. Schrodinger equation and potential energy wells

- Explain why a very deep square well potential is a crude but useful model for a variety of physical systems, including electrons in atoms or wires.
- Calculate the possible energy levels and normalized wave functions and probability distributions for an electron in a very deep square well potential of arbitrary width in one dimension. Be able to use these distributions to predict the results of measurements of these quantities for an electron.
- Explain general method for how to find allowed energies for an electron or atom in any shape potential energy well, although not carry out the detailed calculations required for obtaining values for those energies.

Solving the Schrodinger equation for simple model system (square well). Easiest case of electron confined to solve diff. equation. Form of solutions simpler, easier to understand basic ideas of QM.

one place where this model is "reasonably" accurate

Nanotechnology: how small does an object have to be before movement of electrons starts to depend on size and shape due to quantum effects?

the 3 D Schrodinger equation for hydrogen atom, other atoms much messier because are electron-electron contributions to V

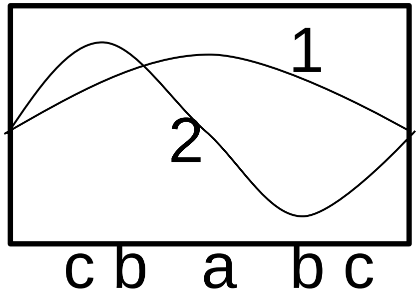
$$-\left[\frac{\hbar^2\partial^2\Psi(x,y,z,t)}{2m\partial x^2}+\frac{\hbar^2\partial^2\Psi(x,y,z,t)}{2m\partial y^2}+\frac{\hbar^2\partial^2\Psi(x,y,z,t)}{2m\partial z^2}\right]+$$
$$-[ke^2/(x^2+y^2+z^2)^{1/2}]\Psi(x,y,zt)=i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t}$$

Reading quiz.

1. a. I read sections 41.3,4, 6, 7.
   b. I read some, but not all of those sections.
   c. I did not do the reading.

Today and Wed. -- will not make much sense if did not do the reading. If questions on material in reading though, ASK!

2. "A particle in a rigid box in the n=2 stationary state is most likely to be found
a. in the center of the box,
b. one third of the way from either end,
c. one quarter of the way from either end,
d. It is equally likely to be found anywhere in the box."



reading quiz

3. In the classically forbidden region for a finite potential well, the physically meaningful solution to the Schrodinger equation is

(*η is always a real positive constant*)

a. a cosine function ($\cos(x/\eta)$)

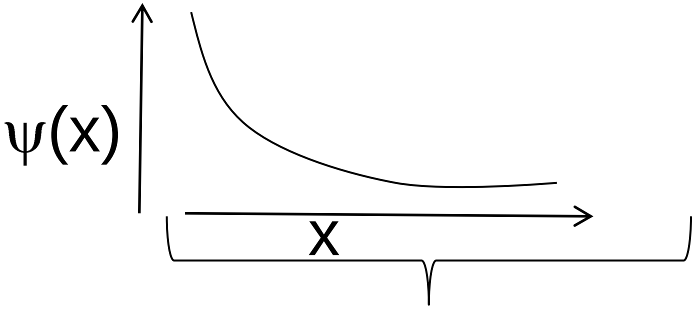
b. the sum of sine and cosine functions

c. an increasing exponential function($e^{+x/\eta}$)

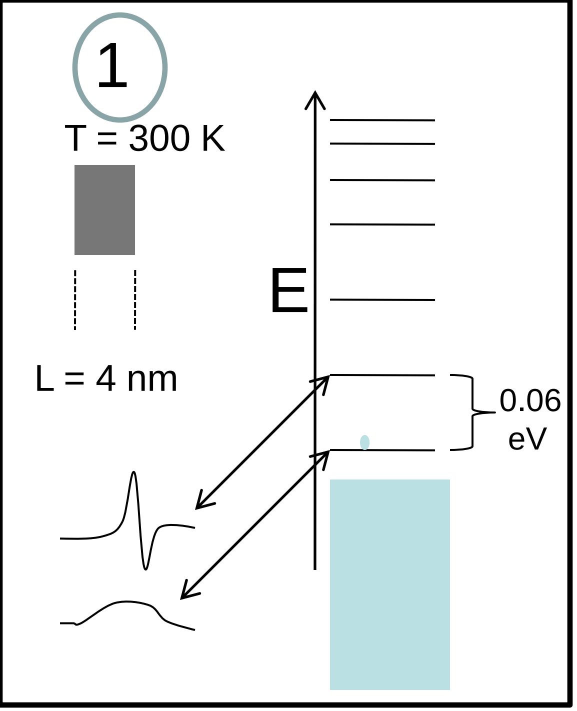
d. a decaying exponential function($e^{-x/\eta}$)

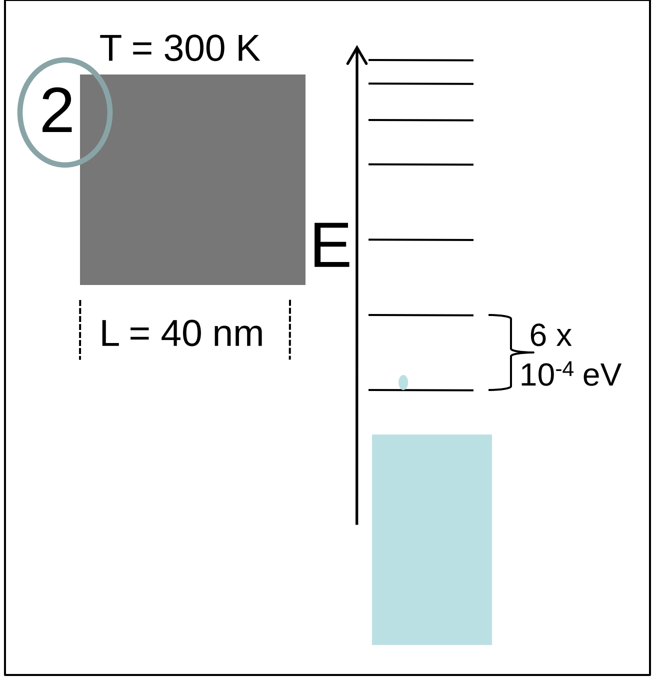
e. this question makes no sense

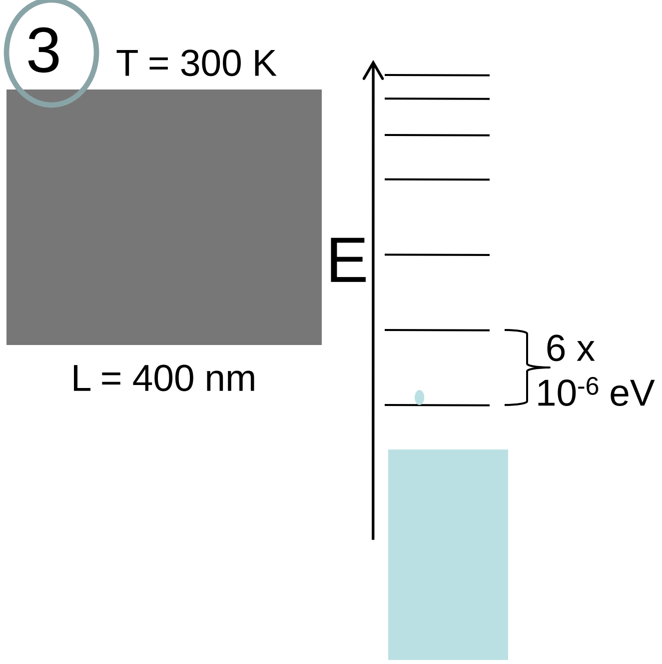
ans. d.

