

PHY1203: General Physics III

Chapter 40

Quantum Mechanics – Part 1

What we have known so far

- Planck: “Energy quanta”, which explains the blackbody radiation
- Einstein: Photoelectric effect can only be explained assuming light behaves like particles → photons
- The nature of light: Particle-wave duality.
- de Broglie: “My essential idea was to extend to all particles the coexistence of waves and particles...” → Matter Waves
- Heisenberg: Uncertainty principle
- Bohr: Atom has discrete “energy levels” and can only transit from one to another, but not somewhere between two levels

Successes and failures of Bohr's theory

- Successes:

- Bohr's theory has correctly explained the atomic spectra, either the emission or absorption ones.
- It is the first “working” model for the atom

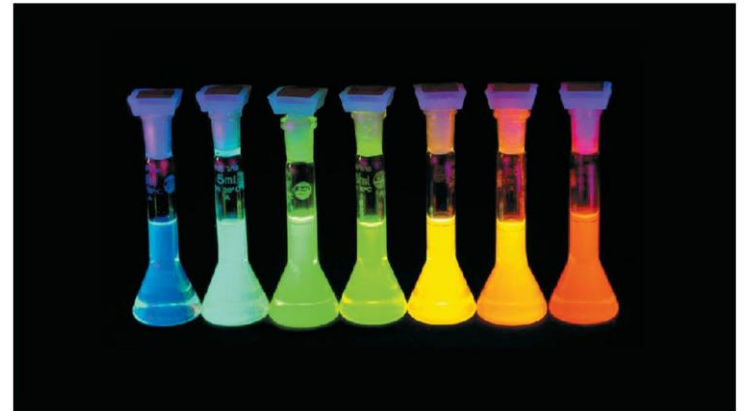
- Failures:

- It is a mixture of classical and quantum ideas.
- It postulates that the electrons do not radiate while orbiting around the nucleus
- It could not explain the maximal electron numbers on one shell
- It could not explain many further experimental observations, including the fine & hyperfine structure of atomic spectra, Zeeman effect, and so on
- It cannot be generalized to more complicated atoms/molecules

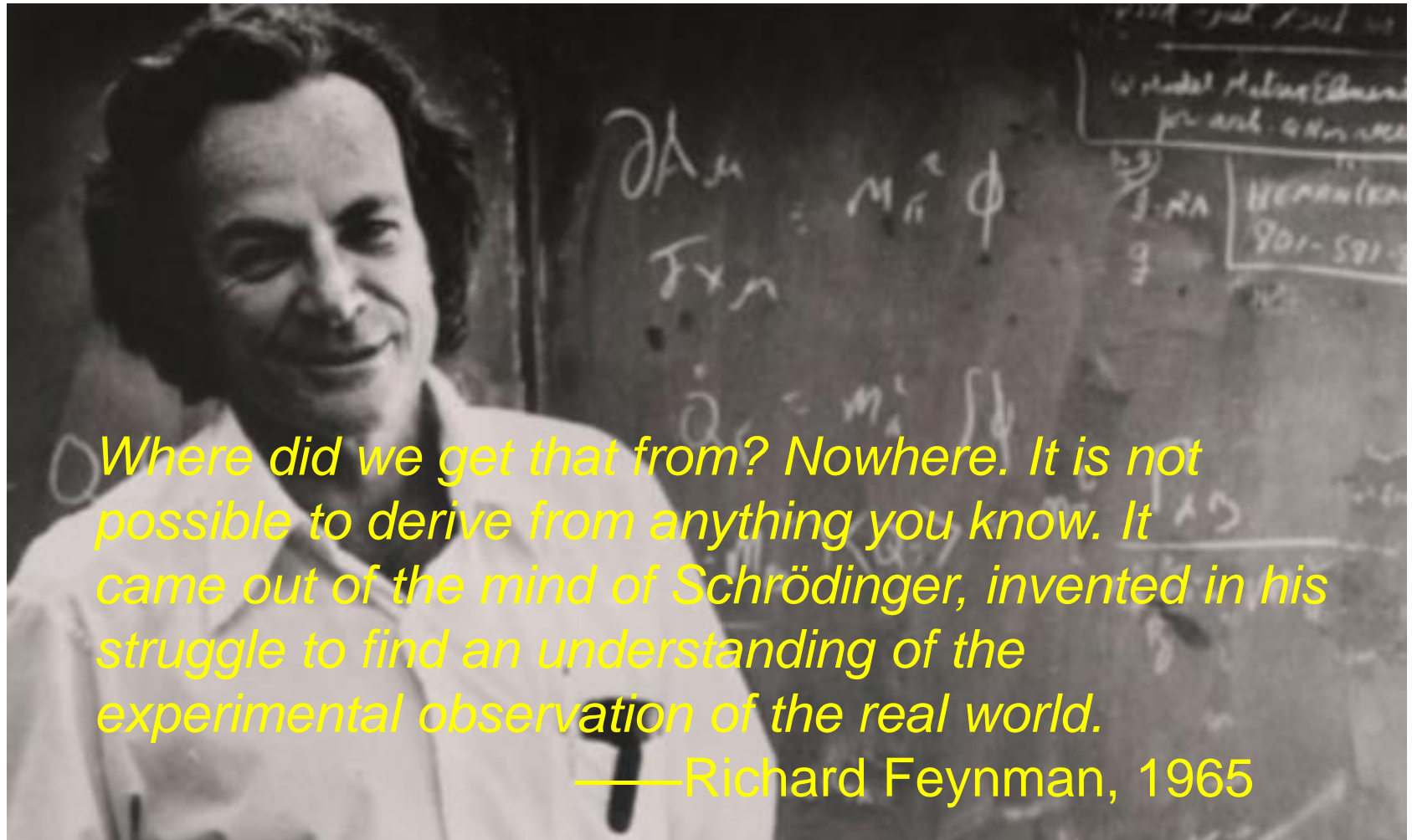


We need a step forward!

- We need a fully quantum theory to explain all those phenomena.
- The starting point: the Schrödinger equation.
- It turns out that the entire quantum world, based on the Schrödinger equation, is remarkably accurate and fascinating.
- In the photograph, microscopic beads of different sizes fluoresce under ultraviolet light.
- The smaller the beads, the shorter the wavelength of visible light they emit.
- The Schrödinger equation can help us understand why. This is just one of the countless intriguing phenomena the quantum world revealed to us.



But where does the Schrödinger equation come from?



Where did we get that from? Nowhere. It is not possible to derive from anything you know. It came out of the mind of Schrödinger, invented in his struggle to find an understanding of the experimental observation of the real world.

—Richard Feynman, 1965

Some history

- On 3 November 1925 Schrödinger wrote to Einstein:
A few days ago I read with great interest the ingenious thesis of Louis de Broglie, which I finally got hold of...
- On 16 November, in another letter, Schrödinger wrote:
I have been intensely concerned these days with Louis de Broglie's ingenious theory. It is extraordinarily exciting, but still has some very grave difficulties.
- One week later Schrödinger gave a seminar on de Broglie's work and a member of the audience suggested that there should be a wave equation.
- Within a few weeks Schrödinger had found his wave equation.



Erwin Schrödinger (1887-1961)

Nobel Prize in
Physics 1933
Prize share ½



"for the discovery of new
productive forms of atomic
theory".

