\lfloor m/2 \rfloor} \sum_{i=0}^{\lfloor (m-2s)/2 \rfloor} \frac{(-1)^m (-1)^j l! \vec{PC}_y^{\,m-2s-2j}}{j!(m-2s-2j)!} \\
&\times \sum_{t=0}^{\lfloor n/2 \rfloor} \sum_{i=0}^{\lfloor (n-2t)/2 \rfloor} \frac{(-1)^n (-1)^k l! \vec{PC}_z^{\,n-2t-2k}}{k!(n-2t-2k)!} .
\end{aligned} \tag{76}$$

Solution.

$$
\begin{aligned}
\frac{\epsilon}{\pi^2}\times C_{RI_x}C_{RI_y}C_{RI_z}\times I'_{k_x}I'_{k_y}I'_{k_z} =& \frac{\epsilon}{\pi^2}\times\left[\left(\frac{\pi}{\gamma}\right)^{1/2}\left(\frac{\pi}{\epsilon}\right)^{1/2}\sum_{r=0}^{\lfloor l/2\rfloor}\sum_{i=0}^{\lfloor (l-2r)/2\rfloor}\mathrm{i}^{2(l-r)}(-1)^r\frac{l!(-1)^i\vec{PC}_x^{\,l-2r-2i}}{i!(l-2r-2i)!}\right]\\
&\times\left[\left(\frac{\pi}{\gamma}\right)^{1/2}\left(\frac{\pi}{\epsilon}\right)^{1/2}\sum_{s=0}^{\lfloor m/2\rfloor}\sum_{j=0}^{\lfloor (m-2s)/2\rfloor}\mathrm{i}^{2(m-s)}(-1)^s\frac{m!(-1)^j\vec{PC}_y^{\,m-2s-2j}}{j!(m-2s-2j)!}\right]\\
&\times\left[\left(\frac{\pi}{\gamma}\right)^{1/2}\left(\frac{\pi}{\epsilon}\right)^{1/2}\sum_{t=0}^{\lfloor n/2\rfloor}\sum_{k=0}^{\lfloor (n-2t)/2\rfloor}\mathrm{i}^{2(n-t)}(-1)^t\frac{n!(-1)^k\vec{PC}_z^{\,n-2t-2k}}{k!(n-2t-2k)!}\right]\\
=&\frac{\epsilon}{\pi^2}\left(\frac{\pi}{\gamma}\right)^{3/2}\left(\frac{\pi}{\epsilon}\right)^{3/2}\\
&\times\sum_{r=0}^{\lfloor l/2\rfloor}\sum_{s=0}^{\lfloor m/2\rfloor}\sum_{t=0}^{\lfloor n/2\rfloor}\overbrace{\mathrm{i}^{2(l+m+n-r-s-t)}}^{(-1)^{l+m+n-(r+s+t)}}(-1)^{r+s+t}l!m!n!\\
&\times\sum_{i=0}^{\lfloor (l-2r)/2\rfloor}\sum_{j=0}^{\lfloor (m-2s)/2\rfloor}\sum_{k=0}^{\lfloor (n-2t)/2\rfloor}\frac{(-1)^{i+j+k}\vec{PC}_x^{\,l-2r-2i}\vec{PC}_y^{\,m-2s-2j}\vec{PC}_z^{\,n-2t-2k}}{i!j!k!(l-2r-2i)!(m-2s-2j)!(n-2t-2k)!}\\
=&\frac{1}{4\gamma}\cdot\frac{\pi^3}{\pi^2}\left(\frac{4\gamma}{\gamma}\right)^{3/2}\\
&\times\sum_{r=0}^{\lfloor l/2\rfloor}\sum_{s=0}^{\lfloor m/2\rfloor}\sum_{t=0}^{\lfloor n/2\rfloor}(-1)^{l+m+n}l!m!n!\\
&\times\sum_{i=0}^{\lfloor (l-2r)/2\rfloor}\sum_{j=0}^{\lfloor (m-2s)/2\rfloor}\sum_{k=0}^{\lfloor (n-2t)/2\rfloor}\frac{(-1)^{i+j+k}\vec{PC}_x^{\,l-2r-2i}\vec{PC}_y^{\,m-2s-2j}\vec{PC}_z^{\,n-2t-2k}}{i!j!k!(l-2r-2i)!(m-2s-2j)!(n-2t-2k)!}\\
=&\frac{2\pi}{\gamma}\sum_{r=0}^{\lfloor l/2\rfloor}\sum_{i=0}^{\lfloor (l-2r)/2\rfloor}\frac{(-1)^l(-1)^i l!\vec{PC}_x^{\,l-2r-2i}}{i!(l-2r-2i)!}\\
&\times\sum_{s=0}^{\lfloor m/2\rfloor}\sum_{i=0}^{\lfloor (m-2s)/2\rfloor}\frac{(-1)^m(-1)^j l!\vec{PC}_y^{\,m-2s-2j}}{j!(m-2s-2j)!}\\
&\times\sum_{t=0}^{\lfloor n/2\rfloor}\sum_{i=0}^{\lfloor (n-2t)/2\rfloor}\frac{(-1)^n(-1)^k l!\vec{PC}_z^{\,n-2t-2k}}{k!(n-2t-2k)!}.
\end{aligned}
$$

[end of solution]

Looking to our original expression for V, Eq. 50, we can substitute in V_{RI} (Eq. 72) using the solution

over the constant terms from Eq. 76.

$$
\begin{aligned}
V = & - Z_C \cdot \widetilde{K}_P \\
& \times \sum_{l=0}^{l_A+l_B} \sum_{m=0}^{m_A+m_B} \sum_{n=0}^{n_A+n_B} c_l(l_A, l_B, \vec{PA}_x, \vec{PB}_x) c_m(m_A, m_B, \vec{PA}_y, \vec{PB}_y) c_n(n_A, n_B, \vec{PA}_z, \vec{PB}z) \\
& \times \underbrace{\int x_P^l y_P^m z_P^n \exp\left(-\gamma r_P^2\right) \left(\frac{1}{\vec{r}_{iC}}\right) \mathrm{d}V}_{V_{RI}} \\
= & - Z_C \times \frac{2\pi}{\gamma} \times \widetilde{K}_P \\
& \times \sum_{l=0}^{l_A+l_B} \sum_{r=0}^{\lfloor l/2 \rfloor} \sum_{i=0}^{\lfloor (l-2r)/2 \rfloor} (-1)^l c_l(l_A, l_B, \vec{PA}_x, \vec{PB}_x) \frac{(-1)^i l! \vec{PC}_x^{\,l-2r-2i}}{i!(l-2r-2i)!} \\
& \times \sum_{m=0}^{m_A+m_B} \sum_{s=0}^{\lfloor m/2 \rfloor} \sum_{j=0}^{\lfloor (m-2s)/2 \rfloor} (-1)^m c_m(m_A, m_B, \vec{PA}_y, \vec{PB}_y) \frac{(-1)^j l! \vec{PC}_y^{\,m-2s-2j}}{j!(m-2s-2j)!} \\
& \times \sum_{n=0}^{n_A+n_B} \sum_{t=0}^{\lfloor n/2 \rfloor} \sum_{k=0}^{\lfloor (n-2t)/2 \rfloor} (-1)^n c_n(n_A, n_B, \vec{PA}_z, \vec{PB}_z) \frac{(-1)^k l! \vec{PC}_z^{\,n-2t-2k}}{k!(n-2t-2k)!} \\
& \times \int_0^1 u^{2\nu} \exp\Big(-\gamma |\vec{PC}|^2 \cdot u^2\Big) \mathrm{d}u
\end{aligned}
\tag{77}
$$

And yet there is *still* an integral! It would seem we are spinning our wheels.

However, this last integral has added significance: It is the Boys function, $F_\nu(t)$.

$$
F_\nu(t) = \int_0^1 t^{2\nu} \exp\big(-xt^2\big) \mathrm{d}t \tag{78}
$$

In fact, the Boys function cannot be analytically solved. We can go no further, and numerical approximations of F_ν are unavoidable in our solutions. For this reason, considerable research has gone into generating good numerical solutions to this essential function, and several have been developed. The one we will implement in Python code (Handout 4) depends on gamma functions.

Exercise.
The solution to the Boys function we will implement in Python depends on the incomplete gamma function $\gamma(\nu + \frac{1}{2}, x)$, which is not to be confused with our *variable* $\gamma = \alpha_a + \alpha_b$. Specifically,

$$
F_\nu(t) = \int_0^1 t^{2\nu} \exp\big(-xt^2\big) \mathrm{d}t = \frac{1}{2x^{(\nu+\frac{1}{2})}} \int_0^x y^{\nu-1/2} \mathrm{e}^{-y} \, \mathrm{d}y = \frac{1}{2x^{(\nu+\frac{1}{2})}} \times \gamma(\nu + \frac{1}{2}, x) \,. \tag{79}
$$

The final two equalities can be found in handbooks of mathematical functions, such as by Abramowitz and Stegun.

Use substitution to show how the Boys Function can be rewritten as the integral that is related to the incomplete gamma function. That is, show that

$$
\int_0^1 t^{2\nu} \exp\big(-xt^2\big) \mathrm{d}t = \frac{1}{2x^{(\nu+\frac{1}{2})}} \int_0^x y^{\nu-1/2} \mathrm{e}^{-y} \, \mathrm{d}y \,.
$$

(Hint: Let $y = xt^2$.)

