UNIVERSITÀ
DEGLI STUDI DI TRIESTE

Scienza dei Materiali
-lezione 6-

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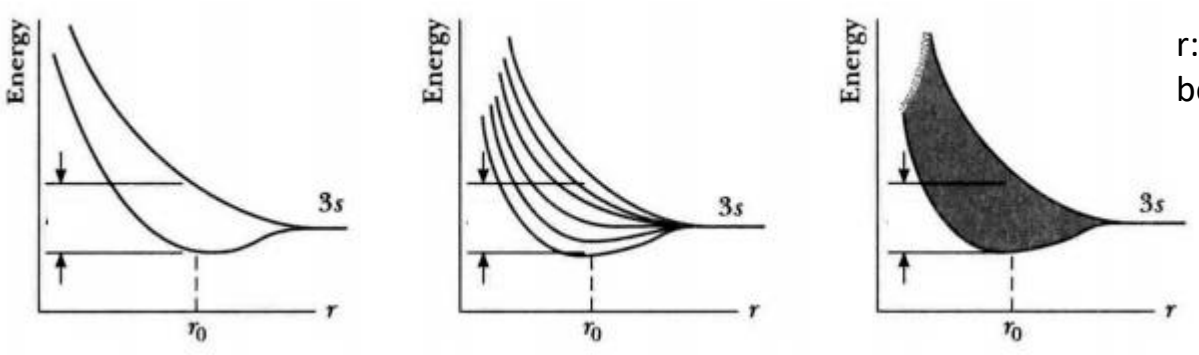
Critical review of bonding

- Bonding states are stable because they have electrons in the middle → this resembles the H_2^+ covalent bonding
- Antibonding states are unstable because they create antialigned dipoles

- If the distance between two atoms (potential wells, boxes) is shortened, splitting of energy levels increases (see example with quantum wells)

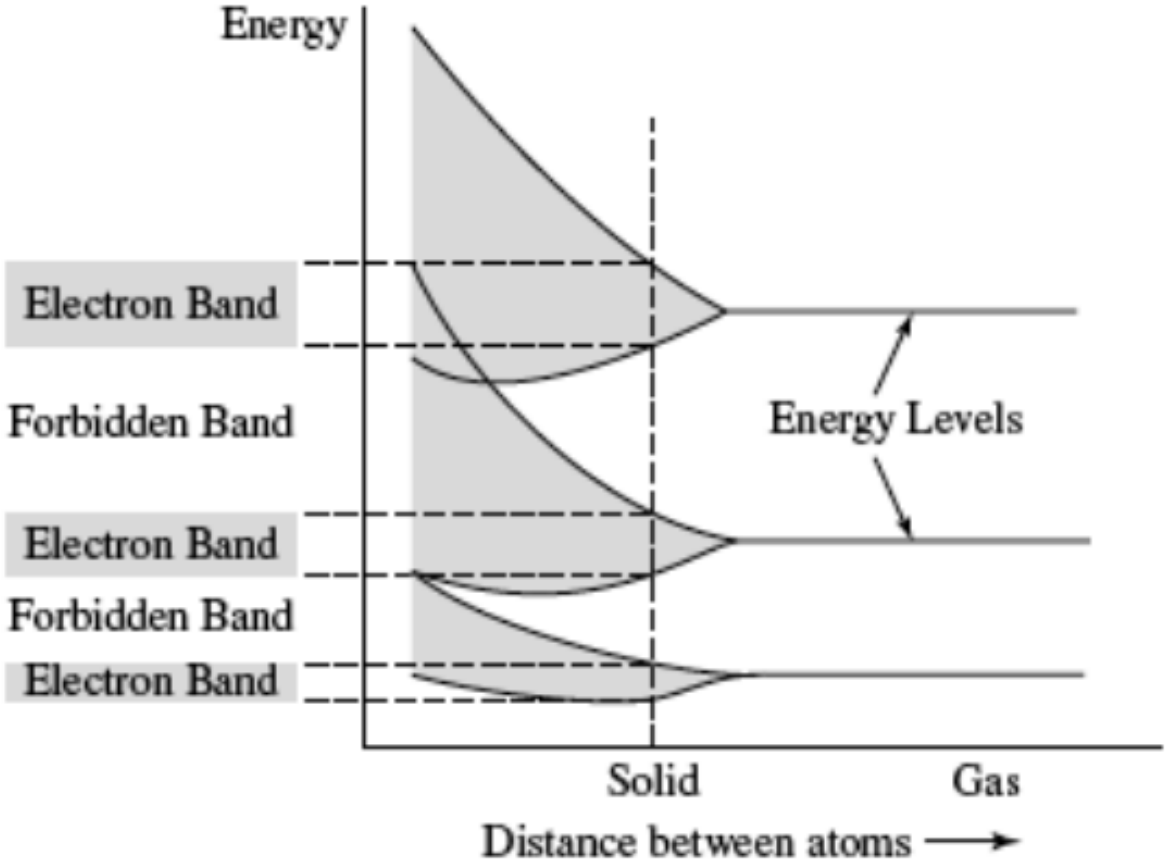
- Adding the repulsion energy (origin: Pauli's exclusion principle) gives the overall bonding energy



