PHYS 250

Lecture 5.1

Applications 1:

Bonds, Bands & Semiconductors

Today

Review
Double Square Well
Chemical Bonds
Multiple Square Wells
Periodic Potential
Energy Bands & Conductivity
Semiconductors
Semiconductor Devices

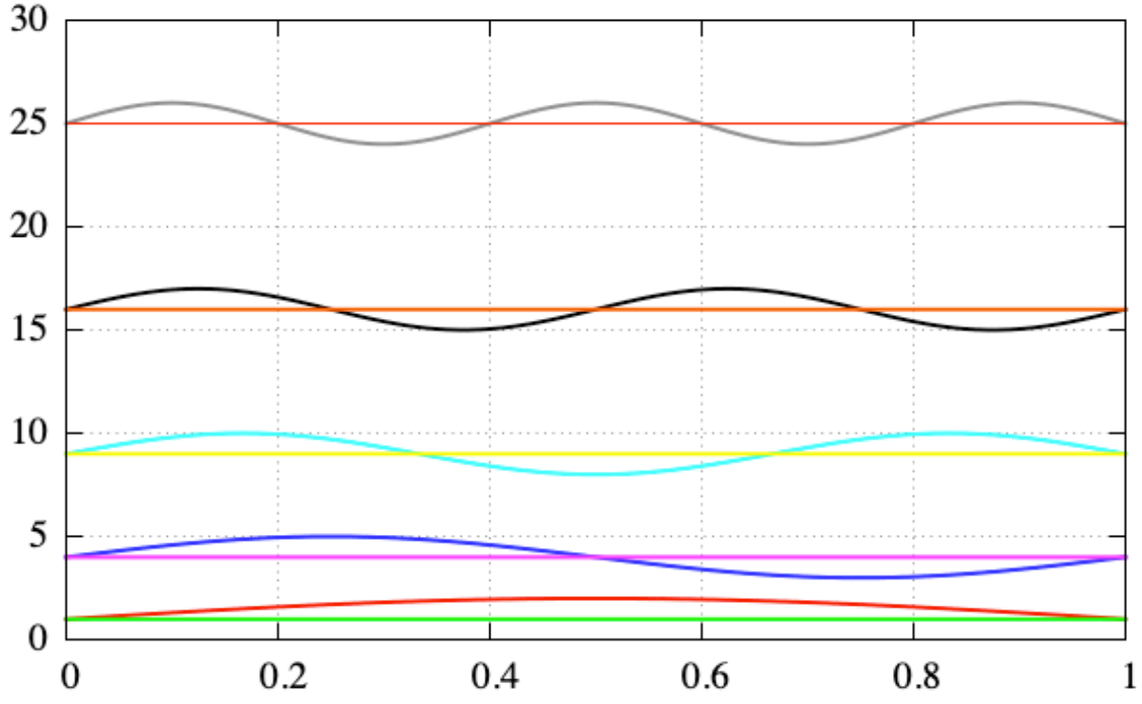
Review 1

For an infinitely tall square well of width w, and $V = 0$ at the bottom,

the energies are $E_n = n^2 \dfrac{\hbar^2 \pi^2}{2mw^2}$ for $n = 1, 2, 3, \ldots$

$= n^2 \dfrac{0.3759 \text{ eV-nm}^2}{w_{\text{nm}}^2}$ for electrons

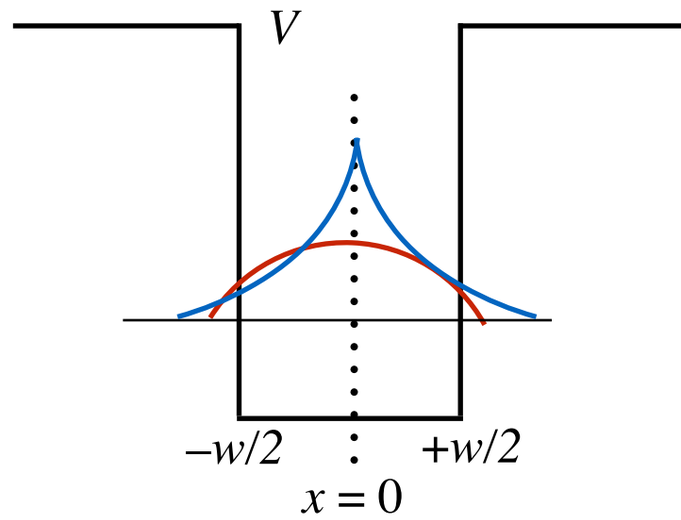
The normalized wavefunctions are $\psi(x) = \sqrt{\dfrac{2}{w}} \sin\left(\dfrac{n\pi}{w} x\right)$



Relative to the potential center at x = 0.5, the lowest wavefunction is even (symmetric), the second is odd, the third is even, the fourth is odd, etc…

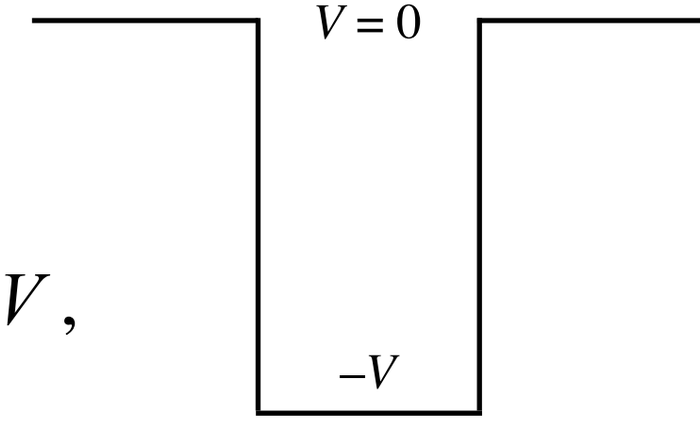
Review 2

For a well with <u>finite</u> height V,
the wavefunction penetrates a bit outside the well.



The energies are a bit lower than the infinite height case,
because the wavelength is a bit longer.

There are only a finite number of bound states, with $E < V$.
For $E > V$, there is a <u>continuum</u> of states.



For a finite square-well potential with $V = 0$ outside
and $-V$ inside, the bound states energies are $E_n \approx n^2 \dfrac{\hbar^2 \pi^2}{2mw^2} - V$,
a bit lower due to the penetration out of the well.

There are a finite number of bound states with negative energy.
There is a continuum of states with positive energy.

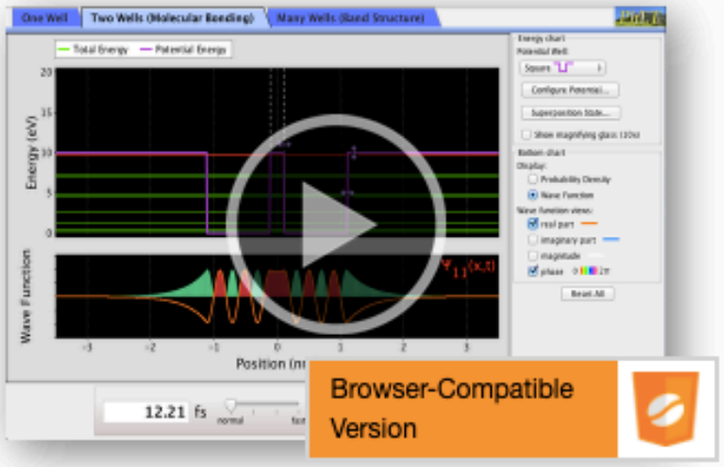
phet.colorado.edu/en/simulation/legacy/bound-states

Apps Google teaching curric amuse MathStudio Reading List

PhET INTERACTIVE SIMULATIONS | University of Colorado Boulder

SIMULATIONS TEACHING RESEARCH ACCESSIBILITY DONATE

Quantum Bound States



- Quantum Particles
- Potential Wells
- Waves

DONATE

PhET is supported by

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and educators like you.

Java via CheerpJ: We've partnered with Leaning Technologies to allow our Java sims to run in a browser.

This sim is not compatible with iPads.

System Requirements and Recommendations

Java Version: Supports offline use and offers improved performance.

JAVA VERSION

Two Ground States

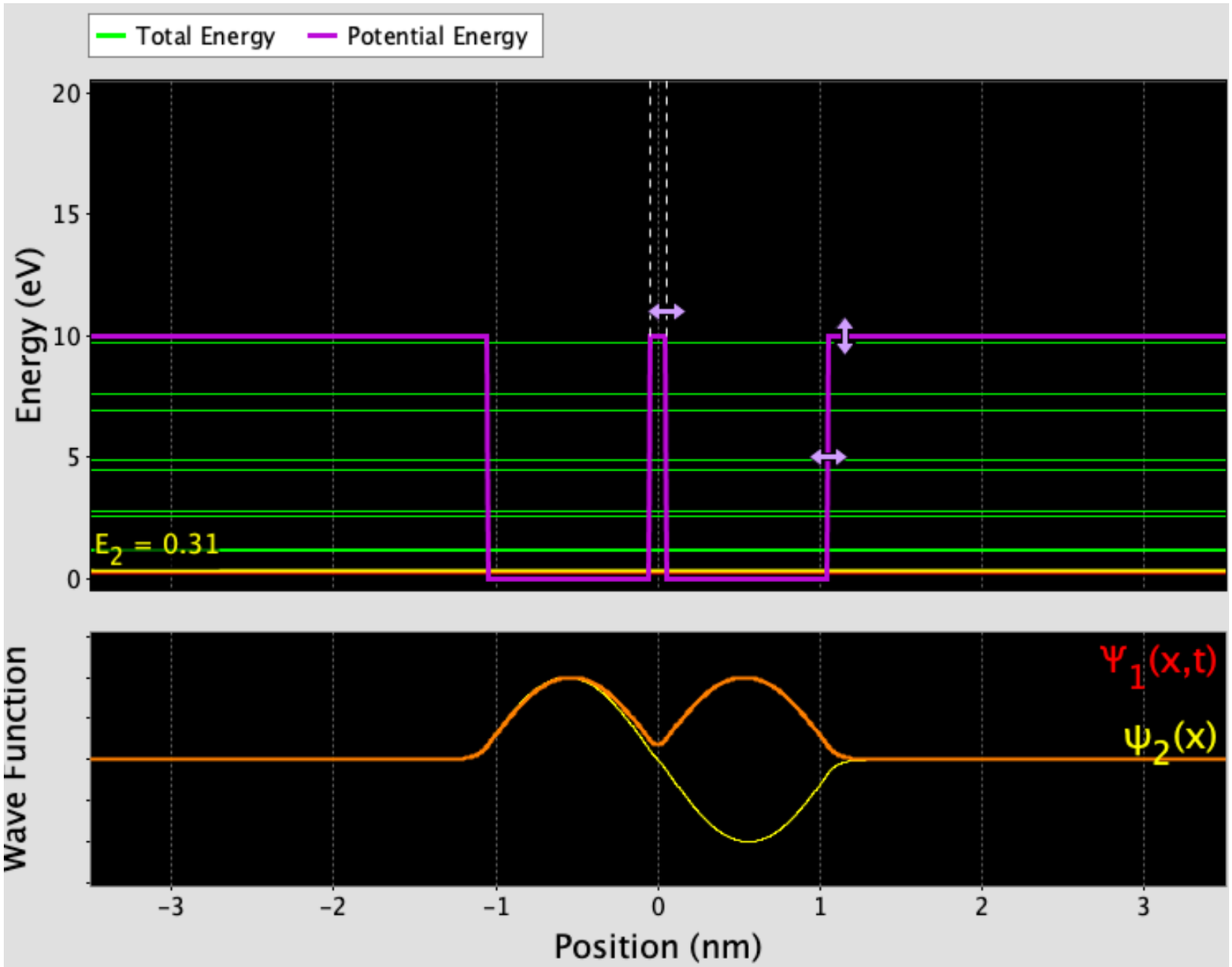
The ground state for a single well with the default dimensions is $E = 0.30$ eV.

With the default two wells, there are two "ground" states, with $E_1 = 0.29$ eV, and $E_2 = 0.31$ eV.

The potential is symmetric.

The "odd" state goes to zero at the middle, so it has a slightly shorter wavelength, so a slightly higher energy.

The "even" state has a slightly lower energy than the single-well ground state.



All the States Split in Two

(Amost) every state that would exist in the single well (6 in this case) splits into two states, one going down in energy, one going up.

(With the default potential settings, for the highest state, the one that goes up is no longer a bound state, it's a continuum state, and isn't shown).

All the wavefunctions are either even or odd.

The even state doesn't go to zero in the middle, so it has a longer wavelength, and a lower energy.

Single-Well Initial State

In "Superposition State" we can add ψ_1 and ψ_2, which gives an initial state that adds in the left well and cancels in the right well.

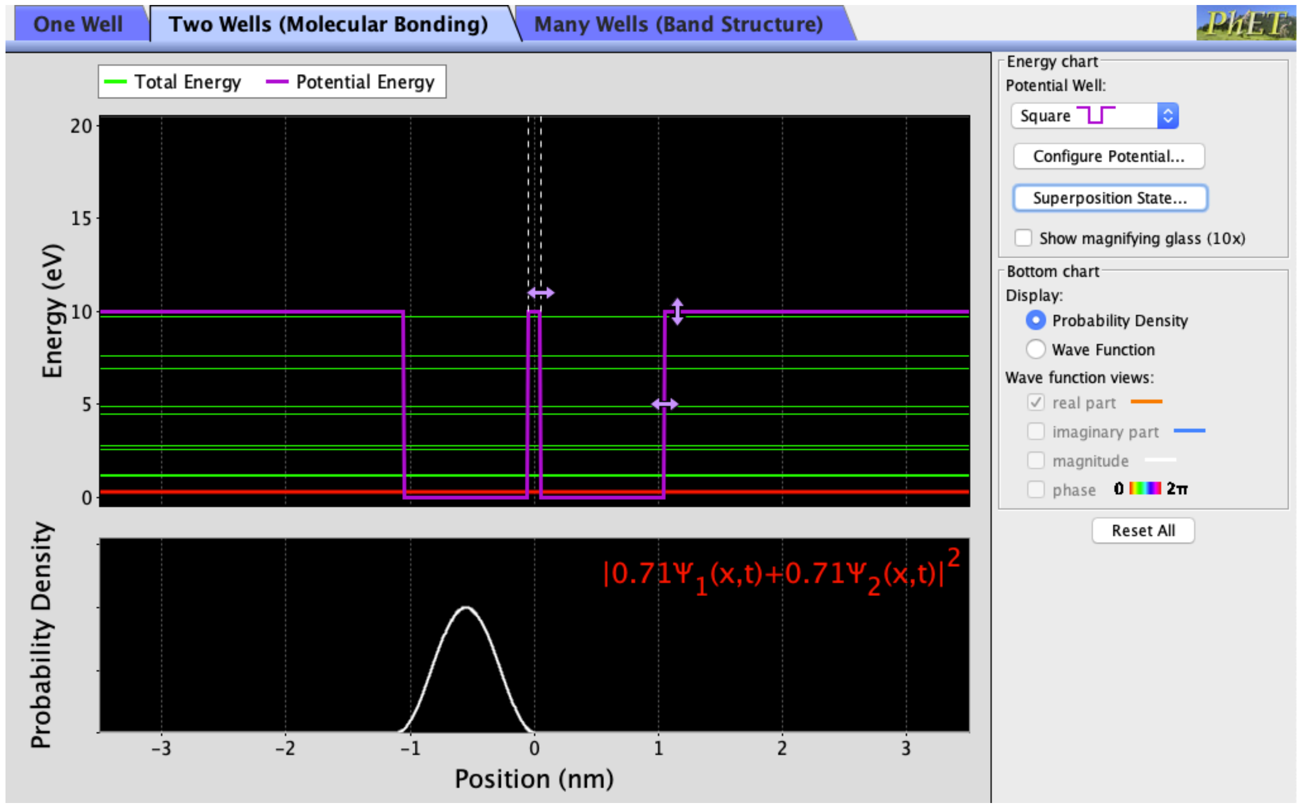
Switch from wavefunction to probability density, and turn on time-stepping.

