Semiconductors

Outline

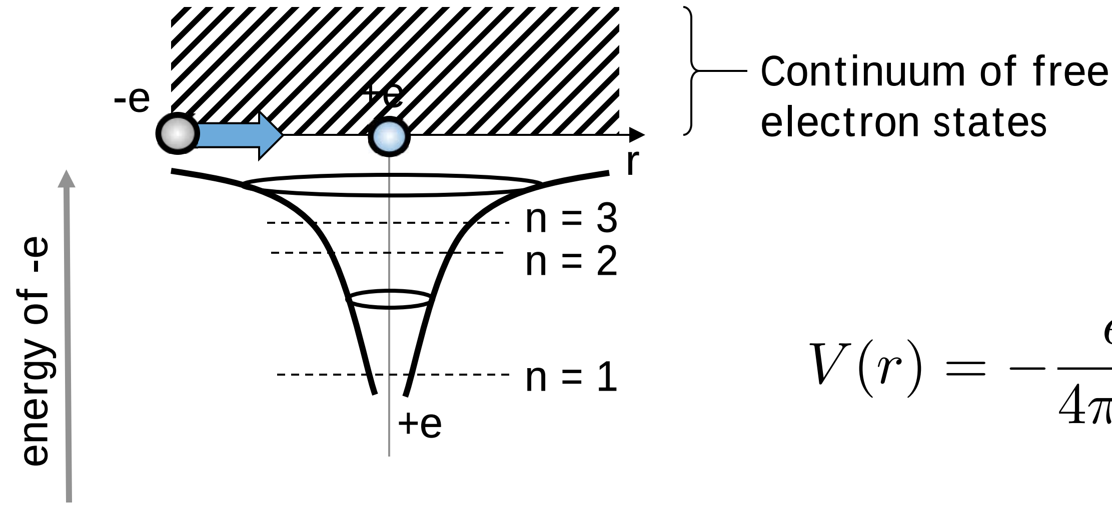
- Crystals: Atomic Solids
- Conductors and Insulators
- Doped Semiconductors

Bonding Between Atoms

How can two neutral objects bind together?

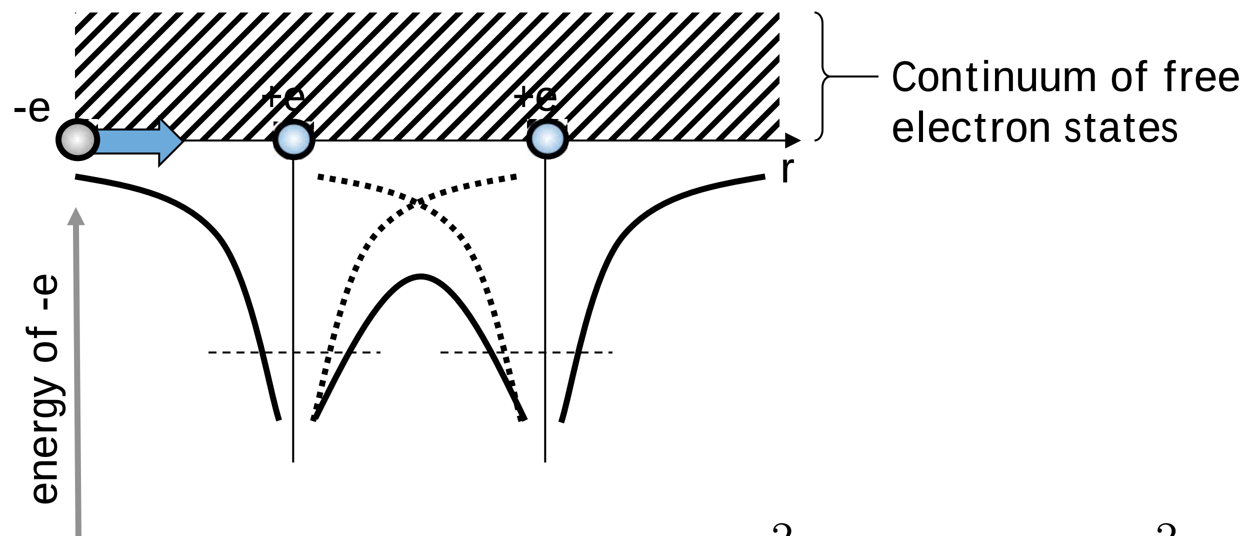
$H + H \rightarrow H_2$

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



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

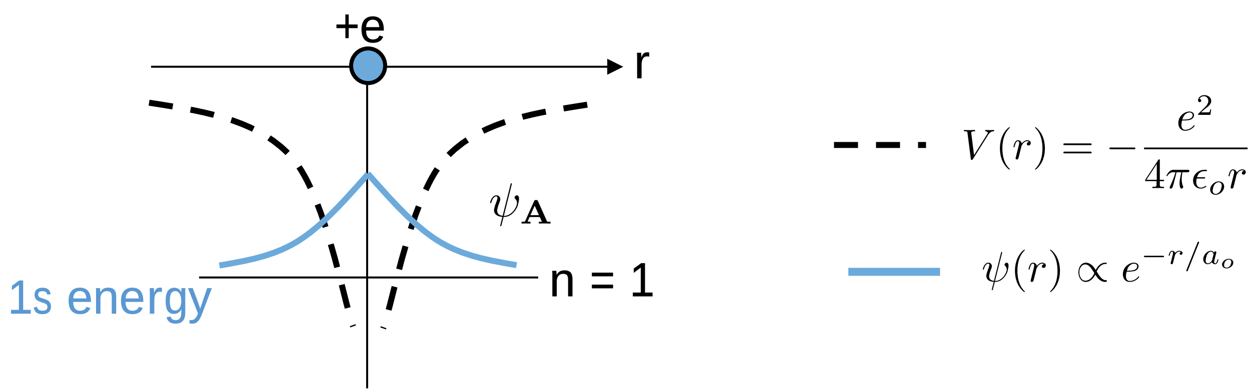
Superposition of Coulomb potentials H_2:



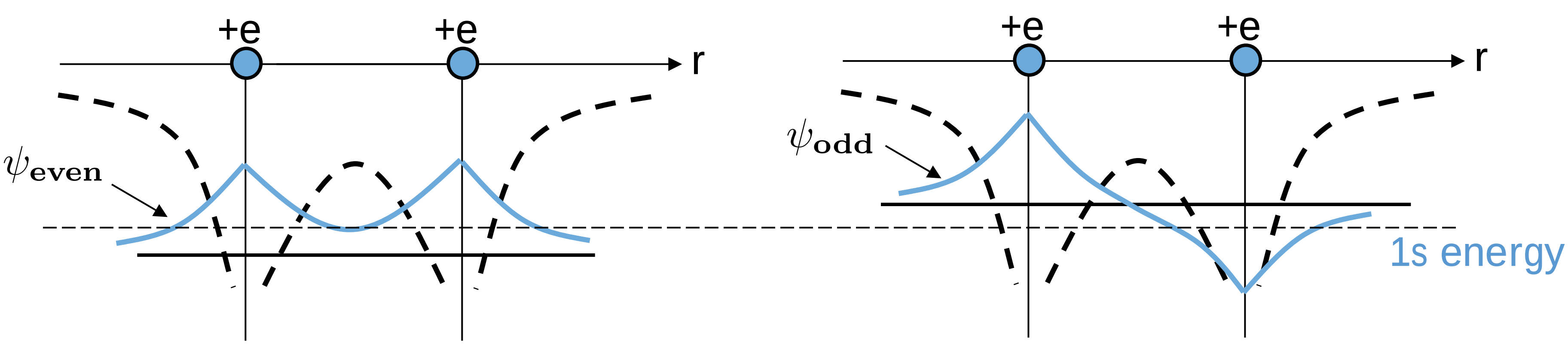
$$V(r) = -\frac{e^2}{4\pi\epsilon_o|r - r_1|} - \frac{e^2}{4\pi\epsilon_o|r - r_2|}$$

Molecular Wavefunctions

Atomic ground state:
(1s)



Molecular states:

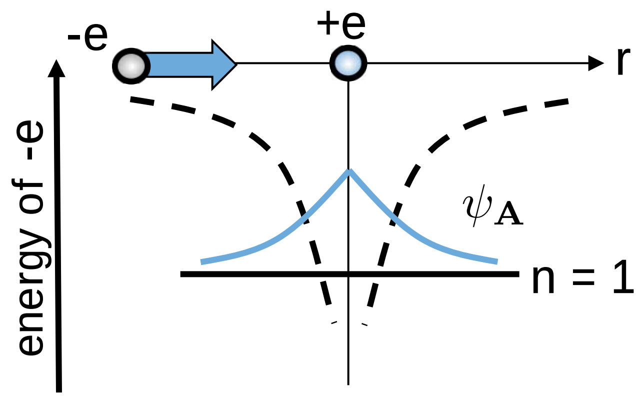


Bonding state

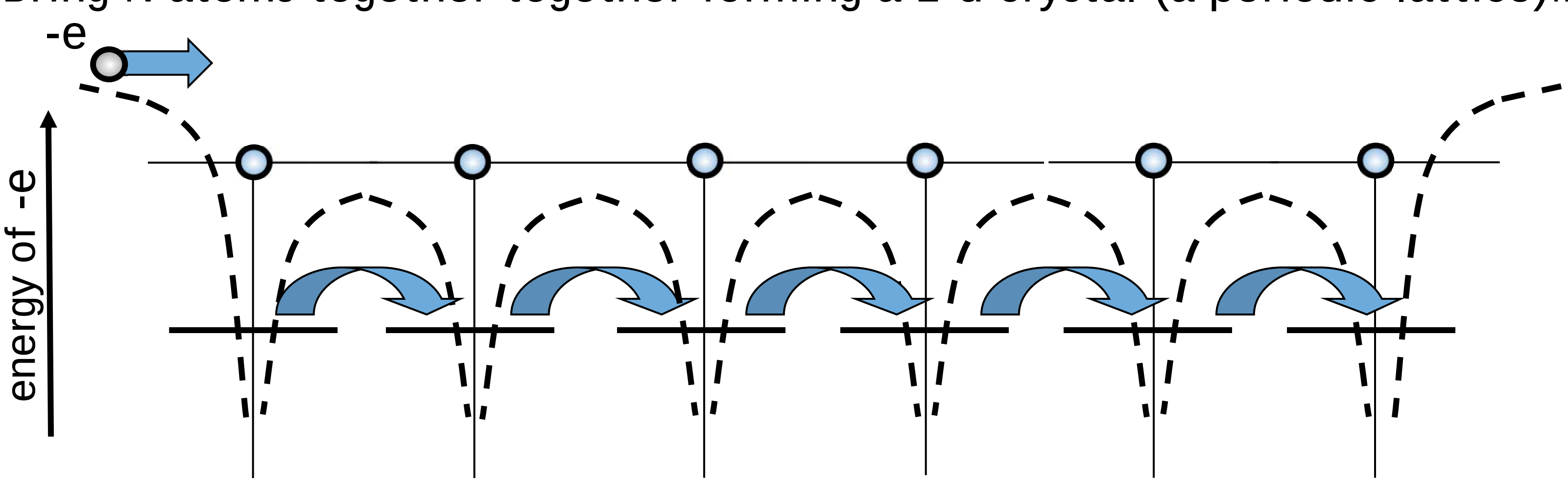
Antibonding state

Tunneling Between Atoms in Solids

Again start with simple atomic state:

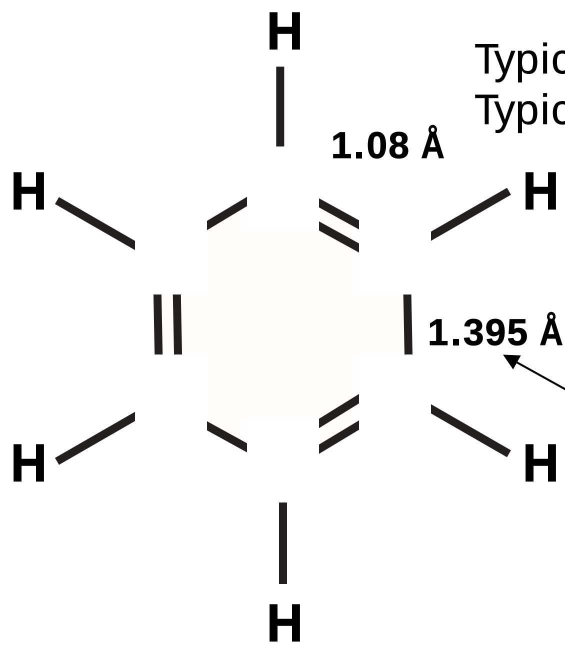


Bring N atoms together together forming a 1-d crystal (a periodic lattice)...



