# ECE 162A
# Mat 162A

# Lecture #16:Band Theory
# Chapter 13

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# Hartree Theory

- Multielectron atomic theory
- First consider a nuclear attractive coulombic force: +Ze
- Include the coulombic repulsion due to the average position of other electrons: -(Z-1)e
- Assume each electron moves independently of each other.
- Schroedinger's equation becomes separable into Z separate equations for the motion of each electron:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

# What is V(r)?

- **First guess:**
  - For r→0,
  $$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

  - For r→infinity
  $$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

- **Then, solve SE and calculate V(r)**

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# Hartree Solution

- Assume V(r) (previous slide)
- Calculate the solutions

$$\psi_\alpha(r,\theta,\phi),\psi_\beta(r,\theta,\phi),\psi_\gamma(r,\theta,\phi),...$$

with energies

$$E_\alpha,E_\beta,E_\gamma,...$$

- Put one electron in each state. Soln is the product of one electron states.

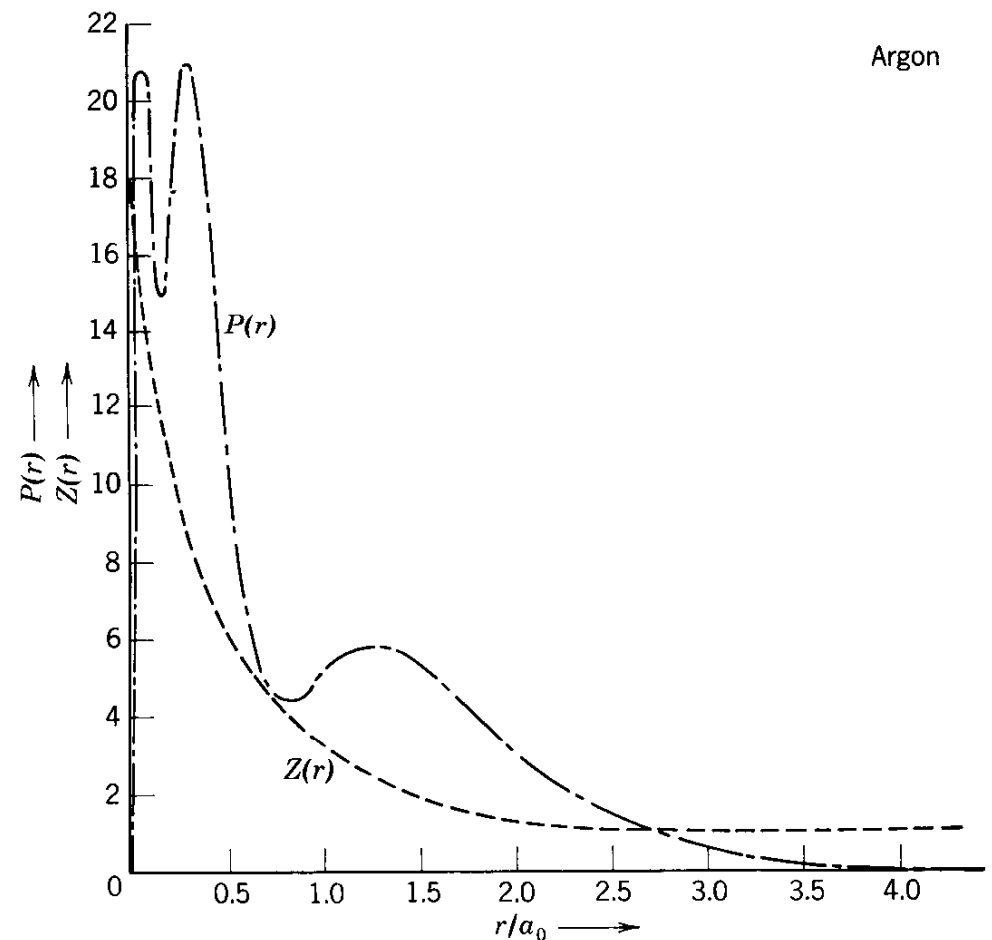$$\psi=\psi_\alpha(r_1,\theta_1,\phi_1),\psi_\beta(r_2,\theta_2,\phi_2),\psi_\gamma(r_3,\theta_3,\phi_3),...$$

- Note: $\alpha,\beta,\gamma$ includes space and spin

$$\alpha:\left|n=1;l=0;m_l=0,\uparrow\right\rangle$$

$$\beta:\left|n=1;l=0;m_l=0,\downarrow\right\rangle$$

# Hartree Solution (cont)

- Use $\psi*\psi$ to calculate V(r)
- Iterate:
  - Soln SE using new V(r)
  - Put one electron in each state to assemble $\psi$
  - Calculate V(r)

Argon

# Hartree Fock Theory

- Hartree theory ignores the requirement of antisymmetric wave functions.

- Fock included this.

- For a N electron atom, N! terms are added in the expression for $\psi$ (It is an N dimensional Slater determinant).

- The effect is only significant for the valence electrons.

# Results of Hartree Theory

- Eigenfunctions labeled by $n, l, m, m_l, m_s$
- (E will not be given by $E_0/n^2$)
- Important for solid state physics.
- Numerical calculation programs exist for Hartree and Hartree-Foch

# Order and Labeling of energy levels (shells)

- N=1,l=0     1s     2 states (up, down)   H,He
- N=2,l=0     2s     2 states (up, down)   Li,Mg
- N=2, l=1     2p     6 states ($2\times(m_l=-1,0,1)$)
- N=3, l=0     3s     2 states ($2\times(m_l=0)$)
- N=3, l=1     3p     6 states ($2\times(m_l=-1,0,1)$)
- <span style="color:red">N=4, l=0     4s     2 states ($2\times(m_l=0)$)</span>
- N=3, l=2     3d     10 states ($2\times(m_l=-2,-1,0,1,2)$)
- N=4, l=1     4p     6 states ($2\times(m_l=-1,0,1)$)

# Order and Labeling of energy levels (shells)

- N=1,l=0      1s      2 states
- N=2,l=0      2s      2 states
- N=2, l=1      2p      6 states
- N=3, l=0      3s      2 states
- N=3, l=1      3p      6 states
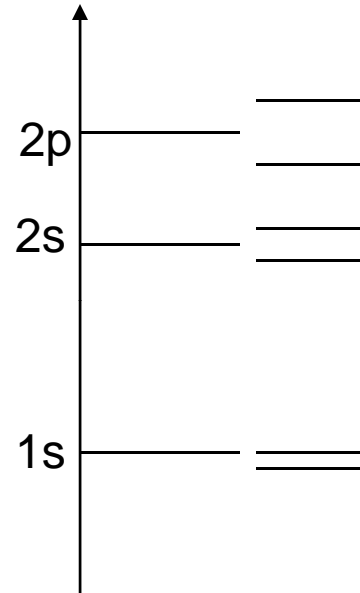- <span style="color:red">N=4, l=0      4s      2 states</span>
- N=3, l=2      3d      10 states
- N=4, l=1      4p      6 states
- N=5, l=0      5s      2 states
- N=5, l=1      5p      6 states
- N=6, l=0      6s      2 states
- N=4, l=3      4f      14 states

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# Chemistry

- Inner electrons affected by nucleus, not other atoms

- Outer electrons see a potential of +e or +2e and are affected by adjacent atoms.

- The outer electrons are called valence electrons and are involved in bonding to other atoms.

- Atoms with the same valence structure behave similarly chemically.

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# Periodic Table (Mendeleev in 1869)

| | $s^1$ | $s^2$ | | $d^1$ | $d^2$ | $d^3$ | $d^4$ | $d^5$ | $d^6$ | $d^7$ | $d^8$ | $d^9$ | $d^{10}$ | | $p^1$ | $p^2$ | $p^3$ | $p^4$ | $p^5$ | $p^6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $1s$ | 1 H | | | | | | | | | | | | | | | | | | | 2 He |
| $2s$ | 3 Li | 4 Be | | | | | | | | | | | | $2p$ | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| $3s$ | 11 Na | 12 Mg | | | | | | | | | | | | $3p$ | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 A |
| $4s$ | 19 K | 20 Ca | $3d$ | 21 Sc | 22 Ti | 23 V | 24 Cr $4s^13d^5$ | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu $4s^13d^{10}$ | 30 Zn | $4p$ | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| $5s$ | 37 Rb | 38 Sr | $4d$ | 39 Y | 40 Zr | 41 Nb $5s^14d^4$ | 42 Mo | 43 Tc | 44 Ru $5s^14d^7$ | 45 Rh $5s^14d^8$ | 46 Pd $5s^04d^{10}$ | 47 Ag $5s^14d^{10}$ | 48 Cd | $5p$ | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| $6s$ | 55 Cs | 56 Ba | $5d$ | 57 La Lantha–nides | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt $6s^15d^9$ | 79 Au $6s^15d^{10}$ | 80 Hg | $6p$ | 81 Ti | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| $7s$ | 87 Fr | 88 Ra | $6d$ | 89 Ac Actinides | | | | | | | | | | $7p$ | | | | | | |

