Quantum Mechanics Part 2

Ch 40 The Schoedinger Eqn.

Making sense of ψ

The Schoedinger Equation

- There are physics laws which are encoded in equations e.g. F=ma; $E_{initial}=E_{final}$ etc
- Is there a rule for ψ ?????
- Schoedinger ~ 1924

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

- Why do we believe it
  - Because it works!

What is the program?

- Justifying it
  - This isn't the real reason we believe it
  - real reason is because of experiment
- Making models of real life and solving
  - Periodic Table of the elements
  - Molecular binding (chemistry)
  - tunneling (decay)
  - transistors
  - Zero point energy of the vacuum!
  - …

A " justification" of the Schroedinger eqn

A wave can be written as a sin so we will guess

$$\psi(x) = \psi_0 \sin\left(\frac{2\pi x}{\lambda}\right)$$

this represents matter waves

hmm

Lets take the second derivative

$$\frac{d\psi}{dx} = \frac{2\pi}{\lambda}\psi_0 \cos\left(\frac{2\pi x}{\lambda}\right) \qquad \frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi_0 \sin\left(\frac{2\pi x}{\lambda}\right) = -\left(\frac{2\pi}{\lambda}\right)^2 \psi(x)$$

now $p=\sqrt{2\,mK}$ where $K = \frac{1}{2}mv^2$

Note: I cheated a bit, since K is really K(x)

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2\,mK}} \text{ (from deBroglie)}$$

$$\frac{d^2\psi}{dx^2} = -\frac{(2\pi)^2}{\lambda^2}\psi(x) = -\frac{(2\pi)^2\, 2\,mK}{h^2}\psi(x) = -\frac{2m}{\hbar^2}K\psi(x)$$

Now setting K(x)=E-U(x) we get

potential energy

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}[E-U(x)]\psi(x) \text{ the Schroeding eqn}$$

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

- This is the 1-D eqn. We should really use a 3-D version (in this class we will stick to 1-D)
- what we need to do is to find appropriate U(x) which describe real situations and then solve for ψ(x)

Boundary Conditions

- We have to require some things about $\psi(x)$ since $P(x)= \psi^2$
  - $\psi(x)$ must be continuous
  - $\psi(x) \rightarrow 0$ as $x \rightarrow \infty$ and $x \rightarrow -\infty$
  - $\psi(x)=0$ in areas it should not be
  - $\psi(x)$ must be normalized (i.e. its total probability = 1 or 100%)

PROBLEM-SOLVING STRATEGY Quantum-mechanics problems

MODEL Determine a potential-energy function that describes the particle's interactions. Make simplifying assumptions.

VISUALIZE The potential-energy curve is the pictorial representation.

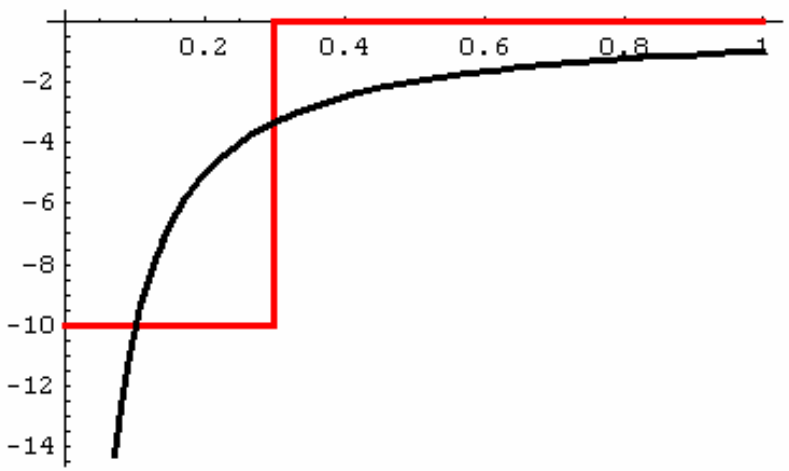
- Draw the potential-energy curve.
- Identify known information.
- Establish the boundary conditions that the wave function must satisfy.

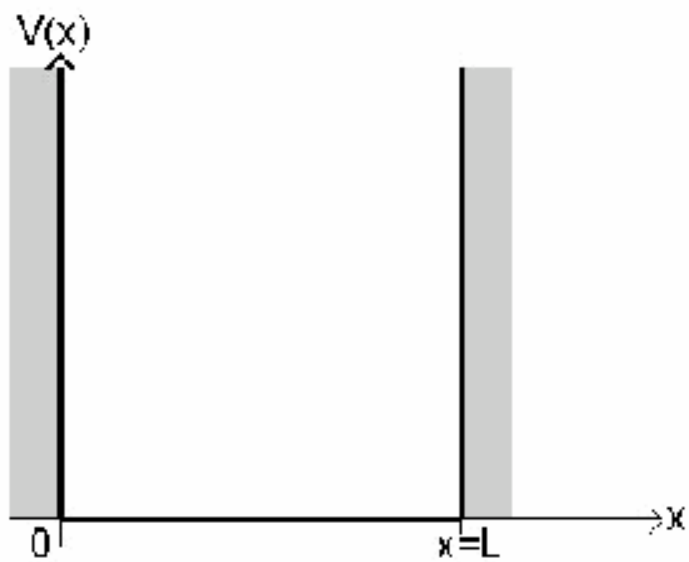
SOLVE The Schrödinger equation is the mathematical representation.

- Utilize the boundary conditions.
- Normalize the wave functions.
- Draw graphs of $\psi(x)$ and $|\psi(x)|^2$.
- Determine the allowed energy levels.
- Calculate probabilities, wavelengths, or other specific quantities.

ASSESS Check that your result has the correct units, is reasonable, and answers the question.

What kinds of problems do we want to solve?

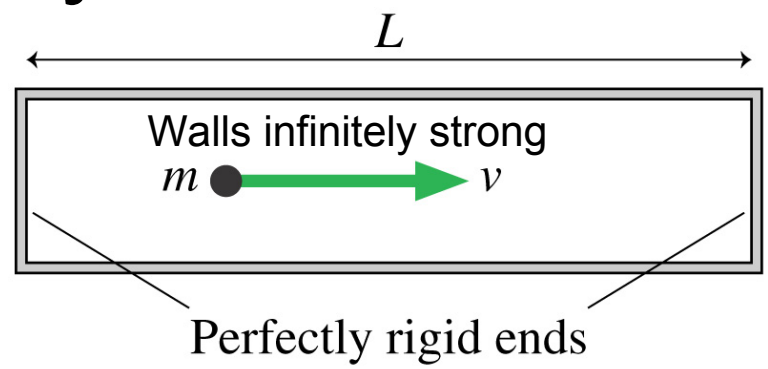


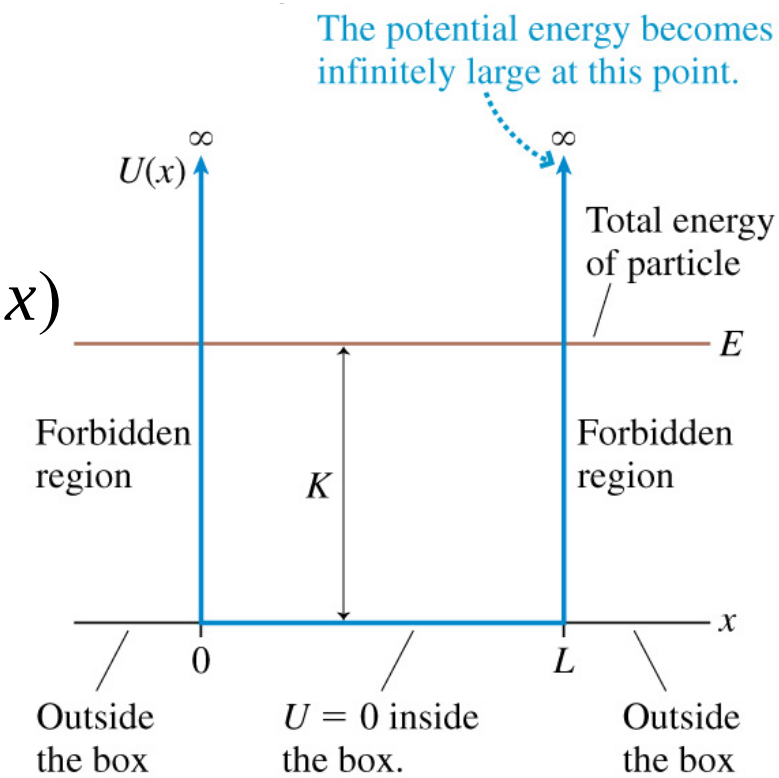


- Atom (to get the Bohr model)
  - $U(X)=-e^2/r$ (Black line)
    - in 3D
  - Too hard –make it 1-D
  - too hard (approx with the red line)
  - Still to hard – approx as a 1D box with infinitely high walls.
    - Maybe not such a good approx, but perhaps we will see some basic things like energy only having some specific values i.e. energy quantization

Particle in a box – a toy model

- 1-D $\frac{d^2\psi(x)}{dx^2} = -\frac{2m}{\hbar^2}[E - U(x)]\psi(x)$
- draw potential
  - U(x)=0 0<x<L
  - U(x)= ∞ x=0; x=L
    - ψ(x)=0 if x≤0 or x ≥L
  - Solutions to $\frac{d^2\psi(x)}{dx^2} = -C\psi(x)$
    - sin, cos
    - choose sin since sin(0)=0
    - try Asin(kx)





Particle in a box

If we assume $\psi(x)=0$ at $x=0$ and $x=L$

and only consider the Sch eqn between 0 and L

we can set $U(x)=0$

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

$\psi(x)=A\sin(kx)$

$\psi(L)=A\sin(kL)=0$ from BC

$kL=n\pi \quad k=n\pi/L \quad n=1,2,\ldots$

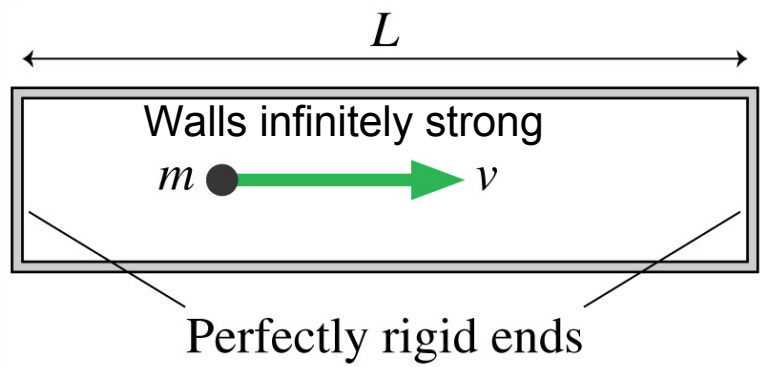
n is called a quantum number

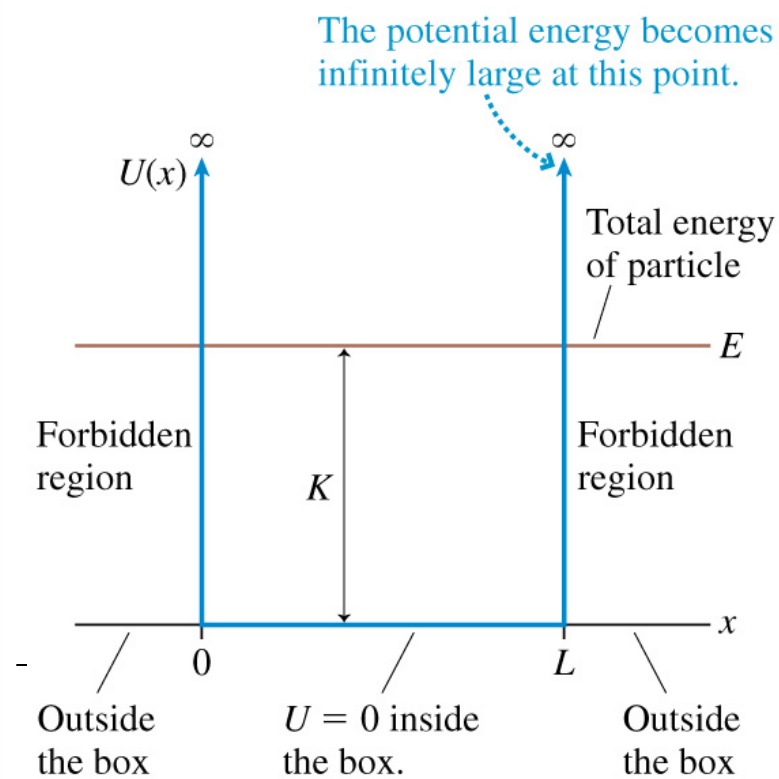
$$\frac{d^2\psi}{dx^2} = -k^2 A\sin(kx)$$

$$-k^2 A\sin(kx) = -\frac{2mE}{\hbar^2} A\sin(kx)$$

$$-k^2 = -\frac{2mE}{\hbar^2} = -n^2\pi^2/L^2$$

$$E = n^2\frac{\pi^2\hbar^2}{2mL^2}$$ (WOW! Energy Quantized)





Normalize and finish

$\psi(x)=A\sin(\frac{n\pi x}{L})$ $0<x<L$ and 0 otherwise. Now normalize

$$1 = \int_{-\infty}^{\infty}\psi^2\, dx = A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = A^2 \frac{L}{n\pi} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) d\left(\frac{n\pi x}{L}\right) =$$

$$A^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2(y)\, d(y) = A^2 \frac{L}{n\pi} \frac{n\pi}{2} = A^2 \frac{L}{2} \qquad A=\sqrt{\frac{2}{L}}$$

Finally our solution is

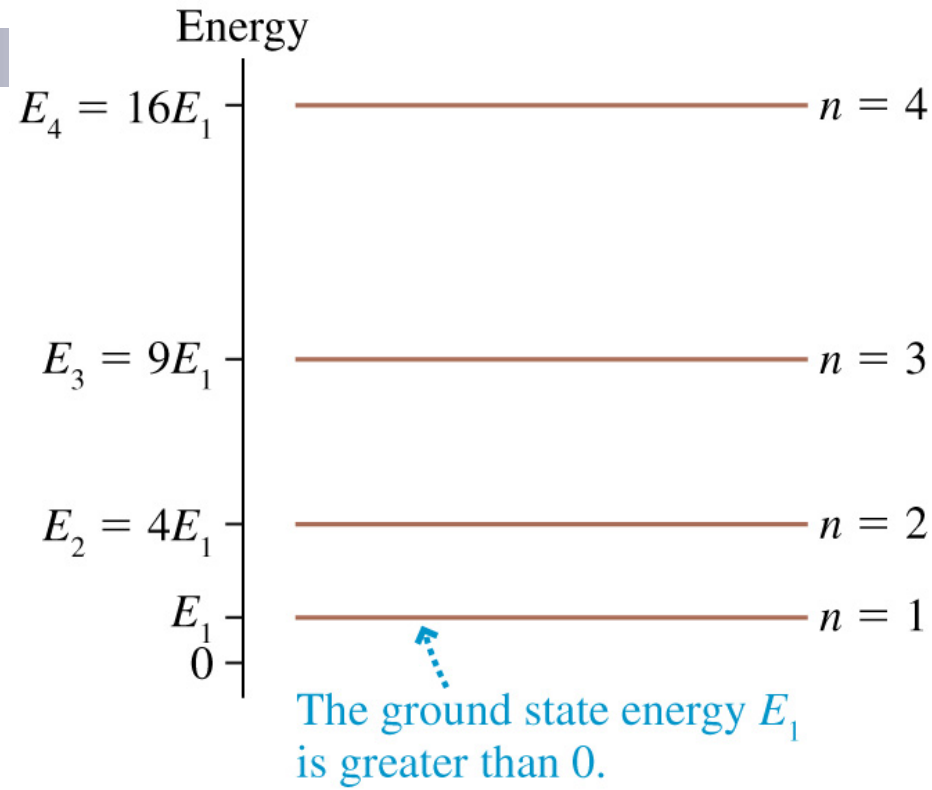
$\psi_n(x)=\sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$ $0<x<L$ and 0 otherwise.

