1.5: The Expansion Theorem

Any arbitrary function of coordinates and time $\Omega(x, y, z, t)$

can be represented exactly in terms of the eigenfunctions $\{\phi_i\}$

(in the same coordinate/time space) of a self-adjoint operator.

→ Ω can be written as a linear combination of the eigenfunctions which are said to form a **complete set**, $\{\Phi_i\}$.

$$\Rightarrow \Omega(x, y, z, t) = \sum_{i=1}^{\infty} c_i \phi_i (x, y, z, t)$$

The $\{c_i\}$ are coefficients to be determined, and $\{\Phi_i\}$ are orthonormal with real eigenvalues since the generating operator is Hermitian.

3-D vector correspondence

Any vector $\vec{G}$ can be written as a linear combination of the orthonormal vectors $\hat{i}, \hat{j}, \hat{k}$

$$\vec{G} = G_x \hat{i} + G_y \hat{j} + G_z \hat{k}$$

$\hat{i}, \hat{j}, \hat{k}$ are the basis vectors for G and span the 3-D vector space.

$$\hat{i}, \hat{j}, \hat{k} \equiv \{\phi_i\};\ G_x, G_y, G_z \equiv \{c_i\}$$

The complete set $\{\Phi_i\}$, are said to span a Hilbert space.

Can determine the expansion coefficients by using orthonormality properties.

$$\Omega = \sum_i c_i \phi_i$$

$$\Rightarrow \phi_k^* \Omega = \sum_i c_i \phi_k^* \phi_i$$

$$\Rightarrow \int \phi_k^* \Omega d\tau = \sum_i c_i \int \phi_k^* \phi_i d\tau = c_k \because \int \phi_k^* \phi_i d\tau = \delta_{ki}$$

Thus: $$c_k = \int \phi_k^* \Omega d\tau$$

Can calculate the expectation value of any property when the system is state Ω

Assuming Ω is normalized:

$$\overline{M} = \int \Omega^* \hat{M} \Omega \, d\tau$$

$$= \int \left(\sum_i c_i^* \phi_i^* \right) \hat{M} \left(\sum_k c_k \phi_k \right) d\tau = \int \left(\sum_i c_i^* \phi_i^* \right) \left(\sum_k c_k m_k \phi_k \right) d\tau$$

$$= \sum_i \sum_k c_i^* c_k m_k \int \phi_i^* \phi_k \, d\tau = \sum_i \sum_k c_i^* c_k m_k \delta_{ik} = \sum_k c_k^* c_k m_k = \sum_k |c_k|^2 m_k$$

Here, m_k represents the value of M when system is in state Φ_k

The value of <M> when the system is in a linear combination of all states is the **weighted** average of all values in each state.

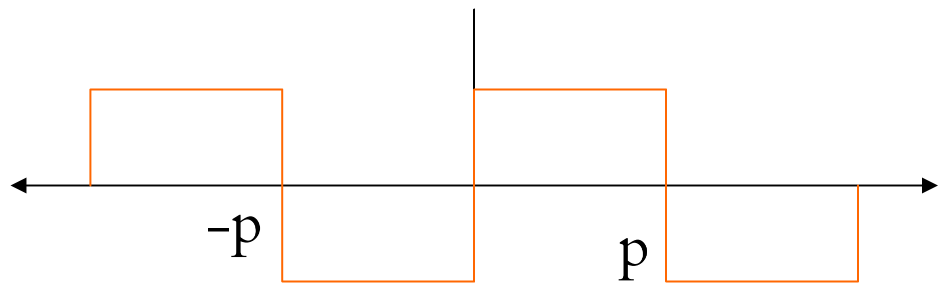
The weights $|c_k|^2$ represent the probability that the system is in state Φ_{k}.
Similarly $|c_k|^2$ = probability of finding m_k when property M is measured when system is in state Ω.

Recall that the solutions of the one-dimensional particle in the box solution are:

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \quad n = 1, 2, 3, \ldots$$

According to the postulate we just invoked, the above wave functions of the particle in a one-dimensional box form a complete set.

