

Chapter 40: Quantum mechanics

- Mechanical wave equations & wave functions
- Schrodinger equation
- Particle in a box
- Potential wells
- Potential barriers and tunneling
- Quantum harmonic oscillator
- The uncertainty principle revisited

Mechanical waves in one dimension

The first semester of the calculus-based physics course covered one dimensional waves on a string. The wave equation was given by

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

where v is the velocity of the wave and $y(x, t)$ is the wave function for the transverse wave.

A wave function solution to the above equation for a wave with wavelength λ and frequency f moving in the positive x -direction along a string is

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

$$\text{or } y(x, t) = C e^{i(kx - \omega t)} + D e^{-i(kx - \omega t)}$$

where A and B (or C and D) are constants, $k = 2\pi/\lambda$ is the wave number, and $\omega = 2\pi f$ is the angular frequency.

You can substitute the above wave functions into the wave equation to show that they are indeed solutions. Also, remember that $\omega = vk$.

One-dimensional Schrodinger equation

The quantum mechanical wave equation cannot be the same as the equation for waves on a string because the relationship between ω and k is different.

Instead of a linear equation of proportionality, last chapter gave us the energy and momentum relationships

$$E = \hbar\omega \quad \text{and} \quad p = \hbar k$$

which after substituting into the equation for the energy for a free particle $E = p^2/2m$ we find the relationship

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

We find that the angular frequency (time derivative part of the wave equation) is proportional to the wave number squared (position derivative part of the wave equation). Thus, we expect the derivatives for time and position to be different, where the actual Schrodinger equation for a free particle is

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

The wave function and probability distribution

Just as the wave functions for an electromagnetic wave describe the distribution of the electric and magnetic fields, the wave function in the Schrodinger equation Ψ describes the distribution of a particle in space.

The square of a particle's wave function $|\Psi|^2$ gives us the probability density of finding that particle. The wave functions can be complex (but not the probability distribution), so it is important to note that the absolute value squared is the wave function Ψ multiplied by its complex conjugate Ψ^* ,

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

To have the probability make sense, it must be normalized. The normalization condition for a one-dimensional wave function is

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

The probability of finding the particle between x_1 and x_2 from the normalized wave function is

$$P(x_1 \leq x \leq x_2) = \int_{x_1}^{x_2} |\Psi(x, t)|^2 dx$$

What does the square of the wave function represent?

- A. The square of the wave function represents the acceleration of the particle as a function of time and position.
- B. The square of the wave function represents the position of the particle as a function of time.
- C. The square of the wave function represents the probability density of finding the particle at a given position and time.
- D. The square of the wave function represents the probability of finding the particle as a function of position.

The wave function for a particle must be normalizable because

- A. the particle's momentum must be conserved.
- B. the particle cannot be in two places at the same time.
- C. the particle must be somewhere.
- D. the particle's charge must be conserved.

Which of the four possible wave functions are normalizable?

$$\psi_1(x) = Ae^{-x}, \text{ for all } x$$

$$\psi_2(x) = A \cos x, \text{ for all } x$$

$$\psi_3(x) = \begin{cases} Ae^x, & 0 \leq x \leq L \\ 0, & \text{for all other } x \end{cases}$$

$$\psi_4(x) = \begin{cases} Ax, & x \geq L \\ 0, & \text{for all other } x \end{cases}$$

A. $\psi_1(x)$

B. $\psi_2(x)$

C. $\psi_3(x)$

D. $\psi_4(x)$

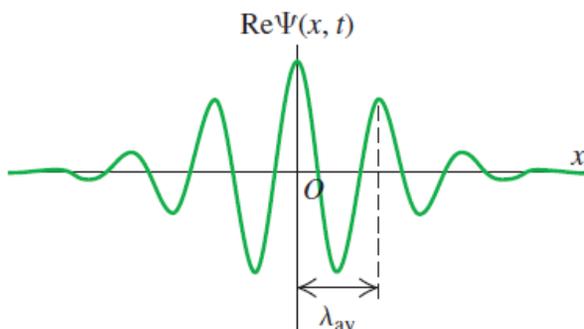
Wave packets

A pure sinusoidal wave extends from $-\infty$ to ∞ with the same amplitude, and therefore it can not be normalized. A wave packet is more localized by allowing the amplitude of a wave to be damped via a pulse-like envelope.