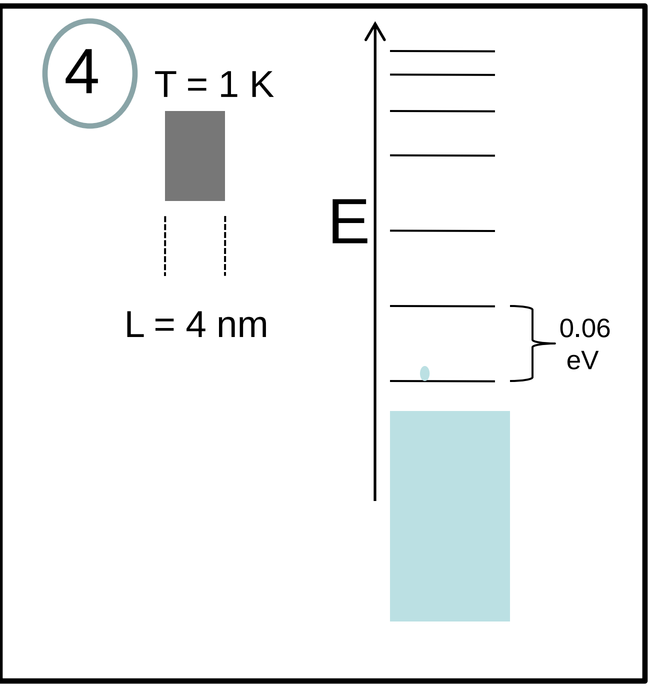


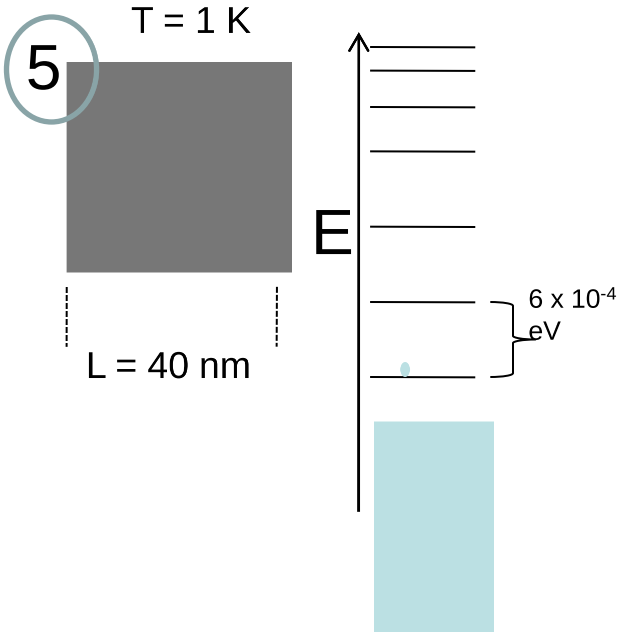
classically forbidden region,
E total less than potential energy V(x)











You have to invent a "quantumticity" parameter. The value of this parameter will characterize if motion of electrons in small blocks of metal is going to be similar to motion in large block, or will be changed by quantum behavior. Parameter should work for all these cases, and any new case.

No single right answer. Will have groups share their parameters when done.

Nanotechnology: how small does a wire have to be before movement of electrons starts to depend on size and shape due to quantum effects?

How to start?

Need to look at

a. size of wire compared to size of atom

b. size of wire compared to size of electron wave function

c. Energy level spacing compared to thermal energy, kT.

d. Energy level spacing compared to some other quantity (what?)

e. something else (what?)

Nanotechnology: how small does a wire have to be before movement of electrons starts to depend on size and shape due to quantum effects?

How to start?

Need to look at

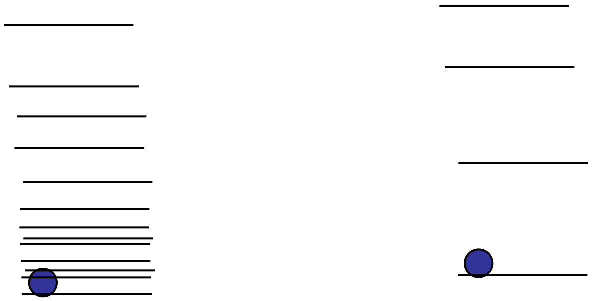
c. Energy level spacing compared to thermal energy, kT.

to move much have higher energy/momentum

Almost always focus on energies in QM.

Electrons, atoms, etc. hopping around with random energy kT.

Larger than spacing, spacing irrelevant. Smaller, spacing big deal.



spacing of levels in pit compared to kT?

Main parameter in behavior of solids

“quantumticity” parameter,
ratio of spacing between energy levels of the electron and thermal energy kT

$\Delta E/kT$ -- small, no quantum effects-- spacing of levels does not matter. Big-- quantum important.

$\Delta E = .06\ \text{eV}/(L/4\text{nm})^2$, $kT = 0.025\ \text{eV}\ (T/300\ \text{kelvin})$

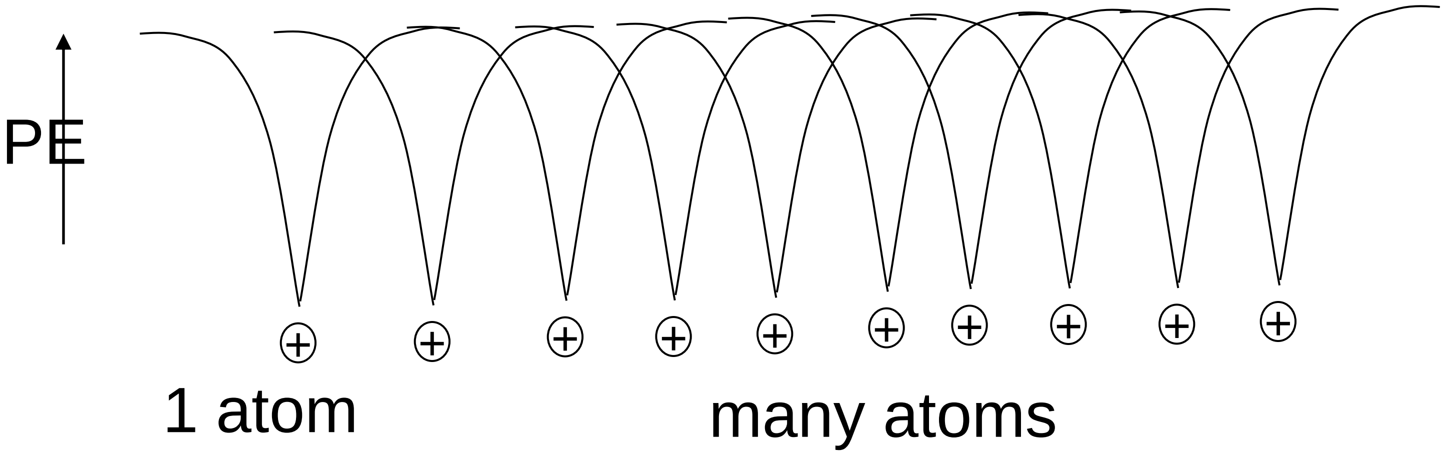
but I just made up ΔE’s for this problem.
Now we need to calculate what they really are.

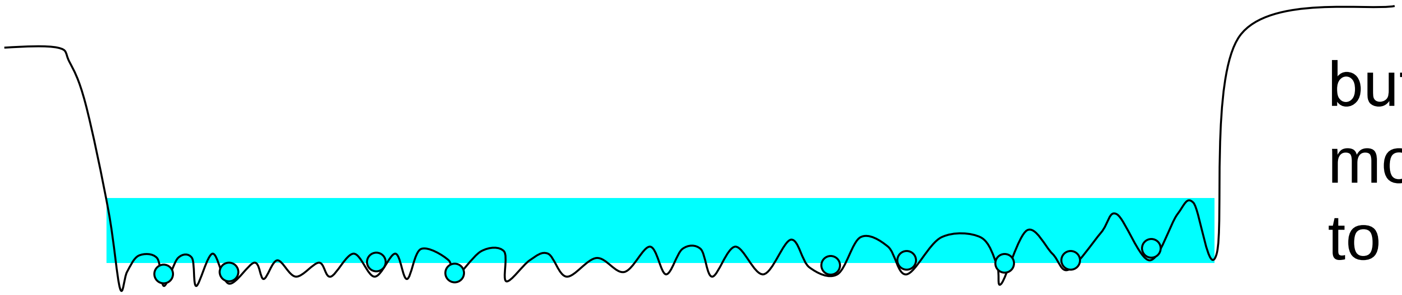
Solving the Schrodinger equation for electron wave in 1 D

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

time independent eq.

1. Figure out what V(x) is, for situation given.
2. Guess or look up functional form of solution.
3. Plug in to check if ψ's, and all x's drop out, leaving equation involving only bunch of constants; showing that trial solution is correct functional form.
4. Figure out what boundary conditions must be to make sense physically.
5. Figure out values of constants to meet boundary conditions and normalization $\int_{-\infty}^{\infty}|\psi(x)|^2dx=1$
6. Multiply by time dependence $\Phi(t)=\exp(-iEt/\hbar)$ to have full solution if needed. STILL TIME DEPENDENCE!

