# 9/4/2024

- General Uncertainty Principle
- Wavefunctions
  - Constraints on wavefunctions
  - Penetration into barriers
  - Quantization
- Exponential solutions to the Schrodinger Equation
  - Free Particle, as a superposition of two or many states
  - Penetration, into a barrier with infinite width and finite height
  - Tunneling, through a barrier with finite width and finite height

- Particle in a box
- Harmonic Oscillator
- This lecture is designed to help you achieve the following learning objectives
  - Use the general uncertainty principle to evaluate limits on the simultaneous specification of a pair of quantities
  - Explain quantum tunneling
  - Obtain and interpret solutions of the Schrodinger equation for tractable systems including the particle in a box, harmonic oscillator, rigid rotor, and hydrogen atom

# General Uncertainty Principle

- Remember that if $[\hat{\mathbf{A}}, \hat{\mathbf{B}}] = 0$, the two operators commute
- According to the uncertainty principle,
  - If two operators commute, then their corresponding observables can be simultaneously specified.
  - If two operators do not commute, then their corresponding observables <u>cannot</u> be simultaneously specified. They are *complementary* observables.
- This is counterintuitive

- Heisenberg uncertainty principle: $\Delta x \Delta p_x \geq \dfrac{1}{2}\hbar$

- General uncertainty principle: $\Delta A \Delta B \geq \dfrac{1}{2}\left| \left\langle [\hat{\mathbf{A}}, \hat{\mathbf{B}}] \right\rangle \right|$, where $\Delta A = \left\{ \left\langle A^2 \right\rangle - \left\langle A \right\rangle^2 \right\}^{\frac{1}{2}}$

# GUT example

- Using the general uncertainty principle, evaluate the limitation on the simultaneous specification of kinetic energy and potential energy

- $$\left[\hat{\mathbf{T}}, \hat{\mathbf{V}}\right] f = \hat{\mathbf{T}}\hat{\mathbf{V}}f - \hat{\mathbf{V}}\hat{\mathbf{T}}f = -\frac{\hbar^2}{2m}\frac{d^2 Vf}{dx} + V\frac{\hbar^2}{2m}\frac{df}{dx}$$

- $$\frac{d^2 Vf}{dx^2} = \frac{d}{dx}\left[f\frac{dV}{dx} + V\frac{df}{dx}\right] = f\frac{d^2 V}{dx^2} + 2\frac{df}{dx}\frac{dV}{dx} + V\frac{d^2 f}{dx^2}$$

- $$\left[\hat{\mathbf{T}}, \hat{\mathbf{V}}\right] f = -\frac{\hbar^2}{2m}\left[f\frac{d^2 V}{dx^2} + 2\frac{df}{dx}\frac{dV}{dx}\right] = i\hat{\mathbf{C}}f$$

- Therefore, $\Delta T \Delta V \geq \dfrac{\hbar^2}{4m}\left|\left\langle \dfrac{d^2 V}{dx^2} + 2\dfrac{dV}{dx}\dfrac{d}{dx}\right\rangle\right|$

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# Properties of Wavefunctions

- Remember from the postulates,
  1. The state of a system is fully described by a function $\Psi(r_1, r_2, \ldots, t)$, known as the wavefunction
  
  4. The probability that a particle will be found in the volume element $d\tau$ at the point $r$ is proportional to $|\Psi(r)|^2 d\tau$.
  
  5. Satisfies the Schrodinger equation, $i\hbar\dfrac{\partial\Psi}{\partial t} = \hat{\mathbf{H}}\Psi$. If the potential energy is time-independent, then $\hat{\mathbf{H}}\Psi = E\Psi$. (In 1D, $\hat{\mathbf{H}}\Psi = -\dfrac{\hbar}{2m}\dfrac{\partial^2\Psi}{\partial x^2} + V(x)\Psi$.)

# Constraints

- Because $|\Psi|^2$ is a probability density that satisfies the Schrodinger equation, $\Psi$,

  - Cannot be infinite over a finite region
  - Must be single-valued
  - Have a second derivative, as the Schrodinger equation includes a second derivative. This implies that the function is continuous and has a continuous first derivative, except in ill-behaved regions of the potential.

# "Curvature" of wavefunctions

- Rearranging the 1D time-independent Schrodinger equation gives, $\frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2}(V-E)\Psi$, showing that "curvature" depends on the difference between the potential and total energy.
- In a classical system, what happens when all of the energy is converted into potential energy?
- In a quantum system, there is some probability of *penetration* into the classically forbidden region.

Potential Energy, V

Energy, E

Position, x

Wavefunction, $\Psi$

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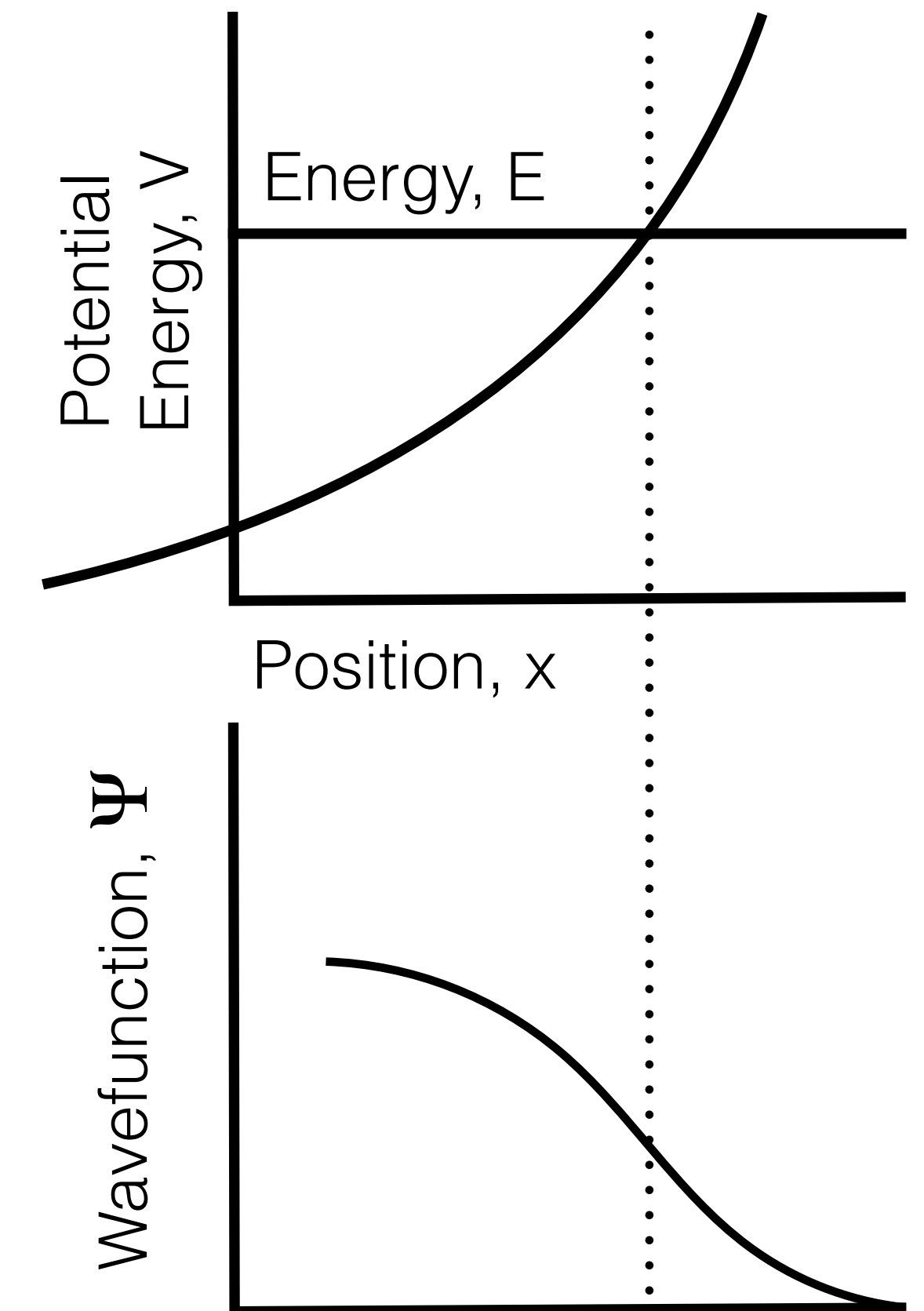
# Boundaries and Quantization

