Week 8

PHY 106 Quantum Physics
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3.2) Introduction to Quantum Mechanics

Seen in week 7 that matter-wave concept can successfully explain a lot about atoms.

However we need now a formal basis.

Classically:

Newton Eq. $\overrightarrow{F} = m\overrightarrow{a}$

Trajectory $\overrightarrow{p}(t)$ $\vec{r}(t)$

Quantum:

???

Q: what is needed here?

A: a **wave-equation** (c.f. section 2.1.2.)

Wave-function $\Psi(\vec{r}, t)$

3.2.1) Time dependent Schrödinger's equation

Re-consider wave function Eq. (57):

$$\Psi(x,t) = A\cos[2\pi\,(\frac{x}{\lambda_{dB}} - \nu t)]$$

We know from week 3 this is a solution of Eq. (13):

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = \frac{1}{\lambda^2\nu^2}\frac{\partial^2}{\partial t^2}\Psi(x,t)$$

$$\lambda = \frac{h}{p} \qquad\qquad \nu = \frac{E}{h}$$

Literature for this part: L. Schiff "quantum-mechanics", item 6, page 20

3.2.1) Time dependent Schrödinger's equation

Re-consider wave function Eq. (57):

$$\Psi(x,t) = A\cos[2\pi\,(\frac{x}{\lambda_{dB}} - \nu t)]$$

We know from week 3 this is a solution of Eq. (13):

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = \boxed{\frac{p^2}{E^2}}\frac{\partial^2}{\partial t^2}\Psi(x,t) \qquad \textbf{(77)}$$

$$= \frac{4m^2}{\boxed{p^2}}$$

Problem: should be part of **solution** only. Not of **equation** (see Newton)

Literature for this part: L. Schiff "quantum-mechanics", item 6, page 20

Turns out can't get it to work with Ψ above, need….

Excursion: Complex numbers and functions

- Earlier, we thought $\sqrt{-1} = ?$ does not work.
- Now let's just define $\sqrt{-1} = i$ (76)

  ***i* imaginary unit**
- We call numbers containing i **complex numbers**

$$z = a + ib$$

real part of z *imaginary part of z*

(a,b) are usual real numbers

Excursion: Complex numbers and functions

- Some ramifications:

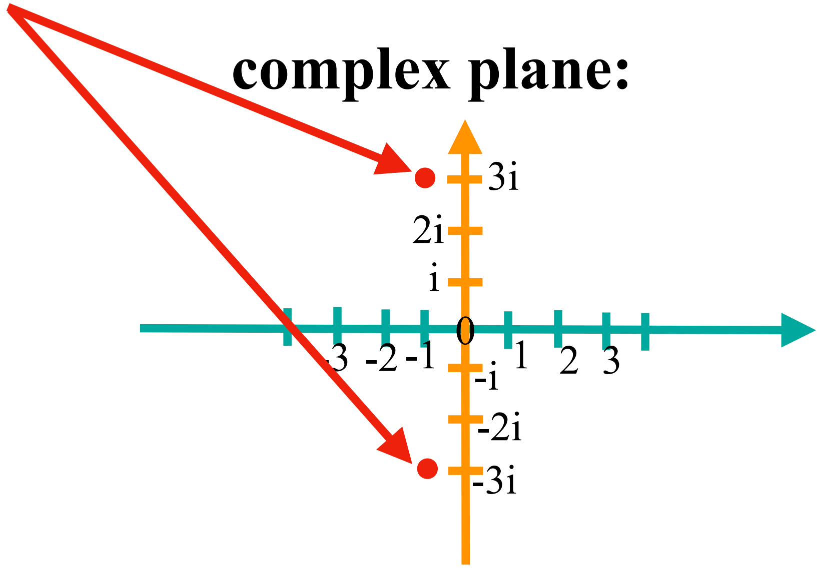
Every polynomial equation now has a solution, e.g.:

$$a_2 z^2 + a_1 z + a_0 = 0$$

Example:

$$z^2 + 2z + 10 = 0 \;\Leftrightarrow\; (z+1)^2 = -9$$

Complex solution: $z_\pm = -1 \pm 3i$



- Visualisation:

Can view z as 2D vector and draw in 2D plane:

$$z \leftrightarrow (a, b)$$

Excursion: Complex numbers and functions

- Functions of complex numbers, e.g. $f(z) = \dfrac{z+5}{z-2}$

- Most important example for this course

$$\exp(z) = \sum_{n=0}^{\infty} \frac{z^n}{n!}$$

- Find formula:

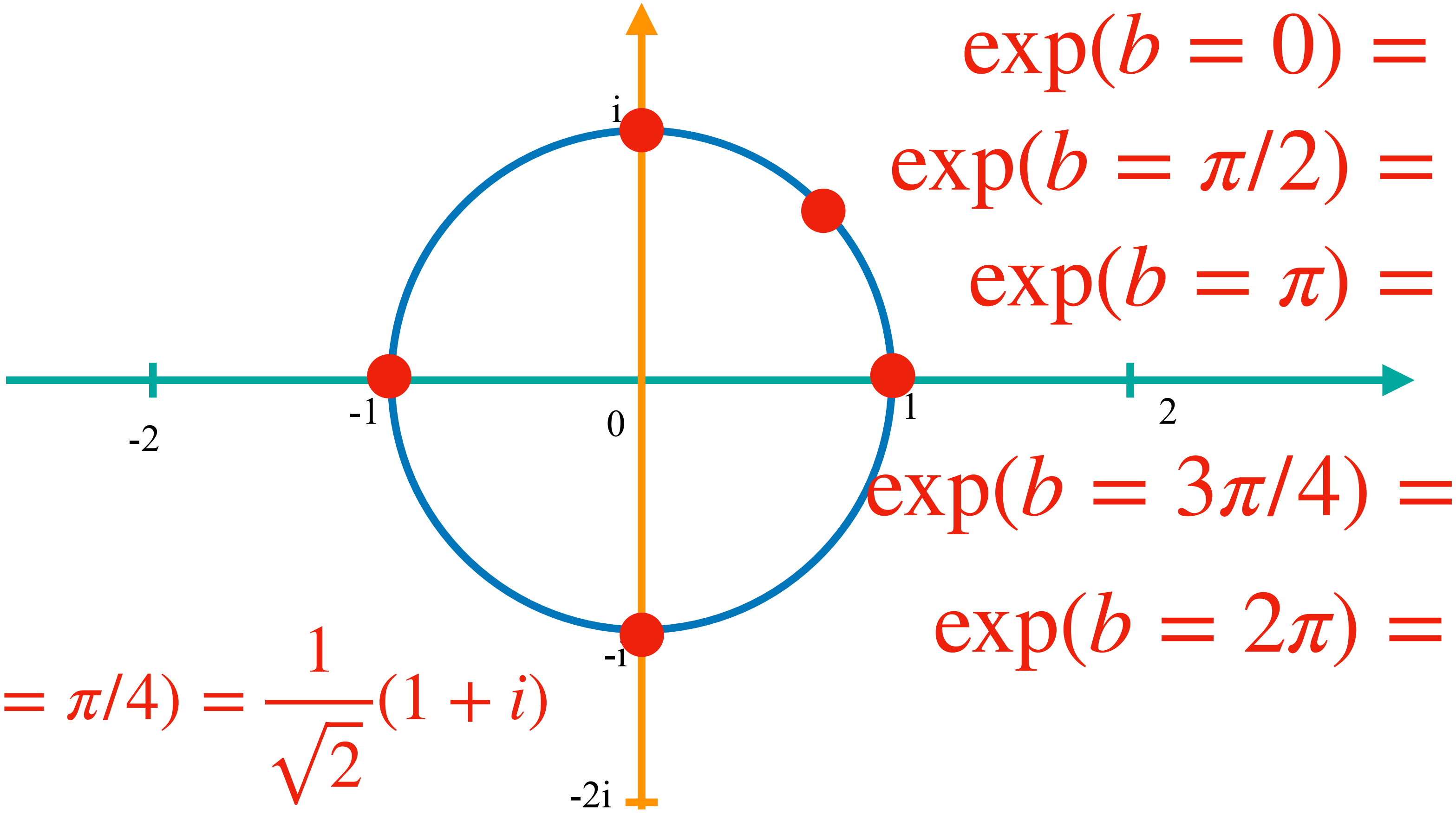
$$\exp(a+ib) = \exp(a)[\cos(b) + i\sin(b)]$$

Excursion: Complex numbers and functions

$$\exp(ib) = \cos(b) + i\sin(b) \qquad \text{(78b)}$$

- In the complex plane:

complex plane:



