Chemistry 331 **Tutorial #3**

What are all these quantum mechanical operators and eigenvalues? Where do they come from? What do they mean? How can we use them?

1. ***The Hamiltonian operator for the total energy.***

a) Prove that

$$\Psi(x,t) = \psi(x)e^{-i2\pi\nu t}$$

is a valid solution of the classical wave equation in the x-direction

$$\frac{\partial^2\Psi(x,t)}{\partial t^2} = \mathrm{v}^2\frac{\partial^2\Psi(x,t)}{\partial x^2}$$

if the x-dependent part of the solution has the form $\psi(x) = A\sin(2\pi x/\lambda) + B\cos(2\pi x/\lambda)$.

b) Show that substitution of $\lambda = h/p$ (from de Broglie's wave-particle duality) and $\nu = E/h$ (from Einstein's equation $E = h\nu$) into the expression for the wave speed $\mathrm{v} = \lambda\nu$ gives

$$\frac{\partial^2\Psi(x,t)}{\partial t^2} = \frac{E^2}{p_x^2}\frac{\partial^2\Psi(x,t)}{\partial x^2}$$

Take the time derivative and verify that

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{4\pi^2 p_x^2}{h^2}\psi(x) = 0$$

The kinetic energy is $T_x = p_x^2/2m = E - V(x)$ and therefore $p_x^2 = 2m(E - V(x))$. Substitute this result into the expression for $d^2\psi(x)/dx^2$ to "derive" the first of Schrodinger's quantum mechanical wave equations (the time-independent equation)

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V(x))\psi(x) = 0$$

Notice that a simple rearrangement gives

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi(x)}{\partial x^2}+V\psi(x)=E\psi(x)$$

So we can define the ***operator***

$$\hat{H}=-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}+V(x)$$

which is equivalent to

$$\hat{H}=\frac{1}{2m}\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2+V(x)$$

and then rewrite Schrodinger's first equation in operator notation

$$\hat{H}\psi(x)=E\psi(x)$$

Operating on the function gives us back the function back times the total energy E. By definition then, the energy is an eigenvalue and $\psi(x)$ an eigenfunction of the operator. This result is more than just convenient notation. Constructing the operator $\hat{H}$ and solving for the eigenvector and eigenfunction gives us the energy of the system and the wave function, from which other information about the system can be obtained.

2. The Hamiltonian for a *classical* particle is the sum of its kinetic energy T (expressed in terms of momentum) and potential energy V. For a particle moving in the x-direction, the kinetic energy is $mv_x^2/2 = p_x^2/2m$ and the classical Hamiltonian is

$$\frac{p_x^2}{2m}+V(x)=E$$

Notice the close analogy with Schrodinger's equation for $\hat{H}\psi(x)=E\psi(x)$:

$$-\frac{1}{2m}\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2\psi(x)+V(x)\psi(x)=E\psi(x)$$

For this reason, $\hat{H}$ is called the "Hamiltonian" operator. Show that the analogy can be made event stronger by defining the momentum operator

$$\hat{p}_x = -\frac{h}{2\pi i}\frac{\partial}{\partial x}$$

And the kinetic energy operator

$$\hat{T}_x = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial}{\partial x}\right)^2$$

3. ***The time-dependent Schrodinger equation.*** In Question 1, we showed that the wave function for a quantum mechanical particle moving in the x-direction

$$\frac{\partial^2\Psi(x,t)}{\partial t^2} = \frac{E^2}{p_x^2}\frac{\partial^2\Psi(x,t)}{\partial x^2}$$

has the general solution

$$\Psi(x,t) = \psi(x)e^{-i2\pi\nu t}$$

Taking the first time derivative gives

$$-\frac{i2\pi\nu p_x^2}{E^2}\frac{\partial\Psi(x,t)}{\partial t} = \frac{\partial^2\Psi(x,t)}{\partial x^2}$$

Use $E = h\nu$ and $p_x^2 = (E - V(x))\, 2m$ to "derive" Schrodinger's ***time-dependent*** wave equation where the energy may change with time.

$$\frac{\partial^2\Psi(x,t)}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left(\frac{h}{2\pi i}\frac{\partial\Psi(x,t)}{\partial t} - V(x)\right)\Psi(x,t) = 0$$

In operator notation, the equivalent result is

$$\hat{H}\Psi(x,t) = -\frac{h}{2\pi i}\frac{\partial\Psi(x,t)}{\partial t} = \frac{ih}{2\pi}\frac{\partial\Psi(x,t)}{\partial t}$$

This equation is used to analyze systems with energies that vary with time, such as molecules or atoms emitting or absorbing radiation.

4. Consider the two vectors $\vec{a} = 2\boldsymbol{i} - \boldsymbol{j} + 3\boldsymbol{k}$ and $\vec{b} = \boldsymbol{i} + 2\boldsymbol{j} + \boldsymbol{k}$.

a) The dot product of vectors $\vec{a} = (a_x, a_y, a_z)$ and $\vec{b} = (b_x, b_y, b_z)$ is the scalar quantity

$$\vec{a} \bullet \vec{b} = a_x b_x + a_y b_y + a_z b_z = |\vec{a}|\,|\vec{b}|\cos\theta$$

given by the products of the magnitudes of the vectors and the cosine of the angle θ between them. Calculate the dot product of $\vec{a}$ and $\vec{b}$ and the angle between the vectors.

b) The **cross product** of vectors $\vec{a}$ and $\vec{b}$ is defined as the vector

$$\vec{a} \times \vec{b} = (a_y b_z - a_z b_y)\boldsymbol{i} + (a_z b_x - a_x b_z)\boldsymbol{j} + (a_x b_y - a_y b_x)\boldsymbol{k}$$

which has magnitude $|\vec{a}|\,|\vec{b}|\sin\theta$ and direction that a right-hand screw would travel as $\vec{a}$ rotates into $\vec{b}$. Calculate the cross product of $\vec{a}$ and $\vec{b}$ and its magnitude.

c) Show that $\vec{a} \times \vec{a} = 0$.

d) Show that $\vec{a} \times \vec{b} = -\vec{b} \times \vec{a}$.

