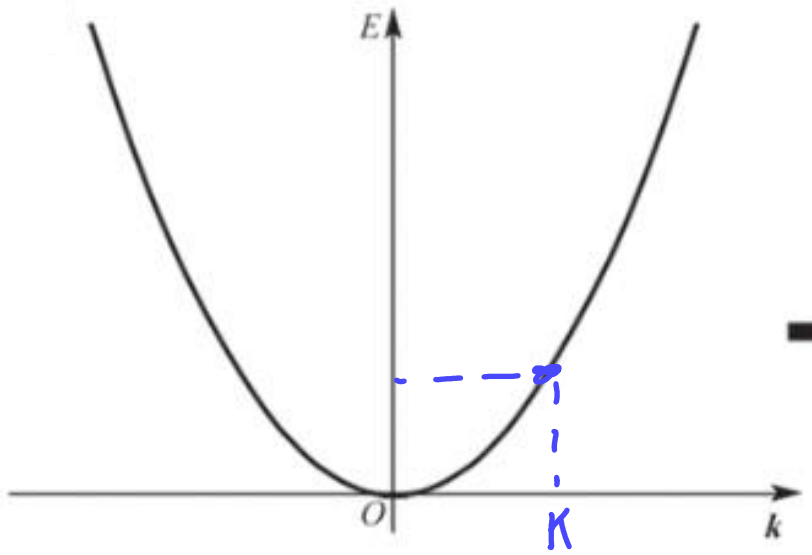
Electronic Band Structure

Lecture 3

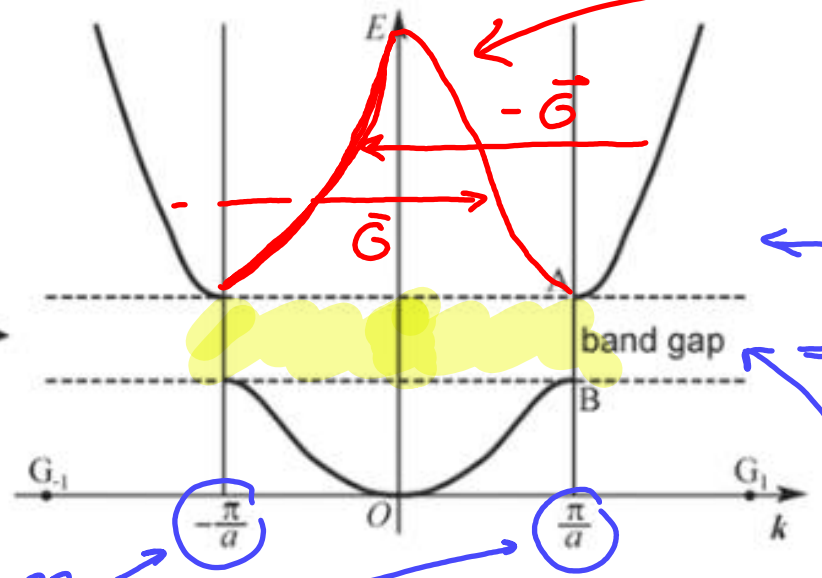
Recap

E(K) dispersion relation curves

Free e⁻ model



Nearly free e⁻ model



Reduced zone

← Extended zone

= Forbidden energies

BZ boundaries

1st B.Z

Magnitude of the gap depends on how strong the nearly free e⁻ model potential is

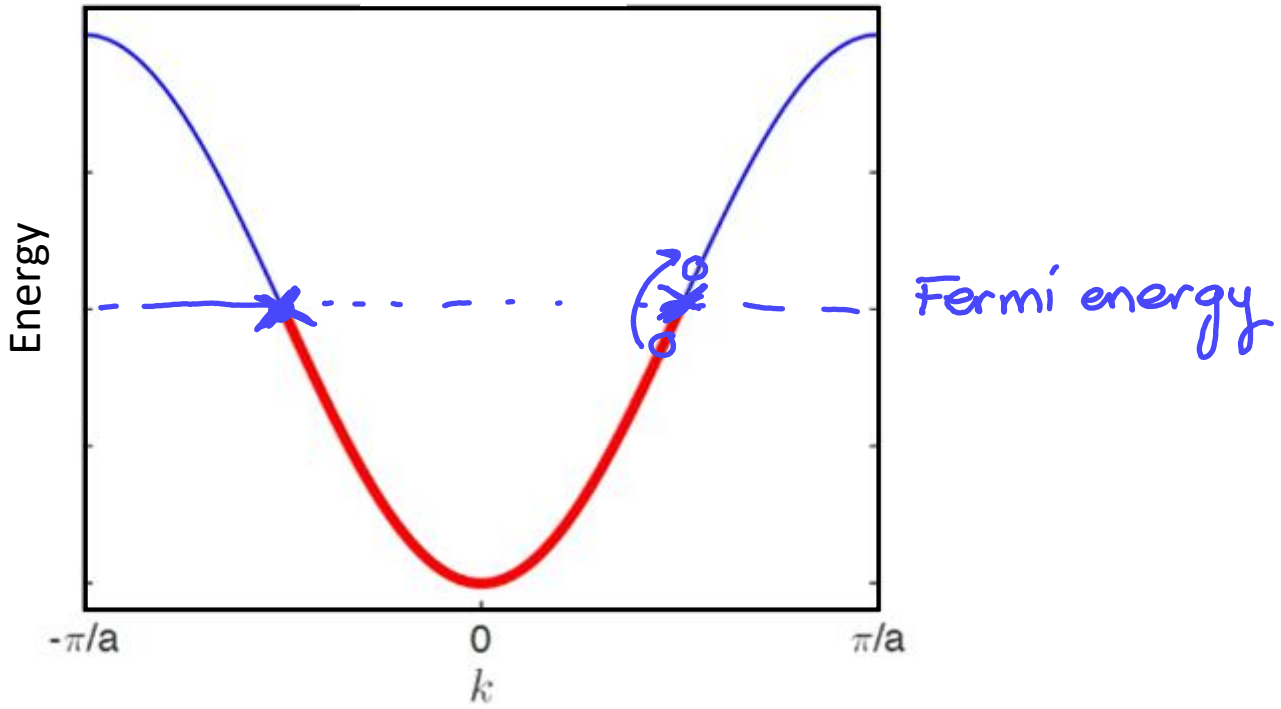
→ 2N e⁻ possible per band !