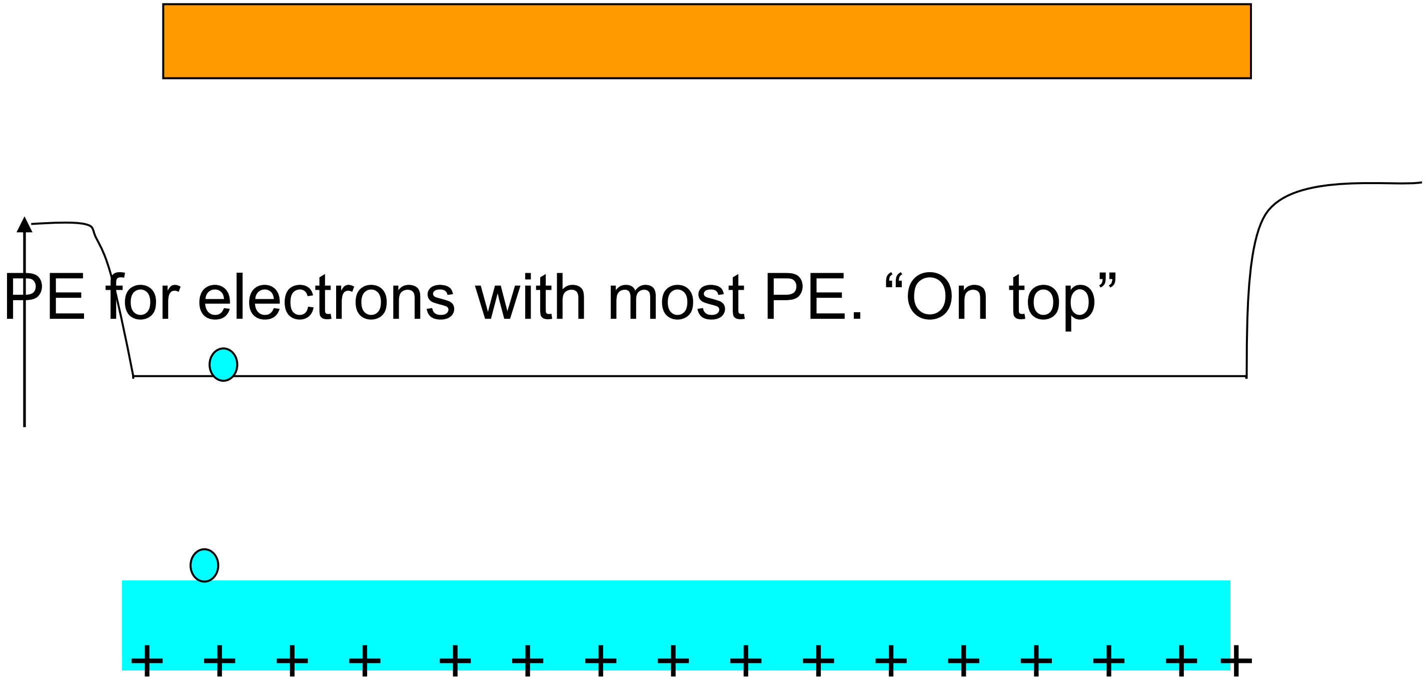




but lot of e's move around to lowest PE

repel other electrons = potential energy near that spot higher.

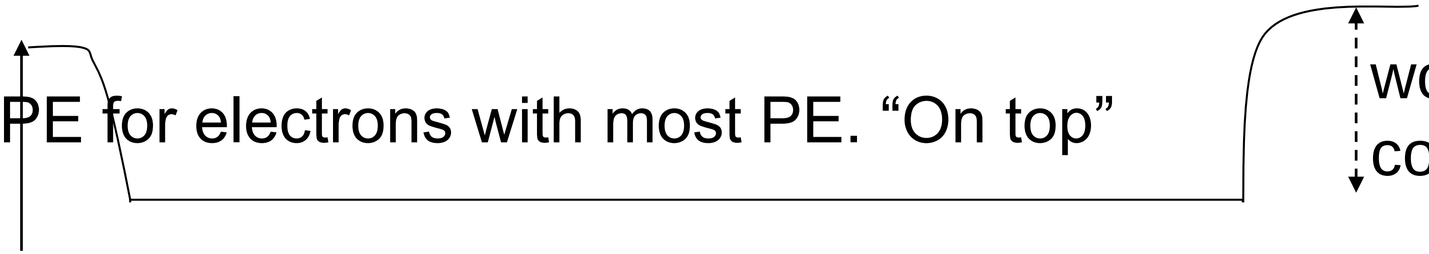
as more electrons fill in, potential energy for later ones gets flatter and flatter. For top ones, is VERY flat.



PE for electrons with most PE. “On top”

as more electrons fill in, potential energy for later ones gets flatter and flatter. For top ones, is VERY flat.

How could you find out how deep the pit is for the top electrons in copper wire?



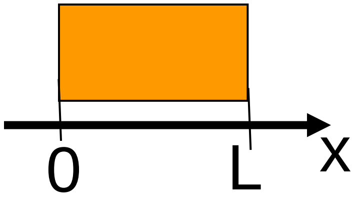
PE for electrons with most PE. “On top”

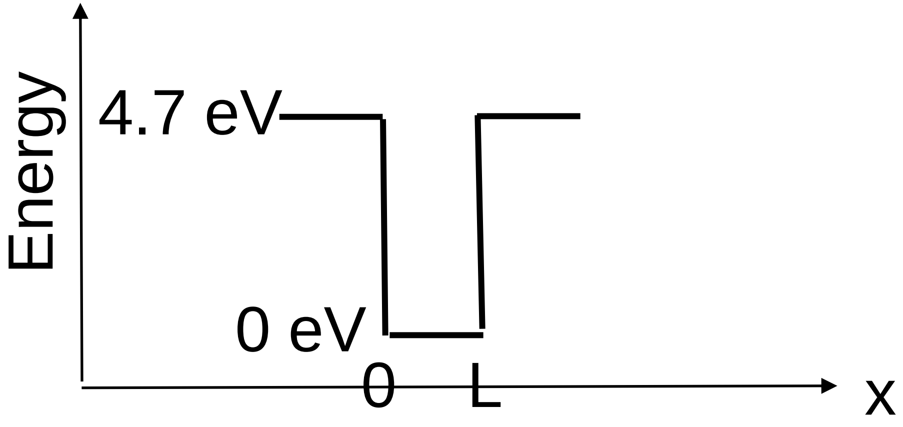
work function of copper = 4.7 eV

How could you find out how deep the pit is for the top electrons in copper wire?

This is just the energy needed to remove them from the metal. That is the work function!!

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



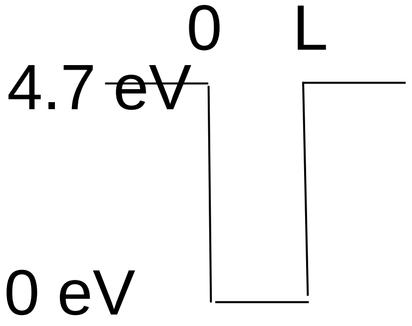


x<0, V(x) = 4.7 eV
x> L, V(x) = 4.7 eV
0<x<L, V(x) =0

How to solve?

a. mindless mathematician approach- find Ψ in each region, make solutions match at boundaries, normalize.

Works, but bunch of math.



mathematically
$V(x) = 4.7$ eV for $x<0$ and $x>L$
$V(x) = 0$ eV for $0>x<L$

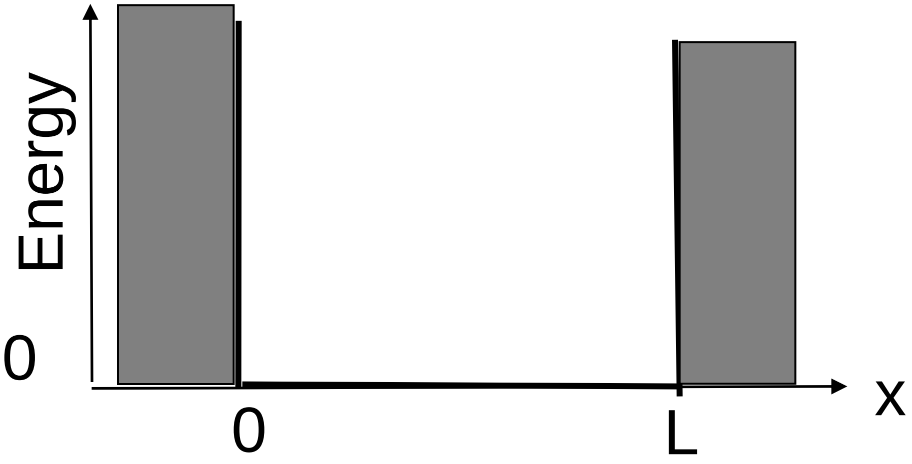
b. Clever physicist approach. Reasoning to simplify how to solve. Electron energy not much more than ~kT=0.025 eV.
Where is electron likely to be? What is chance it will be outside of well?
a. zero chance, b. very small chance, c. small, d. likely

b. 0.025 eV<< 4.7eV. So very small chance an electron could have enough energy get out.