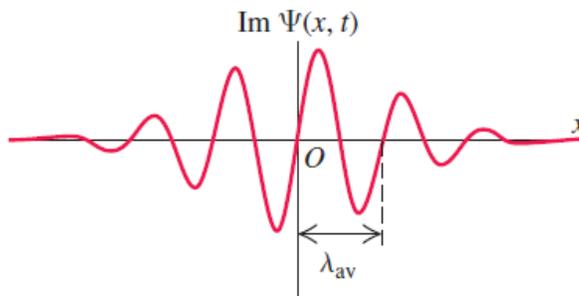
We may use an integral (continuum summation) to represent a superposition of many waves, each with a different wave number k and angular frequency $\omega = \hbar k^2/2m$ along with the k -dependent amplitude $A(k)$. The constructed wave packet is then of the form

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

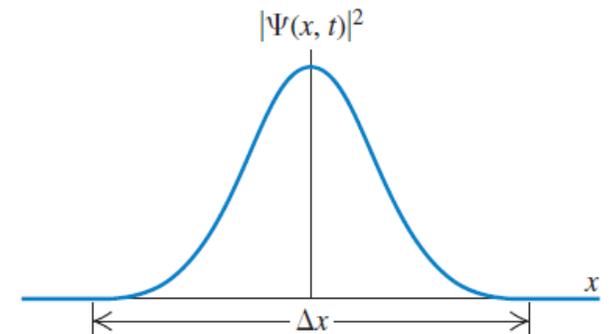
Real part of the wave function at time t



Imaginary part of the wave function at time t



Probability distribution function at time t



1D Schrodinger equation with potential energy

When a particle is influenced by a non-zero potential energy (example: electron trapped by a nucleus in an atom), then we must also portray this physics in the Schrodinger equation.

The one-dimensional Schrodinger equation for a single particle influenced by a position-dependent potential is

$$\left[\underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}}_K + \underbrace{U(x)}_U \right] \Psi(x, t) = \underbrace{i\hbar \frac{\partial}{\partial t}}_E \Psi(x, t)$$

Notice that the potential is not time dependent as written above, where the total energy on the right hand side of the equation is a constant total energy multiplied by the wavefunction (for a closed quantum system only).

Separation of variables & time dependent $\phi(t)$

Because each side of the Schrodinger equation is equal to the constant total energy multiplied by the wave function, we can separate the variables in the wave function and write

$$\Psi(x, t) = \psi(x) \phi(t)$$

Focusing on the right-hand-side of the Schrodinger equation, we know that

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

$$i\hbar \frac{\partial}{\partial t} \psi(x) \phi(t) = E \psi(x) \phi(t)$$

$$i\hbar \frac{d}{dt} \phi(t) = E \phi(t)$$

Setting the phase to zero when $t = 0$, the solution to the last equation is

$$\phi(t) = e^{-i \frac{E}{\hbar} t}$$

Thus, the wave function $\Psi(x, t)$ for a state of definite energy is the product of a time-independent wave function $\psi(x)$ and a factor $e^{-i \frac{E}{\hbar} t}$.

Stationary states

Focusing on the left-hand-side of the Schrodinger equation, we find

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \Psi(x, t) = E\Psi(x, t)$$
$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \psi(x) \phi(t) = E\psi(x) \phi(t)$$
$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E\psi(x)$$

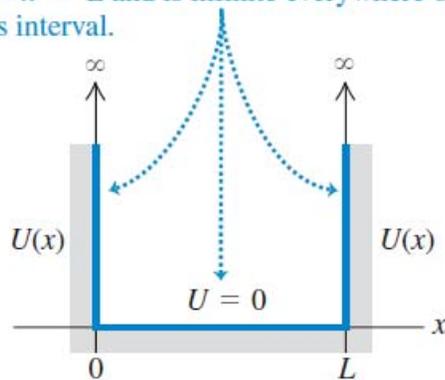
which is an equation that only depends on the position x . To solve this equation, however, we need information about the potential energy function.

An energy state of definite energy is called a stationary state. The probability density of a stationary state has the relationship

$$\begin{aligned} |\Psi(x, t)|^2 &= \Psi^*(x, t) \Psi(x, t) \\ &= \psi^*(x) \psi(x) e^{i\frac{E}{\hbar}t} e^{-i\frac{E}{\hbar}t} \\ &= |\psi(x)|^2 \end{aligned}$$

as determined by the time-independent Schrodinger equation given above.

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



Particle-in-a-box

The one-dimension particle-in-a-box potential (often referred to as the “infinite square well”) is the situation where a particle is “free” to move inside two hard boundaries of infinite potential,

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E\psi(x) \quad \text{where} \quad U(x) = \begin{cases} \infty & \text{for } x \leq 0 \\ 0 & \text{for } 0 < x < L \\ \infty & \text{for } x \geq L \end{cases}$$

The particle’s wave function has the same general form as the free particle, when inside the region $0 < x < L$,

$$\psi(x) = C \sin kx + D \cos kx$$

The probability of being outside the box in the regions $x \leq 0$ and $x \geq L$ is zero. Thus, $\psi(0) = 0$ and $\psi(L) = 0$ at the boundaries. The cosine is not zero when $x = 0$, and therefore we must conclude that the constant $D = 0$, which gives

$$\psi(x) = C \sin kx$$

Also, the condition $\psi(L) = 0$ means that only certain values of k are allowed,