↑ # u.c. in the crystal

Monovalent materials

Each atom "brings" 1e⁻ : N atoms ⇒ Ne⁻

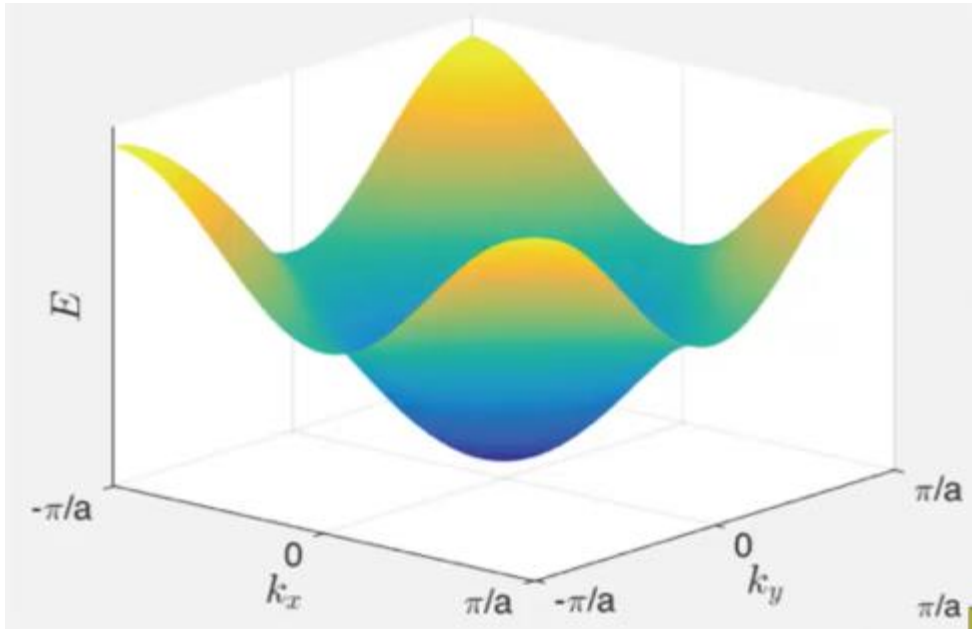
"Half-filled band" → Metal

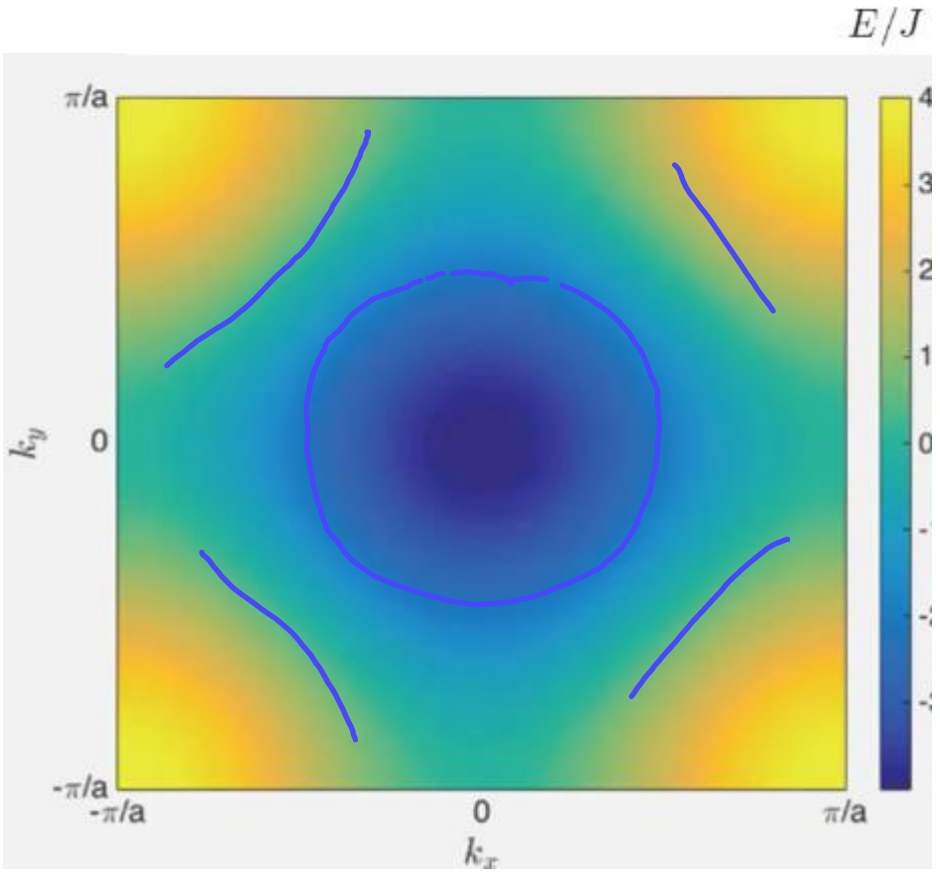


Fermi surface

(in 1D, like here, 2 points)

