

Waves (electron)

In the last class we began our examination of waves

Underlying physics: No brakes → overshoot → oscillation

Led to **Refraction**: Occurs when wave changes speed, the basis for lenses

And to **Reflection**: Why fiber optics work, why dust tends to be white

But in contrasting Nanofabrication with Microfabrication, the key finding was:

Diffraction limited focusing

Waves act like superposition of egotistical "point sources"

Point sources produce circular waves

Long rows of point sources add to make straight ("plane") waves

But short rows of point sources ($< \lambda$) add to make ~ circular waves

So when light focused or confined to widths $< \lambda$, it quickly spreads back out!

If use it immediately (before spreads out!) can do things $< \lambda$

Basis for research "near field" techniques

But in Microfabrication, images must be "projected" some distance

Can't put things receiving light right against lenses / apertures

In mass production that would quickly wear / damage optics

So Microfabrication can't fabricate things $< \lambda$ (now $\sim 50-100$ nm)

Consequence: Nanofabrication MUST be very different than Microfabrication

Even though we don't yet know ideal ways to Nanofabricate!

It's why nanoscientists are exploring so MANY different approaches!

Nanoscience vs. Microscience

But is the difference between Nano and Micro only in fabrication technologies?

NO: I didn't quite finish up the topic of waves

There are still a couple more important wave behaviors left to cover

Electron waves exhibit these particular behaviors VERY strongly

THESE yield key differences between Nanoscience vs. Microscience

Confined Waves → "Standing Waves"

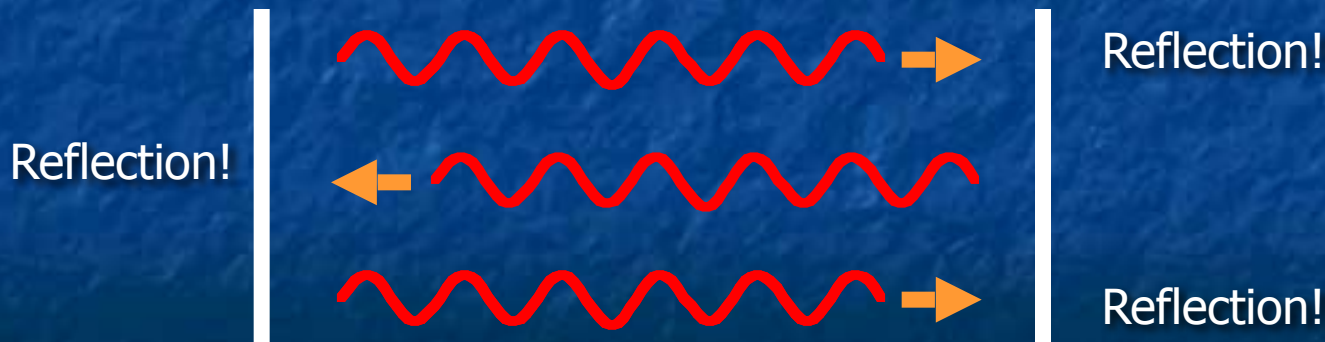
What if confine wave inside a box?

When wave arrives at an edge (which tries to stop the wave)

MUST get reflection (remember conservation of wave energy?)

FYI: Ripple tank has carefully constructed foam edges
INTENDED to absorb / redirect energy, suppressing reflection

Consider wave moving to right inside box with non-absorbing ends:



To get final result, invoke SUPERPOSITION by again adding all waves together

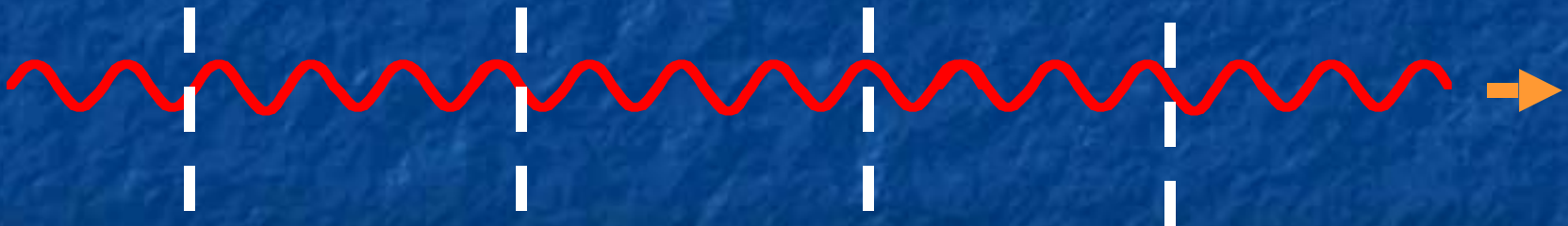
Can sort of see that sometimes waves might ADD → Strong total wave

And sometimes waves might be CANCEL → Little tiny confused ripples

How do we figure out when one or the other happens? Experiment or Simulation

This time, try simulation first (*worked well in last class!*)

TRICK (*always* seems to be a trick with math):



FOLD AT THE DASHED LINES!