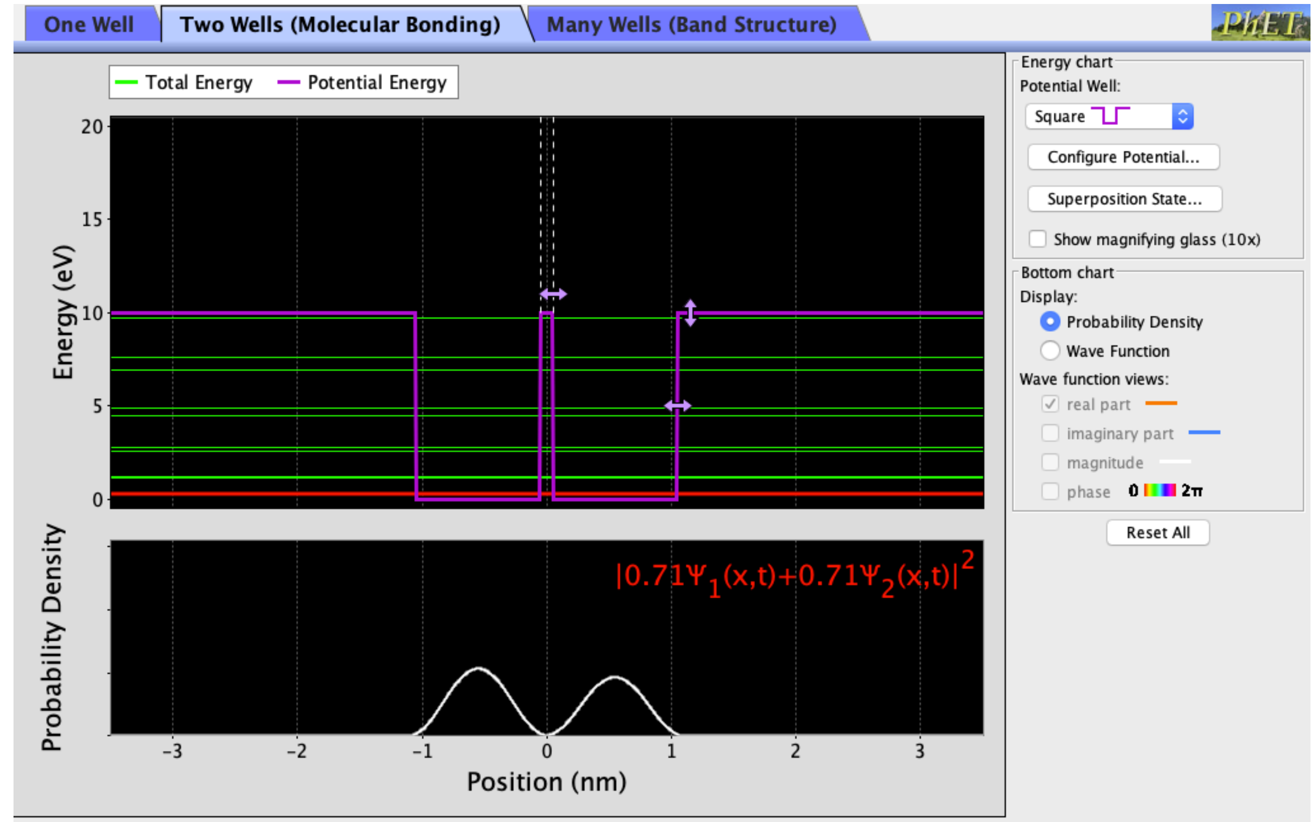
The probability tunnels from the left to the right, then tunnels back to the left.

ψ_1 and ψ_2 have slightly different energies, so they have slightly different frequencies. Initially they added on the left and cancelled on the right.

But after some time, they add on the right and cancel on the left.

After more time, they go back to adding on the right and cancelling on the left.


One Well
Two Wells (Molecular Bonding)
Many Wells (Band Structure)
PhET
Total Energy
Potential Energy
Energy (eV)
20
15
10
5
0
Probability Density
|0.71Ψ1(x,t)+0.71Ψ2(x,t)|2
-3
-2
-1
0
1
2
3
Position (nm)
Energy chart
Potential Well:
Square
Configure Potential...
Superposition State...
Show magnifying glass (10x)
Bottom chart
Display:
Probability Density
Wave Function
Wave function views:
real part
imaginary part
magnitude
phase
0
2π
Reset All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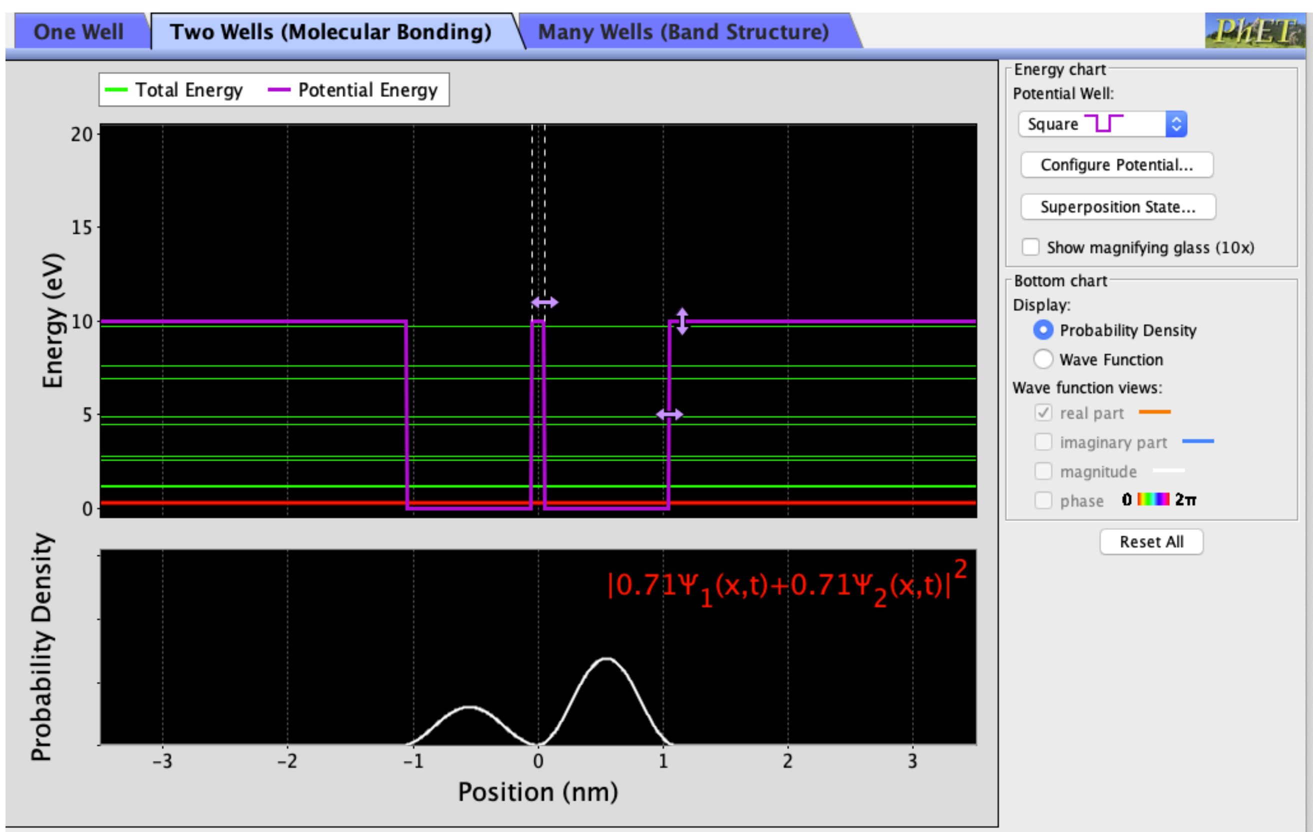
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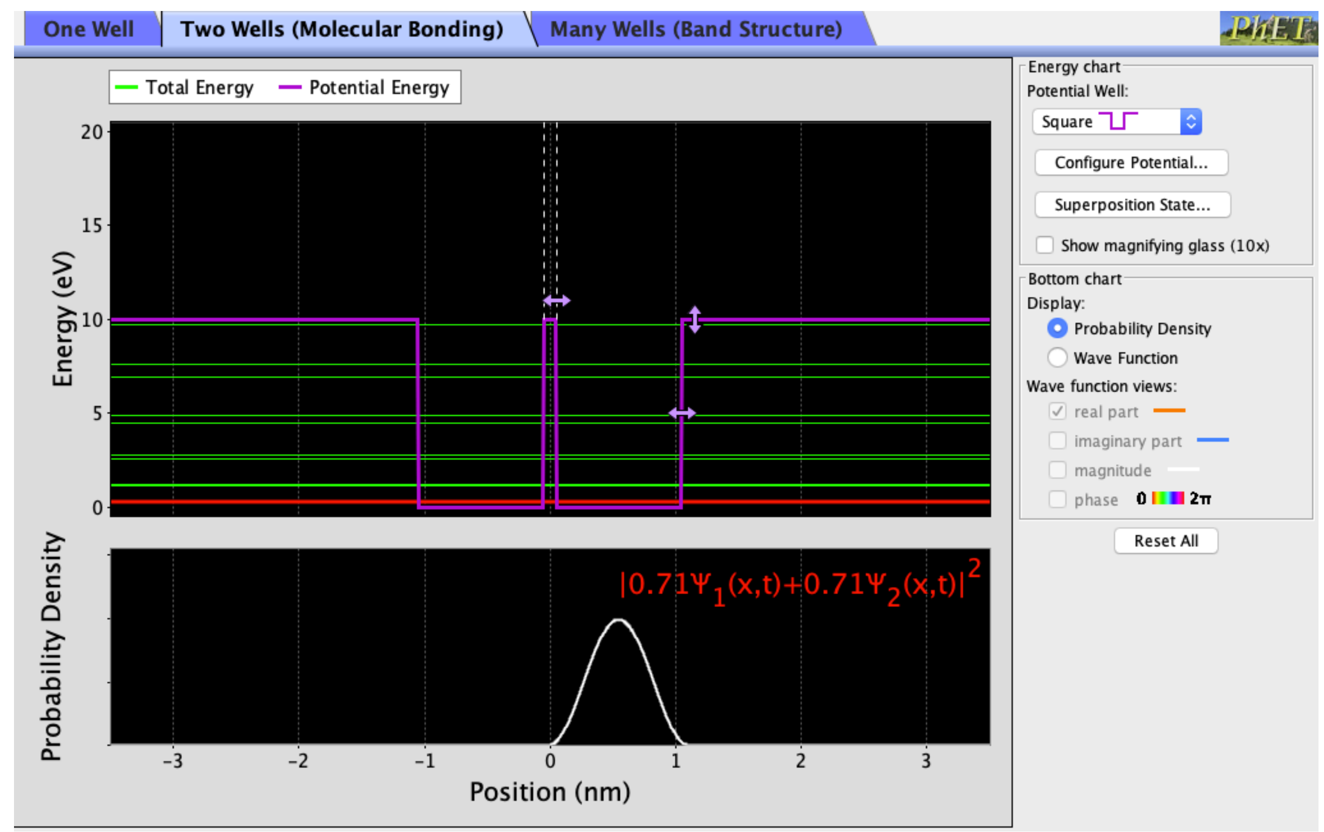
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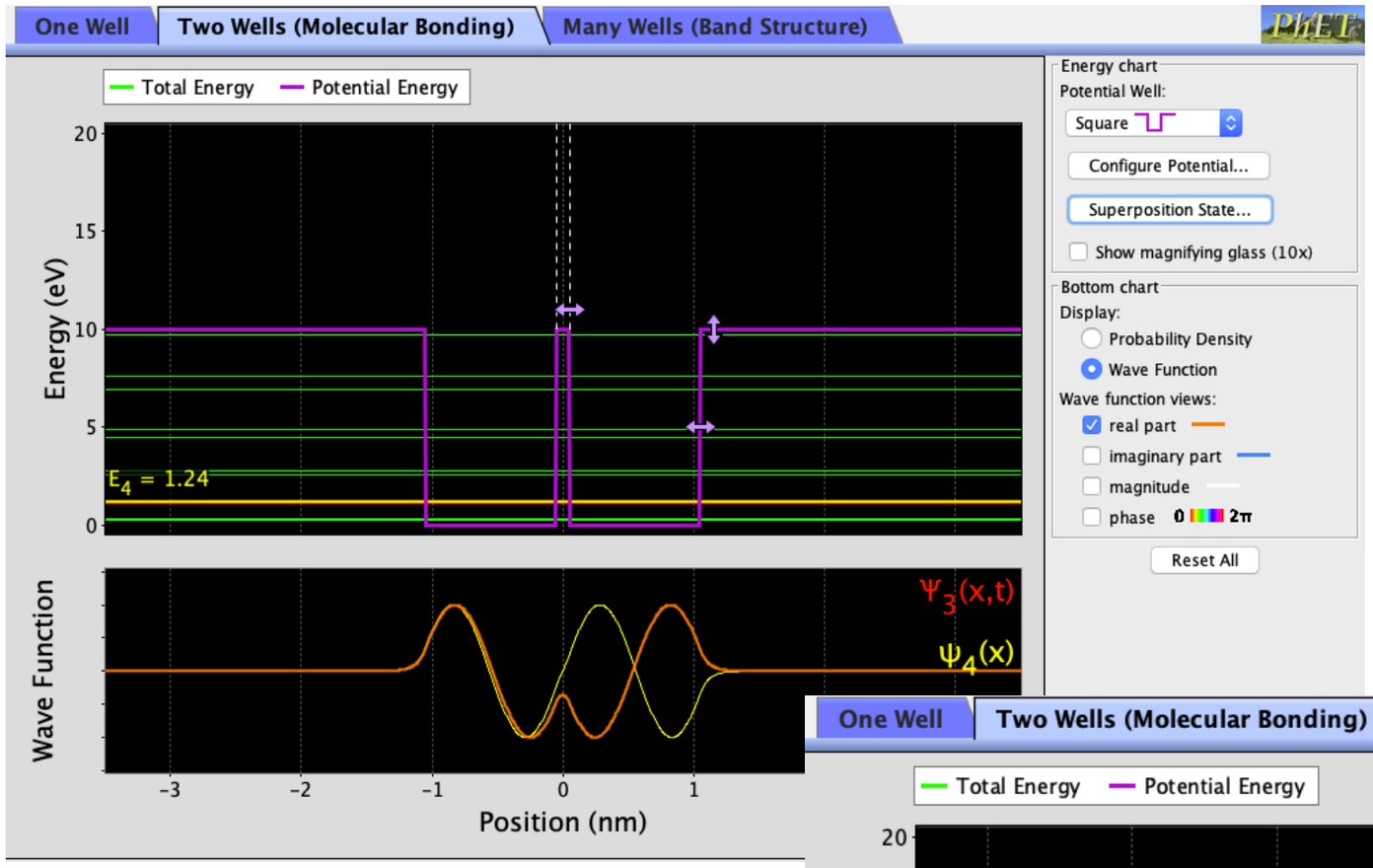
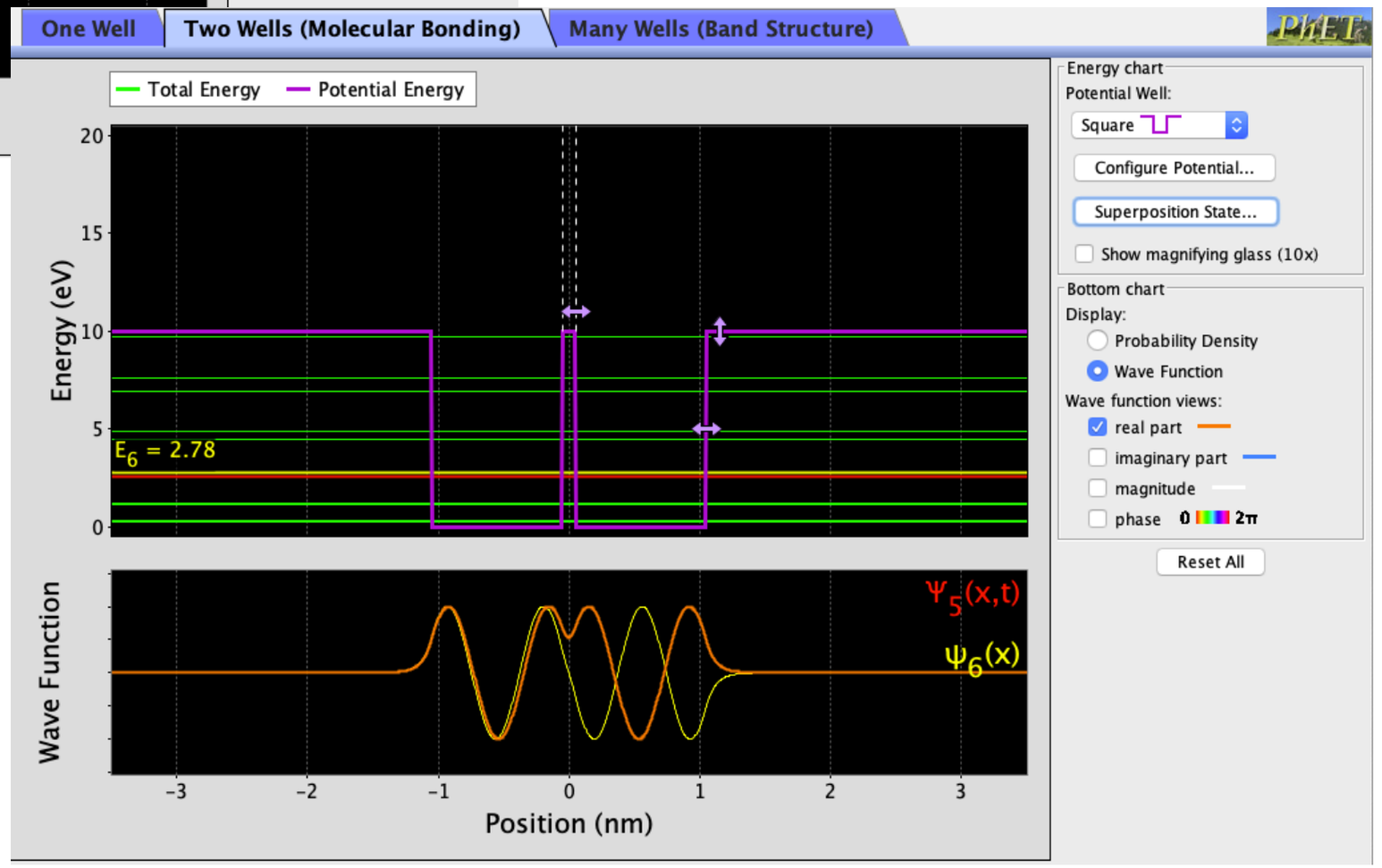
Higher States





Chemical Bonds 1

If the separation of the two wells is large enough, the tunnelling is insignificant.

