Wave Equation for a Quantum Free Particle

Thus, a correct quantum wave function for a quantum free particle must satisfy this quantum dispersion relation for k and ω :

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \qquad (*) \quad \text{(non-relativistic)}$$

We now assume the same fundamental sinusoidal form for the wave function of a quantum free particle with mass m, momentum $p = \hbar k$ and energy $E = \hbar\omega$:

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

Recall from our discussion on the mechanical wave, we have the following:

$\frac{\partial}{\partial x} \rightarrow$ take out an overall k factor from $\Psi(x,t)$

$\frac{\partial}{\partial t} \rightarrow$ take out an overall $-\omega$ factor from $\Psi(x,t)$

Wave Equation for a Quantum Free Particle

So, from the quantum dispersion relation,

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega$$

We can argue that the PDE for the quantum wave function for this free particle must involves:

$$\frac{\partial^2}{\partial x^2} \qquad\qquad -\frac{\partial}{\partial t}$$

Putting in other constants so that units are consistent and one additional dimensionless "fitting" constant C, we then have this trial wave equation,

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

Wave Equation for a Quantum Free Particle

Now, we substitute our trial quantum wave function

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

into the proposed wave equation to solve for the "fitting" constant C:

$$\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} = \frac{\hbar^2}{2m}\left[-Ak^2\cos(kx-\omega t) - Bk^2\sin(kx-\omega t)\right]$$

$$= \frac{\hbar^2 k^2}{2m}\left[-A\cos(kx-\omega t) - B\sin(kx-\omega t)\right]$$

$$-C\hbar\frac{\partial\Psi(x,t)}{\partial t} = -C\hbar\left[-A(-\omega)\sin(kx-\omega t) + B(-\omega)\cos(kx-\omega t)\right]$$

$$= \hbar\omega\left[CB\cos(kx-\omega t) - CA\sin(kx-\omega t)\right]$$

Wave Equation for a Quantum Free Particle

Equating the two terms and using the equality $\frac{\hbar^2 k^2}{2m} = \hbar\omega$, we have,

$$\cancel{\frac{\hbar^2 k^2}{2m}}\left[-A\cos(kx-\omega t) - B\sin(kx-\omega t)\right] \quad = \cancel{\hbar\omega}\left[CB\cos(kx-\omega t) - CA\sin(kx-\omega t)\right]$$

In order for this equality to be true for all (x,t), all coeff's for cos and sin must equal to each other,

$$\Rightarrow \quad \begin{cases} -A = CB \\ B = CA \end{cases}$$

Substituting the first eq into the second, we have,

$$B = C(-CB) \quad \rightarrow \quad C^2 = -1$$

Thus, the "fitting" constant is $C = i$ where $i = \sqrt{-1}$.

Wave Equation for a Quantum Free Particle

Then, finally, putting everything together, we have the desired wave equation for a quantum free particle,

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

This is the 1D **Schrodinger's Equation** for a free particle.

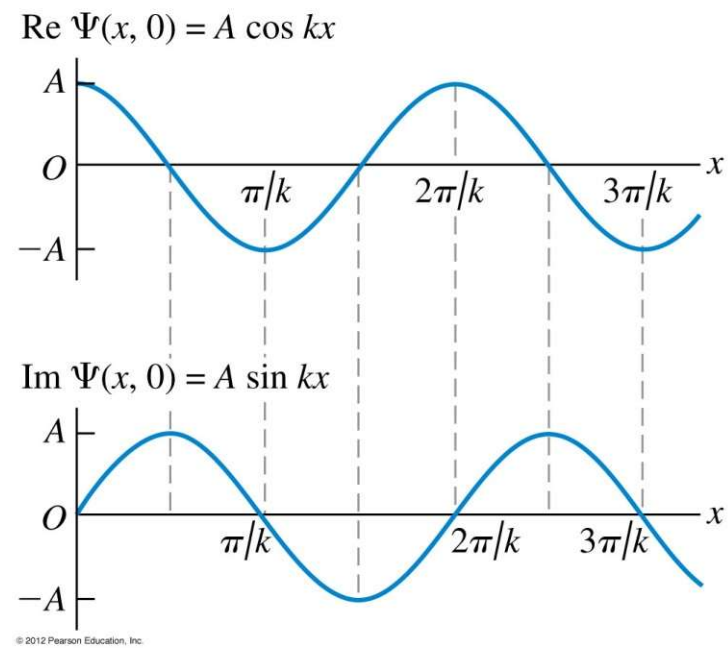
With $B = CA = iA$, the free particle quantum wave function can also be written in a compact exponential form using the Euler's formula,

$$\Psi(x,t) = A\left[\cos(kx-\omega t) + i\sin(kx-\omega t)\right]$$

$$\Psi(x,t) = Ae^{i(kx-\omega t)}$$ (quantum wave function for a free particle)

Free Particle Wave Function & Uncertainty Principle

So, the wave function for a free particle is a *complex* function with *sinusoidal* real and imaginary parts



A quantum *free* particle in principle exists in *all* space $[-\infty, +\infty]$,

$\Delta x = \infty$ & $\Delta t = \infty$ (wave function extends into all space & time)

