Lecture 38
(Trapped Particles)

Physics 262-01 Spring 2019

Douglas Fields

Free Particle Solution Schrödinger's Wave Equation in 1D

- If motion is restricted to one-dimension, the del operator just becomes the partial derivative in one dimension:

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

- And then the wave function, of course, is also just a function of one dimension (plus time):

$$\Psi=\Psi\left(x,t\right)=Ae^{i\left(p_x x-Et\right)/\hbar}=Ae^{ip_x x/\hbar}e^{-iEt/\hbar}$$

- Now, this solution works for when V(x) = 0 everywhere, but fails when not. However, **when the solution has a definite energy**, the general form is:

$$\Psi\left(x,t\right)=\psi\left(x\right)e^{-iEt/\hbar}$$

Time Independent Schrödinger's Wave Equation

- Plugging this into the 1D Schrödinger's equation gives:

$$i\hbar\frac{\partial}{\partial t}\left(\psi(x)e^{-iEt/\hbar}\right)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(\psi(x)e^{-iEt/\hbar}\right)+V(x)\left(\psi(x)e^{-iEt/\hbar}\right)\Rightarrow$$

$$E\psi(x)e^{-iEt/\hbar}=-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}e^{-iEt/\hbar}+V(x)\psi(x)e^{-iEt/\hbar}$$

- And we can divide both sides of the equation by the time dependent part to get:

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

- This is called the time-independent (1D) Schrödinger's equation, which we can use to solve for the position dependence of the wave function.
- One must remember though, that the full wave function needs the time dependent part put back in:

$$\Psi(x,t)=\psi(x)e^{-iEt/\hbar}$$

Example

Consider the wave function $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$, where k is positive. Is this a valid time-independent wave function for a free particle in a stationary state? What is the energy corresponding to this wave function?

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

Example

Consider the wave function $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$, where k is positive. Is this a valid time-independent wave function for a free particle in a stationary state? What is the energy corresponding to this wave function?

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + \cancel{V(x)}^{0}\psi(x)$$

$$\frac{\partial^2}{\partial x^2}\left[A_1 e^{ikx} + A_2 e^{-ikx}\right] = \frac{\partial}{\partial x}\left[ikA_1 e^{ikx} - ikA_2 e^{-ikx}\right] = -k^2 A_1 e^{ikx} - k^2 A_2 e^{-ikx} = -k^2\psi(x) \Rightarrow$$

$$E\psi(x) = \frac{\hbar^2 k^2}{2m}\psi(x) \Rightarrow$$

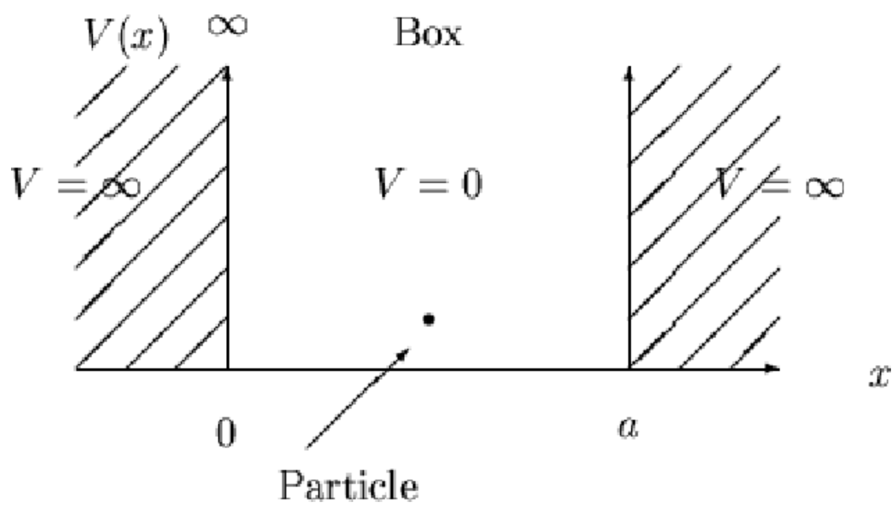
$$E = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = KE$$

This is what we expect, since the potential energy is zero.