Mathcad simulation of trapped wave

Wave (with wavelength, frequency and speed) moving right in box of length L:

$$\text{wave}_{\text{right}_1}(x, t) := \sin(k \cdot x - \omega \cdot t)$$

Fold at L (figuring out new leftward moving wave)

$$\text{wave}_{\text{left}_1}(x, t) := \sin[k \cdot (2L - x) - \omega \cdot t]$$

Fold again at 2L (which after folding is back at $x = 0$)

$$\text{wave}_{\text{right}_2}(x, t) := \sin[k \cdot (2L + x) - \omega \cdot t]$$

Do a few more folds / reflections and figure out pattern of sum (Superposition!):

$$\text{wave}_{\text{total}}(x, t, N) := \sum_{i=0}^N \sin[k \cdot (2 \cdot i \cdot L + x) - \omega \cdot t] + \sum_{i=1}^N \sin[k \cdot (2 \cdot i \cdot L - x) - \omega \cdot t]$$

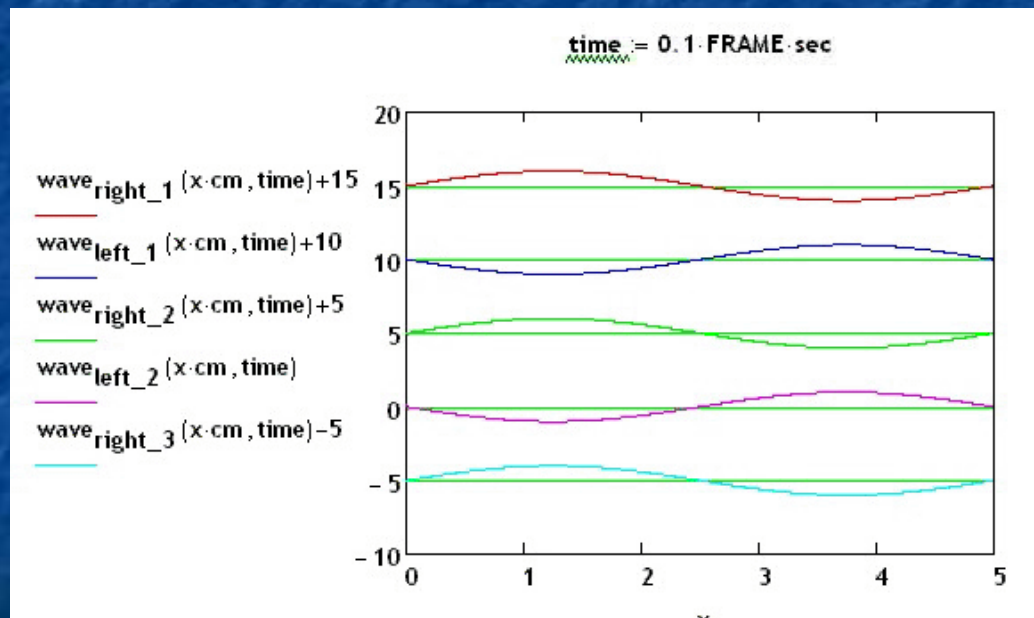
Check Validity of the Math (always!)

As wave reflects at end of the box, its reflection should have the same amplitude

That is, it SHOULD be as if we folded a single wave at that point

So check by plotting subsequent waves (offset so we can see each one clearly)

Then animate to verify that amplitudes of subsequent waves match at ends

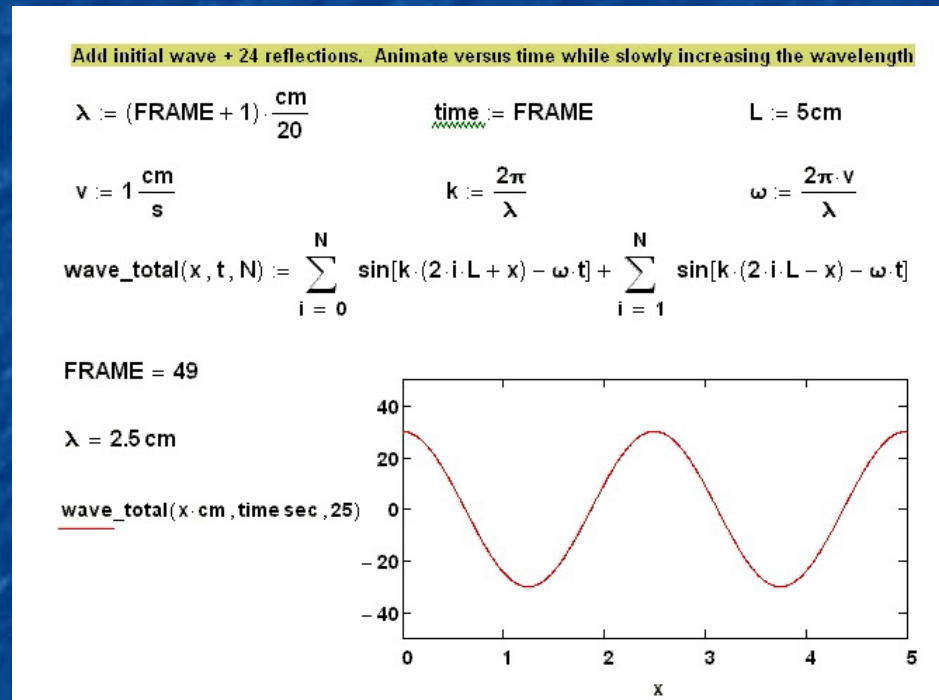


Link to animation embedded in webpage: [Waves: Electron - Supporting Materials - Simulation 1](#)

Now ADD Waves to get the Net Effect

Graph total wave at different times, for a particular fixed wavelength

Then have Mathcad ANIMATE, repeating graphs at different values of wavelength:



Link to animation in webpage: [Waves: Electron - Supporting Materials - Simulation 2](#)

"Standing Waves"

BIG total waves form when:

$$\lambda = 1.25 \text{ cm}, 1.66 \text{ cm}, 2.5 \text{ cm}, 3.33 \text{ cm}, 5 \text{ cm}, 10 \text{ cm}$$
$$= L/4, L/3, L/2, 2L/3, L, 2L \text{ (L is length of box)}$$

These are the wavelengths that FIT in the box (or more accurately, in 2 L):

One wave of $\lambda = L$ fits, Two waves of $\lambda = L/2$ fit . . .

