Exploring Orthonormal Functions©
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Introduction:
A complete orthonormal set of well-behaved functions that satisfy certain boundary
conditions in the specified domain of their variables can be used to express any other
function in the same domain that satisfies the same boundary conditions. The target
function is expressed as an expansion in a convergent series using the given orthonormal
set. The weighting coefficients in the expansion are determined by evaluating the
appropriate overlap integral, the integral that says how much one of the basis set functions
overlaps with the target function. This mathematical definition means that we can under
certain conditions use a convergent series of functions to create a representation of
another function. The Taylor and Fourier series are two examples used frequently in
science. In this document you will explore some of the concepts used in quantum
chemistry, specifically orthogonal and normal functions. The ability to precisely use the
terms orthogonal and normal is essential in modern physical chemistry.

Goal: To have students practice the concept of orthonormal functions and gain
experience with the expansion of some given function in terms of the components of an
orthonormal set of functions.

Prerequisites: Users should
• have had experience with Mathcad through the use of integration in symbolic
  processing;
• have been introduced to the concepts of orthogonal and normalized functions;
• have basic knowledge of the particle-in-a-box (PIB) model and the wavefunctions
  obtained for this model from the solution of the Schrödinger equation for the PIB
• have studied Fourier series and use of Fourier series as an expansion of another
  function in calculus courses;
• be able to compute the sample variance between two functions;
• have had experience with evaluating and Error function with Mathcad.
To the User: this document was prepared and tested with Mathcad 11. Instructions for some steps use the tool bars as found in Mathcad 11. If you are using a newer version you may need to check your Mathcad manual or Help files to see new ways for completing those steps.

Outline:  The five parts in this document are:
1. testing for the normality of functions;
2. testing the orthogonality condition for a set of functions;
3. using linear combination of functions to fit to a target function;
4. computing the goodness of fit between a fitting function and a target function;
5. developing the overlap matrix for a basis set of functions.

Objectives:  At the end of this lesson students will be able to:

1. explain the meaning of orthogonal and normalized functions;
2. write sample equations to express orthogonal and normal properties of functions;
3. use Mathcad to check if a pair of functions is orthogonal;
4. use Mathcad to check if a function is normalized;
5. compute the normalization factor for a function;
6. use an orthonormal basis set to expand a function;
7. compute the goodness of fit of the expansion and make an appropriate decision about when to truncate the expansion;
8. create an overlap matrix for a set of functions.
Part I
Using Mathcad to show that functions are normalized.

Definition: A wavefunction is said to be normalized when the integral of the function times its complex conjugate over the range of the function equals 1.0.

\[ \psi(n,y) := (\sqrt{2}) \sin(n\pi y) \]

This function is one of an infinite set of orthonormal functions. Specifically it is one of the particle-in-a-box functions (PIB) where \( n = 1, 2, 3 \ldots \infty \). The PIB model in quantum mechanics uses a 1-dimensional box with infinite high walls. The walls are the boundaries of the model and boundaries give rise to quantized energy levels and wave functions for the PIB model. You should refer to your physical chemistry text for more details on the PIB model.

\[ n := 1 \]

To the left you have a method for testing if a function is normalized.

\[ A := \int_{0}^{1} \psi(n,y) \cdot \psi(n,y) \, dy \]

The definite integral is created using the calculus pallet. The limits of the integration must match the boundaries of the problem. Since the functions \( \psi(n,y) \) are solutions to the particle in a box problem with unit length, the limits of the integration are 0 and 1, i.e. \( 0 \leq y \leq 1 \). (Recall that the little rectangular symbol here means that this equation is "cold," it is not used in computations on the worksheet). If the function \( \psi \) were complex then the integration would be for \( \psi^*\psi \).