5. If the components of a vector depend on a quantity such as time, then the derivative of the vector is

$$\frac{d\vec{a}}{dt} = \frac{da_x}{dt}\hat{i} + \frac{da_y}{dt}\hat{j} + \frac{da_z}{dt}\hat{k}$$

Show that

$$\frac{d}{dt}(\vec{a} \bullet \vec{b}) = \frac{d\vec{a}}{dt} \bullet \vec{b} + \vec{a} \bullet \frac{d\vec{b}}{dt}$$

$$\frac{d}{dt}(\vec{a} \times \vec{b}) = \frac{d\vec{a}}{dt} \times \vec{b} + \vec{a} \times \frac{d\vec{b}}{dt}$$

What is angular momentum? When is it important?

6. Using the results of problem 5, prove (*Hint*: Start with $\mathrm{d}(\vec{a}\times\vec{a})/\mathrm{d}t = 0$)

$$\vec{a}\times\frac{\mathrm{d}\vec{a}}{\mathrm{d}t} + \frac{\mathrm{d}\vec{a}}{\mathrm{d}t}\times\vec{a} = 0$$

$$\vec{a}\times\frac{\mathrm{d}^2\vec{a}}{\mathrm{d}t^2} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\vec{a}\times\frac{\mathrm{d}\vec{a}}{\mathrm{d}t}\right)$$

7. In vector notation, Newton's equation for a single particle is

$$m\frac{\mathrm{d}^2\vec{r}(x,y,z)}{\mathrm{d}t^2} = \vec{F}(x,y,z)$$

a) Using the results from Question 6 and operating from the left with $\vec{r}\,\times$, show that

$$m\frac{\mathrm{d}}{\mathrm{d}t}\left(\vec{r}\times\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}\right) = \vec{r}\times\vec{F}$$

b) The momentum $\vec{p}$ is defined as

$$\vec{p} = m\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}$$

Show that

$$\frac{\mathrm{d}}{\mathrm{d}t}(\vec{r}\times\vec{p}) = \vec{r}\times\vec{F}$$

This is **Newton's equation of motion for a rotating system.** It shows the origins of the angular momentum $\vec{\ell} = \vec{r}\times\vec{p}$. Notice that the angular momentum is constant if $\vec{r}\times\vec{F} = 0$. ($\vec{r}\times\vec{F}$ is called the "torque".) We will see that angular momentum is an important property of electrons in atoms and molecules, and is quantized.

c) Show that the expression $\vec{r}\times\vec{p}$ reduces to $\ell = mvr$ for magnitude of angular momentum for circular motion. (Recall that we used this result to calculate energy levels for the hydrogen atom.) What is the direction of $\vec{\ell}$ for circular motion?

8. ***Quantum mechanical operators are Hermitian.***

Energy, momentum and other important physical quantities are real numbers (not complex or imaginary like $a + ib$ or ib) evaluated by applying quantum mechanical operators to wave functions. Operators and wave functions, however, can be complex or imaginary. This places important mathematical restrictions on both the operators and wave functions that we should know about.

If eigenvalues a defined by $\hat{O}\Psi = a\Psi$ are real numbers, then we can show

$$\int_{-\infty}^{\infty}\Psi^*\hat{O}\Psi dx = \int_{-\infty}^{\infty}\Psi\hat{O}^*\Psi^* dx \qquad (1)$$

Operators satisfying this condition are called "Hermitian". Multiplying $\hat{O}\Psi = a\Psi$ from the left by Ψ^* and integrating gives

$$\int_{-\infty}^{\infty}\Psi^*\hat{O}\Psi dx = \int_{-\infty}^{\infty}\Psi^* a\Psi dx = a\int_{-\infty}^{\infty}\Psi^*\Psi dx = a$$

Taking the complex conjugate of $\hat{O}\Psi = a\Psi$ and requiring a to be real ($a = a^*$) gives

$$\hat{O}^*\Psi^* = a^*\Psi^* = a\Psi^*$$

Multiplying from the left by Ψ and integrating gives

$$\int_{-\infty}^{\infty}\Psi\hat{O}^*\Psi^* dx = \int_{-\infty}^{\infty}\Psi a\Psi^* dx = a\int_{-\infty}^{\infty}\Psi\Psi^* dx = a$$

which proves equation (1) is valid for a Hermitian operator. Equation (2) is often used for a more general definition of a Hermitian operator

$$\int_{-\infty}^{\infty}\Psi^*\hat{O}\Phi dx = \int_{-\infty}^{\infty}\Phi\hat{O}^*\Psi^* dx \qquad (2)$$

Using equation (1) as the criterion, which of the following operators are Hermitian?

$d/dx \qquad i d/dx \qquad d^2/dx^2 \qquad i d^2/dx^2 \qquad x \qquad x d/dx$

9. ***Quantum mechanical operators are Hermitian and their eigenvalues are real. In addition, the eigenfunctions must satisfy special conditions too: they are orthogonal.***

Consider the two eigenvalue equations: $\hat{O}\Psi_n = a_n\Psi_n$ and $\hat{O}\Psi_m = a_m\Psi_m$

Multiply the first by Ψ_m^* and integrate. Then take the complex conjugate of the second and multiply by Ψ_n and integrate.

$$\int_{-\infty}^{\infty}\Psi_m{}^*\hat{O}\Psi_n\,dx = a_n\int_{-\infty}^{\infty}\Psi_m{}^*\Psi_n\,dx$$

$$\int_{-\infty}^{\infty}\Psi_n\,\hat{O}^*\Psi_m{}^*dx = a_m^*\int_{-\infty}^{\infty}\Psi_n\Psi_m{}^*dx$$

Subtracting the second of these equations from the first gives

$$\int_{-\infty}^{\infty}\Psi_m{}^*\hat{O}\Psi_n\,dx - \int_{-\infty}^{\infty}\Psi_n\,\hat{O}^*\Psi_m{}^*dx = (a_n - a_m^*)\int_{-\infty}^{\infty}\Psi_m{}^*\Psi_n dx$$

Because the operator is Hermitian, the left side is zero and therefore

$$(a_n - a_m^*)\int_{-\infty}^{\infty}\Psi_m{}^*\Psi_n dx = 0$$

There are two possibilities to consider: $n = m$ and $n \neq m$. When $n = m$, because the wave function is normalized, we have

$$(a_n - a_n^*)\int_{-\infty}^{\infty}\Psi_n{}^*\Psi_n dx = (a_n - a_n^*)(1) = 0$$

and therefore $a_n = a_n^*$. This is just another proof the eigenvalues are real.