Particle in a 1D "Box"

- The simplest potential to understand, besides the free particle (V=0 everywhere) is V=0 over some region, and V=∞ otherwise.
- Think of a string stretched between two walls…
  - The wave (particle) can be anywhere between the walls, but nowhere else.
- I will develop the solutions as if you haven't seen the waves on a string solution before.

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



Particle in a box

- So, we start with the 1D time-independent wave equation:

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

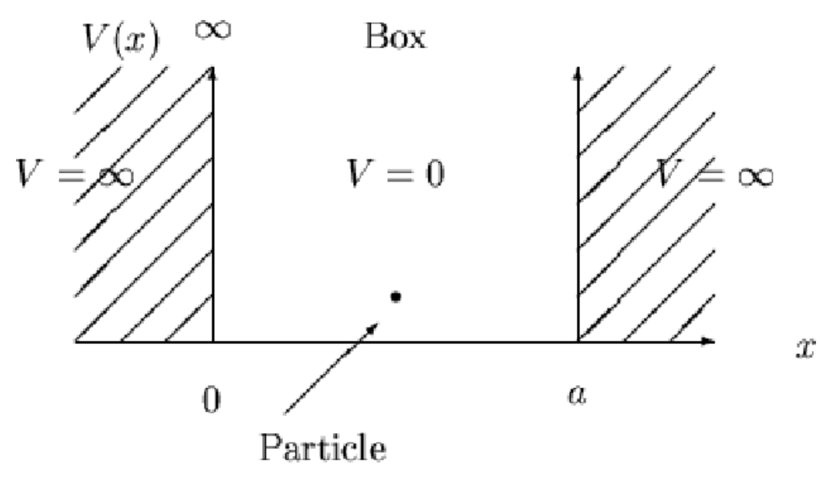
- With the potential defined as:

$$V(x) = 0 \quad (0 \le x \le a)$$
$$V(x) = \infty \quad (x < 0, x > a)$$

- Then, between 0 and a, we can use the solutions we know work:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

- Where we have included both positive and negative exponents to include wave motion in both the positive and negative directions.
- This turns out to be necessary to obey the boundary conditions as well.



Particle in a box

- Now, before we try our solutions, let's consider the boundary conditions of our problem.
- We know that the particle cannot be outside of the box defined by the region where V=0, so:

$$\psi\left(x \le 0\right) = \psi\left(x \ge a\right) = 0 \Rightarrow$$

$$\psi\left(0\right) = Ae^{ik0} + Be^{-ik0} = A + B = 0 \Rightarrow B = -A \Rightarrow$$

$$\psi\left(x\right) = Ae^{ikx} - Ae^{-ikx} = A\left[\left(\cos kx + i\sin kx\right) - \left(\cos\left(-kx\right) + i\sin\left(-kx\right)\right)\right]$$

$$\psi\left(x\right) = A\left[\left(\cos kx + i\sin kx\right) - \left(\cos kx - i\sin kx\right)\right]$$

$$\psi\left(x\right) = 2Ai\sin kx = C\sin kx$$

- Where we have conglomerated the constants together into one for convenience for now.
- Now, let's consider the other boundary, at x =a.

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

$$\psi\left(a\right) = C\sin ka = 0 \Rightarrow$$

$$ka = n\pi \Rightarrow$$

$$k_n = \frac{n\pi}{a}$$

Particle in a box

- So, we have for our wave function:

$$\psi_n(x) = C\sin kx = C\sin k_n x = C\sin\frac{n\pi x}{a}$$

- And we have only one step remaining for a complete solution, we need to determine C, the normalization constant.