$$\exp(b = 0) = 1$$

$$\exp(b = \pi/2) = i$$

$$\exp(b = \pi) = -1$$

$$\exp(b = 3\pi/4) = -i$$

$$\exp(b = 2\pi) = 1$$

$$\exp(b = \pi/4) = \frac{1}{\sqrt{2}}(1 + i)$$

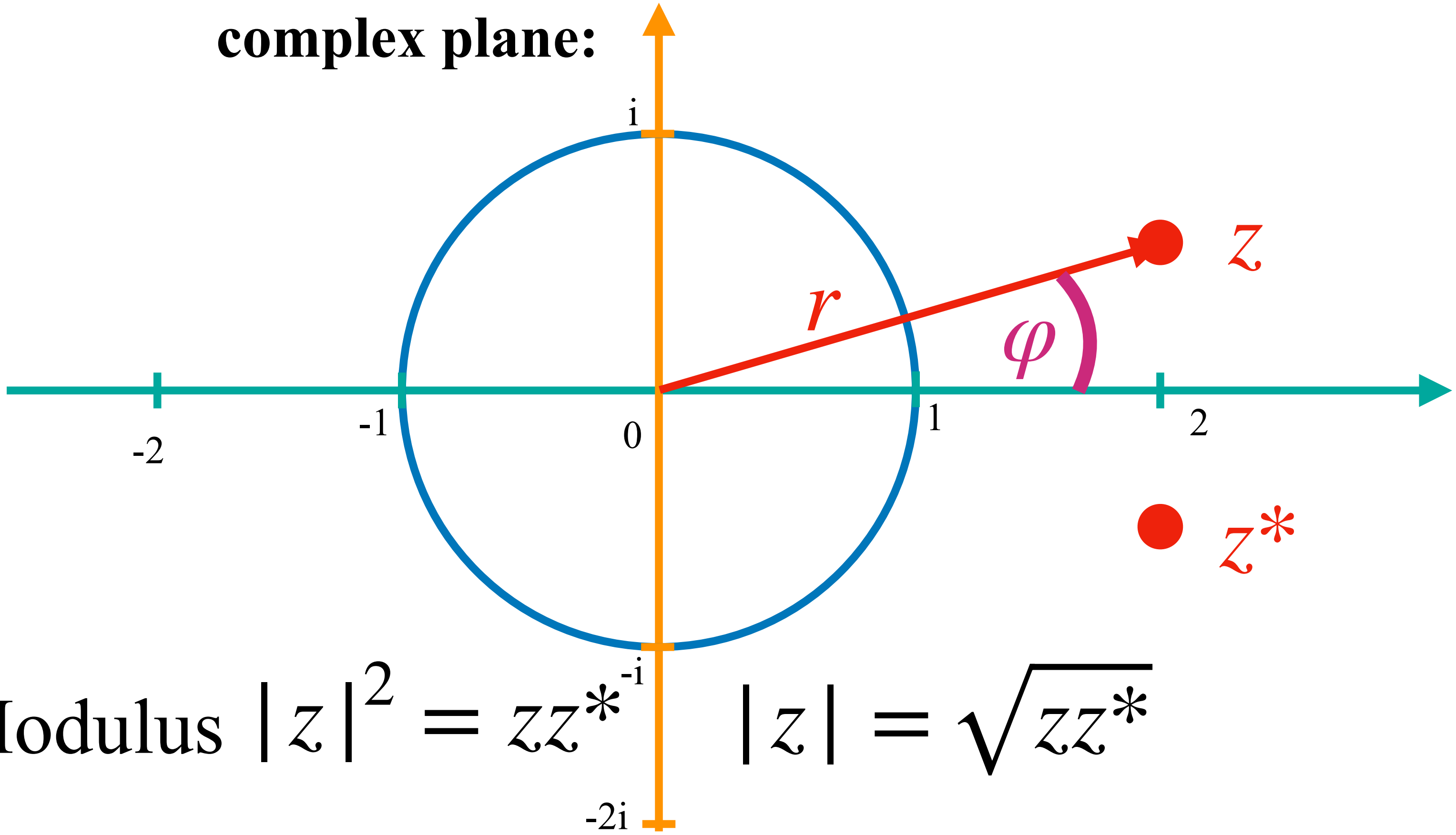
Excursion: Complex numbers and functions

- Can write any complex number as

$$z = r\exp(i\varphi) \tag{79}$$

- Complex conjugate $z^* = a - ib$ (80)

complex plane:



- Modulus $|z|^2 = zz^*$ $|z| = \sqrt{zz^*}$ (81)

Excursion: Complex numbers and functions

- We can now express *sin* and *cos* using Eq. (77b):

$$\cos(x) = \frac{1}{2}\left(e^{ix} + e^{-ix}\right) \qquad \textbf{(82a)}$$

$$\sin(x) = \frac{1}{2i}\left(e^{ix} - e^{-ix}\right) \qquad \textbf{(82b)}$$

- This makes your life better. Can now forget about trig-identities.

- Can simply use

$$\exp(a + b) = \exp(a)\exp(b) \qquad \textbf{(83)}$$

…for manipulations such as in section (2.3.1.)

Schrödinger's equation

With complex numbers, let us fix new:

Quantum wave function of free particle

$$\Psi(x,t) = A\exp[i(kx-\omega t)] \qquad (84)$$

- Still: $k = \dfrac{p}{\hbar}$ $\qquad$ $\omega = \dfrac{E}{\hbar}$
- This replaces Eq. (54). **Forget Eq. (54)!!!**
- Note, probability density:

$$\rho(x,t) = |\Psi(x,t)|^2 = |A|^2 = const\,.$$

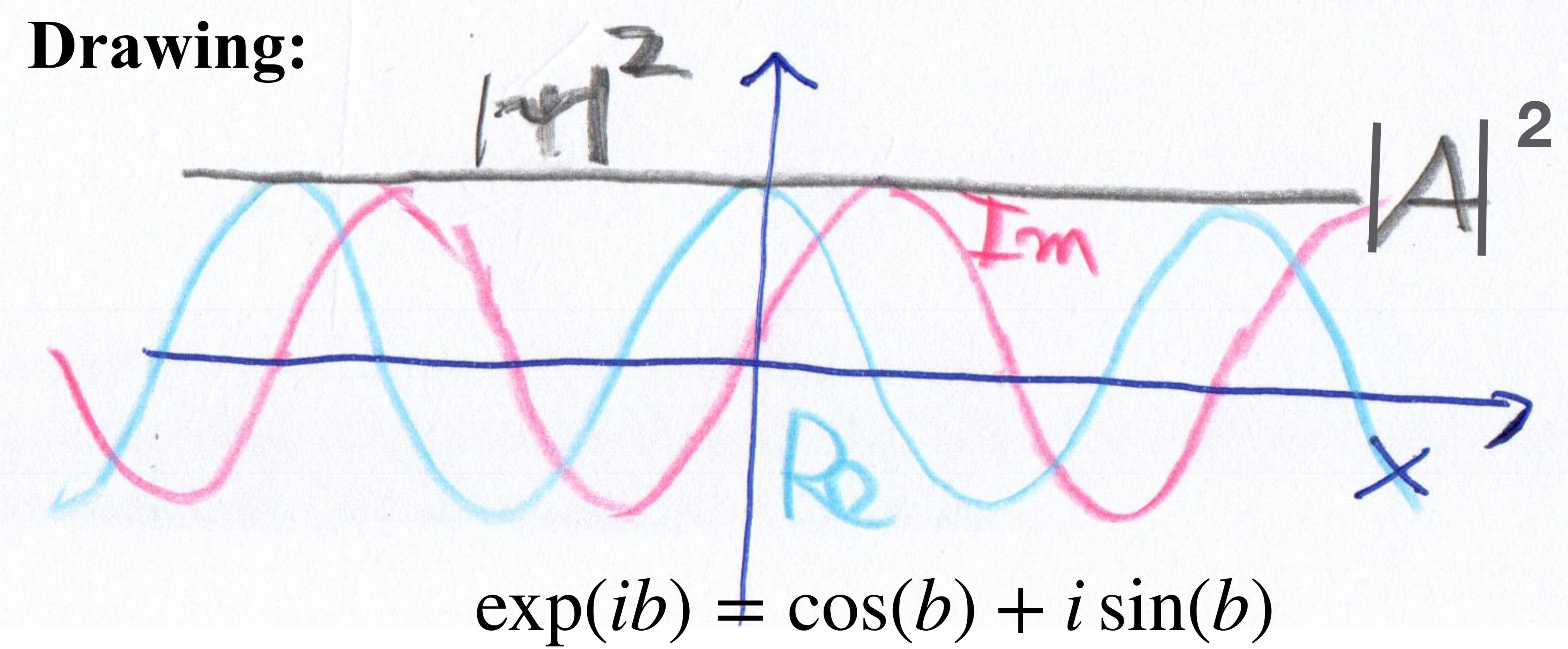
Schrödinger's equation

With complex numbers, let us fix new:

Quantum wave function of free particle

$$\Psi(x,t) = A\exp[i(kx - \omega t)] \qquad (84)$$

Drawing:



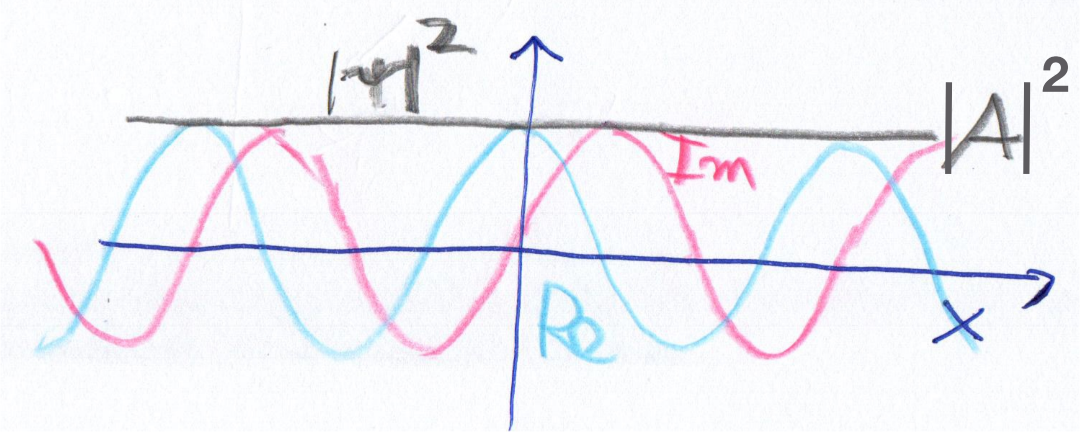
$$\exp(ib) = \cos(b) + i\sin(b)$$

Schrödinger’s equation

With complex numbers, let us fix new:

Quantum wave function of free particle

$$\Psi(x, t) = A \exp[i(kx - \omega t)] \tag{84}$$



Now let us re-attempt finding a wave-equation that has (84) as a solution….

Schrödinger's equation

$$k = \frac{p}{\hbar} \qquad \omega = \frac{E}{\hbar}$$

From Eq. (84): $\Psi(x,t) = A\exp[i(kx - \omega t)]$

$$p\Psi(x,t) = -i\hbar\frac{\partial}{\partial x}\Psi(x,t) \qquad p^2\Psi(x,t) = -\hbar^2\frac{\partial^2}{\partial x^2}\Psi(x,t)$$

(84b)

Also:

$$E\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$

Suppose particle feels potential energy U(x,t):

$$E = \frac{p^2}{2m} + U(x,t)$$

try:

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

Schrödinger's equation

This gives indeed the

Time-dependent Schrödinger equation (TDSE) of particle in 1D in a potential *U(x,t)*

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x,t)\right)\Psi(x,t) \qquad (85)$$

- The classical equivalent is

$$F = ma = m\ddot{x} = -\frac{\partial}{\partial x}U(x,t) \qquad (86)$$

- It contains only the problem (particle, potential) and can give **any** dynamics [unlike Eq. (77)]

Schrödinger's equation

Time-dependent Schrödinger equation (TDSE) of particle in 1D in a potential *U(x,t)*

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x,t)\right)\Psi(x,t) \qquad (85)$$

- In 3D

$$i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t) = \left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U(x,y,z,t)\right)\Psi(x,y,z,t) \qquad (87)$$

- Note, we haven't really derived Eq. (85). It cannot be derived

Example: The *free* particle

We had used the wavefunction

$$\Psi(x,t) = A\exp[i(kx - \omega t)]$$

repeat (84)

to associate
$$E\ldots = i\hbar\frac{\partial}{\partial t}\ldots \qquad p\ldots = -i\hbar\frac{\partial}{\partial x}\ldots$$

in motivating the TDSE Eq. (85).