The result for $n \neq m$ is more interesting.

$$(a_n - a_m^*)\int_{-\infty}^{\infty}\Psi_m{}^*\Psi_n dx = 0 \qquad n \neq m$$

In most cases, all of the eigenvalues are different (for example, the energy levels E_1, E_2, E_3, ... of the hydrogen atom, particle in box, harmonic oscillator, *etc.*). For **nondegenerate eigenvalues** ($a_n \neq a_m$), we have the important result

$$\int_{-\infty}^{\infty} \Psi_m^* \Psi_n \, dx = 0 \qquad n \neq m$$

A set of eigenfunctions that satisfies this condition is said to be **orthogonal**. A set of functions that is normalized and orthogonal is **orthonormal.**

a) Show that the wave functions for a particle in a box of width L

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{L}\right)$$

are orthogonal.

b) Show that the wave functions for a particle moving on a ring of radius R

$$\Psi_m(\theta) = \frac{1}{\sqrt{2\pi}} e^{im\theta} \qquad m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

are orthogonal. θ is the angular position of the particle ($0 \le \theta \le 2\pi$).

10. Sets of orthogonal functions are enormously useful in quantum chemistry and in many other branches of science. Quantum chemistry computer programs such as Gaussian 98, for example, are used to estimate molecular wave functions by taking sums of Gaussian functions.

Consider an arbitrary function $f(x)$ and a set of orthogonal functions $\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, $\psi_4(x)$, … In practice, $f(x)$ could be a quantum mechanical wave function we want to calculate, a voltage in a communication line, a spectrum, *etc.* The set of functions $\psi_n(x)$ is **complete** if it is possible to express $f(x)$ as

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

But what are the values of c_1, c_2, c_3, c_4, … ? Because the set of functions is orthogonal, multiplying both sides of the expression for $f(x)$ by $\psi_m^*(x)$ and integrating gives

$$\int_{-\infty}^{\infty}\psi_m^*(x)f(x)\mathrm{d}x=\sum_{n=1}^{\infty}c_n\int_{-\infty}^{\infty}\psi_m^*(x)\psi_n(x)\mathrm{d}x=c_m\int_{-\infty}^{\infty}\psi_m^*(x)\psi_m(x)\mathrm{d}x$$

This is the formula for calculating the coefficients of the expansion of $f(x)$ in terms of the basis set of functions $\psi_m(x)$.

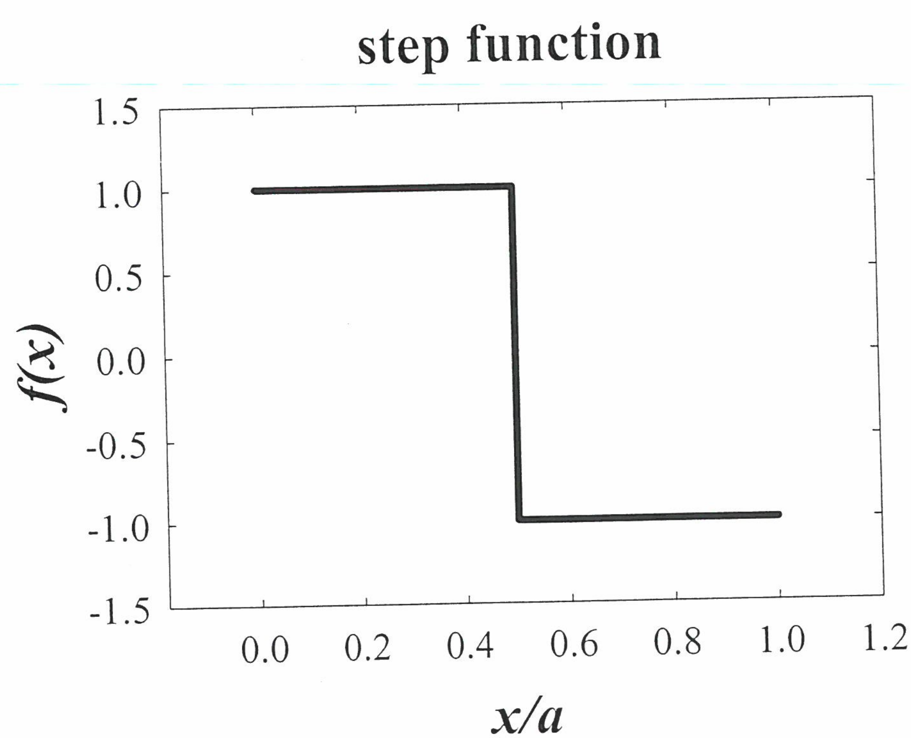
If $\psi_m(x)$ is real and normalized then $\psi_m^*(x) = \psi_m(x)$, $\int \psi_m^* \psi_m \mathrm{d}x = 1$ and

$$c_m = \int_{-\infty}^{\infty}\psi_m(x)f(x)\mathrm{d}x$$

a) Use a sum of the sine functions $\sin(m\pi x/a)$ to represent the step function

$f(x) = 1$ for $0 \le x \le a/2$

$f(x) = -1$ for $a/2 \le x \le a$



Chemistry 331 <u>Tutorial #3</u>

(1.) a) $\frac{\partial \Psi(x,t)}{\partial t} = \psi(x)(-i2\pi\nu)e^{-i2\pi\nu t}$

$\frac{\partial^2 \Psi}{\partial t^2} = \psi(x)(-i2\pi\nu)^2 e^{-i2\pi\nu t}$

$= -4\pi^2\nu^2\psi(x)e^{-i2\pi\nu t}$

$= -4\pi^2\nu^2\Psi(x,t)$

$\frac{\partial \Psi(x,t)}{\partial x} = \left[A\frac{2\pi}{\lambda}\cos\left(\frac{2\pi x}{\lambda}\right) - B\frac{2\pi}{\lambda}\sin\left(\frac{2\pi x}{\lambda}\right)\right]e^{-i2\pi\nu t}$

