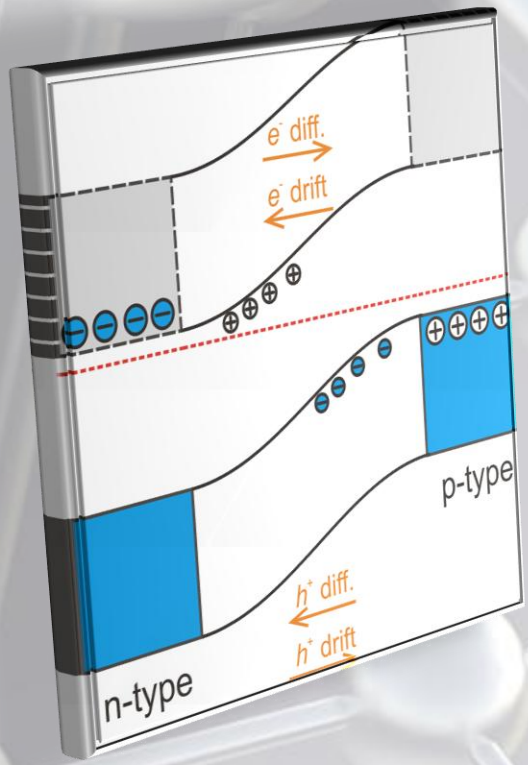
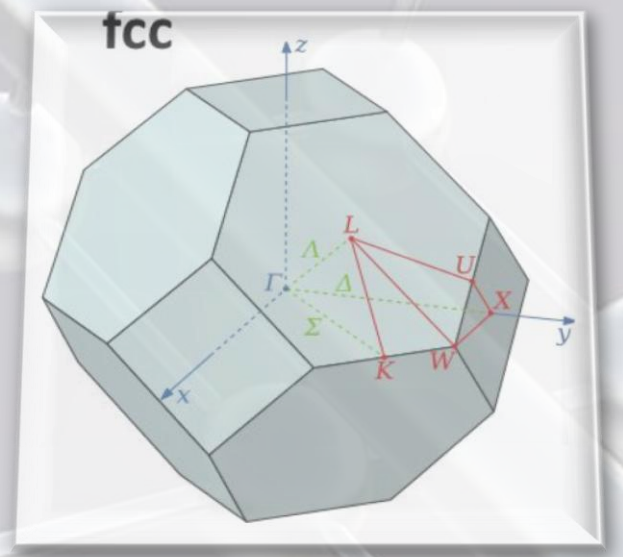
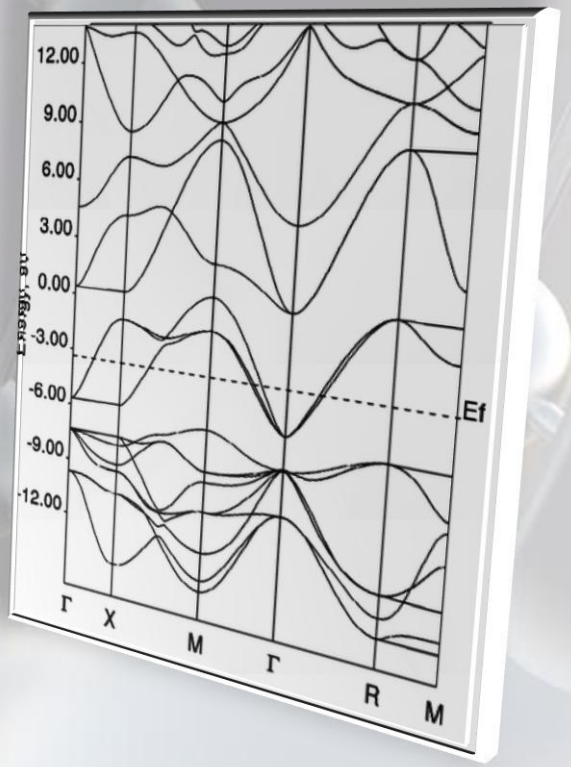
Electronic Structure of Solids

FHI-AC Lecture Series

27th October 2017







Outline

- **Part 1: Basics of Bands**
  - How bands are formed from molecular orbitals
  - The meaning of k-space
  - Density of states
  - Electron filling
  - The Fermi level
  - Metals vs semiconductors
  - Conduction
  - Doping
- **Part 2 : The Fermi level, Work Function and Band Bending**
  - Significance of Fermi level
  - Understanding work function
  - Interfaces and band bending
  - Relevance to catalysts

Part 1:
Basics of Band Structure

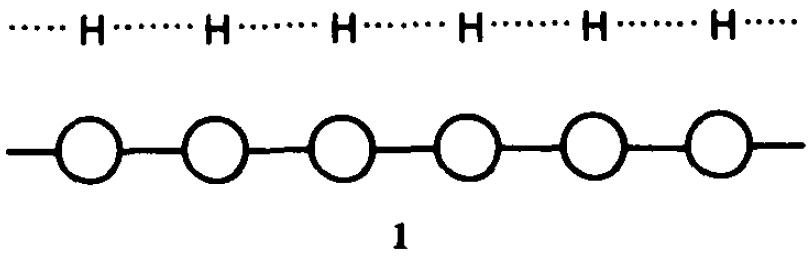
1. Chemist's View of Electronic structure in Solids

- This material is taken from:

"Solids and Surfaces: A Chemist's View of Bonding in Extended Structures"

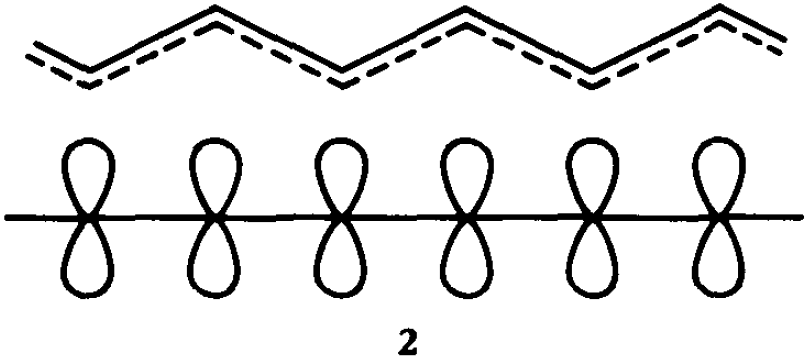
By Ronald Hoffmann

1.1 Orbitals and bands in 1-dimension



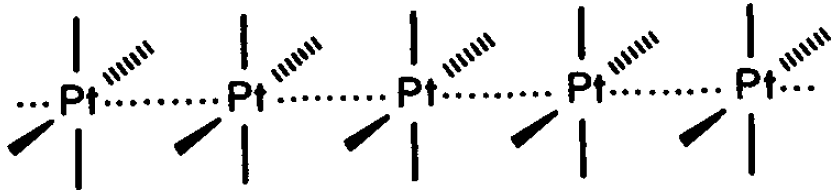
1

Equally-spaced H atoms



2

π-system of delocalized polyene

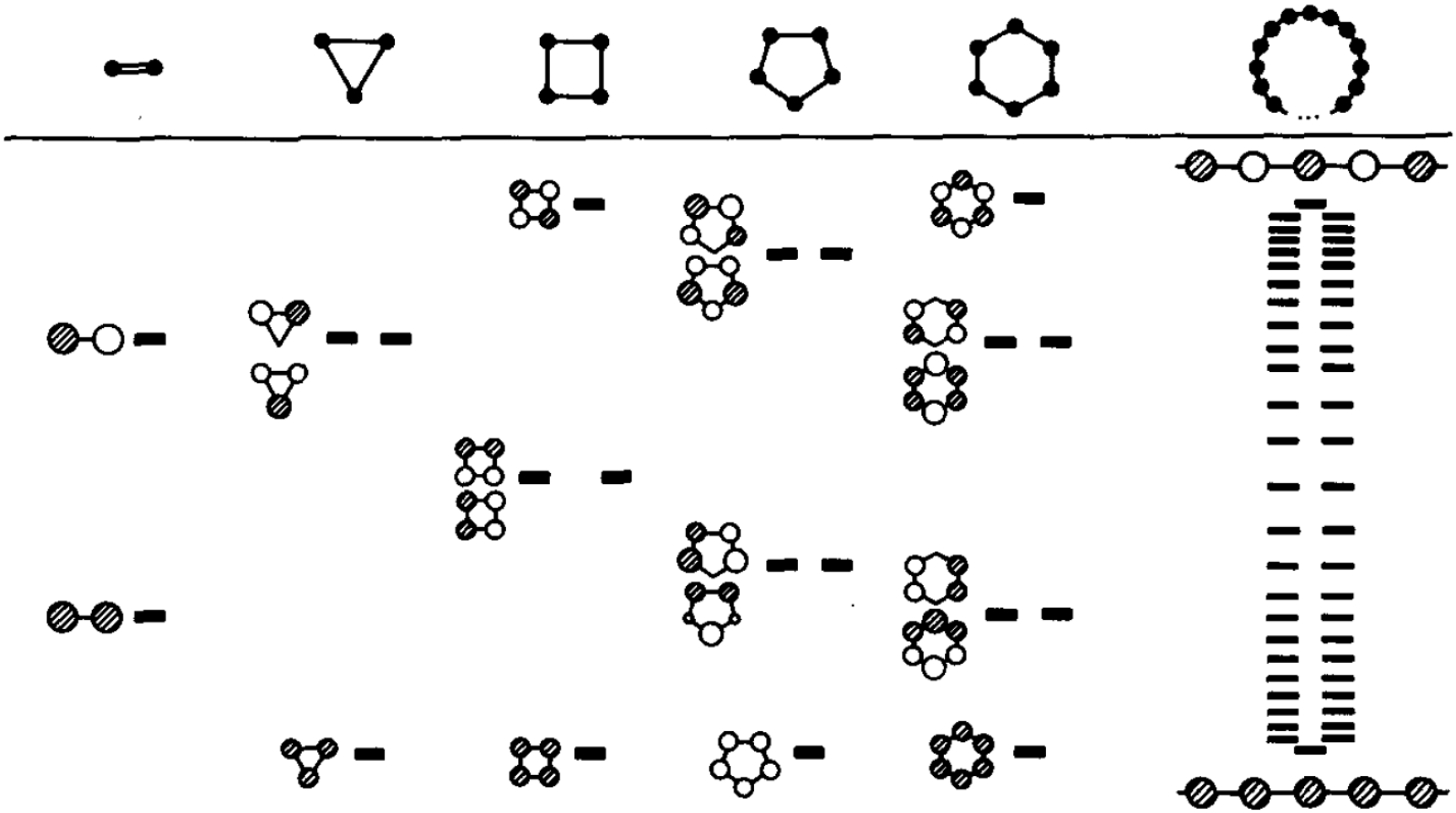


3

Stack of square planar Pt(II) complexes (e.g. PtH_4^{2-})

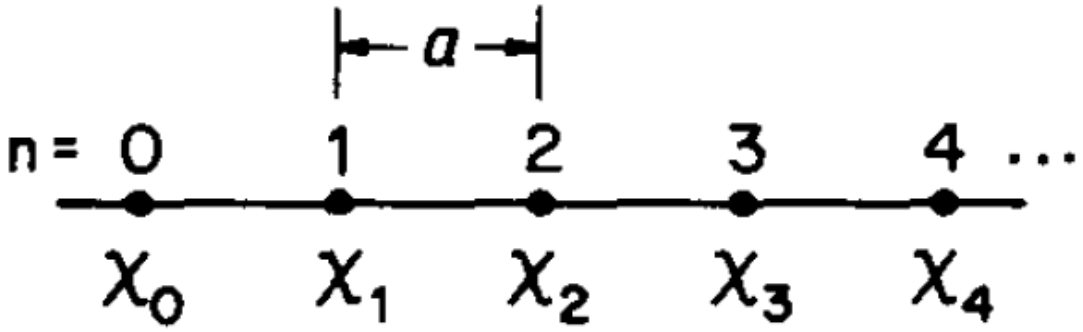
1.1 Infinite chain of H atoms

cyclic boundary condition



1.2 Bloch functions and band structures in k-space

Better way to write … translational symmetry
use an index n = 1, 2, 3, 4, …
Then there is a basis function (an H 1s orbital), χ_0 , χ_1 , χ_2 , χ_3 , … χ_n



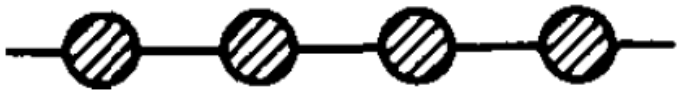
$$\psi_k = \sum_n e^{ikna} \chi_n$$

1.2 Bloch functions and band structures in k-space

Quick test…
does it work for k = 0 and k = π/a ?

$$k = 0 \qquad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n$$

$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$$



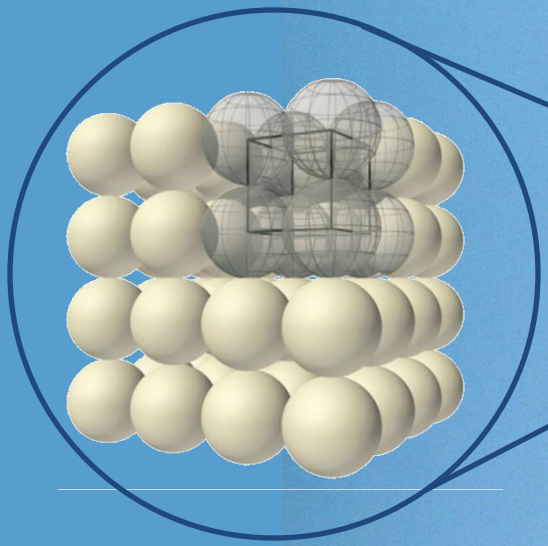
$$k = \frac{\pi}{a} \qquad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n} \chi_n = \sum_n (-1)^n \chi_n$$

$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$$

Higher the magnitude of k, the more number of nodes.
k has a range. Values outside this range are not unique, and reproduce values of lower k
$|k| \leq \pi/a$ (This is called the first Brillouin zone, i.e. the range of unique k)

1.2 k-space

How many values of k are there?



As many as the number of translations in the crystal

(i.e. as many as the number of microscopic unit cells in the macroscopic crystal)

~ 10^{23}

1.2 k-space

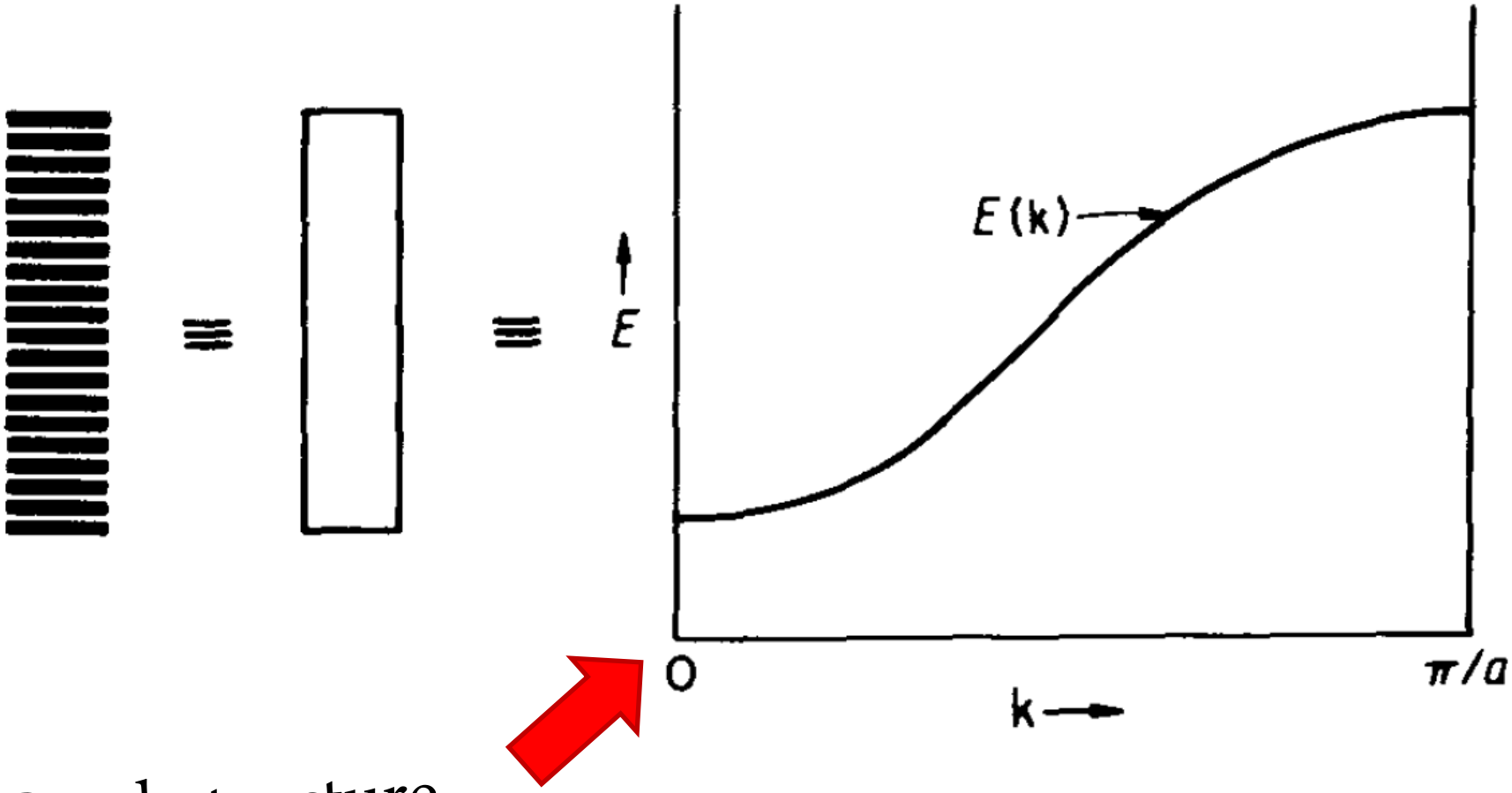
- k-space is also known as reciprocal space or momentum spaces

- Relationship between $k = 2\pi/\lambda$ and momentum is from de Broglie's $\lambda = h/p$

- i.e. k is proportional to p (momentum of the electron wavefunction)

- k is not only a symmetry label and a node counter, it is also a wave vector (i.e. it measures momentum)