For $U(x,t)=0$ the function (84) **is** in fact a solution of the TDSE, if
$$E = \frac{p^2}{2m}$$

This is the case for a **free particle,** which is not subject to any potential.

Verification…

Example (contd.)

Free particle wave function

$$\Psi(x,t) = A\exp[i(kx - \omega t)]$$

repeat (84)

TDSE

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

$$i\hbar(-i\omega)\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\right)(ik)^2\Psi(x,t)$$

$$\hbar\omega\Psi(x,t) = \left(\frac{\hbar^2k^2}{2m}\right)\Psi(x,t)$$

$$\hbar\omega = h\nu = E = \frac{p^2}{2m} \qquad \hbar k = p$$

matches

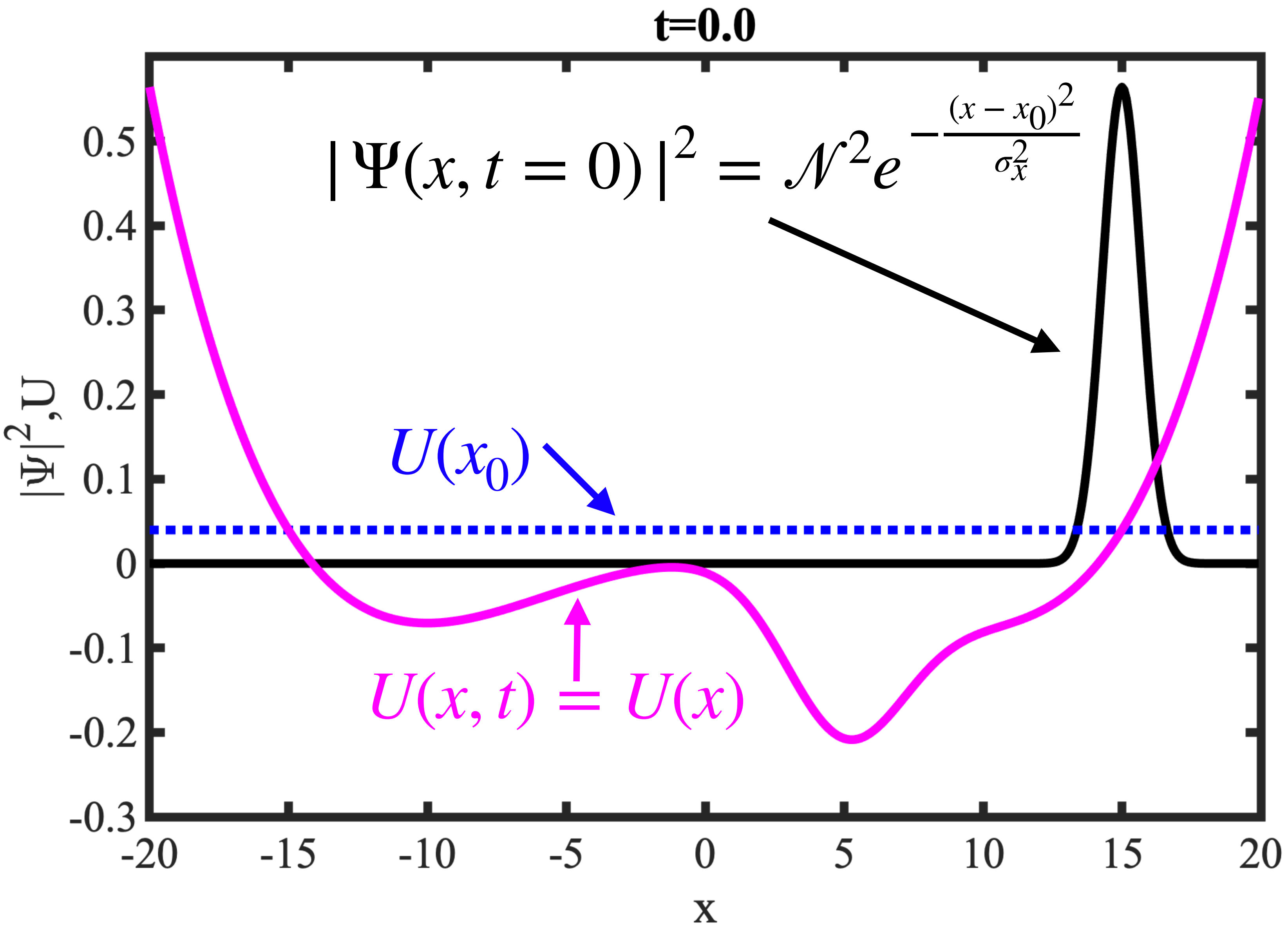
Example: Numerical solution of TDSE

- TDSE is a first-order differential equation in time
- If we know $\Psi(x, t = 0)$ we can find $\Psi(x, t)$ at all later times.
- Let's start with:

$$\Psi(x, t = 0) = \mathcal{N} e^{-\frac{(x - x_0)^2}{2\sigma_x^2}}$$

- Note, this is a **Gaussian wave packet**, c.f. Sec. (2.3.3) with $k_0 = 0$.

Example: Numerical solution of TDSE

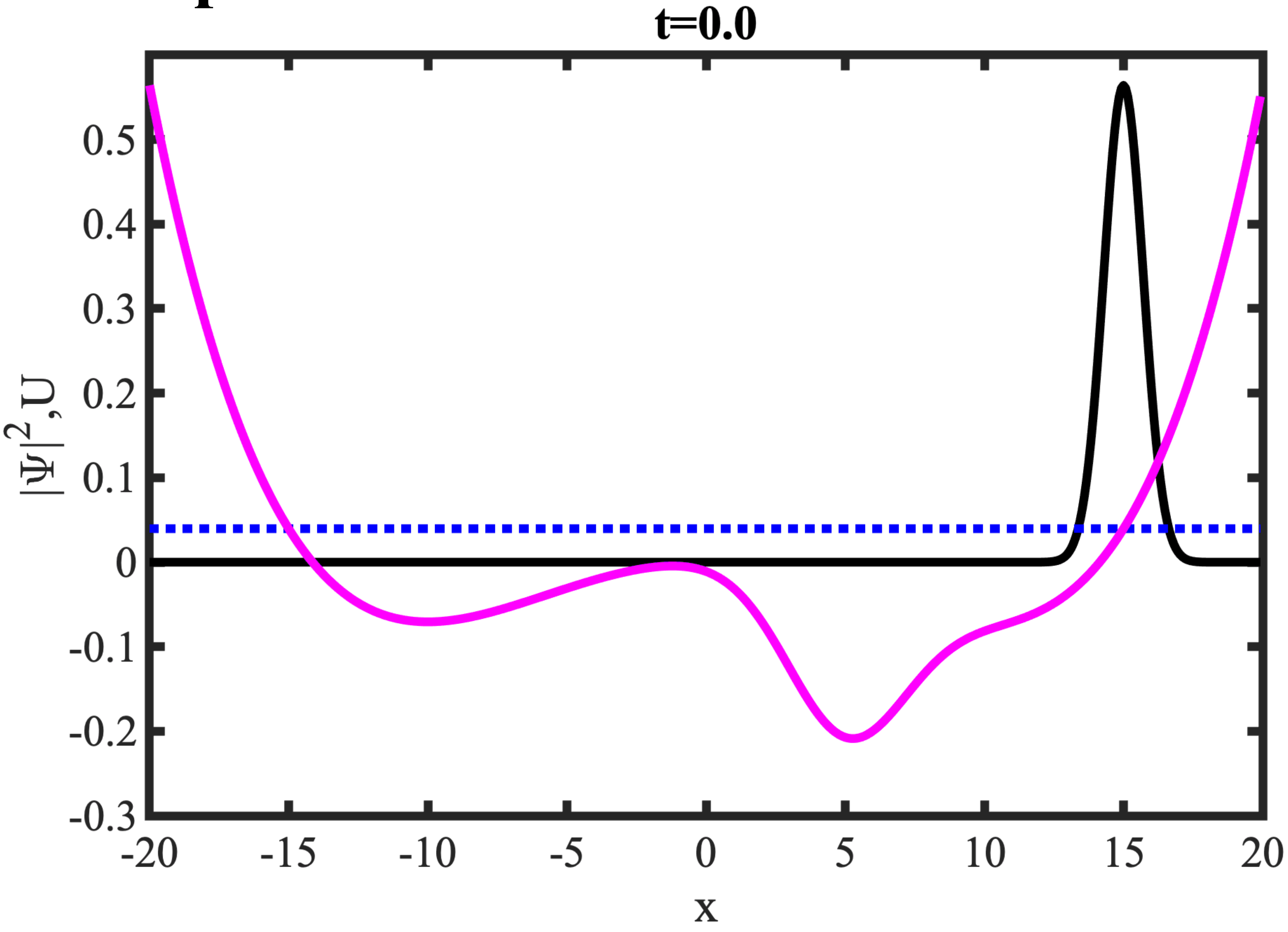


$$|\Psi(x,t=0)|^2 = \mathcal{N}^2 e^{-\frac{(x-x_0)^2}{\sigma_x^2}}$$

$U(x_0)$

$U(x,t) = U(x)$

Example: Numerical solution of TDSE



Example: Numerical solution of TDSE

- We see initially behavior like we would expect classically (particle “**falling down**” potential gradient)

- But already it always has a **distribution** of positions

- At late time, lots of wave like **interference** effects are visible.

