# Contents

# 1 Elementary Basis Function Analysis

## 1.1 Normalization

As you no doubt are aware, the standard basis functions used in *ab initio* MO theory are cartesian gaussian functions, or linear combinations thereof.

$$\phi_\mu(\mathbf{r}) = x^l y^m z^n e^{-\alpha \mathbf{r}^2} \tag{1.1}$$

This is a basis function of angular momentum $(l+m+n)$ centered at the origin, with orbital exponent $\alpha$. Standard notation. These atomic orbital–like basis functions need not be othogonal to one another, but for later convenience, it would be nice to have them normalized. Thus impose the condition

$$\int \phi_\mu^*(\mathbf{r})\phi_\mu(\mathbf{r})d\mathbf{r} = 1. \tag{1.2}$$

Just for fun and to warm up some, evaluate this integral. Assume a Normalization constant of $N$ for $\phi_\mu$, and call 1.2 a self–overlap integral, SO.

$$\begin{aligned} \mathrm{SO} &= \int N^2(x^l y^m z^n e^{-\alpha\mathbf{r}^2})(x^l y^m z^n e^{-\alpha\mathbf{r}^2})d\mathbf{r} && (1.3)\\ &= N^2 \int x^{2l} y^{2m} z^{2n} e^{-2\alpha\mathbf{r}^2} d\mathbf{r} && (1.4) \end{aligned}$$

This integral over all space is separable when done in cartesian coordinates (one of the reasons for using gaussian rather than slater orbitals). Using $\mathbf{r}^2 = x^2 + y^2 + z^2$ and $d\mathbf{r} = dxdydz$, we get

$$\begin{aligned} \mathrm{SO} &= N^2 \int dx x^{2l} e^{-2\alpha x^2} \int dy y^{2m} e^{-2\alpha y^2} \int dz z^{2n} e^{-2\alpha z^2} && (1.5)\\ &= N^2 I_x I_y I_z && (1.6) \end{aligned}$$

Full derivation of these integrals ($I_x$, etc) can be found in Appendix I. The result is that we find

$$I_x = \int_{-\infty}^{\infty} dx x^{2l} e^{-2\alpha x^2} = \frac{(2l-1)!!\sqrt{\pi}}{(4\alpha)^l\sqrt{2\alpha}}. \tag{1.7}$$

Recall that $(2l-1)!! = 1 \cdot 3 \cdot 5 \cdots (2l-1)$. Thus

$$\mathrm{SO} = N^2 \left[ \frac{(2l-1)!!(2m-1)!!(2n-1)!!\pi^{3/2}}{(4\alpha)^{(l+m+n)}(2\alpha)^{3/2}} \right] = 1 \tag{1.8}$$

Rearranging that to solve for $N$, the normalization constant,

$$N = \left[ \left( \frac{2}{\pi} \right)^{3/4} \frac{2^{(l+m+n)}\alpha^{(2l+2m+2n+3)/4}}{[(2l-1)!!(2m-1)!!(2n-1)!!]^{1/2}} \right] \tag{1.9}$$

This result is completly general – for uncontracted functions. But before we go on to contrations, let's consider the product of two gaussian functions on different centers.

### 1.2 The Gaussian Product Theorem

The Gaussian Product Theorem states that the product of two arbitrary angular momentum gaussian functions on different centers can be written as

$$\begin{aligned} G_1G_2 &= G_1(\alpha_1, \mathbf{A}, l_1, m_1, n_1)G_2(\alpha_2, \mathbf{B}, l_2, m_2, n_2) \\ &= \exp[-\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma] \times \\ &\quad \left[ \sum_{i=0}^{l_1+l_2} f_i(l_1, l_2, \overline{\mathbf{PA}}_x, \overline{\mathbf{PB}}_x) x_P^i e^{-\gamma x_P^2} \right] \times \\ &\quad \left[ \sum_{j=0}^{m_1+m_2} f_j(m_1, m_2, \overline{\mathbf{PA}}_y, \overline{\mathbf{PB}}_y) y_P^j e^{-\gamma y_P^2} \right] \times \\ &\quad \left[ \sum_{k=0}^{n_1+n_2} f_k(n_1, n_2, \overline{\mathbf{PA}}_z, \overline{\mathbf{PB}}_z) z_P^k e^{-\gamma z_P^2} \right]. \end{aligned} \tag{1.10}$$

