Quantum Mechanics and Atomic Physics

Lecture 4:

Schodinger's Equation: Part II

http://www.physics.rutgers.edu/ugrad/361

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Announcement

- **<u>Second HW will be due on Monday Sept 19!</u>**
- The text book is on reserve in SERC reading room

Let's recap

- Last time we "derived" time-independent Schroedinger's equation!

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V\cdot\psi = E\psi$$

- We derived this using $\lambda = \frac{h}{p}$ and a prototype wave function $\psi(x,t) = A\cos\left(\frac{2\pi}{\lambda}(x - vt)\right)$
- Today we will derive time-dependent Schroedinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x,t)\cdot\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t)$$

- And discuss the probability interpretation of the wavefunctions

Remember

$$\lambda = \frac{h}{p}, \quad \nu = \frac{E}{h}$$

$$v = \nu \lambda$$

$$\Rightarrow \frac{v}{\lambda} = \nu$$

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

$$\frac{2\pi}{\lambda} v = 2\pi \cdot \nu = 2\pi \frac{E}{h} = \frac{E}{\hbar} \equiv \omega$$

$$\psi(x,t) = A \cos\left[\frac{2\pi}{\lambda}(x - vt)\right]$$

$$= A \cos\left[\frac{1}{\hbar}(px - Et)\right]$$

$$\left[= A \cos(kx - \omega t)\right]$$

Strategy for time-dependent Schroedinger Equation

From $\frac{p^2}{2m} + V = E$ and

$\psi(x,t) = A\cos\left(\frac{1}{\hbar}(px - Et)\right)$,

- Differentiating by "x" allowed replacement of "p" and led to time-independent Schroedinger equation.
- So differentiating by "t" will lead to replacement of E and to the time-dependent Schroedinger equation.

Strategy

- So our goal is to replace ”E” by time-derivative in

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V\cdot\psi = E\psi$$

came from p^2

replace by $\frac{\partial}{\partial t}$

$$\left[\frac{p^2}{2m} + V = E\right]$$

Let's try to include time-dependence

$$\psi = A\cos\frac{2\pi}{\lambda}(x - vt) \qquad \omega = 2\pi\nu = 2\pi\frac{E}{h} = \frac{E}{\hbar}$$

use $\lambda = h/p$, $E = h\nu$,

$$\psi = A\cos\left(\frac{1}{\hbar}(px - Et)\right)$$

$$\frac{\partial\psi}{\partial t} = \frac{E}{\hbar}A\sin(\ldots)$$

$$\Rightarrow \quad A^2\sin^2(\,) + A^2\cos^2(\,) = A^2$$

$$A\sin(\,) = \pm\sqrt{A^2 - A^2\cos^2(\,)}$$

$$= \pm\sqrt{A^2 - \psi^2}$$

$$\Rightarrow \quad \frac{\partial\psi}{\partial t} = \pm\frac{E}{\hbar}\sqrt{A^2 - \psi^2}$$

$$E = \frac{\mp\hbar}{\sqrt{A^2 - \psi^2}}\frac{\partial\psi}{\partial t}$$

Insert into time-independent S.E.:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x,t)\psi = \frac{\mp\hbar\psi}{\sqrt{A^2 - \psi^2}}\frac{\partial\psi}{\partial t}$$

Problems with this result

- Amplitude appears in what we presume to be a general physical law
  - **A** should be dictated by the "boundary conditions" of the problem (more on this next time)
- There is a sign ambiguity
- There is a square root in the denominator!
  - This differential equation is non-linear
  - A sum of independent solutions would not itself be a solution

Plane wave representation for a free particle

- Schroedinger had the idea to modify the wave equation
- So the free particle wave equation becomes:

$$\Psi(x,t) = A\cos\left[\frac{1}{\hbar}(px - Et)\right] + iA\sin\left[\frac{1}{\hbar}(px - Et)\right]$$

$$= Ae^{i\left[\frac{1}{\hbar}(px - Et)\right]}$$

Time-Dependent S.E.