**Lanthanides ($4f$)**

| | $f^1$ | $f^2$ | $f^3$ | $f^4$ | $f^5$ | $f^6$ | $f^7$ | $f^8$ | $f^9$ | $f^{10}$ | $f^{11}$ | $f^{12}$ | $f^{13}$ | $f^{14}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $4f$ Lanthanides | 58 Ce $5d^04f^2$ | 59 Pr $5d^04f^3$ | 60 Nd $5d^04f^4$ | 61 Pm $5d^04f^5$ | 62 Sm $5d^04f^6$ | 63 Eu $5d^04f^7$ | 64 Gd $5d^14f^7$ | 65 Tb $5d^04f^9$ | 66 Dy $5d^04f^{10}$ | 67 Ho $5d^04f^{11}$ | 68 Er $5d^04f^{12}$ | 69 Tm $5d^04f^{13}$ | 70 Yb $5d^04f^{14}$ | 71 Lu $5d^14f^{14}$ |

**Actinides ($5f$)**

| | $f^1$ | $f^2$ | $f^3$ | $f^4$ | $f^5$ | $f^6$ | $f^7$ | $f^8$ | $f^9$ | $f^{10}$ | $f^{11}$ | $f^{12}$ | $f^{13}$ | $f^{14}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $5f$ Actinides | 90 Th $6d^25f^0$ | 91 Pa $6d^15f^2$ | 92 U $6d^15f^3$ | 93 Np $6d^15f^4$ | 94 Pu $6d^15f^5$ | 95 Am $6d^15f^6$ | 96 Cm $6d^15f^7$ | 97 Bk $6d^15f^8$ | 98 Cf $6d^05f^{10}$ | 99 Es $6d^05f^{11}$ | 100 Fm $6d^05f^{12}$ | 101 Md $6d^05f^{13}$ | 102 No $6d^05f^{14}$ | 103 Lw $6d^15f^{14}$ |

# Band Theory of Solids

- Isolated →2 atoms

2p

2s

1s

# Band Theory of Solids

- Isolated →solid

- Splitting higher for outer electrons; more overlap.
- Splitting increases as the separation decreases.

2p

2s

1s
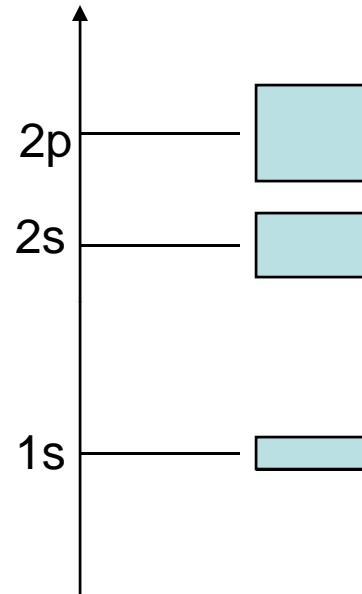
# Energy Bands

- Bands that originate from closed shells (e.g. 1s, 2s for boron) have filled bands
- Shells that are partially filled result in bands that are partially filled.
- Filled bands give insulators
- Partially filled bands give metals.
- Filled bands with empty bands close by (0.1 to 3 eV) are called semiconductors.
- Materials with odd number of electrons/atom are always metals.
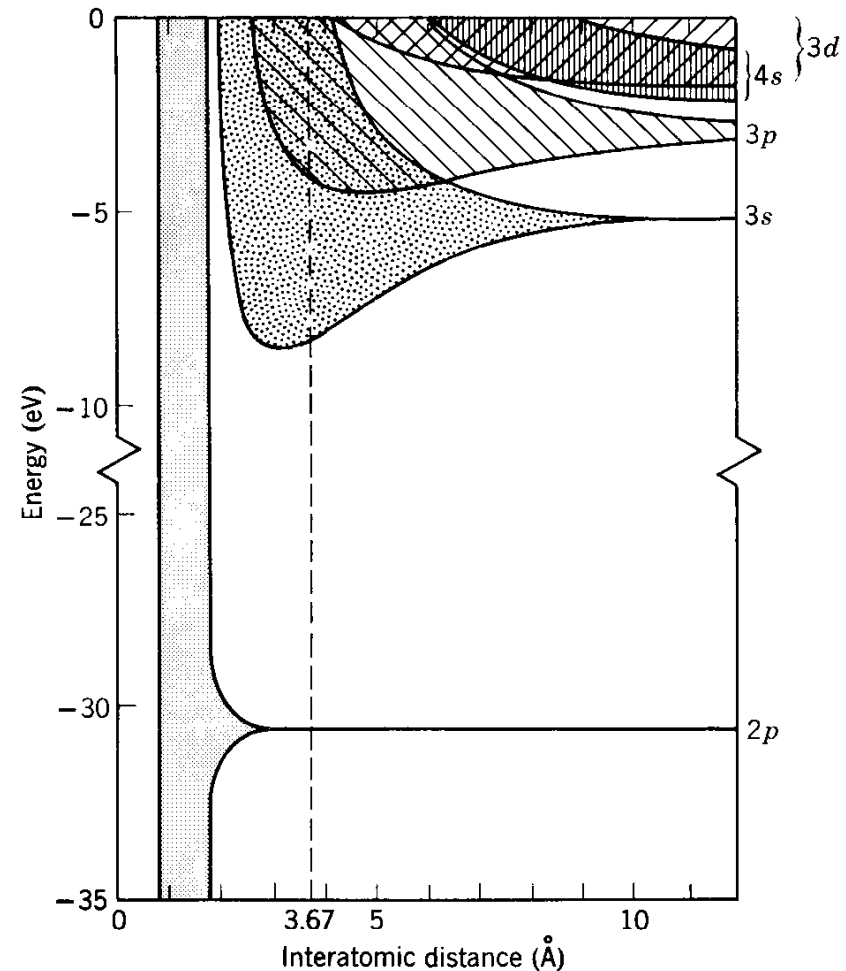
# Quantum Statistics

- How are electrons distributed versus energy?
- Classical answer: Maxwell Boltzman distribution

$$P(E) = Ae^{-E/kT}$$

- However, this has most electrons at low energies, which violates the Pauli exclusion principle.

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# Quantum Statistics

- How are electrons distributed versus energy?
- Classical answer: Maxwell Boltzman distribution

$$P(E) = Ae^{-E/kT}$$

- Quantum mechanical answer: Fermi Dirac distribution

$$P(E) = \frac{A'}{1 + e^{(E-E_0)/kT}}$$

Boltzmann

$\uparrow$ P(E)

