Time independent Schrödinger equation

$$i\hbar\,\partial_t \Psi(x,t) = H\,\Psi(x,t)$$

H: Hamiltonial ⇒ total energy of the system

In 1D:

$$H = \frac{p^2}{2m} + V$$

Correspondence principle $p \to -i\hbar\,\partial_x$

$$i\hbar\,\partial_t \Psi(x,t) = -\frac{\hbar^2}{2m}\partial_x^2 \Psi(x,t) + V(x,t)\,\Psi(x,t)$$ General Schrödinger eq.

Assume $V(x,t) = V(x)$

Method of separation of variables

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

$$\partial_t \Psi(x,t) = \partial_t\big(\psi(x) f(t)\big) = \psi(x)\,\partial_t f(t)$$

$$\partial_x^2 \Psi(x,t) = \partial_x^2\big(\psi(x) f(t)\big) = f(t)\,\partial_x^2 \psi(x)$$

$$\frac{i\hbar\,\psi(x)\,\partial_t f(t)}{\psi(x)\,f(t)} = -\frac{\hbar^2}{2m}\,\frac{f(t)\,\partial_x^2\psi(x)}{\psi(x)\,f(t)} + V(x)\,\frac{\psi(x)\,f(t)}{\psi(x)\,f(t)}$$

$$i\hbar\,\frac{\partial_t f(t)}{f(t)} = -\frac{\hbar^2}{2m}\,\frac{\partial_x^2 \psi(x)}{\psi(x)} + V(x)$$

only depends on time — only depends on space

Both sides must be constant

The equations de-couple

$$i\hbar \frac{\partial_t f(t)}{f(t)} = E = -\frac{\hbar^2}{2m} \frac{\partial_x^2 \psi(x)}{\psi(x)} + V(x)$$

E is a constant

$$\boxed{\begin{aligned} &i\hbar \partial_t f(t) = E f(t) \\ &-\frac{\hbar^2}{2m} \partial_x^2 \psi(x) + V(x)\psi(x) = E\psi(x) \end{aligned}}$$

Two uncoupled differential equations

Solve these equation

- $i\hbar \partial_t f = E f \quad \Rightarrow \quad f(t) = f_0 \exp(-iEt/\hbar)$

check that this solution satisfies the diff. equation

$f_0 = f(t=0)$: Initial condition $\qquad \exp(\alpha) = e^{\alpha}$

$p \to -i\hbar \partial_x \qquad [p] = kg \cdot \frac{m}{s}$

$[\hbar] = [p]/[\partial_x] \qquad [\partial_x] = \frac{1}{m}$

$$= kg \cdot \frac{m}{s} \cdot \frac{1}{1/m} = kg \cdot \frac{m^2}{s}$$

$\left[\frac{Et}{\hbar}\right] = 1$: the argument of an exponential MUST be dimensionless

$$\frac{[E][t]}{[\hbar]} = \frac{[E] \cdot s}{kg \cdot m^2/s} = [E] \cdot \frac{s^2}{kg \cdot m^2} = 1 \Rightarrow [E] = kg \cdot \frac{m^2}{s^2} = \text{Joules} = J$$

$\boxed{E : \text{is an energy (constant)}}$

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

$$\left(-\frac{\hbar^2}{2m}\partial_x^2+V(x)\right)\psi(x)=E\psi(x)$$

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

Eigenvalue problem

Let's assume that we know $\psi(x)$ which solves the $H\psi(x)=E\psi(x)$

$$\Psi(x,t)=\psi(x)\,e^{-iEt/\hbar}$$

f_0 is absorbed by $\psi(x)$

so-called stationary states

Probability: $|\Psi(x,t)|^2=|\psi(x)|^2\,|e^{-iEt/\hbar}|^2$
$=|\psi(x)|^2$: time-independent

The observables are also stationary

For an operator $Q(x,p)$, we have

$$\langle Q(x,p)\rangle=\int\psi^*(x)\,Q(x,-i\hbar\partial_x)\,\psi(x)\,dx$$

In particular $\langle x\rangle$ is time independent

$\langle p\rangle=m\frac{d}{dt}\langle x\rangle=0$ => The particle is not moving => stationary