Exercise 1. Try other values of \( n \) in the integration above. Explore the various display options for numerical format by experimenting with the choices in the Format Result section of Format in the main toolbar.

\[ \frac{1}{4} - \frac{\alpha x^2}{2} \]

Exercise 2. Show that the function \( \left( \frac{\alpha}{\pi} \right)^4 \cdot e^{-\frac{\alpha x^2}{2}} \) is normalized. This function is one of the solutions to the quantum mechanical harmonic oscillator. (The limits of integration for harmonic oscillator functions extend from - infinity to + infinity).

Note: You will get an Error function, err, as part of the result when you use the general form of the function. The Error functions approach 1.0 as \( x \) goes to \( \infty \). This information will enable you to complete the check that the function is normalized. However, if you assign a value to the constant \( \alpha \) you will get a result quickly. Can you explain why?
Exercise 3. Determine if \( \frac{\alpha^4}{4\pi} \cdot \frac{1}{2} \cdot e^{-\frac{\alpha^2}{2}} \cdot x \cdot e^{-\frac{x^2}{2}} \) is a normalized function of \( x \) from \( \infty \) to \( -\infty \). Here you will may again meet the err function and you must recall how \( x \cdot e^{-x} \) behaves as \( x \) goes to \( \infty \). Alternatively you can define \( \alpha \), which is a constant, to some real number. Then follow through with symbolic integrate.

Part II
Using Mathcad to show that the functions are orthogonal.

**Definition:** As pair of functions is said to be orthogonal when the integral of one function times the complex conjugate of the other function over the space of the functions is zero.

\[
\int_{0}^{1} \psi(n,y) \cdot \psi^{*}(m,y) \, dy = 0
\]

The limits of integration are for a unit dimension box, i.e. \( 0 \leq y \leq 1 \). **Why?**

Exercise 4. Do one integration by hand and compare your result to the what Mathcad gives. Do you prefer to do the integration by hand or with Mathcad?
Part III
Linear Combinations of Basis Set Functions.

The set of functions used in linear combinations to create a representation of another function is called a basis set. Some basis sets are specifically designed to be used in research calculations to represent the hydrogen like atomic orbitals that are used to discuss bonding in chemistry. We will start with something simpler. The basis set used in this exercise is the full set of functions that are solutions to the Schrödinger equation for a particle in a box. For a box of unit length these are the \( n \) functions

\[
\psi(n, y) := \sqrt{2} \sin(n \pi y) \quad \text{where} \quad n = 1, 2, 3, \ldots \infty
\]

This set of functions is orthonormal as we tested above. The \( n \) in this equation usually appears in texts as a subscript attached to the symbol for the wave function on the left hand side of the equation. We are using it here as one of the independent variables. The equation written here is "hot," i.e. it is active with respect to being used by Mathcad, until redefined, in all of the remaining pages of the worksheet. Try toggling this equation off by placing the cursor on the equation and then right clicking with the mouse and select "Disable Evaluation" in Mathcad 11.

An example of representing a function with an expansion using a basis set of orthonormal functions.

The basis set used here is the set of solutions to the particle in the box problem. The expansion is confined to the interval \( 0 \leq x \leq 1 \). It is important to know the range of integration for each problem you investigate.

\[
f(y) := y(1 - y)^3 \quad \text{(1)} \quad \text{f}(y) \text{ is the target function to be expressed by the expansion } f(y) := \sum_n (c(n) \cdot \psi(n, y))
\]

\[
n := 1, 2 \ldots 20 \quad \text{(2)} \quad n \text{ is the maximum number of terms to be used in the expansion. Here it is set here to 20.}
\]

\[
y := 0.01 \ldots 1 \quad \text{(3)} \quad y \text{ is the set of values at which } f(y) \text{ and } F(y) \text{ will be evaluated. 101 points will be computed. How do you know there are 101 points to calculate?}
\]

\[
\psi(n, y) := \sqrt{2} \sin(n \pi y) \quad \text{(4)} \quad \text{The } \psi(n, y), \text{ where } n = 1 \text{ to } \infty, \text{ are the full set of basis set functions to use in the expansion. How many are we using?}
\]