Fermi Dirac

E $\longrightarrow$

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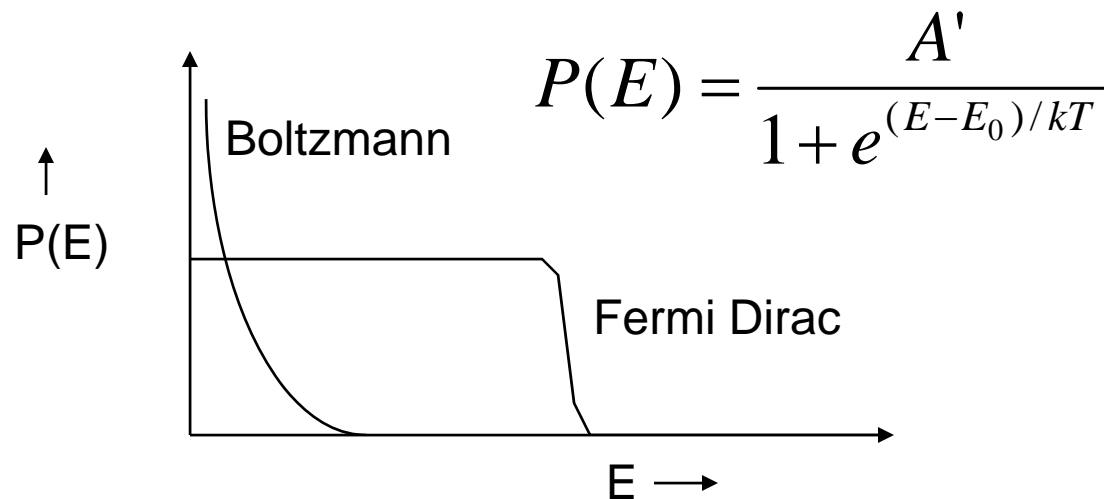
# Electron distribution
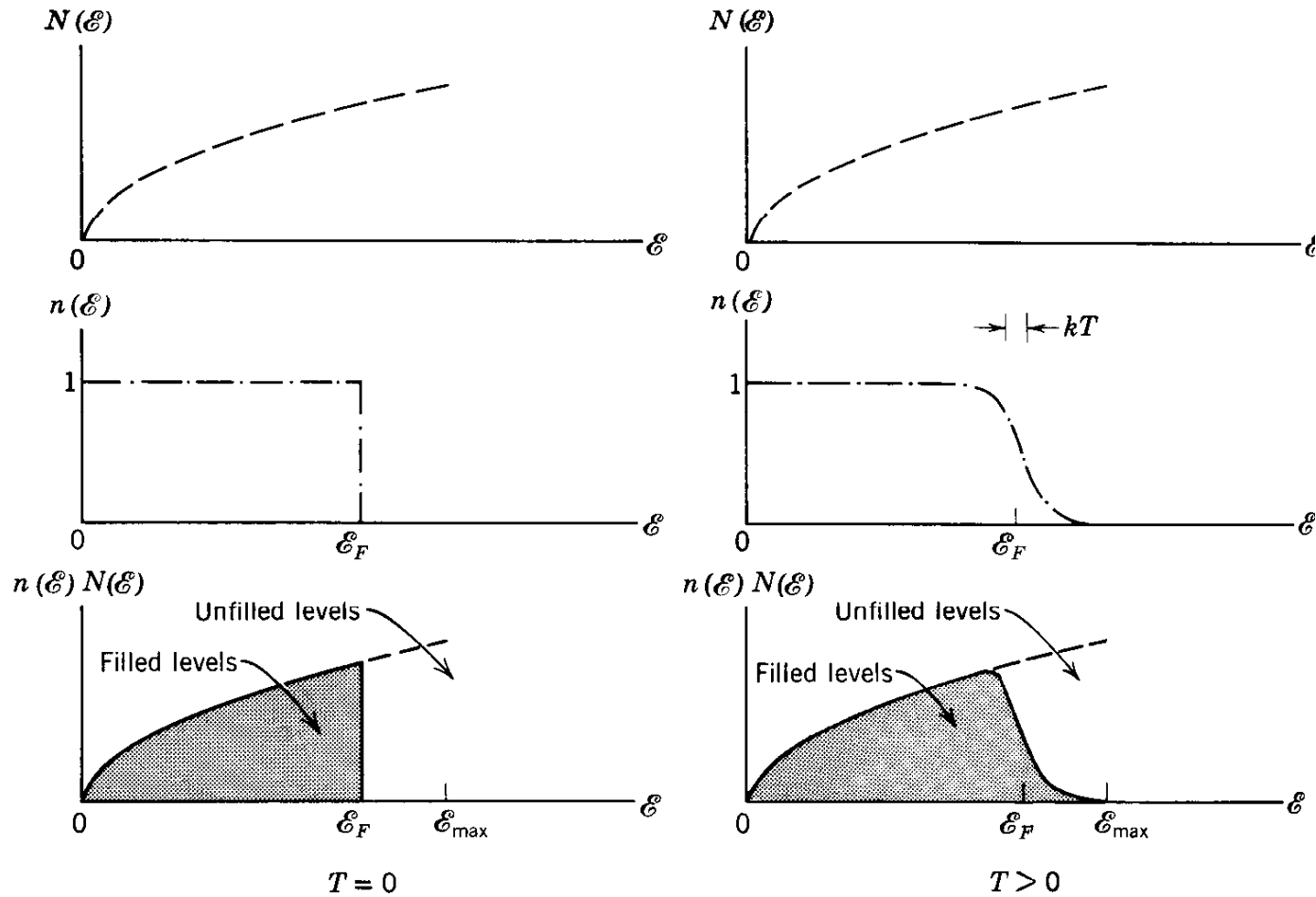


$$n = \int_{-\infty}^{\infty} dE \ N(E) f(E)$$

# Conduction

- A filled band has no net current flow.  For every electron going in one direction, there is an electron going in the opposite direction

# Fermi Energy

- The fermi energy is determined by the doping level:

$$n = \int_{E_C}^{\infty} dE \ N(E) f(E)$$

$$n = N_c \exp(\frac{E_F - E_C}{kT})$$

Where $N_c$ is the effective number of states in the conduction band and $E_F$ is the Fermi energy.

# Hole density

$$p = \int_{-\infty}^{E_V} dE \ N(E)(1 - f(E))$$

$$p = N_V \exp(\frac{E_V - E_F}{kT})$$

Where $N_V$ is the effective density of states in the valence band and $E_v$ is the valence band edge.

# Hole density

$$p = \int_{-\infty}^{E_V} dE \ N(E)(1 - f(E))$$

$$p = N_V \exp(\frac{E_V - E_F}{kT})$$

Where $N_V$ is the effective density of states in the valence band and $E_v$ is the valence band edge.

$$pn = N_C N_V \exp(\frac{E_F - E_C}{kT}) \exp(\frac{E_V - E_F}{kT})$$

$$pn = N_C N_V \exp(-\frac{E_C - E_V}{kT})$$

# How do electrons move through a lattice?

- The potential is periodic:

V(x)

a
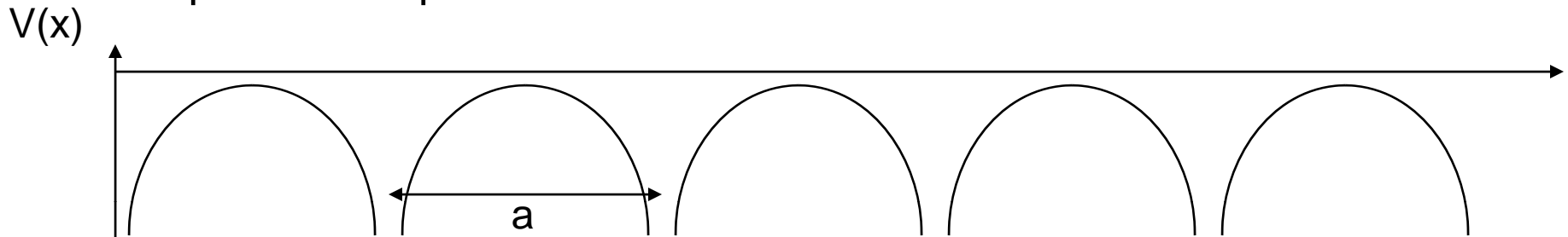
- Bloch found the solution to be $\psi(x) = u_k(x)e^{ikx}$

$$\Psi(x,t) = u_k(x)e^{ikx-\omega t}$$

- The uk(x) are the Bloch functions.

$$u_k(x) = u_k(x+a) = u_k(x+na)$$

- The free motion of the electron through the lattice is given by

$$e^{ikx-\omega t}$$

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# Kronig-Penney Model

V(x)
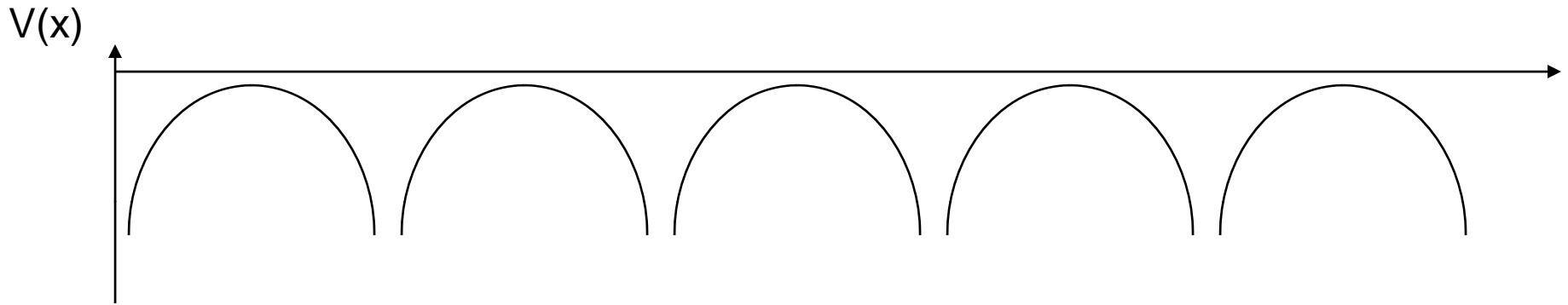
Approximate this potential with the rectilinear one shown below

V(x)

a
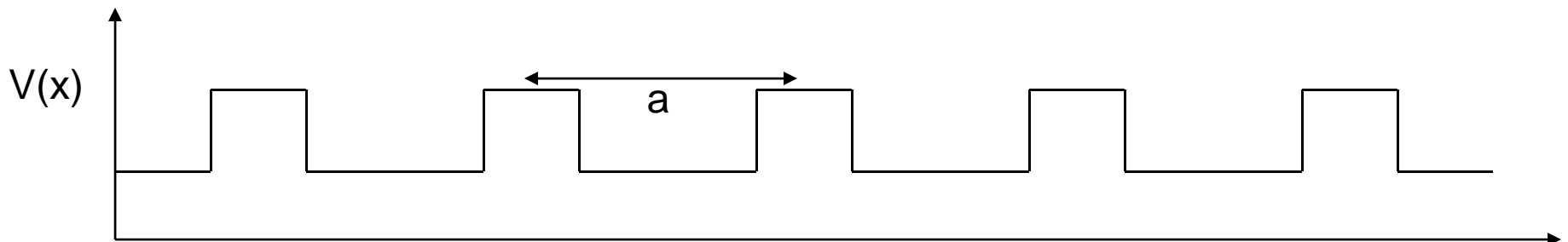
# Energy Bands-Extended Zone

- The region from $-\pi/a$ to $\pi/a$ is the First Brillouin Zone.

