Phys 231 2021

Lecture 22

Fri: No class

Mon: 5.4, 5.6

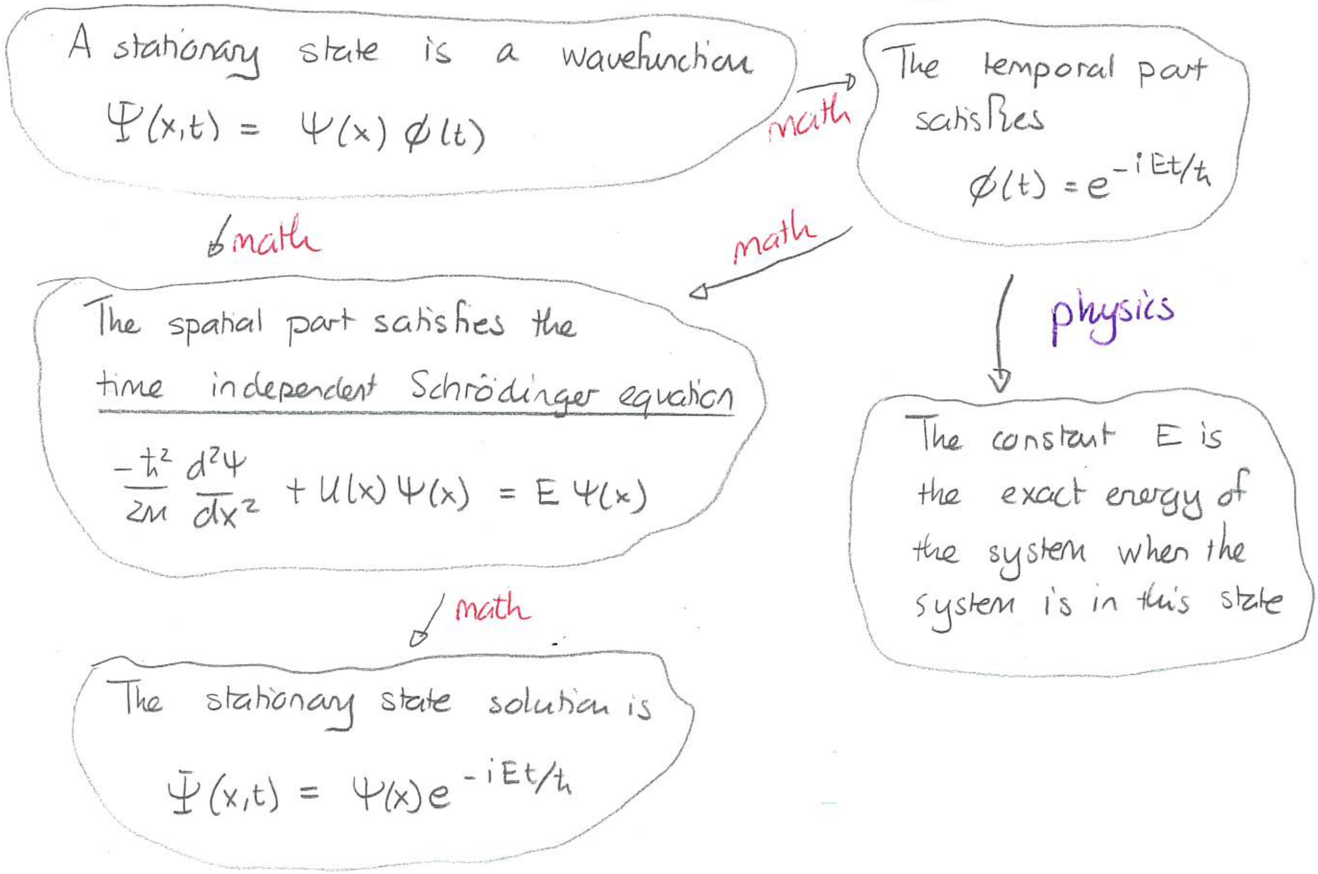
Tues: HW by 5pm

Stationary states / energy eigenstates.

The general time-dependent Schrödinger equation for a particle that can be located along the x-axis is:

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

A special class of solutions are the stationary states.



A stationary state is a wavefunction

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

The temporal part satisfies

$$\phi(t) = e^{-iEt/\hbar}$$

The spatial part satisfies the time independent Schrödinger equation

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

The constant E is the exact energy of the system when the system is in this state

The stationary state solution is

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

Following this procedure, particularly solving the time-independent Schrödinger equation yields all possible states that can each have one definite energy. This is the reason why they are called energy eigenstates.

The term stationary state arises because the position probability density does not vary with respect to time. To see this

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

$$= |\psi(x)|^2 \underbrace{|e^{-iEt/\hbar}|^2}_{1} = |\psi(x)|^2$$

The same will be true of momentum probability densities. In general states with specific energies do not result in any time-varying measurement outcomes. Such an arrangement is clearly consistent with the observed stability of atoms.

Any time variation will have to arise via superpositions of states.