Recall: Wave on a string

- A “wave function” $y(x, t)$ describing a wave on a string must satisfy the “wave equation”

$$\frac{\partial^2 y(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y(x, t)}{\partial t^2}$$

- v is the speed of the wave
- Consider a wave with wavelength λ and frequency f :

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

- Here, $k=2\pi/\lambda$ is the wavenumber and $\omega=2\pi f$ is the angular frequency

Recall: Wave on a string

- Checking: $\frac{\partial y(x, t)}{\partial x} = -kA \sin(kx - \omega t) + kB \cos(kx - \omega t)$

$$\frac{\partial^2 y(x, t)}{\partial x^2} = -k^2 A \cos(kx - \omega t) - k^2 B \sin(kx - \omega t)$$

$$\frac{\partial y(x, t)}{\partial t} = \omega A \sin(kx - \omega t) - \omega B \cos(kx - \omega t)$$

$$\frac{\partial^2 y(x, t)}{\partial t^2} = -\omega^2 A \cos(kx - \omega t) - \omega^2 B \sin(kx - \omega t)$$

$$-k^2 A \cos(kx - \omega t) - k^2 B \sin(kx - \omega t) = \frac{1}{v^2} [-\omega^2 A \cos(kx - \omega t) - \omega^2 B \sin(kx - \omega t)]$$

- The equation is true when $k^2 = \frac{\omega^2}{v^2}$ or $\omega = vk$

“Dispersion relation”

- We also have

$$2\pi f = v \frac{2\pi}{\lambda} \quad \text{or} \quad v = \lambda f$$

Quantum-mechanical version of the wave equation

- Consider a **free** particle with energy

$$E = \frac{1}{2}mv^2 = \frac{m^2v^2}{2m} = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$$

- de Broglie relation: ($\hbar = h/2\pi$)

$$E = hf = \frac{h}{2\pi}2\pi f = \hbar\omega$$

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

- The dispersion relation for a quantum-mechanical free particle is:

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

- It looks different from that for the wave on a string (k^2 instead of k)
- The wave equation is thus different

Quantum-mechanical version of the wave equation

- Consider a sinusoidal **wave function** representing a free particle:

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

- 2nd derivative w.r.t x gives:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= -\frac{\hbar^2}{2m} [-k^2 A \cos(kx - \omega t) - k^2 B \sin(kx - \omega t)] \\ &= \frac{\hbar^2 k^2}{2m} [A \cos(kx - \omega t) + B \sin(kx - \omega t)] \\ &= \frac{\hbar^2 k^2}{2m} \Psi(x, t) \end{aligned}$$

- We guess that this must be related to the 1st derivative w.r.t t

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

Quantum-mechanical version of the wave equation

- Checking:

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

$$A \cos(kx - \omega t) + B \sin(kx - \omega t) = CA \sin(kx - \omega t) - CB \cos(kx - \omega t)$$

- We see that $B = CA$ and $A = -CB$
- Therefore $C^2 = -1$, $C = i$
- Our wave equation therefore becomes

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad \text{(one-dimensional Schrödinger equation for a free particle)}$$

The Schrödinger equation in 1-D

- In a one-dimensional model, a quantum-mechanical particle is described by a wave function $\Psi(x, t)$.
- The one-dimensional Schrödinger equation for a free particle of mass m is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad \text{(one-dimensional Schrödinger equation for a free particle)}$$

- The presence of i (the square root of -1) in the Schrödinger equation means that wave functions are always complex functions.
- The wave function, ψ , can be re-written as

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

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

- But what does “psi” mean?

What does ψ really mean?

- Schrödinger has then applied his equation to several problems including Bohr's atom, and had vast success.
- However, for several years, there wasn't any general agreement to what the wave function actually was.
- A student composed a poem:

*Erwin with his ψ can do
Calculations quite a few.
But one thing has not been seen
Just what does ψ really mean.*

Interpreting the wave function

- In 1926, German physicist Max Born devised an interpretation to the wave function:
- The square of the absolute value of the wave function, $|\Psi(x, t)|^2$, is called the **probability distribution function**. It tells us about the probability of finding the particle near position x at time t .
- Born also coined the term “quantum mechanics” (Quantenmechanik).



Max Born (1882-1970)

Nobel Prize in
Physics 1954
Prize share ½



“for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wavefunction”.

Interpreting the wave function

- Recall: Periodic motion- Energy proportional to A^2 .
- Electromagnetic wave: Intensity (of a interference or diffraction pattern) proportional to E^2 , which is also the probability of finding a photon at certain point
- By analogy, $|\Psi|^2$ at each point tells us about the probability of finding the particle around that point. Absolute value because psi is complex.
- The quantity $|\Psi(x, t)|^2 dx$ is the probability that the particle will be found at time t at a coordinate in the range from x to $x + dx$.

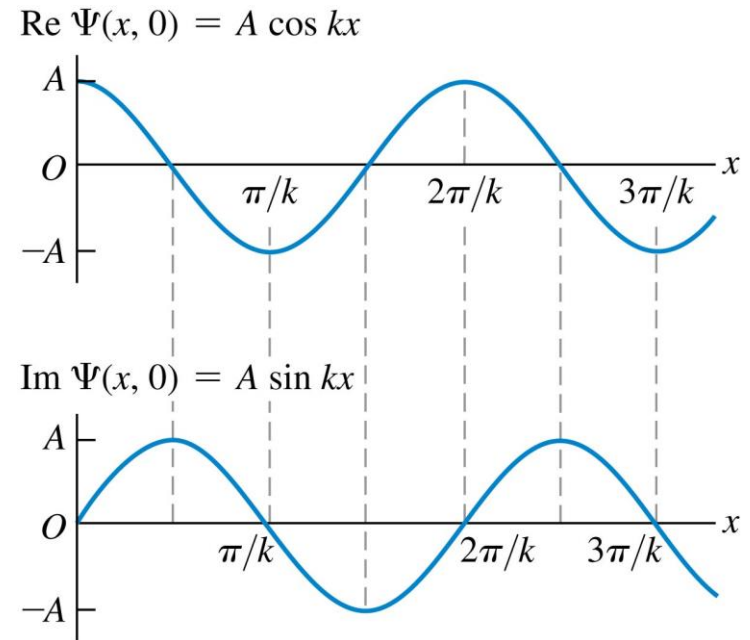
CAUTION Interpreting $|\Psi|^2$ Note that $|\Psi(x, t)|^2$ itself is *not* a probability. Rather, $|\Psi(x, t)|^2 dx$ is the probability of finding the particle between position x and position $x + dx$ at time t . If the length dx is made smaller, it becomes less likely that the particle will be found within that length, so the probability decreases. A better name for $|\Psi(x, t)|^2$ is the **probability distribution function**, since it describes how the probability of finding the particle at different locations is distributed over space. Another common name for $|\Psi(x, t)|^2$ is the *probability density*. ■

The Schrödinger equation in 1-D: A free particle

- A free particle can have a definite momentum $p = \hbar k$ and energy $E = \hbar\omega$.
- Such a particle is not localized at all: The wave function extends to infinity.
- The wave function can be written as a complex exponential:

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

(sinusoidal wave function representing a free particle)



The Schrödinger equation in 1-D: A free particle

- The probability distribution function:

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

- It does not depend on position, which says that we are equally likely to find the particle anywhere along the x -axis
- From the uncertainty principle $\Delta x \Delta p_x \geq \hbar/2$, since we already know $\Delta p_x = 0$, we must have no idea whatsoever where along the x -axis the particle can be found.
- Another way we see it is that $\Delta t \Delta E \geq \hbar$, since we have $\Delta E = 0$, have no idea when the particle will pass a given point on the x -axis.
- This also means that the wave function can't be normalized: The integral of $|\Psi(x, t)|^2$ over all space would be infinite for any value of A . (not an accurate description of a particle)

Example 40.1: A localized free-particle wave function

The wave function $\Psi(x, t) = Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)}$ is a superposition of *two* free-particle wave functions of the form given by Eq. (40.18). Both k_1 and k_2 are positive. (a) Show that this wave function satisfies the Schrödinger equation for a free particle of mass m . (b) Find the probability distribution function for $\Psi(x, t)$.

