

Time-dependent Schrödinger equation

(Quantum Dynamics)

Time-dependent Schrödinger's Equation

Schrödinger postulated the time-dependent equation:

$$i\hbar \frac{\delta\Psi(r, t)}{dt} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(r, t) \right] \Psi(r, t)$$

Which can be also written as:

$$i\hbar \frac{\delta\Psi(r, t)}{dt} = E_i \Psi(r, t)$$

Thus, E_i are eigenvalues of this equation.
It is easy to show that solutions of this equation are
(for V const. in t):

$$\psi(r, t) = \psi_i(r) e^{-iE_i t/\hbar}$$

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$$\psi(r, t) = \psi_i(r) e^{-iE_i t/\hbar}$$

ψ_i is a properly normalized non-time-dependent wavefunction

$$\psi_i(r) = e^{i\mathbf{k}\cdot\mathbf{r}}$$

Thus:

$$\psi(r, t) = e^{i(\mathbf{k}\cdot\mathbf{r} - E_i t)/\hbar}$$

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$$\psi(\mathbf{r}, t) = e^{i(\mathbf{k}\cdot\mathbf{r} - E_i t)/\hbar}$$

Schrödinger chose a specific sign (+) of the spatial part, thus it is definitely a wave propagating in the positive directions for all positive energies E

Contrast to classical wave equations

Remember the classical 3D wave equation

$$\nabla^2 \phi - \frac{1}{c^2} \frac{\delta^2 \phi}{\delta t^2} = 0$$

Were we had also general solutions in the form:

$$\psi(r, t) = \psi_0 e^{i(k \cdot r - \omega t)}$$

Note that this equation has a second derivative with respect to time, as opposed to the first derivative in the time-dependent Schrödinger equation

Relation to the t.i.S.E.

Time-dependent S.E.

$$i\hbar \frac{\delta\Psi(r,t)}{dt} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(r,t) \right] \Psi(r,t)$$

It is easy to show that the solution of this equation is:

$$\psi(r,t) = \psi_i(r) e^{-iE_i t/\hbar}$$

→ If we insert $\psi(r,t)$ explicitly in the S.E. above we obtain (if V constant in t):

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_i(r) = E_i \psi_i(r)$$

Relation to the t.i.S.E.

$$\psi(r, t) = \psi_i(r) e^{-i E_i t / \hbar}$$

ψ_i satisfies the time-independent S.E.:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_i(r) = E_i \psi_i(r)$$

which can be also written as:

$$\hat{H} \psi_i = E_i \psi_i$$

Relation to the t.i.S.E.

$$\psi(r, t) = \psi_i(r) e^{-iE_i t/\hbar}$$

ψ_i satisfies the time-independent S.E.:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_i(r) = E_i \psi_i(r)$$

In fact, we had a solution $\psi(r, t)$ for the time-dependent equation where the spatial behavior of the wavefunction did not change its form with time.

Hence, if the spatial part of the wavefunction is ψ_i steady in time

Relation to the t.i.S.E.

$$\psi(r, t) = \psi_i(r) e^{-iE_i t/\hbar}$$

Hence, if the spatial part of the wavefunction is ψ_i steady in time

Still the full wavefunction, with that choice of the time dependent part $e^{-iE_i t/\hbar}$ guarantees that time-independent and time-dependent Schrödinger equations are consistent.

Stationary states

$$\psi(r, t) = \psi_i(r) e^{-iE_i t/\hbar}$$

$\psi(r, t)$ is a stationary state, because the probability density $|\psi_{E_i}|^2$ is not changing with time, and $\psi(r, t)$ corresponds to a unique value for the energy E_i

$$|\psi(r, t)|^2 = \left[\psi_i(r)^* e^{iE_i t/\hbar} \right] \left[\psi_i(r) e^{-iE_i t/\hbar} \right] = |\psi_i(r)|^2 = |\psi_{E_i}|^2$$

Time-dependent Schrödinger's Equation

$$i\hbar \frac{\delta\Psi(\mathbf{r}, t)}{dt} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t)$$

Unlike the time-independent one, is not an eigenvalue equation. It is not an equation that only has solutions for a particular set of values of some parameter.

It allows us to predict the evolution in time of the system: If we knew $\Psi(\mathbf{r}, t_0)$ for all \mathbf{r} , we could deduce how the wavefunction changes in time at every position, i.e., $\Psi(\mathbf{r}, t)$ at all times.

Superposition Principle

If a quantum system is in one of the two states S_1 and S_2 , where $\psi_1(r, t)$ and $\psi_2(r, t)$ are the corresponding solutions of the S.E., then the quantum system can also be in a state formed by the **linear superposition** of these states. Thus,

$$\Psi_{1+2}(r, t) = a_1 \Psi_1(r, t) + a_2 \Psi_2(r, t)$$

a_1, a_2 are complex
number

is also a solution of the tdSE!

Superposition Principle

We have seen that the solution of the t.d.S.E. (for V const. in t) are:

$$\Psi(r, t) = \psi_i(r) e^{-iE_i t/\hbar}$$

ψ_i is a properly normalized time-independent wavefunction and E_i is the corresponding energy eigenvalue

Because of the linear superposition principle, any sum of such solutions is also a solution.

Let's start by expanding the spatial solution at $t=0$:

$$\psi(x) = \sum_i c_i \psi_i(x)$$

Superposition Principle

We have seen that the solution of the t.d.S.E. (for V const. in t) are:

$$\Psi(r, t) = \psi_i(r) e^{-iE_i t/\hbar}$$

ψ_i is a properly normalized non-time-dependent wavefunction and E_i is the corresponding energy eigenvalue

We can now expand also time-dependent function:

$$\Psi(r, t) = \sum_i c_i \Psi_i(r, t) = \sum_i c_i \psi_i(r) e^{-iE_i t/\hbar}$$

Superposition Principle

$$\Psi(x, t) = \sum_i c_i \psi_i(x) e^{-iE_i t/\hbar}$$

We know this is a solution of the time-dependent Schrödinger equation because it is made up from a linear combination of solutions to the equation.

As a check, at $t = 0$ this correctly gives the known spatial form of the solution.

$$\Psi(x, 0) = \sum_i c_i \psi_i(x) = \psi(x)$$

Expansion in the energy eigenstates

Thus, if we expand the spatial wavefunction in the energy eigenstates at $t = 0$, we have solved for the time evolution of the state thereafter;

we have no further integration to do, merely a calculation of the sum to obtain the w.f. at each time of interest to us.

$$\Psi(x, t) = \sum_i c_i \Psi_i(x, t) = \sum_i c_i \psi_i(x) e^{-iE_i t/\hbar}$$

Time evolution of states

We can predict the evolution of a quantum mechanical state.

$$\Psi(x, 0) = \sum_i c_i \psi_i(x)$$

We take this state, we decompose it into a superposition of the energy eigenstates.

$$\Psi(x, t) = \sum_i c_i \psi_i(x) e^{-iE_i t/\hbar}$$

We add the complex exponential factors and we add up the result to obtain the time evolution of the w.f.

