Hermite Polynomials and Cartisian Gaussian Type Orbitals

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1 Hermite Polynomials

The Hermite polynomials are a set of orthogonal polynomials that are defined by the Rodrigues formula:

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2} \tag{1}$$

The first four Hermite polynomials are:

$$\begin{aligned} H_0(x) &= 1 \\ H_1(x) &= 2x \\ H_2(x) &= 4x^2 - 2 \\ H_3(x) &= 8x^3 - 12x \end{aligned}$$

We also introduce the orthogonality relation for the Hermite polynomials:

$$\int_{-\infty}^{\infty} H_n(x) H_m(x) e^{-x^2} dx = \sqrt{\pi} 2^n n! \delta_{nm} \tag{2}$$

The hermite gaussians are particularly usefull for evaluating integrals of the form:

$$\int_{-\infty}^{\infty} f(x) e^{-x^2} dx \tag{3}$$

where $f(x)$ can be written in terms of the Hermite polynomials. For example, lets consider the integral where $f(x) = x^2$:

$$\begin{aligned}
\int_{-\infty}^{\infty} x^2 e^{-x^2} dx &= \int_{-\infty}^{\infty} \left(\frac{1}{4}H_2(x) + \frac{1}{2}H_0(x)\right) e^{-x^2} dx \\
&= \int_{-\infty}^{\infty} \frac{1}{4}H_2(x)e^{-x^2} dx + \int_{-\infty}^{\infty} \frac{1}{2}H_0(x)e^{-x^2} dx \\
&= \int_{-\infty}^{\infty} \frac{1}{4}H_2(x)H_0(x)e^{-x^2} dx + \int_{-\infty}^{\infty} \frac{1}{2}H_0(x)H_0(x)e^{-x^2} dx \\
&= \frac{1}{2}\sqrt{\pi}
\end{aligned}$$

We can write x^n generally in terms of the Hermite polynomials as:

$$x^n = \frac{n!}{2^n} \sum_{m=0}^{\lfloor \frac{n}{2} \rfloor} \frac{1}{m!(n-2m)!} H_{n-2m}(x) \tag{4}$$

Thus, we can evaluate the integral of $x^n e^{-x^2}$ using equations 2 and 4. We observe that for odd n, the integral evaluates to zero. However, we can obtain a non-zero formula for even n:

$$\begin{aligned}
\int_{-\infty}^{\infty} x^n e^{-x^2} dx &= \int_{-\infty}^{\infty} \left(\frac{n!}{2^n} \sum_{m=0}^{\lfloor \frac{n}{2} \rfloor} \frac{1}{m!(n-2m)!} H_{n-2m}(x)\right) H_0(x)e^{-x^2} dx \\
&= \int_{-\infty}^{\infty} \left(\frac{n!}{2^n \left(\frac{n}{2}\right)!} H_0(x)\right) H_0(x)e^{-x^2} dx \\
&= \frac{n!}{2^n \left(\frac{n}{2}\right)!}\sqrt{\pi}
\end{aligned}$$

Thus, we have obtained the general formula for the integral of $x^n e^{-x^2}$ for even n.

$$\int_{-\infty}^{\infty} x^n e^{-x^2} dx = \begin{cases} 0 & \text{if } n \text{ is odd} \\ \frac{n!}{2^n \left(\frac{n}{2}\right)!}\sqrt{\pi} & \text{if } n \text{ is even} \end{cases} \tag{5}$$

2 Context for Computational Chemistry

In computational chemistry, gaussian type orbitals (GTOs) are commonly used to approximate the wavefunction of electrons. In order to make use of the Hermite polynomials, we need to write the integrals in terms of hermite polynomials. In particular, shperically harmonic GTOs are used to approximate the wavefunction of electrons. This can be written as:

$$\phi_{nlm}(\vec{r}, a, \vec{A}) = R_{nl}^{GTO}(r) Y_{lm}(\theta, \phi) \exp(-ar^2) \tag{6}$$