EXECUTE: (a) If we substitute $\Psi(x, t)$ into Eq. (40.15), the left-hand side of the equation is

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= -\frac{\hbar^2}{2m} \frac{\partial^2 (Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)})}{\partial x^2} \\ &= -\frac{\hbar^2}{2m} [(ik_1)^2 Ae^{i(k_1x - \omega_1t)} + (ik_2)^2 Ae^{i(k_2x - \omega_2t)}] \\ &= \frac{\hbar^2 k_1^2}{2m} Ae^{i(k_1x - \omega_1t)} + \frac{\hbar^2 k_2^2}{2m} Ae^{i(k_2x - \omega_2t)} \end{aligned}$$

The right-hand side is

$$\begin{aligned} i\hbar \frac{\partial \Psi(x, t)}{\partial t} &= i\hbar \frac{\partial (Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)})}{\partial t} \\ &= i\hbar [(-i\omega_1) Ae^{i(k_1x - \omega_1t)} + (-i\omega_2) Ae^{i(k_2x - \omega_2t)}] \\ &= \hbar\omega_1 Ae^{i(k_1x - \omega_1t)} + \hbar\omega_2 Ae^{i(k_2x - \omega_2t)} \end{aligned}$$

Example 40.1: A localized free-particle wave function

The two sides *are* equal, provided that $\hbar\omega_1 = \hbar^2 k_1^2 / 2m$ and $\hbar\omega_2 = \hbar^2 k_2^2 / 2m$. These are just the relationships that we noted above. So we conclude that $\Psi(x, t) = Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)}$ is a valid free-particle wave function. In general, if we take any two wave functions that are solutions of the Schrödinger equation and then make a superposition of these to create a third wave function $\Psi(x, t)$, then $\Psi(x, t)$ is also a solution of the Schrödinger equation.

(b) The complex conjugate of $\Psi(x, t)$ is

$$\Psi^*(x, t) = A^* e^{-i(k_1x - \omega_1t)} + A^* e^{-i(k_2x - \omega_2t)}$$

Hence

$$\begin{aligned} |\Psi(x, t)|^2 &= \Psi^*(x, t) \Psi(x, t) \\ &= (A^* e^{-i(k_1x - \omega_1t)} + A^* e^{-i(k_2x - \omega_2t)}) (A e^{i(k_1x - \omega_1t)} + A e^{i(k_2x - \omega_2t)}) \\ &= A^* A \left[e^{-i(k_1x - \omega_1t)} e^{i(k_1x - \omega_1t)} + e^{-i(k_2x - \omega_2t)} e^{i(k_2x - \omega_2t)} \right. \\ &\quad \left. + e^{-i(k_1x - \omega_1t)} e^{i(k_2x - \omega_2t)} + e^{-i(k_2x - \omega_2t)} e^{i(k_1x - \omega_1t)} \right] \\ &= |A|^2 [e^0 + e^0 + e^{i[(k_2 - k_1)x - (\omega_2 - \omega_1)t]} + e^{-i[(k_2 - k_1)x - (\omega_2 - \omega_1)t]}] \end{aligned}$$

To simplify this expression, recall that $e^0 = 1$. From Euler's formula, $e^{i\theta} = \cos \theta + i \sin \theta$ and $e^{-i\theta} = \cos \theta - i \sin \theta$, so $e^{i\theta} + e^{-i\theta} = 2 \cos \theta$. Hence

$$\begin{aligned} |\Psi(x, t)|^2 &= |A|^2 \{2 + 2 \cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t]\} \\ &= 2|A|^2 \{1 + \cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t]\} \end{aligned}$$

Example 40.1: A localized free-particle wave function

EVALUATE: Figure 40.5 is a graph of the probability distribution function $|\Psi(x, t)|^2$ at $t = 0$. The value of $|\Psi(x, t)|^2$ varies between 0 and $4|A|^2$; probabilities can never be negative! The particle has become *somewhat* localized: The particle is most likely to be found near a point where $|\Psi(x, t)|^2$ is maximum (where the functions $Ae^{i(k_1x - \omega_1t)}$ and $Ae^{i(k_2x - \omega_2t)}$ interfere constructively) and is very unlikely to be found near a point where $|\Psi(x, t)|^2 = 0$ (where $Ae^{i(k_1x - \omega_1t)}$ and $Ae^{i(k_2x - \omega_2t)}$ interfere destructively). This is very similar to the phenomenon of beats for sound waves (see Section 16.7).

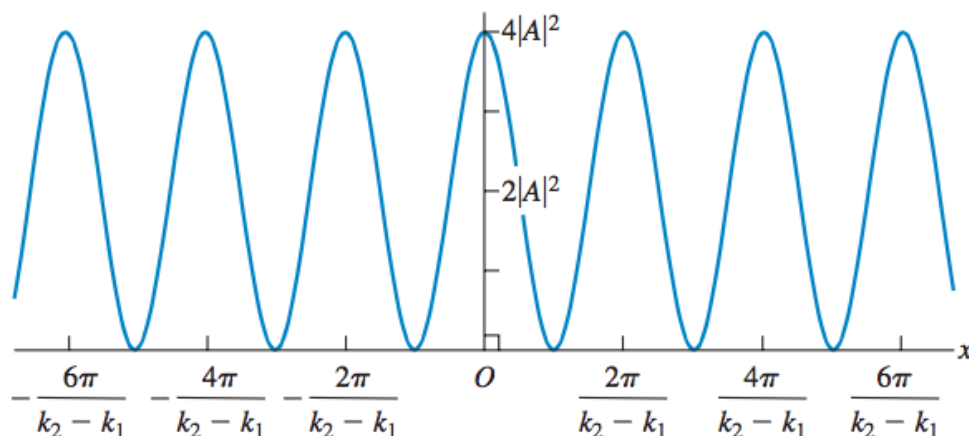
Note also that the probability distribution function is not stationary, but moves in the positive x -direction like the particle that it represents. To see this, recall from Section 15.3 that a sinusoidal wave given by $y(x, t) = A \cos(kx - \omega t)$ moves in the positive x -direction with velocity $v = \omega/k$; since $|\Psi(x, t)|^2$ includes a term $\cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t]$, the probability distribution

moves at a velocity $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$. The subscript “av” reminds us that v_{av} represents the *average* value of the particle’s velocity.

The price we pay for localizing the particle somewhat is that, unlike a particle represented by Eq. (40.18), it no longer has either a definite momentum or a definite energy. That’s consistent with the Heisenberg uncertainty principles: If we decrease the uncertainties about where a particle is and when it passes a certain point, the uncertainties in its momentum and energy must increase.

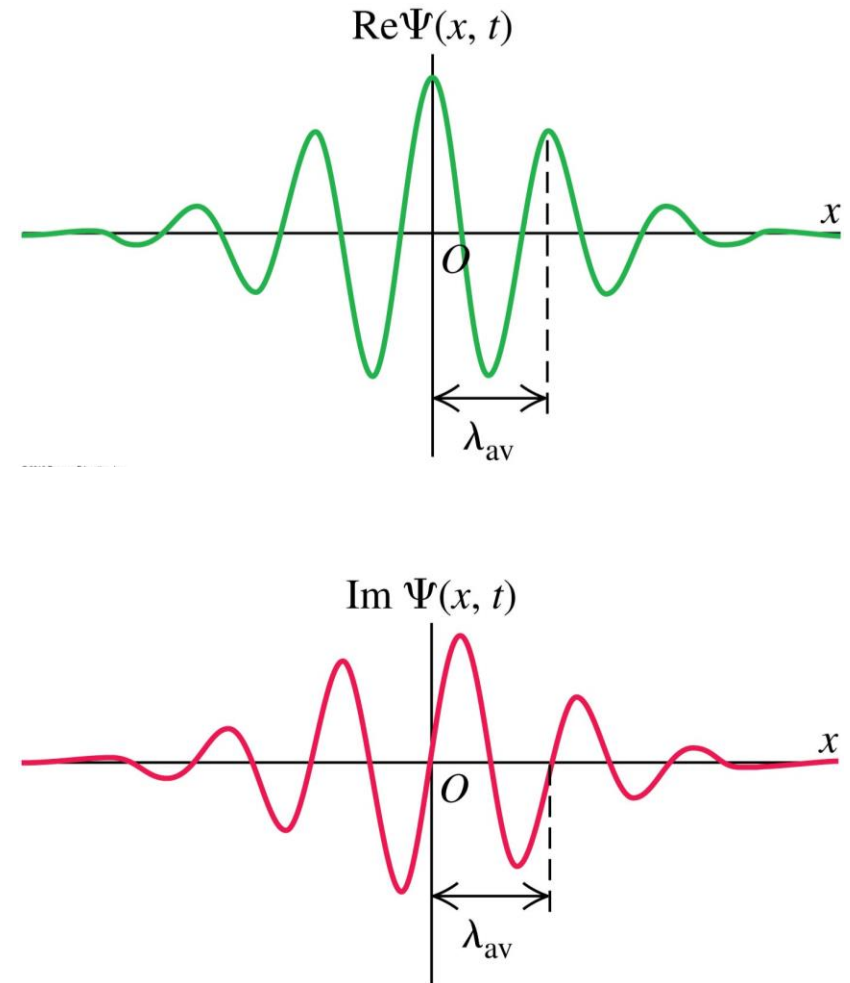
The average momentum of the particle is $p_{av} = (\hbar k_2 + \hbar k_1)/2$, the average of the momenta associated with the free-particle wave functions we added to create $\Psi(x, t)$. This corresponds to the particle having an average velocity $v_{av} = p_{av}/m = (\hbar k_2 + \hbar k_1)/2m$. Can you show that this is equal to the expression $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$ that we found above?