To show this, we first define the multiplicands as

$$G_1 = G_1(\alpha_1, \mathbf{A}, l_1, m_1, n_1) = x_A^{l_1} y_A^{m_1} z_A^{n_1} e^{-\alpha_1 \mathbf{r}_A^2} \tag{1.11}$$

$$G_2 = G_2(\alpha_2, \mathbf{B}, l_2, m_2, n_2) = x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_2 \mathbf{r}_B^2}. \tag{1.12}$$

Here, $\mathbf{r}_A = \mathbf{r} - \mathbf{A}$, etc. For primary analysis, take the angular momentum of $G_1$ and $G_2$ to be zero, so

$$G_1 = e^{-\alpha_1 \mathbf{r}_A^2}; \qquad G_2 = e^{-\alpha_2 \mathbf{r}_B^2}. \tag{1.13}$$

These are unnormalized, but normalization can be calculated as in section 1.1. It would be convenient if this product could be written as a third gaussian, ie. $G_1 \cdot G_2 = G_3$, or

$$e^{-\alpha_1 \mathbf{r}_A^2} e^{-\alpha_2 \mathbf{r}_B^2} = K e^{-\gamma \mathbf{r}_P^2}. \tag{1.14}$$

Expand equation 1.14 using the definition of $\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_P$ given above.

$$\begin{aligned}
e^{-\alpha_1 \mathbf{r}_A^2 - \alpha_2 \mathbf{r}_B^2} &= \exp[-(\alpha_1 + \alpha_2)\mathbf{r} \cdot \mathbf{r} + 2(\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B}) \cdot \mathbf{r} \\
&\quad -\alpha_1 \mathbf{A} \cdot \mathbf{A} - \alpha_2 \mathbf{B} \cdot \mathbf{B}] && (1.15) \\
&= K \exp[-\gamma(\mathbf{r} \cdot \mathbf{r} - \mathbf{r} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{P})] && (1.16)
\end{aligned}$$

Comparing terms,

$$\begin{aligned}
\gamma &= \alpha_1 + \alpha_2 \\
\gamma \mathbf{P} &= (\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B}), \text{thus} \quad \mathbf{P} = \frac{\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B}}{\gamma} && (1.17)
\end{aligned}$$

which leads to the conclusion that

$$\begin{aligned}
K e^{-\gamma \mathbf{P} \cdot \mathbf{P}} &= e^{-\alpha_1 \mathbf{A} \cdot \mathbf{A} - \alpha_2 \mathbf{B} \cdot \mathbf{B}} && (1.18) \\
K &= e^{-\alpha_1 \mathbf{A} \cdot \mathbf{A} - \alpha_2 \mathbf{B} \cdot \mathbf{B} + \gamma \mathbf{P} \cdot \mathbf{P}} && (1.19)
\end{aligned}$$

From equation 1.17, we expand $\mathbf{P} \cdot \mathbf{P}$ and use that to get a final expression for $K$,

$$\begin{aligned}
\gamma \mathbf{P} \cdot \mathbf{P} &= \gamma^{-1} \left[\alpha_1^2 \mathbf{A} \cdot \mathbf{A} + 2\alpha_1 \alpha_2 \mathbf{A} \cdot \mathbf{B} + \alpha_2^2 \mathbf{B} \cdot \mathbf{B}\right] && (1.20) \\
K &= \exp\left[-\alpha_1 \mathbf{A} \cdot \mathbf{A} - \alpha_2 \mathbf{B} \cdot \mathbf{B} + (\alpha_1^2 \mathbf{A} \cdot \mathbf{A} + 2\alpha_1 \alpha_2 \mathbf{A} \cdot \mathbf{B} + \alpha_2^2 \mathbf{B} \cdot \mathbf{B})/\gamma\right] \\
&= \exp\left[(-\alpha_1^2 \mathbf{A} \cdot \mathbf{A} - \alpha_1 \alpha_2 \mathbf{A} \cdot \mathbf{A} - \alpha_1 \alpha_2 \mathbf{B} \cdot \mathbf{B} - \alpha_2^2 \mathbf{B} \cdot \mathbf{B} \right. \\
&\quad \left. + \alpha_1^2 \mathbf{A} \cdot \mathbf{A} + 2\alpha_1 \alpha_2 \mathbf{A} \cdot \mathbf{B} + \alpha_2^2 \mathbf{B} \cdot \mathbf{B})\gamma^{-1}\right] \\
&= e^{-[\alpha_1 \alpha_2 (\overline{\mathbf{AB}}^2)/\gamma]} && (1.21)
\end{aligned}$$

if we define $\overline{\mathbf{AB}} = (\mathbf{A} - \mathbf{B})$. For two 1–s orbitals,

$$e^{-\alpha_1 \mathbf{r}_A^2} e^{-\alpha_2 \mathbf{r}_B^2} = \exp\left[-\alpha_1\alpha_2(\overline{\mathbf{AB}}^2)/\gamma\right] \exp\left[-\gamma(\mathbf{r}-\mathbf{P})^2\right] \tag{1.22}$$