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

- As $x \to \infty$, the wavefunction must approach zero. For $\Psi(x) = y$,
  - If curvature too small, wavefunction goes to $\infty$
  - If curvature too large, wavefunction goes to $-\infty$
  - Thus only certain energies are allowable
- If a system is confined to a finite region of space, the energy is *quantized*
- If there is a single boundary, then energy is not quantized
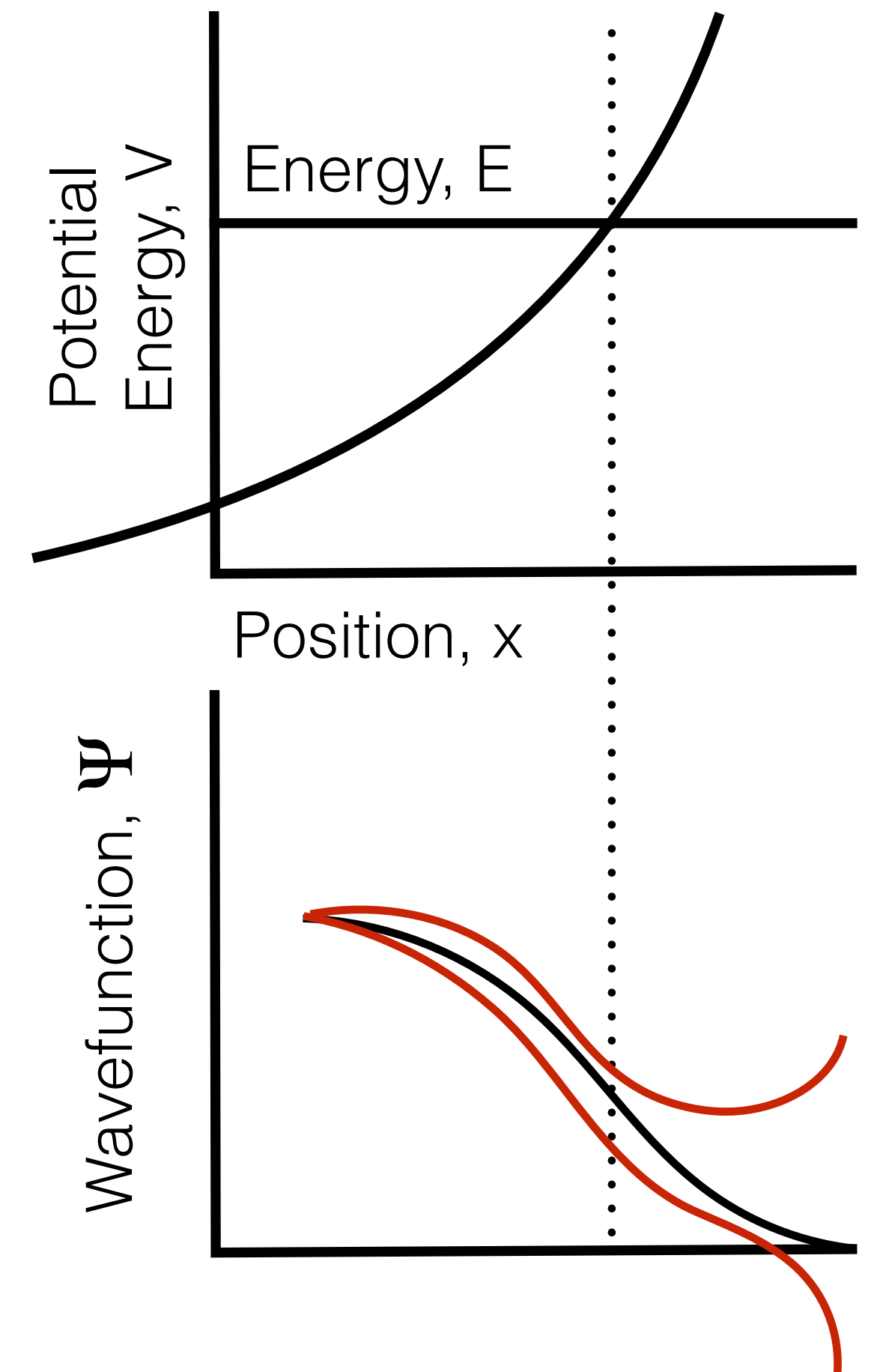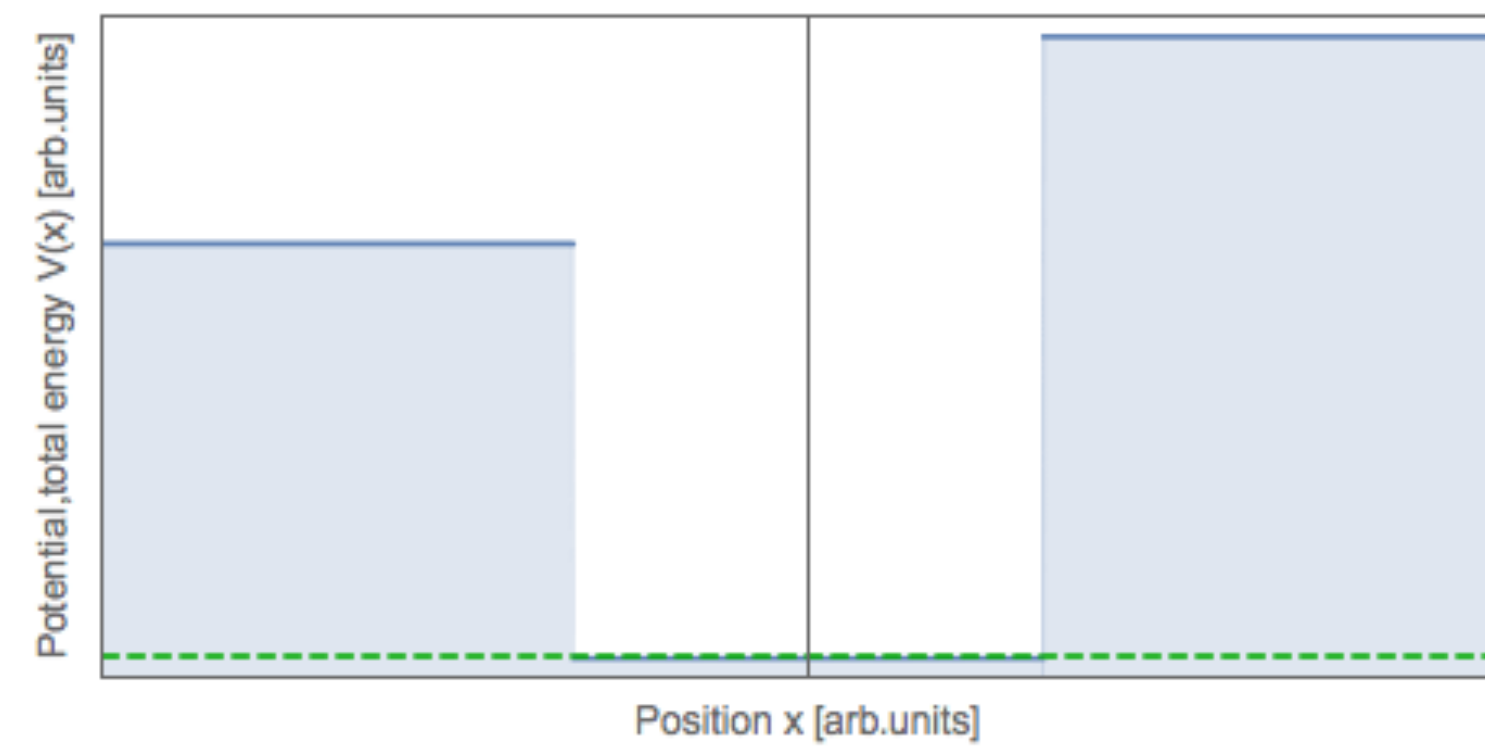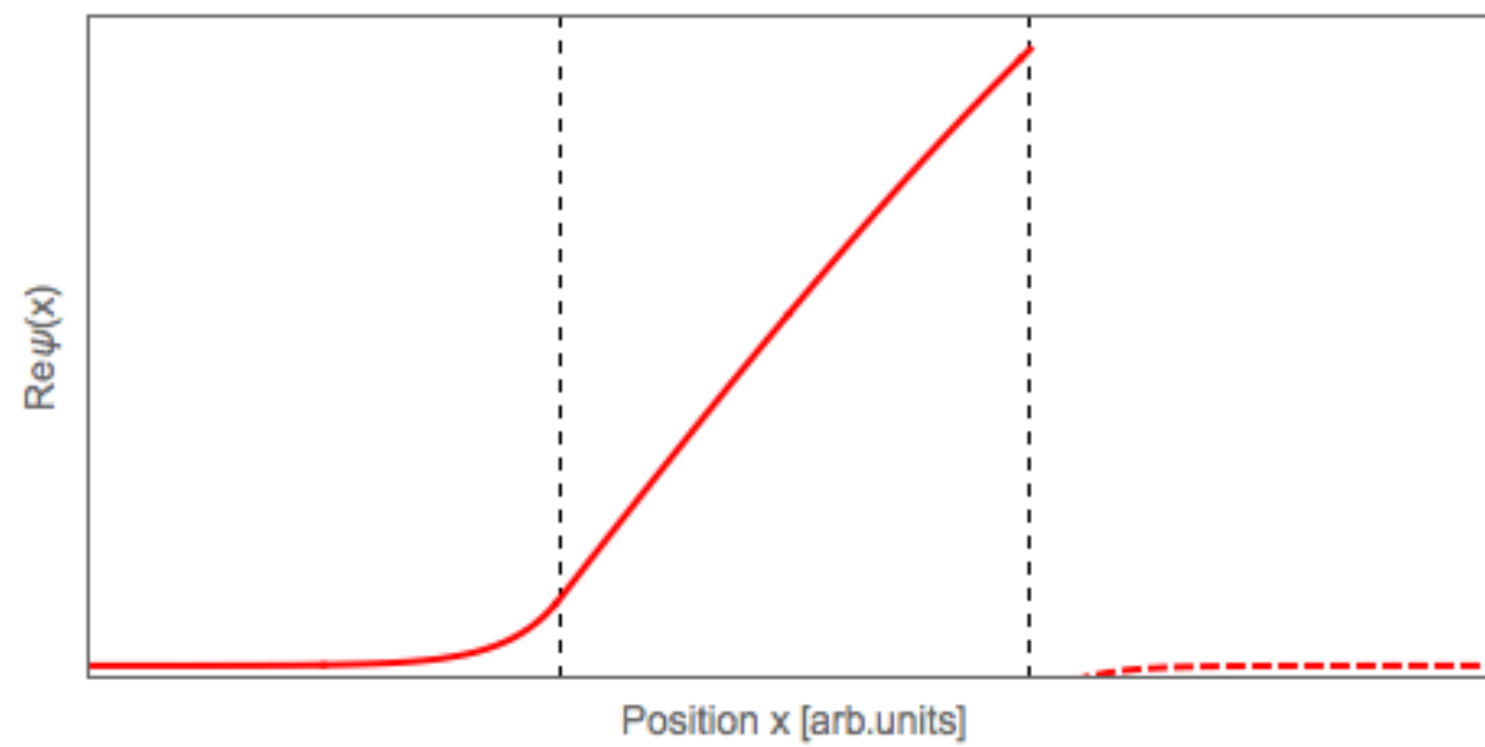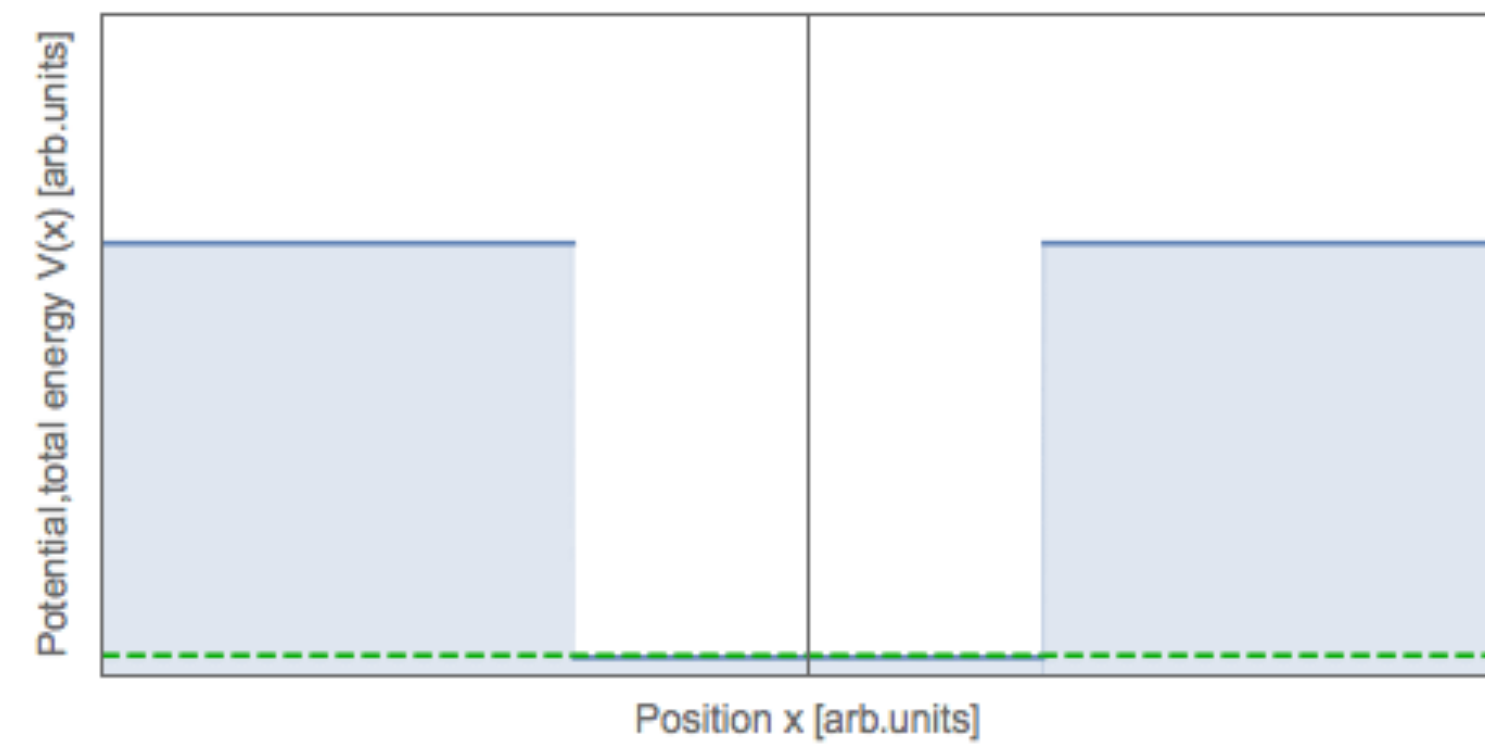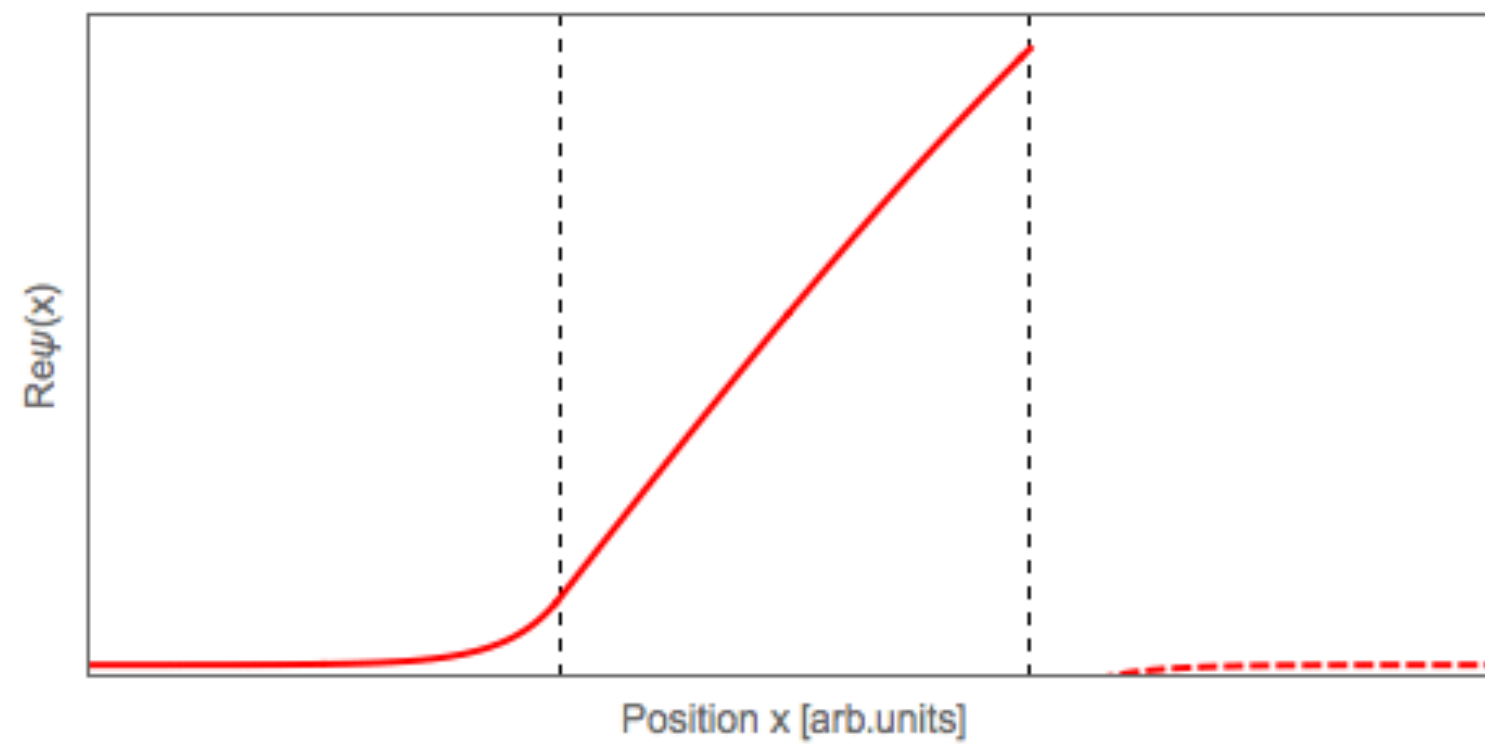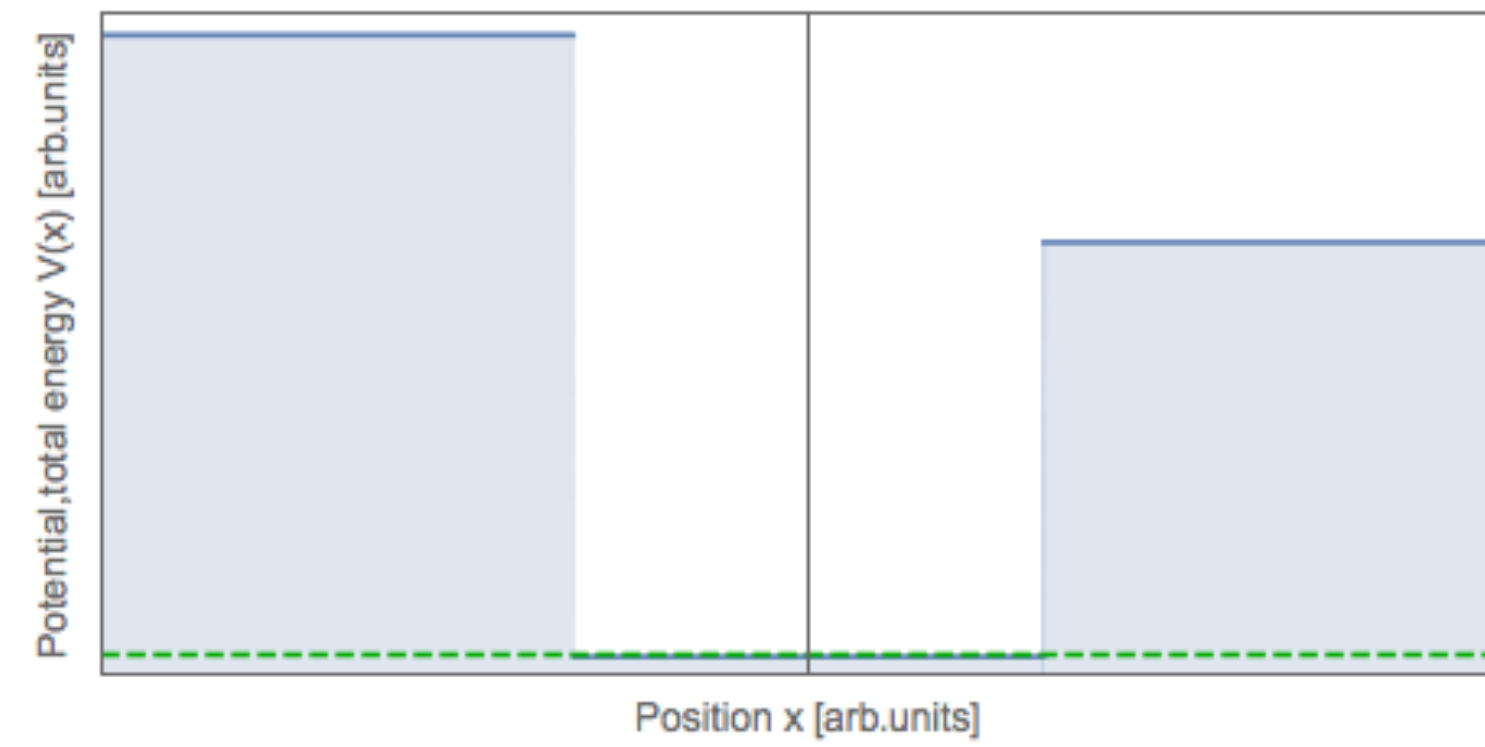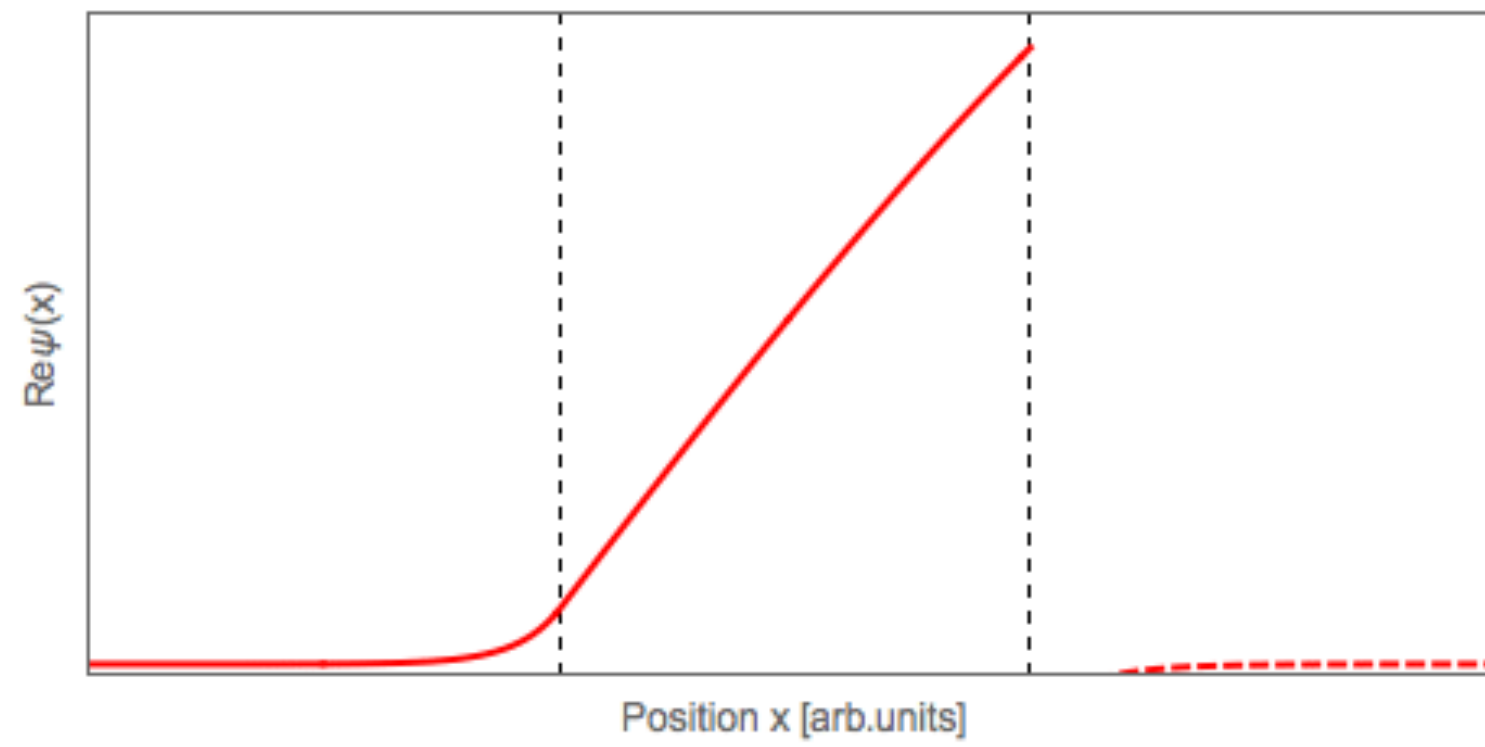
$$\frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2}(V - E)\Psi$$