$$\frac{\partial \psi}{\partial t} = A e^{\frac{i}{\hbar}(px - Et)} \left(-\frac{i}{\hbar} E\right) = -\frac{i}{\hbar} E \psi$$

$$\frac{\partial \psi}{\partial x} = A e^{\frac{i}{\hbar}(px - Et)} \left(\frac{i}{\hbar} p\right) = \frac{i}{\hbar} p \psi$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{i}{\hbar} p \frac{\partial \psi}{\partial x} = \frac{i^2}{\hbar^2} p^2 \psi = -\frac{p^2}{\hbar^2} \psi$$

Now $E = \frac{p^2}{2m} + V(x,t)$

$$\Rightarrow \quad E\psi = \frac{p^2}{2m}\psi + V\psi$$

$$-\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi$$

use: $\frac{1}{i} = \frac{1}{i} \cdot \frac{i}{i} = \frac{i}{i^2} = -i$

$$\Rightarrow \quad \boxed{-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t}}$$

Time Dependent Schrodinger's Equation!

Free Particle Solution to S.E.

$$\Psi(x,t) = A\cos\left[\frac{1}{\hbar}(px - Et)\right] + iA\sin\left[\frac{1}{\hbar}(px - Et)\right]$$

$$= A e^{i\left[\frac{1}{\hbar}(px - Et)\right]}$$

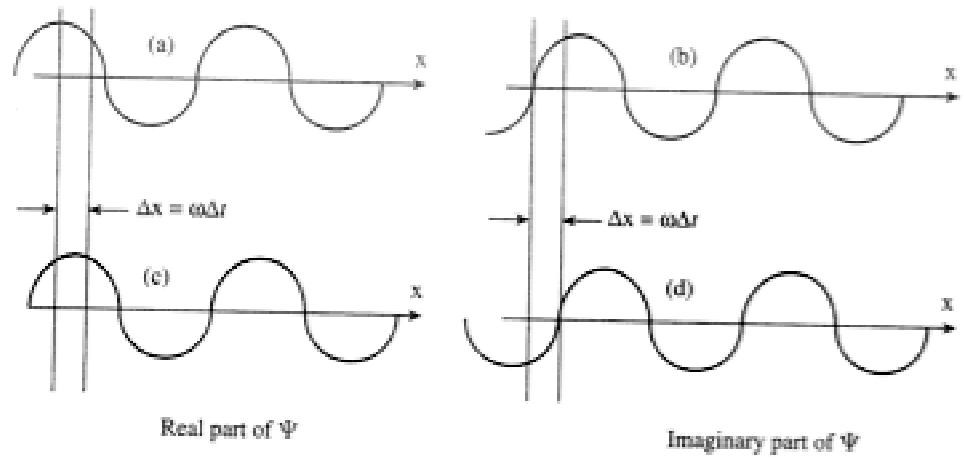


FIGURE 2.2 Real and imaginary parts of $\Psi(x, t)$ at $t = 0$ and $t = \Delta t$.

- Fig. 2.2 in Reed:
  - (a), (b): real (cosine) and imaginary (sine) parts of Ψ at t=0.
  - (c), (d): at a slightly later time Δt
  - The pattern for Ψ behaves as if it has advanced slightly to the right between t=0 and t = Δt.
  - Similarly for motion to the left (~ $e^{-i(kx+\omega t)}$).

Born's interpretation

- Question: how are we to interpret a QM wavefunction Ψ?
  - Interpretation in terms of probabilities by Max Born in 1926.

Wavefunction Ψ

- $\Psi(x,t)$ is a general complex number:

  $\Psi = A + iB$ or $Re^{i\theta}$ where $i = \sqrt{-1}$.

- **<u>Probability</u> of finding particle between x and (x+dx) at time t is:**

  $P(x,t)dx = \Psi^*(x,t)\,\Psi(x,t)dx$ **(Born's Interpretation)**

  where $\Psi^*(x,t)$ is the complex conjugate of Ψ

  $\Psi^*(x,t)\,\Psi(x,t)$ is known as the *probability density*

  $P(x,t) = \Psi^*(x,t)\,\Psi(x,t) = (A-iB)(A+iB) = A^2 - i^2B^2 = A^2 + B^2$

  So $P(x,t)$ is real and positive!