Linear superposition for an infinite potential well

Eigenfunctions

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



We analyze the linear superposition of ψ_1 and ψ_2 resulting in:

$$\Psi(x, t) = \sqrt{1/a} \left[\sin\left(\frac{\pi}{a} x\right) e^{-iE_1 t/\hbar} + \sin\left(\frac{2\pi}{a} x\right) e^{-iE_2 t/\hbar} \right]$$

Note that each eigenfunction is multiplied by the time-dependent complex exponential

$$e^{-iE_i t/\hbar}$$

And the superposition is normalized!

Linear superposition for an infinite potential well

Linear superposition of ψ_1 and ψ_2 resulting in:

$$\Psi(x, t) = \sqrt{1/a} \left[\sin\left(\frac{\pi}{a}x\right) e^{-iE_1 t/\hbar} + \sin\left(\frac{2\pi}{a}x\right) e^{-iE_2 t/\hbar} \right]$$

Let's calculate the probability density:

$$|\Psi(x, t)|^2 = 1/a \left[\sin\left(\frac{\pi}{a}x\right) e^{iE_1 t/\hbar} + \sin\left(\frac{2\pi}{a}x\right) e^{iE_2 t/\hbar} \right] \left[\sin\left(\frac{\pi}{a}x\right) e^{-iE_1 t/\hbar} + \sin\left(\frac{2\pi}{a}x\right) e^{-iE_2 t/\hbar} \right] =$$

$$\frac{\sin^2\left(\frac{\pi}{a}x\right) + \sin^2\left(\frac{2\pi}{a}x\right) + \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) \left[e^{i(E_2 - E_1)t/\hbar} + e^{-i(E_2 - E_1)t/\hbar} \right]}{a}$$

Linear superposition for an infinite potential well

Linear superposition of ψ_1 and ψ_2 .

Let's calculate the probability density:

$$|\Psi(x, t)|^2 = 1/a \sin^2\left(\frac{\pi}{a}x\right) + 1/a \sin^2\left(\frac{2\pi}{a}x\right) +$$
$$+ 1/a \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) \left[e^{i(E_2 - E_1)t/\hbar} + e^{-i(E_2 - E_1)t/\hbar} \right]$$

$$\left[e^{i(E_2 - E_1)t/\hbar} + e^{-i(E_2 - E_1)t/\hbar} \right] = 2 \cos\left(\frac{E_2 - E_1}{\hbar}t\right)$$

$$|\Psi(x, t)|^2 =$$
$$= 1/a \left[\sin^2\left(\frac{\pi}{a}x\right) + \sin^2\left(\frac{2\pi}{a}x\right) + 2 \cos\left(\frac{E_2 - E_1}{\hbar}t\right) \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) \right]$$

Linear superposition for an infinite potential well

Linear superposition of ψ_1 and ψ_2 , the probability density:

$$\begin{aligned} |\Psi(x, t)|^2 &= \\ &= 1/a \left[\sin^2 \left(\frac{\pi}{a} x \right) + \sin^2 \left(\frac{2\pi}{a} x \right) + 2 \cos \left(\frac{E_2 - E_1}{\hbar} t \right) \sin \left(\frac{\pi}{a} x \right) \sin \left(\frac{2\pi}{a} x \right) \right] \end{aligned}$$

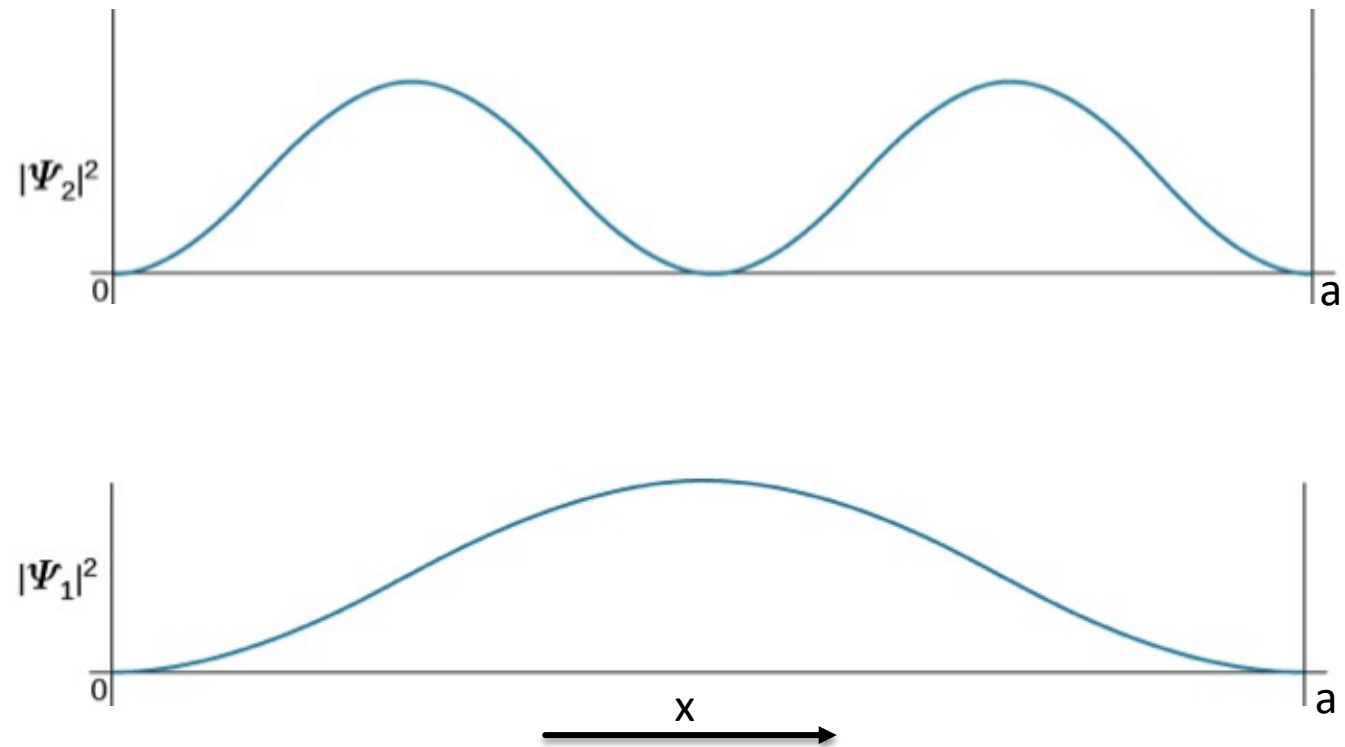
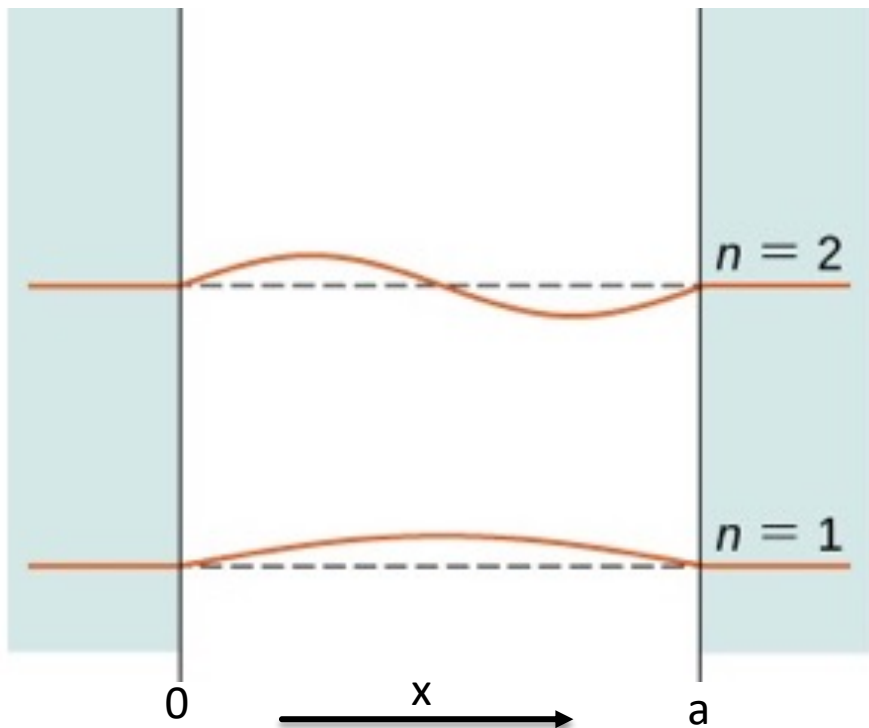
Is oscillating in time at an angular frequency:

$$\omega_{21} = \left(\frac{E_2 - E_1}{\hbar} \right) = \frac{3E_1}{\hbar}$$

The oscillating frequency depends only on the energy difference $E_2 - E_1$, and the absolute energy origin does not matter

Linear superposition for an infinite potential well

Let's remember the single solutions ψ_1 and ψ_2 :

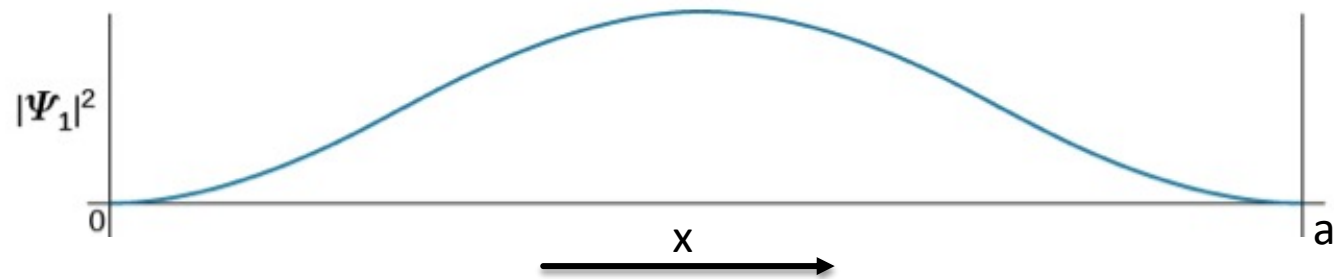


Linear superposition for an infinite potential well

The probability density for $n=1$

$$|\Psi_1(x, t)|^2 = \left[\psi_1(x)^* e^{iE_1 t/\hbar} \right] \left[\psi_1(x) e^{-iE_1 t/\hbar} \right] = |\psi_1(x)|^2$$

The probability density are the same, $|\psi_1(x, t)|^2 = |\psi_1(x)|^2$, do not depend on time: They are stationary!

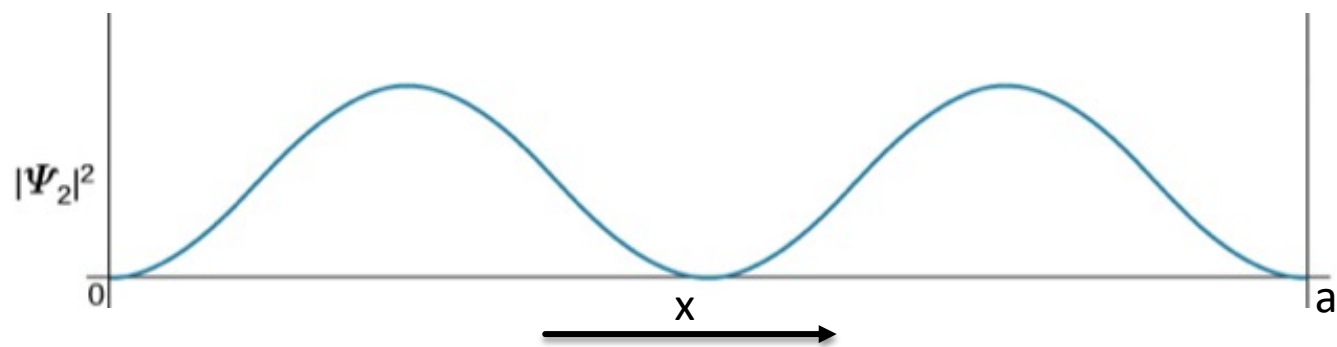


Linear superposition for an infinite potential well

Similarly for for $n=2$

$$|\Psi_2(x, t)|^2 = \left[\psi_2(x)^* e^{i E_2 t / \hbar} \right] \left[\psi_2(x) e^{-i E_1 t / \hbar} \right] = |\psi_2(x)|^2$$

The probability density are the same, $|\psi_2(x, t)|^2 = |\psi_2(x)|^2$, do not depend on time: They are stationary!



Linear superposition for an infinite potential well

Linear superposition of ψ_1 and ψ_2 .

