

# L13. WAVE FUNCTIONS + THE SCHRÖDINGER EQUATION

We've seen that particles behave as waves. But all the waves we know ~ waves of sound ~ electromagnetic waves ~ involve some kind of disturbance that is described by a wave equation.

If electrons are waves, then what is the disturbance, and what is the wavefunction? This brilliant question was posed in Zurich in the Fall of 1925, by Peter Debye to an Austrian visitor to the Eidgenössische Technische Hochschule — Einstein's old university — the visitor's name: Erwin Schrödinger.

Schrödinger could be said to have been the "Bill Clinton" of physics. A brilliant man with a wandering eye. History tells us

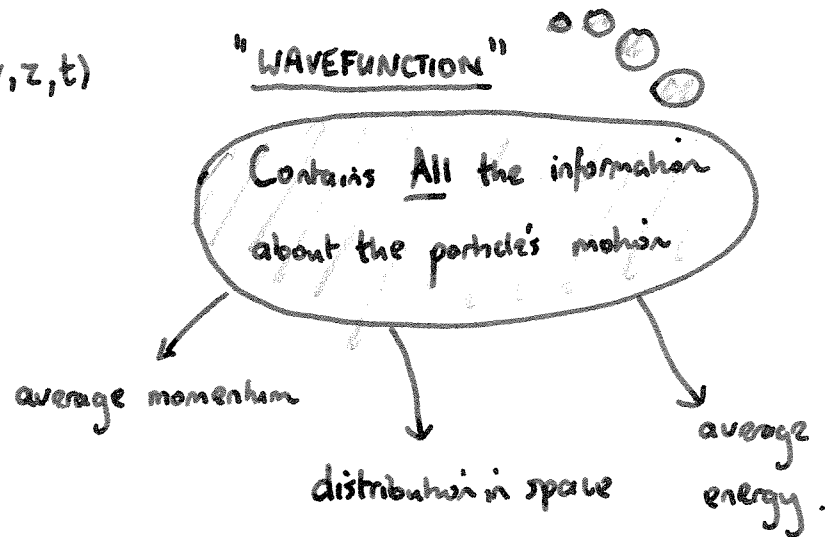
that he pondered Debye's question and tried to compose a wave-equation that would, when applied to hydrogen, recover the Bohr spectrum  $E_n = -\frac{13.6}{n^2} \text{ eV}$ . His first attempt didn't quite work. At the end of 1925, during a romantic interlude with a girlfriend whose name has been lost— he hit upon the equation that describes the electron wave, and on Dec 27th of that year he had derived the Bohr spectrum. Today we will study the famous wave equation he discovered 80 years ago. Remarkably, we shall see that the "intensity" of the electron wave  $|\Psi|^2$  determines the probability of finding it at that location.

# WAVE FUNCTION

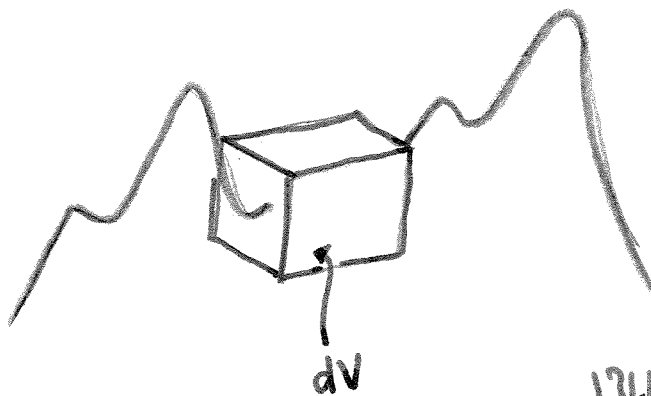


Electromagnetism  $\vec{E}(x,t), \vec{B}(x,t)$

Quantum Physics:  $\Psi(x,y,z,t)$



$\Psi$  is not a disturbance of anything physical



$$dp = \text{probability to be in volume } dV$$

$$= |\Psi(x,y,z,t)|^2 dV$$

$|\Psi|^2 =$  PROBABILITY DISTRIBUTION FUNCTION. (Max Born)