r: distance between atoms

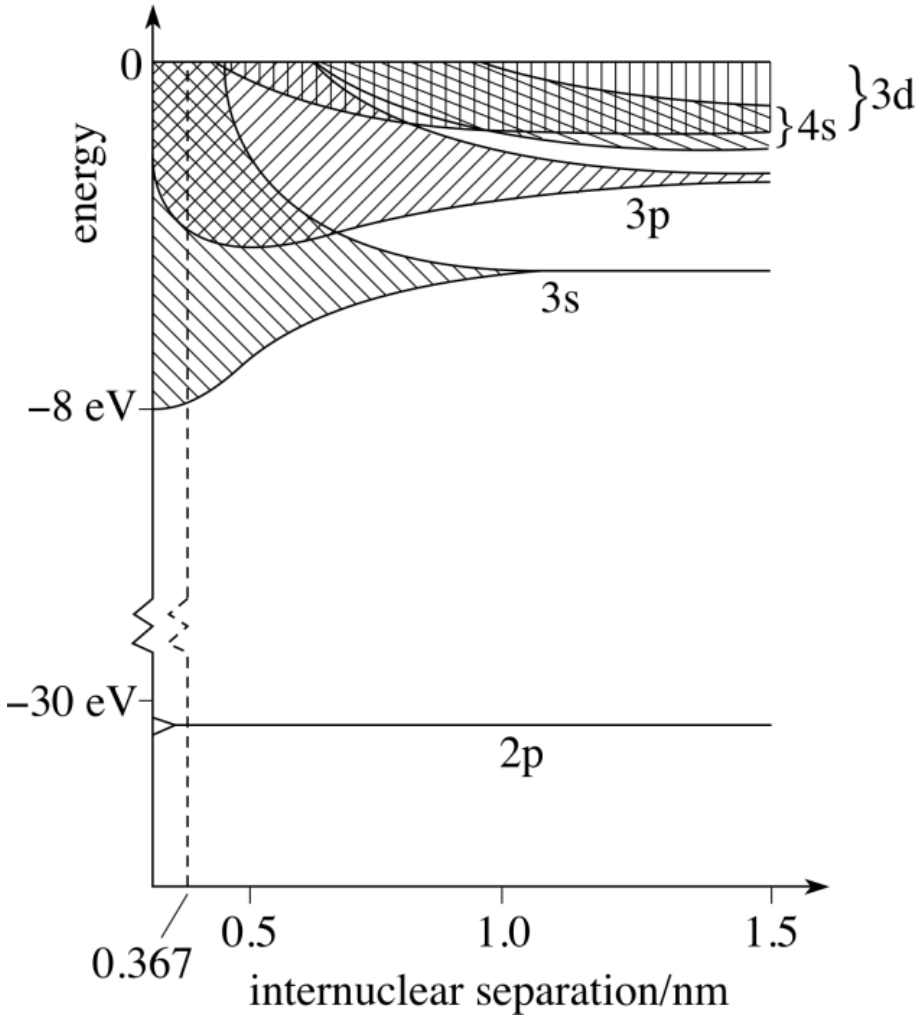
Increasing number of atoms involved

Band Theory of Solids



Band Theory of Solids

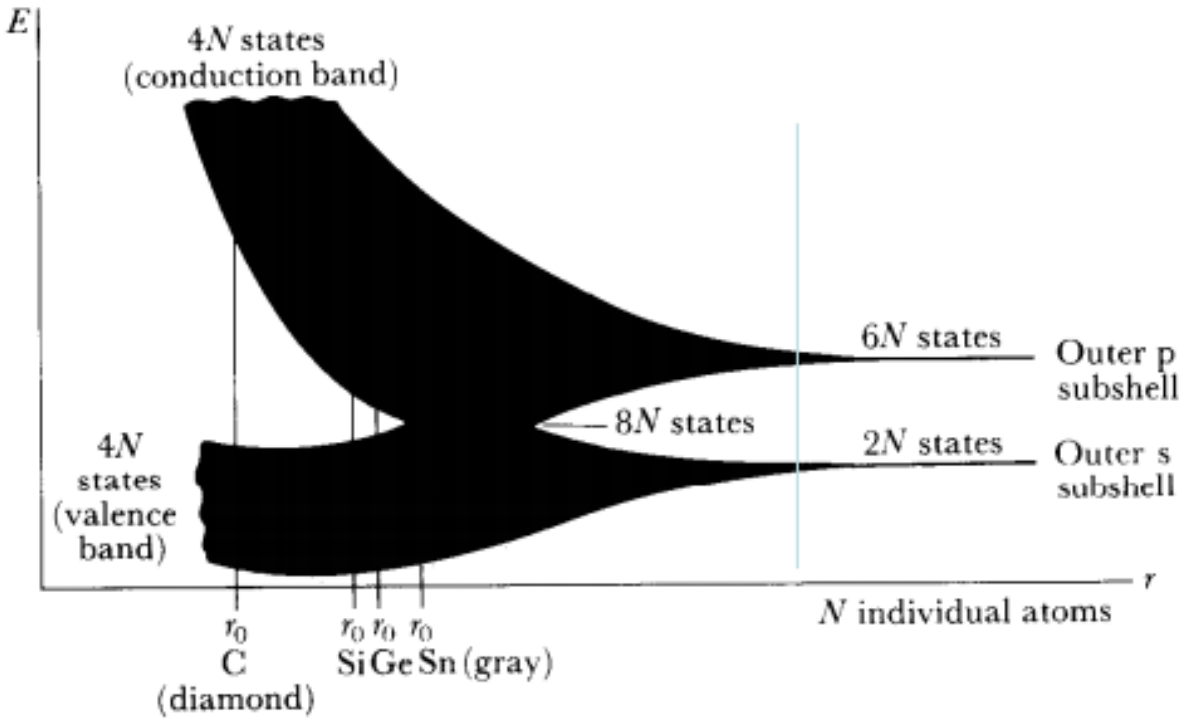
- the example of sodium -



Band Theory of Solids

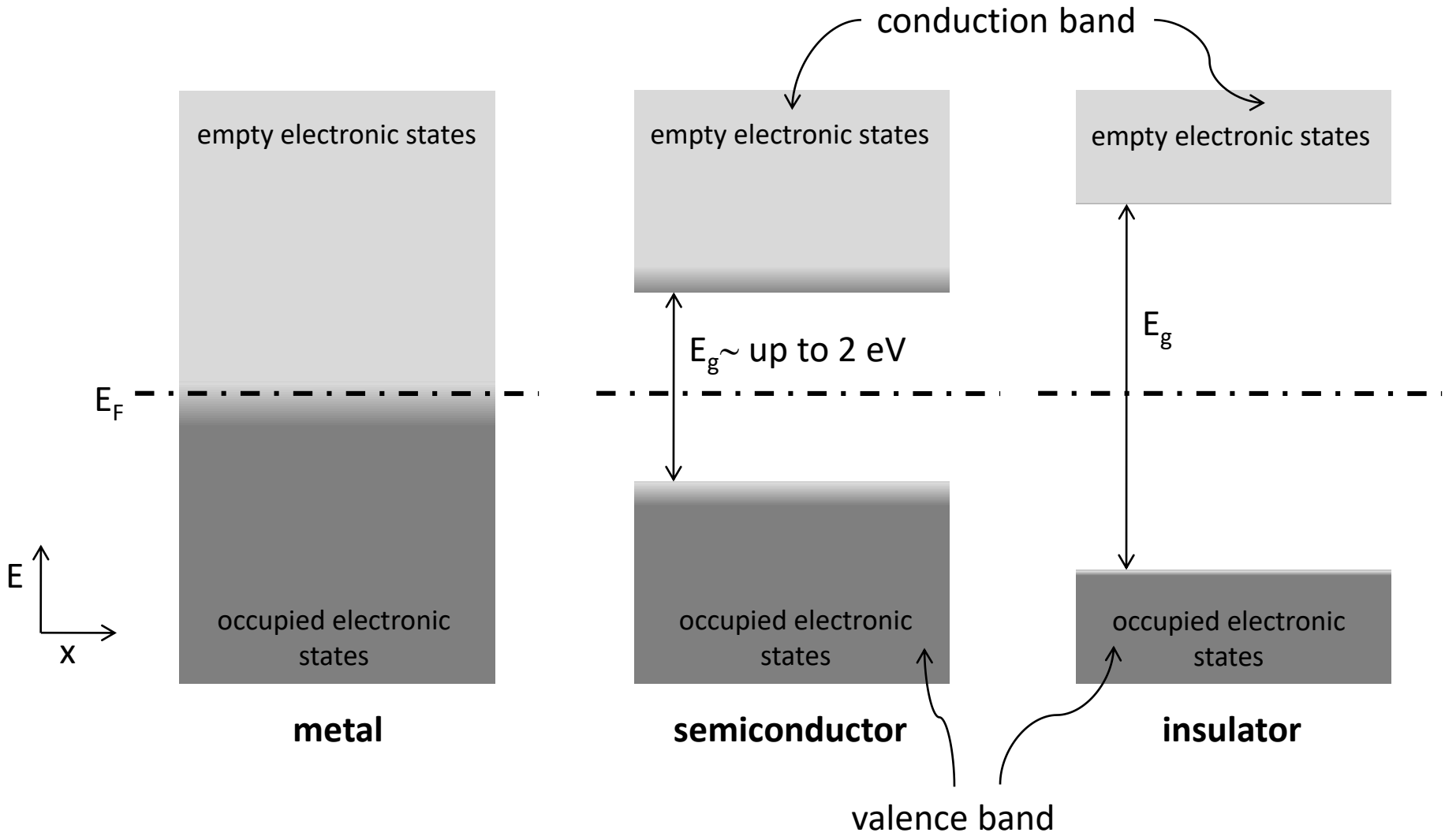
- the example of group IV elemental substances -

5	6	7
B	C	N
Boron	Carbon	Nitrogen
Metalloid	Nonmetal	Nonmetal
13	14	15
Al	Si	P
Aluminum	Silicon	Phosphorus
ost-Transiti	Metalloid	Nonmetal
31	32	33
Ga	Ge	As
Gallium	Germanium	Arsenic
ost-Transiti	Metalloid	Metalloid
49	50	51
In	Sn	Sb
Indium	Tin	Antimony
ost-Transiti	Post-Transiti...	Metalloid



Classification of Solids

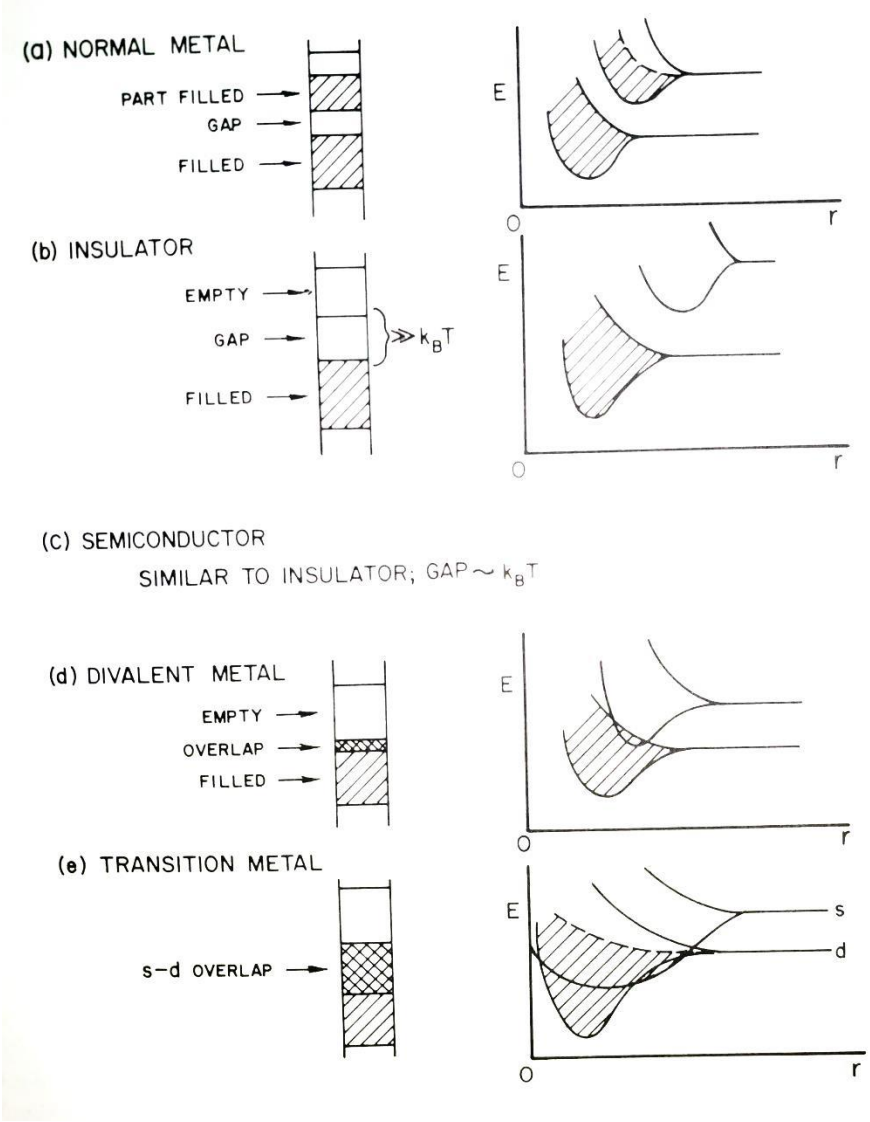
- according to Band Theory -



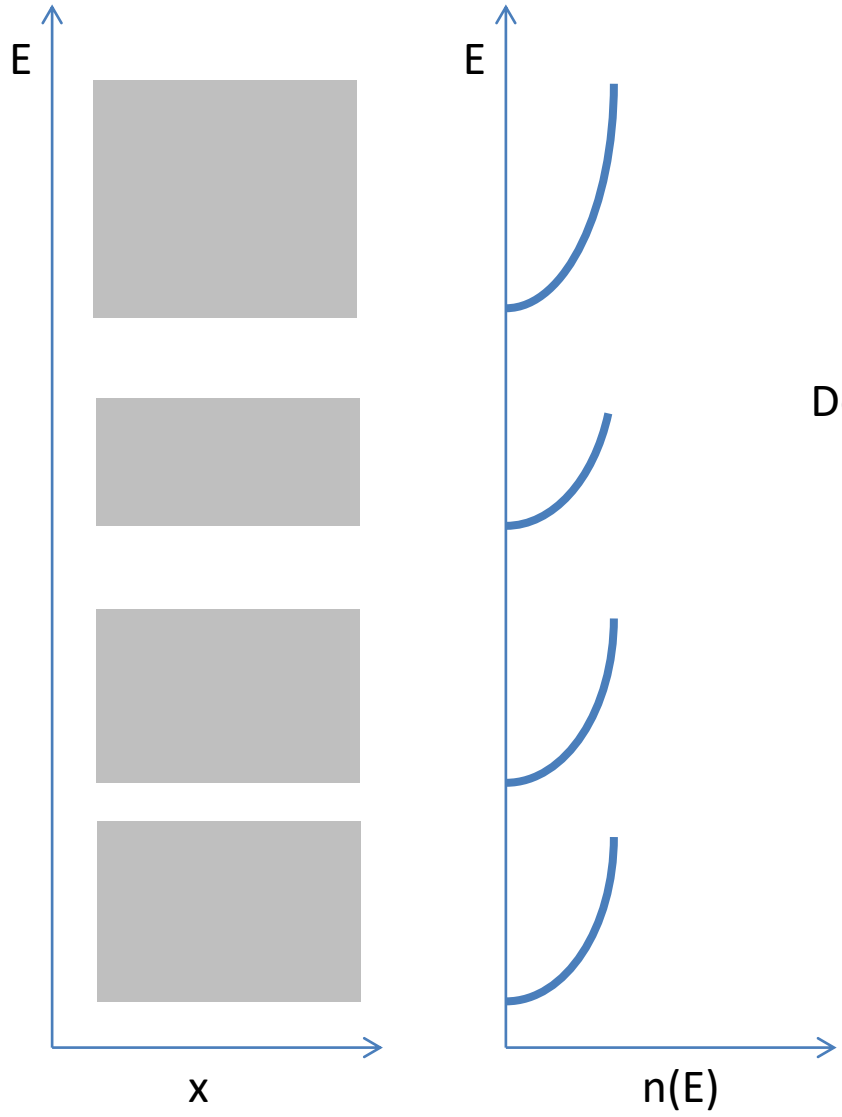
Side note: E_g for semiconductors is much larger than k_bT… What's going on?