Born's interpretation, con't

- Probabilistic interpretation of Ψ does not mean that a particle can be in two or more places simultaneously!
  - Particles do not loose their identity as (essentially) point objects
- In this interpretation, we can only predict the probability of finding the particle in some region of space or of its having momentum within certain limits.
- Ψ itself has no physical reality - it's a mathematical construction to keep account of probabilities.
- The "waviness" of matter is a consequence of its probability distribution.

Normalization

- We say that a wavefunction is normalized if:

$$\int_{-\infty}^{\infty} P(x,t)\,dx = 1 \Rightarrow \int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = 1$$

- If one adds up the probabilities of finding a particle over the entire space it could possibly occupy, the total must be unity.
- The probabilities must add up to a "whole particle"
- In other words, the wavefunction Ψ must be square integrable
    - *This is one of the* **boundary conditions** *that must be imposed on solutions to the S.E.!*

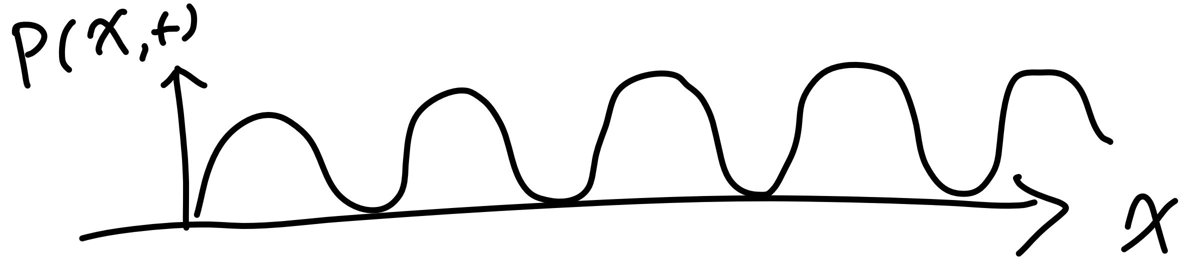
Example

- A free particle's wave function is represented by

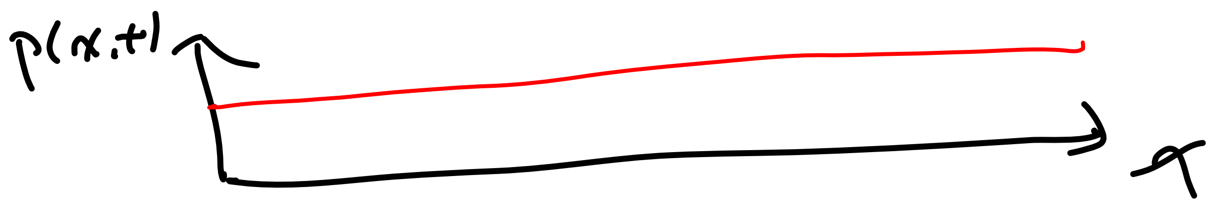
$$\psi(x,t) = A e^{\frac{i}{\hbar}(px - Et)}$$

- Which one of the following depicts the probability of finding the particle correctly?

(a)



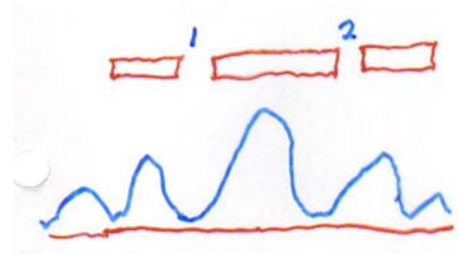
(b)



Recall: Linearity

- If $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are two different solutions to the equation for a given potential energy V, then any arbitrary linear combination of these solutions, $\Psi(x,t) = c_1\Psi_1(x,t) + c_2\Psi_2(x,t)$, is also a solution.
- It involves the first (linear) power of $\Psi_1(x,t)$ and $\Psi_2(x,t)$
- c_1 and c_2 can have any (arbitrary) complex values
- Linearity ensures we can add together wave functions
  - Constructive and destructive interference
  - Principle of superposition