## STATIONARY STATES

It turns out that the most general way to formulate quantum physics involves complex numbers. The wavefunction

$\psi$  has both real & imaginary parts

$$\psi = a + ib \quad i = \sqrt{-1}$$

↑ real part
 ↙ imaginary part

The modulus square  $|\psi|^2 = \psi \times \psi^*$  where  $\psi^* = a - ib$  is the "complex conjugate", so that  $|\psi|^2 = (a + ib)(a - ib) = a^2 - (i^2)b^2 = a^2 + b^2$ . In general  $|\psi|^2$  - the probability density depends on time - but in certain special **STATIONARY STATES**

$$|\psi(x, y, z, t)|^2 = \text{independent of time}$$

$$= |\psi(x, y, z)|^2$$

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

Time dependent wave function for stationary state.

The exponential factor is defined by Euler's formula

$$e^{i\theta} = \cos\theta + i\sin\theta$$

(Euler c.f.  $e^{i\pi} = -1$ )

So  $e^{-i\theta} = \cos(-\theta) + i\sin(-\theta) = \cos\theta - i\sin\theta$  is the complex conjugate of  $e^{i\theta}$

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

and

$$\begin{aligned} |\Psi(x, y, z, t)|^2 &= \Psi^*(x, y, z, t) \Psi(x, y, z, t) \\ &= \psi^*(x, y, z) \psi(x, y, z) e^{+iEt/\hbar} e^{-iEt/\hbar} \\ &= |\psi(x, y, z)|^2 e^0 \\ &= |\psi(x, y, z)|^2 \quad \text{— independent of time.} \end{aligned}$$

STATIONARY STATE  $\equiv$  STATE OF DEFINITE ENERGY.

# SCHRÖDINGER EqN

13.6

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

1d Schrödinger Eq.

↑  
KINETIC↑  
POTENTIAL

Simple electron wave

$$\Psi(x,t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{h} \left( \frac{h}{\lambda} \right) = \frac{2\pi}{h} p \quad \text{wavevector}$$

$$\omega = 2\pi f = \frac{2\pi}{h} (hf) = \frac{2\pi}{h} E \quad \text{angular frequency}$$

Special case  $B = iA$ 

$$\begin{aligned} \Psi(x,t) &= A (\cos(kx - \omega t) + i \sin(kx - \omega t)) \\ &= A e^{i(kx - \omega t)} = A e^{ikx} e^{-i\omega t} \end{aligned}$$

$$\Psi(x) = A e^{ikx}$$

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = -\frac{\hbar^2}{2m} (ik)^2 \psi = \frac{\hbar^2 k^2}{2m} \psi = \frac{p^2}{2m} \psi(x)$$

$$U \psi = 0$$

Free space

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

$$E = p^2/2m \quad \checkmark \quad \text{as expected.}$$

n.b. For non-stationary states we use the time-dependent Schrödinger Eq.

e.g. Is  $\Psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$  a stationary state?

$$\begin{aligned}
 -\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} A_1 e^{ikx} - \frac{\hbar^2}{2m} \frac{d^2}{dx^2} A_2 e^{-ikx} \\
 &= -\frac{\hbar^2}{2m} (ik)^2 A_1 e^{ikx} - \frac{\hbar^2}{2m} (-ik)^2 A_2 e^{-ikx} \\
 &= \frac{\hbar^2 k^2}{2m} (A_1 e^{ikx} + A_2 e^{-ikx})
 \end{aligned}$$

so it satisfies the time-independent Schrödinger equation.