Classification of Solids

- according to Band Theory -



Density of States

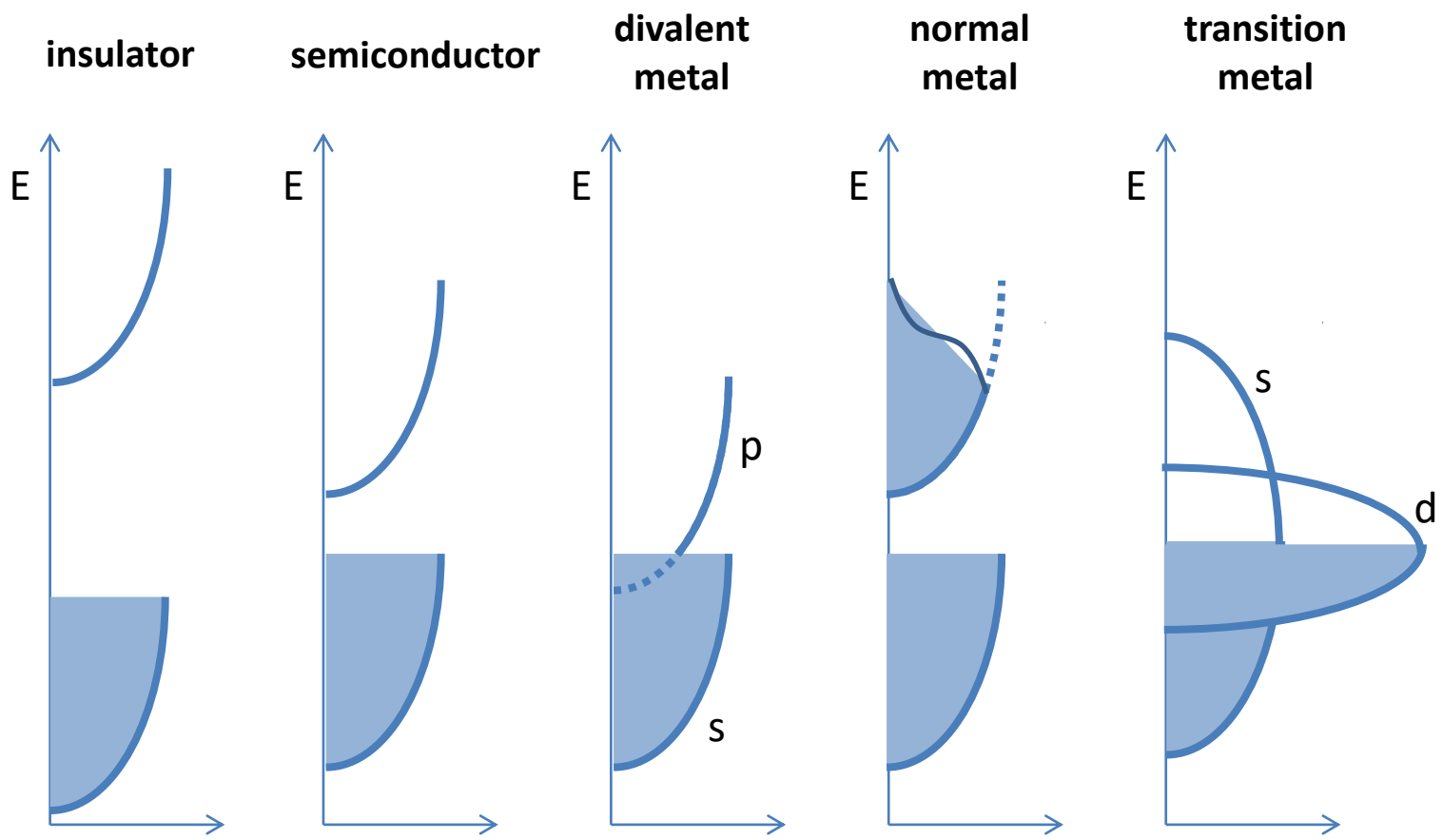


Density of States (DoS)