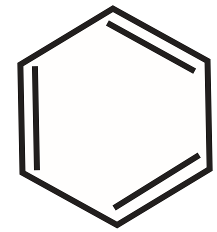
Let's Take a Look at Molecular Orbitals of Benzene

… the simplest "conjugated alkene"

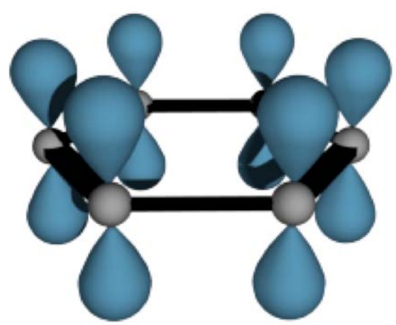


Typical C-C bond length 1.54 Å
Typical C=C bond length 1.33 Å

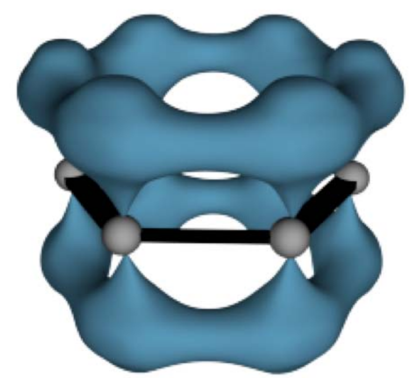
or



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

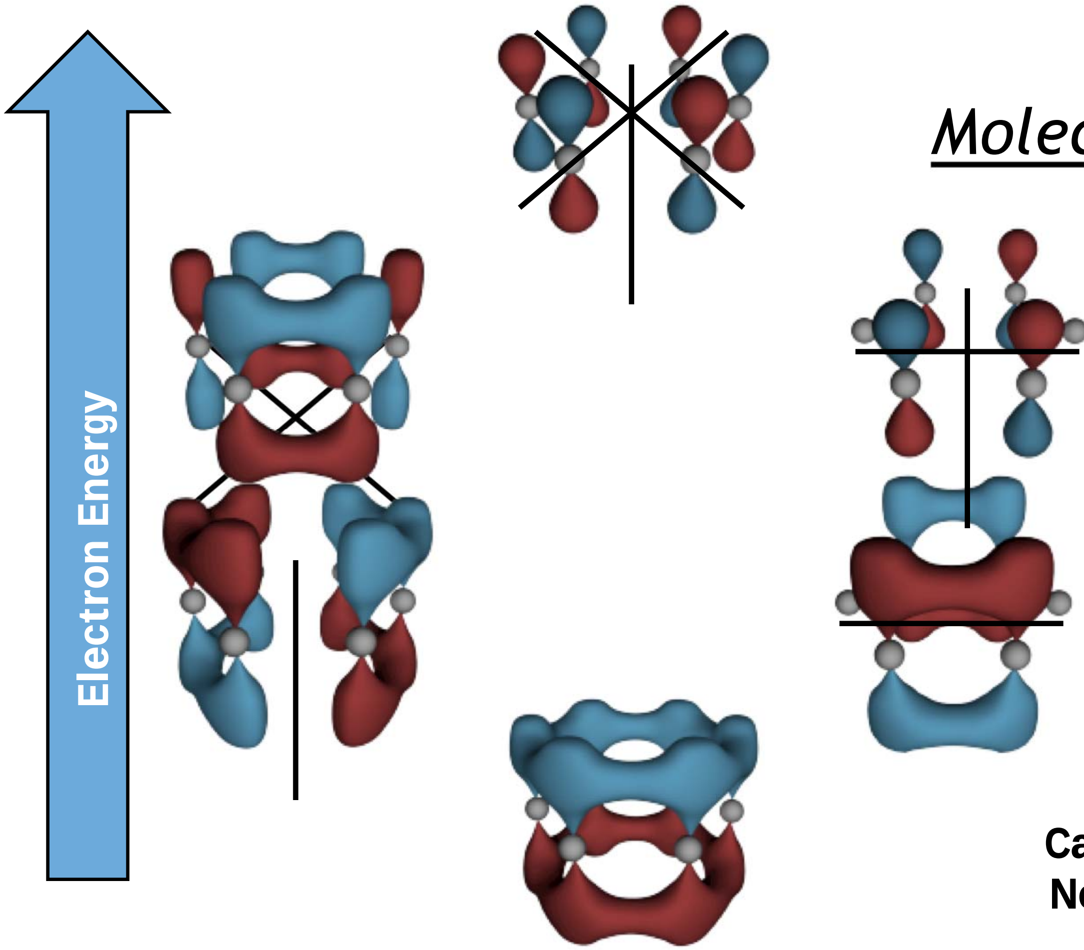


p orbitals



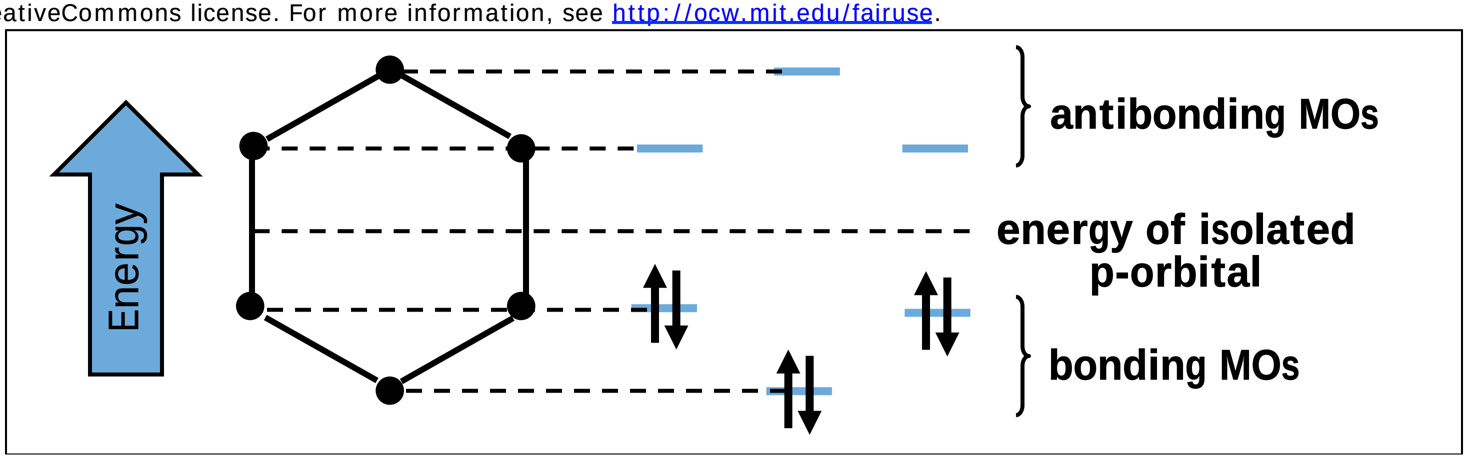
π-electron density

Molecular Orbitals of Benzene



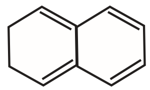
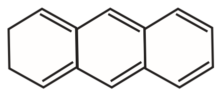
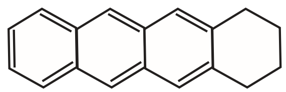
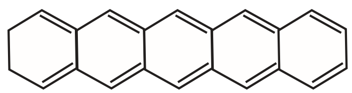
Energy distribution of Benzene π-molecular orbitals

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

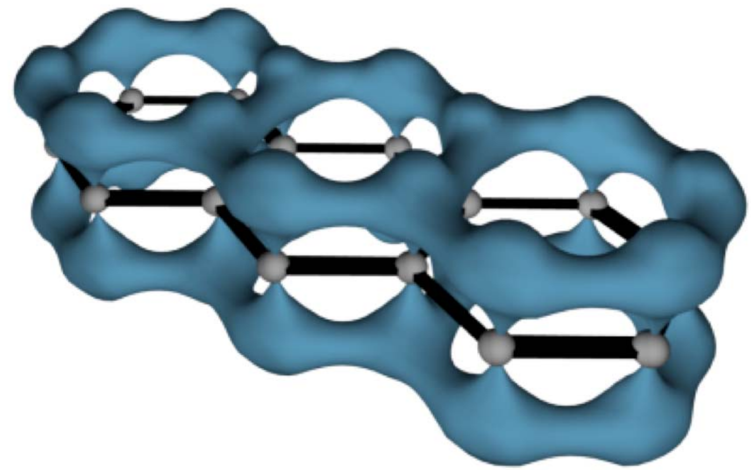


from Loudon

... *More Examples - Series of Polyacene Molecules*

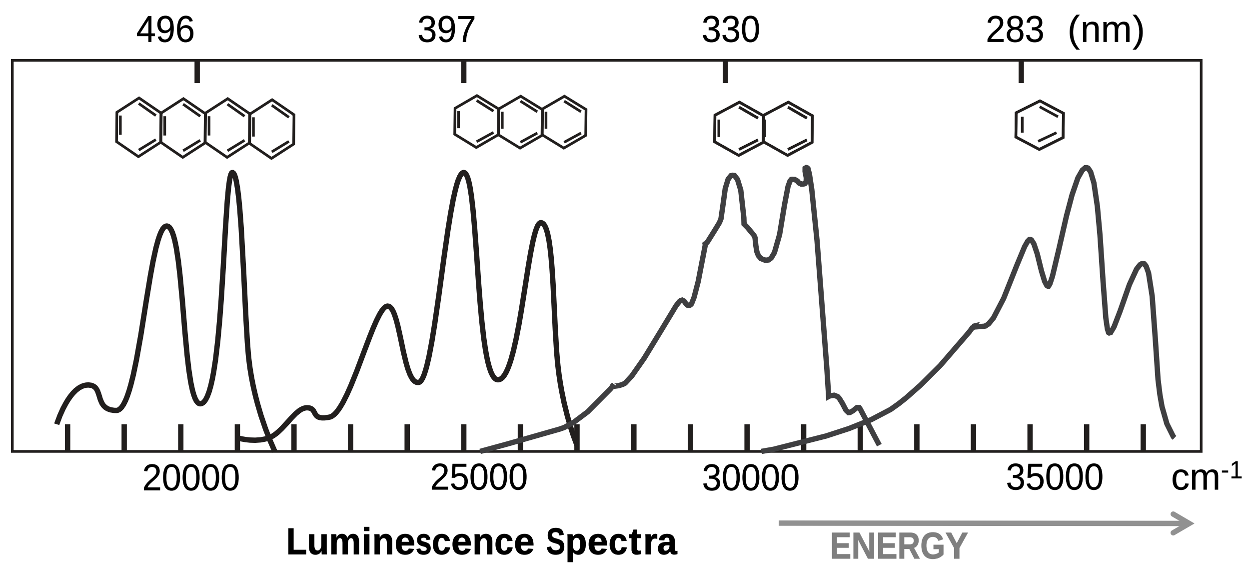
Molecule		**Absorption** ... LOWEST ENERGY ABSORPTION PEAK AT ...
Benzene		255 nm
Naphthaline		315 nm
Anthracene		380 nm
Tetracene		480 nm
Pentacene		580 nm

