Suppose:

- $\Phi(x,t)$ is a general solution of the Schrödinger Equation (SE)
- $\psi_n(x)$ are the solutions ($n = 1, 2, 3 \ldots$) for the time-independent SE
- In the expressions below, c_n are suitable expansion coefficients, E_n are the energies for various solutions $\psi_n(x)$ and E is the average energy of the system.

Which one of the following statements is correct?

a) $\Phi(x,t) = [\sum_n c_n \psi_n(x)] e^{\frac{-iEt}{\hbar}}$

b) $\Phi(x,t) = \sum_n c_n \psi_n(x) e^{\frac{-iE_n t}{\hbar}}$

c) $\Phi(x,t) = \sum_n \psi_n(x) e^{\frac{-E_n t}{\hbar}}$

d) $\Phi(x,t) = \sum_n \psi_n(x) e^{\frac{-iE_n t}{\hbar}}$

CHM 305 The Quantum World
Lecture 4: Free & Confined Particles

Reading: McQuarrie Chap. 3

[and Griffiths Chap. 2]

Quick review of what we learned last time…

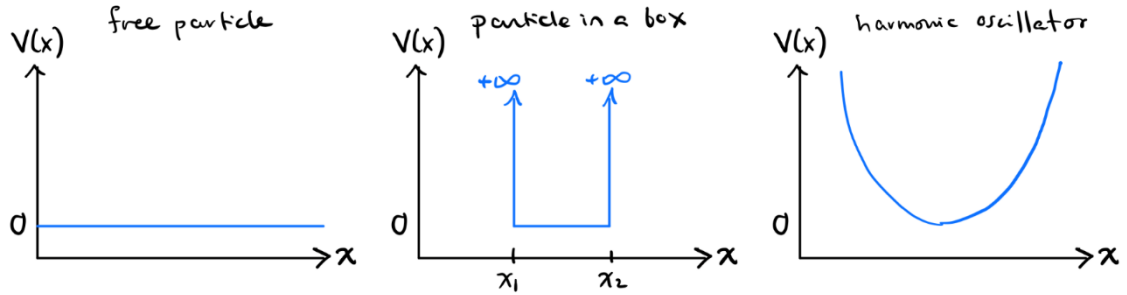
- Motivation of the Schrödinger equation from classical waves plus the deBroglie relation

- The time-*dependent* Schrödinger equation governs the full temporal **and** spatial evolution of quantum wavefunctions

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

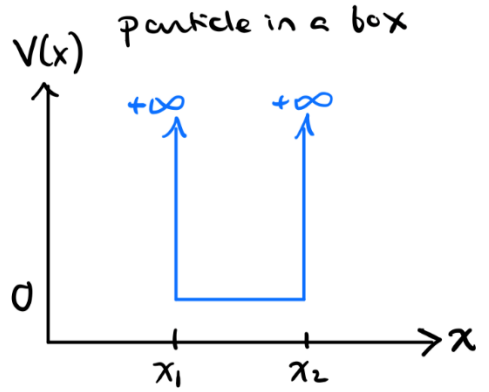
- We solve the time-*independent* Schrödinger equation to find stationary state solutions and their corresponding energies for a given potential V(x)

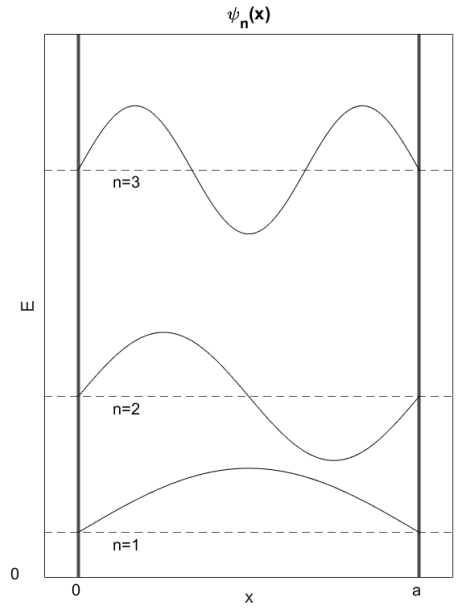
$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\psi(x)=E\psi(x)$$