For more general Cartesian gaussians, ones with arbitrary angular momentum,

$$G_1 G_2 = x_A^{l_1} x_B^{l_2} y_A^{m_1} y_B^{m_2} z_A^{n_1} z_B^{n_2} \underbrace{e^{-(\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma)}}_{K} e^{\gamma \mathbf{r}_P^2} \tag{1.23}$$

where we've used equation 1.22 to take care of the product of the exponentials. Now, $x_A^{l_1}, x_B^{l_2}$ and the like need to be considered.

$$\begin{aligned} x_A^{l_1} x_B^{l_2} &= (x - A_x)^{l_1}(x - B_x)^{l_2} &(1.24)\\ (x - A_x)^{l_1} &= \left[(x - P_x) + (P_x - A_x)\right]^{l_1} = (x_P - (\overline{\mathbf{PA}})_x)^{l_1}. &(1.25)\end{aligned}$$

Using a standard binomial expansion,

$$(x_P - (\overline{\mathbf{PA}})_x)^{l_1} = \sum_{i=0}^{l_1} (x_P)^i (\overline{\mathbf{PA}})_x^{l_1 - i} \frac{l_1!}{i!(l_1 - i)!} = \sum_{i=0}^{l_1} (x_P)^i (\overline{\mathbf{PA}})_x^{l_1 - i} \left(\begin{array}{c} l_1 \\ i \end{array}\right) \tag{1.26}$$

Likewise,

$$(x - B_x)^{l_2} = (x_P - (\overline{\mathbf{PB}})_x)^{l_2} = \sum_{j=0}^{l_2} (x_P)^j (\overline{\mathbf{PB}})_x^{l_2 - j} \left(\begin{array}{c} l_2 \\ j \end{array}\right). \tag{1.27}$$

Using these, we can write $x_A^{l_1} x_B^{l_2}$ as a summation of $x_P$ to various powers.

$$x_A^{l_1} x_B^{l_2} = \sum_{k=0}^{l_1 + l_2} x_P^k f_k(l_1, l_2, (\overline{\mathbf{PA}})_x, (\overline{\mathbf{PB}})_x). \tag{1.28}$$

The coefficient of $x_P^k$ in the product $x_A^{l_1} x_B^{l_2}$ is given by

$$f_k(l_1, l_2, \overline{\mathbf{PA}}_x, \overline{\mathbf{PB}}_x) = \sum_{i=0,l_1}^{i+j=k} \sum_{j=0,l_2} (\overline{\mathbf{PA}})_x^{l_1 - i} \left(\begin{array}{c} l_1 \\ i \end{array}\right) (\overline{\mathbf{PB}})_x^{l_2 - j} \left(\begin{array}{c} l_2 \\ j \end{array}\right) \tag{1.29}$$

Perhaps more conveniently for implementing in a computational scheme, $f_k$ can be redefined as

$$\begin{aligned}
f_k &= \sum_{q=\max(-k,k-2l_2)}^{\min(k,2l_1-k)^*} \begin{pmatrix} l_1 \\ i \end{pmatrix} \begin{pmatrix} l_2 \\ j \end{pmatrix} (\overline{\mathbf{PA}})_x^{l_1-i} (\overline{\mathbf{PB}})_x^{l_2-j} \qquad (1.30) \\
2i &= k+q \\
2j &= k-q \\
& \quad {}^*\text{increments of 2}
\end{aligned}$$

Whence we write the full Gaussian Product Theorem as equation 1.10. A derivation of equation 1.30 might be found in appendix II.