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2\,mL^2} \qquad n=1,2,3....$$

So what does it mean?

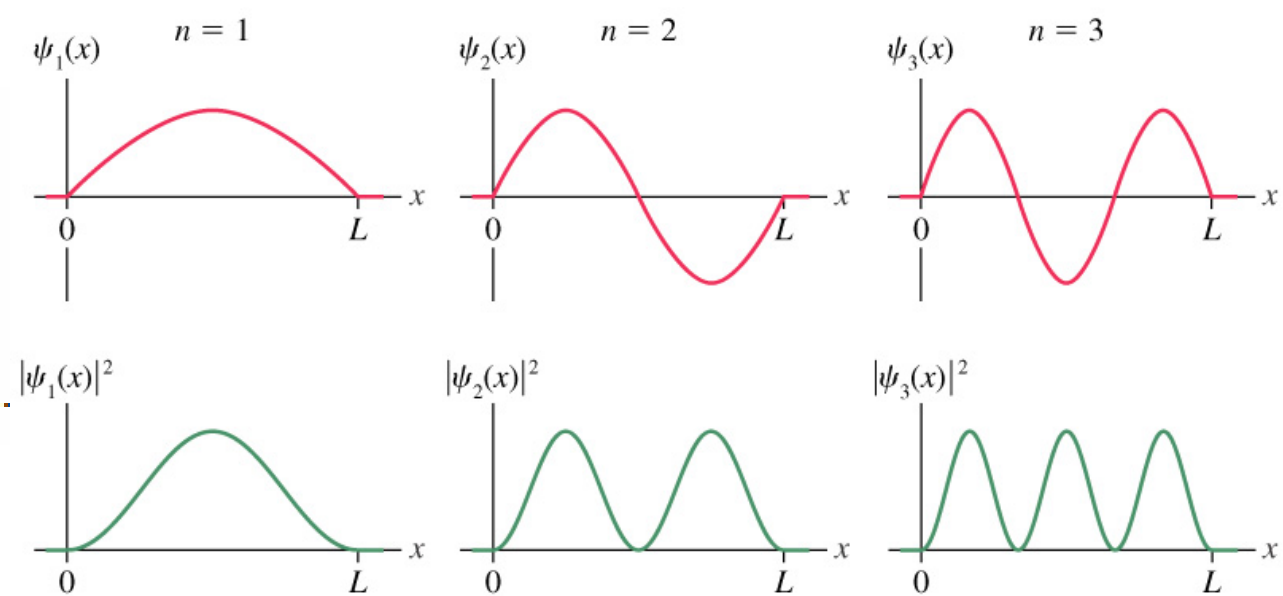
$$E_n = n^2 E_1 \qquad E_1 = \frac{\pi^2 \hbar^2}{2\,mL^2}$$

There is NO E=0 state!
a zero-point energy
Consistent with heisenberg
momentum>0



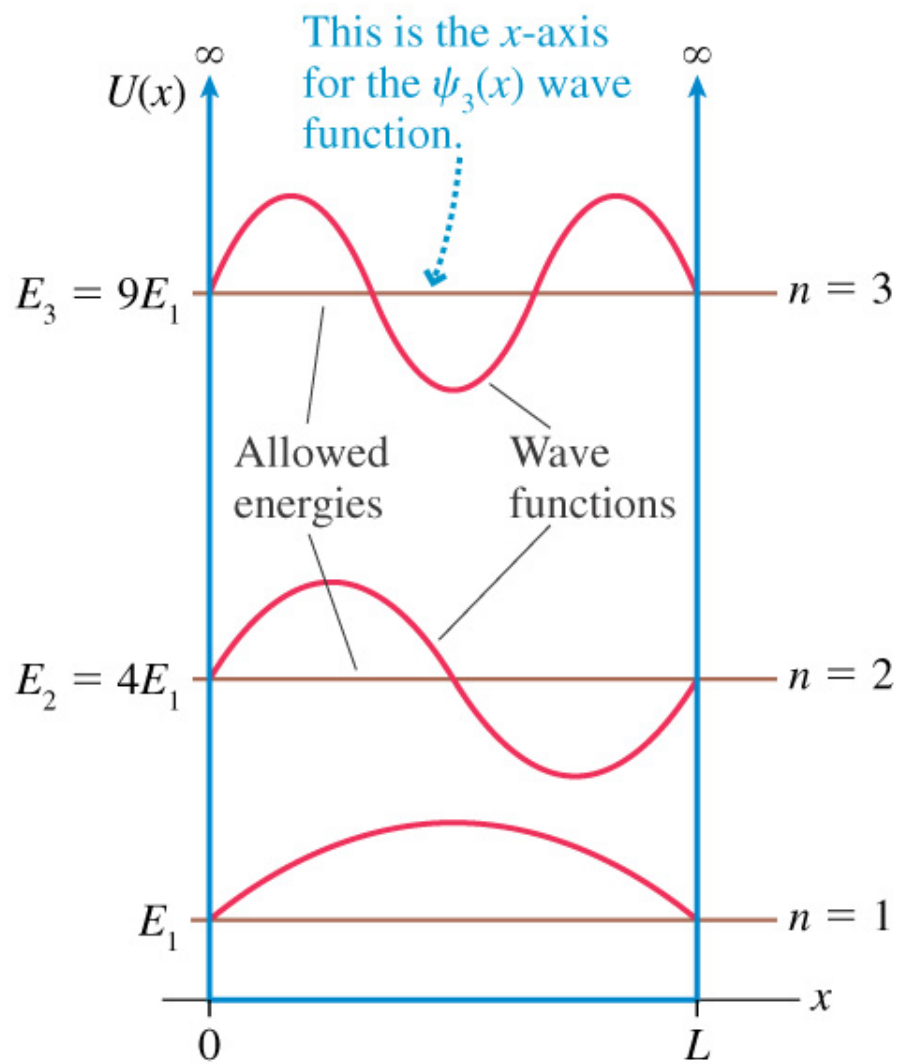
$$\psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right)$$

0<x<L and 0 otherwise.



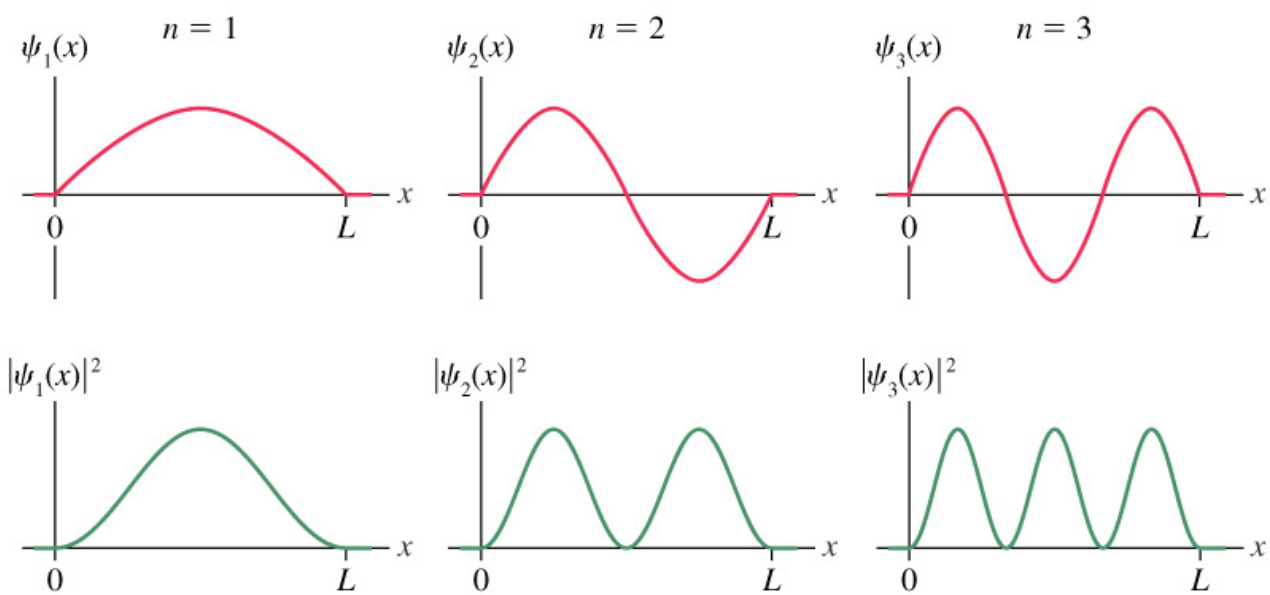
A nice way to picture it

- Sometime we draw a picture like this for clarity.
  - We don't really mean that the wave function starts higher up.

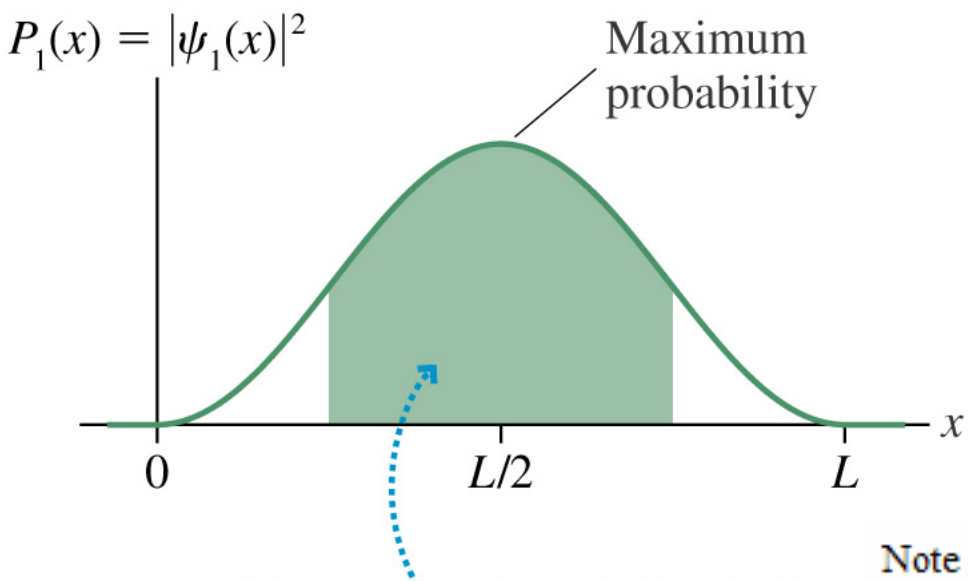


Thought questions

- For the n=2 state the particle is most likely to be found
  - in the middle
  - about ¼ of the way from either end
  - at one of the ends
  - the same everywhere



an example



- Prob of finding a particle between L/4 to 3L/4 if it is in the ground state of a particle in a 1-D box
  - start with normalized wave function!

Note look up in integral table (CRC)

$$\int \sin^2(ax)\, dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax$$

since n=1 $\psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$

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

0<x<L and 0 otherwise.

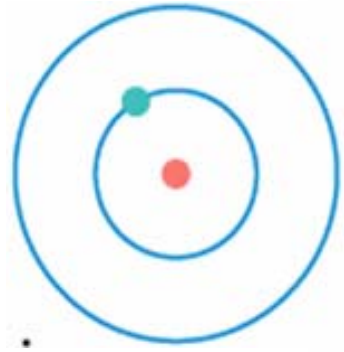
$$\text{Prob}\left(\frac{L}{4} < x < \frac{3L}{4}\right) = \int_{L/4}^{3L/4}\psi^2\, dx = \frac{2}{L}\int_{L/4}^{3L/4}\sin^2\left(\frac{\pi x}{L}\right) dx =$$

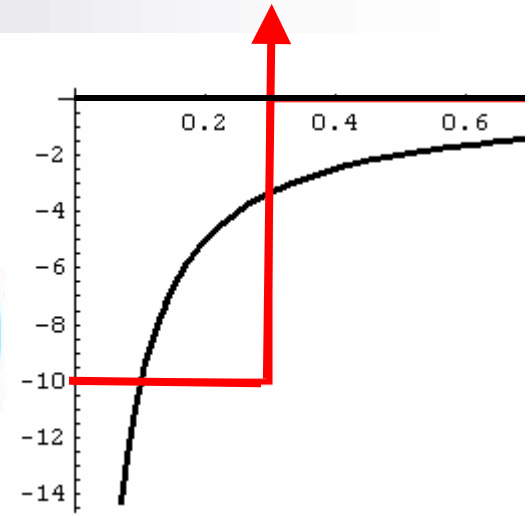
$$\frac{2}{L}\left[\frac{1}{2}x - \frac{L}{4\pi}\sin\left(2\frac{\pi}{L}x\right)\right]_{L/4}^{3L/4} = \left[\frac{x}{L} - \frac{1}{2\pi}\sin\left(2\frac{\pi}{L}x\right)\right]_{L/4}^{3L/4} =$$

$$\frac{3}{4} - \frac{1}{2\pi}\sin\left(3\frac{\pi}{2}\right) - \frac{1}{4} + \frac{1}{2\pi}\sin\left(\frac{\pi}{2}\right) = \frac{1}{2} + \frac{1}{\pi} = 0.818$$

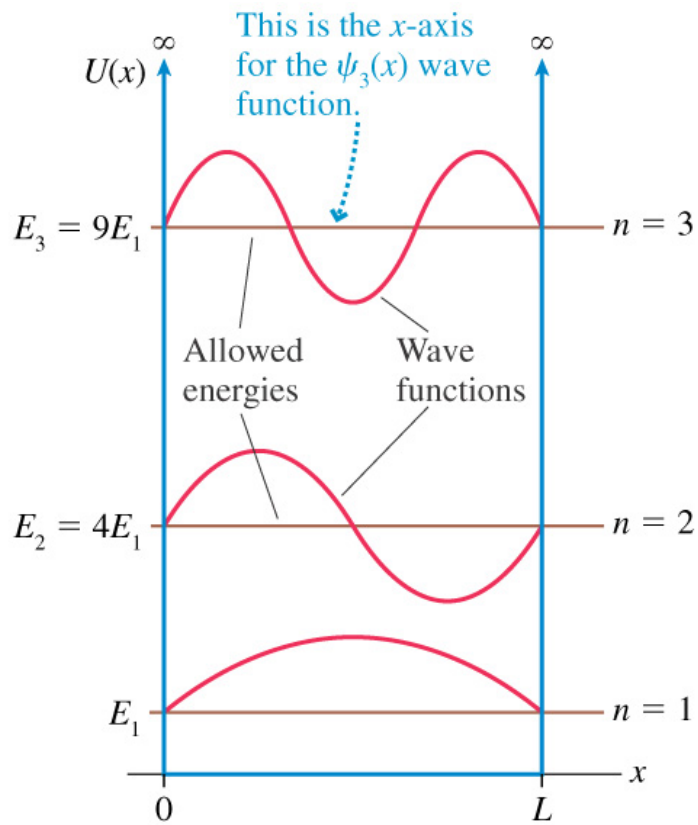
So have we learned anything?