$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\left[A\sin\left(\frac{2\pi x}{\lambda}\right) + B\cos\left(\frac{2\pi x}{\lambda}\right)\right]e^{-i2\pi\nu t} = -\frac{4\pi^2}{\lambda^2}\Psi(x,t)$

$v^2\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\frac{4\pi^2 v^2}{\lambda^2}\Psi(x,t)$

but $v = \lambda\nu$

and $\frac{v}{\lambda} = \nu$

$= -4\pi^2\nu^2\Psi(x,t)$

$= \frac{\partial^2 \Psi(x,t)}{\partial t^2}$

$\nu = \frac{E_x}{h}$ $\lambda = \frac{h}{p_x}$

b) $\frac{\partial^2 \Psi(x,t)}{\partial t^2} = v^2\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \nu^2\lambda^2\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{E_x^2}{h^2}\frac{h^2}{p_x^2}\frac{\partial^2 \Psi(x,t)}{\partial x^2}$

$\frac{\partial^2 \Psi(x,t)}{\partial t^2} = \frac{E_x^2}{p_x^2}\frac{\partial^2 \Psi(x,t)}{\partial x^2}$

$\Psi(x,t) = \psi(x)e^{-2\pi i\nu t}$

$(-2\pi i\nu)^2\psi(x)\cancel{e^{-2\pi i\nu t}} = \frac{E_x^2}{p_x^2}\cancel{e^{-2\pi i\nu t}}\frac{\partial^2\psi(x)}{\partial x^2}$

$\frac{\partial^2\psi(x)}{\partial x^2} = -\frac{p_x^2}{E_x^2}4\pi^2\nu^2\psi(x) = -4\pi^2\frac{p_x^2}{E_x^2}\left(\frac{E_x}{h}\right)^2\psi(x) = -4\pi^2\frac{p_x^2}{h^2}\psi(x)$

but $p_x^2 = 2m(E - V(x))$

(1 b) cont.)

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{4\pi^2 2m(E_x - V(x))}{h^2}\psi(x) \Rightarrow \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2}[E_x - V(x)]\psi(x) = 0$$

(2.) compare $\frac{P_x^2}{2m} + V(x) = E_x$

with $-\frac{1}{2m}\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2 \psi(x) + V(x)\psi(x) = E\psi(x)$

$$\hat{H} = \frac{1}{2m}\left(\frac{-h}{2\pi i}\frac{\partial}{\partial x}\right)^2 + V(x) = \frac{\hat{P}_x^2}{2m} + V(x)$$

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(3) $$-\frac{i2\pi\nu P_x^2}{E_x^2}\frac{\partial \Psi(x,t)}{\partial t} = \frac{\partial^2 \Psi(x,t)}{\partial x^2}$$

$P_x^2 = 2m(E_x - V(x))$

$\nu = \frac{E_x}{h}$

$$= \frac{-i2\pi E_x 2m(E_x - V(x))}{h E_x^2}\frac{\partial \Psi(x,t)}{\partial t}$$

$$= -\frac{2\pi i 2m E_x^2}{h E_x^2}\frac{\partial \Psi(x,t)}{\partial t} + \frac{2\pi i 2m E_x V(x)}{h E_x^2}\frac{\partial \Psi(x,t)}{\partial t}$$

$$= -\frac{4\pi i m}{h}\frac{\partial \Psi(x,t)}{\partial t} + \frac{4\pi i m V(x)}{h E_x}(-2\pi i \nu)\Psi(x,t)$$

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\frac{4\pi i m}{h}\frac{\partial \Psi(x,t)}{\partial t} + \frac{8\pi^2 m V(x)}{h E_x}\frac{E_x}{h}\Psi(x,t)$$

$$\frac{8\pi^2 m}{h^2}\frac{h}{2\pi i} = -\frac{4\pi i m}{h}$$

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{4\pi i m}{h}\frac{\partial \Psi(x,t)}{\partial t} - \frac{8\pi^2 m}{h^2}V(x) = 0$$

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left(\frac{-h}{2\pi i}\frac{\partial \Psi(x,t)}{\partial t} - V(x)\right)\Psi(x,t) = 0$$

$\vec{a} = 2\hat{i} - \hat{j} + 3\hat{k}$ $\qquad$ $\vec{b} = \hat{i} + 2\hat{j} + \hat{k}$

(4) a) $\vec{a}\cdot\vec{b} = 2(1) + (-1)(2) + 3(1) = 3$

$|\vec{a}| = \sqrt{2^2 + (-1)^2 + 3^2} = \sqrt{14} = 3.741$

$|\vec{b}| = \sqrt{1^2 + 2^2 + 1^2} = \sqrt{6} = 2.449$

$\vec{a}\cdot\vec{b} = 3 = \sqrt{14}\sqrt{6}\cos\theta$ $\qquad$ $\cos\theta = \frac{3}{\sqrt{84}} = 0.3273\ldots$

$\theta = 70.89°$

b) $\vec{a}\times\vec{b} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ a_x & a_y & a_z \\ b_x & b_y & b_z \end{vmatrix} = \hat{i}(a_y b_z - b_y a_z) + \hat{j}(a_z b_x - a_x b_z) + \hat{k}(a_x b_y - a_y b_x)$

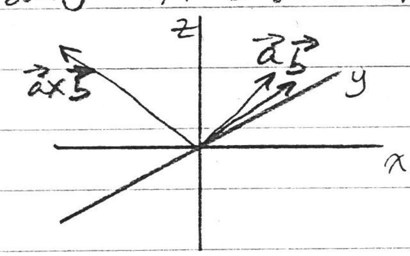
$\vec{a}\times\vec{b} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ 2 & -1 & 3 \\ 1 & 2 & 1 \end{vmatrix} = \hat{i}(-1-6) + \hat{j}(3-2) + \hat{k}(4+2)$