### 1.3 Products of Contracted Cartesian Gaussians

Examine some contracted 1–s functions. Let

$$\phi(\mathbf{r}) = N \sum_i^n a_i e^{-\alpha_i \mathbf{r}^2} \qquad (1.31)$$

where $n$ is the number of primitive functions in the contracted function $\phi(\mathbf{r})$, and $a_i$ are the contraction coefficients. The product $\phi^*(\mathbf{r})\phi(\mathbf{r})$ can be written

$$\phi^*(\mathbf{r})\phi(\mathbf{r}) = N^2 \left[ \sum_i^n a_i e^{-\alpha_i \mathbf{r}^2} \sum_j^n a_j e^{-\alpha_j \mathbf{r}^2} \right]. \qquad (1.32)$$

Since the bracketed term contains a product of two polynomials, only two types of terms can result; the square of each uncontracted function and the products of all different pairs of uncontracted functions. Take an example where $n$ is three:

$$\begin{aligned}
[a_1 e^{-\alpha_1 \mathbf{r}^2} + a_2 e^{-\alpha_2 \mathbf{r}^2} + a_3 e^{-\alpha_3 \mathbf{r}^2}]^2 &= [a_1^2 e^{-2\alpha_1 \mathbf{r}^2} + a_2^2 e^{-2\alpha_2 \mathbf{r}^2} + a_3^2 e^{-2\alpha_3 \mathbf{r}^2} \\
& +2\alpha_1\alpha_2 e^{-(\alpha_1+\alpha_2)\mathbf{r}^2} + 2\alpha_1\alpha_3 e^{-(\alpha_1+\alpha_3)\mathbf{r}^2} \\
& +2\alpha_2\alpha_3 e^{-(\alpha_2+\alpha_3)\mathbf{r}^2}] \qquad (1.33)
\end{aligned}$$

In this case, as in all others, there are only two types of terms of which the integral needs to be taken. They may be written and evaluated as

$$1. \int a_i^2 e^{-2\alpha_i \mathbf{r}^2} d\mathbf{r} = a_i^2 \left(\frac{\pi}{2\alpha_i}\right)^{3/2} \tag{1.34}$$

$$2. \int 2a_i a_j e^{-(\alpha_i+\alpha_j)\mathbf{r}^2} d\mathbf{r} = 2a_i a_j \left(\frac{\pi}{\alpha_i+\alpha_j}\right)^{3/2}. \tag{1.35}$$

It is realized that 1. above can be obtained by setting $i = j$ in 2., and henceforth only the general case need be considered. Generalizing to arbitrary $n$ is straightforward, and so the normalization of contracted gaussian functions can proceed as

$$\begin{aligned} \int \phi^*(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} &= N^2\pi^{3/2}\left[\frac{a_1^2}{(2\alpha_1)^{3/2}} + \cdots + \frac{2\alpha_1\alpha_2}{(\alpha_1+\alpha_2)^{3/2}} + \cdots\right] \\ &= N^2\pi^{3/2}\sum_i^n\sum_j^n \frac{a_i a_j}{(\alpha_i+\alpha_j)^{3/2}} = 1, \end{aligned} \tag{1.36}$$

thus the normalization constant for the entire contraction will be

$$N = \pi^{-3/4}\left[\sum_{i,j}^n \frac{a_i a_j}{(\alpha_i+\alpha_j)^{3/2}}\right]^{-1/2} \tag{1.37}$$

General contractions (of arbitrary angular momentum) are a tad worse, but if we assume all of the contracted functions to be of the same angular momentum

$$\begin{aligned} \phi(\mathbf{r}) &= N\left[a_1 x^l y^m z^n e^{-\alpha_1\mathbf{r}^2} + a_2 x^l y^m z^n e^{-\alpha_2\mathbf{r}^2} + \cdots\right] \\ &= N x^l y^m z^n \sum_i^n a_i e^{-\alpha_i\mathbf{r}^2} \end{aligned} \tag{1.38}$$

$$\int \phi^*(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} = N^2 \int x^{2l}y^{2m}z^{2n}\left[\sum_i^n a_i e^{-\alpha_i\mathbf{r}^2} \cdot \sum_j^n a_j e^{-\alpha_j\mathbf{r}^2}\right] d\mathbf{r} \tag{1.39}$$

$$\int \phi^*(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} = N^2 \sum_{i=o}^n \sum j = 0^n \left[x^{2l}y^{2m}z^{2n}e^{-\alpha_i\mathbf{r}^2}e^{-\alpha_2\mathbf{r}^2}\right] \tag{1.40}$$

The product in brackets in equation 1.40 we've encountered before. Analogous to equation 1.7, the general form for one integral in the double sum is

$$\int x^{2l} y^{2m} z^{2n} a_i^2 e^{-2\alpha_i \mathbf{r}^2} d\mathbf{r} = a_i^2 \pi^{3/2} \frac{(2l-1)!!(2m-1)!!(2n-1)!!}{2^{(l+m+n)}(2\alpha_i)^{(l+m+n+3/2)}}. \tag{1.41}$$