Technically, each level still splits into even and odd wavefunctions,
but the energy differences are insignificant.

But the closer together the wells are, the bigger the splitting gets.

So if there is an electron in the state that goes down in energy,
the total energy goes down as the wells get closer.

This is the quantum mechanical basis of chemical bonds,
although greatly over-simplified.

Chemical Bonds 2

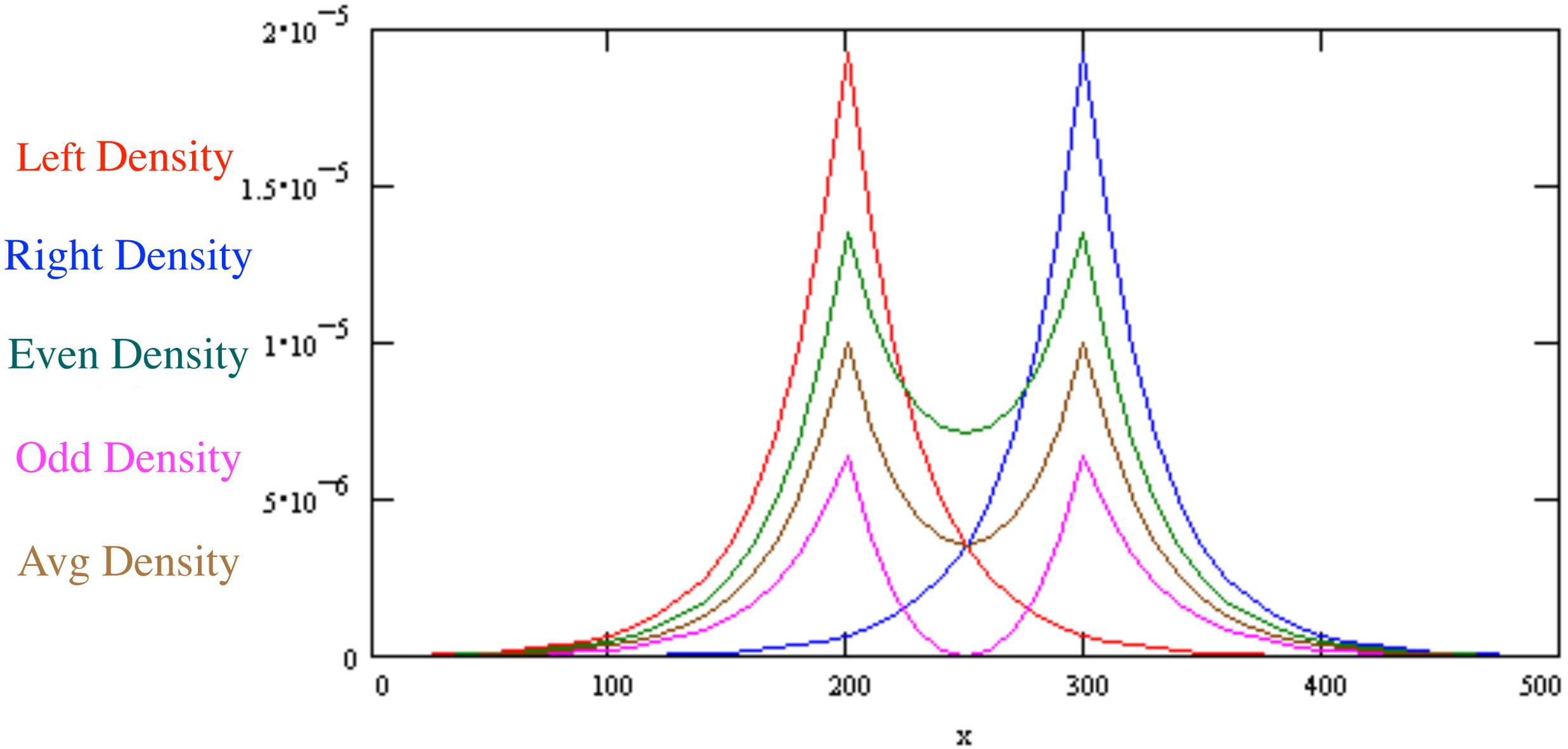
The simplest real case is two hydrogen nuclei (protons) and one electron.

If the protons are far apart, we normally think of the electron being attached to one proton, and the other proton is naked.

But in quantum mechanics, we should think of the even wavefunction, where the electron is attached to both protons with the same sign, and the odd wavefunction where it's attached to both with opposite signs.

The sum of even and odd has the electron on one proton, the difference has the electron on the other.

Chemical Bonds 3



The “even” wavefunction has the highest probability of finding the electron between the protons, which allows it to pull them closer together.

The “odd” wavefunction has the lowest probability of finding the electron between the protons, so the attraction is less (but still non-zero).

Chemical Bonds 4

If the protons were closer together, the electron density between them would get even greater, resulting in more attraction.

But the protons still repel each other, so there would be an equilibrium separation where the energy would be minimized. That sets the bond length.

What about the more common case of <u>both</u> protons having an electron?

Then both electrons can be in the "even" state, attached to both protons, and give stronger attraction. But they have to have their "spins" pointed in opposite directions (Pauli Exclusion Principle).

Why can't 3 hydrogen atoms bond? There is more electrostatic repulsion between the protons, and Pauli would require that the third electron go into the "odd" state, where it can't help much in holding the protons together. So the third atom apparently doesn't stick.

Three Potential Wells

Let the left well always have a positive bump, since the overall sign of a wavefunction is irrelevant.

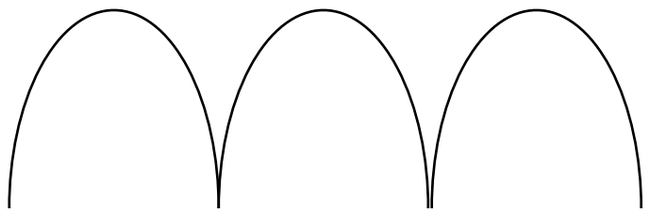
The second well could have either sign of bump.
The third well could have either sign of bump.
So it sounds like there are 4 basic “shapes.”

But if the potential is symmetric, so the wavefunction be either even or odd, and not all the shapes satisfy that.

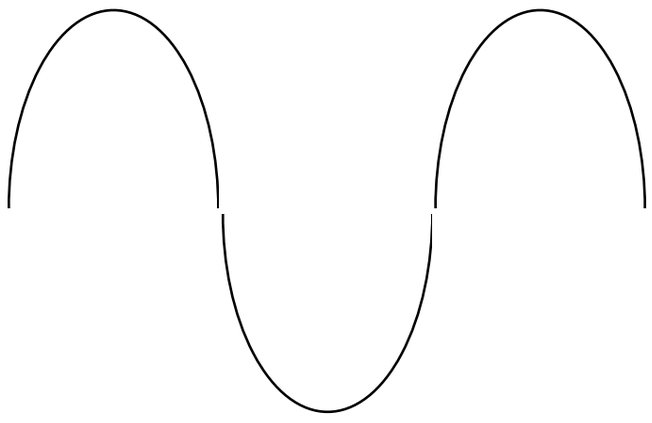
Two are symmetric (even).

The other two are not, but if we add them, we can make a symmetric (odd) state.

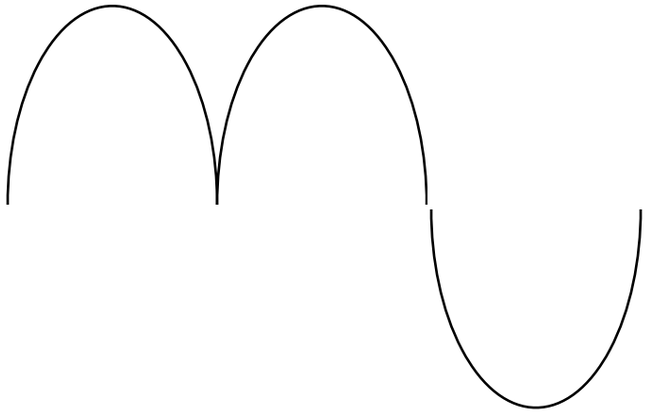
Three Potential Wells 2



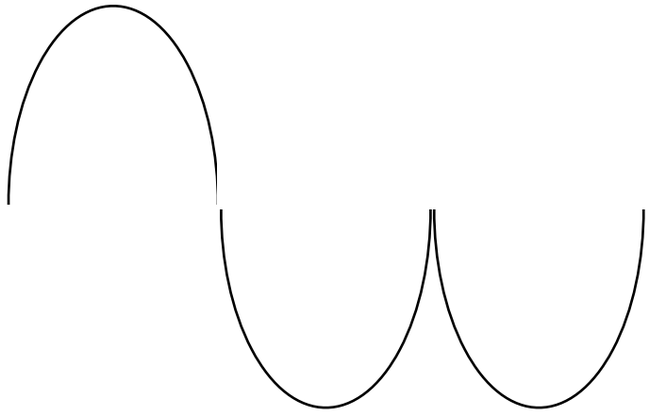
Even



Even



Not Symmetric



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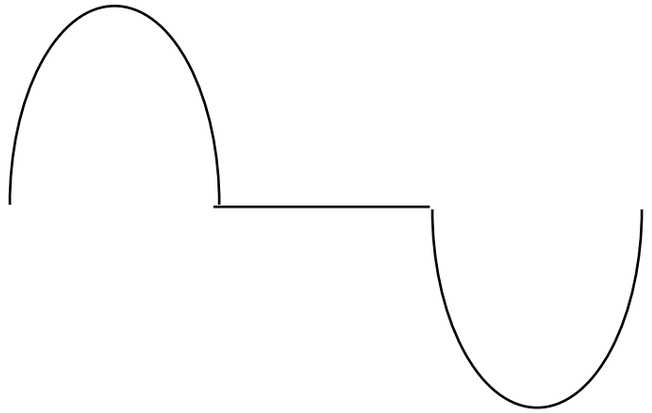
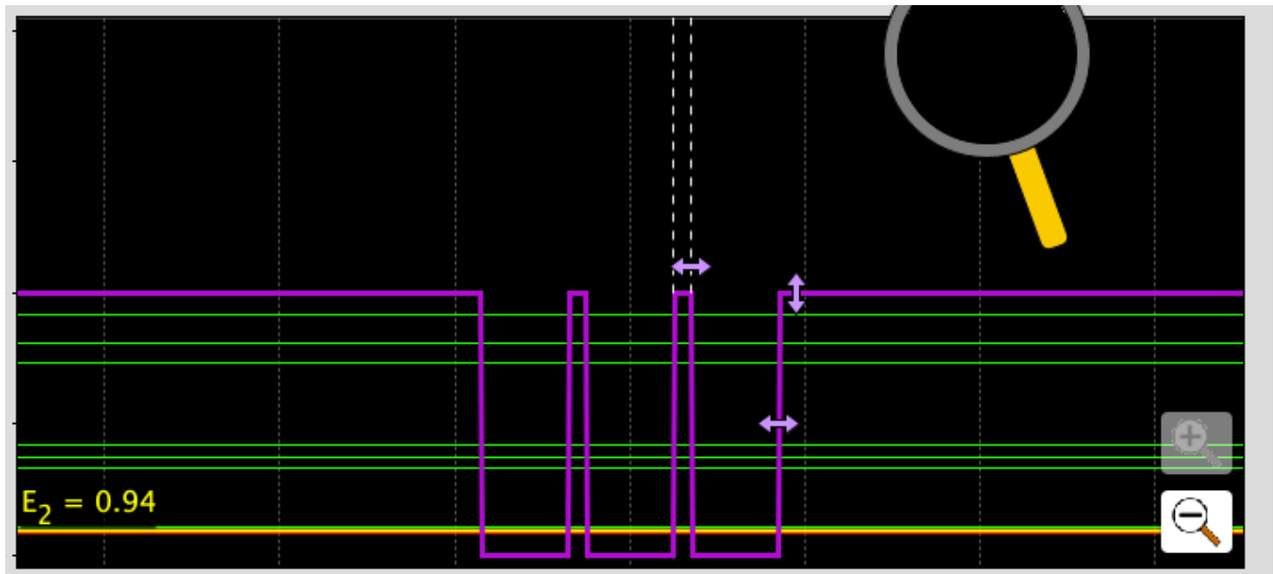
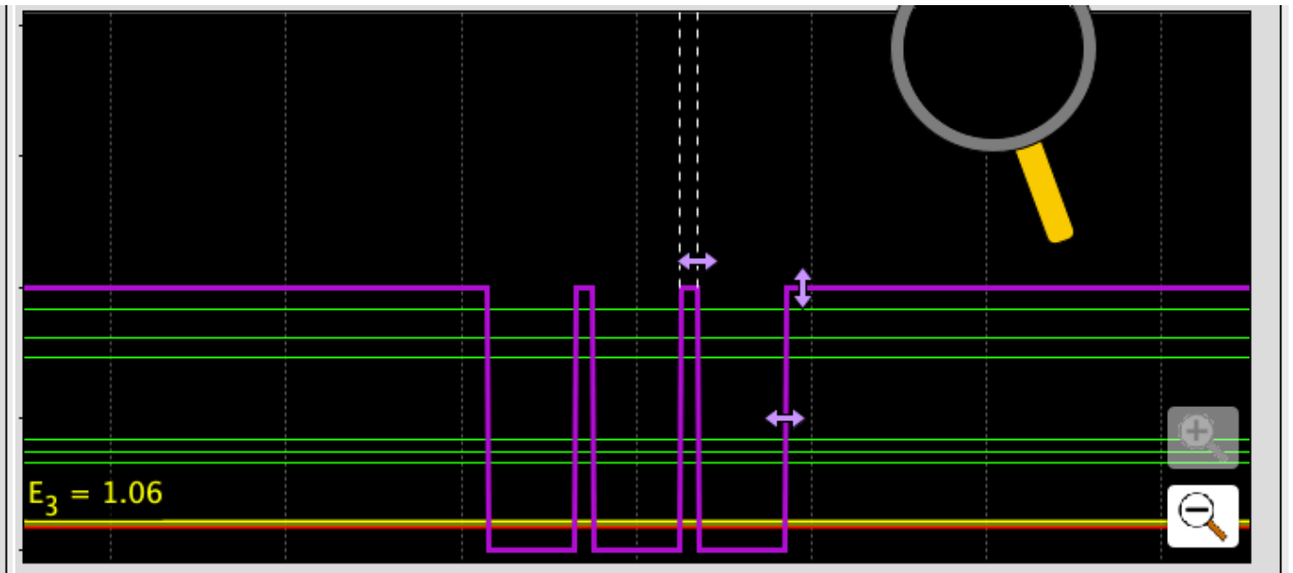