Particle-in-a-box (continued)

The sine function is zero at the position L when $k_n = \frac{n\pi}{L}$. Therefore we may write

$$\psi_n(x) = C \sin\left(\frac{n\pi}{L}x\right) \quad \text{for } n = 1, 2, 3, \dots$$

The constant C is determined from the normalization condition

$$\begin{aligned} 1 &= \int_0^L \psi^*(x) \psi(x) dx \\ &= \int_0^L C^2 \sin^2\left(\frac{n\pi}{L}x\right) dx \\ &= C^2 \int_0^L \frac{1}{2} \left[1 - \cos\left(\frac{2n\pi}{L}x\right)\right] dx \\ &= C^2 \left[\frac{x}{2} - \frac{L}{2n\pi} \sin\left(\frac{2n\pi}{L}x\right)\right]_0^L = C^2 \frac{L}{2} \end{aligned}$$

We can solve for C , which gives $C = \sqrt{\frac{2}{L}}$. The wave function follows as

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

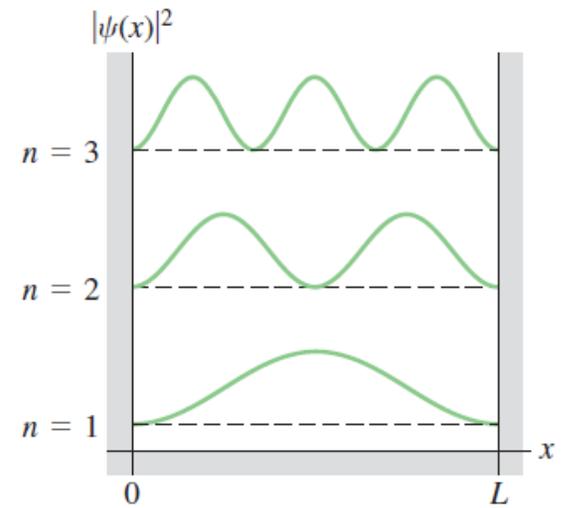
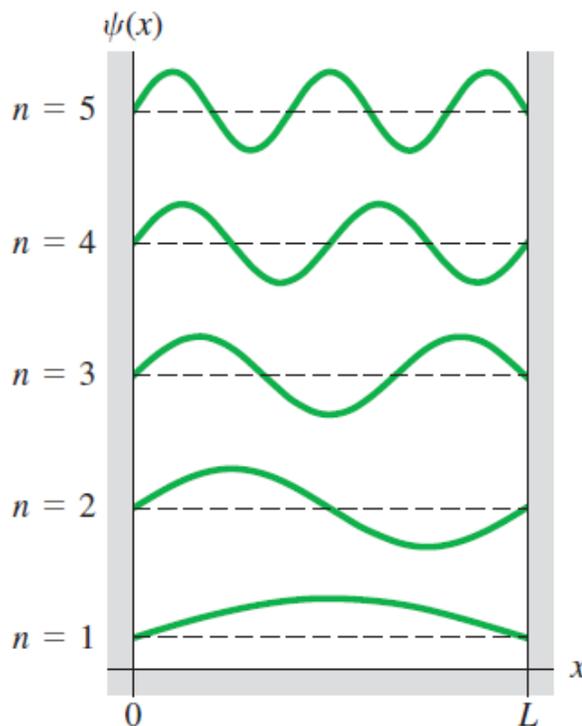
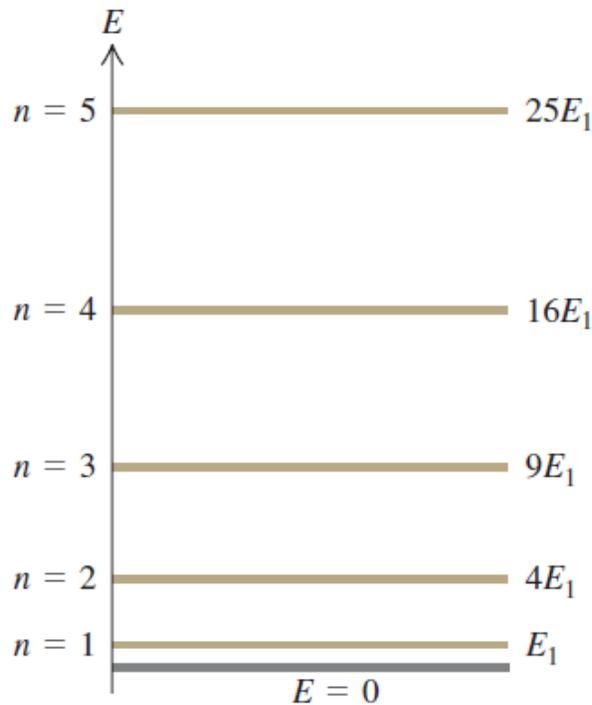
Particle-in-a-box (continued)

We previously learned particles behave like waves with momentum $p = \hbar k$.