Principle of superposition: Double-slit experiment

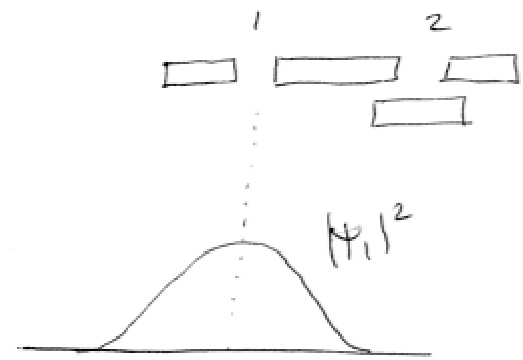


- Only slit 1 open, we have:

$$\Psi_1(x,t) = R_1(x,t)\, e^{i\theta_1}$$

- Probability distribution with only slit 1 open:

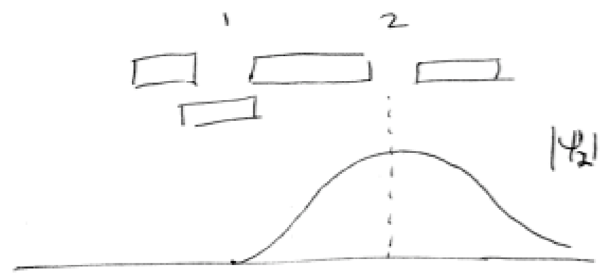
$$P_1 = \Psi_1^* \Psi_1 = R_1 e^{-i\theta_1} R_1 e^{i\theta_1} = R_1^2$$



Probability distribution

- If only slit 2 open:

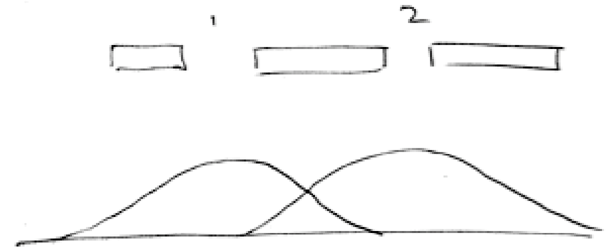
$$\Psi_2 = R_2 e^{i\theta_2} \Rightarrow P_2 = \Psi_2^* \Psi_2 = R_2^2$$



Probability distribution

Principle of superposition, con't

- Both slits open:



Individual counts/min

$$\psi = \psi_1 + \psi_2 = R_1 e^{i\theta_1} + R_2 e^{i\theta_2}$$

$$P_{12} = \psi^* \psi = (R_1 e^{-i\theta_1} + R_2 e^{-i\theta_2})(R_1 e^{i\theta_1} + R_2 e^{i\theta_2})$$

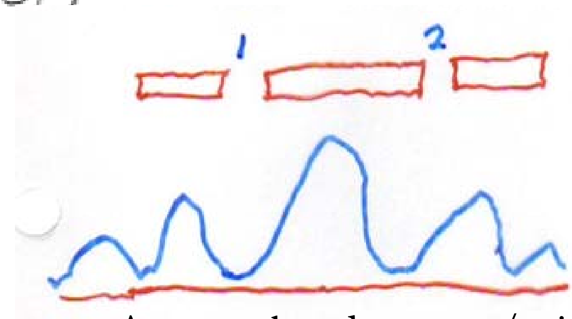
$$= R_1^2 + R_2^2 + R_1 R_2 e^{i(\theta_1 - \theta_2)} + R_1 R_2 e^{i(\theta_2 - \theta_1)}$$

$$P_{12} = R_1^2 + R_2^2 + 2 R_1 R_2 \cos(\theta_1 - \theta_2)$$

So,

$$P_{12} \neq P_1 + P_2 \quad !$$

Interference term!