Sum = Odd
Probably looks like this

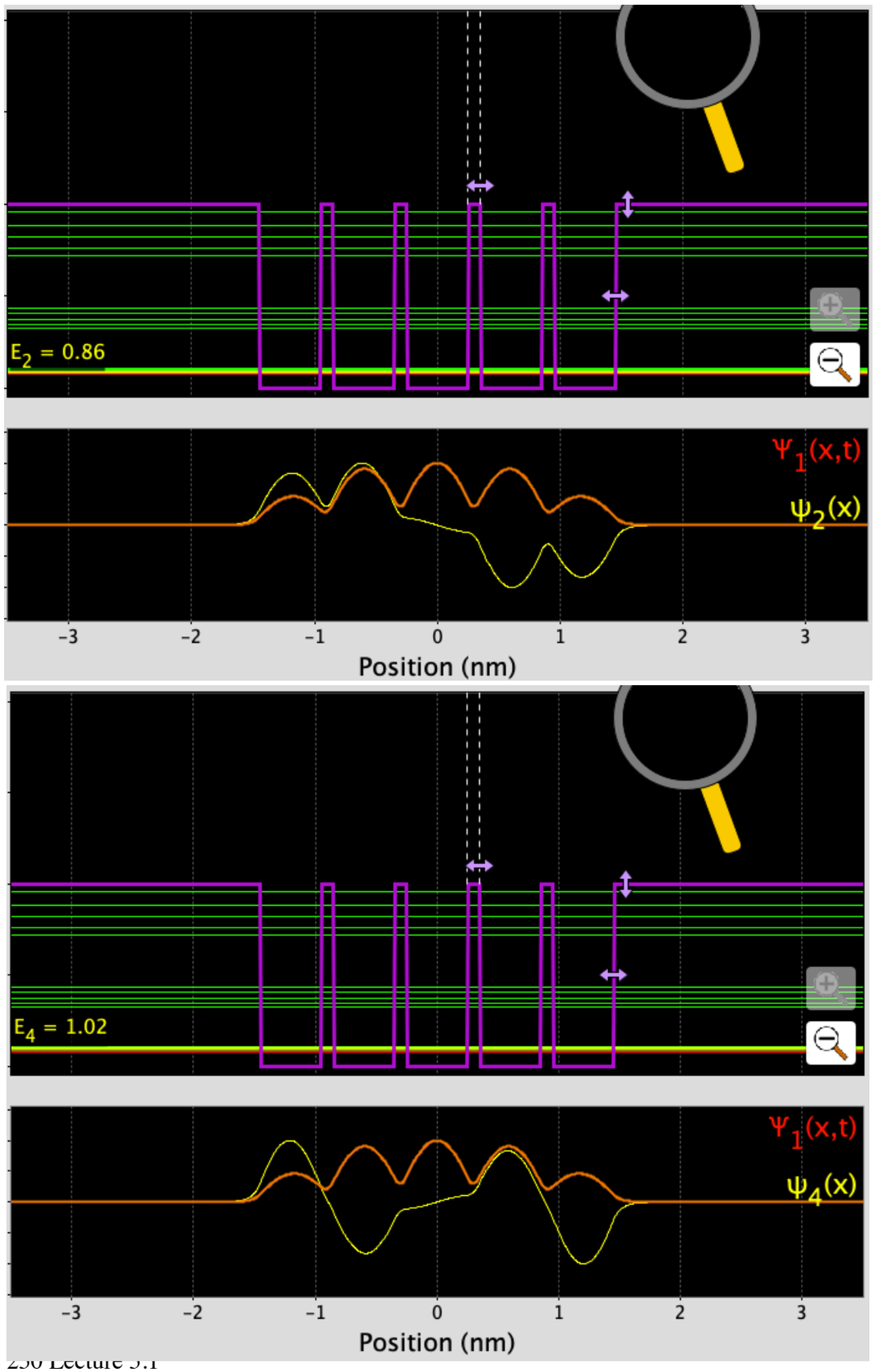
Three Potential Wells 3

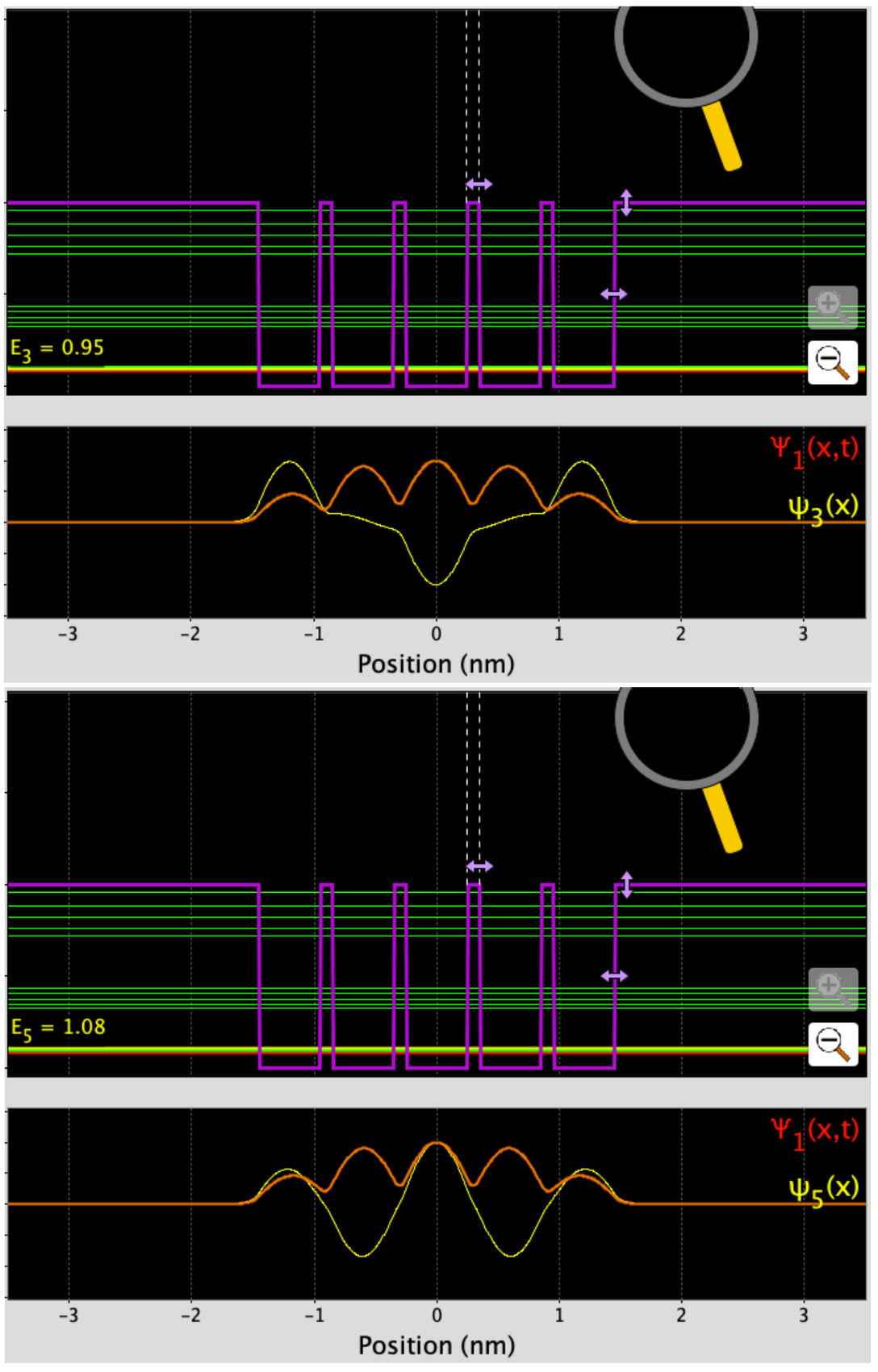




The lowest state is even, with no zero crossings and the longest wavelength. The odd state is higher energy. The other even state is the highest energy, with the shortest wavelength.

Five Potential Wells





N Potential Wells

In general, if there are N potential wells, each energy level splits into N closely-spaced energy level.

The amount of splitting depends on how close together the wells are, and the height of the barriers between them.

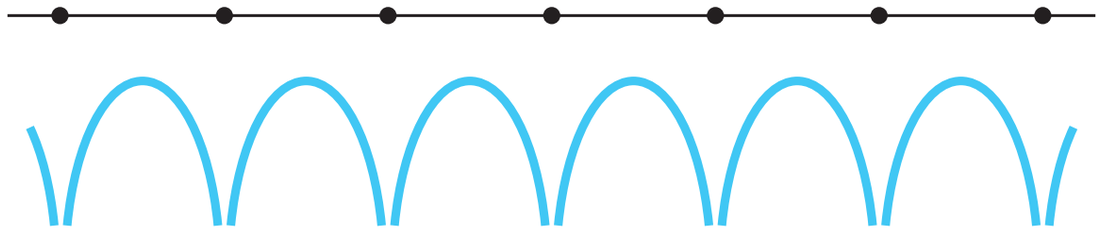
The lowest of the split levels is even, with no zero-crossings in the wavefunction, and is lower than the corresponding energy level of a single well.

Some other levels may be lower than a single well. Others will be higher.

Periodic Potential

An infinite number of identical potential wells is called a periodic potential.

A crystal of identical atoms would make a periodic potential for electrons.



Bloch Theorem: The Schrodinger solution for a periodic potential has the form $\psi(x) = u_K(x) \cdot e^{iKx}$, where $u_K(x)$ has the same period as the potential.

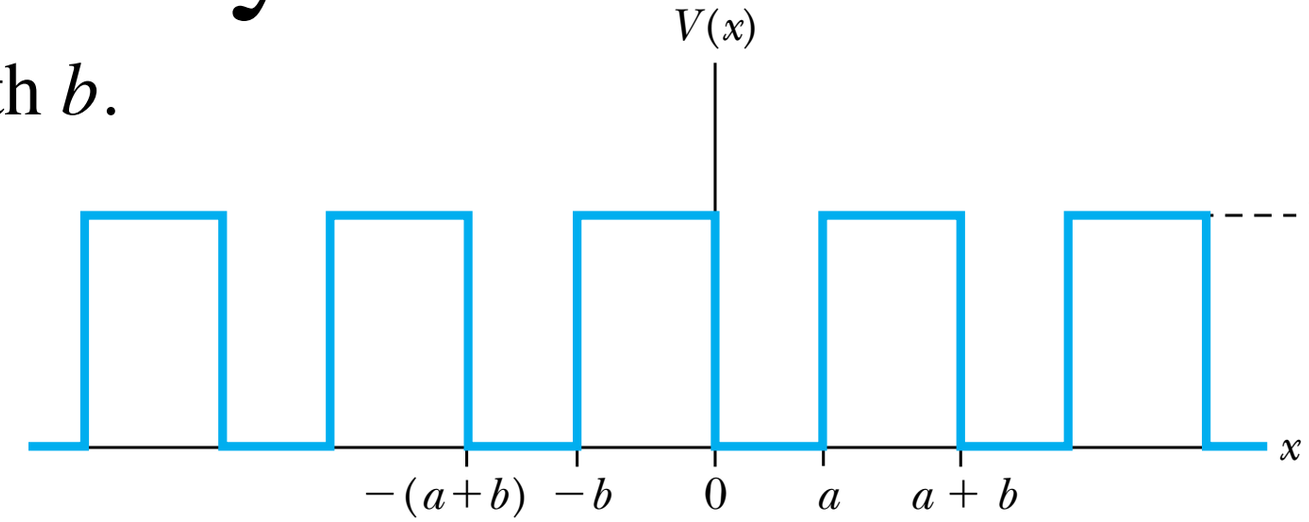
The e^{iKx} factor is a phase-shift with magnitude 1. So this says that the wavefunction has the same shape at each atom, but with a complex phase-shift.

There is a different $u_K(x)$ for each K, and they aren't easy to solve for.

Every K-value corresponds to an electron energy.

Kronig-Penney Model

$V = 0$ for length a, and $V = V_0$ for length b.



For the a zones, $\psi(x) = Ae^{ikx} + Be^{-ikx}$

with $k = \sqrt{2mE}/\hbar$.

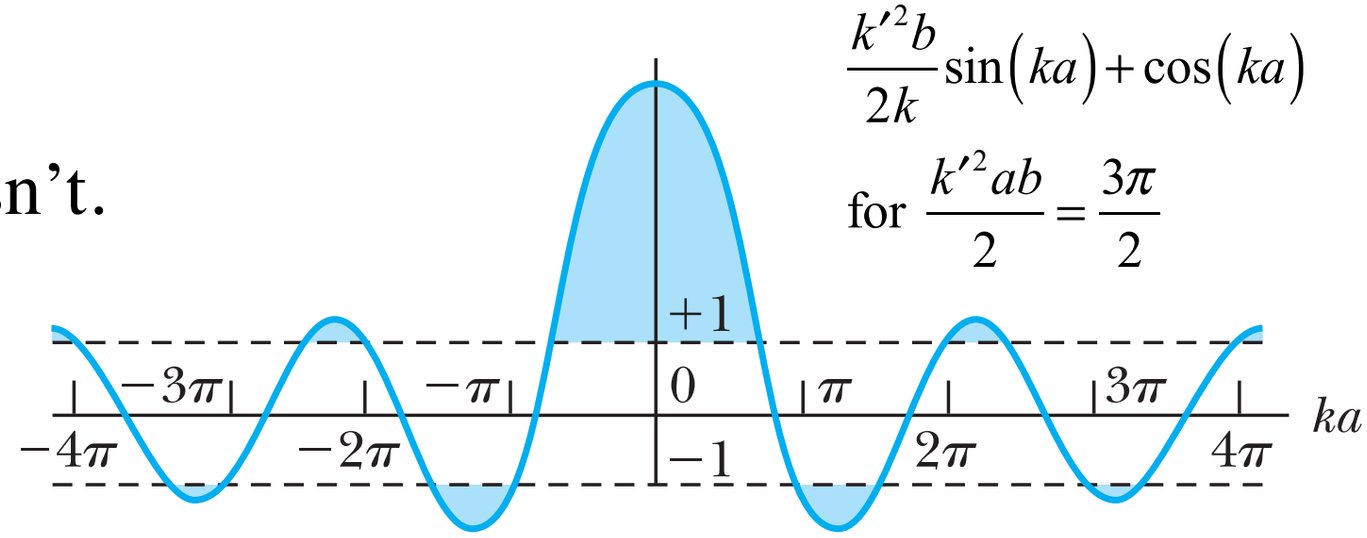
For the b zones, $\psi(x) = Ce^{+k'x} + De^{-k'x}$ with $k' = \sqrt{2m \cdot (V_0 - E)}/\hbar$.

Boundary conditions give $\frac{k'^2 b}{2k}\sin(ka) + \cos(ka) = \cos(Ka)$

where K is the Bloch-Theorem wavenumber.

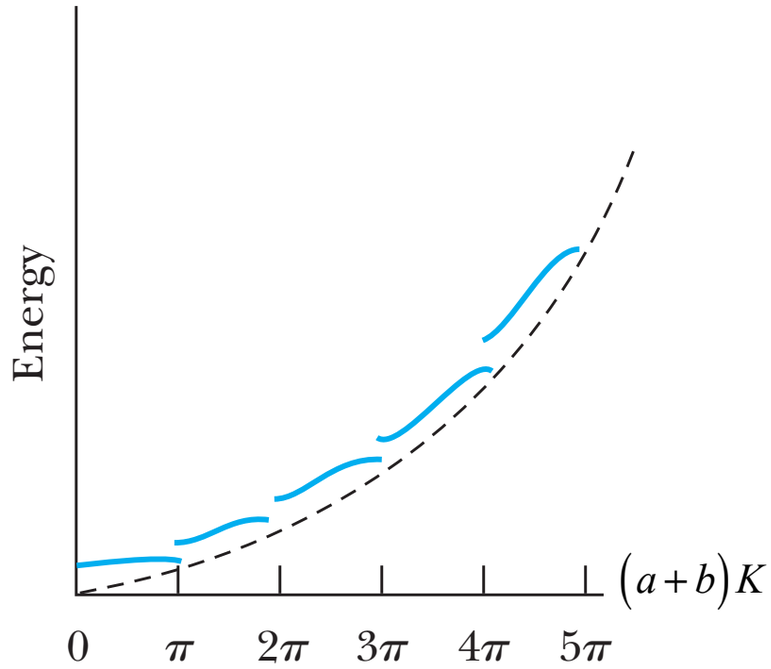
The right side is limited to –1 to +1,
but for some k-values, the left side isn't.

So some E-values are not allowed!