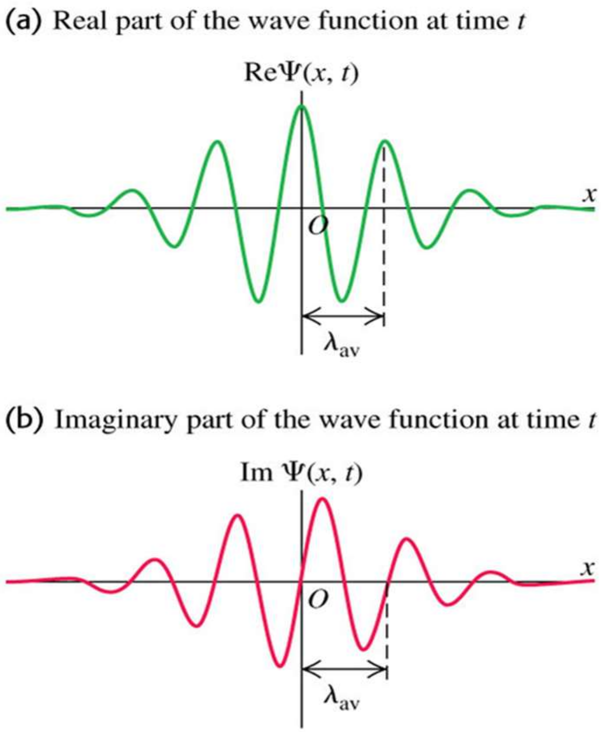
but $\Delta p = 0$ & $\Delta E = 0$ (energy and momentum is fixed)

Note: $\Delta x \Delta p \geq \hbar/2$ & $\Delta t \Delta E \geq \hbar/2$ can still be satisfied.

More Realistic Particle (Wave Packets)

Under more realistic circumstance, a particle will have a relatively well defined position and momentum so that *both* Δx and Δp will be *finite* with limited spatial extents.

A more *localized* quantum particle can *not* be a pure sine wave and it must be described by a **wave packet** with a combination of many sine waves.



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

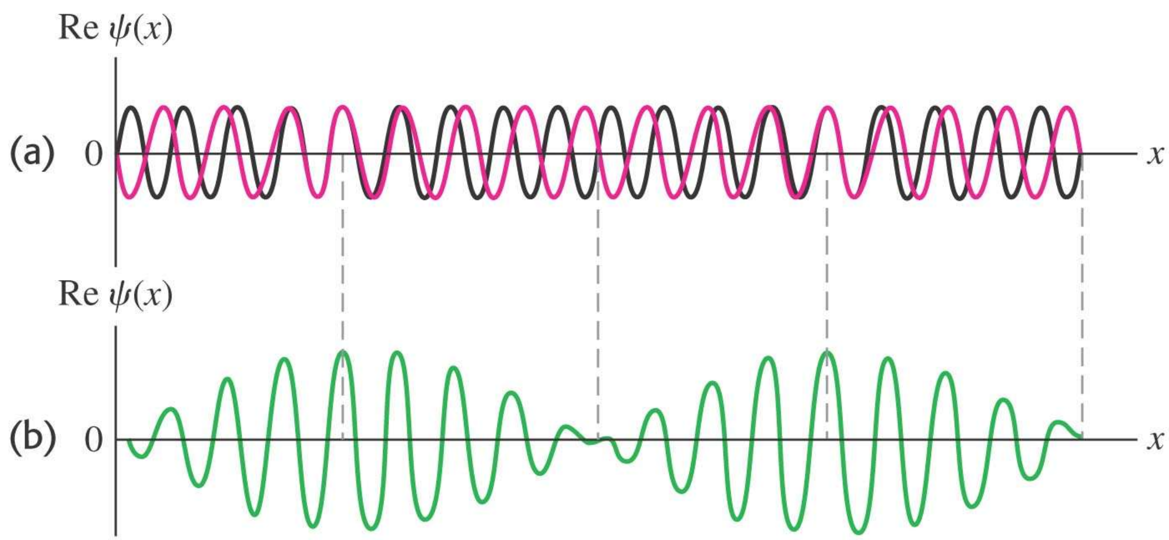
(a linear combination of many sine waves.)

The coefficient $A(k)$ gives the relative proportion of the various sine waves with diff. k (wave number).

Wave Packets

Recall: Combination of *two* sine waves

→ more localized than a pure sine wave.



Wave Packets

A **wave packet** is a linear combination of many sine waves.

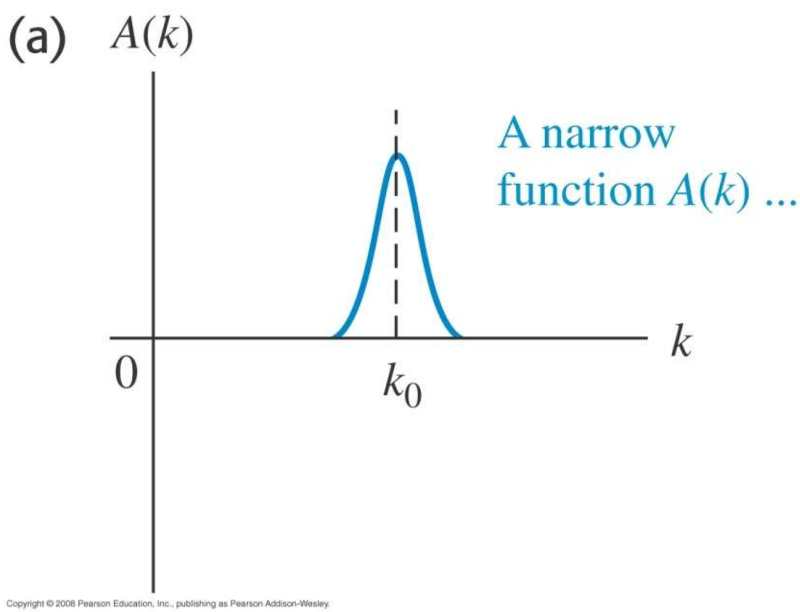
$$\Psi(x,t)=\int_{-\infty}^{\infty}A(k)e^{i(kx-\omega t)}dk$$