Solution.
To begin with,

$$y = xt^2 \implies t = \frac{\sqrt{y}}{\sqrt{x}} = y^{1/2} \cdot x^{-1/2}$$

Thus,

$$\mathrm{d}y = 2xt\,\mathrm{d}t = 2xy^{1/2}x^{-1/2}\mathrm{d}t = 2x^{1/2}y^{1/2}\mathrm{d}t\,.$$

Rearranging,

$$\mathrm{d}t = \frac{1}{2} \cdot x^{-1/2}y^{-1/2}\,\mathrm{d}y\,. \tag{80}$$

Clearly, because $y = xt^2$, then for the exponential function

$$\mathrm{e}^{-xt^2} = \mathrm{e}^{-y}\,. \tag{81}$$

Next, based on our definition of t,

$$t^{2\nu} = \left(\frac{y}{x}\right)^{\nu} = y^{\nu}x^{-\nu}\,. \tag{82}$$

Changing the integration bounds from t to y:

$$\int_{t=\sqrt{y/x}=0 \implies y=0}^{t=\sqrt{y/x}=1 \implies y=x} \implies \int_0^x\,. \tag{83}$$

Piecing together each of these substitutions (Eqs. 80 – 83) into a complete integral gives

$$\int_0^1 t^{2\nu}\mathrm{e}^{-xt^2}\mathrm{d}t = \frac{1}{2x^{(\nu+\frac{1}{2})}}\int_0^x y^{\nu-1/2}\mathrm{e}^{-y}\,\mathrm{d}y$$

as we set out to show.
[end of solution]

Now that we have a means of evaluating the Boys function (using the gamma function, which is featured in Python), we have derived a completed solution to Eq. 50, and can couple Eq. 77 with 79. For tidiness of Eq. 77, we define

Essential Equation

$$v_{l,r,i}(l_A, l_B, \vec{A}_x, \vec{B}_x, \vec{C}_x, \gamma) = (-1)^l c_l(l_A, l_B, \vec{PA}_x\vec{PB}_x)\frac{(-1)^i l!\vec{PC}_x^{\,l-2r-2i}\epsilon^{r+i}}{r!i!(l-2r-2i)!} \tag{84}$$

with analogous expressions for $v_{m,s,j}$ and $v_{n,t,k}$, such that

Essential Equation

$$
\begin{aligned}
V = & -Z_C \times \frac{2\pi}{\gamma} \times \exp\left(-\frac{\alpha_a \alpha_b}{\gamma}|\vec{AB}|^2\right) \\
& \times \sum_{l=0}^{l_A+l_B} \sum_{r=0}^{\lfloor l/2 \rfloor} \sum_{i=0}^{\lfloor (l-2r)/2 \rfloor} v_{l,r,i}(l_A, l_B, \vec{A}_x, \vec{B}_x, \vec{C}_x, \gamma) \\
& \times \sum_{m=0}^{m_A+m_B} \sum_{s=0}^{\lfloor m/2 \rfloor} \sum_{j=0}^{\lfloor (m-2s)/2 \rfloor} v_{m,s,j}(m_A, m_B, \vec{A}_y, \vec{B}_y, \vec{C}_y, \gamma) \\
& \times \sum_{n=0}^{n_A+n_B} \sum_{t=0}^{\lfloor n/2 \rfloor} \sum_{k=0}^{\lfloor (n-2t)/2 \rfloor} v_{n,t,k}(n_A, n_B, \vec{A}_z, \vec{B}_z, \vec{C}_z, \gamma) \\
& \times F_{l+m+n-2(r+s+t)-(i+j+k)}(\gamma|\vec{PC}|^2)
\end{aligned}
\tag{85}
$$

and the complete matrix element, first shown in Eq. 50, can be evaluated as

Essential Equation

$$
(A|\frac{-Z_C}{\vec{r}_{iC}}|B) = \sum_{a=1}^{K_\alpha} \sum_{b=1}^{K_\beta} \mathrm{d}_a \mathrm{d}_b N_a N_b \times V \tag{86}
$$

2.4 Electron-electron repulsion integrals

The final operator in the Hamiltonian ($1/\vec{r}_{ij}$) corresponds to potential energy, as did electron-nuclear attraction ($1/\vec{r}_{iC}$). Now, rather than an operator describing the electrostatic attraction (potential energy) between one electron i and the nucleus of an atom C, this final operator describes the electrostatic repulsion (potential energy) between two electrons i and j. In the electron-nuclear attraction integrals, we had three spatial coordinates to integrate over: x, y, and z. The present electron repulsion integrals (ERI), as they are sometimes called, necessitate six spatial coordinates to integrate over: the x, y, and z coordinates of electron i, and the x, y, and z coordinates of electron j.

Just as describing the overlap or kinetic energy of one electron was predicated on two orbitals (for orbitals are the "space" that electrons occupy), it follows that the description of two electrons depends on four orbitals: one electron i in orbitals ϕ_A and ϕ_B, and one electron j in orbitals ϕ_C and ϕ_D.

Because the electron-electron repulsion operator is a potential operator like the electron-nuclear attraction operator, deriving the analytical form of the expectation value using atomic, Gaussian basis functions is very similar. The techniques employed in the previous section to derive the analytical solution to the electron-nuclear attraction integral are the only ones necessary to derive the analytical solution to the electron-electron repulsion integral. As you might expect, it just happens to involve about twice as much manipulation.

The idea of a rank-4 tensor may initially seem a little abstract, but at least for our purposes it can simply be thought of as a generalization of a matrix. Where **S**, **T**, and **V** matrices are $K \times K$ in dimension, electron-electron repulsion integral matrices **G** are $K \times K \times K \times K$ in dimension. As a simple example, Fig. 7 shows the form of the $2 \times 2 \times 2 \times 2$ tensor of electron-electron repulsion for the dihydrogen molecule, which has $K = 2$ atomic orbitals; evaluation of each integral shown on the left-hand side of the equivalence sign yields the Hartree energy values shown on the right-hand side.

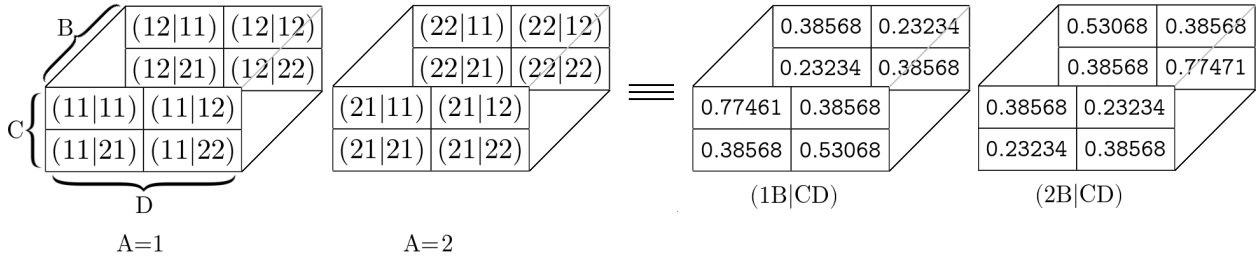

Figure 7: The $2 \times 2 \times 2 \times 2$ four-dimensional structure of the electron-electron repulsion tensor for the hydrogen molecule in the STO-3G basis, corresponding to the four indices of $(AB|CD)$. The results are based on a geometry where the interatomic distance is 1.6 a_0; the input `.xyz` file is available in SI 6.

A more complex example is the water molecule, which has $K = 7$ atomic orbitals in its basis; the general form of its electron repulsion tensor is shown in Fig. 8.

Now consider the general form of a tensor *element* $(AB|CD)$, which we will refer to as a matrix element of **G**:

$$\begin{aligned}(AB|CD) &= \int\int \phi_A(\vec{A},\alpha_a,l_A,m_A,n_A)(\vec{r}_{Ai})\,\phi_B(\vec{B},\alpha_b,l_B,m_B,n_B)(\vec{r}_{Bi}) \\ &\quad\times \frac{1}{\vec{r}_{ij}}\,\phi_C(\vec{C},\alpha_c,l_C,m_C,n_C)(\vec{r}_{Cj})\,\phi_D(\vec{D},\alpha_d,l_D,m_D,n_D)(\vec{r}_{Dj})\,\mathrm{d}V_i\,\mathrm{d}V_j \\ &= \sum_{a=1}^{K_a}\sum_{b=1}^{K_b}\sum_{c=1}^{K_c}\sum_{d=1}^{K_d} \mathrm{d}_a\mathrm{d}_b\mathrm{d}_c\mathrm{d}_d N_a N_b N_c N_d \times \underbrace{\int\int \chi_a\chi_b\left(\frac{1}{\vec{r}_{ij}}\right)\chi_c\chi_d\,\mathrm{d}V_i\,\mathrm{d}V_j}_{G}\,.\end{aligned} \tag{87}$$

Every "box" of this four-dimensional matrix must include the contraction coefficients and normalization constants for primitives within the four orbitals (or CGTFs) ϕ_A, ϕ_B, ϕ_C, and ϕ_D; recall that there are three primitives per orbital in the case of STO-3G. As before, we have identified the integral over individual primitives that needs to be analytically resolved, which we call G. By expanding the expression for G in

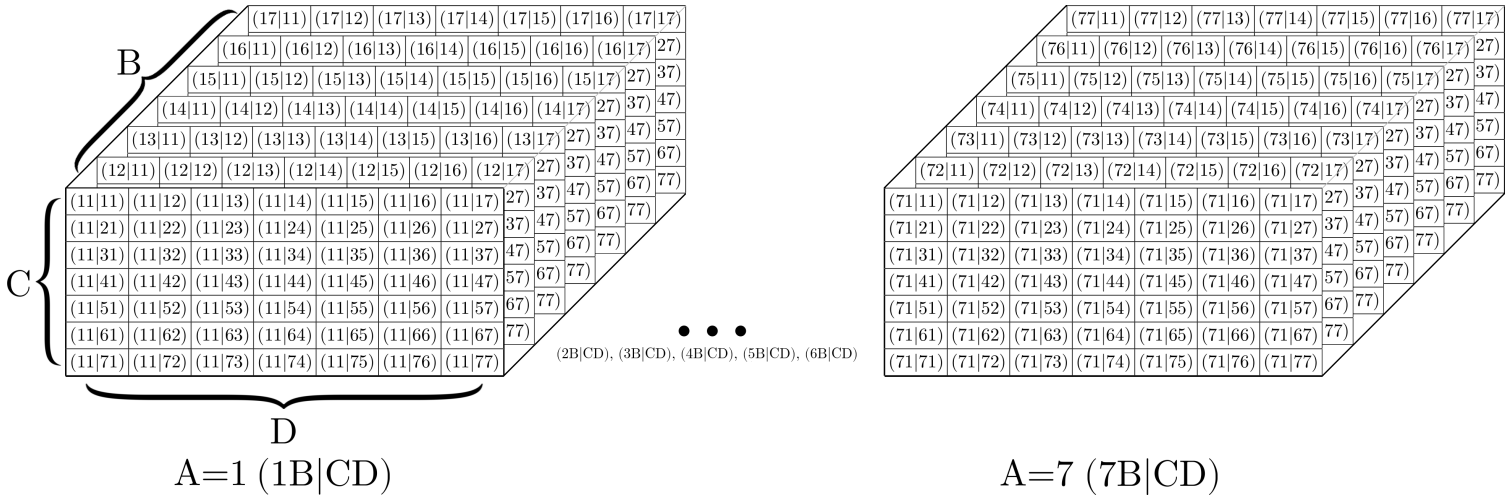

Figure 8: The $7 \times 7 \times 7 \times 7$ four-dimensional structure of the electron repulsion tensor for the water molecule in the minimal basis, corresponding to the four indices of $(AB|CD)$. As this image reveals, the presence of a greater number of orbitals leads rapidly to the the growth and complexity of the tensor.

terms of functional dependencies, we see that there is some new notation to consider.