Another way to look at it: if we force the wavefunction of a bound system to not blow up, it will only be continuous *for certain energies*

# Exponential Solutions

- For a 1D system with constant V, the time-independent Schrodinger equation is $-\dfrac{\hbar^2}{2m}\dfrac{d^2\Psi}{dx^2} + V\Psi = E\Psi$. When V = 0, the system is known as a free particle.

- The general solution is $\Psi = Ae^{ikx} + Be^{-ikx}$, with $k = \left(\dfrac{2m(E-V)}{\hbar^2}\right)^{1/2}$

- As Euler's formula is $e^{ix} = \cos(x) + i\sin(x)$, another way to write the general solution is, $\Psi = C\cos(kx) + D\sin(kx)$.

- Is there quantization? In other words, is E restricted to specific values?

  - No

# Self-test of Postulate 3

- Remember from postulate 3 that for an eigenfunction expansion $\Psi = \sum_m c_m \Psi_m$, the probability of measuring a particular eigenvalue $\omega_n$ is proportional to $|c_m|^2$.

- Given that $\Psi = Ae^{ikx} + Be^{-ikx}$, $k = \left( \dfrac{2mE}{\hbar^2} \right)^{1/2}$, and $\hat{\mathbf{p}} = \dfrac{\hbar}{i}\dfrac{d}{dx}$, what values of the linear momentum may be observed? What are their probabilities?