What does that say about boundary condition on $\psi(x)$?
a. $\psi(x)$ must be same $x<0$, $0<x<L$, $x>L$,
b. $\psi(x<0)\sim0$, $\psi(x>0) \neq 0$ c. $\psi(x) \sim 0$ except for $0<x<L$

ans c. So pretty good approximation to say never gets out

x<0, V(x) ~ infinite
x> L, V(x) ~ infinite
0<x<L, V(x) =0



so clever physicist just has to solve

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

with boundary conditions,
$\psi(0)=\psi(L)=0$

solution a lot like microwave & guitar string

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

A solution to this diff. eq. is
A cos(kx) and B sin (kx), so sum is also solution.

Check-- plug in.

$$\frac{\hbar^2}{2m}\frac{k^2 A\cos kx}{}=EA\cos kx$$

solution if $\frac{\hbar^2}{2m}\frac{k^2}{}=E$

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

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

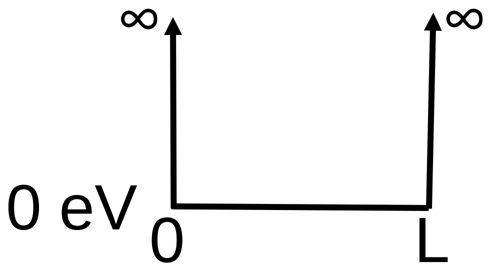
$$\frac{\hbar^2}{2m}\frac{k^2}{}=E$$

makes sense, because $p=\hbar k$

so condition on k is just saying that $(p^2)/2m = E$.
V=0, so E= KE = ½ $mv^2 = p^2/2m$

This result implies that the total energy of electron is
a. quantized according to E_n = const. x n^2, n= 1,2, 3, …
b. quantized according to E_n = const x n
c. quantized according to E_n = const. x $1/n^2$
d. quantized according to some other condition but don't know what it is.
e. not quantized, energy can take on any value.

e. no boundary, not quantized, energy can take on any value.



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

functional form of solution: $\psi(x)=A\cos(kx)+B\sin(kx)$

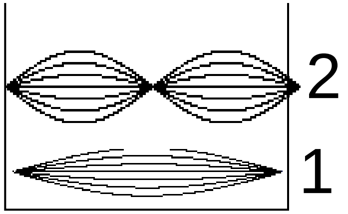
Apply boundary conditions

x=0 → ? $\psi(0)=A$ → A=0

x=L → $\psi(L)=B\sin(kL)=0$ ⇒? kL=nπ (n=1,2,3,4 …)

→ k=nπ/L

$k=\frac{2\pi}{\lambda}$ $\lambda=\frac{2L}{n}$



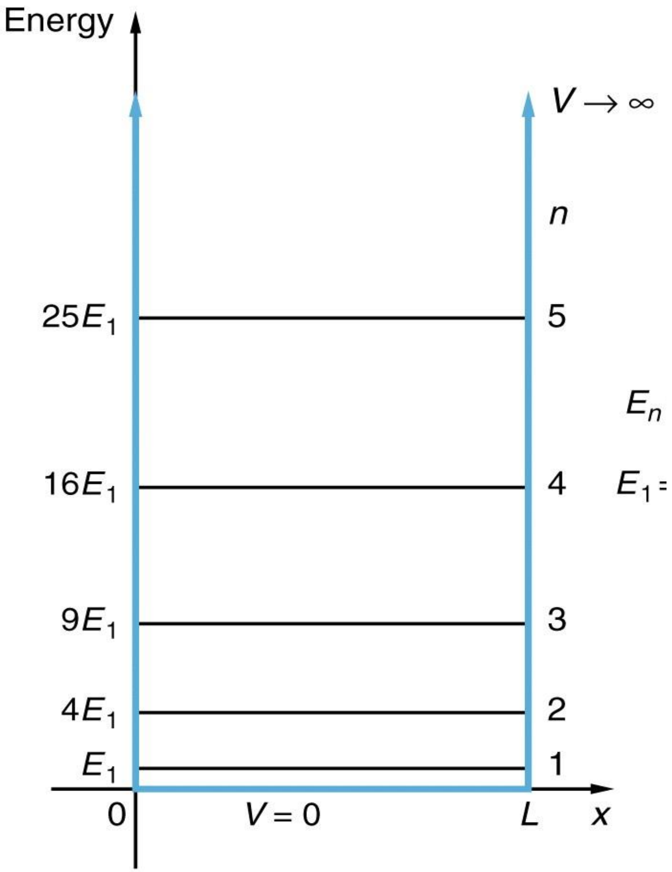
$$p = \hbar k = \hbar(n\pi / L) \qquad \lambda = \frac{2L}{n}$$

$$\boxed{E = \frac{p^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2}}$$

Energy quantized by boundary conditions. Why bound electrons have only certain discrete energies, unbound can have any energy.

Does this L dependence make sense?

leave it to you to calculate L when
ΔE = kT room temp
How many atomic diameters?
What if cooled to 1 Kelvin?



Solving completely-

$$\Psi(x,t) = \psi(x)\phi(t) = B\sin(\frac{n\pi x}{L})e^{-iEt/\hbar}$$

Normalize wavefunction …

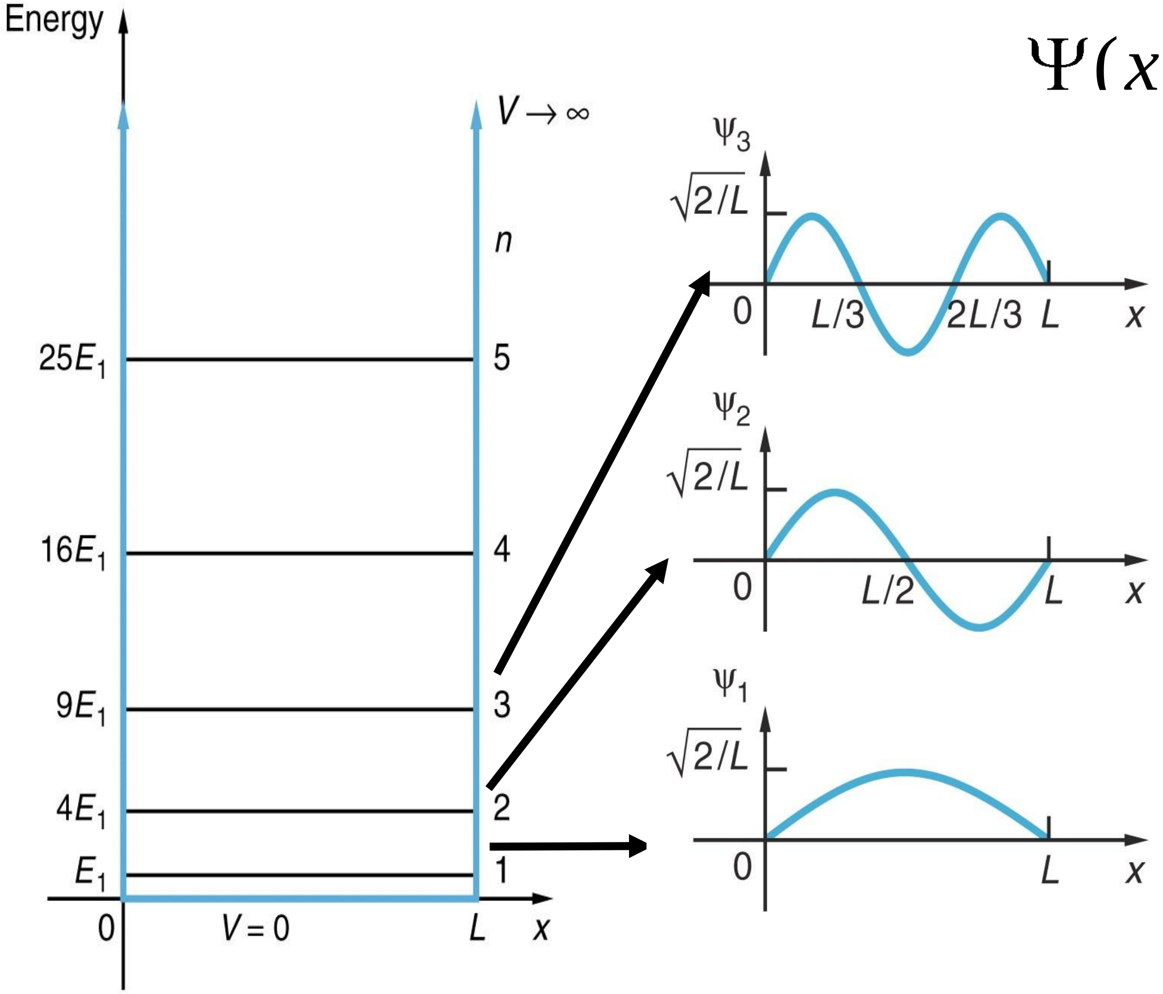
Probability of finding electron between -∞ and ∞ must be 1.