40.5 The probability distribution function at $t = 0$ for $\Psi(x, t) = Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)}$.



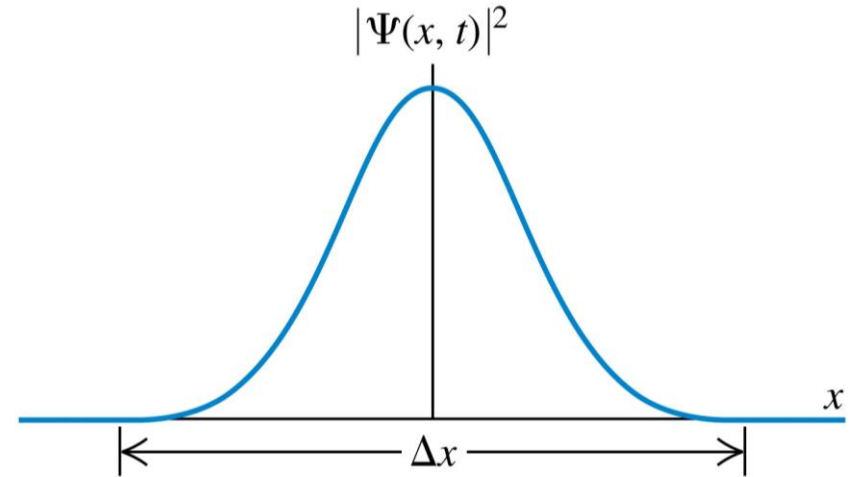
The Schrödinger equation in 1-D: Wave packets

- Superposing a large number of sinusoidal waves with different wave numbers and appropriate amplitudes can produce a wave pulse that has a wavelength $\lambda_{av} = 2\pi/k_{av}$ and is localized within a region of space of length Δx .
- Shown are the real and imaginary components of such a wave packet at time t .



The Schrödinger equation in 1-D: Wave packets

- The resulting probability distribution has only one maximum.
- This localized pulse has aspects of both particle and wave.
- It is a particle in the sense that it is localized in space; if we look from a distance, it may look like a point.
- But it also has a periodic structure that is characteristic of a wave.
- Such a localized wave pulse is called a **wave packet**.



The Schrödinger equation in 1-D

- If a particle of mass m moves in the presence of a potential energy function $U(x)$, the one-dimensional Schrödinger equation for the particle is:

General one-dimensional Schrödinger equation:

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

Diagram illustrating the components of the Schrödinger equation:

- \hbar : Planck's constant divided by 2π
- m : Particle's mass
- $\Psi(x, t)$: Particle's wave function
- $U(x)$: Potential-energy function

- Note that if $U(x) = 0$, this reduces to the free-particle Schrödinger equation.

The Schrödinger equation in 1-D

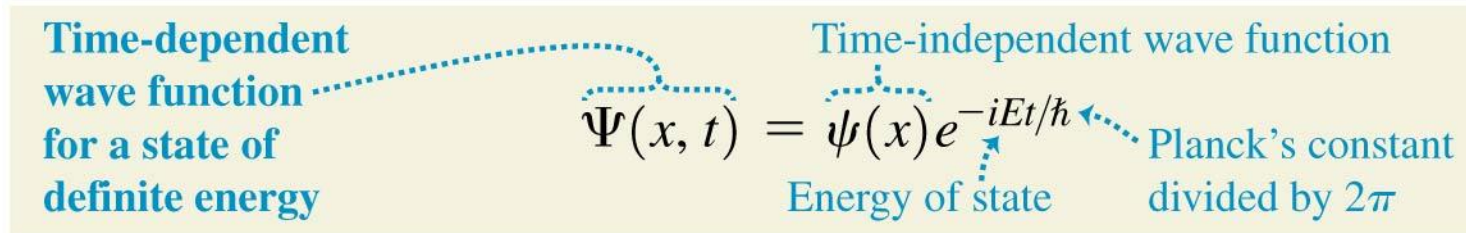
- The motivation is as follows: for a free particle,

$$\begin{aligned}-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} (Ae^{ikx} e^{-i\omega t}) = -\frac{\hbar^2}{2m} (ik)^2 (Ae^{ikx} e^{-i\omega t}) \\ &= \frac{\hbar^2 k^2}{2m} \Psi(x, t) \\ i\hbar \frac{\partial \Psi(x, t)}{\partial t} &= i\hbar \frac{\partial}{\partial t} (Ae^{ikx} e^{-i\omega t}) = i\hbar (-i\omega) (Ae^{ikx} e^{-i\omega t}) = \hbar\omega \Psi(x, t)\end{aligned}$$

- The l.h.s. is the kinetic energy, while the r.h.s. is the total energy. Therefore it is natural to add the potential energy (if present) on the l.h.s.
- This is NOT a proof. The only way we know that the Schrödinger equation is correct is that it works: Predictions made with this equation agree with experimental results.

The Schrödinger equation in 1-D: Stationary states

- If a particle has a definite energy E , the wave function $\Psi(x, t)$ is a product of a time-independent wave function $\psi(x)$ and a factor that depends on time t but not position:



The diagram shows the equation $\Psi(x, t) = \psi(x) e^{-iEt/\hbar}$ with several labels and arrows. A bracket on the left side of the equation is labeled "Time-dependent wave function for a state of definite energy". A bracket under $\psi(x)$ is labeled "Time-independent wave function". A bracket under E is labeled "Energy of state". A bracket under \hbar is labeled "Planck's constant divided by 2π ".

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

- For such a *stationary state* the probability distribution function $|\Psi(x, t)|^2 = |\psi(x)|^2$ does not depend on time.

CAUTION A stationary state does not mean a stationary particle The name *stationary state* may lead you to think that the particle is not in motion if it is described by such a wave function. That's not the case. It's the *probability distribution* (that is, the relative likelihood of finding the particle at various positions), not the particle itself, that's stationary. ■

The Schrödinger equation in 1-D: Stationary states

- Substituting $\Psi(x, t)$ into the Schrödinger equation, we have

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 [\psi(x)e^{-iEt/\hbar}]}{\partial x^2} + U(x)\psi(x)e^{-iEt/\hbar} &= i\hbar \frac{\partial [\psi(x)e^{-iEt/\hbar}]}{\partial t} \\ -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} e^{-iEt/\hbar} + U(x)\psi(x)e^{-iEt/\hbar} &= i\hbar \left(\frac{-iE}{\hbar} \right) [\psi(x)e^{-iEt/\hbar}] \\ &= E\psi(x)e^{-iEt/\hbar} \end{aligned}$$

- Dividing both sides by $e^{-iEt/\hbar}$, we have

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

The Schrödinger equation in 1-D: Stationary states

- The time-independent one-dimensional Schrödinger equation for a stationary state of energy E is:

The diagram shows the time-independent one-dimensional Schrödinger equation with labels for its components:

Time-independent one-dimensional Schrödinger equation:

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

Labels and arrows:

- Planck's constant divided by 2π** points to \hbar .
- Particle's mass** points to m .
- Potential-energy function** points to $U(x)$.
- Time-independent wave function** points to $\psi(x)$.
- Energy of state** points to E .