Thus the product can be written as one sum if we're clever. The self overlap is then

$$\int \phi^*(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} = \frac{N^2\pi^{3/2}(2l-1)!!(2m-1)!!(2n-1)!!}{2^{l+m+n}} \sum_{i,j}^{n} \frac{a_i a_j}{(\alpha_i+\alpha_j)^{l+m+n+3/2}}. \tag{1.42}$$

Calling $l+m+n=L$, the angular momentum of the shell, and solving for $N$,

$$\int \phi^*\phi = \frac{N^2\pi^{3/2}(2l-1)!!(2m-1)!!(2n-1)!!}{2^L} \sum_{i,j}^{n} \frac{a_i a_j}{(\alpha_i+\alpha_j)^{L+3/2}} = 1 \tag{1.43}$$

$$N = \left[\frac{\pi^{3/2}(2l-1)!!(2m-1)!!(2n-1)!!}{2^L} \sum_{i,j}^{n} \frac{a_i a_j}{(\alpha_i+\alpha_j)^{L+3/2}}\right]^{-1/2} \tag{1.44}$$

## 2 $\mathbf{S}_{ij}$ – Overlap Integrals

### 2.1 Overlap of primitive $1s$ functions on different centers

$$\int \phi_1^*(\mathbf{r})\phi_2(\mathbf{r})d\mathbf{r} = \int e^{-\alpha_1 \mathbf{r}_A^2} e^{-\alpha_2 \mathbf{r}_B^2} d\mathbf{r} \tag{2.1}$$

Using the gaussian product theorem as it appears in equation 1.22

$$\begin{aligned} S_{12} &= \int e^{-\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma} e^{-\gamma \mathbf{r}_P^2} d\mathbf{r} && (2.2) \\ &= e^{-\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma} \int_{-\infty}^{\infty} e^{-\gamma x_P^2} dx \int_{-\infty}^{\infty} e^{-\gamma y_P^2} dy \int_{-\infty}^{\infty} e^{-\gamma z_P^2} dz && (2.3) \\ S_{12} &= e^{-\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma} \left(\frac{\pi}{\gamma}\right)^{3/2} && (2.4) \end{aligned}$$

### 2.2 Overlap of generally contracted $1s$ functions

Take now $\phi_1(\mathbf{r})$ to be centered on $\mathbf{A}$ and $\phi_2(\mathbf{r})$ to be centered on $\mathbf{B}$, as

$$\phi_1(\mathbf{r}) = N_1 \sum_i^n a_i e^{-\alpha_i \mathbf{r}_A^2}, \phi_2(\mathbf{r}) = N_2 \sum_j^m b_j e^{-\beta_j \mathbf{r}_B^2} \tag{2.5}$$

$$S_{12} = \int \phi_1^*(\mathbf{r})\phi_2(\mathbf{r})d\mathbf{r} = N_1 N_2 \sum_i^n \sum_j^m a_i b_j \int e^{-\alpha_i \mathbf{r}_A^2} e^{-\beta_j \mathbf{r}_B^2} d\mathbf{r} \tag{2.6}$$

Examining one term in the double sum,

$$\begin{aligned} \int e^{-\alpha_i \mathbf{r}_A^2} e^{-\beta_j \mathbf{r}_B^2} d\mathbf{r} &= \int e^{-\alpha_i\beta_j(\overline{\mathbf{AB}})^2/\gamma} e^{-\gamma \mathbf{r}_P^2} d\mathbf{r} && (2.7) \\ &= e^{-\alpha_i\beta_j(\overline{\mathbf{AB}})^2/\gamma_{ij}} \left(\frac{\pi}{\gamma_{ij}}\right)^{3/2} && (2.8) \end{aligned}$$

where $\gamma_{ij} = \alpha_i + \beta_j$ and $\mathbf{P}_{ij} = \frac{\alpha_i \mathbf{A} + \beta_j \mathbf{B}}{\gamma_{ij}}$. So

$$S_{12} = N_1 N_2 \sum_i^n \sum_j^m a_i b_j e^{-\alpha_i\beta_j(\overline{\mathbf{AB}})^2/\gamma_{ij}} \left[\frac{\pi}{\gamma_{ij}}\right]^{3/2} \tag{2.9}$$