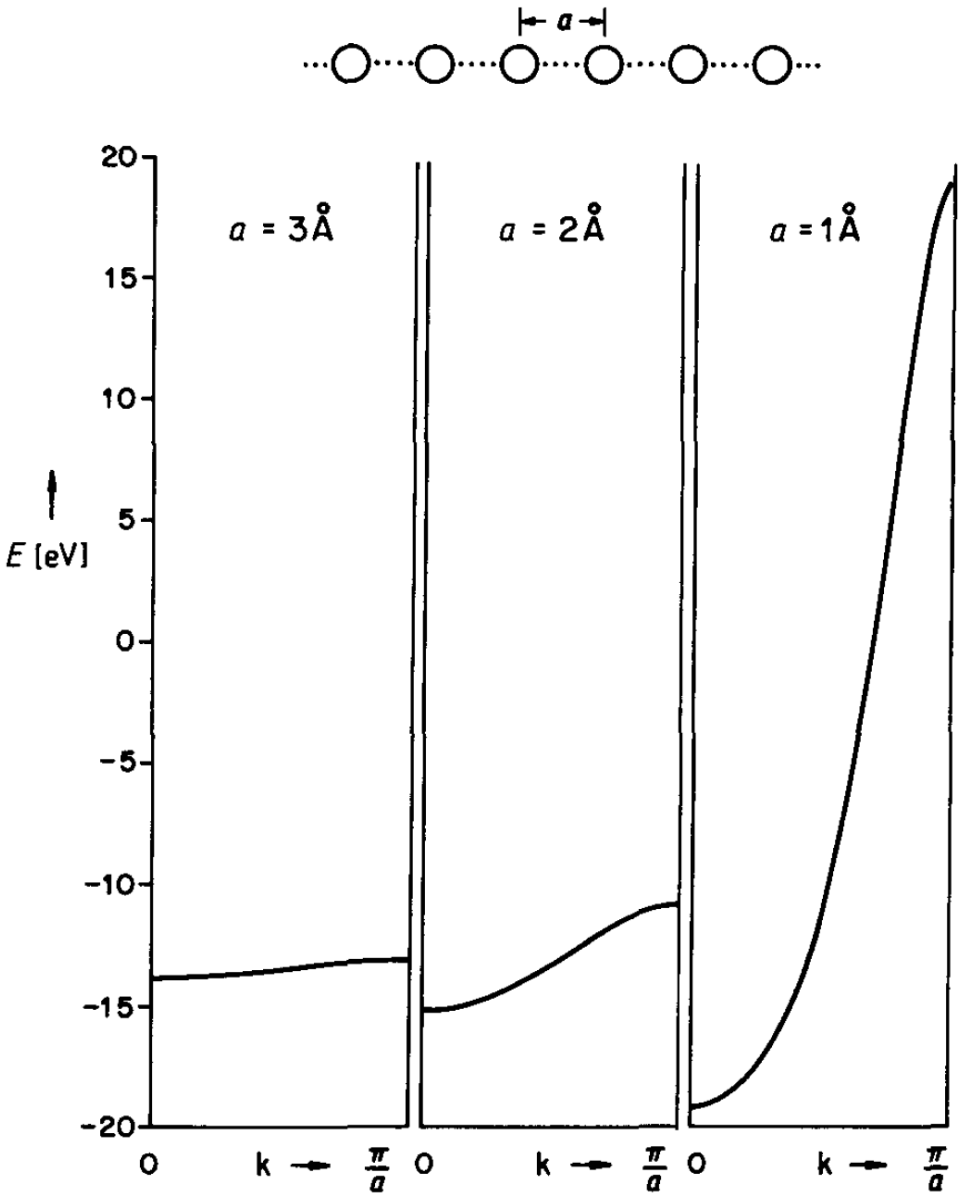
1.2 k-space



Band structure

1.2 Bandwidth

a.k.a. dispersion



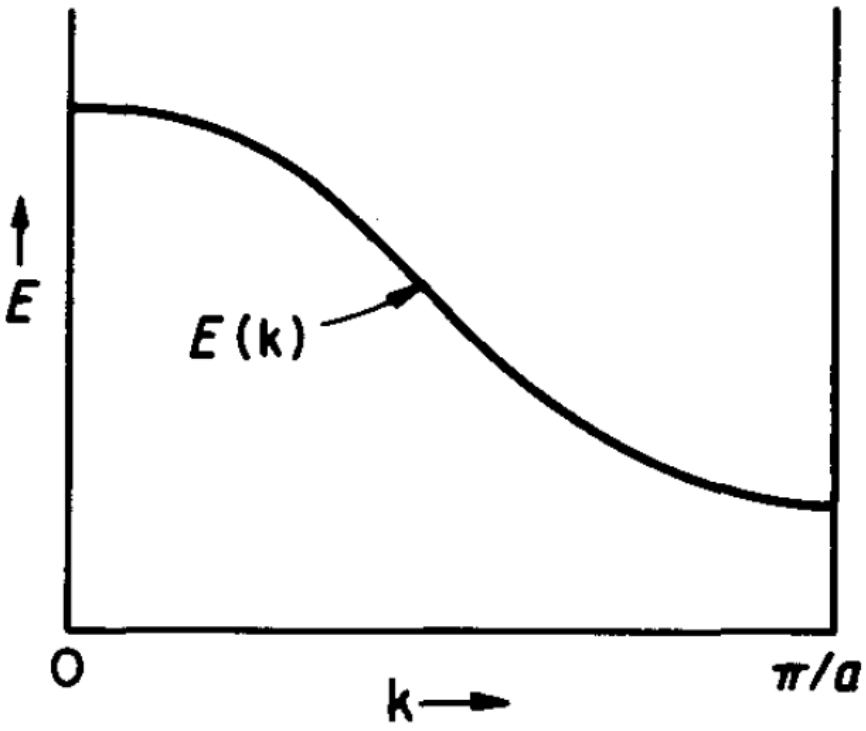
The larger the atomic spacing, the closer the band resembles a free H atom.

1.3 p-orbitals in solids

When the basis set (i.e. orbitals) have inversion symmetry (e.g. p-orbitals) then bands run in the opposite direction (i.e. k = 0 has higher energy than k = π/a)

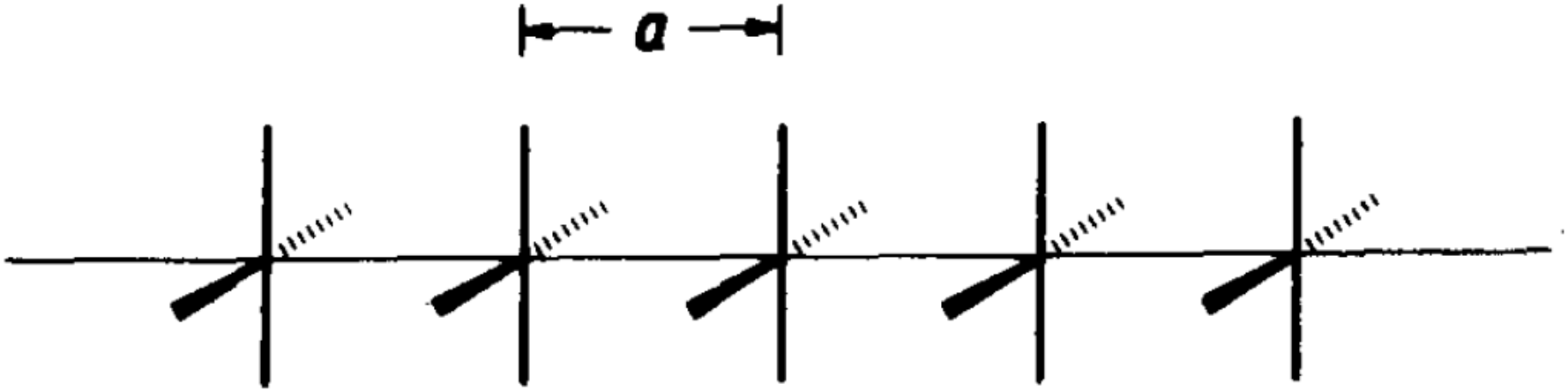
$$\psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$$

$$\psi_{\frac{\pi}{a}} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$$

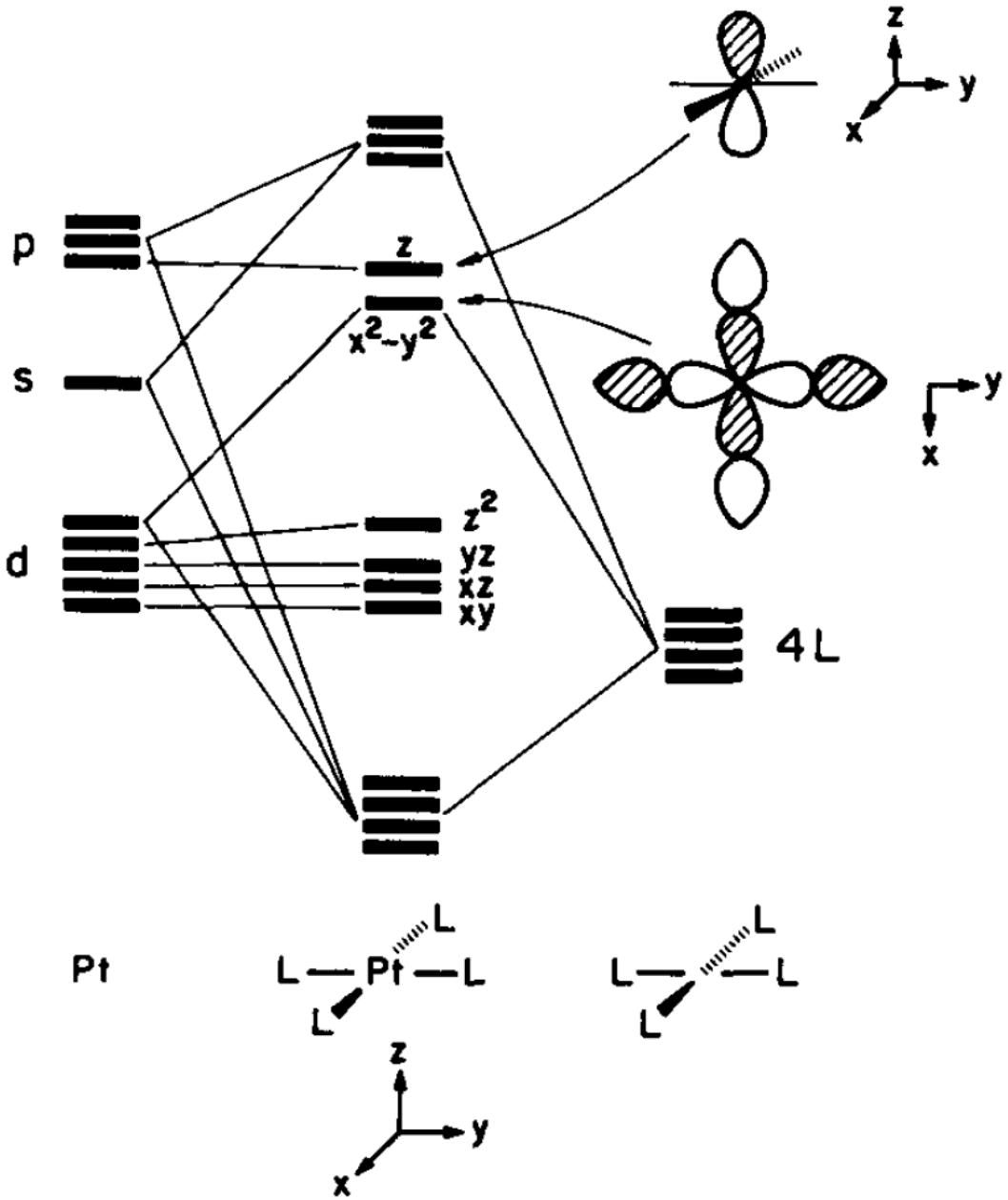


1.3 Stacks in solids

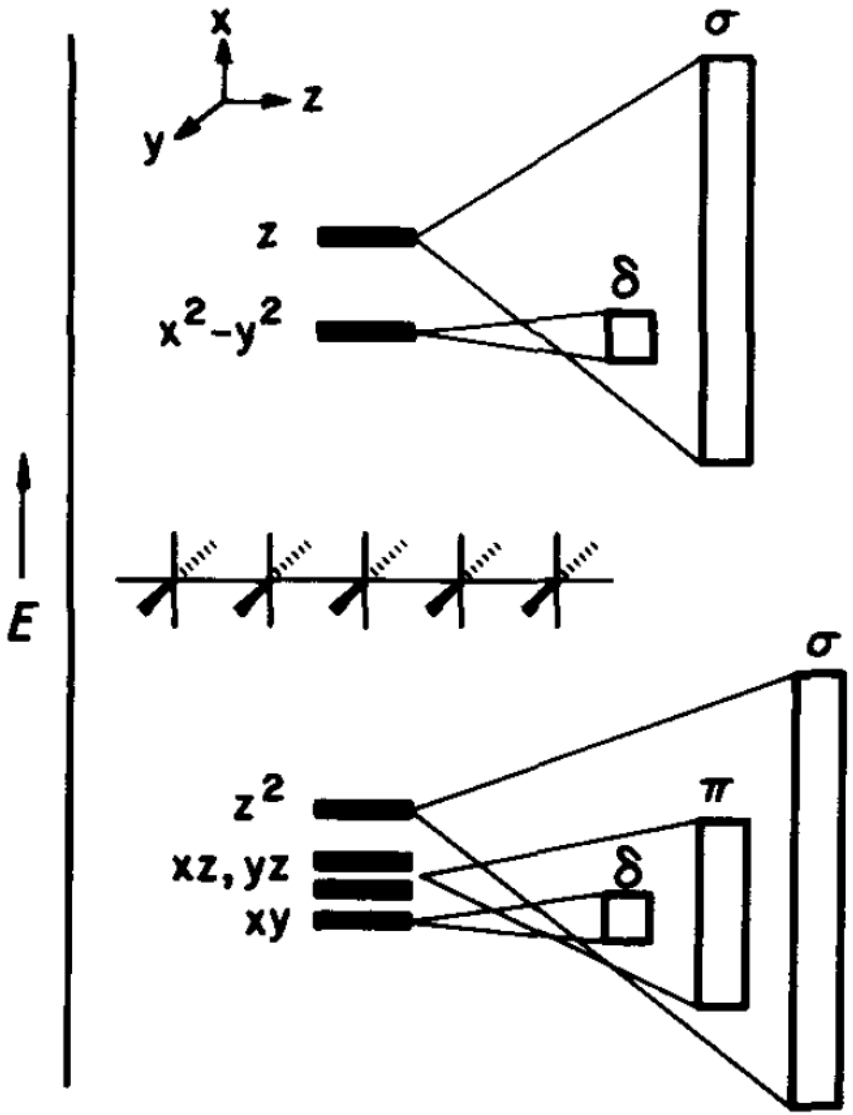
Getting more complicated
with d^8 PtL_4 complexes