- we modeled an coulomb potential as an infinite well
- we used 1-D instead of 3-D





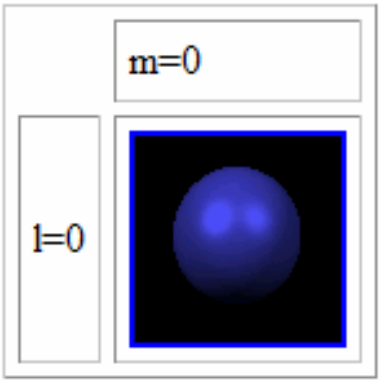
- BUT
  - ☺ we got quantized energies
  - ☺ quantized radii
  - ☹ The shapes of the wave functions don't tell us much about real life
- Maybe if we go to a 3-D model with a real 1/r coulomb potential we might get something that makes sense



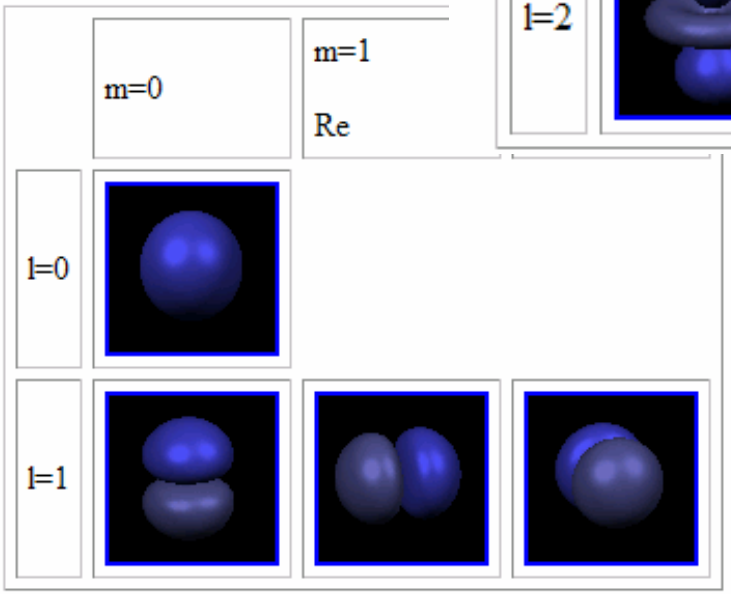
Do it

chapter 41

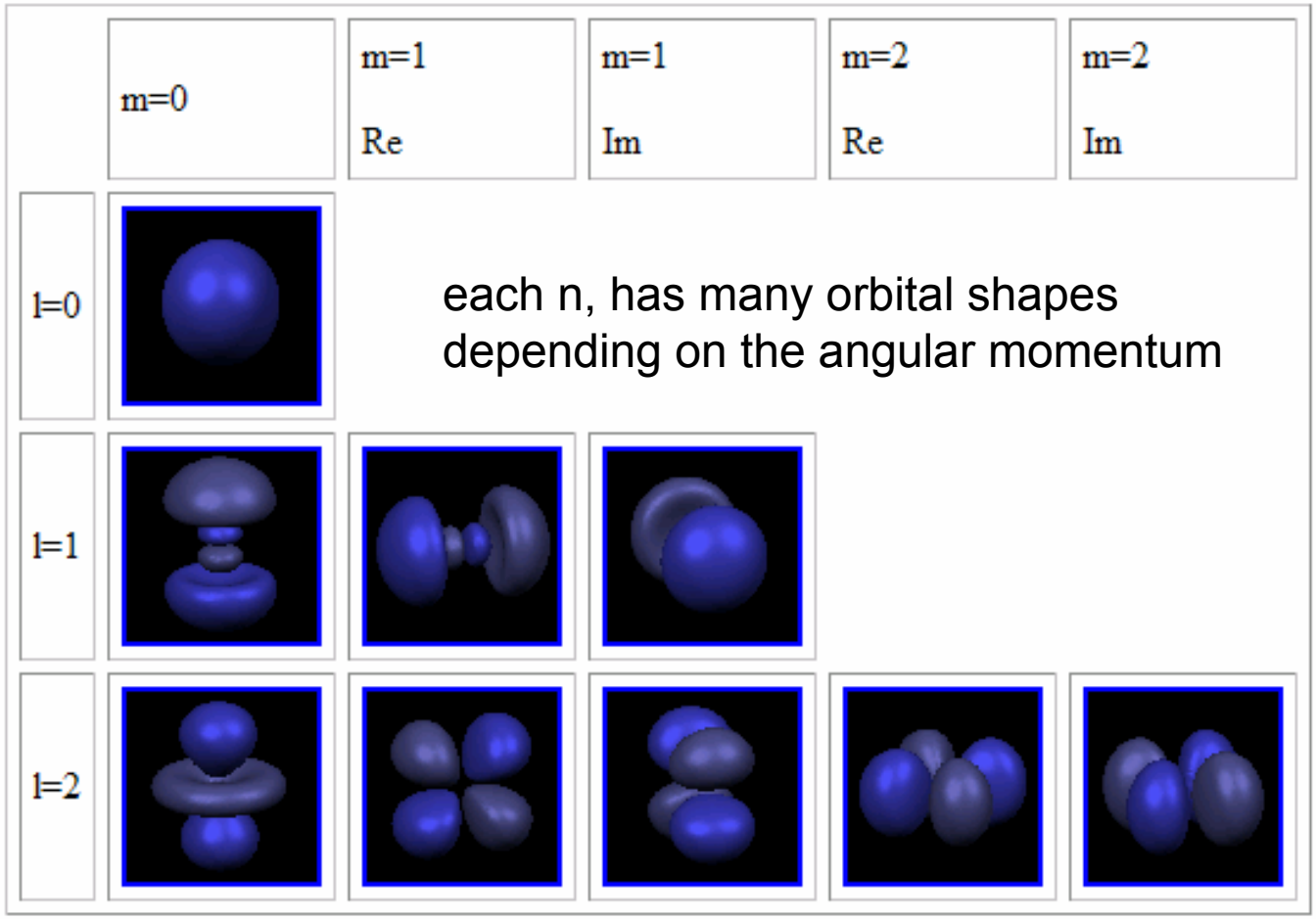
- **n=1:**



- **n=2:**



- **n=3:**

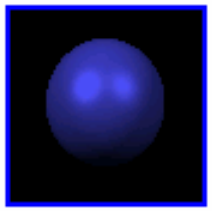
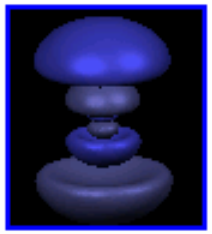
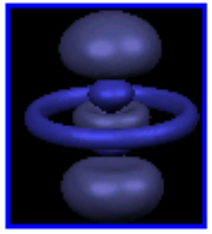
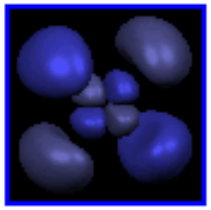
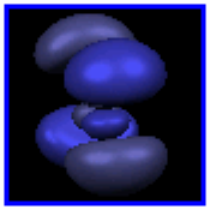
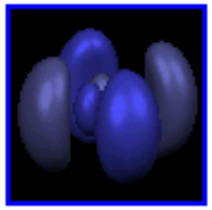
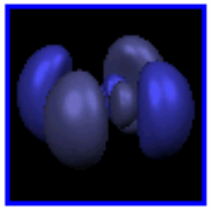
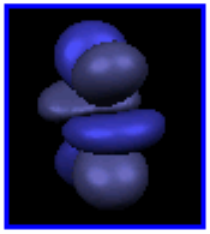


each n, has many orbital shapes depending on the angular momentum

- Get the right energies!
  - $E=-13.6ev/n^2$
- Get orbital shapes
  - Chemistry!

it Gets pretty complicated

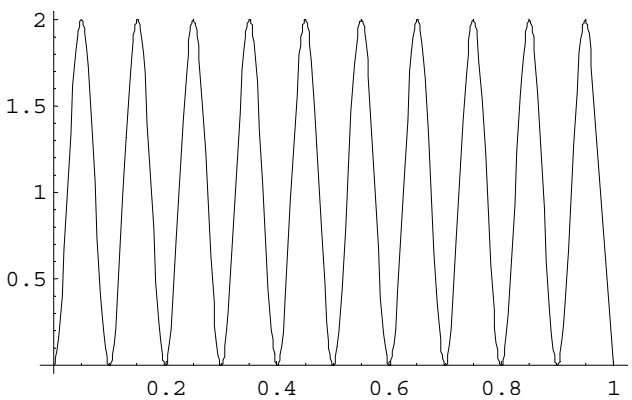
- **n=4:**

	m=0	m=1 Re	m=1 Im	m=2 Re	m=2 Im	m=3 Re	m=3 Im
l=0							
l=1							
l=2							
l=3							

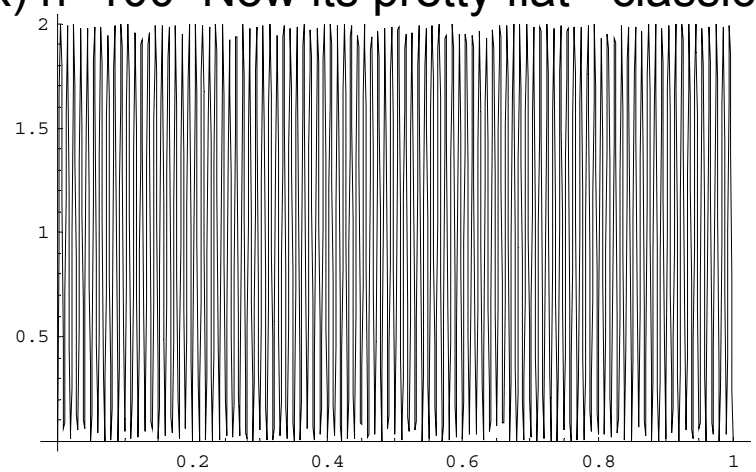
The correspondence principle

- If you put a ball in a box and let it rattle around, the probability of finding it anywhere in the box is pretty much the same
- How does this square with QM??
- Answer: For large quantum number n the probabilities approach the classical value

P(x) n=10

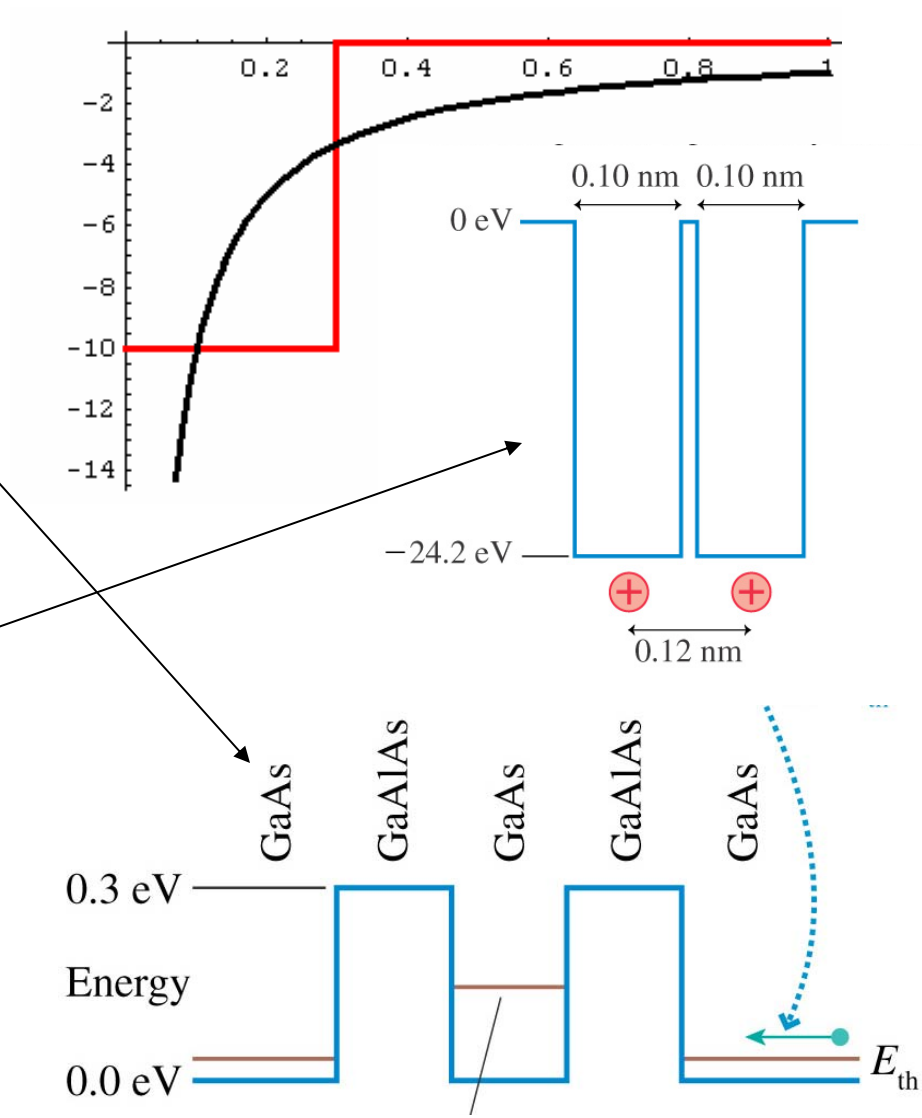


P(x) n=100 Now its pretty flat ~classical

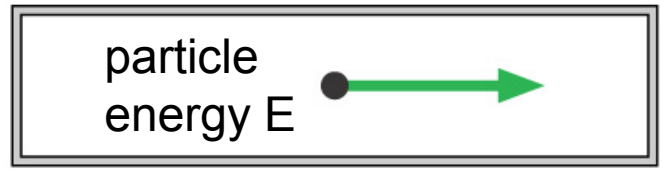


Now for something more realistic

- Finite potential wells
  - Better approx to Coulomb potential
  - Pretty good model for an electron in semiconductor
    - transistors, your cell phone etc
  - Two potential finite potential wells can be like a H_2 atom
  - We can learn a lot from these…