$$\begin{aligned} G = \int \int \chi_a(\vec{A}, \alpha_a, l_A, m_a, n_A)(\vec{r}_{Ai})\chi_b(\vec{B}, \alpha_b, l_B, m_B, n_B)(\vec{r}_{Bi}) \\ \times \left(\frac{1}{\vec{r}_{ij}}\right) \chi_c(\vec{C}, \alpha_c, l_C, m_C, n_C)(\vec{r}_{Cj})\chi_d(\vec{D}, \alpha_d, l_D, m_D, n_D)(\vec{r}_{Dj})\, \mathrm{d}V_i\, \mathrm{d}V_j \end{aligned} \tag{88}$$

$$\vec{r}_{Ai} = \vec{r}_i - \vec{A},\ \vec{r}_{Bi} = \vec{r}_i - \vec{B},\ \vec{r}_{Cj} = \vec{r}_j - \vec{C},\ \vec{r}_{Dj} = \vec{r}_j - \vec{D},\ \vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$$

Thus, $\vec{r}_{Ai}$ is the distance between the coordinates of electron i (denoted $\vec{r}_i$) and the coordinates $\vec{A}$ corresponding to the center of the atom-centered orbital ϕ_A. A more explicit expression of what we need to solve is

$$\begin{aligned} G = \int_0^\infty \int_0^\infty x_{Ai}^{l_A} y_{Ai}^{m_A} z_{Ai}^{n_A} e^{-\alpha_a r_{Ai}^2} x_{Bi}^{l_B} y_{Bi}^{m_B} z_{Bi}^{n_B} e^{-\alpha_b r_{Bi}^2} \\ \times \left(\frac{1}{\vec{r}_{ij}}\right) x_{Cj}^{l_C} y_{Cj}^{m_C} z_{Cj}^{n_C} e^{-\alpha_c r_{Cj}^2} x_{Dj}^{l_D} y_{Dj}^{m_D} z_{Dj}^{n_D} e^{-\alpha_d r_{Dj}^2}\, , \mathrm{d}V_i\, , \mathrm{d}V_j\, , \end{aligned} \tag{89}$$

$$\begin{aligned} \mathrm{d}V_i &= \mathrm{d}x_i\, \mathrm{d}y_i\, \mathrm{d}z_i \\ \mathrm{d}V_j &= \mathrm{d}x_j\, \mathrm{d}y_j\, \mathrm{d}z_j \end{aligned}$$

where vector notation on $\vec{r}$ has been removed in the exponential function arguments for clarity. Study this expression carefully to ensure that you are aware of all that we are contending with as we move forward in the derivation. Note that x_i is notation for the x-component of $\vec{r}_i$; and so on. As before, $r^2 = x^2 + y^2 + z^2$, and so you should be able to see how exponential functions can be separated based on their Cartesian coordinates.

Dropping the subscripts of the angular terms $x_{Ai}^{l_A}$, *etc.*, let us rearrange Eq. 89 in terms of spatial coordinates, because this will form an important part of how we solve the problem.

$$\begin{aligned} G = \int_0^\infty x^{l_A} x^{l_B} e^{-(\alpha_a+\alpha_b)x_i^2} \mathrm{d}x_i \int_0^\infty y^{m_A} y^{m_B} e^{-(\alpha_a+\alpha_b)y_i^2} \mathrm{d}y_i \int_0^\infty z^{n_A} z^{n_B} e^{-(\alpha_a+\alpha_b)z_i^2} \mathrm{d}z_i \\ \times \left(\frac{1}{\vec{r}_{ij}}\right) \int_0^\infty x^{l_C} x^{l_D} e^{-(\alpha_c+\alpha_d)x_j^2} \mathrm{d}x_j \int_0^\infty y^{m_C} y^{m_D} e^{-(\alpha_c+\alpha_d)y_j^2} \mathrm{d}y_j \int_0^\infty z^{n_C} z^{n_D} e^{-(\alpha_c+\alpha_d)z_j^2} \mathrm{d}z_j \end{aligned} \tag{90}$$

The Gaussian product theorem is once again the gateway to simplification. We can reduce the four centers ($\vec{A}$, $\vec{B}$, $\vec{C}$, $\vec{D}$) to just two, by considering two products of orbitals, $\phi_A\phi_B$, and $\phi_C\phi_D$ – each of which

provides the "space" for electrons i and j, respectively, to occupy. These four centers are reduced to two, $\vec{P}$ and $\vec{Q}$. Thus, information about electron i will ultimately be described in terms of center $\vec{P}$, and information about electron j will be described in terms of center $\vec{Q}$. (See Fig. 9.)

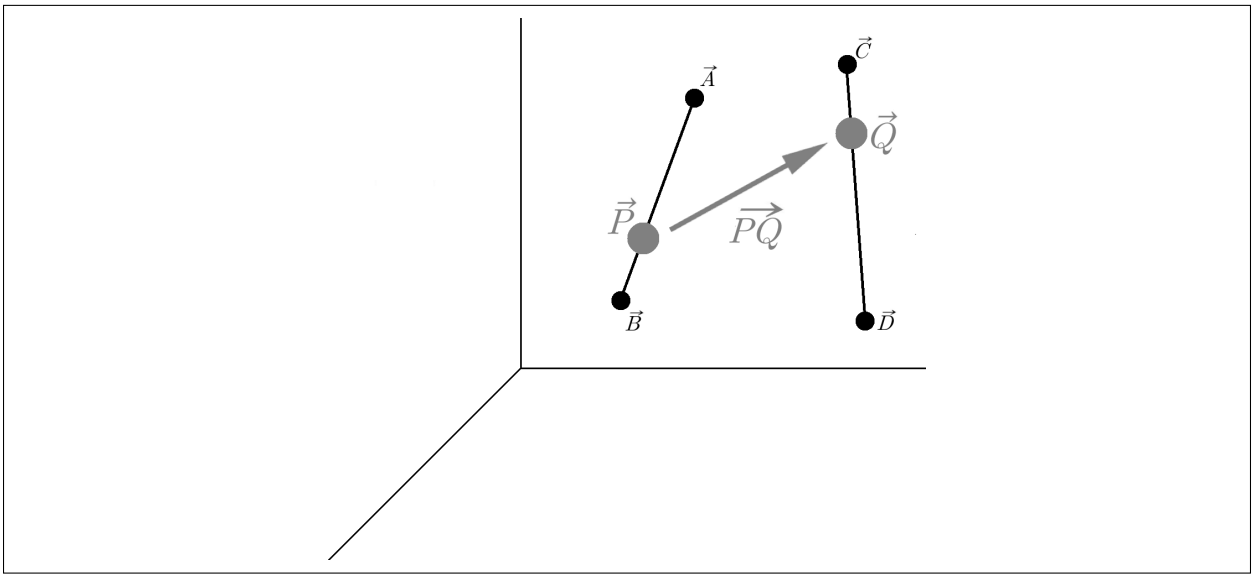

Figure 9: The six centers involved in a two-electron integral. Centers $\vec{A}$ and $\vec{B}$ have the third center $\vec{P}$, which describes the space for the first electron, i; centers $\vec{C}$ and $\vec{D}$ have the third center $\vec{Q}$, which describes the space for the second electron, j.

Exercise.
Calculate the Gaussian product for the radial portion of primitives χ_a and χ_b (each contributing to orbitals ϕ_A and ϕ_B, respectively), where the radial portion of χ_a is

$$\exp\bigl(-\alpha_a r_{Ai}^2\bigr),$$

and the radial portion portion of χ_b has the same form by analogy. Calculate the Gaussian product for the radial portions of primitives χ_c and χ_d also. Let $\gamma_P = \alpha_a + \alpha_b$ and $\gamma_Q = \alpha_c + \alpha_d$.

Solution.

$$\begin{aligned}
\exp\bigl(-\alpha_a r_{Ai}^2\bigr)\exp\bigl(-\alpha_b r_{Bi}^2\bigr) &= \exp\left(-\frac{\alpha_a\alpha_b}{\gamma_P}|\vec{AB}|^2\right)\exp\bigl(-\gamma_P r_{Pi}^2\bigr)\\
&= \widetilde{K}_P\exp\bigl(-\gamma_P r_{Pi}^2\bigr)\\
\exp\bigl(-\alpha_c r_{Cj}^2\bigr)\exp\bigl(-\alpha_c r_{Dj}^2\bigr) &= \exp\left(-\frac{\alpha_c\alpha_d}{\gamma_Q}|\vec{CD}|^2\right)\exp\bigl(-\gamma_Q r_{Qj}^2\bigr)\\
&= \widetilde{K}_Q\exp\bigl(-\gamma_Q r_{Qj}^2\bigr)
\end{aligned} \tag{91}$$

$$\begin{aligned}
\gamma_P = \alpha_a+\alpha_b, \quad \vec{P} &= \frac{(\alpha_a\vec{A}+\alpha_b\vec{B})}{\gamma_P}\\
\gamma_Q = \alpha_c+\alpha_d, \quad \vec{Q} &= \frac{(\alpha_c\vec{C}+\alpha_d\vec{D})}{\gamma_Q}\\
\vec{AB} = \vec{A}-\vec{B}, \quad \vec{CD} &= \vec{C}-\vec{D}\\
\vec{r}_{Pi} = \vec{r}_i-\vec{P}, \quad \vec{r}_{Qj} &= \vec{r}_j-\vec{Q}\\
\vec{x}_{Pi} = x_i-\vec{P}_x, \quad \vec{x}_{Qj} &= x_j-\vec{Q}_x
\end{aligned}$$

[end of solution]

What of the angular portion of these orbitals? We proceed as we have done before with all of the preceding integrals.

Exercise.
Calculate the x-component of the product of angular components of primitives χ_a and χ_b,

$$x^{l_A}x^{l_B}.$$

Do the same for the y- and z- components.

Solution. Following the example of Eqs. 13, 15, and 20, the angular components over the product of primitives χ_a and χ_b are

$$\begin{aligned}
x^{l_A}x^{l_B} &= \sum_{l_P=0}^{l_A+l_B} c_{l_P}(l_A,l_B,\vec{PA}_x,\vec{PB}_x)x^{l_P}\,,\\
y^{m_A}y^{m_B} &= \sum_{m_P=0}^{m_A+m_B} c_{m_P}(m_A,m_B,\vec{PA}_y,\vec{PB}_y)y^{n_P}\,,\\
z^{n_A}z^{n_B} &= \sum_{n_P=0}^{n_A+n_B} c_{n_P}(n_A,n_B,\vec{PA}_z,\vec{PB}_z)z^{m_P}\,.
\end{aligned}$$

The new subscripts on the coefficients c_k and coordinates x^l, y^m, z^n, *etc.*, will be necessary to distinguish between centers $\vec{P}$ and $\vec{Q}$.
[end of solution]

Exercise.
Repeat the previous exercise for the product of the angular components of the primitives corresponding to electron j.