- The second Brillouin Zone extends from $\pi/a$ to $3\pi/a$.

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# Energy Bands

- Extended zone
- Reduced zone
- Repeating zone



Energy bands
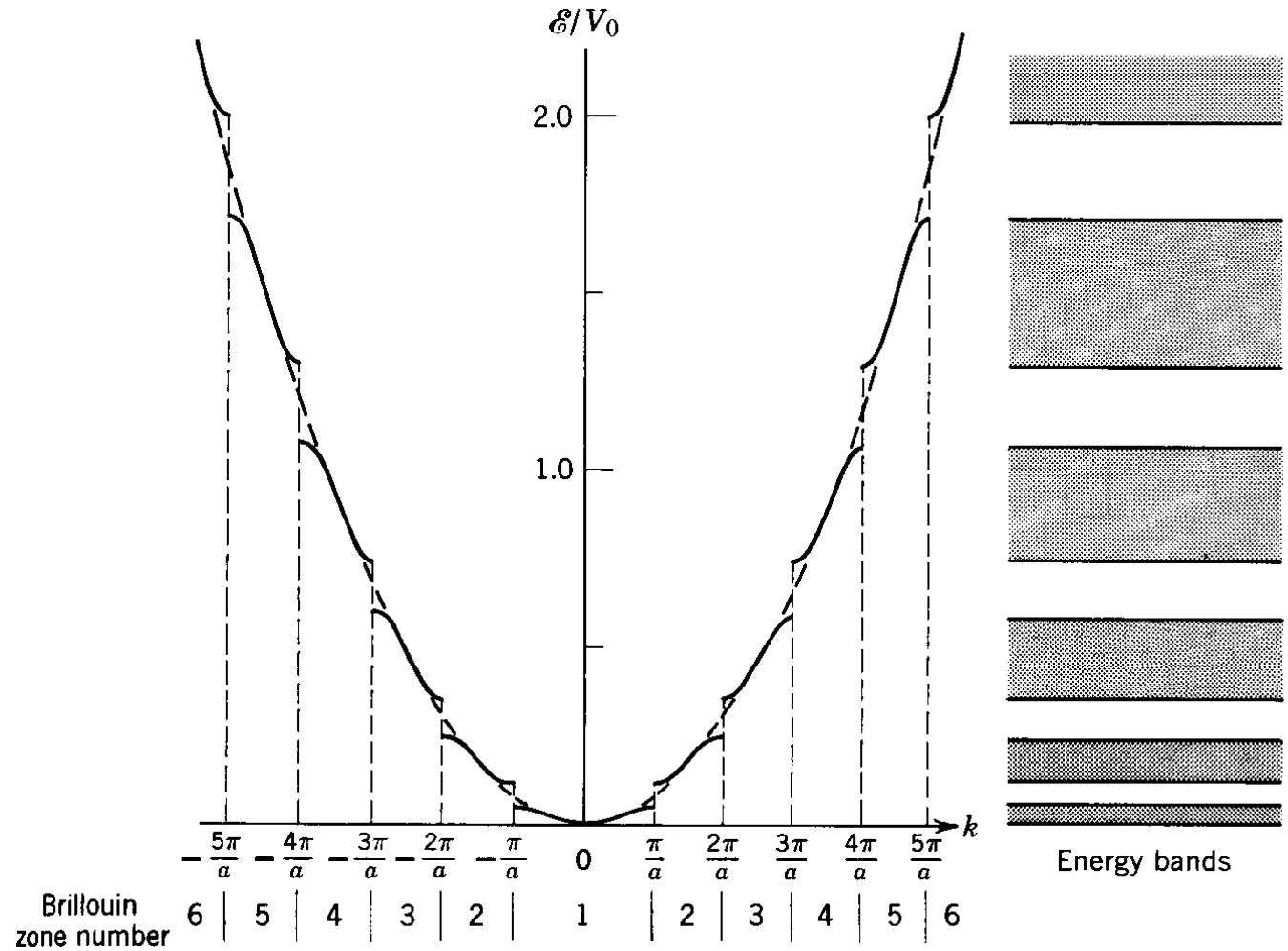
# Direct Gap vs. Indirect Gap

- Semiconductors where the minimum in the conduction band and the maximum in the valence band are located at the same point in k space are called direct gap semiconductors.
- Semiconductors where the minimum in the conduction band and the maximum in the valence band are located at different point in k space are called direct gap semiconductors.
- Silicon and AlAs are indirect gap semiconductors.
- GaAs and InP are direct gap semiconductors.

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$\Gamma$ (k=0)

Direct

$\Gamma$ (k=0)
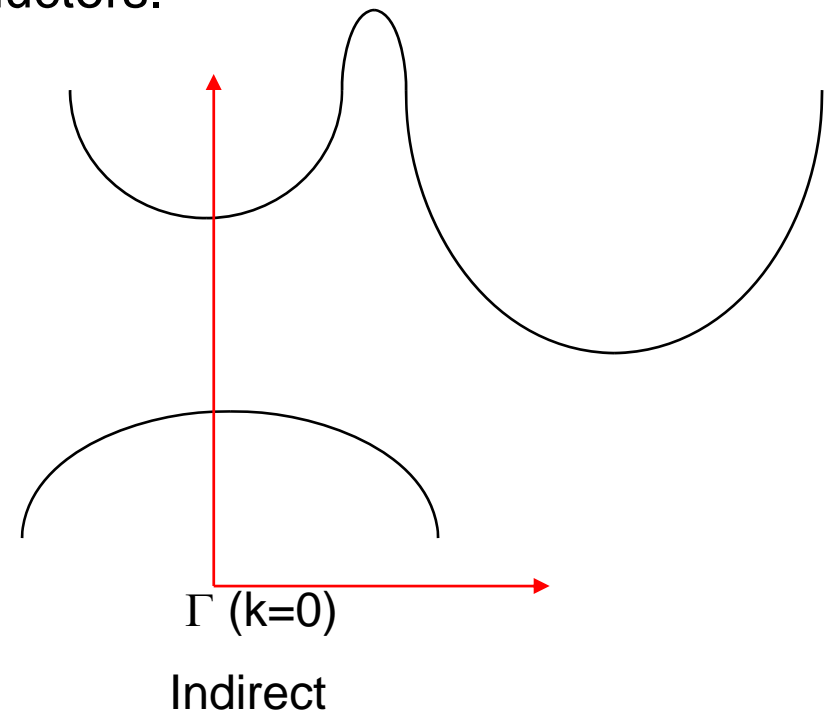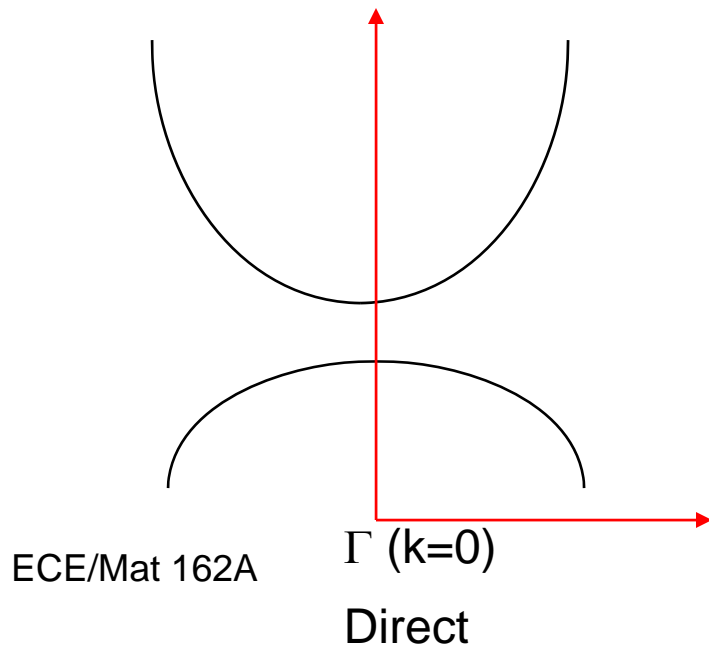
Indirect

# Direct Gap vs. Indirect Gap

- Direct gap semiconductors:  Good absorption and good emission because photons can be directly absorbed or emitted.

