

Time-independent Schrödinger equation

SE (time-dependent)

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

If $V(x, t) = V(x)$ (i.e., potential energy does not change with time), then simplification: SE can be solved by separation of variables

Assume $\Psi(x, t) = \psi(x) f(t)$

$$\frac{\partial \Psi}{\partial t} = \psi(x) \frac{df}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} f(t), \quad i\hbar \psi \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} f + V(x) \psi f$$

$$\times \frac{1}{\psi f} \Rightarrow i\hbar \frac{1}{f} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V(x) = \text{const} = E \quad \text{will be energy, now just a constant}$$

Now two equations (in time and in space)

$$i\hbar \frac{1}{f} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V(x) = E \quad \Psi(x, t) = \psi(x) f(t)$$

First equation: $\frac{df}{dt} = -i \frac{E}{\hbar} f \quad \Rightarrow \quad f(t) = C e^{-\frac{iE}{\hbar} t}$

Can choose $C = 1$
 E must be real
 (for normalization)

$$f(t) = \exp\left(-i \frac{E}{\hbar} t\right)$$

Second equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x)$$

$$\hat{H}\psi = E \psi$$

Time-independent Schrödinger equation (TISE)

(this hints that
 E is energy)

$$\Psi(x, t) = \psi(x) \exp\left(-i \frac{E}{\hbar} t\right)$$

Normalization $\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$, while $\left| \exp\left(-i \frac{E}{\hbar} t\right) \right| = 1$

therefore $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$

ψ normalized in
 the same way as Ψ

General solution of SE (for time-independent $V(x)$)

TISE solutions (infinitely many):

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi_n}{dx^2} + V(x) \psi_n = E_n \psi_n \quad n = 1, 2, 3, \dots$$

SE is linear \Rightarrow any linear combination of solutions is a solution

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) \exp\left(-i \frac{E_n}{\hbar} t\right)$$

Any complex coefficients c_n ; however, Ψ should be normalized.

As we will see, with normalized ψ_n , this requires normalization for c_n as

$$\sum_{n=1}^{\infty} |c_n|^2 = 1$$

Orthogonality of stationary states

Theorem Stationary states $\psi_n(x)$ and $\psi_m(x)$ with different energies, $E_n \neq E_m$, are orthogonal: $\int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx = 0$.

Remarks:

- orthonormal (since normalized)
- we treat functions as vectors, inner product (generalized dot-product)
 $\langle f|g \rangle \equiv \int_{-\infty}^{\infty} f^*(x) g(x) dx$, orthogonal: $\langle f|g \rangle = 0$

Proof Start with $-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} + V \psi_n = E_n \psi_n$

$\times \psi_m^*$, integrate: $-\frac{\hbar^2}{2m} \int \psi_m^* \frac{d^2\psi_n}{dx^2} dx + \int \psi_m^* V \psi_n dx = E_n \int \psi_m^* \psi_n dx$

\updownarrow equal (by parts) \updownarrow equal \Rightarrow also equal

exchange $n \leftrightarrow m$,
conjugate: $-\frac{\hbar^2}{2m} \int \psi_n \frac{d^2\psi_m^*}{dx^2} dx + \int \psi_n V \psi_m^* dx = E_m \int \psi_n \psi_m^* dx$

$$(E_n - E_m) \int \psi_m^* \psi_n dx = 0 \quad \text{if } E_n \neq E_m, \text{ then } \int \psi_m^* \psi_n dx = 0$$

Q.E.D.

If energies are the same, usually also choose orthogonal functions $\psi_n(x)$

Normalization for coefficients c_n

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) \exp\left(-i \frac{E_n}{\hbar} t\right)$$

Use orthogonality of ψ_n
only $n=m$

$$1 = \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = \sum_{n,m} c_m^* c_n \exp\left(-i \frac{E_n - E_m}{\hbar} t\right) \int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx$$

$$= \sum_n |c_n|^2 \times 1 \times \int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = \sum_n |c_n|^2$$

This is how we obtain normalization for c_n :

$$\sum_{n=1}^{\infty} |c_n|^2 = 1$$

General solution for evolution of $\Psi(x, t)$

Suppose we know wave function at $t = 0$: $\Psi(x, 0)$

Then we can find coefficients c_n in $\Psi(x, 0) = \sum_n c_n \psi_n(x)$

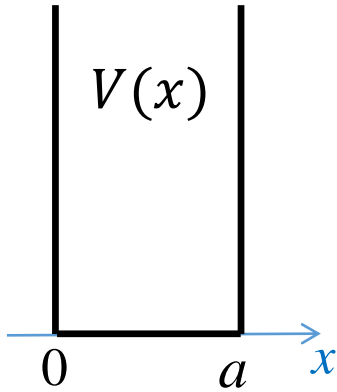
Again use orthogonality: multiply by $\psi_m^*(x)$ and integrate

$$\int \psi_m^*(x) \Psi(x, 0) dx = \sum_n c_n \underbrace{\int \psi_m^*(x) \psi_n(x) dx}_{\delta_{nm}} = c_m$$