Sort of makes sense:

Waves with λ unrelated to L could never get into step and ADD

Those big (summed) waves are called "Standing Waves"

They don't really STAND (still oscillate up and down)

But because they don't seem to be moving side to side, are called "standing"

"Fidgeting waves" (at one point but moving a lot) might be better name

Verify with water ripple tank experiment:

Set up wave generator with single point touching water

Enclose that point at the center of a circular ring

I cut sections of plastic drain pipes \sim 6 and 14 cm inside diameter

Then halved (giving pair of C's I could place without disturbing generator)

Experiment 1) With small ring, scan the generator frequency

Get any BIG Standing Waves ? Record their frequencies, f ?

PREDICT frequencies that will produce **SAME PATTERN** inside the larger ring

Experiment 2) Swap in the larger circular ring

Tune to your **PREDICTED** frequencies

DO you indeed get the same strong standing waves?

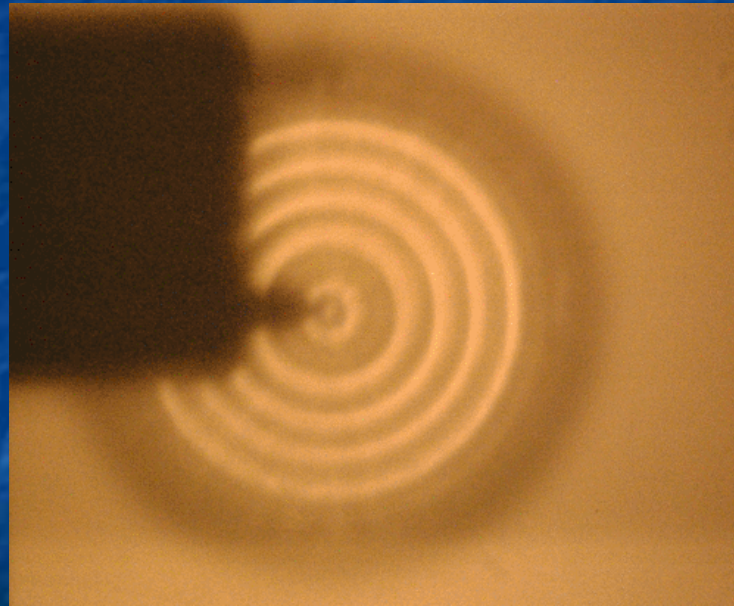
Actual ripple tank images:

Here I was using the larger ring

I scanned generator frequency from 1-20 Hz in 0.5 Hz increments

Took one photograph at each of these 39 frequencies, then combined into movie

NOTE: Did not necessarily capture biggest waves at each f (matter of luck)



Link to animation in webpage: [Waves: Electron - supporting Materials - Animation 1](#)

"A Hands-on Introduction to Nanoscience: WeCanFigureThisOut.org/NANO/Nano_home.htm"

"Magic" wavelengths → magic energies

The strong "standing waves" have different wavelengths and frequencies

Your intuition tells you that they must also have different energy

Would expect energy of a wave to increase with its frequency (f)

In fact, it increases as: **Energy \propto (frequency)²**

(I prove this in lecture's appendix for a common situation)

Which implies that **Energy $\propto 1 / (\text{wavelength})^2$**

From fact that wave moves one wavelength (λ) in each cycle time ($1/f$):

$$\text{velocity} = \lambda f \quad \Rightarrow \quad f = \text{velocity} / \lambda$$

So fact that in a box we ONLY have strong waves a certain specific f 's and λ 's →

Trapped waves are QUANTIZED in energy (. . . drum roll!)

"Quantum Size Effect"

Or just "QSE" - The sexy name this is given for electron waves

The strong standing waves were those that "fit" in the box:

$$\lambda_1 = L_{\text{box}}$$

$$\lambda_2 = L_{\text{box}} / 2$$

$$\lambda_3 = L_{\text{box}} / 3 \dots$$

Their energies increase as frequency $^2 = (\text{velocity} / \lambda)^2 \rightarrow$ "allowed energies" $\propto 1 / \lambda^2$

$$E_1 \propto 1 / L_{\text{box}}^2$$

$$E_2 \propto 4 / L_{\text{box}}^2$$

$$E_3 \propto 9 / L_{\text{box}}^2$$

Energy



Small Box



Large Box



Huge Box

(and so on)

1) LARGER THE BOX - smaller the energies

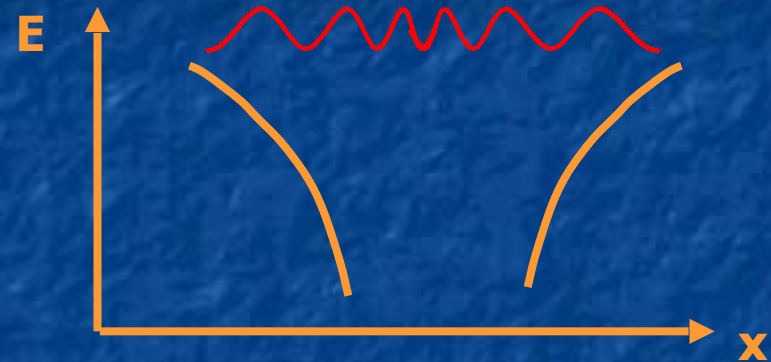
2) Energies \sim SAME for same sized particles (if electron wave velocities \sim same)

Atoms = 3D electron boxes (a bit more complicated):

For 1D water wells above, standing wave energies were pretty easy to figure out

But what if well got sharply deeper in center?

Wave's velocity & wavelength
change as depth of well changes:



"Standing wave" energies shift from those on previous page

Further modified if well goes from 1D → 2D → 3D

Atoms = 3D energy wells: $-q_{\text{electron}} q_{\text{nucleus}} / R =$



Math is more complex! Takes longer to solve (!@#%#!!) But in the end:

Atomic Energy Levels = Electron Standing Wave Energies

Size dependence + insensitivity to composition = Hallmark of Nanoscience

But why just hallmark of Nanoscience?

