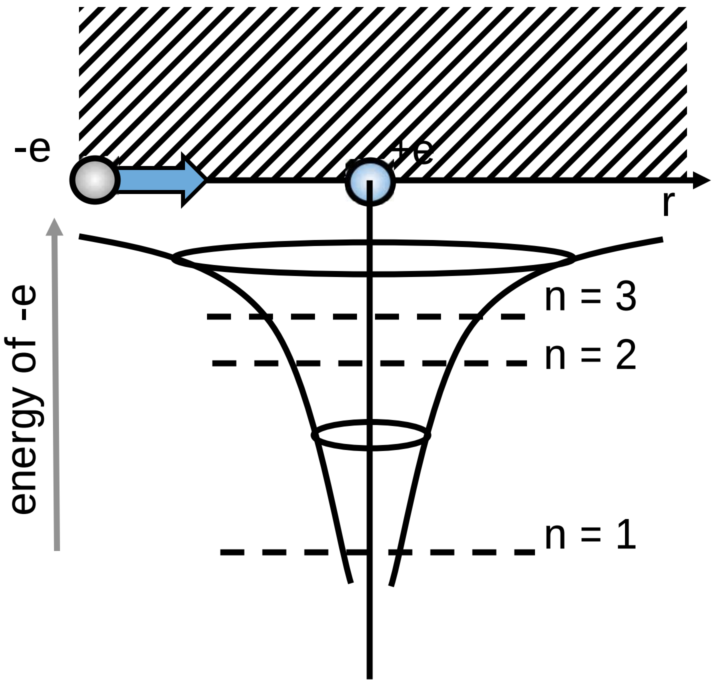
# *From Atoms to Solids*

## Outline

- Atomic and Molecular Wavefunctions
- Molecular Hydrogen
- Benzene

# *A Simple Approximation for an Atom*

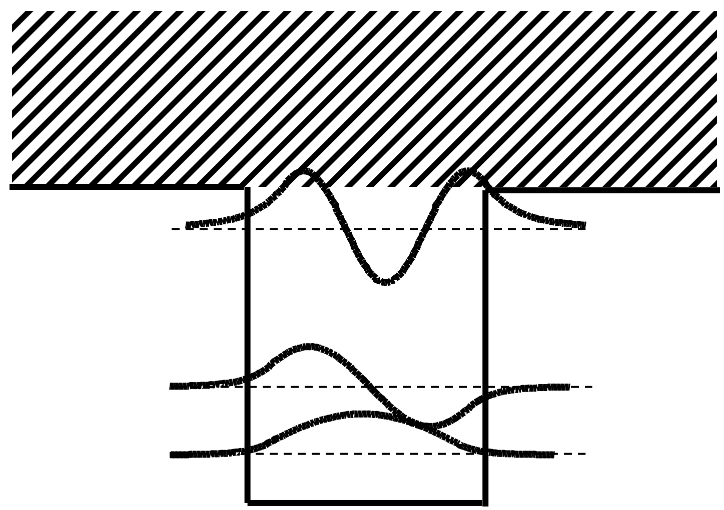
Let's represent the atom in space by its <u>Coulomb potential</u> centered on the proton (+e):




Continuum of free electron states

$$V(r) = -\frac{e^2}{4\pi\epsilon_o r}$$

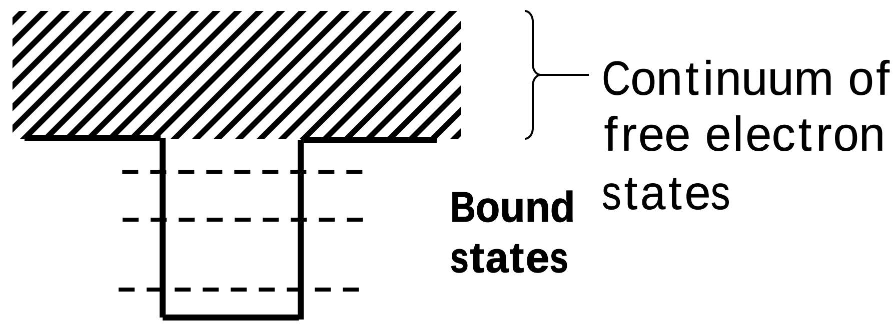
Finite Quantum Well:



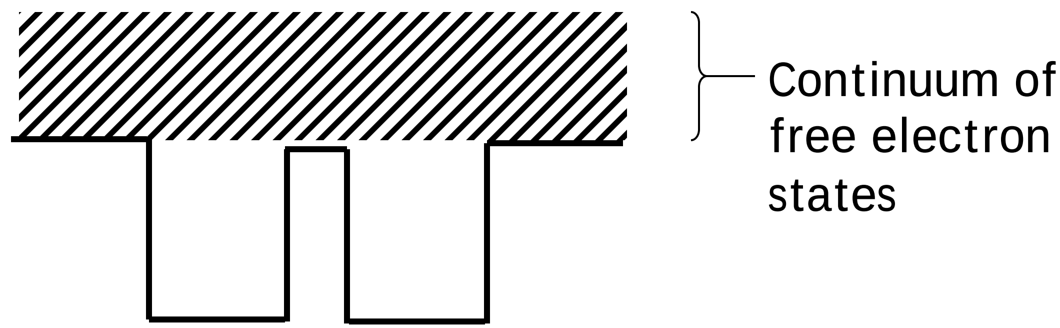
Continuum of free electron states

# *A Simple Approximation for a Molecule*

If this were the 'atomic' potential,



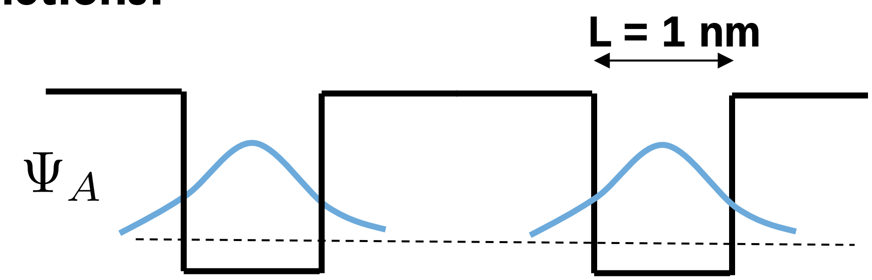

then this would be the 'molecular' potential:




We do not know exactly what the energy levels are, although in 1-D we could solve the equation exactly if we had to

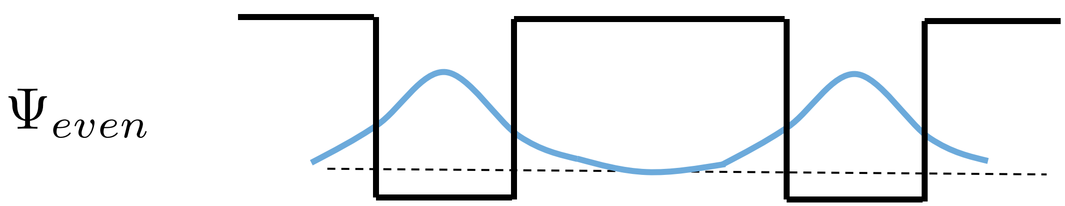
# 'Molecular' Wavefunctions

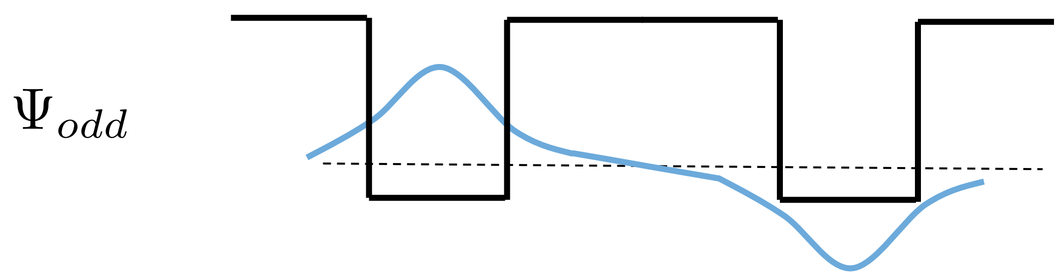
**"Atomic" Wavefunctions:**




$$E \approx \frac{1.505\ \mathrm{eV \cdot nm^2}}{(2L)^2} = 0.4\ \mathrm{eV}$$

**"Molecular" Wavefunctions:** 2 'atomic' states → 2 'molecular' states



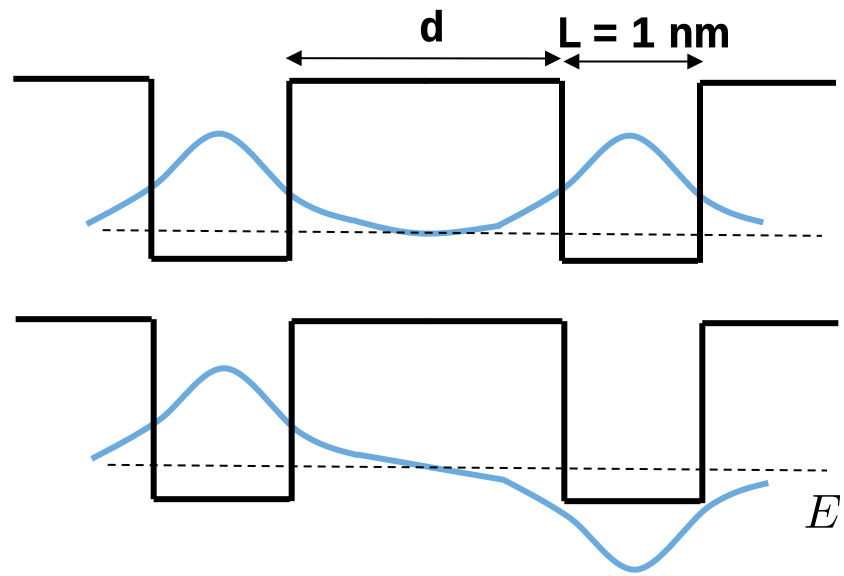

When the wells are far apart, 'atomic' functions don't overlap.
A <u>single electron</u> can be in either well with equal probability, and E = 0.4 eV.