  - $p = \hbar k$ with probability $|A|^2$ and $p = -\hbar k$ with probability $|B|^2$

# Wave Packet

- If the wavefunction has the form $\Psi = Ae^{ikx} + Be^{-ikx}$, then there are
  - two possible momenta
  - one possible energy
- How well defined is the position?
  - It is a free particle
- A wave packet is a superposition of $\Psi = Ae^{ikx} + Be^{-ikx}$ with different k. The energy is less well defined, but position is better defined.



https://dkirkby.github.io/quantum-demo/
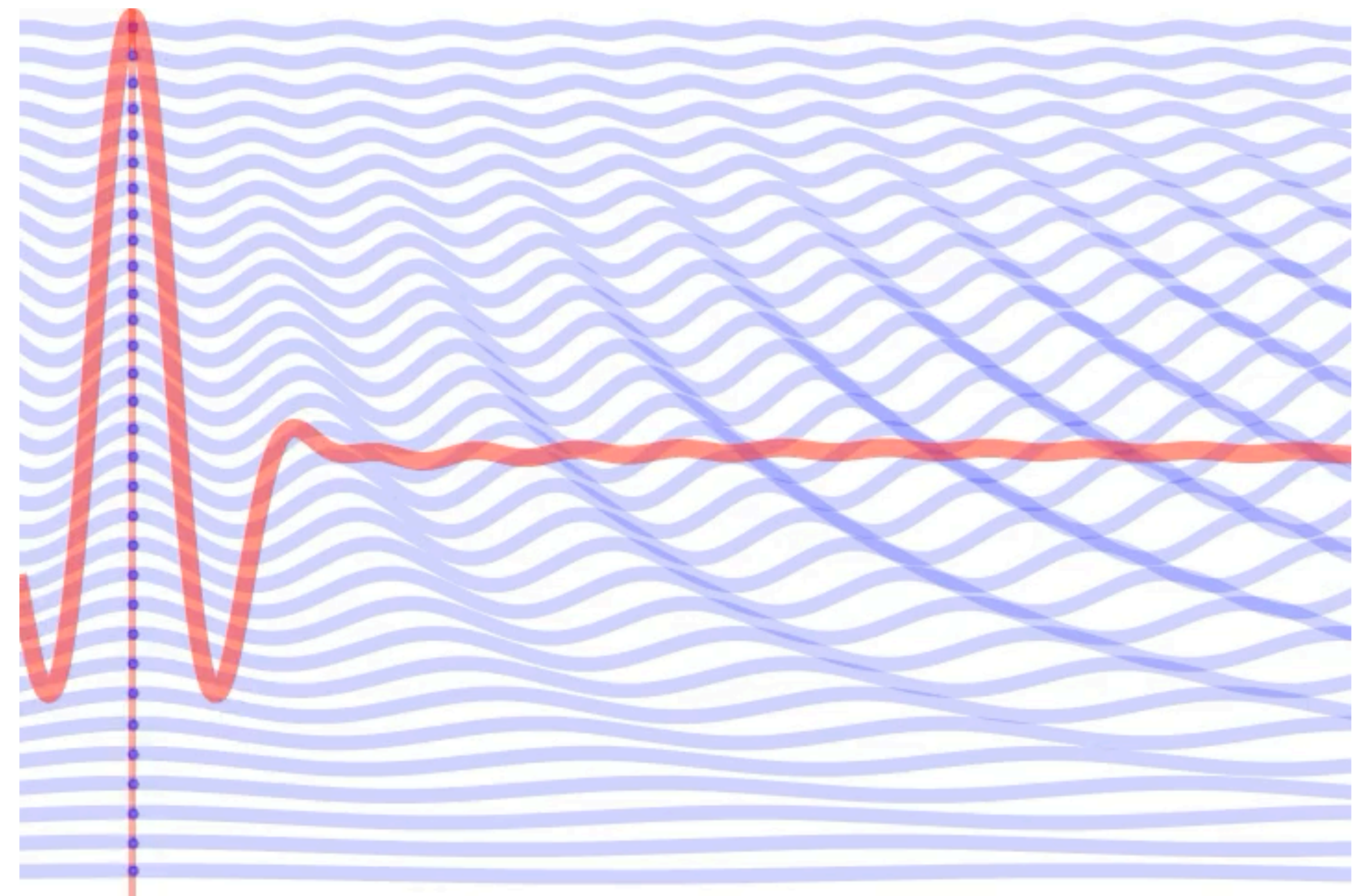
# Barrier with finite height & infinite width

- $V(x) = \begin{cases} 0 & \text{if } x < 0 \\ V & \text{if } x \geq 0 \end{cases}$

- Same general solution, different coefficients in different regions

$\infty \rightarrow$

0
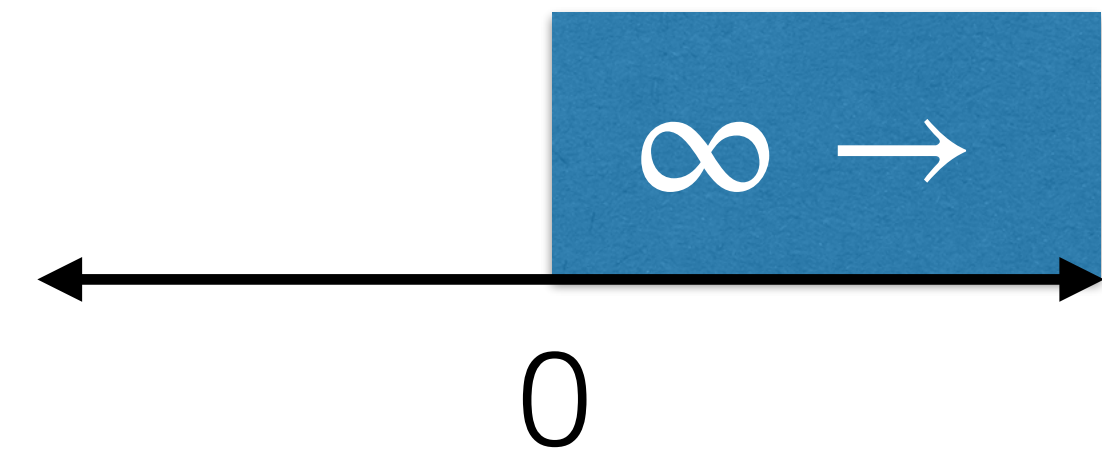
# Quantum Penetration

- Zone I (x < 0, V(x) = 0)
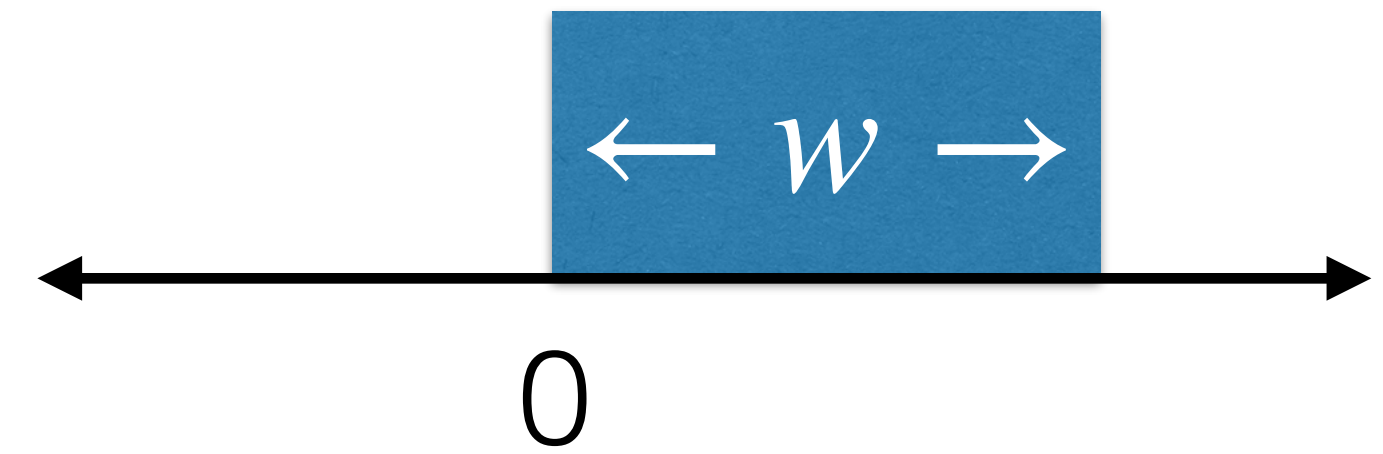
$$\Psi = Ae^{ikx} + Be^{-ikx}, k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$
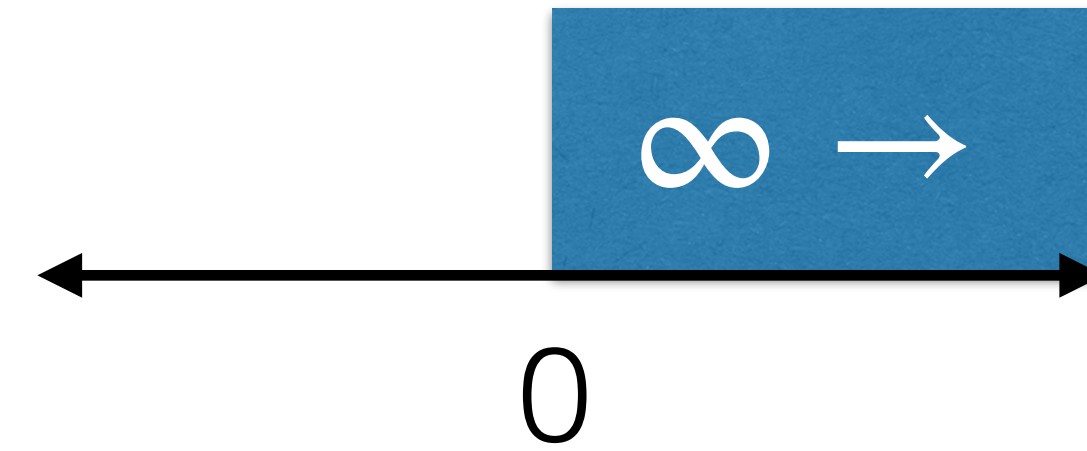
- Zone II (x > 0, V(x) = V):

$$\Psi = A'e^{ik'x} + B'e^{-ik'x}, k' = \left[\frac{2m(E-V)}{\hbar^2}\right]^{1/2}$$, where k' is imaginary. This is

nonzero, showing penetration

$$\Psi = A'e^{-\kappa'x} + B'e^{\kappa'x}, k = \left[\frac{2m(V-E)}{\hbar^2}\right]^{1/2}$$, where $k' = i\kappa'$. Thus, B' must be

zero. The wave function decays <u>exponentially</u> into the barrier.
- How does the extent of penetration depend on particle mass and energy?

# Barrier with finite height & finite width



$$V(x) = \begin{cases} 0 & \text{if } x < 0 \\ V & \text{if } 0 \le x < w \\ 0 & \text{if } x \ge w \end{cases}$$

- 
- Same general solution, different coefficients in different regions

# Quantum Tunneling

- Zone I (x < 0, V(x) = 0)
  - $\Psi = Ae^{ikx} + Be^{-ikx}$,
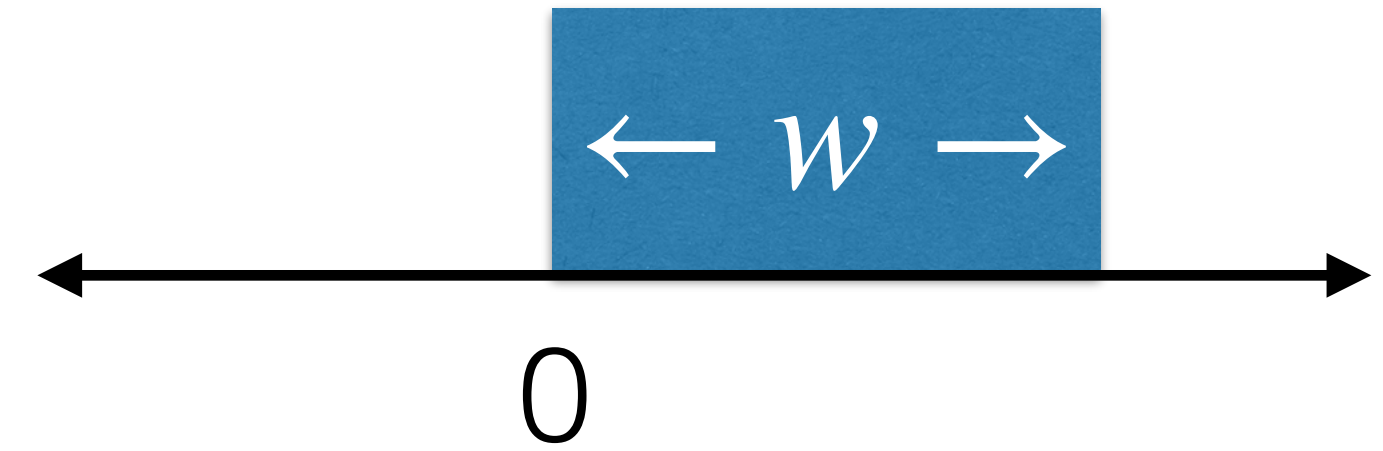
  $$k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