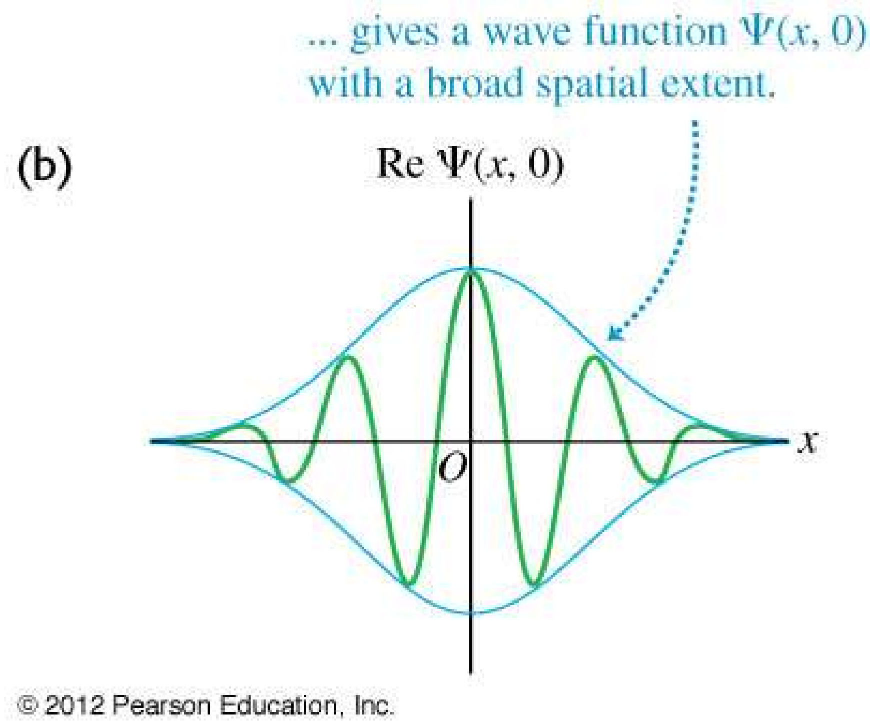
Recall $$P=\frac{h}{\lambda}=\frac{h}{2\pi}\frac{2\pi}{\lambda}=\hbar k$$

So, the wave number k is directlly proportional to the momentum of the quantum particle.

Wave Packets (characteristic)

$A(k)$ gives the spread in k (momentum P)

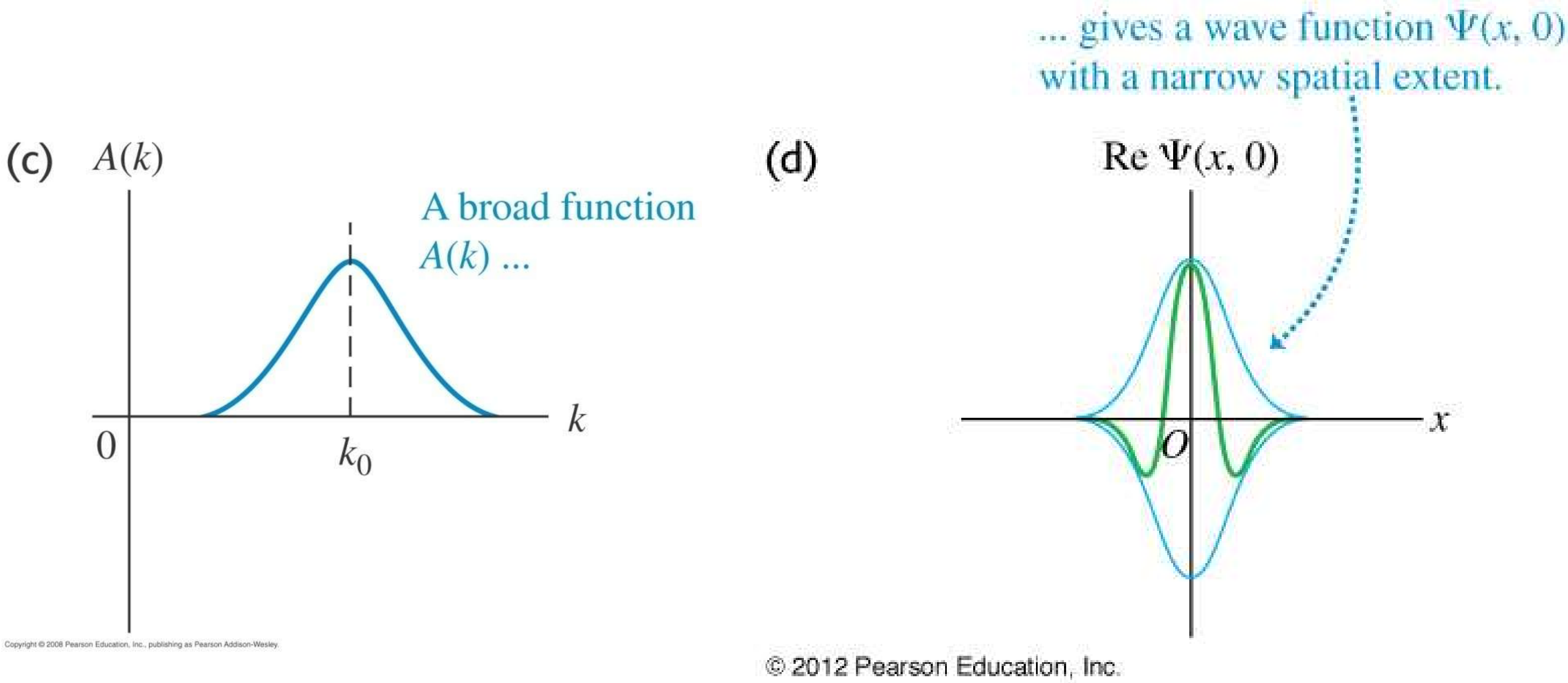




Δp smaller

Δx bigger

Wave Packets (characteristic)



Δp bigger

Δx smaller

The is consistent with: $\Delta x \Delta p \geq \hbar$!