Solution.
The angular components over the product of primitives χ_c and χ_d are

$$
\begin{aligned}
x^{l_C} x^{l_D} &= \sum_{l_Q=0}^{l_C+l_D} c_{l_Q}(l_C, l_D, \vec{PC}_x, \vec{PD}_x) x^{l_Q} \,, \\
y^{m_C} y^{m_D} &= \sum_{m_Q=0}^{m_C+m_D} c_{m_Q}(m_C, m_D, \vec{PC}_y, \vec{PD}_y) y^{n_Q} \,, \\
z^{n_C} z^{n_D} &= \sum_{n_Q=0}^{n_C+n_D} c_{n_Q}(n_C, n_D, \vec{PC}_z, \vec{PD}_z) z^{m_Q} \,.
\end{aligned}
$$

[end of solution]

Let us consider the expression for G we've derived up to this point. It features two $\widetilde{K}$ constants, one for each new intermediate center $\vec{P}$ and $\vec{Q}$, as well as six c_k factors resulting from the treatment of angular momentum over these two centers. Because we are integrating over third center coordinates ($\vec{P}$, $\vec{Q}$), we integrate over the range $(-\infty, \infty)$ instead of $[0, \infty)$.

$$
\begin{aligned}
G = & \widetilde{K}_P \, \widetilde{K}_Q \\
& \times \sum_{l_P=0}^{l_A+l_B} \sum_{m_P=0}^{m_A+m_B} \sum_{n_P=0}^{n_A+n_B} c_{l_P}(l_A, l_B, \vec{PA}_x, \vec{PB}_x) c_{m_P}(m_A, m_B, \vec{PA}_y, \vec{PB}_y) c_{n_P}(n_A, n_B, \vec{PA}_z, \vec{PB}z) \\
& \times \sum_{l_Q=0}^{l_C+l_D} \sum_{m_Q=0}^{m_C+m_D} \sum_{n_Q=0}^{n_C+n_D} c_{l_Q}(l_C, l_D, \vec{PC}_x, \vec{PD}_x) c_{m_Q}(m_C, m_D, \vec{PC}_y, \vec{PD}_y) c_{n_Q}(n_A, n_B, \vec{PC}_z, \vec{PD}_z) \\
& \times \underbrace{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x^{l_P} y^{m_P} z^{n_P} \exp\!\left(-\gamma_P r_{Pi}^2\right) \left(\frac{1}{\vec{r}_{ij}}\right) x^{l_Q} y^{m_Q} z^{n_Q} \exp\!\left(-\gamma_Q r_{Qj}^2\right) \mathrm{d}V_i \, \mathrm{d}V_j}_{G_{RI}}
\end{aligned}
\tag{92}
$$

We've succeeded in deriving a general expression for the electron-electron repulsion integral in terms of two centers instead of four. Because we know exactly the form of $\widetilde{K}$ and c_k, the remaining work in resolving the analytical form of G will be in solving the last line of Eq. 92, which we call G_{RI} to imply the "remaining integral" of G. There is much to be done to resolve G_{RI}.

Perhaps most obviously, there is the matter of the inverse operator. Much as we did with the electron-nuclear attraction integral, we pull $\vec{r}_{ij}$ from the denominator by subjecting it to a Fourier transform. Before we do so, we recast the denominator of the operator in terms of the two new centers $\vec{P}$ and $\vec{Q}$.

Exercise.
Expand $\vec{r}_{ij}$ in terms of the two new centers $\vec{P}$ and $\vec{Q}$, analogous to what was done with recasting $\vec{r}_{iC}$ in terms of one new center, $\vec{P}$.

Solution.

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j = (\vec{r}_i - \vec{P}) - (\vec{r}_j - \vec{Q}) = \vec{r}_{Pi} - \vec{r}_{Qj} + \vec{PQ}\,, \tag{93}$$

$$\vec{PQ} = \vec{P} - \vec{Q}.$$

[end of solution]

Now we transform the operator.

Exercise.
Use Eq. 52, the canonical Fourier transform, to transform the operator as expressed in Eq. 93.

Solution.

$$\begin{aligned}
\frac{1}{\vec{r}_{ij}} &= \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\left[\mathrm{i}\vec{k}\cdot(\vec{r}_{ij})\right]\mathrm{d}\vec{k} \\
&= \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\left[\mathrm{i}\vec{k}\cdot(\vec{r}_{Pi} - \vec{r}_{Qj} + \vec{PQ})\right]\mathrm{d}\vec{k} \\
&= \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot\vec{r}_{Pi}\Big)\exp\Big(\mathrm{i}\vec{k}\cdot -\vec{r}_{Qj}\Big)\exp\Big(\mathrm{i}\vec{k}\cdot\vec{PQ}\Big)\mathrm{d}\vec{k}
\end{aligned} \tag{94}$$

[end of solution]

Exercise.
Insert the solution of Eq. 94 into G_{RI}, the last line of Eq. 92.

Solution.

$$\begin{aligned}
G_{RI} &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^{l_P} y^{m_P} z^{n_P}\exp\left(-\gamma_P r_{Pi}^2\right)\left(\frac{1}{\vec{r}_{ij}}\right)x^{l_Q} y^{m_Q} z^{n_Q}\exp\left(-\gamma_Q r_{Qj}^2\right)\mathrm{d}V_i\,\mathrm{d}V_j \\
&= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^{l_P} y^{m_P} z^{n_P}\exp\left(-\gamma_P r_{Pi}^2\right) \\
&\quad\times\left[\frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot\vec{r}_{Pi}\Big)\exp\Big(\mathrm{i}\vec{k}\cdot -\vec{r}_{Qj}\Big)\exp\Big(\mathrm{i}\vec{k}\cdot\vec{PQ}\Big)\mathrm{d}\vec{k}\right] x^{l_Q} y^{m_Q} z^{n_Q}\exp\left(-\gamma_Q r_{Qj}^2\right)\mathrm{d}V_i\,\mathrm{d}V_j
\end{aligned} \tag{95}$$

[end of solution]

Exercise.
With the exception of the terms $\left(\frac{1}{\vec{k}^2}\right)$ and $\exp\left(\mathrm{i}\vec{k}\cdot\vec{PQ}\right)$, expand G_{RI} in terms of the x, y, and z components of $\vec{r}_{Pi}$, $\vec{r}_{Qj}$, and $\vec{k}$. Note that the differential volume elements are

$$\begin{aligned}\mathrm{d}V_i &= \mathrm{d}x_P\,\mathrm{d}y_P\,\mathrm{d}z_P\,,\\ \mathrm{d}V_j &= \mathrm{d}x_Q\,\mathrm{d}y_Q\,\mathrm{d}z_Q\,,\\ \mathrm{d}\vec{k} &= \mathrm{d}\vec{k}_x\,\mathrm{d}\vec{k}_y\,\mathrm{d}\vec{k}_z\,.\end{aligned}$$

Collect terms by these spatial components. You should end up with one integral that is

$$\frac{1}{2\pi^2}\int\frac{1}{\vec{k}^2}\exp\left(\mathrm{i}\vec{k}\cdot\vec{PQ}\right)\mathrm{d}\vec{k}\,,$$

multiplied by six integrals in the general form of

$$\int_{-\infty}^{\infty}x^n\exp\left(-ax^2+bx\right)\mathrm{d}x\,.$$

Solution.

$$
\begin{aligned}
G_{RI} =& \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^{l_P} y^{m_P} z^{n_P} \exp\left(-\gamma_P r_{Pi}^2\right) \\
&\times \left[\frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\left(\mathrm{i}\vec{k}\cdot\vec{r}_{Pi}\right)\exp\left(\mathrm{i}\vec{k}\cdot -\vec{r}_{Qj}\right)\exp\left(\mathrm{i}\vec{k}\cdot\vec{PQ}\right)\mathrm{d}\vec{k}\right] x^{l_Q} y^{m_Q} z^{n_Q}\exp\left(-\gamma_Q r_{Qj}^2\right)\mathrm{d}V_i\,\mathrm{d}V_j \\
=&\frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\left(\mathrm{i}\vec{k}\cdot\vec{r}_{Pi}\right)\exp\left(\mathrm{i}\vec{k}\cdot -\vec{r}_{Qj}\right)\exp\left(\mathrm{i}\vec{k}\cdot\vec{PQ}\right)\mathrm{d}\vec{k} \\
&\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^{l_P} y^{m_P} z^{n_P}\exp\left(-\gamma_P x_P^2\right)\exp\left(-\gamma_P y_P^2\right)\exp\left(-\gamma_P z_P^2\right)\mathrm{d}x_P\,\mathrm{d}y_P\,\mathrm{d}z_P \\
&\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^{l_Q} y^{m_Q} z^{n_Q}\exp\left(-\gamma_Q x_Q^2\right)\exp\left(-\gamma_Q y_Q^2\right)\exp\left(-\gamma_Q z_Q^2\right)\mathrm{d}x_Q\,\mathrm{d}y_Q\,\mathrm{d}z_Q \\
=&\frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big[\mathrm{i}\vec{k}\cdot(x_P+y_P+z_P)\Big]\exp\Big[\mathrm{i}\vec{k}\cdot -(x_Q+y_Q+z_Q)\Big]\exp\left(\mathrm{i}\vec{k}\cdot\vec{PQ}\right)\mathrm{d}\vec{k} \\
&\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^{l_P} y^{m_P} z^{n_P}\exp\left(-\gamma_P x_P^2\right)\exp\left(-\gamma_P y_P^2\right)\exp\left(-\gamma_P z_P^2\right)\mathrm{d}x_P\,\mathrm{d}y_P\,\mathrm{d}z_P \\
&\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^{l_Q} y^{m_Q} z^{n_Q}\exp\left(-\gamma_Q x_Q^2\right)\exp\left(-\gamma_Q y_Q^2\right)\exp\left(-\gamma_Q z_Q^2\right)\mathrm{d}x_Q\,\mathrm{d}y_Q\,\mathrm{d}z_Q \\
=&\frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\left(\mathrm{i}\vec{k}\cdot\vec{PQ}\right)\mathrm{d}\vec{k} \\
&\times \int_{-\infty}^{\infty} x^{l_P}\exp\left(-\gamma_P x_P^2\right)\exp\left(\mathrm{i}\vec{k}_x\cdot x_P\right)\mathrm{d}x_P \times \int_{-\infty}^{\infty} x^{l_Q}\exp\left(-\gamma_Q x_Q^2\right)\exp\Big[\mathrm{i}\vec{k}_x\cdot(-x_Q)\Big]\mathrm{d}x_Q \\
&\times \int_{-\infty}^{\infty} y^{m_P}\exp\left(-\gamma_P y_P^2\right)\exp\left(\mathrm{i}\vec{k}_y\cdot y_P\right)\mathrm{d}y_P \times \int_{-\infty}^{\infty} y^{m_Q}\exp\left(-\gamma_Q y_Q^2\right)\exp\Big[\mathrm{i}\vec{k}_y\cdot(-y_Q)\Big]\mathrm{d}y_Q \\
&\times \int_{-\infty}^{\infty} z^{n_P}\exp\left(-\gamma_P z_P^2\right)\exp\left(\mathrm{i}\vec{k}_z\cdot z_P\right)\mathrm{d}z_P \times \int_{-\infty}^{\infty} z^{n_Q}\exp\left(-\gamma_Q z_Q^2\right)\exp\Big[\mathrm{i}\vec{k}_z\cdot(-z_Q)\Big]\mathrm{d}z_Q \\
=&\frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\left(\mathrm{i}\vec{k}\cdot\vec{PQ}\right)\mathrm{d}\vec{k} \\
&\times \int_{-\infty}^{\infty} x^{l_P}\exp\left(-\gamma_P x_P^2+\mathrm{i}\vec{k}_x\cdot x_P\right)\mathrm{d}x_P \times \int_{-\infty}^{\infty} x^{l_Q}\exp\left(-\gamma_Q x_Q^2-\mathrm{i}\vec{k}_x\cdot x_Q\right)\mathrm{d}x_Q \\
&\times \int_{-\infty}^{\infty} y^{m_P}\exp\left(-\gamma_P y_P^2+\mathrm{i}\vec{k}_y\cdot y_P\right)\mathrm{d}y_P \times \int_{-\infty}^{\infty} y^{m_Q}\exp\left(-\gamma_Q y_Q^2-\mathrm{i}\vec{k}_y\cdot y_Q\right)\mathrm{d}y_Q \\
&\times \int_{-\infty}^{\infty} z^{n_P}\exp\left(-\gamma_P z_P^2+\mathrm{i}\vec{k}_z\cdot z_P\right)\mathrm{d}z_P \times \int_{-\infty}^{\infty} z^{n_Q}\exp\left(-\gamma_Q z_Q^2-\mathrm{i}\vec{k}_z\cdot z_Q\right)\mathrm{d}z_Q
\end{aligned}
\tag{96}
$$

