PH101: Physics 1

Module 3: Introduction to Quantum Mechanics

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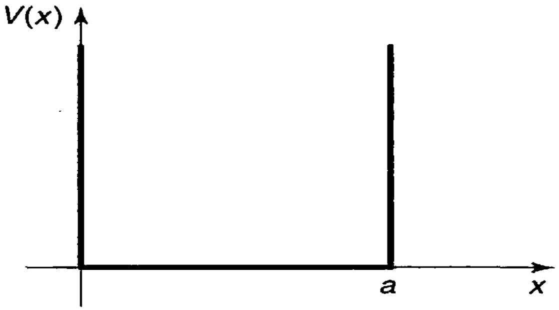
RECAP

Particle in a box (infinite square well)



$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a, \\ \infty, & \text{otherwise} \end{cases}$$

V = 0 (particle is completely free)

Particle doesn't exist at all in the region

x > a and x < 0

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi,$$

or $$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

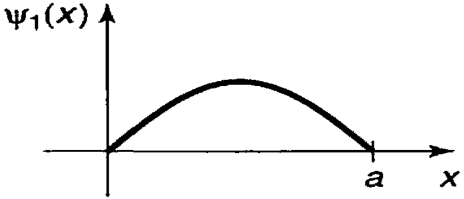
Inside the well, the solutions are (the phase of *A* carries no physical significance, hence is taken as positive)

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

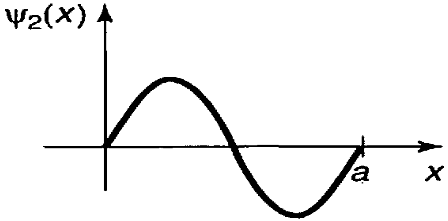
The time-independent Schrodinger equation has an infinite set of solutions (one for each positive integer n).

contd...

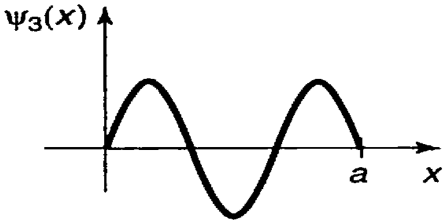
Plot the ground state, first and second excited states



Ground state



First excited state



Second excited state

Important properties of the wave function:

1. They are alternately even and odd, with respect to the center of the well: ψ_1 is even, ψ_2 is odd, ψ_3 is even, and so on.

2. As you go up in energy, each successive state has one more node (zero-crossing): ψ_1 has none (the end points don't count), ψ_2 has one, ψ_3 has two, and so on.

3. They are mutually orthogonal, in the sense tha $\int \psi_m(x)^* \psi_n(x)\, dx = 0$, whenever $m \neq n$.

To understand why this idea corresponds to orthogonality we have to understand the geometry of Hilbert space.

Geometry of Hilbert Space

- In rigid bodies, we saw that there were special directions [principal directions] called $\hat{e}_1$, $\hat{e}_2$, $\hat{e}_3$ such that the moment of inertia matrix **I** which is a 3x3 matrix when acting on any one these special directions resulted in a vector which was parallel to it. In other words,

$$\mathbf{I}\,\hat{e}_j = \mathrm{I}_j\,\hat{e}_j$$

where I_j are pure numbers with j = 1, 2, 3. In quantum mechanics, the time independent Schrodinger equation has a similar form –

$$H\,\varphi_j(x) = \mathrm{E}_j\,\varphi_j(x)$$

where instead of the 3x3 moment of inertia matrix we have the Hamiltonian operator –

$$H = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)$$

$$H = \left(- \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right)$$

While in case of rigid bodies there are only three special vectors that have this property, in quantum mechanics it is always the case that the number of special "directions" [in this case, functions] $\varphi_j(x)$, j =1,2,3,…. are infinitely many. The space generated by the unit vectors $\hat{e}_1$, $\hat{e}_2$, $\hat{e}_3$ is the usual three dimensional space of vectors. The space generated by the functions

$\varphi_j(x)$, j =1,2,3,…. is an infinite dimensional space where the most general object is a general function of x, just as in three dimensional vector space, the most general object was a general vector in 3D. This infinitely dimensional space of functions is called a Hilbert space.