WAVE PACKETS

$$\Psi(x,t) = A e^{i(kx - \omega t)}$$

describes a particle of definite momentum  $p = \hbar k$ .

but

$$\begin{aligned} |\Psi(x,t)|^2 &= \Psi^*(x,t) \Psi(x,t) \\ &= (A^* e^{-i(kx - \omega t)}) (A e^{i(kx - \omega t)}) \\ &= A^* A e^0 \\ &= |A|^2 \end{aligned}$$

- time & space independent  $\Leftrightarrow \Delta x = \infty$ .

But consider two waves of different momenta, which are superimposed

$$\begin{aligned} \Psi(x) &= A_1 e^{ik_1 x} + A_2 e^{ik_2 x} \\ &= A_1 (\cos k_1 x + i \sin k_1 x) + A_2 (\cos k_2 x + i \sin k_2 x) \\ &= \underbrace{(A_1 \cos k_1 x + A_2 \cos k_2 x)}_{\text{REAL}} + i \underbrace{(A_1 \sin k_1 x + A_2 \sin k_2 x)}_{\text{IM PART.}} \end{aligned}$$

eg  $A_1 = -A_2$

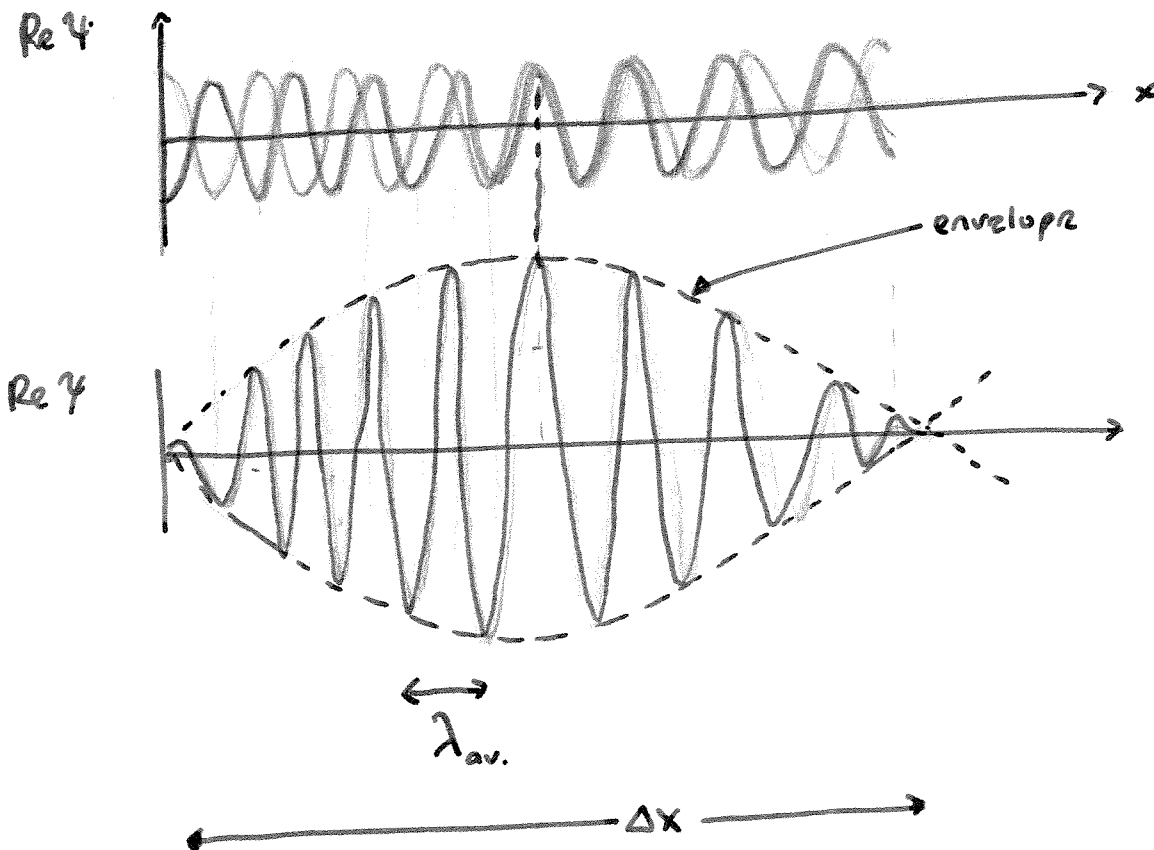
$$\operatorname{Re} \psi(x) = A_1 (\cos k_1 x - \cos k_2 x)$$