[end of solution]

It will prove useful to use some shorthand notation:

$$
G_{l_P}^{x_P} = \int_{-\infty}^{\infty} x^{l_P}\exp\left(-\gamma_P x_P^2+\mathrm{i}\vec{k}_x\cdot x_P\right)\mathrm{d}x_P \tag{97}
$$

so that the last line of Eq. 96 can be expressed as

$$
G_{RI} = \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\left(\mathrm{i}\vec{k}\cdot\vec{PQ}\right)\mathrm{d}\vec{k} \times G_{l_P}^{x_P} \times G_{m_P}^{y_Q} \times G_{n_P}^{z_P} \times G_{l_Q}^{x_Q} \times G_{m_Q}^{y_Q} \times G_{n_Q}^{z_Q} \tag{98}
$$

The form of $G_{l_P}^{x_P}$ as it appears in Eq. 97 should be familiar, and we know how to solve it.

Exercise.
Let $\epsilon_P = (4\gamma_P)^{-1}$, and provide the solution to Eq. 97, for $G_{l_P}^{x_P}$, using Eq. 56. Repeat the exercise for $G_{l_Q}^{x_Q}$.

Solution.

$$\begin{aligned} G_{l_P}^{x_P} &= \int_{-\infty}^{\infty} x^{l_P} \exp\Big(-\gamma_P x_P^2 + \mathrm{i}\vec{k}_x \cdot x_P\Big)\,\mathrm{d}x_P \\ &= \mathrm{i}^l \left(\frac{\pi}{\gamma_P}\right)^{1/2} l_P! \epsilon_P^{l_P/2} \exp\Big(-\epsilon_P \vec{k}_x^2\Big) \times \sum_{r_P=0}^{\lfloor l_P/2 \rfloor} \frac{(-1)^{r_P} (2\sqrt{\epsilon_P}\vec{k}_x)^{l_P - 2r_P}}{r_P!(l_P - 2r_P)!} \end{aligned} \tag{99}$$

$$\begin{aligned} G_{l_Q}^{x_Q} &= \int_{-\infty}^{\infty} x^{l_Q} \exp\Big(-\gamma_Q x_P^2 - \mathrm{i}\vec{k}_x \cdot x_Q\Big)\,\mathrm{d}x_Q \\ &= \mathrm{i}^l \left(\frac{\pi}{\gamma_Q}\right)^{1/2} l_Q! \epsilon_P^{l_Q/2} \exp\Big(-\epsilon_P \vec{k}_x^2\Big) \times \sum_{r_Q=0}^{\lfloor l_Q/2 \rfloor} \frac{(-1)^{r_Q} (-1 \cdot 2\sqrt{\epsilon_Q}\vec{k}_x)^{l_Q - 2r_Q}}{r_Q!(l_Q - 2r_Q)!} \end{aligned} \tag{100}$$

Take notice that, in addition to different indices, Eq. 100 is distinguished from Eq. 99 by the presence of a $(-1)^{l_Q - 2r_Q}$ term. Additionally, in the square root fraction, we reverted $\epsilon/4$ to γ, which will be useful in the final steps of the derivation of G.
[end of solution]

Exercise.
Using the form derived in Eqs. 99 and 100, calculate the product $G_{l_P}^{x_P} G_{m_P}^{y_P} G_{n_P}^{z_P} G_{l_Q}^{x_Q} G_{m_Q}^{y_Q} G_{n_Q}^{z_Q}$, collecting terms like so:

$$(G_{l_P}^{x_P} G_{l_Q}^{x_Q}) \times (G_{m_P}^{y_P} G_{m_Q}^{y_Q}) \times (G_{n_P}^{z_P} G_{n_Q}^{z_Q})$$

Finally, collect an $\exp\Big[-(\epsilon_P + \epsilon_Q)\vec{k}^2\Big]$ term as a multiplicative factor of the remaining, decomposed terms, without decomposing $\vec{k}^2$ into its spatial coordinates.

Solution.

$$\begin{aligned} G_{l_P}^{x_P} G_{m_P}^{y_P} G_{n_P}^{z_P} G_{l_Q}^{x_Q} G_{m_Q}^{y_Q} G_{n_Q}^{z_Q} &= \exp\left[-(\overbrace{\epsilon_P + \epsilon_Q}^{\delta})\vec{k}^2\right] \\ \times \mathrm{i}^{l_P + l_Q} \left(\frac{\pi}{\gamma_P}\right)^{1/2} \left(\frac{\pi}{\gamma_Q}\right)^{1/2} & l_P! l_Q! \epsilon_P^{l_P/2} \epsilon_Q^{l_Q/2} \times \sum_{r_P=0}^{\lfloor l_P/2 \rfloor} \sum_{r_Q=0}^{\lfloor l_Q/2 \rfloor} \frac{(-1)^{r_P} (2\sqrt{\epsilon_P}\vec{k}_x)^{l_P - 2r_P}}{r_P!(l_P - 2r_P)!} \frac{(-1)^{r_Q} (-1 \cdot 2\sqrt{\epsilon_Q}\vec{k}_x)^{l_Q - 2r_Q}}{r_Q!(l_Q - 2r_Q)!} \\ \times \mathrm{i}^{m_P + m_Q} \left(\frac{\pi}{\gamma_P}\right)^{1/2} \left(\frac{\pi}{\gamma_Q}\right)^{1/2} & m_P! m_Q! \epsilon_P^{m_P/2} \epsilon_Q^{m_Q/2} \times \sum_{s_P=0}^{\lfloor m_P/2 \rfloor} \sum_{s_Q=0}^{\lfloor m_Q/2 \rfloor} \frac{(-1)^{s_P} (2\sqrt{\epsilon_P}\vec{k}_y)^{m_P - 2s_P}}{s_P!(m_P - 2s_P)!} \frac{(-1)^{s_Q} (-1 \cdot 2\sqrt{\epsilon_Q}\vec{k}_y)^{m_Q - 2s_Q}}{s_Q!(m_Q - 2s_Q)!} \\ \times \mathrm{i}^{n_P + n_Q} \left(\frac{\pi}{\gamma_P}\right)^{1/2} \left(\frac{\pi}{\gamma_Q}\right)^{1/2} & n_P! n_Q! \epsilon_P^{n_P/2} \epsilon_Q^{n_Q/2} \times \sum_{t_P=0}^{\lfloor n_P/2 \rfloor} \sum_{t_Q=0}^{\lfloor n_Q/2 \rfloor} \frac{(-1)^{t_P} (2\sqrt{\epsilon_P}\vec{k}_z)^{n_P - 2t_P}}{t_P!(n_P - 2t_P)!} \frac{(-1)^{t_Q} (-1 \cdot 2\sqrt{\epsilon_Q}\vec{k}_z)^{n_Q - 2t_Q}}{t_Q!(n_Q - 2t_Q)!} \end{aligned} \tag{101}$$

You may have ordered some specific terms differently than that presented here in Eq. 101. If so, ensure that, with appropriate manipulation, the two forms are equivalent.
[end of solution]

By this point we have succeeded in integrating over $\mathrm{d}V_i$ and $\mathrm{d}V_j$, because we solved each G_l^x term and took their product. We can expand out Eq. 98 in terms of these solutions, by simply inserting Eq. 101 into

Eq. 98. Even doing so, it remains for us to integrate over $\mathrm{d}\vec{k}$, which was introduced in the Fourier transform to draw $\vec{r}_{ij}$ out of the denominator. Since we are interested in those terms involving $\vec{k}$, the following equation features the result of substituting Eq. 101 into Eq. 98.

$$\begin{aligned} G_{RI} &= \frac{1}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot P\vec{Q}\Big)\overbrace{\exp\Big(-\delta\vec{k}^2\Big)\times C_{RI}\times \vec{k}_x^{\,l_P-2r_P}\vec{k}_x^{\,l_Q-2r_Q}\vec{k}_y^{\,m_P-2s_P}\vec{k}_y^{\,m_Q-2s_Q}\vec{k}_x^{\,n_P-2t_P}\vec{k}_x^{\,n_Q-2t_Q}}^{G_{l_P}^{x_P}G_{m_P}^{y_P}G_{n_P}^{z_P}G_{l_Q}^{x_Q}G_{m_Q}^{y_Q}G_{n_Q}^{z_Q}}\mathrm{d}\vec{k} \\ &= \frac{C_{RI}}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot P\vec{Q}\Big)\exp\Big(-\delta\vec{k}^2\Big)\vec{k}_x^{\,l_P-2r_P+l_Q-2r_Q}\vec{k}_y^{\,m_P-2s_P+m_Q-2s_Q}\vec{k}_x^{\,n_P-2t_P+n_Q-2t_Q}\mathrm{d}\vec{k}\,, \end{aligned} \tag{102}$$

where C_{RI} is a collection of all constant terms in G_{RI} that are not dependent on $\vec{k}$,