In case of rigid bodies, the three directions (unit vectors) $\hat{e}_1$, $\hat{e}_2$, $\hat{e}_3$ were linearly independent and mutually orthogonal so that any other general vector may be expressed as,

$$\vec{\mathrm{v}} = c_1\ \hat{e}_1 + c_2\ \hat{e}_2 + c_3\ \hat{e}_3$$

Similarly we may expect that a general function $\psi(x)$ may be expressed as linear combinations of special "directions" $\varphi_j(x)$, j =1,2,3,….

$$\psi(x)\ = c_1\,\varphi_1(x)\ +\ c_2\,\varphi_2(x)\ +\ \ldots\ldots$$

The notion of unit vector, parallelism, orthogonality e.t.c. are geometrical notions. We would like to find analogous notions in the case of the Hilbert space of functions. Just as we know that $\hat{e}_1$ is perpendicular to $\hat{e}_2$ because $\hat{e}_1 . \ \hat{e}_2 = 0$ and we know that $\hat{e}_1$ is a unit vector because $\hat{e}_1 . \ \hat{e}_1 = 1$, can we make similar statements about the special functions $\varphi_1(x)$ and $\varphi_2(x)$? What does it mean for $\varphi_1(x)$ and $\varphi_2(x)$ to be mutually orthogonal? What does it mean for $\varphi_1(x)$ to be a unit vector? Answering these amounts to studying the "geometry" of the Hilbert space of functions.

One word of notation: We prefer to denote the dot product $\hat{e}_i . \hat{e}_j$ as $< \hat{e}_i \mid \hat{e}_j >$

One way to answer both these questions [dot product and unit vector] is to define the "dot product" between any two functions $\psi(x)$ and $\phi(x)$ is

$$\int_{-\infty}^{\infty} \psi^*(x)\, \phi(x)\, dx \equiv < \psi|\phi > = < \phi|\psi >^*$$

This means the statement that different special directions $\varphi_1(x)$ and $\varphi_2(x)$ are "mutually orthogonal" is the statement that,

$$< \varphi_1|\varphi_2 > \equiv \int_{-\infty}^{\infty} \varphi_1^*(x)\, \varphi_2(x)\, dx = 0$$

The statement that the basis function $\varphi_1(x)$ has length one (unit vector) is,

$$< \varphi_1 | \varphi_1 > \equiv \int_{-\infty}^{\infty} \varphi_1^*(x)\, \varphi_1(x)\ dx \ = \ 1$$

We also recognize this as the statement that the total probability of finding the particle somewhere on the real axis is unity.

Thus once we pin down the meaning of the dot product in the Hilbert space of functions we have understood how to do geometry in this space.

Just as a general vector in three dimensions may be written in terms of the principal directions of the rigid body as,

$$\vec{\mathrm{v}} = c_1 \, \hat{e}_1 + c_2 \, \hat{e}_2 + c_3 \, \hat{e}_3$$

and using orthogonality of these unit vectors we may write,

$$c_1 = \hat{e}_1.\vec{\mathrm{v}} \, , \, c_2 = \hat{e}_2.\vec{\mathrm{v}} \, , \, c_3 = \hat{e}_3.\vec{\mathrm{v}}$$

or, $$c_j = \hat{e}_j.\vec{\mathrm{v}} \equiv < \hat{e}_j | \vec{\mathrm{v}} >$$

In Hilbert space a general function has the expansion in terms of the basis functions,

$$\psi(x) = c_1\,\varphi_1(x) + c_2\,\varphi_2(x) + \;\ldots\ldots \qquad [1]$$

and the coefficients are similarly given as,

$$c_j \equiv <\varphi_j\,|\psi> = \int_{-\infty}^{\infty} \varphi_j^*(x)\psi(x)\;dx$$

HW: Prove this by multiplying [1] above on both sides by $\boldsymbol{\varphi_j^*(x)}$ and integrate with respect to x and use the orthogonality and normalization of the basis functions $\boldsymbol{\varphi_j(x)}$.

contd...

$$\textit{Proof}: \quad \int \psi_m(x)^* \psi_n(x)\, dx = \frac{2}{a}\int_0^a \sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{a}x\right)\, dx$$

$$= \frac{1}{a}\int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right)\right] dx$$

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

$$= \frac{1}{\pi}\left\{\frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)}\right\} = 0.$$

We can combine orthogonality and normalization into a single statement:

$$\int \psi_m(x)^* \psi_n(x)\, dx = \delta_{mn},$$

where δ_{mn} (the so-called **Kronecker delta**) is defined in the usual way,

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n; \\ 1, & \text{if } m = n. \end{cases}$$

contd...

4. They are complete, in the sense that any other function, $f(x)$, can be expressed as a linear combination of them:

$$f(x)=\sum_{n=1}^{\infty} c_n \psi_n(x)=\sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right).$$

This represents **Fourier series** for f(x), and the fact that "any" function can be expanded in this way is sometimes called **Dirichlet's theorem**.
The coefficients c_n can be evaluated by Fourier's trick, which exploits the orthonormality of $\{\psi_n\}$ Multiply both sides of the above equation by $\psi_m(x)^*$ and integrate.

$$\int \psi_m(x)^* f(x)\, dx=\sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)\, dx=\sum_{n=1}^{\infty} c_n \delta_{mn}=c_m.$$