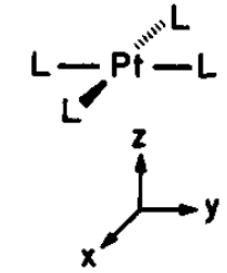


1.3 Frontier orbitals of monomer

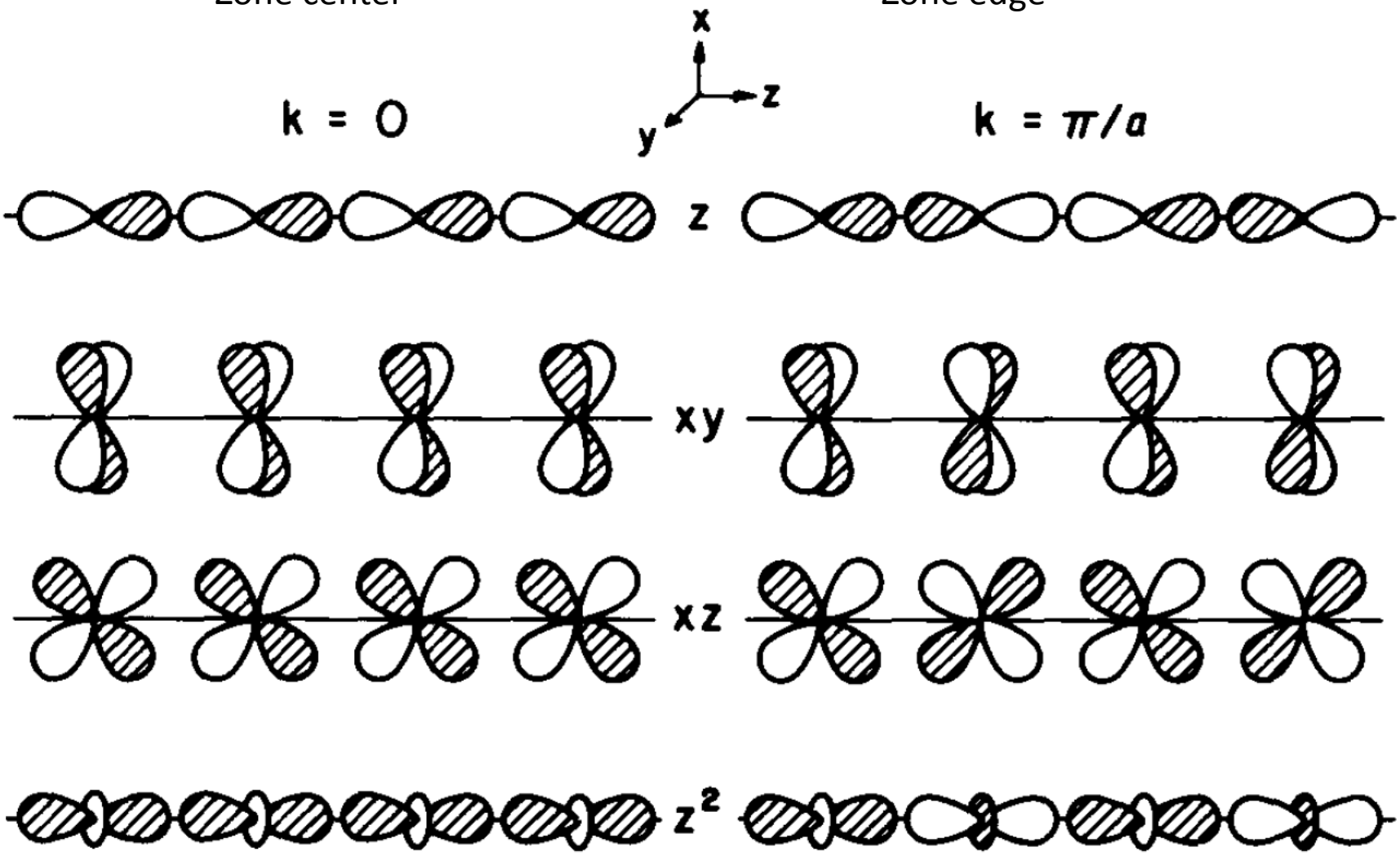


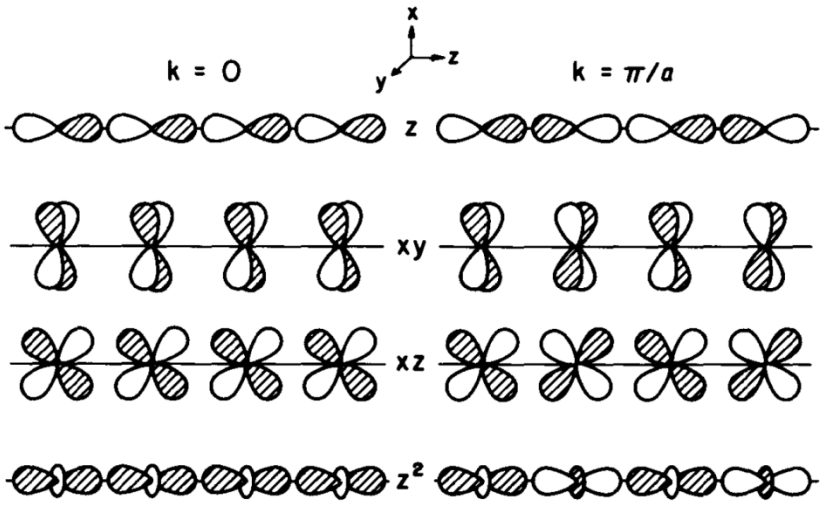
1.3 Bands from frontier orbitals

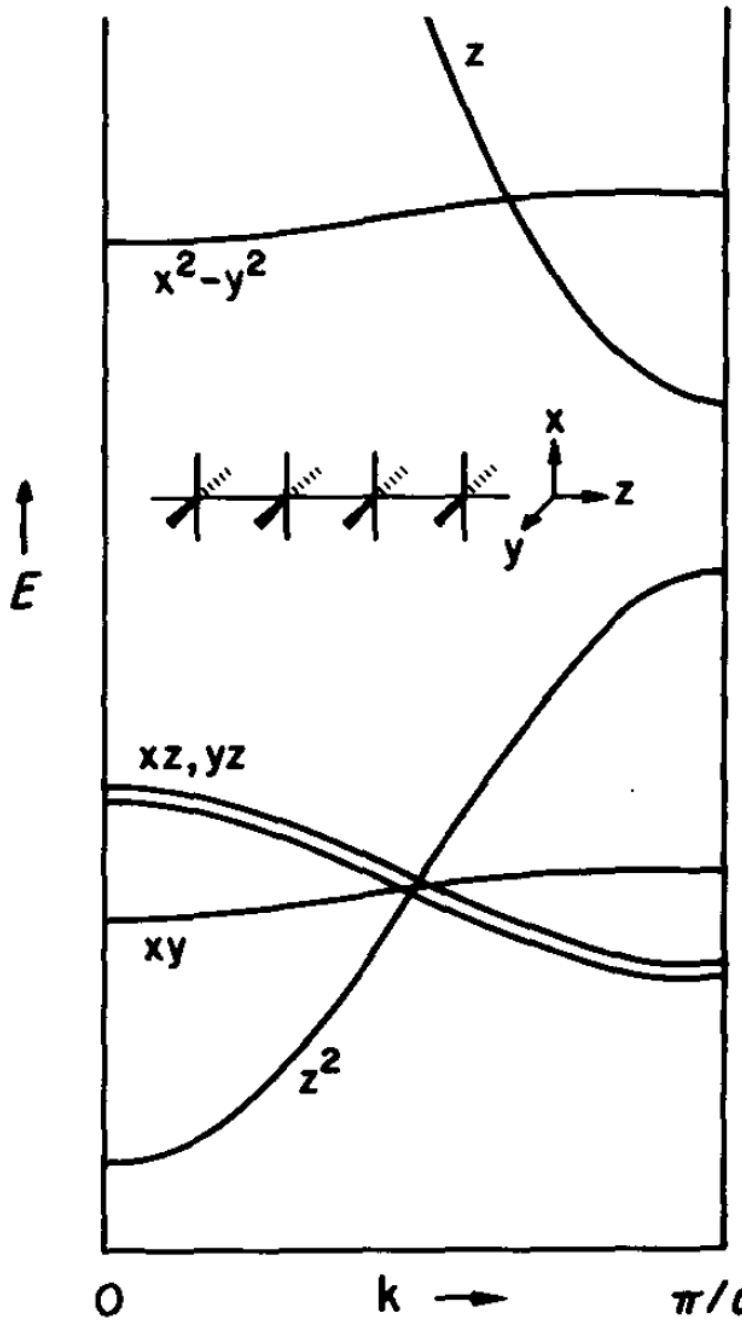




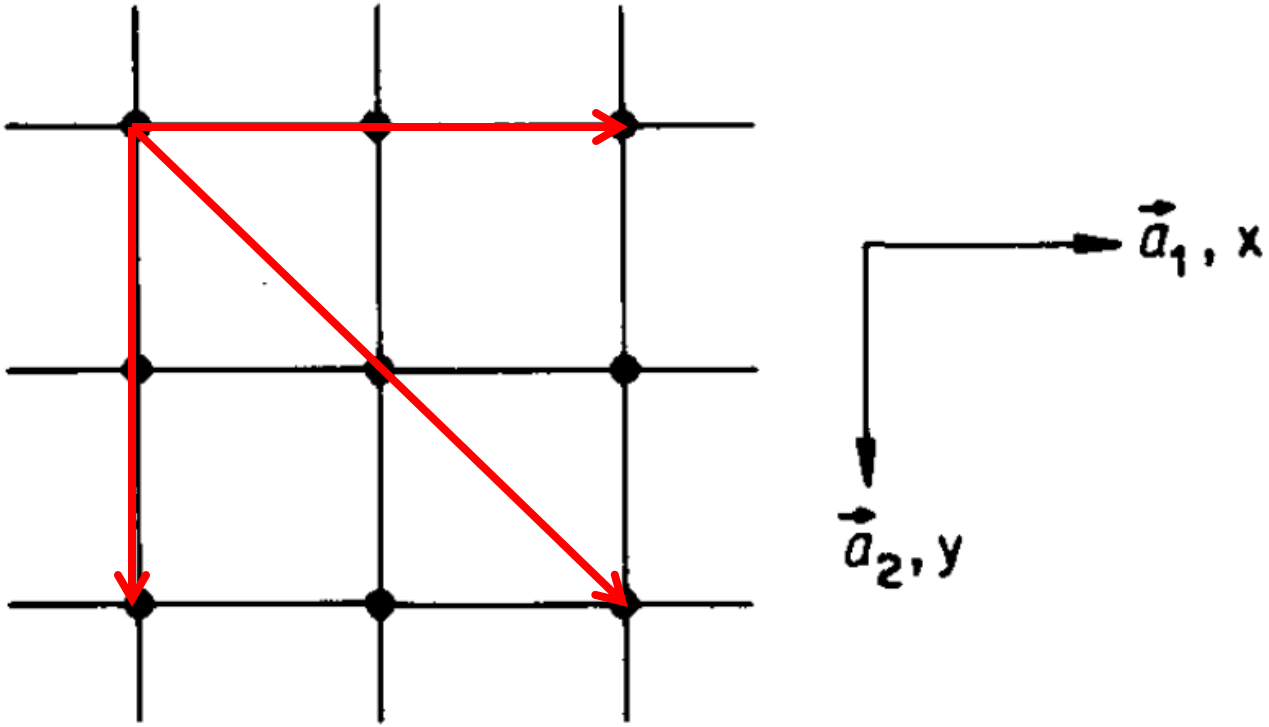
1.3 Orbitals at k = 0 and k = π/a




k = 0
x
y
z
k = π/a
z
xy
xz
z²


z
x²-y²
x
z
y
E
xz, yz
xy
z²
0
k
π/a

1.4 Bands in 2 Dimensions

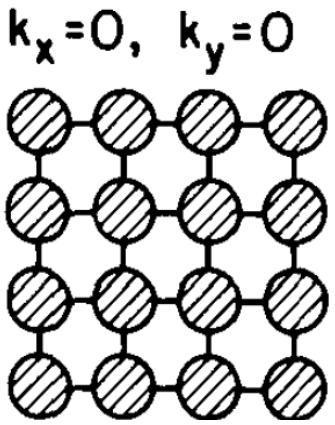


We can factor the Schrödinger equation of the crystal into wavefunctions along the x- and y-axis, each being identical to the 1D representations.

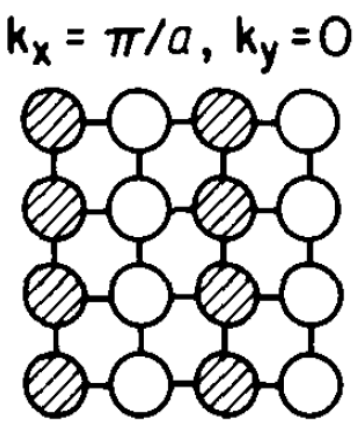
Then we have two kinds of wave vectors, k_x and k_y

$0 \leq |k_x|, |k_y| \leq \pi/a$ $\quad\quad$ $(a = |\mathbf{a_1}| = |\mathbf{a_2}|)$