# *'Molecular' Wavefunctions*

**WELLS FAR APART:**

$\Psi_{even}$

$\Psi_{odd}$



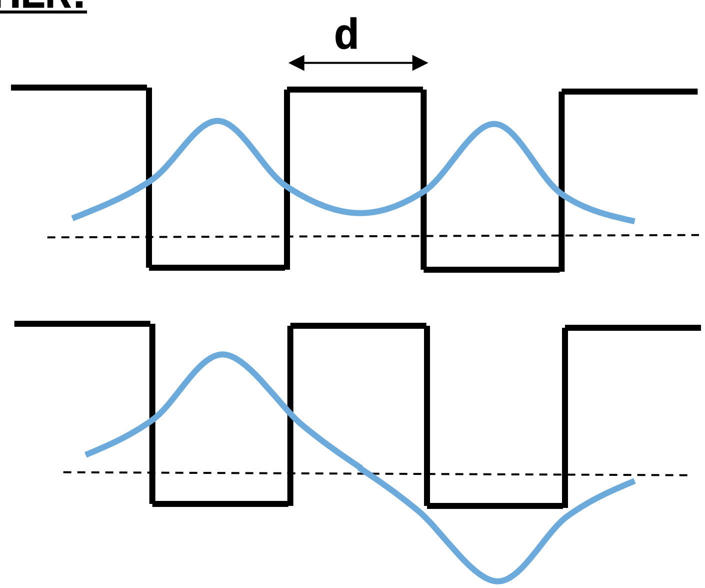

$$E \approx \frac{1.505 \text{ eV} \cdot \text{nm}^2}{(2L)^2} = 0.4 \text{ eV}$$

**("Degenerate" states)**

**WELLS CLOSER TOGETHER:**

$\Psi_{even}$

$\Psi_{odd}$

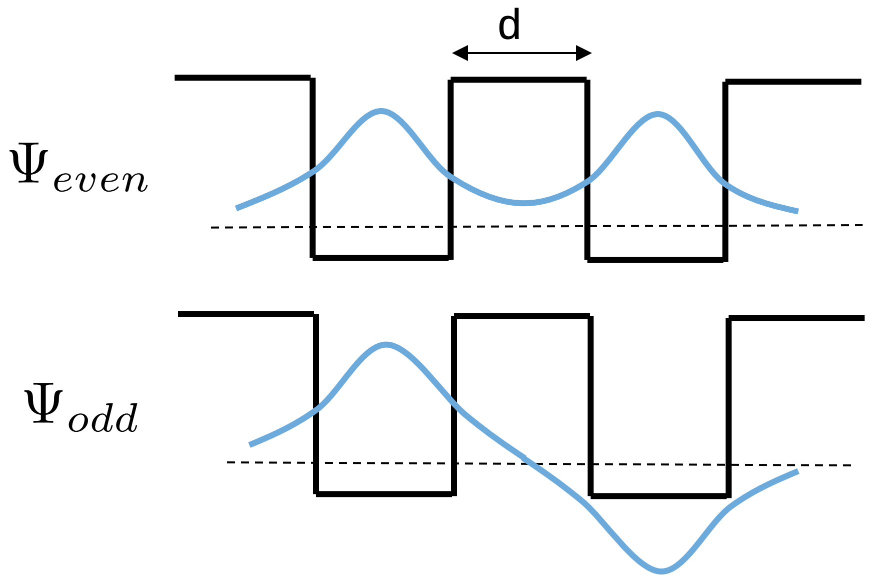



'Atomic' states are beginning to overlap and distort. $|\Psi_{even}|^2$ and $|\Psi_{odd}|^2$ are not the same (note center point). Energies for these two states are not equal. (The degeneracy is broken.)

# *'Molecular' Wavefunctions*

1. Which state has the lower energy?

   (a) $\Psi_{even}$
   (b) $\Psi_{odd}$




2. What will happen to the energy of $\Psi_{even}$ as the two wells come together (i.e., as d is reduced)?

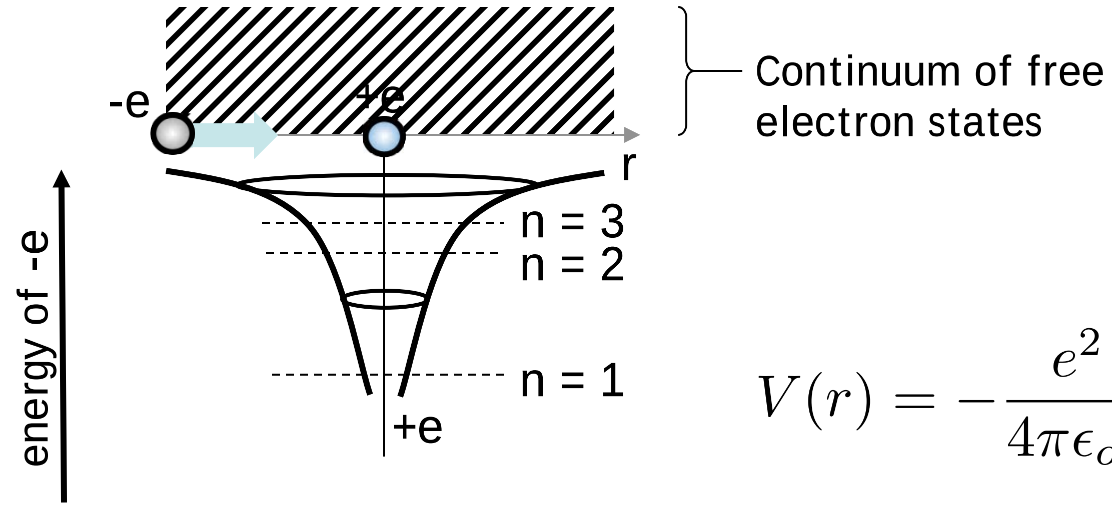
   (a) E increases
   (b) E decreases
   (c) E stays the same

# *Bonding Between Atoms*

How can two neutral objects bind together?

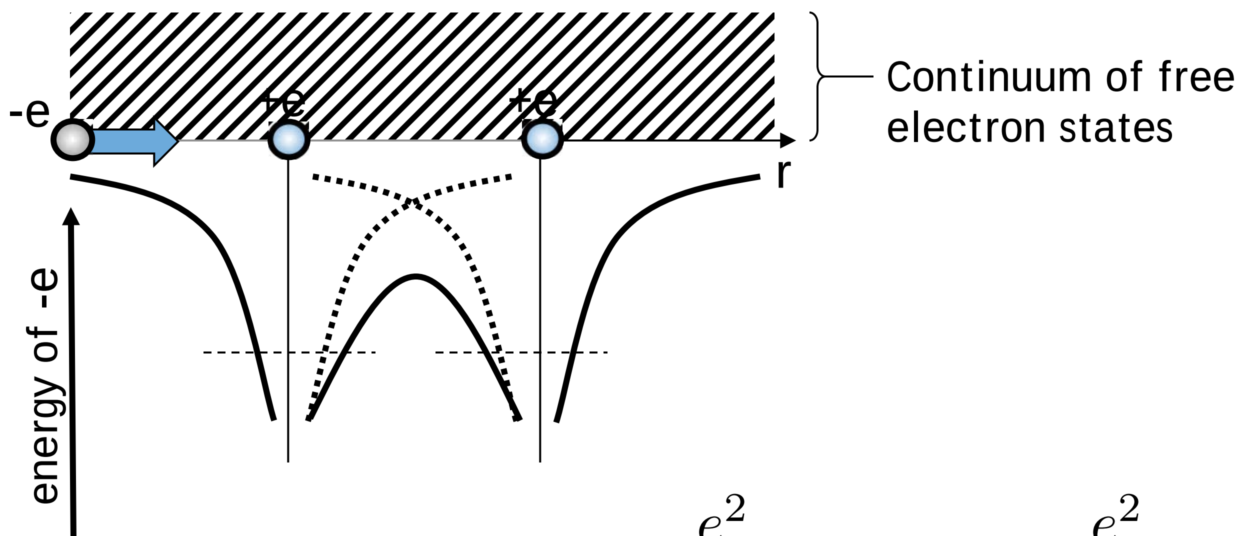
$H + H \rightarrow H_2$

Let's represent the atom in space by its Coulomb potential centered on the proton (+e):