Let's calculate the probability density:

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

$$\begin{aligned} |\Psi(x, t)|^2 &= \\ &= 1/a \left[\sin^2\left(\frac{\pi}{a}x\right) + \sin^2\left(\frac{2\pi}{a}x\right) + 2 \cos\left(\frac{E_2 - E_1}{\hbar}t\right) \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) \right] = \\ &= A \left[|\psi_1(x)|^2 + |\psi_2(x)|^2 + 2 \cos\left(\frac{E_2 - E_1}{\hbar}t\right) \psi_1(x) \psi_2(x) \right] \end{aligned}$$

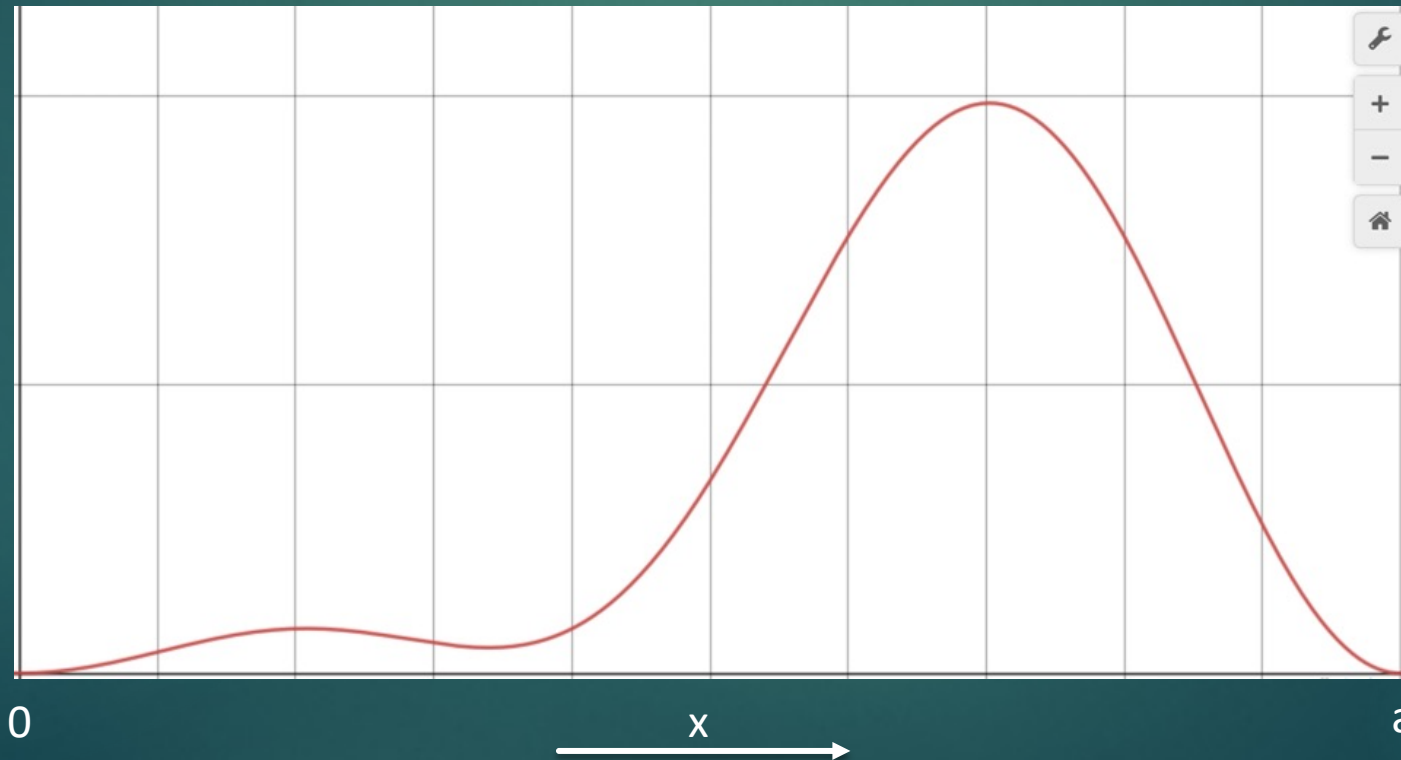
Linear superposition for an infinite potential well

Linear superposition of ψ_1 and ψ_2 .

Let's calculate the probability density:

$$|\Psi(x, t)|^2 = A \left[|\psi_1(x)|^2 + |\psi_2(x)|^2 + 2 \cos\left(\frac{E_2 - E_1}{\hbar} t\right) \psi_1(x) \psi_2(x) \right]$$

$|\Psi(x, t)|^2$



Linear superposition for the harmonic oscillator

Generally, a linear superposition of two energy eigenstates ψ_a and ψ_b , with energy E_a and E_b gives a probability density that oscillates at the angular frequency

$$\omega_{ab} = \left| \frac{E_a - E_b}{\hbar} \right|$$

Hence, if we have a superposition wavefunction

$$\Psi_{ab}(x, t) = C_a \psi_a(x) e^{-iE_a t/\hbar} + C_b \psi_b(x) e^{-iE_b t/\hbar}$$

The probability density will be:

$$|\Psi(x, t)|^2 = \dots$$

Linear superposition for the harmonic oscillator

Hence, if we have a superposition wavefunction

$$\Psi_{ab}(x, t) = C_a \psi_a(x) e^{-iE_a t/\hbar} + C_b \psi_b(x) e^{-iE_b t/\hbar}$$

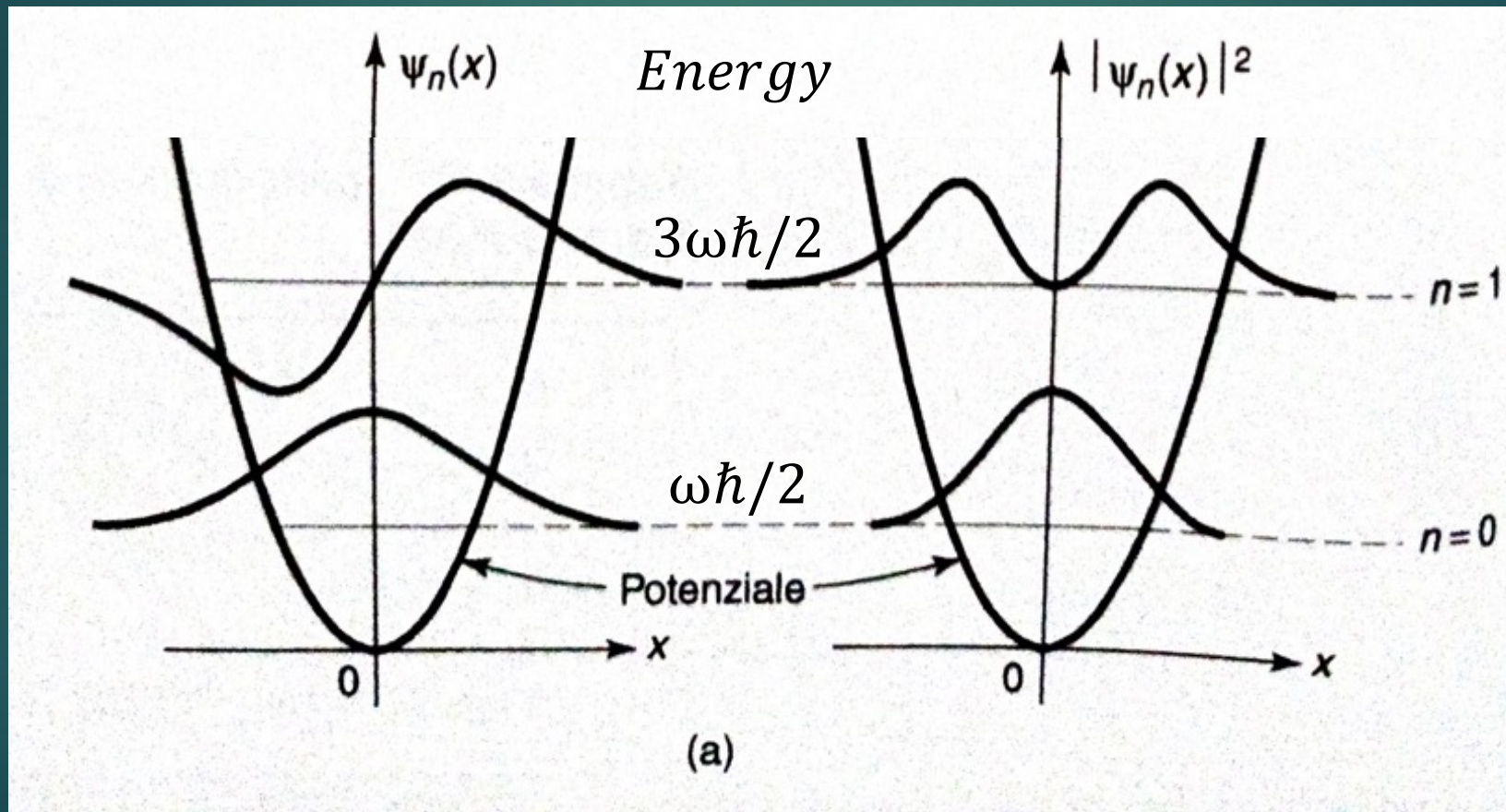
The probability density will be:

$$\begin{aligned} |\Psi(x, t)|^2 &= |C_a|^2 |\psi_a(x)|^2 + |C_b|^2 |\psi_b(x)|^2 \\ &+ 2|C_a^* \psi_a^*(x) C_b \psi_b(x)| \cos \left[\left(\frac{E_a - E_b}{\hbar} t \right) - \Theta_{ab} \right] \end{aligned}$$

Where $\Theta_{ab} = \arg(C_a \psi_a(x) C_b^* \psi_b^*(x))$

Linear superposition for the harmonic oscillator

Let's remember the ψ_0 and ψ_1 for the harmonic oscillator



Linear superposition for the harmonic oscillator

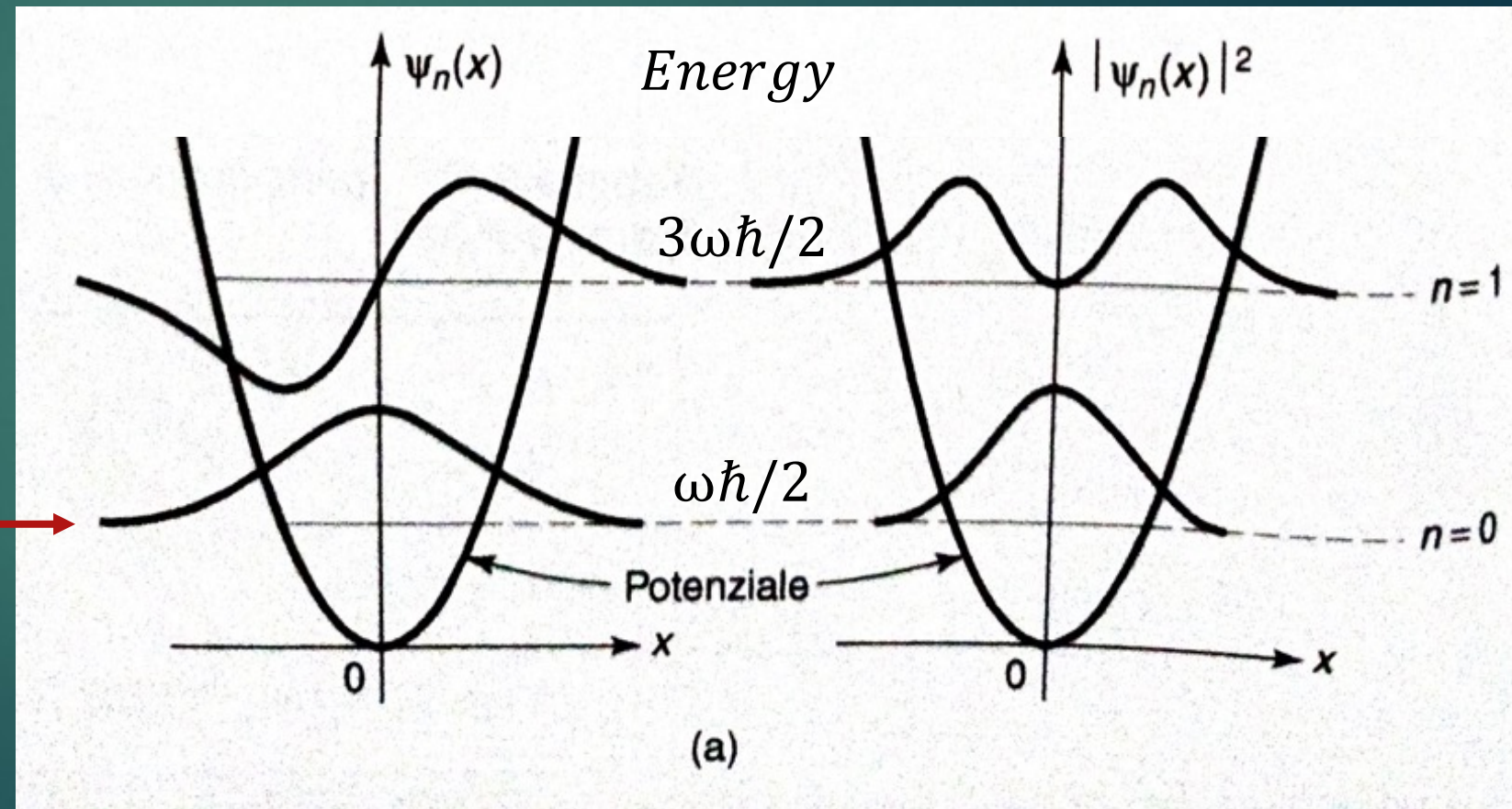
Let's remember the ψ_0 for the harmonic oscillator