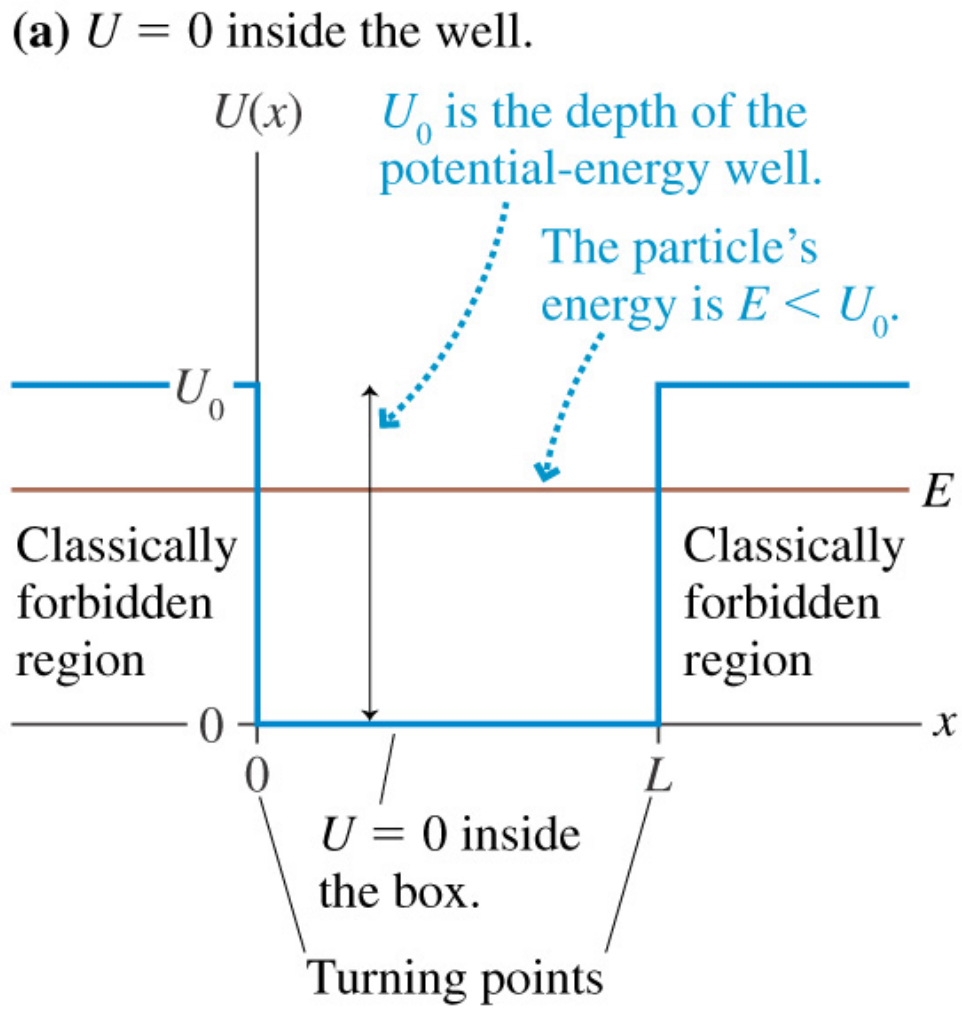


A finite potential well

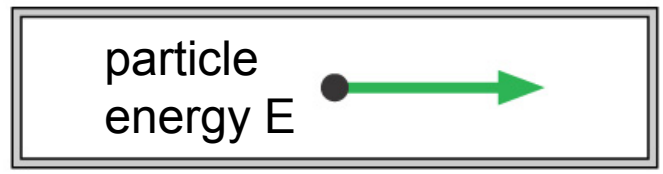


Walls are not infinitely strong

- U=0 0<x<L
- U=U_0 x<0 or x>L
- Particle with energy E
  - E can be
    - >U_0 Free particle
      - energy enough to puncture walls
    - <U_0 Particle "trapped in well"
      - X<0 and X>L is the "classically forbidden region"



wave function Inside the box



Walls are not infinitely strong

Lets start with the Schroedinger eqn

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

Inside the well U(x)=0 so we have

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2m}{\hbar^2}E\psi(x)$$ just like we had before.

The problem is that we now longer have the boundary condition $\psi(x)=0$ at x=0 and x=L

A general solution to this eqn is

$\psi(x) = A\sin(kx)+B\cos(kx)$ Lets check it

$$\frac{d^2\psi(x)}{dx^2} = -k^2 A\sin(kx) - k^2 B\cos(kx)$$ so we have

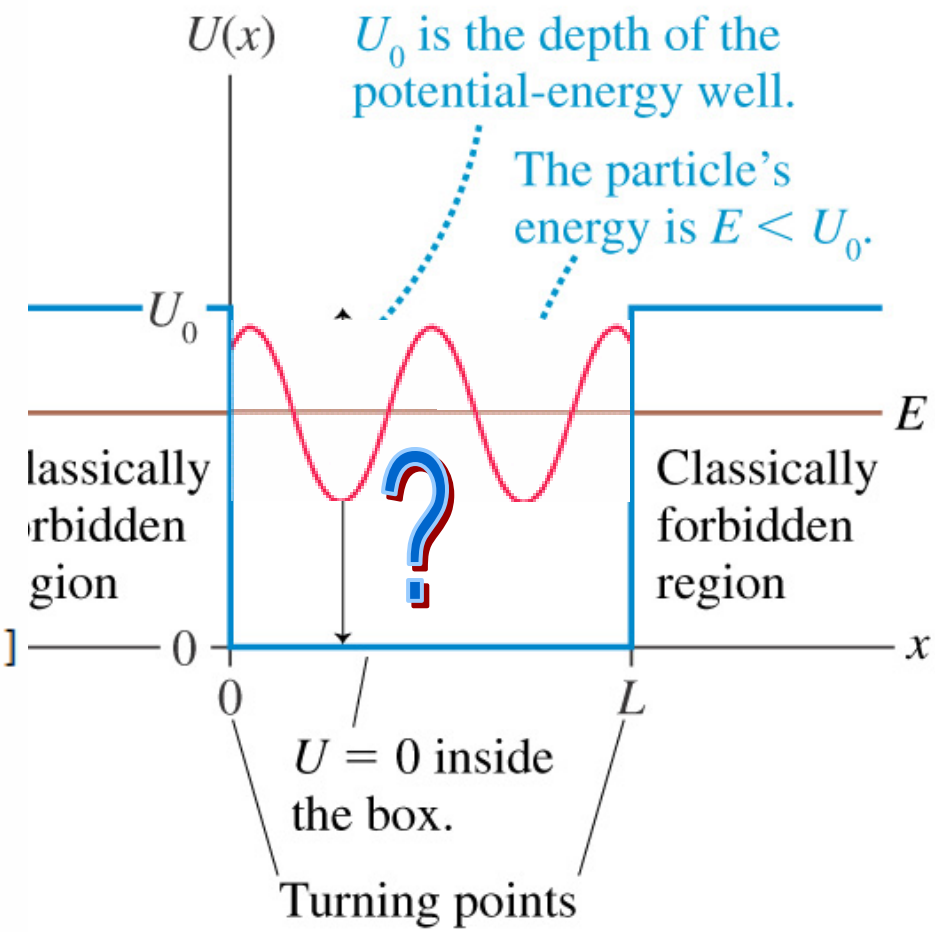
$$-k^2 A\sin(kx) - k^2 B\cos(kx) = -\frac{2m}{\hbar^2}E[A\sin(kx)+B\cos(kx)]$$

So it works and we also have $k=\sqrt{\frac{2mE}{\hbar^2}}$

the solution INSIDE the well is then

$\psi(x) = A\sin(kx)+B\cos(kx)$ where $k=\sqrt{\frac{2mE}{\hbar^2}}$

) $U = 0$ inside the well.



wave function OUTSIDE the box

Lets start with the Schroedinger eqn again

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

OUTSIDE well $U(x) = U_0$ so we have

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2m}{\hbar^2}[E-U_0]\psi(x)$$

BUT $E - U_0 < 0$ so lets turn it around

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}[U_0-E]\psi(x)$$ and remember that U_0-E > 0

Note that there is no more negative sign so sin and cos

will NOT solve the solution (try it) The general solution is

$\psi(x) = Fe^{\kappa x}+Ge^{-\kappa x}$ (Outside) let check

we remember that $\frac{d}{dx}(e^{\kappa x}) = \kappa e^{\kappa x}$

$$\frac{d^2\psi(x)}{dx^2} = \kappa^2 Fe^{\kappa x} + \kappa^2 G e^{-\kappa x}$$ so we have

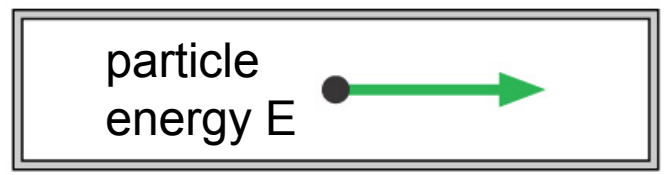
$$\kappa^2 Fe^{\kappa x} + \kappa^2 G e^{-\kappa x} = \frac{2m}{\hbar^2}[U_0-E](Fe^{\kappa x}+Ge^{-\kappa x})$$

So it works and we also have $\kappa = \sqrt{\frac{2m(U_0-E)}{\hbar^2}}$

good thing that U_0-E > 0 or we would have a problem

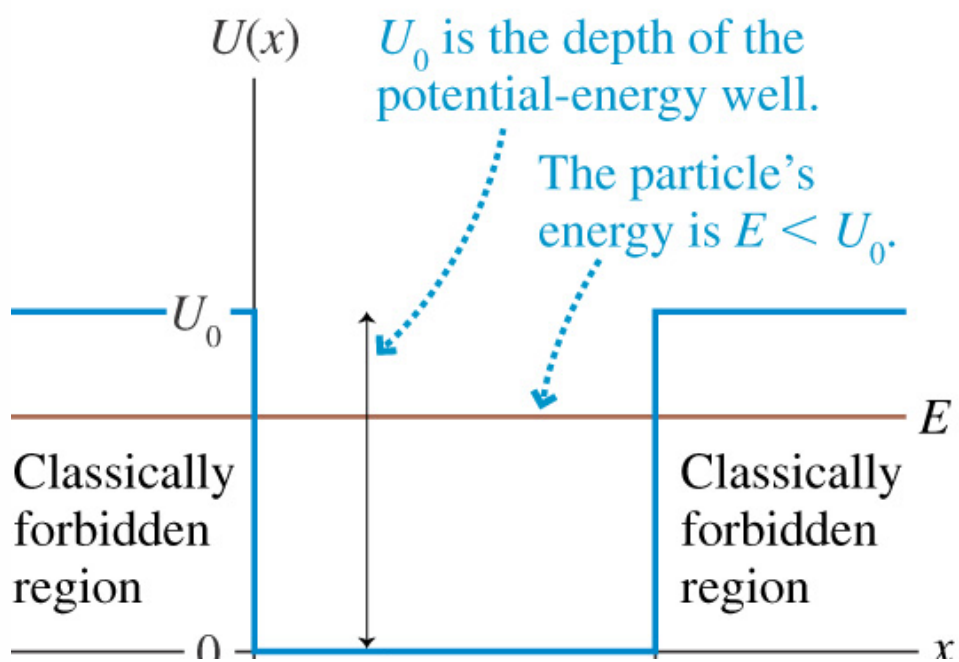
the solution OUTSIDE the well is then

$\psi(x) = Fe^{\kappa x}+Ge^{-\kappa x}$ where $\kappa = \sqrt{\frac{2m(U_0-E)}{\hbar^2}}$



Walls are not infinitely strong

(a) $U = 0$ inside the well.



More boundary conditions

$\psi(x) = Fe^{\kappa x} + Ge^{-\kappa x}$ where $\kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$

Now $\psi(x) \longrightarrow 0$ and $x \longrightarrow \infty$ or $x \longrightarrow -\infty$

So to the left of the well G=0

and to the right of the well F=0 so

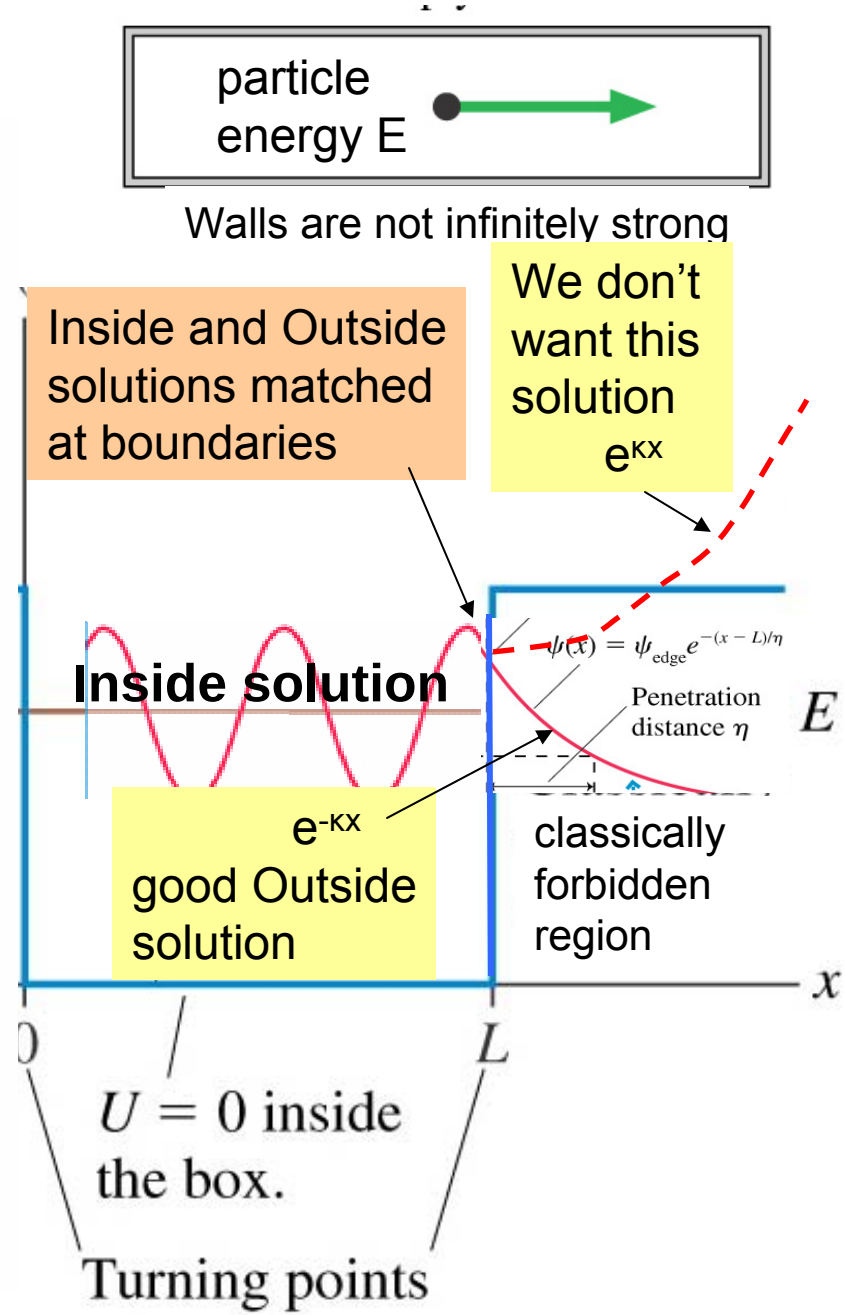
$$\left.\begin{array}{l} \psi_L(x) = Fe^{\kappa x} \text{ left of well} \\ \psi_R(x) = G\,e^{-\kappa x} \text{ right of well} \end{array}\right\} \text{with } \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

and $\psi_I(x) = A\sin(kx) + B\cos(kx)$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$ inside the well

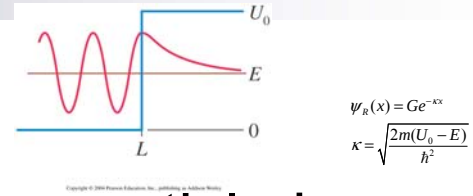
We need to "match" the the wave functions at the boundary so they give the same answer at x=0 and x=L (We want one answer from the solution, not two)

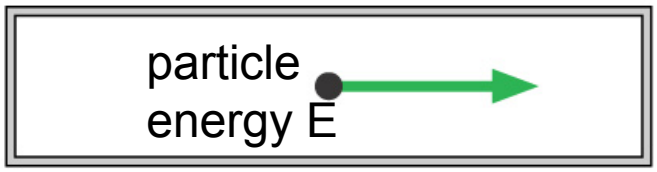
$\psi_L(0) = \psi_I(0)$ and $\psi_I(L) = \psi_R(L)$ (watch it L means x=L)

BTW we also need the derivative to match up also. I am not going to do this since it gives some rather ugly algebraic solutions, but we can solve them on a computer.