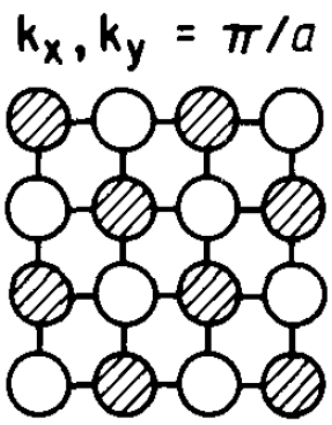
1.4 Solutions in 2D for s-orbtials



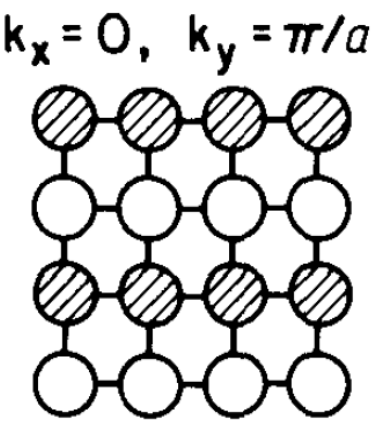
Γ



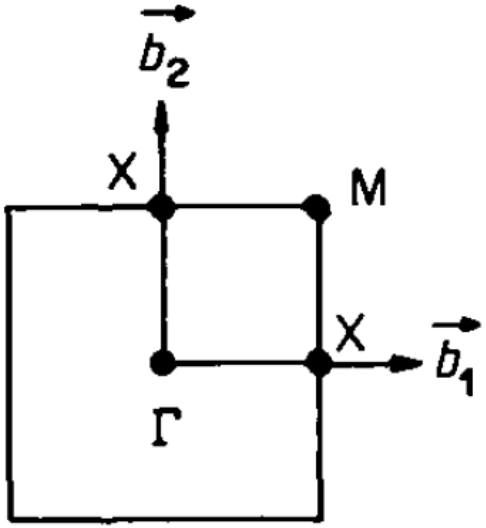
X

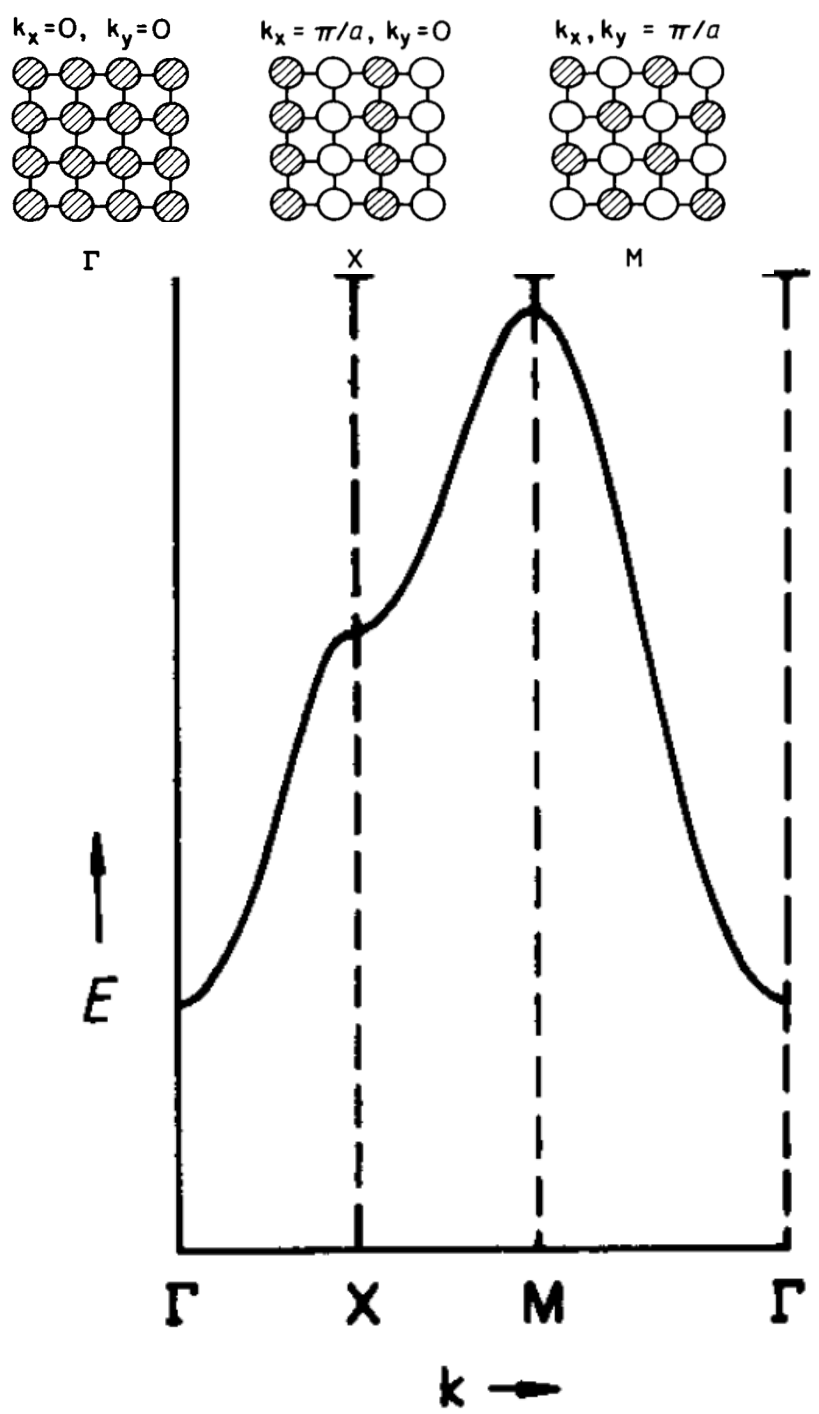


M

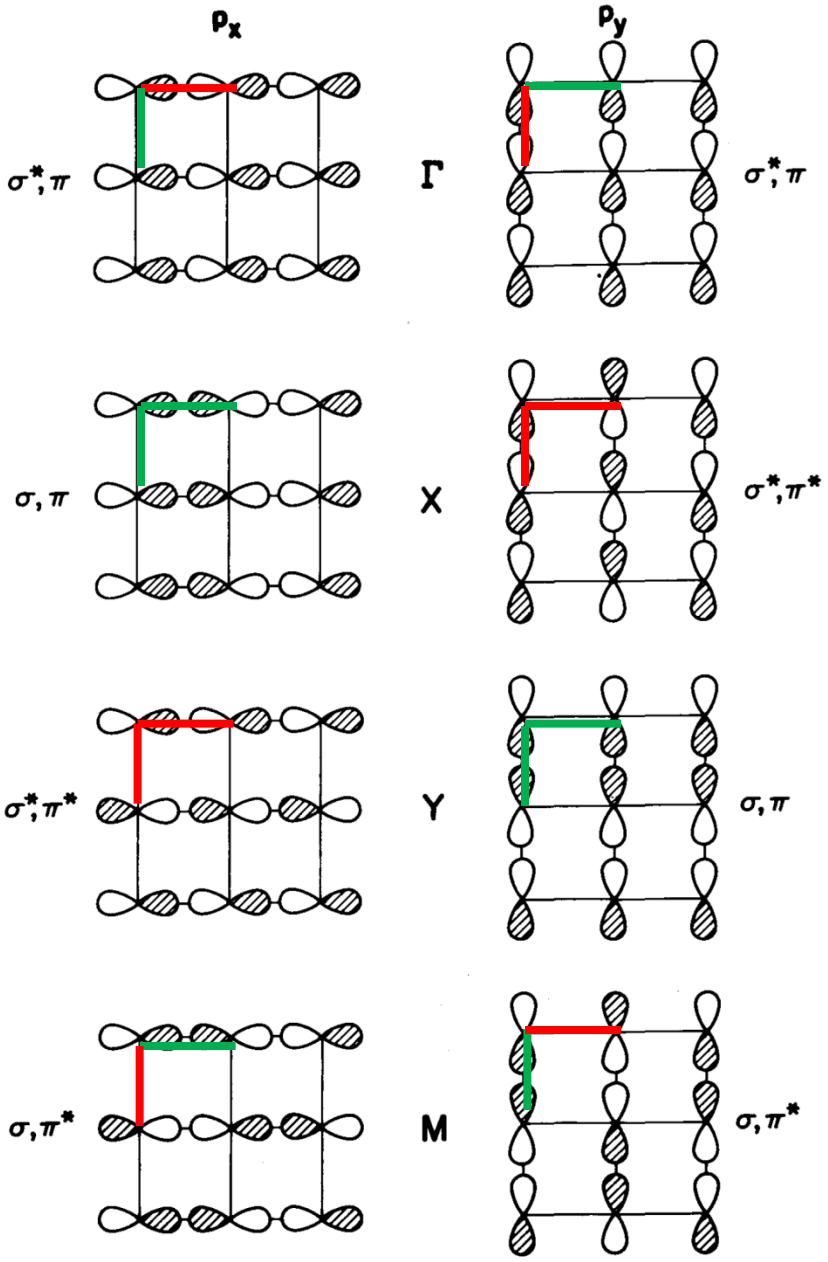


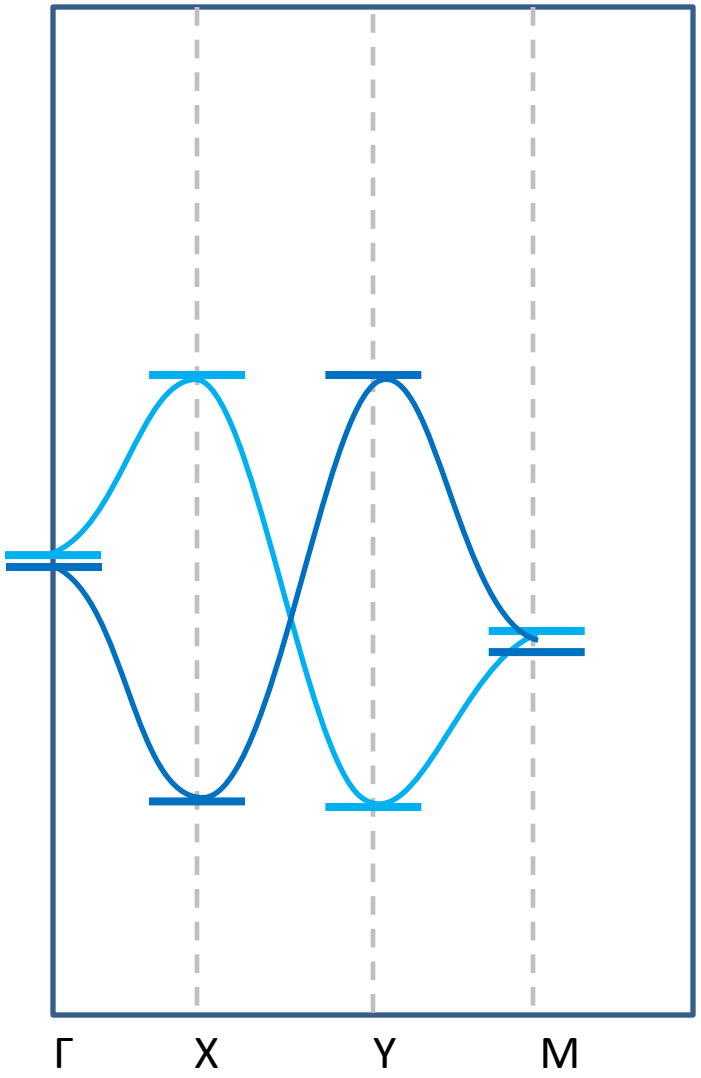
X

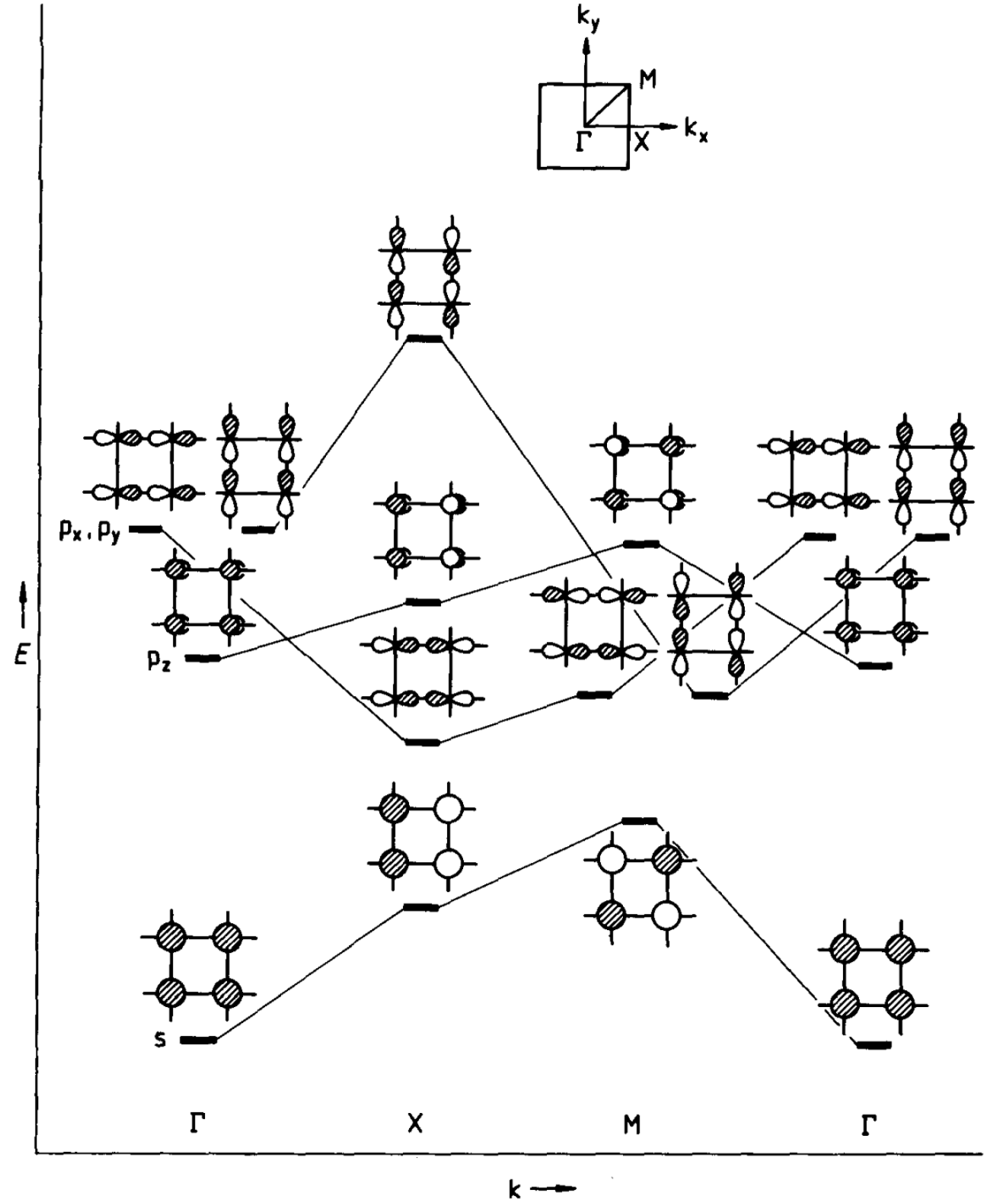

$\vec{b}_2$
X
M
X
$\vec{b}_1$
Γ


$k_x=0,\ k_y=0$
$k_x=\pi/a,\ k_y=0$
$k_x, k_y=\pi/a$
Γ
X
M
E
Γ
X
M
Γ
k

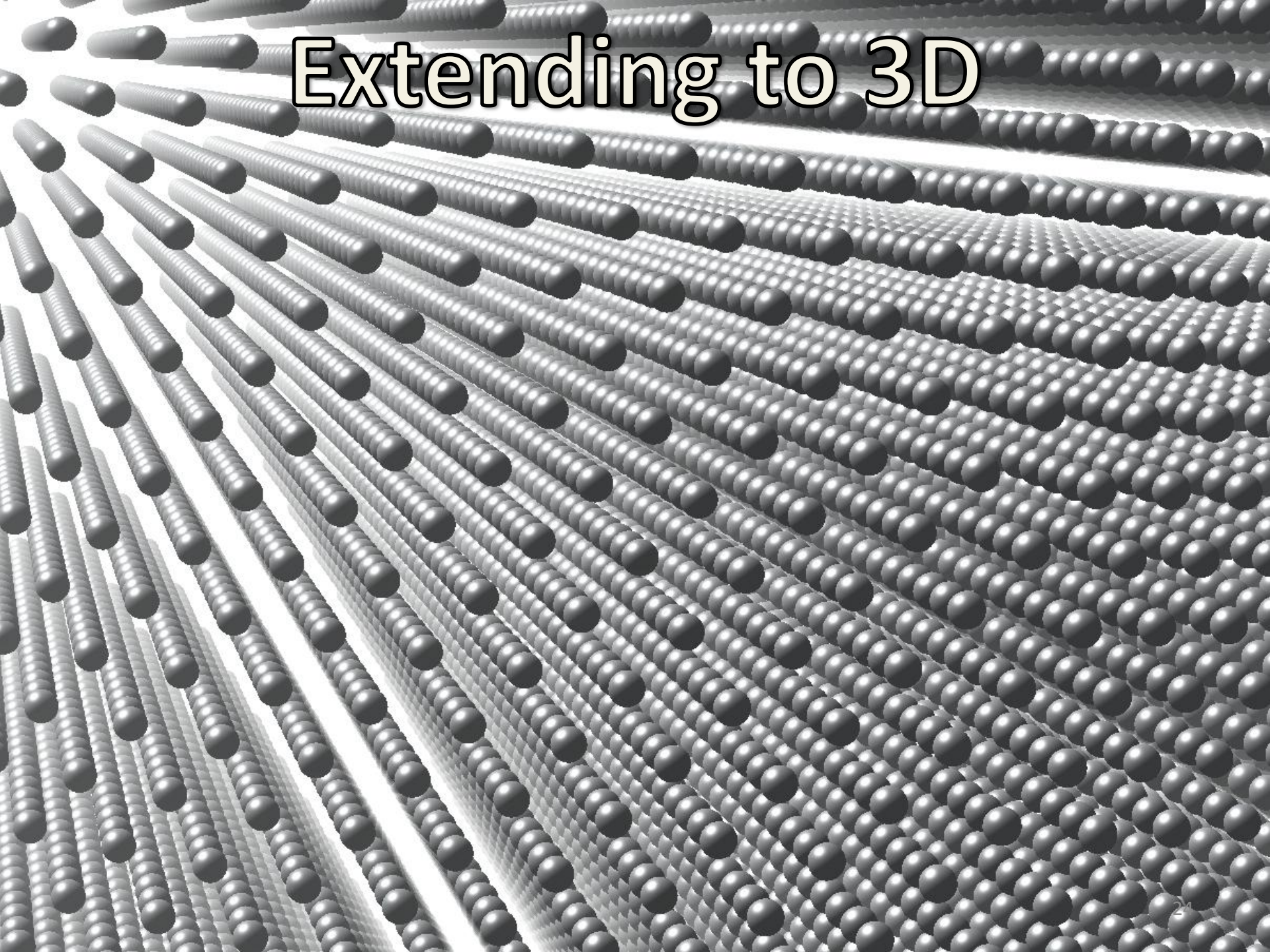
2D Solutions for p-orbtials



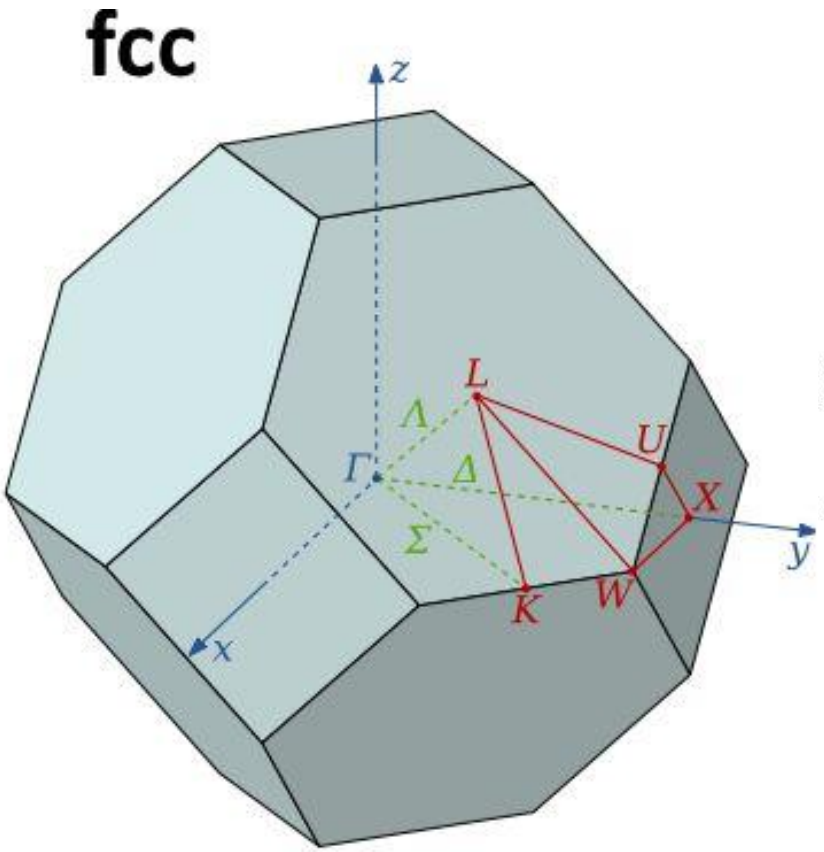


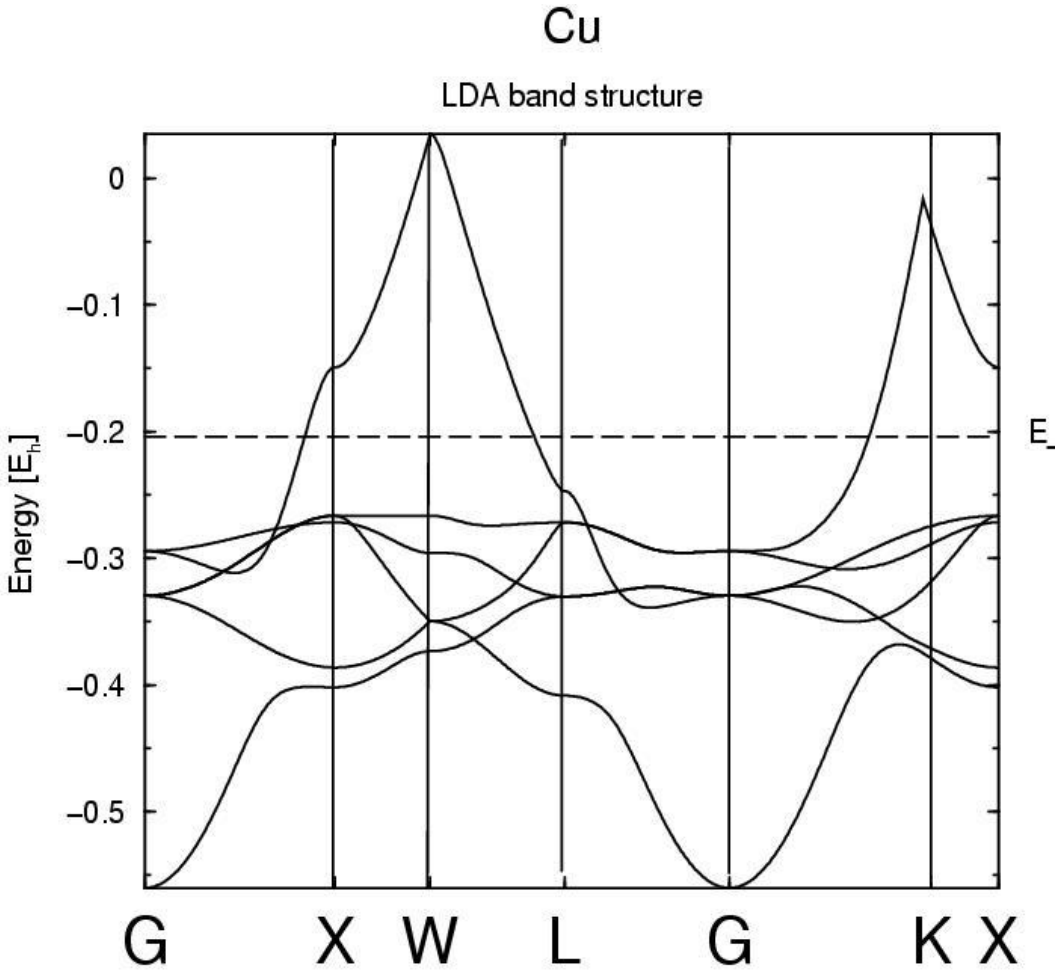

k_y
M
Γ
X
k_x
p_x , p_y
p_z
s
E
Γ
X
M
Γ
k

Extending to 3D



1.5 Brillouin Zone in 3D



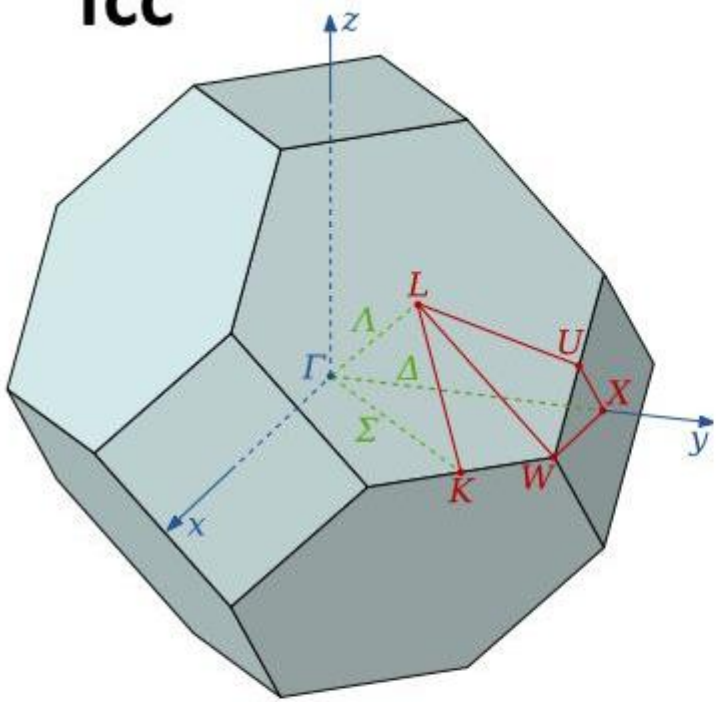


http://slideplayer.com/slide/8814870/26/images/12/Brillouin+Zones+in+3D+fcc+bcc+hcp+The+BZ+reflects+lattice+symmetry.jpg

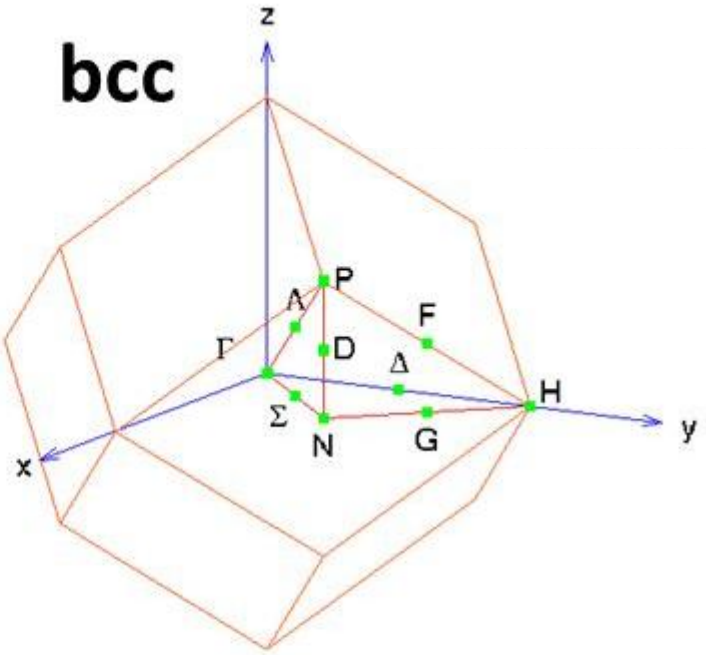
http://www.theochem.unito.it/crystal_tuto/mssc2008_cd/tutorials/metals/metalklaus_files/cuLDAband.jpg