"Standing waves" are almost unavoidable in small boxes: e.g. coffee in cup

But are not seen in large boxes ($L \gg \lambda$): e.g. water in swimming pool

Reason 1) Waves die out before crossing large box

Reason 2) Wave energies/wavelengths are SO close to one another (QSE!)
that we can't tell them apart:



Huge Box

Same degradation occurs for electron waves

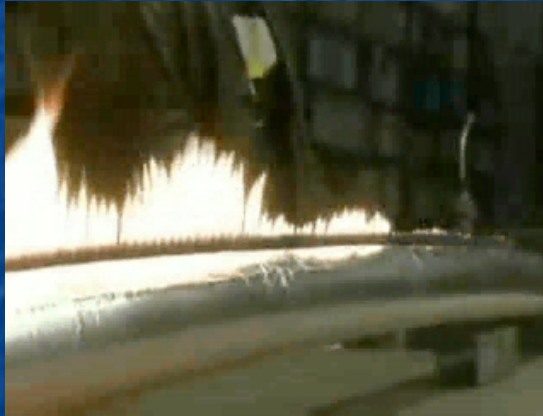
For electrons in a large "box," wave energies squeeze together
and, with thermal energy, electrons can dance between levels

So effects of trapped electron waves seldom seen for $L \gg \lambda$ (for electrons ~ 50 nm)

Additional reason why ~ 50 nm = Boundary between Nano & Micro

Standing waves DO also occur in non-water or non-Nano situations:

For instance in YouTube demonstrations of "Reuben's Tubes:"



And in patterns of salt on a vibrating plate:



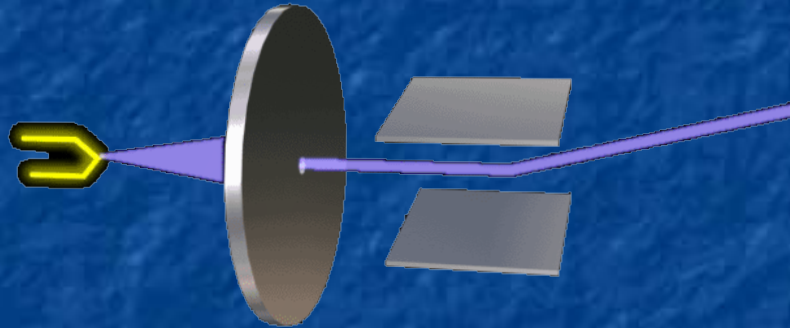
Link to YouTube standing wave videos: [Waves: Electron - Supporting Materials - Other](#)

OK, but ARE electrons really waves?

Scientists came to this conclusion only very slowly and very painfully

They HAD thought electrons were ~ little B-B's:

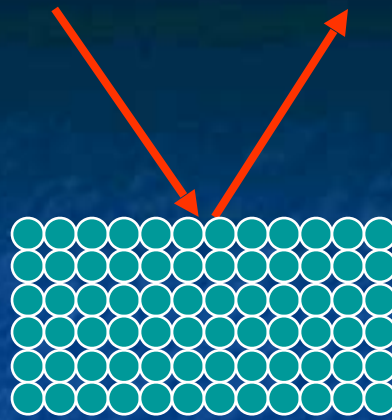
In "Crooke's Tube" (early 1900 name for CRT) they could form beams of electrons



Behaved just as they expected (in E and B fields) for little charged particles

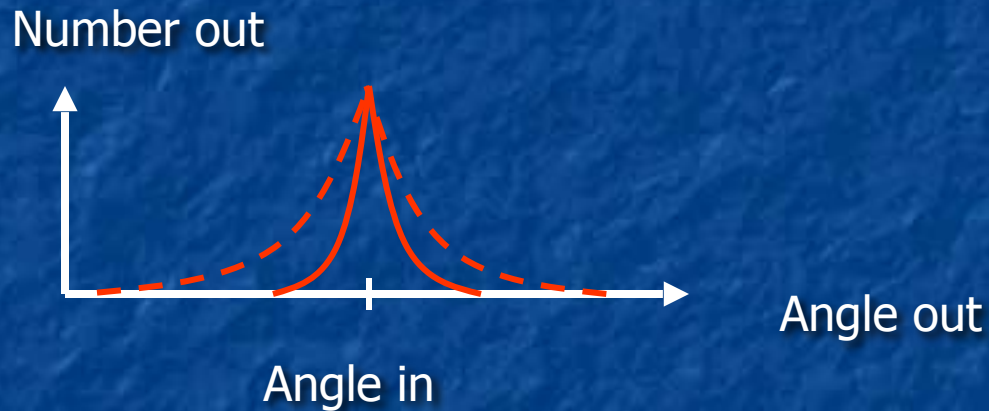
But then stumbled across many NEW situations where electrons acted as waves!!!

One of these was when they bounced beam of electrons off a crystal of nickel:



The measured number bouncing off (for one incoming angle) vs. outgoing angle

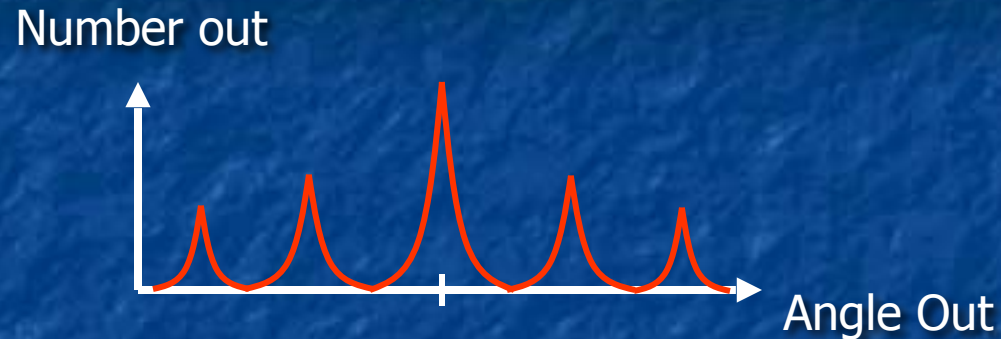
EXPECTED:



Made SENSE: Outgoing angle = Incoming angle if smooth enough (\sim pool table)

OR Scattered about incoming angle if rough (on scale of electron size)

BUT WHAT THEY GOT WAS:



They could ONLY explain above behavior IF:

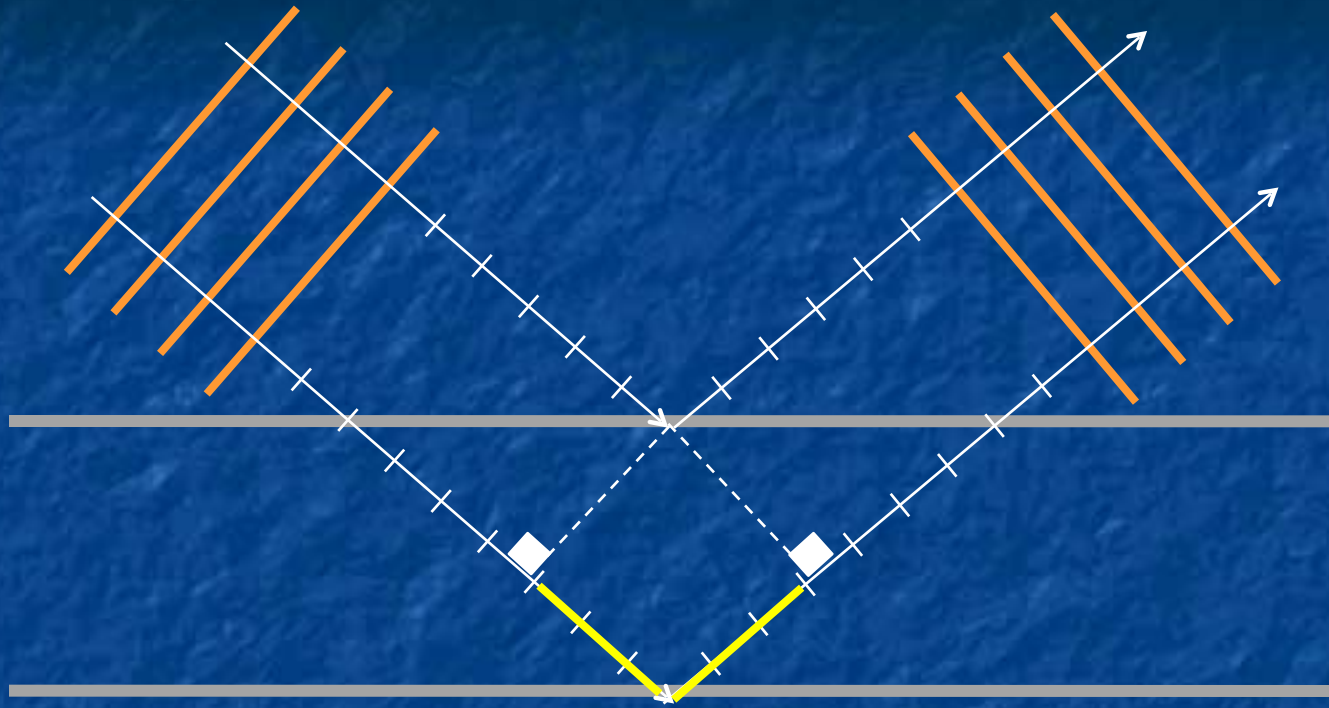
ELECTRONS were acting as waves

Atomic planes in crystal acted as partially reflecting electron mirrors

In certain directions sum of reflected WAVES added, in others it cancelled

Really need a drawing to visualize:

Waves entering from upper left, bouncing off crystal's planes:



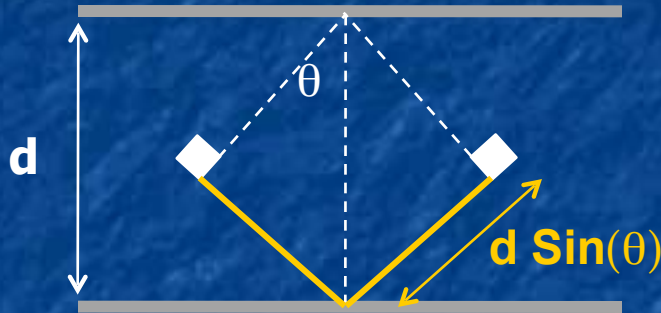
Compare parts of waves traveling along indicated paths:

Top part of wave travels certain distance

Bottom part of wave travels same distance + PLUS extra yellow distance

For strong net reflection, waves must end up back in phase

Figure out extra distance traveled by lower portion of wave:

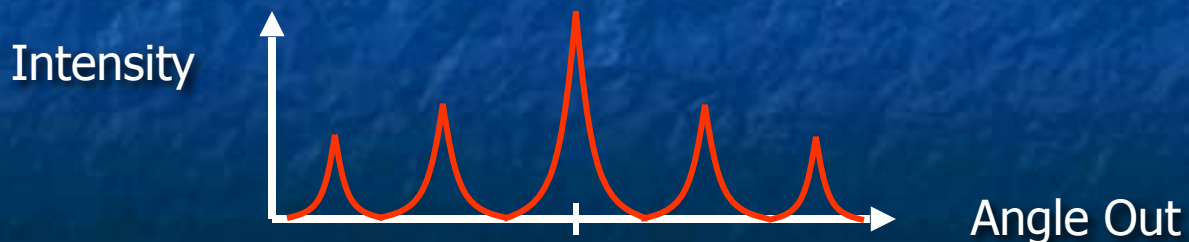


Total extra travel: $2 d \sin(\theta)$

If extra travel = multiple of wave's wavelength, two waves DO end up back in phase

So condition for strong net reflection is: $2 d \sin(\theta) \Rightarrow n \lambda$

For each integer value of n , there is a corresponding angle of strong reflection:



How on earth did they come up with that explanation?