- Zone II (0 < x < w, V(x) = V):
  - $\Psi = A'e^{ik'x} + B'e^{-ik'x}$,

  $$k' = \left[\frac{2m(E - V)}{\hbar^2}\right]^{1/2}$$

- Zone III (x > w, V(x) = 0)
  - $\Psi = A''e^{ikx} + B''e^{-ikx}$
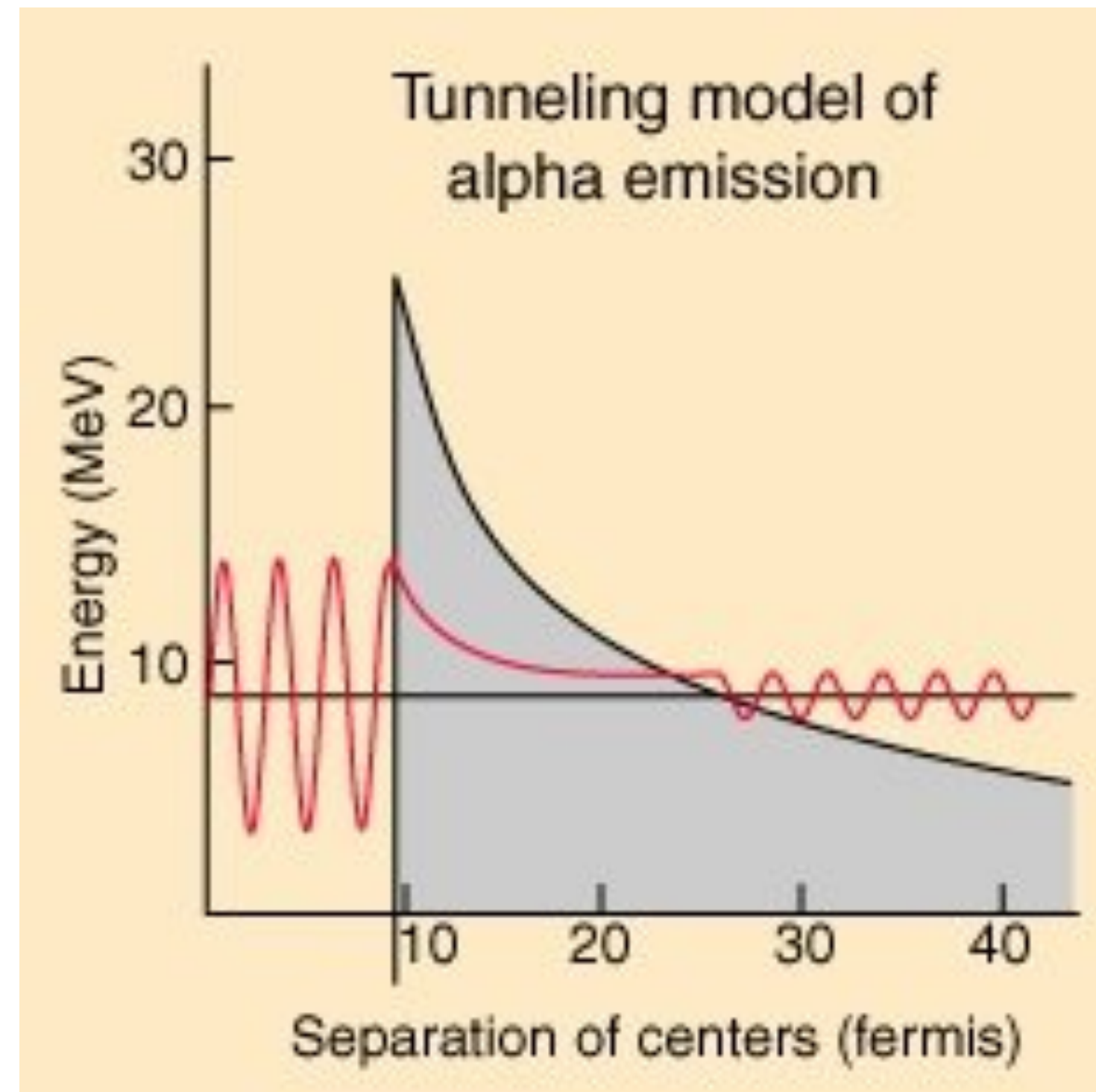
$$\leftarrow w \rightarrow$$

0

- For E<V, solution for tunneling probability is,
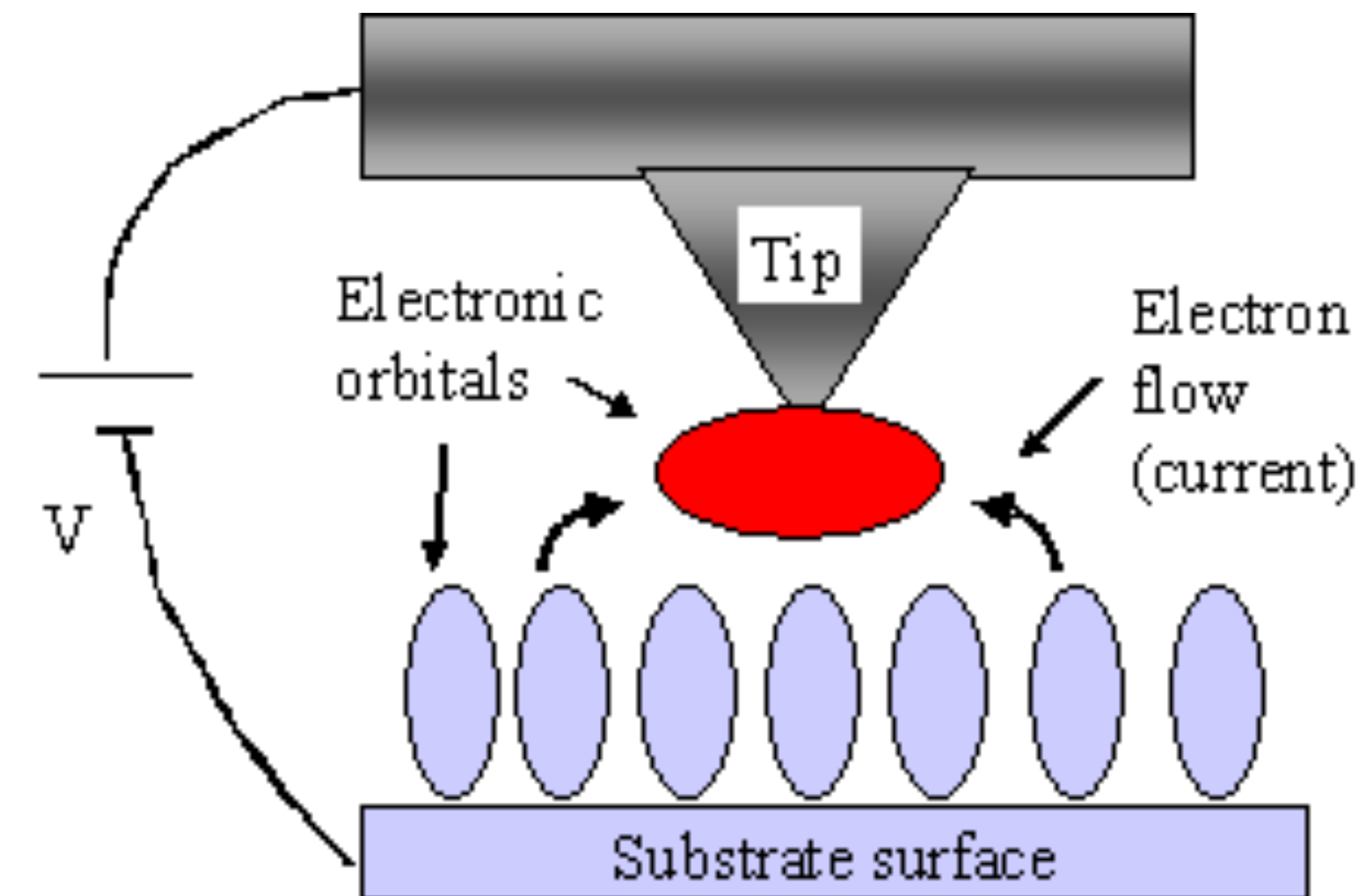  - $$T = \cfrac{1}{1 + \cfrac{e^{\kappa L} - e^{-\kappa L}}{16(E/V)(1 - E/V)}}$$
- Based on continuity of function and slopes

# Quantum Tunneling Applications



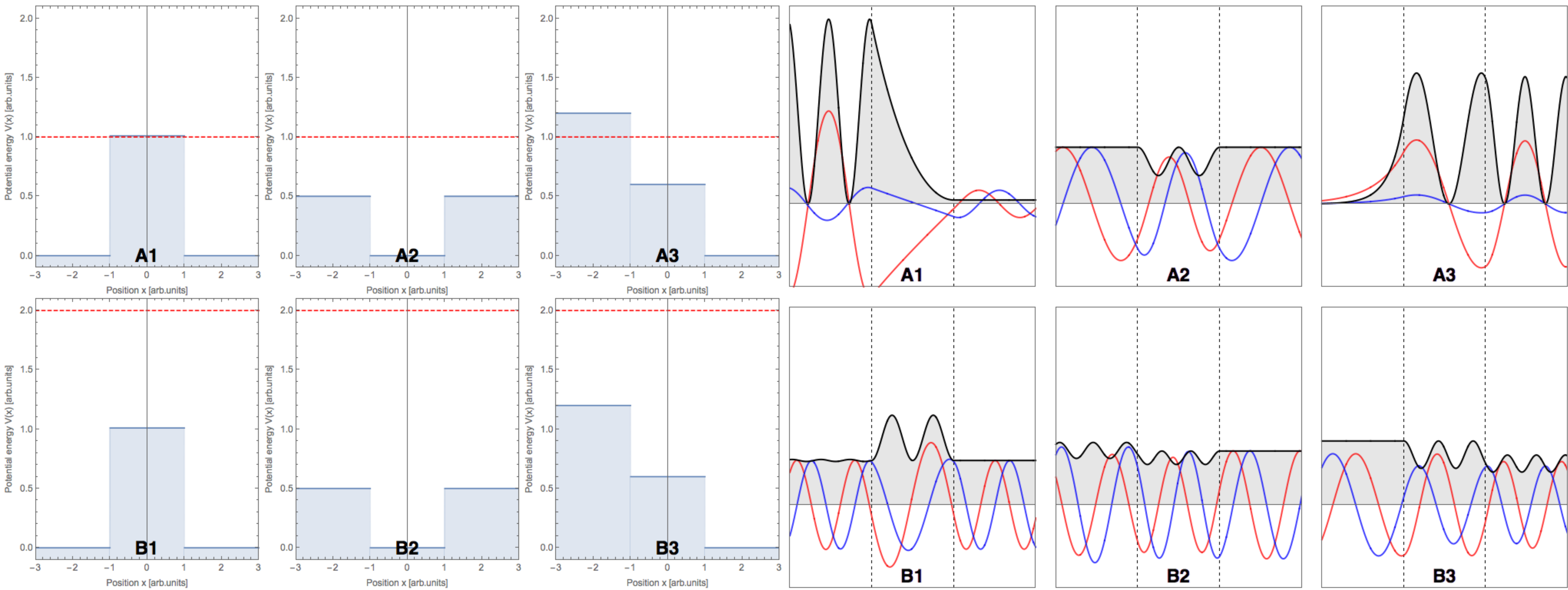https://physicsopenlab.org/2017/05/30/tunnel-effect/