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\, dx = \int_0^L \Psi^*\Psi dx = \int_0^L B^2 \sin^2(n\pi x/L)dx = 1$$

$$B = \sqrt{\frac{2}{L}}$$

$$\boxed{\Psi(x,t) = \psi(x)\phi(t) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})e^{-iEt/\hbar}}$$

$$\Psi(x.t) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})e^{-iEt/\hbar}$$



Quantized: k=nπ/L

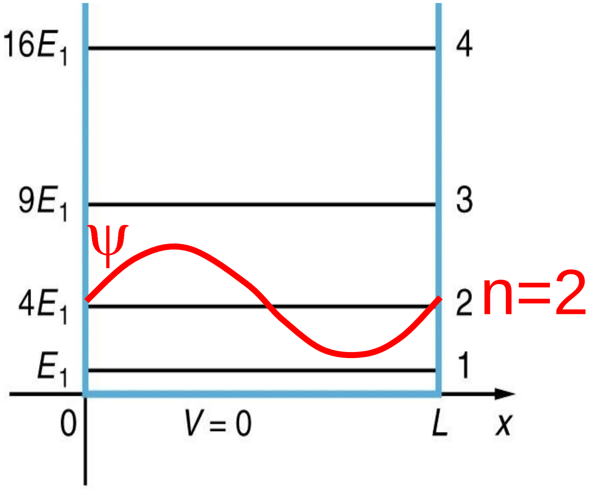
Quantized:

$$E = n^2\frac{\pi^2\hbar^2}{2mL^2} = n^2 E_1$$

energies are
“eigen values”

wave functions
“eigenfunctions”

show sim-- vary L, n



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

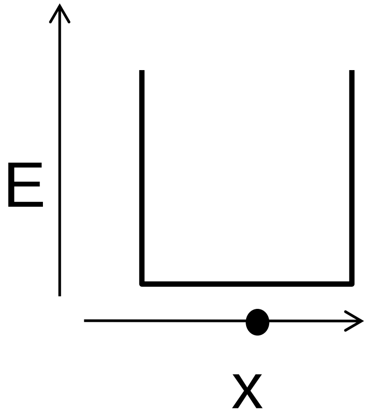
Quantized: k=nπ/L

Quantized: $E = n^2 \dfrac{\pi^2\hbar^2}{2mL^2} = n^2 E_1$

<u>What you expect classically:</u>	<u>What you get quantum mechanically:</u>
Electron can have any energy	Electron can only have specific energies. (quantized)
Electron is localized	Electron is delocalized … spread out between 0 and L

CQ. Can electron be in combination of n=1 and n=3?

a. yes, b. no

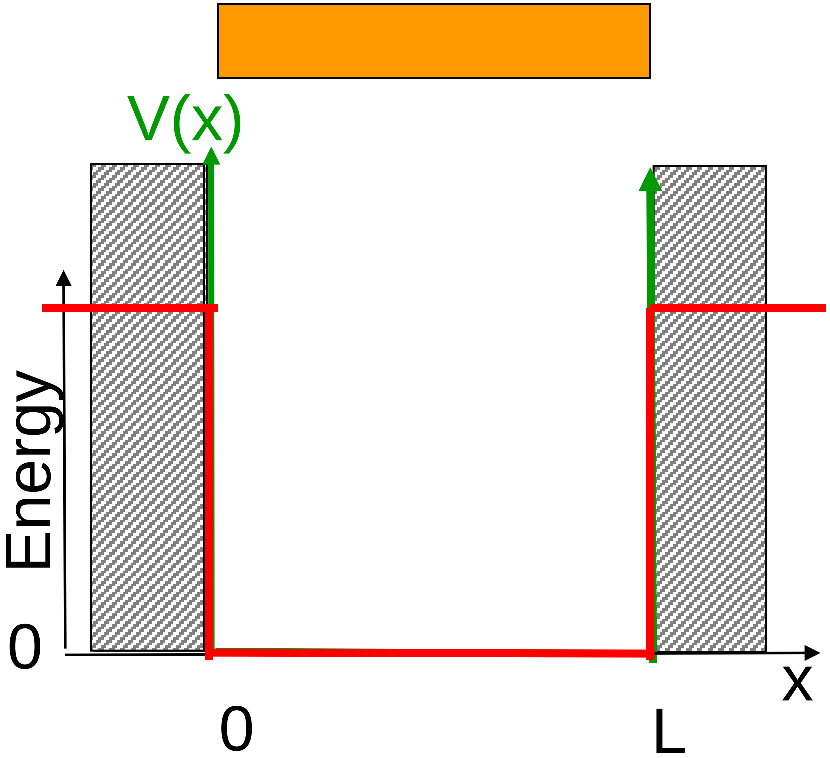


CQ. if went in and measured position of electron in potential well and found it at x =2+-.01 nm, what would that mean its energy would be?

think, then will give choices.

a. one particular discrete energy but cannot know which.
b. sum of many different energies.
c. would be impossible to do the measurement
d. the energy for which wave function had peak at that spot
e. some other answer

When does clever physicist model that wavefunction never gets outside potential well fail?
(look at sim)



Good Approximation:

Electrons never got out of wire

$\psi(x<0 \text{ or } x>L) = 0$.

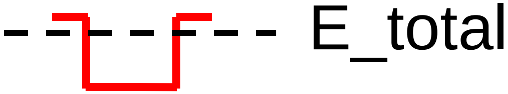
(OK when Energy << work function)

Exact Potential Energy curve:

V. small chance electrons get out of wire

$\psi(x<0 \text{ or } x>L) \sim 0$, but not exactly 0!

What happens if electron Energy bigger?



What if two wires very close to each other?

Then if ψ leaks out a little or not, is very important.

How much coupling to other wire?

When does clever physicist model that wavefunction never gets outside potential well fail?
(look at sim)

If energy of electron not too far below top of well, starts to extend out a bit. (classically forbidden region)

Some special situations, VERY important. Sticks out a bit where something important happens to it.

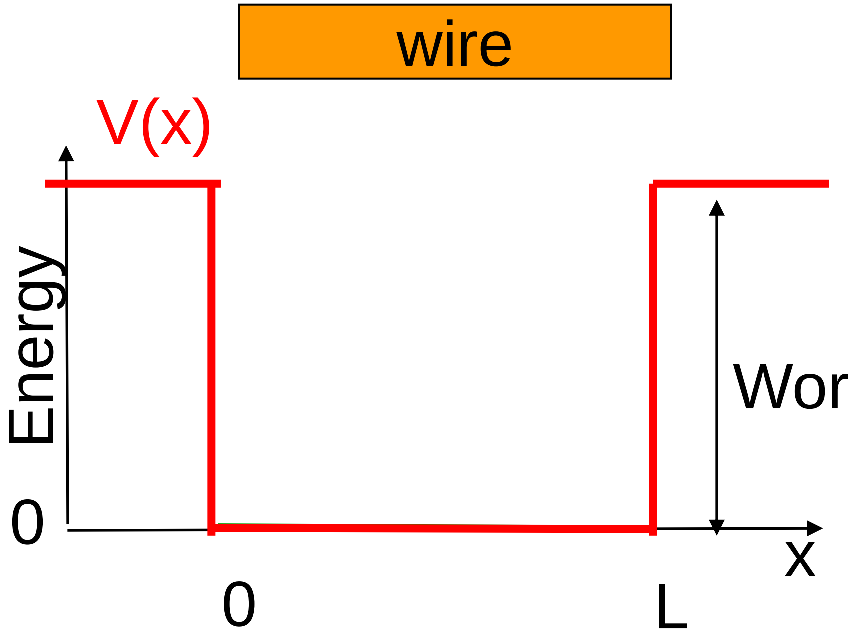
a. two wires close together
b. nuclear decay,
c. tunneling microscope-- see single atoms on surfaces
d. most modern electronics
e. electrons coming out of hot metal
f....

Detect electron position-- see it outside wire?