Linearity and superposition

- Since now all information about the dynamics/motion of a particle is encoded in the wave function, mechanics becomes **probabilistic**

- The TDSE is linear. This means we have again:

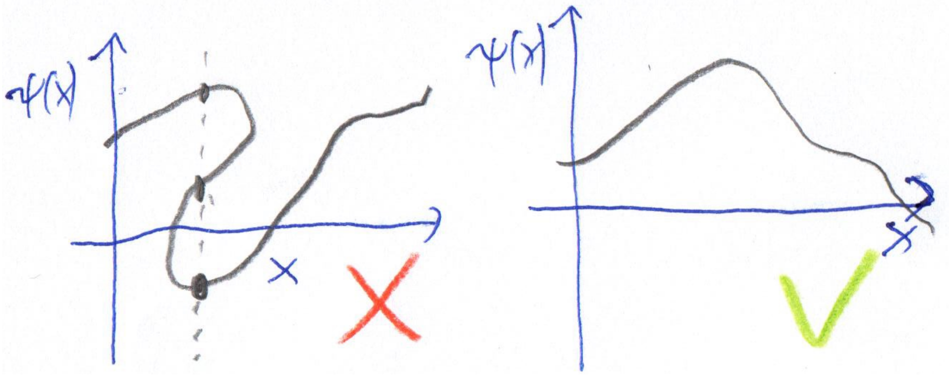
Superposition principle

If $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are solutions to the TDSE, so is $\Psi_3(x,t) = d_1\Psi_1(x,t) + d_2\Psi_2(x,t)$ **(88)**

In analytical solutions, we have to take care of….

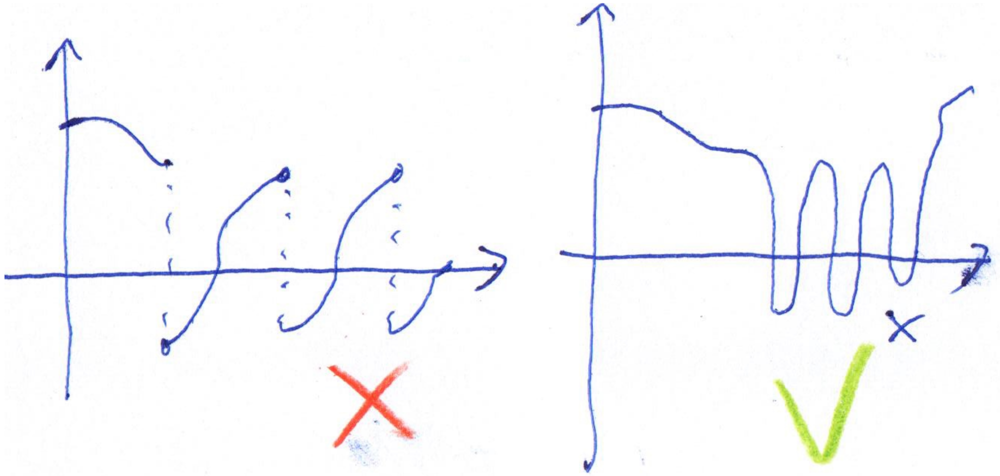
Schrödinger's equation, admissible solutions

- single-valued



- Normalizable $$\int dx\,|\Psi(x,t)|^2 = 1$$

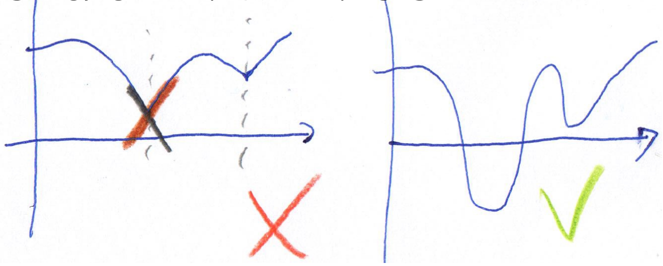
- continuous



$$\lim_{x\downarrow x_0}\Psi(x) = \lim_{x\uparrow x_0}\Psi(x)$$

- differentiable with continuous derivatives

$$\lim_{x\downarrow x_0}\frac{d}{dx}\Psi(x) = \lim_{x\uparrow x_0}\frac{d}{dx}\Psi(x)$$



Expectation values

Statistics:

If x is a random variables which can have outcomes x_k with probability ρ_k we define

Expectation value $$E[x] = \sum_k x_k \rho_k \quad (89)$$

- Expectation values corresponds to the average over a very large number of realisations.

- Example: Throw a 6-sided dice.

$$x_k = k \ , k = 1,\ldots,6$$

$$\rho_k = \frac{1}{6}$$

$$E[x] = \frac{1+2+3+4+5+6}{6} = 3.5$$

Expectation values

- For a continuous range of possible outcomes, Eq. (89) becomes

$$E[x] = \int dx\, x\, \rho(x) \qquad \textbf{(90)}$$

- We can now apply this to the quantum wave function to find the

Position expectation value of particle with wavefunction $\Psi(x,t)$

$$\langle x \rangle = \int_{-\infty}^{\infty} dx \;\; x\,|\,\Psi(x,t)\,|^2 \qquad \textbf{(91)}$$

- This is the **average** over many position measurements of identically prepared particles

Operators

How do we find expectation values of **momentum** or **energy**?

- Statistics: $\langle p \rangle = \int dp \, p \, \rho(p)$

But wave-function does not give us **probability** of momentum directly. We must use….

Momentum operator $$\hat{p} = -i\hbar \frac{\partial}{\partial x} \qquad (92)$$

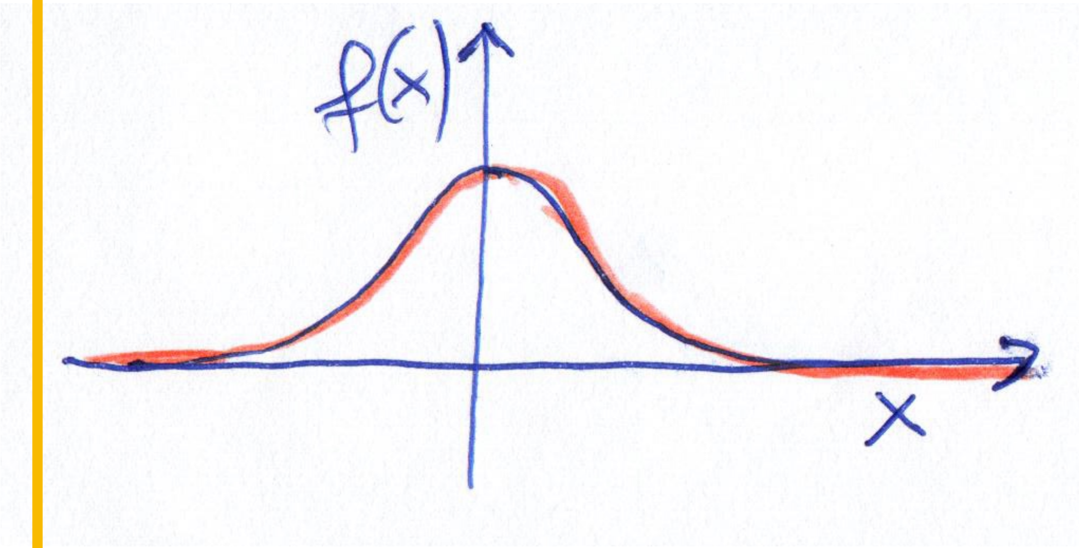
- Motivation: Eq. (84b)
- Notation: We denote all operators with “$\widehat{\text{hat}}$”.

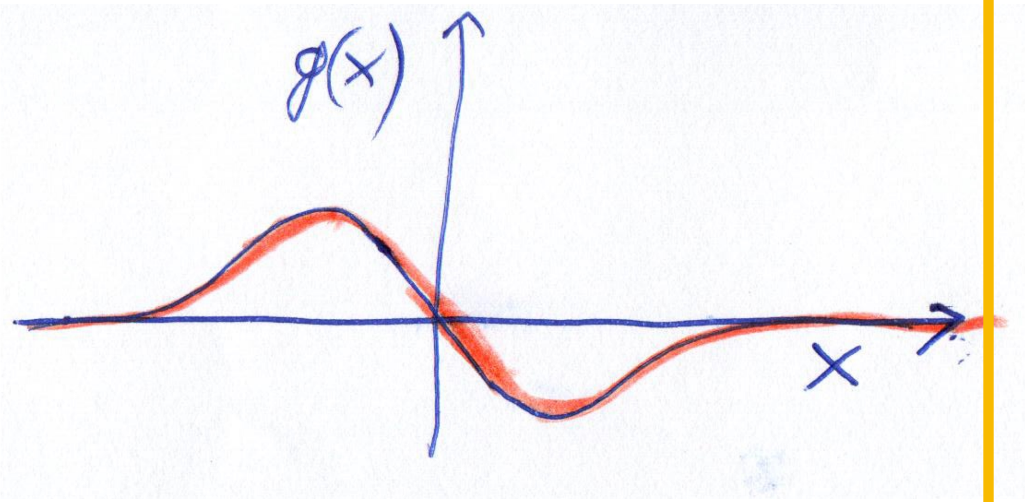
Operators An operator $\hat{O}$ is a map of a function onto another function: $\hat{O} : f(x) \to g(x)$