$$\int_0^a |\psi(x)|^2\,dx = \int_0^a C^2\sin^2(kx)\,dx$$

$$= C^2\left[\frac{x}{2} - \frac{\sin 2kx}{4k}\right]_0^a = C^2\left[\frac{a}{2} - \frac{\sin\frac{2n\pi a}{a}}{4\frac{n\pi}{a}}\right] = C^2\frac{a}{2} \equiv 1 \Rightarrow$$

$$C = \sqrt{\frac{2}{a}}$$

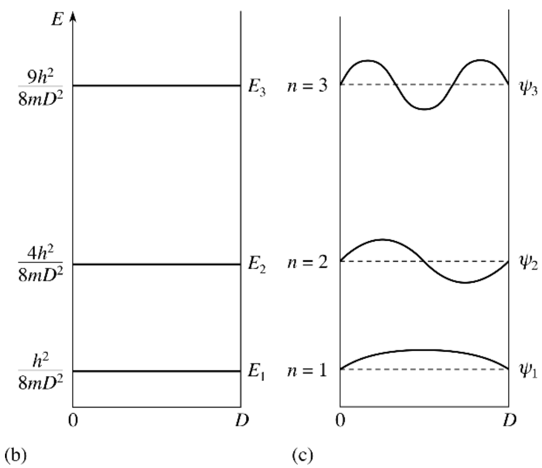
- So, we have our completed spatial wave functions:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$$

Energy Eigenvalues

- Now, these wave functions represent a series of solutions with definite energies, E_n.

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$



$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} + \cancel{V(x)}^{0}\psi(x) \Rightarrow$$

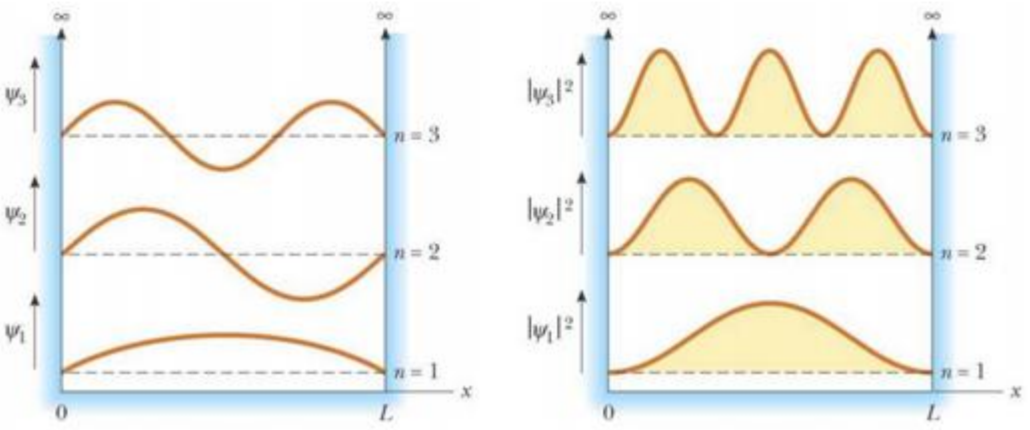
$$E\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\right) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\right) = \frac{\hbar^2 n^2 \pi^2}{2ma^2}\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\right) \Rightarrow$$

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2} = \frac{h^2 n^2}{8ma^2}$$

- The stationary states are called eigenstates, and their energies are called energy eigenvalues.
- One thing to note is that the higher the eigenvalues (energy), the more wiggly the eigenfunctions.
- This is because the kinetic energy (all there is here, since the potential is zero in the allowed region) is given by the momentum operator squared, which is proportional to the second derivative of the wave function with respect to position – its curvature!

Particle in a box

- We can also plot ψ(x), and the probability distribution for each of theses solutions:
- Note that there ARE locations inside the box where you would not expect to find the particle.