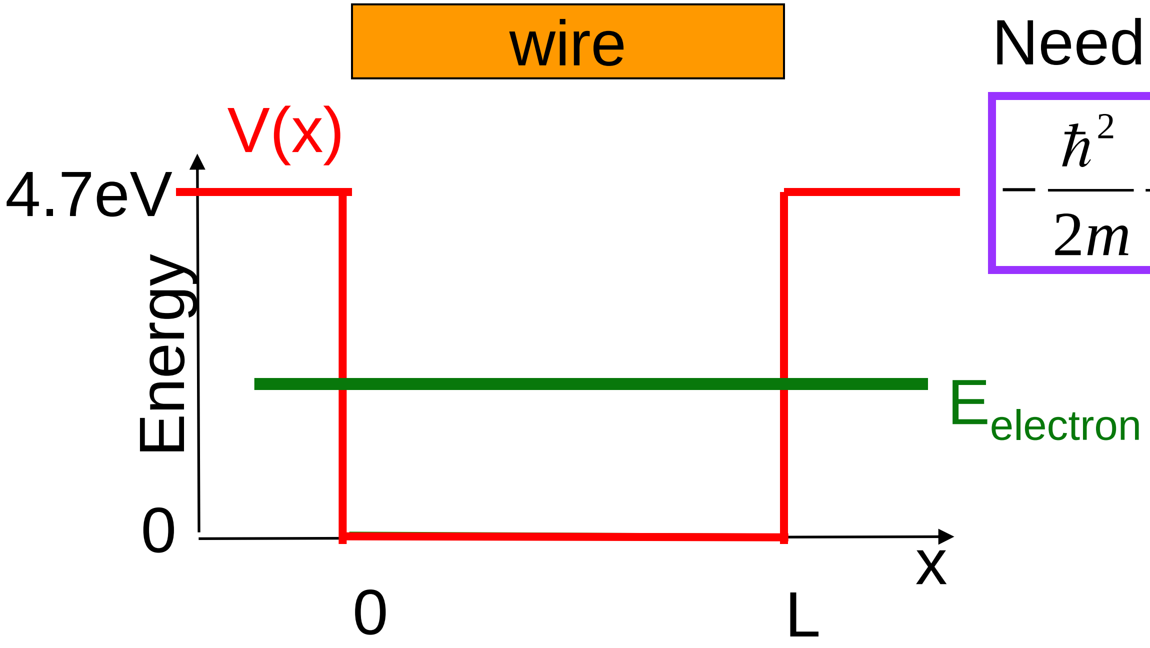
sketching how how solve for wave function for finite potential wells-- for reference if interested, not covered in class, you are not expected to be able to do.

V. small chance electrons get out of wire

$\psi(x<0 \text{ or } x>L) \sim 0$, but not exactly 0!



Finite Square Well



Need to solve Schrodinger Eqn:

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

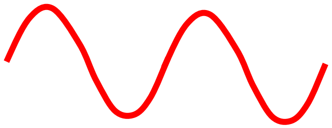
Region I | Region II | Region III

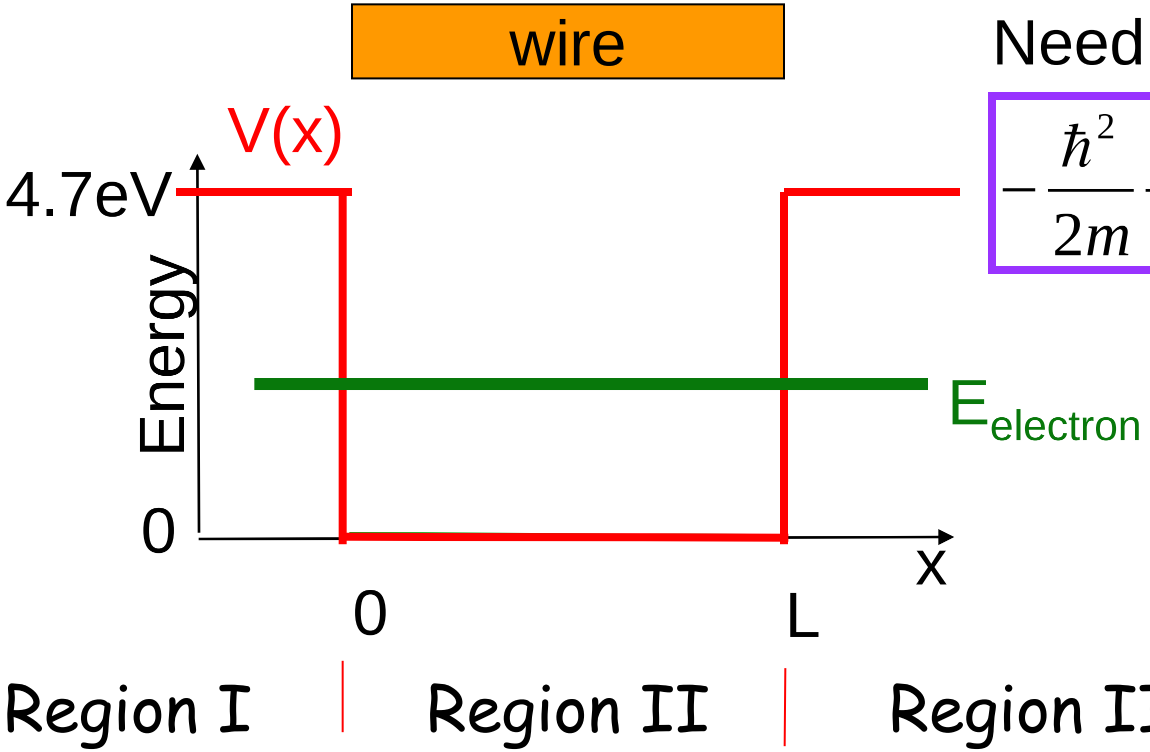
In Region II … total energy E > potential energy V

$$\frac{d^2\psi(x)}{dx^2}=\underbrace{\frac{2m}{\hbar^2}(V-E)}_{\text{Negative number}}\psi(x)\;=-k^2\psi(x)$$

k is real

When E>V: Solutions = sin(kx), cos(kx), e^{ikx}.
Always expect sinusoidal functions





Need to solve Schrodinger Eqn:

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

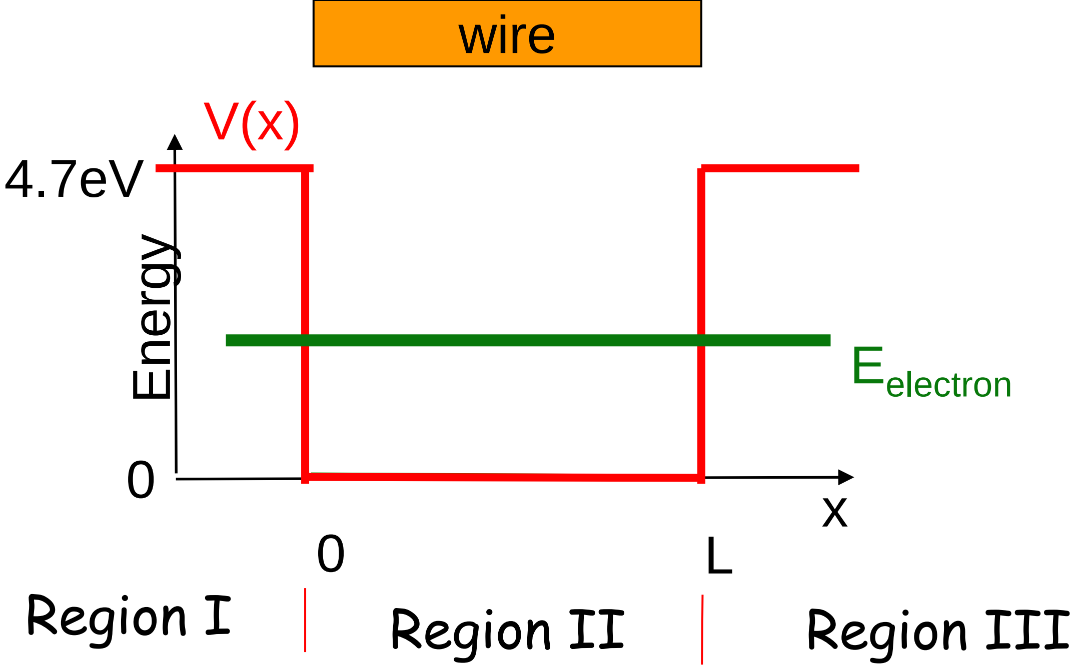
<u>In Region III</u> … total energy E < potential energy V

$$\frac{d^2\psi(x)}{dx^2} = \underbrace{\frac{2m}{\hbar^2}(V-E)}_{\text{Positive}}\psi(x) \quad = \alpha^2\psi(x)$$