$= -7\hat{i} + \hat{j} + 6\hat{k}$

magnitude of $\vec{a}\times\vec{b} = |\vec{a}\times\vec{b}| = |\vec{a}||\vec{b}|\sin\theta = \sqrt{14}\sqrt{6}\sin 70.89°$

$= 9.165(0.9449)$

$= 8.660$



c) $\vec{a}\times\vec{a} = (a_y a_z - a_z a_y)\hat{i} + (a_z a_x - a_x a_z)\hat{j} + (a_x a_y - a_y a_x)\hat{k} = 0$

d) $-\vec{b}\times\vec{a} = [-b_y a_z - (-b_z)a_y]\hat{i} + [(-b_z)a_x - (-b_x)a_z]\hat{j} + [(-b_x)a_y - (-b_y)a_x]\hat{k}$

$= (a_y b_z - a_z b_y)\hat{i} + (a_z b_x - a_x b_z)\hat{j} + (a_x b_y - a_y b_x)\hat{k}$

$= \vec{a}\times\vec{b}$

(5) $\vec{a} \cdot \vec{b} = a_x b_x + a_y b_y + a_z b_z$

$$\frac{d(\vec{a}\cdot\vec{b})}{dt} = \frac{d}{dt}(a_x b_x + a_y b_y + a_z b_z)$$

$$= b_x \frac{da_x}{dt} + b_y \frac{da_y}{dt} + b_z \frac{da_z}{dt} + a_x \frac{db_x}{dt} + a_y \frac{db_y}{dt} + a_z \frac{db_z}{dt}$$

$$= \frac{d\vec{a}}{dt} \cdot \vec{b} + \vec{a} \cdot \frac{d\vec{b}}{dt}$$

$$\frac{d(\vec{a}\times\vec{b})}{dt} = \frac{d}{dt}(a_y b_z - a_z b_y)\hat{\imath} + \frac{d}{dt}(a_z b_x - a_x b_z)\hat{\jmath} + \frac{d}{dt}(a_x b_y - a_y b_x)\hat{k}$$

$$= \left(\frac{da_y}{dt} b_z - \frac{da_z}{dt} b_y\right)\hat{\imath} + \left(\frac{da_z}{dt} b_x - \frac{da_x}{dt} b_z\right)\hat{\jmath} + \left(\frac{da_x}{dt} b_y - \frac{da_y}{dt} b_x\right)\hat{k}$$

$$+ \left(a_y \frac{db_z}{dt} - a_z \frac{db_y}{dt}\right)\hat{\imath} + \left(a_z \frac{db_x}{dt} - a_x \frac{db_z}{dt}\right)\hat{\jmath} + \left(a_x \frac{db_y}{dt} - a_y \frac{db_x}{dt}\right)\hat{k}$$

$$= \frac{d\vec{a}}{dt} \times \vec{b} + \vec{a} \times \frac{d\vec{b}}{dt}$$

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from 4C: from 5:

(6) $$\frac{d(\vec{a}\times\vec{a})}{dt} = 0 = \frac{d\vec{a}}{dt} \times \vec{a} + \vec{a} \times \frac{d\vec{a}}{dt}$$

from 5:

$$\frac{d}{dt}\left(\vec{a} \times \frac{d\vec{a}}{dt}\right) = \frac{d\vec{a}}{dt} \times \frac{d\vec{a}}{dt} \,(\to 0) + \vec{a}\, \frac{d}{dt}\frac{d\vec{a}}{dt} = \vec{a}\, \frac{d^2\vec{a}}{dt^2}$$

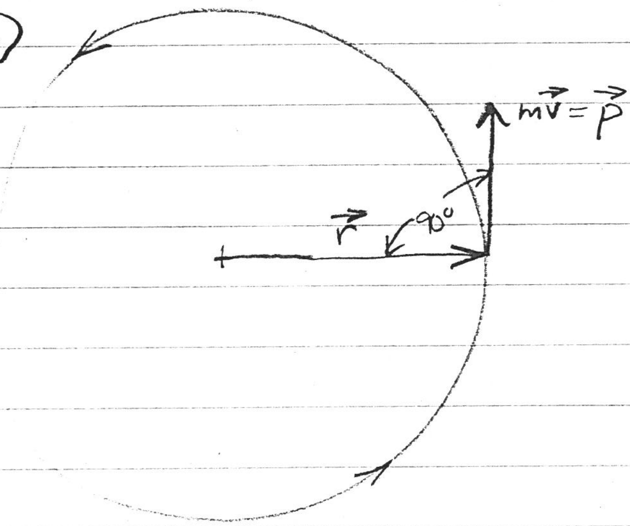
(m scalar)

⑦ a) $m \frac{d}{dt}\left(\vec{r} \times \frac{d\vec{r}}{dt}\right) = m\left(\vec{r} \times \frac{d^2\vec{r}}{dt^2}\right) = \vec{r} \times \left(m\frac{d^2\vec{r}}{dt^2}\right) = \vec{r} \times \vec{F}$

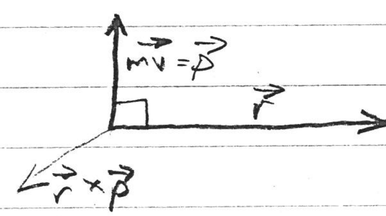
b) $\frac{d}{dt}(\vec{r} \times \vec{p}) = \vec{r} \times \frac{d\vec{p}}{dt} = \vec{r} \times \left(\frac{d}{dt}\left(m\frac{d\vec{r}}{dt}\right)\right) = \vec{r} \times \left(m\frac{d^2\vec{r}}{dt^2}\right)$

$\frac{d(\vec{r} \times \vec{p})}{dt} = \vec{r} \times \vec{F}$

c)



equivalent to



$$\vec{r} \times \vec{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ r & 0 & 0 \\ 0 & mv & 0 \end{vmatrix} = rmv\,\hat{k}$$

magnitude rmv

in +ve z direction

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⑧ a) Is $\boxed{\frac{d}{dx}}$ a Hermitian operator? (integrate by parts)

assume $f \to 0$, $x \to \pm\infty$

$$\int_{-\infty}^{\infty} f^* \frac{d}{dx} f \, dx = \int_{-\infty}^{\infty} f^* \frac{df}{dx} dx = \int_{-\infty}^{\infty} f^* df = \left.(f^* f)\right|_{-\infty}^{\infty} - \int f \, df^*$$

($(f^*f)\big|_{-\infty}^{\infty} \to 0$)

$\int f^* \frac{df}{dx} dx = - \int f \frac{df^*}{dx} dx$ ← not Hermitian

(8 cont.)

