(4) Eigenvalue Equation in $\{|\vec{r}\rangle\}$ representation.

In the abstract state space, an eigenvalue equation is

$$\hat{A}\,|\psi\rangle = a\,|\psi\rangle$$

Where $\hat{A}$ — observable operator, $|\psi\rangle$ — state vector,

a — a complex constant (real number in reality)

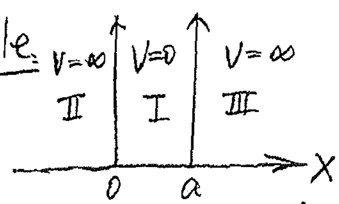
It can be proven that in the $\{|\vec{r}\rangle\}$ representation, the eigen value equation becomes

$$\hat{A}\,\psi(\vec{r}) = a\,\psi(\vec{r})$$

Where $\hat{A}$ is the representation of $\hat{A}$ operator in $\{|\vec{r}\rangle\}$.

$\psi(\vec{r})$ called the eigen wave function, is the projection of the eigen state $|\psi\rangle$ on the $\{|\vec{r}\rangle\}$ representation.

Example.



(1-D) Infinite High Potential Well

A particle moves within a potential well between $x=0$ and $x=a$. The normalized wave function is given by

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right), & 0<x<a \\ 0. & \text{elsewhere} \end{cases}$$

① Try to derive the mean of the particle's momentum and kinetic energy

② Verify whether this wave function is an eigen-function of momentum, whether an eigen wave function of kinetic energy.

Solution: In $\{|x\rangle\}$ representation, $\hat{\vec{p}} = -i\hbar\frac{\partial}{\partial x}$, $\frac{\hat{\vec{p}}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$.

$$\bar{p} = \int_{-\infty}^{+\infty} dx\, \psi_n^*(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi_n(x) = -\frac{2i\hbar}{a}\int_0^a dx\, \sin\left(\frac{n\pi x}{a}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)\sin\left(\frac{n\pi x}{a}\right)$$

$$= -i\hbar\frac{2}{a}\cdot\frac{n\pi}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cos\left(\frac{n\pi}{a}\right)dx$$

$$= -i\hbar\frac{2}{a}\cdot\frac{1}{2}\sin^2\left(\frac{n\pi x}{a}\right)\Big|_0^a = 0-0=0.$$

Kinetic energy mean:

$$\overline{\frac{p^2}{2m}} = \int_{-\infty}^{+\infty} \psi_n^*(x) \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right) \psi_n(x)\, dx$$

$$= -\frac{\hbar^2}{ma}\int_0^a \sin\left(\frac{n\pi x}{a}\right) \frac{\partial^2}{\partial x^2} \sin\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{\hbar^2}{ma}\left(\frac{n\pi}{a}\right)^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

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

Verifying eigen wave function: to see whether "Apply the operator to the wave function you can obtain a number times the same wave function".

(1) $\hat{p}\psi_n(x) = -i\hbar\frac{\partial}{\partial x}\psi_n(x) = -i\hbar\sqrt{\frac{2}{a}}\frac{\partial}{\partial x}\sin\left(\frac{n\pi x}{a}\right) = i\sqrt{\frac{2}{a}}\frac{\hbar n\pi}{a}\cos\left(\frac{n\pi x}{a}\right)$

— $\psi_n(x)$ is NOT $\hat{p}$'s eigen function.

(2) $\frac{\hat{p}^2}{2m}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_n(x) = -\frac{\hbar^2}{2m}\sqrt{\frac{2}{a}}\frac{\partial^2}{\partial x^2}\sin\left(\frac{n\pi x}{a}\right)$

$= \frac{\hbar^2}{2m}\sqrt{\frac{2}{a}}\left(\frac{n\pi}{a}\right)^2 \sin\left(\frac{n\pi x}{a}\right) = \frac{\hbar^2\pi^2 n^2}{2ma^2}\psi_n(x)$

$\therefore$ $\psi_n(x)$ is the eigen function of kinetic energy.

The eigen value is $\frac{\hbar^2\pi^2 n^2}{2ma^2}$, the same as the mean we derived above — of course, the mean of the kinetic energy in its own eigenstate is equal to the eigenvalue.

Thus, we solved the HW #3, Problem #3. You may practice it yourself. Then apply similar technique to HW #3, Problem #2.

(5) Schrödinger Equation in $\{|\vec{r}\rangle\}$ and $\{|\vec{p}\rangle\}$ representations.

In the abstract state space, the Schrödinger equation is

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}(t)\,|\psi(t)\rangle.$$

For a (spinless) particle in a scalar potential $V(\vec{r})$, the operator $\hat{H} = \frac{\hat{\vec{p}}^{\,2}}{2m} + V(\hat{\vec{r}})$.