$\boxed{\underline{\alpha \text{ is real}}}$

What functional forms of $\psi(x)$ work?

a. $e^{i\alpha x}$ b. $\sin(\alpha x)$ c. $e^{\alpha x}$ d. more than one of these



$$\boxed{\psi_{III}(x) = Ae^{\alpha x} + Be^{-\alpha x}}$$

In Region III … total energy E < potential energy V

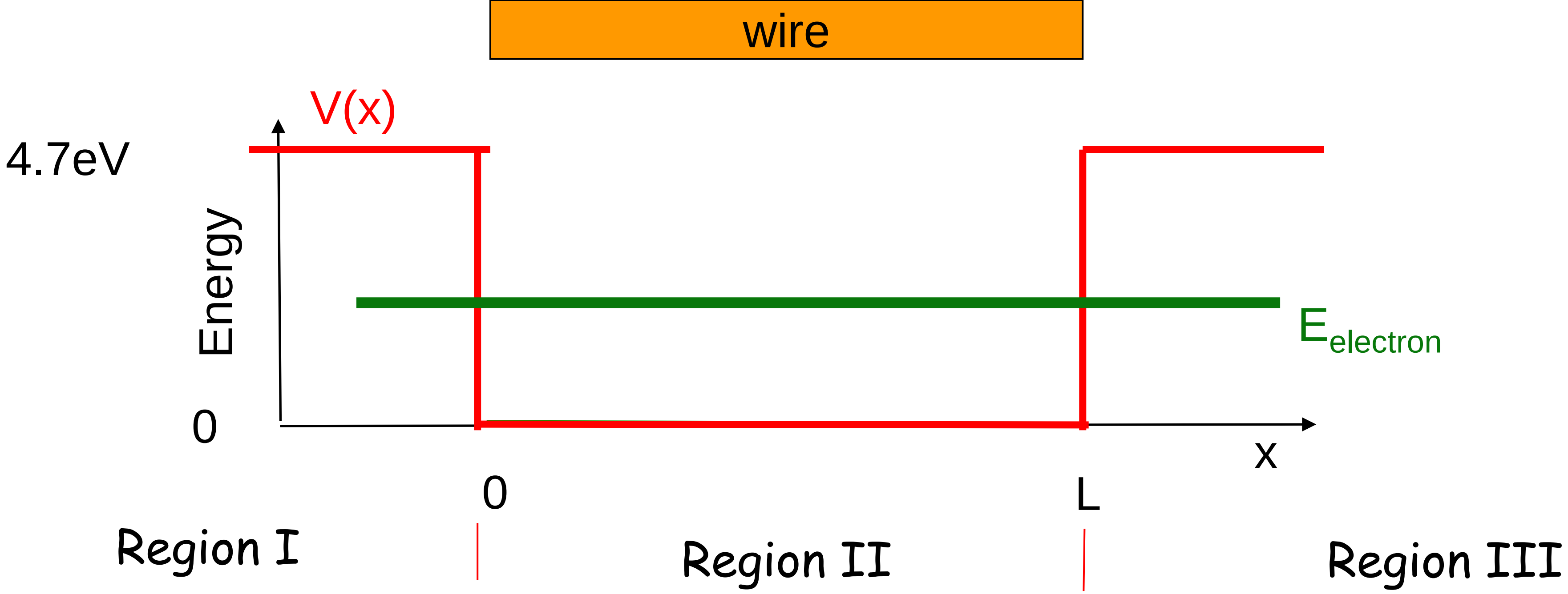
$$\frac{d^2\psi(x)}{dx^2} = \underbrace{\frac{2m}{\hbar^2}(V-E)}_{\text{Positive}}\psi(x) = \alpha^2\psi(x)$$

α is real

Answer is C: $e^{\alpha x}$ … could also be $e^{-\alpha x}$.
Exponential decay or growth

Why not $e^{i\alpha x}$?

LHS	RHS
$-\alpha^2\psi(x)$	$\neq \alpha^2\psi(x)$



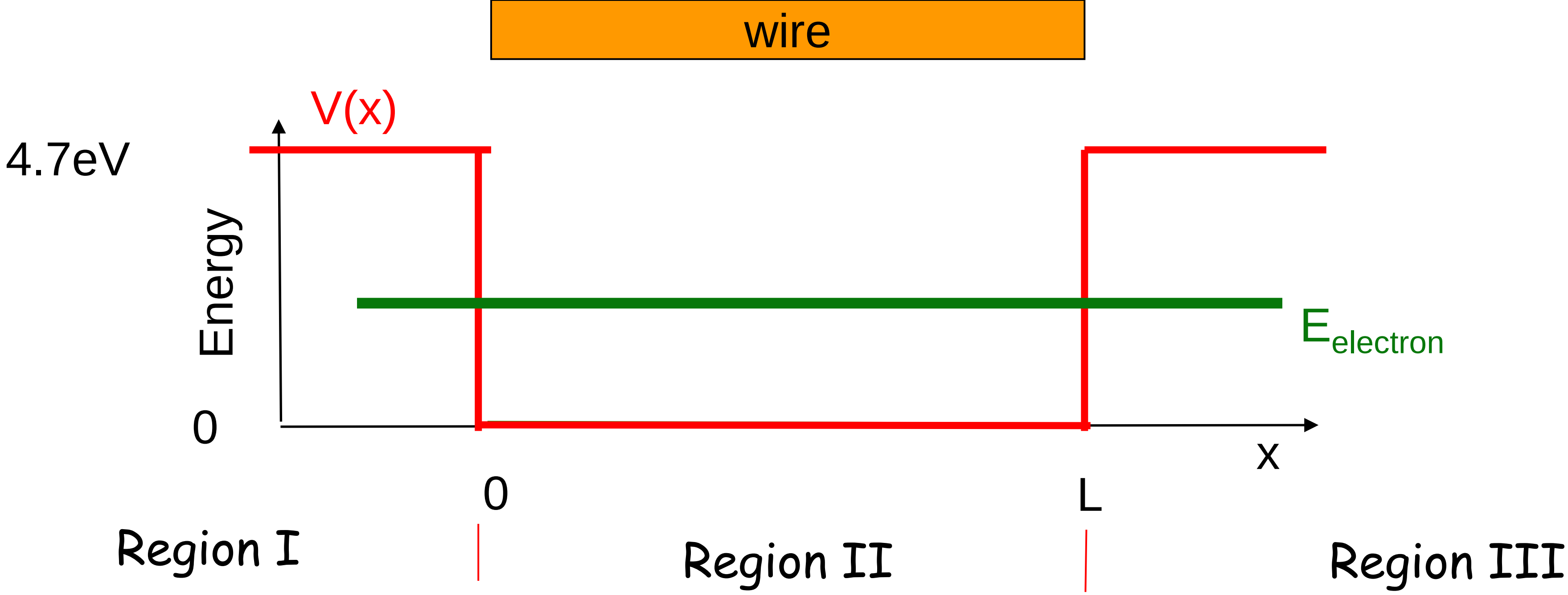
$$\psi_I(x) = Ee^{\alpha x} + Fe^{-\alpha x}$$

$$\psi_{III}(x) = Ae^{\alpha x} + Be^{-\alpha x}$$

$$\psi_{II}(x) = C\sin(kx) + D\cos(kx)$$

What will wave function in Region III look like?
What makes sense for constants A and B?

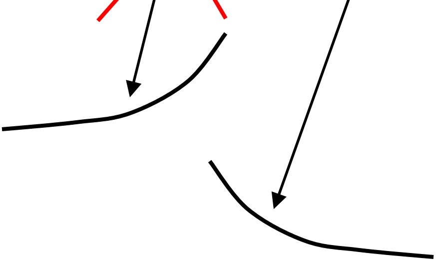
a. A must be 0
b. B must be 0
c. A and B must be equal
d. A=0 and B=0
e. A and B can be anything, need more info.



$$\psi_I(x) = Ee^{\alpha x} + Fe^{-\alpha x}$$

$$\psi_{II}(x) = C\sin(kx) + D\cos(kx)$$

$$\psi_{III}(x) = \cancel{Ae^{\alpha x}} + Be^{-\alpha x}$$



What will wave function in Region III look like?
What <u>makes sense</u> for constants A and B?

Answer is a. A must be 0 .. otherwise ψ blows up as x gets bigger.
This doesn't make sense!