1.5 Brillouin Zone of other lattices

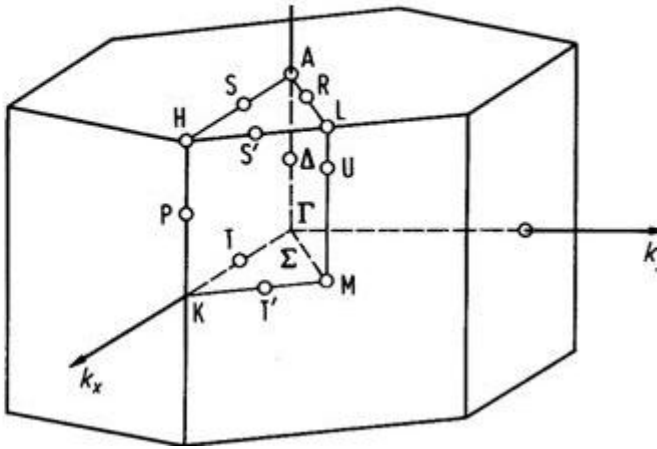
fcc



bcc

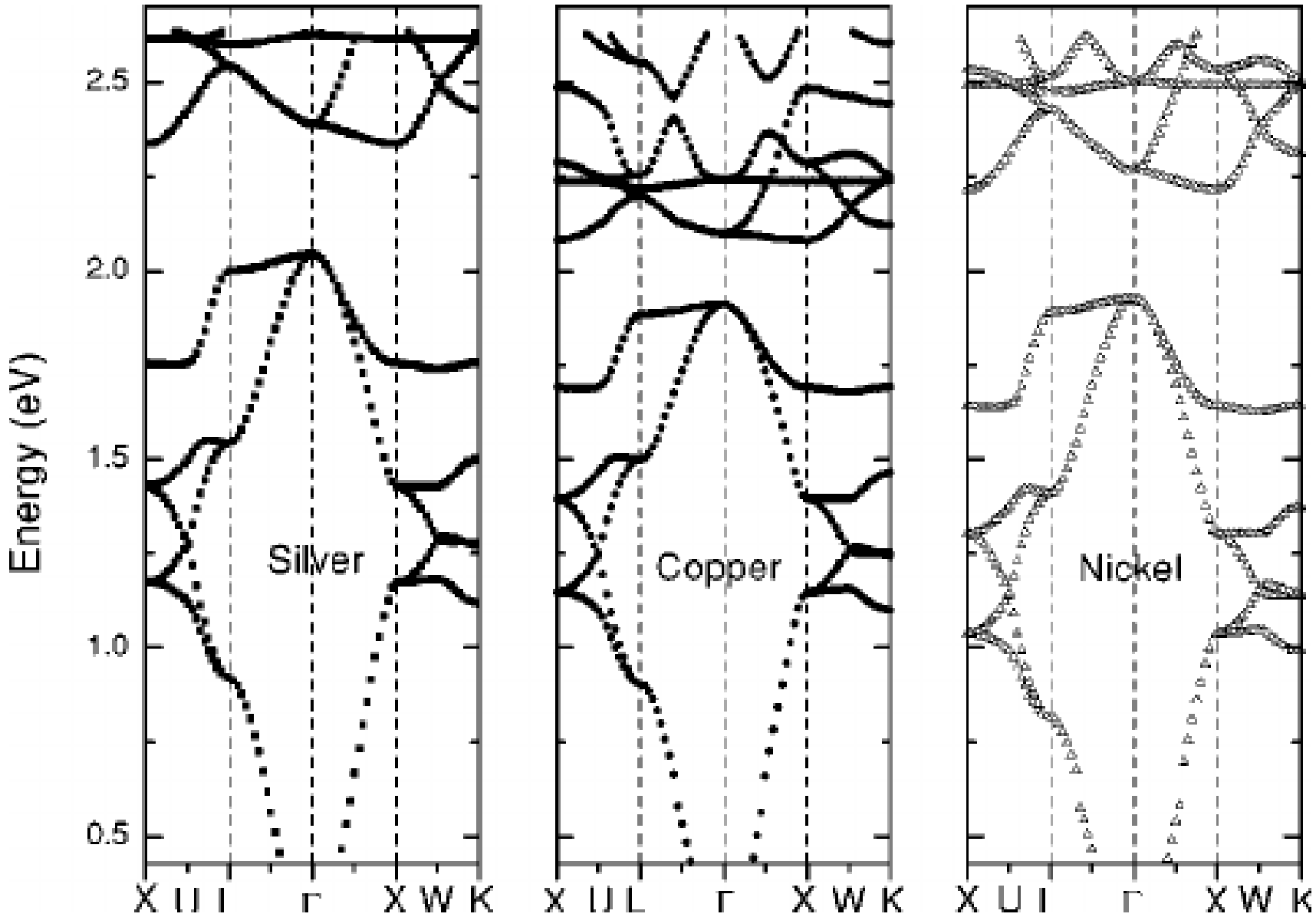


hcp

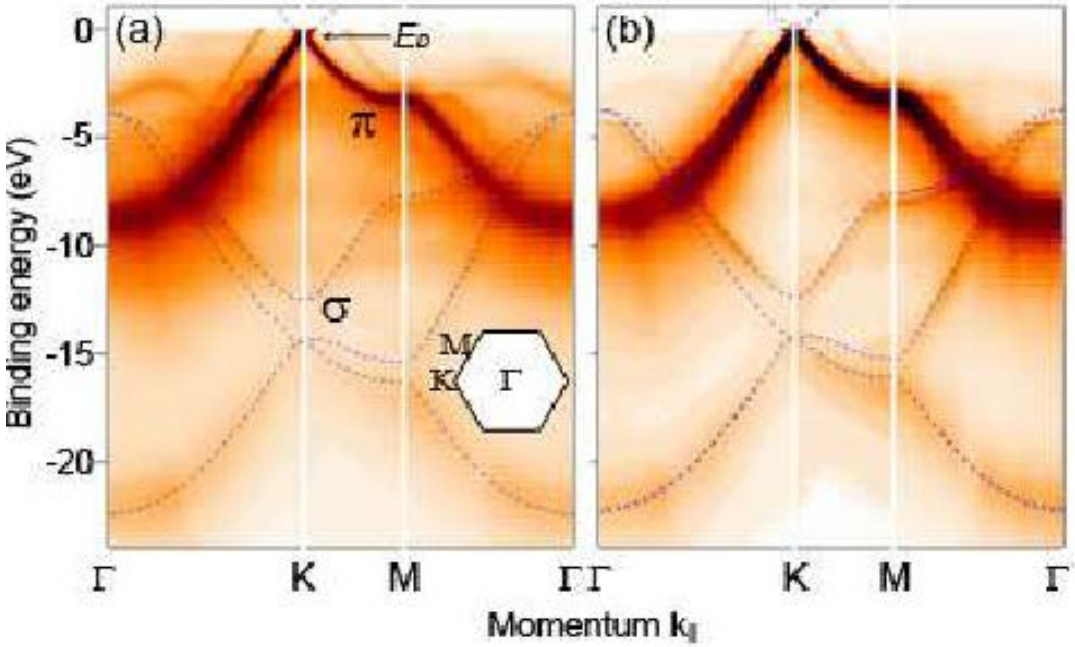


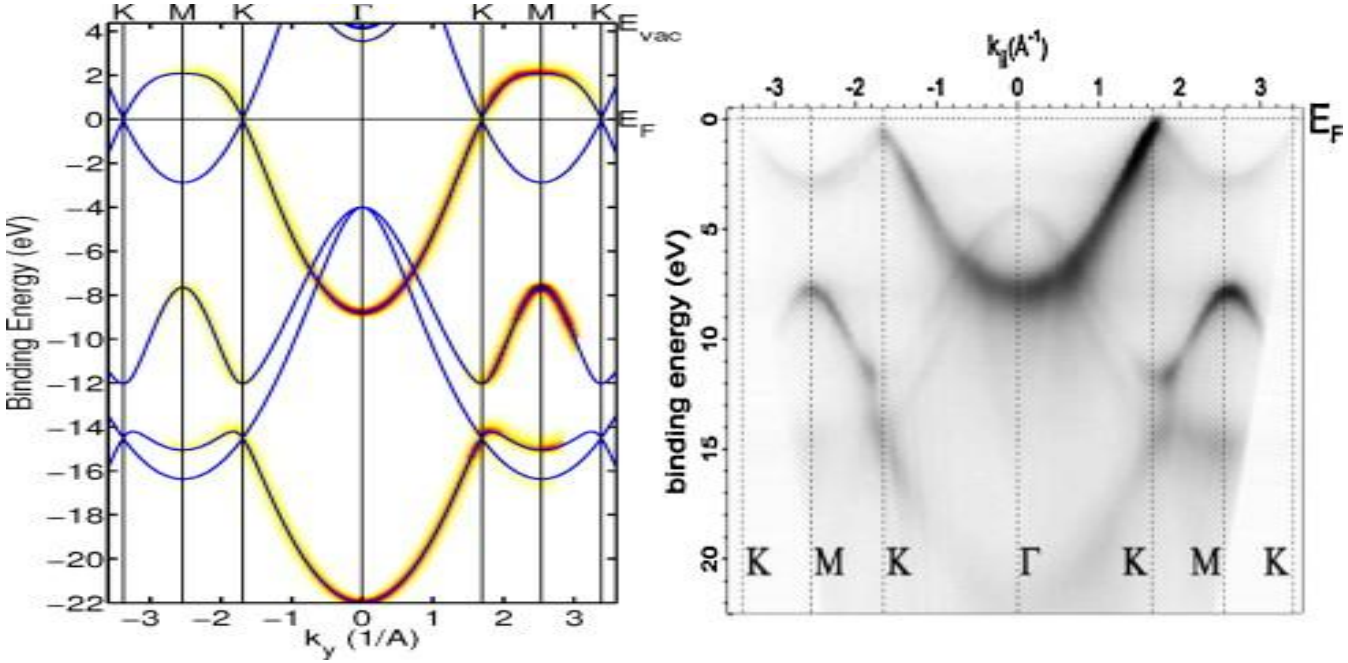
- The BZ reflects lattice symmetry

http://slideplayer.com/slide/8814870/26/images/12/Brillouin+Zones+in+3D+fcc+bcc+hcp+The+BZ+reflects+lattice+symmetry.jpg



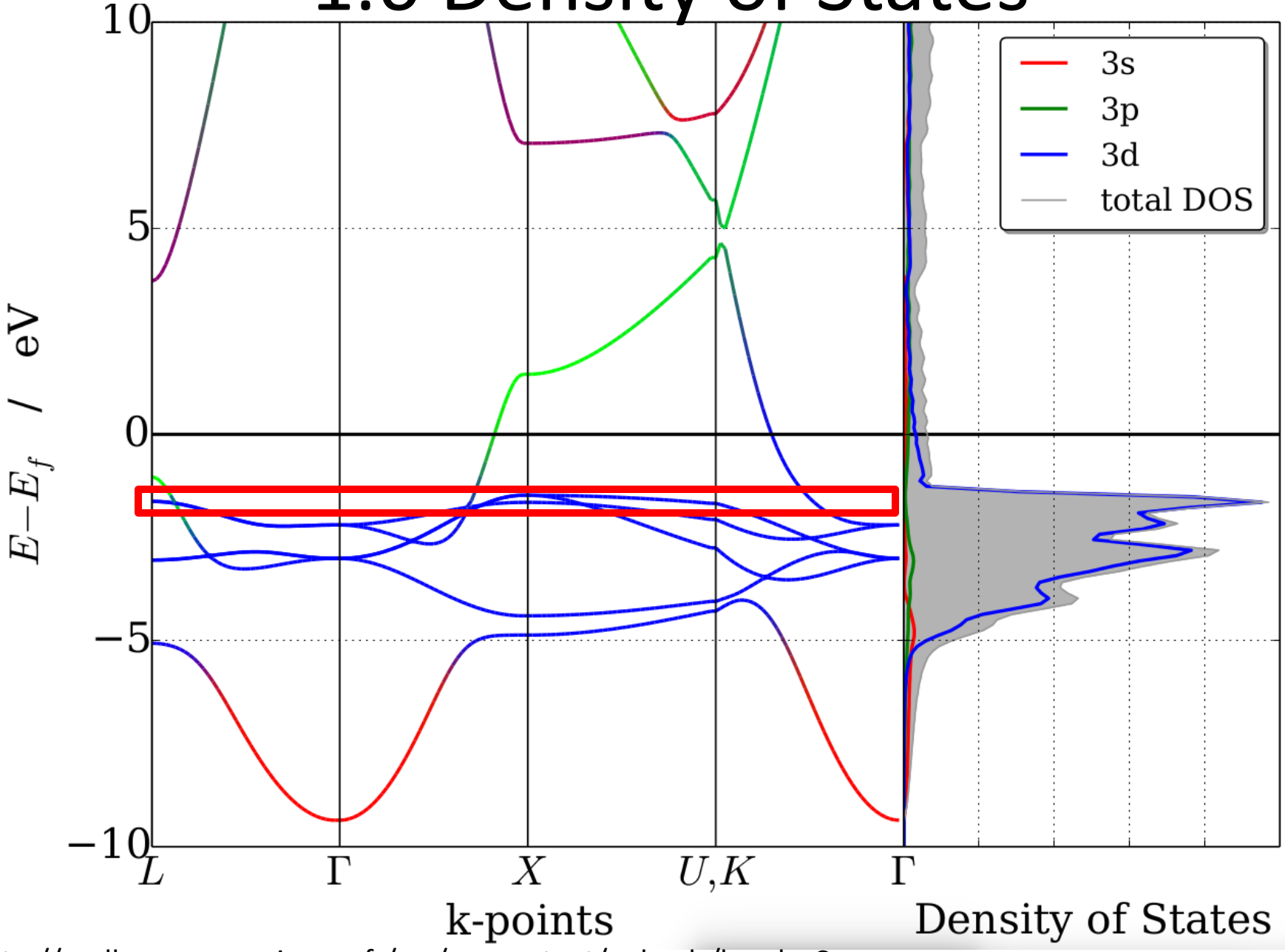
https://www.researchgate.net/profile/Weiyi_Zhang4/publication/235593434/figure/fig1/AS:299884272996390@1448509390741/FIG-1-Calculated-band-structure-for-fcc-photonic-crystals-con-sisting-of.png





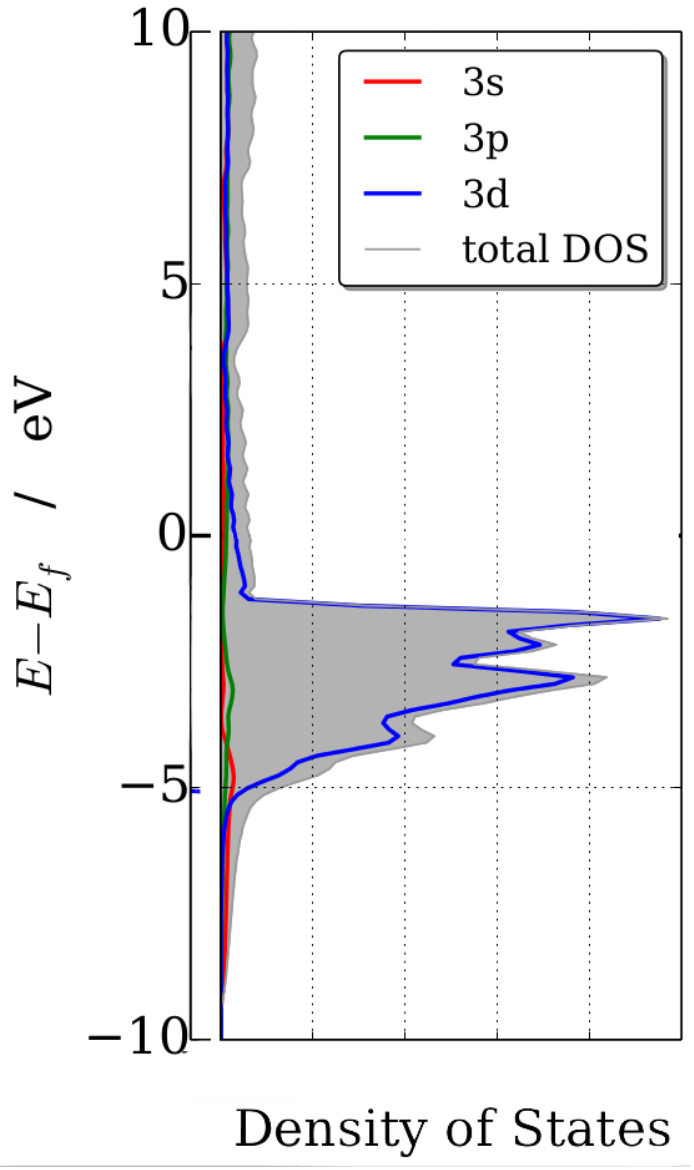
https://www.researchgate.net/profile/Peter_Puschnig/publication/278686642/figure/fig4/AS:268832665239556@1441106110198/Left-panel-Band-structure-blue-lines-and-simulated-photoemission-intensities.png

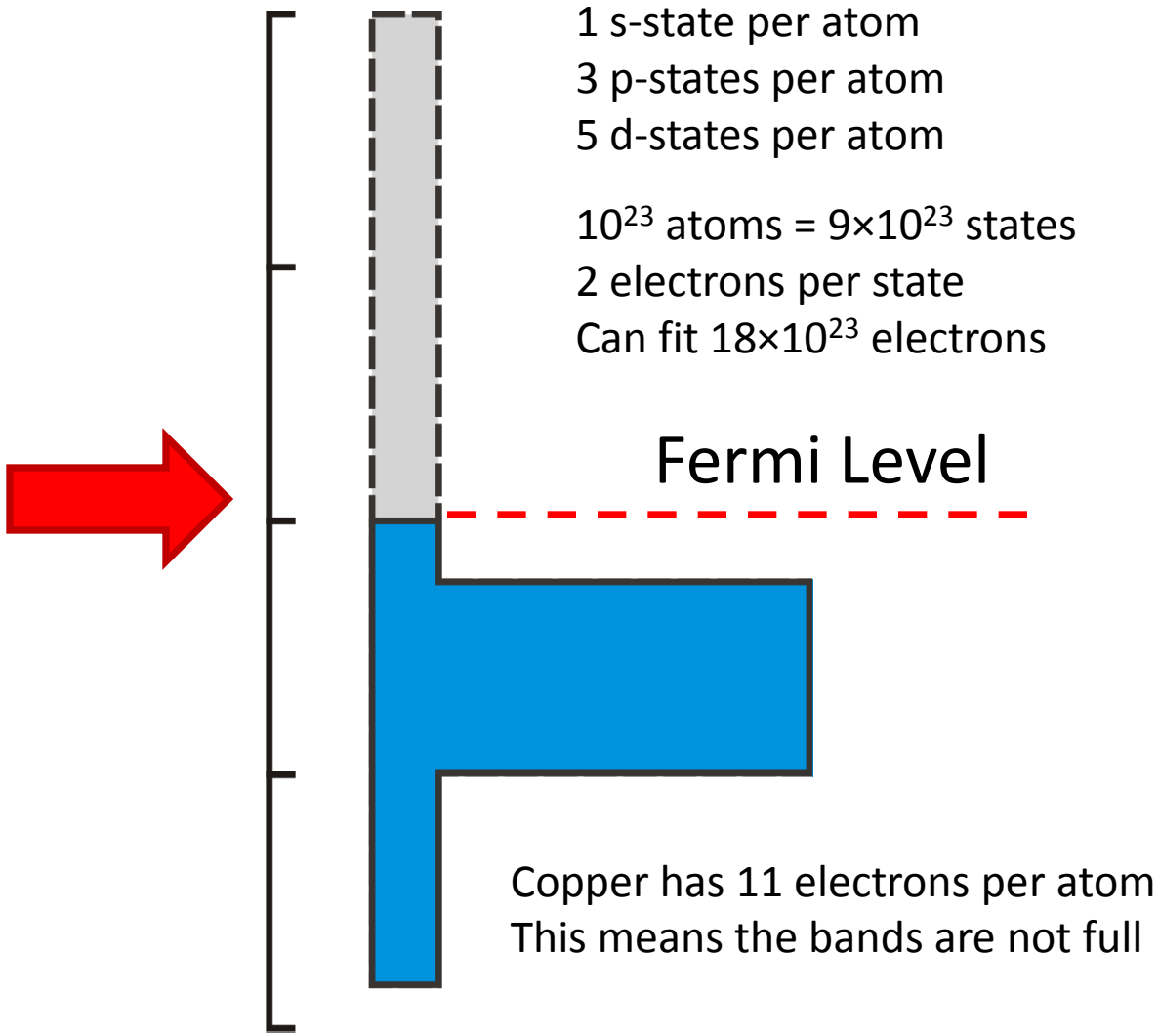
1.6 Density of States



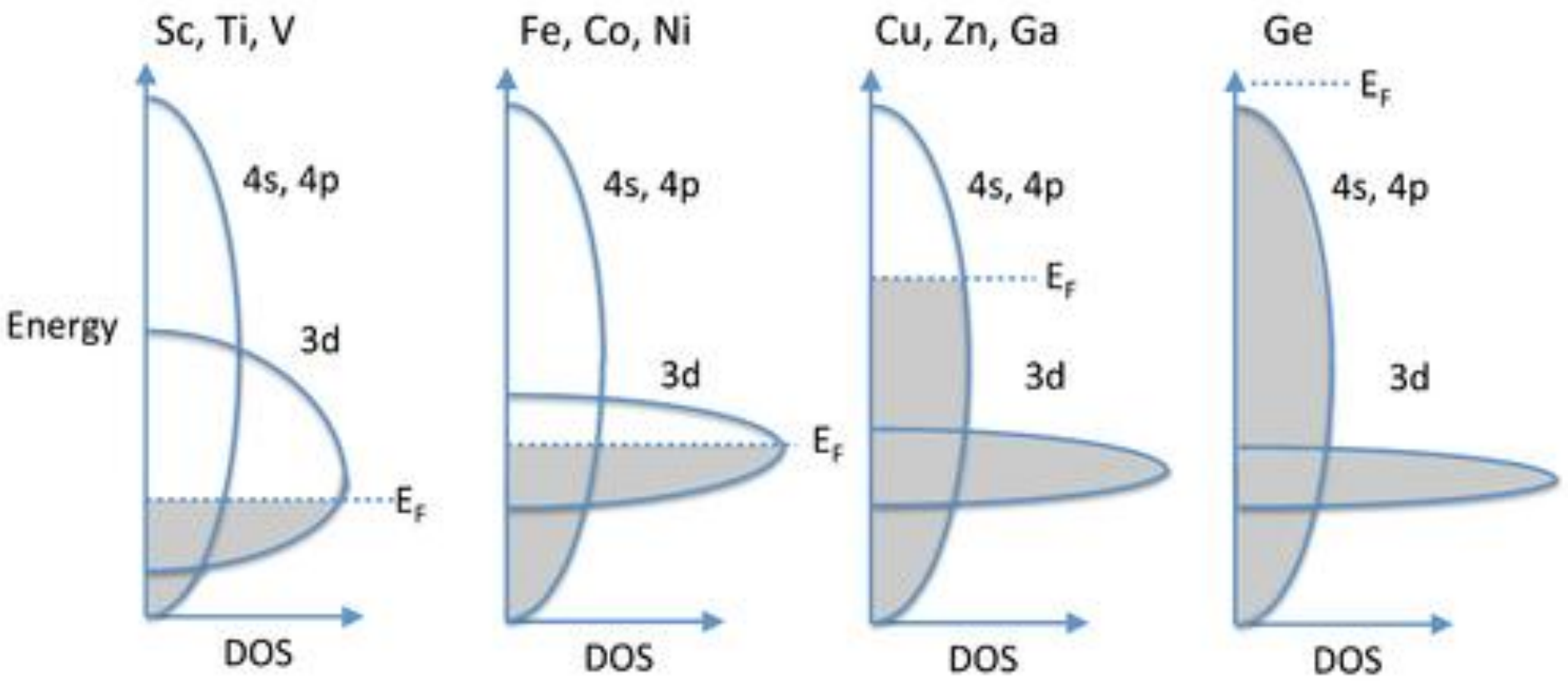
http://gvallver.perso.univ-pau.fr/wp/wp-content/uploads/bands_Cu.png