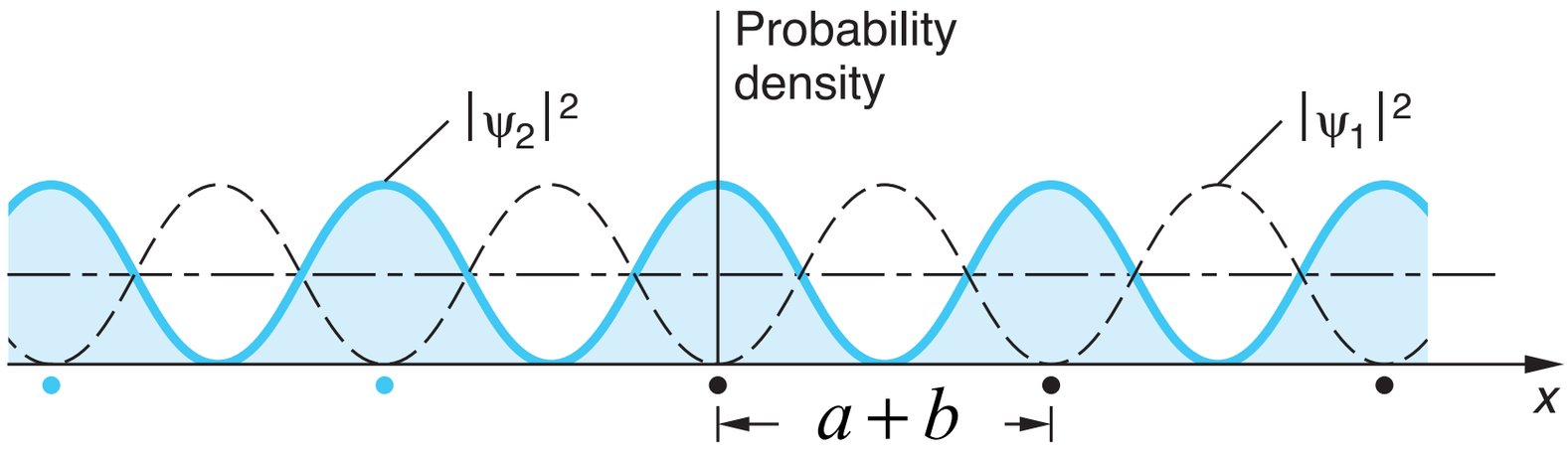
Kronig-Penney Model 2

If we plot the energy $E = \dfrac{\hbar^2 k^2}{2m}$ versus $a + b$ times Bloch-Theorem K, we find that the energy is roughly parabolic, but there are jumps in the energy whenever $(a+b)\cdot K = n\pi$.



At those values, the period of the wavefunction (including the phase) matches the period of the potential.

One solution has maxima of the conjugate-square at the low-potential points, and the other has maxima at the high-potential points.

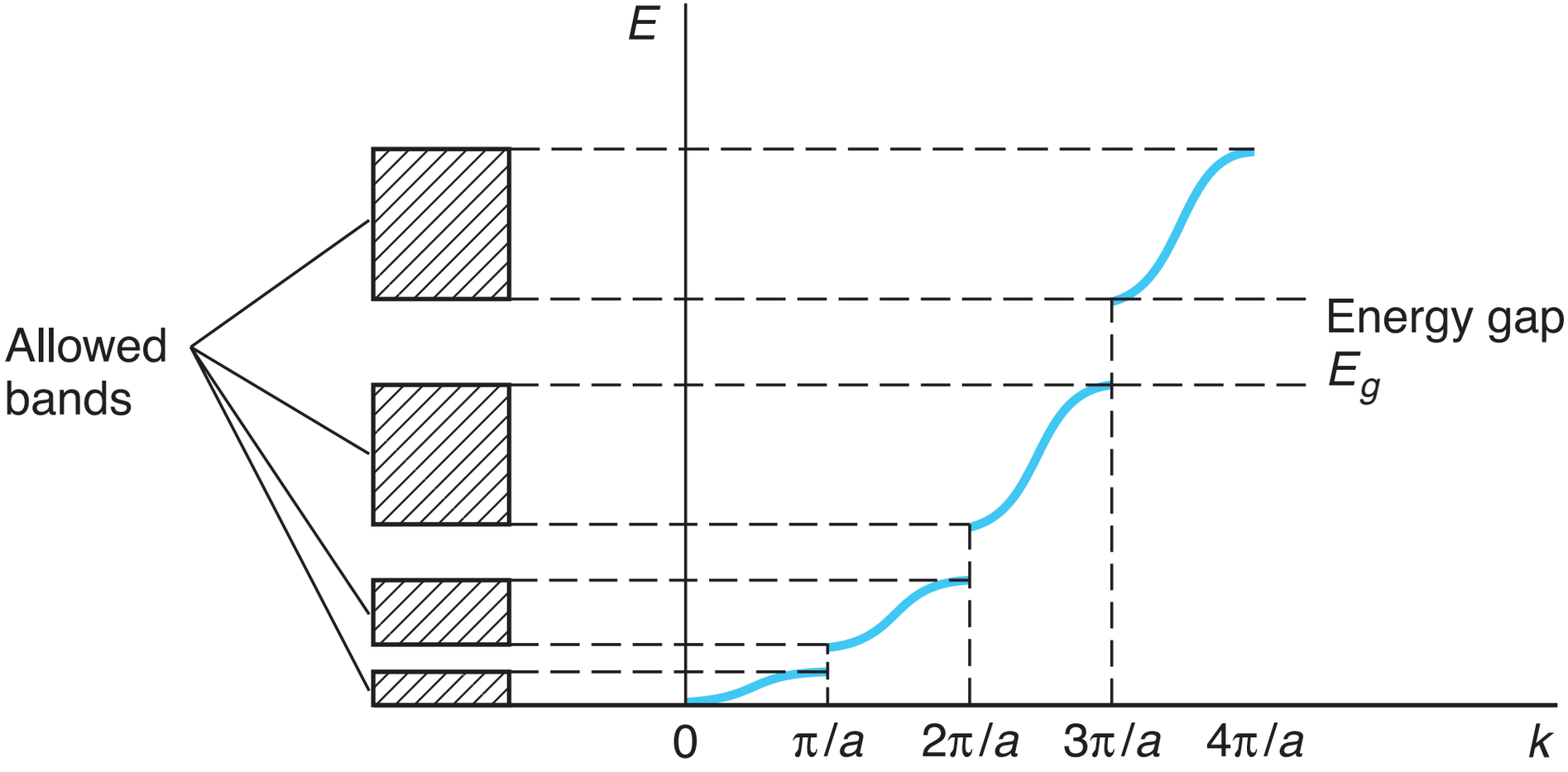


Energy Bands

For <u>any</u> periodic potential, a particle that would be bound in an isolated well with <u>discrete</u> energies, can "tunnel" from well to well with a <u>range</u> of energies.

Any value of the Bloch Theorem K is allowed. And the energy E is roughly parabolic in K. But the there are gaps in the E vs K relation.

The allowed energy ranges are called <u>energy bands</u>.



Level Splitting in Crystals

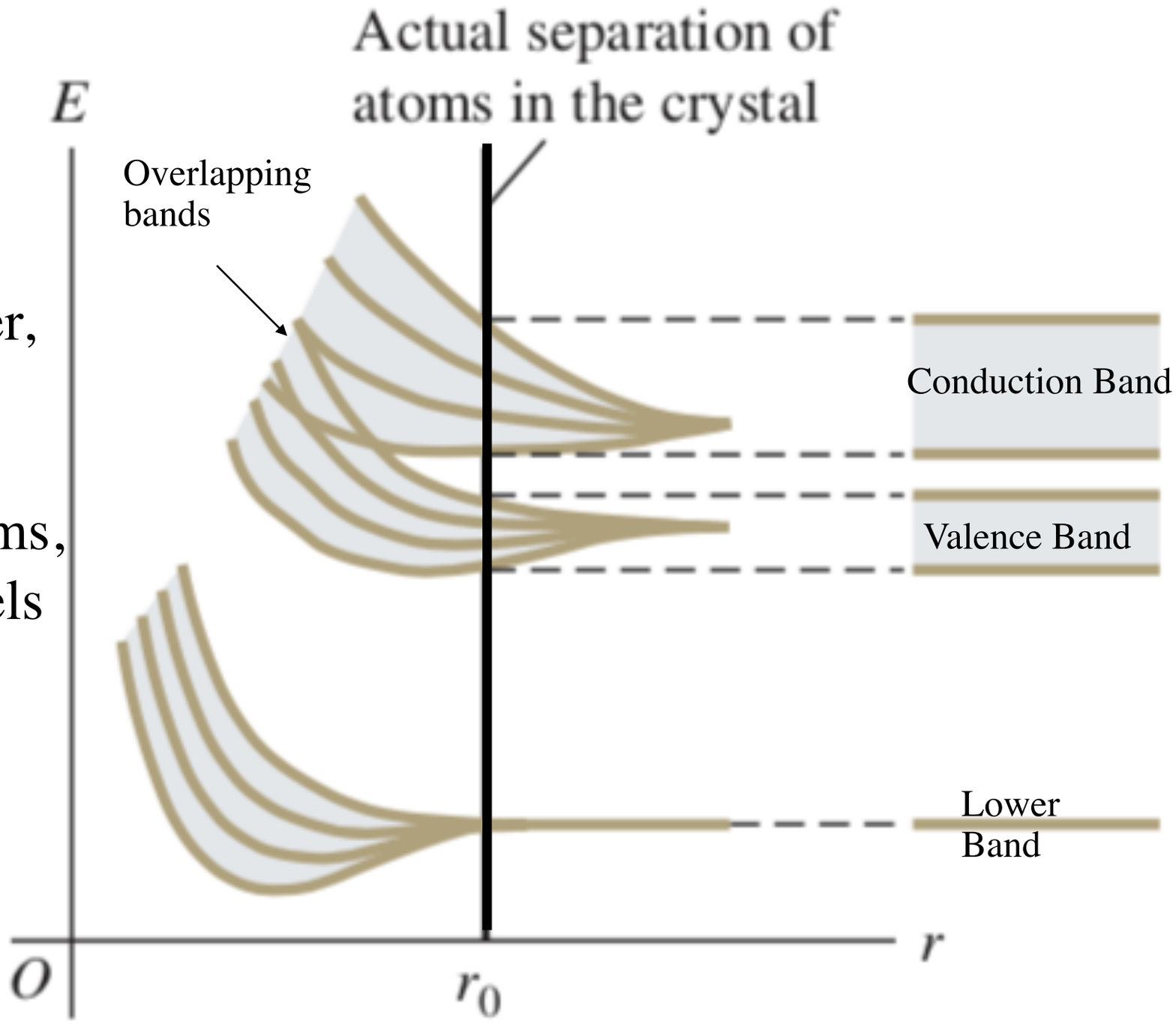
If crystal atoms were far apart, they would have the usual Schrodinger Equation levels, the same for each atom.

As we move the N atoms closer, the levels split more and more.

At the actual separation of atoms, there are N closely spaced levels split from the original levels.

There can be energy gaps between different bands.

Or the splitting can be so large that the bands overlap.



Pauli Principle and Conductivity

If we have N atoms, each level splits into N states.

The Pauli Exclusion Principle says there can be only 2 electrons per state.

The first 2N electrons go into the lowest band of N states.
The next 2N electrons go into the next band of N states.
This continues until we have assigned all the electrons.

If a band is not full, there are un-occupied states that electrons can use to move.
That gives us conductivity.

If a band is fully occupied, there are no empty states for electrons to move into.
So full bands don't conduct.

If a band is completely empty, there are no electrons to move.
So that doesn't conduct either.

Conductivity in Metals

Sodium (Z = 11) has a single electron in the 3s level $\left(\ell = 0, n = 3\right)$.

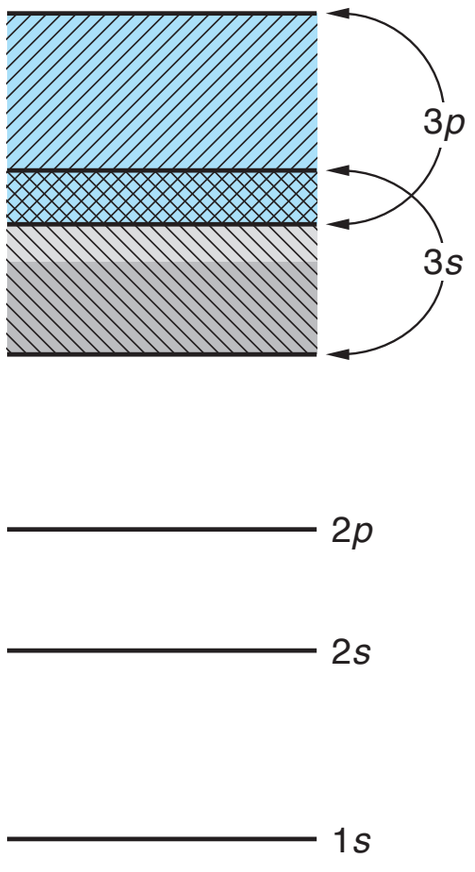
For a crystal of N Sodium atoms, there are N electrons in the split 3s level.
But the level could accommodate 2N electrons. So the band is only half full.
So Sodium is a good conductor.

Magnesium (Z = 12) has two electrons in the 3s level. So the band will be full.
But Magnesium is <u>also</u> a good conductor. How does that happen?

The 3p energy levels still exist in Mangesium,
they are just empty in isolated atoms.

But the splitting of the 3s and 3p levels in a Magnesium <u>crystal</u>
causes them to overlap. So Magnesium is also a conductor.

For nearly every element that can crystallize, the bands overlap
so they are conducting metals.



Insulators

If Sodium loses an electron, the remaining ones form a “closed shell” that has the electron structure of Neon (although with a positive charge).

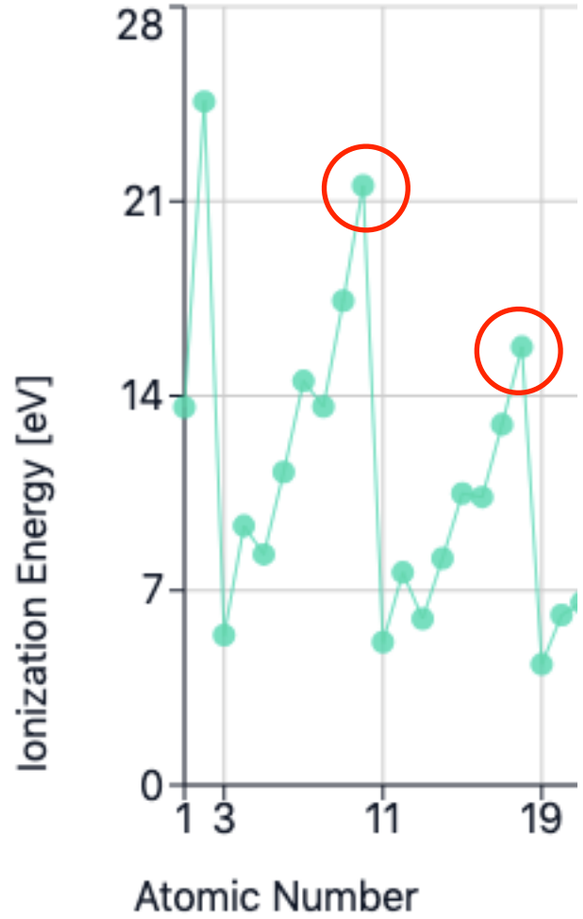
If Chlorine gains an electron, its outer electrons form a “closed shell” that has the electron structure of Argon (although with a negative charge).

The atoms can arrange themselves into a crystal of NaCl (table salt).

The highest occupied energy band is completely full, so NaCl is an insulator.

There are unoccupied levels, but they correspond to ionizing Neon or Argon. And they have very high ionization energies.

So there is a large energy gap to the higher states, and very few electrons are thermally excited into them.

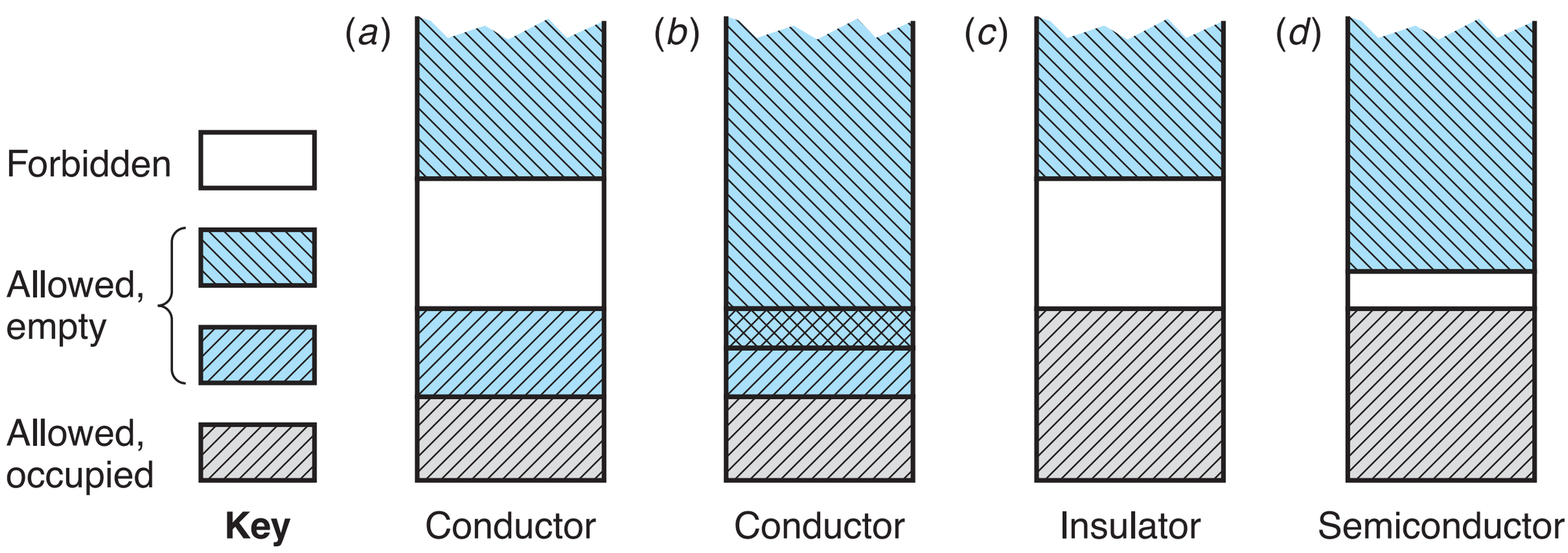


Conductor, Insulator, Semiconductor

A conductor has either (a) a half-filled energy band, or (b) overlapping bands.