- Much of this chapter is devoted to solving this equation to find the definite-energy, stationary-state wave functions $\psi(x)$ and the corresponding values of E —that is, the energies of the allowed levels—for different physical situations.

Q40.1

Which of the following wave functions for a free particle represent(s) a stationary state?

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

B. $\Psi(x, t) = Ae^{ikx}e^{-i\omega t} + Ae^{-ikx}e^{-i\omega t}$

C. $\Psi(x, t) = Ae^{ikx}e^{-i\omega t} + 2Ae^{-ikx}e^{-i\omega t}$

D. Two of A, B, and C represent a stationary state.



E. All three of A, B, and C represent a stationary state.

Example 40.2: A stationary state

Consider the wave function $\psi(x) = A_1e^{ikx} + A_2e^{-ikx}$, where k is positive. Is this a valid time-independent wave function for a free particle in a stationary state? What is the energy corresponding to this wave function?

IDENTIFY and SET UP: A valid stationary-state wave function for a free particle must satisfy the time-independent Schrödinger equation, Eq. (40.23), with $U(x) = 0$. To test the given function $\psi(x)$, we simply substitute it into the left-hand side of the equation. If the result is a constant times $\psi(x)$, then the wave function is indeed a solution and the constant is equal to the particle energy E .

EXECUTE: Substituting $\psi(x) = A_1e^{ikx} + A_2e^{-ikx}$ and $U(x) = 0$ into Eq. (40.23), we obtain

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} &= -\frac{\hbar^2}{2m} \frac{d^2(A_1e^{ikx} + A_2e^{-ikx})}{dx^2} \\ &= -\frac{\hbar^2}{2m} [(ik)^2 A_1e^{ikx} + (-ik)^2 A_2e^{-ikx}] \\ &= \frac{\hbar^2 k^2}{2m} (A_1e^{ikx} + A_2e^{-ikx}) = \frac{\hbar^2 k^2}{2m} \psi(x) \end{aligned}$$

Example 40.2: A stationary state

Consider the wave function $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$, where k is positive. Is this a valid time-independent wave function for a free particle in a stationary state? What is the energy corresponding to this wave function?

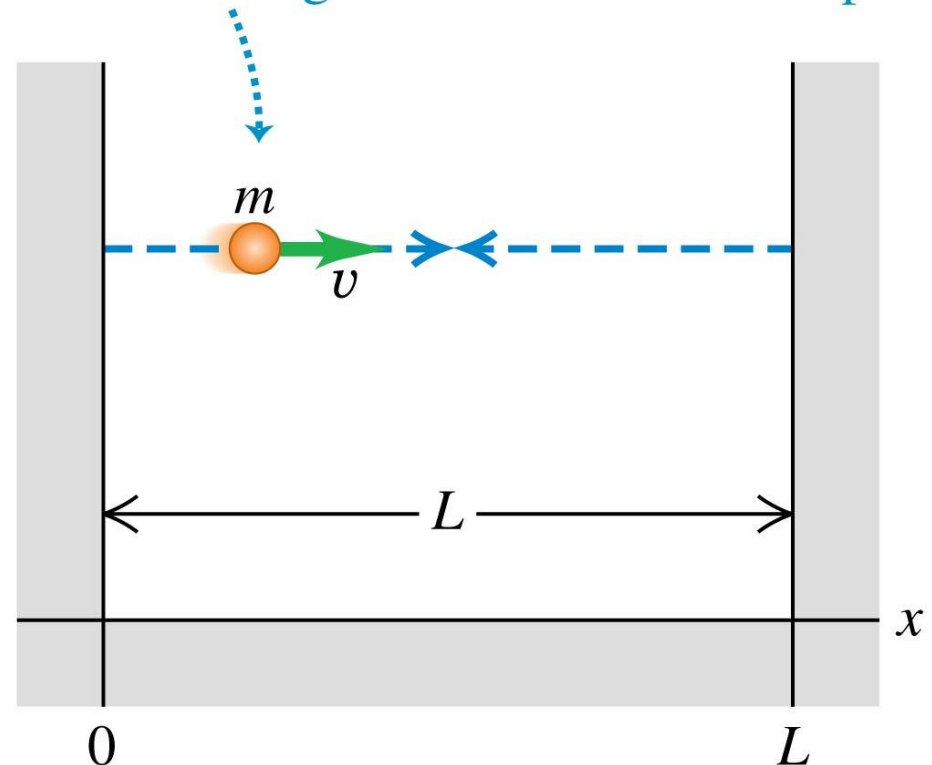
The result is a constant times $\psi(x)$, so this $\psi(x)$ is indeed a valid stationary-state wave function for a free particle. Comparing with Eq. (40.23) shows that the constant on the right-hand side is the particle energy: $E = \hbar^2 k^2 / 2m$.

EVALUATE: Note that $\psi(x)$ is a *superposition* of two different wave functions: one function ($A_1 e^{ikx}$) that represents a particle with magnitude of momentum $p = \hbar k$ moving in the positive x -direction, and one function ($A_2 e^{-ikx}$) that represents a particle with the same magnitude of momentum moving in the negative x -direction. So while the combined wave function $\psi(x)$ represents a stationary state with a definite energy, this state does *not* have a definite momentum. We'll see in Section 40.2 that such a wave function can represent a *standing wave*, and we'll explore situations in which such standing matter waves can arise.

Particle in a box: Newtonian view

- Let's look at a simple model in which a particle is bound so that it cannot escape to infinity, but rather is confined to a restricted region of space.
- Our system consists of a particle confined between two rigid walls separated by a distance L .

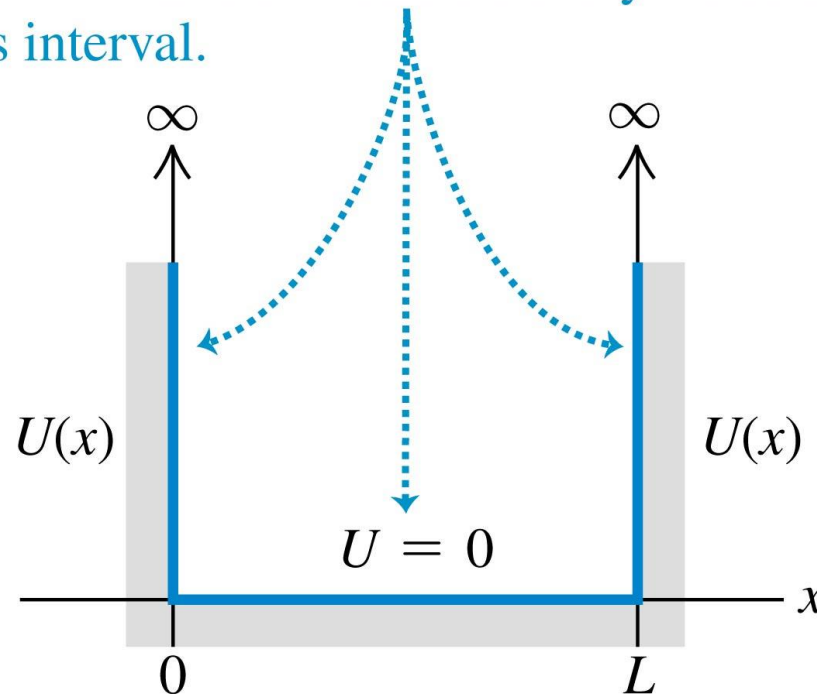
A particle with mass m moves along a straight line at constant speed, bouncing between two rigid walls a distance L apart.



Potential energy for a particle in a box

- The potential energy corresponding to the rigid walls is infinite, so the particle cannot escape.
- This model might represent an electron that is free to move within a long, straight molecule or along a very thin wire.

The potential energy U is zero in the interval $0 < x < L$ and is infinite everywhere outside this interval.