### 2.3 Overlap of primitive arbitrary angular momentum functions

Overlap of arbitrary–$l$ functions:

$$\begin{aligned} S_{12} &= \int G_1(\alpha_1, \mathbf{A}, l_1, m_1, n_1) G_2(\alpha_2, \mathbf{B}, l_2, m_2, n_2) d\mathbf{r} && (2.10) \\ &= \int x_A^{l_1} x_B^{l_2} y_A^{m_1} y_B^{m_2} z_A^{n_1} z_B^{n_2} \exp[-\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma] e^{-\gamma x_P^2} e^{-\gamma y_P^2} e^{-\gamma z_P^2} && (2.11) \end{aligned}$$

with $\gamma$ and $\mathbf{P}$ defined as before. Applying the fullness of the gaussian product theorem (equation 1.10),

$$S_{12} = \exp[-\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma] I_x I_y I_z. \tag{2.12}$$

where

$$\begin{aligned} I_x &= \int \sum_{i=0}^{l_1+l_2} f_i(l_1, l_2, \overline{\mathbf{PA}}_x, \overline{\mathbf{PB}}_x) x_P^i e^{-\gamma x_P^2} dx && (2.13) \\ &= \sum_{i=0}^{l_1+l_2} f_i(l_1, l_2, \overline{\mathbf{PA}}_x, \overline{\mathbf{PB}}_x) \int_{-\infty}^{\infty} x_P^i e^{-\gamma x_P^2} dx && (2.14) \end{aligned}$$

Noting that any odd value of $i$ produces a zero integral, and then using equation 1.41 for $\int x_P^i e^{-\gamma x_P^2} dx$,

$$I_x = \sum_{i=0}^{(l_1+l_2)/2} f_{2i}(l_1, l_2, \overline{\mathbf{PA}}_x, PB_x) \frac{(2i-1)!!}{(2\gamma)^i} \left(\frac{\pi}{\gamma}\right)^{1/2} \tag{2.15}$$

by equation 860.17 in Dwight.

## 3 $T_{ij}$–Kinetic Energy Integrals

### 3.1 $\nabla^2\phi(\mathbf{r})$

The kinetic energy operator is $-\frac{1}{2}\nabla^2$, or $-\frac{1}{2}(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$ in cartesian coordinates. So the kinetic energy integral over general, uncontracted gaussian functions is

$$\begin{aligned}
\mathbf{T}_{12} &= \int \phi_1^*(\mathbf{r})(-\frac{1}{2}\nabla^2)\phi_2 d\mathbf{r} \\
&= -\frac{1}{2}\int x_A^{l_1} y_A^{m_1} z_A^{n_1} e^{-\alpha_1 r_A^2}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_1 r_A^2} d\mathbf{r} \\
&= I_x + I_y + I_z
\end{aligned} \tag{3.1}$$

where we now define $I_x$ as

$$I_x = -\frac{1}{2}\int x_A^{l_1} y_A^{m_1} z_A^{n_1} e^{-\alpha_1 r_A^2}(\frac{\partial^2}{\partial x^2}) x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_1 r_A^2} d\mathbf{r} \tag{3.2}$$

Now we need to determine the action of the lagrangian (or any piece thereof) on a particular gaussian function. Sequentially applying the differential operator,

$$\frac{\partial}{\partial x}(x_B^{l_2} e^{-\alpha_2 x_B^2}) = l_2 x_B^{l_2-1} e^{-\alpha_2 x_B^2} - 2\alpha_2 x_B^{l_2+1} e^{-\alpha_2 x_B^2} \tag{3.3}$$

$$\begin{aligned}
\frac{\partial}{\partial x}(\frac{\partial}{\partial x}(x_B^{l_2} e^{-\alpha_2 x_B^2})) &= l_2(l_2-1) x_B^{l_2-2} e^{-\alpha_2 x_B^2} + \alpha_2(2l_2+1) x_B^{l_2} e^{-\alpha_2 x_B^2} \\
&\quad -2\alpha_2(l_2+1) x_B^{l_2} e^{-\alpha_2 x_B^2} + 4\alpha_2^2 x_B^{l_2+2} e^{-\alpha_2 x_B^2}
\end{aligned} \tag{3.4}$$

$$\begin{aligned}
-\frac{1}{2}\frac{\partial^2}{\partial x^2}(x_b^{l_2} e^{-\alpha_2 x_B^2}) &= -\frac{l_2(l_2-1)}{2} x_B^{l_2-2} e^{-\alpha_2 x_B^2} \\
&\quad +\alpha_2(2l_2+1) x_B^{l_2} e^{-\alpha_2 x_B^2} - 2\alpha_2^2 x_B^{l_2+2} e^{-\alpha_2 x_B^2}
\end{aligned} \tag{3.5}$$

Clearly, this is just a sum of three gaussian functions related to the original by a shift of 0, 2, or -2 in the angular momentum portion, aside from some constants.