Explaining α decay



https://minerva.union.edu/malekis/ESC24/KoskywebModules/cp_intr2.htm

Scanning Tunneling Microscopy

Potentials

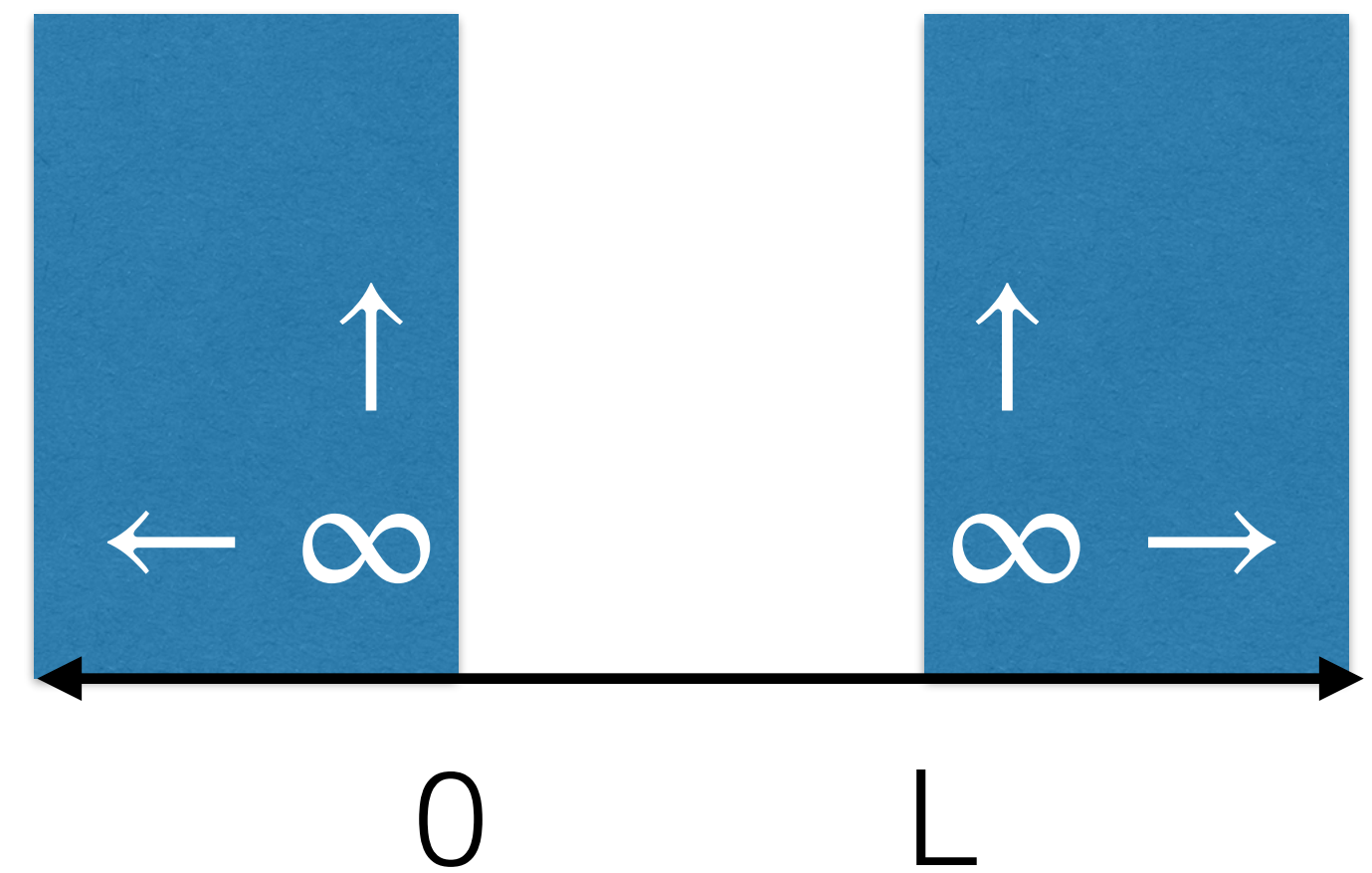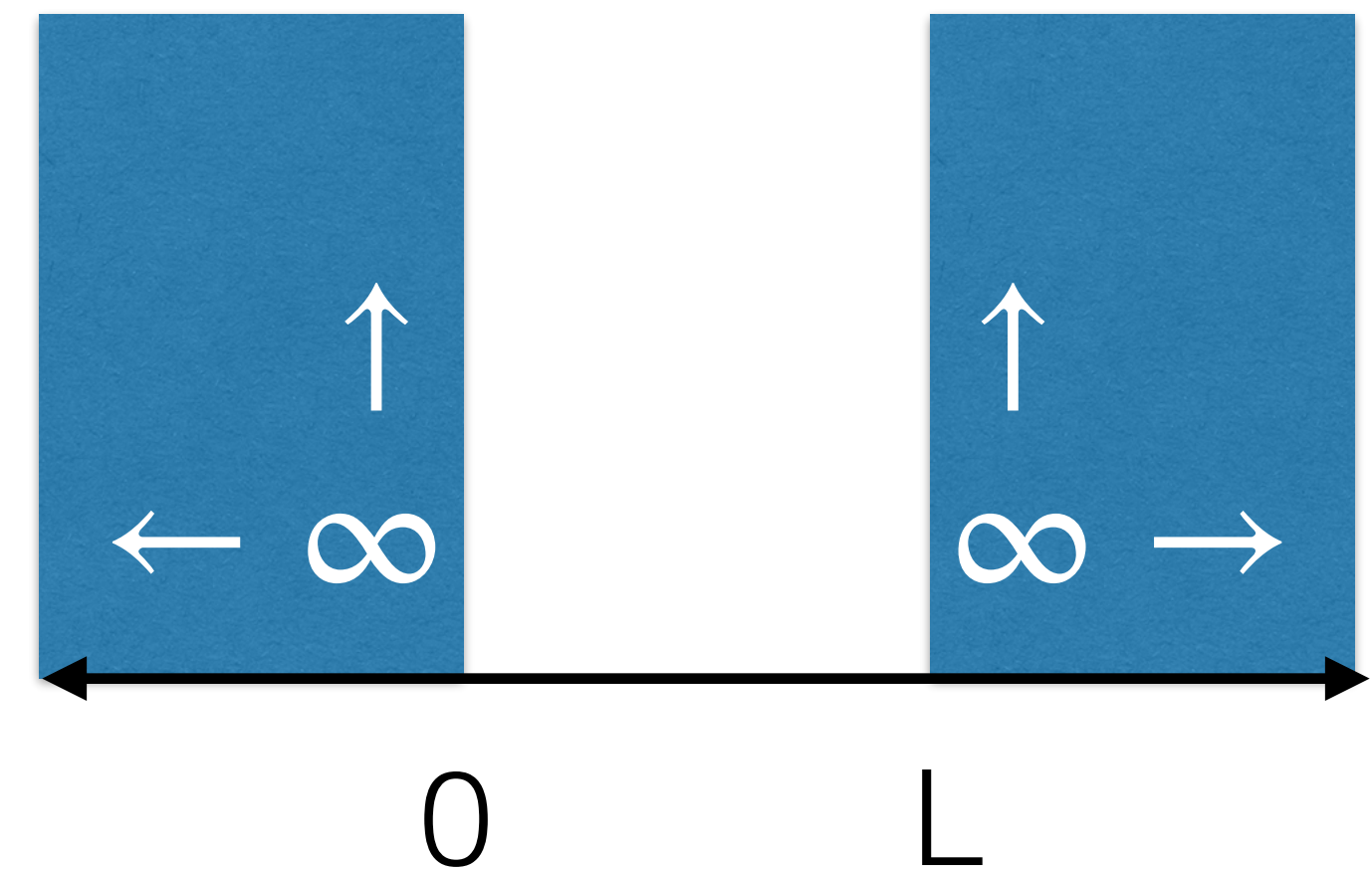Wavefunctions

# Particle in a Box

$$V(x) = \begin{cases} \infty & \text{if } x < 0 \\ 0 & \text{if } 0 \leq x < L \\ \infty & \text{if } x \geq L \end{cases}$$

# Solving the PIB

- Inside the box, the general solution is $\Psi = C\cos(kx) + D\sin(kx)$, where

$$k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

- Outside the box, $\Psi = 0$
- Because $\Psi(0) = 0$ and $\Psi(L) = 0, C = 0$.
- The solutions are $\Psi(x) = D\sin(kL)$, where

$$k = \frac{n\pi}{L}$$ to be zero at the boundaries



0      L

# PIB energies

- Setting two expressions for k equal, $\dfrac{\sqrt{2mE}}{\hbar} = \dfrac{n\pi}{L}$

- The allowable energies are $E = \dfrac{n^2\pi^2\hbar^2}{2mL^2} = \dfrac{n^2 h^2}{8mL^2}$, for n = 1, 2, …

- The PIB is a bound state with quantization

- The lowest possible energy for a particle is NOT zero (even at 0 K). This means the particle always has some kinetic energy.
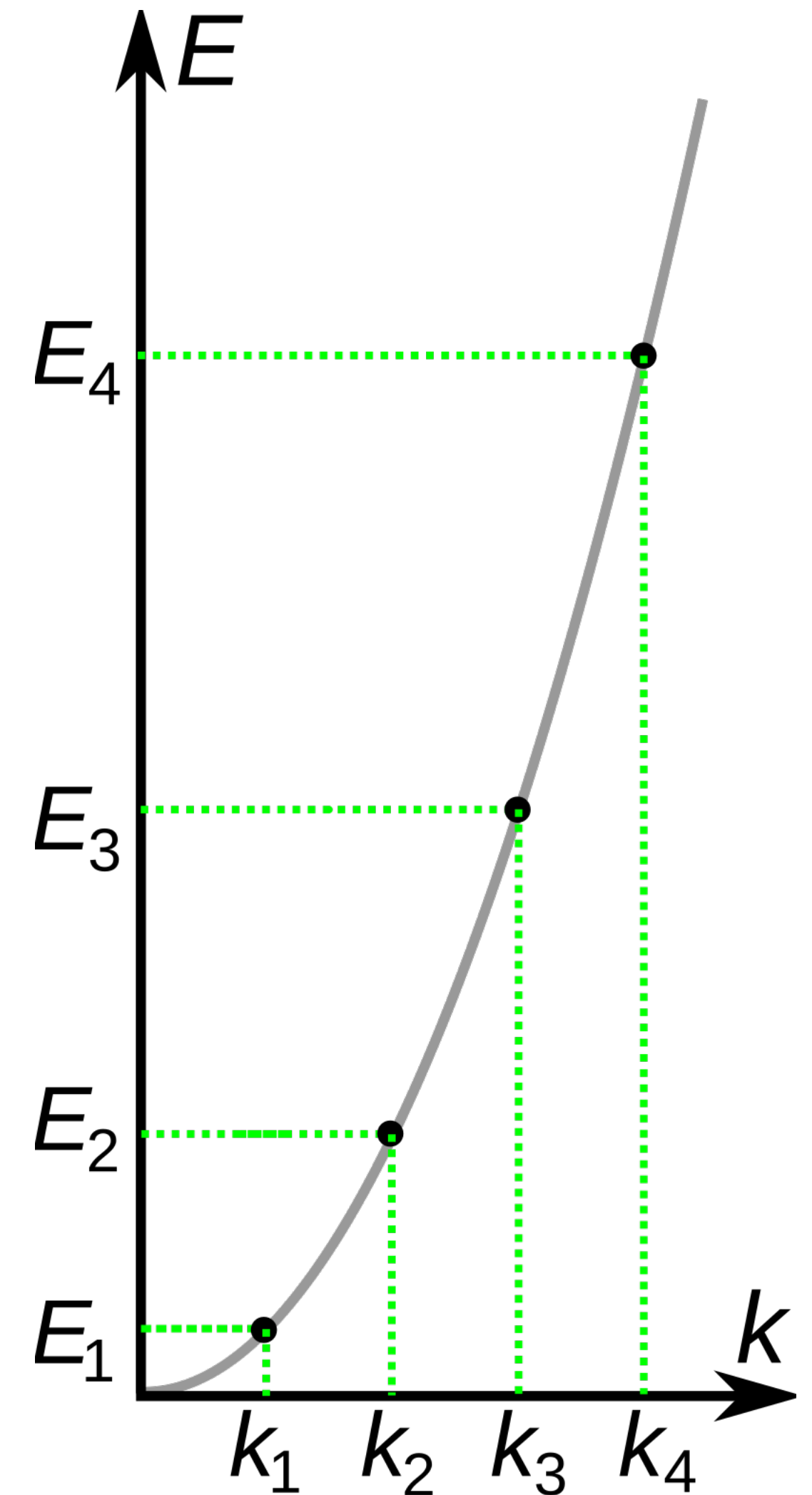


By Papa November - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=8652690

Nanocrystals are zero dimensional nanomaterials, which exhibit strong quantum confinement in all three dimensions, and thus they are also called "*quantum dots*".