2D





Monovalent compounds – effect of potential strength

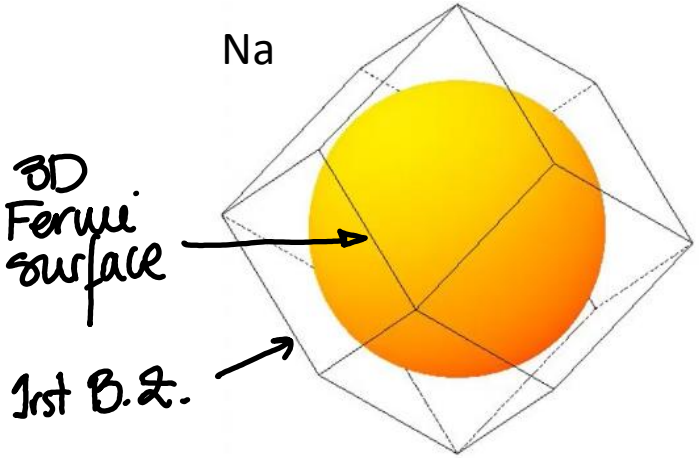
Half-filled Brillouin zone

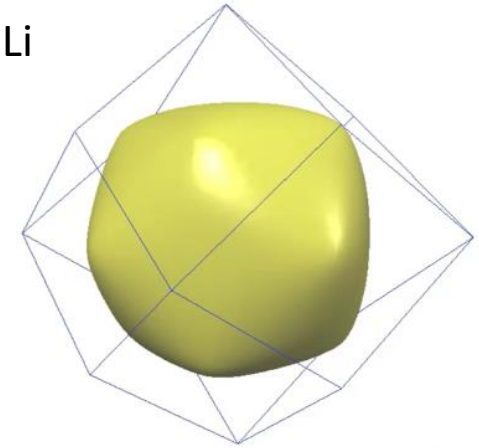
increasing potential

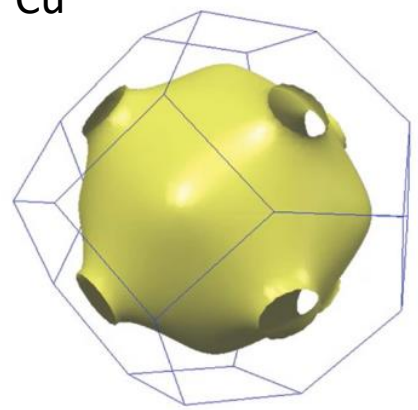
Na

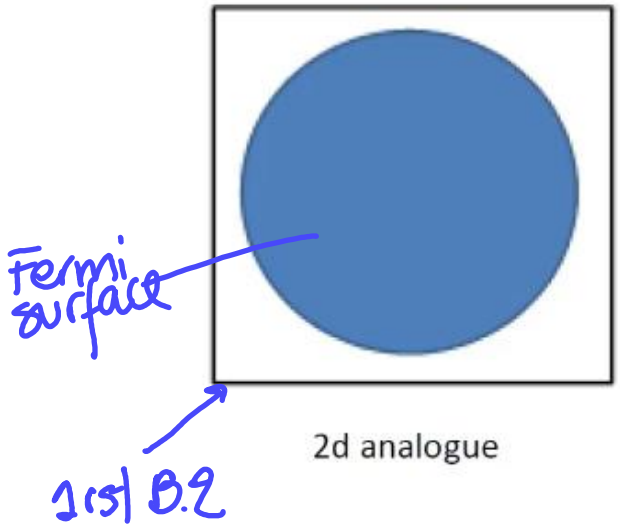
Li

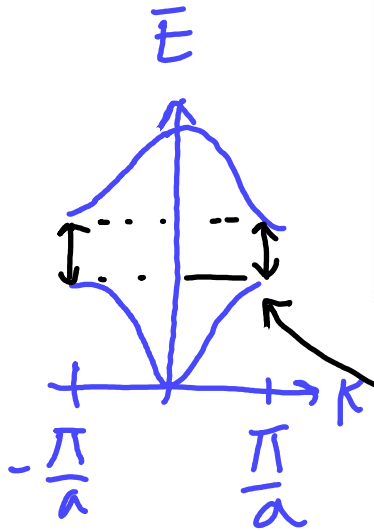
Cu

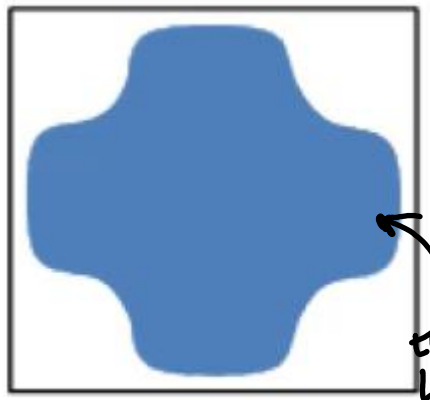


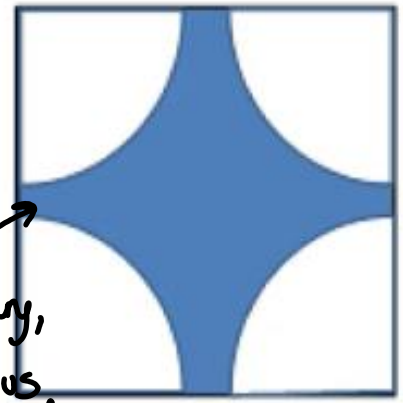












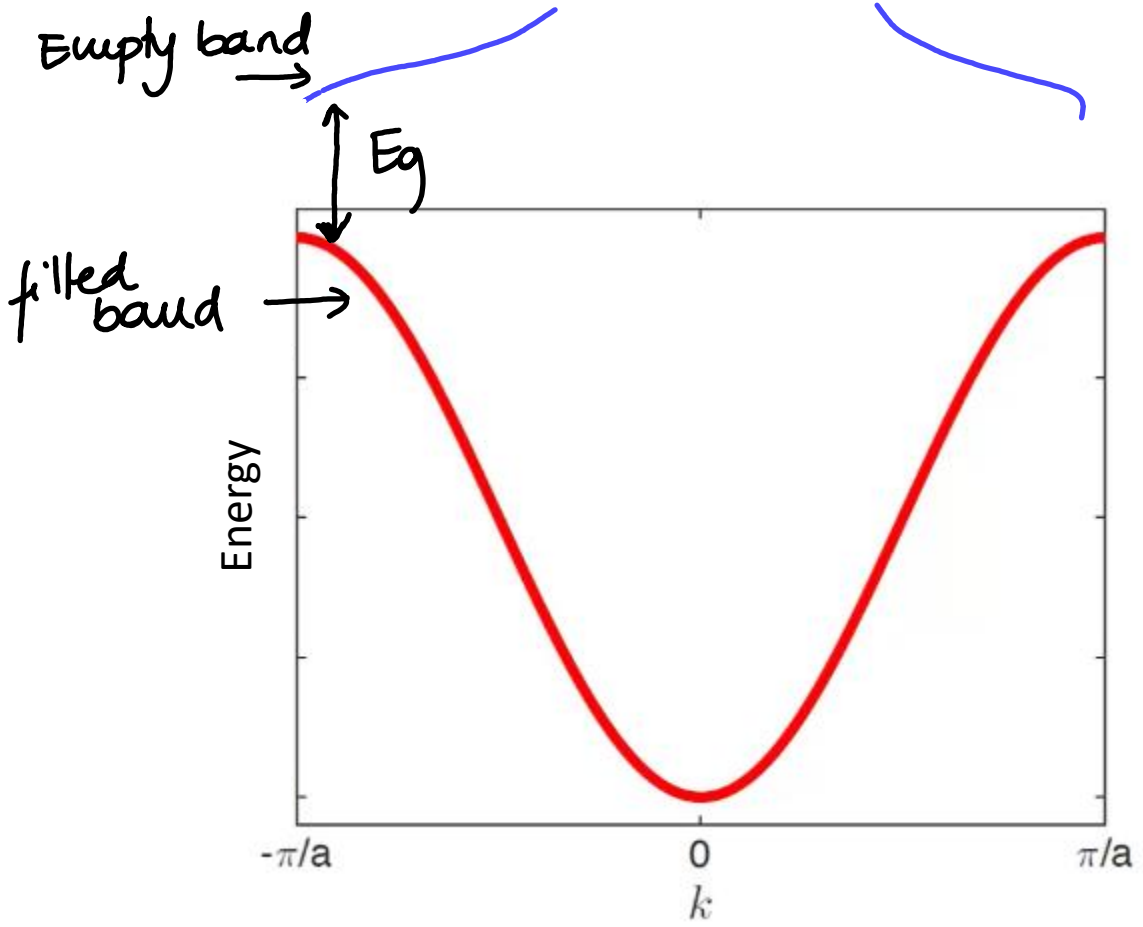
Close to the boundary, the states will have lower energy and thus the compound will prefer to fill them first

⇒ Fermi surface becomes distorted

(but # occupied states is still the same!)