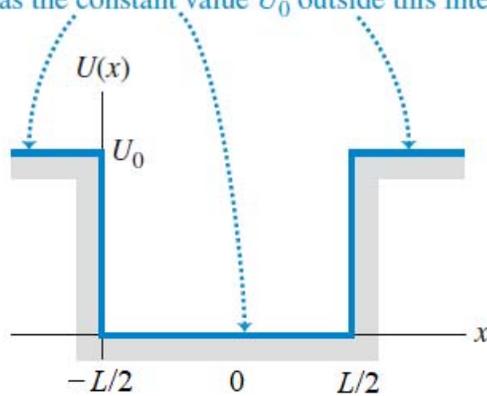
Substituting our the relationship for k_n , we find $p_n = \frac{n\pi\hbar}{L}$.

Finally, the energy is given by $E_n = \frac{p_n^2}{2m} + U$. Therefore, we may write the expression for the energy states,

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$



The potential energy U is zero within the potential well (in the interval $0 \leq x \leq L$) and has the constant value U_0 outside this interval.



Finite square well (FSW)

The finite square-well has a potential of zero over a certain length with a surrounding potential of U_0 stretching to infinity in both directions.

When the total energy of the particle is greater than U_0 , the particle is not trapped within the well. When the total energy of the particle is less than U_0 , then the particle will be bounded by the potential.

The Schrodinger equation is of the form

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E\psi(x) \quad \text{where} \quad U(x) = \begin{cases} U_0 & \text{for } x \leq -\frac{L}{2} \\ 0 & \text{for } -\frac{L}{2} < x < \frac{L}{2} \\ U_0 & \text{for } x \geq \frac{L}{2} \end{cases}$$

If the particle is not bound by the potential, and instead passes by it, then we expect to see a change in the wave function at the well's location. If the particle is bound, then we expect to see quantum mechanical bound states for sufficiently small L .

Finite square well's bound states

The potential inside the well is zero, and therefore we may write the free particle Schrodinger equation for the wave equation (inside the well only),

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

The wave function must satisfy the free particle wave equation in this region, where we have

$$\psi(x) = Ae^{i\frac{\sqrt{2mE}}{\hbar}x} + Be^{-i\frac{\sqrt{2mE}}{\hbar}x} \quad (\text{bound states inside})$$

$$\text{or } \psi(x) = C \sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) + D \cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) \quad (\text{bound states inside})$$

The potential outside the well is U_0 , where the Schrodinger equation is

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U_0\right] \psi(x) = E\psi(x) \quad \Longrightarrow \quad \frac{d^2}{dx^2} \psi(x) = \frac{2m(U_0 - E)}{\hbar^2} \psi(x)$$

For bound states, $E < U_0$. Thus, we get a real exponent for the wave function,

$$\psi(x) = Ge^{\kappa x} + He^{-\kappa x} \quad (\text{bound states outside})$$

where we have defined the parameter $\kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$ for simplicity.

Finite square well's bound states (continued)

The area under the curve is the probability, which must be normalizable.

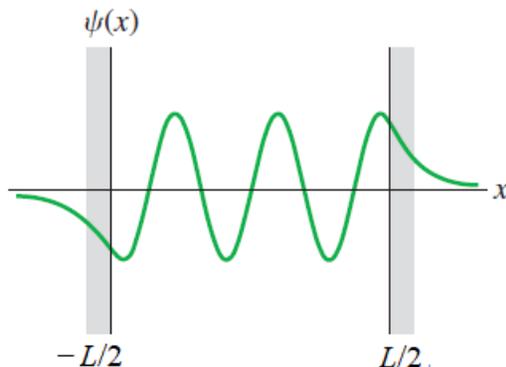
When $x < -L/2$ or when $x > L/2$, the wave function must not tend to infinity.

Thus, H must be zero when $x < -L/2$ and G must be zero when $x > L/2$.

We have to *match* the wave functions inside and outside the well so that they satisfy the boundary conditions for a physical system, i.e.,

$$\begin{aligned} \psi_{\text{out}}(-L/2) = \psi_{\text{in}}(-L/2) & \quad \text{and} \quad \frac{d}{dx}\psi_{\text{out}}(-L/2) = \frac{d}{dx}\psi_{\text{in}}(-L/2) \\ \psi_{\text{out}}(L/2) = \psi_{\text{in}}(L/2) & \quad \frac{d}{dx}\psi_{\text{out}}(L/2) = \frac{d}{dx}\psi_{\text{in}}(L/2) \end{aligned}$$

Matching the sinusoidal and exponential functions at both boundaries so that they join smoothly is possible only for specific values of the total energy E .