UV light

Ambient light
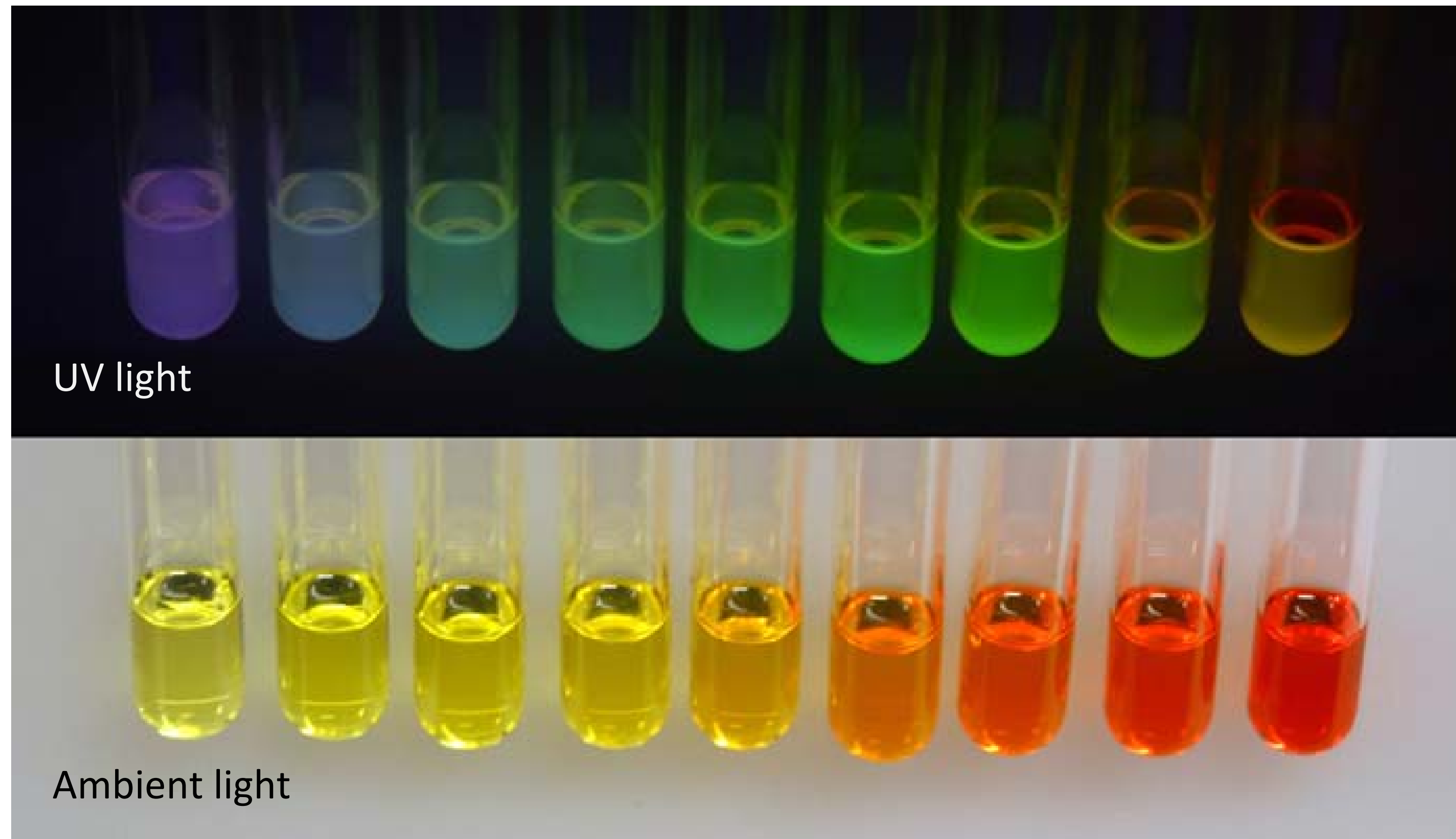
*Size dependent optical properties!*

# PIB wavefunctions

- In classical physics, the probability of finding the particle is independent of the energy and the same at all points in the box
- In QM, the square of the wavefunction is related to the probability of finding the particle in a specific position for a given energy level.
  - There are nodes where particles cannot be found!
  - At higher energy, the probability is more uniform

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



$n = 4$

$n = 3$

$n = 2$

$n = 1$
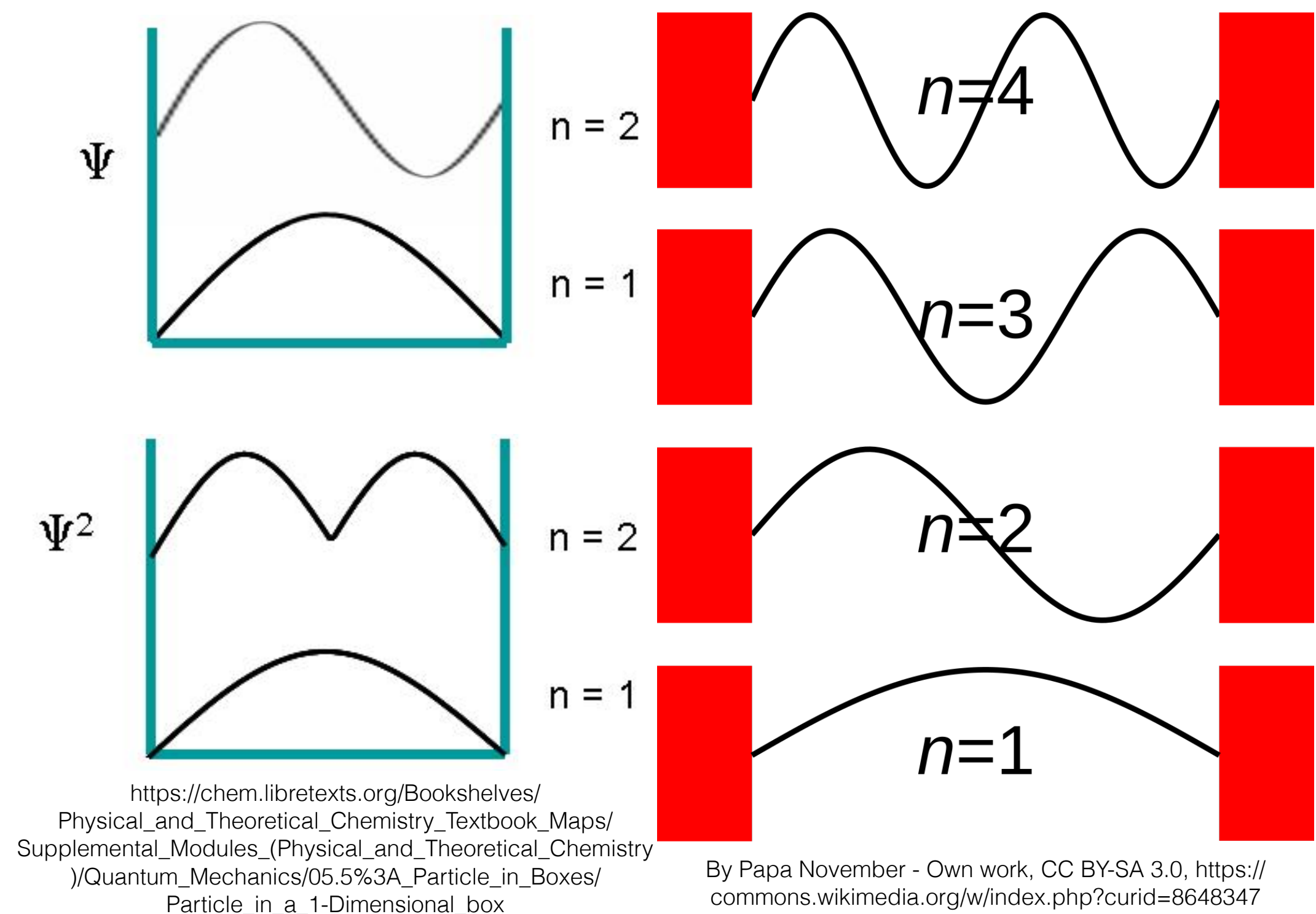
# 2D PIB

- Solution is based on separation of variables

- $\Psi_{n_1, n_2} = \dfrac{2}{\sqrt{L_1 L_2}} \sin\left(\dfrac{n_1 \pi x}{L_1}\right) \sin\left(\dfrac{n_2 \pi x}{L_2}\right)$

- $E_{n_1, n_2} = \dfrac{h^2}{8m}\left(\dfrac{n_1^2}{L_1^2} + \dfrac{n_2^2}{L_2^2}\right)$

- $n_1 = 1, 2, \ldots; n_2 = 1, 2, \ldots$

- Note that

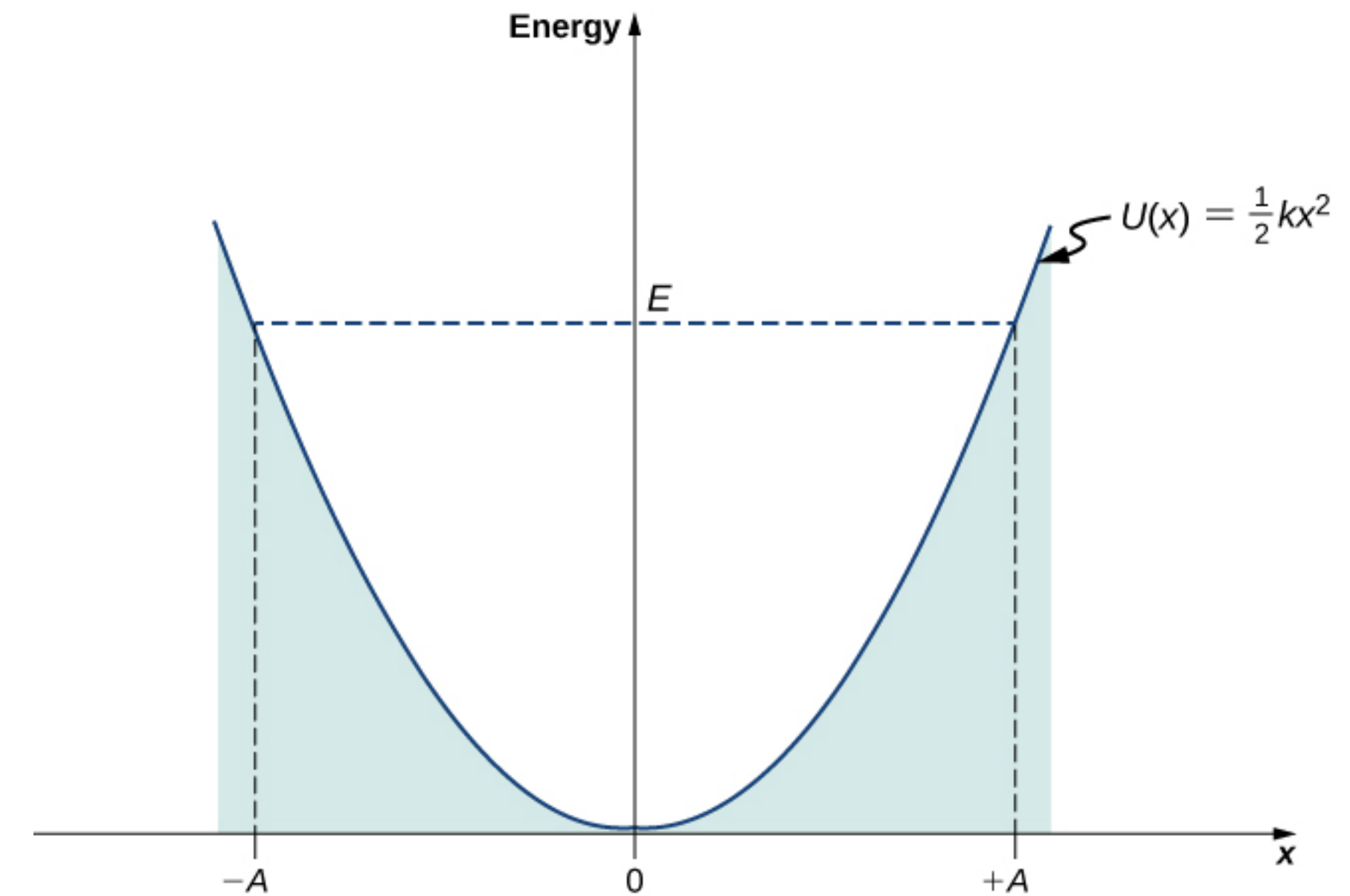- Like 1D, has a zero-point energy and is quantized

- If $L_1 = L_2$, then $E_{n_1, n_2} = \dfrac{h}{8mL^2}\left(n_1^2 + n_2^2\right)$ and there can be degeneracy, multiple states with the same energy

# Harmonic Oscillator

- $V(x) = \dfrac{1}{2}kx^2$

- It is qualitatively similar to a particle in a box. Are energies continuous or quantized?

