

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 cannot be simultaneously specified. They are *complementary* observables.
- This is counterintuitive
- Heisenberg uncertainty principle: $\Delta x \Delta p_x \geq \frac{1}{2} \hbar$
- General uncertainty principle: $\Delta A \Delta B \geq \frac{1}{2} \left| \left\langle [\hat{\mathbf{A}}, \hat{\mathbf{B}}] \right\rangle \right|$, where $\Delta A = \left\{ \langle A^2 \rangle - \langle A \rangle^2 \right\}^{\frac{1}{2}}$

Properties of Wavefunctions

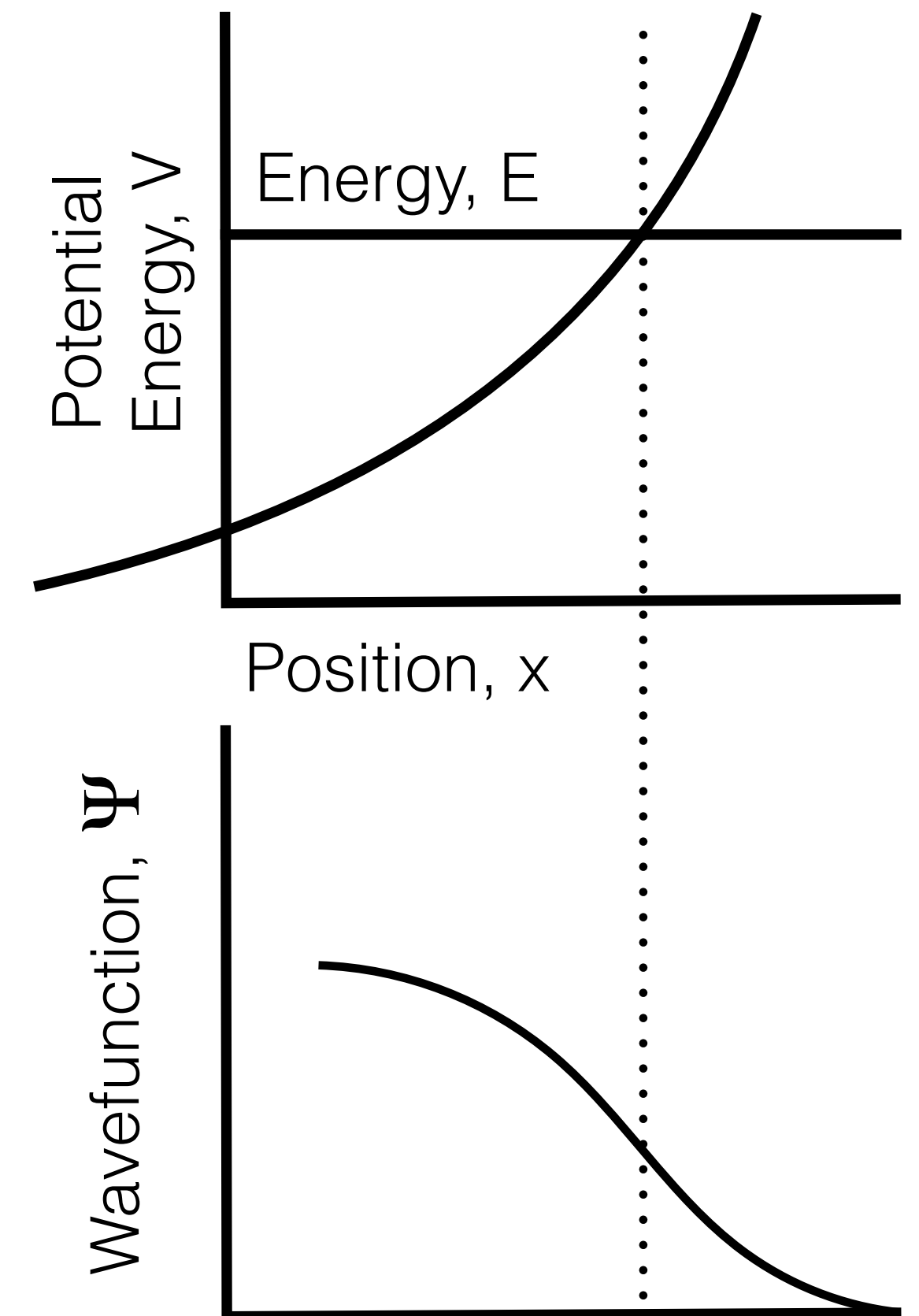
- Remember from the postulates,
 1. The state of a system is fully described by a function $\Psi(r_1, r_2, \dots, t)$, known as the wavefunction
 4. The probability that a particle will be found in the volume element $d\tau$ at the point r is proportional to $|\Psi(r)|^2 d\tau$.
 5. Satisfies the Schrodinger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

Constraints

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

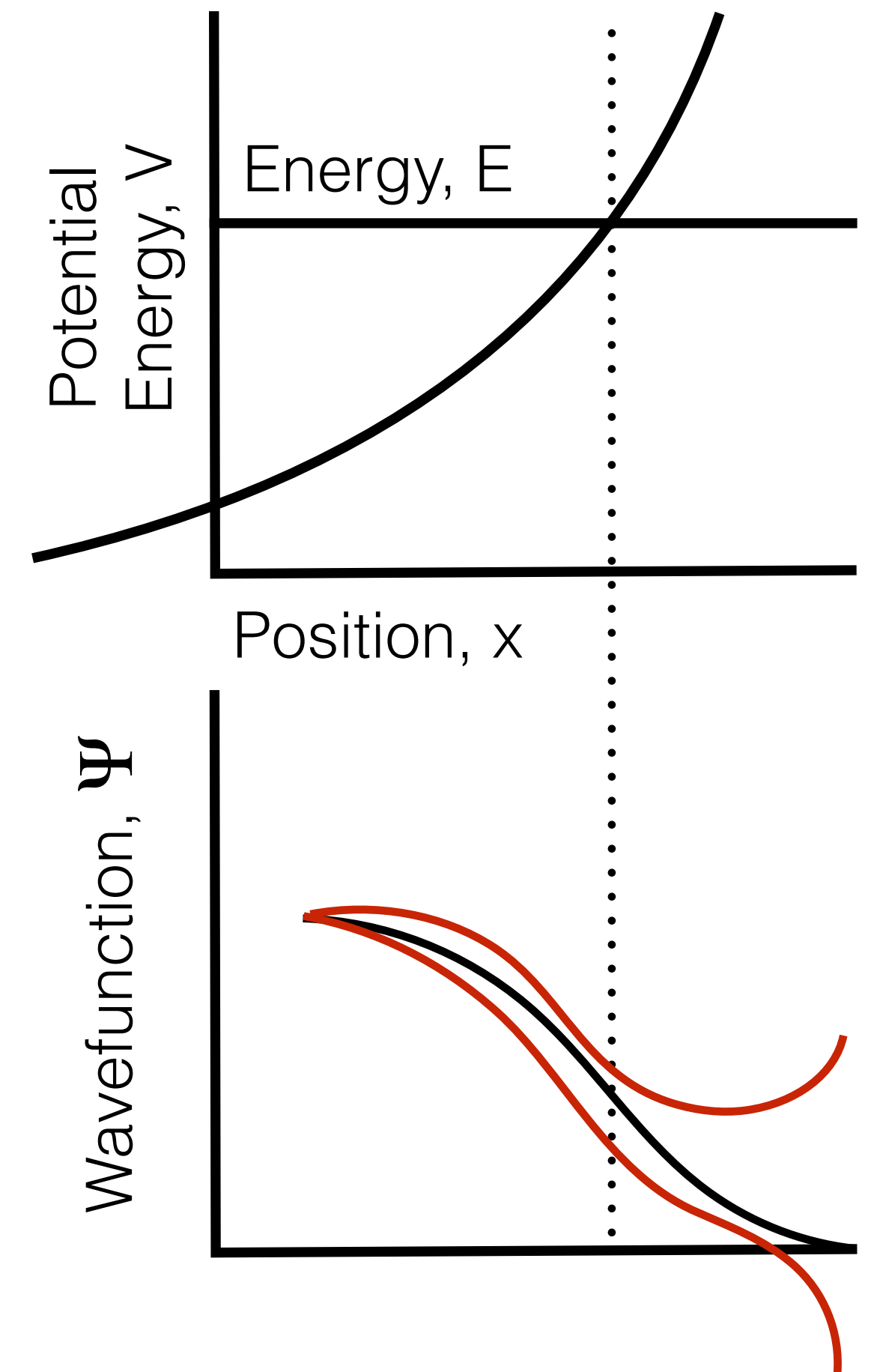
- Rearranging the 1D time-independent Schrodinger equation gives, $\frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2}(V - E)\Psi$, showing that “curvature” depends on the difference between the potential and total energy.
- In a classical system, what happens when all of the energy is converted into potential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