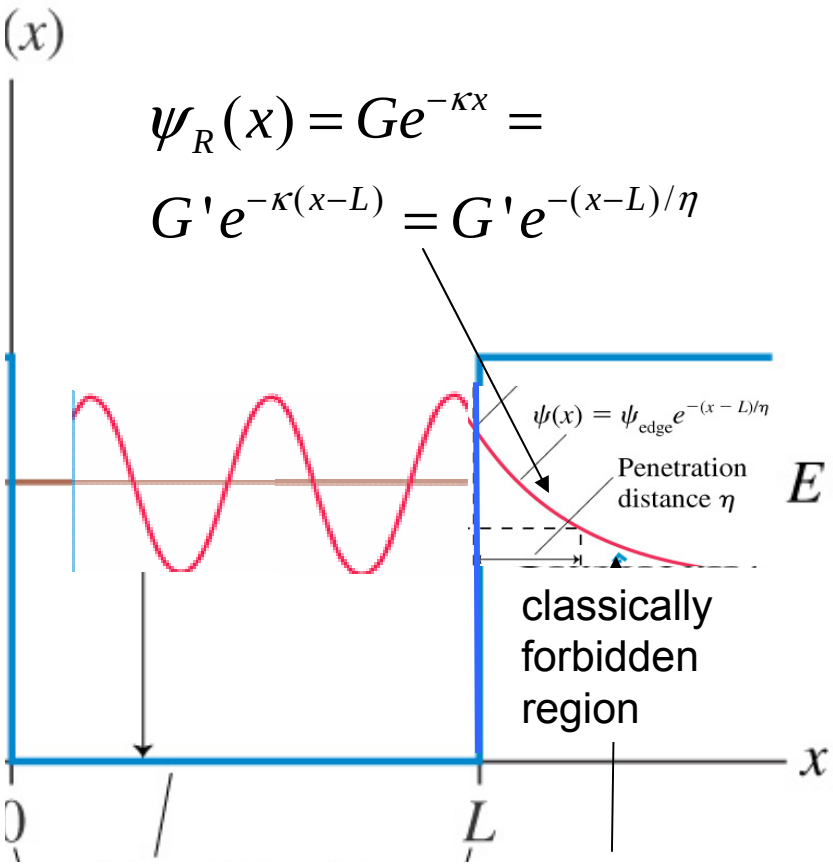


What is this Outside the box stuff?





Walls are not infinitely strong



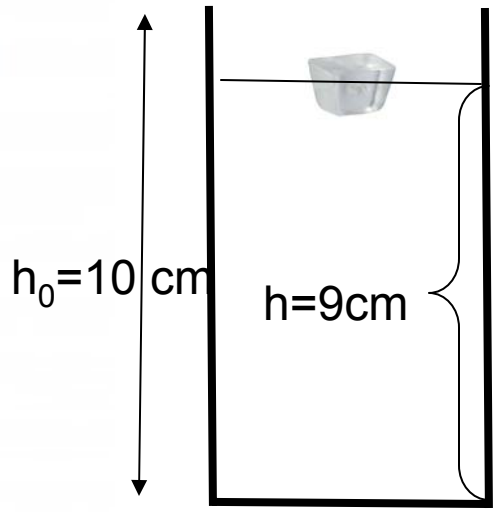
- If we put a particle in a box (say a match box) it doesn't get out.
- QM tells us that there is a small probability that the particle is OUTSIDE THE BOX! (the classically forbidden region)
- Penetration depth=1/κ
  - related to probablility for particle to "tunnel" outside box

$$\kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

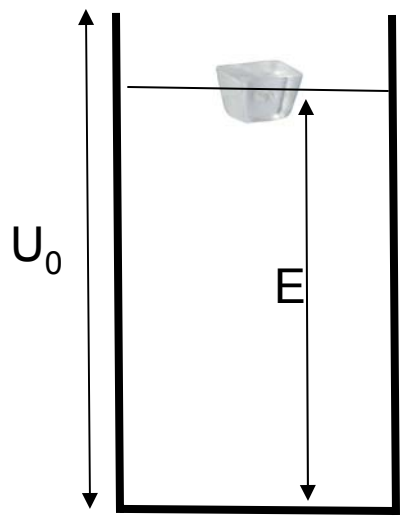
How big is the effect?

$$\psi_R(x) = Ge^{-\kappa x}$$

$$\kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$



The well



$U_0 = mgh_0$
$E = mgh$
$U_0 - E = mg(h_0 - h)$

$= .01\ (9.8\ )(.1 - .09)$
$= .00098J$

- find how far a cube of ice with mass 10g sits outside the glass

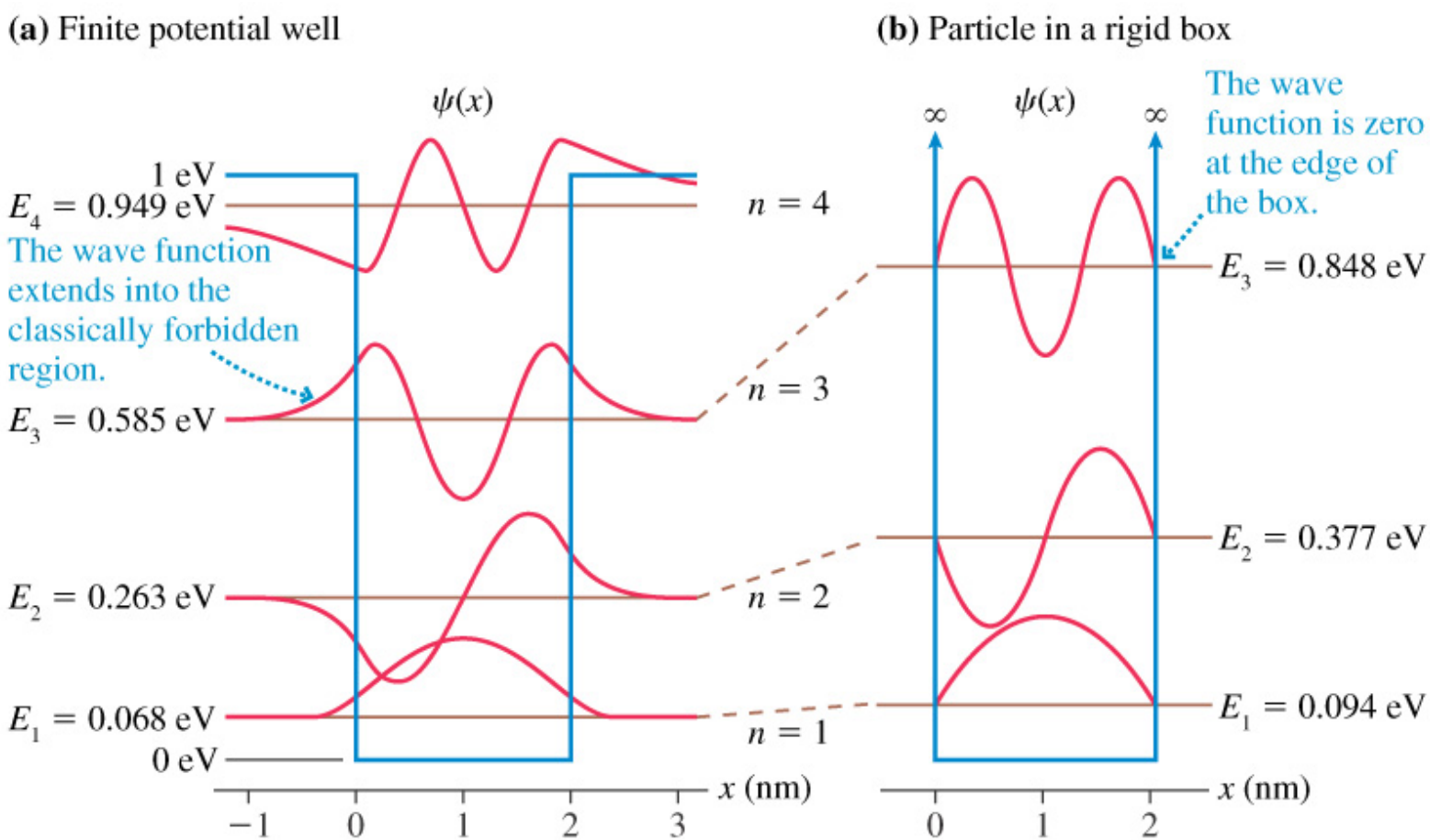
$$\kappa = \sqrt{\frac{2(.01)(.00098)}{(1\times10^{-34})^2}} = 4.4\times10^{31}$$

penetration depth = $1/\kappa = 2\times10^{-32}$ m
your ice stays in your glass (we will calculate a probability later)

the effect is big on atomic scales

What do the wave function look like?

- electron in a 1eV potential well
  - Energies are shifted relative to inifinite well
  - wave function penetrates into classically “forbidden region”



So to summarize

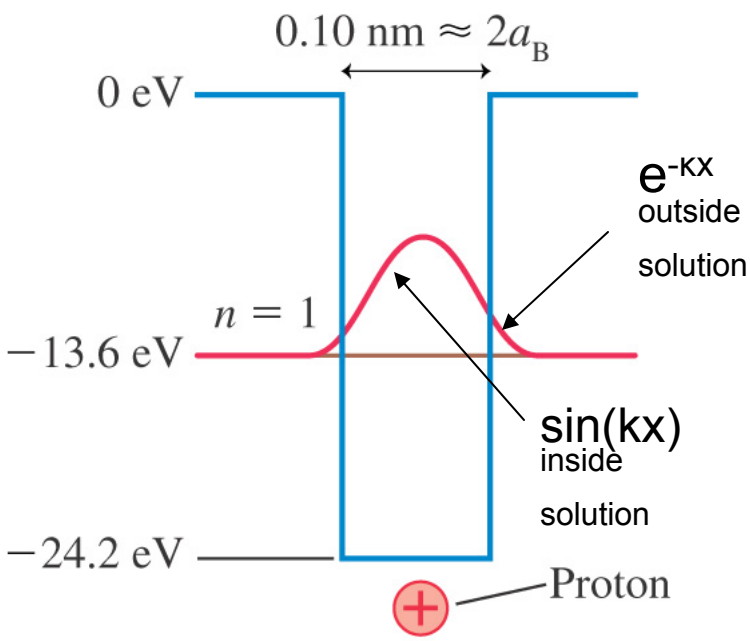
- QM has told us that particles penetrate into classically forbidden regions
  - Tunneling
  - decay
- Crazy – your car has a small probability of being OUTSIDE your garage

Covalent bonds

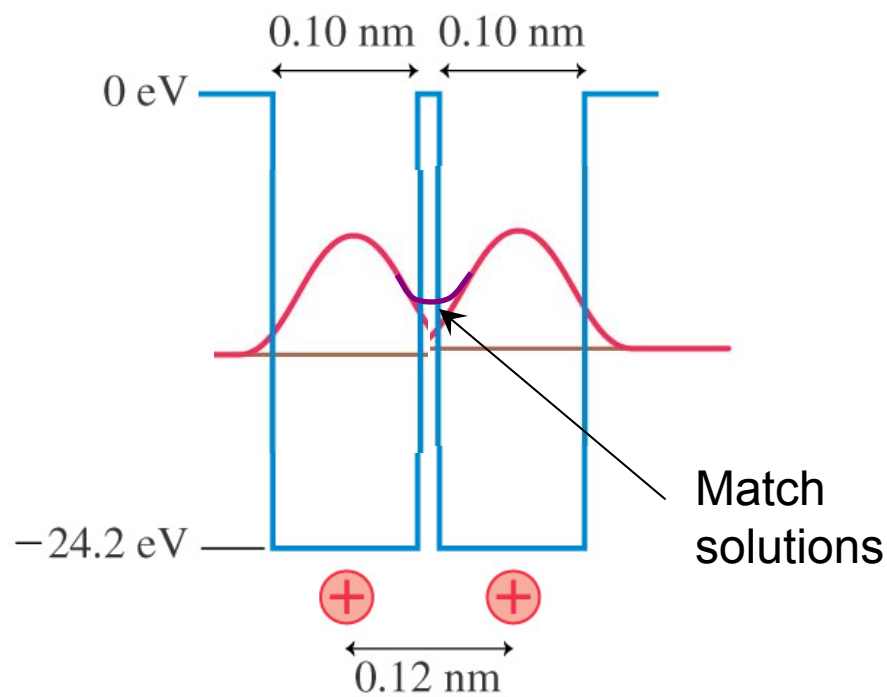
- Model of H atom
  - particle in a box
  - E=-13.6 ev (n=1 state)
  - top of the box be at zero
  - width of the box is ~ $2a_B$~0.1 nm

- 2 H atoms for a bond
  - Separation =.12 nm
  - match solutions at boundary

(a) Simple one-dimensional model of an electron in a hydrogen atom

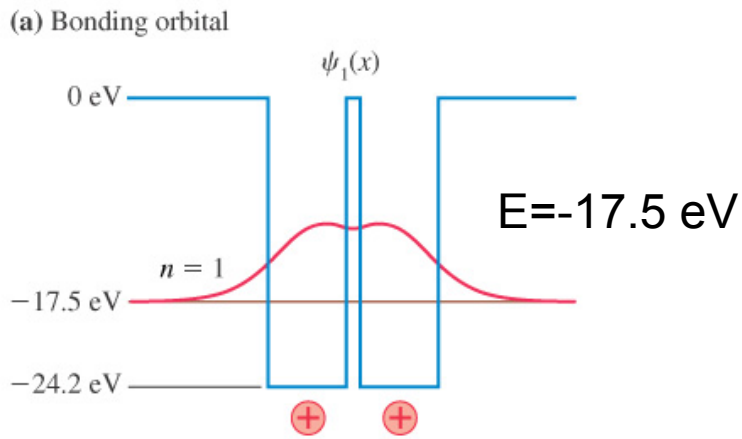


(b) An H_2^+ molecule modeled as an electron with two protons separated by 0.12 nm



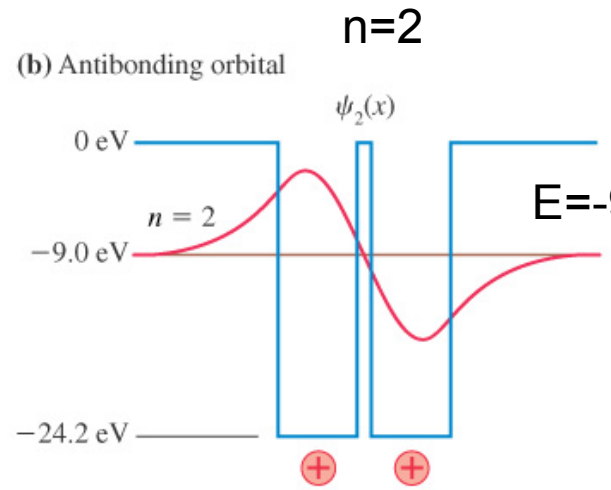
Now solve for the new energies

n=1



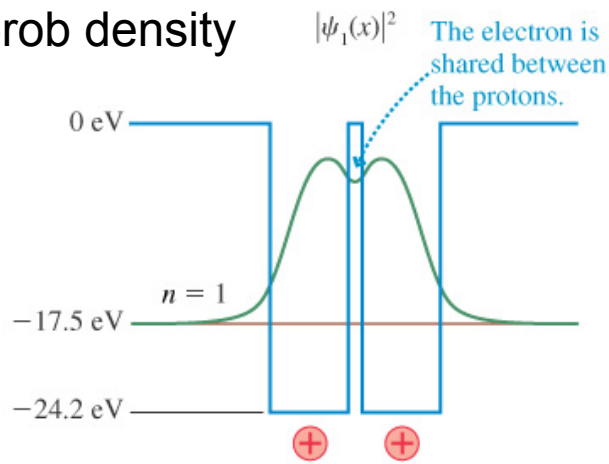
E=-17.5 eV

n=2

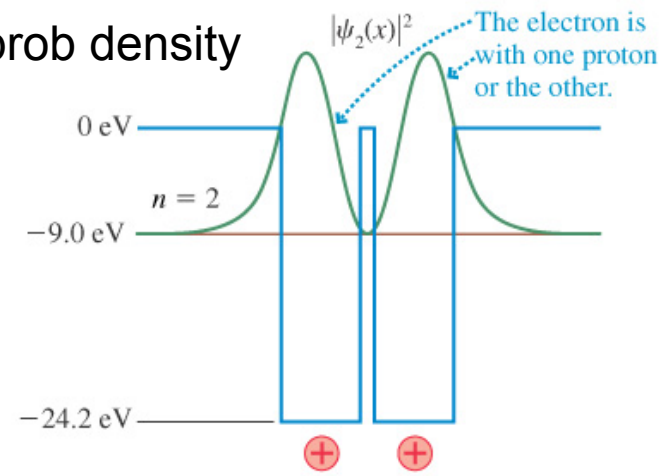


E=-9 eV

prob density



prob density



Total energy – the covalent bond

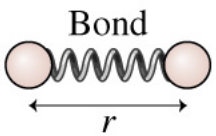
- If the total energy is negative, then the particles are bound.
  - pp repulsive energy = $\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} = 12eV \quad r = .12nm$
  - n=1 E=12 eV-17.5eV = -5.5eV
    - covalent bond!!
  - n=2 E=12 eV – 9 eV=+3eV
    - doesn't bind