It can be proven that in the $\{|\vec{r}\rangle\}$ representation, the Schrödinger equation becomes:

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r},t).$$

In the $\{|\vec{p}\rangle\}$ representation, the Schrödinger equation is

$$i\hbar\frac{\partial}{\partial t}\bar{\psi}(\vec{p},t) = \frac{\vec{p}^{\,2}}{2m}\bar{\psi}(\vec{p},t) + (2\pi\hbar)^{-3/2}\int d^3p'\, \bar{V}(\vec{p}-\vec{p}\,')\,\bar{\psi}(\vec{p}\,',t).$$

Here, $\psi(\vec{r},t) \equiv \langle\vec{r}|\psi\rangle$

$\bar{\psi}(\vec{p},t) \equiv \langle\vec{p}|\psi\rangle.$

$\bar{V}(\vec{p}) = (2\pi\hbar)^{-3/2}\int d^3r\; e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\,V(\vec{r}).$

§3.6 Solutions to Eigenvalue Equation and Schrödinger Equation

16. Solution to Eigenvalue Equation and Schrödinger Equation.

Schrödinger equation: $i\hbar \frac{\partial}{\partial t} \psi(\vec{r},t) = [-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})]\psi(\vec{r},t)$.

If $V(\vec{r})$ is not explicitly dependent on time t, then we have

$$\psi(\vec{r},t) = \psi(\vec{r})\,T(t).$$

Substituting this into the Schrödinger equation:

$$\frac{i\hbar}{T}\frac{dT}{dt} = \frac{1}{\psi(\vec{r})}[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})]\psi(\vec{r}) = \underset{\substack{\uparrow \\ \text{total energy}}}{E}$$

$$\therefore \begin{cases} \frac{i\hbar}{T}\frac{dT}{dt} = E \Rightarrow T = T_0 e^{-iEt/\hbar} \\ [-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})]\psi(\vec{r}) = E\,\psi(\vec{r}) \end{cases}$$

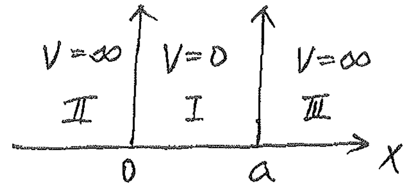
$$\therefore \psi(\vec{r},t) = \psi(\vec{r})\,e^{-iEt/\hbar}.$$

Probability density $= |\psi(\vec{r},t)|^2 = |\psi(\vec{r})|^2$ is independent of t.
i.e., the probability of the particle appearing at position $\vec{r}$ does not change with time!

Equation $[-\frac{\hbar^2}{2m}\nabla^2 + \vec{V}(\vec{r})]\psi(\vec{r}) = E\,\psi(\vec{r})$
is called the stationary state Schrödinger equation. Essentially, it is the energy eigenvalue equation.

Here, we show a few examples of how to solve the stationary state Schrödinger equation, i.e., the energy eigenvalue equation, to derive the system states and eigenvalues.

(1) 1-Dimension Infinite potential well



The stationary-state Schrödinger equation is: $\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\right]\psi(x)=E\psi(x)$.

$$V(x)=\begin{cases}\infty, & x<0\\ 0, & 0<x<a\\ \infty, & x>a\end{cases}$$

Since a particle cannot be in an infinite potential, $\therefore \psi=0$ in regions II and III. (Physics)

In region I, $V=0$, the equation is simplified to

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)=E\psi(x)$$

Let $k=\sqrt{\frac{2mE}{\hbar^2}}$, then, $\frac{d^2\psi}{dx}+k^2\psi=0$

The general solution to this equation is

$$\psi=A\sin(kx+\delta),$$

where A and δ are constants to be determined from boundary conditions and normalization requirements.

Considering from physics aspects, since the particle cannot be in the $V=\infty$ region, i.e., the probability to be in regions II and III is zero. Therefore, $\psi(x=0)=0$, $\psi(x=a)=0$.

At $x=0$, $0=A\sin\delta$.

Since $A\neq0$ (otherwise, the solution is no meaning),

$$\therefore \delta=0$$

At $x=a$, $0=A\sin ka$.

Since $A\neq0$, $\therefore \sin ka=0 \Rightarrow ka=n\pi$ (n = 1,2,3,...)

$$\therefore k=\frac{n\pi}{a}.$$

Here, we kick out $n=0$ and $n<0$ solutions, as they have no meaning in reality. Now: $\psi_n=A\sin(\frac{n\pi}{a}x)$.

$\because k=\frac{n\pi}{a}=\sqrt{\frac{2mE}{\hbar^2}} \Rightarrow E_n=\frac{\hbar^2\pi^2n^2}{2ma^2}$, $n=1,2,3,\cdots$

$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$ indicates that the particle energy is quantized in the infinit high potential well.