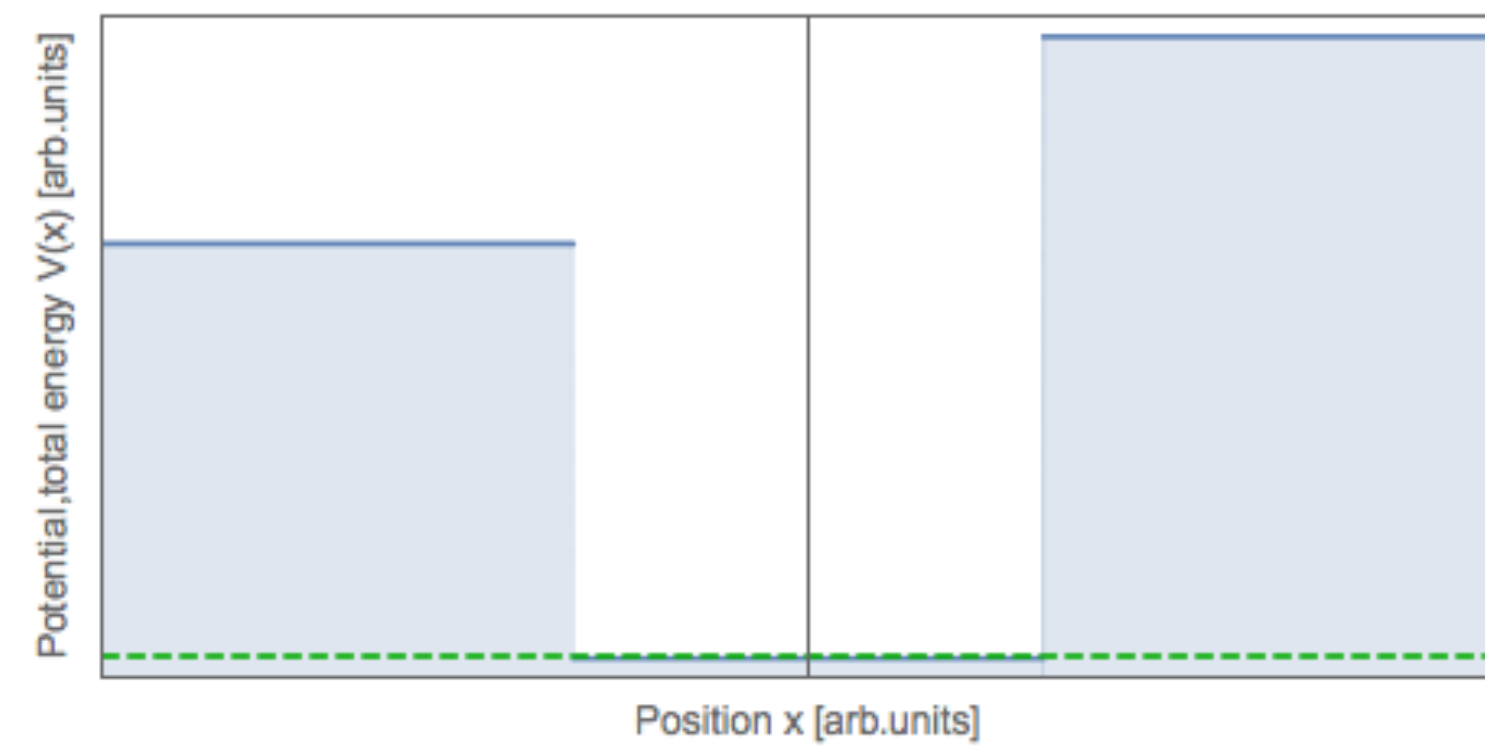
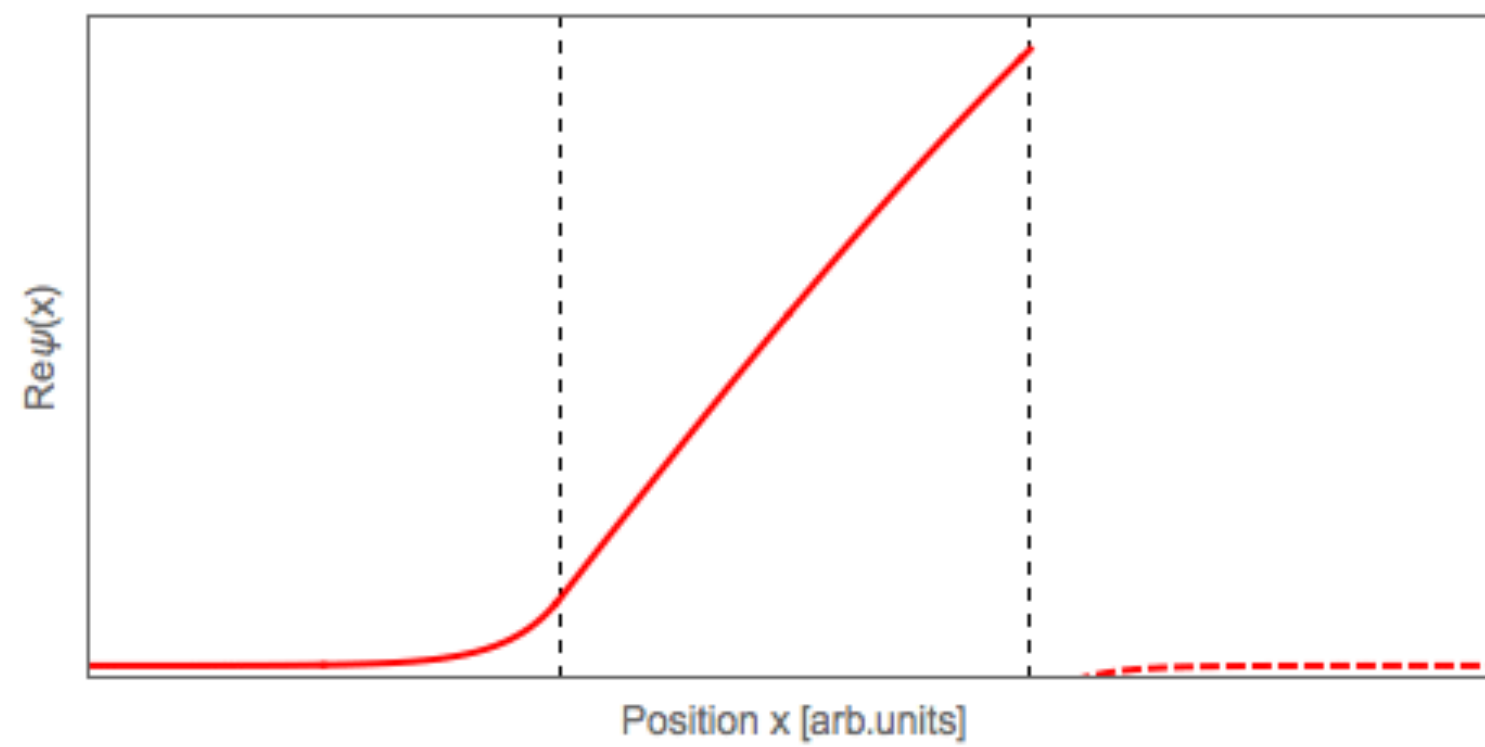
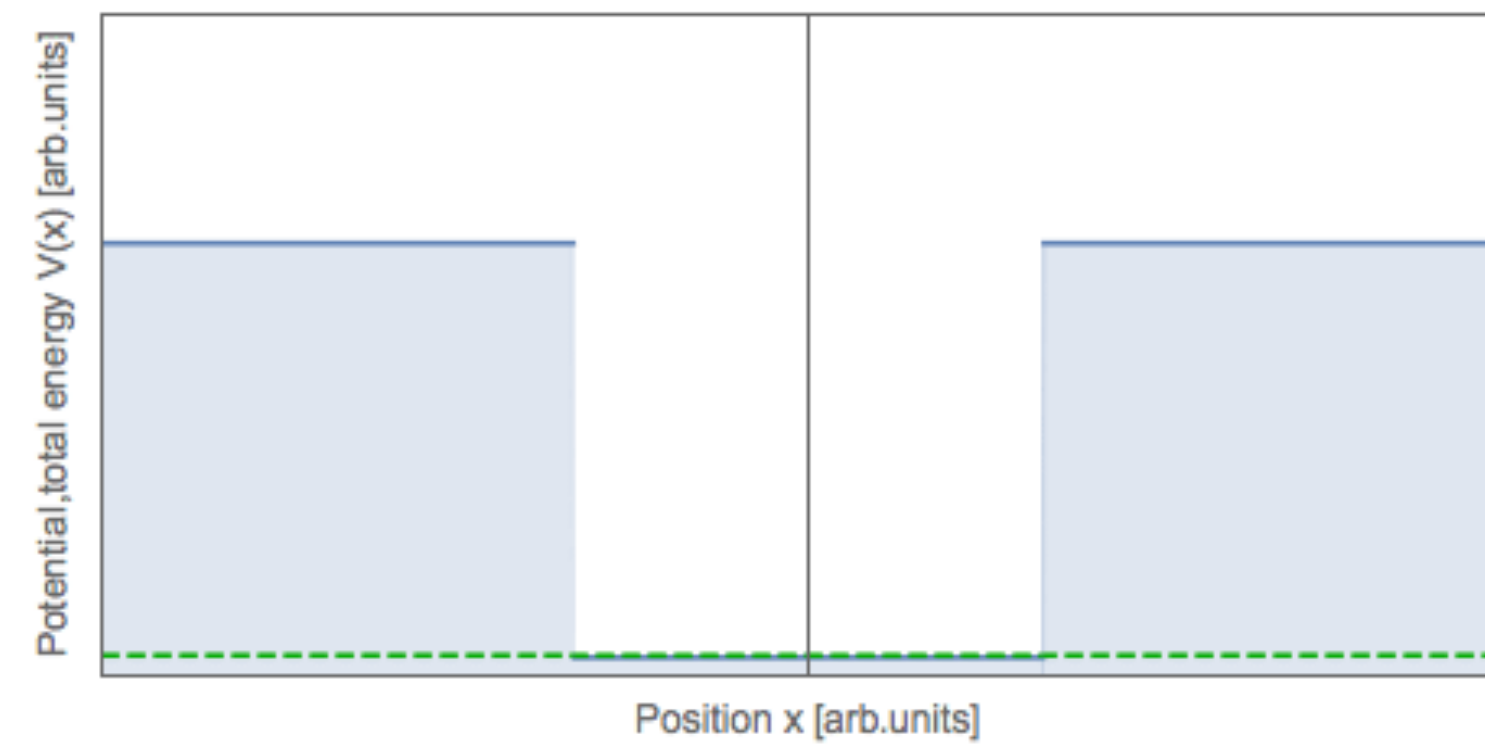
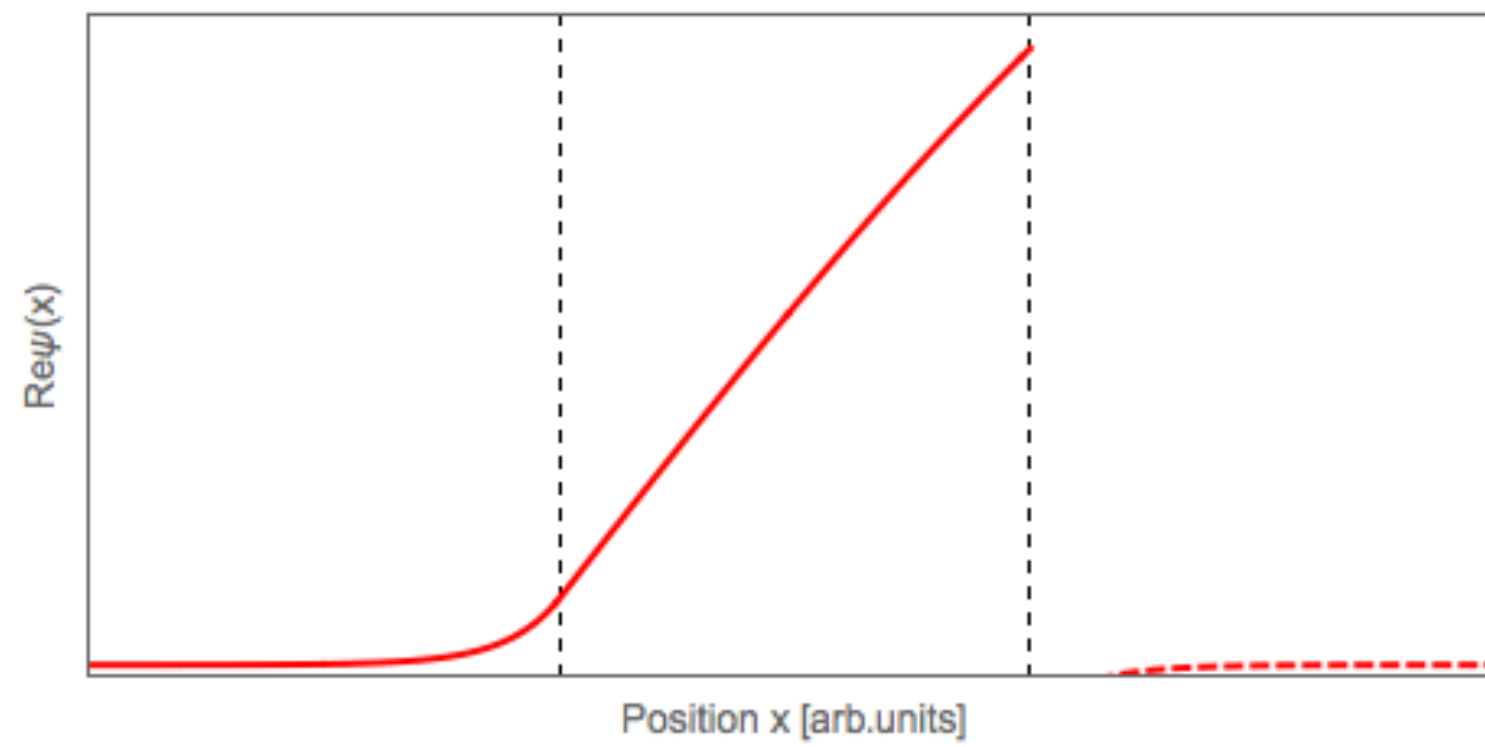
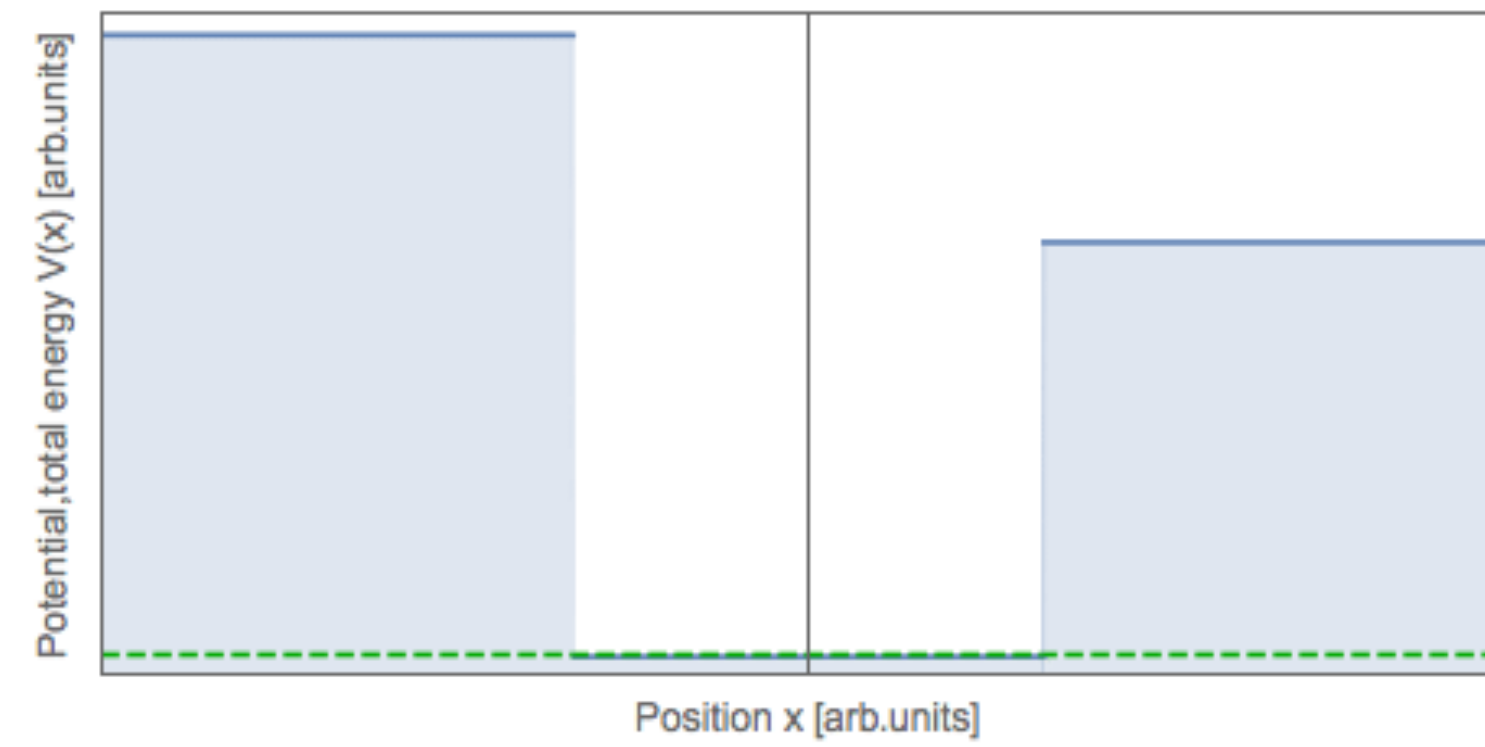
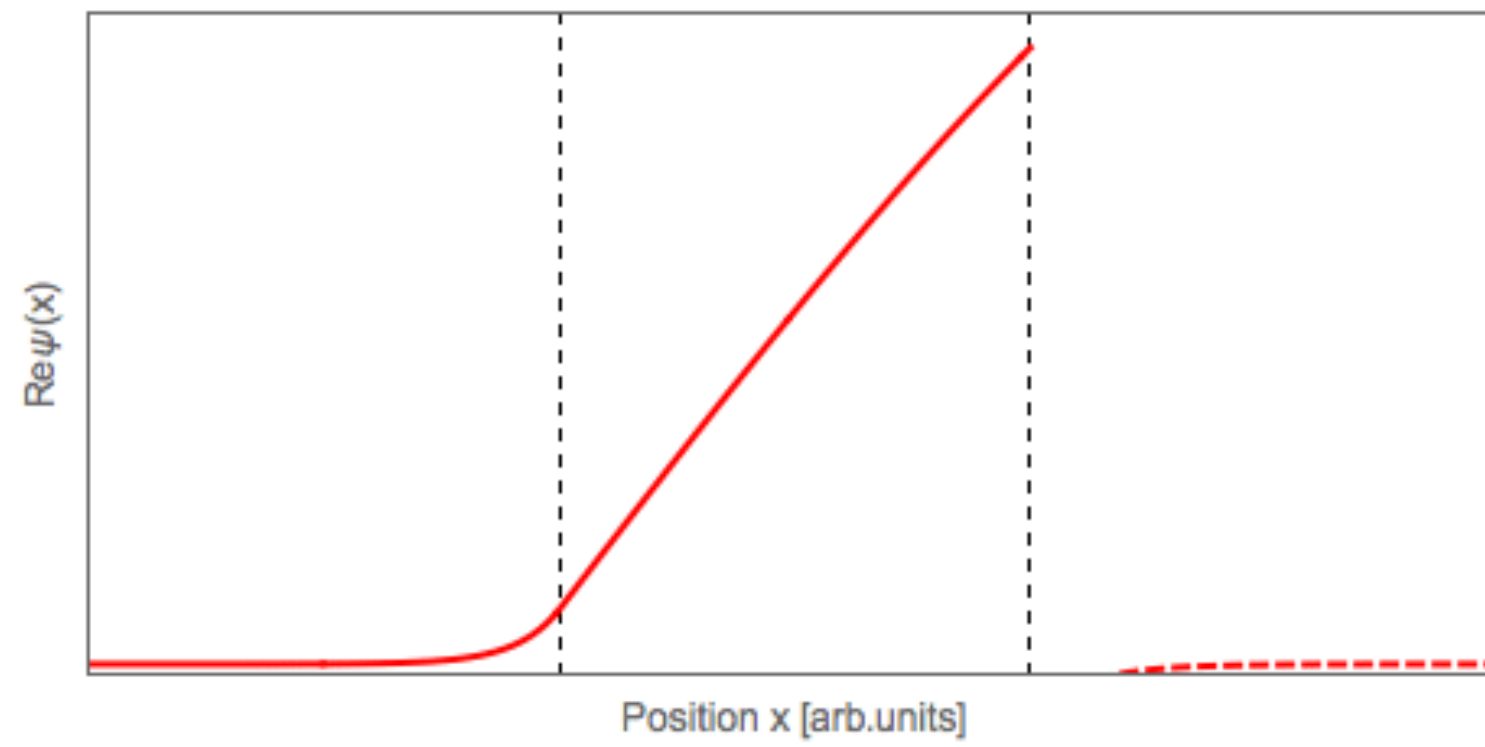