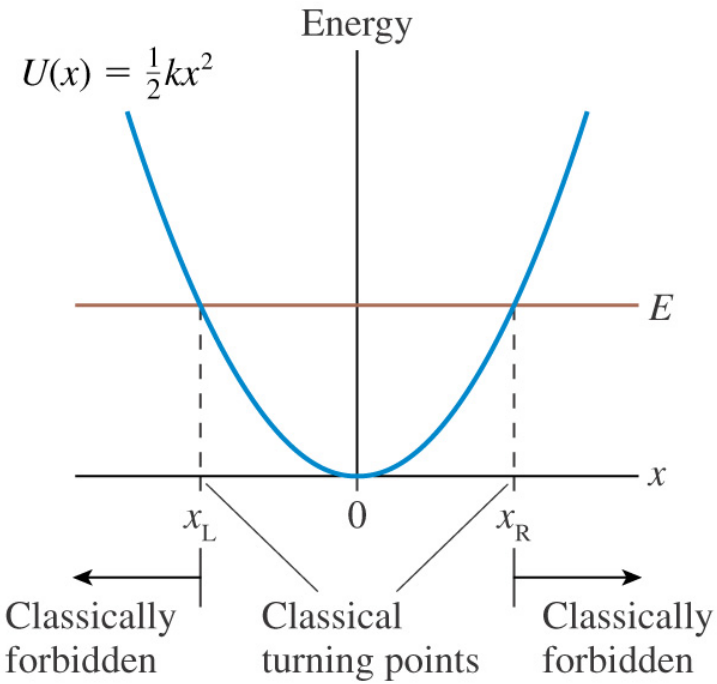
The Quantum Simple Harmonic Oscillator and molecular vibrations

- 1-D particle in a box $E \sim n^2$ i.e. not evenly spaced.
- A better model for a molecule and vibrations.
  - A spring
  - $U(x)=\frac{1}{2}kx^2$
- Classical solution
  - vibrates between turning points
  - frequency $\omega = \sqrt{\frac{k}{m}}$
  - Solving the Sch eqn we get

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi$$

$$E_n = \left(n - \frac{1}{2}\right)\hbar\omega \quad n=1,2,3..$$



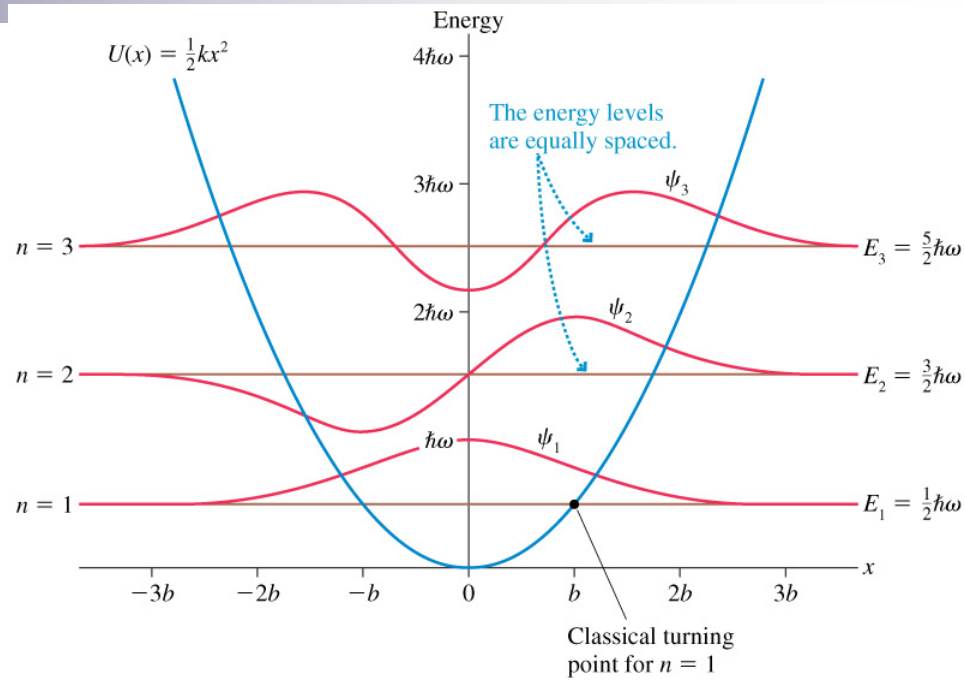


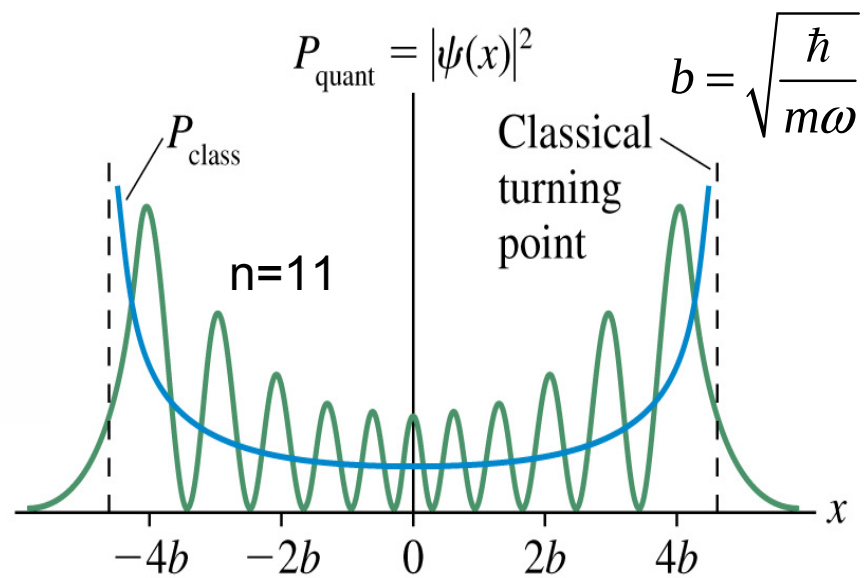
Wave functions

- Here is what the wave functions look like
- Note at high n (n=11) the probability starts looking classical
  - particle spends most of time near turning points
  - Notice the energy states are evenly spaced

$$E_n = \left(n - \frac{1}{2}\right)\hbar\omega \qquad n=1,2,3..$$

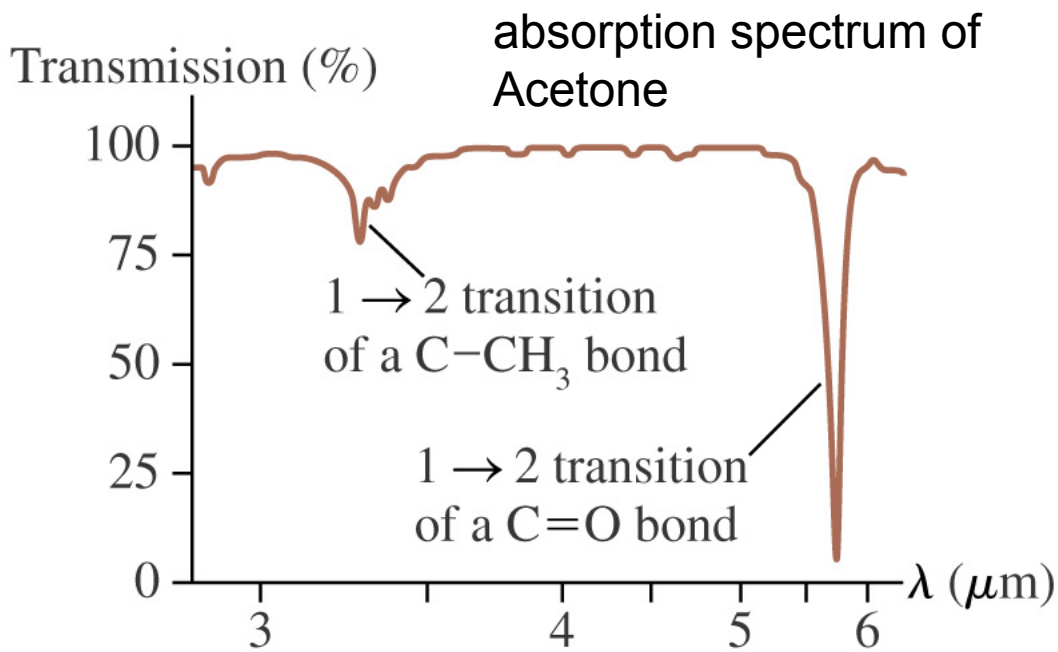
  - Again, lowest energy>0!
    - $E_0 = \frac{1}{2}\hbar\omega$

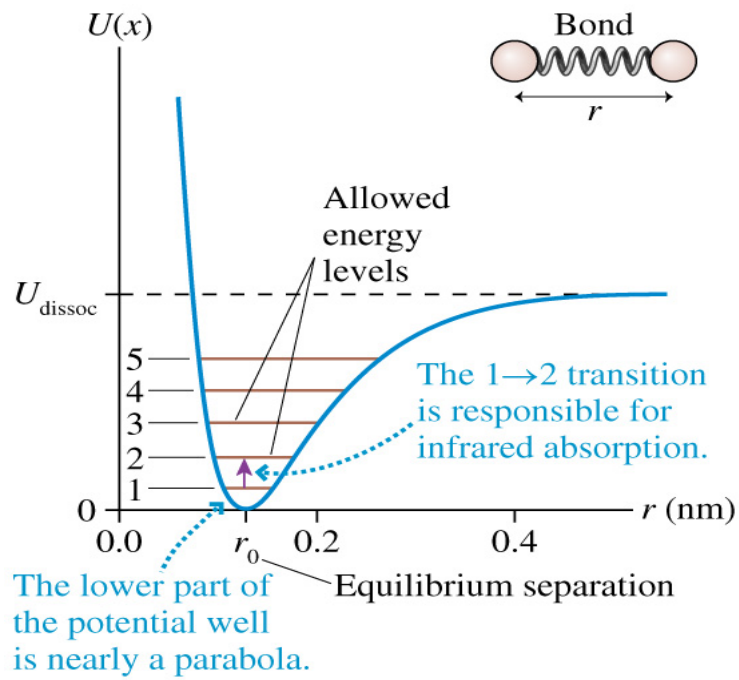




Sping constant of a bond?

$$E_n = \left(n - \frac{1}{2}\right)\hbar\omega \quad n=1,2,3..$$





- What is the spring constant of the carbon-oxygen double bond?
  - λ=5.8μm line is absorbed 1→2 transition

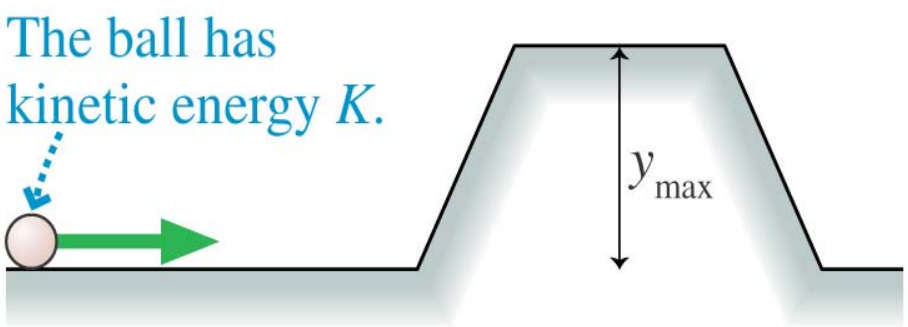
$$\Delta E = E_2 - E_1 = (2-\frac{1}{2})\hbar\omega - (1-\frac{1}{2})\hbar\omega = \hbar\omega$$

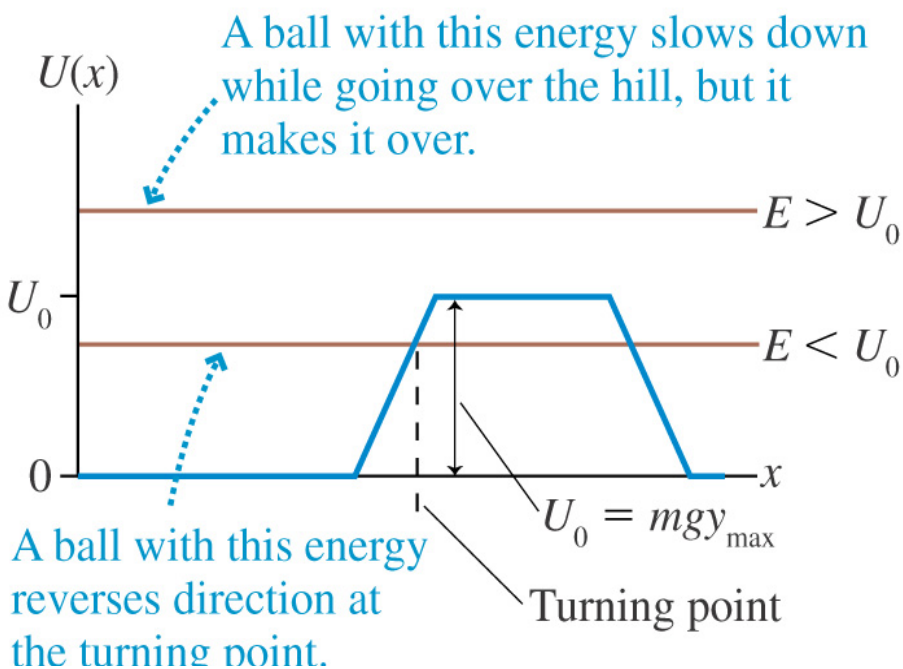
$$\hbar\omega_{spring} = \frac{hc}{\lambda_{photon}} \qquad \omega_{spring} = \frac{2\pi c}{\lambda} \qquad but \qquad \omega_{spring} = \sqrt{\frac{k}{m}}$$

$$k_{sping} = \left(\frac{2\pi c}{\lambda}\right)^2 m_e = \left[\frac{2\pi(3\times10^8)}{5.8\times10^{-6}}\right]^2 9.11\times10^{-31} = 0.1N/m$$