Particle in a box: qualitative considerations

- $\psi(x)$ must be zero outside $[0, L]$ [$U(x)\psi(x)$ is finite]
- $\psi(x)$ must be a continuous function to be mathematically well-behaved. \rightarrow Boundary conditions: $\psi(0) = \psi(L) = 0$.
- In order for $d^2\psi(x)/dx^2$ to be well behaved, $d\psi(x)/dx$ should also be continuous except at $x = 0$ and L .
- Within $[0, L]$, the Schrödinger equation can be written as

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

The same as the free particle. We take the solution $\psi(x) = Ae^{ikx}$ and found that it does not satisfy the boundary condition at $x = L$.

Particle in a box: solution

- Recall Example 40.2: a more general trial wave function can be taken as

$$\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$$

- $\psi(0)=0 \rightarrow A_1 + A_2 = 0, A_1 = -A_2;$
- $\psi(L)=0 \rightarrow 2iA_1 \sin(kL) = C \sin(kL) = 0$

$$k = \frac{n\pi}{L} \quad \text{and} \quad \lambda = \frac{2\pi}{k} = \frac{2L}{n} \quad (n = 1, 2, 3, \dots)$$

- Since we already know that the energy is given as

$$E = \hbar^2 k^2 / 2m = p^2 / 2m, \text{ where } p = \hbar k = (h/2\pi)(2\pi/\lambda) = h/\lambda$$

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2L}$$

Particle in a box: Wave functions, energy levels

- The energy levels for a particle in a box are:

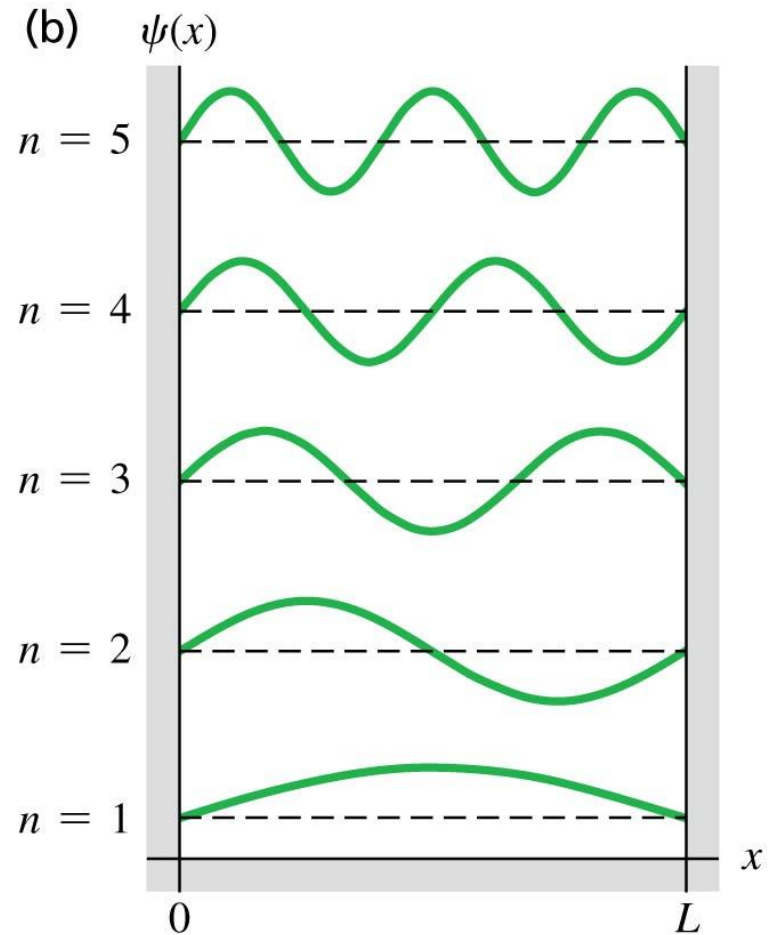
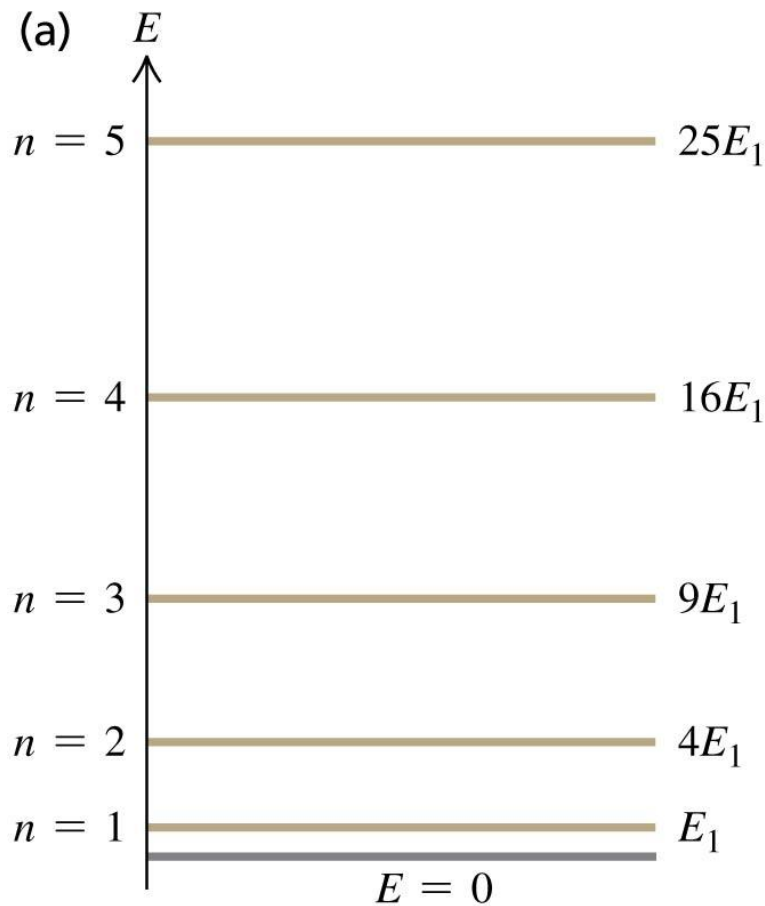
$$E_n = \frac{p_n^2}{2m} = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \dots)$$

- Each energy level has its own value of the quantum number n and a corresponding wave function (The determination of C , the normalization constant, will be explained later)

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (n = 1, 2, 3, \dots)$$

Particle in a box: Wave functions, energy levels

- Shown are energy levels and associated stationary-state wave functions for a particle in a box.