Boundaries and Quantization

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

- As $x \rightarrow \infty$, the wavefunction must approach zero. For $\Psi(x) = y$,
 - If curvature too small, wavefunction goes to ∞
 - 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

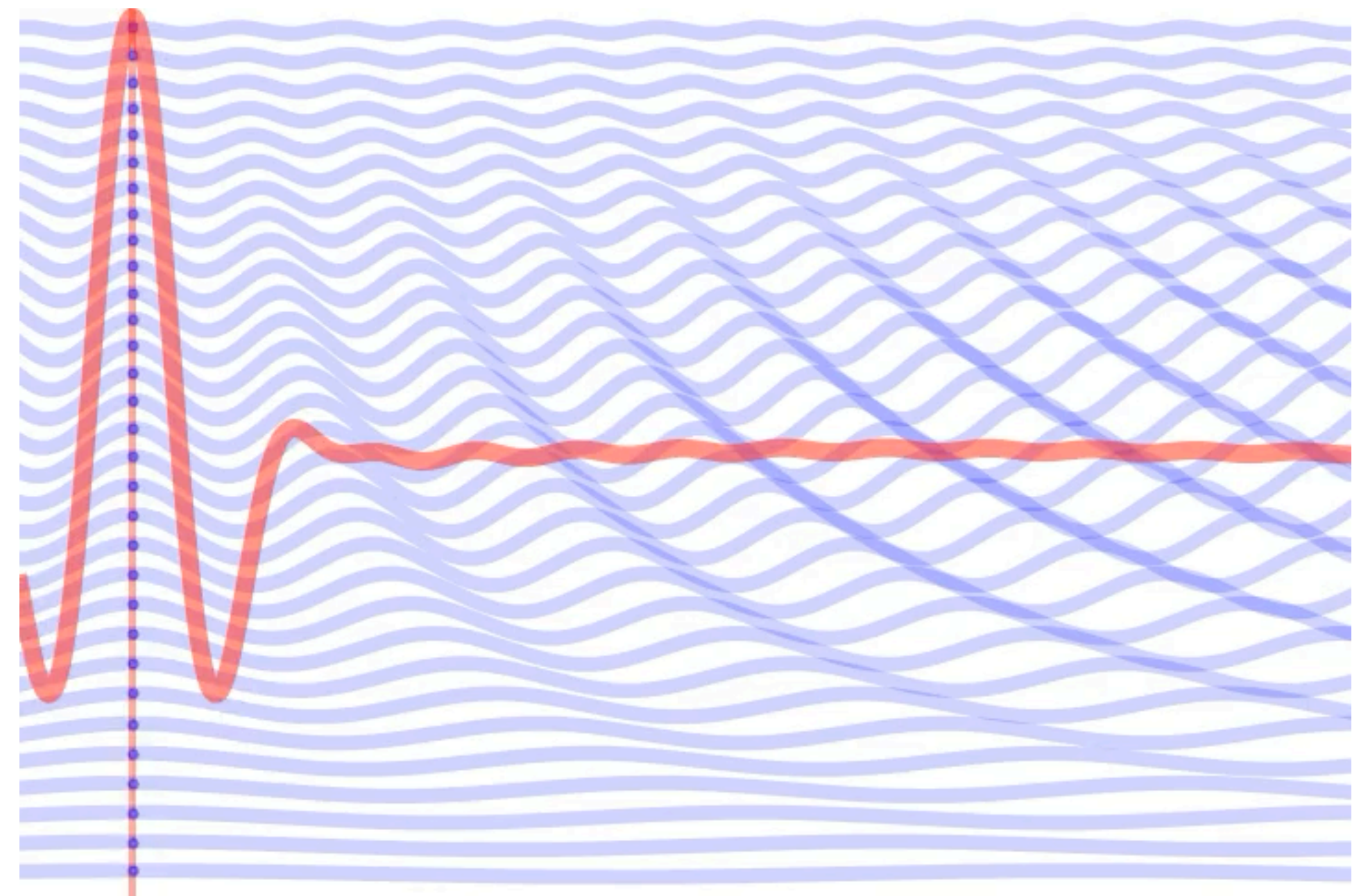
- For a 1D system with constant V , the time-independent Schrodinger equation is $-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V\Psi = E\Psi$. When $V = 0$, the system is known as a free particle.
- The general solution is $\Psi = Ae^{ikx} + Be^{-ikx}$, with $k = \left(\frac{2m(E - V)}{\hbar^2} \right)^{1/2}$
- 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 ω_n is proportional to $|c_m|^2$.
- Given that $\Psi = Ae^{ikx} + Be^{-ikx}$, $k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$, and $\hat{\mathbf{p}} = \frac{\hbar}{i} \frac{d}{dx}$, 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