Quantum Wave Function

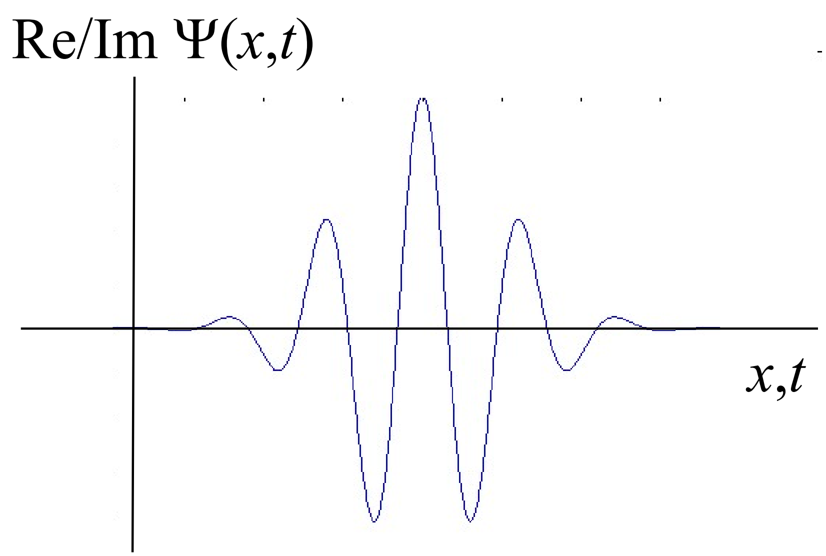
In QM, the **matter wave** postulated by de Broglie is described by a *complex-valued* **wavefunction** $\Psi(x,t)$ which is the fundamental descriptor for a quantum particle.

1. Its absolute value squared $|\Psi(x,t)|^2\,dx$ gives the probability of finding the particle in an infinitesimal volume dx at time t.
2. For any Q problem:

→ The goal is to find $\Psi(x,t)$ for the particle for all time.

→ Physical interactions involves "operations" (O) on this wave function: $O\,\Psi(x,t)$

→ Experimental measurements will involve the "products", $\Psi^*(x,t)\,O\Psi(x,t)$



$\Psi(x,t)$ is a complex-valued function of space and time.

The **General** 1D Schrodinger Equation for a Quantum Particle (not free)

Recall that the wave equation for a quantum *free* particle is

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

KE = Total E

It is basically a statement on the conservation of energy!

The **General** 1D Schrodinger Equation for a Quantum Particle (not free)

Now, for the general case:

The **Schrodinger equation** is again a statement on the conservation of energy.

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

KE + PE = Total E

As we have seen for the free quantum particle case,

- the *first term* (2^{nd} order spatial derivative term) in the Schrodinger equation is associated with the Kinetic Energy of the particle
- the last term (the 1^{st} order time derivative term) is associated with the total energy of the particle
- now we also include the Potential Energy term $U(x)\,\Psi(x)$

The Schrodinger Equation

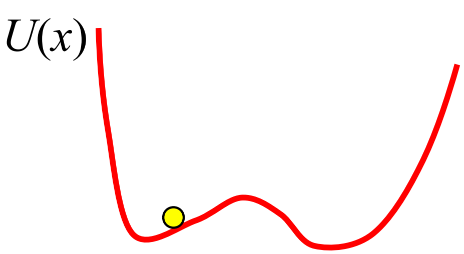
In Classical Mechanics, we have the Newton's equation which describes the trajectory $\mathbf{x}(t)$ of a particle:

$$\mathbf{F} = m\ddot{\mathbf{x}}$$

In EM, we have the wave equation for the propagation of the *E, B* fields:

$$\frac{\partial^2 E,B}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 E,B}{\partial t^2}$$ (derived from Maxwell's eqns)

In QM, **Schrodinger equation** prescribes the evolution of the wavefunction for a particle in time t and space x under the influence of a potential energy $U(x)$,

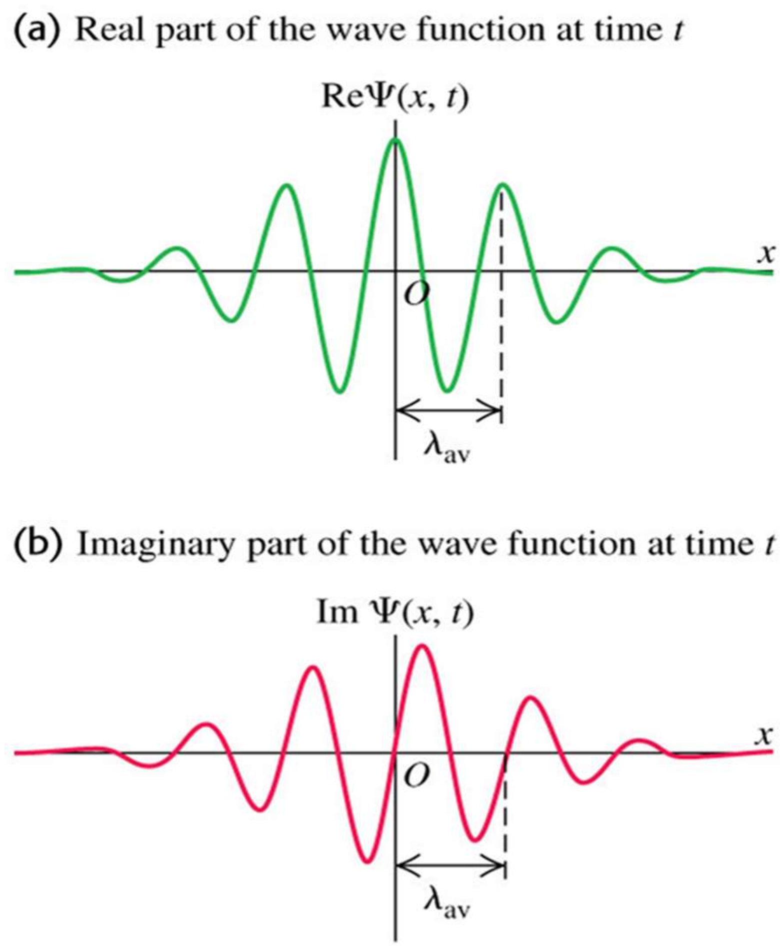


$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

(general 1D Schrödinger equation)