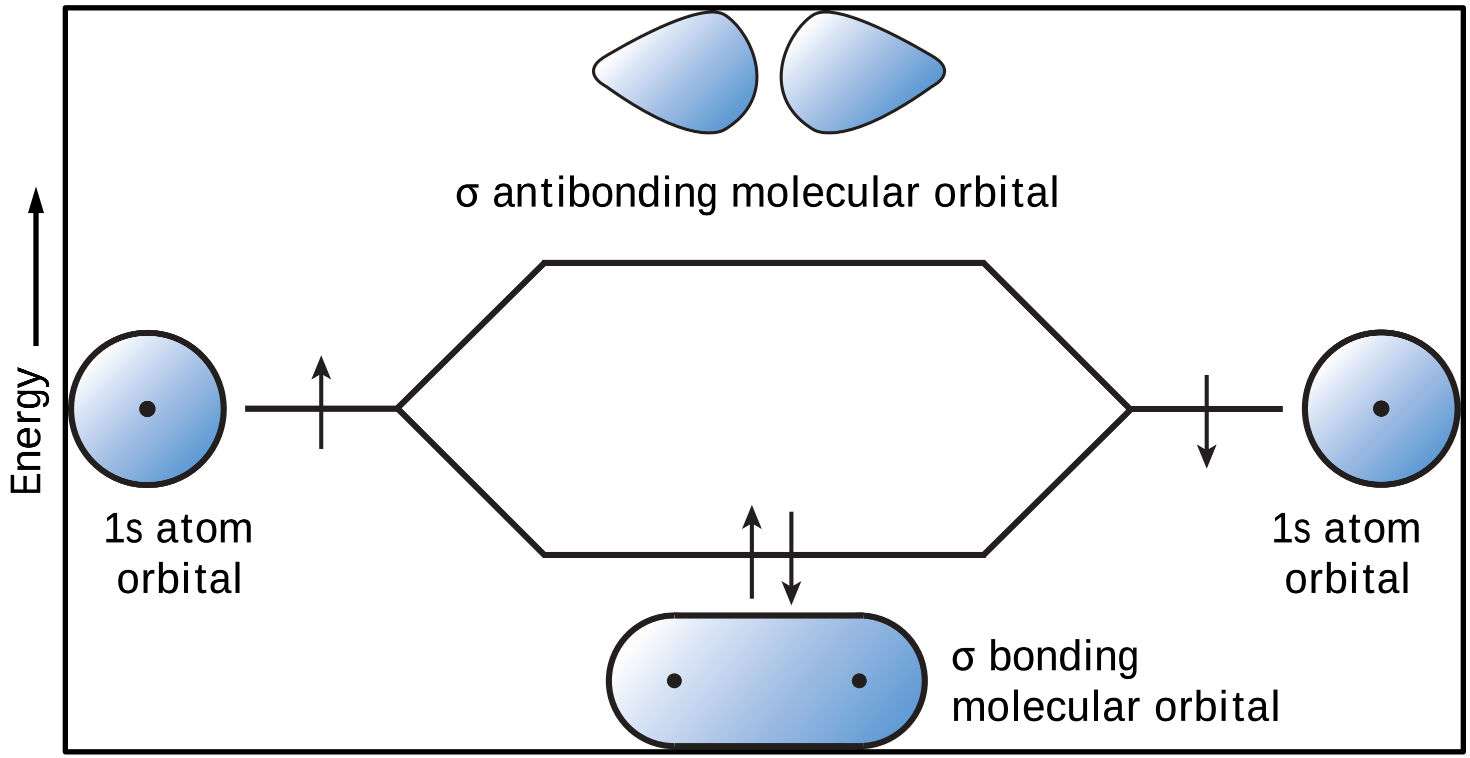

$$V(r) = -\frac{e^2}{4\pi\epsilon_o r}$$

Superposition of Coulomb potentials $H_2$:

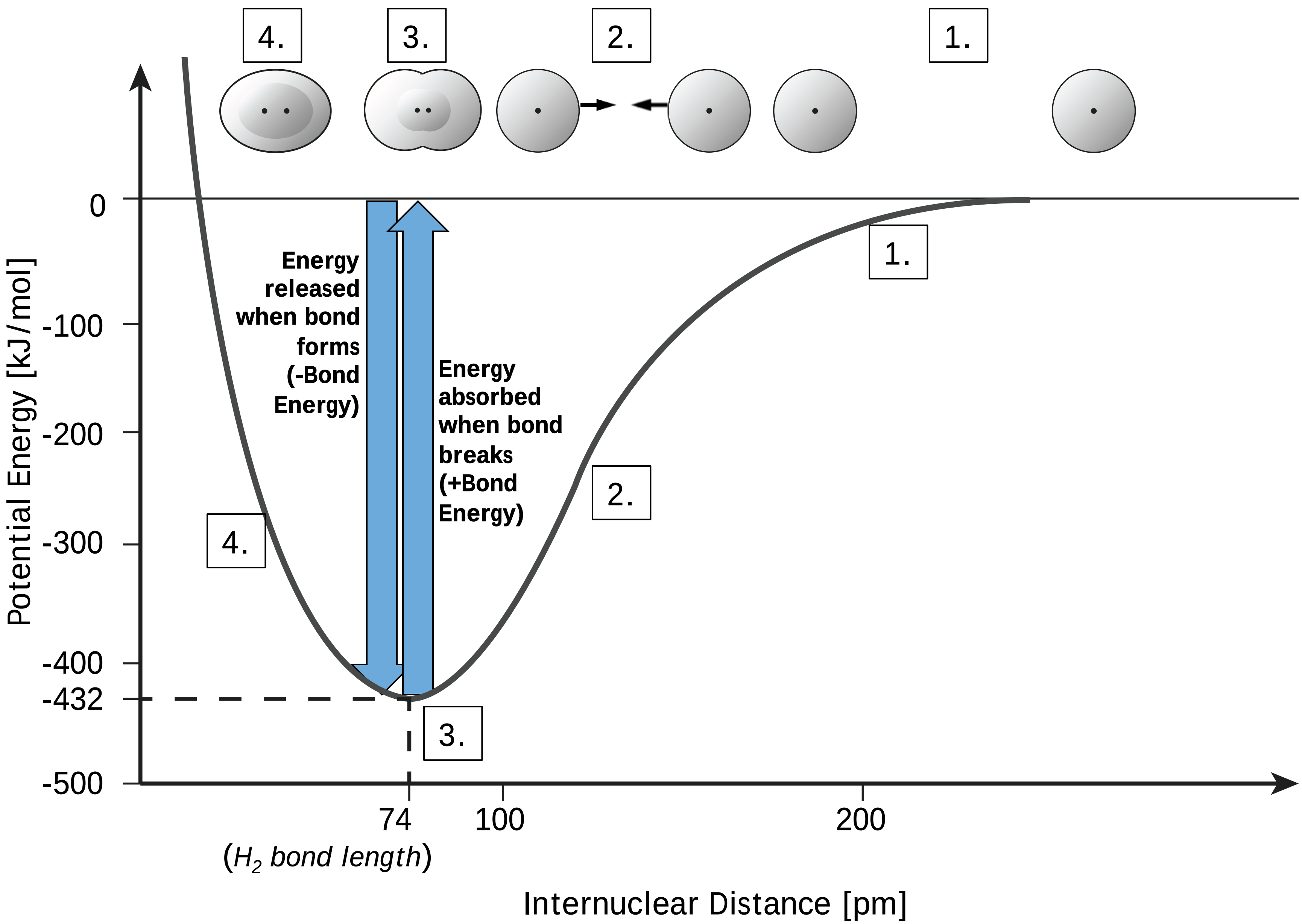



$$V(r) = -\frac{e^2}{4\pi\epsilon_o |r - r_1|} - \frac{e^2}{4\pi\epsilon_o |r - r_2|}$$

# *Molecular Hydrogen*

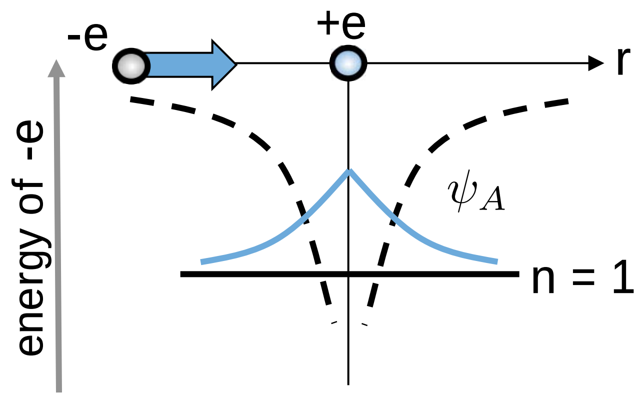


# Molecular Hydrogen Binding Energy

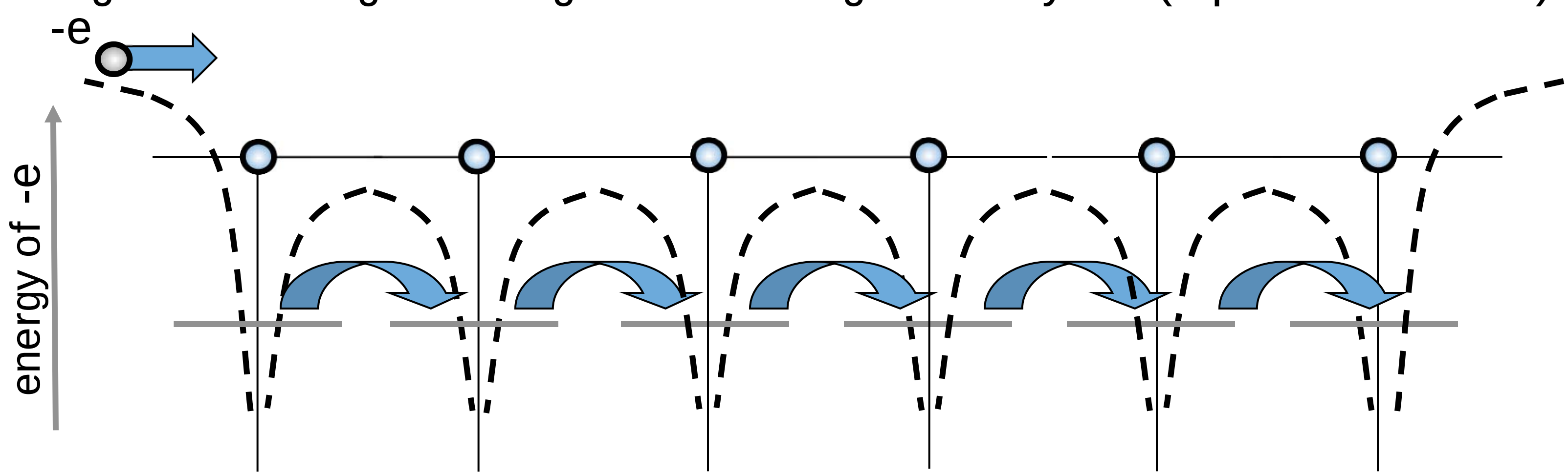


# *Tunneling Between Atoms in Solids*

Again start with simple atomic state:

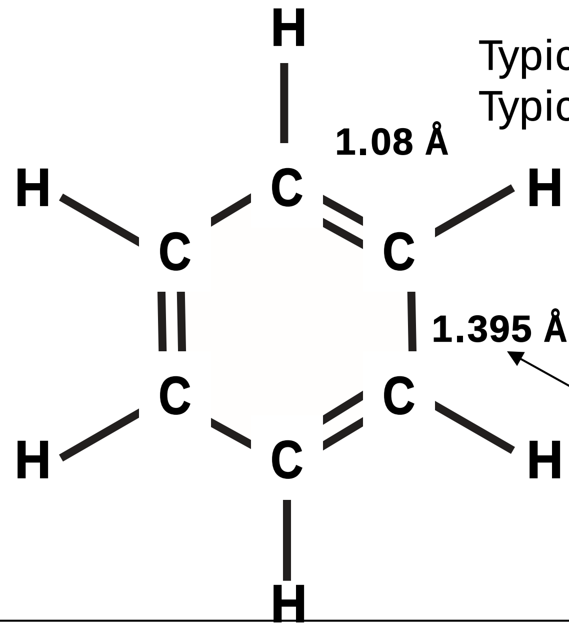



Bring N atoms together together forming a 1-d crystal (a periodic lattice)...



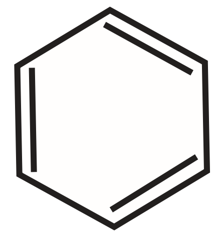
# *Let Take a Look at Molecular Orbitals of Benzene*

**... the simplest "conjugated alkene"**

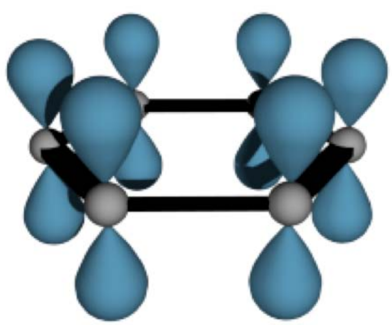



Typical C-C bond length 1.54 Å
Typical C=C bond length 1.33 Å

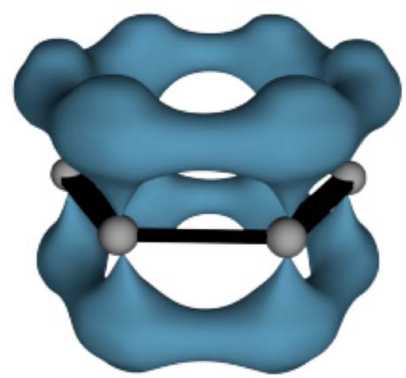
or



Length of benzene carbon-carbon bonds is between C-C and C=C bond lengths

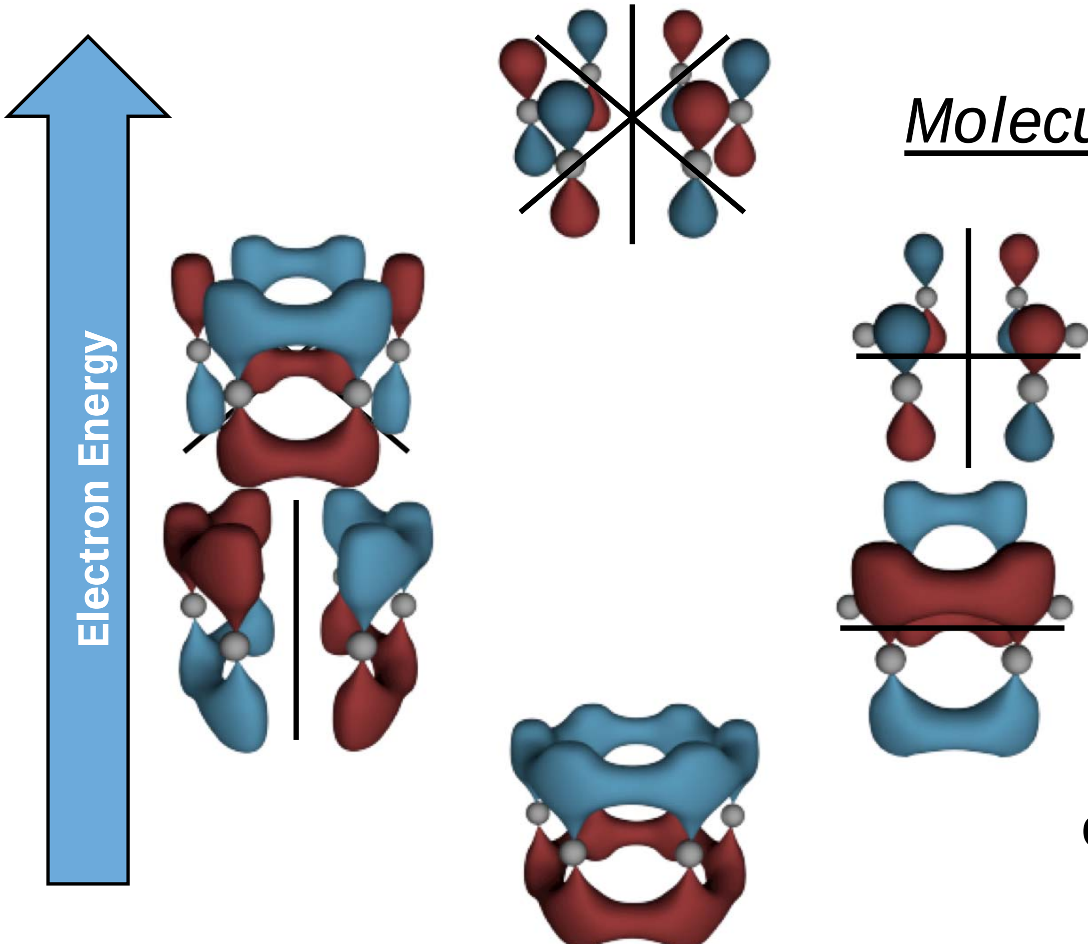


**p orbitals**



**π-electron density**

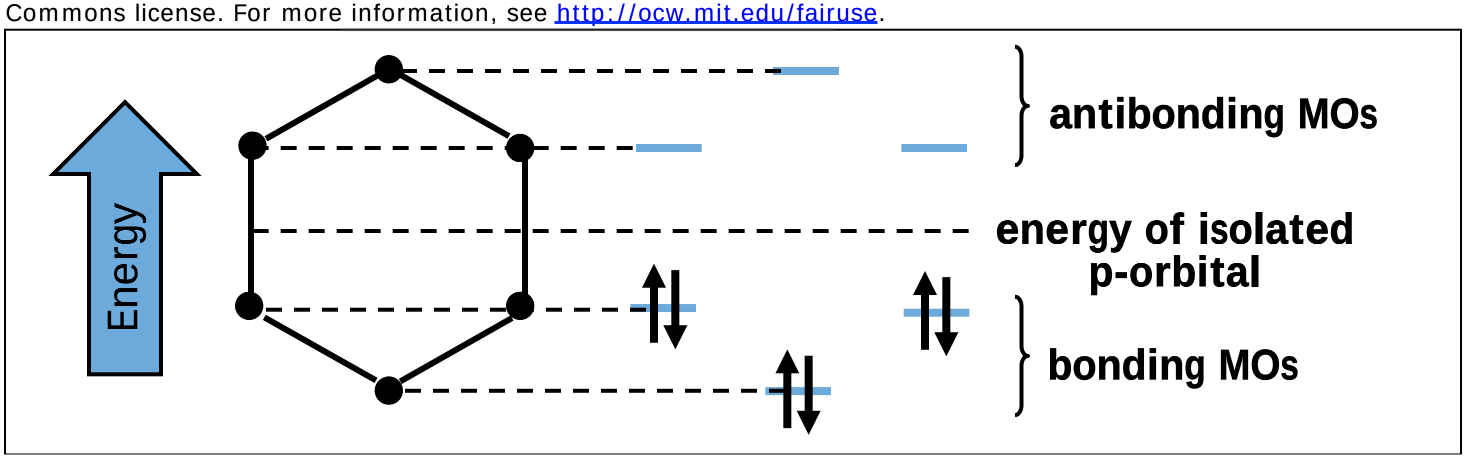
# *Molecular Orbitals of Benzene*




**Energy distribution of Benzene $\pi$-molecular orbitals**

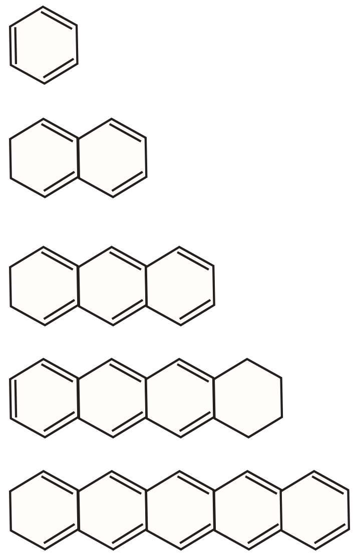
**Carbon atoms are represented by dots**
**Nodal planes are represented by lines**