$$\begin{aligned} C_{RI} = \mathrm{i}^{l_P+l_Q}&\left(\frac{\pi}{\gamma_P}\right)^{1/2}\left(\frac{\pi}{\gamma_Q}\right)^{1/2} l_P!l_Q!\epsilon_P^{l_P/2}\epsilon_Q^{l_Q/2}\times\sum_{r_P=0}^{\lfloor l_P/2\rfloor}\sum_{r_Q=0}^{\lfloor l_Q/2\rfloor}\frac{(-1)^{r_P}(2\sqrt{\epsilon_P})^{l_P-2r_P}}{r_P!(l_P-2r_P)!}\frac{(-1)^{r_Q}(-1\cdot 2\sqrt{\epsilon_Q})^{l_Q-2r_Q}}{r_Q!(l_Q-2r_Q)!} \\ \times\mathrm{i}^{m_P+m_Q}&\left(\frac{\pi}{\gamma_P}\right)^{1/2}\left(\frac{\pi}{\gamma_Q}\right)^{1/2} m_P!m_Q!\epsilon_P^{m_P/2}\epsilon_Q^{m_Q/2}\times\sum_{s_P=0}^{\lfloor m_P/2\rfloor}\sum_{s_Q=0}^{\lfloor m_Q/2\rfloor}\frac{(-1)^{s_P}(2\sqrt{\epsilon_P})^{m_P-2s_P}}{s_P!(m_P-2s_P)!}\frac{(-1)^{s_Q}(-1\cdot 2\sqrt{\epsilon_Q})^{m_Q-2s_Q}}{s_Q!(m_Q-2s_Q)!} \\ \times\mathrm{i}^{n_P+n_Q}&\left(\frac{\pi}{\gamma_P}\right)^{1/2}\left(\frac{\pi}{\gamma_Q}\right)^{1/2} n_P!n_Q!\epsilon_P^{n_P/2}\epsilon_Q^{n_Q/2}\times\sum_{t_P=0}^{\lfloor n_P/2\rfloor}\sum_{t_Q=0}^{\lfloor n_Q/2\rfloor}\frac{(-1)^{t_P}(2\sqrt{\epsilon_P})^{n_P-2t_P}}{t_P!(n_P-2t_P)!}\frac{(-1)^{t_Q}(-1\cdot 2\sqrt{\epsilon_Q})^{n_Q-2t_Q}}{t_Q!(n_Q-2t_Q)!}\,, \end{aligned} \tag{103}$$

and which can be safely set aside for the moment. Doing so allows us to focus on the manipulations of $\vec{k}$.

Eq. 102 suffers from the presence of $\vec{k}^2$ in a denominator. How do you think we will ameliorate this problem? If you have not already guessed as much, we will use the same technique as we did with electron-nuclear attraction integrals. As before, we do so at the price of a new integral.

Exercise.
Employ the identity of Eq. 63 in Eq. 102. At the end of the exercise, combine the two exponential functions into one.

Solution.

$$\begin{aligned} G_{RI} =& \frac{C_{RI}}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot P\vec{Q}\Big)\exp\Big(-\delta\vec{k}^2\Big)\vec{k}_x^{\,l_P-2r_P+l_Q-2r_Q}\vec{k}_y^{\,m_P-2s_P+m_Q-2s_Q}\vec{k}_x^{\,n_P-2t_P+n_Q-2t_Q}\mathrm{d}\vec{k} \\ =& \frac{C_{RI}}{2\pi^2}\int \frac{1}{\vec{k}^2}\exp\Big(\mathrm{i}\vec{k}\cdot P\vec{Q}\Big)2\delta\vec{k}^2\int_0^1\frac{\mathrm{d}u}{u^3}\exp\Big(-\delta\vec{k}^2u^{-2}\Big) \\ &\times\vec{k}_x^{\,l_P-2r_P+l_Q-2r_Q}\vec{k}_y^{\,m_P-2s_P+m_Q-2s_Q}\vec{k}_x^{\,n_P-2t_P+n_Q-2t_Q}\mathrm{d}\vec{k} \\ =& \frac{\delta\cdot C_{RI}}{\pi^2}\int_0^1\frac{\mathrm{d}u}{u^3}\int_{-\infty}^{\infty}\exp\Big(-\delta\vec{k}^2u^{-2}+\mathrm{i}\vec{k}\cdot P\vec{Q}\Big)\vec{k}_x^{\,l_P-2r_P+l_Q-2r_Q}\vec{k}_y^{\,m_P-2s_P+m_Q-2s_Q}\vec{k}_x^{\,n_P-2t_P+n_Q-2t_Q}\mathrm{d}\vec{k} \end{aligned} \tag{104}$$

Now it should be clear why we had not decomposed $\exp\Big(-\delta\vec{k}^2\Big)$ into its components, so that we could make this identity substitution.
[end of solution]

If we consider the components of $\vec{k}$ ($\vec{k}_x$, $\vec{k}_y$, $\vec{k}_z$), then there are now four multiple integrals to be solved in G_{RI}.

$$G_{RI}\approx\int_0^1\frac{\mathrm{d}u}{u^3}\int_{-\infty}^{\infty}\cdots\mathrm{d}\vec{k}_x\int_{-\infty}^{\infty}\cdots\mathrm{d}\vec{k}_y\int_{-\infty}^{\infty}\cdots\mathrm{d}\vec{k}_z$$

Exercise.
Derive the solution to the integral over $\mathrm{d}\vec{k}_x$,

$$\int_{-\infty}^{\infty} \vec{k}_x^{(l_P-2r_P)+(l_Q-2r_Q)} \exp\Big(-\delta\vec{k}_x^2 u^{-2} + \mathrm{i}\vec{k}_x P\vec{Q}_x\Big)\mathrm{d}\vec{k}_x \,.$$

(Hint: You've solved integrals with this general form before.)

Repeat the exercise for the integrals over $\mathrm{d}\vec{k}_y$ and $\mathrm{d}\vec{k}_z$.

Solution.
Proceed by using the standard integral of Eq. 56.

$$\begin{aligned}\int_{-\infty}^{\infty} \vec{k}_x^{(l_P-2r_P)+(l_Q-2r_Q)} \exp\Big(-\delta\vec{k}_x^2 u^{-2} + \mathrm{i}\vec{k}_x P\vec{Q}_x\Big)\mathrm{d}\vec{k}_x = \\ \sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2\rfloor} u\cdot u^{(l_P-2r_P)+(l_Q-2r_Q)}\cdot u^{(l_P-2r_P)+(l_Q-2r_Q)-2i}\cdot \exp\Big(-P\vec{Q}_x^{\,2}/(4\delta)u^2\Big)\cdot \mathrm{i}^{(l_P-2r_P)+(l_Q-2r_Q)} \\ \times\left(\frac{\pi}{\delta}\right)^{1/2}\left(\frac{1}{2}\right)^{(l_P-2r_P)+(l_Q-2r_Q)}\left(\frac{1}{\sqrt{\delta}}\right)^{(l_P-2r_P)+(l_Q-2r_Q)}\left(\frac{1}{\sqrt{\delta}}\right)^{(l_P-2r_P)+(l_Q-2r_Q)-2i} \\ \times P\vec{Q}_x^{(l_P-2r_P)+(l_Q-2r_Q)-2i}\frac{(-1)^i(l_P-2r_P+l_Q-2r_Q)!}{i!(l_P-2r_P+l_Q-2r_Q-2i)!}\end{aligned} \tag{105}$$

We have separated out some terms here for future utility. Ensure that, with proper manipulation, your solution agrees with Eq. 105.

The solutions over $\mathrm{d}\vec{k}_y$ and $\mathrm{d}\vec{k}_z$ are entirely analogous, with summation indices j and k in lieu of i.
[end of solution]

Exercise.
Extract all terms that include contain u from the previous exercise (Eq. 105) and introduce them as arguments of the integral over $\mathrm{d}u$ that appears in Eq. 104.

$$\int_0^1 \frac{\mathrm{d}u}{u^3}$$

Introduce also the u terms that appear in the analogous solutions to integration over $\mathrm{d}\vec{k}_y$ and $\mathrm{d}\vec{k}_z$. In other words, fill in the bracketed part of

$$\int_0^1 u^{-3}\cdot[\text{additional } u \text{ terms}]\cdot \mathrm{d}u \,.$$

Simplify the resulting integral, letting ν equal the collection of powers outside of the exponential factors. Do not attempt to solve the integral.

Solution.

$$\begin{aligned}\int_0^1 \frac{\mathrm{d}u}{u^3} \Big\{ u \cdot u^{(l_P-2r_P)+(l_Q-2r_Q)} \cdot u^{(l_P-2r_P)+(l_Q-2r_Q)-2a} \cdot \exp\Big[-\vec{PQ}_x^{\,2}/(4\delta)u^2\Big] \\ \times u \cdot u^{(m_P-2s_P)+(m_Q-2s_Q)} \cdot u^{(m_P-2s_P)+(m_Q-2s_Q)-2b} \cdot \exp\Big[-\vec{PQ}_y^{\,2}/(4\delta)u^2\Big] \\ \times u \cdot u^{(n_P-2t_P)+(n_Q-2t_Q)} \cdot u^{(n_P-2t_P)+(n_Q-2t_Q)-2c} \cdot \exp\Big[-\delta\vec{PQ}_z^{\,2}/(4\delta)u^2\Big] \Big\} = \\ \int_0^1 \frac{\mathrm{d}u}{u^3} \cdot u^3 \cdot u^{2\nu} \cdot \exp\Big[-(\vec{PC}_x^{\,2} + \vec{PC}_y^{\,2} + \vec{PC}_z^{\,2})/(4\delta)u^2\Big]\end{aligned} \tag{106}$$

where

$$\nu = l_P + l_Q + m_P + m_Q + n_P + n_Q - 2(r_P + r_Q + s_P + s_Q + t_P + t_Q) - (i + j + k)$$

which simplifies to the Boys Function,

$$\int_0^1 u^{2\nu} \exp\Big[-\vec{PC}^{\,2}/(4\delta)u^2\Big]\mathrm{d}u = F_\nu[\vec{PQ}^{\,2}/(4\delta)]\,. \tag{107}$$

[end of solution]

Now all terms involving u (a variable that was introduced to remove $\vec{k}^2$ from the denominator) are resolved. Additionally, all terms involving $\vec{k}$ have been integrated out. All integrals over $\mathrm{d}V_i$ and $\mathrm{d}V_j$ were also solved several exercises before. Thus, all integrals have been solved. What we are left with is the complex assemblage of their solutions, which we will now simplify as fully as possible.