1.6 Filling with electrons



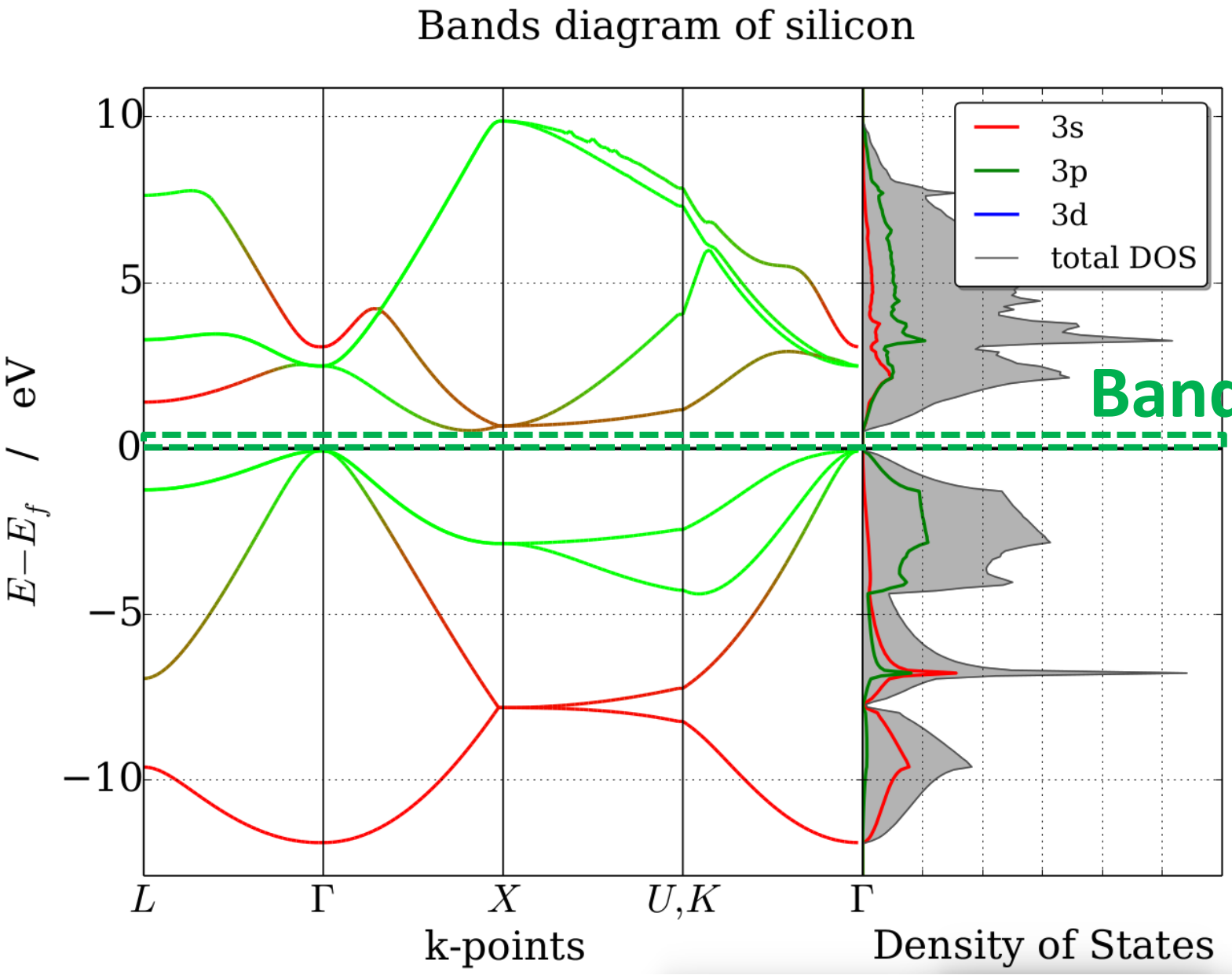


1.6 Band filling of the transition metals



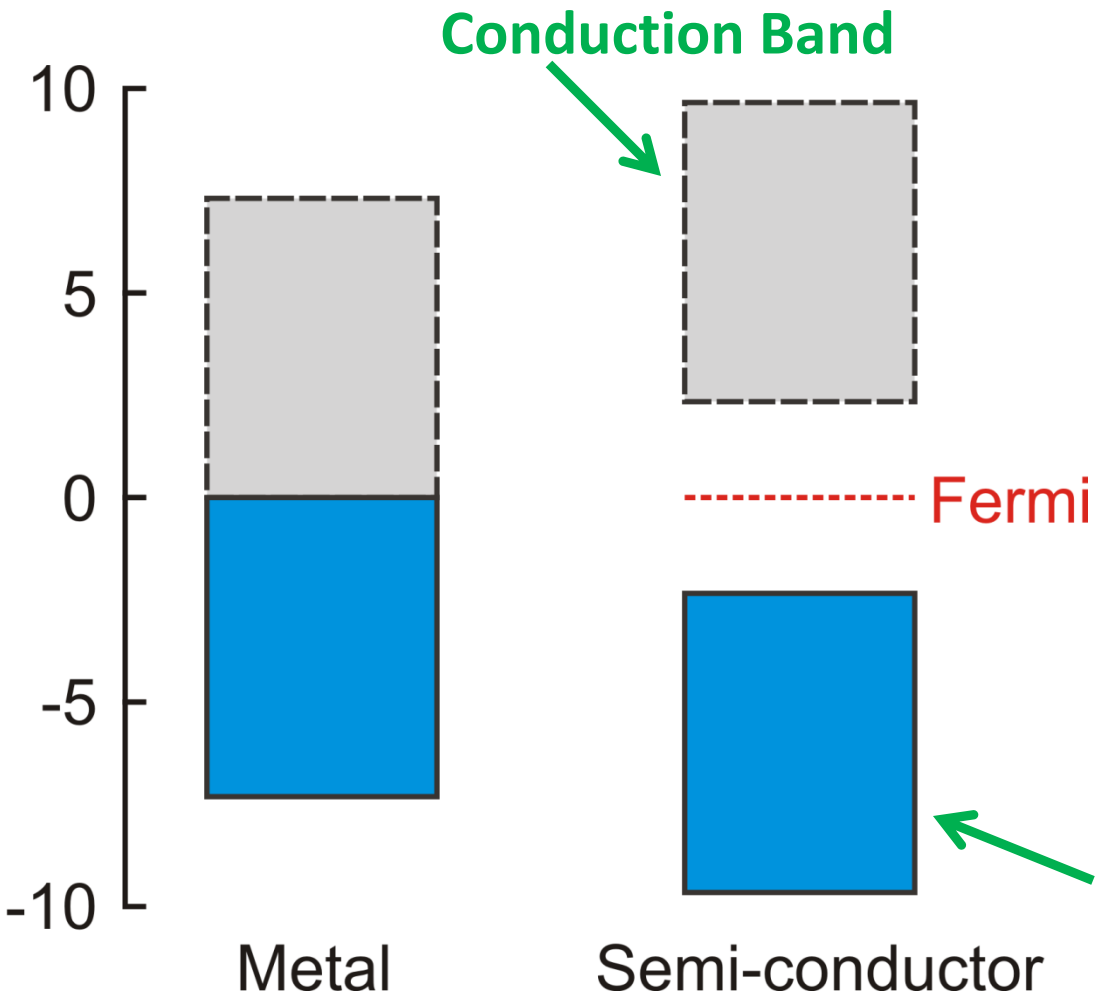
https://chem.libretexts.org/@api/deki/files/51236/D-band_filling.png?revision=1&size=bestfit&width=500&height=221

1.7 Semiconductors and band gaps



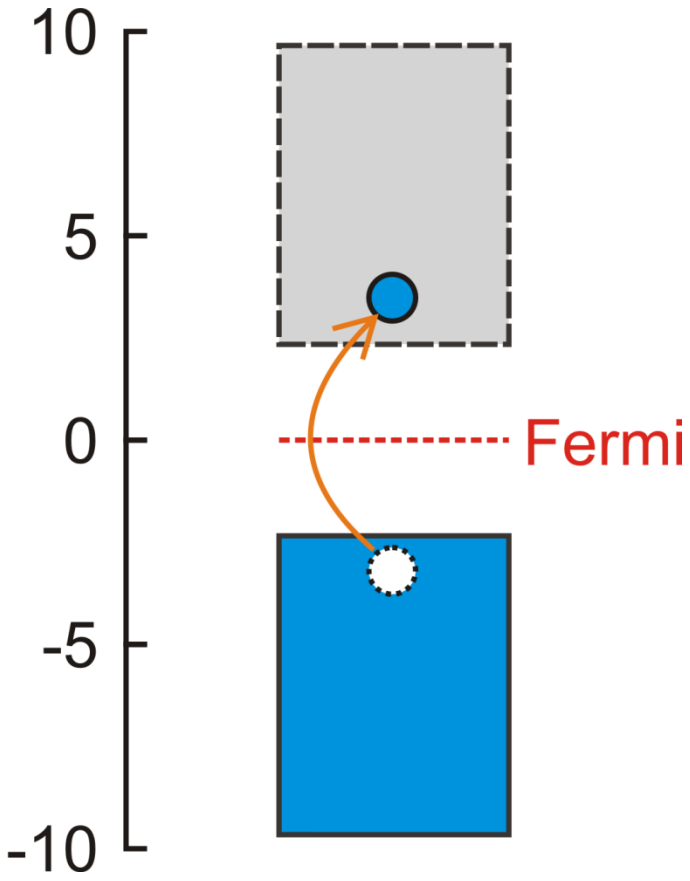
http://gvallver.perso.univ-pau.fr/wp/wp-content/uploads/bands_Si.png

1.7 Metals vs Semiconductors



- Metals have states at Fermi level
- SC's and insulators do not
- "Band Gap" is the difference between CB and VB.
- For intrinsic SC's the Fermi level is in the middle of the gap

1.7 Conduction



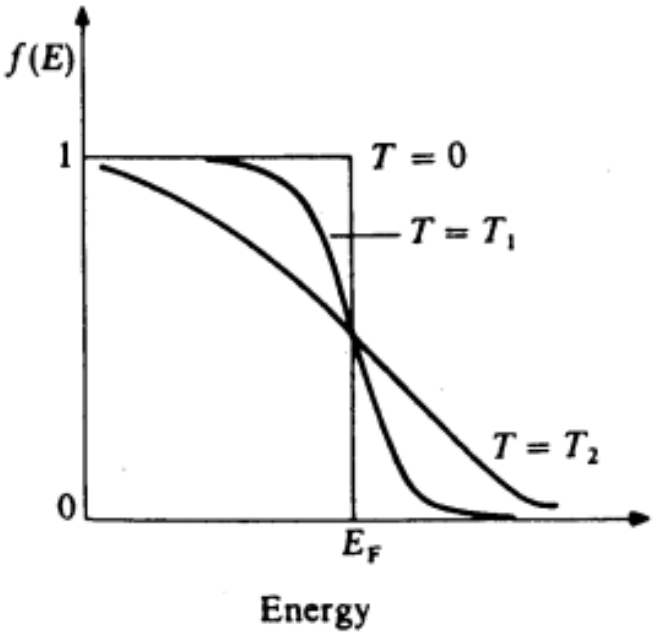
- Elect. Conduction occurs via excitation of e^- into unoccup. States
- This generates electrons in the CB and holes (i.e. electron vacancies) in the VB.
- Both lead to conductivity
- Average thermal energy (kT) at room temp. is 0.013 eV
- Only the electrons within a few kT of the Fermi level can contribute to conduction

1.7 Fermi-Dirac Function

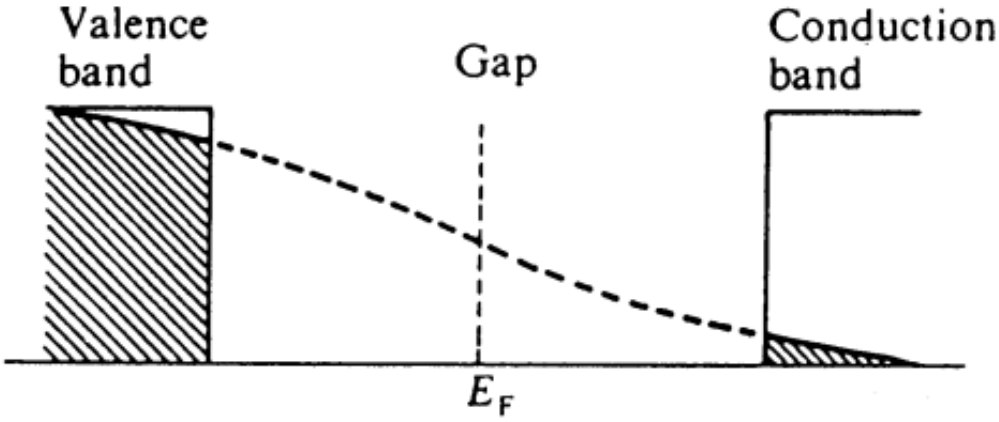
$$f(E)_{\text{Fermi-Dirac}} = \frac{1}{e^{(E - E_F)/kT} + 1}$$

http://ummalqura-phy.com/HYPER1/disfd3.gif

1.7 Carrier Concentrations

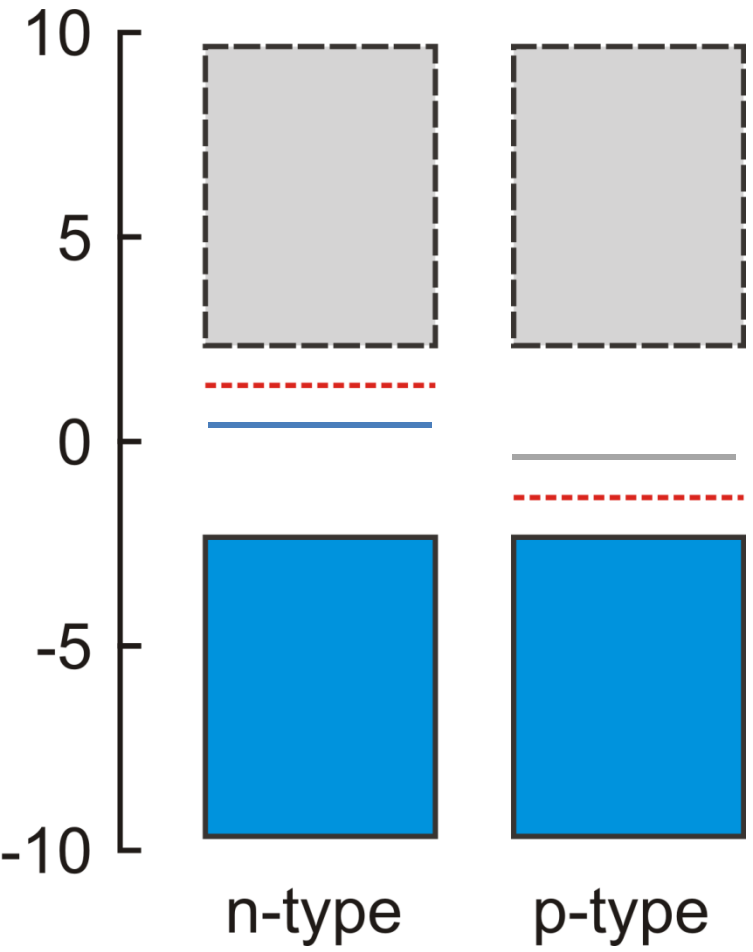


- At 0 K, the electron population distribution is a step function
- As T increases, CB states become filled and VB states become unoccupied.
- Fermi function is used to calculate this.
- Fermi function can be used to calculate charge carrier concentrations in semi-conductors.



https://cbc-wb01x.chemistry.ohio-state.edu/~woodward/ch754/lect2003/conductivity_lect20.pdf

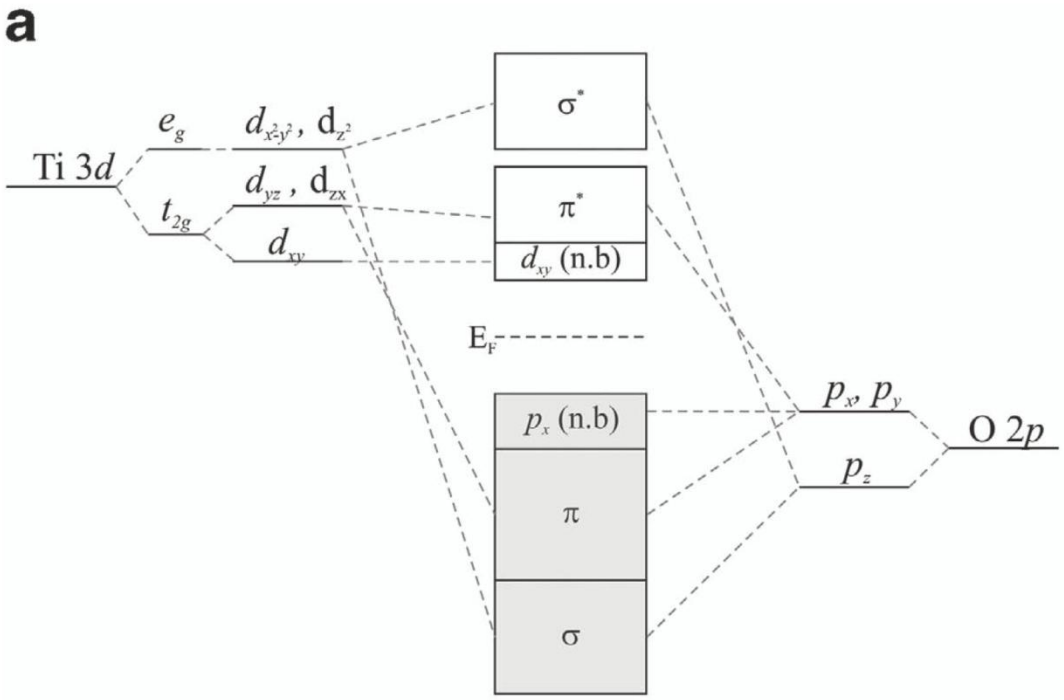
1.8 Doping Semiconductors

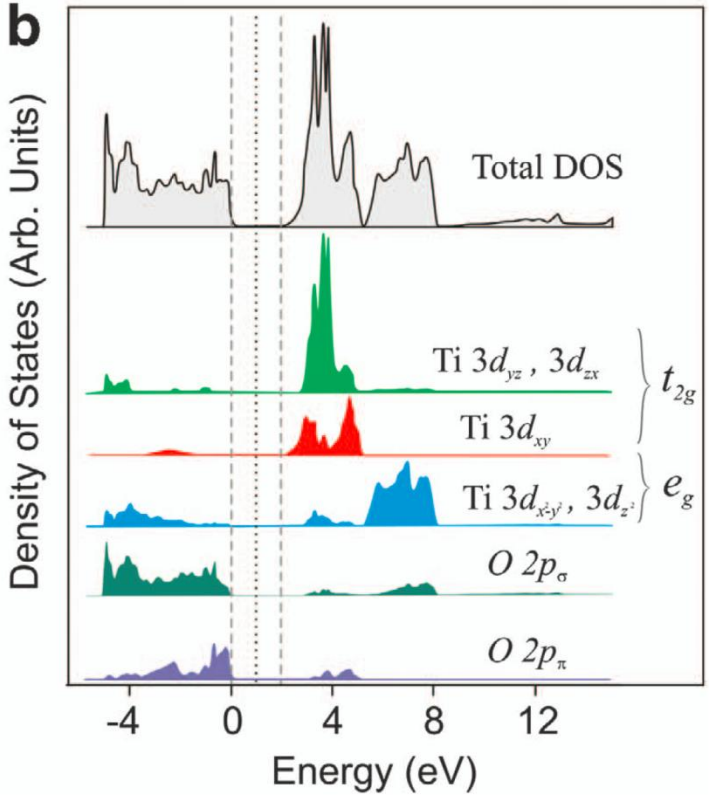


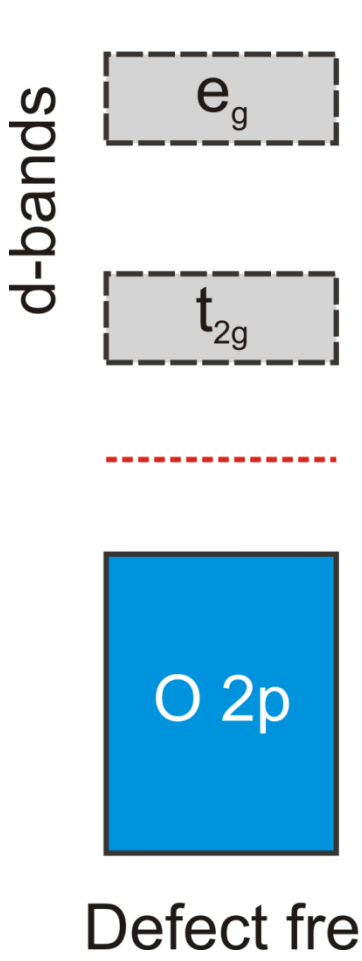
- Impurities can be added to SC's to increase conductivity
- N-type dopants add filled states close to the CB
- P-type dopants add empty states close to the VB
- N-type shifts Fermi toward CB
- P-type shifts Fermi toward VB
- In Si, P is an n-type dopant, B is a P-type dopant.