Normalization of energy eigenstates

The position probability density must be normalized. Thus

$$\int_{-\infty}^{\infty} P(x,t)\, dx = 1$$

For stationary states this implies:

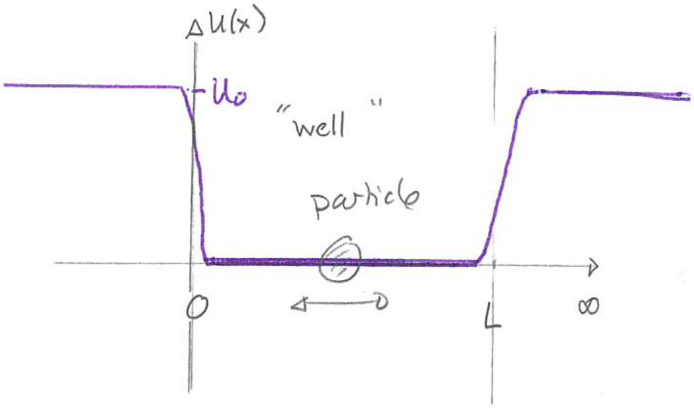
$$\boxed{\int_{-\infty}^{\infty} |\psi(x)|^2\, dx = 1}$$ normalization

We have to apply this normalization condition to any solution to the time-independent Schrödinger equation.

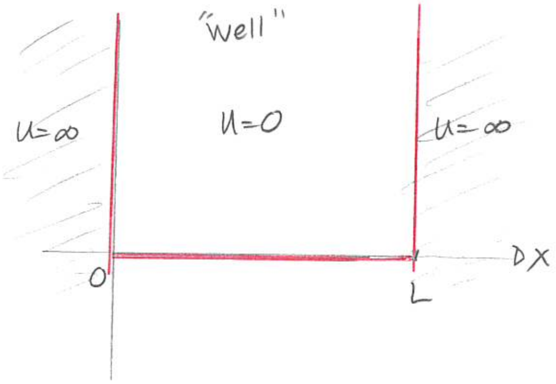
Infinite Well

We now apply the general scheme to a particle trapped in a region. Inside this region it will be free. The first step is to describe the potential. We assume that the region extends from $x=0$ to $x=L$

"Realistic"



"Idealized

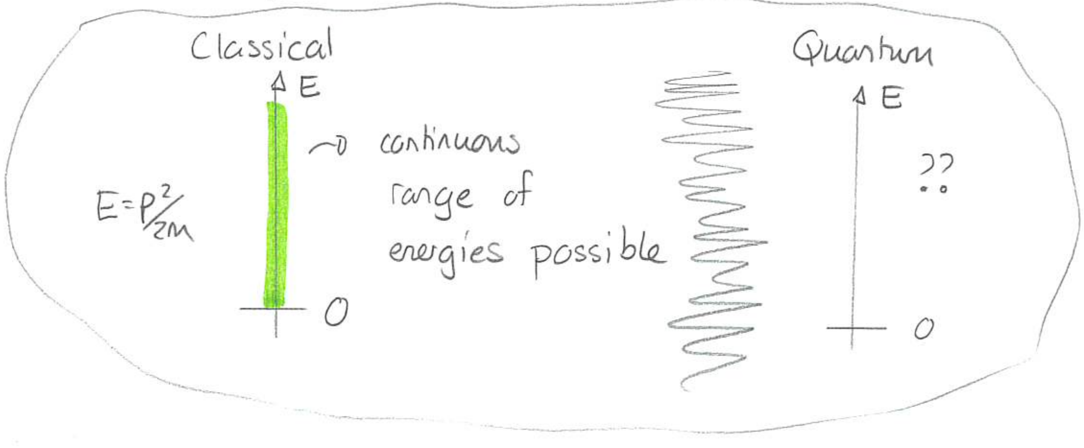


In the idealized case

$$U(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{elsewhere.} \end{cases}$$

Our first task is to find the energy eigenstates and hence the possible energies for the particle.

For comparison a classical particle in this situation has momentum p and energy $E = p^2/2M$. In principle any value of energy is possible.



The technique for solving the TISE in such cases is

Inside well $0 < x < L$	Outside well $x \leq 0$ $x \geq L$
$U(x) = 0$	$U(x) = \infty$
$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\,\psi(x)$	Only possible solution is $\psi(x) = 0$

We then solve the equation in each region and ensure that the solutions match at the boundary. This means:

Solve

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

in region $0 \leq x \leq L$

AND

match on boundary

$$\psi(0) = 0$$

$$\psi(L) = 0$$

Solve

Boundary conditions

1 Energy eigenstates for a particle in an infinite well

Consider an infinite well for $0 \leqslant x \leqslant L$. Within the well the time-independent Schrödinger equation (TISE) is

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

a) Consider each of the following possible solutions:

   i) $\psi(x) = Akx(x-L)$

   ii) $\psi(x) = A\sin(kx+\varphi)$

   where A and k are constants. Determine which of these satisfy the TISE and, for those that do, and expression for the energy in terms of the constants. At this point what are the possible energy values?

b) Apply the boundary condition at $x = 0$ to simplify the wavefunction.

c) Apply the boundary condition at $x = L$ and determine the possible values of k that satisfy this condition.

d) Determine the possible values of the energy of the particle.