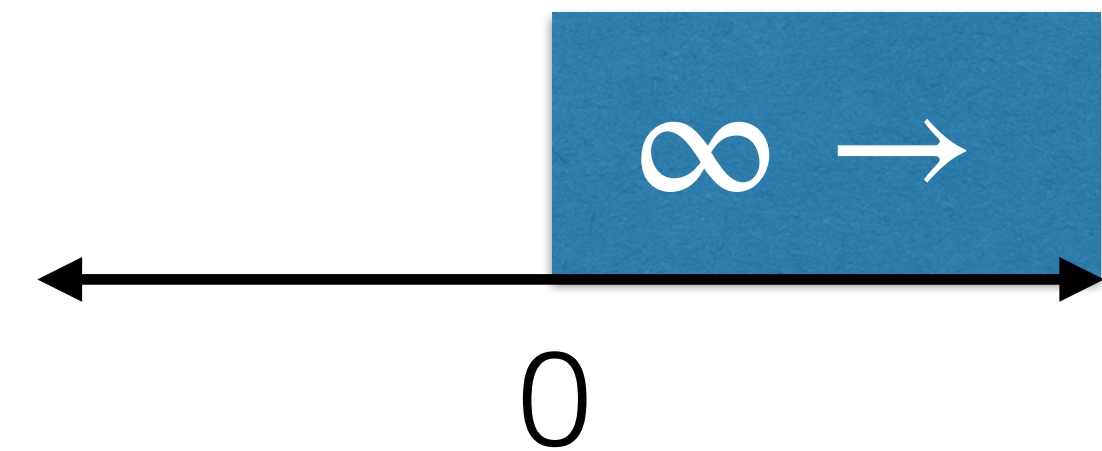
- If the wavefunction has the form $\Psi = Ae^{ikx} + Be^{-ikx}$, then there are
 - two possible momenta
 - one possible energy
- How well defined is the position?
 - It is a free particle
- A wave packet is a superposition of $\Psi = Ae^{ikx} + Be^{-ikx}$ with different k. The energy is less well defined,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



<https://dkirkby.github.io/quantum-demo/>

Barrier with finite height & infinite width

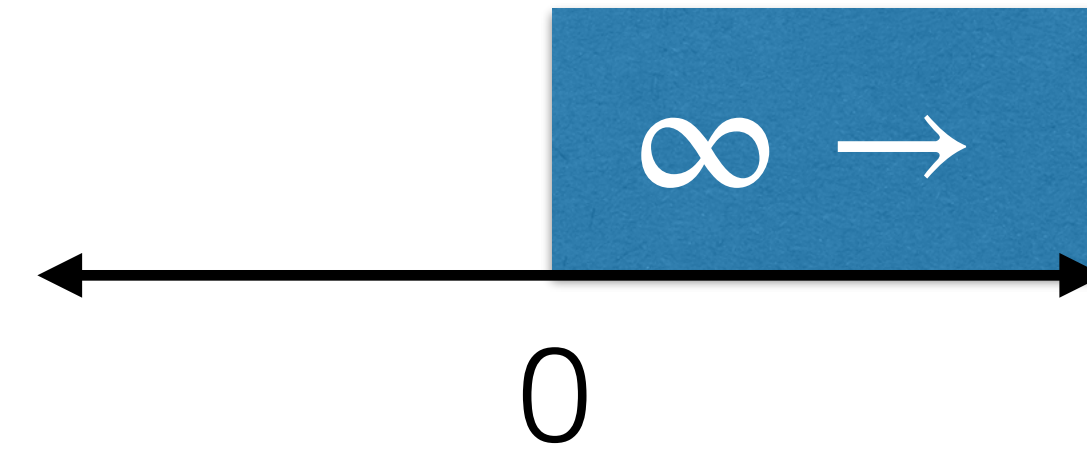
- $V(x) = \begin{cases} 0 & \text{if } x < 0 \\ V & \text{if } x \geq 0 \end{cases}$
- Same general solution, different coefficients in different regions



Quantum Penetration

- Zone I ($x < 0$, $V(x) = 0$)

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



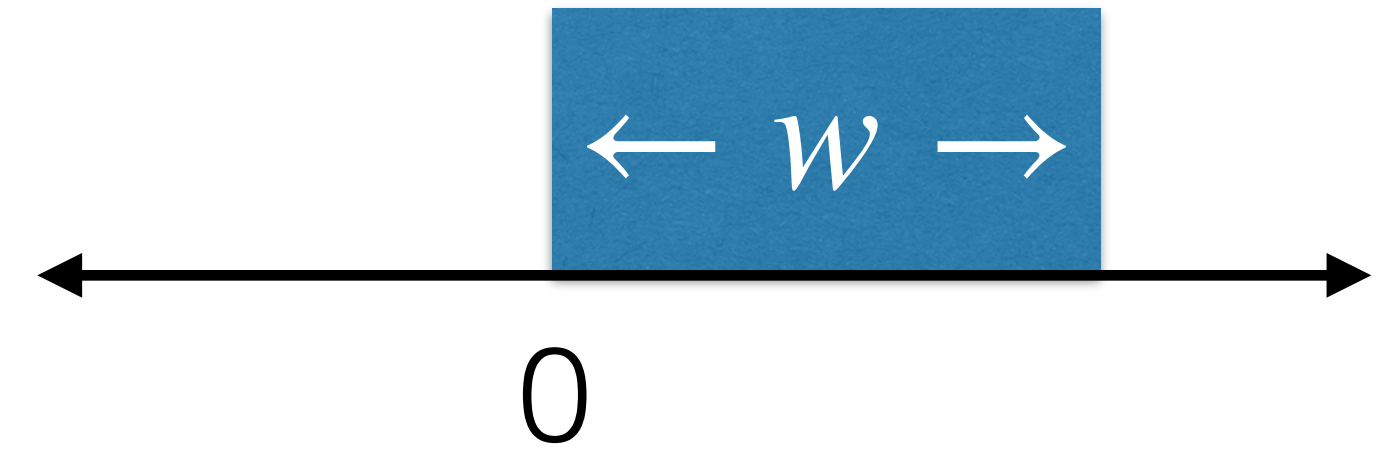
- Zone II ($x > 0$, $V(x) = V$):

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

- How does the extent of penetration depend on particle mass and energy?

Barrier with finite height & finite width



- $$V(x) = \begin{cases} 0 & \text{if } x < 0 \\ V & \text{if } 0 \leq x < w \\ 0 & \text{if } x \geq w \end{cases}$$
- Same general solution, different coefficients in different regions

Quantum Tunneling

- Zone I ($x < 0$, $V(x) = 0$)

- $\Psi = Ae^{ikx} + Be^{-ikx}$,

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

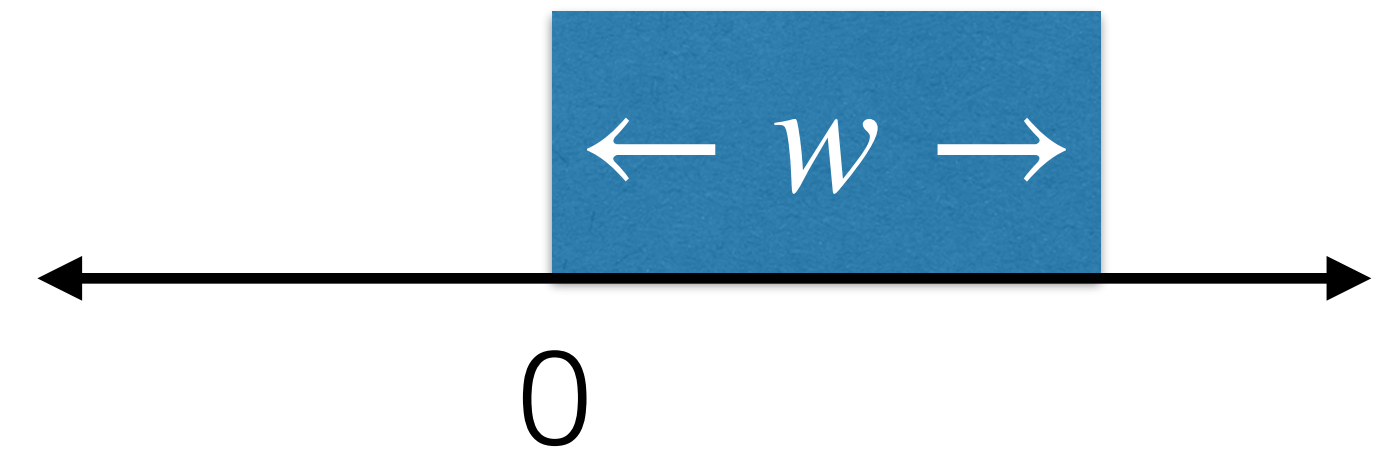
- Zone II ($0 < x < w$, $V(x) = V$):

- $\Psi = A'e^{ik'x} + B'e^{-ik'x}$,

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

- Zone III ($x > w$, $V(x) = 0$)