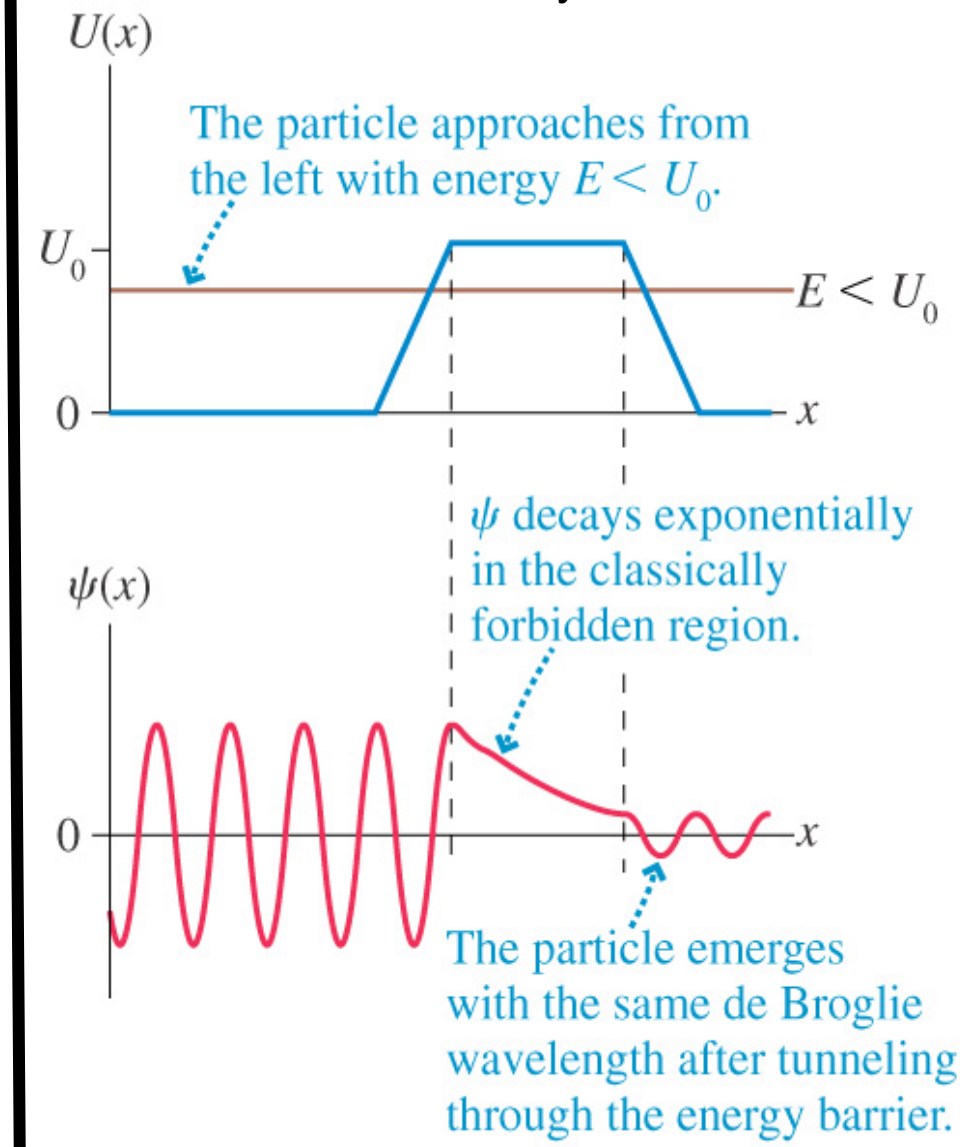
Tunneling

Classical Physics

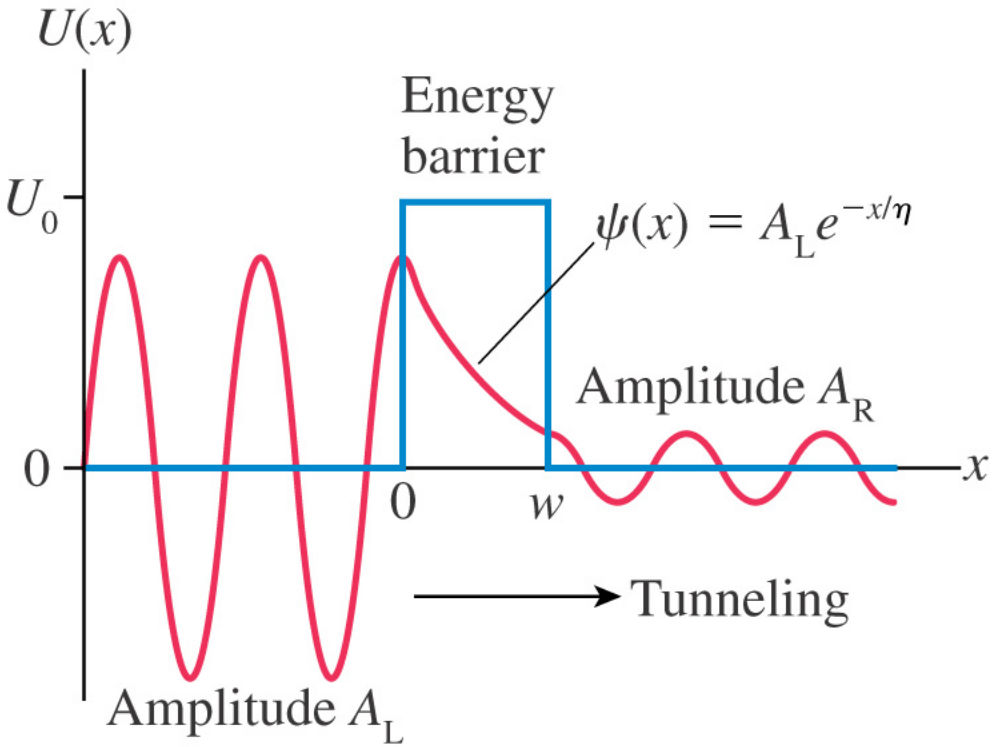




Quantum Physics



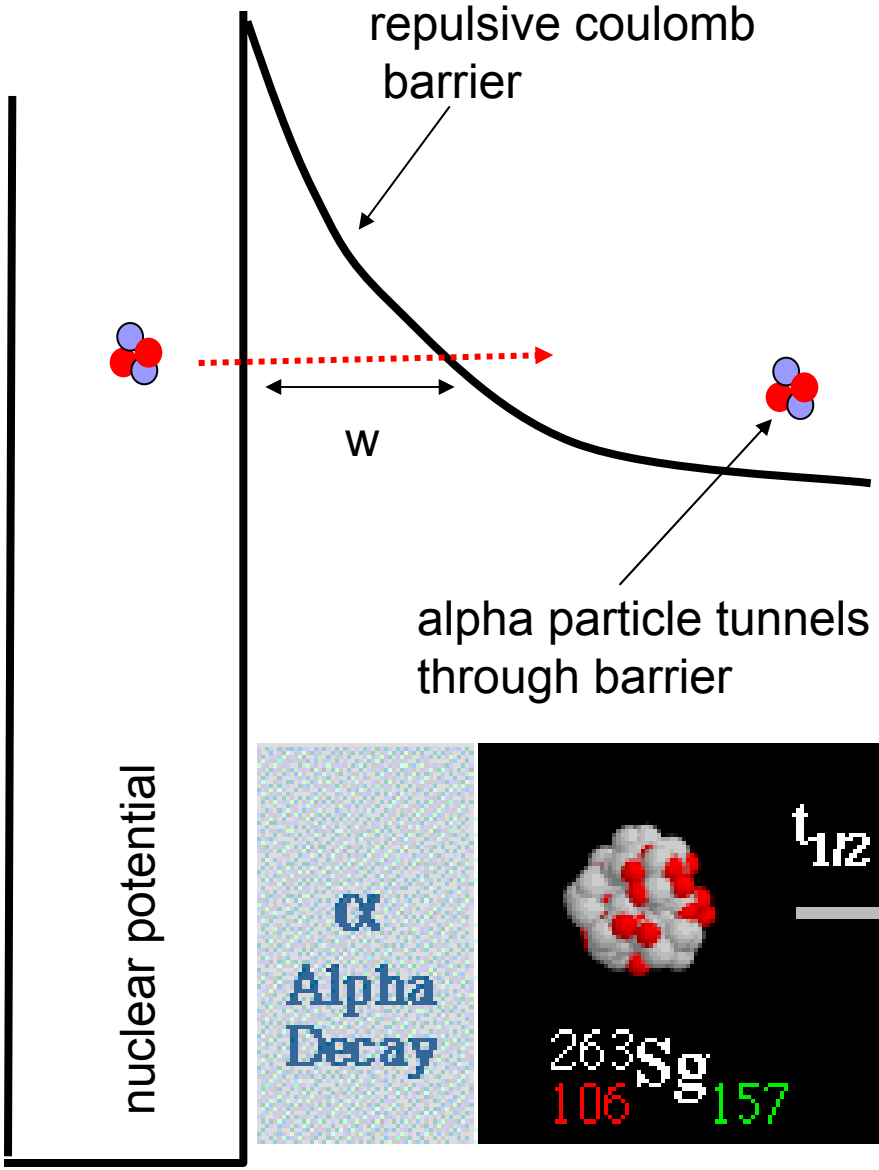
Knight's toy model



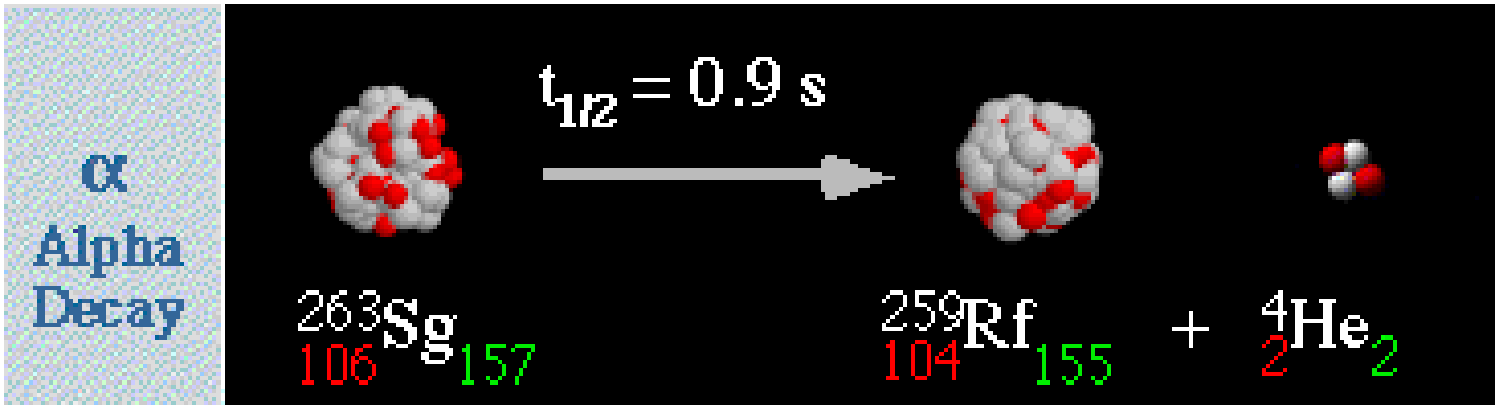
so $A_R = A_L e^{-w/\eta}$
w=width of barrier
remember $\eta = 1/\kappa$

$$P_{tunnel} = |A_R|^2/|A_L|^2 = e^{-2w/\eta}$$

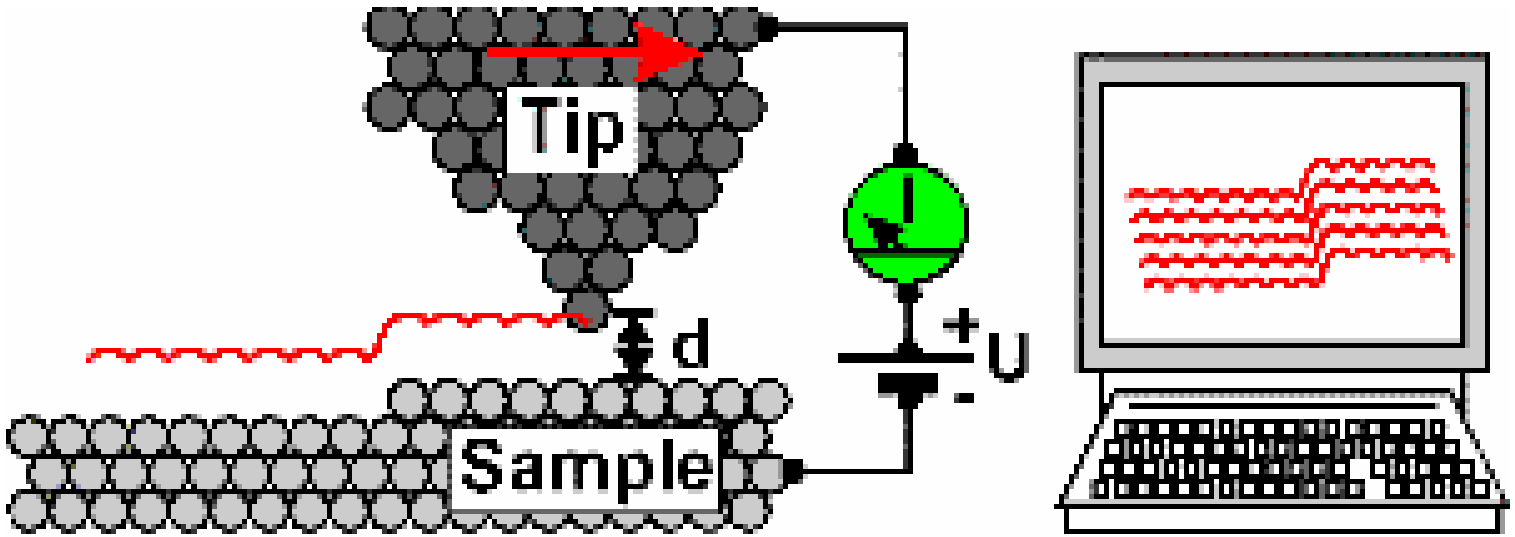
Nuclear Decay and Spontaneous Fission



- Problem
  - similar nuclei have radically different lifetimes
  - U^{238} 4.5B years
  - U^{234} 244 K years
  - different by 20,000
- Answer: Decay is from tunneling, exceedingly sensitive to width of barrier
  - $P \sim e^{-1} = 0.4$
  - $P \sim e^{-11} = 1.7 \times 10^{-5}$
  - different by 20,000