Therefore $c_n = \int_{-\infty}^{\infty} \psi_n^*(x) \Psi(x, 0) dx$

Then we can find $\Psi(x, t)$ at any time t :

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) \exp\left(-i \frac{E_n}{\hbar} t\right)$$



Example: Infinite square well

(one of the most important systems in this course)

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

(similar to quantum well in semiconductors, except different effective mass and finite depth)

Solve TISE inside

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E \psi(x) \quad \Rightarrow \quad \psi(x) = A \sin(kx) + B \cos(kx)$$

Boundary conditions: $\begin{cases} \psi(0) = 0 \\ \psi(a) = 0 \end{cases}$ $k = \frac{\sqrt{2mE}}{\hbar}$

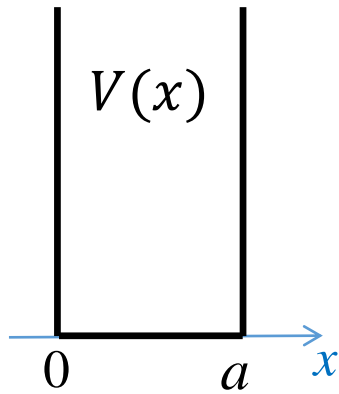
(because $\psi(x) = 0$ outside and $\psi(x)$ is always continuous)

therefore

$$\psi(x) = A \sin(k_n x)$$

$$k_n = \frac{\pi n}{a}, \quad n = 1, 2, 3, \dots$$

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



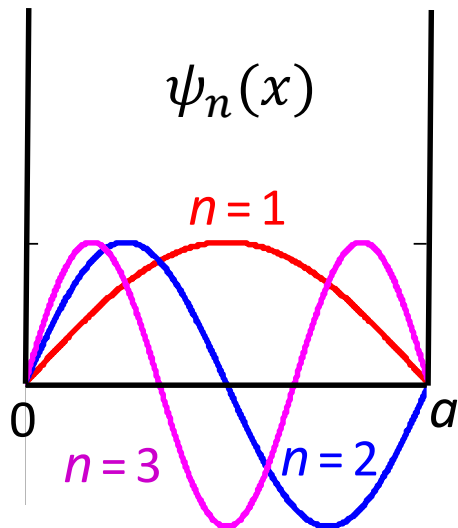
Infinite square well

$$\psi_n(x) = A \sin(k_n x), \quad k_n = \frac{n\pi}{a} \quad n = 1, 2, 3, \dots$$

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

Normalization $1 = \int_0^a |\psi(x)|^2 dx = |A|^2 \frac{1}{2} a \Rightarrow A = \sqrt{2/a}$
 (because $\overline{\sin^2(x)} = 1/2$)

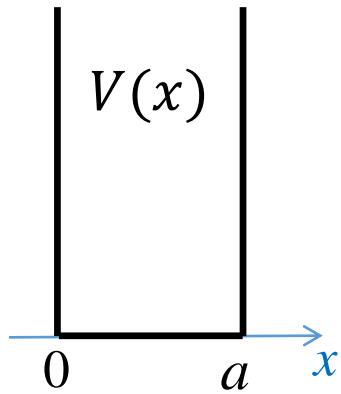
$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$$



$n = 1$ – lowest energy,
 “ground state”
 $n \geq 2$ – “excited states”

- Similar to atom states
- Even lowest state has positive energy (understanding from uncertainty principle)