Elements with even number of valence electrons

$2N\ e^- \Rightarrow$ bands completly filled to the gap



T = 0K : Insulator

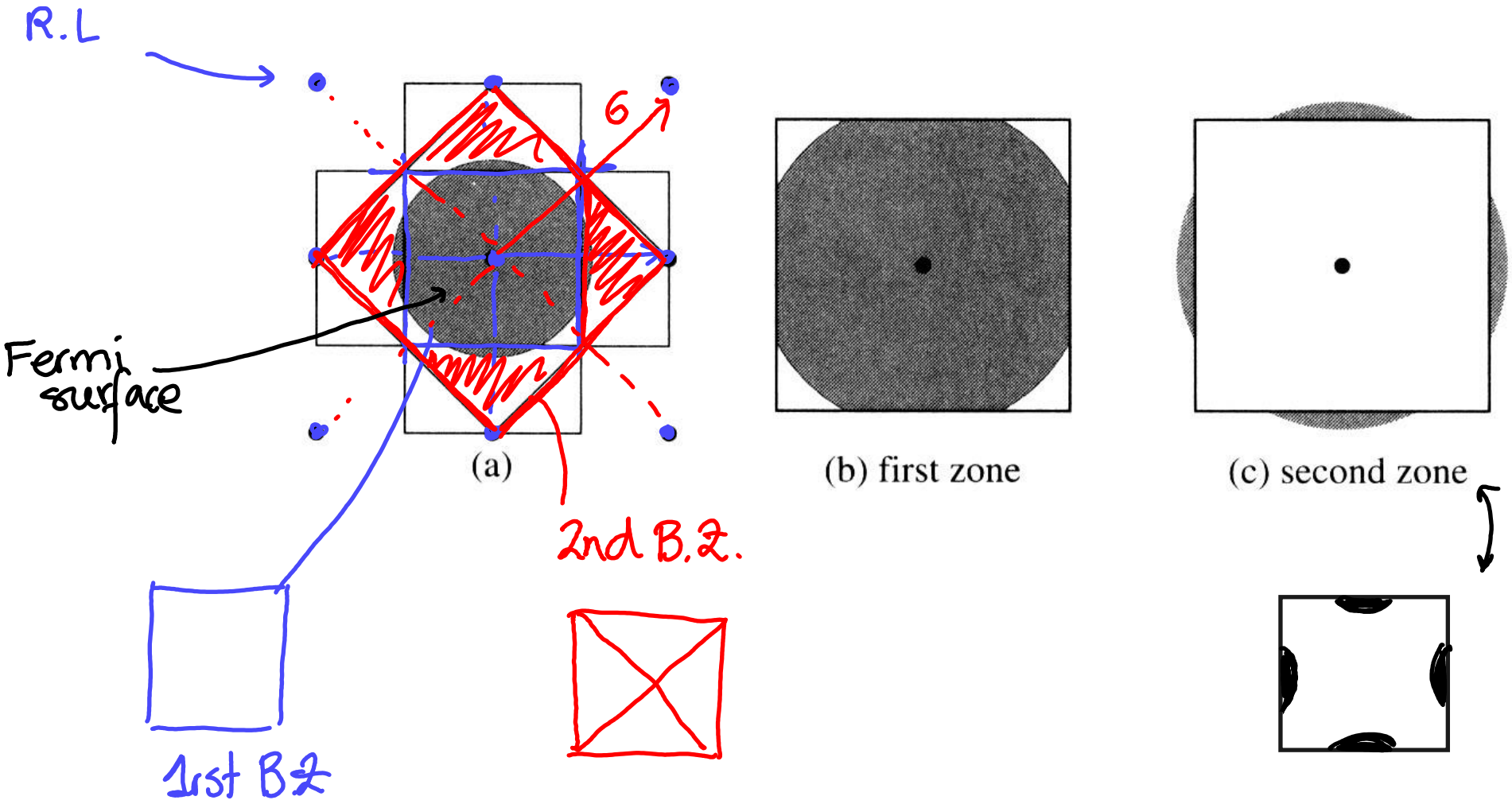
T > 0K : e^- can be thermally excited and go to the conduction band

Ex. Diamond : Insulator
Si, Ge : Semiconductors

! However, there are some divalent crystals that conduct electricity (i.e. Ca, Sr, etc.)

see next →

Reminder 2D square lattice



Elements with even number of valence electrons

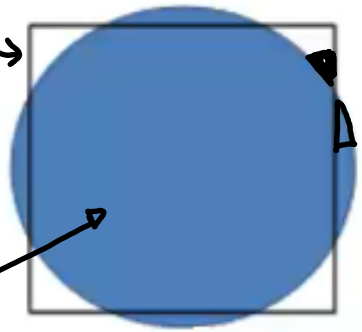
Divalent: enough e^- to fill 1st Brillouin zone

Let's assume square lattice again

Despite there are exactly $2N$ e^-, they go into $2 \neq$ bands
$\Rightarrow$ neither of the 2 are competly fill $\Rightarrow$ they can conduct

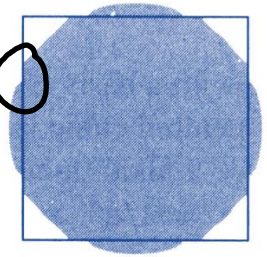
1rst B.Z.

Fermi "sphere" for free e-



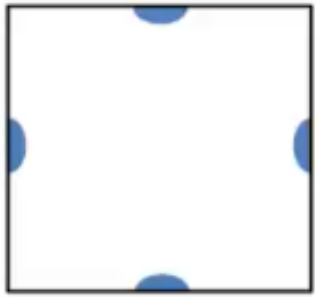
No periodic potential

Distortion of Fermi surface due to the Band gap



with weak periodic potential

with weak periodic potential Lowest Band (in 1st BZ)