An insulator has (c) a large energy gap between the highest filled band and the lowest empty band. There are negligible thermally excited carriers.

A semi-conductor has (d) a small energy gap between a full and empty band. A semi-conductor is an insulator, but with a few thermally excited carriers.



Level Splitting in Semiconductors

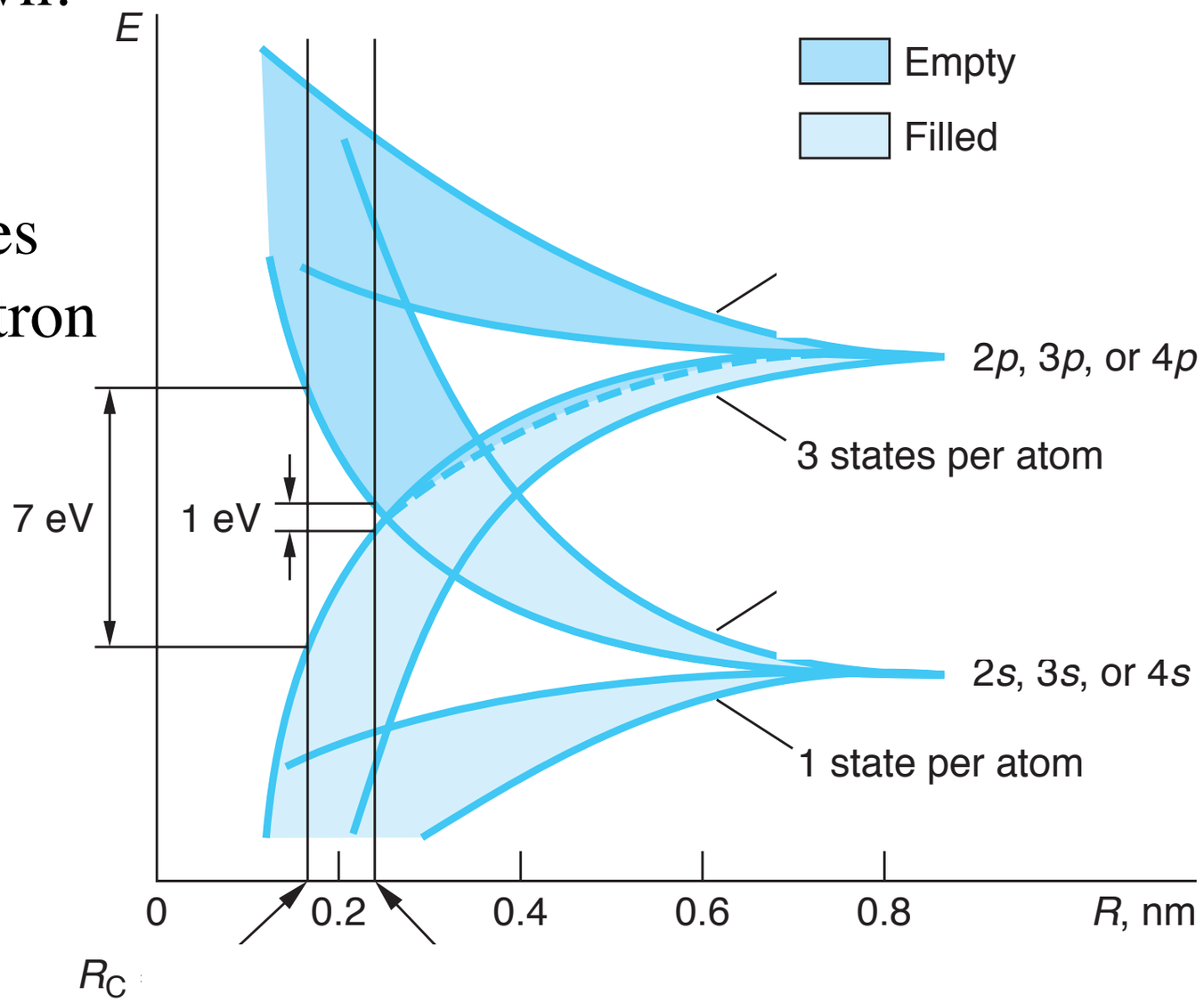
Carbon, Silicon, and Germanium have 4 electrons in their outer shells.

When the atoms are brought close,
half the levels go up, and half go down.

At the actual separation in a crystal,
three electrons are in the three *p*-states
that go down in energy, and one electron
is in the *s*-state that goes down.

The *s*-state that goes up in energy
is slightly higher than the three
p-states that go down.

The band-gap is 7 eV in Carbon
(because the atoms are small),
but about 1 eV in Silicon and Germanium.



Semiconductor Band Gaps

Silicon is the most common semiconductor, with band gap of 1.1 eV.

A lot of early devices used Germanium (because people hadn't learned how to purify silicon yet) with bandgap of 0.7 eV.

Compounds of a column 3 element with a column 5 element are also semiconductors.

They can have much lower band gaps, or much higher band gaps, than silicon.

Table 11.2 Energy Gaps for Selected Semiconductor Materials at $T = 0$ K and $T = 300$ K

	E_g (eV)	
Material	$T = 0$ K	$T = 300$ K
Si	1.17	1.11
Ge	0.74	0.66
InSb	0.23	0.17
InAs	0.43	0.36
InP	1.42	1.27
GaP	2.32	2.25
GaAs	1.52	1.43
GaSb	0.81	0.68
CdSe	1.84	1.74
CdTe	1.61	1.44
ZnO	3.44	3.2
ZnS	3.91	3.6

Conductivity in Semiconductors

The highest occupied band is called the valence band,
and the lowest un-occupied band is called the conduction band.

In a (pure) semiconductor (and an insulator), the valence band is full,
and the conduction band is empty, except a few thermally excited electrons.

If an electron somehow gets into the conduction band, it can tunnel
from atom to atom, and there is conductivity.

If an electron is somehow missing from the valence band, that is called a hole.

An electron from a neighboring atom can tunnel across and fill the hole.
But that leaves a hole at the neighbor atom.

An electron can tunnel across from the next neighbor and fill that hole.

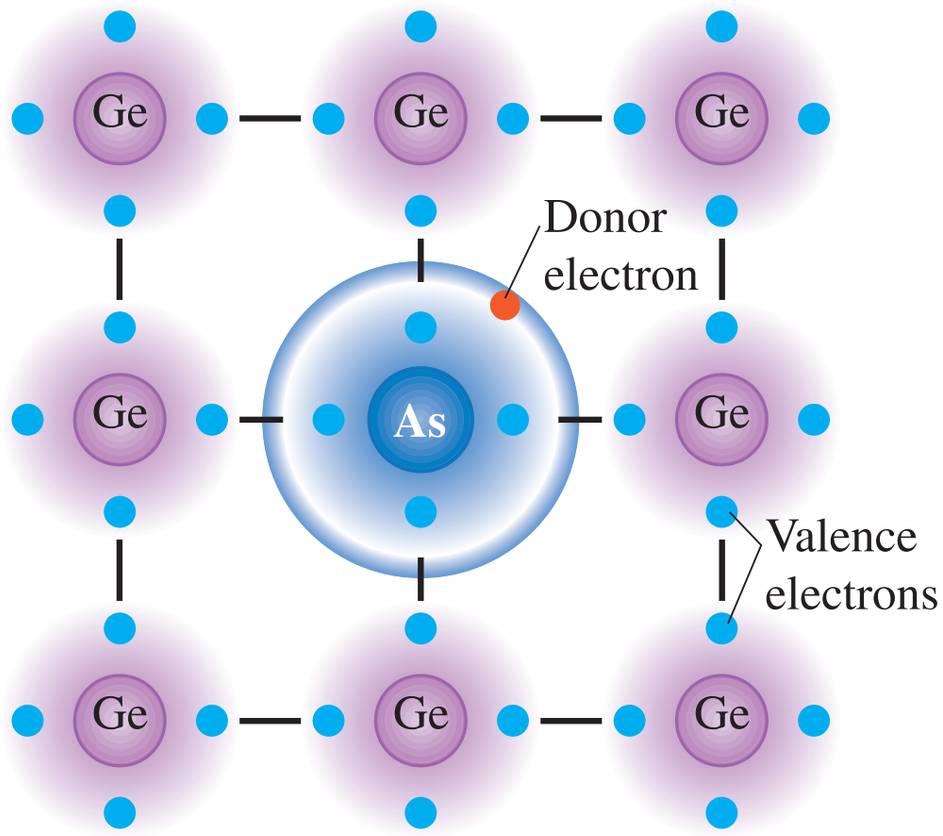
The motion of the hole also contributes to conductivity.

Donor Doping

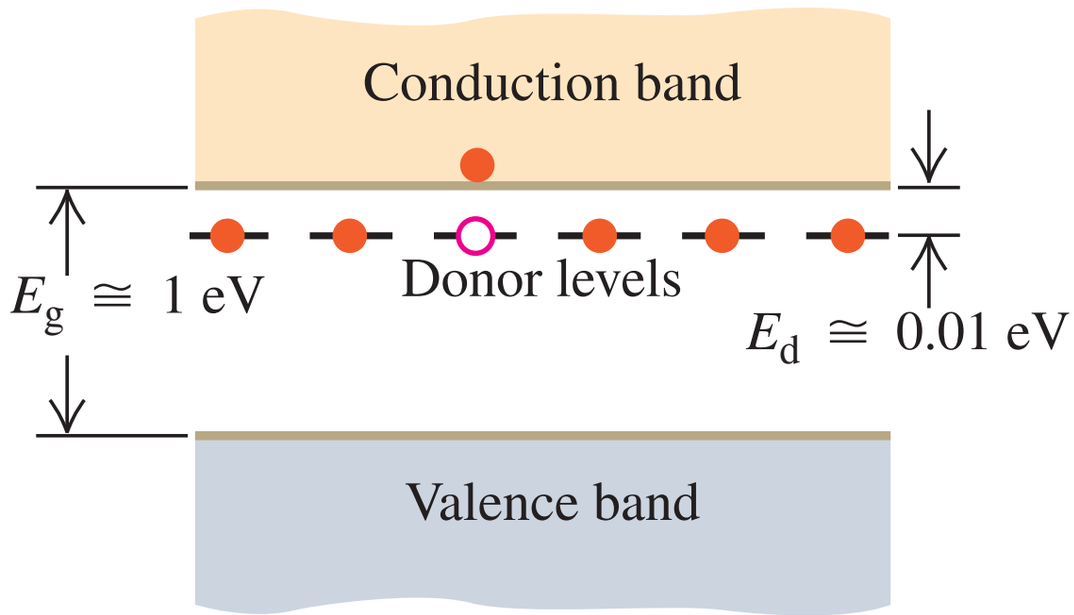
Arsenic has almost the same size as Germanium, and has 5 outer electrons, vs 4 for germanium or silicon.

Replacing N atoms of Germanium by Arsenic puts N extra electrons into the lattice (balanced by N extra charges from immobile Arsenic atoms).

The “donor levels” are very close to the conduction band,
so the donor electron is easily thermally excited into the conduction band.



(b) Energy-band diagram for an *n*-type semiconductor at a low temperature. One donor electron has been excited from the donor levels into the conduction band.

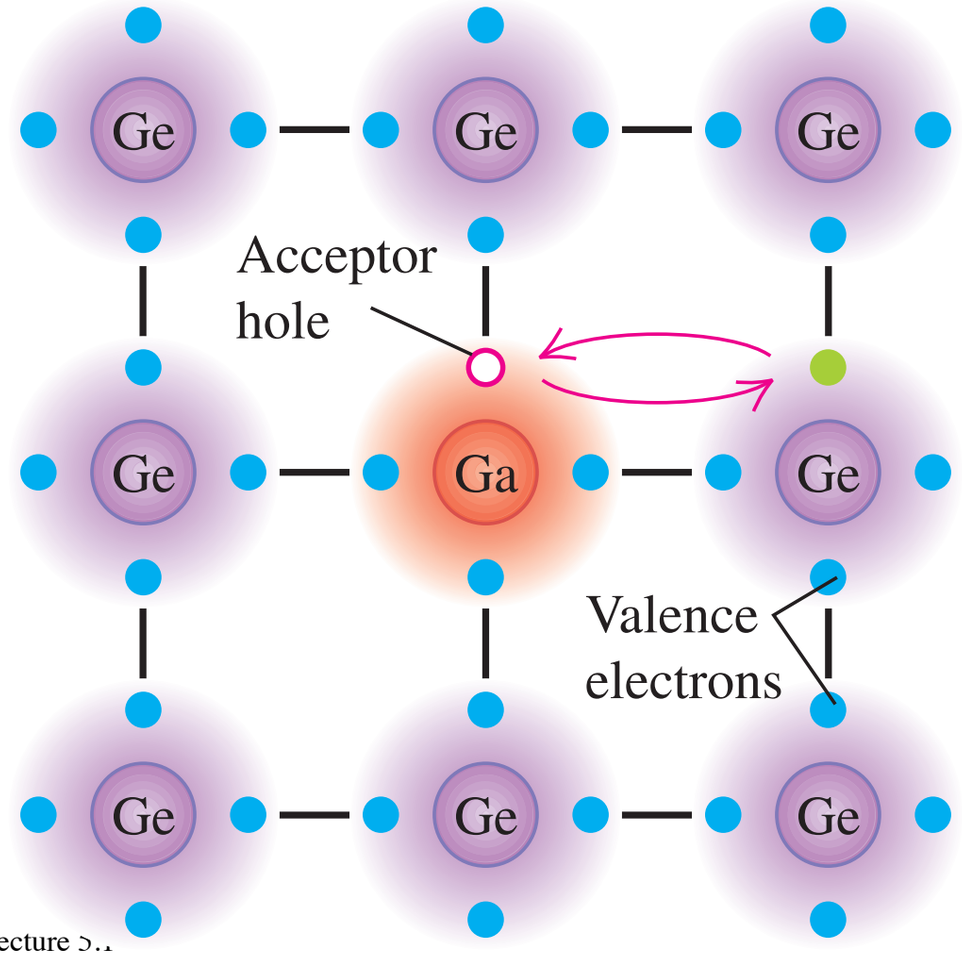


Acceptor Doping

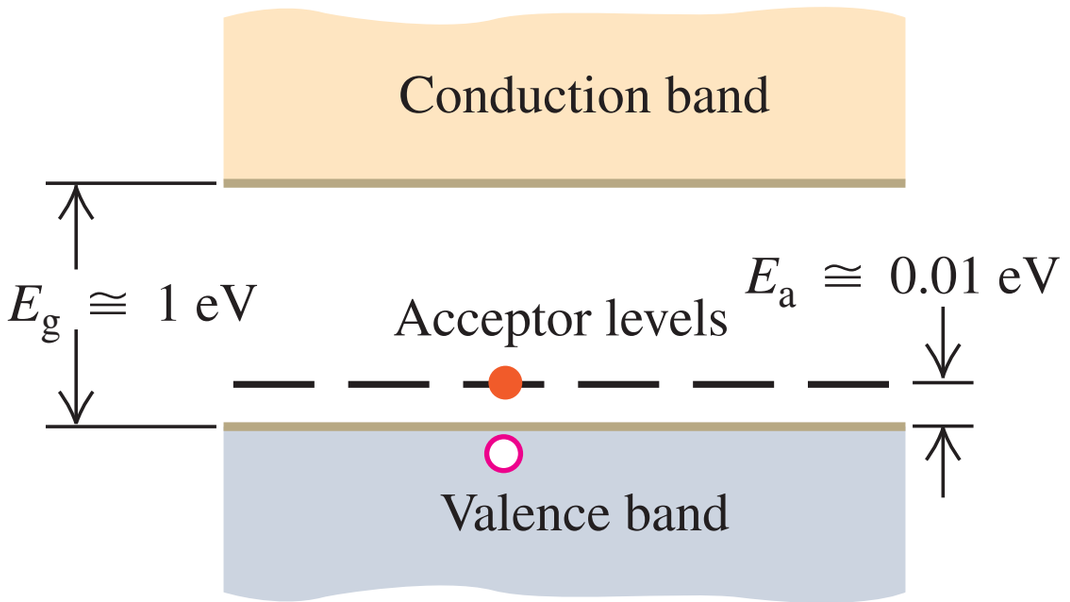
Gallium is almost the same size as Germanium, but has 3 outer electrons.