The lowest bonding MO of anthracene



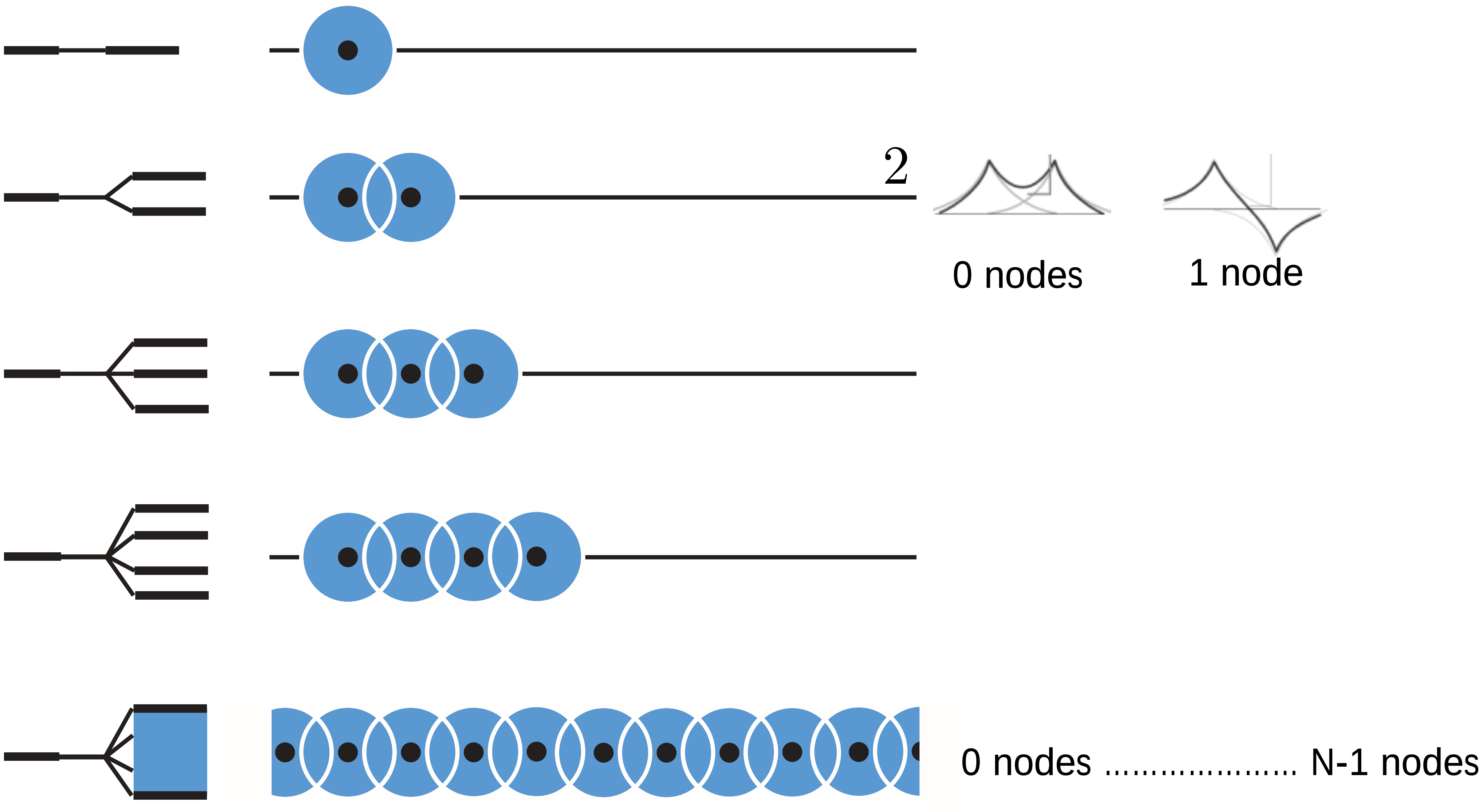
Red: bigger molecules !

Blue: smaller molecules !



Luminescence Spectra

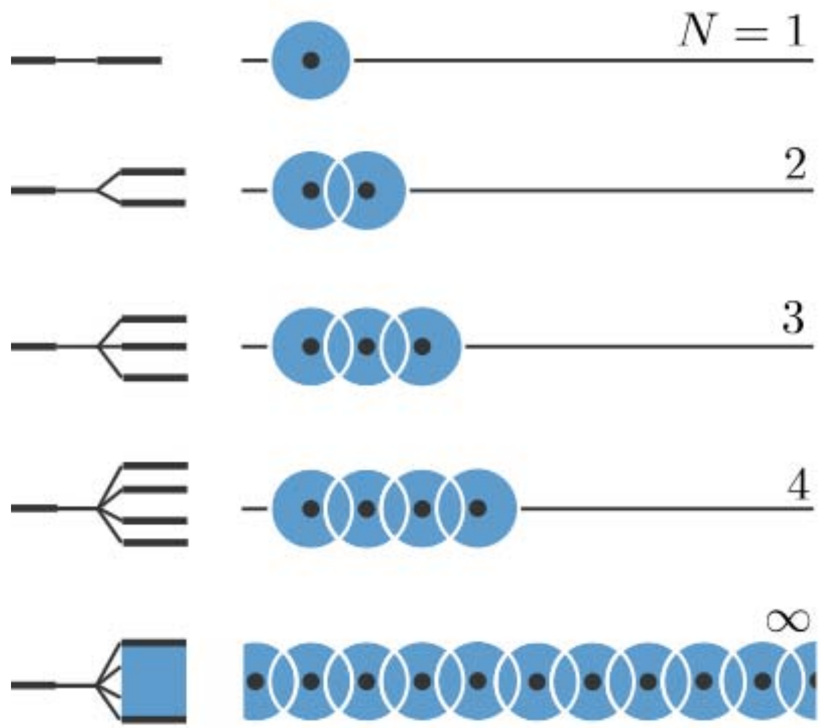
From Molecules to Solids



Number of atoms = number of states

1-D Lattice of Atoms

Single orbital, single atom basis



Adding atoms…

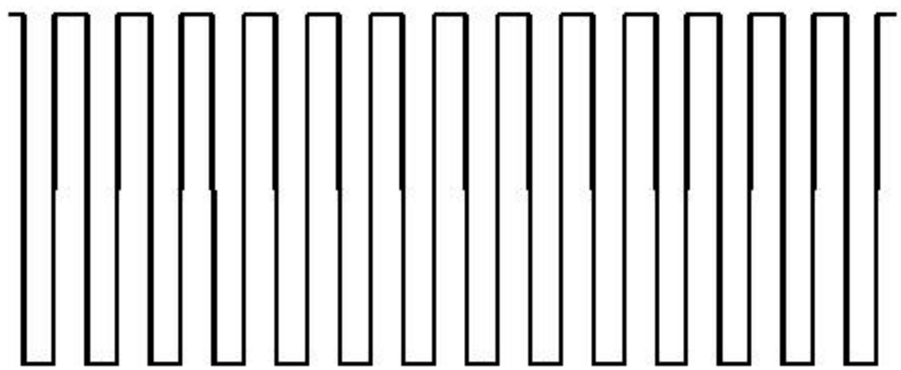
- reduces curvature of lowest energy state (incrementally)
- increases number of states (nodes)
- beyond ~10 atoms the bandwidth does not change with crystal size