- $\Psi = A''e^{ikx} + B''e^{-ikx}$

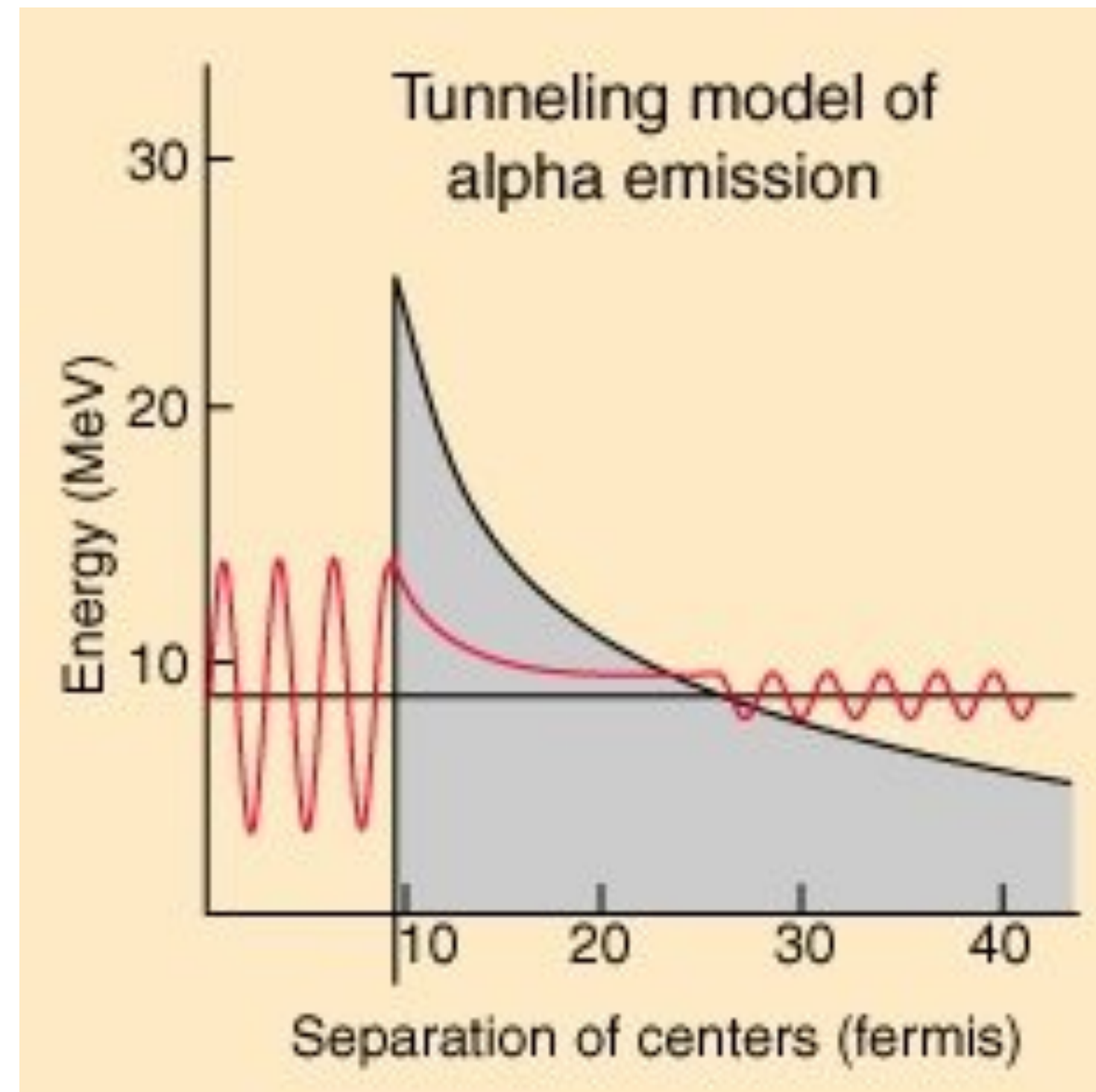


- For $E < V$, solution for tunneling probability is,

$$T = \frac{1}{1 + \frac{e^{\kappa L} - e^{-\kappa L}}{16(E/V)(1 - E/V)}}$$

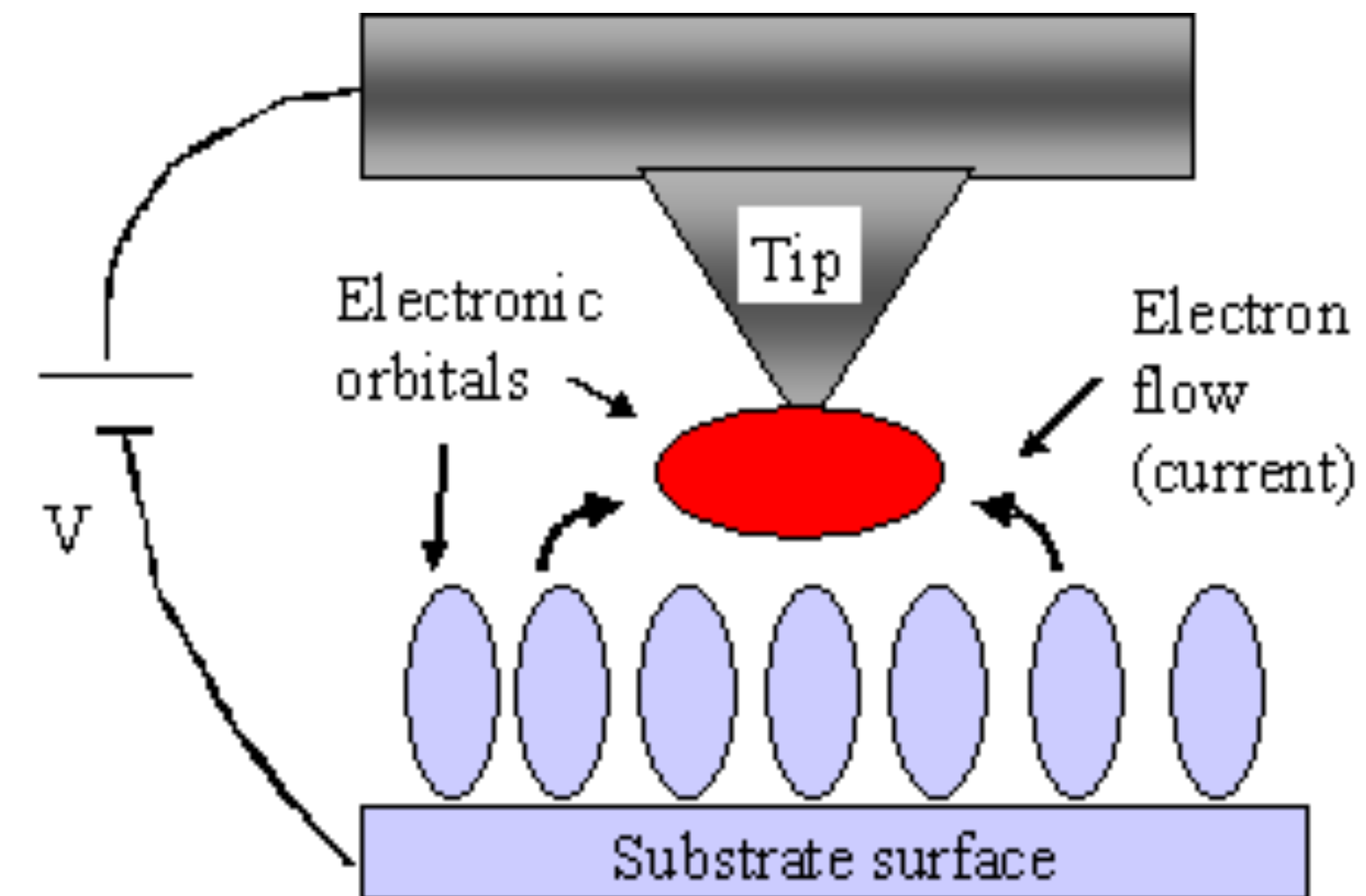
- Based on continuity of function and slopes

Quantum Tunneling Applications



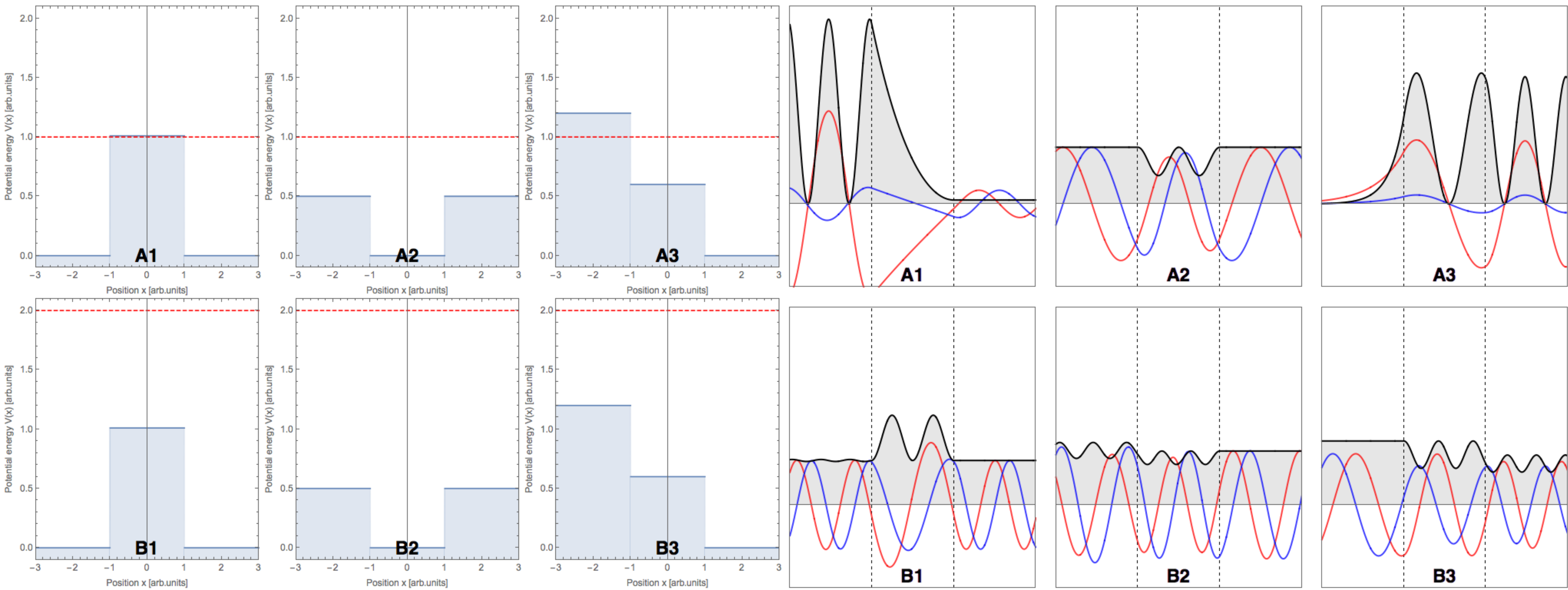
<https://physicsopenlab.org/2017/05/30/tunnel-effect/>