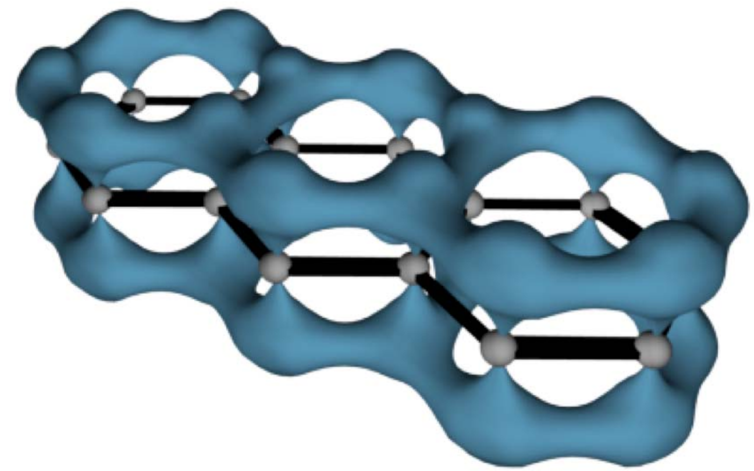

*from Loudon*

# *… More Examples – Series of Polyacene Molecules*



| | |
|---|---|
| Benzene | 255 nm |
| Naphthaline | 315 nm |
| Anthracene | 380 nm |
| Tetracene | 480 nm |
| Pentacene | 580 nm |

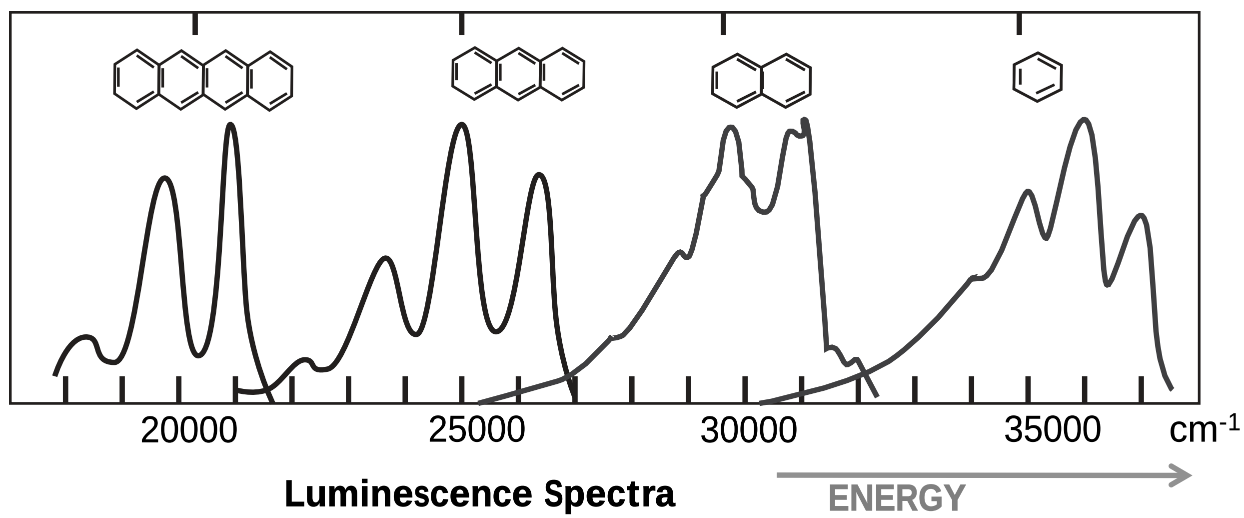
The lowest bonding MO of anthracene





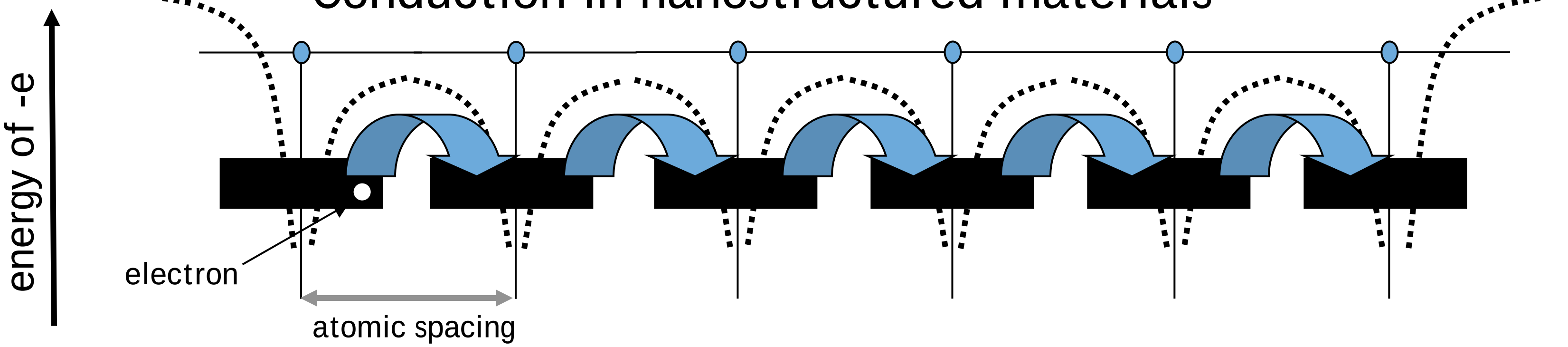
**Red: bigger molecules !**

**Blue: smaller molecules !**

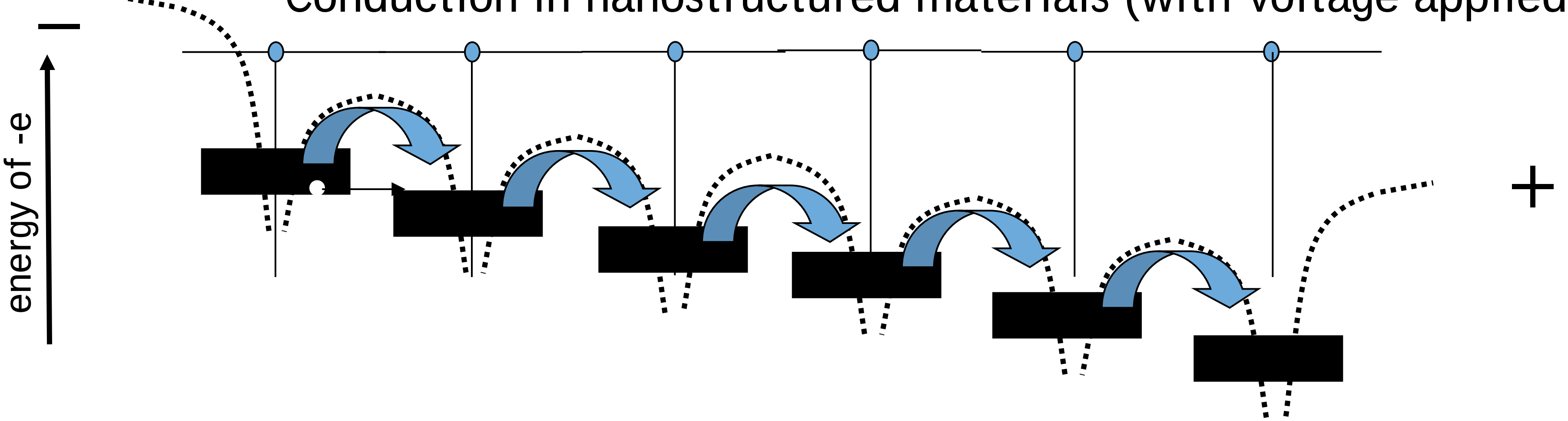


# *Tunneling Between Atoms in Solids*

Conduction in nanostructured materials



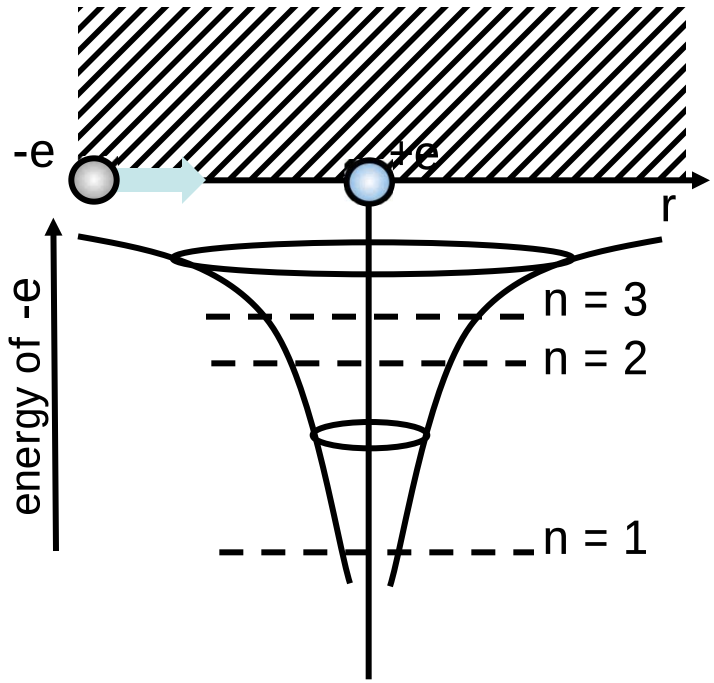

Conduction in nanostructured materials (with Voltage applied)