$$k_{av} = \frac{k_1 + k_2}{2}$$

$$\Delta k_{av} = (k_2 - k_1)$$

$$= A_1 \left( \cos(k_{av} x - \frac{\Delta k}{2} x) - \cos(k_{av} x + \frac{\Delta k}{2} x) \right)$$

$$= 2A_1 \left( \sin k_{av} x \sin \frac{\Delta k}{2} x \right)$$



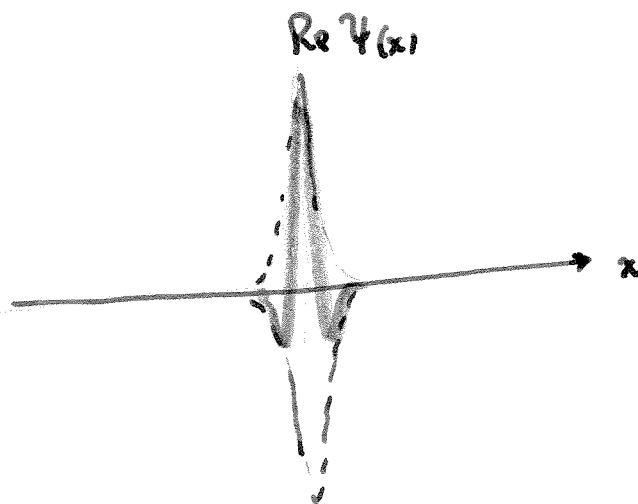
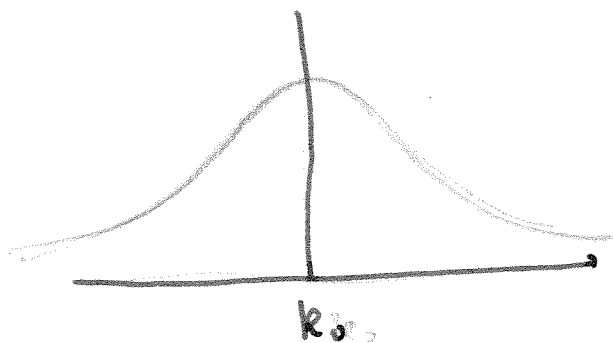
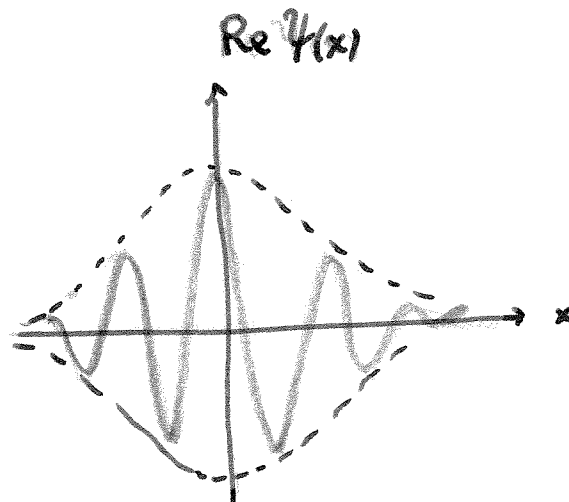
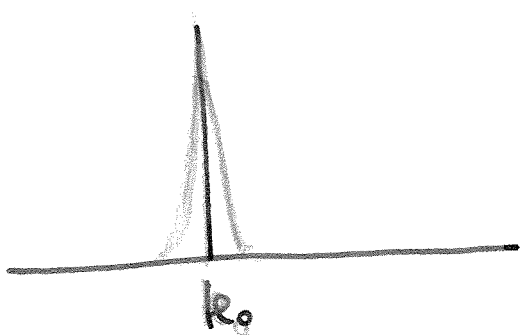
$$\Delta x \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) = 1$$

$$\Delta x \overbrace{\left( \frac{h}{\lambda_2} - \frac{h}{\lambda_1} \right)}^{\Delta p} = h$$