Physicists circa 1900 were the ALL TIME EXPERTS ON WAVES!

Triumph of 17th and 18th century physics:

~ 1600 Galileo and others started using light waves to explore the heavens

"Natural Philosophers" learned how light focused, reflected, diffracted . . .

Began to see how KNOWN waves (e.g. water) behaved similarly

Eventually identified light as waves

Triumph of 19th century physics:

James Clerk Maxwell came
up with four little equations:

$$\begin{aligned}\nabla \cdot \xi &= \frac{\rho}{\epsilon_0} \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \xi &= -\left(\frac{d}{dt} \mathbf{B}\right) \\ \nabla \times \mathbf{B} &= \frac{1}{c^2} \frac{d}{dt} \xi + \mu_0 \cdot \mathbf{J}\end{aligned}$$

EXPLAINED:

Electricity & Magnetism

AND that

LIGHT was wave combining both

They REALLY didn't like idea that electrons were waves!

But treating as waves explained DOZENS of otherwise UNEXPLAINABLE results!

So they ultimately came up with a new set of rules (a.k.a. "Quantum Mechanics")

Centered on one NEW wave equation (from Erwin Schrodinger):

$$\frac{d^2}{dx^2} \Psi(x) + [2m(E - V) / \hbar^2] \Psi(x) = 0$$

m = Mass of Electron

E = Its total energy

V = Its potential energy

\hbar = Planck's constant / 2π = "fudge factor" so solutions fit experimental data

Looks strange (primarily because uses strange Greek letter for function, Ψ)

But is really just a variant on the form of ALL equations describing waves

Difficult parts were:

DIFFICULTY 1:

Coming up with exact arrangement of things inside the [] bracket

It HAD to produce results consistent with experiments!

DIFFICULTY 2:

Figuring out HOW equation's solutions $\Psi(x)$ described electron behavior

Here they sort of borrowed from Maxwell's theory of light waves:

What you **measure** about light waves is the ENERGY they carry

It's proportional to the amplitudes² of E and B fields in light wave

So GUESSED $\Psi(x)^2$ described **measurable** feature of electron: Probability it's at x

Physicists "GUESSED" this?

Well, it took **THIRTY YEARS** to come up with that equation and its interpretation

If it was a process of logical deduction it was sure glacial!

REALLY hard part was that it seemed utterly inconsistent with Newtonian physics

Had to throw out everything that had worked so BRILLIANTLY in previous century

And install in its place this weird new equation

And THEN spend more decades proving that QM results at nanoscale

DO EVENTUALLY

produce results we recognize as Newtonian physics at human and larger scales

Why in class avoiding math did I drag you through this?

Because there's a UNIQUE electron behavior based on Schrodinger Wave equation

Occurs when Schrodinger's equation ceases to be a wave equation!!

So grit your teeth and look more closely at wave type equations:

$d^2/dx^2 f(x) + f(x) = 0$ but that's the **SAME** as saying:

$d^2/dx^2 f(x) = -f(x)$ or that the function's second derivative = - the function

Math teacher can PROVE this implies sums of **Sin(x)** and **Cos(x)**

Or a second type of equation where we just change the plus to a minus:

$d^2/dx^2 f(x) - f(x) = 0$ but that's the **SAME** as saying:

$d^2/dx^2 f(x) = +f(x)$ or that the function's second derivative = + the function

Same math teacher can prove this implies sum of **e^x** and **e^{-x}**

But then just goof things up a little bit by sticking a constant A into the equations

$$d^2/dx^2 f(x) + A f(x) = 0 \rightarrow \text{solutions } \cos(x\sqrt{A}) \text{ and } \sin(x\sqrt{A})$$

$$d^2/dx^2 f(x) - A f(x) = 0 \rightarrow \text{solutions } e^{+x\sqrt{A}} \text{ and } e^{-x\sqrt{A}}$$

Our Quantum Mechanical Shrodinger equation fits one of these two forms:

$$d^2/dx^2 \Psi(x) + A \Psi(x) = 0 \quad \text{with } A = [2m(E - V) / \hbar^2] \text{ is Schrodinger!}$$

If A is positive, we get classic wave solutions involving Sin and Cos

But if A is negative, we'd instead get exponential solutions:

$$\Psi(x) = e^{+kx} \text{ or } e^{-kx} \quad \text{with } k = \sqrt{A} = \sqrt{[2m(V - E) / \hbar^2]}$$

Is coefficient ever negative in Schrodinger equation?

Yes!
$$\frac{d^2}{dx^2} \Psi(x) + [2m(E - V) / \hbar^2] \Psi(x) = 0$$

If $E < V$ the factor in [] must be negative

E is the electron's total energy, V is its potential energy

So if Newton still ruled, $E - V$ would be the electron's kinetic energy

AND as Newton said kinetic energy = $1/2 mv^2$ it couldn't be negative!

But kinetic energy is not central to QM! While potential energy still is (the V):

Electron potential energy rises when moves from region with net positive charge to region with net negative charge

More negative charge, more potential energy! Eventually might exceed E

Electron sure doesn't WANT to go there, but doesn't mean can't happen!