**TUNNELING IS THE MECHANISM FOR CONDUCTION**

# *Coulomb's Law and Atomic Hydrogen*

Let's represent the atom in space by its Coulomb potential centered on the proton (+e):



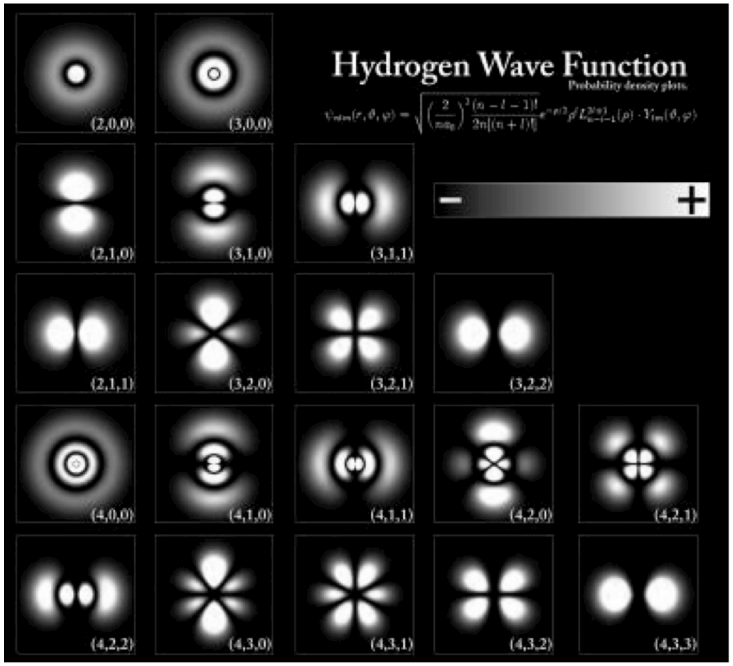

Continuum of free electron states

$$V(r) = -\frac{e^2}{4\pi\epsilon_o r}$$

Time-Independent Schrödinger Equation

$$E\psi(\overset{\mathbf{r}}{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\overset{\mathbf{r}}{r}) - \frac{e^2}{4\pi\epsilon_o r}\psi(\overset{\mathbf{r}}{r})$$

## *Solutions*

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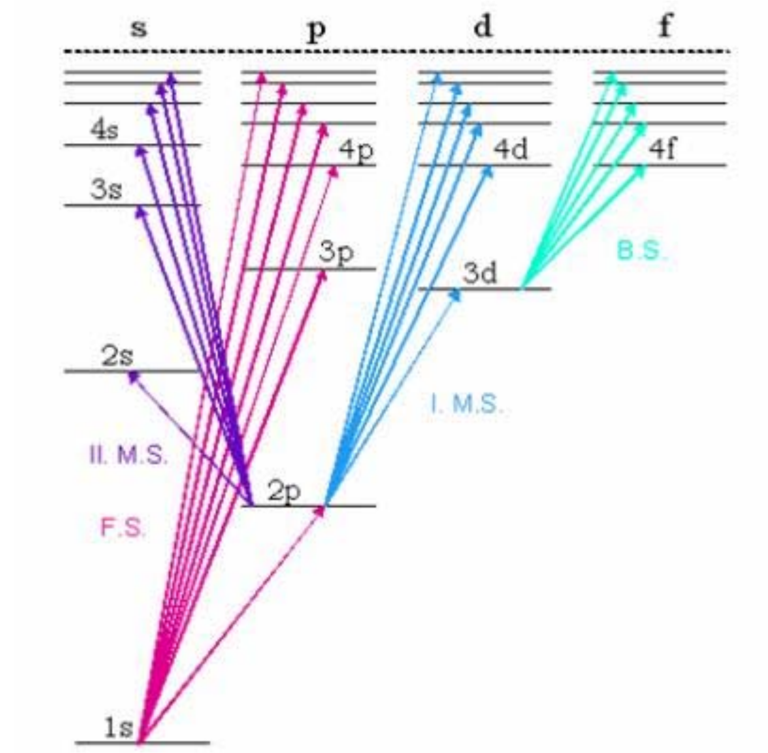



Image by Szdori on Wikipedia.