### 3.2 Asymmetric form of $T_{ij}$

Simply applying the results shown in equation 3.5 within equation 3.1 gives a form of $T_{ij}$ which appears as a sum of three overlap–type integrals with various multiplicative constants. To display the particular overlap integrals involved in that sum we will use a particular notation derived from the bra and ket notation common in physics. Let $\langle \pm n|_\gamma$ denote a gaussian where the angular momentum has been increased or decreased by $n$ in the $\gamma$ coordinate. In other words,

$$\langle +2|_x = x^{l+2} y^m z^n e^{-\alpha r^2} \tag{3.6}$$

Thus, given that the overlap between two gaussians $G_1$ and $G_2$ is

$$\int G_1 G_2 = \langle 0|0\rangle, \tag{3.7}$$

the construction $\langle 0| + 2\rangle_x$ denotes an overlap integral between $G_1$ and a gaussian derived from $G_2$ by incrementing the exponent of $x$ by 2. In this way, we can write the asymmetric form of the kinetic energy integral using equations 3.2 and 3.5 as

$$I_x = \alpha_2(2l_2+1)\langle 0|0\rangle - 2\alpha_2^2\langle 0| + 2\rangle_x - \frac{l_2(l_2-1)}{2}\langle 0| - 2\rangle_x \tag{3.8}$$

I havn't yet got this to work in my program.

### 3.3 Symmetric form of $T_{ij}$

Time to try a different approach. Starting with the old definition of $I_x$,

$$I_x = -\frac{1}{2}\int\int\int \phi_1^*(\mathbf{r})\frac{\partial^2}{\partial x^2}\phi_2(\mathbf{r})dxdydz \tag{3.9}$$

and integrating by parts in $x$,

$$I_x = -\frac{1}{2}\left[\int\int\left(\phi_1^*(\mathbf{r})\frac{\partial\phi_2(\mathbf{r})}{\partial x}\right|_{-\infty}^{+\infty} dydz - \int\int\int\frac{\partial\phi_1^*(\mathbf{r})}{\partial x}\frac{\partial\phi_2(\mathbf{r})}{\partial x}dxdydz\right] \tag{3.10}$$

The first term is of course zero because both $\phi_1(\mathbf{r})$ and $\partial\phi_2(\mathbf{r})/\partial x$ go to zero as $x \rightarrow \pm\infty$. So

$$I_x = \frac{1}{2}\int\int\int \frac{\partial\phi_1}{\partial x}\frac{\partial\phi_2}{\partial x}dxdydz \tag{3.11}$$

Recalling equation 3.3,

$$\begin{aligned} I_x &= \frac{1}{2}\int\int\int \left[l_2 x_A^{l_1-1} - 2\alpha_1 x_A^{l_1+1}\right] y_A^{m_1} z_A^{n_1} e^{\alpha_1 r_A^2} \\ &\quad \cdot \left[l_2 x_B^{l_2-1} - 2\alpha_2 x_B^{l_2+1}\right] y_B^{m_2} z_B^{n_2} e^{-\alpha_2 r_B^2} dxdydz. \end{aligned} \tag{3.12}$$

Thus we can reduce this cumbersome notation to something a little simpler for those of us with overlap integrals all coded up already as a simple subroutine...

$$\begin{aligned} I_x &= \frac{1}{2} l_1 l_2 \langle -1| - 1\rangle_x + 4\alpha_1\alpha_2\langle +1| + 1\rangle_x \\ &\quad -2\alpha_1 l_2 \langle +1| - 1\rangle_x - 2\alpha_2 l_1 \langle -1| + 1\rangle_x \end{aligned} \tag{3.13}$$

This I got to work. It is somewhat more appealing, since $\mathrm{T}_{ij}$ should be a symmetric matrix, i.e. $\mathrm{T}_{ij} = \mathrm{T}_{ji}$. This is an obvious truth when equation 3.13 is used to calculate T, but is not so from the asymmetric form. There is no good reason for this – Wesley Allen and I proved all this quite rigorously, so there must be something wrong with my coding of it.