The w.f. adding the
time dependent factor:

$$\Psi_0(x, t) = \psi_0(x) e^{-iE_0 t/\hbar}$$

The probability density
is still the same

$$|\Psi_0(x, t)|^2 = |\psi_0(x)|^2$$



Linear superposition for the harmonic oscillator

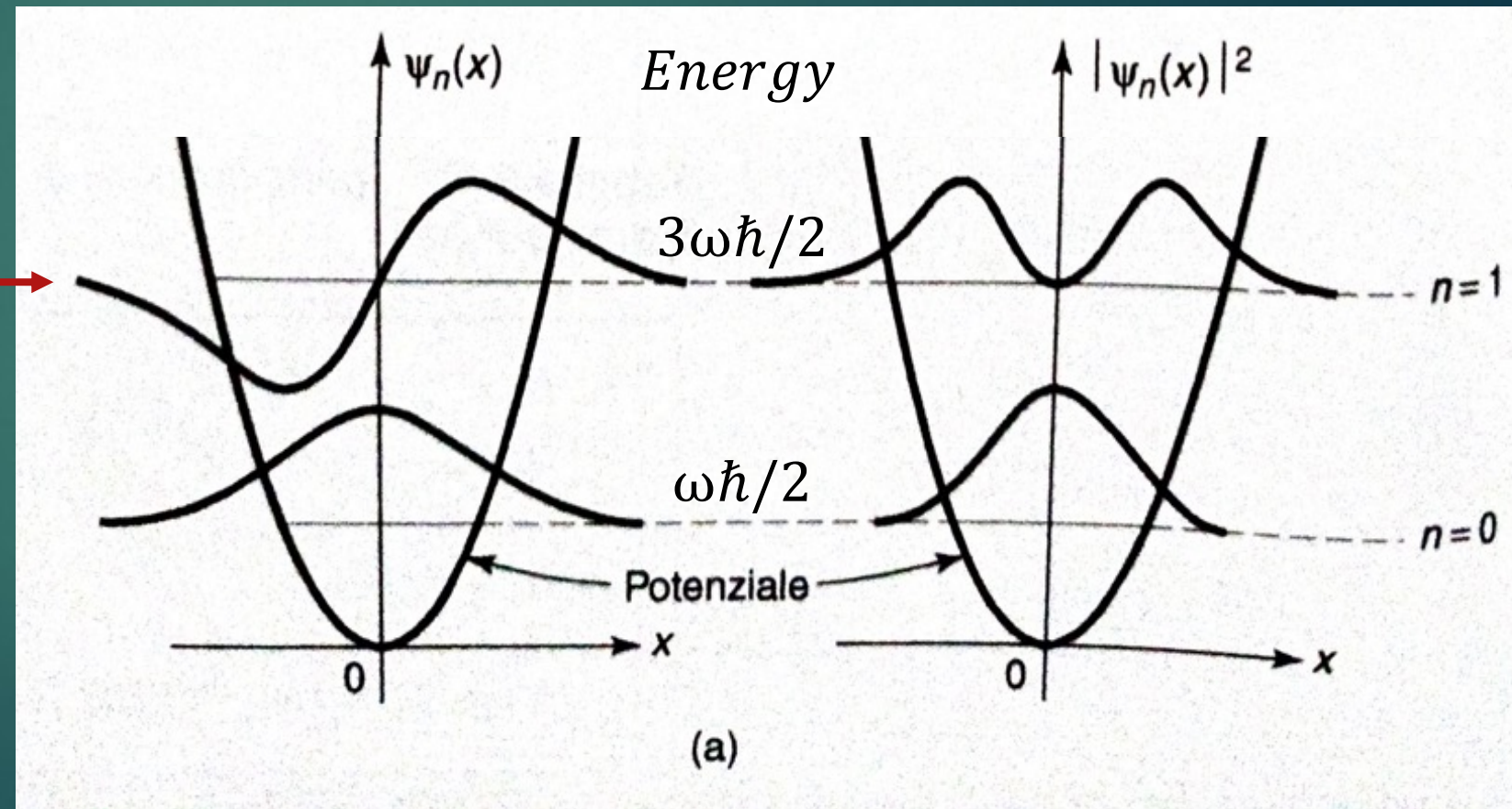
Let's remember the ψ_0 for the harmonic oscillator

The w.f. adding the
time dependent factor:

$$\Psi_1(x, t) = \psi_1(x) e^{-iE_1 t/\hbar}$$

The probability density
is still the same

$$|\Psi_1(x, t)|^2 = |\psi_1(x)|^2$$



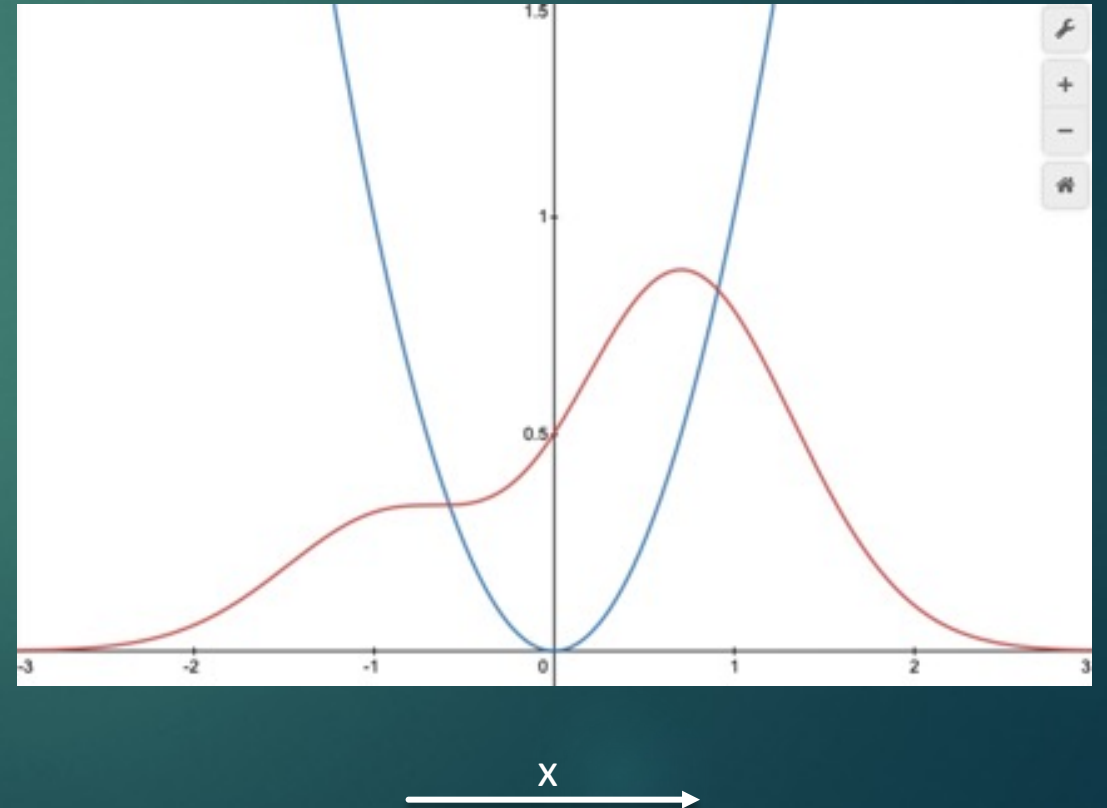
Linear superposition for the harmonic oscillator

A superposition of ψ_0 and ψ_1 will get a probability density oscillating at the angular frequency

$$\omega = \left| \frac{E_1 - E_0}{\hbar} \right|$$

The probability density will be:

$$\begin{aligned} |\Psi(x, t)|^2 &= |\psi_0(x) + \psi_1(x)|^2 \\ &= |\psi_0(x)|^2 + |\psi_1(x)|^2 \\ &\quad + 2\cos(\omega t)\psi_0(x)\psi_1(x) \end{aligned}$$



Coherent state for the harmonic oscillator

The linear superpositions that correspond best to our classical understanding of harmonic oscillators are known as “coherent states”.