Road map for today's lecture

- Review the rules for solving the Schrödinger equation
- Description of the simplest quantum system: the ***free particle*** in a potential with V(x) = 0
- Description of the next simplest quantum system: the **particle in a box**
  - stationary states & energies for a 1D box
  - boxes of 2 and 3 dimensions
  - some real-world examples





Practice Problem #1

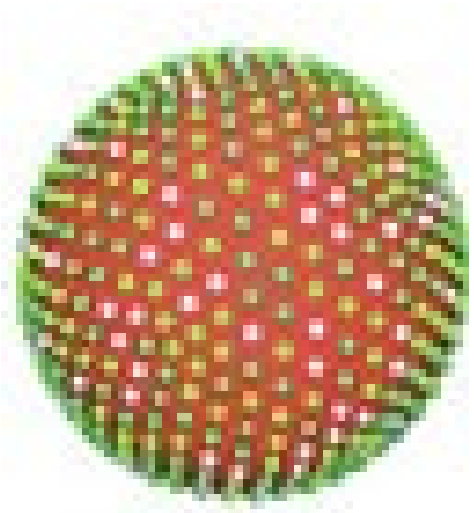
We found that a stationary state of the free particle Hamiltonian might look like:

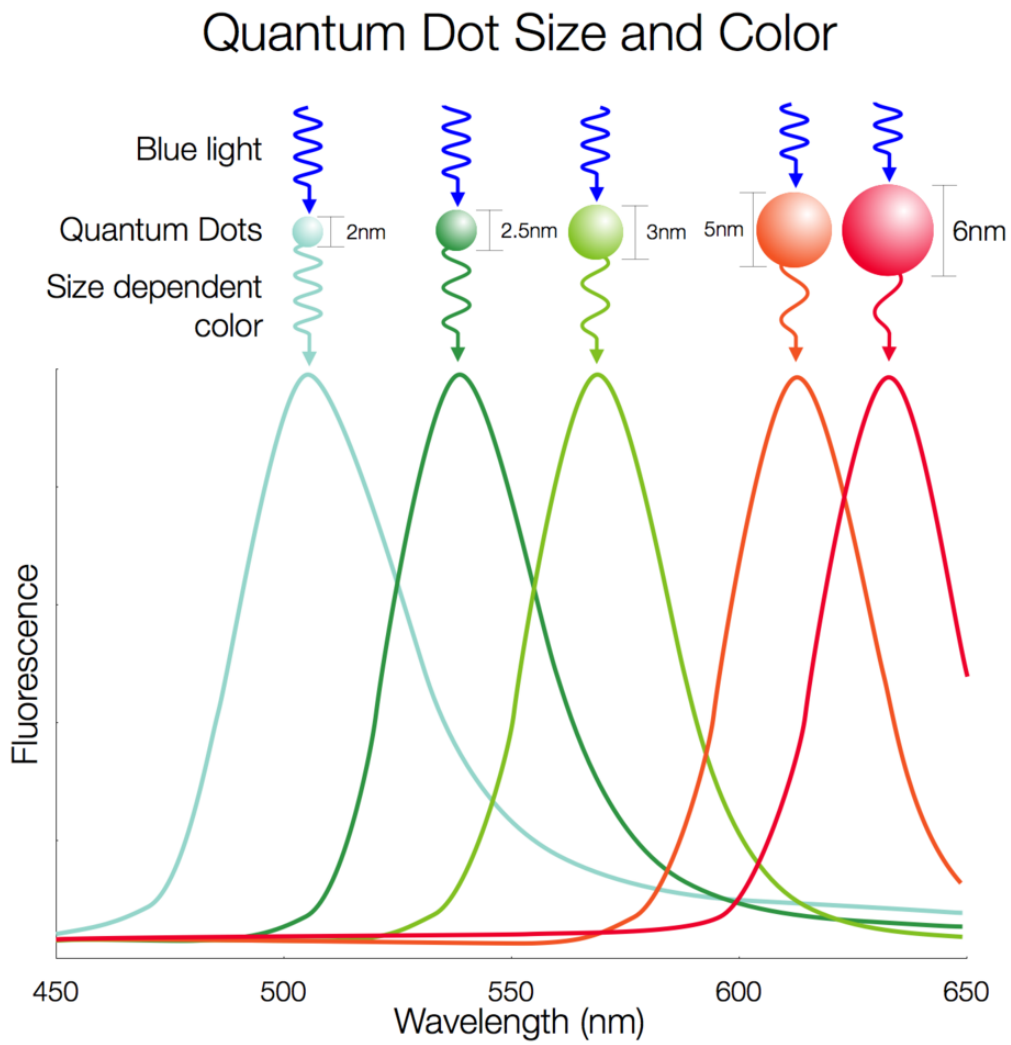
$$\psi_k(x) = Ae^{-ikx}$$

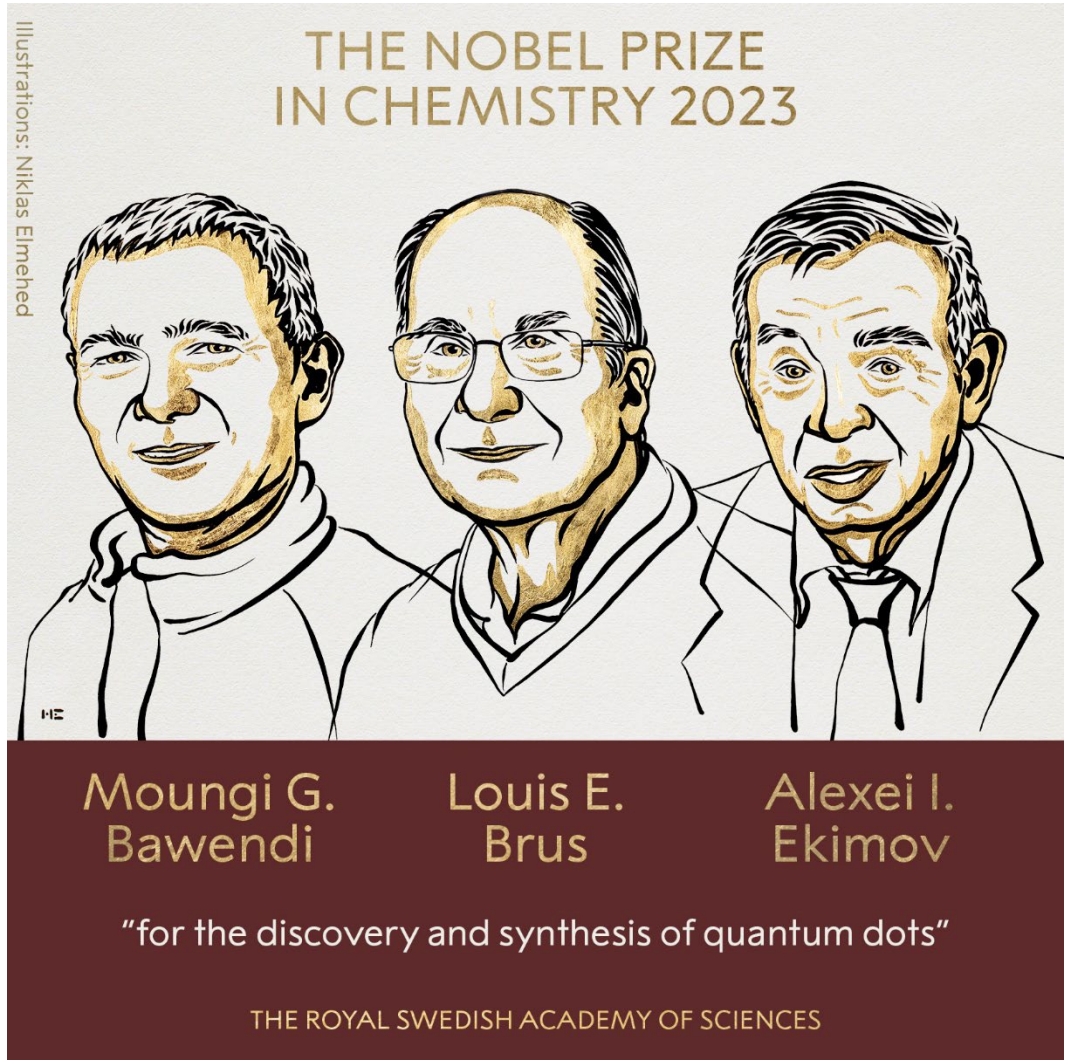
where $k = (2mE)^{1/2}/\hbar$.