Look again at Eq. 105. Since we removed the u terms to collect the Boys Function (Eq. 107), then Eq. 105 takes on the following form, which we will call I_{k_x}, as we did for the electron-nuclear attraction integral.

$$\begin{aligned} I_{k_x} = & \sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2 \rfloor} \mathrm{i}^{(l_P-2r_P)+(l_Q-2r_Q)} \left(\frac{\pi}{\delta}\right)^{1/2} \left(\frac{1}{2}\right)^{(l_P-2r_P)+(l_Q-2r_Q)} \\ & \times \left(\frac{1}{\sqrt{\delta}}\right)^{(l_P-2r_P)+(l_Q-2r_Q)} \left(\frac{1}{\sqrt{\delta}}\right)^{(l_P-2r_P)+(l_Q-2r_Q)-2i} \\ & \times \vec{PQ}_x^{\,(l_P-2r_P)+(l_Q-2r_Q)-2i} \frac{(-1)^i (l_P - 2r_P + l_Q - 2r_Q)!}{i!(l_P - 2r_P + l_Q - 2r_Q - 2i)!} \\ = & \left(\frac{\pi}{\delta}\right)^{1/2} \sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2 \rfloor} \mathrm{i}^{(l_P-2r_P)+(l_Q-2r_Q)} \left(\frac{1}{2}\right)^{(l_P-2r_P)+(l_Q-2r_Q)} \\ & \times \left(\frac{1}{\delta}\right)^{l_P+l_Q-2(r_P+2r_Q)} \delta^i \vec{PQ}_x^{\,(l_P-2r_P)+(l_Q-2r_Q)-2i} \frac{(-1)^i (l_P - 2r_P + l_Q - 2r_Q)!}{i!(l_P - 2r_P + l_Q - 2r_Q - 2i)!} \end{aligned} \tag{108}$$

We know there are analogous expressions for the y and z components, which we will term I_{k_y} and I_{k_z}.

Consider I_{k_x} (Eq. 108) in the context of G_{RI}, which we last saw expressed in Eq. 104.

$$\begin{aligned} G_{RI} &= \frac{\delta \cdot C_{RI}}{\pi^2} \times I_{k_x} I_{k_y} I_{k_z} \times F_\nu[\vec{PQ}^{\,2}/(4\delta)] \\ &= \frac{\delta}{\pi^2} \times C_{RI_x} C_{RI_y} C_{RI_z} \times I_{k_x} I_{k_y} I_{k_z} \times F_\nu[\vec{PQ}^{\,2}/(4\delta)] \end{aligned} \tag{109}$$

where C_{RI} is expressed in Eq. 103, and $C_{RI} = C_{RI_x} C_{RI_y} C_{RI_z}$ is the product of the spatial decomposition of C_{RI}, just as each line of Eq. 103 clearly shows the delineated x, y, and z contributions. (Take a look again at Eqs. 92 and 88 to remind yourself of G_{RI} in the context of G and $(AB|CD)$, respectively.)

We proceed with the simplification of G_{RI} by considering the x component product of C_{RI} and I_k.

Exercise.
Using the x-component of C_{RI} shown in Eq. 103, and I_{k_x} as expressed in Eq. 108, show that the product of C_{RI_x} and I_{k_x} is

$$\begin{aligned} C_{RI_x} \times I_{k_x} = & \left(\frac{\pi}{\gamma_P}\right)^{1/2} \left(\frac{\pi}{\gamma_Q}\right)^{1/2} \left(\frac{\pi}{\delta}\right)^{1/2} \\ & \times \sum_{r_P=0}^{\lfloor l_P/2 \rfloor} \sum_{r_Q=0}^{\lfloor l_Q/2 \rfloor} \sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2 \rfloor} \frac{l_P! \gamma^{r_P-l_P}}{r_P!(l_P-2r_P)!} \times \frac{l_Q! \gamma^{r_Q-l_Q}}{r_Q!(l_Q-2r_Q)!} \\ & \times \frac{(-1)^{l_P} (2\delta)^{2(r_P+r_Q)} (l_P+l_Q-2r_P-r_Q)! \delta^i \vec{PQ}_x^{\,l_P+l_Q-2(r_P+r_Q+i)}}{(4\delta)^{l_P+l_Q} i!(l_P+l_Q-2r_P-2r_Q-2i)!} \end{aligned}$$

This will test your algebraic process!

Solution.

$$
\begin{aligned}
C_{RI_x} \times I_{k_x} =& \mathrm{i}^{l_P+l_Q}\left(\frac{\pi}{\gamma_P}\right)^{1/2}\left(\frac{\pi}{\gamma_Q}\right)^{1/2} l_P! l_Q! \epsilon_P^{l_P/2}\epsilon_Q^{l_Q/2} \times \sum_{r_P=0}^{\lfloor l_P/2\rfloor}\sum_{r_Q=0}^{\lfloor l_Q/2\rfloor} \frac{(-1)^{r_P}(2\sqrt{\epsilon_P})^{l_P-2r_P}}{r_P!(l_P-2r_P)!}\frac{(-1)^{r_Q}(-1\cdot 2\sqrt{\epsilon_Q})^{l_Q-2r_Q}}{r_Q!(l_Q-2r_Q)!} \\
&\times \left(\frac{\pi}{\delta}\right)^{1/2}\sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2\rfloor} \mathrm{i}^{(l_P-2r_P)+(l_Q-2r_Q)}\left(\frac{1}{2}\right)^{(l_P-2r_P)+(l_Q-2r_Q)} \\
&\times \left(\frac{1}{\delta}\right)^{l_P+l_Q-2(r_P+2r_Q)} \delta^i \vec{PQ}_x^{(l_P-2r_P)+(l_Q-2r_Q)-2i}\frac{(-1)^i(l_P-2r_P+l_Q-2r_Q)!}{i!(l_P-2r_P+l_Q-2r_Q-2i)!} \\
=& \left(\frac{\pi}{\gamma_P}\right)^{1/2}\left(\frac{\pi}{\gamma_Q}\right)^{1/2}\left(\frac{\pi}{\delta}\right)^{1/2} l_P! l_Q! \epsilon_P^{l_P/2}\epsilon_Q^{l_Q/2} \\
&\times \sum_{r_P=0}^{\lfloor l_P/2\rfloor}\sum_{r_Q=0}^{\lfloor l_Q/2\rfloor}\sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2\rfloor} \mathrm{i}^{l_P+l_Q}\mathrm{i}^{(l_P-2r_P)+(l_Q-2r_Q)}(-1)^{r_P+r_Q}(-1)^{l_Q-2r_Q} \\
&\times \left(\frac{1}{\delta}\right)^{l_P+l_Q-2(r_P+2r_Q)}\delta^i\left(\frac{1}{2}\right)^{(l_P-2r_P)+(l_Q-2r_Q)} 2^{(l_P-2r_P)+(l_Q-2r_Q)} \\
&\times \sqrt{\epsilon_P}^{l_P-2r_P}\sqrt{\epsilon_Q}^{l_Q-2r_Q}\frac{\vec{PQ}_x^{(l_P-2r_P)+(l_Q-2r_Q)-2i}}{r_P!(l_P-2r_P)!r_Q!(l_Q-2r_Q)!}\frac{(-1)^i(l_P-2r_P+l_Q-2r_Q)!}{i!(l_P-2r_P+l_Q-2r_Q-2i)!} \\
=& \left(\frac{\pi}{\gamma_P}\right)^{1/2}\left(\frac{\pi}{\gamma_Q}\right)^{1/2}\left(\frac{\pi}{\delta}\right)^{1/2} \\
&\times \sum_{r_P=0}^{\lfloor l_P/2\rfloor}\sum_{r_Q=0}^{\lfloor l_Q/2\rfloor}\sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2\rfloor} \overbrace{\mathrm{i}^{2(l_P-r_P+l_Q-r_Q)}}^{(-1)^{l_P+l_Q-r_P-r_Q}}(-1)^{r_P+r_Q}(-1)^{l_Q-2r_Q} \\
&\times \delta^{-(l_P+l_Q-2r_P-2r_Q)}\delta^i\epsilon_P^{(2l_P-2r_P)/2}\epsilon_Q^{(2l_Q-2r_Q)/2} \\
&\times \frac{\vec{PQ}_x^{(l_P-2r_P)+(l_Q-2r_Q)-2i}}{r_P!(l_P-2r_P)!r_Q!(l_Q-2r_Q)!}\frac{l_P!l_Q!(-1)^i(l_P-2r_P+l_Q-2r_Q)!}{i!(l_P-2r_P+l_Q-2r_Q-2i)!} \\
=& \left(\frac{\pi}{\gamma_P}\right)^{1/2}\left(\frac{\pi}{\gamma_Q}\right)^{1/2}\left(\frac{\pi}{\delta}\right)^{1/2} \\
&\times \sum_{r_P=0}^{\lfloor l_P/2\rfloor}\sum_{r_Q=0}^{\lfloor l_Q/2\rfloor}\sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2\rfloor} \overbrace{(-1)^{l_P+2(l_Q-2r_Q)}}^{(-1)^{l_P}} \\
&\times \delta^{-(l_P+l_Q)}\delta^{2(r_P+r_Q)}\delta^i(4\gamma_P)^{-(l_P-r_P)}(4\gamma_Q)^{-(l_Q-r_Q)} \\
&\times \frac{\vec{PQ}_x^{(l_P-2r_P)+(l_Q-2r_Q)-2i}}{r_P!(l_P-2r_P)!r_Q!(l_Q-2r_Q)!}\frac{l_P!l_Q!(-1)^i(l_P-2r_P+l_Q-2r_Q)!}{i!(l_P-2r_P+l_Q-2r_Q-2i)!} \\
=& \left(\frac{\pi}{\gamma_P}\right)^{1/2}\left(\frac{\pi}{\gamma_Q}\right)^{1/2}\left(\frac{\pi}{\delta}\right)^{1/2} \\
&\times \sum_{r_P=0}^{\lfloor l_P/2\rfloor}\sum_{r_Q=0}^{\lfloor l_Q/2\rfloor}\sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2\rfloor} (-1)^{l_P} \\
&\times (4\delta)^{-(l_P+l_Q)}(2\delta)^{2(r_P+r_Q)}\delta^i\gamma_P^{r_P-l_P}\gamma_Q^{r_Q-l_Q} \\
&\times \frac{\vec{PQ}_x^{(l_P-2r_P)+(l_Q-2r_Q)-2i}}{r_P!(l_P-2r_P)!r_Q!(l_Q-2r_Q)!}\frac{l_P!l_Q!(-1)^i(l_P-2r_P+l_Q-2r_Q)!}{i!(l_P-2r_P+l_Q-2r_Q-2i)!}
\end{aligned}
$$

Finally,

$$C_{RI_x} \times I_{k_x} = \left(\frac{\pi}{\gamma_P}\right)^{1/2} \left(\frac{\pi}{\gamma_Q}\right)^{1/2} \left(\frac{\pi}{\delta}\right)^{1/2} \times \sum_{r_P=0}^{\lfloor l_P/2 \rfloor} \sum_{r_Q=0}^{\lfloor l_Q/2 \rfloor} \sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2 \rfloor} \frac{l_P! \gamma^{r_P-l_P}}{r_P!(l_P-2r_P)!} \times \frac{l_Q! \gamma^{r_Q-l_Q}}{r_Q!(l_Q-2r_Q)!} \times \frac{(-1)^{l_P}(2\delta)^{2(r_P+r_Q)}(l_P+l_Q-2r_P-r_Q)! \delta^i \vec{PQ}_x^{\,l_P+l_Q-2(r_P+r_Q+i)}}{(4\delta)^{l_P+l_Q} i!(l_P+l_Q-2r_P-2r_Q-2i)!} \tag{110}$$