Decreasing distance between atoms (lattice constant) …

- increases bandwidth

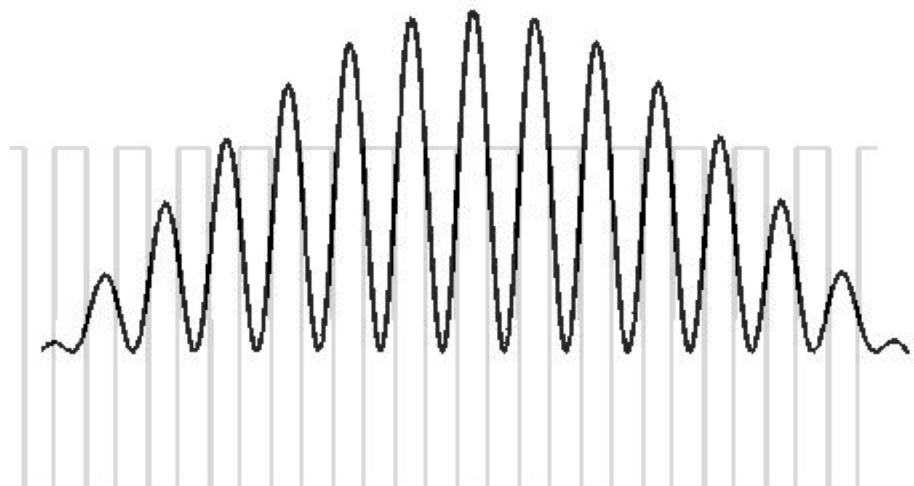
Consider a set of quantum wells

$V(x)$



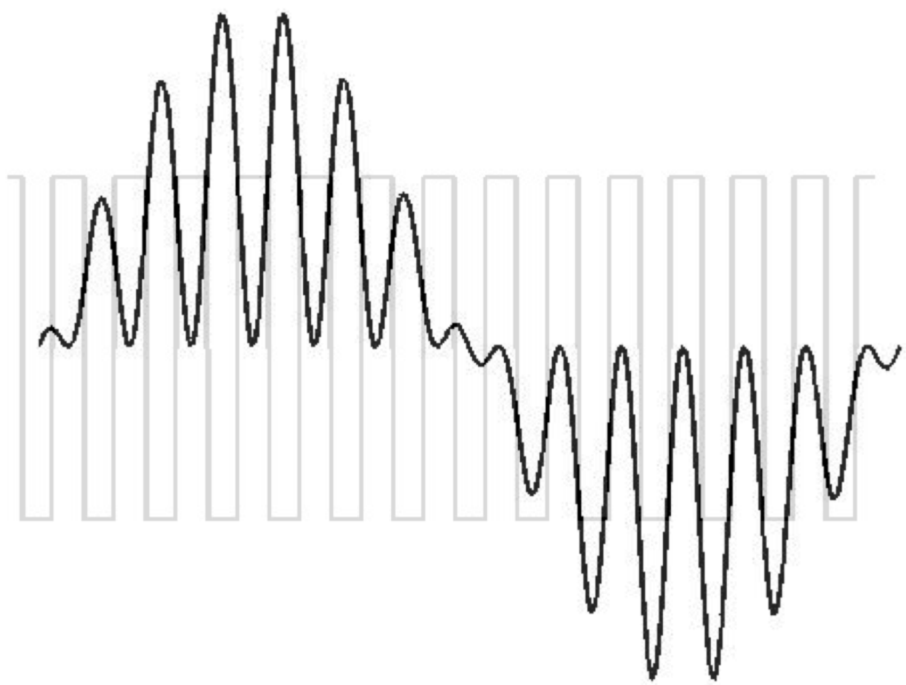
Ground state solution

$\Psi_0(x)$



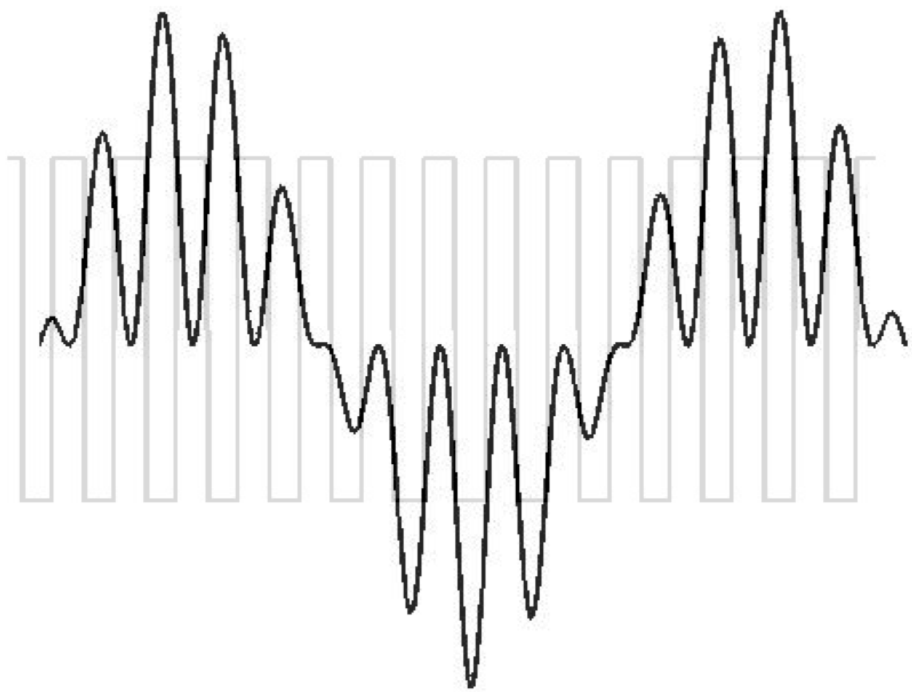
First excited state solution

$\Psi_1(x)$



Second excited state solution

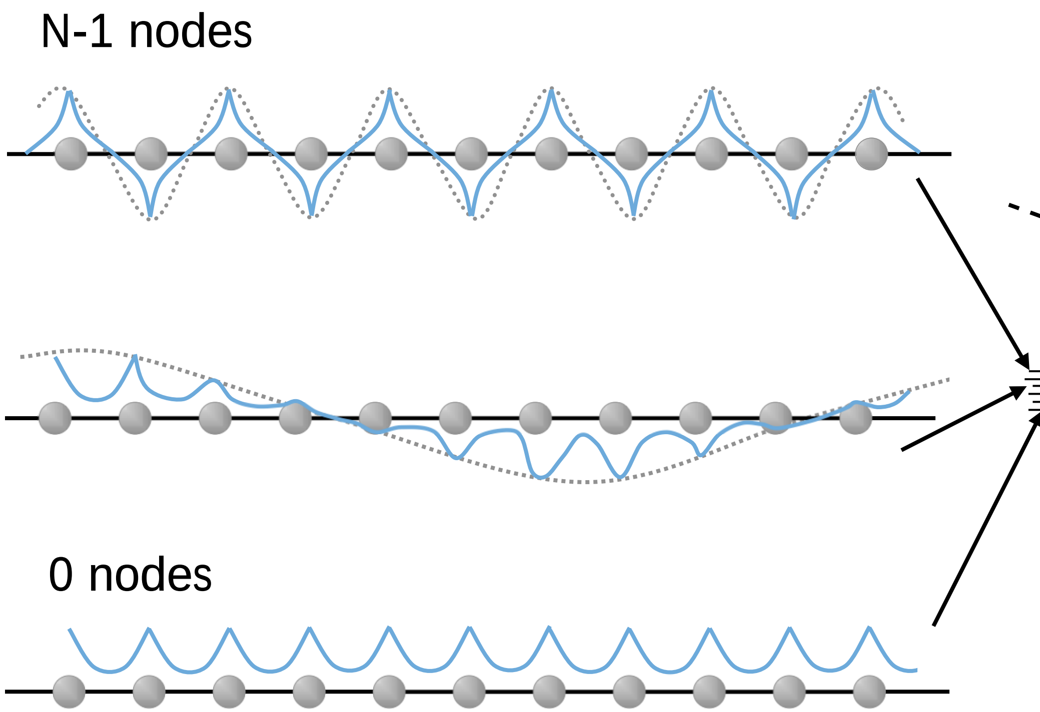
$$\Psi_2(x)$$

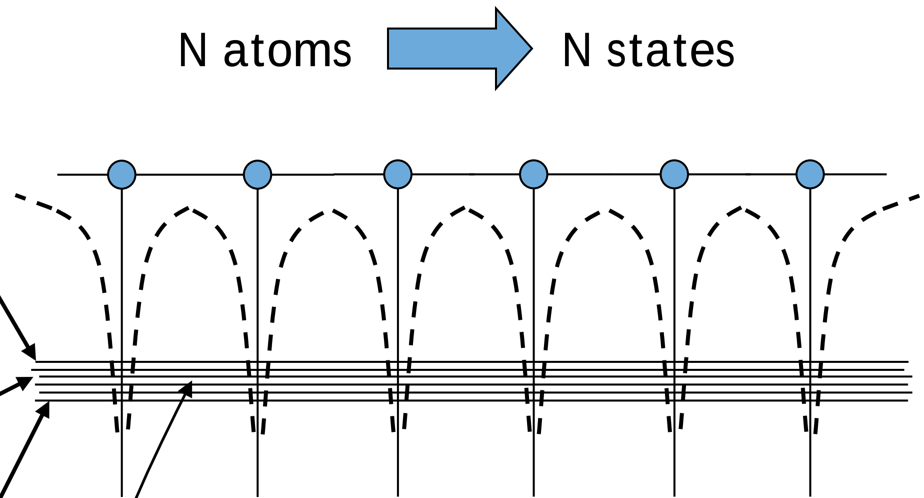


Interpretation of the Wavefunction Shapes

- Envelope of wavefunction seems to work like wavefunction for a particle in a box
- Wavefunctions local to a single well look like ground state wavefunction for a well in isolation
- Same kind of effect occurs with atomic potentials instead of quantum well potentials

From Molecules to Solids

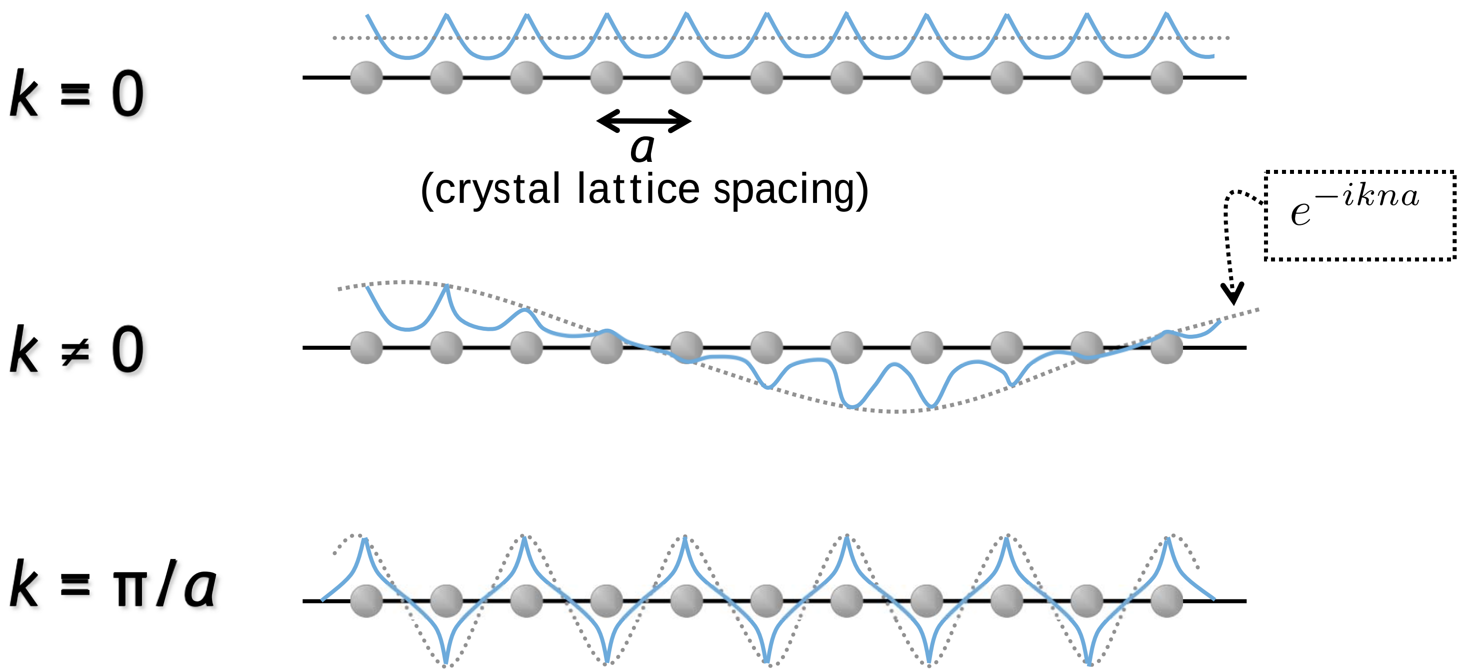




Closely spaced energy levels form a "band" of energies between the max and min energies

Approximate Wavefunction for 1-D Lattice

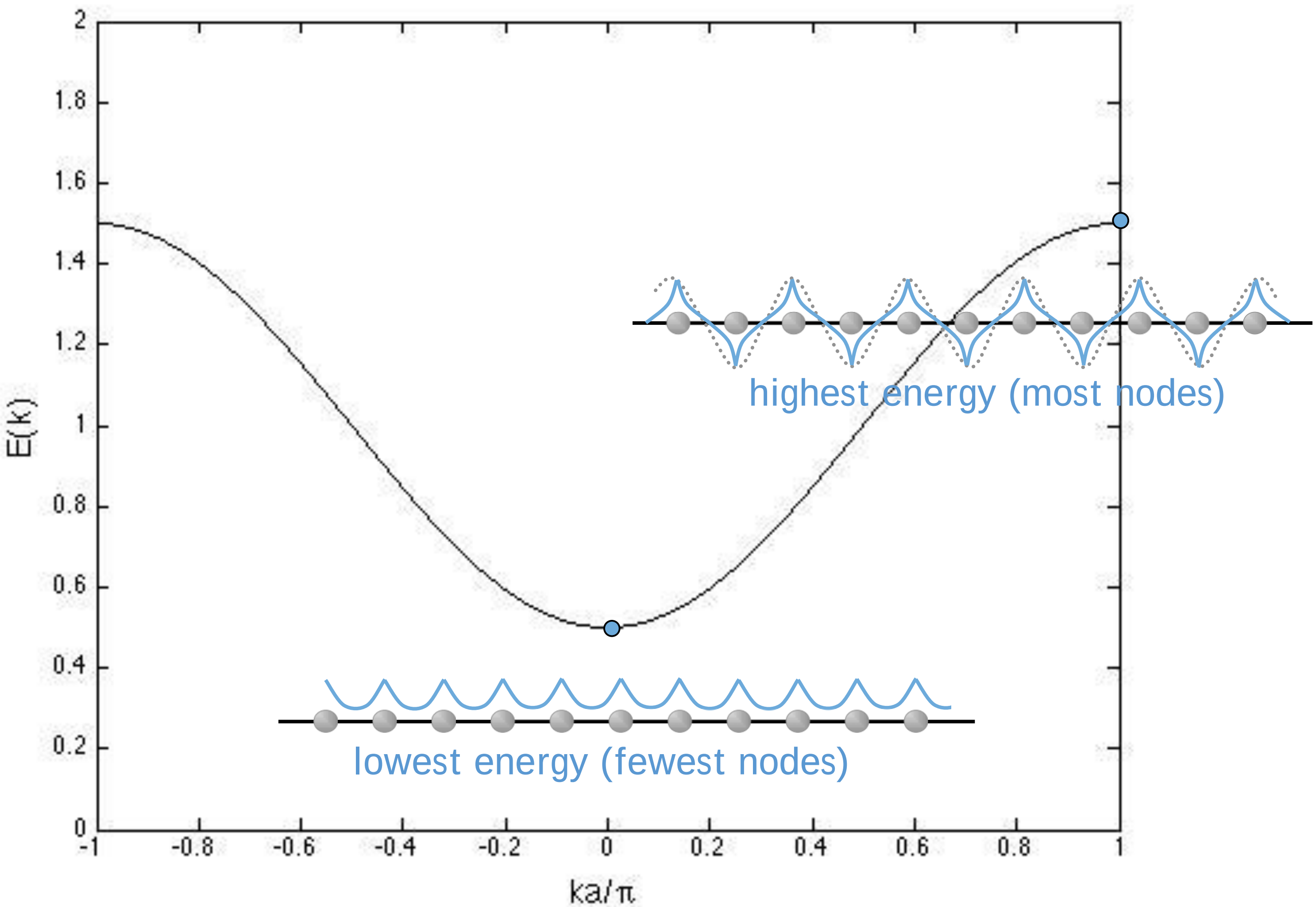
Single orbital, single atom basis



k is a convenient way to enumerate the different energy levels
(count the nodes)