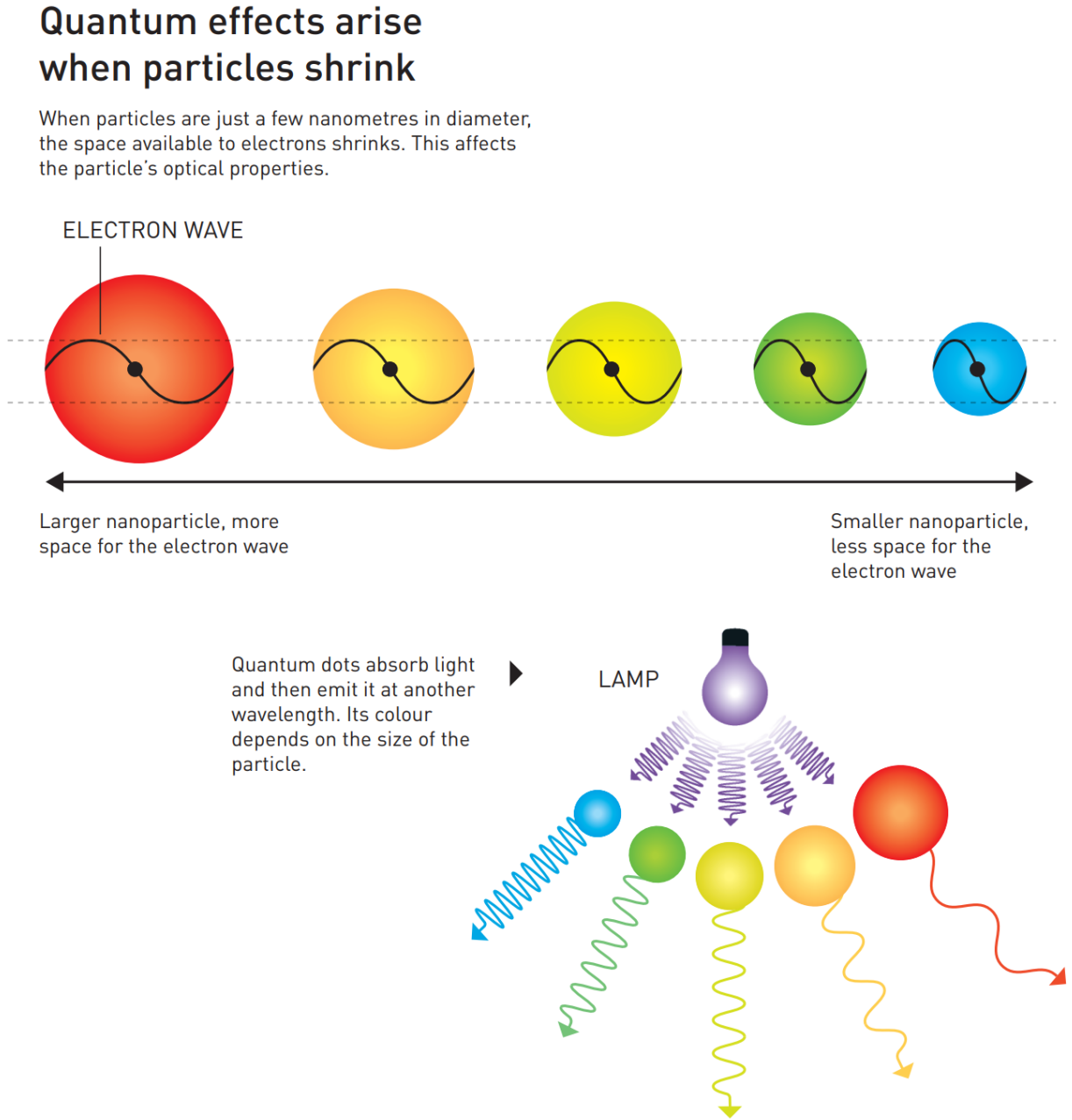
We will require that the energy of the system E be a positive real number. Let's consider why this is. What would go wrong if E is allowed to take on a negative value?