<u>Answer:</u> a) Case i

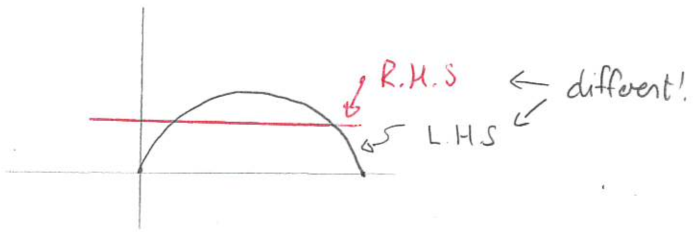
$$\psi(x) = Akx^2 - AkLx$$

$$\frac{d\psi}{dx} = 2Akx - AkL$$

$$\frac{d^2\psi}{dx^2} = 2Ak$$

Substitute $\Rightarrow$ $$-\frac{\hbar^2}{\cancel{2}m}\cancel{2}\cancel{A}\cancel{k} = E\cancel{A}\cancel{k}x(x-L)$$

$$\Rightarrow \underbrace{x(x-L)}_{\text{depends on } x} = \underbrace{-\frac{\hbar^2}{mE}}_{\text{indep. of } x}$$



Case ii

$$\frac{d\psi}{dx} = -kA\cos(kx+\varphi)$$

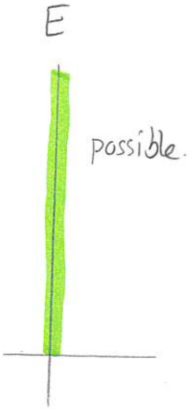
$$\frac{d^2\psi}{dx^2} = -k^2 A\sin(kx+\varphi)$$

substitute:

$$\frac{-\hbar^2}{2M}\left(-k^2 \cancel{A}\,\cancel{\sin(kx+\varphi)}\right) = E\cancel{A}\,\cancel{\sin(kx+\varphi)}$$

$$\Rightarrow \quad \frac{\hbar^2 k^2}{2M} = E$$

This is a solution if $E = \frac{\hbar^2 k^2}{2M}$ any $E>0$ possible



b) $\psi(0)=0 \Rightarrow A\sin(\varphi)=0 \Rightarrow A=0 \Rightarrow \psi=0$ trivial

OR $\varphi=0$

So

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

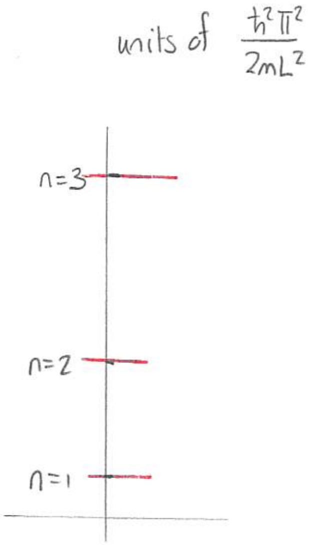
c) $\psi(L) = A\sin(kL) = 0 \Rightarrow kL = n\pi$ $n=1,2,3,\dots$

$\Rightarrow \boxed{k = \frac{n\pi}{L}}$ $\Rightarrow$ only some k possible

d) $E = \frac{\hbar^2}{2M}\left(\frac{n\pi}{L}\right)^2 = n^2 \frac{\hbar^2\pi^2}{2ML^2}$

So the possible energies are

$$E_n = \frac{\hbar^2\pi^2}{2ML^2} n^2 \qquad n=1,2,3,\dots$$



Thus we find the solutions to the TISE are:

$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right)$ for $0 < x < L$

with energy $E_n = n^2 \frac{\hbar^2\pi^2}{2mL^2}$

We can normalize these using

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = 1 \Rightarrow \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

$$\Rightarrow A^2 \frac{L}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$

Thus

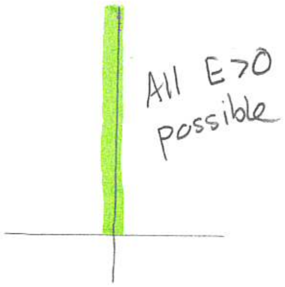
For a particle in an infinite well the energy eigenstates are labeled by an integer $n = 1, 2, 3, \ldots$ The wavefunctions are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad 0 < x < L$$

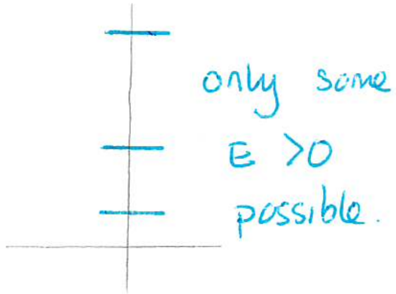
and the possible energies are

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

Note that the possible energies are discretely distributed (i.e. quantized). This is a consequence of the bound nature of the wavefunctions.



Classical



Quantum