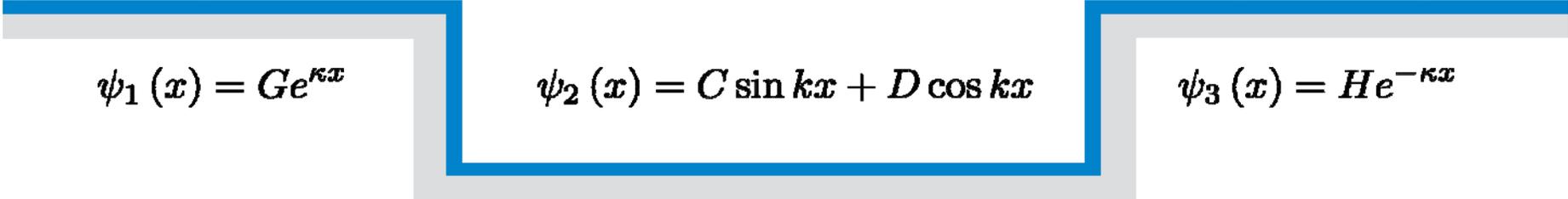


The bound states are sinusoidal functions that become exponential decaying curves outside the well. The finite decay means that there is some probability of finding it beyond the well, which is not at all like a classical phenomenon!!!

Bound energy levels of the FSW

There is no analytical solution to the finite square well; however, we can numerically determine the energy levels from our analysis of the bound states.

We can start by rewriting the wavefunction corresponding to the regions: (1) to the left of the well, (2) inside the well, (3) to the right of the well.


$$\psi_1(x) = Ge^{\kappa x}$$

$$\psi_2(x) = C \sin kx + D \cos kx$$

$$\psi_3(x) = He^{-\kappa x}$$

Again, the constants are given by $\kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$ and $k = \frac{\sqrt{2mE}}{\hbar}$.

The allowed wave modes can be symmetric ($n = 1, 3, 5, \dots$) where $C = 0$ and $G = H$ or antisymmetric ($n = 2, 4, 6, \dots$) where $D = 0$ and $G = -H$. Using our four boundary conditions, we get the following conditions:

symmetric ($n = \text{odd}$)

$$He^{-\kappa L/2} = D \cos\left(\frac{kL}{2}\right)$$

$$-\kappa He^{-\kappa L/2} = -Dk \sin\left(\frac{kL}{2}\right)$$

antisymmetric ($n = \text{even}$)

$$He^{-\kappa L/2} = C \sin\left(\frac{kL}{2}\right)$$

$$-\kappa He^{-\kappa L/2} = Ck \cos\left(\frac{kL}{2}\right)$$

Bound energy levels of the FSW (cont.)

We can divide the bottom condition equations by the top condition equations to get

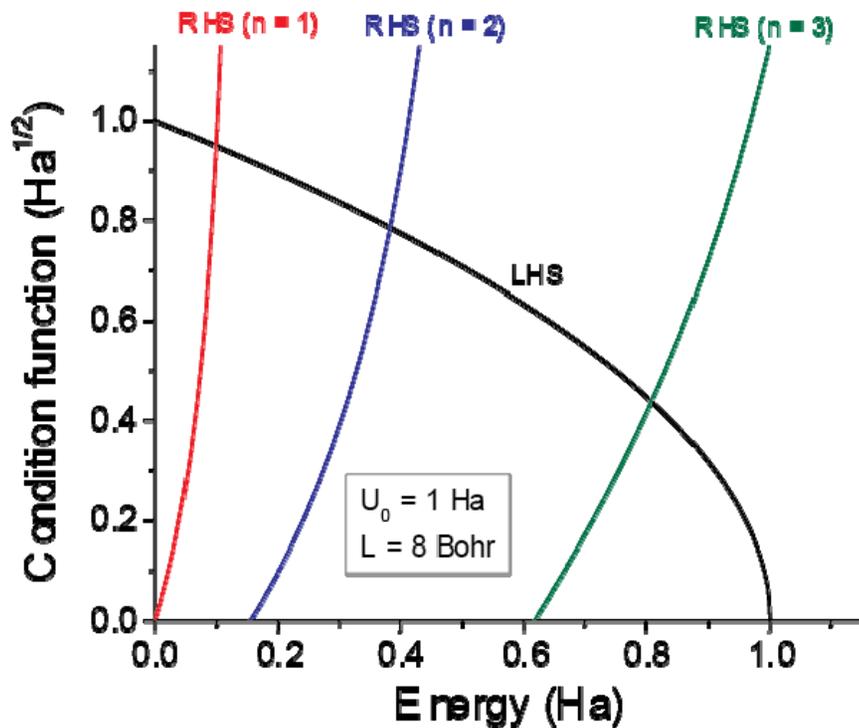
Symmetric (n = odd)