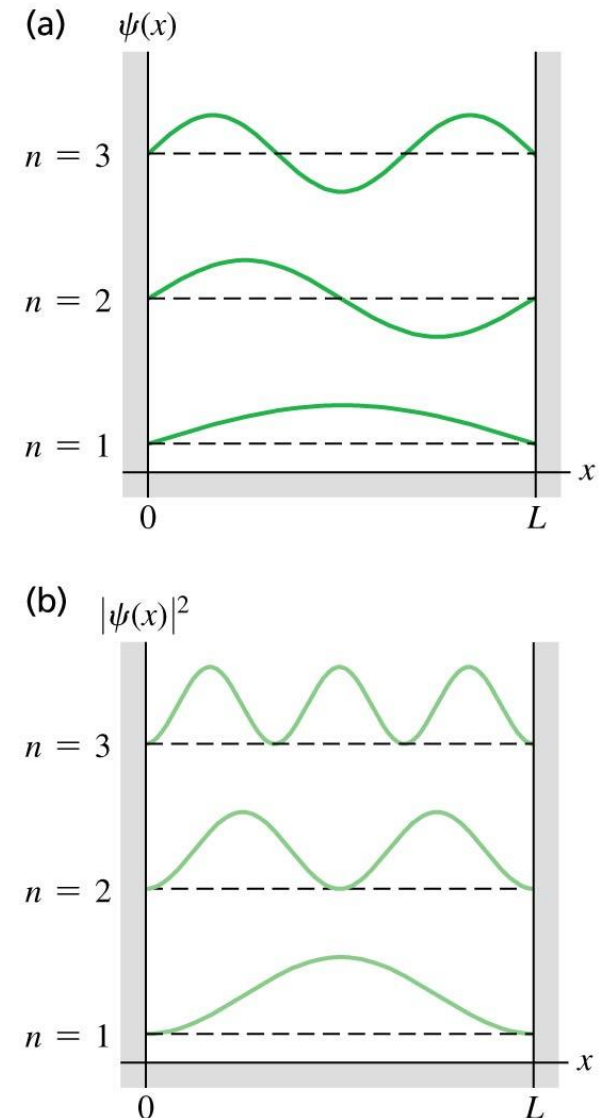


Particle in a box: Wave functions, energy levels

CAUTION **A particle in a box cannot have zero energy** Note that the energy of a particle in a box *cannot* be zero. Equation (40.31) shows that $E = 0$ would require $n = 0$, but substituting $n = 0$ into Eq. (40.32) gives a zero wave function. Since a particle is described by a *nonzero* wave function, this means that there cannot be a particle with $E = 0$. This is a consequence of the Heisenberg uncertainty principle: A particle in a zero-energy state would have a definite value of momentum (precisely zero), so its position uncertainty would be infinite and the particle could be found anywhere along the x -axis. But this is impossible, since a particle in a box can be found only between $x = 0$ and $x = L$. Hence $E = 0$ is not allowed. By contrast, the allowed stationary-state wave functions with $n = 1, 2, 3, \dots$ do not represent states of definite momentum (each is an equal mixture of a state of x -momentum $+p_n = nh/2L$ and a state of x -momentum $-p_n = -nh/2L$). Hence each stationary state has a nonzero momentum uncertainty, consistent with having a finite position uncertainty. ■

Particle in a box: Probability and normalization

- Shown are the first three stationary-state wave functions $\psi(x)$ for a particle in a box (a) and the associated probability distribution functions $|\psi(x)|^2$ (b).
- There are locations where there is *zero* probability of finding the particle.
- Wave functions must be normalized so that the integral of $|\psi(x)|^2$ over all x equals 1 (which means there is 100% probability of finding the particle *somewhere*).



Particle in a box: Wave function normalization

- The normalization condition:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad (\text{normalization condition})$$

- Within $[0, L]$ we have

$$|\psi(x)|^2 dx = C^2 \sin^2 \frac{n\pi x}{L} dx$$

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

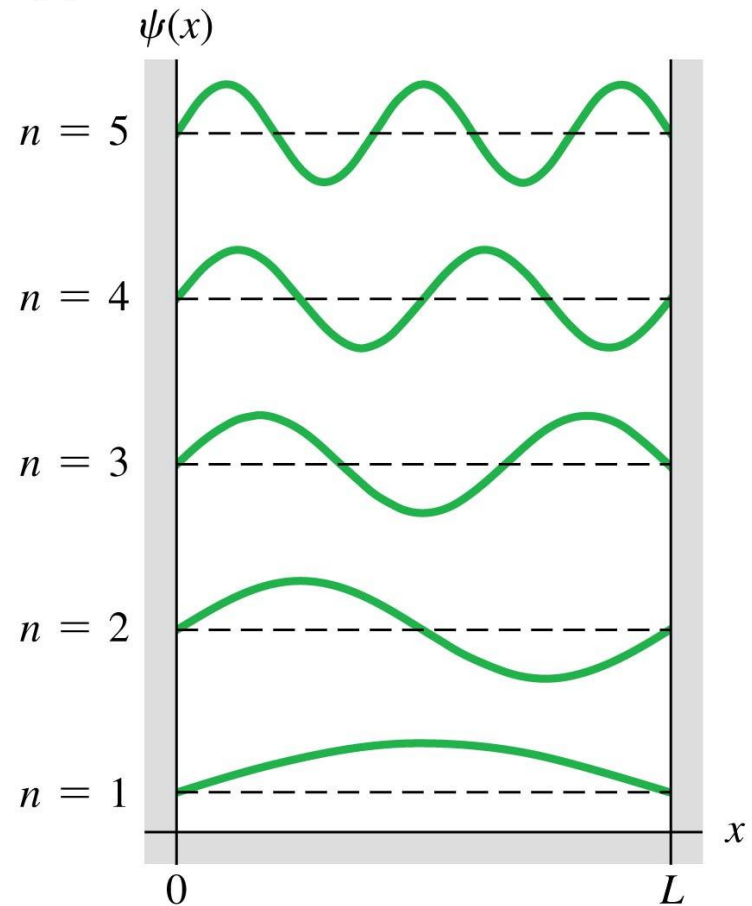
- Using the identity $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$, we evaluate the integral and get

$$C = (2/L)^{1/2}$$

Q40.2

The first five wave functions ($n = 1$ through $n = 5$) for a particle in a box are shown. The probability of finding the particle near $x = L/2$ is

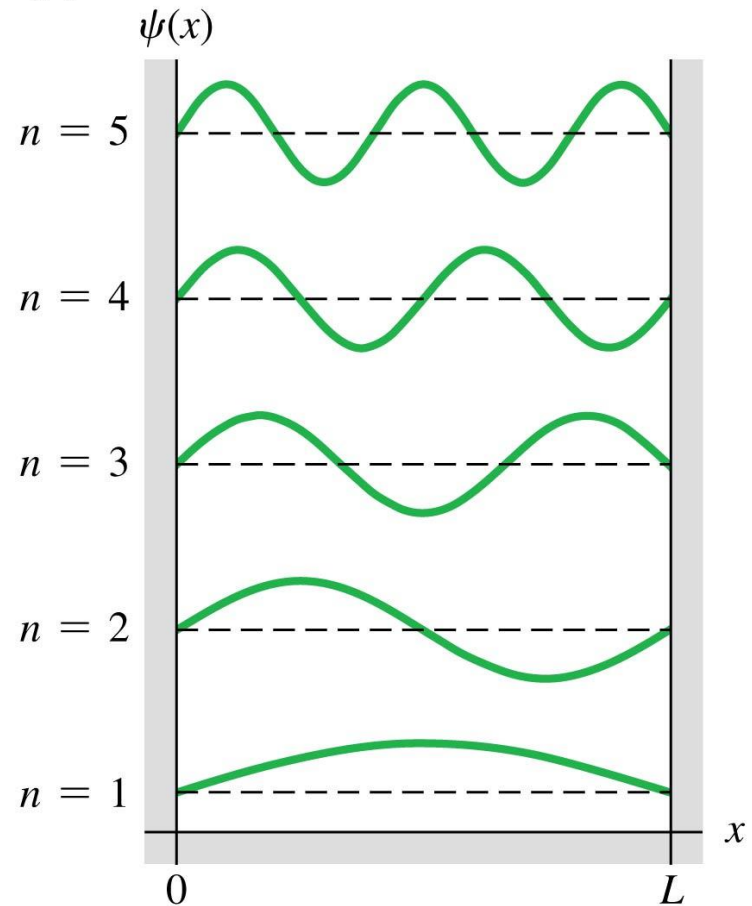
- A. least for $n = 1$.
- ✓ B. least for $n = 2$ and $n = 4$.
- C. least for $n = 5$.
- D. the same (and nonzero) for $n = 1, 2, 3, 4$, and 5 .
- E. zero for $n = 1, 2, 3, 4$, and 5 .