$$n(E) \propto E^{1/2}$$

Classification of Solids

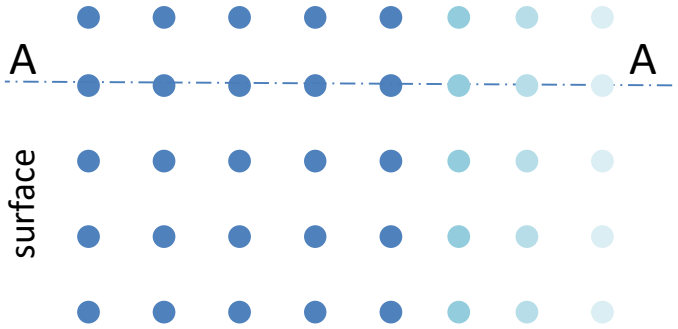
- according to Band Theory -

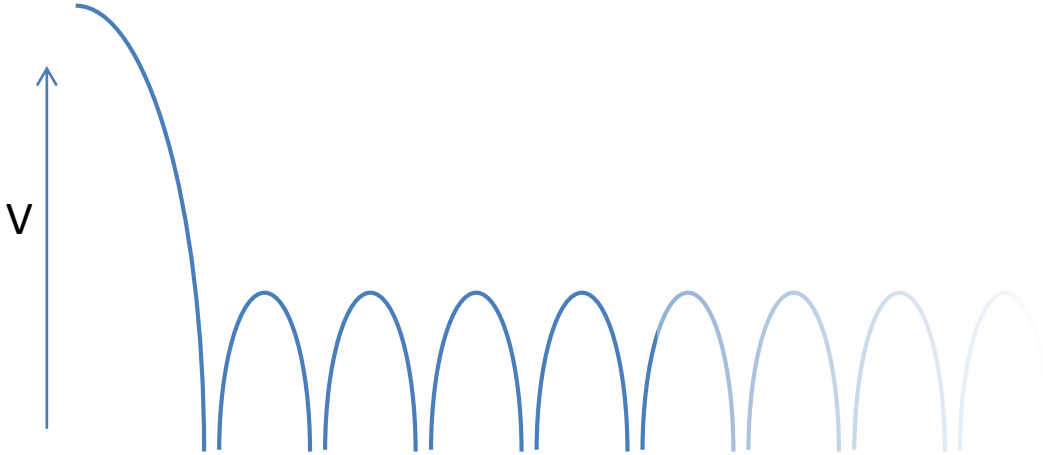


$$N(E) = n(E)f(E)$$

Periodicity of Crystal Potential

Potential in solids is not constant, it is periodic
Direction is important

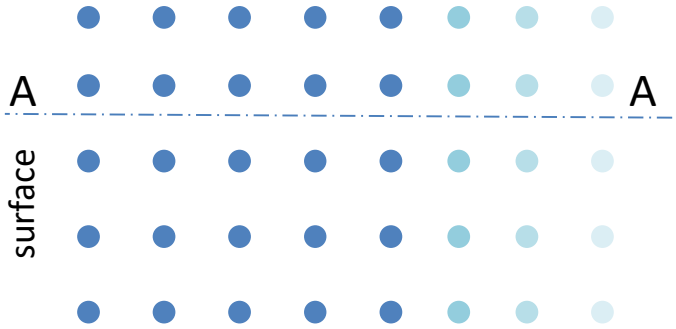


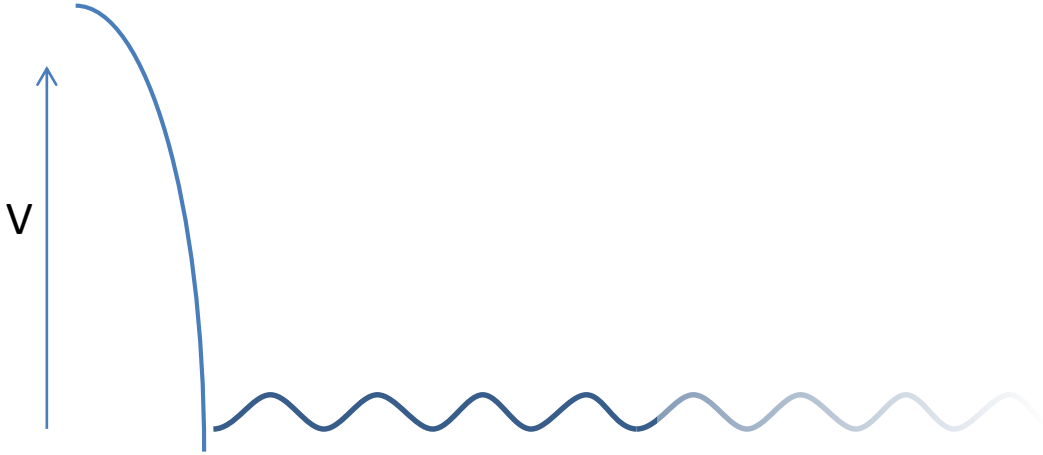


Potential along A-A

Periodicity of Crystal Potential

Potential in solids is not constant, it is periodic
Direction is important





Potential along A-A

Periodicity of Crystal Potential

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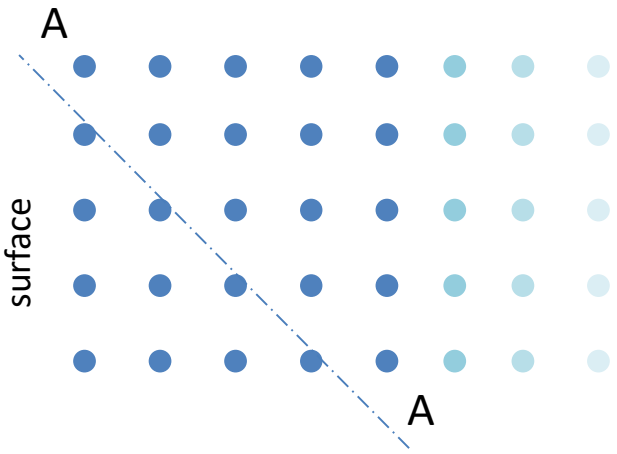
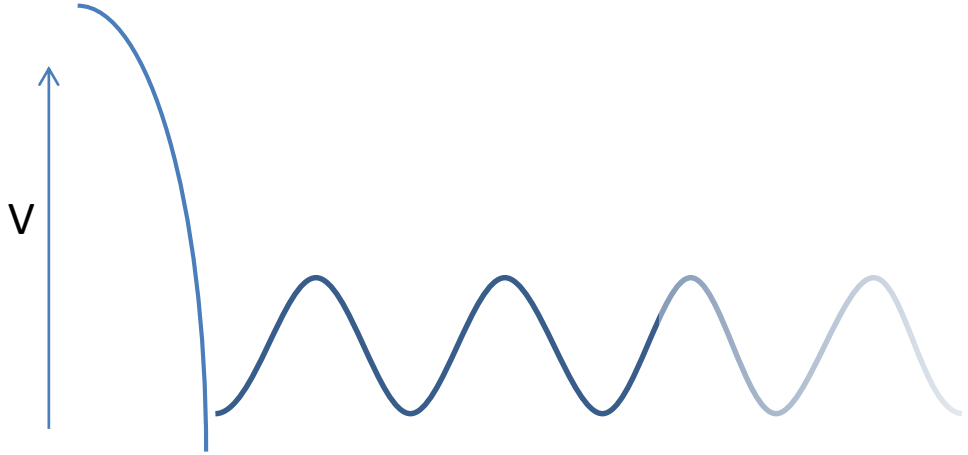
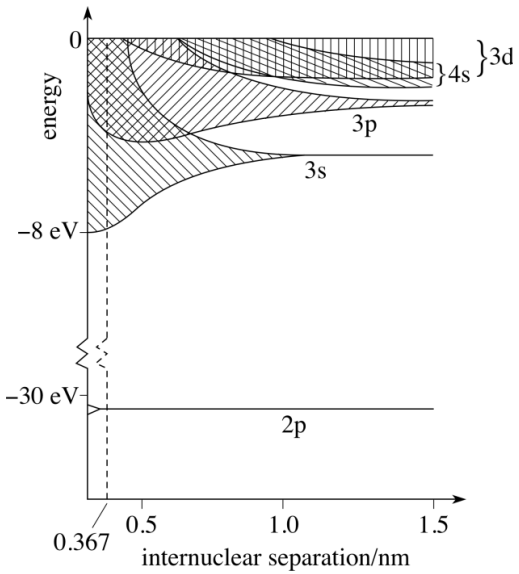
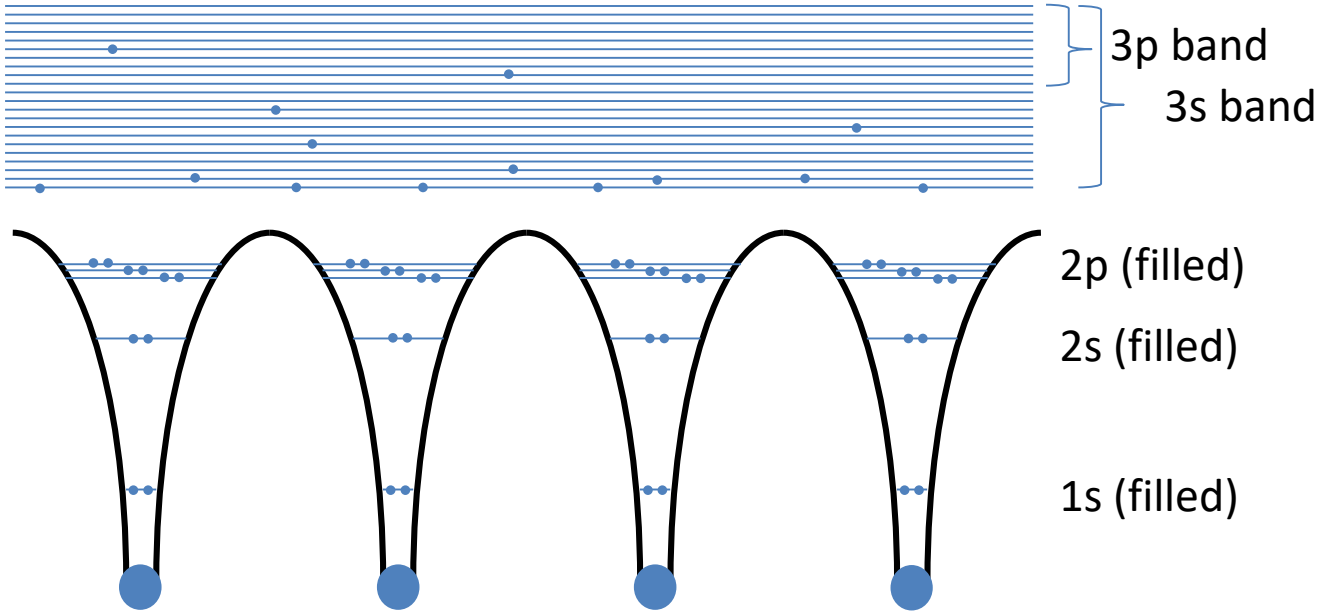




Potential along A-A

Band Theory of Solids





CRYSTAL LATTICES

A crystal lattice is defined by the **unit cell vectors**:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

with $\vec{a}_1,\ \vec{a}_2,\ \vec{a}_3$ linearly independent: $(\vec{a}_1 \wedge \vec{a}_2)\cdot\vec{a}_3 \neq 0$

$n_i \in \mathbb{Z}$: 0; ±1; ±2; ±3; …

Volume

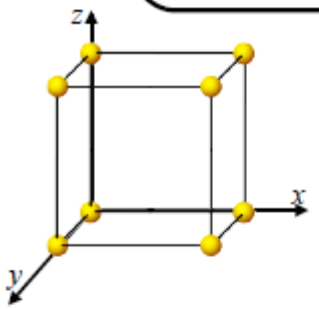
$$\begin{vmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{vmatrix} = \vec{a}_1 \cdot (\vec{a}_2 \wedge \vec{a}_3)$$

Examples:

SC – Simple Cubic

$$Vol = a^3$$

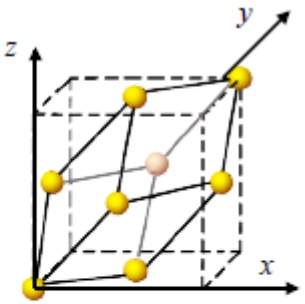
$\vec{a}_1 = a\ (1,\ 0,\ 0)$
$\vec{a}_2 = a\ (0,\ 1,\ 0)$
$\vec{a}_3 = a\ (0,\ 0,\ 1)$



FCC – Face Centred Cubic

$$Vol = \frac{a^3}{8}\begin{vmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \\ 1 & 0 & 1 \end{vmatrix} = \frac{a^3}{4}$$

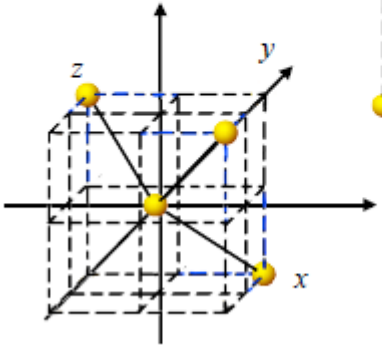
$\vec{a}_1 = a/2\ (1,\ 1,\ 0)$
$\vec{a}_2 = a/2\ (0,\ 1,\ 1)$
$\vec{a}_3 = a/2\ (1,\ 0,\ 1)$



BCC – Body Centred Cubic

$$Vol = \frac{a^3}{8}\begin{vmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{vmatrix} = \frac{a^3}{2}$$

$\vec{a}_1 = a/2\ (-1,\ 1,\ 1)$
$\vec{a}_2 = a/2\ (1,\ -1,\ 1)$
$\vec{a}_3 = a/2\ (1,\ 1,\ -1)$



THE RECIPROCAL LATTICE

It is a lattice of **wave vectors** $\vec{k}$ (dimension $\left[\frac{1}{L}\right]$).

$$\vec{b}_i = 2\pi \frac{\vec{a}_j \wedge \vec{a}_k}{\vec{a}_i \cdot \left[\vec{a}_j \wedge \vec{a}_k\right]}$$

where i, j, k, are *ordered* triplets (1,2,3 – 3,1,2 – 2,3,1)

$$\begin{cases} \vec{b}_1 = 2\pi \dfrac{\vec{a}_2 \wedge \vec{a}_3}{\vec{a}_1 \cdot \left[\vec{a}_2 \wedge \vec{a}_3\right]} \\ \vec{b}_2 = 2\pi \dfrac{\vec{a}_3 \wedge \vec{a}_1}{\vec{a}_2 \cdot \left[\vec{a}_3 \wedge \vec{a}_1\right]} \\ \vec{b}_3 = 2\pi \dfrac{\vec{a}_1 \wedge \vec{a}_2}{\vec{a}_3 \cdot \left[\vec{a}_1 \wedge \vec{a}_2\right]} \end{cases}$$

→ **reciprocal lattice:**

$$\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$$

we construct it this way because of the following property of the **plane waves** $e^{i\vec{G}\cdot\vec{r}}$:

RECIPROCAL LATTICES

Theorem:

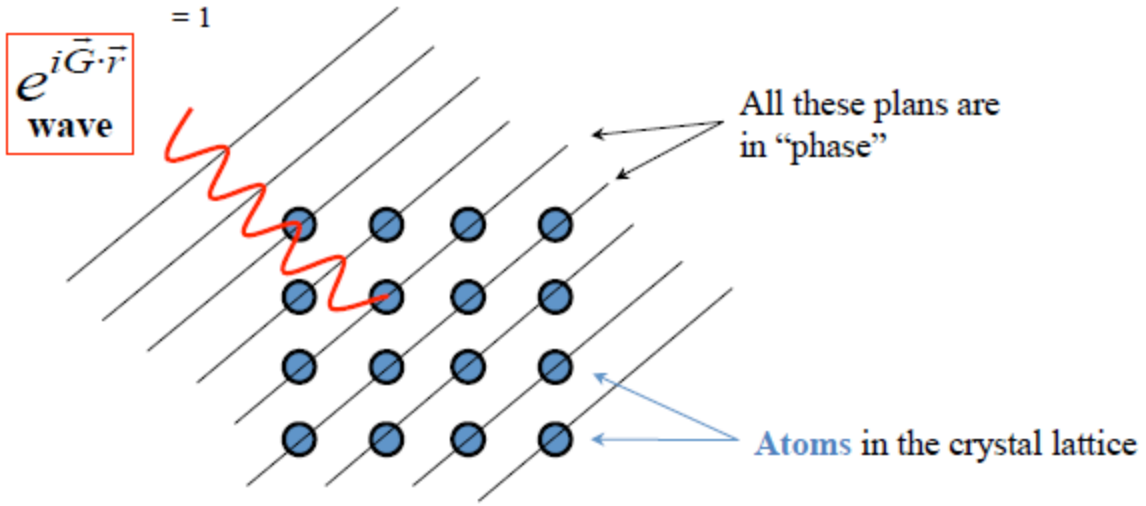
The function $e^{i\vec{G}\cdot\vec{r}}\ \forall \vec{G} \in$ reciprocal lattice, has the lattice periodicity:

$$e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r}}\ \forall \vec{R} \in \text{direct lattice}$$

Proof:

$$\begin{cases} \vec{G}\cdot\vec{R} = (n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3)(m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3) \\ \vec{a}_i\cdot\vec{b}_j = 2\pi\delta_{ij} \qquad \delta_{ij}\begin{cases} 1 & \text{if } i=j \\ 0 & \text{otherwise} \end{cases} \end{cases} \Longrightarrow \quad \therefore \vec{G}\cdot\vec{R} = 2\pi\underbrace{(n_1m_1 + n_2m_2 + n_3m_3)}_{\text{an integer}}$$