Accumulated counts/min

$|\Psi_1 + \Psi_2|^2$

NOT $|\Psi_1|^2 + |\Psi_2|^2$

Boundary Conditions

1. As we already covered, Ψ must be square integrable:

$$\int_{-\infty}^{\infty} P(x,t)\,dx = 1 \Rightarrow \int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = 1$$

2. The wavefunction Ψ must be a continuous function!
   - This means forcing two solutions at the boundary to agree: $\Psi^<(\text{boundary}) = \Psi^>(\text{boundary})$

Fig. 2.3 from Reed

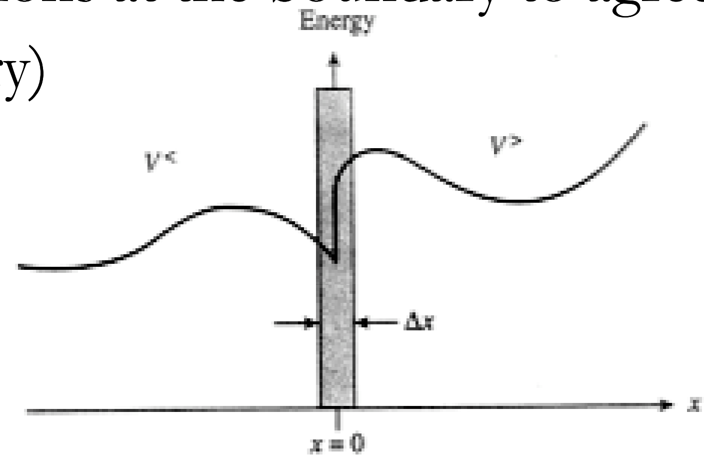


FIGURE 2.3 Potential function with a discontinuity at $x = 0$.

3. If V(x) is continuous or finitely discontinuous across a boundary, then the first derivative of Ψ, $d\Psi/dx$, must be made continuous across the boundary. But if V(x) is infinitely discontinuous across the boundary, then $d\Psi/dx$ can be discontinuous across the boundary.

- These will become clear once we start doing some examples.

Error in the book

- In Eq. 2.4.7, $v^{>}(0) - v^{<}(0)$

$$\Rightarrow \quad v^{>}(0) + v^{<}(0)$$

Change of Potential by a constant amount

- Suppose we have a particle with potential V(x), with a wavefunction solution Ψ and energy state E.
- If the potential changes to $V'(x) = V(x) + V_0$, where V_0 is constant, what will be new Ψ' and E'?

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi \qquad (1)$$

New:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi' + [V(x)+V_0]\Psi' = E'\Psi'$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\Psi'}{dx^2} + V(x)\Psi' = (E'-V_0)\Psi' \qquad (2)$$

… continued

- (1) and (2) will be identical if $E=E'+V_0$.
- So the new wavefunction will be identical $\Psi' = \Psi$. But the new energy state will be $E=E'+V_0$.
- All that happens is that the "zero" of the potential has shifted.
- This is true for all wavefunction solutions, Ψ_n (or *eignefunctions*) and E_n (or *energy eignevalues*). More on eigenfunctions and eigenvalues next time.

Example: “particle-in-a-box”

- Consider a particle of mass m which can move freely along the x axis anywhere from x=-a/2 to x=+a/2, but is strictly prohibited from being found outside this region. The particle bounces back and forth between the walls at x=±a/2 of a (1-dim) box. Assume the walls to be completely impenetrable, no matter how energetic the particle is (this is an idealization!).
- The wave function of the particle is:

$$\Psi(x,t) = \begin{cases} A\cos\frac{\pi x}{a}\, e^{-iEt/\hbar} & -\frac{a}{2} < x < +\frac{a}{2} \\ 0 & x \leq -\frac{a}{2} \text{ or } x \geq +\frac{a}{2} \end{cases}$$

Example, con't

- Verify that it is a solution to the S.E. in the region -a/2≤ x ≤ +a/2 and determine the value of the lowest energy state.

Since there are no forces acting on particle, V = constant in the region.