2nd band

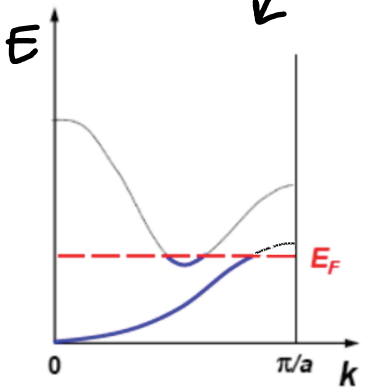
with strong periodic potential

just one band completly filled
$\Rightarrow$ insulator

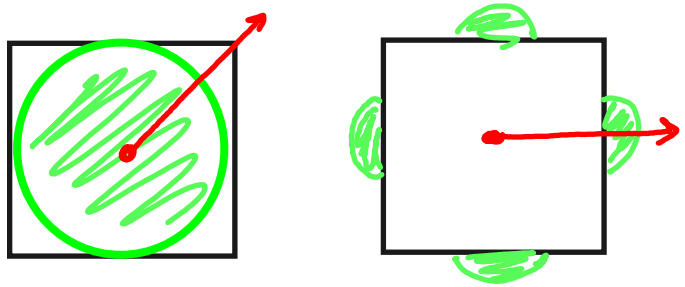
1st band

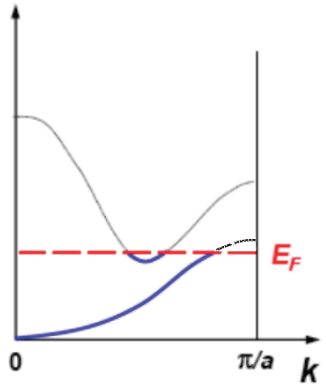
Calcium FCC (Divalent)

2nd band

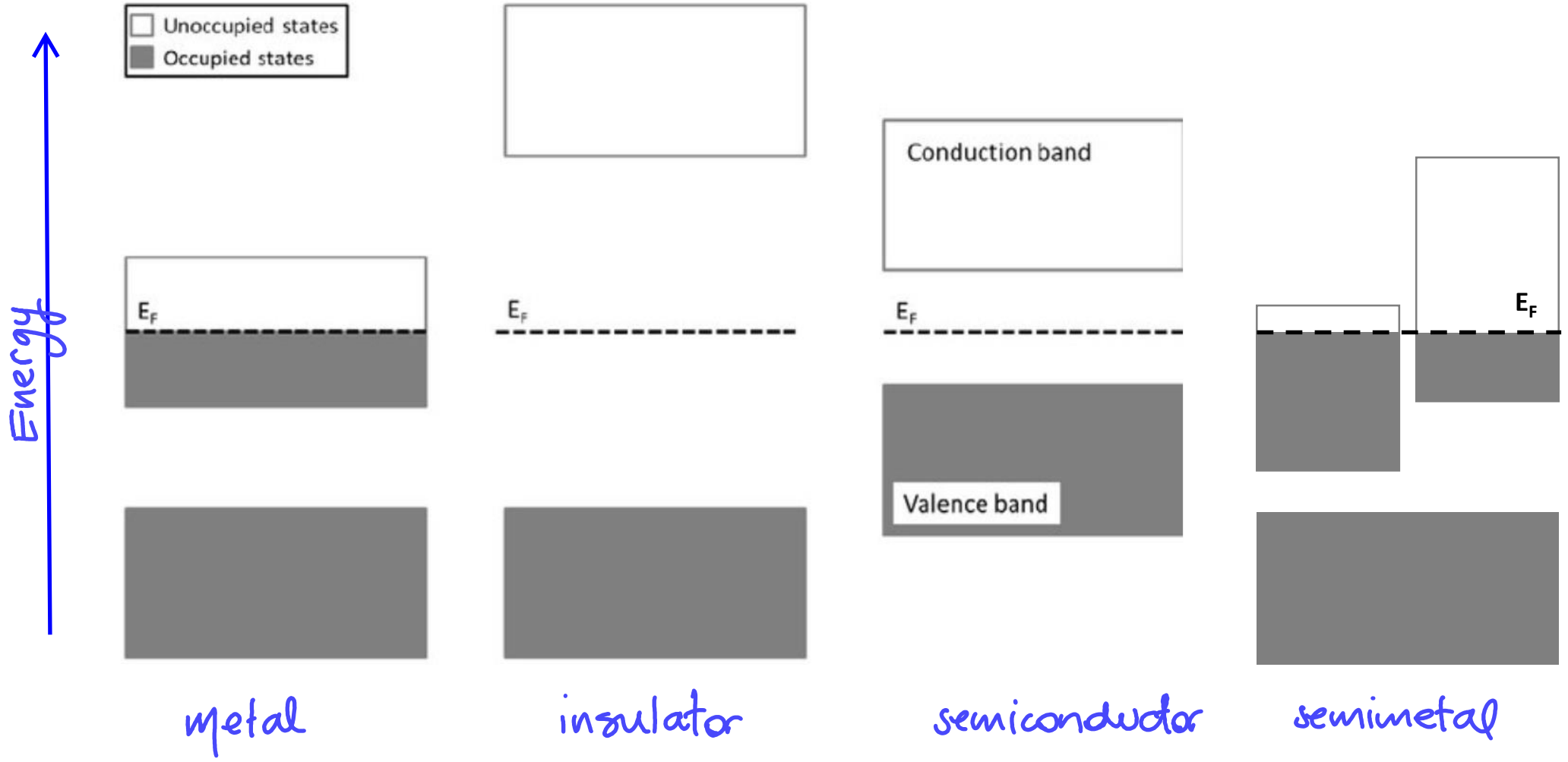


* Condition for the two bands being partially filled. Exercise!





Quiz


Unoccupied states
Occupied states
Energy
E_F
E_F
Conduction band
E_F
Valence band
E_F
metal
insulator
semiconductor
semimetal