ψ and probability should → 0 at large x!
Need to be able to normalize ψ

Outside well (E<V): (Region I)

On HW next week

Inside well (E>V): (Region II)

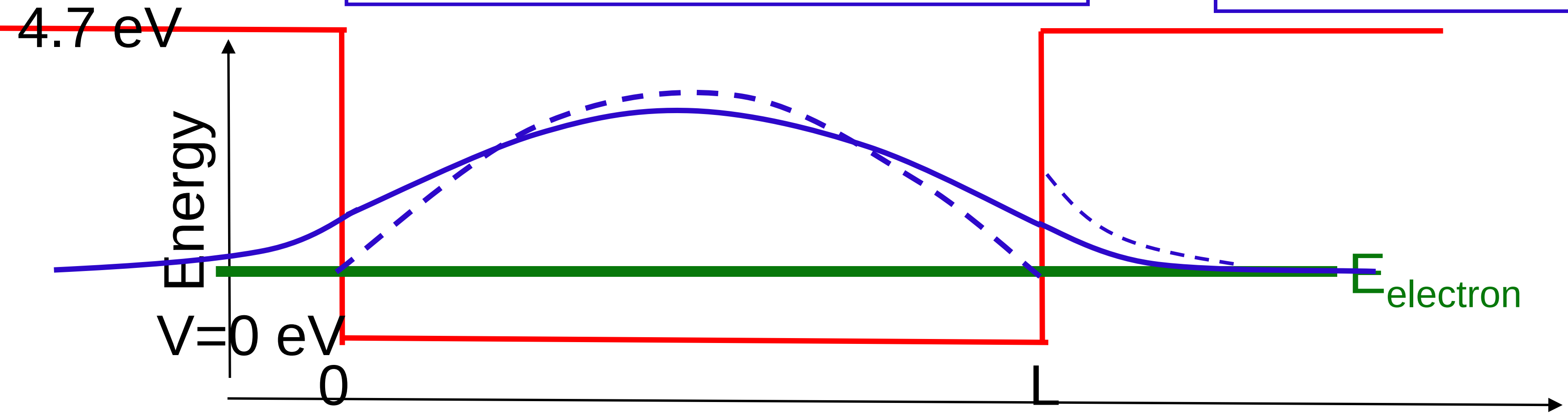
$$\frac{d^2\psi_{II}(x)}{dx^2} = -k^2\psi_{II}(x)$$

$$\boxed{\psi_{II}(x) = C\sin(kx) + D\cos(kx)}$$

Outside well (E<V): (Region III)

$$\frac{d^2\psi_{III}(x)}{dx^2} = \alpha^2\psi_{III}(x)$$

$$\boxed{\psi_{III}(x) = Be^{-\alpha x}}$$

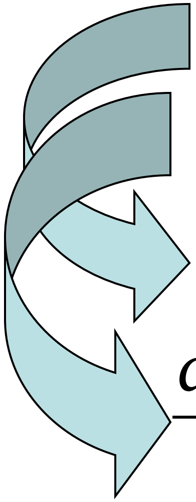


$$\psi(L) = \text{continuous}$$

$$\psi \longrightarrow 0 \quad \text{as x} \longrightarrow \infty$$

$$\frac{d\psi(L)}{dx} = \text{continuous}$$

Boundary Conditions:



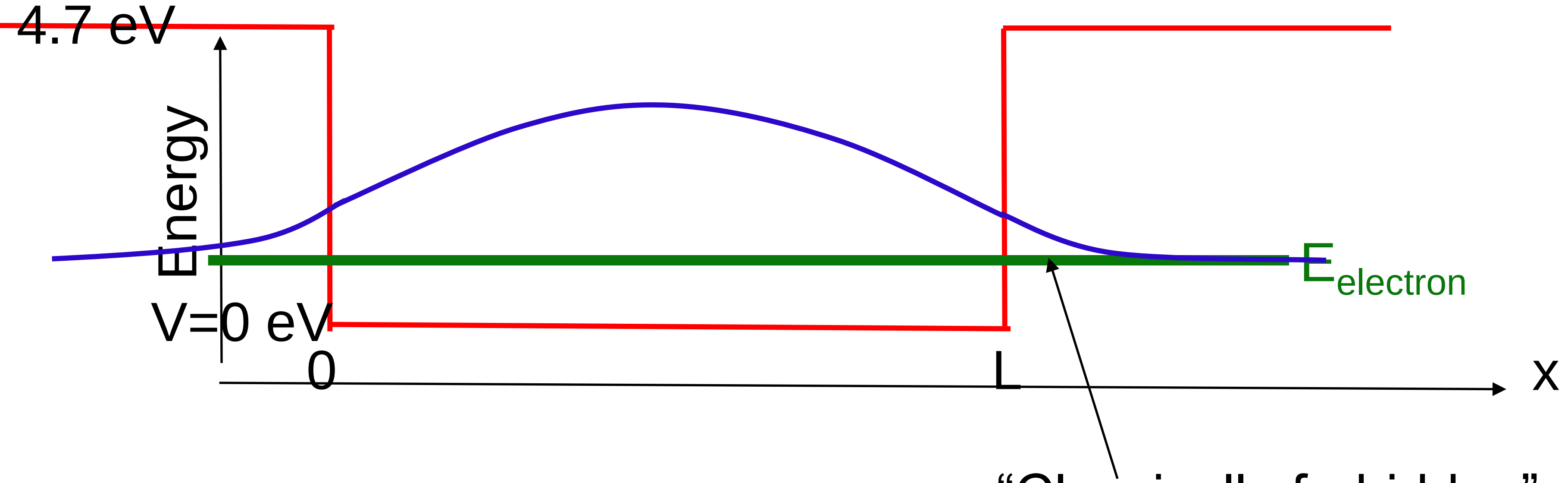
$$\psi_{II}(L) = \psi_{III}(L)$$

$$\frac{d\psi_{II}(L)}{dx} = \frac{d\psi_{III}(L)}{dx}$$

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

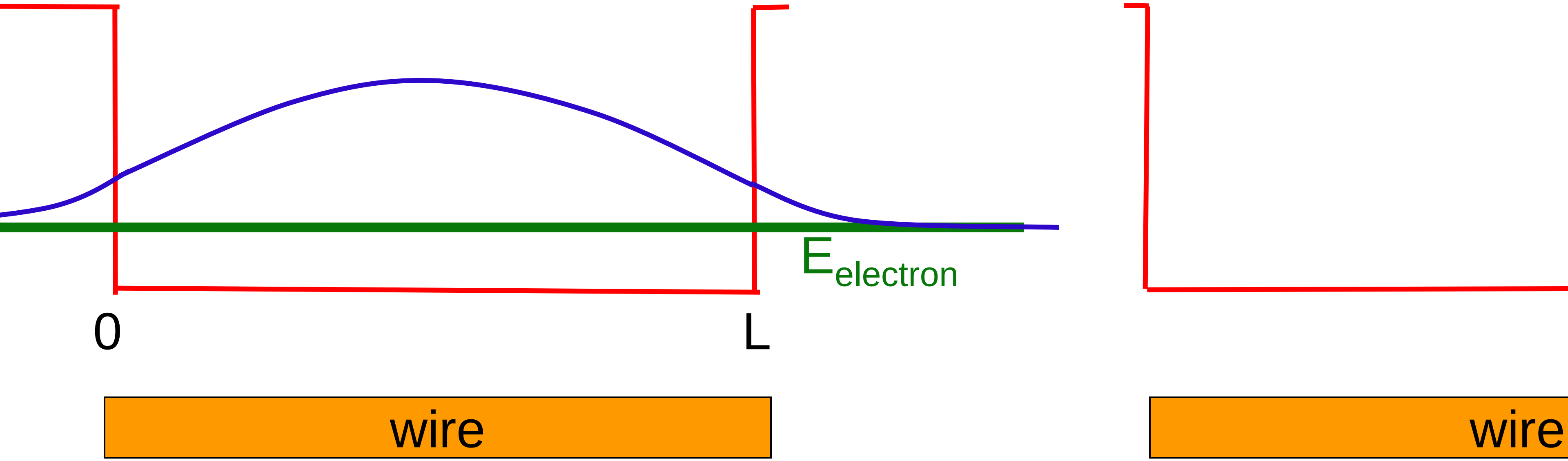
Inside well (E>V):

Outside well (E<V):



“Classically forbidden” region.

Electron is delocalized … spread out.
Some small part of wave is where Total energy is less than potential energy!



If wire gets closer and closer, what will happen?

a. electron is “shared” between wires, with fraction in each constant over time

b. the electron will flow away through wire 2

c. electron will jump back and forth between wire 1 and wire 2

d. electron stays in wire 1.

e. something else happens.