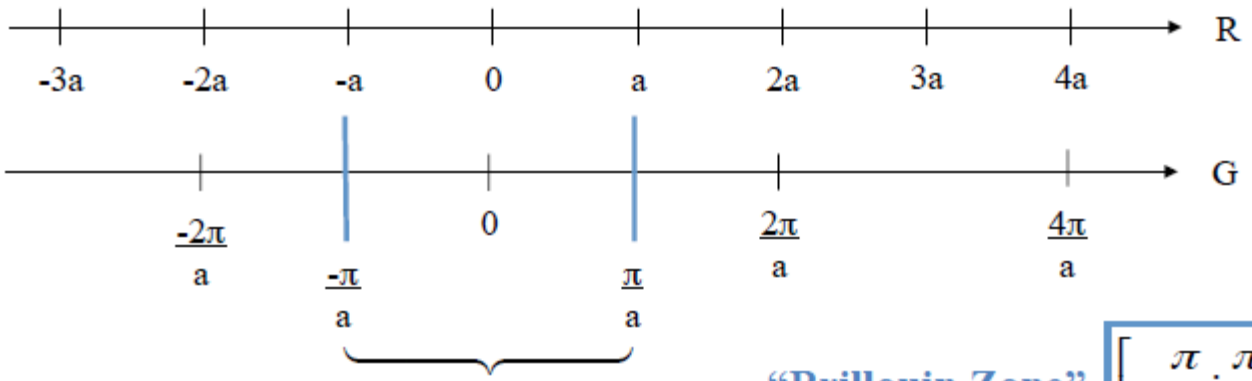
so $e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r}}\cdot\underbrace{e^{i\vec{G}\cdot\vec{R}}}_{=1} = e^{i\vec{G}\cdot\vec{r}}$



RECIPROCAL LATTICES

a simple example: 1d

$$\begin{cases} \text{lattice} & R = na \\ \text{r. lattice} & G = \dfrac{2\pi}{a} m \\ R \cdot G = \left[\left(\dfrac{2\pi}{a} \right) \cdot a \right] n\, m = 2\pi\, n\, m \end{cases} \qquad \therefore e^{i\frac{2\pi}{a}mx} = \cos\left(\frac{2\pi}{a} mx\right) + i \sin\left(\frac{2\pi}{a} mx\right)$$



"Brillouin Zone" $\left[-\dfrac{\pi}{a}; \dfrac{\pi}{a} \right[$

Note that $f(\vec{r}) = \sum_{G \in RL} c_G \cdot e^{i\vec{G}\cdot\vec{r}}$ is a general periodic function

$\Rightarrow$ $e^{i\vec{G}\cdot\vec{r}}$ = (Fourier) **basis for all those functions periodic** over the lattice

RECIPROCAL LATTICES

Exercise 1: Reciprocal lattice of a simple cubic?

$$\begin{cases} \vec{b}_1 = 2\pi \dfrac{\vec{a}_2 \wedge \vec{a}_3}{Volume} = \dfrac{2\pi}{a^3} a^2 \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = \dfrac{2\pi}{a}(1,\ 0,\ 0) \\ \vec{b}_2 = \dfrac{2\pi}{a}(0,\ 1,\ 0\ ) \\ \vec{b}_3 = \dfrac{2\pi}{a}(0,\ 0,\ 1) \end{cases}$$

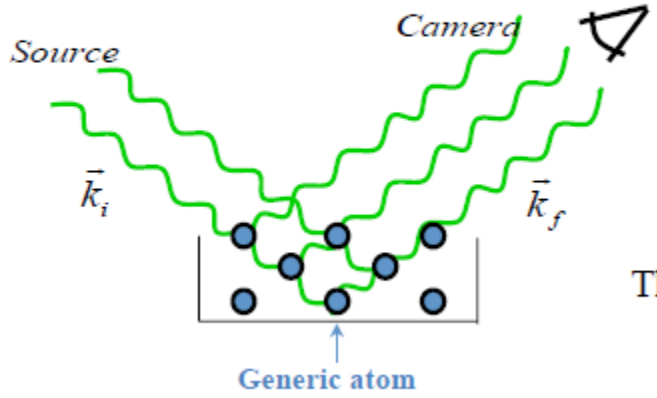
Q: what is the volume of the RL unit cell?

A: clearly $\left(\dfrac{2\pi}{a}\right)^3 = V_G$

➡ product of direct and reciprocal unit cell volumes $= V_R V_G = (2\pi)^3 \qquad (3D)$

Exercise 2: prove that the RL of a BCC lattice is a FCC lattice
prove that the RL of a FCC lattice is a BCC lattice
prove that the volumes product is $(2\pi)^3$ in each of these cases.

DIFFUSION OF LIGHT



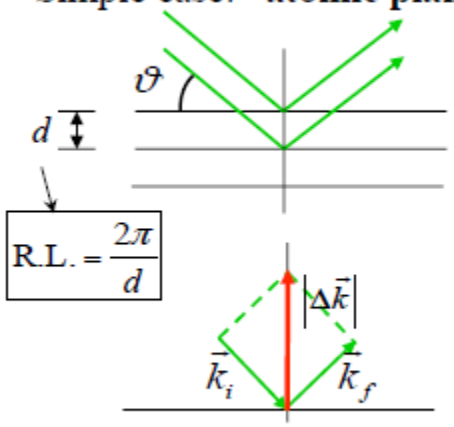
For positive interference at the receiving point $\vec{R}$ all waves must be in phase $\vec{R}_I$.

Total Phase: $e^{i\,\vec{k}_i\cdot\vec{R}_I}\cdot e^{i\,\vec{k}_f\cdot(\vec{R}-\vec{R}_I)}$

The ion-dependent part is: $e^{-i\,(\vec{k}_f-\vec{k}_i)\cdot\vec{R}_I}$

So a criterium for a **diffraction peak** is the: **Bragg condition:** $\boxed{\Delta\vec{k}=\vec{G}}$

Simple case: **"atomic planes"**



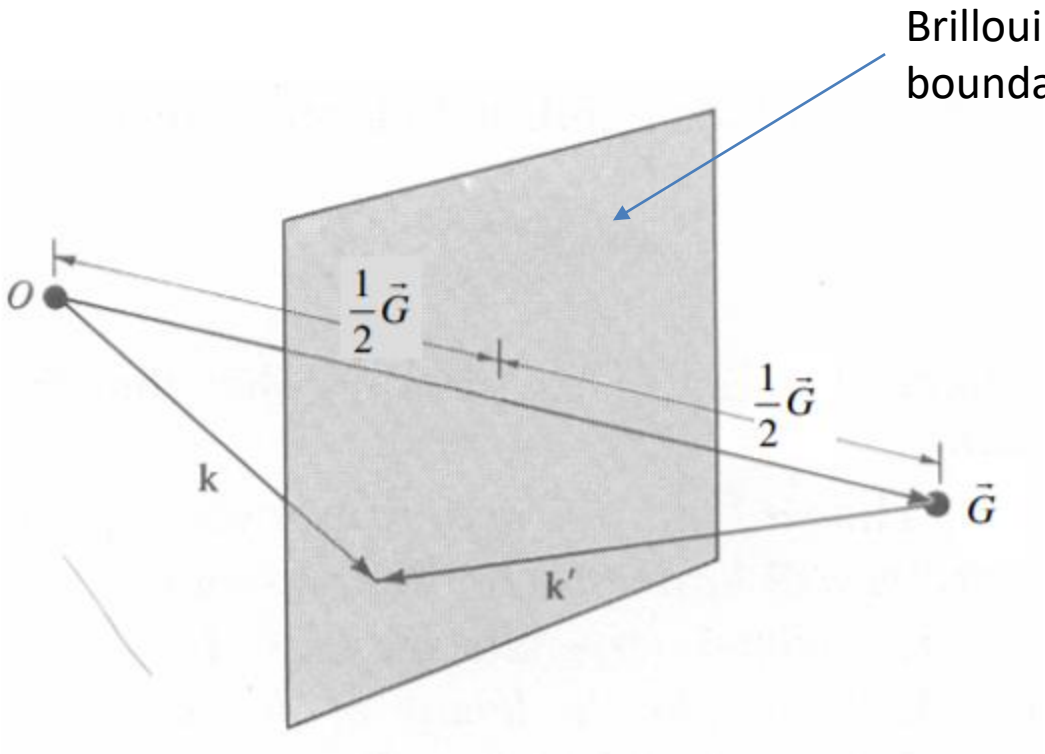
$2d\sin\vartheta$ = difference of path $= n\lambda$

$|\Delta\vec{k}| = 2k\sin\vartheta$ but is also $|\Delta\vec{k}| = m\frac{2\pi}{d}$ and remember $k=\frac{2\pi}{\lambda}$

$\Rightarrow\ 2\frac{2\pi}{\lambda}\sin\vartheta = m\frac{2\pi}{d}$ $\Rightarrow$ $\boxed{2d\sin\vartheta = m\lambda}$ as above.

Note $|\vec{k}_i| = |\vec{k}_f| = k$ $\Rightarrow$ "Elastic scattering" = the energy of the photon is conserved!

we know that $E=\hbar\omega$ $\Rightarrow$ same $\upsilon,\ \lambda,\ k$...!


Brillouin zone boundary!!!
O
$\frac{1}{2}\vec{G}$
$\frac{1}{2}\vec{G}$
k
$\vec{G}$
k′