∴ We can take V=0 in the region.

So,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t} \qquad -\frac{a}{2} < x < +a/2$$

$$\Rightarrow \frac{\partial\psi}{\partial x} = -\frac{\pi}{a} A \sin\frac{\pi x}{a}\, e^{-iEt/\hbar}$$

$$\frac{\partial^2\psi}{\partial x^2} = -\left(\frac{\pi}{a}\right)^2 A \cos\frac{\pi x}{a}\, e^{-iEt/\hbar} = -\left(\frac{\pi}{a}\right)^2 \psi$$

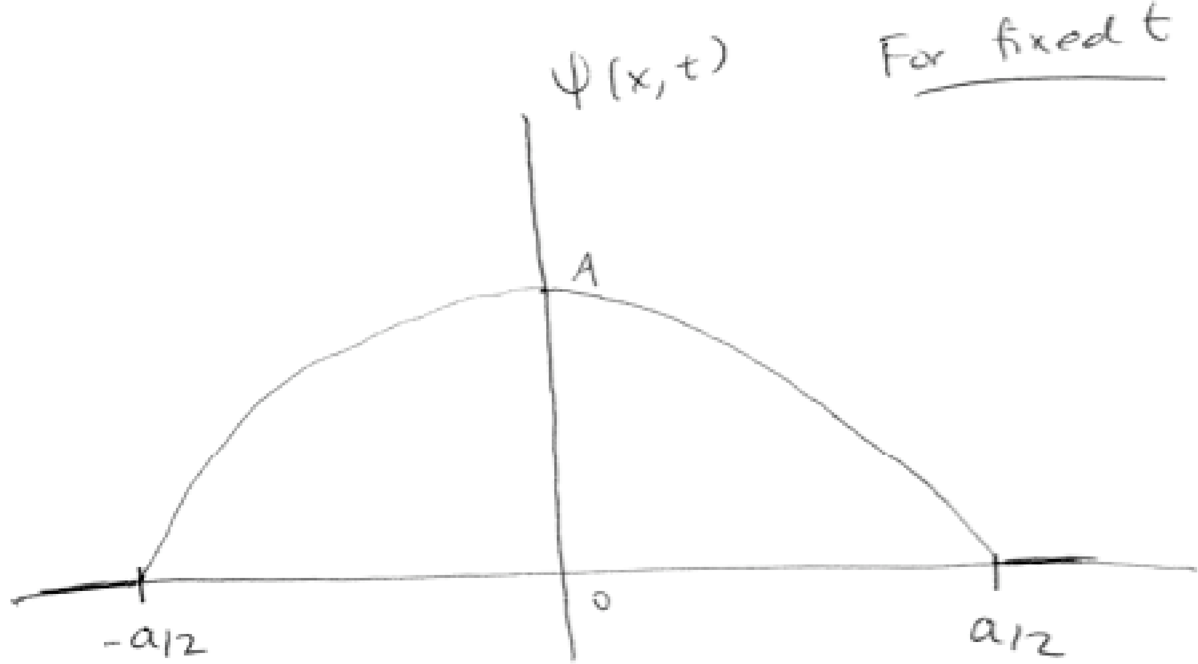
$$\frac{\partial\psi}{\partial t} = -\frac{iE}{\hbar} A \cos\frac{\pi x}{a}\, e^{-iEt/\hbar} = -\frac{iE}{\hbar}\psi$$

$$\Rightarrow +\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 \psi = -i\hbar\frac{iE}{\hbar}\psi$$

$$\frac{1}{2m}\left(\frac{\hbar\pi}{a}\right)^2 \psi = E\psi \Rightarrow \boxed{E = \frac{\pi^2\hbar^2}{2ma^2}}$$

Example, con't

- Plot the space dependence of the wave function (for fixed time).



Summary/Announcements

- We derived time-dependent Schroedinger equation
- Born's interpretation of probability density for wavefunctions
- Boundary conditions

- Next time:
  - Solutions to Schrodinger's Equation in 1 dimension

- Next homework due on Monday Sept 19!