\[
c(n) := \int_0^1 f(y) \cdot \psi(n, y) \, dy \quad \text{(5)} \quad \text{The } c(n) \text{ are found by evaluating the overlap integral, equation (5). } c(n) \text{ is the degree of overlap of the target function and the } n^{\text{th}} \text{ member of the basis set.}
\]

\[
c(1) = 5.184 \times 10^{-2} \quad \text{(6)}
\]
ψ(n,y) are the PIB wavefunctions. ψ is written as a function of n instead of using a running index in order to provide opportunities for exploring the results for different n values.

Other c(n) values can be computed and inspected on this worksheet.

**Exercise 5: Typing c(n)= on the right of this document.**

How does the value of c(n) vary as n increases? Increase the n value above to get 50 terms in the expansion. How does the value of c(50) compare with that of c(1)? What is the significance of these observations when you make an expansion of a function with an orthonormal basis set? Plot several of the wavefunctions (n = 1 through 8) multiplied by their c(n) values. On the same plot show the target function. Write on the contribution an individual member of the basis set makes to the overall target function.

F1(y) on the right below is the fit to the target function f(y) when only one term is used in the expansion.

**Exercise 6**

The plot of f(y), F1(y), and F(y) as a function of y is shown to the right.

- How good is the fit shown in the plot when only one term is used in the expansion given by F1(y)?
- How many terms are in the sum that created F(y)?
- Has the fit improved by using F(y)?
- What can you do to improve the fit between the given function and the expansion?
- Implement your strategy and record your results.
- What criteria would you use to ensure that a suitable fit is obtained?

\[
f(y) := y(1 - y)^3
\]

\[
F1(y) := c(1) \cdot \psi(1, y)
\]

\[
F(y) := \sum_{n=1}^{2} (c(n) \cdot \psi(n, y))
\]
Changing the notation to make computation of the variance easier.

It is important to remember that usually there is more than one way to accomplish a mathematical task. Although not all ways are equally elegant, appropriate solutions to any problem require a good understanding of mathematical principles and their relationship to the situation under study. In physical chemistry this means linking mathematics, and physics to chemical phenomena. Sometimes the connection is not immediately apparent.

Below is an alternate way of computing the values of \( y \) given by the target function and the fitting function. The definitions below make it easier to design a strategy to determine the standard deviation of the fit over all data points.

\[
\begin{align*}
  y_0 & := 0 \quad i := 1 \ldots 100 \\
  y_i & := y_{i-1} + .01 \\
  f_{yi} & := y_i \left(1 - y_i\right)^3 \\
  F_{yi} & := \sum_{n=1}^{2} \left(c(n) \cdot \psi(n,y_i)\right) 
\end{align*}
\]

First we identify the variables and their extent.

N.B. Use the [ to create the step variable index subscripts shown on this page.

Target function

Fitted Function

The target and fitted function are plotted again here to the right.

Exercise 7:
Adjust the number of terms in the sum, equation 7, to get a good fit between the target function and the fit function.
Part IV

Sample Variance for Goodness of Fit between Two Functions

In this section we define SV, the sample variance of the fit between the target function and the fitting function. From SV we can obtain SD, the standard deviation. SV is defined as

\[
SV := \frac{1}{n_{\text{max}} - 1} \left[ \sum_{i=1}^{n_{\text{max}}} (f_{y_i} - F_{y_i})^2 \right]
\]

Remember that \( n_{\text{max}} \) is the number of terms in the expansion and \( i \) is the number of points over which the expansion is tested and compared to values for the target function.

\[ n_{\text{max}} := 2 \]

\[
SV := \frac{1}{n_{\text{max}} - 1} \left[ \sum_{i} (f_{y_i} - F_{y_i})^2 \right]
\]

\[
SV = 1.107 \times 10^{-2}
\]

\[
SD := \sqrt{SV}
\]

\[
SD = 1.052 \times 10^{-1}
\]

Exercise 8. Vary \( n \) and \( n_{\text{max}} \) and tabulate \( n \) and \( SV \) for several values of \( n \). How does the fit improve with increasing number of basis functions? When would you consider the fit between the target function and the Fitted function sufficiently close?