The energy of stationary states is well defined

Energy => Hamiltonian

$\langle H\rangle$: average energy

$$\langle H\rangle=\int\psi^*H\psi\,dx=\int\psi^*E\psi\,dx=E\underbrace{\int\psi^*\psi\,dx}_{\text{must be 1 because }\psi(x)\text{ has to be normalized}}$$

$=E$

$\langle H^2\rangle=E^2$ Check on your own!

$$\mathrm{Var}(H) = \langle H^2 \rangle - \langle H \rangle^2$$
$$= E^2 - E^2 = 0$$

The variance of this energy is zero

Principle of superposition

→ Schrödinger eq. is linear

If ψ_1 and ψ_2 are solutions to S.E.
then $\alpha\psi_1 + \beta\psi_2$ are also solutions to S.E.

If we find a set of solutions with energies E_j (with $j = 1, 2, \ldots$)

$$\Psi_j(x,t) = \psi_j(x)\, e^{-iE_j t/\hbar}$$

then

$$\Psi(x,t) = \sum_{k=0}^{\infty} \alpha_k \psi_k(x) e^{-iE_k t/\hbar}$$

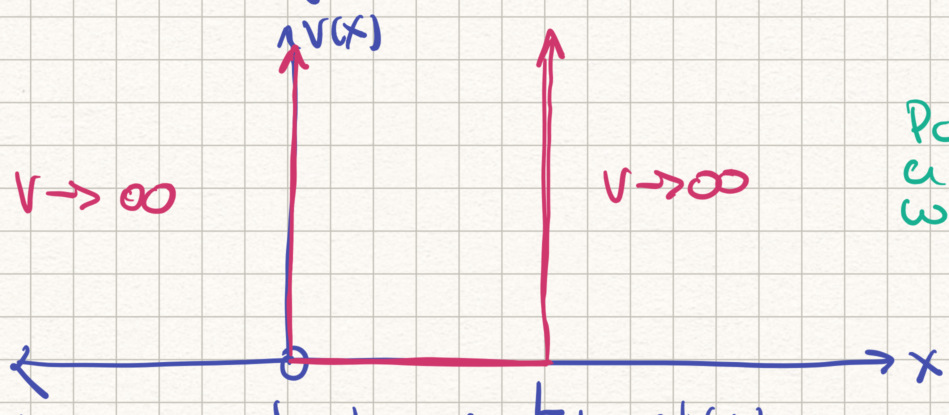
Also a solution to S.E.

But these are NOT stationary anymore.

Check that this is true for the superposition of two states with the energies E_1 and E_2.

Particle in a box

Schrödinger Eq. in 1D for $V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{elsewhere} \end{cases}$



Particle is within a box of inpenetrable walls

$$\psi(x) = \begin{cases} 0 & x > L \\ 0 & x < 0 \\ ? & 0 < x < L \end{cases}$$

we need to find $\psi(x)$ for $0 < x < L$.

$$H = \frac{P^2}{2m} \quad (\text{there } V(x) = 0)$$

Schrödinger Eq. then reads

$$H\psi(x) = E\psi(x)$$

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

With the boundary condition

$\left.\begin{array}{l}\psi(x=0)=0\\ \psi(x=L)=0\end{array}\right\}$ Continuity of the $\psi(x)$

$E \geq 0$: Physical requirement

$$\partial_x^2\psi(x) = -\frac{2mE}{\hbar^2}\psi(x) = -k^2\psi(x) \qquad \text{with } k^2 = \frac{2mE}{\hbar^2}$$

$$\psi(x) = A\sin(kx) + B\cos(kx) :$$

General solution to this diff. eq.

From the Boundary conditions

$$\psi(x=0) = B = 0$$

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

$$\psi(x=L) = 0 = \psi(x=L) = A\sin(kL)$$

The case $A=0$ is not interesting $\Rightarrow \psi(x)=0$

$$\sin(kL) = 0 \Rightarrow kL = n\pi \qquad n\text{: an integer}$$

$$k = \frac{n\pi}{L} \qquad n\in\mathbb{Z}$$

Our solution becomes $\boxed{\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right)}$

we had

$$k^2 = \frac{2mE}{\hbar^2} \qquad k^2 = \left(\frac{n\pi}{L}\right)^2 \Rightarrow \frac{2mE}{\hbar^2} = \left(\frac{n\pi}{L}\right)^2$$