Explaining α decay



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

Scanning Tunneling Microscopy

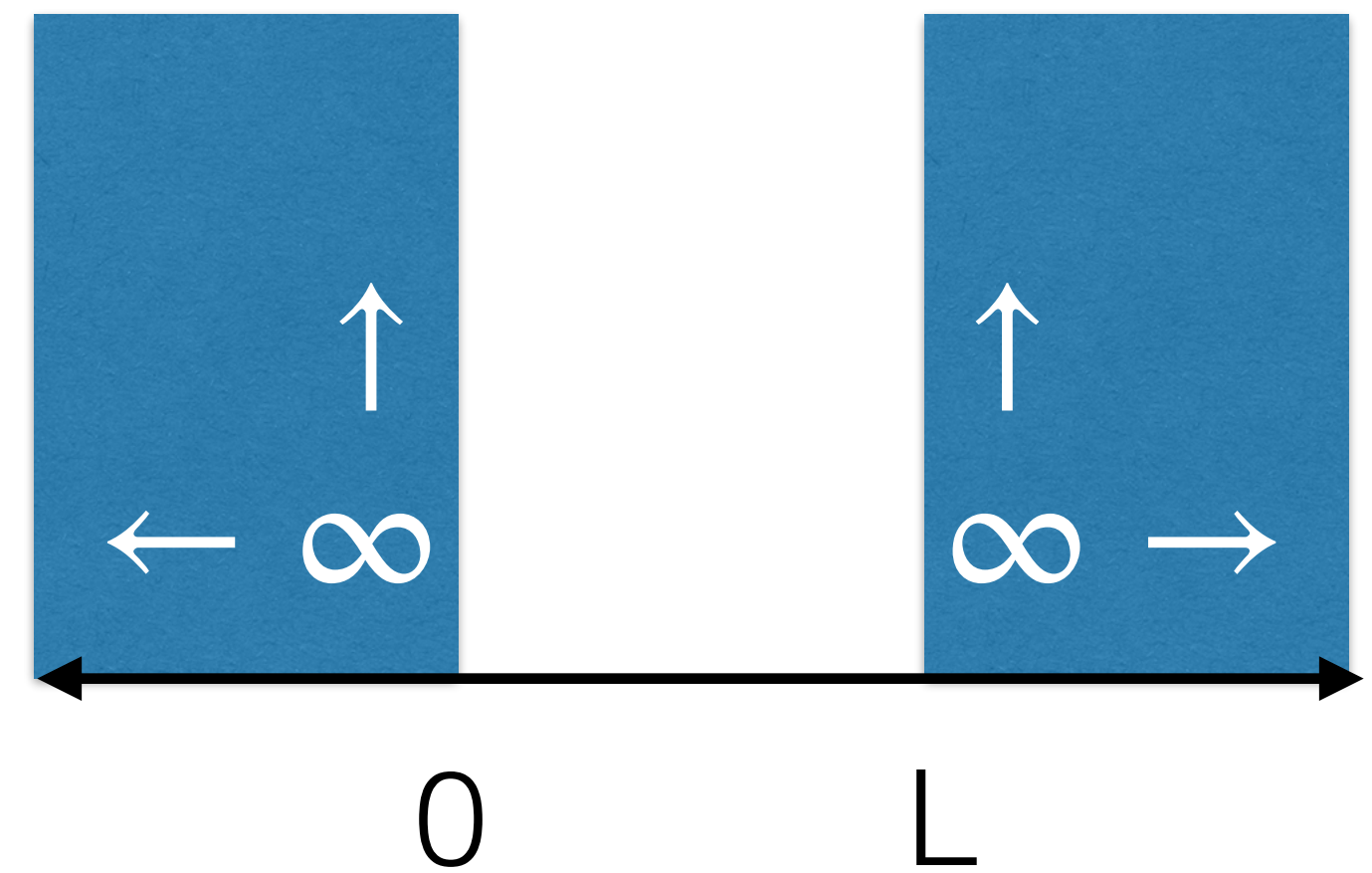


Potentials

Wavefunctions

Particle in a Box

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

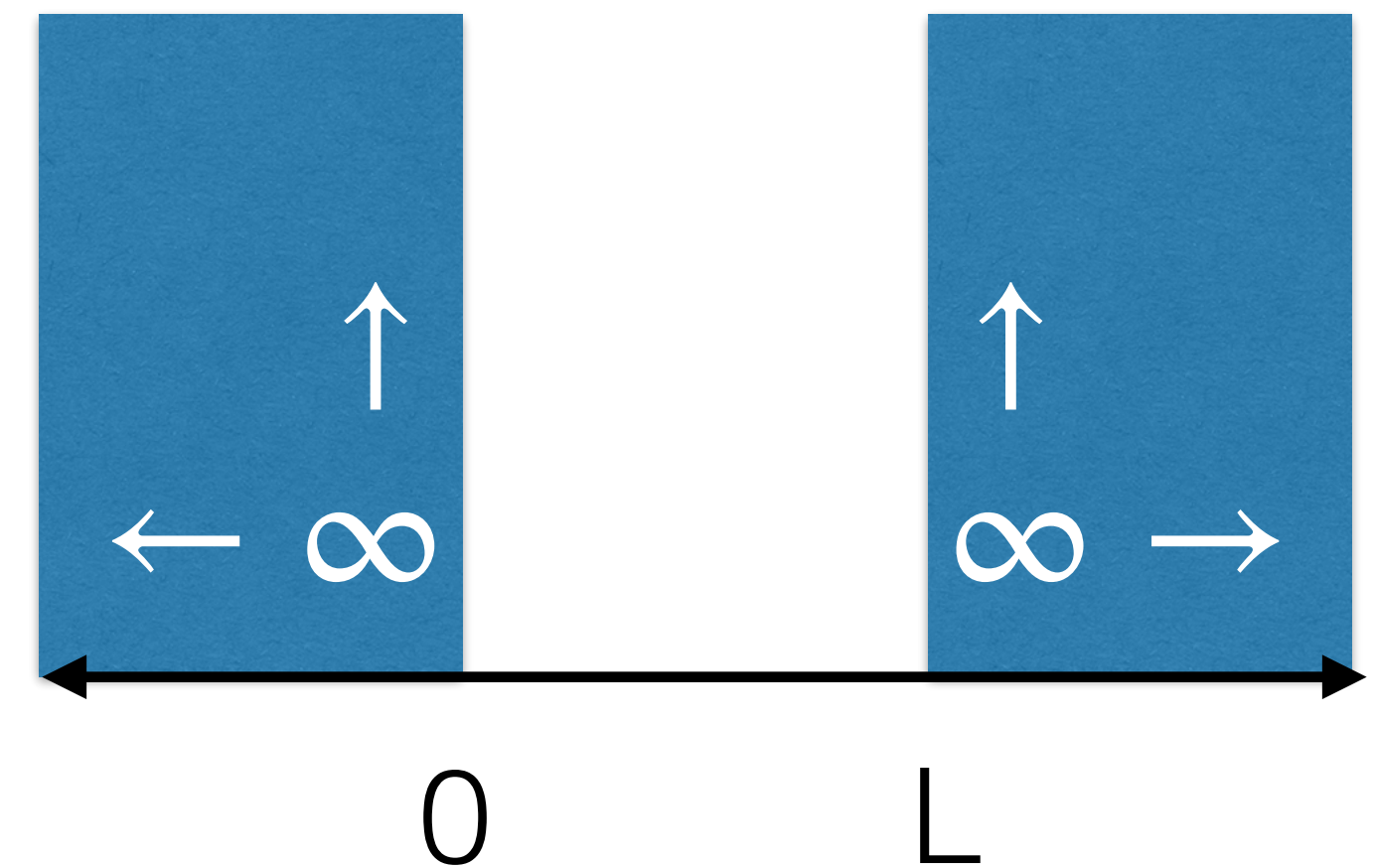


Solving the PIB

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

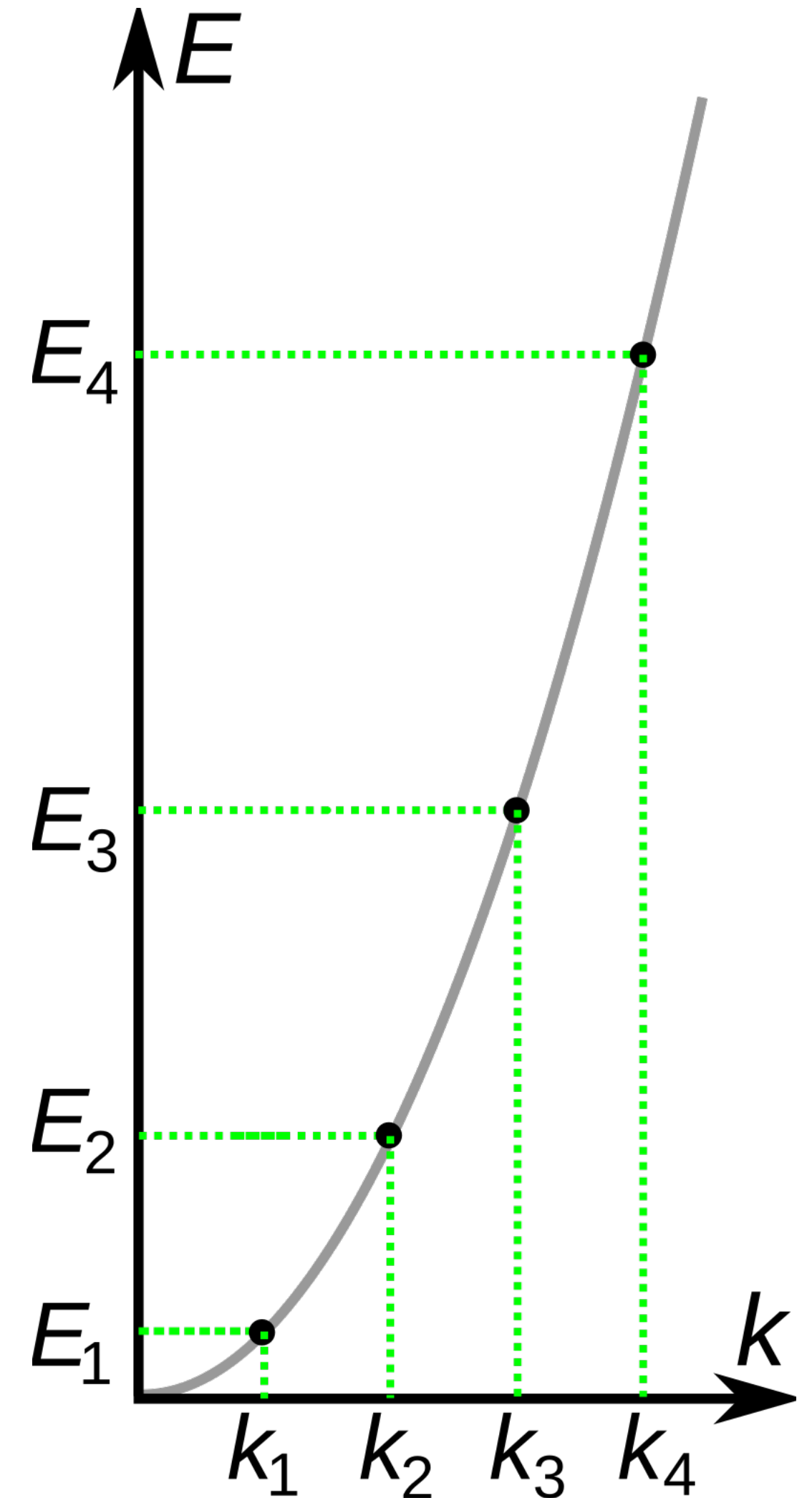
$$k = \left(\frac{2mE}{\hbar^2} \right)^{1/2}$$
- Outside the box, $\Psi = 0$
- Because $\Psi(0) = 0$ and $\Psi(L) = 0$, $C = 0$.
- The solutions are $\Psi(x) = D \sin(kL)$, where