$$\kappa = k \tan\left(\frac{kL}{2}\right)$$

antisymmetric (n = even)

$$\kappa = -k \cot\left(\frac{kL}{2}\right)$$

Substituting the constants $\kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$ and $k = \frac{\sqrt{2mE}}{\hbar}$ back into the equations gives



symmetric (n = odd)

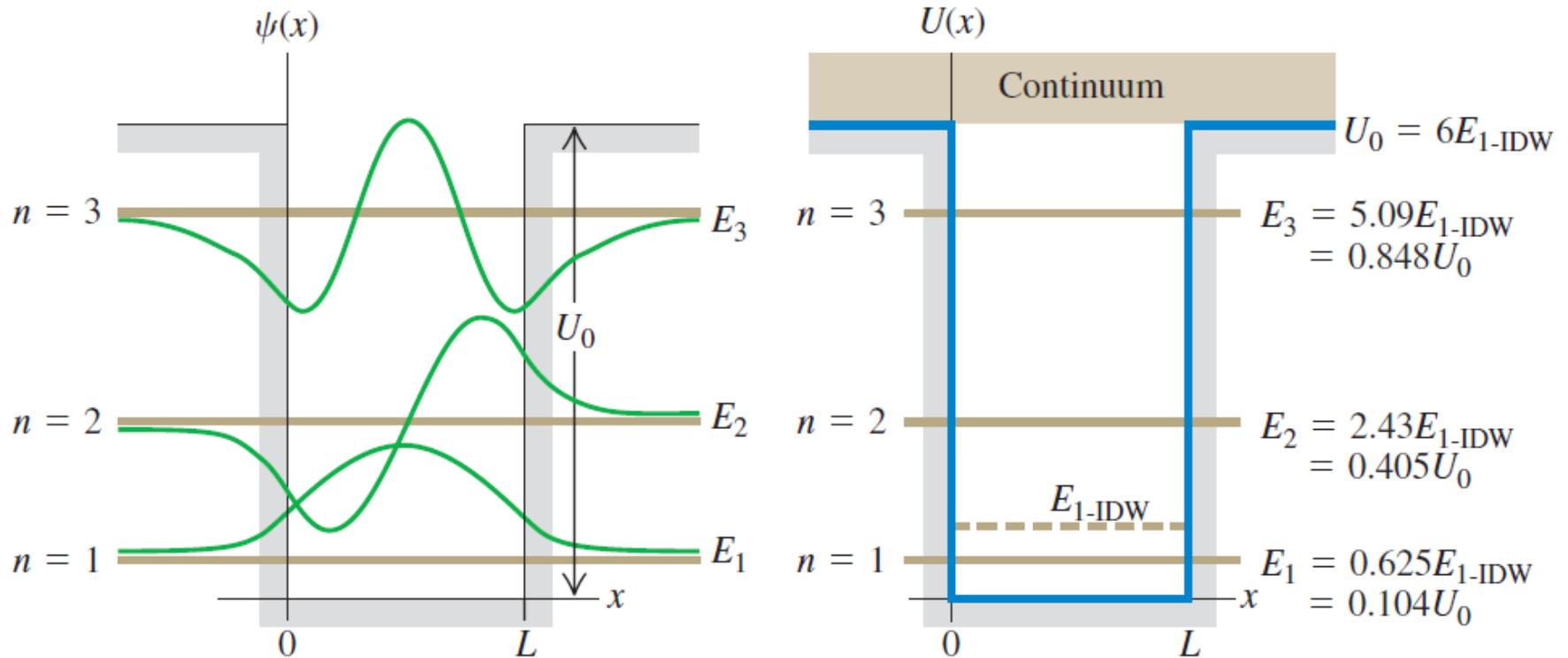
$$\frac{\sqrt{2m(U_0 - E)}}{\hbar} = \frac{\sqrt{2mE}}{\hbar} \tan\left(\frac{\sqrt{2mE}}{2\hbar}L\right)$$

antisymmetric (n = even)

$$\frac{\sqrt{2m(U_0 - E)}}{\hbar} = -\frac{\sqrt{2mE}}{\hbar} \cot\left(\frac{\sqrt{2mE}}{2\hbar}L\right)$$

Allowed energy levels occur when the left-hand-side equals the right-hand-side. Thus, we can scan through energies E until we find all E_n energy levels.