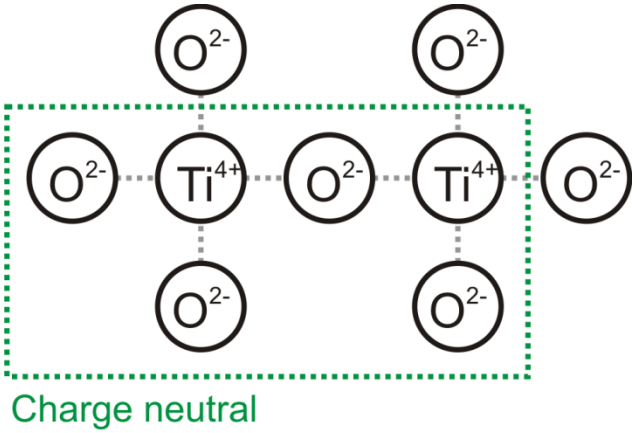
1.8 Doping with defects

- Consider d^0 oxides
- d-orbitals are empty, O 2p orbitals are full
- Examples: TiO_2, MoO_3, V_2O_5, WO_3

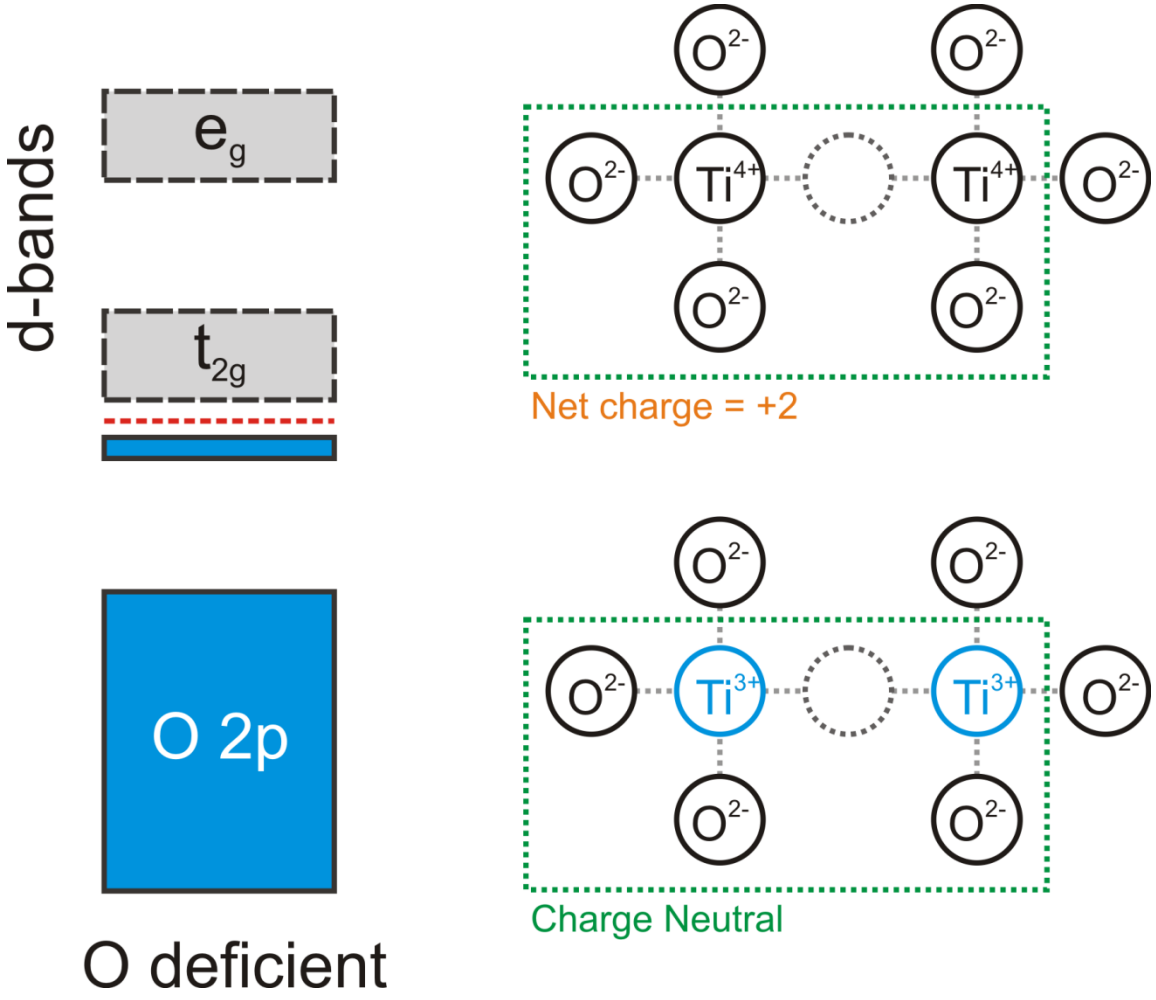








- Perfect crystal has Fermi at mid-gap



- O vacancy requires two Ti^{4+} to become Ti^{3+}
- Therefore, Ti 3d band not empty
- Electrons on Ti^{3+} sites are n-type dopants

Doping with defects

- Due to entropy, there is always some finite concentration of defects.
- Therefore, oxides are always intrinsically “doped”
- Type of doping depends on thermodynamic stability of defects
- O vacancies are n-type dopants
- Metal vacancies are p-type dopants
- O interstitials are p-type dopants
- Metal interstitials are n-type dopants
- Doping degree changes with temperature and O-partial pressure

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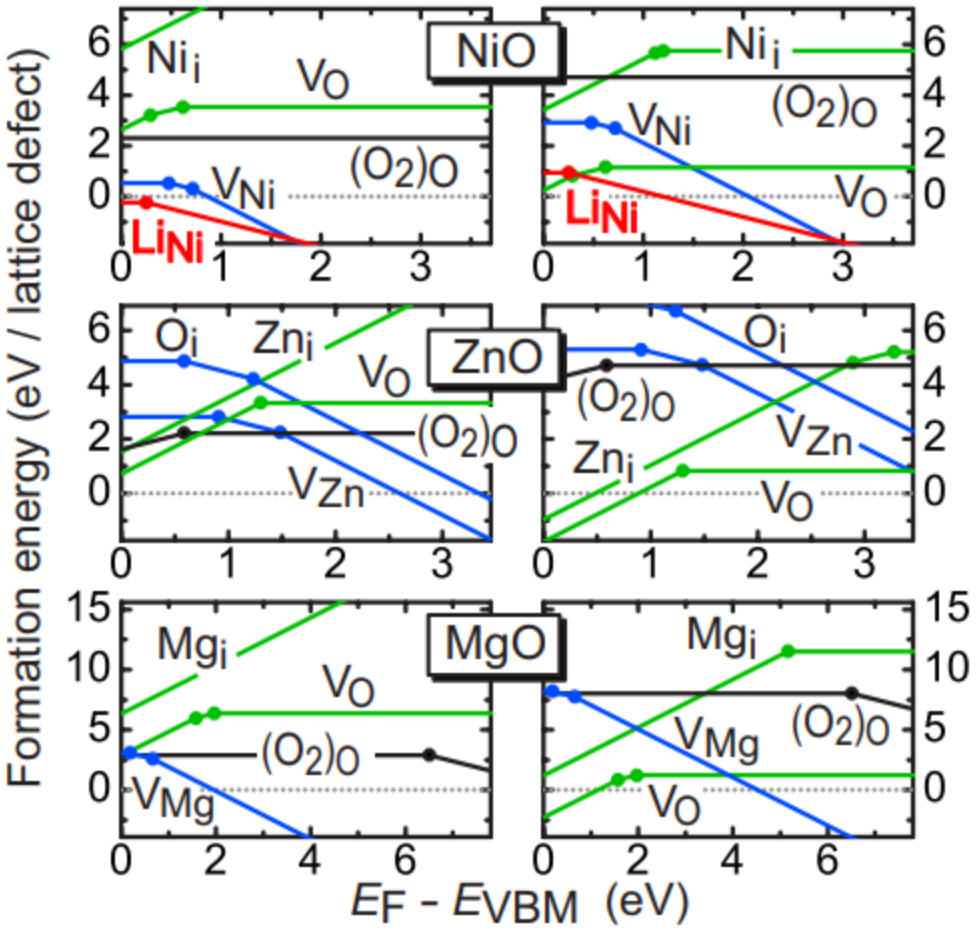
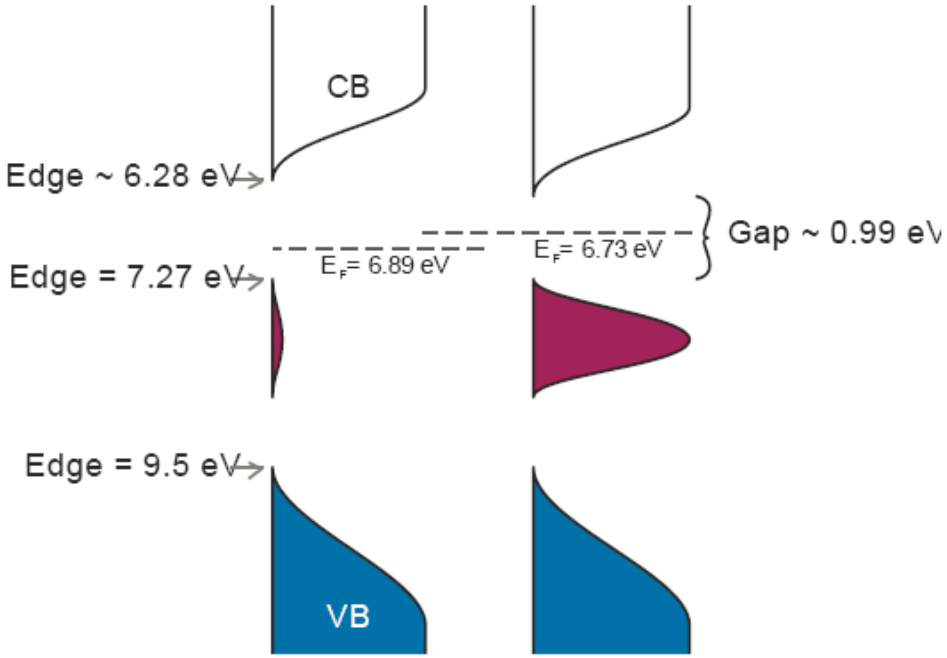
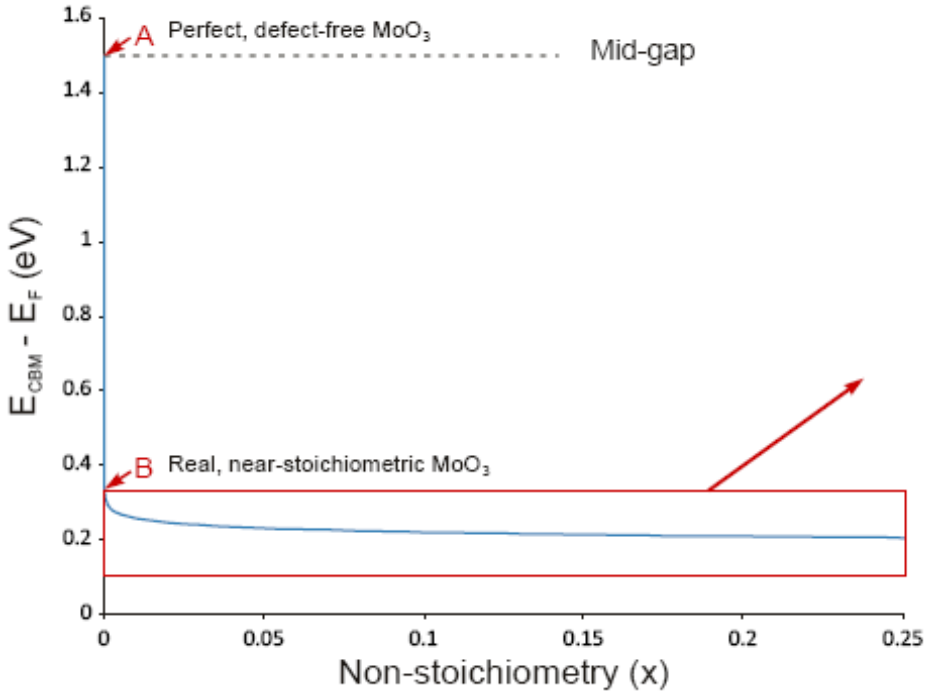
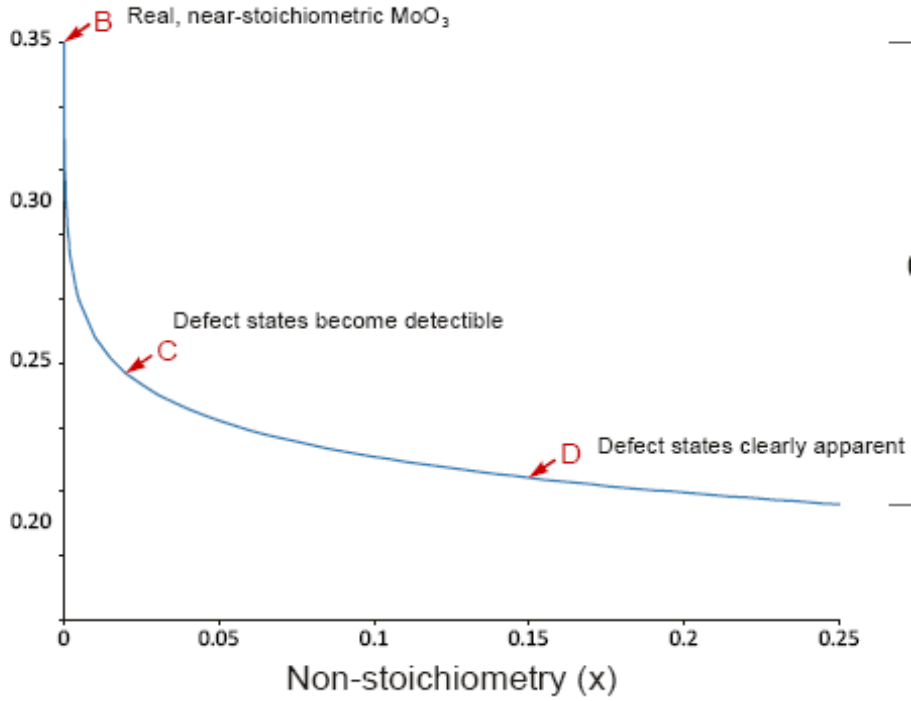
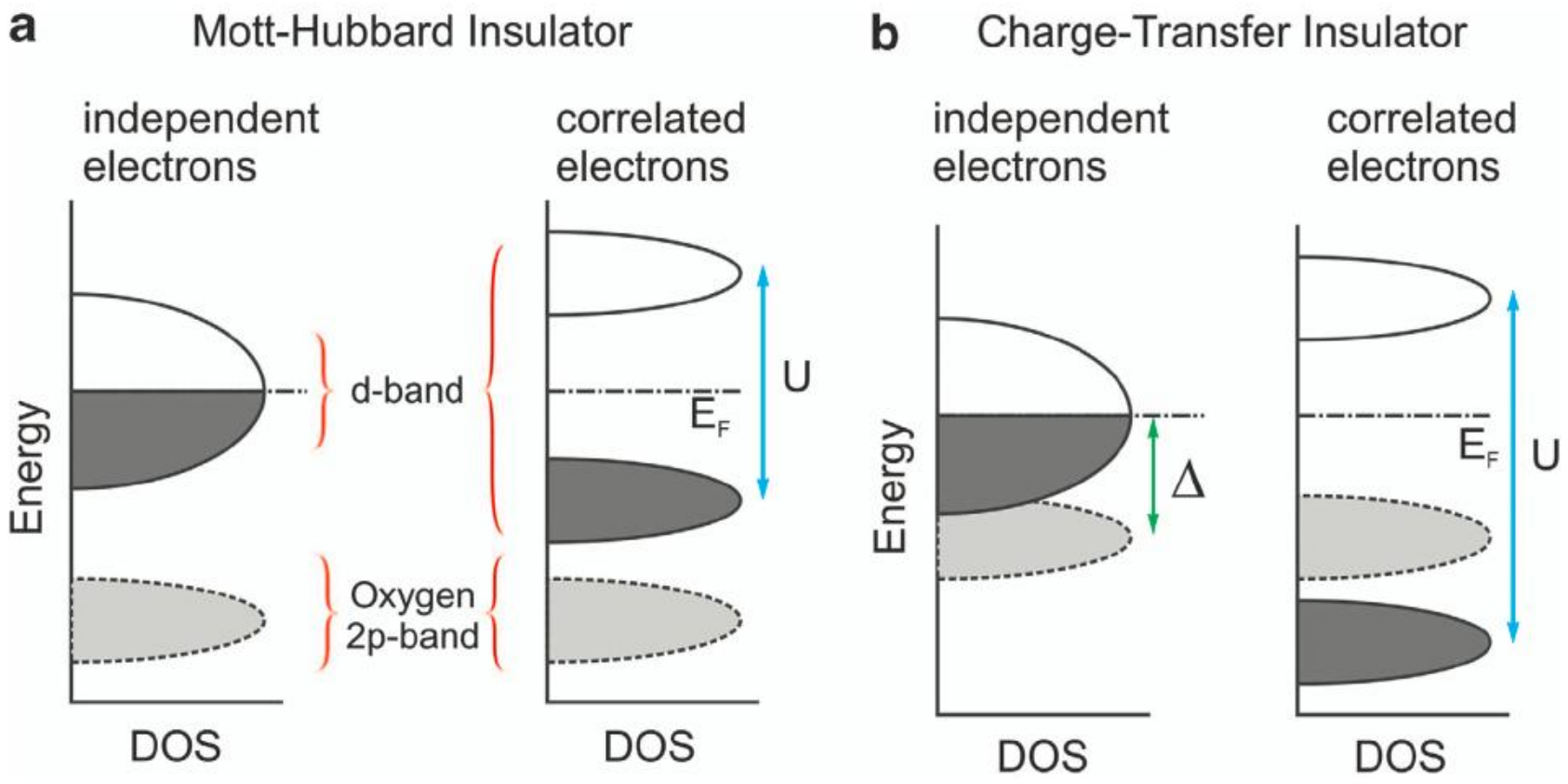



CB
Edge ~ 6.28 eV
Gap ~ 0.99 eV
E_F= 6.89 eV
E_F= 6.73 eV
Edge = 7.27 eV
Edge = 9.5 eV
VB


A Perfect, defect-free MoO_3
Mid-gap
B Real, near-stoichiometric MoO_3
E_{CBM} - E_F (eV)
Non-stoichiometry (x)