Band Theory of Solids

- Brillouin theory and the dependence on k -

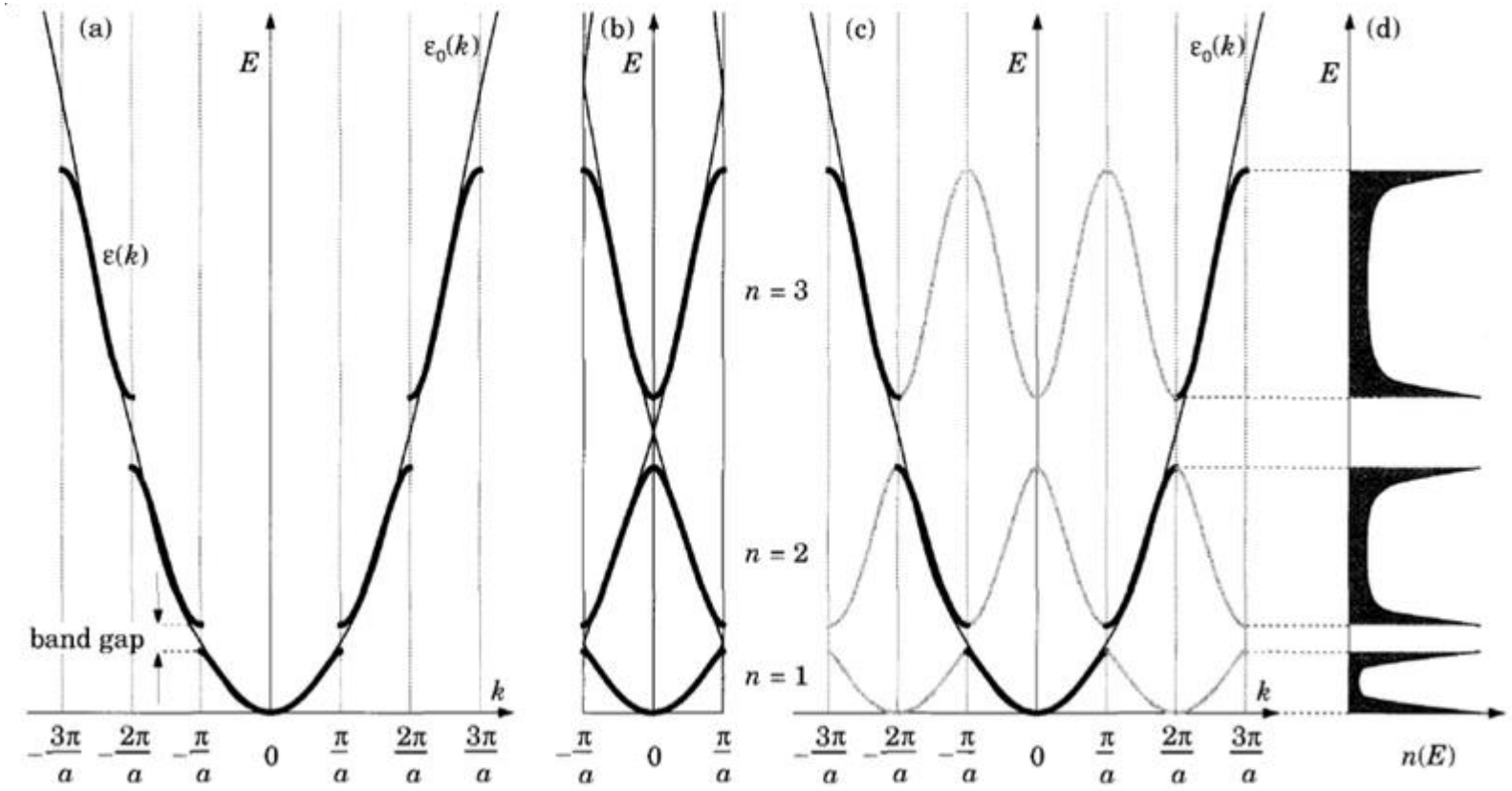


Figure 2.2. Band structure of a one-dimensional crystal in the (a) extended, (b) reduced, and (c) repeated zone schemes, and (d) the density of states as a function of energy. The thick lines show $\varepsilon(k)$ in a weak periodic potential, with bands labelled by n, while the thin parabola is $\varepsilon_0(k)$ for free electrons. The grey lines are periodic repeats.