Example: $\hat{O} = \frac{\partial}{\partial x} = \frac{i}{\hbar}\hat{p}$

$f(x) = \exp[-x^2]$

$g(x) = -\,2x\exp[-x^2]$

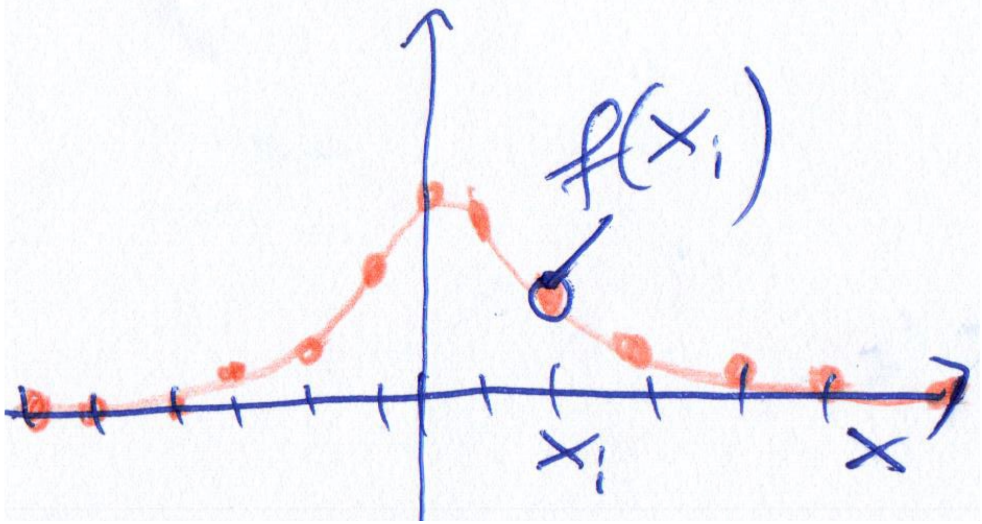


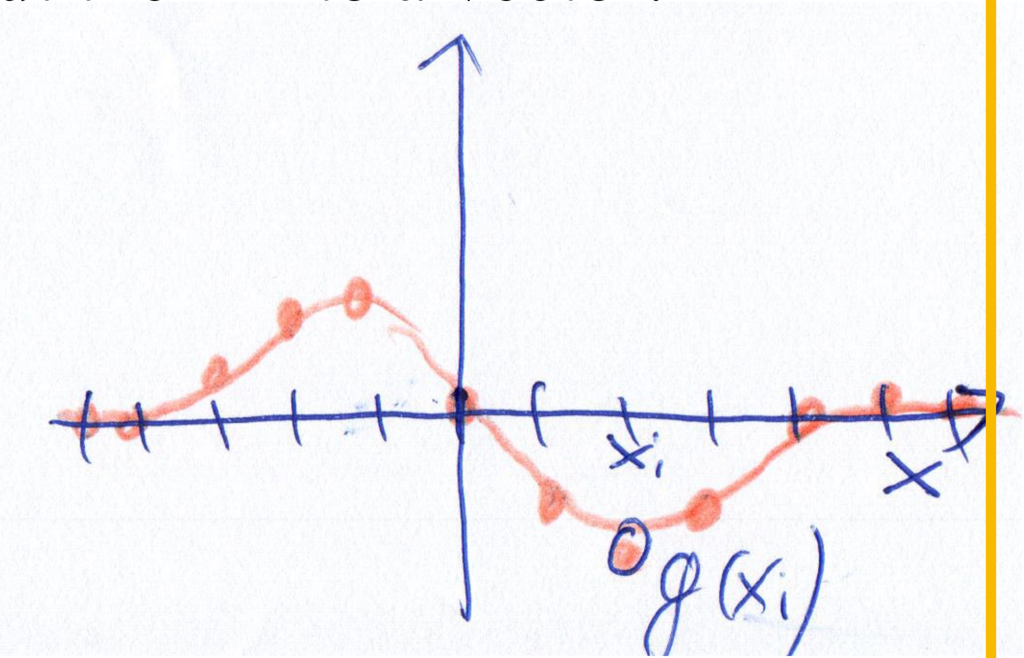


[recall “differentiation by drawing” chapter 1]

Operators

Discretize the functions and put them into a vector:





$$\vec{f} = \begin{bmatrix} f(x_0) \\ f(x_1) \\ \vdots \\ f(x_k) \\ \vdots \\ f(x_N) \end{bmatrix}$$

Now: $g(x) = \dfrac{\partial}{\partial x} f(x)$

Can map operator onto matrix: $\overrightarrow{g} = \underline{\underline{D}}\vec{f}$

$$\vec{g} = \begin{bmatrix} g(x_0) \\ g(x_1) \\ \vdots \\ g(x_k) \\ \vdots \\ g(x_N) \end{bmatrix}$$

Operators

For the specific derivative operator, we can even approximately write an explicit form:

Definition of **derivative / slope**: $\frac{\partial}{\partial x} f(x)\,|_{x=x_0} = \frac{f(x_0+\Delta x)-f(x_0-\Delta x)}{\Delta x}$

Thus:

$$\underline{\underline{O}}\,\vec{f} = \frac{1}{\Delta x}\begin{bmatrix} 0 & 1 & & & \cdots & 0 \\ -1 & 0 & 1 & & & \vdots \\ & -1 & \ddots & 1 & & \\ & & -1 & \ddots & & \\ \vdots & & & \ddots & 1 & 0 \\ & & & -1 & 0 & 1 \\ 0 & \cdots & & 0 & -1 & 0 \end{bmatrix}\begin{bmatrix} f(x_0) \\ f(x_1) \\ \vdots \\ \vdots \\ f(x_N) \end{bmatrix}$$

Summary, operators

We can then think of **operators** as **matrices**

$$\hat{O} \rightarrow \underline{\underline{O}}$$

(matrices map vectors onto other vectors,
Operators map functions onto other functions)

$$\underline{\underline{O}} : \overrightarrow{v} \rightarrow \overrightarrow{w}, \quad \overrightarrow{w} = \underline{\underline{O}}\,\overrightarrow{v}$$

$$\hat{O} : f(x) \rightarrow g(x)$$

Operators

measurable quantity

It turns out:…

In quantum mechanics, every observable is represented by an operator

Its expectation value is then:

Expectation value of any operator

$$\langle \hat{O} \rangle = \int_{-\infty}^{\infty} dx\, \Psi^*(x,t) \hat{O} \Psi(x,t) \tag{93}$$

- e.g. momentum expectation value:

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} dx\, \Psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(x,t) \tag{94}$$

- !! Ordering in Eq. (93) is important for differential operators

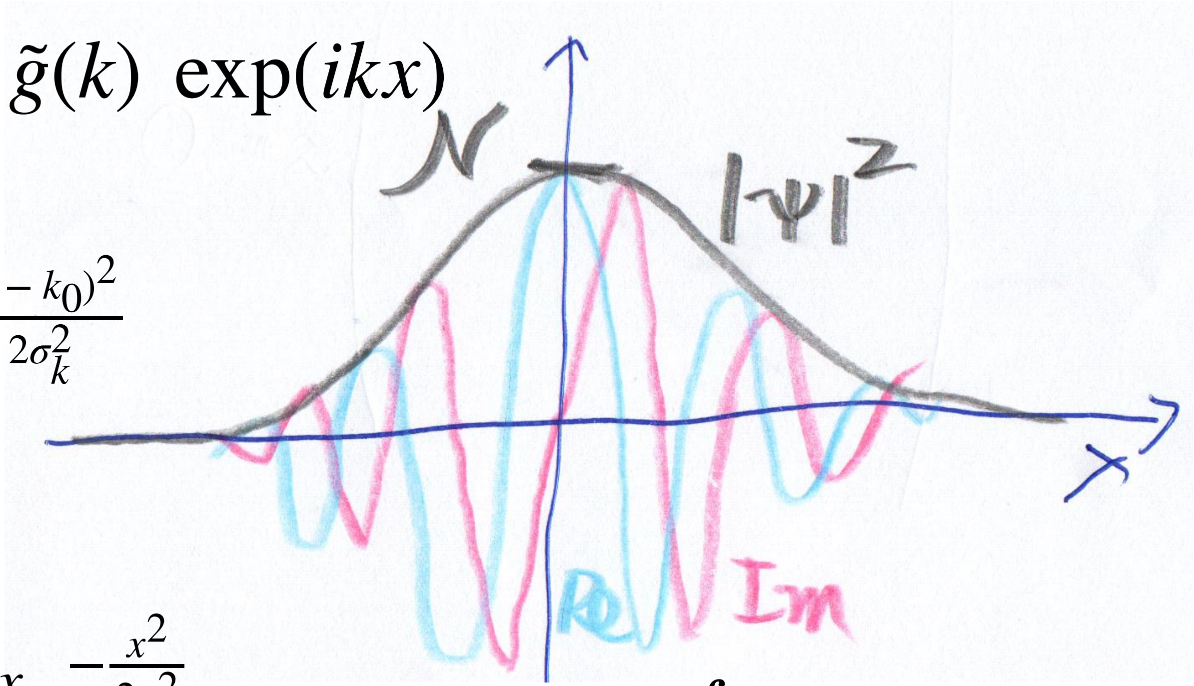
Example: Gaussian wave packet

Convert our earlier Gaussian wave-packet Eq. (42), into one for complex waves, as Eq. (84)

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk \;\; \tilde{g}(k) \;\; \exp(ikx)$$

(95)

$$\tilde{g}(k) = \frac{1}{\sqrt{\sqrt{\pi}\sigma_k}} e^{-\frac{(k-k_0)^2}{2\sigma_k^2}}$$

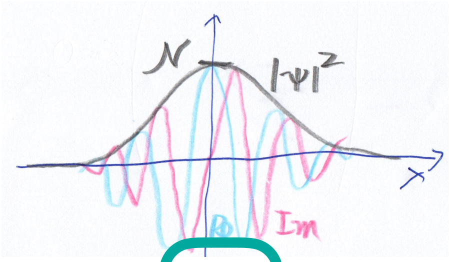


$$\Psi(x) = \frac{1}{(\pi\sigma_x^2)^{1/4}} e^{ik_0x} e^{-\frac{x^2}{2\sigma_x^2}}$$

(96)

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

Example (contd.)



$\boxed{x_0}$

Let us calculate the **expectation value** of position $\langle\hat{x}\rangle$ and momentum $\langle\hat{p}\rangle$

Let's slightly shift wave packet: **(97)** $\Psi(x) = \dfrac{1}{(\pi\sigma_x^2)^{1/4}} e^{ik_0x} e^{-\frac{(x-\boxed{x_0})^2}{2\sigma_x^2}}$

$$\langle\hat{x}\rangle = \int_{-\infty}^{\infty} dx\, \Psi^*(x)\hat{x}\;\Psi(x)$$

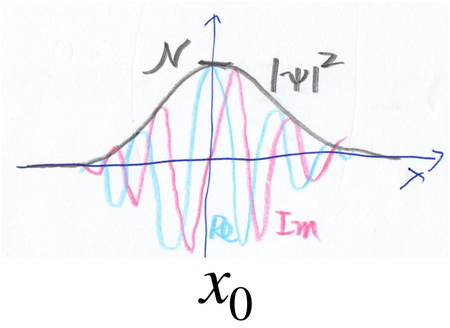
$$= \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{\pi\sigma_x}} |e^{ik_0x}|^2 |e^{-\frac{(x-x_0)^2}{2\sigma_x^2}}|^2 x$$

$\tilde{x} = x - x_0$

$$= \frac{1}{\sqrt{\pi\sigma_x}}\int_{-\infty}^{\infty} dx\, e^{-\frac{(x-x_0)^2}{\sigma_x^2}} x \quad = \frac{1}{\sqrt{\pi\sigma_x}}\int_{-\infty}^{\infty} d\tilde{x} e^{-\frac{\tilde{x}^2}{\sigma_x^2}} (\tilde{x}+x_0)$$

$d\tilde{x} = dx$

Example (contd.)



$$\Psi(x) = \frac{1}{(\pi\sigma_x^2)^{1/4}} e^{ik_0 x} e^{-\frac{(x-x_0)^2}{2\sigma_x^2}} \quad \textbf{(97)}$$

Split integral into two:

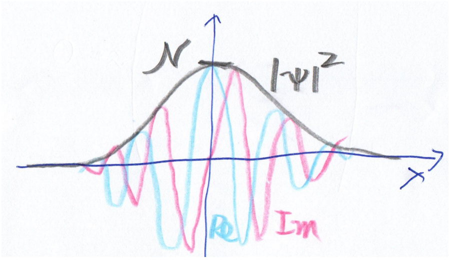
$$\langle \hat{x} \rangle = \cdots \quad = \frac{1}{\sqrt{\pi}\sigma_x} \int_{-\infty}^{\infty} d\tilde{x} e^{-\frac{\tilde{x}^2}{\sigma_x^2}} (\tilde{x} + x_0)$$

$$= \underbrace{\frac{1}{\sqrt{\pi}\sigma_x} \int_{-\infty}^{\infty} d\tilde{x} e^{-\frac{\tilde{x}^2}{\sigma_x^2}} \tilde{x}}_{\substack{= 0 \\ \text{asymmetric integrand!}}} + x_0 \underbrace{\frac{1}{\sqrt{\pi}\sigma_x} \int_{-\infty}^{\infty} d\tilde{x} e^{-\frac{\tilde{x}^2}{\sigma_x^2}}}_{\substack{= 1 \quad = \int_{-\infty}^{\infty} |\Psi|^2 dx \\ \text{normalisation}}} \quad = x_0$$

Thus on **average**, this particle is **found** at position x_0

Example (contd.)