- Indirect gap semiconductors: Low absorption and low emission rates because a phonon is required to conserve energy and momentum

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$\Gamma$ (k=0)

Direct

$\Gamma$ (k=0)

Indirect

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+++

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+++
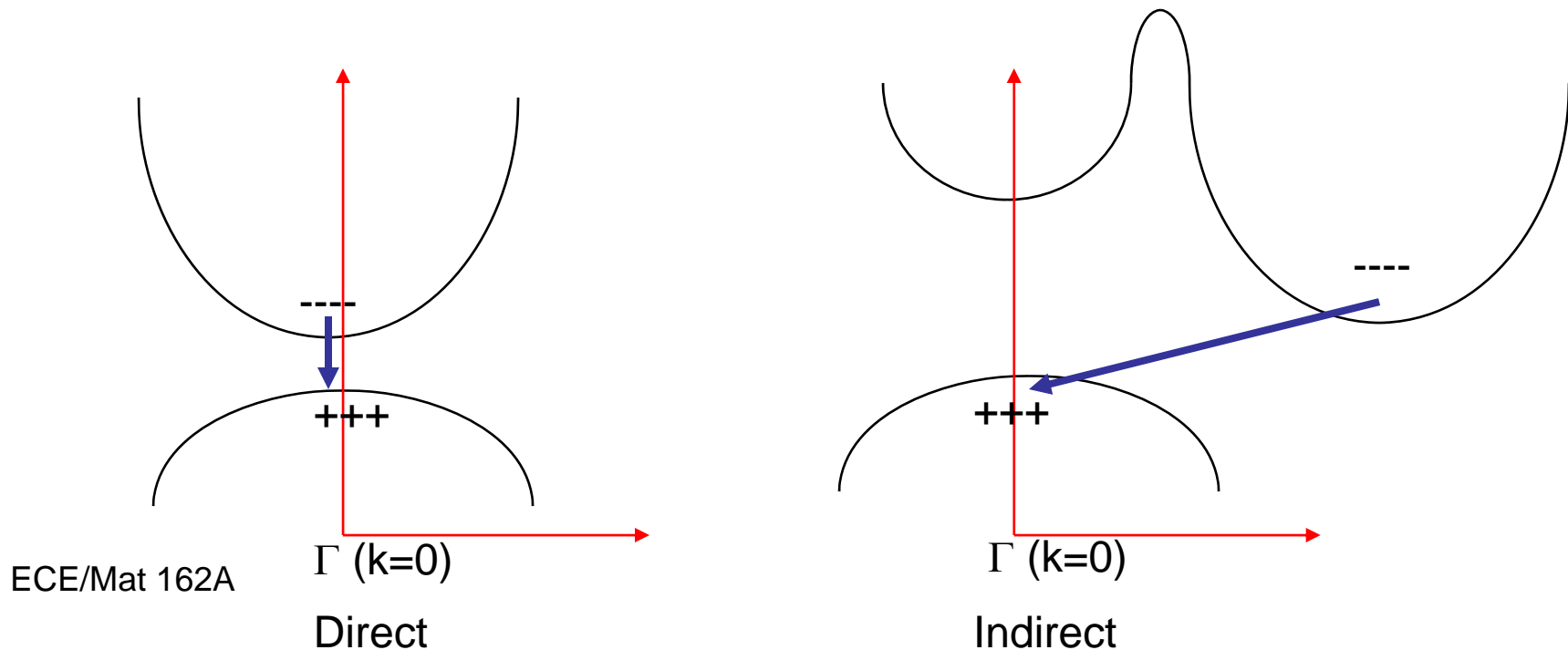
- Photons travel at the speed of light so the transitions are almost vertical lines (momentum change is very small).

E

Photon (E=pc)

Electron

p

---
+++

$\Gamma$ (k=0)

phonon

photon

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+++

$\Gamma$ (k=0)

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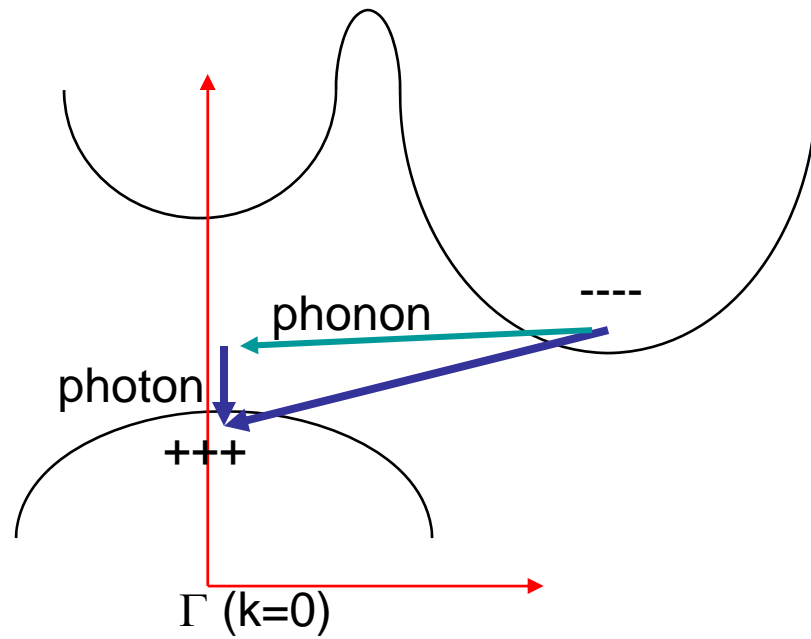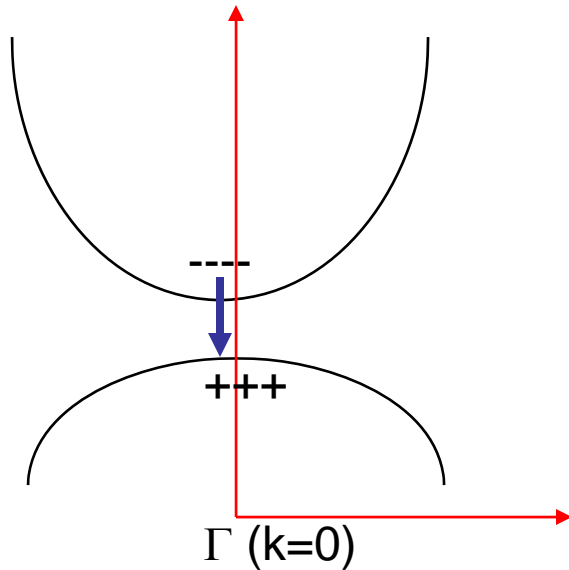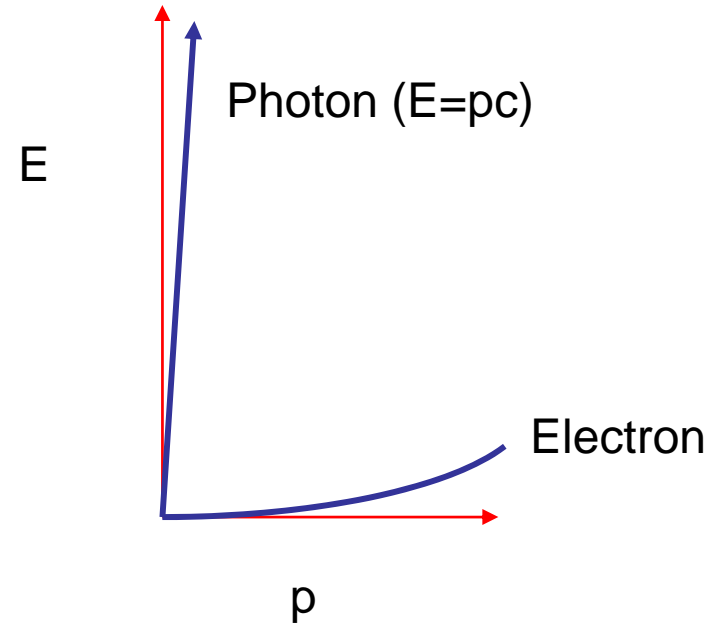
# Compound Semiconductors

- Tetrahedrally bonded in a zinc blende structure.

- Several varieties:  III-V compounds

- II-VI compounds.