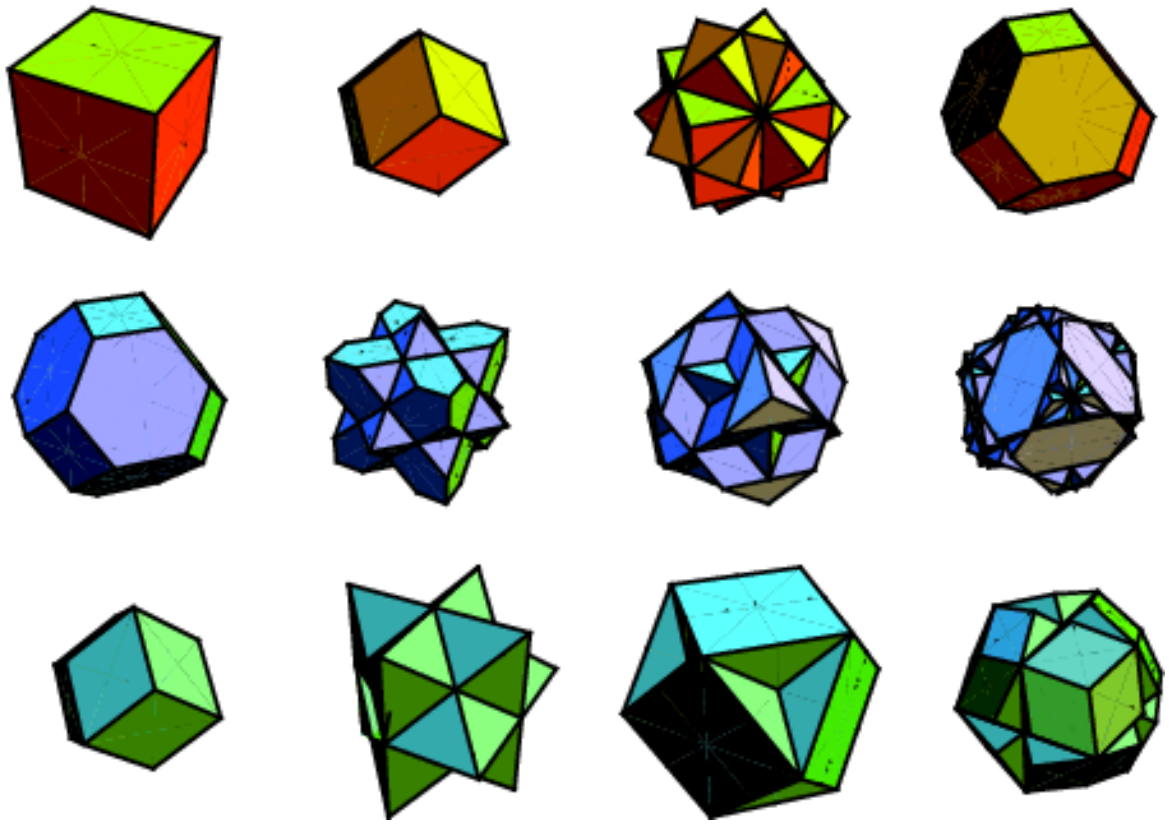
Band Theory of Solids

- Brillouin zones in 3D -

simple cubic

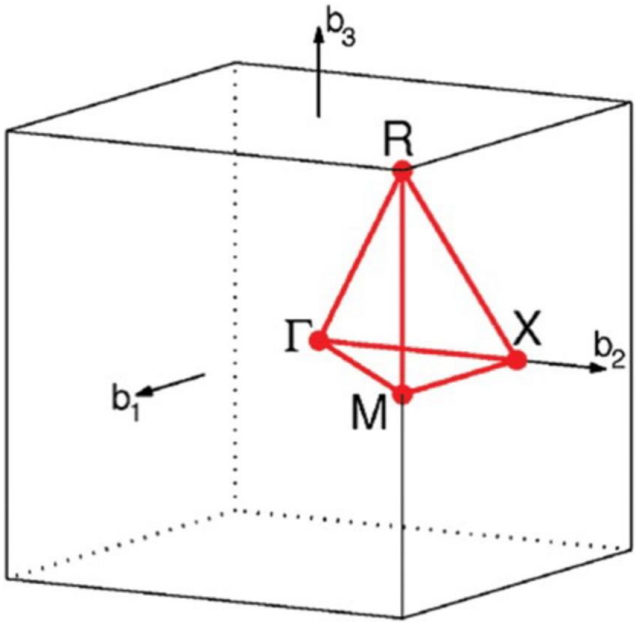
face-centered cubic

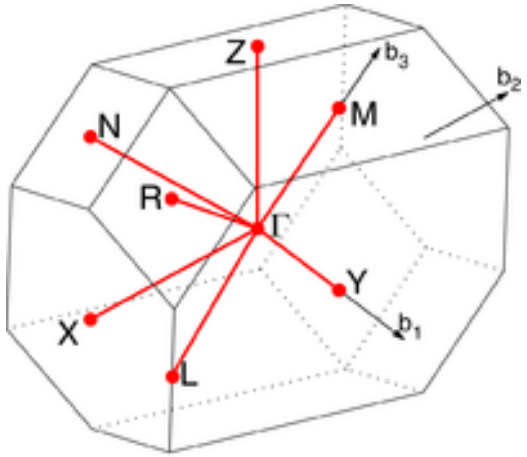
body-centered cubic



Band Theory of Solids

- Brillouin zones in 3D -

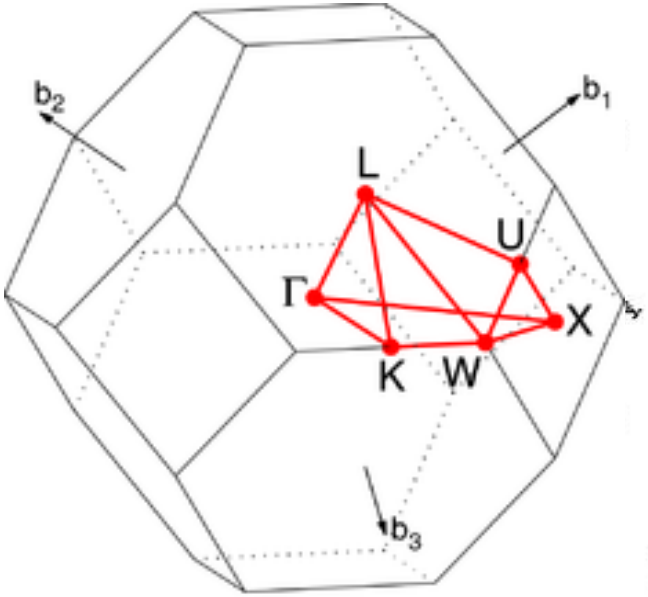




Band Theory of Solids

- Brillouin zones in 3D -

Free electron bands for fcc structure



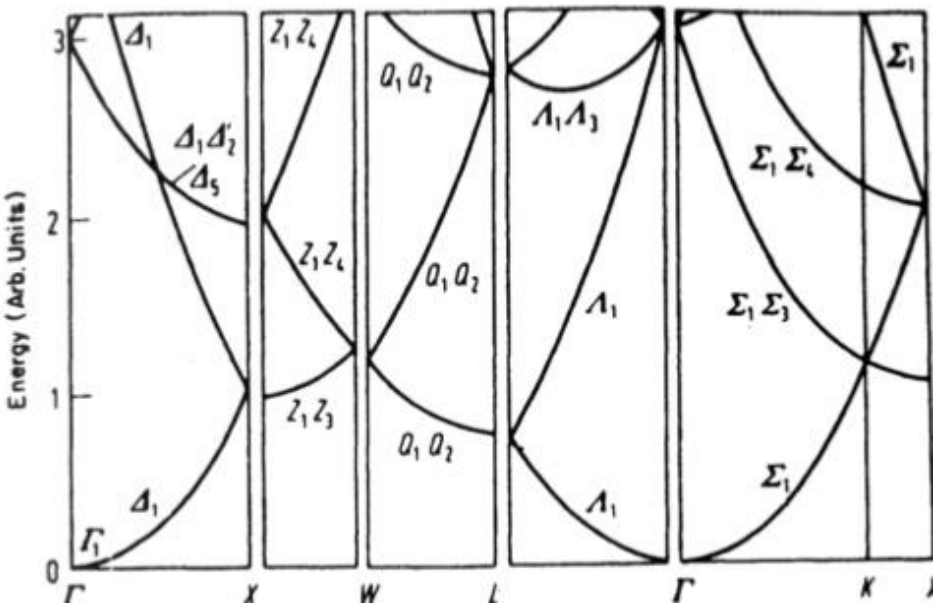
FCC path: Γ-X-W-K-Γ-L-U-W-L-K|U-X

Γ – center of the BZ

X – [100] intercept; Γ – X path Δ

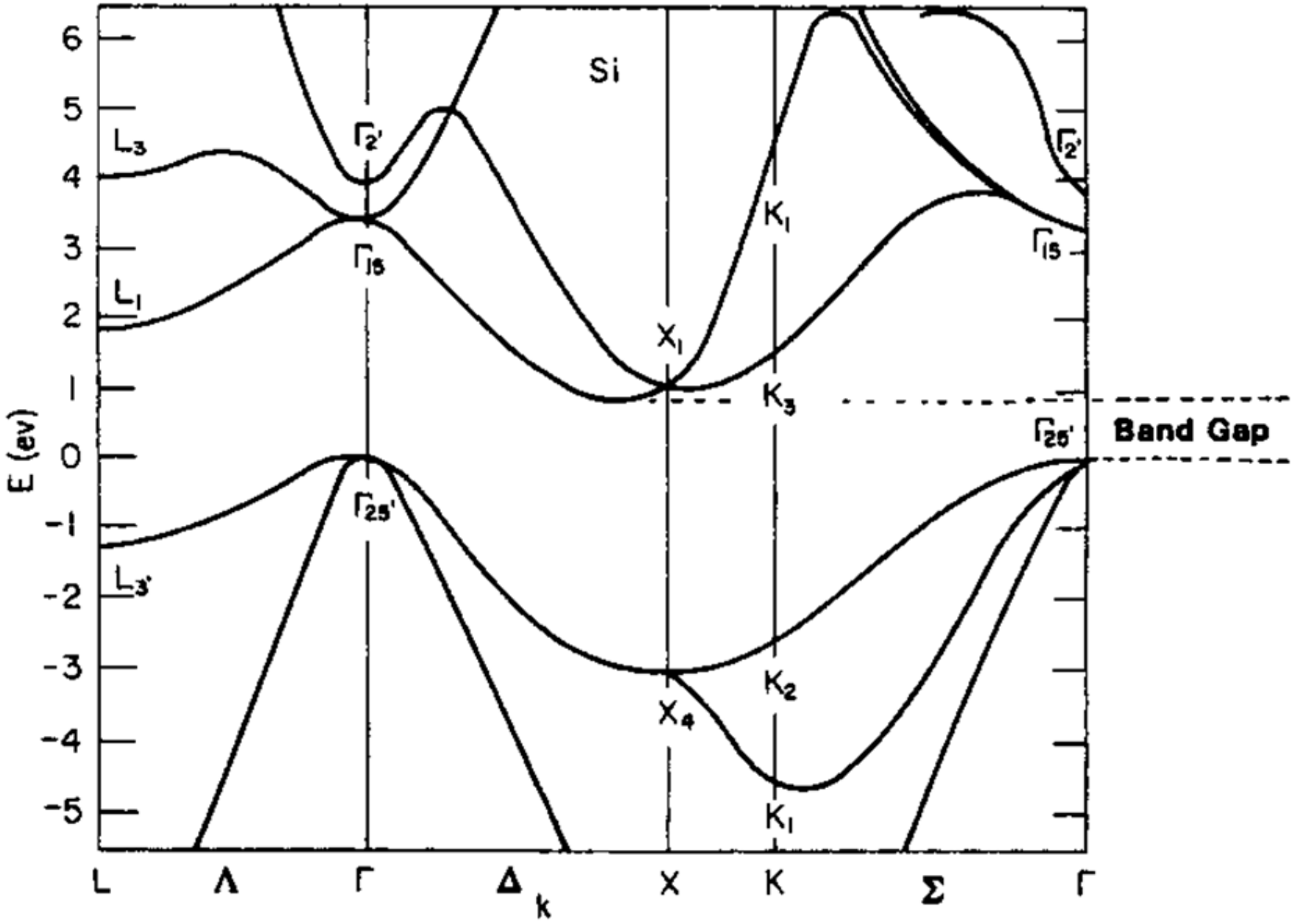
K – [110] intercept; Γ – K path Σ

L – [111] intercept; Γ – L path Λ

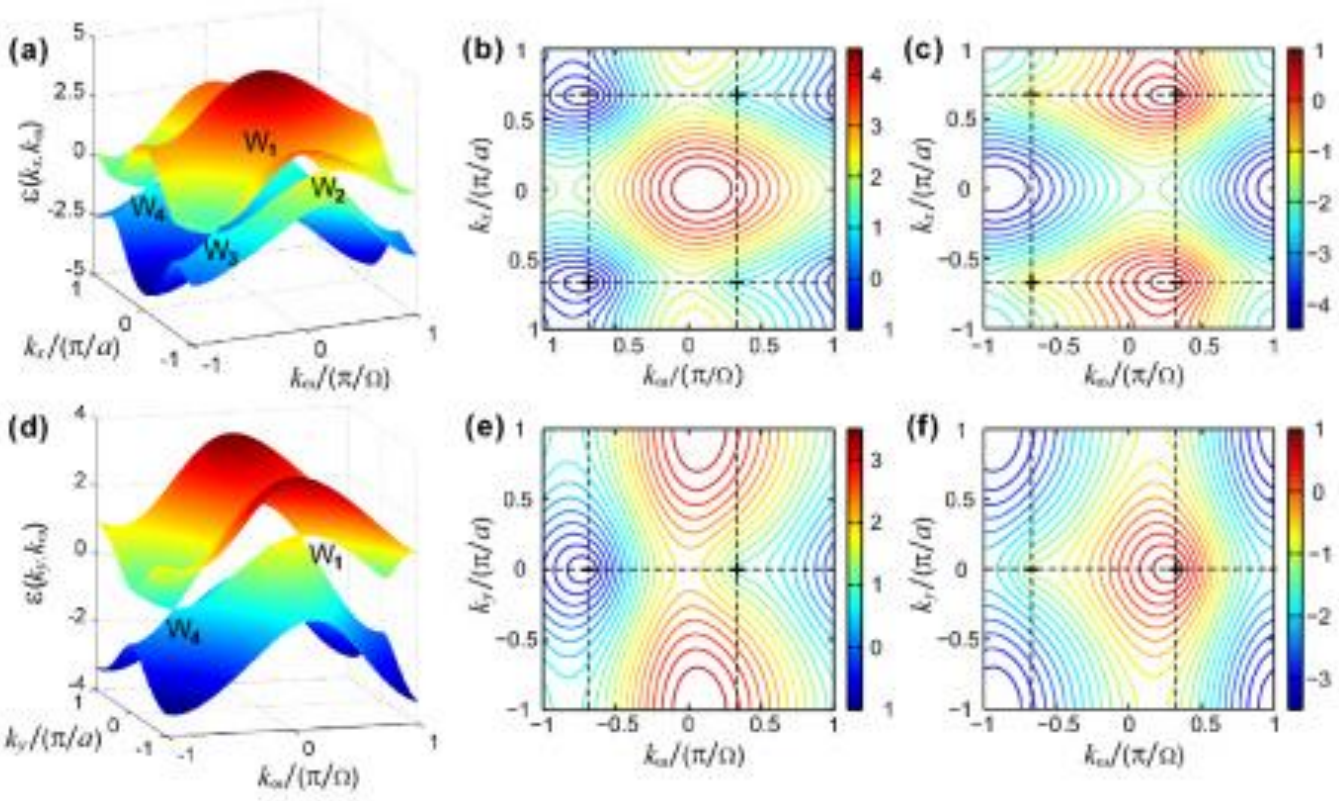


Band Theory of Solids

- Brillouin zones in 3D -



Representing Bands – a different way



Statistics

- Probability of occupation of a state

$$\bar{n} = \frac{n_s}{g_s}$$

number of particles
number of states with energy E_s

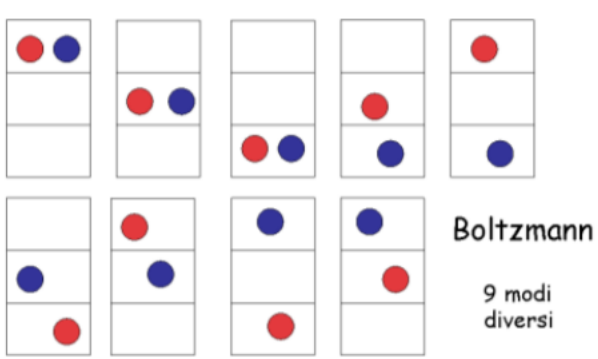
Boltzmann	Bose Einstein	Fermi Dirac
$\bar{n}_k = \frac{1}{\exp\left(\frac{\varepsilon-\mu}{k_B T}\right)}$	$\bar{n}_k = \frac{1}{\exp\left(\frac{\varepsilon-\mu}{k_B T}\right)-1}$	$\bar{n}_k = \frac{1}{\exp\left(\frac{\varepsilon-\mu}{k_B T}\right)+1}$
indistinguishable $Z=(Z_1)^N/\mathbf{N!}$ $n_K<<1$	indistinguishable integer spin 0,1,2 …	indistinguishable half-integer spin 1/2,3/2,5/2 …
spin doesn't matter	bosons	fermions
localized particles Ψ don't overlap	wavefunctions overlap total Ψ symmetric	wavefunctions overlap total Ψ anti-symmetric
gas molecules at low densities	photons ^{4}He atoms	free electrons in metals electrons in white dwarfs
"unlimited" number of particles per state	unlimited number of particles per state	never more than 1 particle per state