Tight Binding model

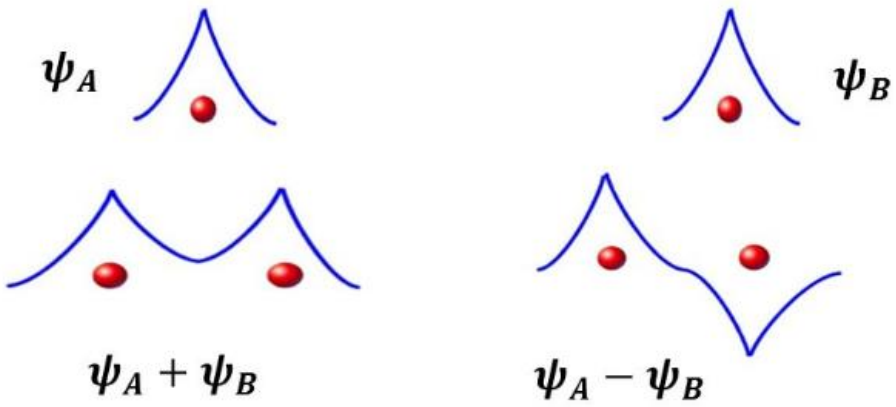
Tight binding model

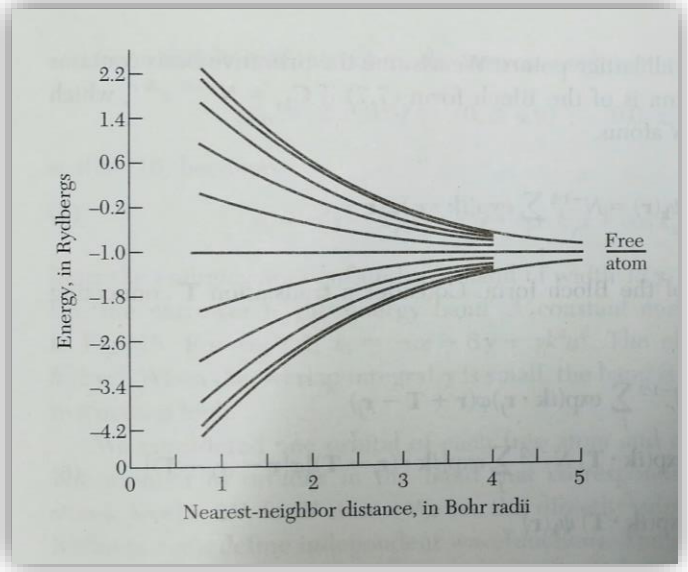
Opposite limit to the nearly free e⁻

↓

e⁻ stays most of the time bound to the ions because potential is very large.

Case of 2 hydrogen atoms example.





Bands from a single electronic level

$$\hat{H}_{at}\,\phi_i(\vec{r}) = E_i\,\phi_i(\vec{r})$$

$\hat{H}_{at}$: Hamiltonian 1 atom; $\phi_i(\vec{r})$: atomic wavefunction

Make Bloch functions from linear combinations of atomic wavefunctions:

$$\psi_{i,\vec{K}}(\vec{r}) = \sum_{\vec{T}} a_{\vec{K}\vec{T}}\,\phi_i(\vec{r}-\vec{T})$$

Bloch theorem $\psi_{\vec{K}}(\vec{r}+\vec{T}) = e^{i\vec{K}\vec{T}}\,\psi_{\vec{K}}(\vec{r})$

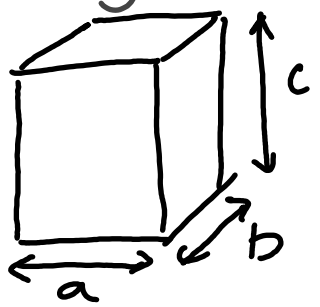
$$\Rightarrow \psi_{\vec{K}}(\vec{r}) = \sum_{\vec{T}} e^{i\vec{K}\vec{T}}\,\phi(\vec{r}-\vec{T})$$

Let's consider now only the highest occupied orbital of an atom $\phi(\vec{r})$ with energy E_ϕ

$$H = H_{at} + \{V(\bar{r}) - V_0(\bar{r})\}$$

$$\int \phi^* H_{at} \underbrace{\sum_T e^{iKT} \phi(r-T)}_{\Psi_K} d^3r + \int \phi^* \{(V(\bar{r}) - V_0(\bar{r})\} \sum_T e^{iKT} \phi(r-T) d^3r = \int \phi^* E(K) \sum_T e^{iKT} \phi(r-T) d^3$$

to obtain $E(K)$:



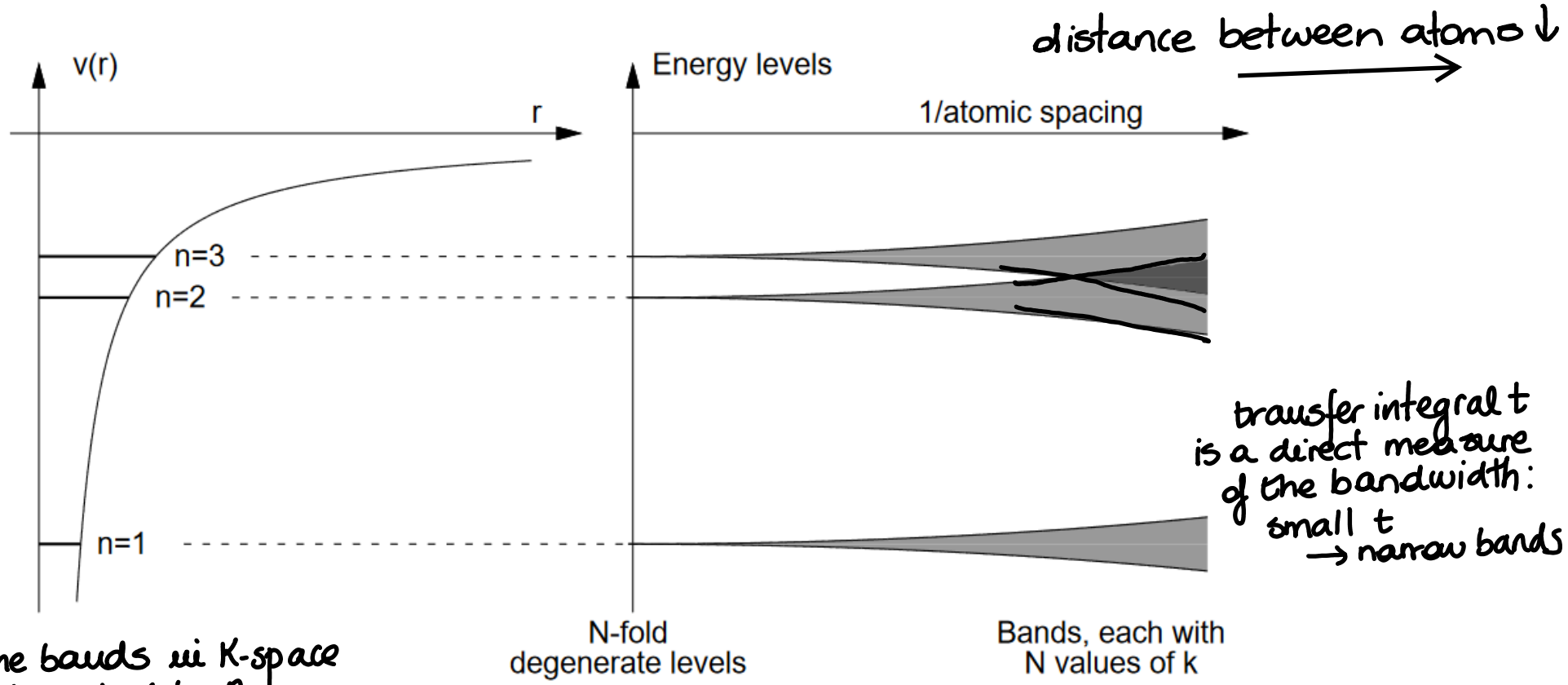
$$\bar{a}_1 = a\bar{e}_1$$
$$\bar{a}_2 = b\bar{e}_2$$
$$\bar{a}_3 = c\bar{e}_3$$