The coherent state for a harmonic oscillator of frequency ω is

$$\Psi_N(\xi, t) = \sum_{n=0}^{\infty} C_{Nn} \psi_n(\xi) e^{-i \left(n + \frac{1}{2}\right) \omega t / \hbar}$$

Where

$$C_{Nn} = \sqrt{\frac{N^n e^{-N}}{n!}}$$

and

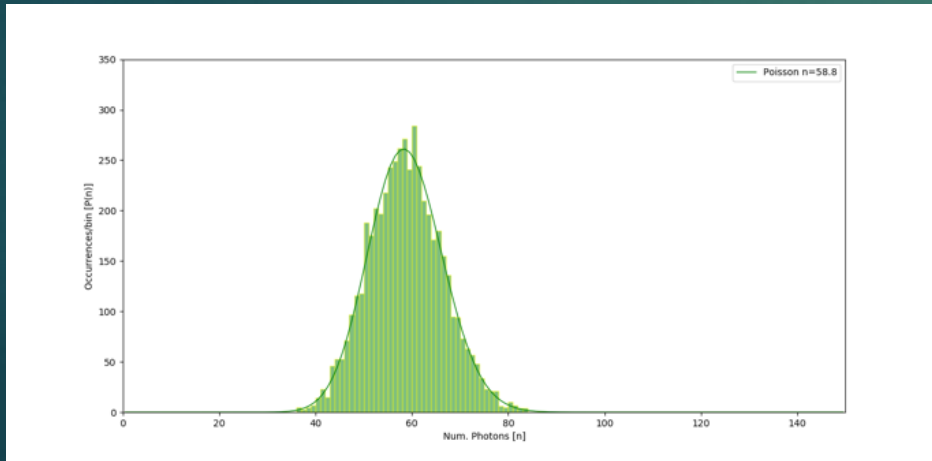
$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}$$

Coherent state for the harmonic oscillator

The modulus squared of the expansion coefficients

$$|C_{Nn}|^2 = \frac{N^n e^{-N}}{n!}$$

Is the Poisson distribution with mean value N
and standard deviation \sqrt{N}



This is explaining, for example, the Poissonian distribution in a laser beam

Coherent state for the harmonic oscillator

Let's plot the probability density:

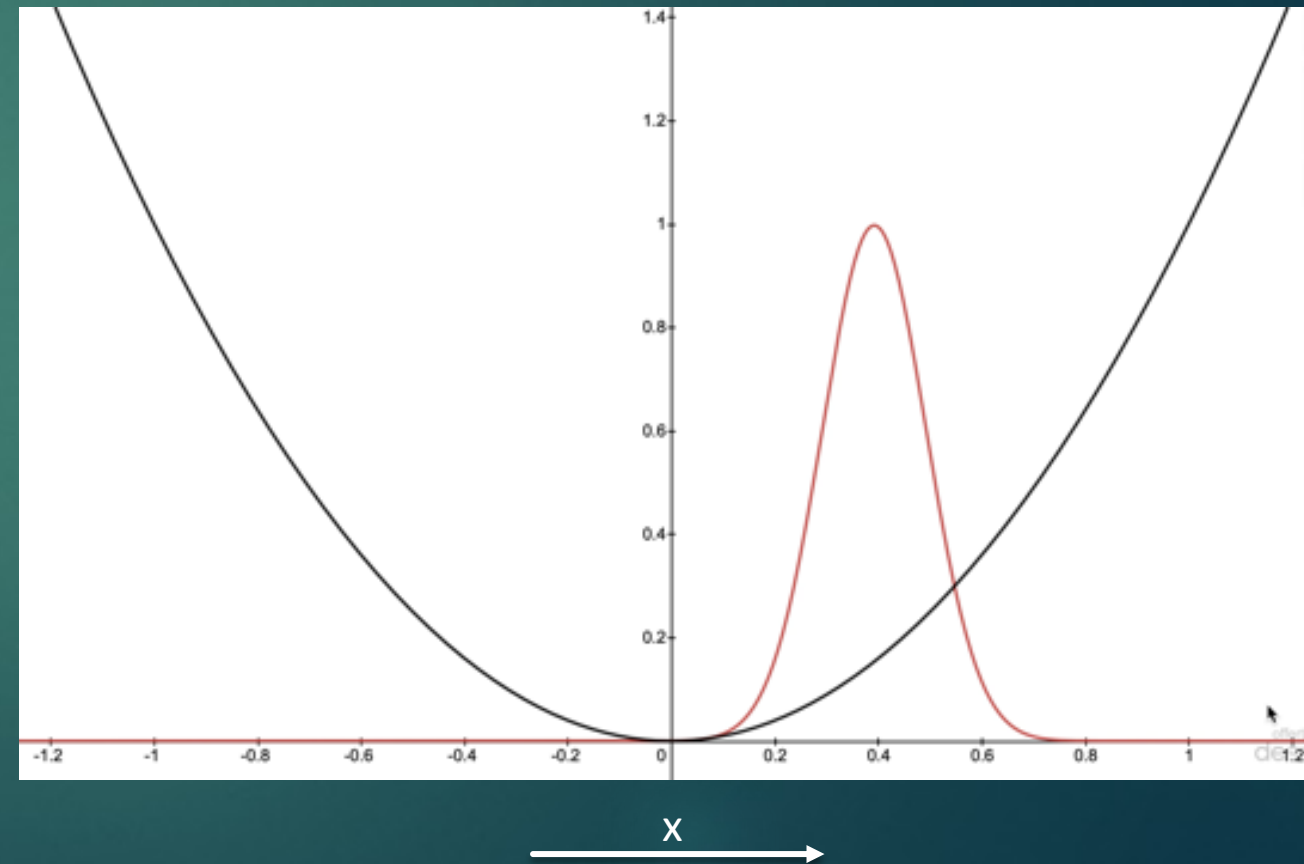
$$\Psi_N(\xi, t) = \sum_{n=0}^{\infty} C_{Nn} \psi_n(\xi) e^{-i(n+\frac{1}{2})\omega t/\hbar}$$

Where

$$C_{Nn} = \sqrt{\frac{N^n e^{-N}}{n!}}$$

$N=1$

$$|\Psi_N(\xi, t)|^2$$



Coherent state for the harmonic oscillator

Let's plot the probability density:

$$\Psi_N(\xi, t) = \sum_{n=0}^{\infty} C_{Nn} \psi_n(\xi) e^{-i(n+\frac{1}{2})\omega t/\hbar}$$