$$\psi_{1s}(\mathbf{r}) = e^{-r/a_0}$$

$$\psi_{2px}(\mathbf{r}) = xe^{-r/2a_0}$$

$$\psi_{2py}(\mathbf{r}) = ye^{-r/2a_0}$$

$$\psi_{2pz}(\mathbf{r}) = ze^{-r/2a_0}$$

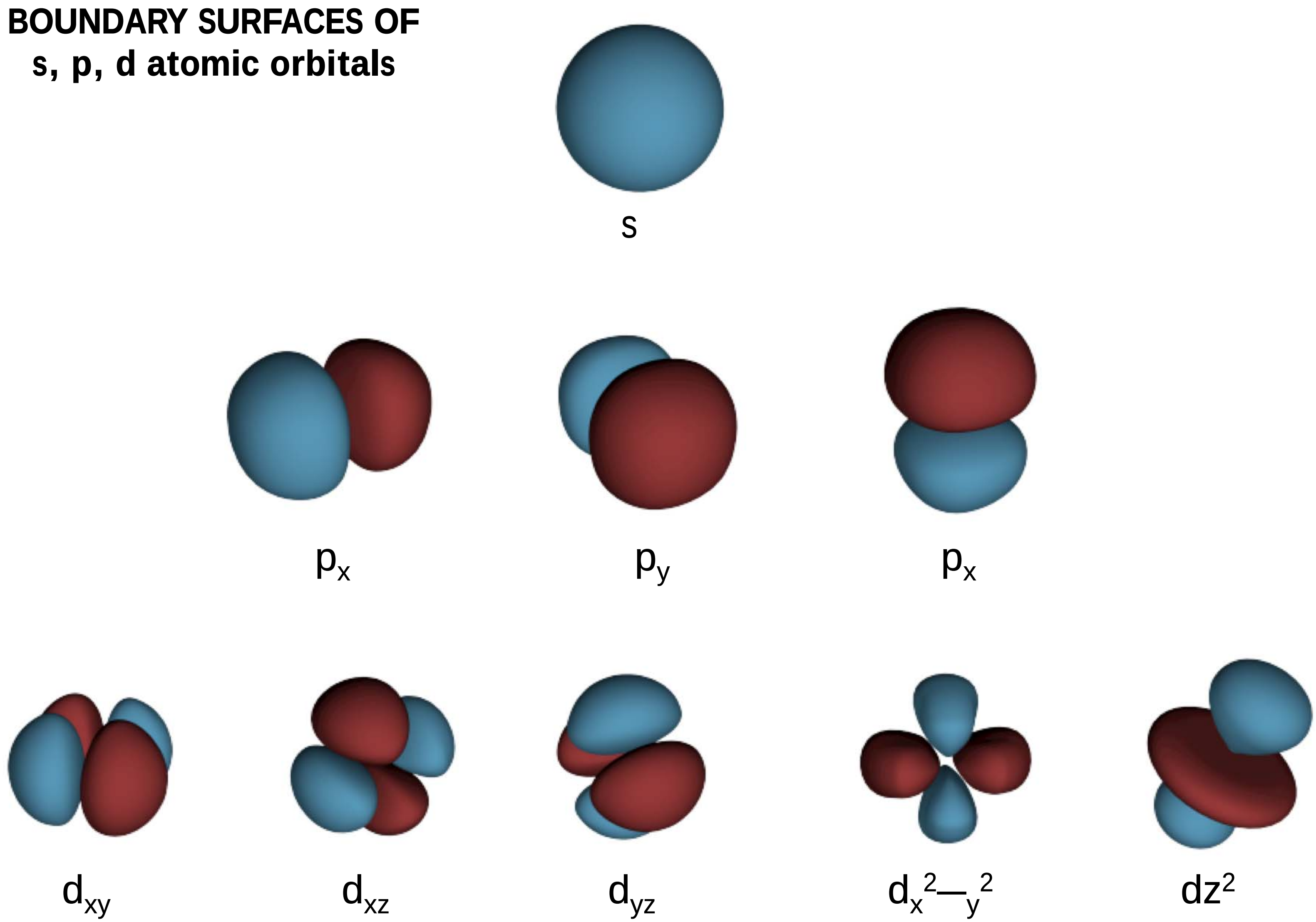
$$E_{1s} = -I_H$$

$$E_{2p} = -I_H/4$$

$a_0$ = 0.0529 nm
$I_H$ = 13.606 eV

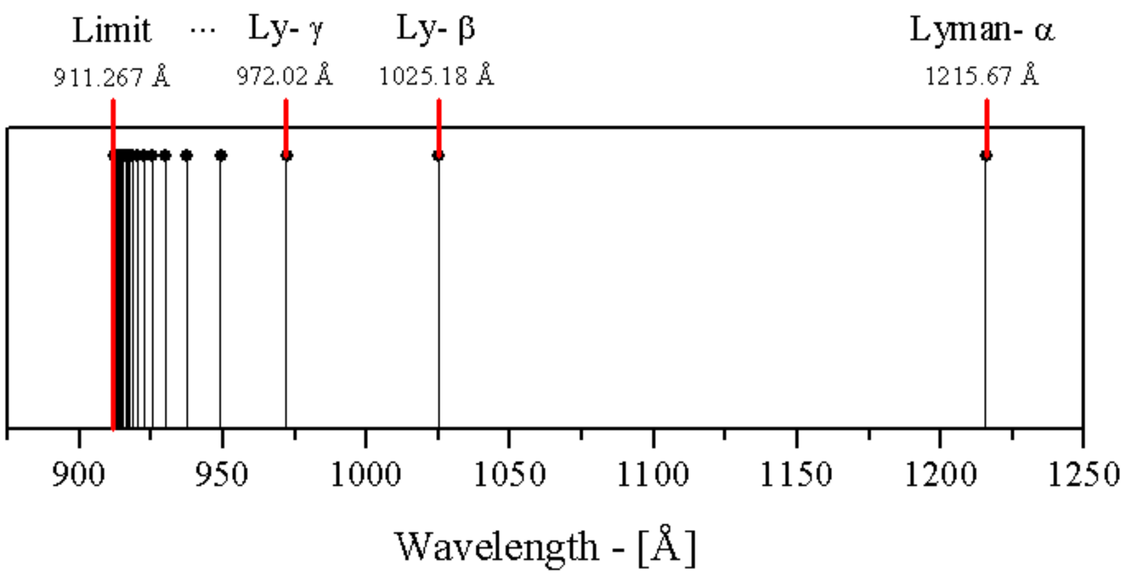
These are some solutions, without normalization.

# *Solutions*



**BOUNDARY SURFACES OF**
**s, p, d atomic orbitals**
s
$p_x$
$p_y$
$p_x$
$d_{xy}$
$d_{xz}$
$d_{yz}$
$d_{x^2—y^2}$
$dz^2$

# *1s-np transitions in atomic hydrogen*

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The Lyman alpha blob, so called because of its Lyman alpha emission line, photons must be redshifted to be transmitted through the atmosphere

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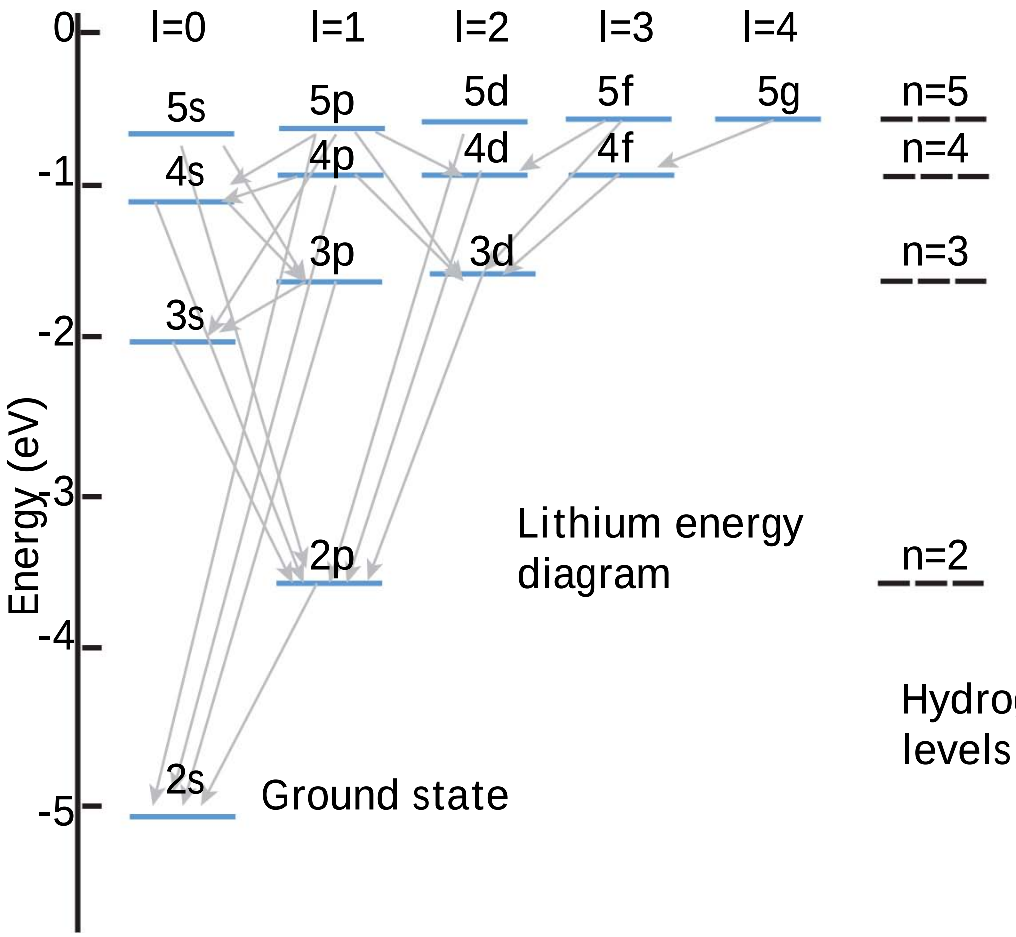
# *Energy Levels of Atomic Lithium*

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Ground state is $1s^2 2s$, excited states shown are $1s^2 np$

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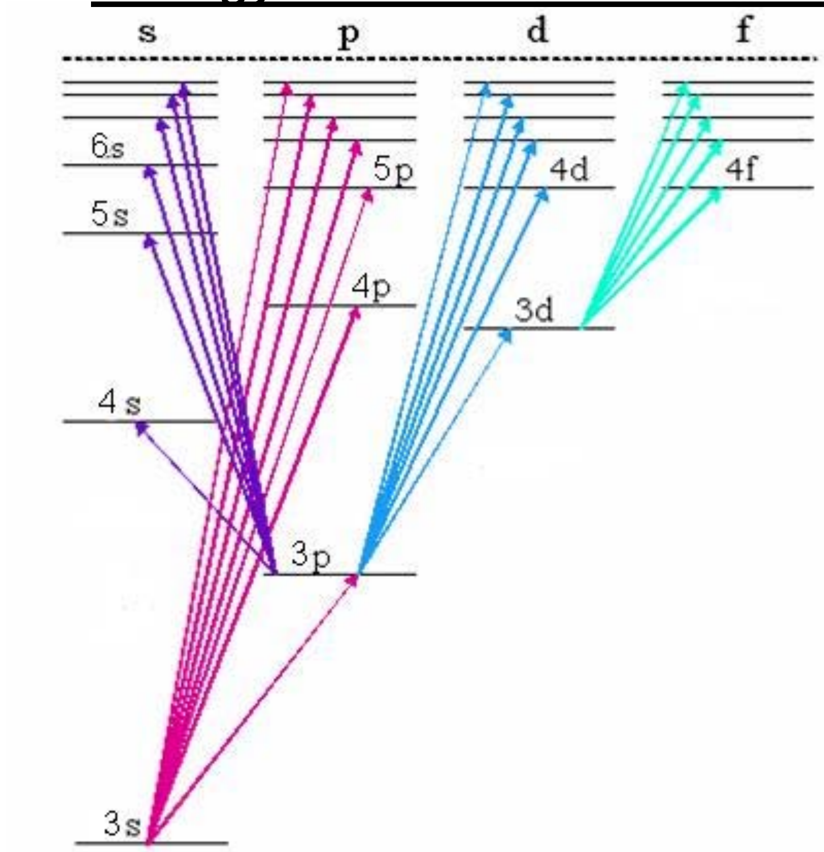
# *Energy Levels of Atomic Sodium*

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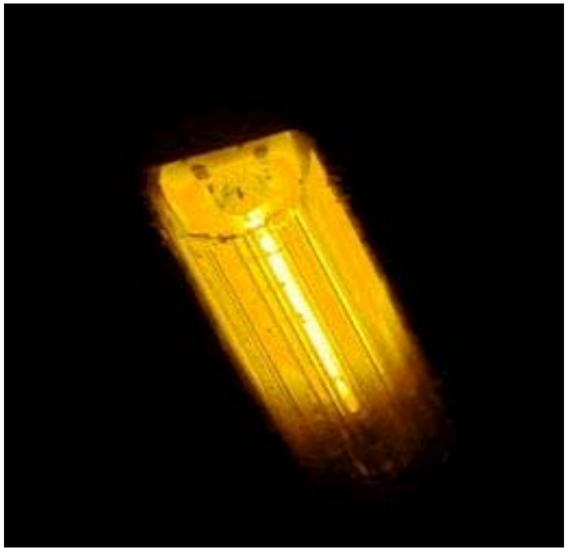