(proportional to momentum operator $\hat{P}_x$)

b) is $i\frac{d}{dx}$ Hermitian?

assume f vanishes at $x = \infty$ and $x = -\infty$

$$\int_{-\infty}^{\infty} f^* i\frac{d}{dx} f\,dx = i\int_{-\infty}^{\infty} f^*\frac{df}{dx}\,dx = -i\int_{-\infty}^{\infty} f\frac{df^*}{dx}\,dx$$

$$= \int_{-\infty}^{\infty} f\left(i\frac{d}{dx}\right)^* f^*\,dx$$

Hermitian

c) is $\frac{d^2}{dx^2}$ Hermitian?

proportional to the kinetic energy operator

$$\int f^*\frac{d^2f}{dx^2}\,dx = \int f^*\frac{d}{dx}\left(\frac{df}{dx}\right)dx = f^*\frac{df}{dx}\Big|_{-\infty}^{\infty}{}^{\nearrow 0} - \int_{-\infty}^{\infty}\frac{df}{dx}\,df^*$$

$$= -\int_{-\infty}^{\infty}\frac{df}{dx}\frac{df^*}{dx}\,dx = -\int_{-\infty}^{\infty}\frac{df^*}{dx}\frac{df}{dx}\,dx$$

$$= -\left(f\frac{df^*}{dx}\right)\Big|_{-\infty}^{\infty}{}^{\nearrow 0} + \int_{-\infty}^{\infty} f\frac{d\frac{df^*}{dx}}{dx}\,dx = \int_{-\infty}^{\infty} f\frac{d^2f^*}{dx^2}\,dx$$

Hermitian

d) is $i\frac{d^2}{dx^2}$ Hermitian?

$$\int f^* i\frac{d^2f}{dx^2}\,dx = f^* i\frac{df}{dx}\Big|_{-\infty}^{\infty}{}^{\nearrow 0} - i\int_{-\infty}^{\infty}\frac{df^*}{dx}\frac{df}{dx}\,dx$$

$$= -i f\frac{df^*}{dx}\Big|_{-\infty}^{\infty}{}^{0} + i\int_{-\infty}^{\infty} f\frac{d^2f^*}{dx^2} = -\int_{-\infty}^{\infty} f\left(i f\frac{d^2f^*}{dx^2}\right)^* dx$$

Not Hermitian

(9a cont.)

if $n = m$, then $\int_0^L \psi_n^* \psi_n \, dx = \frac{2}{L}\int_0^L \sin\frac{n\pi x}{L} \sin\frac{n\pi x}{L}\, dx$

$$= \frac{2}{L}\int_0^L \left(\frac{\cos 0}{2} - \frac{\cos\frac{2n\pi x}{L}}{2}\right) dx = \frac{2}{L}\int_0^L \frac{1}{2}\,dx - \frac{2}{L}\int \frac{\cos\frac{2n\pi x}{L}}{2}\,dx$$

$$= \frac{L-0}{L} + \frac{1}{L}\frac{L}{2n\pi}\sin\frac{2n\pi x}{L}\Big|_0^L = \frac{L}{L} + 0 = 1$$

orthogonal and normalized $\Longrightarrow$ orthonormal

what if you can't remember trig. identities!

could also use:

$$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} \qquad \cos\theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

then:

$$\int_0^L \psi_n^* \psi_m \, dx = \frac{2}{L}\int_0^L \left(\sin\frac{n\pi x}{L}\right)\left(\sin\frac{m\pi x}{L}\right) dx$$

$$= \frac{2}{L}\int_0^L \left(\frac{e^{in\pi x/L} - e^{-in\pi x/L}}{2i}\right)\left(\frac{e^{im\pi x/L} - e^{-im\pi x/L}}{2i}\right) dx$$

$$= \frac{2}{L}\frac{1}{4i^2}\int_0^L \left(e^{i(n+m)\pi x/L} - e^{i(n-m)\pi x/L} - e^{i(m-n)\pi x/L} + e^{-i(n+m)x\pi/L}\right) dx$$

$$= \frac{-2}{L}\frac{1}{2}\int_0^L \left[\left(\frac{e^{i(n+m)\pi x/L} + e^{-i(n+m)\pi x/L}}{2}\right) - \left(\frac{e^{i(n-m)\frac{\pi x}{L}} + e^{-i(n-m)\pi x/L}}{2}\right)\right] dx$$

(9a) cont.)

$$= \frac{2}{L}\int_0^L \left(\frac{\cos\frac{(n-m)\pi x}{L}}{2} - \frac{\cos\frac{(n+m)\pi x}{L}}{2}\right) dx$$

then same derivation as used previously

⋮

b) shows that $\psi_m(\theta) = \frac{1}{\sqrt{2\pi}} e^{im\theta}$ $m = 0, \pm 1, \pm 2, \ldots$

is an orthonormal set of functions.