For **momentum** expectation value:



x_0

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} dx\, \Psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(x,t) \qquad \Psi(x) = \frac{1}{(\pi\sigma_x^2)^{1/4}} e^{ik_0x} e^{-\frac{(x-x_0)^2}{2\sigma_x^2}}$$

$$= \frac{1}{\sqrt{\pi}\sigma_x} \int_{-\infty}^{\infty} dx\, e^{-ik_0x} e^{-\frac{(x-x_0)^2}{2\sigma_x^2}} \left(-i\hbar \frac{\partial}{\partial x} \right) e^{ik_0x} e^{-\frac{(x-x_0)^2}{2\sigma_x^2}}$$

$$= \frac{1}{\sqrt{\pi}\sigma_x} \int_{-\infty}^{\infty} dx\, e^{-ik_0x} e^{-\frac{(x-x_0)^2}{2\sigma_x^2}} \left(\hbar k_0 e^{-ik_0x} e^{-\frac{(x-x_0)^2}{2\sigma_x^2}} + e^{-ik_0x} \left(-\frac{(x-x_0)}{2\sigma_x^2} \right) e^{-\frac{(x-x_0)^2}{2\sigma_x^2}} \right)$$

excercise

$$= \cdots = \hbar k_0 \equiv p_0$$

Thus on **average**, this particle has **momentum** p_0

3.2.2) Time independent Schrödinger equation

Frequently, e.g.) examples in 3.2.1), potential does **not** actually depend on time $U(x,t) = U(x)$

For example free particle $U(x,t) = 0$

Note we can write Eq. (84) as

$$\Psi(x,t) = A\exp[i(kx - \omega t)]$$

$$\Psi(x,t) = \phi(x)\exp[-i\omega t] \qquad (98)$$

Insert into TDSE:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \ldots \qquad \hbar\omega\Psi(x,t) = \ldots \qquad E\Psi(x,t) = \ldots$$

Time independent Schrödinger equation

Using this replacement on the lhs, we are led to the

Time-independent Schrödinger equation (TISE) of particle in 1D in a potential *U(x)*

$$E_n\phi_n(x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\phi_n(x) \qquad \textbf{(99)}$$

- The equation has many solutions *n=0,1,2,…*with different energies E_n

- If we start the TDSE on such a solution, i.e. $\Psi(x,0) = \phi_n(x)$ we get (see Eq. 107b later) $\Psi_n(x,t) = \phi_n(x)e^{-i\frac{E_n}{\hbar}t}$ **(99b)**

Thus: $|\Psi(x,t)|^2 = |\phi_n(x)|^2$ **probability density const!!**

Time independent Schrödinger equation

Time-independent Schrödinger equation (TISE) of particle in 1D in a potential *U(x,t)*

$$E_n\phi_n(x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \right)\phi_n(x) \qquad (100)$$

- The operator on the rhs. of the TISE is so important that it has a special name:

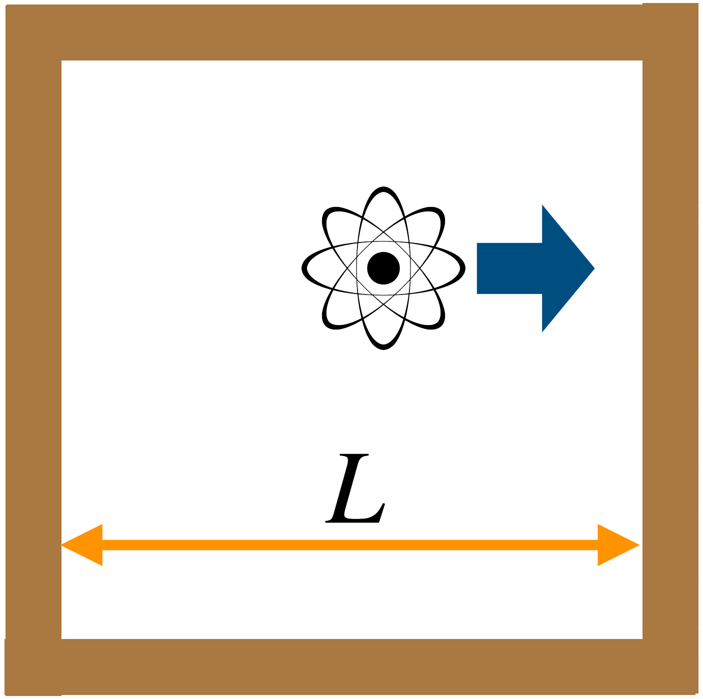
Hamiltonian (operator):

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \qquad (101)$$

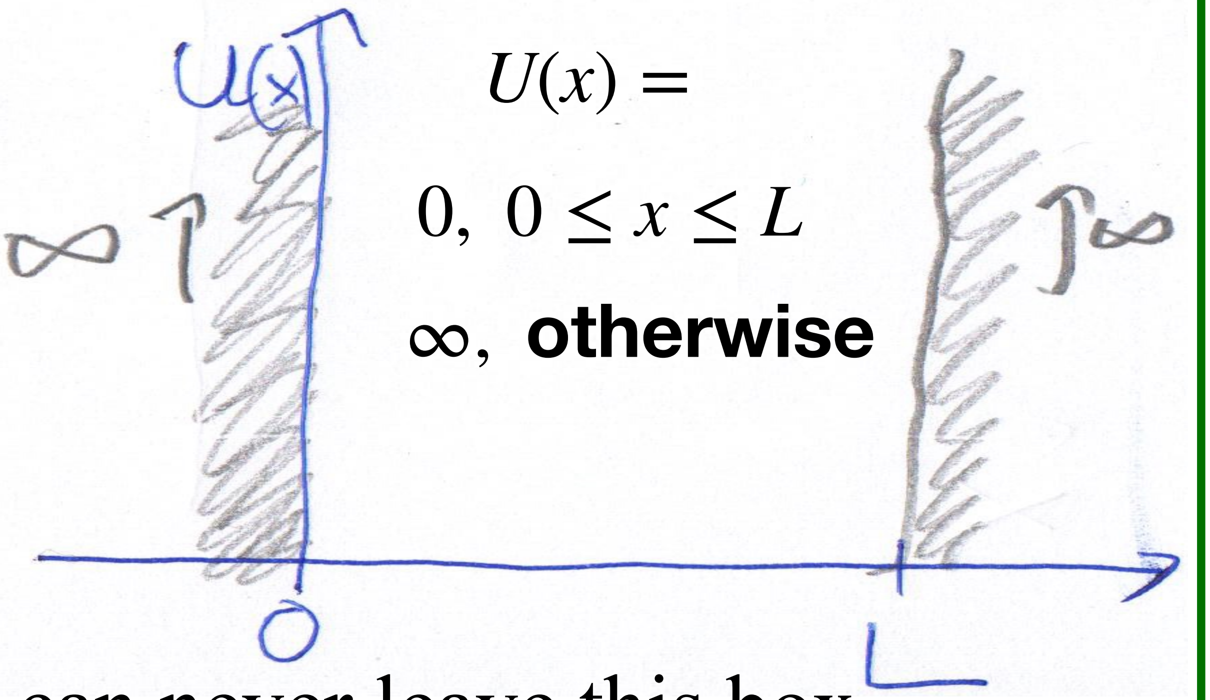
- It represents the **total** energy of the particle

3.2.2.1.) Example: Particle in a box

We can best understand the relevance of the TISE by revisiting the example from section 2.4.3) more mathematically:



We first need a **box potential**:



$U(x) =$

$0,\ 0 \le x \le L$

∞, **otherwise**

Finite energy particle can never leave this box…

Example *(contd.)*

We shall solve: $E_n\phi_n(x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\phi_n(x)$

First note: $\phi_n(x) = 0$ outside the box.

Reason: (A) Let's use Eq. (93) with $\hat{O} = U(\hat{x})$

Expectation value of potential energy

$$\langle U(\hat{x})\rangle = \int_{-\infty}^{\infty} dx\, U(x)\,|\,\phi_n(x)\,|^2$$

This would be **infinite** if $\phi_n(x) \neq 0$ outside box.

(B) Wavefunction must be **continuous**

[proof: advanced courses]

$\Rightarrow$ **Boundary condition** $\phi_n(0) = \phi_n(L) = 0$

(c.f. section 2.4.3)

Example *(contd.)*

Inside the box *U=0*

$$E_n\phi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi_n(x) \qquad \textbf{(102)}$$

Solution? Revisit section 1.2):

$$\phi_n(x) = A\sin\left(\frac{\sqrt{2mE_n}}{\hbar}x\right) + B\cos\left(\frac{\sqrt{2mE_n}}{\hbar}x\right) \qquad \textbf{(103)}$$

[verify by insertion into (98)]

To fulfill B.C. $\phi_n(0) = 0$ $\qquad B = 0$

$$\phi_n(L) = 0 \qquad \frac{\sqrt{2mE_n}}{\hbar}L = n\pi$$

$$n = 1,2,\ldots$$

We thus again arrive at $E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}$ [= Eq. (65)]

Example *(contd.)*

We have also found the wave-function:

$$\phi_n(x) = A\sin(k_n x) \qquad k_n = \frac{n\pi}{L} \tag{104}$$

Finally can find A by requiring **normalisation** [Eq.(59)]

$$1 = \int_{-\infty}^{\infty} |\phi_n(x)|^2 dx \qquad \Rightarrow \qquad A = \sqrt{\frac{2}{L}}$$

[exercise!]