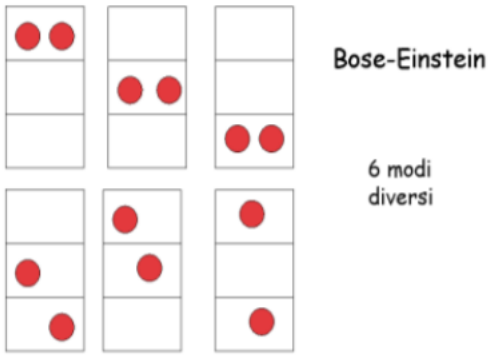
Statistics

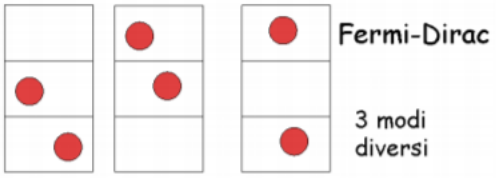
- Probability of occupation of a state

$$\bar{n} = \frac{n_s}{g_s}$$

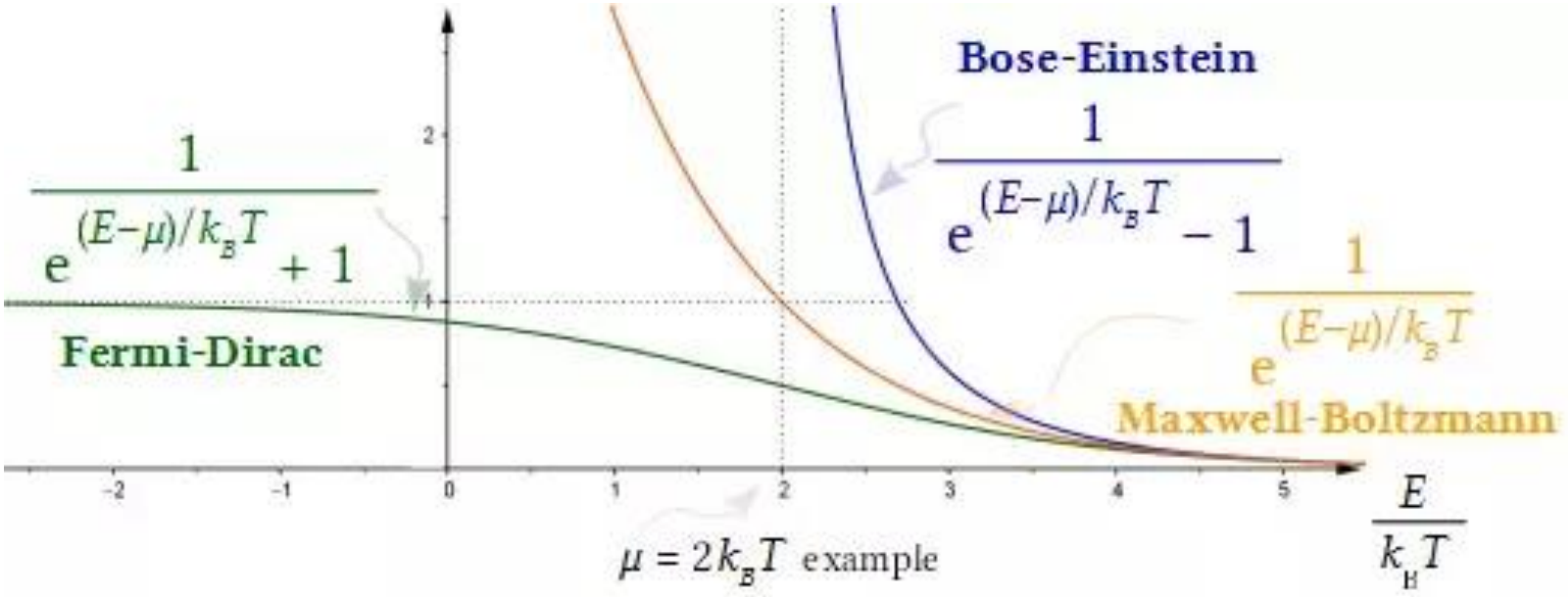
n_s: number of particles
g_s: number of states with energy E_s



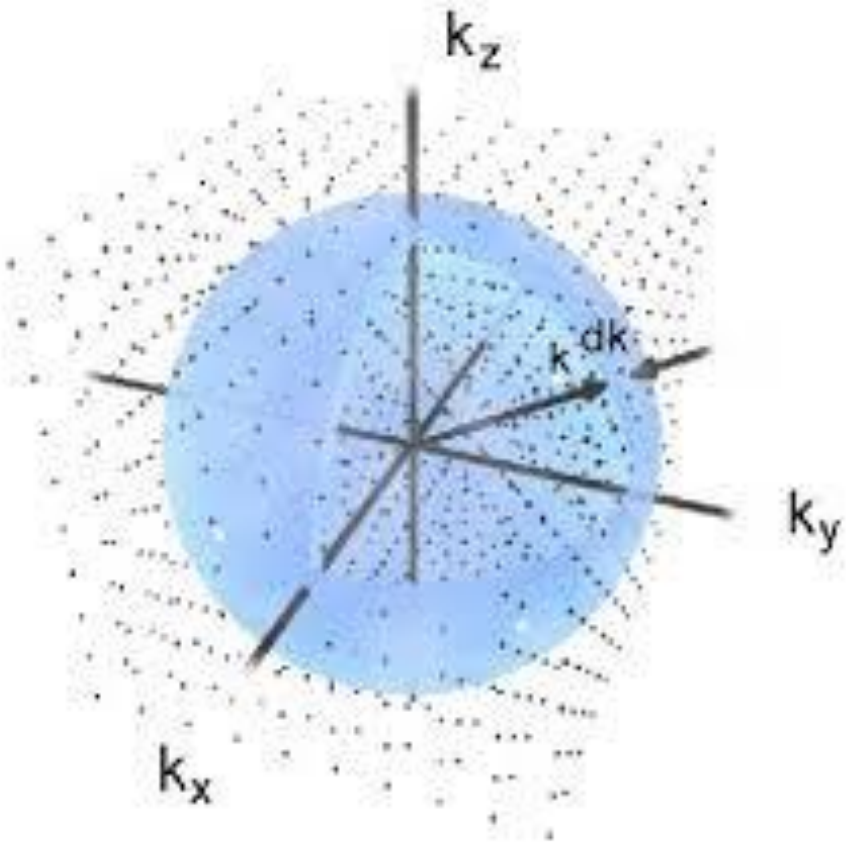




Statistics


Bose-Einstein
$\frac{1}{e^{(E-\mu)/k_BT} - 1}$
$\frac{1}{e^{(E-\mu)/k_BT} + 1}$
Fermi-Dirac
$\frac{1}{e^{(E-\mu)/k_BT}}$
Maxwell-Boltzmann
$\mu = 2k_BT$ example
$\frac{E}{k_BT}$
-2
-1
0
1
2
3
4
5

Calculating the density of states



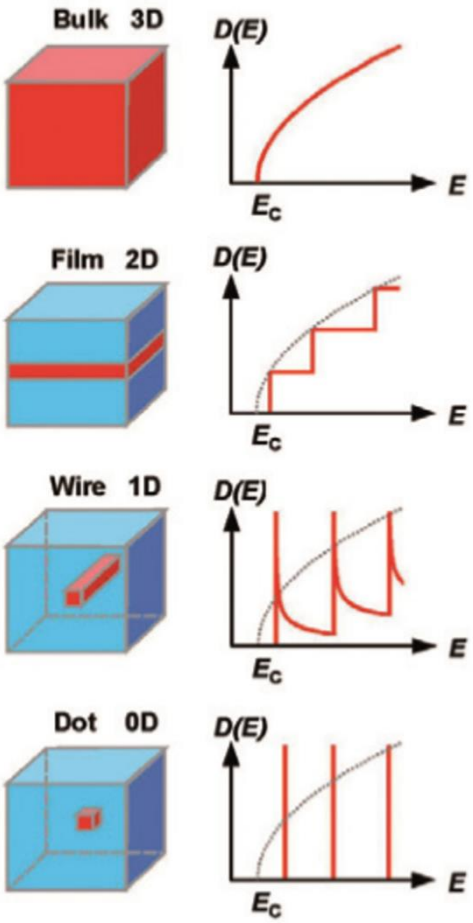
Densità degli stati per unità di volume reale

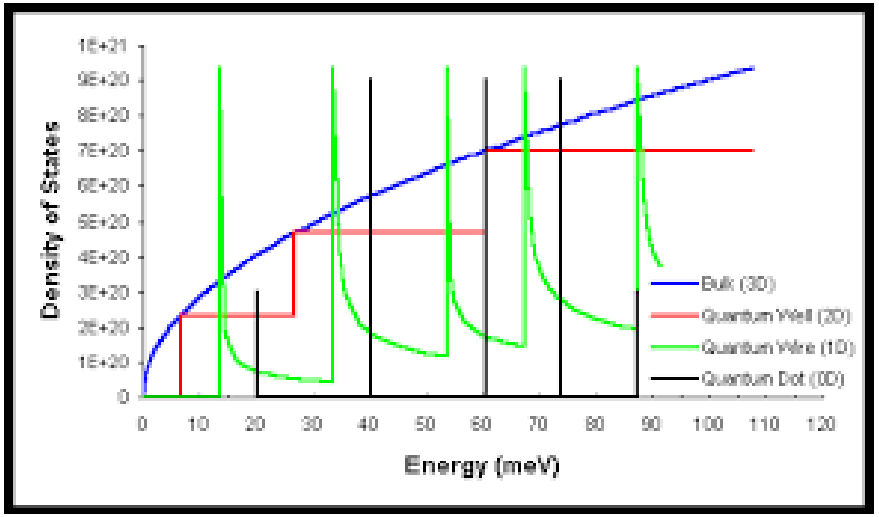
$$n(k) = 2 \cdot \frac{1}{V} \cdot \frac{1}{\Omega}$$

V: volume della cella unitaria nello spazio reciproco

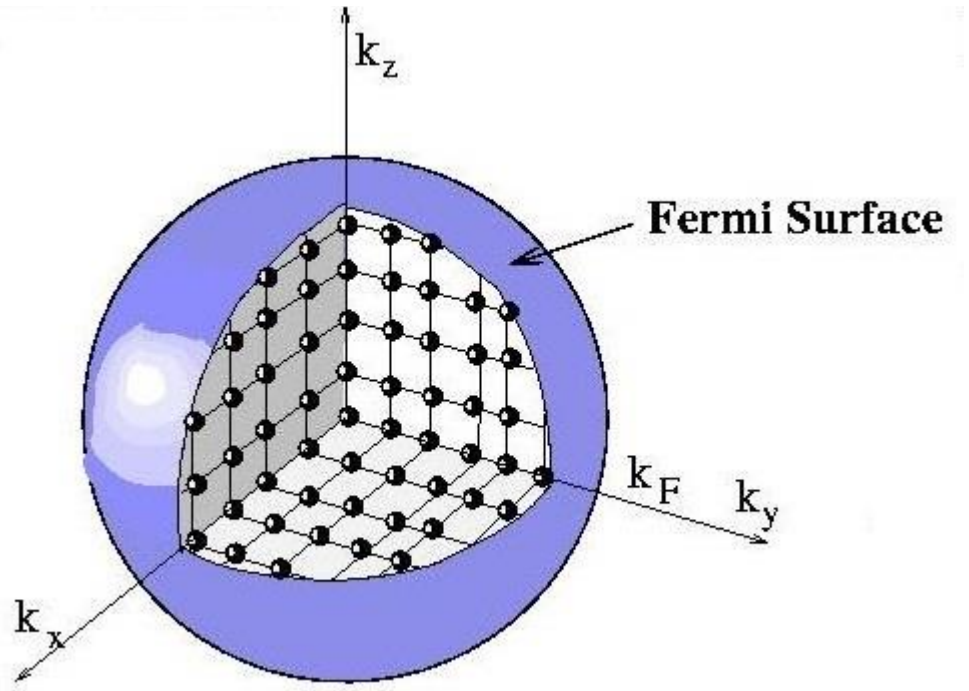
$$n(E) = \frac{8m\pi}{h^3}\sqrt{2mE}$$

Density of States in 3D, 2D, 1D, 0D





Fermi Energy and Average Electron Energy



$$E_F = \frac{h^2}{8m}\left[\frac{3N}{\pi V}\right]^{2/3}$$

$$\bar{E} = \frac{3}{5}E_F$$

$$E_F \sim units\ of\ eV$$

Transport in solids

Energy (approximate with a sin function)

$$E(k) = W \sin^2 \frac{ka}{2}$$

$$E(k) \sim \frac{W}{4} a^2 k^2$$

Velocity

$$v(k) = \frac{a}{2\hbar} W \sin ka$$

Effective mass

$$m^*(k) = \frac{2\hbar^2}{m_0 a^2 W} \sec ka$$