Quantum Wave Function

The **wave function** $\Psi(x,t)$ for a quantum particle is a *complex* function with *sinusoidal* real and imaginary parts



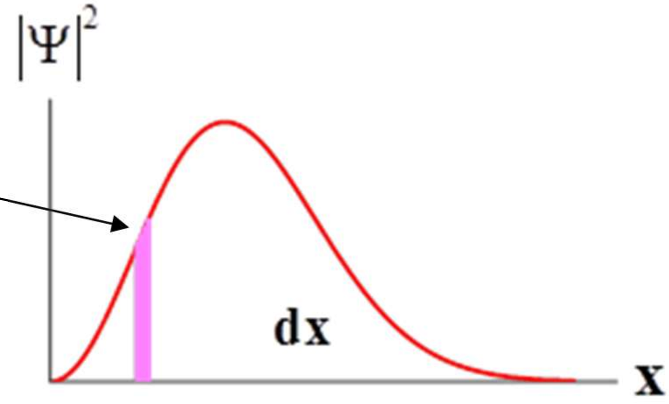
Wave Function and Probability

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

is the **probability distribution function** for the quantum particle.

In other words, $|\Psi(x,t)|^2\,dx$ (shaded area)

is the *probability* in finding the particle in the interval $[x, x+dx]$ at time t.



Since $p(x)dx \equiv |\Psi(x,t)|^2\,dx$ is a probability, it has to be **normalized** !

$$\int_{-\infty}^{+\infty} p(x)dx = \int_{-\infty}^{+\infty} |\Psi(x,t)|^2\,dx = 1$$

(At any instance of time t, the particle must be somewhere in space !)

Stationary States

For most problems, we can factor out the *time dependence* by assuming the following harmonic form for the time dependence,

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

[Recall the free particle case: $\Psi(x,t)=Ae^{i(kx-\omega t)}=Ae^{ikx}e^{-i\omega t}$.]

With $\omega=E/\hbar$, we can rewrite the time exponent in terms of E,

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

$\Psi(x,t)$ is a state with a definite energy E and is called a **stationary state**.

$\psi(x)$ is called the *time-independent* wave function.

The Time-Independent Schrödinger Equation

Substituting this factorization into the general time-dependent Schrodinger Eq, we have

RHS $\Rightarrow$ $$i\hbar\frac{\partial\Psi(x,t)}{\partial t}=i\hbar\frac{\partial}{\partial t}\left(\psi(x)e^{-iEt/\hbar}\right)=i\hbar\psi(x)\left(\frac{-iE}{\hbar}\right)e^{-iEt/\hbar}=E\psi(x)e^{-iEt/\hbar}$$

and,

LHS $\Rightarrow$ $$\frac{\partial^2\Psi(x,t)}{\partial x^2}=\frac{d^2\psi(x)}{dx^2}e^{-iEt/\hbar}$$

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

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

(time dependence can be cancelled out !)

(*time-independent* Schrodinger equation)

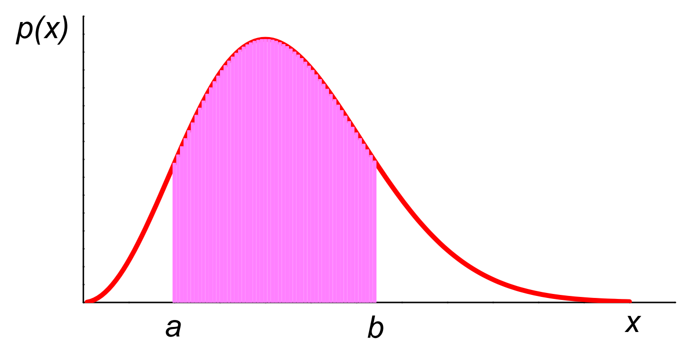
More on (time-independent) Wavefunction

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

$$= \psi^*(x)\psi(x)e^{i(-Et/\hbar+Et/\hbar)} = \psi^*(x)\psi(x) = |\psi(x)|^2$$

So, in general, the probability in finding the particle in the interval $[a,b]$ is given by:

$$p_{ab} = \int_a^b |\psi(x)|^2 dx$$



Note: $\psi(x)$ is *not* the probability density

$|\psi(x)|^2$ is the probability density.

More on (time-independent) Wavefunction

Other physical **observables** can be obtained from $\psi(x)$ by the following operation:

example (position x): $\langle x \rangle = \int_{-\infty}^{\infty} x p(x) dx = \int_{-\infty}^{\infty} x |\psi(x)|^2 dx$

- $\langle x \rangle$ is called the **expectation value** (of x): it is the experimental value that one should expect to measure in real experiments !

In general, any experimental observable (position, momentum, energy, etc.) $O(x)$ will have an expectation value given by:

$$\langle O \rangle = \int_{-\infty}^{\infty} O(x) |\psi(x)|^2 dx$$

O can be x, p, E, etc.

Note:

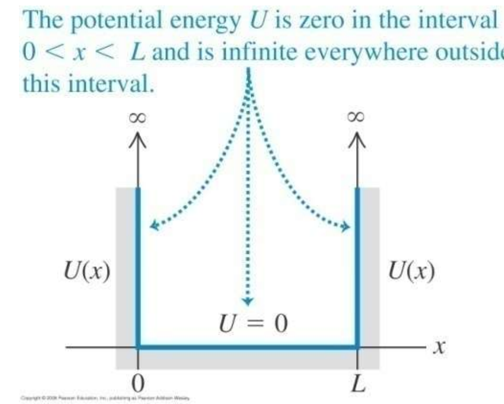
- Expectation values of physically measurable functions are the only experimentally accessible quantities in QM.
- Wavefunction $\psi(x)$ itself is not a physically measurable quantity.