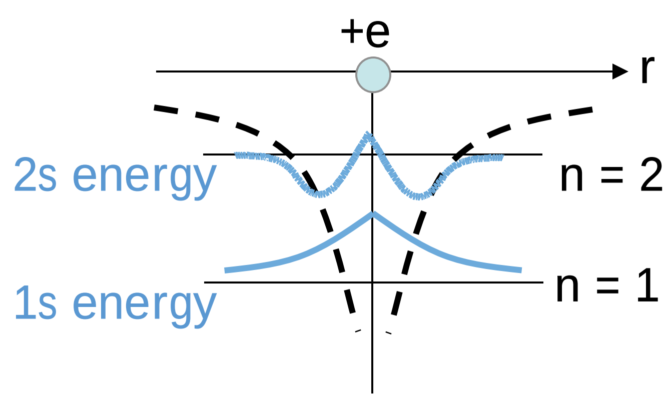
Bloch Functions: $\psi_{n,k}(r) = u_{n,k}(r)e^{ikr}$ $\quad u_{n,k}(r) \approx \text{orbitals}$

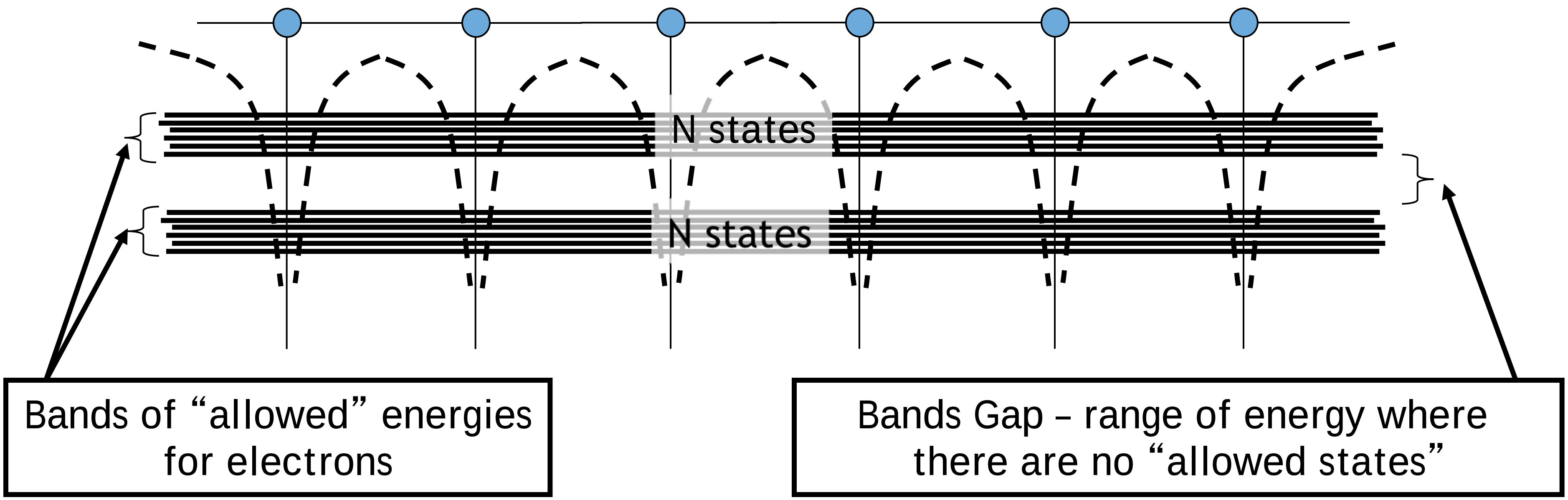
Energy Band for 1-D Lattice
Single orbital, single atom basis



- Number of states in band = number of atoms
- Number of electrons to <u>fill</u> band = number of atoms x 2 (spin)

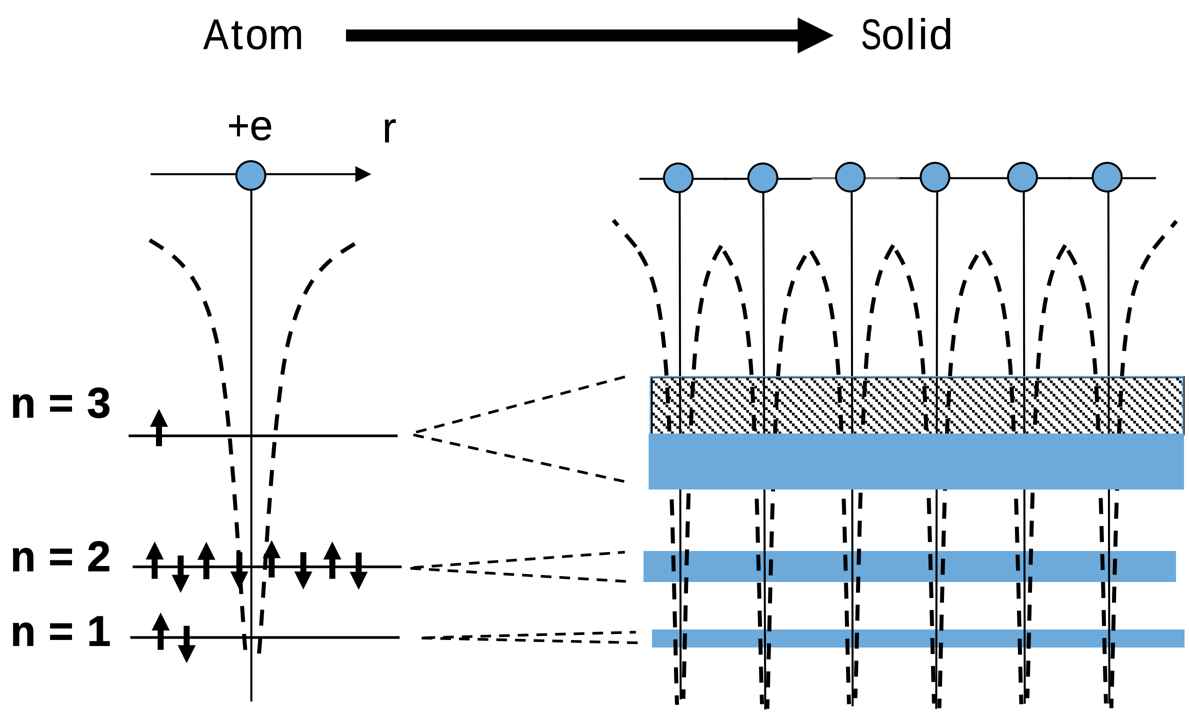
From Molecules to Solids





The total number of states = (number of atoms) x (number of orbitals in each atom)

Bands from Multiple Orbitals



Example of Na

Z = 11 $1s^2 2s^2 2p^6 3s^1$

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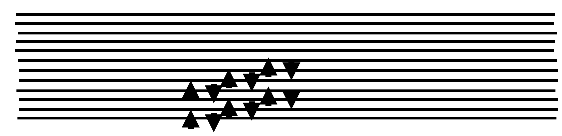


These two facts are the basis for our understanding of metals, semiconductors, and insulators !!!

- Each atomic state → a band of states in the crystal

  These are the "allowed" states for electrons in the crystal
  → Fill according to Pauli Exclusion Principle

- There may be gaps between the bands
  These are "forbidden" energies where there are no states for electrons

What do you expect to be a metal ?

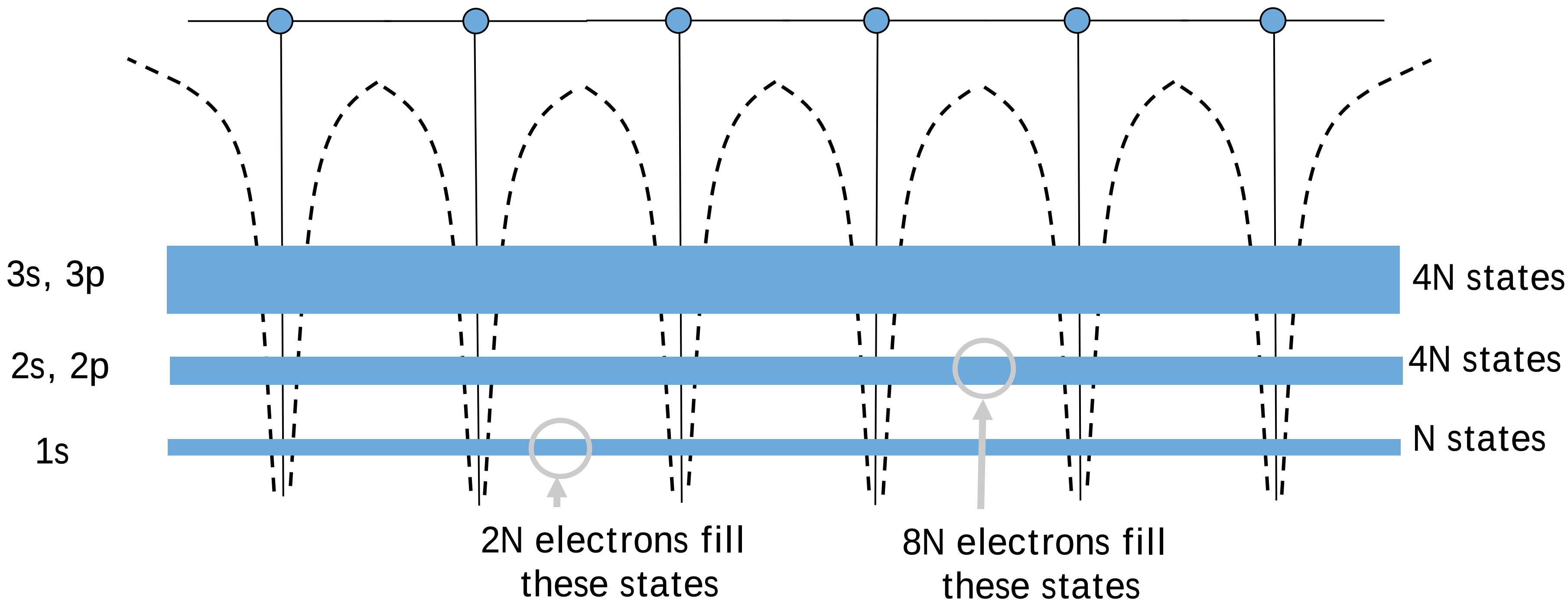
Na? Mg? Al? Si? P?

What about semiconductors like silicon?

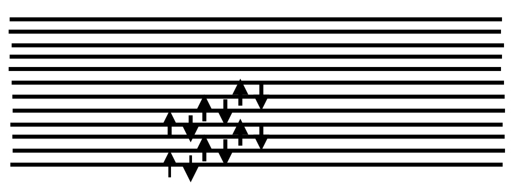
Fill the Bloch states according to Pauli Principle

$Z = 14$	$1s^2 2s^2 2p^6 3s^2 3p^2$

Total # atoms = N
Total # electrons = 14N



It appears that, like Na, Si will also have a half filled band: The 3s3p band has 4N orbital states and 4N electrons.



By this analysis, Si should be a good metal, just like Na.