$e^{i\theta} = \cos\theta + i\sin\theta$

$$\int_0^{2\pi} \psi_m^*(\theta)\,\psi_n(\theta)\,d\theta = \int_0^{2\pi} \left(\frac{1}{\sqrt{2\pi}} e^{im\theta}\right)^* \left(\frac{1}{\sqrt{2\pi}} e^{in\theta}\right) d\theta$$

$$= \frac{1}{2\pi}\int_0^{2\pi} e^{-im\theta} e^{in\theta}\,d\theta = \frac{1}{2\pi}\int_0^{2\pi} e^{i(n-m)\theta}\,d\theta$$

$$= \frac{1}{2\pi}\int_0^{2\pi} [\cos(n-m)\theta + i\sin(n-m)\theta]\,d\theta$$

if $n \neq m$:

$$\int_0^{2\pi} \psi_m^*(\theta)\psi_n(\theta)\,d\theta = \frac{1}{2\pi}\frac{1}{n-m}\sin(n-m)\theta\Big|_0^{\theta=2\pi} - \frac{i}{2\pi}\frac{1}{n-m}\cos(n-m)\theta\Big|_0^{2\pi}$$

$$= \frac{1}{2\pi}\frac{1}{n-m}(0-0) - \frac{i}{2\pi}\frac{1}{n-m}(1-1) = 0$$

if $n = m$:

$$\int_0^{2\pi} \psi_n^*\psi_n\,d\theta = \frac{1}{2\pi}\int_0^{2\pi}[\cos(0) + i\sin(0)]\,d\theta = \frac{1}{2\pi}\int_0^{2\pi} d\theta = \frac{2\pi}{2\pi} = 1$$

($\cos(0) \to 1$, $\sin(0) \to 0$)

orthonormal

(10.) step function (or square wave with wavelength a):

$$f(x) = 1 \quad \text{for} \quad 0 \leq x \leq a/2$$

$$f(x) = -1 \quad \text{for} \quad a/2 \leq x \leq a$$

use a series of sine and cosine functions to represents f(x)

$$f(x) = \sum_{m=1}^{\infty}\left(c_m \sin\frac{2m\pi x}{a} + b_m \cos\frac{2m\pi x}{a}\right)$$

often called "Fourier" analysis

$$\int_0^a f(x)\cos\left(\frac{2m\pi x}{a}\right)dx = \int_0^{a/2}\cos\left(\frac{2m\pi x}{a}\right)dx - \int_0^{a/2}\cos\frac{2m\pi x}{a}\,dx$$

$$= \frac{a}{2m\pi}\left[\sin\frac{2m\pi x}{a}\Big|_0^{a/2} - \sin\frac{2m\pi x}{a}\Big|_{a/2}^{a}\right]$$

$$= \frac{a}{2m\pi}\left(\sin m\pi - 0 - \sin 2m\pi + \sin m\pi\right)$$

$$= 0$$ all the b_n coefficients are zero

why?

the square wave is an "odd" function $f(x) = -f(-x)$

$\cos\frac{2m\pi x}{a}$ is an even function $\cos\theta = \cos(-\theta)$

f(x) can be expressed as a sum of $\sin\frac{2m\pi x}{a}$ functions

$\sin\theta = -\sin(-\theta)$

(10 cont.)

$$f(x) = \sum_{m=1}^{\infty} c_m \sin \frac{2m\pi x}{a} \qquad \psi_m = \sin\frac{2m\pi x}{a}$$

$$= \sum_{m=1}^{\infty} c_m \psi_m(x)$$

multiply by ψ_n^* and integrate:

$$\int_0^a \psi_n^* f(x)\,dx = \sum_{m=1}^{\infty} c_m \int \psi_n^*(x)\,\psi_m(x)\,dx$$

(orthogonal set of functions Q. 9a)

$$= c_n \int_0^a \psi_n^*(x)\,\psi_n(x)\,dx$$

$$c_n = \frac{\int_0^a \psi_n^*(x) f(x)\,dx}{\int_0^a \psi_n^*(x)\,\psi_n(x)\,dx}$$

real functions: $\psi_n^*(x) = \psi_n(x)$

$$\sin^2\theta = \frac{1}{2} - \frac{\cos 2\theta}{2}$$

normalization factor

$$\int_0^a \psi_n^*(x)\,\psi_n(x)\,dx = \int_0^a \sin^2\left(\frac{2n\pi x}{a}\right) dx$$

$$= \int_0^a \left(\frac{\cos 0}{2} - \cos\frac{4n\pi x}{a}\right) dx = \int_0^a \frac{1}{2}\,dx + \int_0^a \cos\frac{4n\pi x}{a}\,dx$$

$$= \frac{a}{2} + \frac{a}{4n\pi} \sin\frac{4n\pi}{a} x \Big|_0^a = \frac{a}{2} + 0 - 0 = \frac{a}{2}$$

$$c_n = \frac{2}{a} \int_0^a \psi_n^*(x)\, f(x)\,dx$$

(10 cont.)

$$f(x) = +1 \quad \text{for} \quad 0 \le x \le a/2$$
$$= -1 \quad \text{for} \quad a/2 \le x \le a$$

$$c_n = \frac{2}{a}\int_0^{a/2} (+1) \sin\frac{2n\pi x}{a}\,dx + \frac{2}{a}\int_{a/2}^{a} (-1) \sin\frac{2n\pi x}{a}\,dx$$

$$= -\frac{2}{a}\frac{a}{2n\pi}\cos\frac{2n\pi x}{a}\Big|_0^{a/2} + \frac{2}{a}\frac{a}{2n\pi}\cos\frac{2n\pi x}{a}\Big|_{a/2}^{a}$$

$$= \frac{1}{n\pi}\left[-\cos n\pi + 1 + \cos 2n\pi - \cos n\pi\right]$$

$$= -\frac{2}{n\pi}\cos n\pi \qquad \cos n\pi = -1 \quad n = 1, 3, 5, \ldots$$

$$\cos n\pi = 1 \quad n = 2, 4, 6, \ldots$$

<u>n odd</u> $(1, 3, 5, \ldots)$

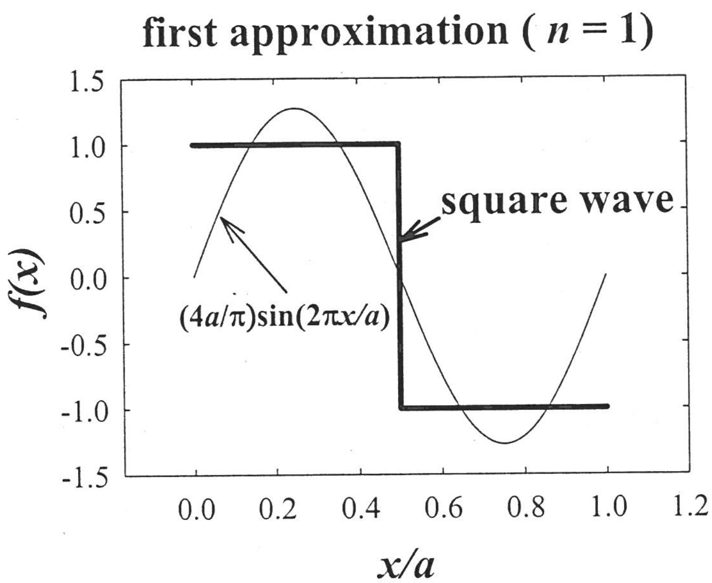
$$c_n = \frac{1}{n\pi}\left[-(-1) + 1 + 1 - (-1)\right] = \frac{4}{n\pi}$$