- But, if we put a particle (say, an electron) in a 1D box (say, a nano-wire) in a particular initial location, then it may not be in one of the eigenstates – it could be in a superposition of several (or many)…

Particle in a box

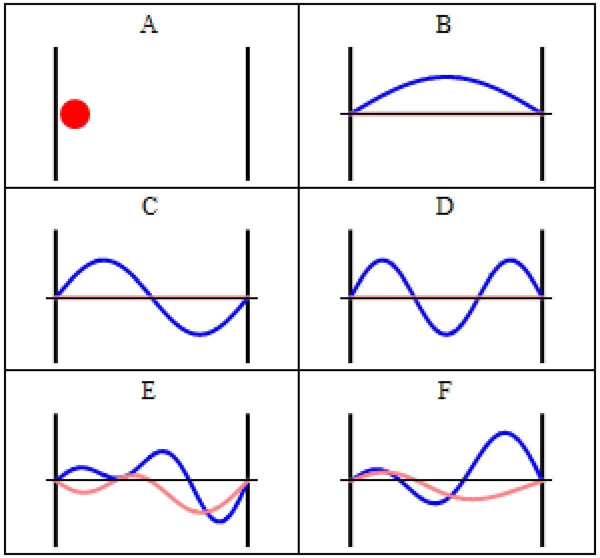
- But, we cannot forget the time dependence:

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} e^{-iE_n t/\hbar}$$

- Why? Because while states of definite energy are “stationary states” (their position probability distribution remains constant with time), if we set the initial condition as a certain position within the box, the particle will not have a definite energy – it will be a superposition of several stationary states with time dependences that will create cross terms in the probability distribution, that will change with time.

Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-F). In (B-F), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wave function. The states (B,C,D) are energy eigenstates, but (E,F) are not.

http://chemwiki.ucdavis.edu/Wikitexts/New_York_University/CHEM-UA_127%3A_Advanced_General_Chemistry_I/06%3A_The_Schr%C3%B6dinger_equation%3A_Predicting_energy_levels_and_the_particle-in-a-box_model



Orthonormal Sets

- The set of wave functions form a complete set for this geometry:

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} e^{-iE_n t/\hbar}$$

for any function $f(x,t)$ that obeys the boundary conditions:

$$f(x,t) = \sum_{n=1}^{\infty} w_n \Psi_n(x,t)$$

- Let's look at the probability density for one of the "eigenstates":

$$\Psi(x,t) = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} e^{-iE_1 t/\hbar}$$

$$P = \Psi^*(x,t)\Psi(x,t) = \frac{2}{a}\left(\sin \frac{\pi x}{a} e^{iE_1 t/\hbar}\right)\left(\sin \frac{\pi x}{a} e^{-iE_1 t/\hbar}\right)$$

$$= \frac{2}{a}\left[\sin^2\left(\frac{\pi x}{a}\right) \cancel{e^{i(E_1 - E_1)t/\hbar}}\right]$$

$$= \frac{2}{a}\sin^2\left(\frac{\pi x}{a}\right)$$

← Time independent!

Orthonormal Sets

- Let's just look at the probability density for a superposition of two energy "eigenstates":

$$\Psi(x,t)=\frac{1}{\sqrt{2}}\left(\Psi_1(x,t)+\Psi_2(x,t)\right)=\sqrt{\frac{1}{a}}\left(\sin\frac{\pi x}{a}e^{-iE_1t/\hbar}+\sin\frac{2\pi x}{a}e^{-iE_2t/\hbar}\right)$$

$$P=\Psi^*(x,t)\Psi(x,t)=\frac{1}{a}\left(\sin\frac{\pi x}{a}e^{iE_1t/\hbar}+\sin\frac{2\pi x}{a}e^{iE_2t/\hbar}\right)\left(\sin\frac{\pi x}{a}e^{-iE_1t/\hbar}+\sin\frac{2\pi x}{a}e^{-iE_2t/\hbar}\right)$$