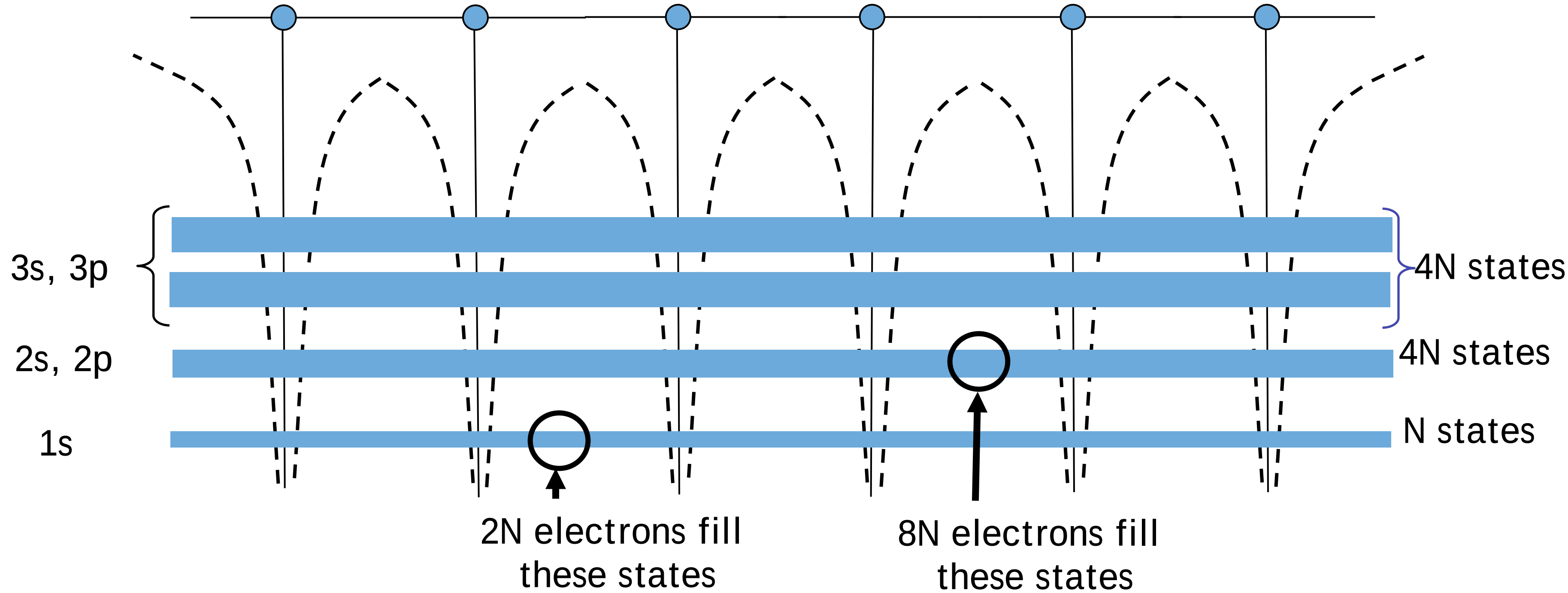
But something special happens for Group IV elements.

Silicon Bandgap

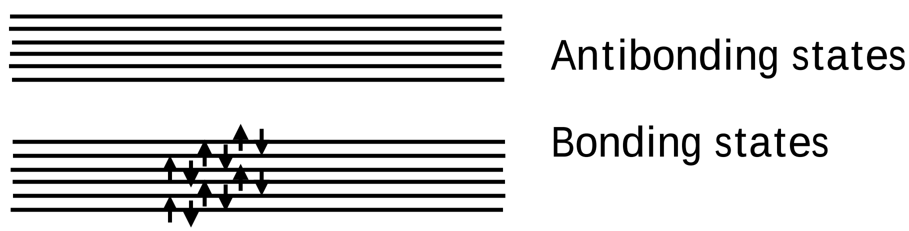
Fill the Bloch states according to Pauli Principle

Z = 14	$1s^2 2s^2 2p^6 3s^2 3p^2$

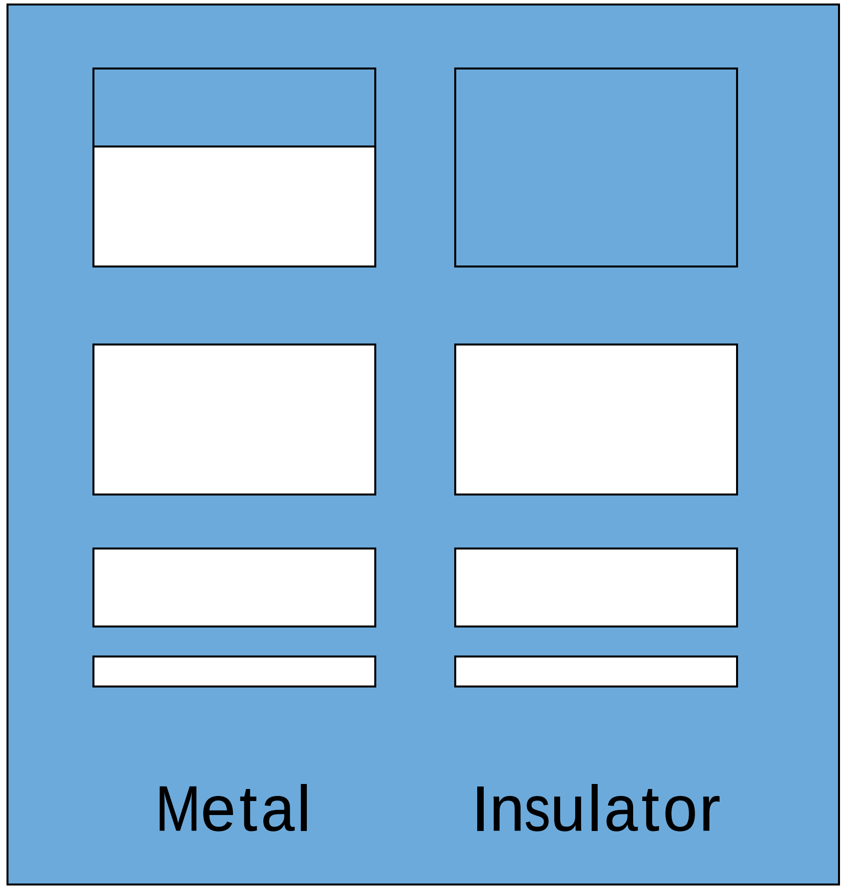
Total # atoms = N
Total # electrons = 14N



The 3s-3p band splits into two:



Conduction and Band-filling



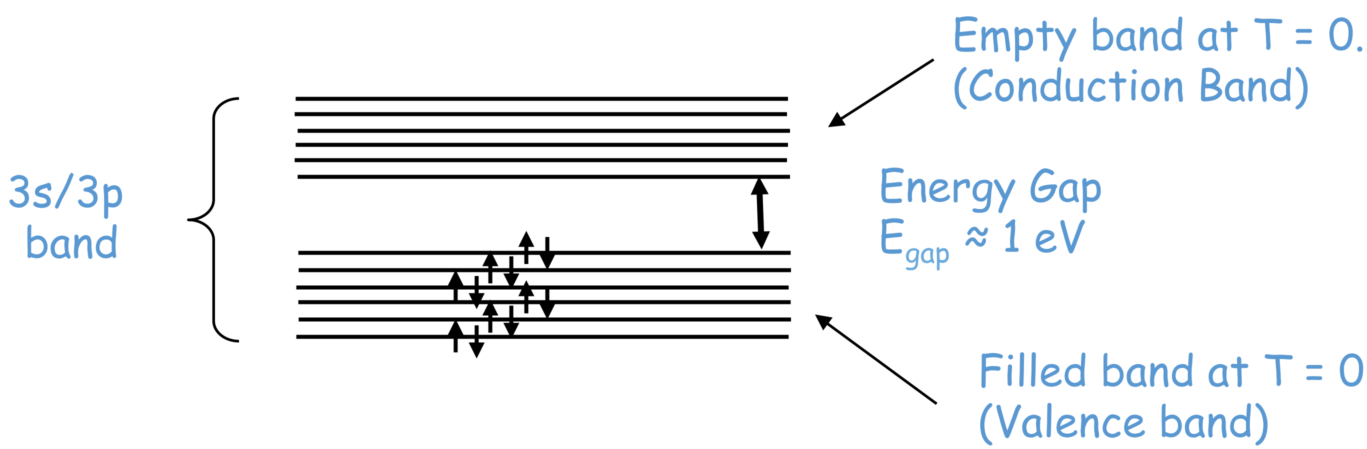
The electrons in a filled band cannot contribute to conduction, because with reasonable E fields they cannot be promoted to a higher kinetic energy.

Therefore, at T = 0, Si is an insulator. At higher temperatures, however, electrons are thermally promoted into the conduction band.

Electron States in Silicon

Electronic Conduction in a Semiconductor
- example: Si **Z = 14** **$1s^2 2s^2 2p^6 3s^2 3p^2$**

valence electrons



The electrons in a <u>filled band</u> cannot contribute to conduction, because with reasonable E fields they cannot be promoted to a higher kinetic energy.

Therefore, at T = 0, Si is an <u>insulator</u>. At higher temperatures, however, electrons are thermally promoted into the conduction band.

Making Silicon Conduct

Consider electrons in a semiconductor, e.g., silicon. In a perfect crystal at T=0 the valence bands are filled and the conduction bands are empty - no conduction. Which of the following could be done to make the material conductve?

a. heat the material

As we increase the temperature, such that $kT \rightarrow E_{gap}$, some electrons are excited to the conduction band

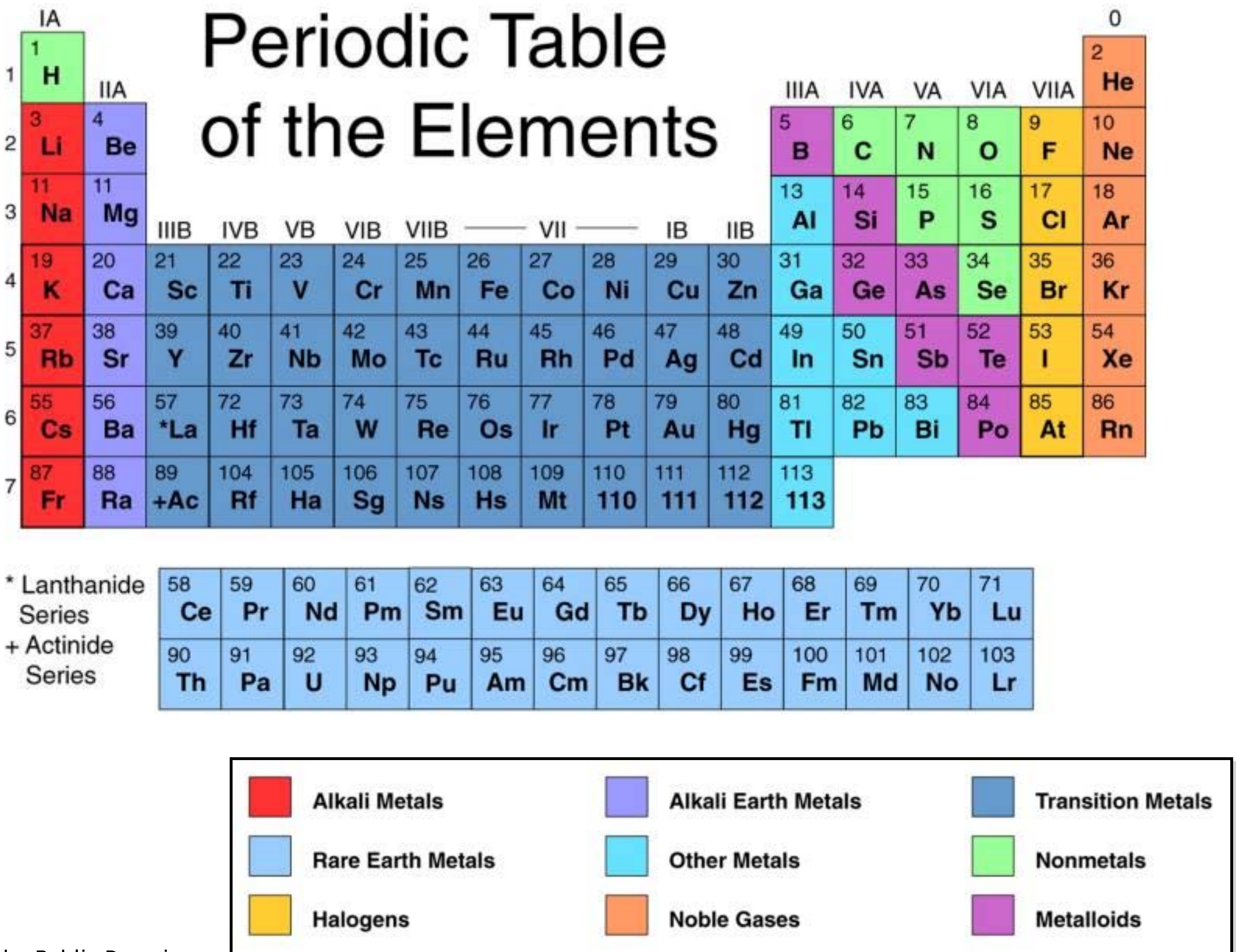
b. shine light on it

As we shine light on the material (with energy $E_{photon} > E_{gap}$), electron-hole pairs are created

c. add foreign atoms that change the number of electrons

"Donor" atoms (like P) have extra electrons to add to the crystal. The electrons are "donated" to the conduction band and they can conduct electricity.