Mastery Exercise 1: For a particular number of basis functions how does the fit vary at different positions of the range of the function (values of \( i \))? What do you need to plot to see this? (Hint: compute the deviation point by point and plot the deviations as a function of \( y \).)
Another Approach to Computing the Variance.

It is easy to write the standard deviation of the fit over all points in terms of the reduction of the identity, i.e. if $F_k(y)$ is the approximation for $f(y)$ with $k$ terms from a set of orthonormal functions and $f(y)$ is normalized, we have:

$$\sigma^2 = \int_0^1 (f(y) - F_k(y))^2 \, dy = 1 - \sum_{j=1}^{k} \left| c_j \right|^2$$

Mastery Exercise 2: Demonstrate that the right hand side of this expression is true and then use it to compute the variance for the work done in the previous section. (Hint, expand the square term and evaluate each integral. Use the definition of the coefficients you have from this document.)

Part V

Orthonormality of Basis Functions Through an Overlap Matrix.

An overlap matrix can be constructed for a set of $n$ functions by computing the integral

$$\int_{\text{all space}} \psi(n,y) \cdot \psi(m,y) \, dy$$

for all unique combinations of $n$ and $m$. For the basis set we used in this document, PIB wavefunctions, the range for the variable is $0 \leq y \leq 1$.

Given that we know the PIB wavefunctions are orthonormal we expect to discover that the overlap matrix will be a unit matrix, one with 1.0 on the diagonal and zeros on all off diagonal positions.

Overlap Extension Exercise:

Consider the functions $\psi(m,\phi)$ defined as follows:

$$\psi(m,\phi) := \frac{1}{\sqrt{2\pi}} \cdot \exp(j \cdot m \cdot \phi)$$

The range of integration is $0$ to $2\pi$ for this function. The range of integers used in the basis set functions will be $m = -M$ to $M$. This requires us to set the ORIGIN to -5. (Recall that the default ORIGIN, where Mathcad initializes arrays, is zero.)

We first set up the parameters for the calculation and then compute the overlap integral values to check the orthonormal property of the function. (When you do this be careful about the case of the PSI, $\Psi$ or $\psi$, function. function names are case sensitive in Mathcad.)
M := 5  j := \sqrt{-1}  ORIGIN := -5  

Defining some parameters for this exercise.

m := -M, -M + 1 .. M  n := -M, -M + 1 .. M  

Setting the range for the exercise.

\[ \psi(m, \phi) := \frac{1}{\sqrt{2\pi}} \exp(j \cdot m \cdot \phi) \]

The function in Mathcad active form.

To show that the functions where m and n vary from -M to +M are orthonormal one creates the overlap integral in a general form. The overlap integral is then evaluated for the whole set of possibilities. This is described next. First examine the Notes for this exercise.

Notes:

An overlap integral is written as

\[ S_{i,j} := \int_{-\tau}^{\tau} f_i \cdot f_j \cdot d\tau \]

where d\tau calls for integration over the full range of coordinates for the system. In the overlap integral the function on the left is the complex conjugate form of the function of the function on the right. An overlap matrix is a two dimensional array of all of the overlap integrals. The array can be built in Mathcad by writing the equation for \( S_{m,n} \) where m and n are the integers identifying the function used.

To make the complex conjugate of a function select the function and then press the double quote, i.e. ".

Exercise 9. Write the overlap integral for four different function, two where \( m = n \) and two where \( m \neq n \). Evaluate these integrals. Record the values you obtain.

Mastery Exercise 3.