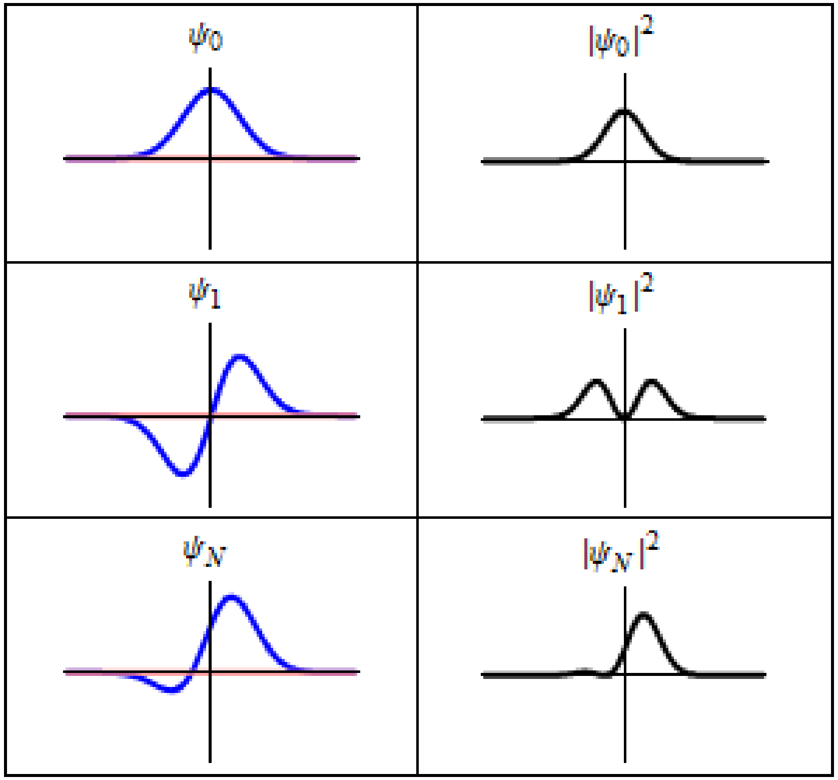
$$=\frac{1}{a}\left[\sin^2\left(\frac{\pi x}{a}\right)+\sin^2\left(\frac{2\pi x}{a}\right)+\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)\left\{e^{i(E_2-E_1)t/\hbar}+e^{-i(E_2-E_1)t/\hbar}\right\}\right]$$

$$=\frac{1}{a}\left[\sin^2\left(\frac{\pi x}{a}\right)+\sin^2\left(\frac{2\pi x}{a}\right)+\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)2\cos\left(\Delta Et/\hbar\right)\right]$$

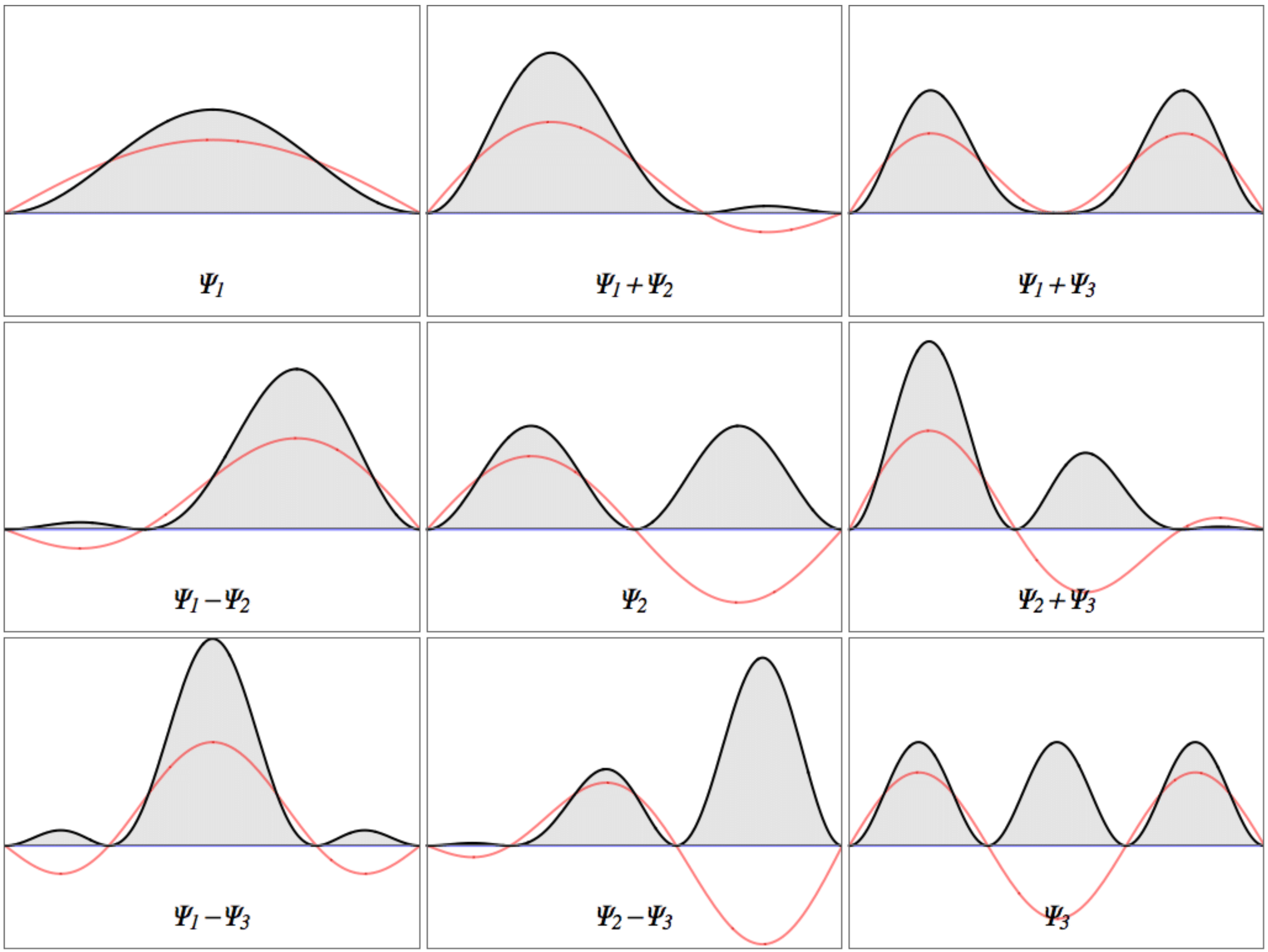
Time dependent!