"Acceptor" atoms (like B) have fewer electrons and they "accept" electrons from the crystal. This leaves missing electrons – called "holes" in the valence band so that it is not completely filled and can conduct electricity.



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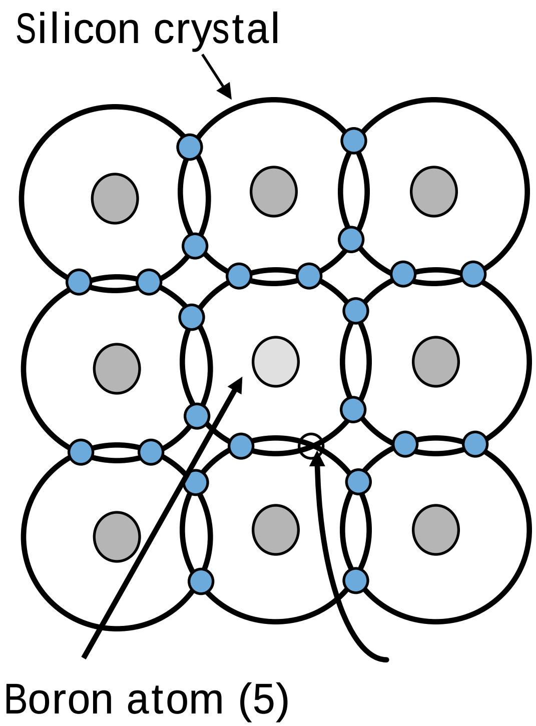
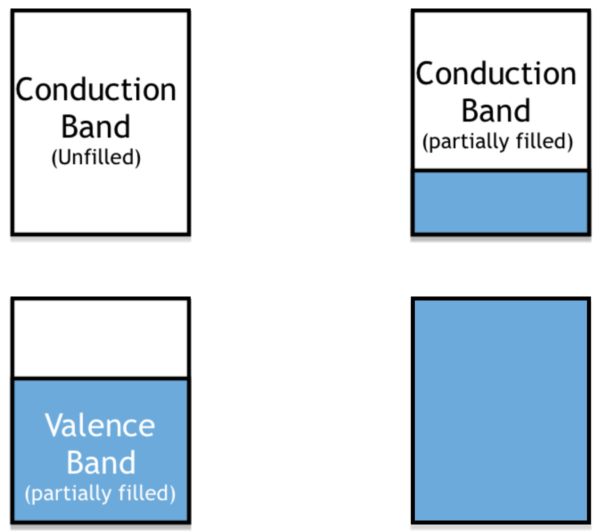
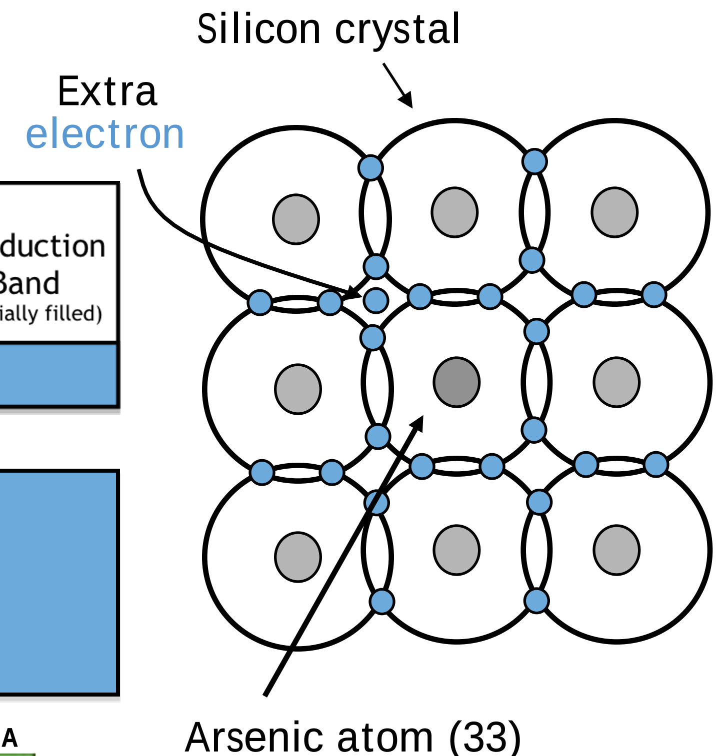
Controlling Conductivity: Doping Solids

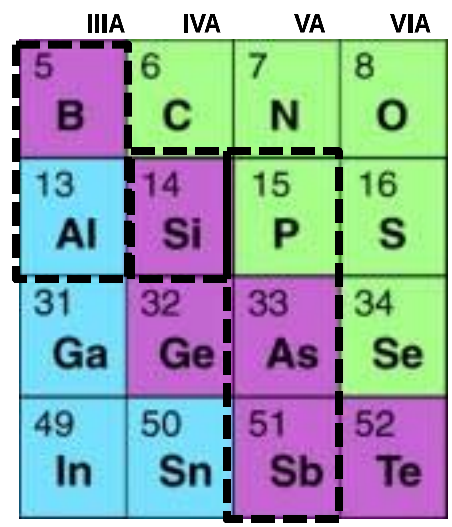


ACCEPTOR DOPING:
P-type Semiconductor
Dopants: B, Al





DONOR DOPING
N-type Semiconductor
Dopants: As, P, Sb



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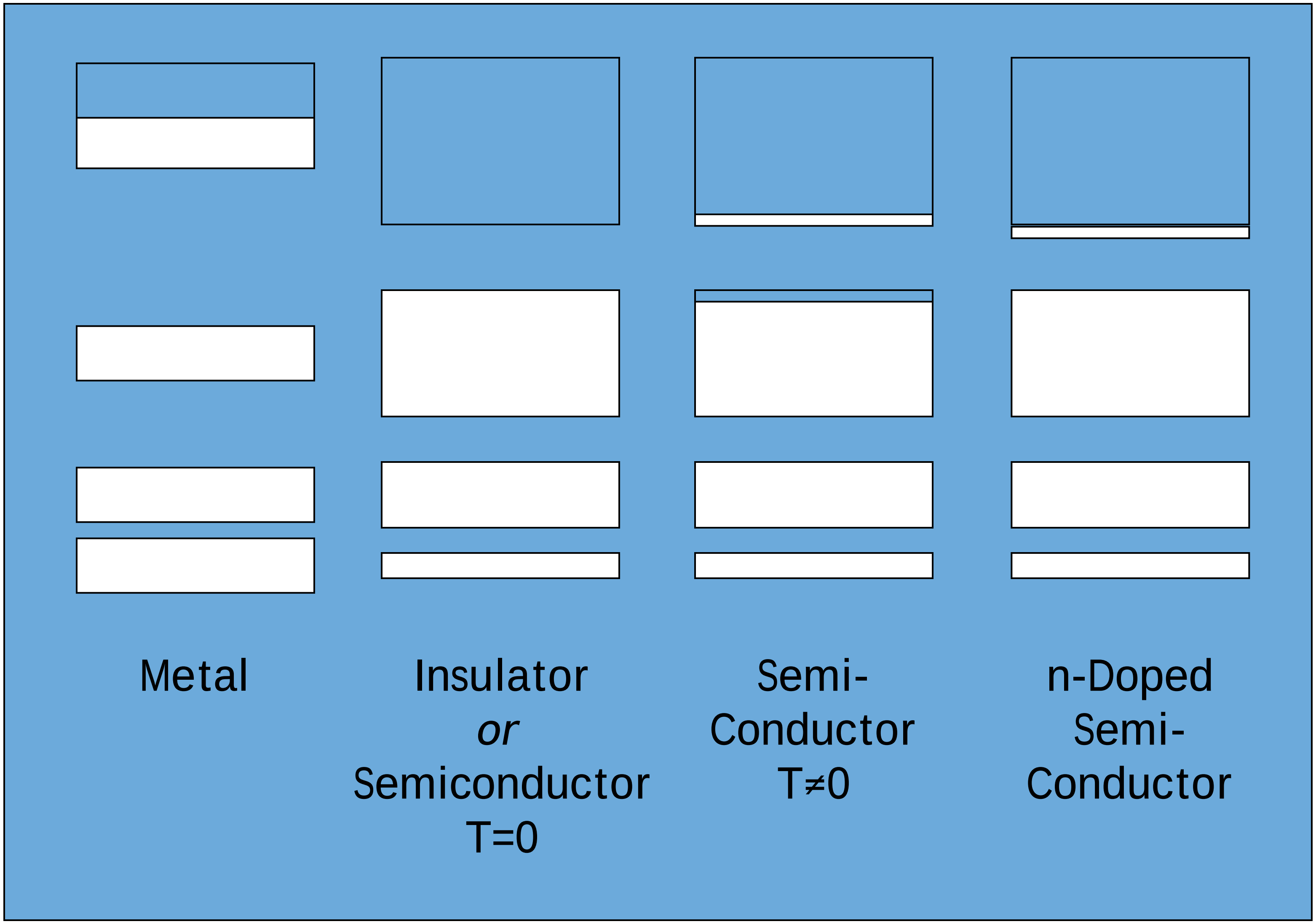
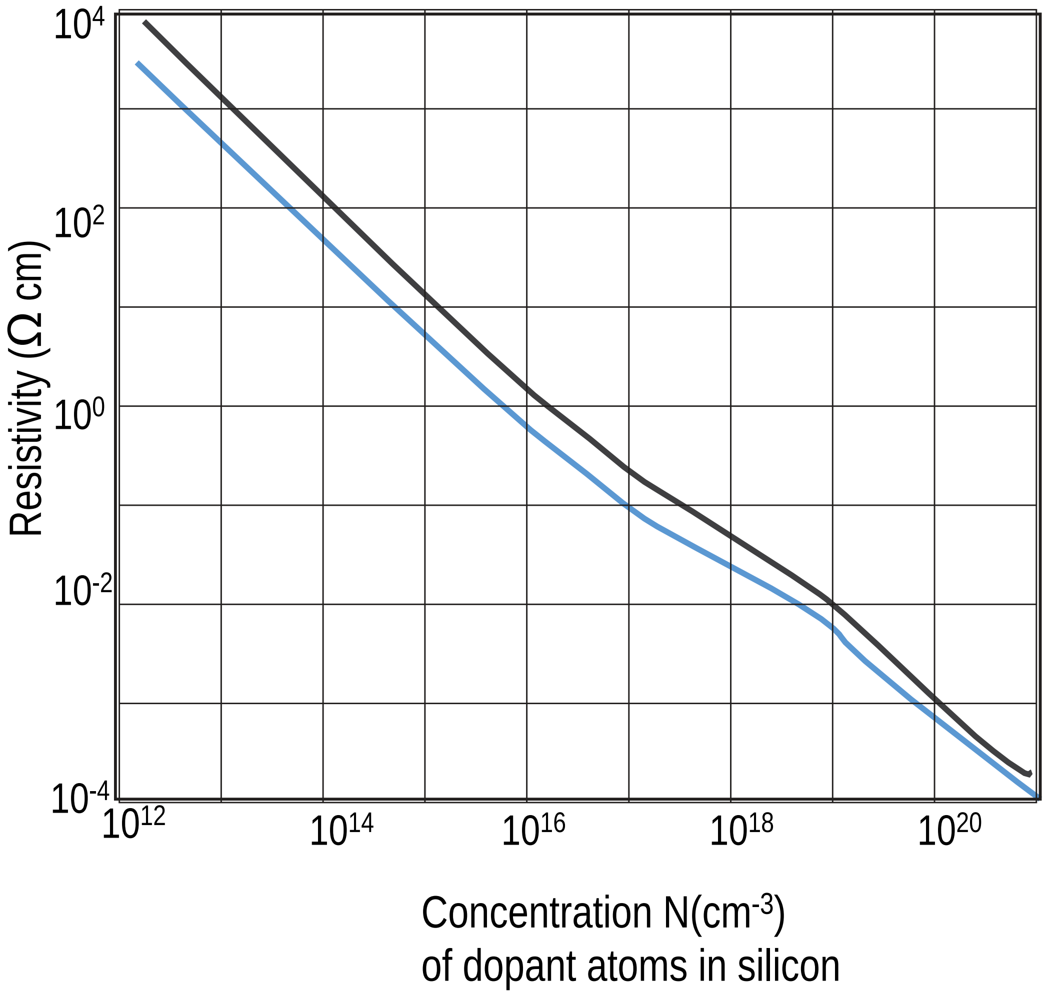
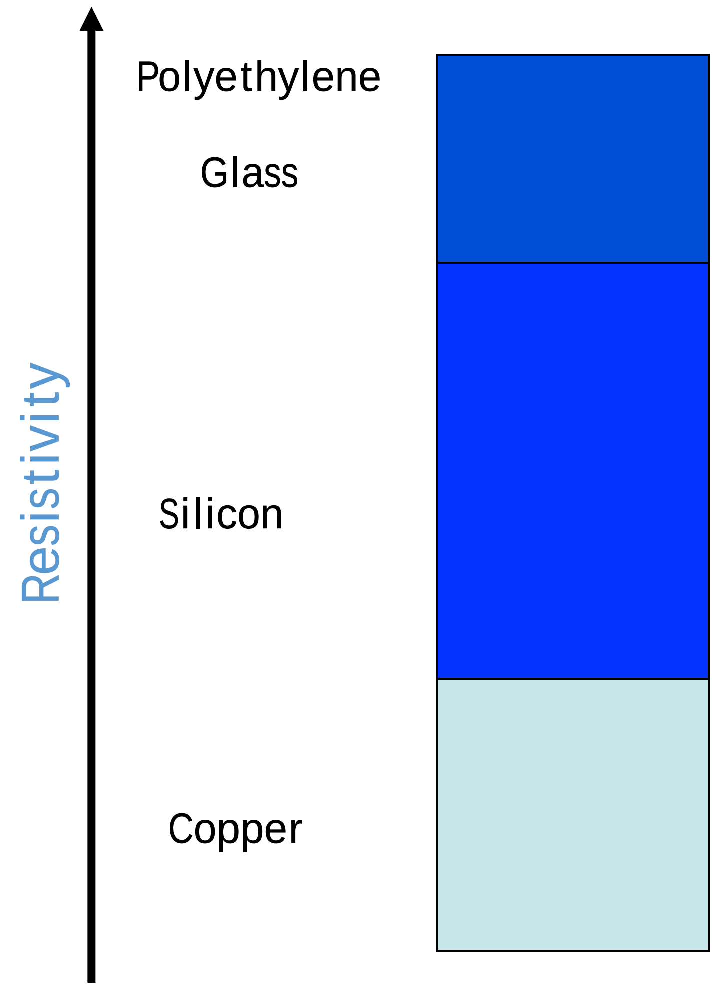
Making Silicon Conduct