Evaluate the entire "overlap matrix" for the function

\[ \psi(m, \phi) := \frac{1}{\sqrt{2\pi}} \exp(j \cdot m \cdot \phi) \]

Display the overlap matrix as a matrix on the Mathcad worksheet.

Explain how this matrix shows that the set of functions (\( \gamma(m,f) \)) are orthonormal.

Carefully read the notes below to help you complete this exercise.
Notes:

When creating a matrix in Mathcad the default range for the matrix is 0 to the maximum size of the matrix. This means that the labels of the columns and rows of the overlap matrix would start at zero. The functions in the overlap exercise are identified by integers that start at -5. We want the overlap matrix rows and columns to be labeled by the same integers. This requires us to reset the ORIGIN.

Making changes in the Tools, Worksheet Options Built in Variables menu. A change here changes the ORIGIN for the entire worksheet. Check the user guide for your version of Mathcad for resetting the ORIGIN.

Alternatively a new ORIGIN can be set for a part of a worksheet, the current position forward, by typing ORIGIN:= - 5.

More Notes

Remember the orthogonal functions have different values for m. The normalized functions have the same values for m in the appropriate integral.

You must design a general overlap matrix element of the form $B(m,n)$ by using the general overlap integral definition given above. If you designed the $B(m,n)$ correctly Mathcad will compute all the overlap matrix elements for you. There will not be a need to do all 100 matrix elements individually. After all of the elements of the overlap matrix are computed the matrix can be displayed by typing the symbol for the matrix without the range variable indices and pressing the plain =, that is $B=.$

Once you see the matrix you can experiment with the numerical format of the numbers in the matrix. With the cursor outside the Matrix, select Format, Format Result and then observe the matrix output when Scientific is chosen for the Number Format. **What do you observe?**

$B_{m,n} := \int_{-\frac{2\pi}{\sqrt{2\pi}}}^{\frac{2\pi}{\sqrt{2\pi}}} \frac{\exp(j\cdot m\cdot \phi)}{\sqrt{2\pi}} \cdot \frac{\exp(j\cdot n\cdot \phi)}{\sqrt{2\pi}} \, d\phi \quad \text{Type } B= \text{ and see what you get.}$

Double click on the little right pointing arrow to compare your overlap matrix to mine.
Conclusion

After completing the exercises in this document you should have a clear understanding and working knowledge of orthonormal functions. You also have used a complete set of orthonormal functions as a basis set to expand into a function that matches a target function. The goodness of fit between a fitting function and a target function was determined by the sum of squares of the deviations. You were also able to construct a general overlap matrix for the basis set used in this document.

The fundamental skills learned through this document are preparation for similar skills required to understand the more detailed methods used in computational chemistry by standard software packages that perform molecular orbital calculations.

Partial answer for Exercise 2.

To normalize the function $\psi(x) = e^{-\frac{(\alpha \cdot x)^2}{2}}$

Write the 'overlap integral' as shown here. Be sure you have the correct limits for the integration

Highlight the entire integral and choose Evaluate from the Symbolic Menu.

Evaluate the Error Function $\text{erf}(\alpha x)$ at the limit of $\infty$

Below the integral the value appears.

Write the final result using cut and paste.

This is the value of the integral. The Normalization constant is the square root of the inverse.

The normalized function is:

Highlight the whole expression and choose Symbolic, Simplify.
\[
\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{\alpha^2} \cdot \exp\left(-\frac{1}{2} \cdot \alpha^2 \cdot x^2\right)
\]
or
\[
\frac{\sqrt{2\alpha}}{\sqrt{\pi}} \cdot \exp\left(-\frac{1}{2} \cdot \alpha^2 \cdot x^2\right)
\]

Extension Exercise:

Determine if the function \( x \cdot e^{-\frac{\alpha x^2}{2}} \) is normalized. If it is not then normalize it.

References


See also standard physical chemistry texts.

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