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# III-V Compound Semiconductors

III  V

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 1 H | | | | | | | | | | | | | | | | | 2 He |

| | | |
|---|---|---|
| 2s | 3 Li | 4 Be |
| 3s | 11 Na | 12 Mg |
| 4s | 19 K | 20 Ca |
| 5s | 37 Rb | 38 Sr |
| 6s | 55 Cs | 56 Ba |
| 7s | 87 Fr | 88 Ra |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 3d | 21 Sc | 22 Ti | 23 V | 24 Cr $4s^1 3d^5$ | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu $4s^1 3d^{10}$ | 30 Zn |
| 4d | 39 Y | 40 Zr | 41 Nb $5s^1 4d^4$ | 42 Mo | 43 Tc | 44 Ru $5s^1 4d^7$ | 45 Rh $5s^1 4d^8$ | 46 Pd $5s^0 4d^{10}$ | 47 Ag $5s^1 4d^{10}$ | 48 Cd |
| 5d | 57 La Lantha–nides | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt $6s^1 5d^9$ | 79 Au $6s^1 5d^{10}$ | 80 Hg |
| 6d | 89 Ac Actinides | | | | | | | | | |

$s^1$ $s^2$  $d^1$ $d^2$ $d^3$ $d^4$ $d^5$ $d^6$ $d^7$ $d^8$ $d^9$ $d^{10}$

| | | | | | |
|---|---|---|---|---|---|
| 2p | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 3p | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 A |
| 4p | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 5p | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 6p | 81 Ti | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 7p | | | | | | |

$p^1$ $p^2$ $p^3$ $p^4$ $p^5$ $p^6$

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4f Lanthanides | 58 Ce $5d^0 4f^2$ | 59 Pr $5d^0 4f^3$ | 60 Nd $5d^0 4f^4$ | 61 Pm $5d^0 4f^5$ | 62 Sm $5d^0 4f^6$ | 63 Eu $5d^0 4f^7$ | 64 Gd $5d^1 4f^7$ | 65 Tb $5d^0 4f^9$ | 66 Dy $5d^0 4f^{10}$ | 67 Ho $5d^0 4f^{11}$ | 68 Er $5d^0 4f^{12}$ | 69 Tm $5d^0 4f^{13}$ | 70 Yb $5d^0 4f^{14}$ | 71 Lu $5d^1 4f^{14}$ |
| 5f Actinides | 90 Th $6d^2 5f^0$ | 91 Pa $6d^1 5f^2$ | 92 U $6d^1 5f^3$ | 93 Np $6d^1 5f^4$ | 94 Pu $6d^1 5f^5$ | 95 Am $6d^1 5f^6$ | 96 Cm $6d^1 5f^7$ | 97 Bk $6d^1 5f^8$ | 98 Cf $6d^0 5f^{10}$ | 99 Es $6d^0 5f^{11}$ | 100 Fm $6d^0 5f^{12}$ | 101 Md $6d^0 5f^{13}$ | 102 No $6d^0 5f^{14}$ | 103 Lw $6d^1 5f^{14}$ |

$f^1$ $f^2$ $f^3$ $f^4$ $f^5$ $f^6$ $f^7$ $f^8$ $f^9$ $f^{10}$ $f^{11}$ $f^{12}$ $f^{13}$ $f^{14}$

GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, AlN, AlP, AlSb, …

# II-Vi Compound Semiconductors

# Semiconductor Problems

- p-n junction in GaAs

- $E_G$=1.42 eV

- $N_C$=4.7 x $10^{17}$ cm$^{-3}$

- $N_V$=7x$10^{18}$ cm$^{-3}$

- $n_i$=2.1x$10^6$ cm$^{-3}$

- In equilibrium, the Fermi level is constant across the structure.

- Draw a p-n junction in GaAs for $N_D$=$10^{18}$ cm$^{-3}$ and $N_A$=$10^{17}$ cm$^{-3}$

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# p-n junction in GaAs



$E_F$

$E_V$

$E_C$

# p-n junction in GaAs

$E_F$

$E_C$

$E_V$

**Rules**
1. Valence bands and conduction bands equadistant and parallel everywhere (constant bandgap).
2. Fermi energy $E_F$ is constant in equilibrium.
3. Quadratic variation of band edge (constant doping, depletion edge approximation).
4. Fermi level to band edge separation appropriate for doping.

$$\frac{d^2\Phi}{dx^2} = -\frac{\rho}{\varepsilon} = -\frac{p - n + N_D - N_A}{\varepsilon}$$

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# Binaries

- Bandgap always fixed.

- Lattice constant always fixed.

- Consequently, you can grow large boules of binaries, and cut identical substrates out of the boule.

- Fermi level depends on doping.

# Ternary Materials

- Binary materials always have a particular bandgap and a particular lattice constant.

- However, many times we need intermediate bandgaps, not provided in nature.  Or we wish to make a square well, or some other heterostructure.

- Ternaries:
  - $Ga_xAl_{1-x}As$
  - $Hg_xCd_{1-x}Te$
  - These are both mixtures on the group III site. Mixtures on the group V site are also possible.

# Ternary Materials

- Mix two binaries together.  The bandgap is approximately the arithmetic average of the two (Vegard's law) e.g. $Ga_xAl_{1-x}As$

- There are two types of sites: group III and group V. (II-VI compounds also possible).

- Ternaries cannot be grown on binary substrates in general because the lattice constants don't line up and dislocations occur.  Special case: $Ga_xAl_{1-x}As$ because the lattice constants of GaAs and AlAs are almost equal.

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# Quaternary materials

- To match bandgap and lattice constant, two degrees of freedom are required.

- Example: $Ga_xIn_{1-x}As_yP_{1-y}$
  - X is the fraction of group III sites occupied by Ga.
  - Y is the fraction of group V sites occupied by As.

- In a bandgap chart, the dots are binaries, the lines are ternaries, and the regions bounded by 4 lines are quaternaries.
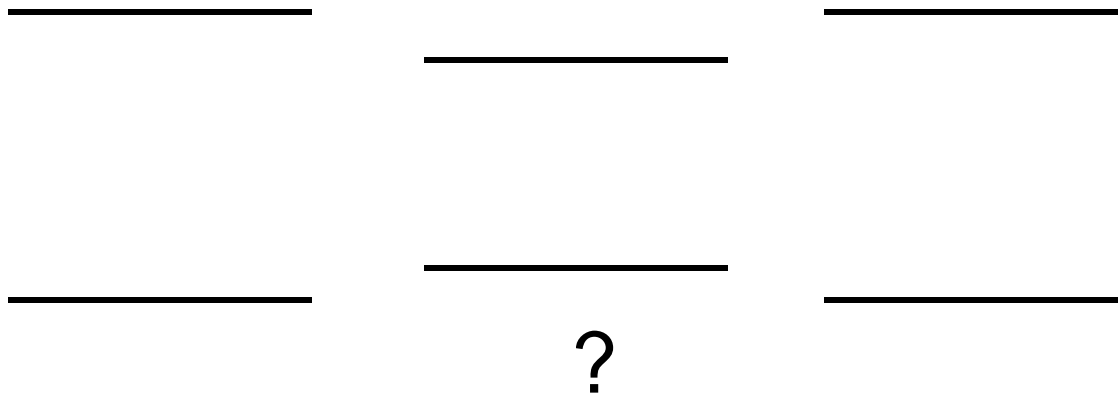
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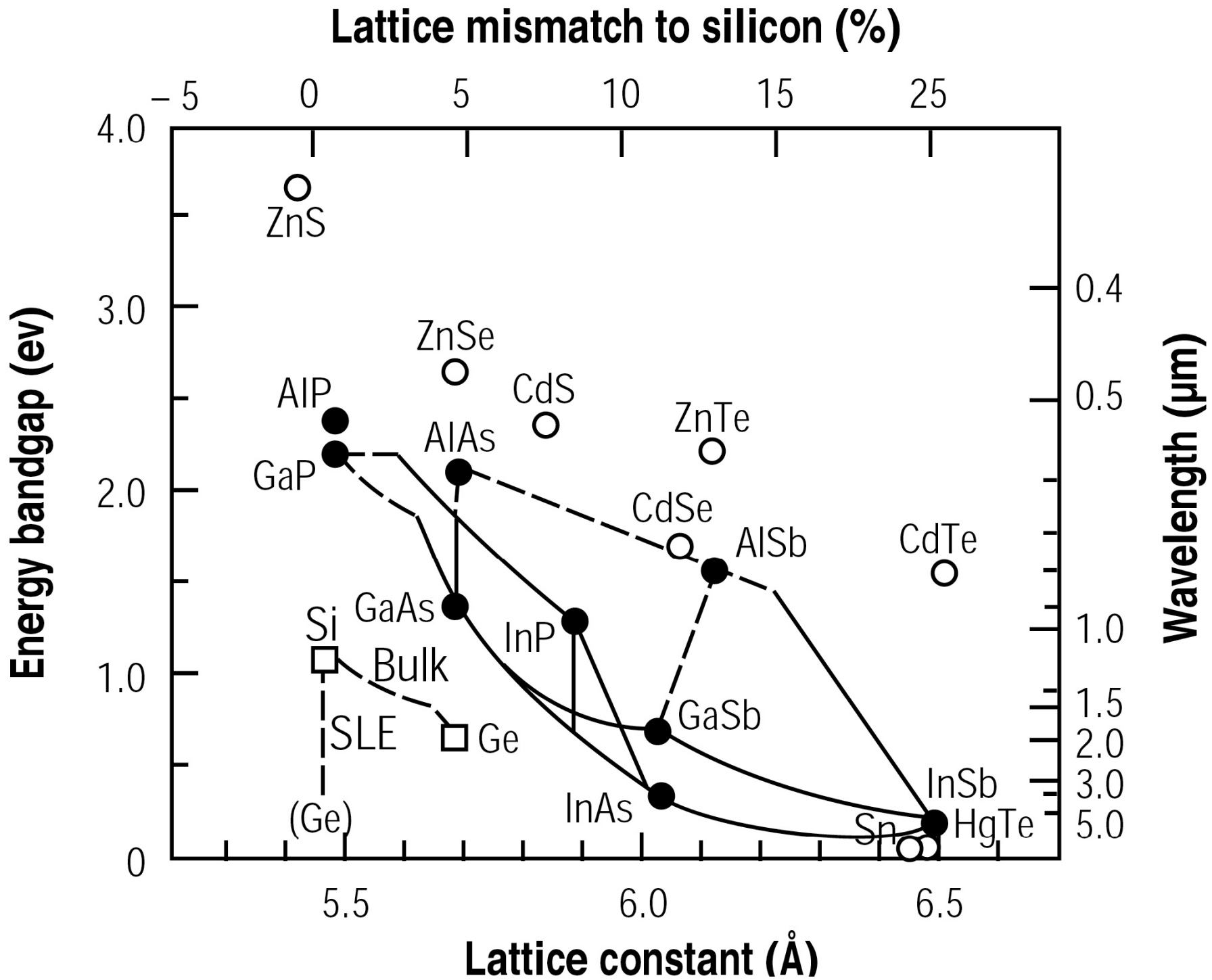
# Epitaxial Layers