Q40.3

The first five wave functions ($n = 1$ through $n = 5$) for a particle in a box are shown. The average value of the x -component of momentum is

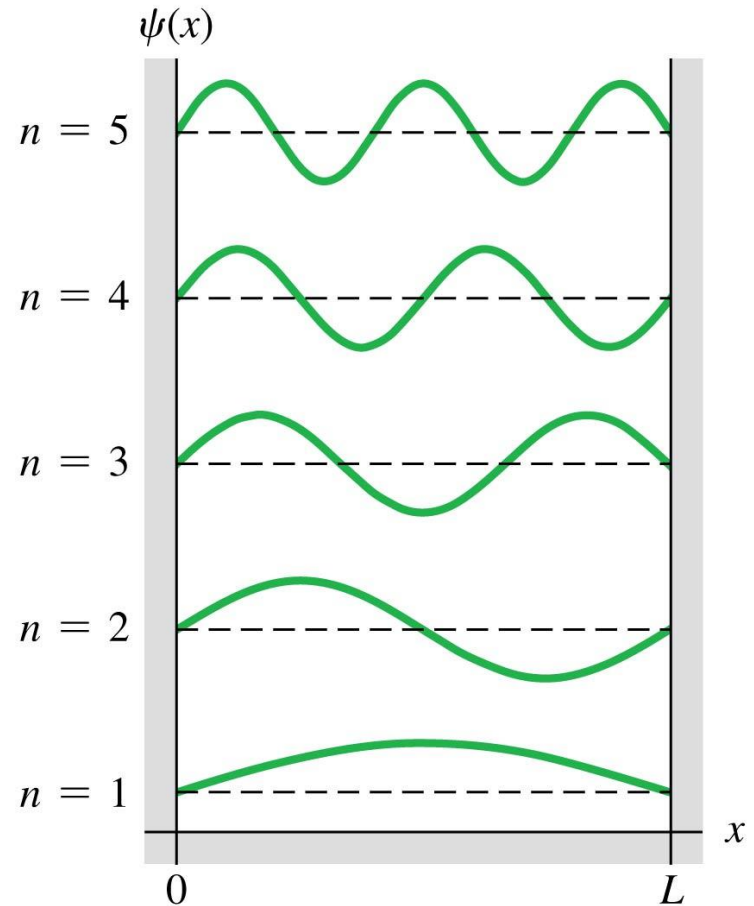
- A. greatest for $n = 1$.
- B. greatest for $n = 5$.
- C. equally great (and nonzero) for all odd values of n .
- D. equally great (and nonzero) for all values of n , odd or even.
- ✓ E. zero for all values of n , odd or even.



Q40.4

The first five wave functions ($n = 1$ through $n = 5$) for a particle in a box are shown. Compared to the $n = 1$ energy level, the $n = 5$ energy level has

- A. the same kinetic energy (KE).
- B. 5 times the KE.
- ✓ C. 25 times the KE.
- D. 125 times the KE.
- E. none of the above.



Example 40.3: Electron in an atom-size box

Find the first two energy levels for an electron confined to a one-dimensional box 5.0×10^{-10} m across (about the diameter of an atom).

EXECUTE: From Eq. (40.31),

$$\begin{aligned} E_1 &= \frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.109 \times 10^{-31} \text{ kg})(5.0 \times 10^{-10} \text{ m})^2} \\ &= 2.4 \times 10^{-19} \text{ J} = 1.5 \text{ eV} \\ E_2 &= \frac{2^2 h^2}{8mL^2} = 4E_1 = 9.6 \times 10^{-19} \text{ J} = 6.0 \text{ eV} \end{aligned}$$

Example 40.3: Electron in an atom-size box

Find the first two energy levels for an electron confined to a one-dimensional box 5.0×10^{-10} m across (about the diameter of an atom).

EVALUATE: The difference between the first two energy levels is $E_2 - E_1 = 4.5$ eV. An electron confined to a box is different from an electron bound in an atom, but it is reassuring that this result is of the same order of magnitude as the difference between actual atomic energy levels.

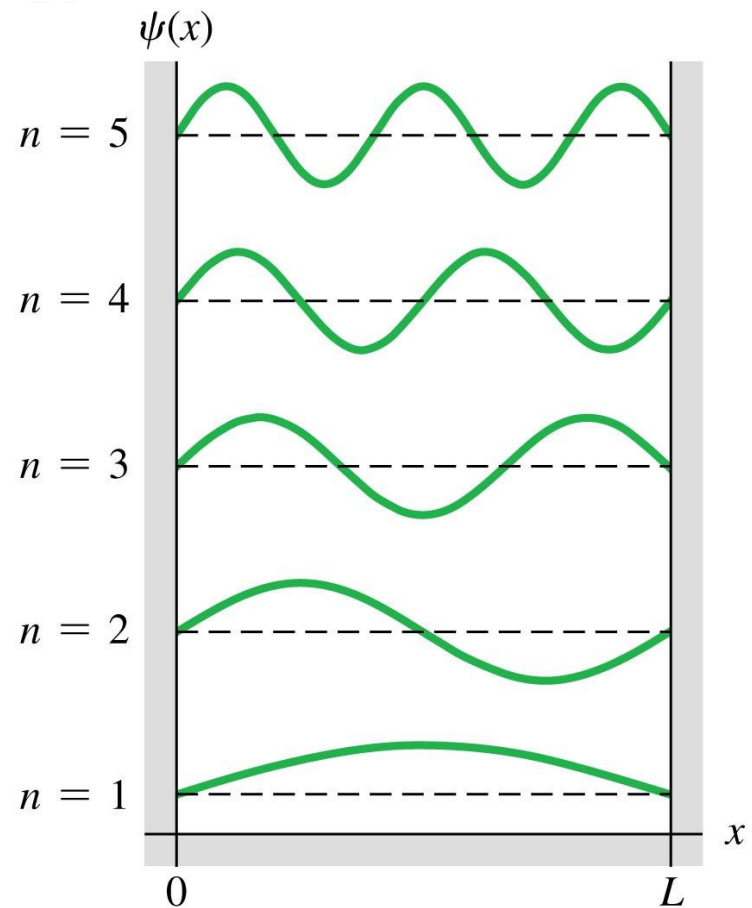
You can also show that for a proton or neutron ($m = 1.67 \times 10^{-27}$ kg) confined to a box 1.1×10^{-14} m across (the width of a medium-sized atomic nucleus), the energies of the first two levels are about a million times larger: $E_1 = 1.7 \times 10^6$ eV = 1.7 MeV, $E_2 = 4E_1 = 6.8$ MeV, $E_2 - E_1 = 5.1$ MeV. This suggests why nuclear reactions (which involve transitions between energy levels in nuclei) release so much more energy than chemical reactions (which involve transitions between energy levels of electrons in atoms).

Finally, you can show (see Exercise 40.11) that the energy levels of a billiard ball ($m = 0.2$ kg) confined to a box 1.3 m across—the width of a billiard table—are separated by about 5×10^{-67} J. Quantum effects won't disturb a game of billiards.

Q-RT40.1

The figure shows the first five wave functions ($n = 1$ through $n = 5$) for a particle in a box of width L . **Rank** the energy of a particle in the $n = 1$ state for the four following situations, from greatest energy to least energy. (The mass of the proton is 1836 times greater than the mass of the electron.)

- A. proton in a box, $L = 1.0$ nm
- B. proton in a box, $L = 2.0$ nm
- C. electron in a box, $L = 1.0$ nm
- D. electron in a box, $L = 2.0$ nm



✓ Answer: CDAB

Example 40.4: A nonsinusoidal wave function?

(a) Show that $\psi(x) = Ax + B$, where A and B are constants, is a solution of the Schrödinger equation for an $E = 0$ energy level of a particle in a box. (b) What constraints do the boundary conditions at $x = 0$ and $x = L$ place on the constants A and B ?

EXECUTE: (a) From Eq. (40.25), the Schrödinger equation for an $E = 0$ energy level of a particle in a box is

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

in the region $0 \leq x \leq L$. Differentiating $\psi(x) = Ax + B$ twice with respect to x gives $d^2\psi(x)/dx^2 = 0$, so the left side of the equation is zero, and so $\psi(x) = Ax + B$ is a solution of this Schrödinger equation for $E = 0$. (Note that both $\psi(x)$ and its derivative $d\psi(x)/dx = A$ are continuous functions, as they must be.)

(b) Applying the boundary condition at $x = 0$ gives $\psi(0) = B = 0$, and so $\psi(x) = Ax$. Applying the boundary condition at $x = L$ gives $\psi(L) = AL = 0$, so $A = 0$. Hence $\psi(x) = 0$ both inside the box ($0 \leq x \leq L$) and *outside*: There is *zero* probability of finding the particle anywhere with this wave function, and so $\psi(x) = Ax + B$ is *not* a physically valid wave function.