Wave functions and energy spectrum of FSW



E_{1-IDW} is the ground-level energy for an infinite well of the same width.



The ground state energy of a particle in a one-dimensional infinite potential well of width 1.5 nm is 20 eV. The ground state energy of the same particle in a one-dimensional finite potential well with $U_0 = 0$ in the region $0 < x < 1.5$ nm, and $U_0 = 50$ eV everywhere else, would be

A. equal to 20 eV.

B. greater than 20 eV.

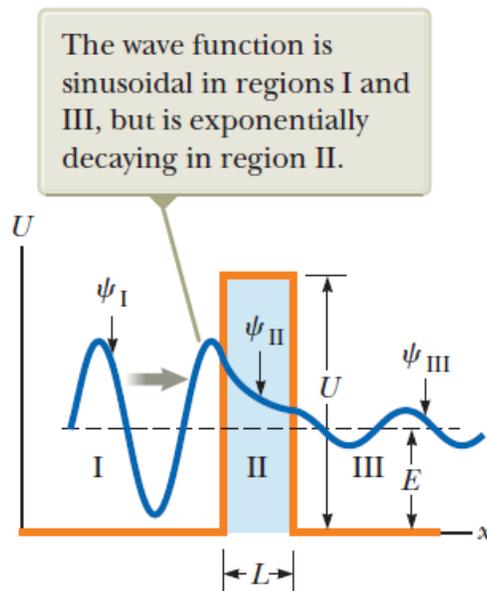
C. less than 20 eV.

D. The particle would not have a ground state.

Tunneling through a square barrier

Remember that we saw a probability of the particle existing outside the finite square well, even while in a bound state inside the square well.

This nonzero probability concept can be used to understand quantum tunneling phenomena, where particles can tunnel through barriers at the quantum scale.



Let us apply this concept to a finite square barrier.

$$U(x) = \begin{cases} 0 & \text{for } x \leq 0 \\ U_0 & \text{for } 0 < x < L \\ 0 & \text{for } x \geq L \end{cases}$$

The tunneling probability (transmission coefficient) T that the particle gets through the barrier is proportional to the square of the ratio of the amplitudes of the sinusoidal wave functions on the two sides of the barrier. The particle cannot disappear in this scenario, so there must be a reflection coefficient R .

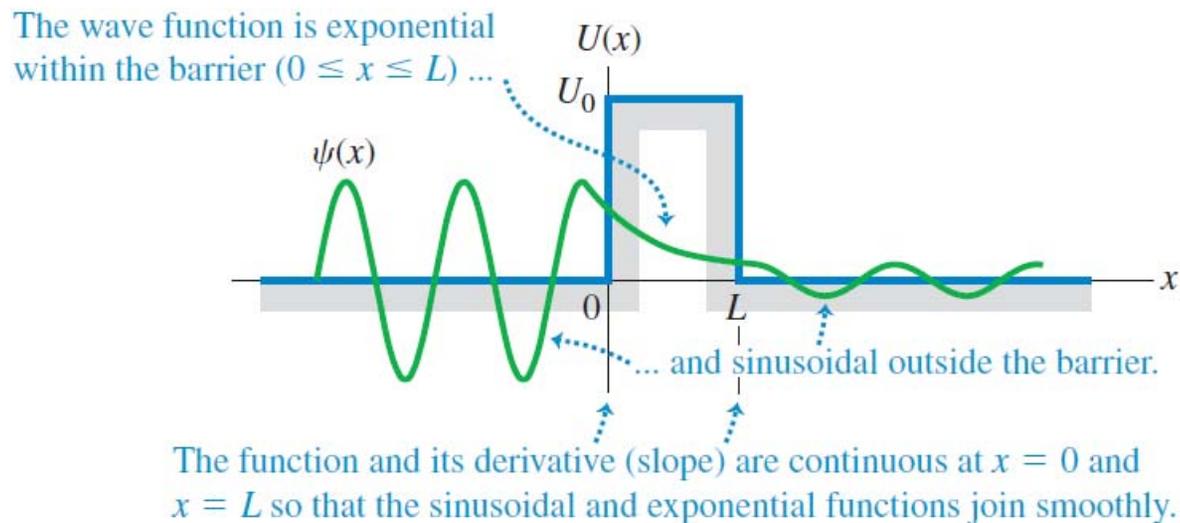
$$T + R = 1$$

Tunneling through a square barrier (cont.)

Matching the boundary conditions will give transmission coefficient. This process is quite mathematically rigorous. A good approximation can be used for the transmission coefficient when $E \ll U_0$ or when the barrier is lengthy,

$$T = 16 \frac{E}{U_0} \left(1 - \frac{E}{U_0} \right) e^{-2\kappa L}$$

where $\kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$ and E is the energy of the particle incident on the barrier.