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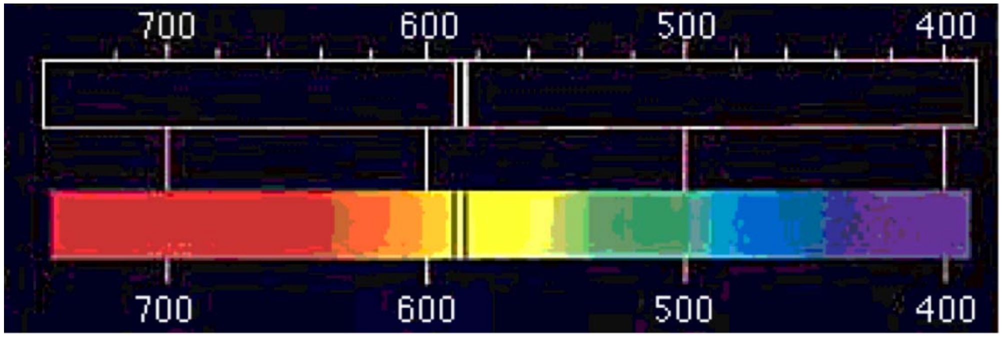


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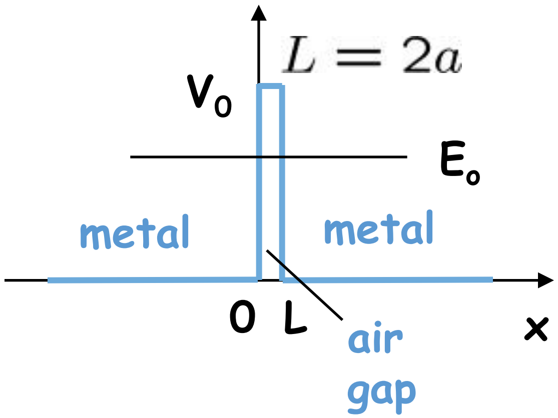
# *Example: Barrier Tunneling*

- Let's consider a tunneling problem:

An electron with a total energy of $E_o = 6$ eV approaches a potential barrier with a height of $V_0 = 12$ eV. If the width of the barrier is L = 0.18 nm, what is the probability that the electron will tunnel through the barrier?




$$T = \left|\frac{F}{A}\right|^2 \approx \frac{16E_o(V - E_o)}{V^2} e^{-2\kappa L}$$

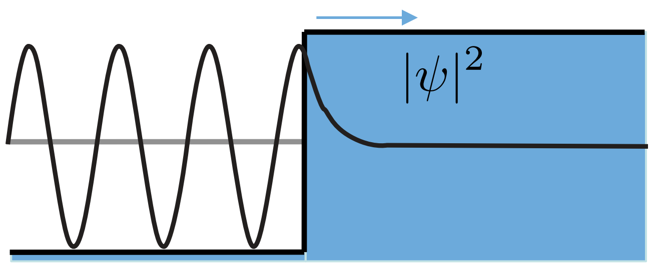
$$\kappa = \sqrt{\frac{2m_e}{\hbar^2}(V_o - E)} = 2\pi\sqrt{\frac{2m_e}{\hbar^2}(V_o - E)} = 2\pi\sqrt{\frac{6\text{ eV}}{1.505\text{ eV-nm}^2}} \approx 12.6\text{ nm}^{-1}$$

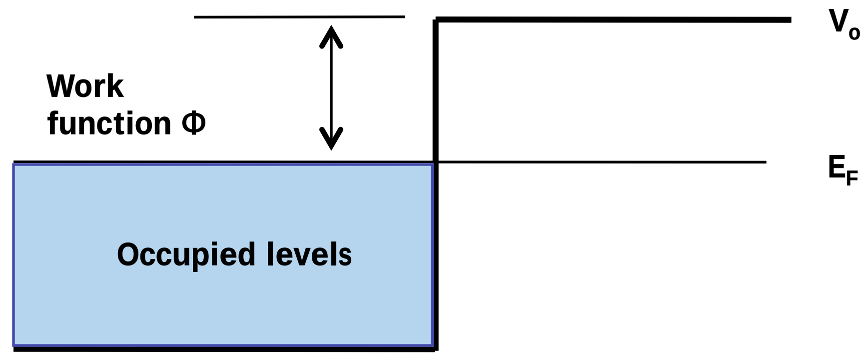
$$T = 4e^{-2(12.6\text{ nm}^{-1})(0.18\text{ nm})} = 4(0.011) = \boxed{4.4\%}$$

**Question: What will T be if we double the width of the gap?**

# *Leaky Particles*

Due to “barrier penetration”, the electron density of a metal actually extends outside the surface of the metal !



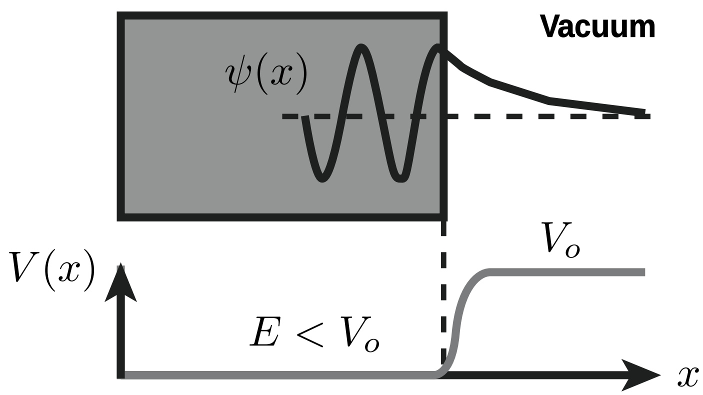

Assume that the work function (i.e., the energy difference between the most energetic conduction electrons and the potential barrier at the surface) of a certain metal is $\Phi = 5$ eV. Estimate the distance $x$ outside the surface of the metal at which the electron probability density drops to 1/1000 of that just inside the metal.

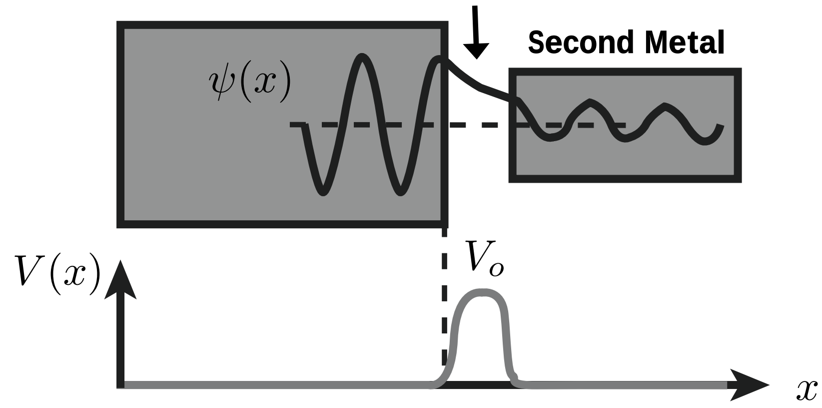
(Note: in previous slides the thickness of the potential barrier was defined as $x = 2a$)

$$\frac{|\psi(x)|^2}{|\psi(0)|^2} = e^{-2\kappa x} \approx \frac{1}{1000} \quad \Rightarrow \quad x = -\frac{1}{2\kappa}\ln\left(\frac{1}{1000}\right) \approx 0.3 \text{ nm}$$

using $\kappa = \sqrt{\frac{2m_e}{\hbar^2}(V_o - E)} = 2\pi\sqrt{\frac{2m_e}{h^2}\Phi} = 2\pi\sqrt{\frac{5 \text{ eV}}{1.505 \text{ eV}\cdot\text{nm}^2}} = 11.5 \text{ nm}^{-1}$

# *Application: Scanning Tunneling Microscopy*



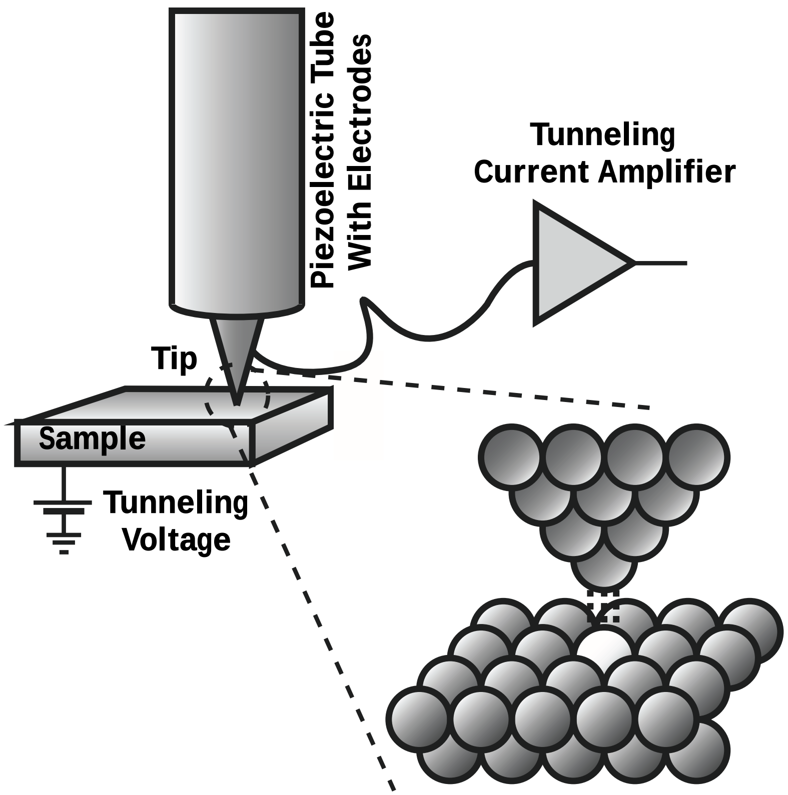




Image originally created by IBM Corporation.

6.007 Electromagnetic Energy: From Motors to Lasers
Spring 2011