Replacing N atoms of Germanium with Gallium makes the lattice have
N fewer electrons (balanced by immobile Gallium atoms with fewer protons).

The “acceptor levels” are very close to the valence band, so a valence-band electron can jump to a Gallium atom, leaving a mobile hole in the valence band.



(b) Energy-band diagram for a *p*-type semiconductor at a low temperature. One acceptor level has accepted an electron from the valence band, leaving a hole behind.



N-Type and P-Type

Doping with electron donors (5 valence electrons) makes what is called N-type material, which has mobile electrons and fixed positive charges.

Doping with electron acceptors (3 valence electrons) makes P-type material, which has mobile holes and fixed negative charges.

Both N-type and P-type materials have zero net electric charge.

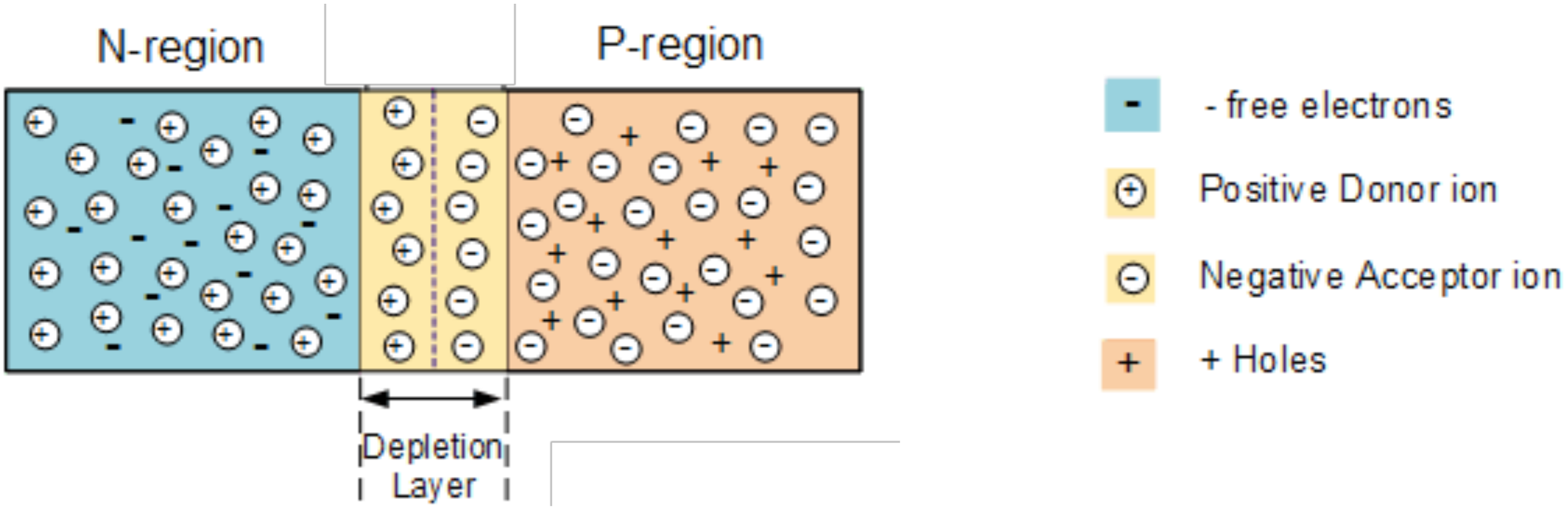
It's best to dope with atoms that are close to the same size as the lattice, which happens when the doping atoms are in the same periodic table row.

Phosphorous doping makes N-type Silicon. Boron doping makes P-type silicon.

Arsenic doping makes N-type Germanium. Gallium doping makes P-type.

PN Junction

Start with a pure silicon wafer. Diffuse some P-type impurity into the whole thickness. Then diffuse enough N-type impurity to reverse the polarity, but just of the surface.

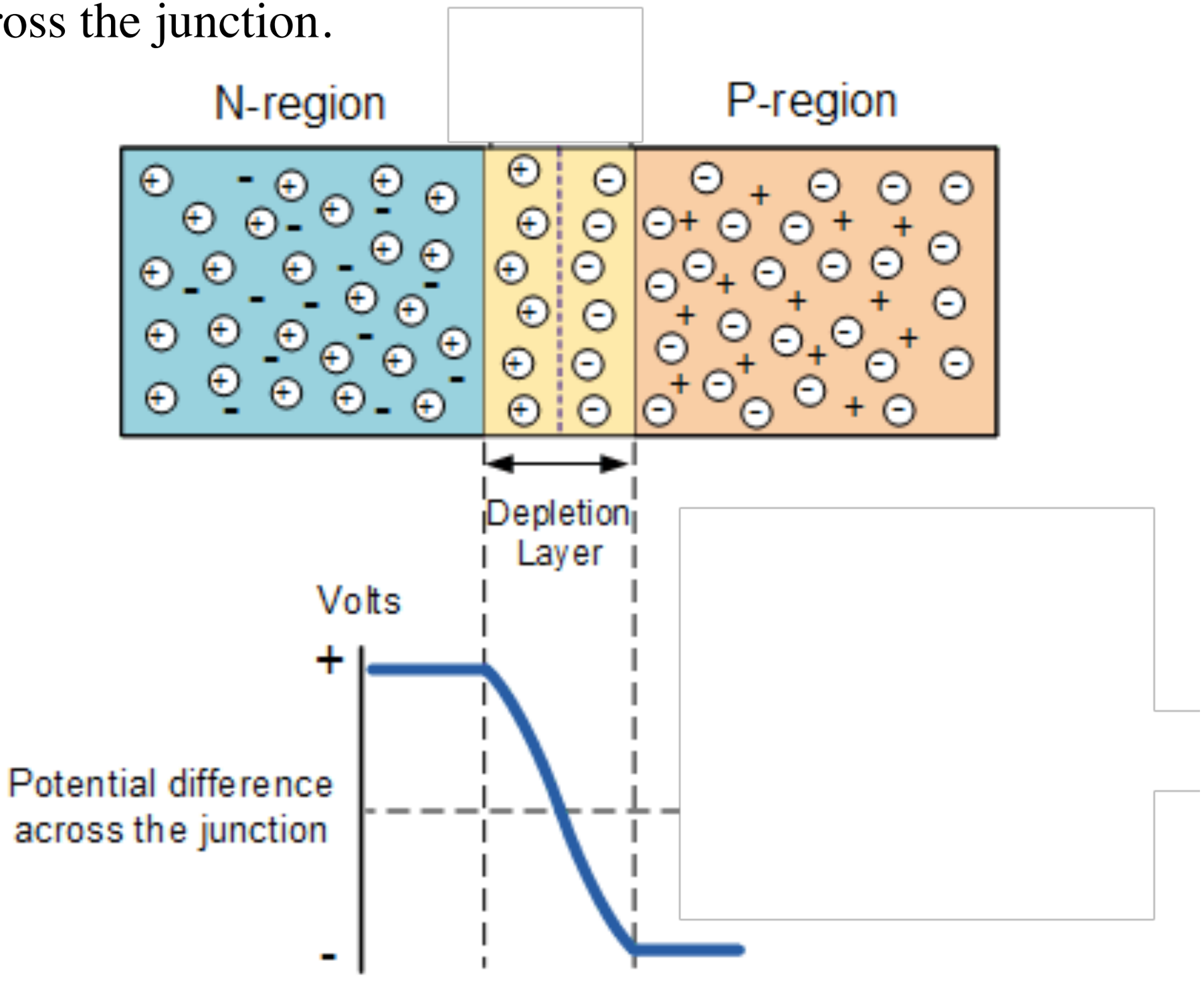


The electrons and holes neutralize each other in a thin depletion layer that has the low conductivity of pure silicon.

The N-region and P-region do conduct.

PN Junction 2

The charge flow to form the depletion layer results in a built-in potential difference across the junction.



Solar Cell

Photons that enter the silicon can detach an electron from an atom, leaving a hole behind.

The built-in electric field separates the electron from the hole, causing an electric current to flow.

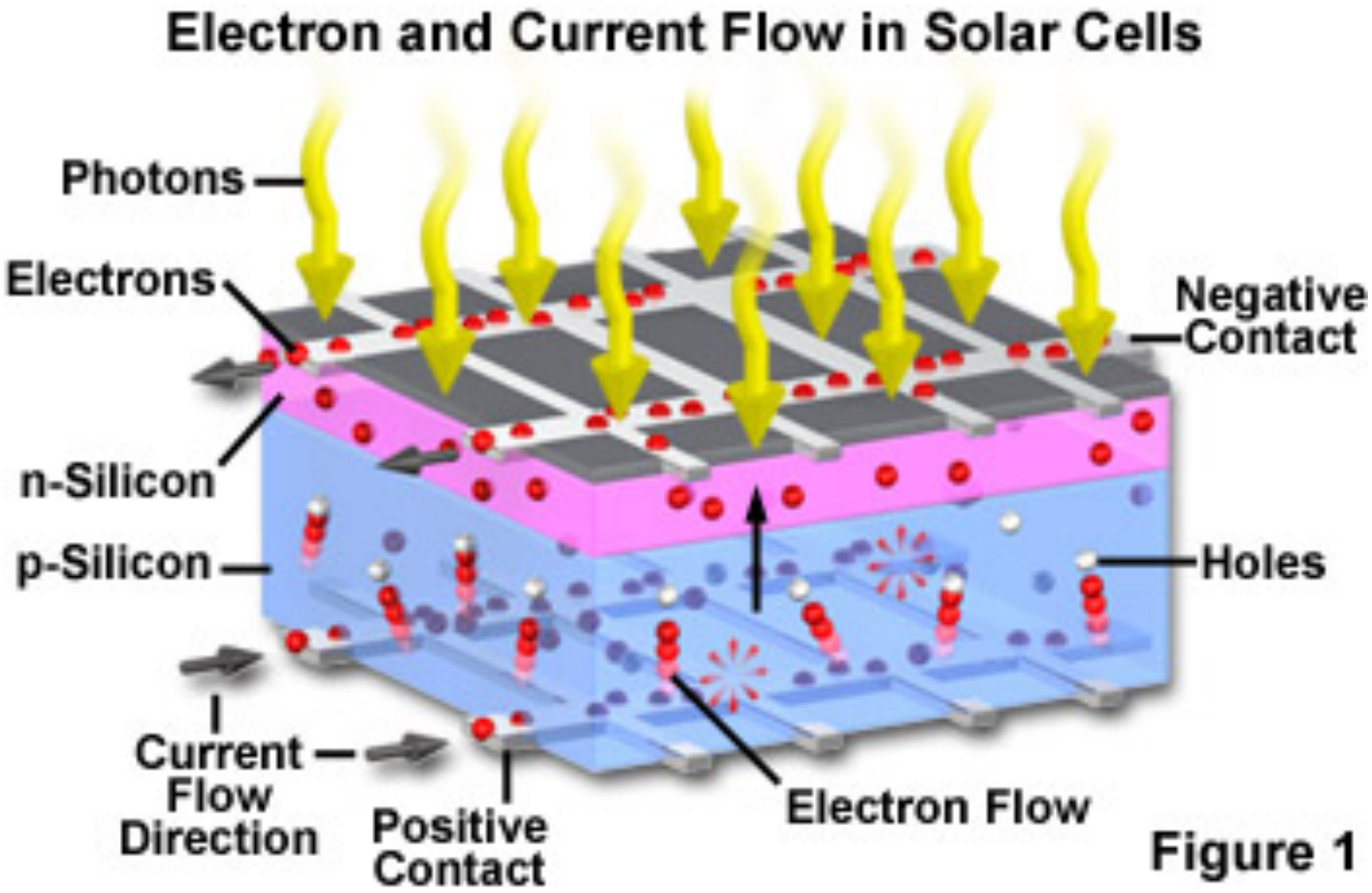


Figure 1

Rectifier Diode

The thickness of the depletion layer can be changed by applying an external voltage to the PN junction.

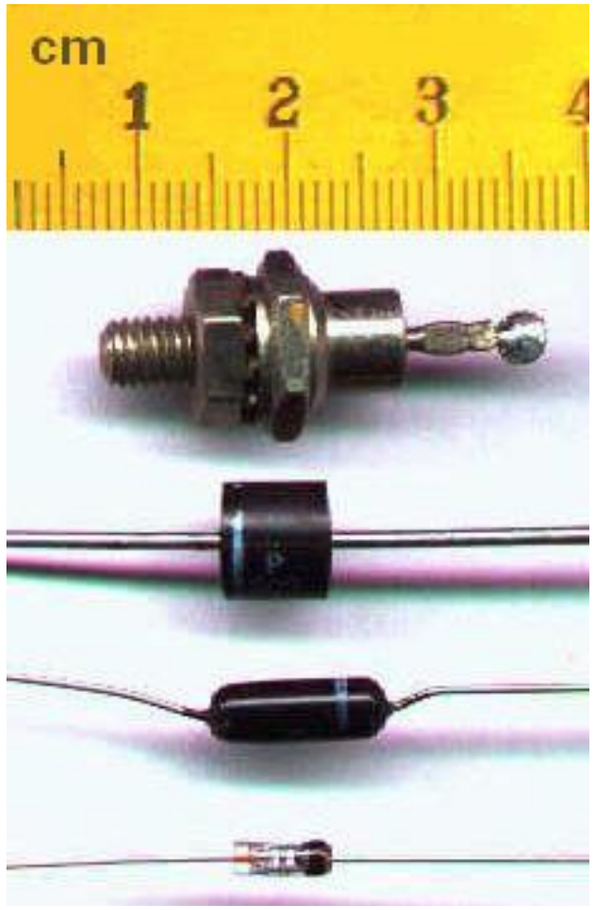
If a large enough positive voltage is applied to the P-side, the depletion layer gets so thin that significant conduction occurs. This is the standard rectifier.

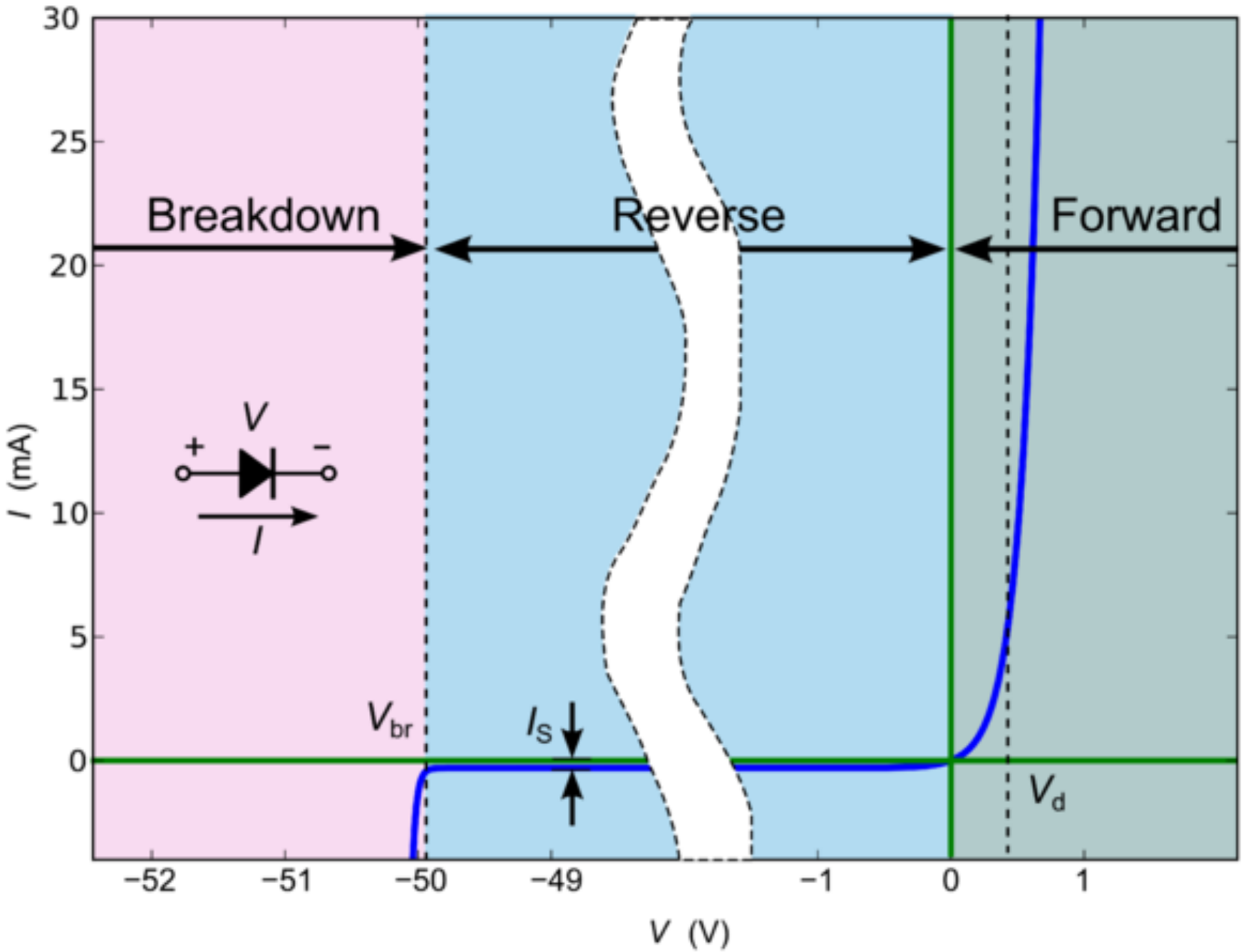
For negative voltage, the depletion layer gets thicker. There is a reverse current that is almost independent of voltage, but usually immeasurably small.