Quantum harmonic oscillator

The classical harmonic oscillator is a mass subject to a force $F_x = -k'x$, where the equilibrium position is set to zero. Here k' is the spring constant, where the prime ' is used to keep it from being mistaken for the wave number.

The classical harmonic oscillator's potential energy follows as $U(x) = \frac{1}{2}k'x^2$.

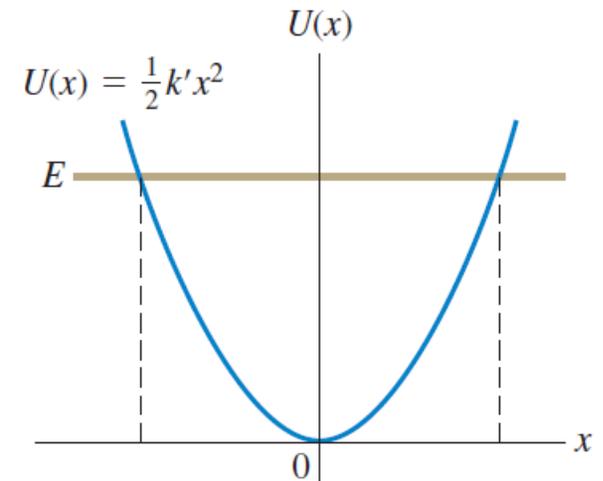
The quantum harmonic oscillator describes a particle in the harmonic oscillator potential at small quantum scales, *e.g.*, the oscillation between molecular bonds.

Just like the classical harmonic oscillator, the spring constant is related to the angular frequency,

$$\omega = \sqrt{\frac{k'}{m}}$$

The time-independent Schrodinger equation for the one-dimensional quantum harmonic oscillator is

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \right] \psi(x) = E\psi(x)$$



Quantum harmonic oscillator (cont.)

Although a rigorous pursuit, the one-dimensional quantum harmonic oscillator's stationary wave functions can be obtained from the Schrodinger equation. The normalized wave functions are based on the Hermite polynomials,

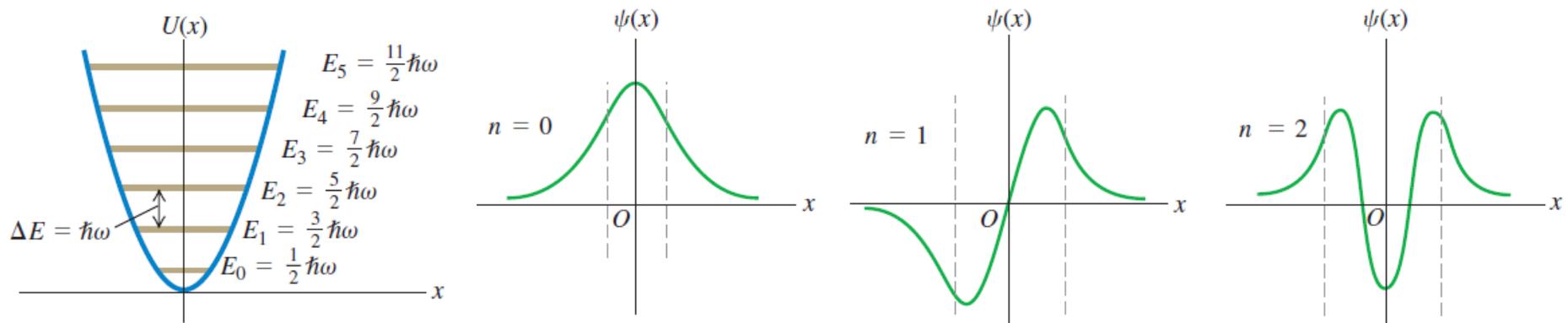
$$\psi(x) = \frac{1}{\sqrt{2^n n!}} \sqrt{\frac{m\omega}{\pi\hbar}} e^{-\frac{m\omega}{2\hbar}x^2} \mathcal{H}_n\left(\frac{m\omega}{\hbar}x\right)$$

where $n = 0, 1, 2, \dots$ and the Hermite polynomials are given by

$$\mathcal{H}_n(\rho) = (-1)^n e^{\rho^2} \frac{d^n e^{-\rho^2}}{d\rho^n}$$

The energy levels are linearly spaced,

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$





What is the main difference between Newtonian mechanics and quantum mechanics?

- A. Newtonian mechanics can be used to predict exactly where a particle will be at any given time, whereas quantum mechanics only gives probabilities.
- B. Newtonian mechanics is valid only for large objects, whereas quantum mechanics is valid only for very small objects.
- C. Energy is conserved only in Newtonian mechanics, not in quantum mechanics.
- D. Momentum is conserved only in quantum mechanics, not in Newtonian mechanics.