  - Quantized

# HO Solutions

- The Hamiltonian is $\hat{\mathbf{H}} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2} + \dfrac{1}{2}k_f x^2$

- $\Psi_\nu(x) = N_\nu H_\nu(\alpha x)e^{-\alpha^2 x^2/2}$, where

- $N_\nu = \left(\dfrac{\alpha}{2^\nu \nu! \pi^{1/2}}\right)^{1/2}$ is for normalization

- $H_\nu(y) = (-1)^\nu e^{y^2}\dfrac{d^\nu}{dy^\nu}e^{-y^2}$

- $\alpha = \left(\dfrac{mk_f}{\hbar^2}\right)^{1/4}$

- $H_\nu$ are known as Hermite polynomials

- For $\nu = 0$, the solution is Gaussian

- The energies are $E_\nu = \left(\nu + \dfrac{1}{2}\right)\hbar\omega$, where

  $\nu = 0,1,2,...$

- $\omega = \sqrt{\dfrac{k_f}{m}}$

- $\nu$ starts at 0, not 1

- As energy increases, energy level spacings (a) increase, (b) decrease, or (c) stay constant?

  - (c) Stay constant

# HO Wavefunctions and Probability Densities
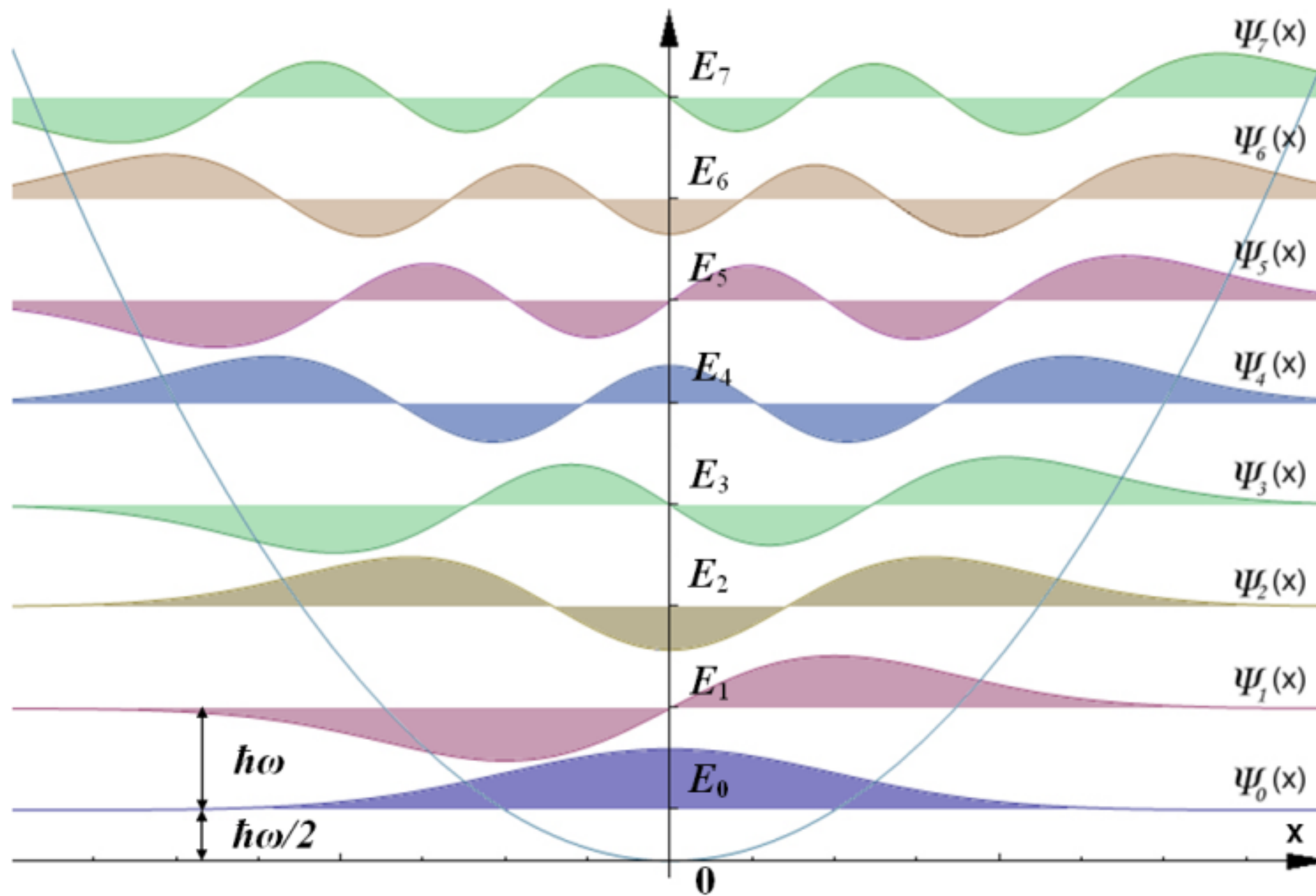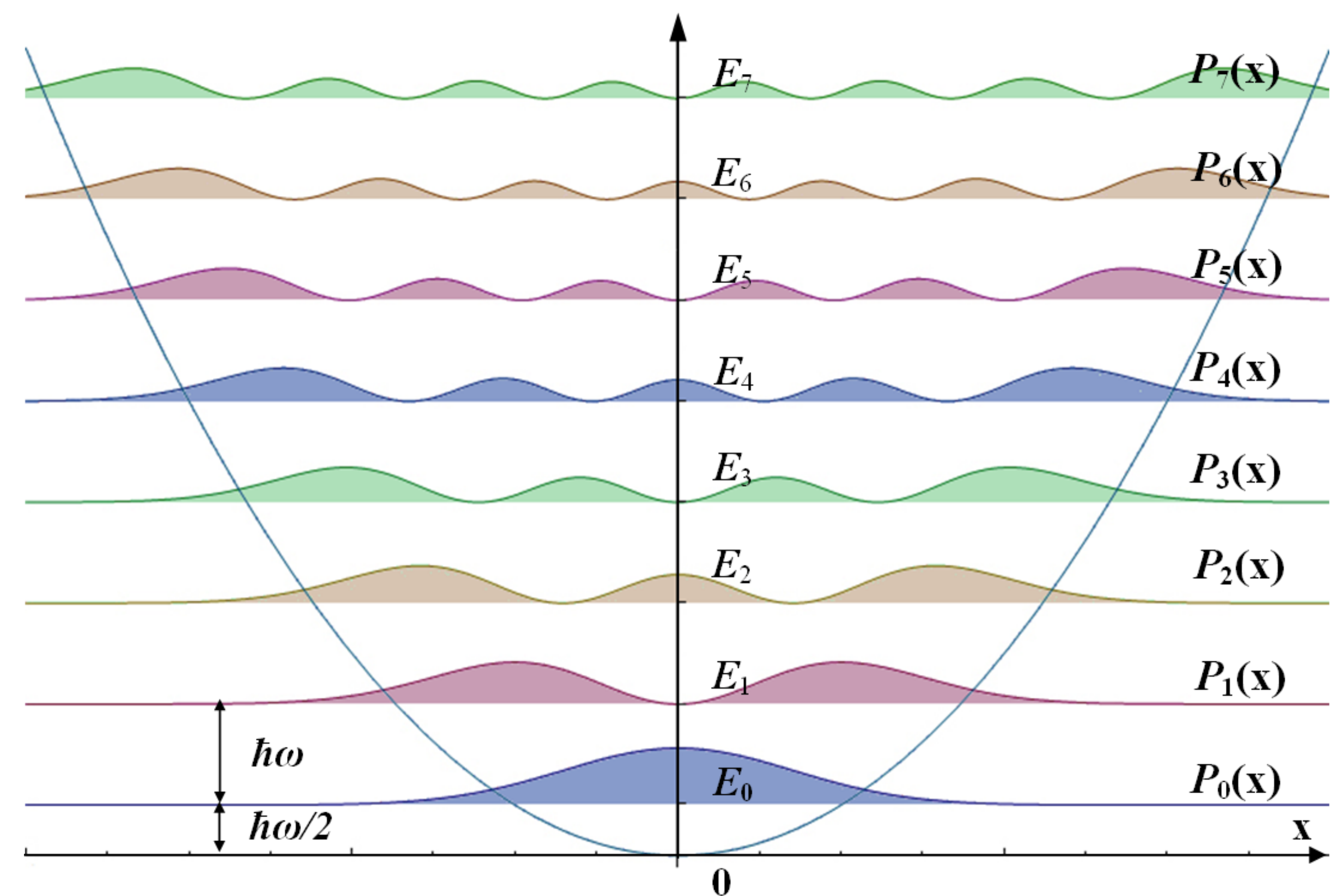
# HO Applications

- A good first-order model for any potential energy surface. There are anharmonicity corrections that are useful to better model potential energies.

- IR spectrum of a diatomic molecule

  - Only transitions between adjacent energy levels where there is a change in dipole moment are allowed.

  - These all have the same energy, the *fundamental vibrational frequency.*

  - 
$$\Delta E = \hbar\nu_{obs}, \text{ where } \nu_{obs} = \sqrt{\frac{k}{\mu}} \text{ and } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

# HO Example

- The oscillation of the atoms around their equilibrium positions in the molecule HI can be modeled as a harmonic oscillator of mass $m \approx m_H$ (the iodine atom is almost stationary) and force constant $k_f = 313.8 \ N \ m^{-1}$. Evaluate the separation of energy levels and predict the wavelength of light needed to induce a transition between neighboring levels.

- $$\omega = \sqrt{\frac{k_f}{m}} = \sqrt{\frac{313.8 \ \text{N m}^{-1}}{1.008 \times 10^{-3} \ \text{kg mol}^{-1}/6.022 \times 10^{23} \ \text{particles/mol}}}$$
$$= 4.33 \times 10^{14} \ \text{s}^{-1}$$

- $$\lambda = \frac{hc}{\Delta E} = \frac{hc}{\hbar \omega} = \frac{2\pi c}{\omega} = 4.35 \ \mu m$$

# Review

- What is the relationship between uncertainty and the commutator?
- When is energy quantized?
- What is the general solution of the time-independent Schrodinger equation for a free particle?
- What is quantum penetration and tunneling?
- How do PIB wavefunctions and energies differ from classical expectations?
- How do PIB and HO energy levels differ from each other?
- Name systems that the PIB and HO are good models for.