$$E(K) = E_\phi - B - 2t_x \cos(K_x a) - 2t_y \cos(K_y b) - 2t_z \cos(K_z c)$$

$$B = -\int \phi^*(r)(V - V_0)\phi(\bar{r})\, d^3r$$
$$t_x = -\int \phi^*(\bar{r})(V - V_0)\phi(\bar{r} + \bar{a}_1)\, d^3r$$
$$t_y = -\int \phi^*(r)(V - V_0)\phi(\bar{r} + \bar{a}_2)\, d^3r$$
$$t_z = -\int \phi(\bar{r})(V - V_0)\phi(r + \bar{a}_3)\, d^3r$$

t_i : TRANSFER INTEGRALS
("how easy is for an e⁻ to jump from atom to atom")

Schematics of the origin of bands in a tight binding picture



- "shape" of the bands in K-space is in part determined by the real crystal structure!
- the bands also reflect the character of the atomic levels that contribute to make them

Process involved in forming tight-binding bands:
N single atoms with j (double-degenerate) atomic levels become j 2N-fold deg bands.

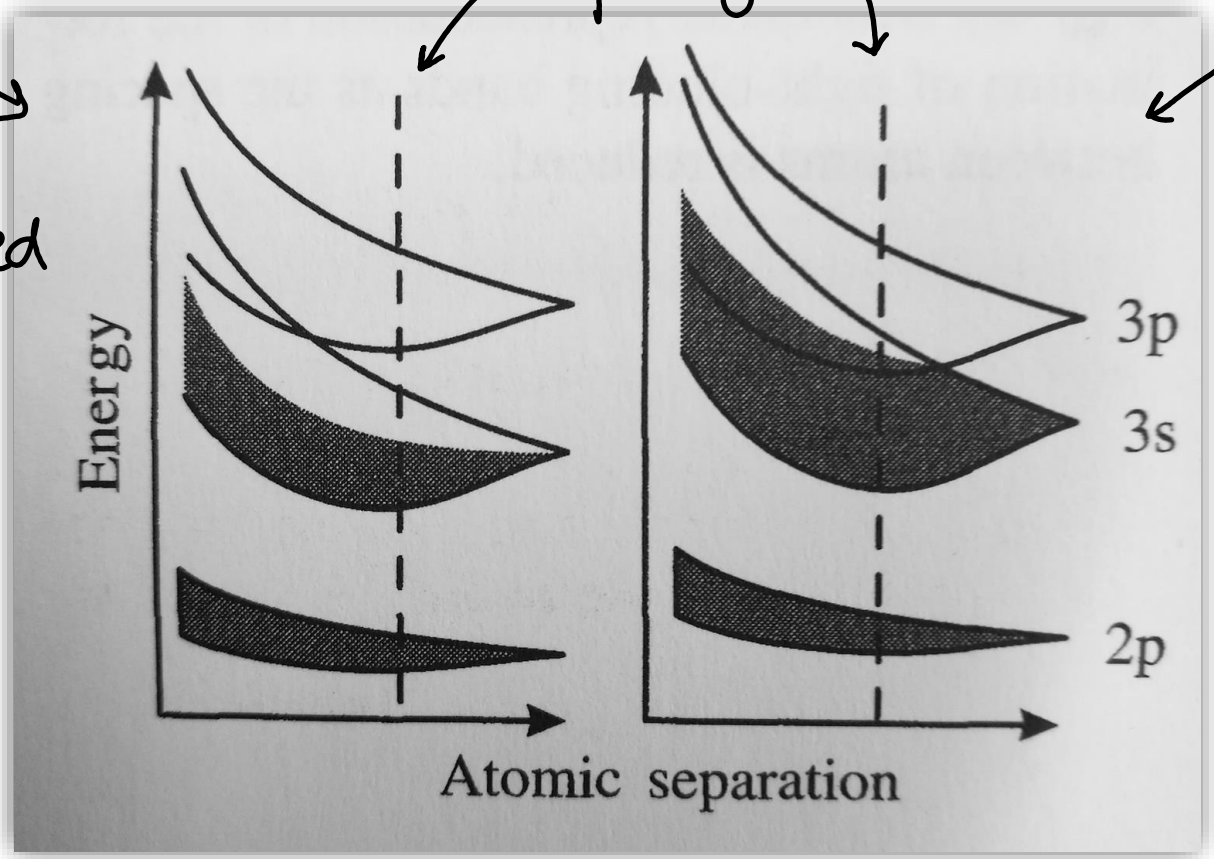
Group IA and IIA metals – tight-binding point of view