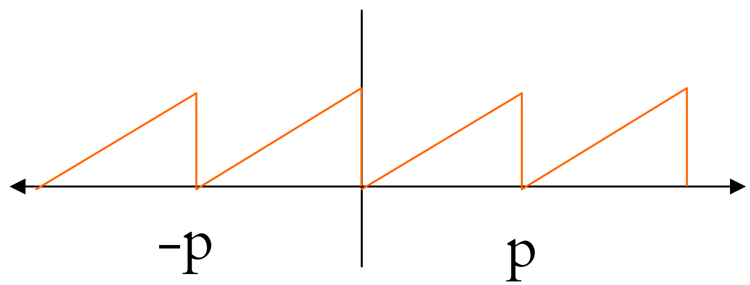
They can be used in the Fourier Series for odd parity periodic functions! We can even construct nasty functions as below with an infinite series of sine functions.

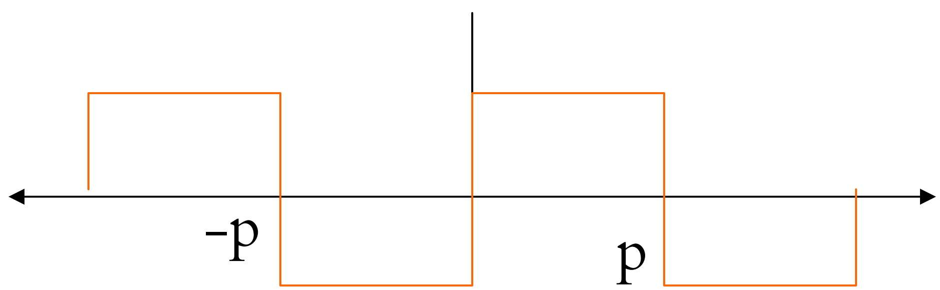


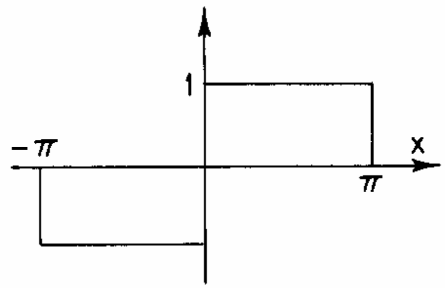
We can expand any well behaved one-dimensional periodic function as a series of sines and cosines! This is known as a Fourier series.

$$f(x) = a_o + \sum_{n=1}^{\infty}(a_n \cos nx + b_n \sin nx) \longleftarrow \text{complete set!}$$

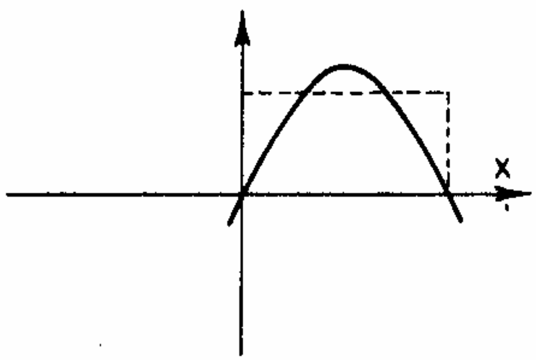
We if we use enough sine and cosine functions can represent any periodic well behaved functions, including those below:



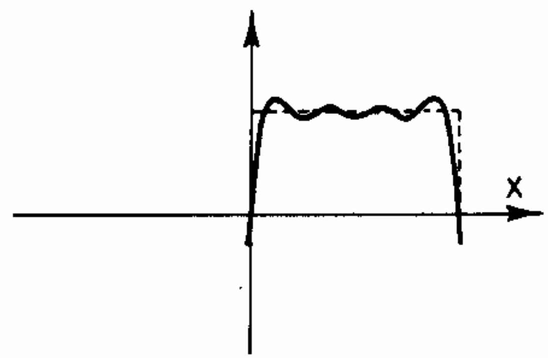




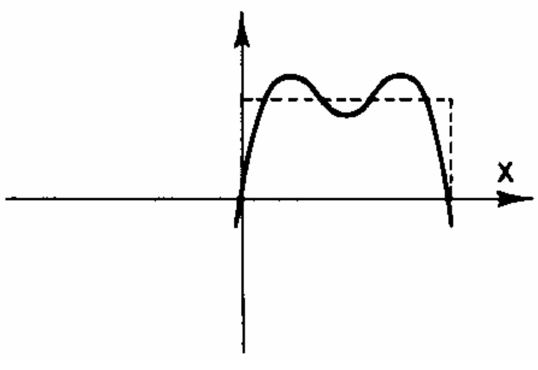
$$\widetilde{f}(x) = c_1 \sin x$$



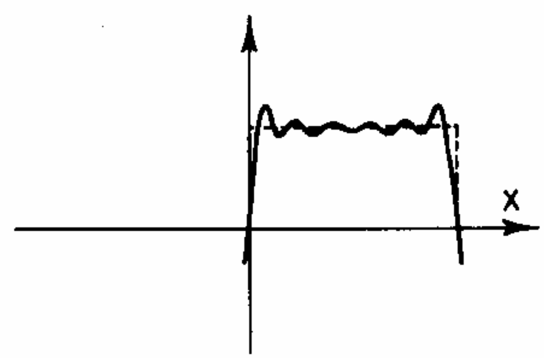
$$\widetilde{f}(x) = c_1 \sin x + c_3 \sin 3x + c_5 \sin 5x + c_7 \sin 7x$$



$$\widetilde{f}(x) = c_1 \sin x + c_3 \sin 3x$$



$$\widetilde{f}(x) = c_1 \sin x + c_3 \sin 3x + \ldots + c_{11} \sin 11x$$



1.6: A first look at transition probabilities

When the Hamiltonian is independent of time, the state of the system and its properties are independent of time

If at t=0 the system is in state Φ_1 with energy E_1, it will remain there unless **perturbed.**

When the system interacts with a time-dependent perturbation; for example, light

$$\hat{H}_{new}(t) = \hat{H}_{old} + \hat{V}(t)$$

Isolated molecule Hamiltonian → stationary state

External perturbation (light, particle collisions, etc)

Stationary states will be gone: in fact, there will be exchange of population among these levels = **transitions**= **spectroscopy**

Approach mathematically: express time varying system in terms of the original stationary states; that is, Ω(r,t) in terms of {Φ_i(r)}.

$$\Rightarrow \Omega(\vec{r},t) = \sum_i c_i \phi_i(\vec{r})$$

$$\Rightarrow c_i = c_i(t)$$

$$\Rightarrow \Omega(\vec{r},t) = \sum_i c_i(t) \phi_i(\vec{r})$$

Here, $c_i(t)$ = expansion coefficient, and Φ_i satisfies:

1.) $H_{old}(r)\Phi_i(r)=E_i\Phi_i(r)$
2.) {Φ_i} form a complete set
3.) {Φ_i} are orthonormal

Obtain $c_i(t)$ values by solving: $\hat{H}_{new}\Omega(\vec{r},t) = -\frac{\hbar}{i}\frac{\partial \Omega(\vec{r},t)}{\partial t}$

subject to initial conditions

In the old-stationary state expansion $|c_i|^2$ = probability that the expectation value of an observable M would be m_i.

Now $$\left|c_i(t)\right|^2 = c_i^*(t)c_i(t)$$

= probability of finding system in state Φ_i at time t
= probability that transitions occur into/out of state Φ_i
= transition probability

1.7: Introduce bra-ket notation: for an operator $\hat{M}$

The integral

$$m_{mn} = \int \psi_m^* \hat{M} \psi_n d\tau = \langle \psi_m | \hat{M} | \psi_n \rangle = \langle m | \hat{M} | n \rangle$$

Thus: $$\psi_m = |\psi_m\rangle = |m\rangle; \quad \psi_m^* = \langle \psi_m | = \langle m |$$

and $$\int \psi_m^* \psi_n d\tau = \langle \psi_m | \psi_n \rangle = \langle m | n \rangle = \delta_{mn}$$

and $$c_k = \langle \phi_k^* | \Omega \rangle = \langle k | \Omega \rangle$$

Will use this notation throughout the course.