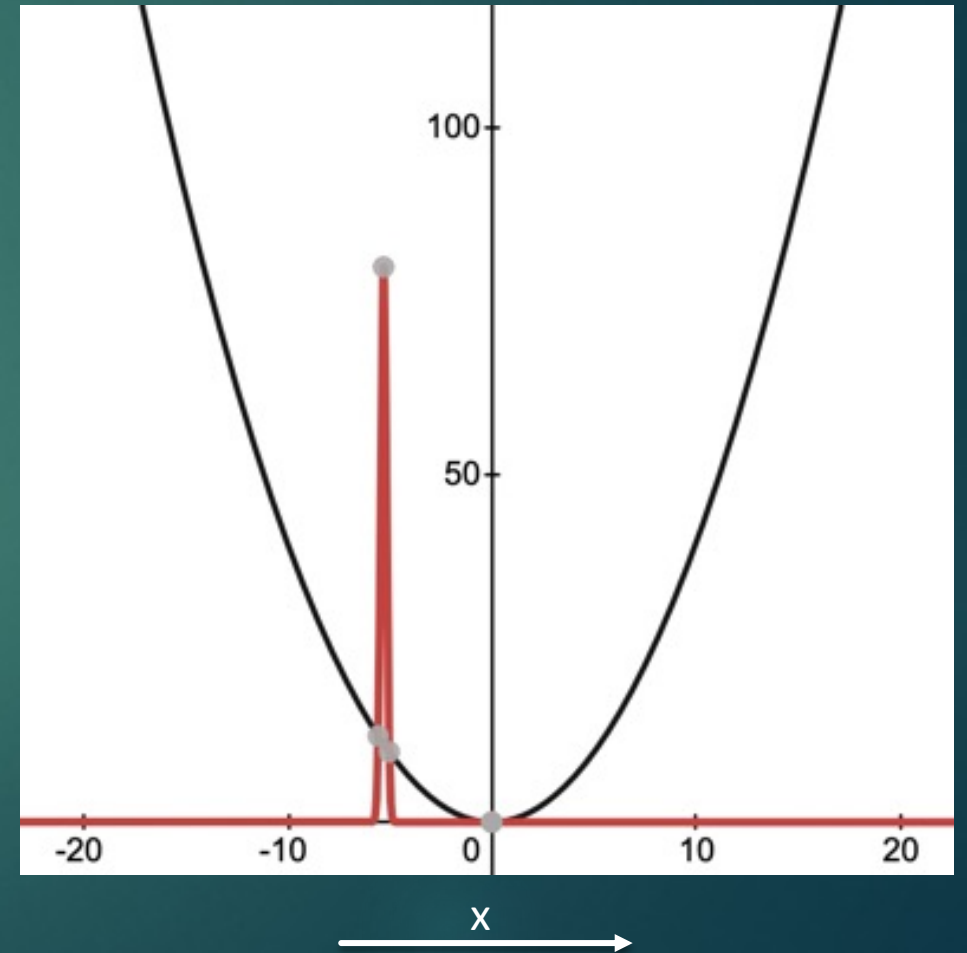
Where

$$C_{Nn} = \sqrt{\frac{N^n e^{-N}}{n!}}$$

$N=100$

The distribution is now much sharper, but the amplitude is increasing, keeping same area.

$$|\Psi_N(\xi, t)|^2$$



Coherent state for the harmonic oscillator

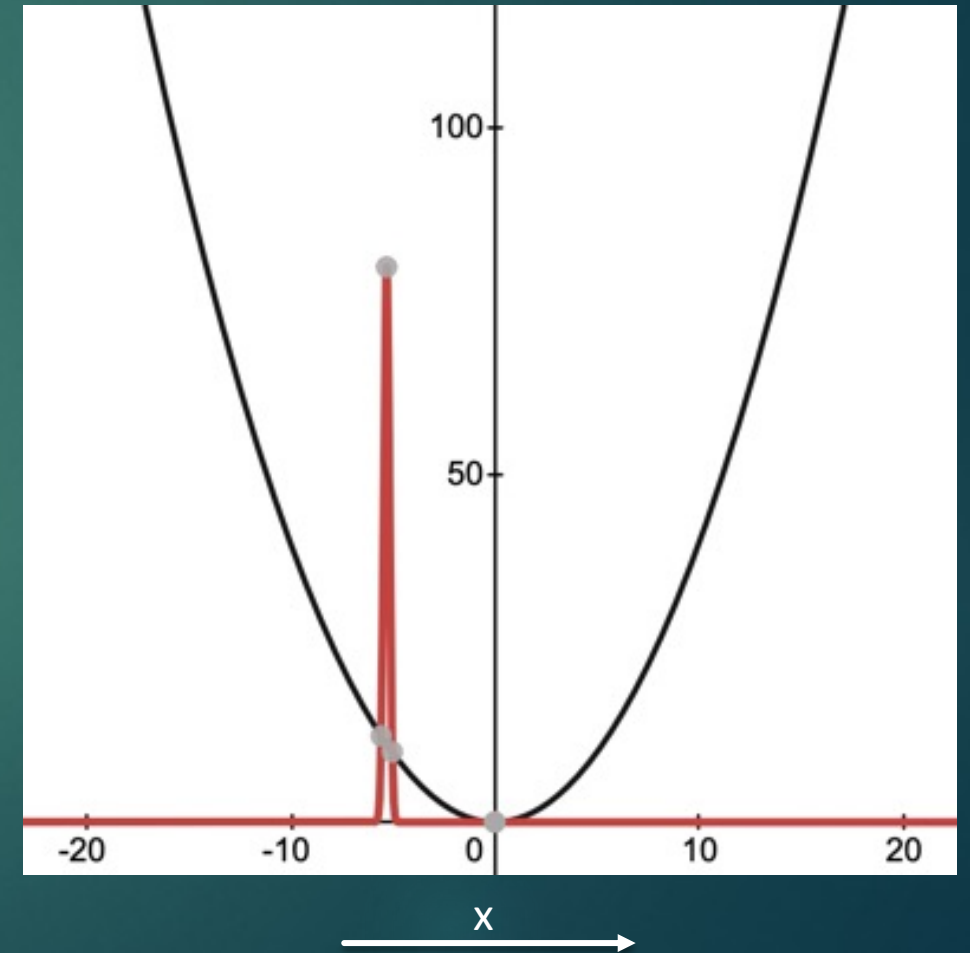
The sharp peak here is going backwards and forwards, beginning to look quite like a classical oscillator.

For large N , the probability distribution will appear to be very localized relative to the size of the oscillation.

Thus, we do have a correspondence that we can get from the quantum back to the classical.

$$|\Psi_N(\xi, t)|^2$$

$N=100$



Coherent state for the harmonic oscillator

In general, a system in a linear superposition of multiple energy eigen states does not have a simple harmonic motion

Any linear superposition of two different states will oscillate at a frequency corresponding to the energy separation of the two states.

But the simple oscillatory motion, when we have a complicated superposition of a large number of states, as in the coherent state, is a special consequence of the fact that all the energy levels are equally spaced (or with integer ratio).

$$|\Psi_N(\xi, t)|^2$$

N=100