We now solved our first **quantum problem:**

Solution of TISE for particle in the box

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} \qquad \phi_n(x) = \sqrt{\frac{2}{L}}\sin(k_n x) \qquad k_n = \frac{n\pi}{L} \tag{105}$$

Solution of TISE for particle in the box

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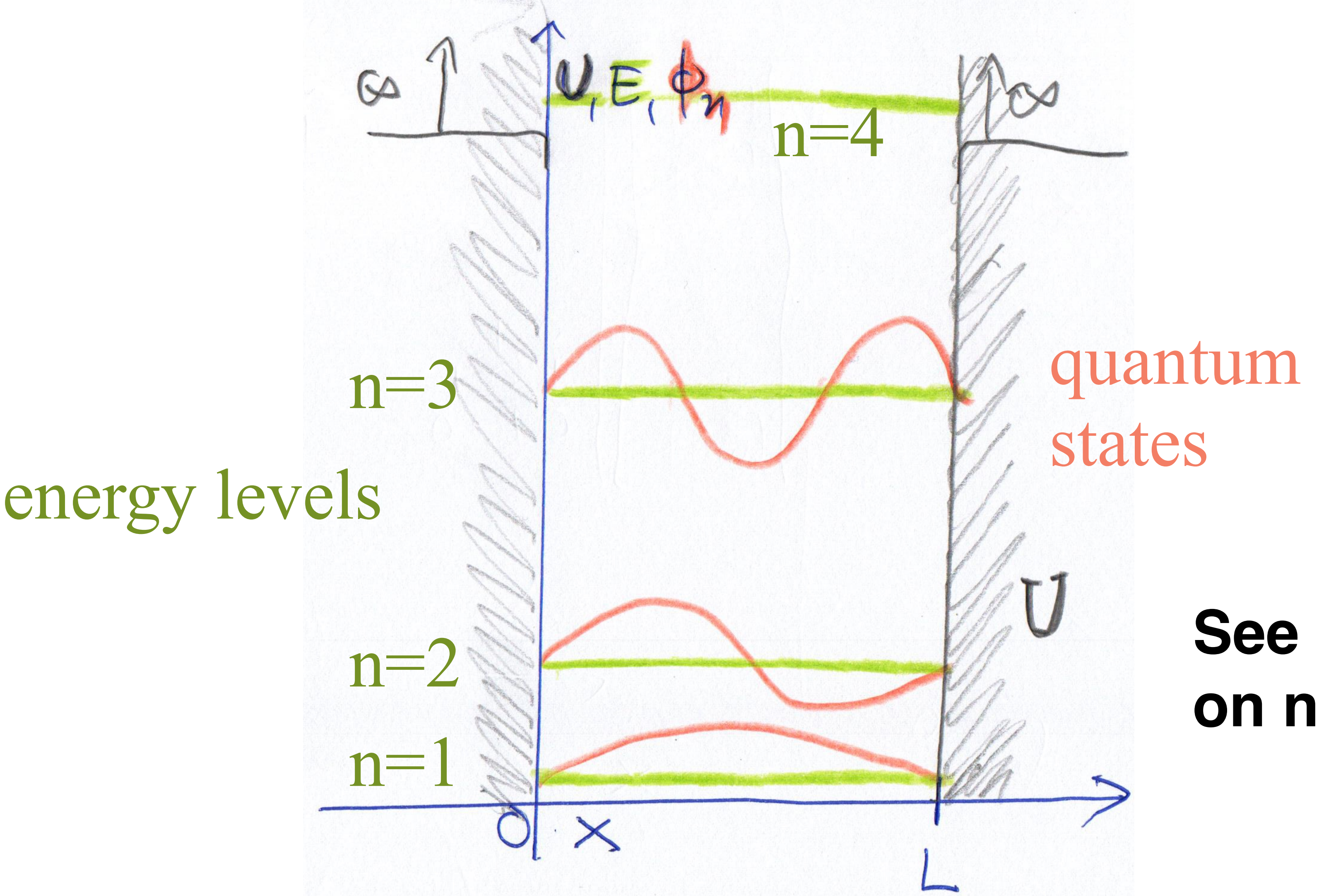
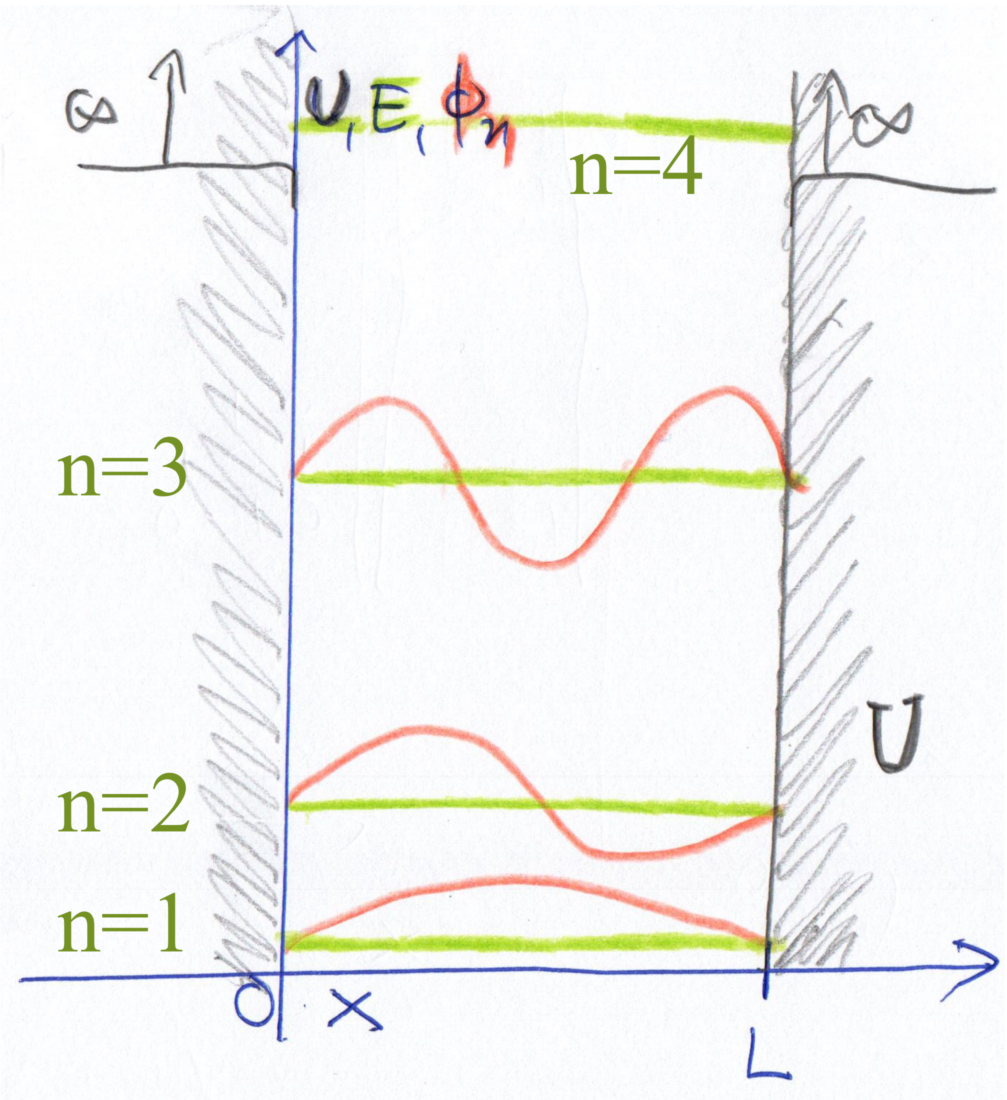


See plot legend on next slide!

Legend: Diagrams as on he previous slide will occur frequently throughout this section