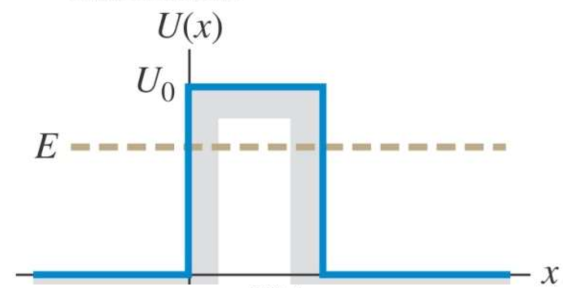
Solving QM Problems with (time-independent) Schrodinger Equation

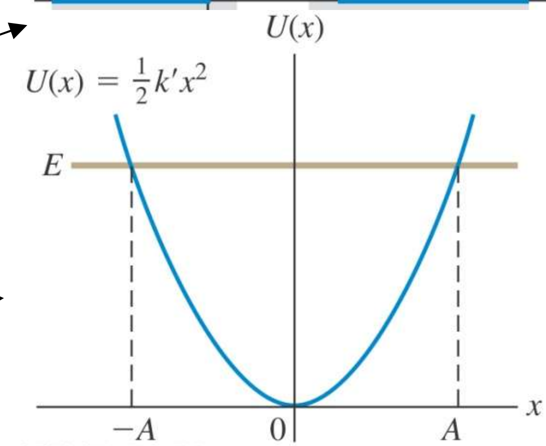
Given: A particle is moving under the influence of a potential $U(x)$.

Examples:

- Free particle: $U(x) = 0$
- Particle in a box: $U(x) = \begin{cases} 0, & 0 \le x \le L \\ \infty, & elsewhere \end{cases}$
- Barrier: $U(x) = \begin{cases} U_0, & 0 \le x \le L \\ 0, & elsewhere \end{cases}$
- HMO: $U(x) = \frac{1}{2} k' x^2$







Solving QM Problems with (time-independent) Schrodinger Equation

The general process in solving a quantum problem under the influence of a given potential $U(x)$ involves:

Solve time-independent Schrodinger equation for $\psi(x)$ as a function of energy E,

with the restrictions:

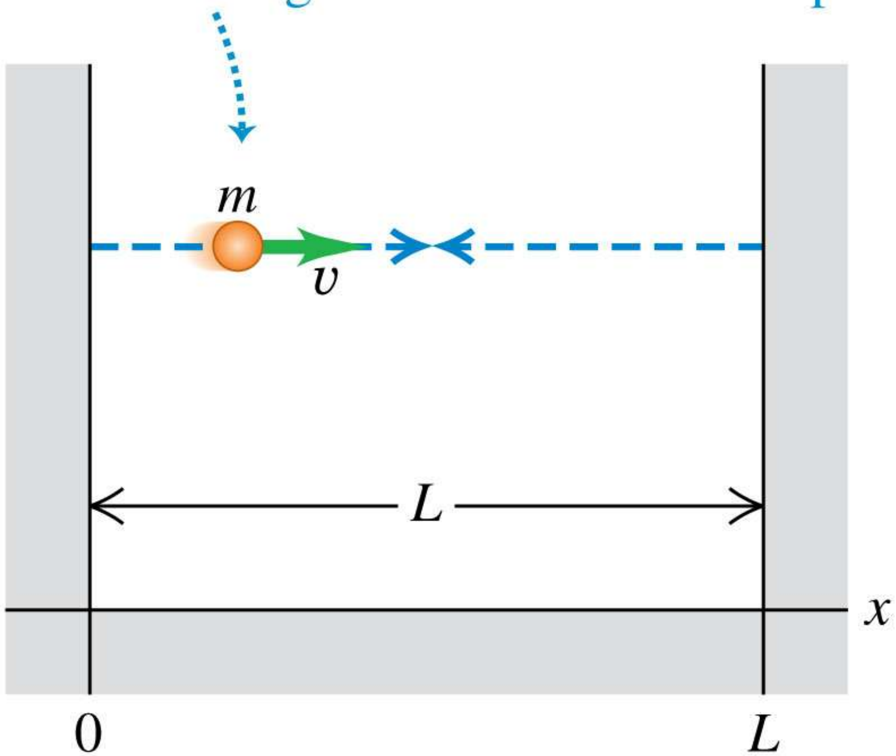
- $\psi(x)$ and $\dfrac{d\psi(x)}{dx}$ are *continuous* everywhere for smooth $U(x)$.
- $\psi(x)$ is *normalized*, i.e., $\int_{-\infty}^{\infty} \left|\psi(x)\right|^2 dx = 1$
- *Bounded* solution: $\psi(x) \to 0 \quad as \quad x \to \pm\infty$

Then, *expectation values* of physical measurable quantities can be calculated from $\psi(x)$.

Particle in a Box

Classical Picture

A particle with mass m moves along a straight line at constant speed, bouncing between two rigid walls a distance L apart.



A 1-*D* box with *hard* walls:

$$U(0) = U(L) = \infty \quad \text{(non-penetrable)}$$

A free particle *inside* the box:

$$U(x) = 0 \qquad \text{(inside box)}$$

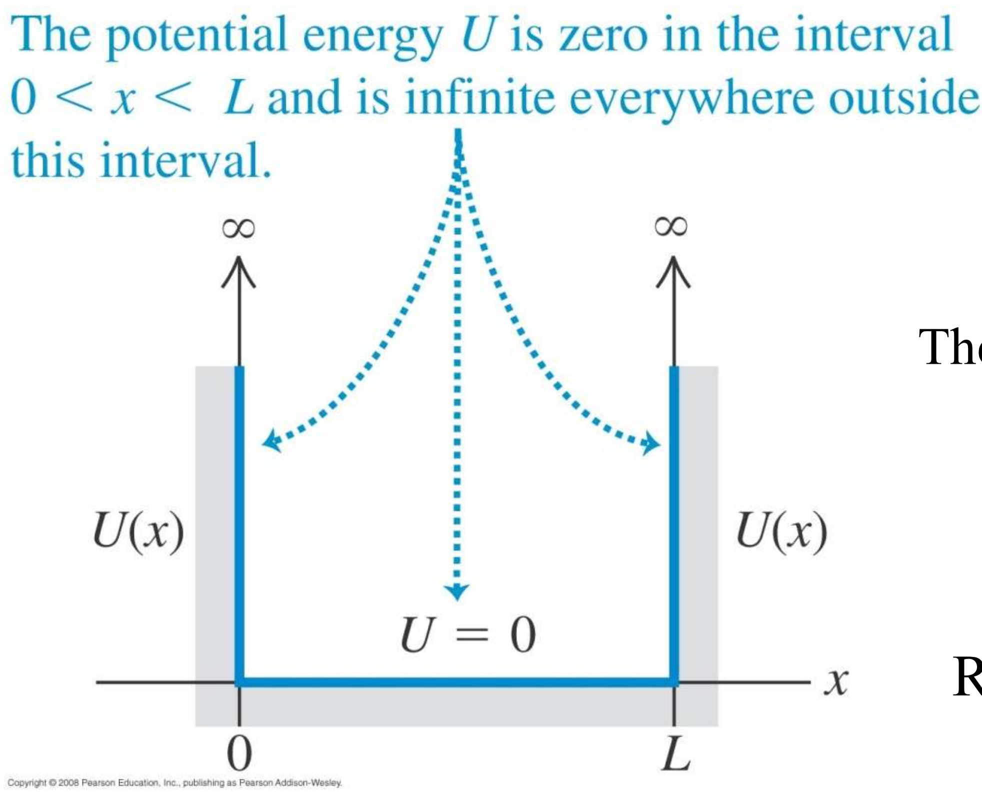
No forces acting on the particle except at hard walls.

P (in x) is conserved between bounces

→ |**P**| is fixed but **P** switches sign between bounces.

Particle in a Box (Quantum Picture)

The situation can be described by the following potential energy $U(x)$:



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

The *time-independent* Schrodinger equation is:

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

Recall, this is basically

KE + PE = Total E

Problem statement: For this $U(x)$, what are the possible wave functions $\psi(x)$ and their corresponding allowed energies E ?

Wave functions for a Particle in a Box

Inside the box, $0 < x < L$, $U(x) = 0$, and the particle is free. From before, we know that the wave function for a free particle has the following form:

$$\psi_{inside}(x) = A_1 e^{ikx} + A_2 e^{-ikx}$$ (linear combination of the two possible solutions.)

where A_1 and A_2 are constants that will be determined later.

$$\left(E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \right)$$

Outside the box, $U(x) = \infty$, and the particle cannot exist outside the box and

$$\psi_{outside}(x) = 0 \qquad \text{(outside the box)}$$

At the boundary, $x = 0$ and $x = L$, the wavefunction has to be *continuous*:

$$\Rightarrow \quad \psi_{inside}(0, L) = \psi_{outside}(0, L) = 0$$

Wavefunctions for a Particle in a Box

Let see how this **boundary condition** imposes restrictions on the two constants, A_1 and A_2, for the wave function.

Using the Euler's formula, we can rewrite the *interior* wave function in terms of sine and cosine:

$$\psi_{inside}(x) = A_1 \underbrace{\left(\cos kx + i \sin kx\right)}_{e^{+ikx}} + A_2 \underbrace{\left(\cos kx - i \sin kx\right)}_{e^{-ikx}}$$
$$= \left(A_1 + A_2\right)\cos kx + i\left(A_1 - A_2\right)\sin kx$$

Imposing the **boundary condition** at $x = 0$,

$$\psi_{inside}(0) = \left(A_1 + A_2\right)\cos 0 + \cancel{i\left(A_1 - A_2\right)\sin 0} = \left(A_1 + A_2\right) = 0$$

$\Rightarrow$ $A_1 = -A_2$ $\Rightarrow$ $\psi_{inside}(x) = 2iA_1 \sin kx = C \sin kx$ (where $C = 2iA_1$)

Wavefunctions for a Particle in a Box

Now, consider the **boundary condition** at $x = L$:

$$\psi_{inside}(L) = C \sin kL = 0$$

For a non-trivial solution ($C \neq 0$), only certain sine waves with a particular choice of wave numbers (k) can satisfy this condition:

$$k_n L = n\pi \quad \text{or} \quad k_n = \frac{n\pi}{L}, \quad n = 1, 2, 3, \cdots$$

This implies that the wavelengths within the box is *quantized* !

$$\lambda_n = \frac{2\pi}{k_n} = 2\cancel{\pi}\frac{L}{n\cancel{\pi}} = \frac{2L}{n}, \quad n = 1, 2, 3, \cdots$$