Infinite square well: Summary

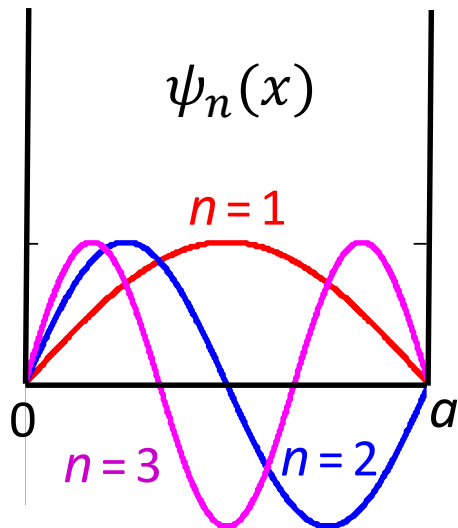


$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

$$n = 1, 2, 3, \dots$$

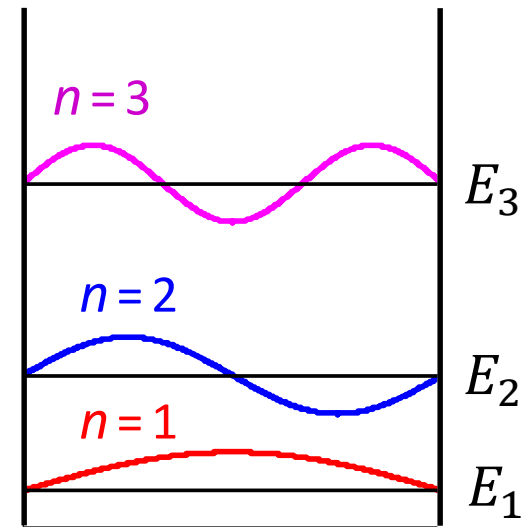
$$k_n = \frac{n\pi}{a}$$

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

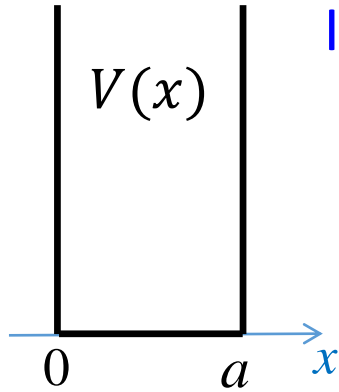


$n = 1$ – lowest energy,
“ground state”

$n \geq 2$ – “excited states”



Infinite square well: properties of stationary states



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

- **orthogonal to each other,**

$$\int_0^a \psi_m^*(x) \psi_n(x) dx = \delta_{mn}$$

- **complete set,** any $f(x)$ can be represented as

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \quad \text{if } f(0) = f(a) = 0$$

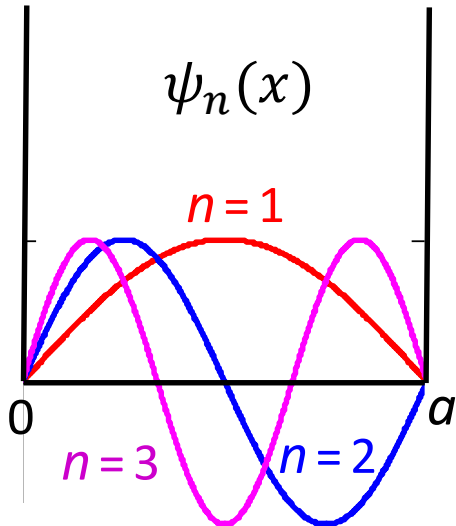
(i.e., orthonormal basis)

How to find c_n ? Already know the trick:

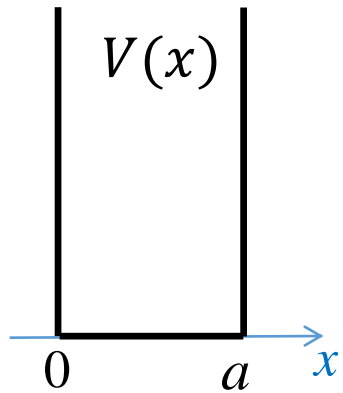
$$\int \psi_m^*(x) f(x) dx = \sum_n c_n \int \psi_m^*(x) \psi_n(x) dx = c_m$$

Therefore

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

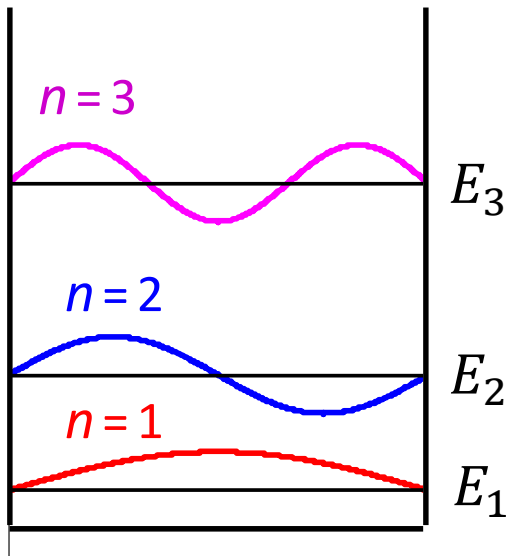


General solution



$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) \exp\left(-i \frac{n^2 \pi^2 \hbar}{2ma^2} t\right)$$

$$\sum_{n=1}^{\infty} |c_n|^2 = 1$$



If only one coefficient c_n is non-zero, then stationary state

If more than one level occupied (“**superposition**”), then non-stationary, state evolves in time (interference)

Classical motion can be represented as combination of many high-numbered states (transition to classical picture when energies are $\gg E_{1,2,3}$)

Is a general (superposition) state localized in space? – No

Is it localized in energy? – Also no!

However, if we measure energy, then we will get some result: some E_n (nothing in between!)

If measure again – will get the same result (collapse)