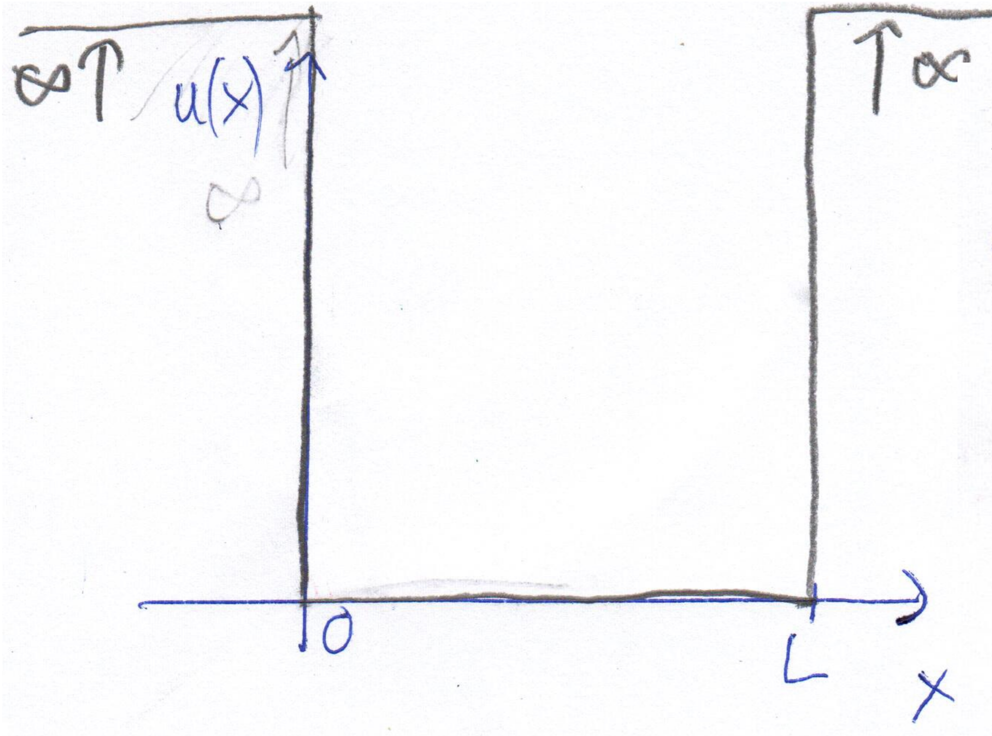


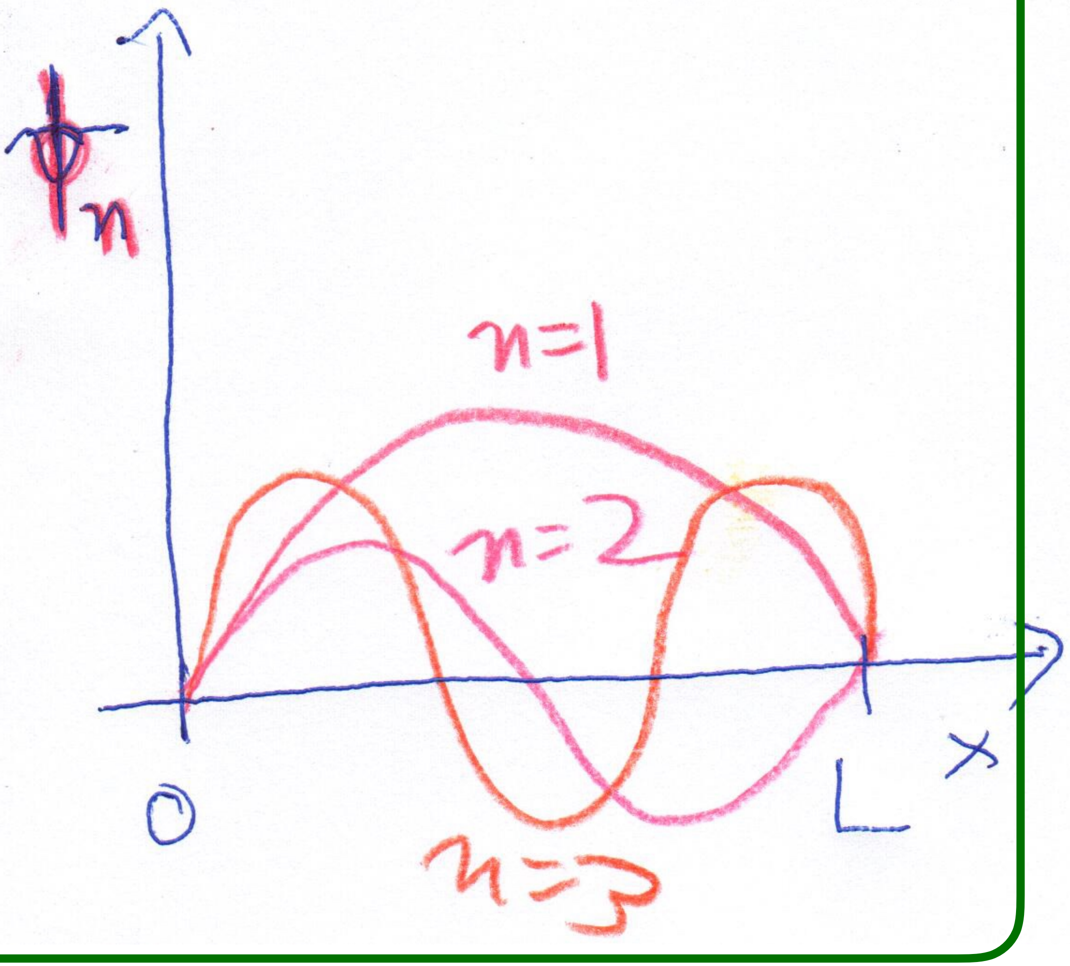
Potential energy U(x) (grey shade/line)

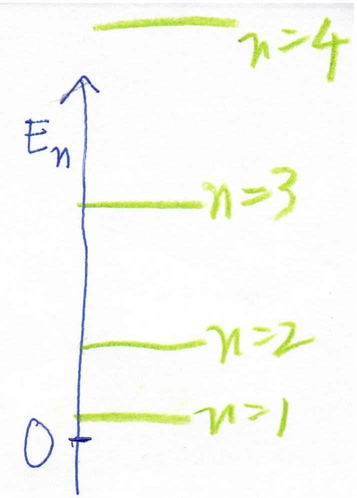
Energy values (green lines, same axes as U)

Wave-function (red line), **not to scale** [has different units!]. The zero for each of these is the **green** line

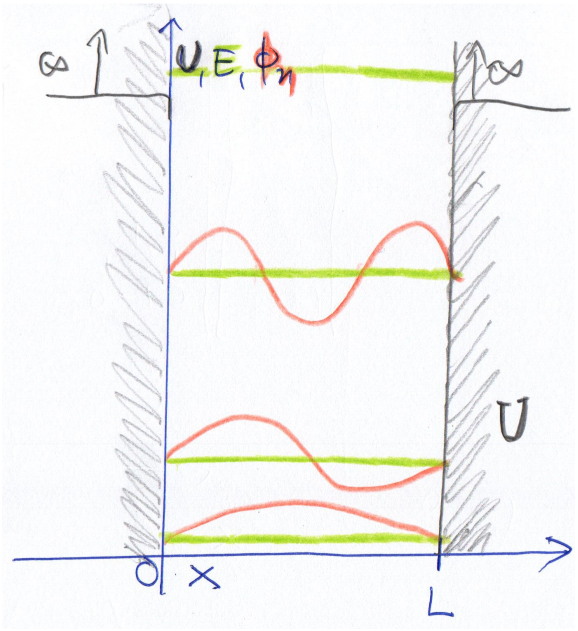
Legend: … thus if we were carefully drawing this information into separate diagrams we get:







Example *(contd.)*



Again we can calculate expectation values…

We find: $\langle \hat{x} \rangle = \dfrac{L}{2}$ $\qquad \langle \hat{p} \rangle = 0$

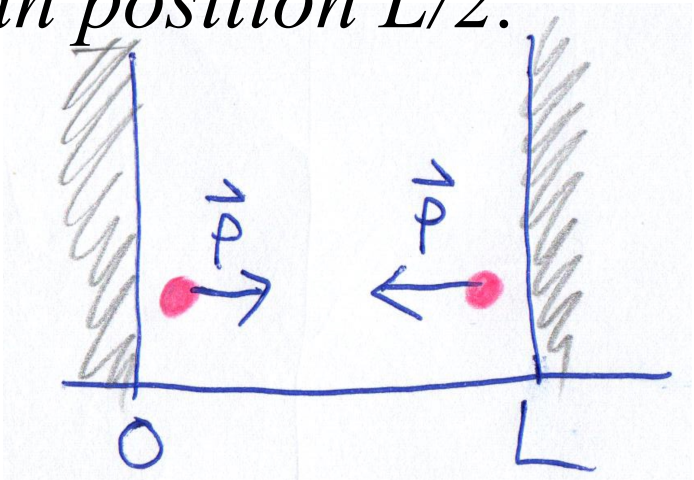
Q: E

A: For position, we see probability density in any state is symmetric wrt. L/2. So mean position L/2.

For momentum, use Eq. (82b)

$$\sin(kx) = \frac{1}{2i}\left(e^{ikx} - e^{-ikx}\right)$$

contains p>0 and p<0!!! (Eq. 55)



3.2.3) Operators and eigenvalues

Let us rewrite the TISE we just solved using $\hat{H}$(Eq. 101):

$$\hat{H}\phi_n(x) = E_n\phi_n(x) \qquad \textbf{(106)}$$

Q: what does that remind you of?

A: Matrix eigenvalue problem:

$$A\overrightarrow{v} = \lambda\overrightarrow{v} \qquad \textbf{(103)}$$

- Here A is an (NxN) matrix, $\overrightarrow{v}$ an N component vector. λ a real number.

Operators and eigenvalues

We define in general

Operator eigenvalue problem

$$\hat{O}\varphi_n(x) = o_n\varphi_n(x) \qquad (107)$$

- $\hat{O}$ is an operator
- $\varphi_n(x)$ is called **eigen-function** ("own-function")
- o_n is called **eigen-value** ("own-value")

Example:

$$\hat{O} = \hat{p} = -i\hbar\frac{\partial}{\partial x} \qquad \varphi_n(x) = \exp(ik_n x) \qquad o_n = p_n = \hbar k_n$$

Free particle wavefct. $\varphi(x)$ is an eigen-function of $\hat{p}$

Operators and eigenvalues

In this language we understand the

TISE as eigenvalue problem

$$\hat{H}\phi_n(x) = E_n\phi_n(x) \qquad \text{(106, rep)}$$

of the **Hamiltonian**

- the solutions $\varphi_n(x)$ are called **eigen-states** of the problem
- E_n are the allowed **eigen-energies** of the problem

(c.f. e.g. atom energies Eq. (75))

3.2.4.) Time-dependence from TISE

While the TISE is time-independent, it still allows us to find the time-evolution:

Suppose the initial state for particle in the box is

$$\Psi(x, t = 0) = \phi_n(x)$$

with $\phi_n(x)$ from Eq. (105). Assume $\Psi(x, t) = c(t)\phi_n(x)$

Then we have

Eq. (99) TISE

$$i\hbar\left[\frac{\partial}{\partial t}c(t)\right]\phi_n(x) = i\hbar\frac{\partial}{\partial t}\Psi(x, t) \underset{\uparrow}{=} \hat{H}\Psi(x, t) = c(t)\hat{H}\phi_n(x) \overset{\downarrow}{=} c(t)E_n\phi_n(x)$$

Eq. (85) TDSE, using Hamiltonian

Time-dependence from TISE

Overall

$$i\hbar \frac{\partial}{\partial t} c(t) = E_n \; c(t)$$

Which has the solution $c(t) = e^{-i\frac{E_n}{\hbar}t}$, thus…

Time-dependence of eigen state

$$\Psi(x,t) = \phi_n(x) e^{-i\frac{E_n}{\hbar}t} \qquad \textbf{(107b)}$$

- this justifies comment after Eq. (99)

Time-dependence from TISE

According to (88), we have the superposition principle. What if we now start in a superposition of eigenstates?

$$\Psi(x, t=0) = \frac{1}{\sqrt{2}}\left[\phi_a(x) + \phi_b(x)\right]$$

Time-dependence of superposition

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left(\phi_a(x)e^{-i\frac{E_a}{\hbar}t} + \phi_b(x)e^{-i\frac{E_b}{\hbar}t}\right) \qquad \textbf{(107c)}$$

- proof: PHY 304 QM
- ramifications: Tutorial 10, online app: http://www.falstad.com/qm1d/