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



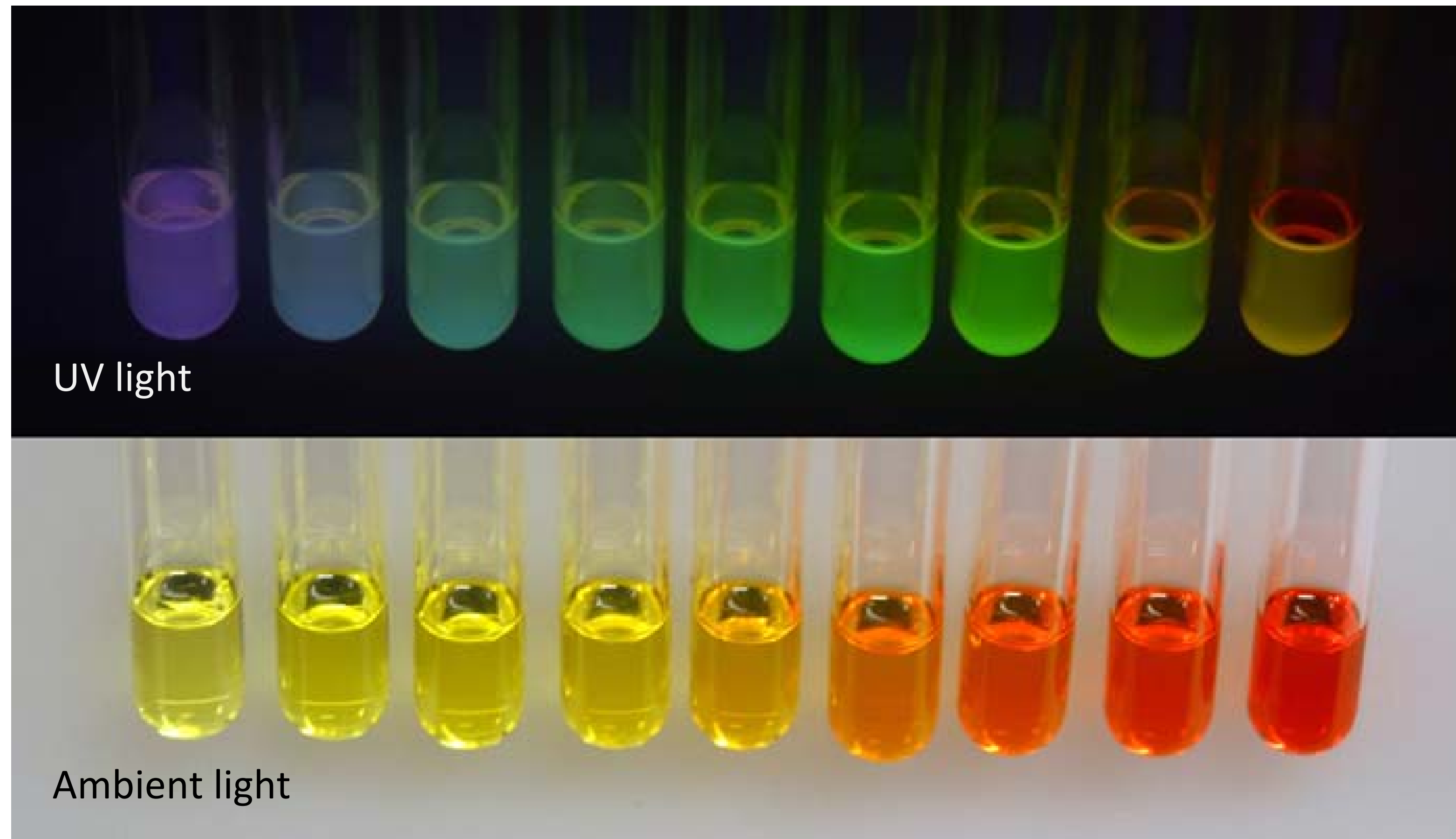
PIB energies

- Setting two expressions for k equal, $\frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{L}$
- The allowable energies are $E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$, for $n = 1, 2, \dots$
- 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.



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

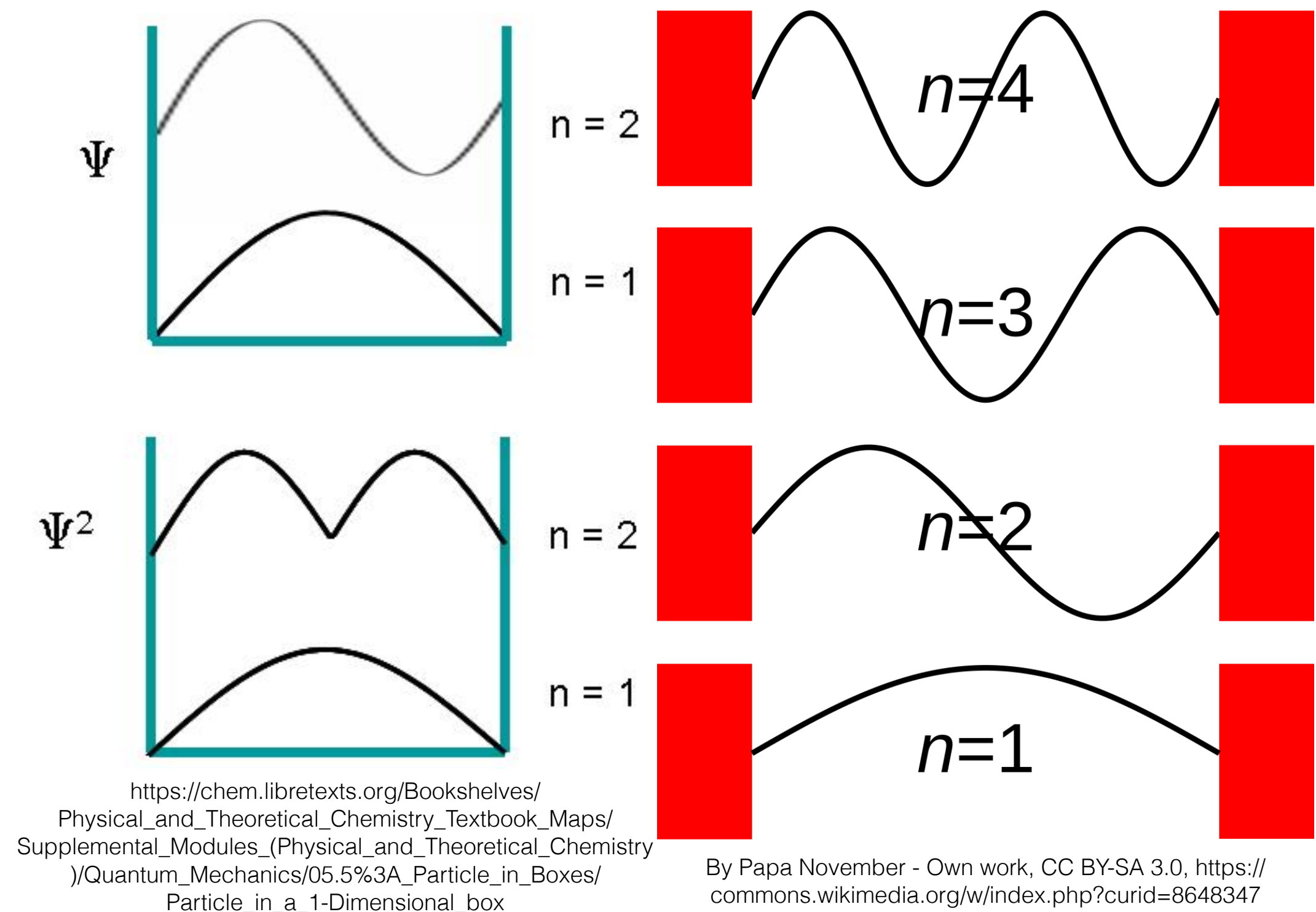


Size dependent optical properties!