$$\boxed{E_n = \frac{1}{2m}\left(\frac{n\pi\hbar}{L}\right)^2}$$

To find A, we need to normalize the $\psi(x)$

$$\int_{-\infty}^{\infty}|\psi(x)|^2dx = 1 = \cancelto{0}{\int_{-\infty}^{0}|\psi(x)|^2dx} + \int_0^L|\psi(x)|^2dx + \cancelto{0}{\int_L^{\infty}|\psi(x)|^2dx}$$

$$1 = \int_0^L |\psi_n(x)|^2 \, dx$$ check on your own that $A = \sqrt{\frac{2}{L}}$

Put everything together

$\Psi_n(x,t) = \psi_n(x) f(t)$ $\quad f(t) = \exp\left(-\frac{i E_n t}{\hbar}\right)$

$$\boxed{\Psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \exp\left[-\frac{i}{2m\hbar}\left(\frac{n\pi\hbar}{L}\right)^2 t\right]}$$

Prob. $|\Psi_n(x,t)|^2$ is time-independent!!

$\langle x \rangle$ is constant in time $\Rightarrow \langle p \rangle = 0$

The particle is "at rest" in the box.

Energy is well defined:

$\langle H \rangle = E_n \Rightarrow \boxed{E_n = \frac{1}{2m}\left(\frac{n\pi\hbar}{L}\right)^2}$ $\quad$ check $\mathrm{Var}(H) = 0$

The energy doesn't fluctuate; it's known with total precision.

Orthogonality of $\psi_n(x)$

$$\int_0^L \psi_m^*(x) \psi_n(x) \, dx = \delta_{nm} = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{otherwise} \end{cases}$$

δ_{nm}: "delta kronecker" of m and n

Therefore

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

we can write any function inside the box as a superposition of these functions

True for any functon $F(x)$ within the box

"Making the Fourier transform of $F(x)$"

We need to find C_n using the orthogonality of $\psi_n(x)$.

$$C_n = \int_0^L F(x)\, \psi_n^*(x)\, dx$$

Due to the linearity of S.E.

$$f(x,t) = \sum_{n=1}^{\infty} C_n \psi_n(x) \exp(-iE_n t/\hbar)$$

is a solution of S.E.

$$\partial_t [\psi_n \exp(-iE_n t/\hbar)] = H \psi_n \exp(-iE_n t/\hbar)$$

do this for $f(x,t) \Rightarrow H f(x,t)$

$f(x,t)$ is a wavefunction, provided that it is normalized

$$\int |f(x,t)|^2\, dx = 1$$

$$= \int \sum_{m=0}^{\infty} C_m^* \psi_m^*(x) e^{iE_m t/\hbar} \sum_{n=0}^{\infty} C_n \psi_n(x)\, e^{-iE_n t/\hbar}\, dx$$

$$= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} C_m^* C_n e^{-i(E_n - E_m)t/\hbar} \int \psi_m^*(x) \psi_n(x)\, dx$$

$$= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} C_m^* C_n e^{-i(E_n - E_m)t/\hbar}\, \delta_{nm}$$

$$= \sum_{n=0}^{\infty} C_n^* C_n = \boxed{1 = \sum_{n=0}^{\infty} |C_n|^2}$$

Compute the average value of $\Omega(x,p)$

$$\langle \Omega(x,p) \rangle = \int f^*(x,t)\, \Omega(x, -i\hbar\partial_x)\, f(x,t)\, dx$$

$$= \int \left(\sum_{m=0}^{\infty} c_m^* \psi_m^*(x) e^{iE_m t/\hbar} \right) \Omega(x, -i\hbar\partial_x) \left(\sum_{n=0}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} \right) dx$$

$$= \sum_{m,n} c_m^* c_n e^{-i(E_n - E_m)t/\hbar} \int \psi_m^*(x) \Omega(x, -i\hbar\partial_x) \psi_n(x) \, dx$$

we have cross-termes $\Rightarrow$ mixing ψ_m and ψ_n

$\Rightarrow$ time dependence doesn't cancel ... thing start moving $\Rightarrow$ $\langle \Omega(x,p) \rangle (t)$