For large enough negative voltage, the few charges that cross the depletion region get enough energy that they can knock electrons from the valence band up to the conduction band, causing a large current. This is reverse breakdown.

Zener diodes are engineered to have a precise reverse breakdown voltage.

Silicon Diodes



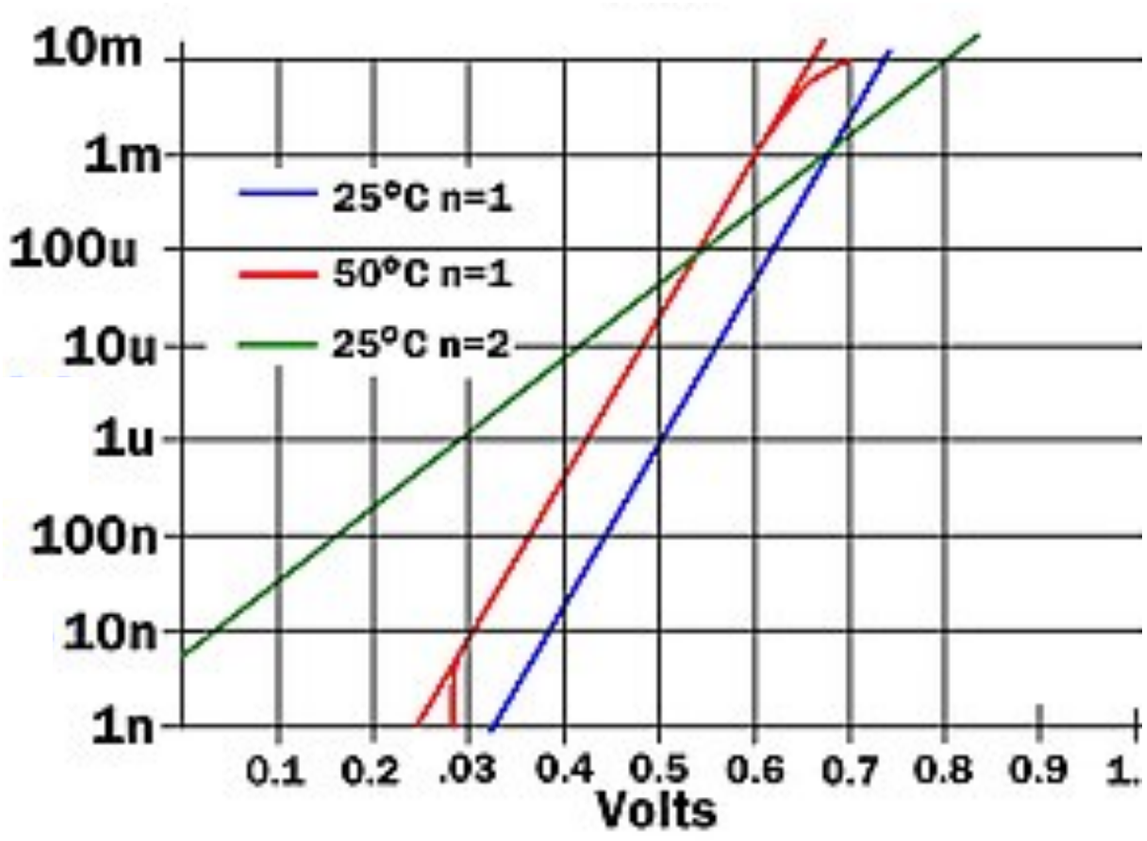


Shockley Diode Equation

For voltages greater than the reverse breakdown voltage, the current-voltage relationship is described by the Shockley Equation $I(V) = I_S \cdot \left(\exp \frac{qV}{nk_BT} - 1 \right)$

At $V = 0$, the exponential is +1,
and the current is zero.

I_S is the saturation current, which is the current at negative voltage. It depends on the area of the junction, doping level, etc.



$\frac{k_BT}{q} = V_T$ is called the thermal voltage.
It's ~25 milliVolts at room temperature.

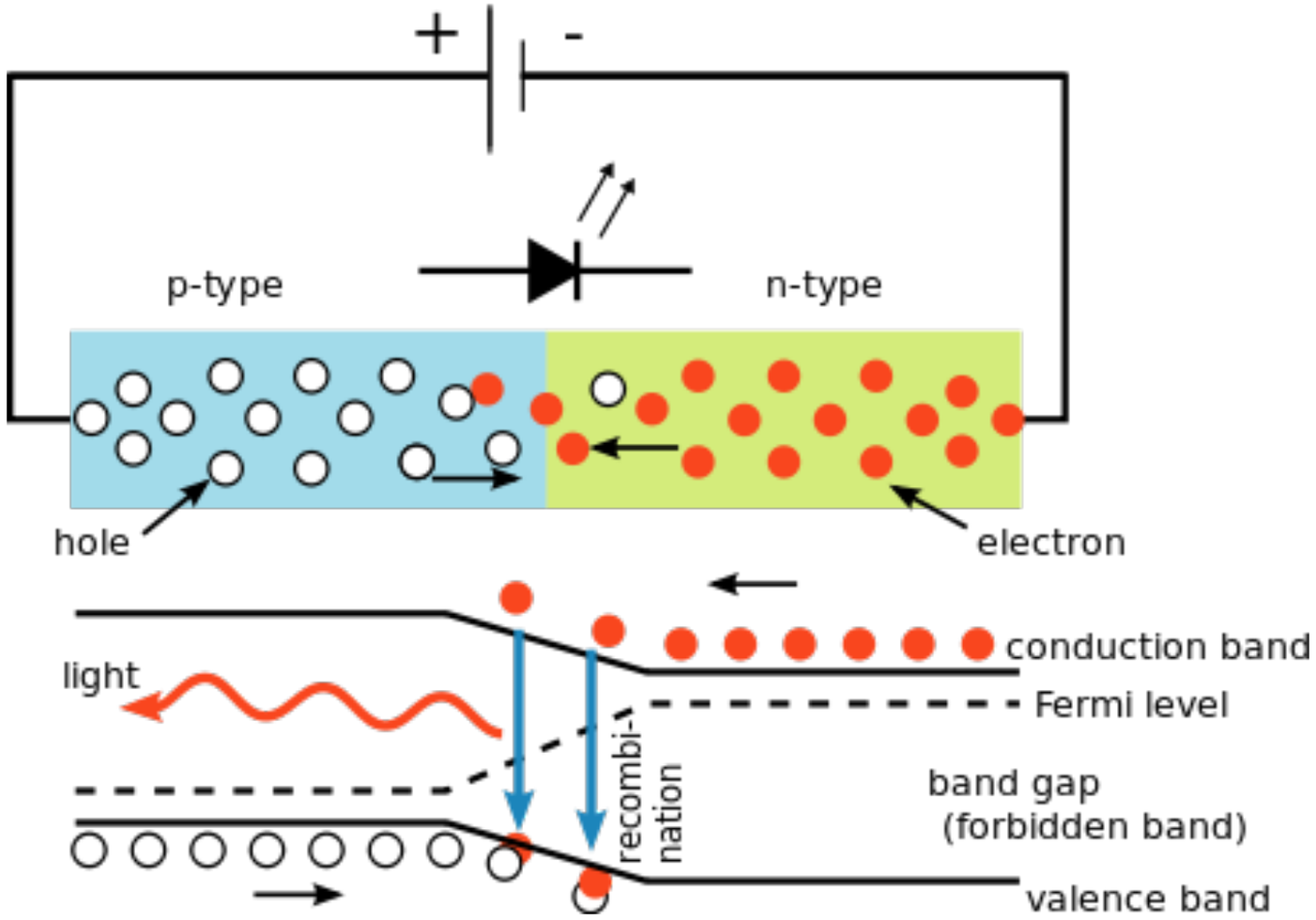
The n is called the "ideality factor."
It's ~1 for Germanium, ~2 for Silicon.

Light Emitting Diode

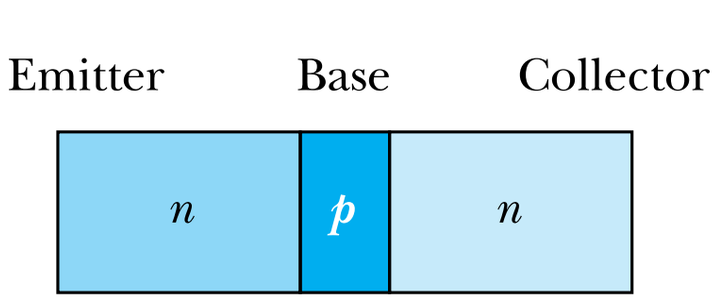
When a diode is conducting, there are lots of electrons and holes in the depletion region.

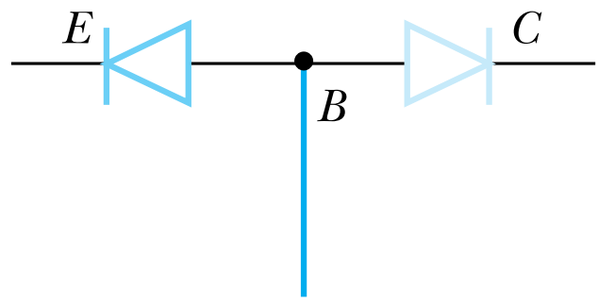
They can re-combine, essentially annihilating each other.
That's a nuisance if you are trying to make a good rectifier.

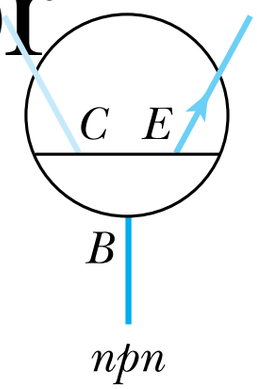
But the energy of the recombination can turn into a photon.

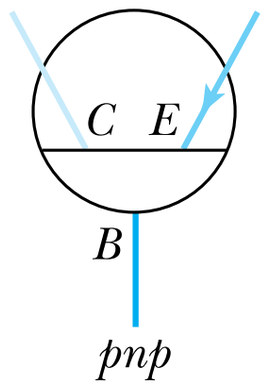


Bipolar Transistor









A bipolar transistor has two PN junctions back to back. It can be NPN or PNP.

The middle region is called the base. It's usually made quite thin.

One end is intended to be forward-biased relative to the base, so its voltage is normally about 0.6 V different from the base. It's called the emitter, because that junction emits either electrons or holes into the base region.

The other end is reverse-biased relative to the base and is called the collector.

The collector current would normally be very small. But the electrons or holes from the emitter-base junction in the depletion region allow current to flow.

The emitter-base current controls the collector current.

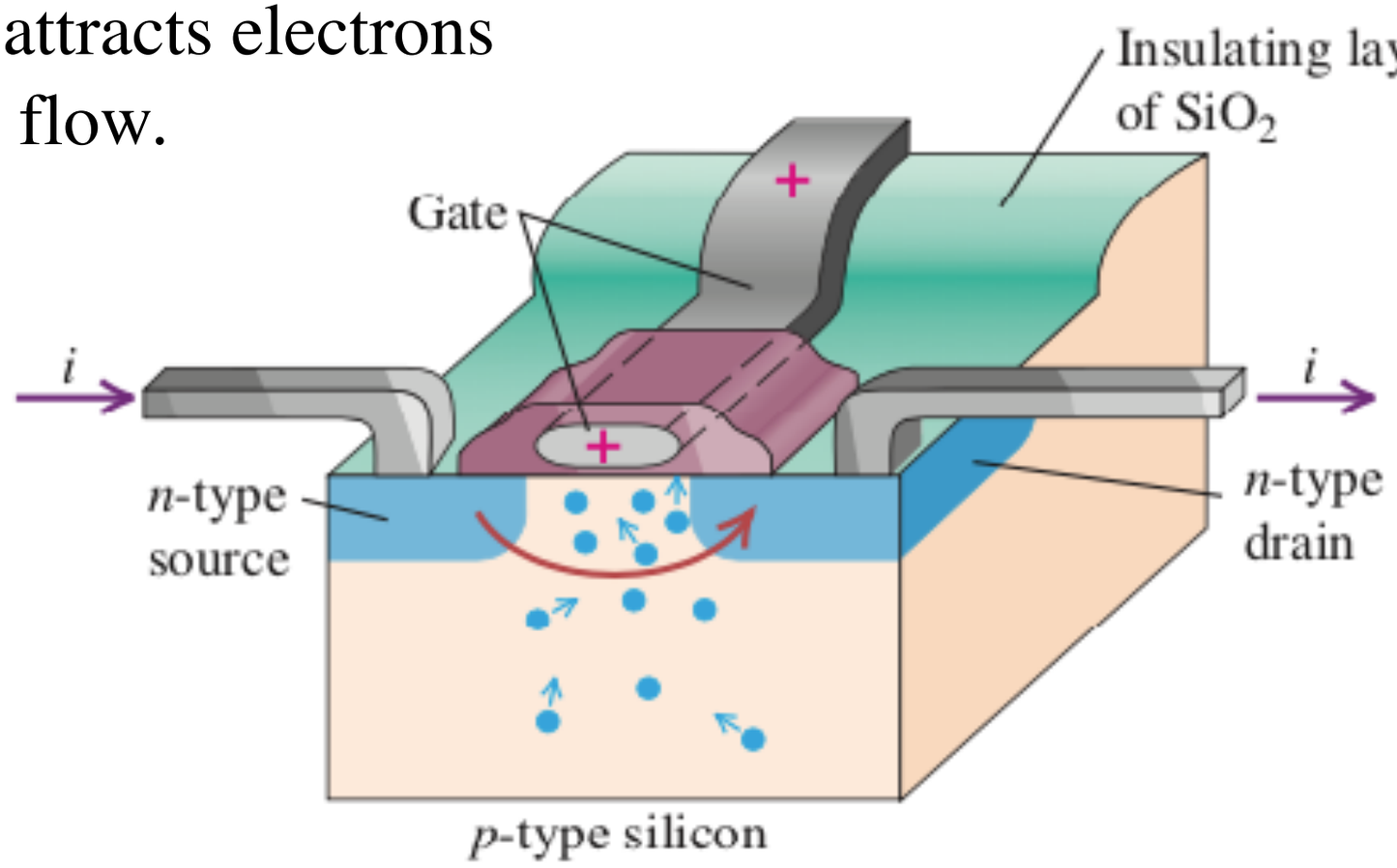
Field Effect Transistor

Make 2 N-type islands in P-type silicon. Grow an insulating layer of oxide on top. Etch holes above the N-type islands and deposit metal connecting wires. Deposit another metal wire over the region between the N-type islands, without a hole.

One of the PN junctions is always reverse-biased, so there is normally no current flow between the <u>source</u> and the <u>drain</u>.

But a voltage applied to the gate attracts electrons to the region, allowing current to flow.

Since the gate is insulated, there is negligible gate current, so MOSFETs are far more energy-efficient than bipolar transistors.



For Next Time

Homework 4 is due tonight.

Wednesday will be Lasers.

Worksheet on Friday as usual.

Next week will be Schrodinger in 3 dimensions.