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

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



2D PIB

- Solution is based on separation of variables

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

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

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

- Note that

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

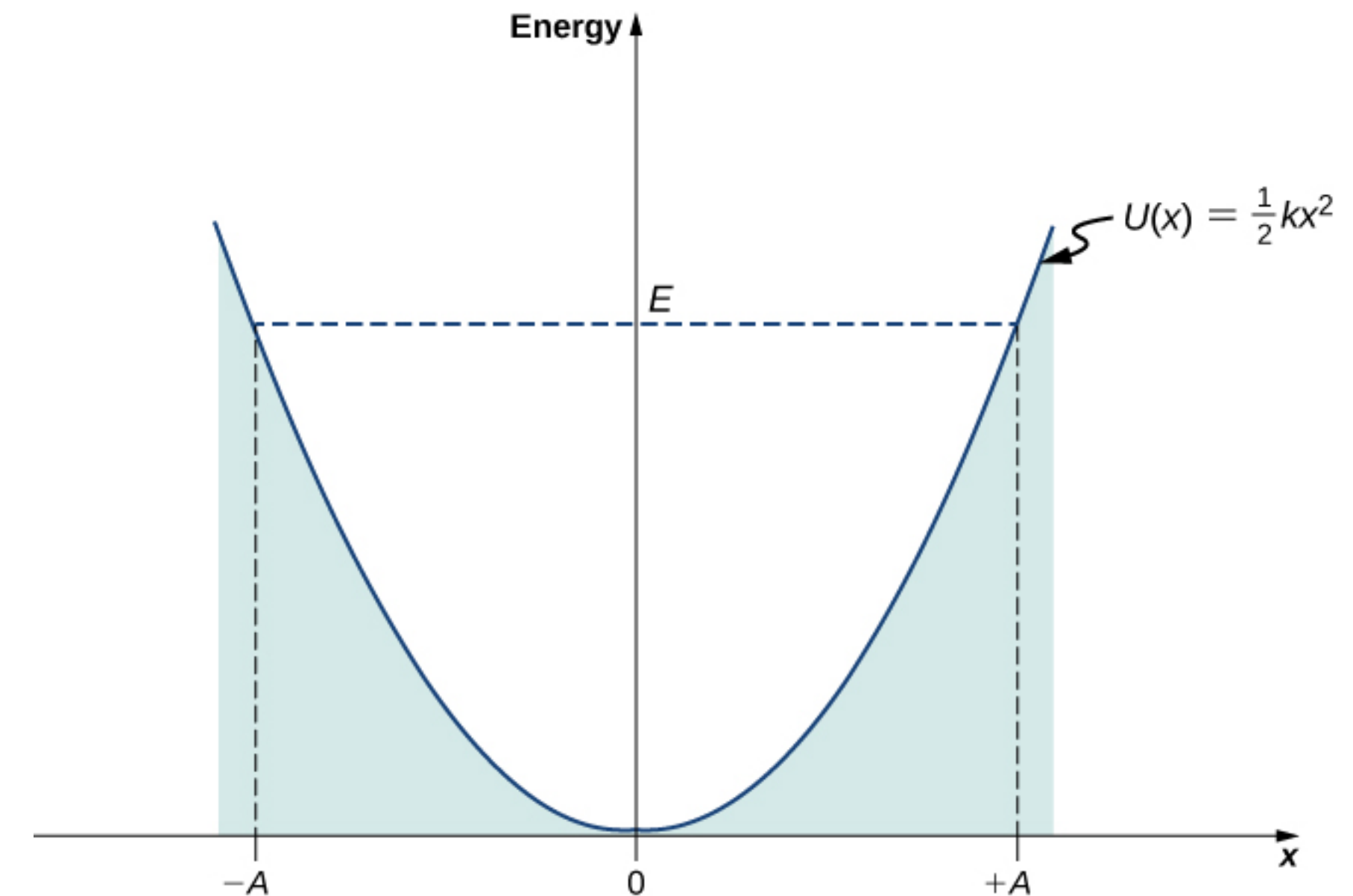
- If $L_1 = L_2$, then

$$E_{n_1, n_2} = \frac{h^2}{8mL^2} (n_1^2 + n_2^2) \text{ and}$$

there can be degeneracy, multiple states with the same energy

Harmonic Oscillator

- $V(x) = \frac{1}{2}kx^2$
- It is qualitatively similar to a particle in a box. Are energies continuous or quantized?
- Quantized

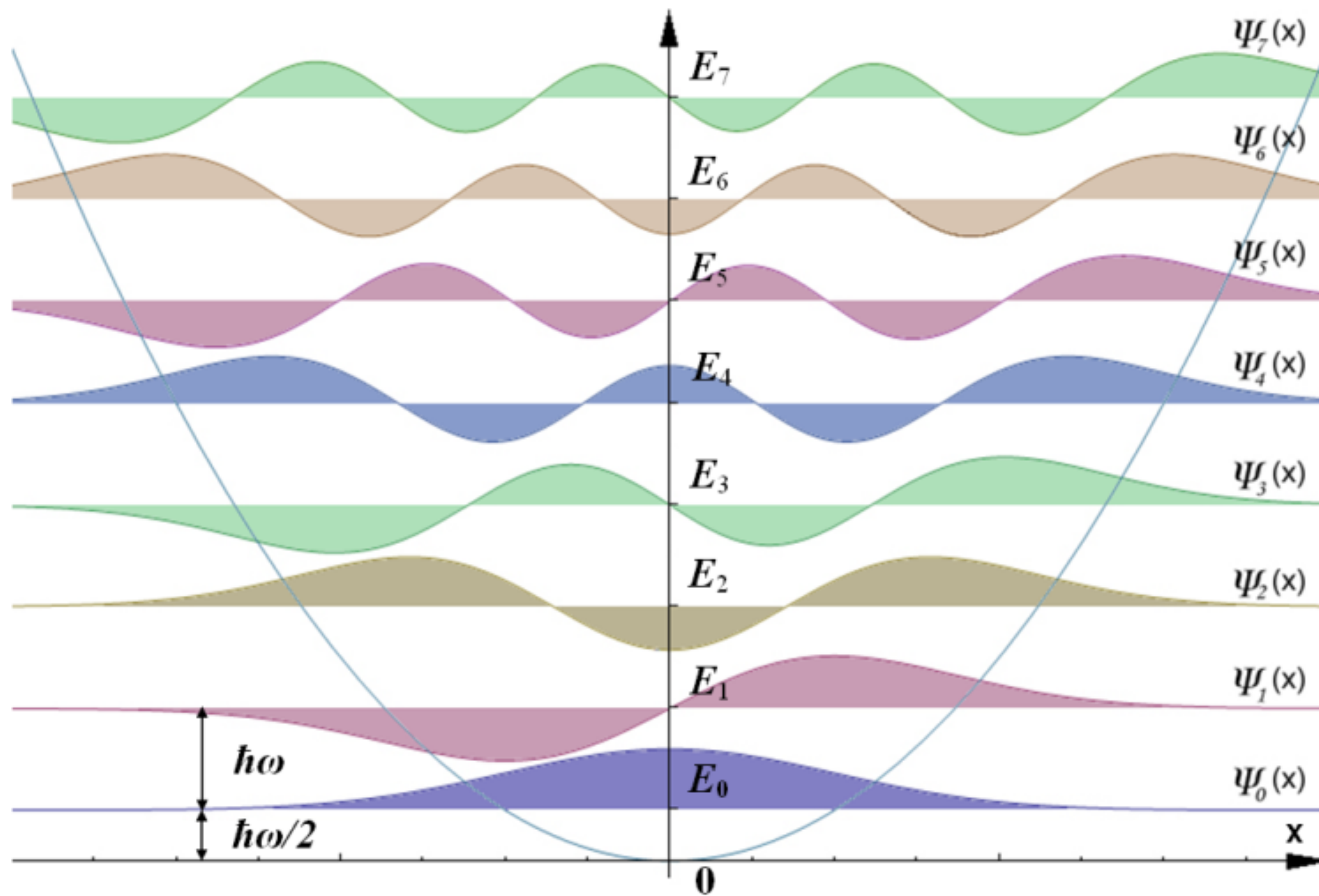


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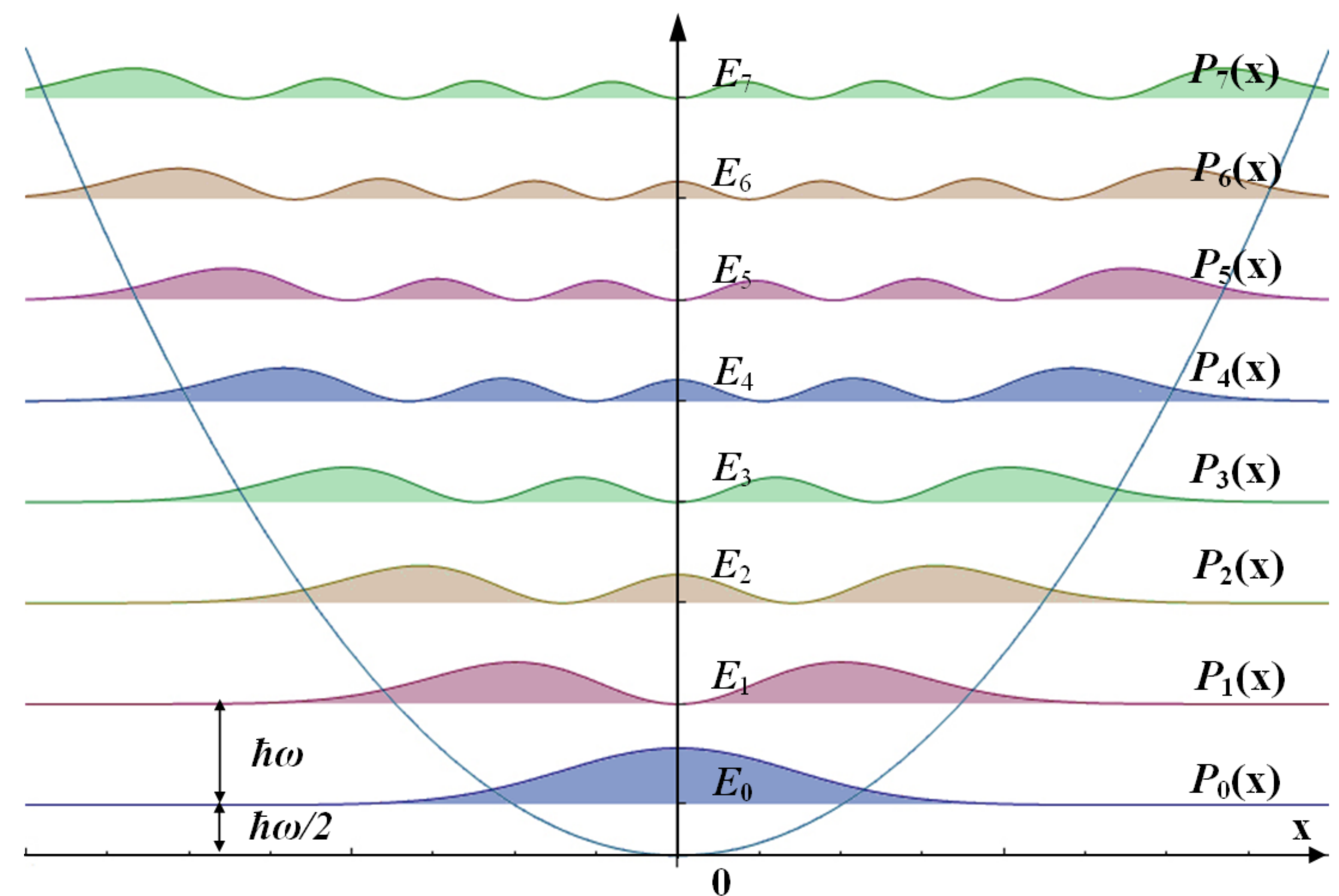
HO Solutions

- The Hamiltonian is $\hat{\mathbf{H}} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}k_f x^2$
- $\Psi_\nu(x) = N_\nu H_\nu(\alpha x) e^{-\alpha^2 x^2/2}$, where
- $N_\nu = \left(\frac{\alpha}{2^\nu \nu! \pi^{1/2}} \right)^{1/2}$ is for normalization
- $H_\nu(y) = (-1)^\nu e^{y^2} \frac{d^\nu}{dy^\nu} e^{-y^2}$
- $\alpha = \left(\frac{mk_f}{\hbar^2} \right)^{1/4}$
- H_ν are known as Hermite polynomials
- For $\nu = 1$, the solution is Gaussian
- The energies are $E_\nu = \left(\nu + \frac{1}{2} \right) \hbar \omega$, where $\nu = 0, 1, 2, \dots$
- ν starts at 0, not 1
- Spacings between energy levels are constant

HO Wavefunctions and Probability Densities



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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*.

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

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.