$|\psi(x)|^2$ is the probability density of finding the particle at position x. Since the probability of finding the particle in all space is 1 (i.e., normalization requirement), we have

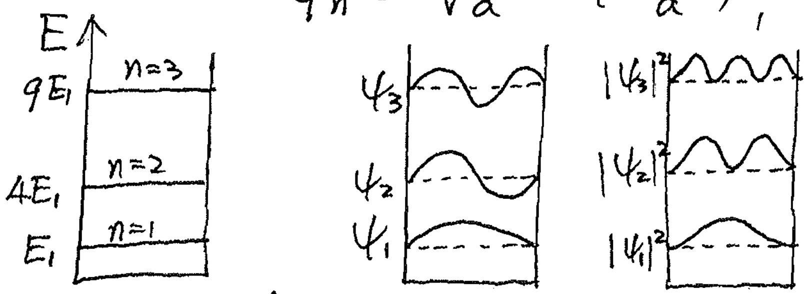
$$\int |\psi(x)|^2 dx = 1$$

$$\therefore \int_0^a A^2 \sin^2 kx \, dx = \int_0^a A^2 \sin^2 \frac{n\pi}{a} x \, dx = A^2 \cdot \frac{a}{2} = 1$$

$$\Rightarrow A = \sqrt{\frac{2}{a}}.$$

$\therefore$ the normalized wave function (eigen wave function) is

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad n = 1, 2, 3, \cdots$$



(a) energy level E_n (b) ψ_n (c) $|\psi_n|^2$

Particle's motion in a potential well is a common phenomenon, e.g., the electron in hydrogen atom does 3-D motion in the Coulomb potential, just the wall is not a square, but distributes along $-\frac{1}{r}$.

* Note: the lowest energy $E_1 \neq 0$, which is completely different from classical mechanics. This is due to the wave nature of particle — "a wave at rest" does not exist!

* Note: the full wave function $\psi_n(x,t) \propto \sin\left(\frac{n\pi x}{a}\right) e^{-iE_n t/\hbar}$, which is a standing wave.

(2) Harmonic Oscillator (1-D):

The force that a particle experiences $F = -kx$,
where x is the displacement of particle relative to its balance point O. $\therefore E_{potential} = \frac{1}{2}kx^2 = V$.

The stationary-state Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x} + \frac{1}{2}kx^2\right)\psi = E\psi.$$

Let $\beta = \alpha x$, where $\alpha = (mk/\hbar^2)^{1/4}$.

$$\therefore \frac{d^2\psi}{d\beta^2} + (\lambda - \beta^2)\psi = 0$$

where $\lambda = \frac{2mE}{\hbar^2 a^2} = \frac{2E}{\hbar}\sqrt{\frac{m}{k}} = \frac{2E}{\hbar\omega}$. $\omega = \sqrt{k/m}$.

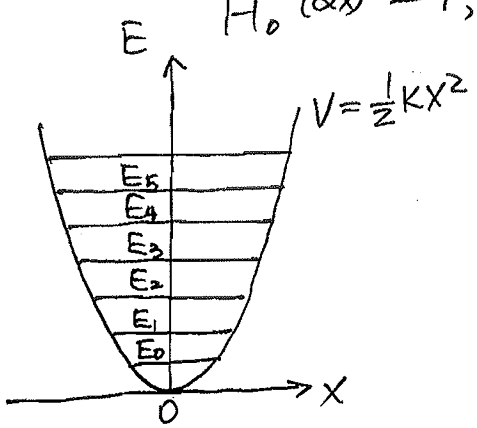
The solution to the equation is:

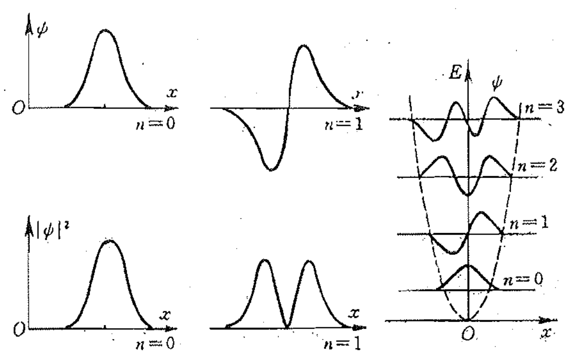
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots$$

$$\psi_n = \left(\frac{\alpha}{\sqrt{\pi}\,2^n \cdot n!}\right)^{1/2} e^{-\frac{1}{2}\alpha^2 x^2} H_n(\alpha x),$$

Where $H_n(\alpha x)$ is Hermitian polynomial

$H_0(\alpha x) = 1$, $H_1(\alpha x) = 2\alpha x$, $H_2(\alpha x) = 4(\alpha x)^2 - 2, \cdots$





① Plot energy levels within the potential energy curve. The length of horizontal lines shows the oscillator motion range.

② When $n = 0$, $E_0 = \frac{1}{2}\hbar\omega \neq 0$. $\Rightarrow$ no oscillator at rest!

③ E_n are equally separated — similar to Planck's hypothesis — quanta of oscillator energy!