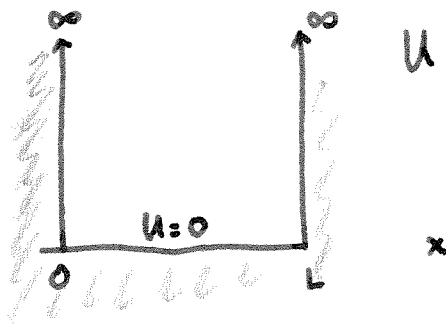
UNCERTAINTY PRINCIPLE.

$$\hat{\Psi}(x) = \int dk A(k) e^{ikx}$$

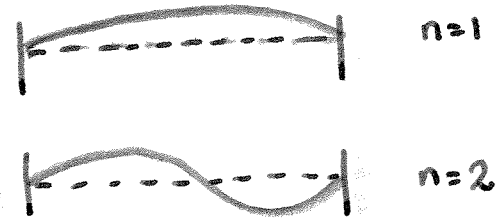
"FOURIER"  
SUPERPOSITION  
OF LARGE #  
OF WAVES



# 40.1 PARTICLE IN A BOX



STRING



In the region  $0 < x < L$   $U(x) = 0$ , so the wavefunction satisfies

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + 0 = E \psi(x)$$

In free space solution of this equation is  $\psi(x) = A e^{ikx}$ ,  $E = \frac{\hbar^2 k^2}{2m}$ .

Now wave is reflected off walls to form a STANDING WAVE

$$\psi(x) = \underbrace{A_1 e^{ikx}}_{\text{Right moving}} + \underbrace{A_2 e^{-ikx}}_{\text{Left moving}}$$

$$\begin{aligned}\Psi(x) &= A_1 (\cos kx + i \sin kx) + A_2 (\cos kx - i \sin kx) \\ &= (A_1 + A_2) \cos kx + i(A_1 - A_2) \sin kx.\end{aligned}$$

$$\Psi(x=0) = A_1 + A_2 = 0 \quad \text{since wave must vanish.}$$

for all  $x \leq 0$

$$\Psi(x) = 2iA_1 \sin kx = C \sin kx$$

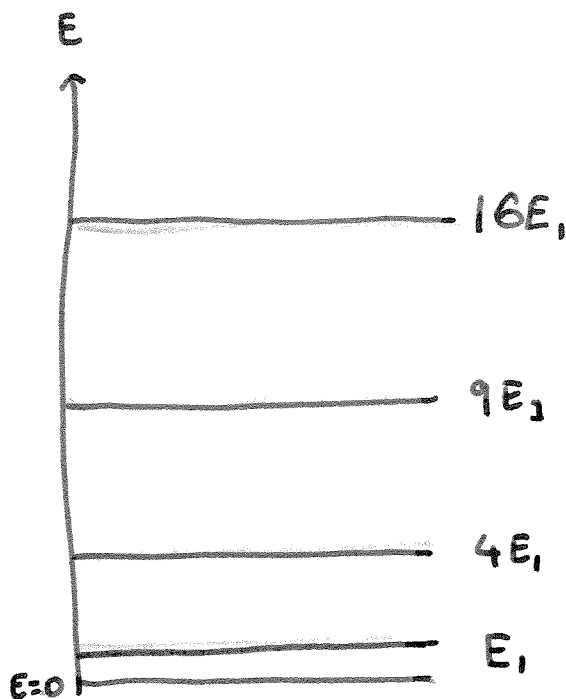
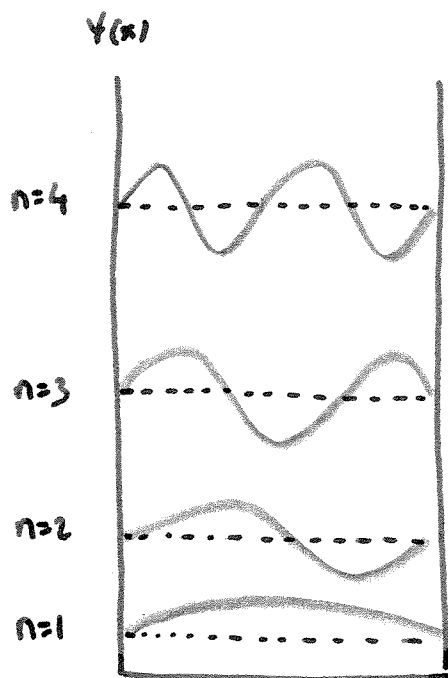
But also