Eigenstates and mixed states

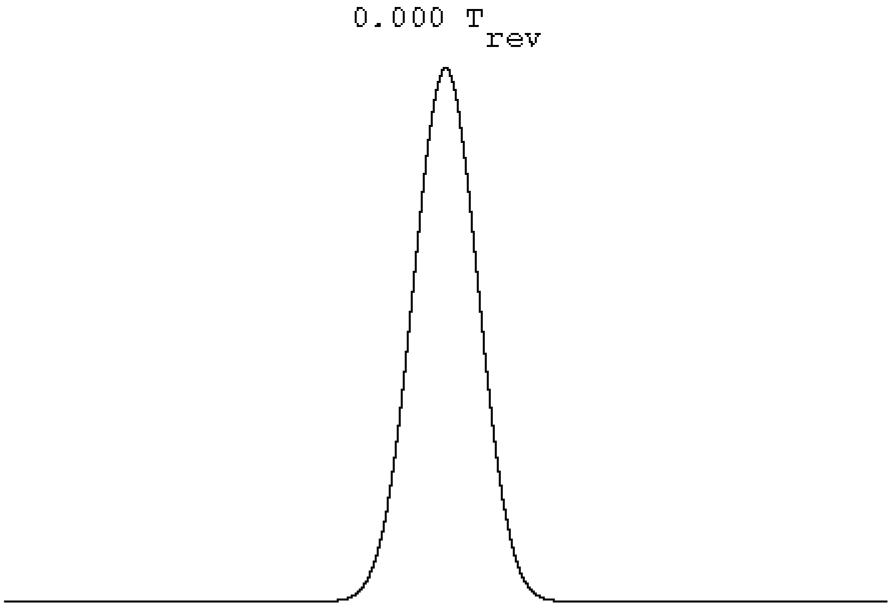
- So, eigenstates are characteristic states of the Schrodinger equation with determined energy.
- These states correspond to a position dependence that doesn't depend on time.
- But combinations of these states CAN have time dependence of the position.



Infinite Square Well



Gaussian position wavefunction in an infinite potential well



Hamiltonians…

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

let,

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

then,

$$\hat{H}\psi_E = E\psi_E$$