[end of solution]

Exercise.
From Eq. 110 of the previous exercise, extract the first line of square root constants. These will have identical form in $C_{RI_y} \times I_{k_y}$ and $C_{RI_z} \times I_{k_z}$. That is, across $C_{RI_x} I_{k_x} C_{RI_y} I_{k_y} C_{RI_z} I_{k_z}$, we will have the factor

$$\left(\frac{\pi}{\gamma_P}\right)^{3/2} \left(\frac{\pi}{\gamma_Q}\right)^{3/2} \left(\frac{\pi}{\delta}\right)^{3/2}.$$

Show that the product of this and the first factor that appears in the last line of G_{RI} (Eq. 109), (δ/π^2), is

$$\frac{2\pi^2}{\gamma_P \gamma_Q} \left(\frac{\pi}{\gamma_P+\gamma_Q}\right)^{1/2}.$$

Solution.

$$\left(\frac{\pi}{\gamma_P}\right)^{3/2} \left(\frac{\pi}{\gamma_Q}\right)^{3/2} \left(\frac{\pi}{\delta}\right)^{3/2} \times \frac{\delta}{\pi^2} = \pi^3 (\gamma_P\gamma_Q)^{-3/2} \pi^{3/2} \cdot \delta^{-3/2} \frac{\delta}{\pi^2}$$

$$= \pi (\gamma_P\gamma_Q)^{-3/2} \pi^{3/2} \cdot \overbrace{\delta^{-3/2}\delta}^{\delta^{-1/2}}$$

Because

$$\delta = \left(\frac{1}{4\gamma_P}\right) + \left(\frac{1}{4\gamma_Q}\right) = \frac{4(\gamma_P+\gamma_Q)}{16\gamma_P\gamma_Q} = \frac{\gamma_P+\gamma_Q}{4\gamma_P\gamma_Q},$$

then

$$\delta^{-1/2} = \left(\frac{4\gamma_P\gamma_Q}{\gamma_P+\gamma_Q}\right)^{1/2}.$$

Thus,

$$\pi (\gamma_P\gamma_Q)^{-3/2} \pi^{3/2} \left(\frac{4\gamma_P\gamma_Q}{\gamma_P+\gamma_Q}\right)^{1/2} = \frac{2\pi^2}{\gamma_P\gamma_Q} \left(\frac{\pi}{\gamma_P+\gamma_Q}\right)^{1/2}.$$

[end of solution]

Consider $C_{RI_x} \times I_{k_x}$ (Eq. 110) with the factors featuring π removed, as in the last exercise. When we multiply this by the x-component coefficients c_{l_P} and c_{l_Q}, which are factors of G_{RI} in the expression for G

(Eq. 88), then we have what we might call $C'_{RI_x} \times I'_{k_x}$:

$$\begin{aligned} C'_{RI_x} \times I'_{k_x} = & \sum_{r_P=0}^{\lfloor l_P/2 \rfloor} \sum_{r_Q=0}^{\lfloor l_Q/2 \rfloor} \sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2 \rfloor} \frac{l_P! \gamma^{r_P-l_P} \cdot c_{l_P}}{r_P!(l_P-2r_P)!} \times \frac{l_Q! \gamma^{r_Q-l_Q} \cdot c_{l_Q}}{r_Q!(l_Q-2r_Q)!} \\ & \times \frac{(-1)^{l_P} (2\delta)^{2(r_P+r_Q)} (l_P+l_Q-2r_P-r_Q)! \delta^i \vec{PQ}_x^{\,l_P+l_Q-2(r_P+r_Q+i)}}{(4\delta)^{l_P+l_Q} i!(l_P+l_Q-2r_P-2r_Q-2i)!} \\ = & \sum_{r_P=0}^{\lfloor l_P/2 \rfloor} \sum_{r_Q=0}^{\lfloor l_Q/2 \rfloor} \sum_{i=0}^{\lfloor (l_P-2r_P+l_Q-2r_Q)/2 \rfloor} \theta_P \times \theta_Q \\ & \times \frac{(-1)^{l_P} (2\delta)^{2(r_P+r_Q)} (l_P+l_Q-2r_P-r_Q)! \delta^i \vec{PQ}_x^{\,l_P+l_Q-2(r_P+r_Q+i)}}{(4\delta)^{l_P+l_Q} i!(l_P+l_Q-2r_P-2r_Q-2i)!}, \end{aligned} \tag{111}$$

where

$$\theta = \frac{l! \gamma^{r-l} \cdot c_l}{r!(l-2r)!} \tag{112}$$

As such, by incorporating the results of the previous exercise and the new definitions C'_{RI} and I'_k,

$$\begin{aligned} G = & \widetilde{K}_P \widetilde{K}_Q \\ & \times \sum_{l_P=0}^{l_A+l_B} \sum_{m_P=0}^{m_A+m_B} \sum_{n_P=0}^{n_A+n_B} c_{l_P} c_{m_P} c_{n_P} \\ & \times \sum_{l_Q=0}^{l_A+l_B} \sum_{m_Q=0}^{m_A+m_B} \sum_{n_Q=0}^{n_A+n_B} c_{l_Q} c_{m_Q} c_{n_Q} \\ & \times G_{RI} \\ = & \frac{2\pi^2}{\gamma_P \gamma_Q} \left(\frac{\pi}{\gamma_P+\gamma_Q} \right)^{1/2} \widetilde{K}_P \widetilde{K}_Q \\ & \times \sum_{l_P=0}^{l_A+l_B} \sum_{l_Q=0}^{l_A+l_B} C'_{RI_x} \times I'_{k_x} \\ & \times \sum_{m_P=0}^{m_A+m_B} \sum_{m_Q=0}^{m_A+m_B} C'_{RI_y} \times I'_{k_y} \\ & \times \sum_{n_P=0}^{n_A+n_B} \sum_{n_Q=0}^{n_A+n_B} C'_{RI_z} \times I'_{k_z} \\ & \times F_\nu[\vec{PQ}^{\,2}/(4\delta)]. \end{aligned} \tag{113}$$

Only a few steps remain.

Exercise.
Complete the derivation of G by performing the following rearrangements.

1. Extract the summation symbols from every C'_{RI} and I'_{k_x}, and fuse the remaining part of C'_{RI} and I'_k to create expressions labelled g_x, g_y, and g_z.
2. Move the summation symbols into Eq. 113, alongside g_x, g_y, and g_z, so that there are five summation symbols per coordinate, for a total of 15.
3. Collect the terms containing π and $\widetilde{K}$ (*i.e.*, the first line in the last equality of Eq. 113) into a new term called Ω.
4. Show the final expression for G in terms of this rearrangement of Eq. 113 and its new set of definitions.
5. As a separate, one-line equation, show the expression for $(AB|CD)$ in terms of G.

Solution.

Essential Equation

$$(AB|CD) = \sum_{a=1}^{K_a}\sum_{b=1}^{K_b}\sum_{c=1}^{K_c}\sum_{d=1}^{K_d} \mathrm{d}_a \mathrm{d}_b \mathrm{d}_c \mathrm{d}_d N_a N_b N_c N_d \times G \tag{114}$$

Essential Equation

$$\begin{aligned} G =& \Omega \sum_{l_P=0}^{l_A+l_B}\sum_{r_P=0}^{\lfloor l_P/2\rfloor}\sum_{l_Q=0}^{l_C+l_D}\sum_{r_Q=0}^{\lfloor l_Q/2\rfloor}\sum_{i=0}^{\lfloor (l_P+l_Q-2r_P-2r_Q)/2\rfloor} g_x \\ &\times \sum_{m_P=0}^{m_A+m_B}\sum_{s_P=0}^{\lfloor m_P/2\rfloor}\sum_{m_Q=0}^{m_C+m_D}\sum_{s_Q=0}^{\lfloor m_Q/2\rfloor}\sum_{j=0}^{\lfloor (m_P+m_Q-2s_P-2r_Q)/2\rfloor} g_y \\ &\times \sum_{n_P=0}^{n_A+n_B}\sum_{t_P=0}^{\lfloor n_P/2\rfloor}\sum_{n_Q=0}^{n_C+n_D}\sum_{t_Q=0}^{\lfloor n_Q/2\rfloor}\sum_{k=0}^{\lfloor (n_P+n_Q-2t_Q-2t_Q)/2\rfloor} g_z \\ &\times F_\nu(|\vec{PQ}|^2/4\delta) \end{aligned} \tag{115}$$

$$\nu = l_P + l_Q + m_P + m_Q + n_P + n_Q - 2(r_P + r_Q + s_P + s_Q + t_P + t_Q) - (i + j + k)$$

$$\delta = \frac{1}{4\gamma_P} + \frac{1}{4\gamma_Q}$$

where

Essential Equation

$$\Omega = \frac{2\pi^2}{\gamma_P\gamma_Q}\left(\frac{\pi}{\gamma_P+\gamma_Q}\right)^{1/2} \exp\left(-\frac{\alpha_a\alpha_b}{\gamma_P}|\vec{AB}|^2\right)\exp\left(-\frac{\alpha_c\alpha_d}{\gamma_Q}|\vec{CD}|^2\right) \tag{116}$$

and for the x-components

Essential Equation

$$
\begin{aligned}
g_x \equiv & \, g_{l_P,l_Q,r_P,r_Q,i}(l_A, l_B, \vec{A}_x, \vec{B}_x, \vec{P}_x, \gamma_P; l_C, l_D, \vec{C}_x, \vec{D}_x, \vec{Q}_x, \gamma_Q) \\
= & (-1)^{l_P} \cdot \theta(l_P, l_A, l_B, \vec{PA}_x, \vec{PB}_x, r, \gamma_P) \cdot \theta(l_Q, l_C, l_D, \vec{QC}_x, \vec{QD}_x, r_Q, \gamma_Q) \\
& \times \frac{(-1)^i (2\delta)^{2(r_P+r_Q)} (l_P + l_Q - 2r_P - 2r_Q)! \delta^i \vec{PQ}_x^{\,l_P+l_Q-2(r_P+r_Q+i)}}{(4\delta)^{l_P+l_Q} i! [l_P + l_Q - 2(r_P + r_Q + i)]!}
\end{aligned}
\tag{117}
$$

$$
\theta(l, l_A, l_B, a, b, \gamma) = c_l(l_A, l_B, a, b) \frac{l! \gamma^{r-l}}{r!(l-2r)!} \tag{118}
$$

with analogous expressions for the other two g factors.
[end of solution]

Congratulations! You have derived the code-able solutions to the molecular integrals. You are ready to proceed to Handout 3 (or Handout 4 if you are an experienced programmer) and implement them in computer code.