Quantum dots as 3D PIBs





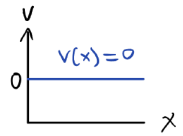
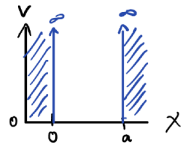
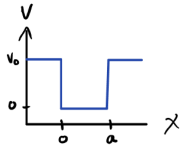
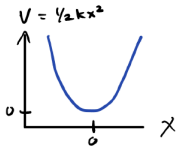
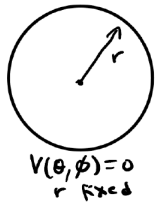




https://www.nobelprize.org/prizes/chemistry/2023/prize-announcement/

try filling out the "quantum model systems" chart as we go along...

CHM 305 - Important Quantum Model Systems

	free particle	particle in a box	particle in a finite box	harmonic oscillator	rigid rotor
$V(x)$					
$\psi_n(x)$					
E_n					

Wrapping up

- **Next time:** the postulates of quantum mechanics
- **Today's reading:** McQuarrie Chap. 3
- **Problem Set 2:** out today, due next Monday at midnight
- **In the last minute or two**: think about your muddiest point from this lecture. What was confusing, what lingering questions do you have?

Practice Problem #2

In solving the time-independent Schrodinger equation for a free particle, we are working with the expression:

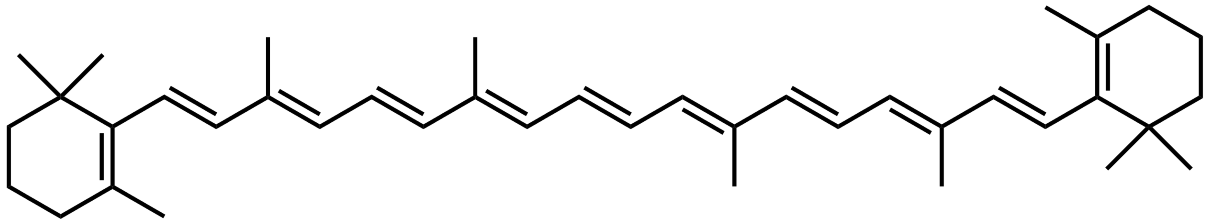
$$\frac{d^2\psi(x)}{dx^2} = -\frac{2m}{\hbar^2}E\psi(x)$$

Our solutions will be complex exponentials of the form:

$$\psi_k(x) = A_+ e^{ikx}$$

Write down an expression for *k* that solves the differential equation. Does it look familiar?

Practice Problem #3: beta carotene



β-carotene can be approximated as a 1D particle in a box.

This molecule has a conjugated region that is approximately 2.4 nm long and contains 11 π bonds. There are therefore 22 π electrons filling the lowest 11 orbitals of the π network.

Write down an expression for the lowest-energy electronic transition of β-carotene? What wavelength of light is needed to excite this transition?