$$\Psi(x=L) = C \sin kL = 0 \quad \text{since } \Psi=0 \text{ for all } x \geq L.$$

$$\Rightarrow kL = n\pi$$

$$\Rightarrow k = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots = n \frac{\pi}{L} \quad |p_n| = \frac{\hbar \pi}{L} n$$

$$\Psi_n(x) = C \sin \left( \frac{\pi n}{L} x \right), \quad E_n = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 n^2$$



### Probability + Normalization

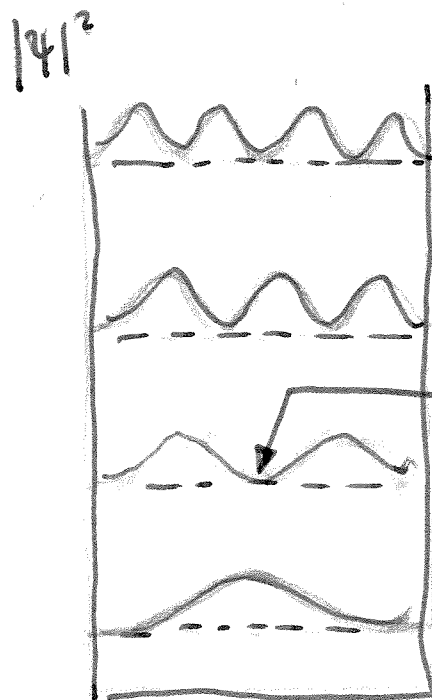
$$|\Psi(x)|^2 = C^2 \sin^2\left(\frac{n\pi x}{L}\right)$$

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

NORMALIZATION OF  
PROBABILITY DISTRIBUTION.

$$\int_0^L dx C^2 \sin^2\left(\frac{n\pi x}{L}\right) = C^2 L \left(\frac{1}{2}\right)$$

$$\Rightarrow C^2 = \frac{2}{L} \Rightarrow C = \sqrt{\frac{2}{L}}$$



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

40.5 3D Motion

For a free particle in 1D

$$K = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

$$\frac{\hbar^2 k^2}{2m} e^{ikx} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} e^{ikx}$$

In 3D

$$K = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m}$$

$$\Psi(x, y, z) = e^{ik_x x} e^{ik_y y} e^{ik_z z} = e^{i(k_x x + k_y y + k_z z)}$$

$$K \Psi(x, y, z) = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z)$$

General 3.D Schrödinger equation

$$\boxed{-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + U(x, y, z) \Psi = E \Psi}$$

In atomic structure, often we use spherical polar coords.  $(r, \theta, \phi)$

Convenient when  $U = U(r)$ . e.g. H atom  $U = e^2 / (4\pi\epsilon_0 r)$ .