Controlling Conductivity: Doping Solids

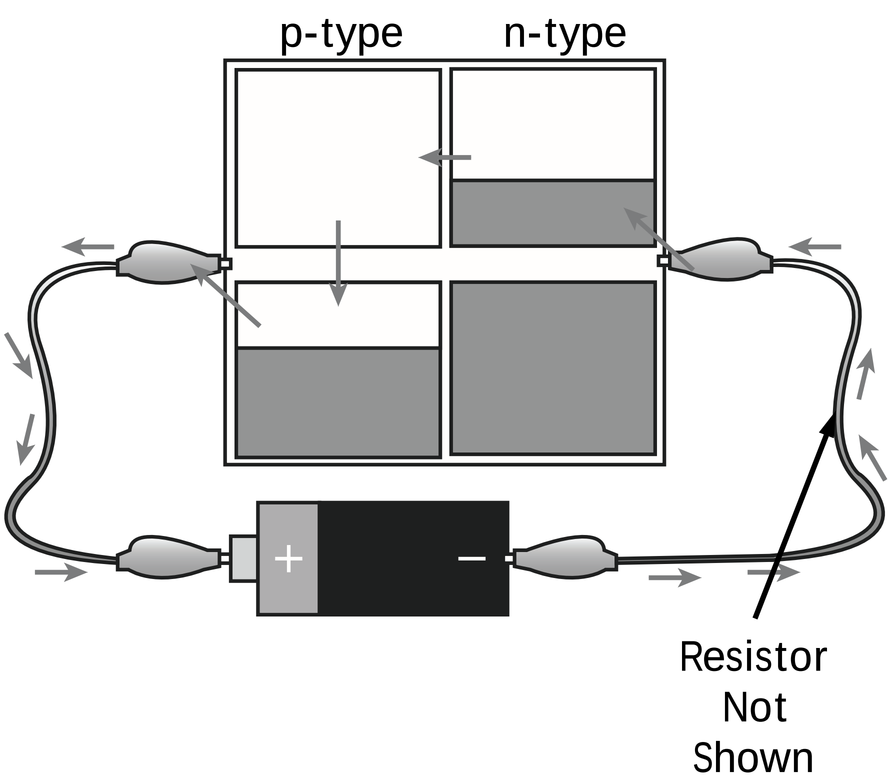
Adding impurities can change the conductivity from 'insulator' to 'metal'

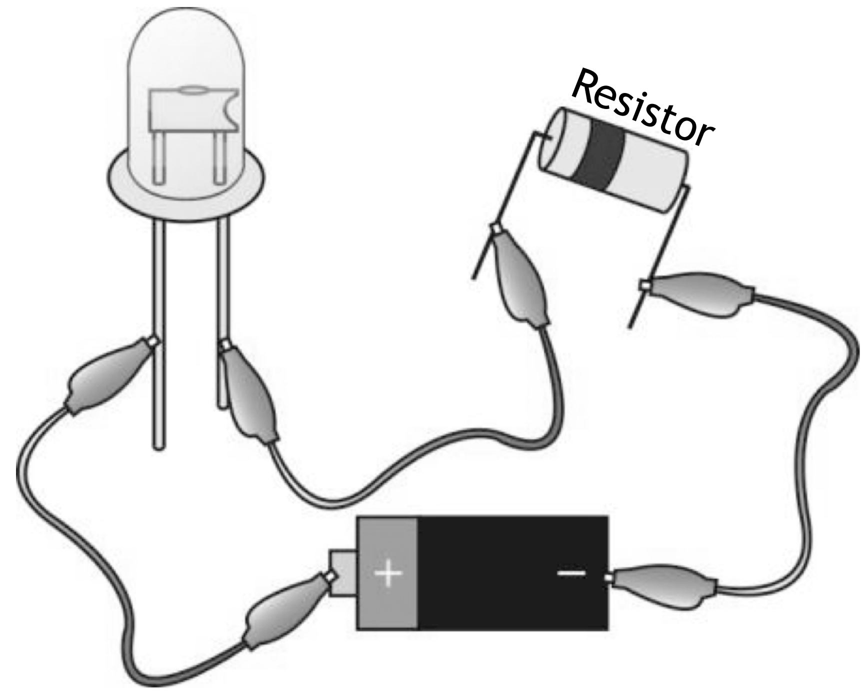




Note: Density of silicon atoms in a perfect (undoped) crystal of silicon is 5×10^{22} cm^{-3}

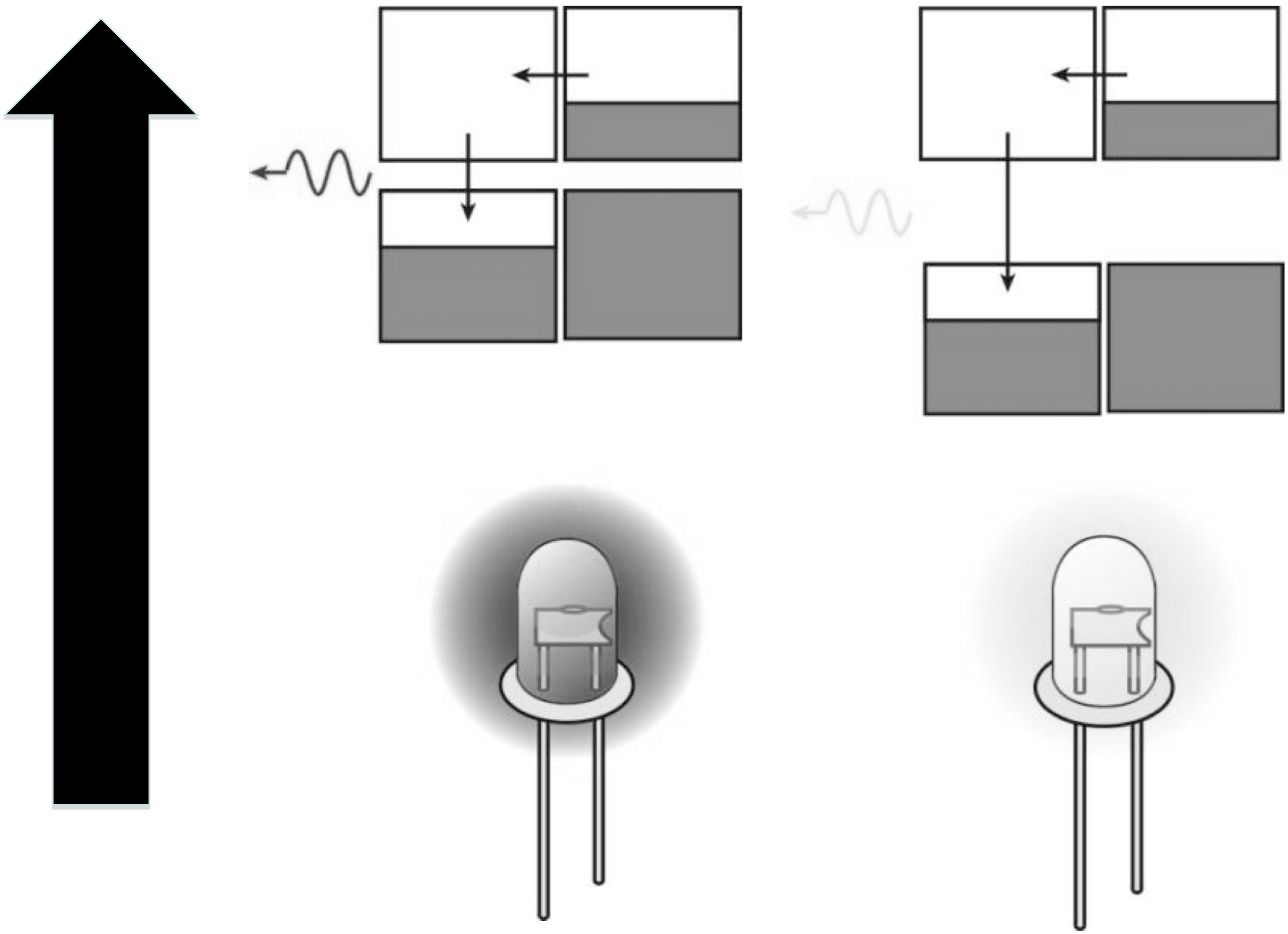
p-n Junctions and LEDs





High energy electrons (n-type) fall into low energy holes (p-type)

p-n Junctions and LEDs



Bandgaps of Different Semiconductors

Symbol	Band gap (eV) 300 K
Si	1.11
Ge	0.67
SiC	2.86
AlP	2.45
AlAs	2.16
AlSb	1.6
AlN	6.3
C	5.5
GaP	2.26
GaAs	1.43
GaN	3.4
GaS	2.5 (@ 295 K)
GaSb	0.7
InP	1.35

Symbol	Band gap (eV) 300 K
InAs	0.36
ZnO	3.37
ZnS	3.6
ZnSe	2.7
ZnTe	2.25
CdS	2.42
CdSe	1.73
CdTe	1.49
PbS	0.37
PbSe	0.27
PbTe	0.29