typical interatomic spacing

Na

1s, 2s, 2p : narrow bands completly filled

3s : half-filled → metal

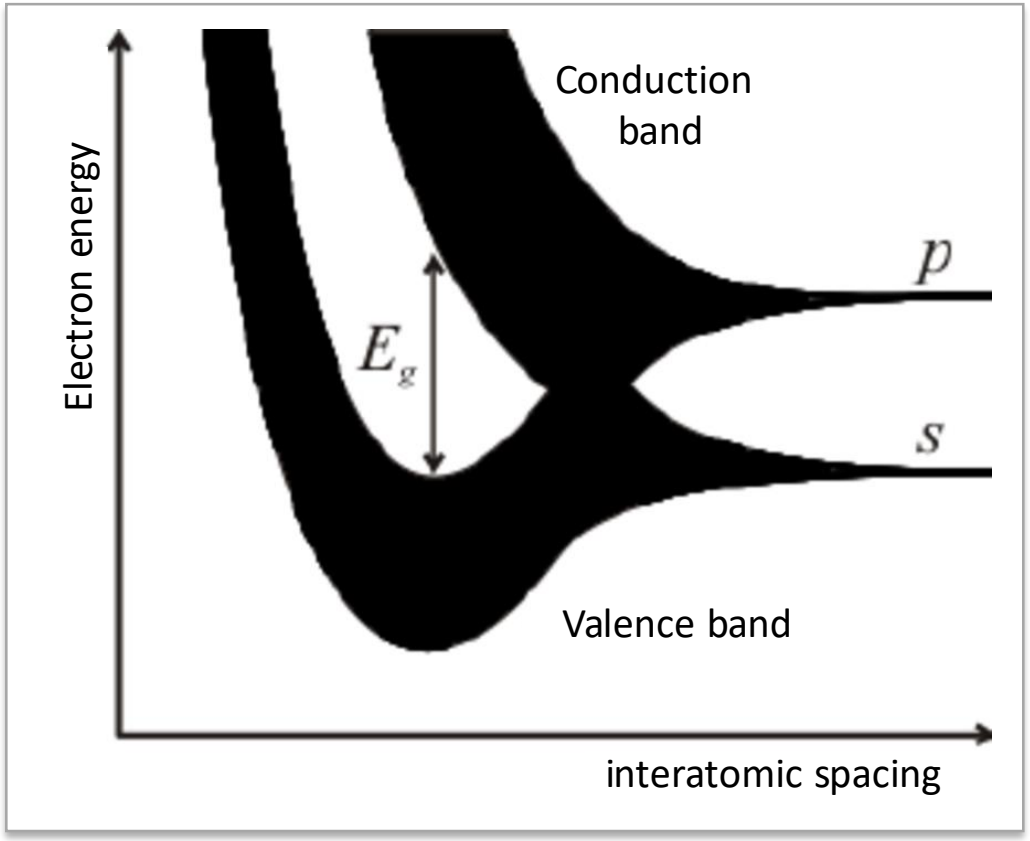


Ca

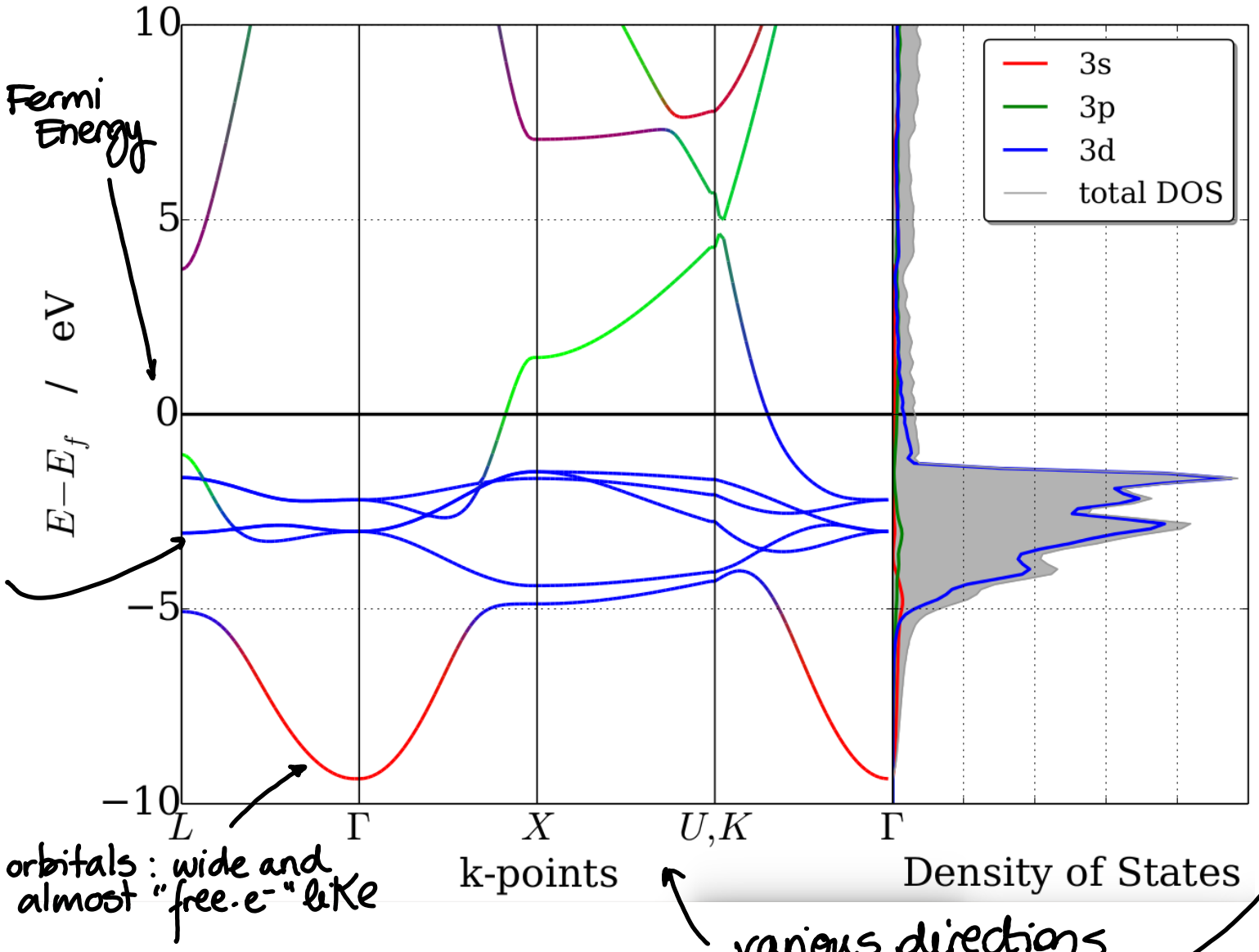
atoms are sufficiently close together for bands derived from 3s and 3p to overlap → metal

Group IV elements

Element	E_g	a
C	5 eV	0.356 nm
Si	1.1 eV	0.543 nm
Ge	1.0 eV	0.566 nm
Sn	metallic	0.646 nm



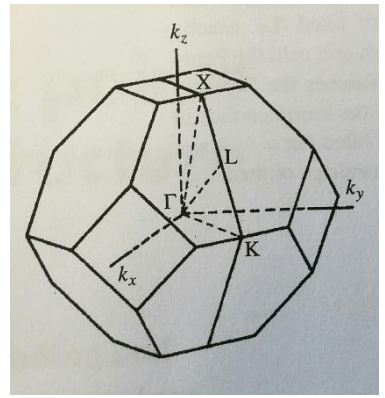
Properties transition metals are strongly related to where the position of E_F is with respect the "mess" of d-orbitals.

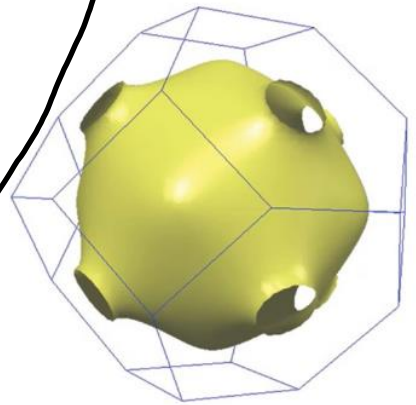


d-orbitals more compact and anisotropic
→ 5 narrow and complex bands

s-orbitals : wide and almost "free-e⁻" like

various directions in K-space





Γ: origin

http://gvallver.perso.univ-pau.fr/wp/wp-content/uploads/bands_Cu.png