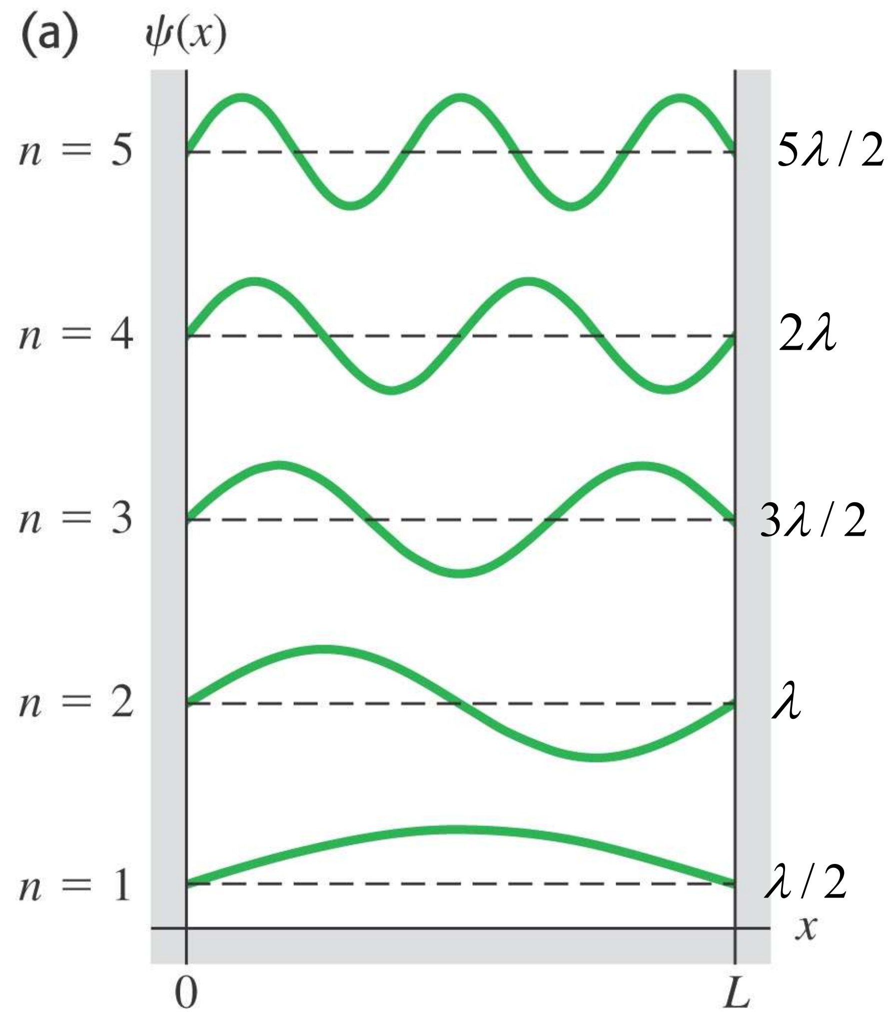
Allowed wavefunctions must have wavelengths exactly fit within the box !

Wavefunction for a Particle in a Box

Rewriting this, we have,

$$L = n\,\lambda_n/2\,, \quad n = 1, 2, 3, \cdots$$

Graphically, it looks like



Since k_n is *quantized*, only a discrete set of $\psi_n(x)$ is allowed as solutions,

$$\psi_n(x) = C\sin\left(k_n x\right) = C\sin\left(\frac{n\pi}{L}x\right),$$
$$n = 1, 2, 3, \cdots$$

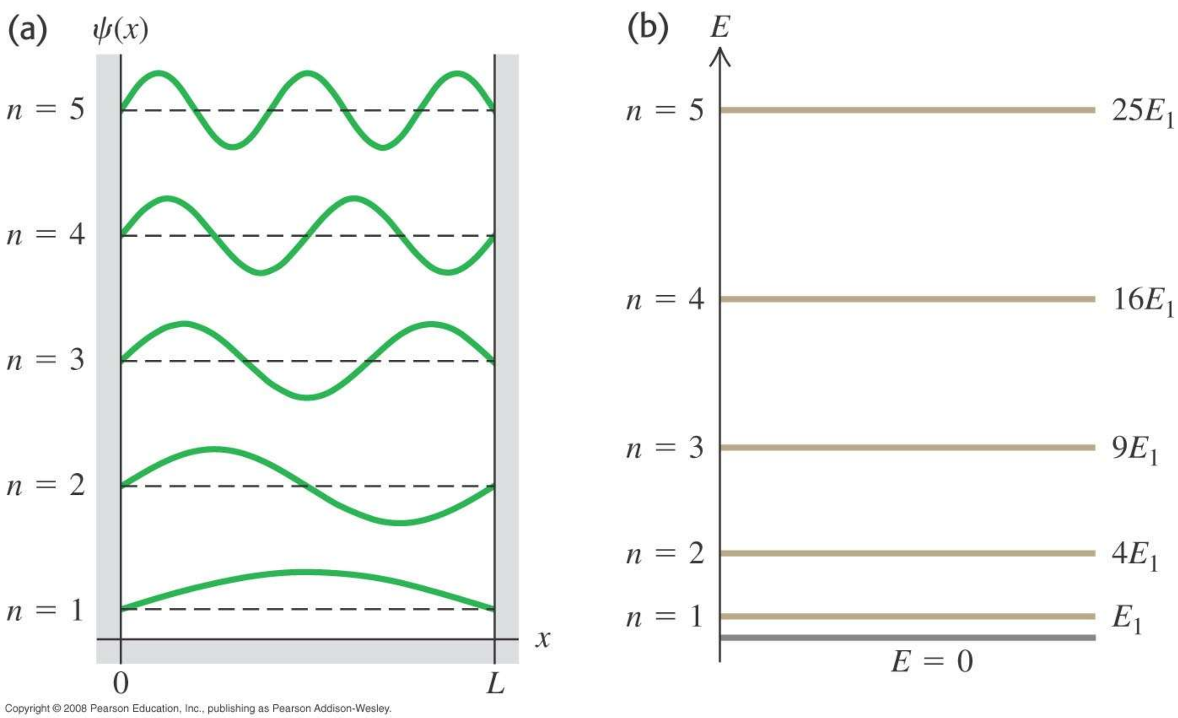
(similar to *standing waves* on a cramped string)

Quantized Energies for a Particle in a Box

Since the wave number k_n is quantized, the energy for the particle in the box is also quantized:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 = \frac{n^2\pi^2\hbar^2}{2mL^2}\left(\text{or } = \frac{n^2h^2}{8mL^2}\right), \quad n = 1, 2, 3, \cdots$$

(n is called the **quantum number**)



Note: the lowest energy with $n = 1$ is not zero:

$$E_1 = \frac{h^2}{8mL^2} > 0$$

$n = 0$ gives $\psi(x) = 0$ and it means *no* particle.