- Epitaxial layers of different compound semiconductors can be grown on top of each other.

- Small differences in lattice constants can be accommodated for thin layers (strained layers: Compressive or tensile).

- Too much accumulated strain results in dislocations.

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# InP/InGaAs/InP Square Well
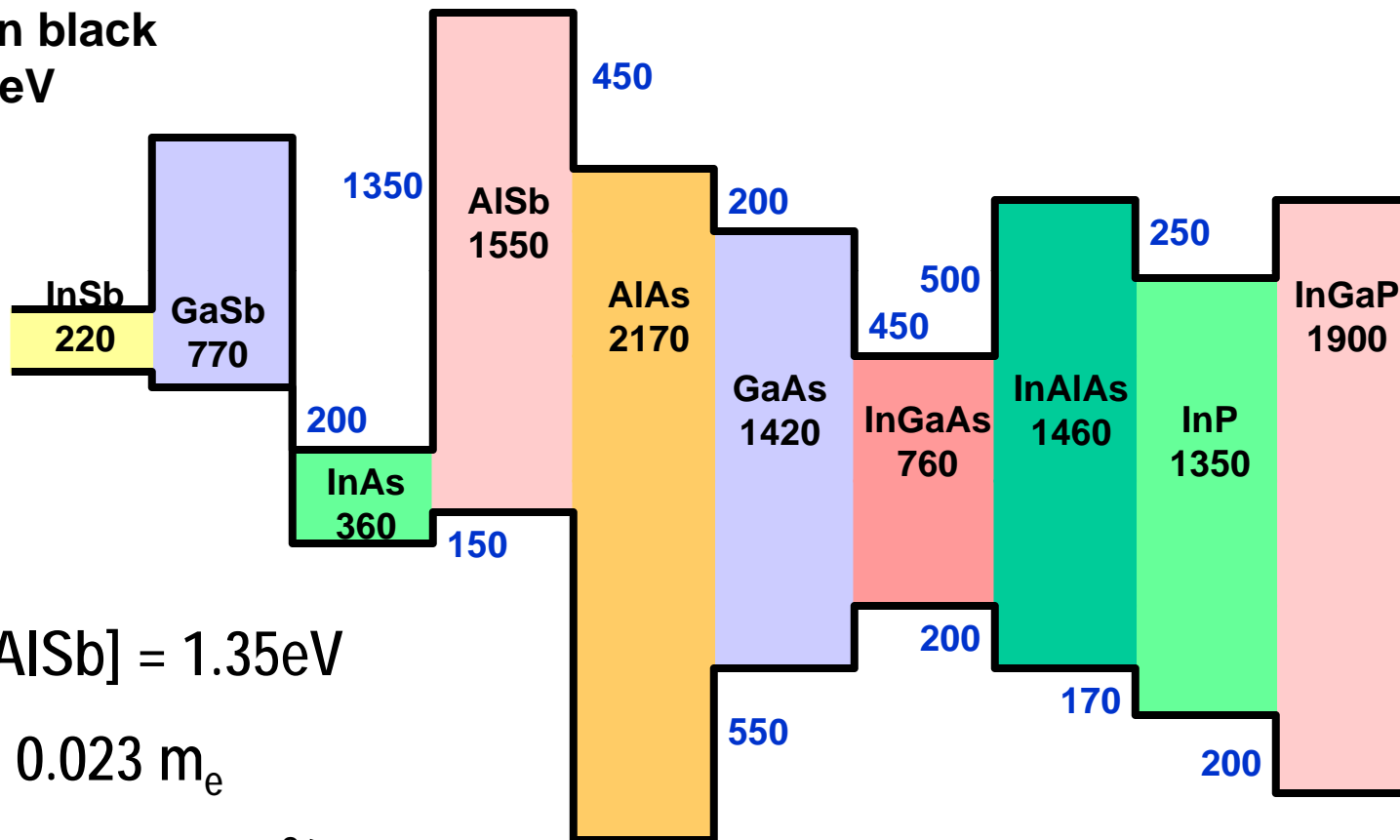
- InGaAs: $E_g = .76$ eV
- InP: $E_g = 1.35$ eV

——————    ——————    ——————

——————    ——————    ——————

?

How do bands line up?
It depends on the electron affinity: Energy to bring an
electron from the conduction band edge to vacuum.

# Bandgap Heaven

# Guidelines

- Figure out bandgaps. (draw horizontal where there is no depletion).

- Figure out conduction band and valence band discontinuity.

- Figure out Fermi level for each material.

- Draw flat band first, then flaten out the Fermi level.

- Keep the band separation constant for any region where the bandgap is not changing.

# Semiconductor Problems

- p-n junction in GaAs
- $E_G$=1.42 eV
- $N_C$=4.7 x $10^{17}$ cm$^{-3}$
- $N_V$=7x$10^{18}$ cm$^{-3}$
- $n_i$=2.1x$10^6$ cm$^{-3}$
- In equilibrium, the Fermi level is constant across the structure.
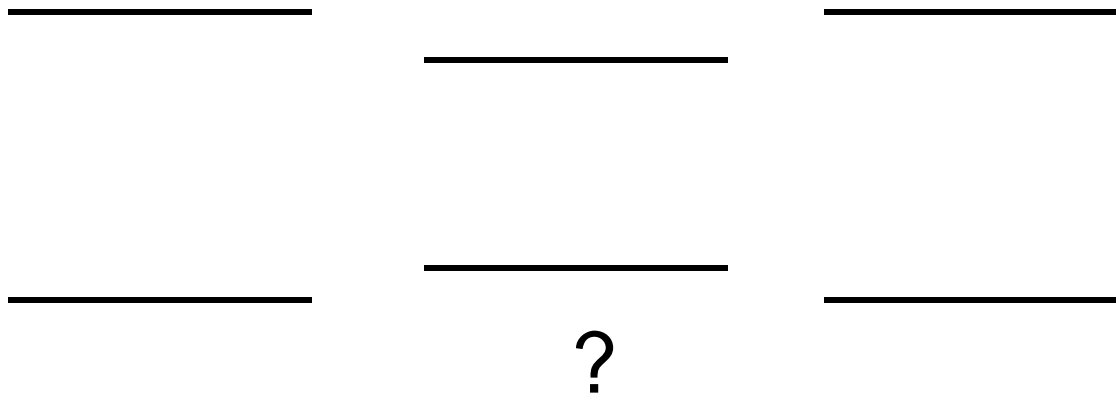- Draw a p-n junction in GaAs for $N_D$=$10^{18}$ cm$^{-3}$ and $N_A$=$10^{17}$ cm$^{-3}$