In general, the radial part of the spherical-harmonic GTOs can be written as:

$$R_{nl}^{GTO}(r) \propto r^l \exp(-\alpha_n r^2) \tag{7}$$

The spherical-harmonic GTO's are simple linear combinations of Cartisian GTO's. We can map $Y_{lm} \to S_{lm}$ (using equation 6.4.48 pg 215 in Molecular Electronic Structure Theory) [1]:

$$S_{lm} = N_{lm} \sum_{t=0}^{(l-|m|)/2} \sum_{u=0}^{t} \sum_{v=v_m}^{|m|/(2-v_m)+v_m} C_{tuv}^{lm} x^{2t+|m|-2(u+v)} y^{2(u+v)} z^{l-2t-|m|} \tag{8}$$

$$\begin{aligned}
N_{lm} &= \frac{1}{2^{|m|} l!} \sqrt{\frac{(2l+|m|)!(l-|m|)!}{2^{\delta_{0m}}}} \\
C_{tuv}^{lm} &= (-1)^{t+v-v_m} \left(\frac{1}{4}\right)^t \binom{l}{t} \binom{l-t}{|m|+t} \binom{t}{u} \binom{|m|}{2v} \\
v_m &= \begin{cases} 0 & \text{if } m \geq 0 \\ \frac{1}{2} & \text{if } m < 0 \end{cases}
\end{aligned}$$

Thus the final result can be expressed as:

$$\phi_{nlm} = N_{lm} S_{lm} \exp(-\alpha_n r^2) \tag{9}$$

3 Cartisian Gaussian Type Orbitals

Following the begining of chapter 9 [1], we start with an anzatz of gaussian orbitals is given by:

$$\phi_{ijk}(\vec{x}, a, \vec{A}) = (x_1 - A_1)^i (x_2 - A_2)^j (x_3 - A_3)^k \exp\left(-a \left|\vec{x} - \vec{A}\right|^2\right) \tag{10}$$

where $\vec{x} = (x_1, x_2, x_3)$ and $\vec{A} = (A_1, A_2, A_3)$. We can write this in a simplified form where $x_{1,A} = x_1 - A_1$ and similarly for x_2 and x_3:

$$\phi_{ijk}(\vec{x}, a, \vec{A}) = x_{1,A}^i x_{2,A}^j x_{3,A}^k \exp\left(-a\left(x_{1,A}^2 + x_{2,A}^2 + x_{3,A}^2\right)\right) \tag{11}$$

We can now seperate phi into the product of the x_1, x_2, and x_3 parts:

$$\phi_{ijk}(\vec{x}, a, \vec{A}) = \phi_i(x_1, a, A_1)\phi_j(x_2, a, A_2)\phi_k(x_3, a, A_3) \tag{12}$$

where the x_1 part is:

$$\phi_i(x_1, a, A_1) = x_{1,A}^i \exp(-a x_{1,A}^2) \tag{13}$$

We now want to consider two orbitals relative to points A and B. We thus have the following integrand for the overlap integral in the x_1 direction:

$$\langle i| \, |l\rangle = \int_{-\infty}^{\infty} \phi_i^*(x_1, a, A_1)\phi_l(x_1, b, B_1)dx_1 = \int_{-\infty}^{\infty} x_{1,A}^i \exp(-a x_{1,A}^2) x_{1,B}^l \exp(-b x_{1,B}^2)dx_1 \tag{14}$$

The goal is now to evaluate this integral. To do this, we want to bring the equation into a form where we can use the Hermite polynomials to evaluate the integral. We can do this by completing the square in the exponent of the gaussian. We can write the exponent as:

$$\begin{aligned}
-a x_{1,A}^2 - b x_{1,B}^2 &= -a\left(x_{1,A} - A_1\right)^2 - b\left(x_{1,B} - B_1\right)^2 \\
&= \left(-a - b\right) x_1^2 + 2\left(aA_1 + bB_1\right) x_1 - aA_1^2 - bB_1^2 \\
&= \left(-a - b\right)\left(x_1 + \frac{aA_1 + bB_1}{(a+b)}\right)^2 - \frac{ab(A_1 - B_1)^2}{(a+b)}
\end{aligned}$$