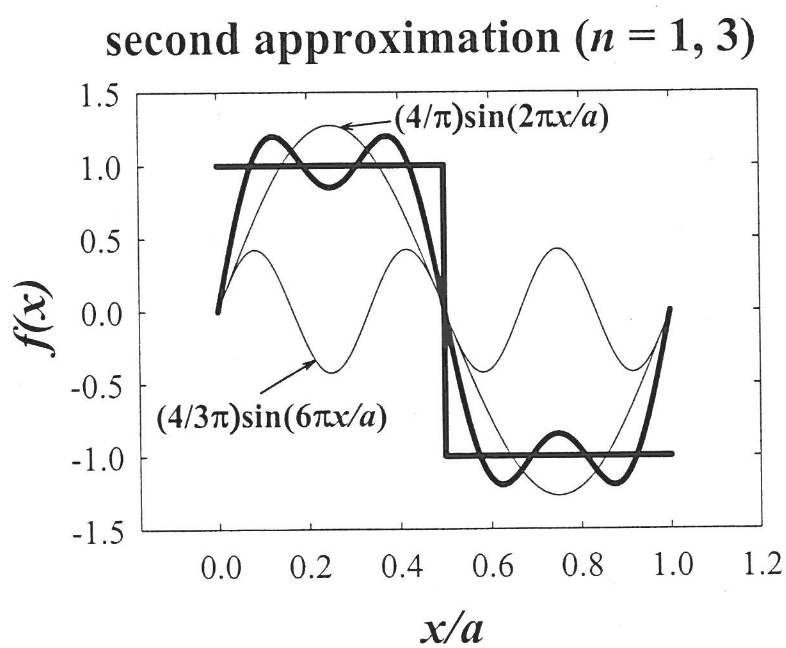
<u>n even</u> $(2, 4, 6, \ldots)$

$$c_n = \frac{1}{n\pi}\left(-1 + 1 + 1 - 1\right) = 0$$

$$\boxed{f(x) = \frac{4}{\pi}\sin\frac{2\pi x}{a} + \frac{4}{3\pi}\sin\frac{3\pi x}{a} + \frac{4}{5\pi}\sin\frac{5\pi x}{a} + \cdots}$$

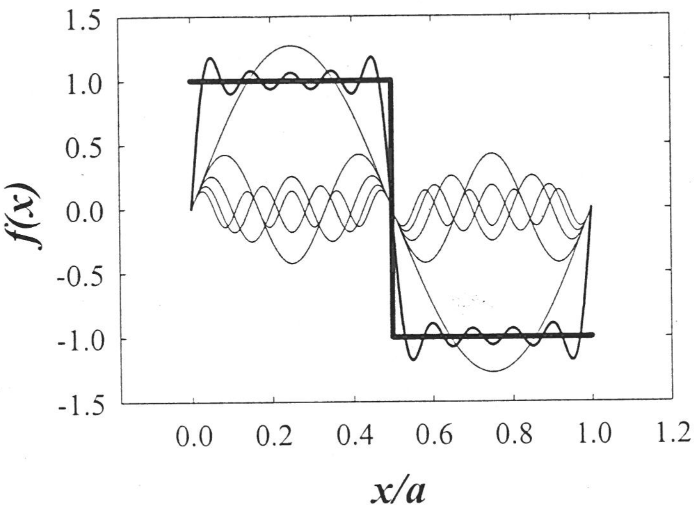
(10 cont.)


first approximation (n = 1)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
square wave
(4a/π)sin(2πx/a)
f(x)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
x/a


second approximation (n = 1, 3)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
(4/π)sin(2πx/a)
(4/3π)sin(6πx/a)
f(x)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
x/a

(10 cont.)

$n = 1, 3, 5, 7, 9$



e) is x Hermitian? x is real, so $x^* = x$

$$\int f^* x f \, dx = \int f (xf)^* dx \qquad \text{Hermitian}$$

f) $$\int f^* x \frac{df}{dx} dx = f^* x f \Big|_{-\infty}^{\infty} - \int f \left(x \frac{df^*}{dx} + f^* \right) dx$$

$$\neq \int_{-\infty}^{\infty} f x \frac{df^*}{dx} dx \qquad \text{not Hermitian}$$

(real functions, so: $\psi_n^* = \psi_n$)

9a) $$\int_0^L \psi_n^* \psi_m \, dx = \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx$$

could use the trigonometric identity:

$$\sin\alpha \sin\beta = \frac{\cos(\alpha - \beta)}{2} - \frac{\cos(\alpha + \beta)}{2}$$

$n \neq m$:

$$\frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx = \frac{2}{L} \int_0^L \left(\frac{\cos\frac{(n-m)\pi x}{L}}{2} - \frac{\cos\frac{(n+m)\pi x}{L}}{2} \right) dx$$

$$= \frac{1}{L}\left(\frac{-L}{(n-m)\pi}\right) \sin\frac{(n-m)\pi x}{L} \Big|_0^L - \frac{1}{L}\left(\frac{-L}{(n+m)\pi}\right) \sin\frac{(n+m)\pi x}{L} \Big|_0^L$$

... $\sin(2\pi)$, $\sin\pi$, $\sin 0$, $\sin\pi$, $\sin 2\pi$, ... are all zero

So if $n \neq m$, then $\int_0^L \psi_n \psi_m \, dx = 0$ (orthogonal)