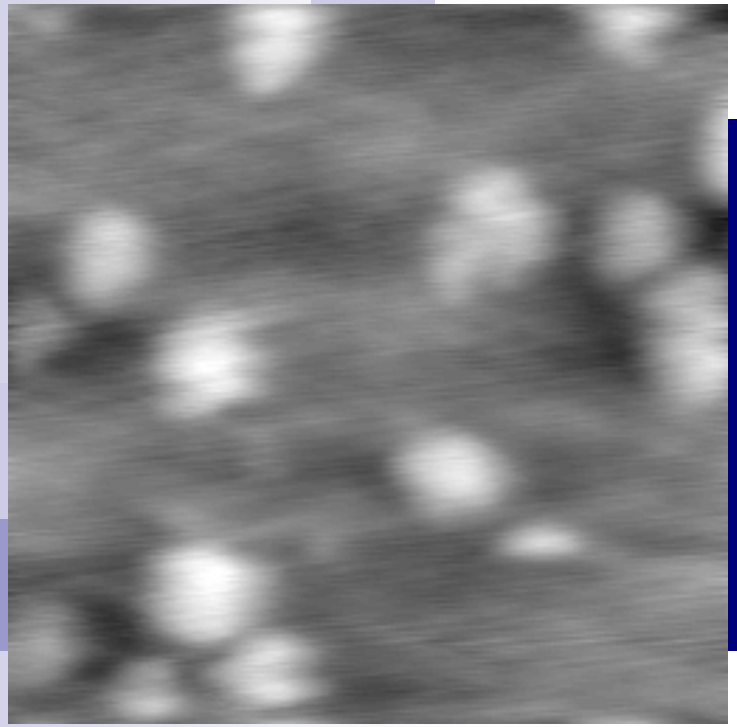
Scanning Tunneling Microscope

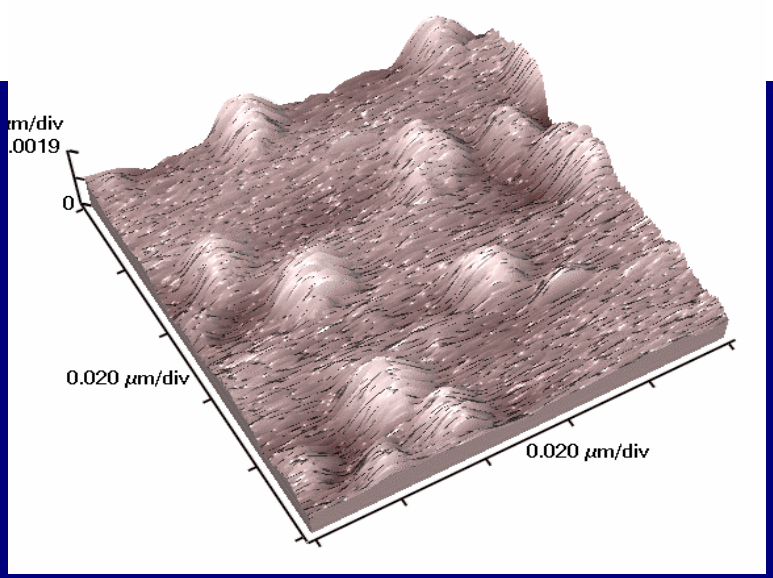


$P_{tunnel}=e^{-2w/\eta}$

tunneling probability is very sensitive to w

STM of Gold Nanoclusters in Ultra-High Vacuum

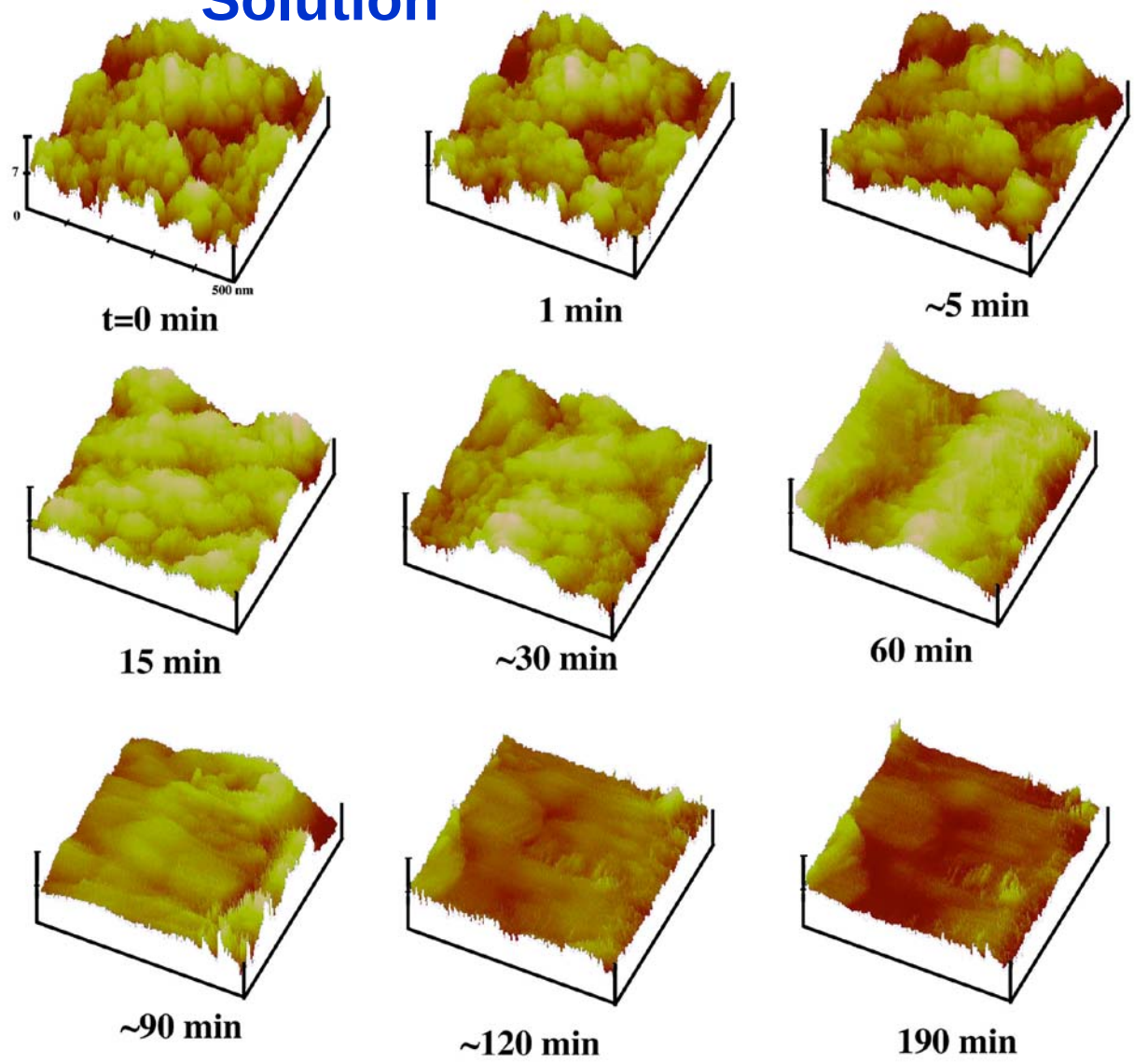




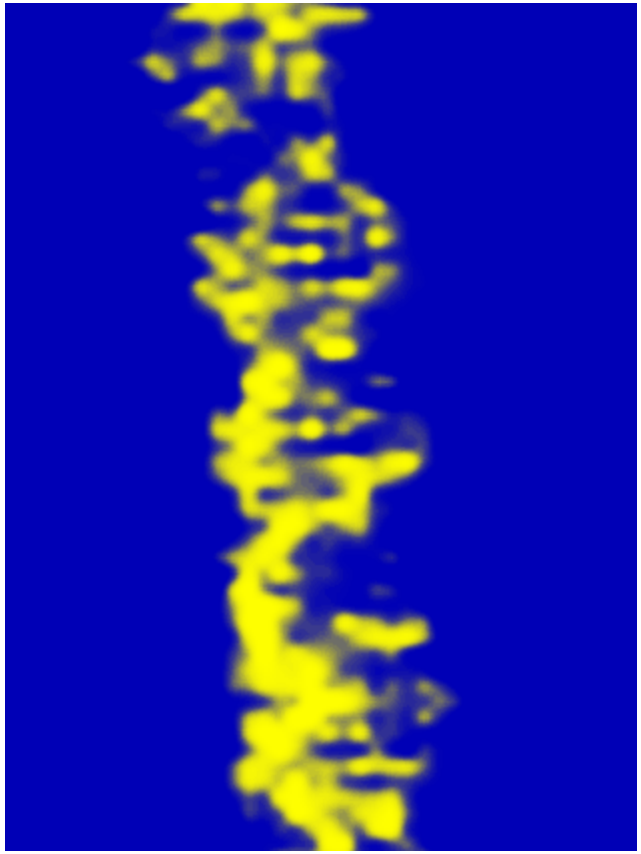
STM images (100 nm × 100 nm) collected from Au nanoclusters on a TiO_2(110) substrate. They were grown by depositing 1 ML of Au and annealing to 600° C.

STM of Iron foil in a Uranyl Nitrate Solution

The surface of an iron foil was monitored with *in situ* STM in a solution containing uranyl nitrate. The 500x500 nm images show the rough surface, characteristic of a native iron oxide, becoming smoother as the reaction proceeds.



DNA

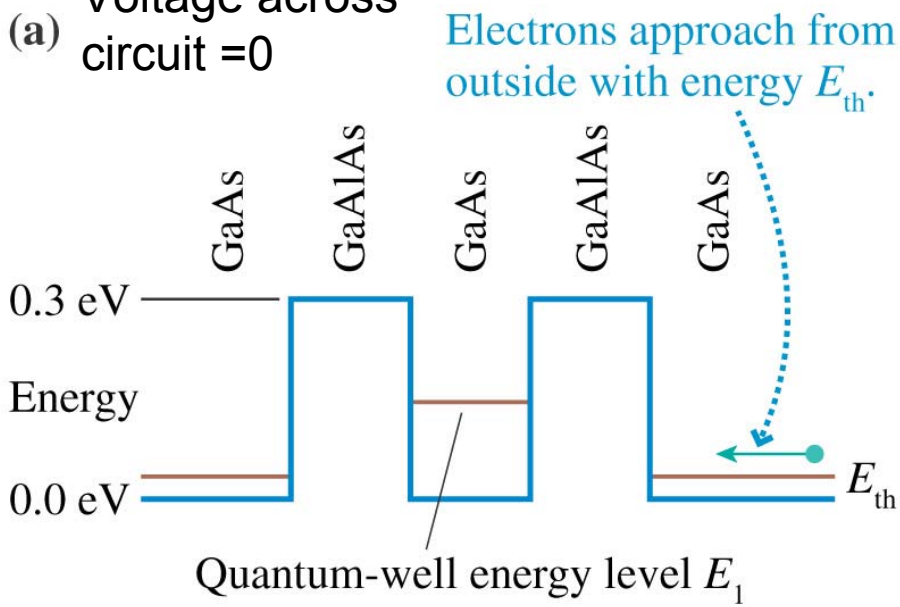


Wolfgang Schonert
GSI

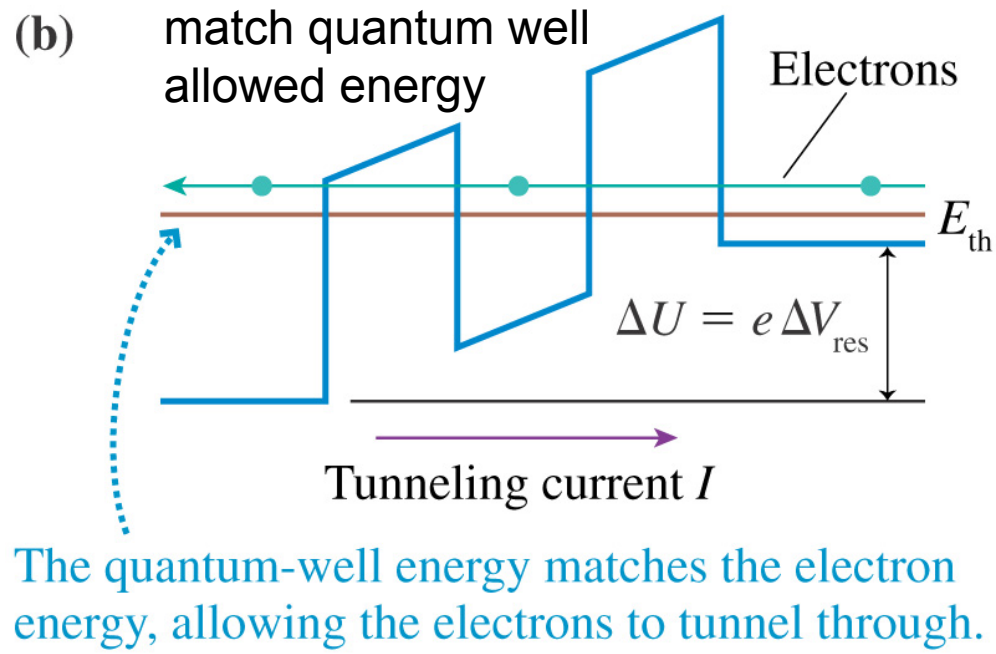
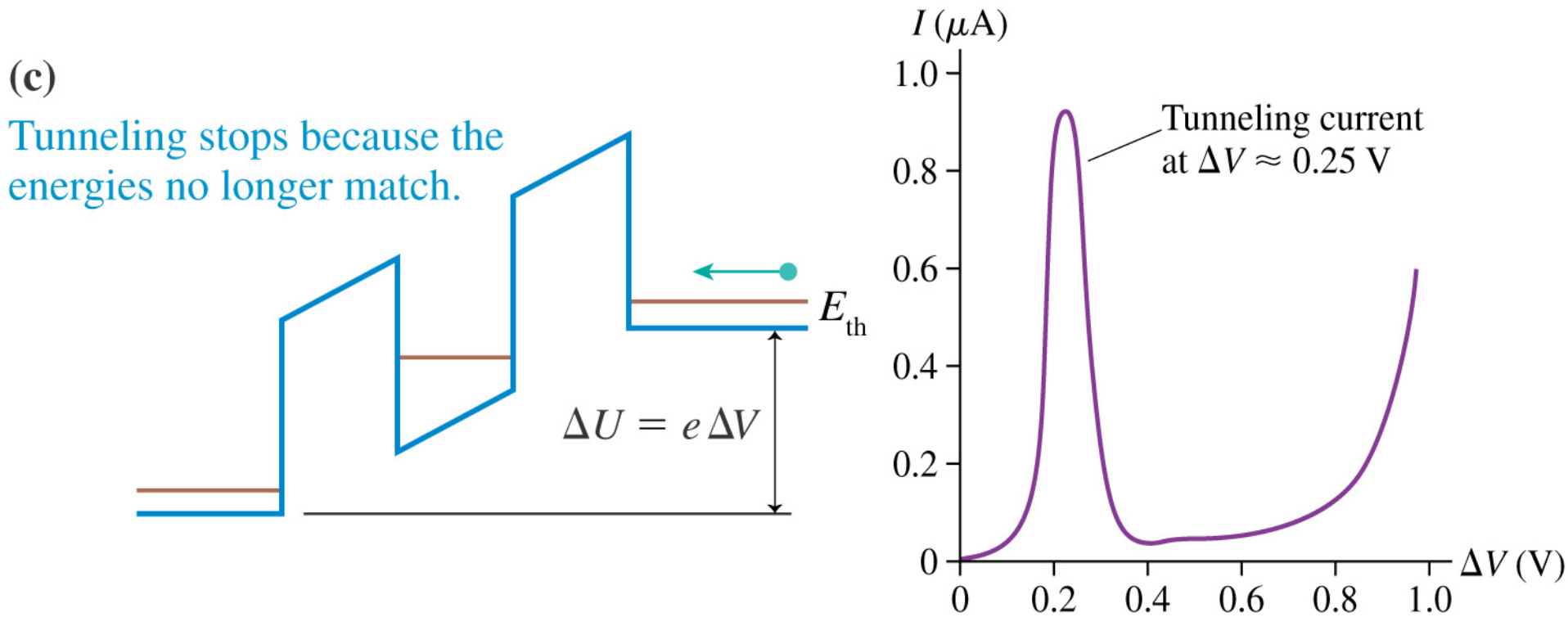
Resonant Tunneling diode

- High speed gate 500 GHz??
- When tunneling occurs energy must be conserved
  - Energy of incoming electron must equal energy of well for tunneling to occur

Gate closed
Voltage across circuit =0



Gate open:
Voltage across circuit such that electrons match quantum well allowed energy



If voltage is too high gate closes