To simplify this expression, we can define the following:

$$\begin{aligned}
p &= a + b \\
\mu &= \frac{ab}{a+b} \\
P_1 &= \frac{aA_1 + bB_1}{a+b} = \frac{aA_1 + bB_1}{p} \\
x_{1,P} &= x_1 + P_1 \\
P_{1,AB} &= A_1 - B_1
\end{aligned}$$

We can now write the exponent as:

$$-a x_{1,A}^2 - b x_{1,B}^2 = -p x_{1,P}^2 - \mu P_{1,AB}^2$$

Thus, we can write the integrand as:

$$\langle i| \, |l\rangle = \exp(-\mu P_{1,AB}^2) \int_{-\infty}^{\infty} x_{1,A}^i x_{1,B}^l \exp(-p x_{1,P}^2)dx_1 \tag{15}$$

Now, we want to use the binomial theorem to expand the product $x_{1,A}^i x_{1,B}^l$ in terms of $C_{i,j}$. We start with the definitions of $x_{1,A}$ and $x_{1,B}$:

$$\begin{aligned} x_{1,A} &= x_1 - A_1 \\ x_{1,B} &= x_1 - B_1 \end{aligned}$$

We can now expand the product $x_{1,A}^i x_{1,B}^l$:

$$\begin{aligned} x_{1,A}^i x_{1,B}^l &= (x_1 - A_1)^i (x_1 - B_1)^l \\ &= (x_{1,P} + P_1 - A_1)^i \, (x_{1,P} + P_1 - B_1)^l \\ &= \left(x_{1,P} + \frac{aA_1 + bB_1}{p} - A_1\right)^i \left(x_{1,P} + \frac{aA_1 + bB_1}{p} - B_1\right)^l \\ &= \left(x_{1,P} + \frac{aA_1 + bB_1 - A_1(a+b)}{p}\right)^i \left(x_{1,P} + \frac{aA_1 + bB_1 - B_1(a+b)}{p}\right)^l \\ &= \left(x_{1,P} - \frac{bP_{1,AB}}{p}\right)^i \left(x_{1,P} + \frac{aP_{1,AB}}{p}\right)^l \end{aligned}$$

We can now write the integrand as:

$$\langle i| \, |l\rangle = \exp(-\mu P_{1,AB}^2) \int_{-\infty}^{\infty} \sum_{k=0}^{i+l} C_k^{il} x_{1,P}^k \exp(-p x_{1,P}^2) dx_1 \tag{16}$$

To evaluate this integral, we set $u = \sqrt{p} x_{1,P}$ and thus $dx_1 = \frac{1}{\sqrt{p}} du$. We can now write the integral as:

$$\langle i| \, |l\rangle = \exp(-\mu P_{1,AB}^2) \sum_{k=0}^{i+l} C_k^{il} \left(\frac{1}{\sqrt{p}}\right)^{k+1} \int_{-\infty}^{\infty} u^k \exp(-u^2) du$$

Using equation 5, we can evaluate the integral to obtain:

$$\langle i| \, |l\rangle = \exp(-\mu P_{1,AB}^2) \sum_{k=0}^{\lfloor \frac{i+l}{2} \rfloor} C_{2k}^{il} \left(\frac{1}{\sqrt{p}}\right)^{2k+1} \frac{2k!}{2^{2k} \, (k)!} \sqrt{\pi} \tag{17}$$

4 Conclusion

Thus far we have shown simply the utility of the Hermite polynomials in evaluating integrals of the form $x^n e^{-x^2}$ and why it aids in the computation of Gaussian type orbitals. We have also shown how to evaluate the overlap integral of two Cartisian Gaussian Type Orbitals, which is equivalent to the overlap integral of two spherical-harmonic GTOs. This is a key step in the evaluation of the integrals in computational chemistry.

References

[1] Trygve Helgaker, Poul Jorgensen, and Jeppe Olsen. *Molecular Electronic Structure Theory*. 1st. Hoboken, NJ: Wiley, 2014.