# 4 $V_ij$ – Nuclear Attraction Integrals

## 4.1 The need for a transformation

Since the potential energy is due to coulombic interaction of the nuclei with the electron in question, the operator to deal with is $1/r_C$. Thus the integral we need to evaluate is

$$\begin{aligned} V_{ij}^C &= \int \phi_i \frac{1}{r_C} \phi_j d\mathbf{r} \\ &= \int x_A^{l_1} y_A^{m_1} z_A^{n_1} e^{-\alpha_1 r_A^2} \frac{1}{r_c} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_2 r_B^2} d\mathbf{r} \end{aligned} \tag{4.1}$$

Since the operator does not affect the operand ($\phi$), we can combine the two orbitals via the gaussian product theorem, and make the final statement

$$\begin{aligned} V_{ij}^C &= K \sum_l \sum_m \sum_n f_l(l_1, l_2, \overline{\mathbf{PA}}_x, \overline{\mathbf{PB}}_x) f_m(m_1, m_2, \overline{\mathbf{PA}}_y, \overline{\mathbf{PB}}_y) \\ &\quad \cdot f_n(n_1, n_2, \overline{\mathbf{PA}}_z, \overline{\mathbf{PB}}_z) \int x_P^l y_P^m z_P^n e^{-\gamma r_P^2} \frac{1}{r_C} d\mathbf{r} \end{aligned} \tag{4.2}$$

where $K = e^{-\alpha_1 \alpha_2 (\overline{\mathbf{AB}}^2/\gamma)}$. This is still intractible, since we've failed to write everything in terms of the integration variables, $\mathbf{r}_P$. At this point, we want to apply some sort of transform to the $\frac{1}{r_C}$ to turn it into some sort of an exponential which can be combined with the other gaussians and result in resolution of the variables. There are two standard possibilities – the one I like and the one everyone uses. First things first...

## 4.2 Laplace transform

Use the standard Laplace transform,

$$r^{-\lambda} = \left[\Gamma(\frac{\lambda}{2})\right]^{-1} \int_0^\infty e^{-sr^2} s^{\lambda/2-1} ds. \tag{4.3}$$

You can just evaluate the rhs to confirm this. We want the instance where $\lambda = 1$, thus

$$\frac{1}{r_C} = \pi^{-1/2} \int_0^\infty e^{-sr_C^2} s^{-1/2} ds. \tag{4.4}$$

What occurs when we use this in the context of a potential energy integral involving only 1s functions?

$$\begin{aligned} V &= \int e^{-\alpha_1 r_A^2} e^{-\alpha_2 r_B^2} \frac{1}{r_C} d\mathbf{r} \\ &= K \int e^{-\gamma r_P^2} \frac{1}{r_C} d\mathbf{r} \\ &= K\pi^{-1/2} \int e^{-\gamma r_P^2} \int_0^\infty e^{-sr_C^2} s^{-1/2} ds d\mathbf{r} \end{aligned} \tag{4.5}$$

Conveniently, the laplace transform takes $r_c^{-1}$ into a function with the appearance of a 1s gaussian of orbital exponent $s$ centered on $\mathbf{C}$. A second application of the GPT and we can switch the order of integration, evaluating the integral over $s$ second.

$$\begin{aligned} V &= K\pi^{-1/2} \int_0^\infty ds s^{-1/2} \int e^{-\gamma r_P^2} e^{-sr_C^2} d\mathbf{r} \\ &= K\pi^{-1/2} \int_0^\infty ds s^{-1/2} e^{-\gamma s \overline{\mathbf{PC}}^2/(\gamma+s)} \int d\mathbf{r} e^{-(\gamma+s) r_D^2} \qquad (4.6) \\ &= K\pi \int_0^\infty ds s^{-1/2} (\gamma + s)^{-3/2} e^{-\gamma s \overline{\mathbf{PC}}^2/(\gamma+s)}. \qquad (4.7) \end{aligned}$$

Now making the substitution $t^2 = \frac{s}{(\gamma+s)}, ds = \frac{2}{\gamma} s^{1/2} (\gamma + s)^{3/2} dt$ amazingly cancels just about everything leaving

$$V = \frac{K\pi^2}{\gamma} \int_0^1 e^{-\gamma \overline{\mathbf{PC}}^2 t^2} dt \tag{4.8}$$

which everyone recognizes as a standard error function,

$$V = \frac{K\pi^{5/2}}{2\gamma^{3/2} \overline{\mathbf{PC}}} \mathrm{erf}(\gamma^{1/2} \overline{\mathbf{PC}}). \tag{4.9}$$

### 4.3 Fourier transform

When I get around to typesetting this, it will be here, but it is non-essential to the lecture.

## 5 Electron Repulsion Integrals

These are just a little more complicated than potential energy integrals.