Thus the nth coefficient in the expansion of $f(x)$ is

$$c_n=\int \psi_n(x)^* f(x)\, dx.$$

Thus, the **stationary states** are given by **contd...**

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.$$

and the most general solution is $$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.$$

Above equation gives $$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x).$$

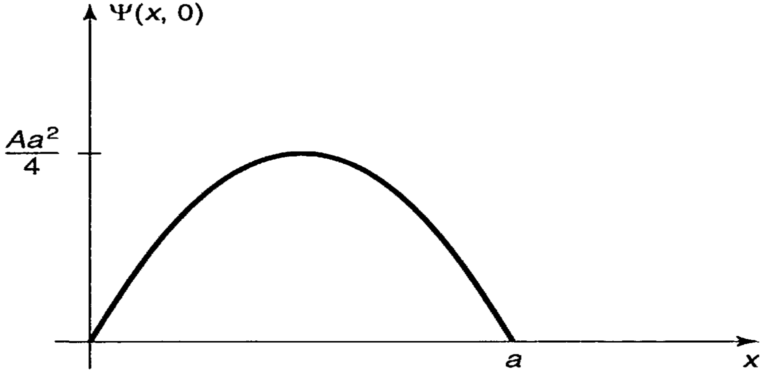
And using the Fourier's trick, we get $$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0)\,dx.$$

Given the initial wave function ψ (*x*, 0), we first compute the expansion coefficients c_n, and then obtain ψ(*x*, *t*).

Example: A particle in the infinite square well has the initial wave function

$$\Psi(x,0) = Ax(a-x), \qquad (0 \le x \le a).$$

for some constant *A* . Outside the well, of course, $\psi = 0$. Plot $\psi(x, 0)$. Find $\psi(x, t)$.



Normalize the wave function,

$$1 = \int_0^a |\Psi(x,0)|^2\, dx = |A|^2 \int_0^a x^2(a-x)^2\, dx = |A|^2 \frac{a^5}{30},$$

$$A = \sqrt{\frac{30}{a^5}}.$$

contd...

$$
\begin{aligned}
c_n &= \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{30}{a^5}}\, x(a-x)\, dx \\
&= \frac{2\sqrt{15}}{a^3}\left[a \int_0^a x \sin\left(\frac{n\pi}{a}x\right) dx - \int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right) dx\right] \\
&= \frac{2\sqrt{15}}{a^3}\left\{a\left[\left(\frac{a}{n\pi}\right)^2 \sin\left(\frac{n\pi}{a}x\right) - \frac{ax}{n\pi}\cos\left(\frac{n\pi}{a}x\right)\right]\Bigg|_0^a\right. \\
&\quad \left. - \left[2\left(\frac{a}{n\pi}\right)^2 x \sin\left(\frac{n\pi}{a}x\right) - \frac{(n\pi x/a)^2 - 2}{(n\pi/a)^3}\cos\left(\frac{n\pi}{a}x\right)\right]\Bigg|_0^a\right\} \\
&= \frac{2\sqrt{15}}{a^3}\left[-\frac{a^3}{n\pi}\cos(n\pi) + a^3\frac{(n\pi)^2-2}{(n\pi)^3}\cos(n\pi) + a^3\frac{2}{(n\pi)^3}\cos(0)\right] \\
&= \frac{4\sqrt{15}}{(n\pi)^3}[\cos(0) - \cos(n\pi)] \\
&= \begin{cases} 0, & \text{if } n \text{ is even.} \\ 8\sqrt{15}/(n\pi)^3, & \text{if } n \text{ is odd.} \end{cases}
\end{aligned}
$$

so that, $\Psi(x,t) = \sqrt{\frac{30}{a}}\left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5\ldots} \frac{1}{n^3}\sin\left(\frac{n\pi}{a}x\right) e^{-in^2\pi^2\hbar t/2ma^2}.$

What is the probability to find the system in the ground state at time t=0 ?

Consider another example. Let $\psi(x,t) = c_1\,\varphi_1(x,t) + c_2\,\varphi_2(x,t)$

where $\varphi_1(x,t)$ and $\varphi_2(x,t)$ are normalised wavefunctions, orthogonal to each other.

Total probability $\int \psi^*(x,t)\psi(x,t)\,dx = |c_1|^2 + |c_2|^2 = 1$

Probability to find the system in $\varphi_1(x,t) = |c_1|^2$

Probability to find the system in $\varphi_2(x,t) = |c_2|^2$

Given $$\psi(x,t) = \sum_n c_n \psi_n(x,t)$$

What is the probability to find the system in the ground state at time t=0?

$$P_1 = |c_1|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 = 0.9985550143640185$$

What is the probability to find the system in the second excited state?

$$P_3 = |c_3|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 \frac{1}{3^6} = 0.00136976$$

Similarly,

$$P_5 = 0.0000639075, \quad P_7 = 8.48758 \times 10^{-6}$$