Would then have to use exponential solutions:

$$\Psi(x) = B e^{+kx} \quad \text{OR} \quad \Psi(x) = C e^{-kx} \quad \text{where } k = \sqrt{[2m(V-E) / \hbar^2]}$$

Remembering that this thing squared gives probability of finding electron at x:

First solution GROWS farther the electron goes

Electrons are MORE likely to be found deeper in repulsive region?

Makes NO sense – the constant "B" must be 0!

Second solution DECREASES farther the electron goes

Electrons are LESS likely to be found deeper in a repulsive region?

Makes GOOD sense - constant C can be non-zero

This produces the phenomenon of: **"Quantum Mechanical Tunneling"**

Electrons tunneling INTO and even THROUGH otherwise insurmountable energy barriers

Through what thickness "barrier" can an electron tunnel?

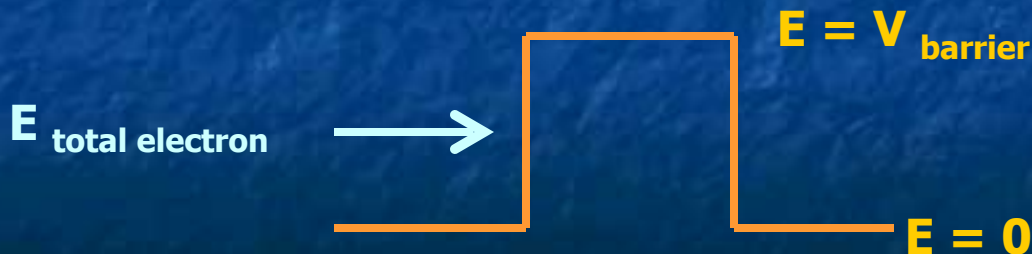
First make sure you understand these barriers! They are due to charge interaction:



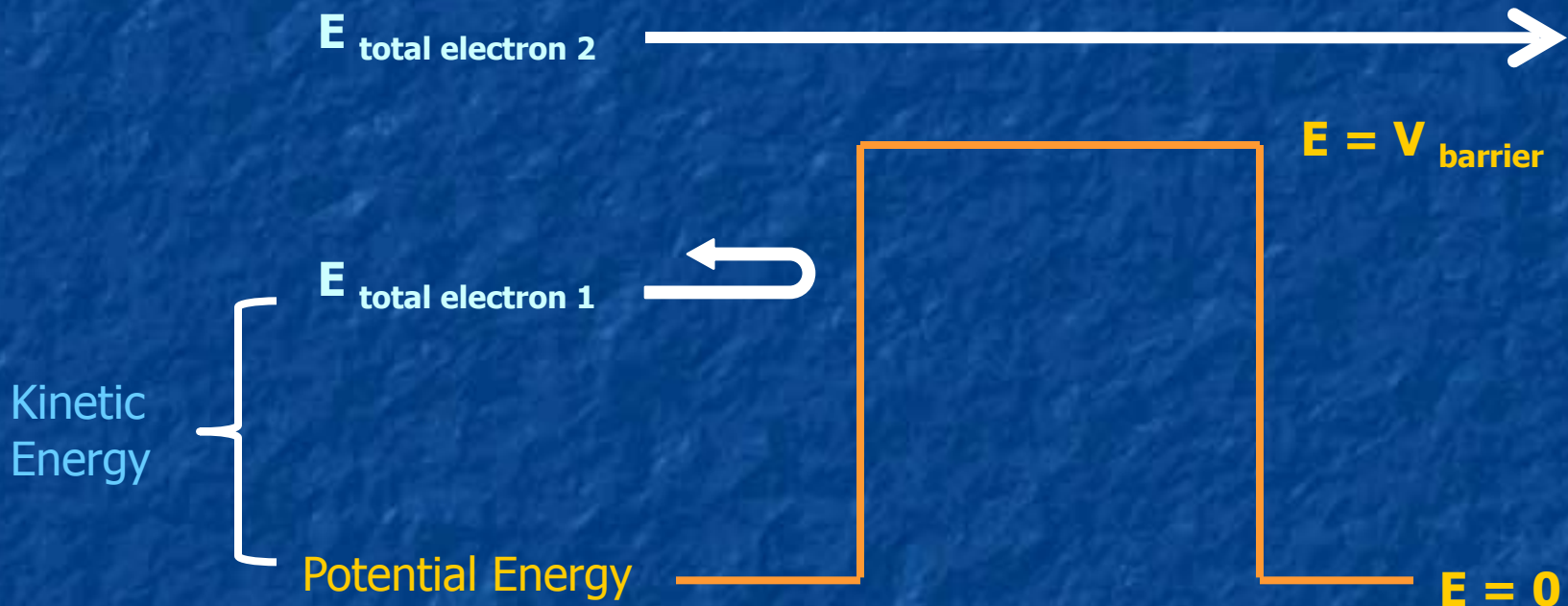
Matter on left or right: Lots of positive atom cores = happy place for electron to be!

Gap in middle is empty (or very different), NOT a happy place for an electron to be

So electrons face an "electrostatic" potential energy barrier:

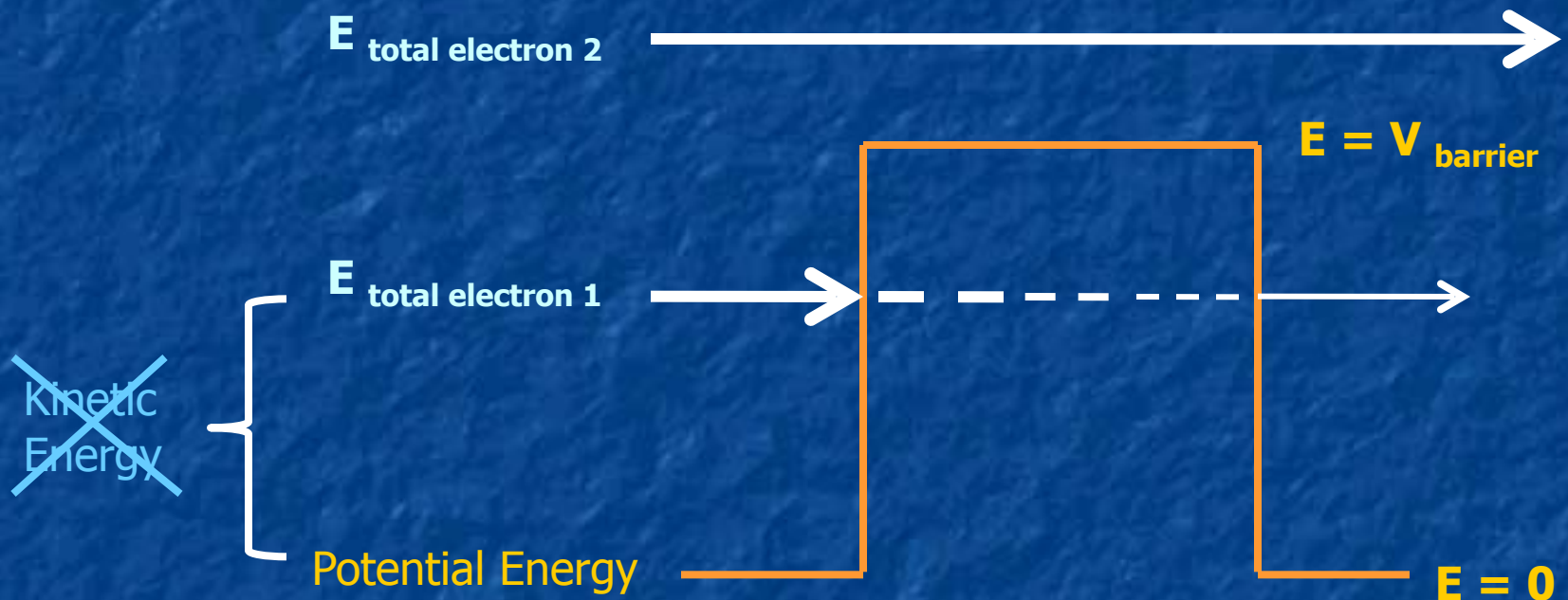
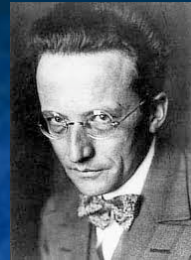


If Sir Isaac Newton were still in charge:



Newton: "Can't go through barrier, must have enough energy to go over!"

But with Erwin Schrodinger in charge:



Schrodinger: "No Problemo!"

So, proceeding with "tunneling" calculation:

Probability of exiting barrier = $\Psi(L_{\text{barrier}})^2 = e^{-2kL}$ which diminishes as:

- 1) Height of barrier (which is embedded in k)
- 2) Thickness of barrier (L)

To get barrier heights, we need to select barrier material (\Rightarrow value of k)

- a) Electron trying to escape atom(s) completely \rightarrow vacuum (e.g. as with ionization)

Barrier to escape into vacuum = "Work Function" ~ 4 eV

- b) But in most nanodevices only ask electron to pass through insulator

Barrier to enter insulator ~ 2 eV

- c) Or pass through slightly different material (e.g. semiconductor 1 \rightarrow semiconductor 2)

Barrier to enter different semiconductor ~ 0.2 eV

These are only ball park numbers, but let's see what they get us:

Probability of electron tunneling through potential energy barrier (V-E):

$$\Psi (L_{\text{barrier}})^2 = e^{-2kL} \text{ with } k = \sqrt{[2m(V-E) / \hbar^2]}$$

Barrier:	0.1 nm	0.3 nm	1 nm	3 nm	10 nm
Similar material (0.2 eV)	0.63	0.25	0.01	1×10^{-6}	$< 10^{-15}$
Insulator (2 eV)	0.36	0.046	3×10^{-5}	4×10^{-14}	$< 10^{-15}$
Air/ Vacuum (4 eV)	0.13	2×10^{-3}	1×10^{-9}	$< 10^{-15}$	$< 10^{-15}$

Barrier height and width make **HUGE** differences!

Through vacuum ($\Delta E \sim 4$ eV) electron can only go fraction of nm

But for lower barriers, electron can "tunnel" for 1-3 nanometers

Bottom Lines:

Nanoscience is DOMINATED by two electron phenomena

Quantum Size Effect: Controls energies INSIDE nanoparticles

Electron (quantized) energy levels are $\propto 1 / (\text{size of box})^2$

Tunneling: Controls movement BETWEEN nanoparticles

Electrons can tunnel THROUGH energy barriers $< \sim 1 \text{ nm}$

Credits / Acknowledgements

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This set of notes was authored by John C. Bean who also created all figures not explicitly credited above.

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Short appendix on wave energy vs. frequency is given below:

Appendix on Wave Energy vs. Frequency

In this class, my goal is to present intuitive explanations rather than math

But math above is already enough to demonstrate that wave energy can scale as $1/\lambda^2$

So I might as well complete the math:

From above, $\sin(x\sqrt{A})$ solves a wave equation of the form $d^2/dx^2 F(x) + A f(x) = 0$

In regions where potential energy (V) is constant, the Schrodinger equation has this form:

$$\text{with } A = [2 m (E - V) / \hbar^2]$$

But for a sine wave, going a distance λ advances its argument by one cycle = 2π , thus

$$\lambda \sqrt{A} = 2 \pi$$

Substituting in Schrodinger value of A , and solving for energy (E):

$$\lambda \sqrt{[2 m (E - V) / \hbar^2]} = 2 \pi \quad \text{So:} \quad E = V + 2 \pi^2 \hbar^2 / m \lambda^2$$