# p-n junction in GaAs

$E_F$

$E_V$

$E_C$

$$\frac{d^2\Phi}{dx^2} = -\frac{\rho}{\varepsilon} = -\frac{p - n + N_D - N_A}{\varepsilon}$$

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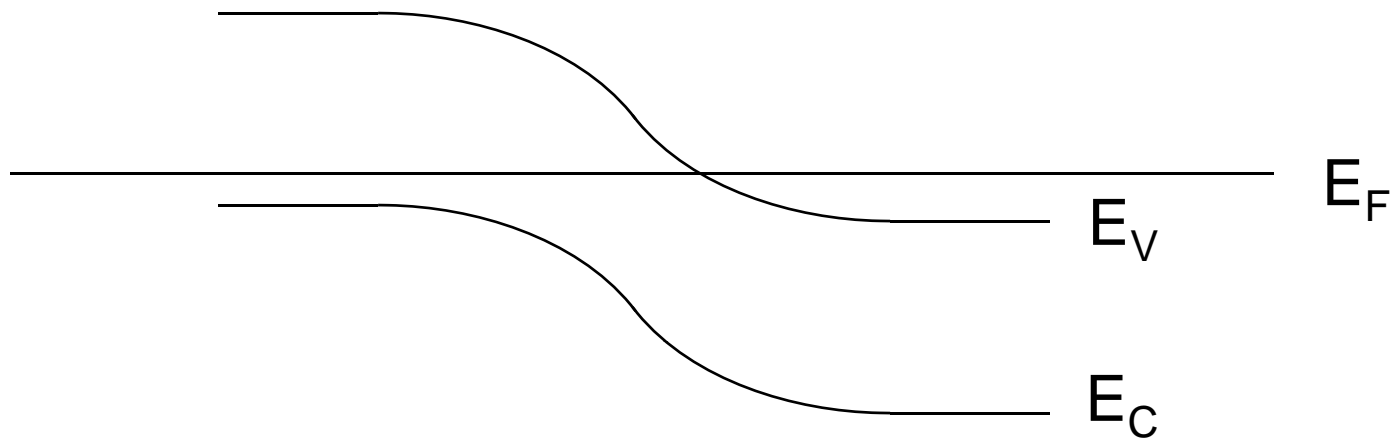
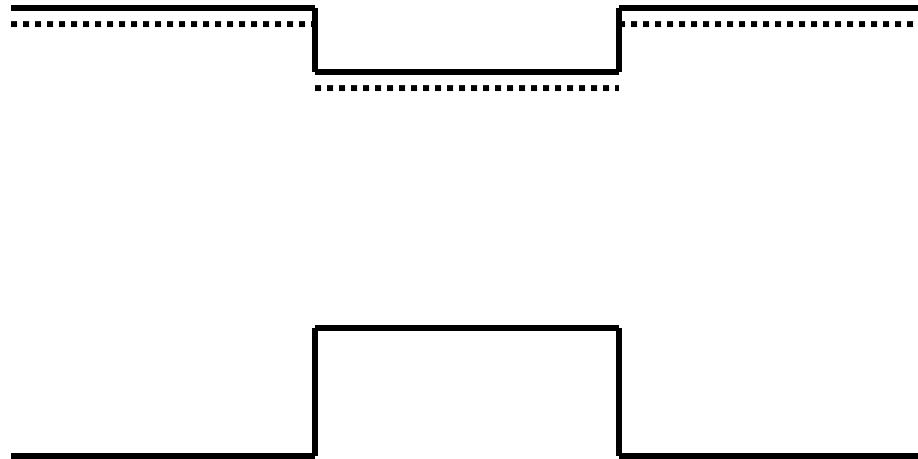# InP/InGaAs/InP Square Well
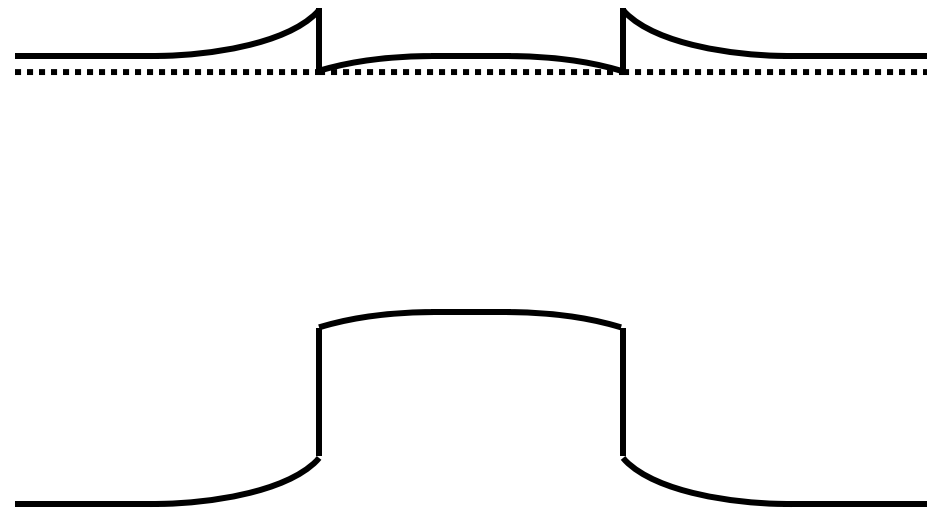
- N+ InGaAs: $E_g$=.76 eV
- N+ InP: $E_g$=1.35 eV

?

# InP/InGaAs/InP Square Well

- N+ InGaAs: $E_g$=.76 eV

- N+ InP: $E_g$=1.35 eV

- $\Delta E_g$=.59 eV
- $\Delta E_c$=.25 eV
- $\Delta E_v$=.34 eV

- Draw the flatband diagram first, ignoring doping.

# InP/InGaAs/InP Square Well

- N+ InGaAs: $E_g$=.76 eV

- N+ InP: $E_g$=1.35 eV

- $\Delta E_g$=.59 eV

- $\Delta E_c$=.20 eV

- $\Delta E_v$=.39 eV

# General comments

- If the composition is constant, the bandgap is constant. Hence, the separation of conduction band and valence band are constant.

- If there is no field, the bands are horizontal.

- Use the depletion edge approximation; either the material is depleted of free carriers (and the bands are bent) or there is no field and the bands are flat.

- Depleted doped material has a quadratic bend and linearly increasing field.

- Depleted undoped material has constant electric field and linear band bending.

$$\frac{d^2\Phi}{dx^2} = -\frac{\rho}{\varepsilon} = -\frac{p - n + N_D - N_A}{\varepsilon}$$

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# InP/InGaAs/InP Square Well

- N+ InGaAs: $E_g = .76$ eV
- N+ InP: $E_g = 1.35$ eV
- ☐ $\Delta E_g = .59$ eV
- ☐ $\Delta E_c = .20$ eV
- ☐ $\Delta E_v = .39$ eV
- Adjust Fermi level to account for bias.
- Keep bandgaps constant.
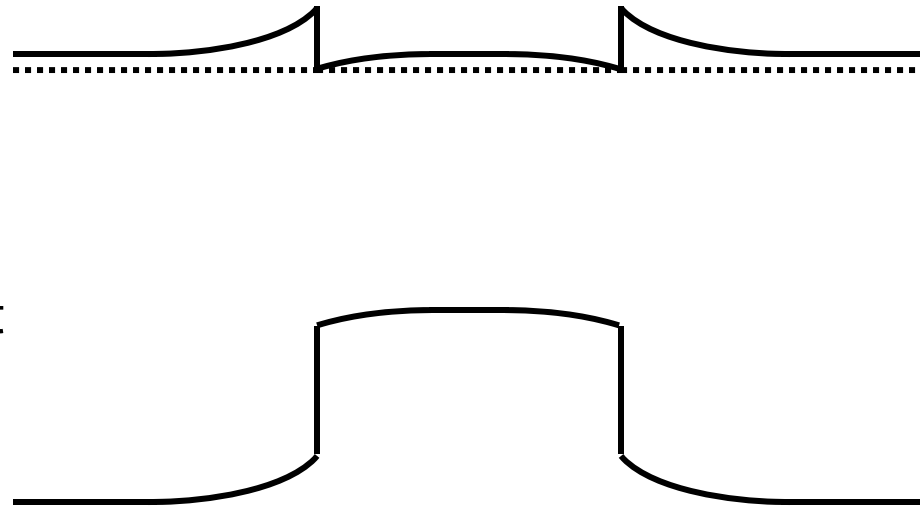
Calculate the absorption bandedge assuming a 100 Angstrom quantum well and $m_e^* = 0.1\ m_e$ and $m_h^* = 1\ m_e$

Calculate the absorption bandedge assuming a 100 Angstrom quantum dot and $m_e^* = 0.1\ m_e$ and $m_h^* = 1\ m_e$

Check the validity of your assumptions.