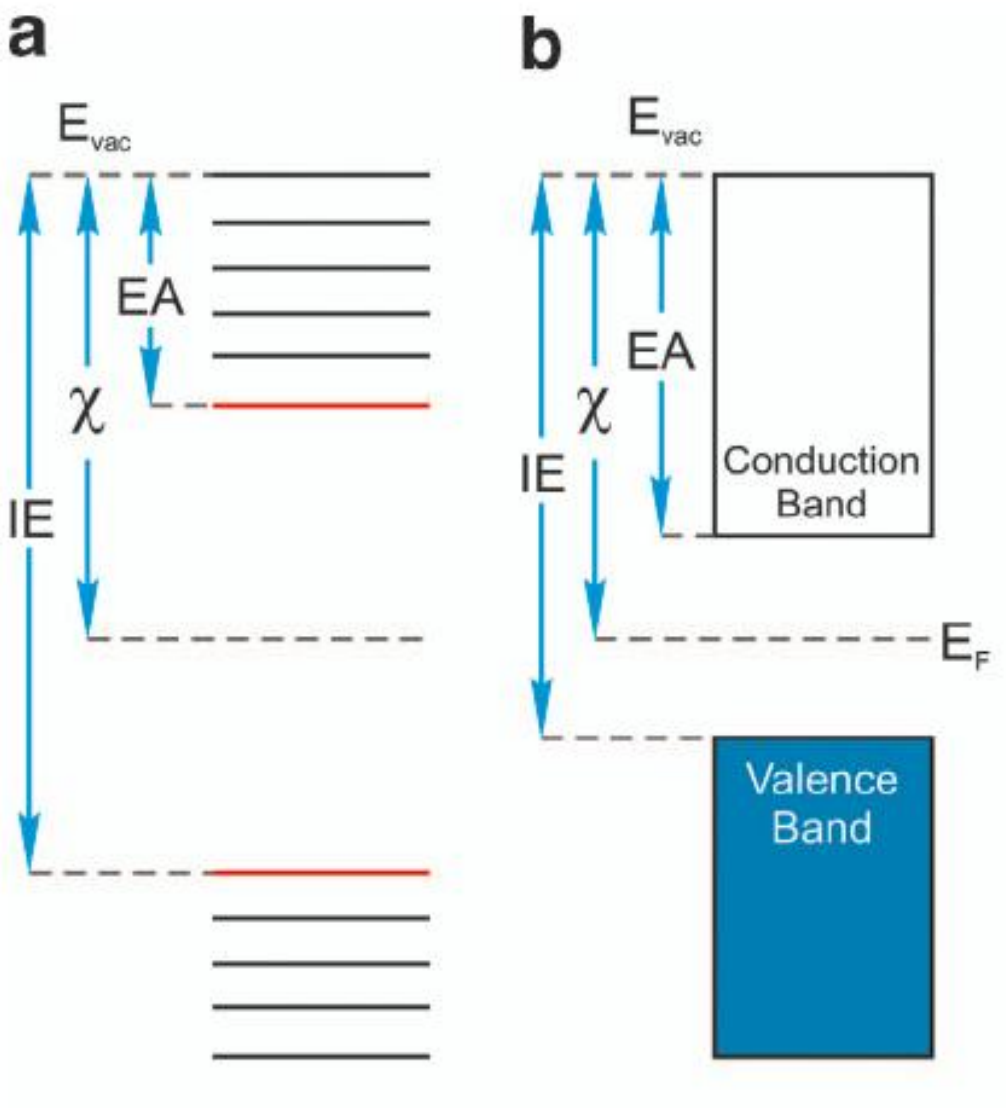

B Real, near-stoichiometric MoO_3
Defect states become detectible
C
D
Defect states clearly apparent
Non-stoichiometry (x)

Non-classical Insulators



Part 2:
The Fermi Level, Work Function and Band Bending

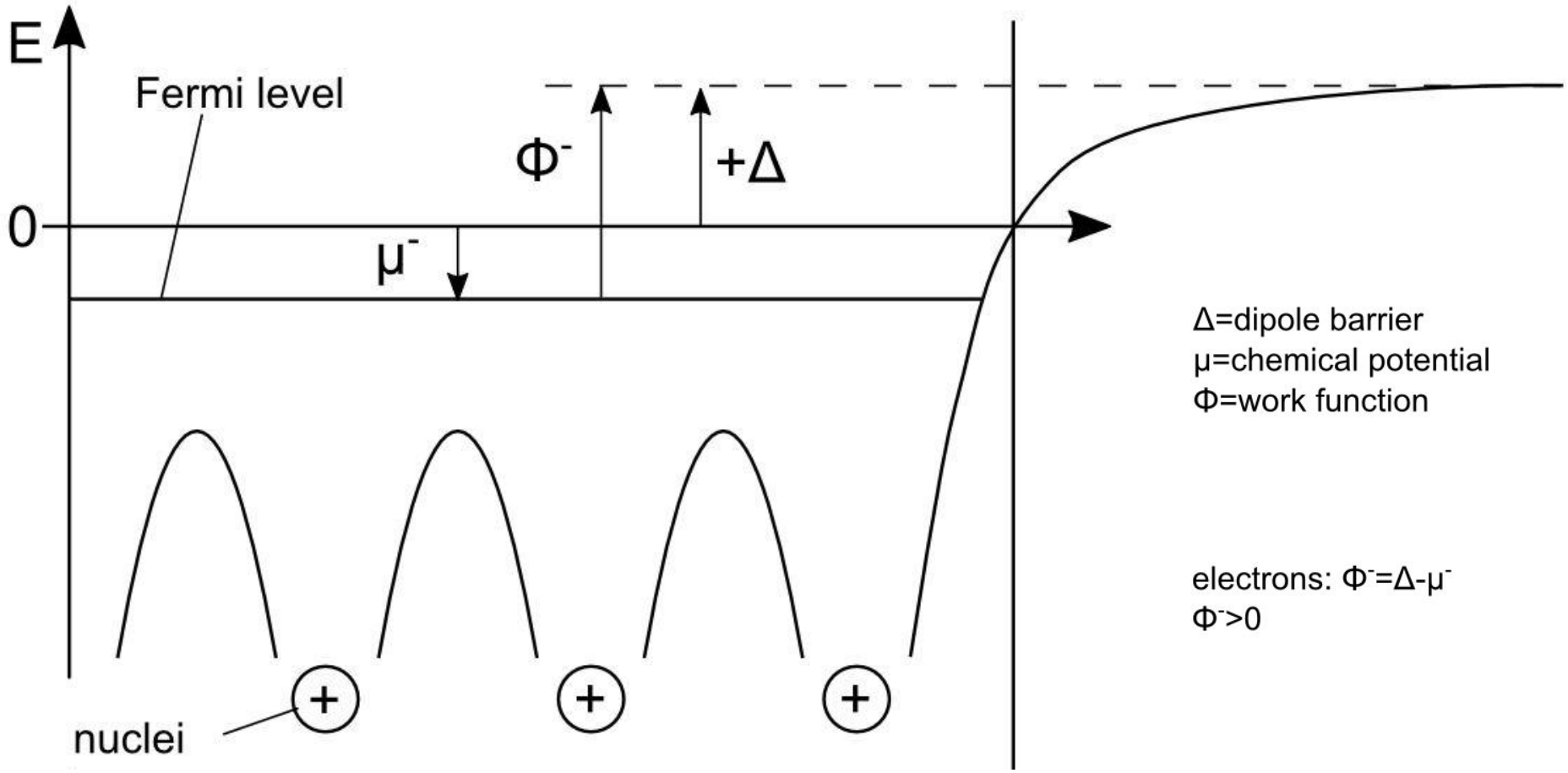
2.1 Fermi level is related to electronegativity



2.1 Work Function

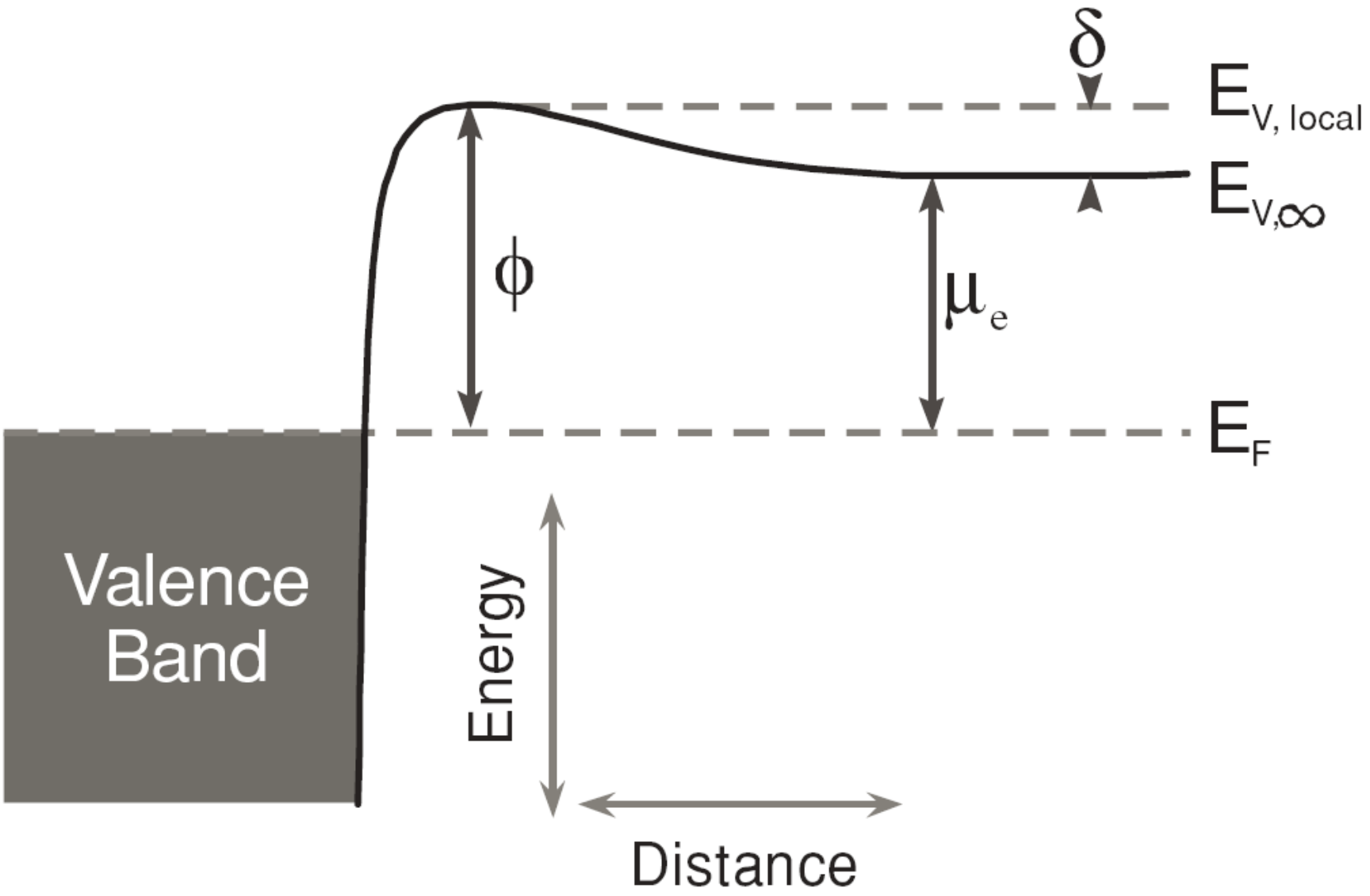
- Work function is the minimum energy required to remove an electron from a solid.
- It is the energy difference between the “local” vacuum level and the Fermi level.
- Local is to be distinguished from absolute vacuum level
- Work function is a characteristic of surfaces.
- If is related to the Fermi level (which is a property of solids), but contains an additional term that is a property of the surface
- This term is the surface dipole.

2.1 Surface Dipole



http://inspirehep.net/record/1497822/files/workfunctions.png

2.1 Surface Dipole



2.1 Local vs. Absolute Vacuum Level

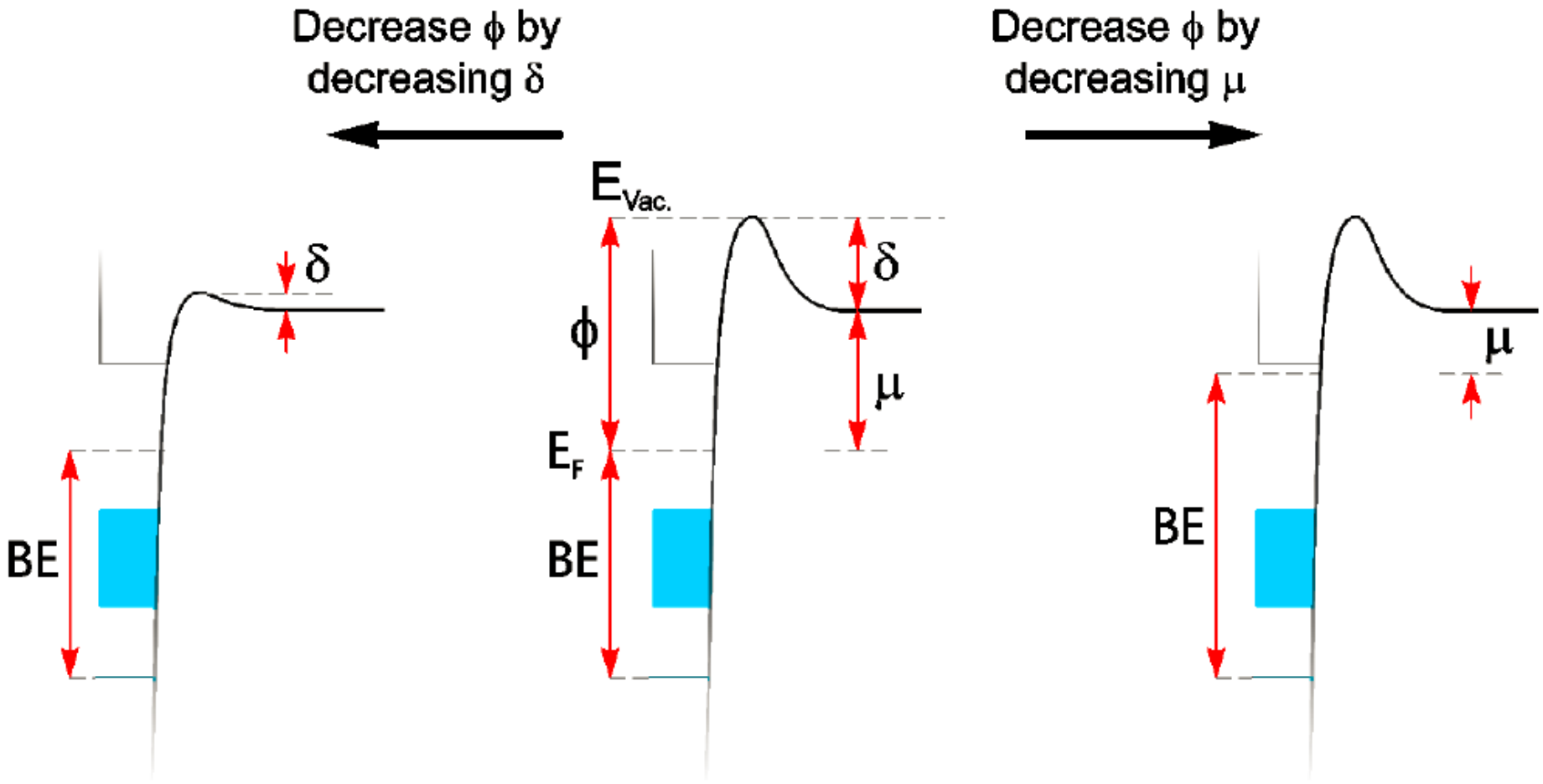
- Absolute vacuum is a universal constant, however, it is not directly measureable
- It is the rest energy of a test charge in absolute vacuum, at infinite distance away from all other particles.
- All we can measure is energy required to eject an electron.
- This is the sum of Fermi energy + surface dipole
- We cannot disentangle these two contributions
- Thus work function is not really Fermi energy or electron chemical potential, but it is the our best measureable approximation.

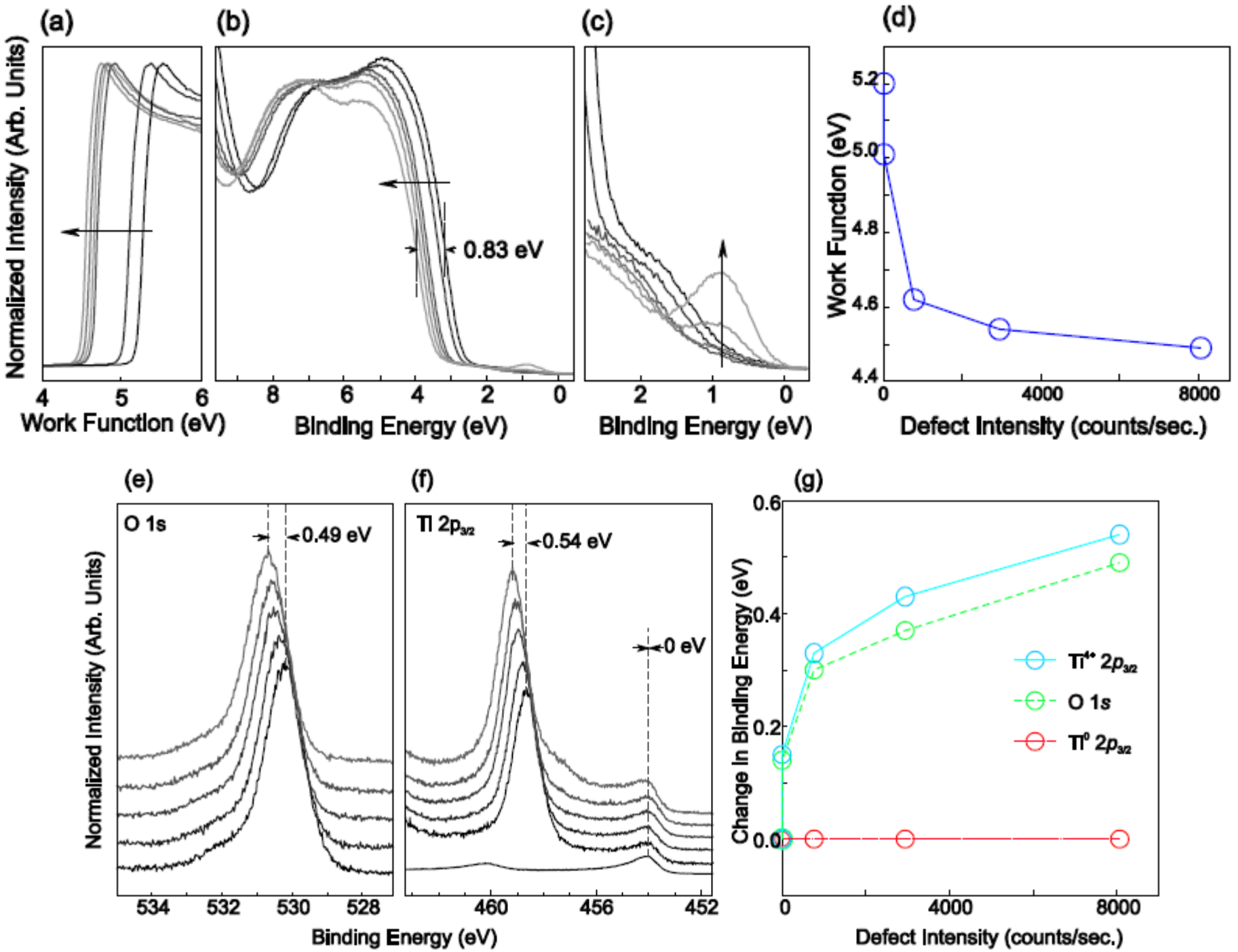
2.1 Work Function Anisotropy

- Different crystal faces have different surface dipoles due to differing atomic packing and resulting electron density
- Thus different crystal faces have different work functions.

	Work Function (eV)
Cu(111)	4.91
Cu(100)	4.81
Cu(110)	4.53

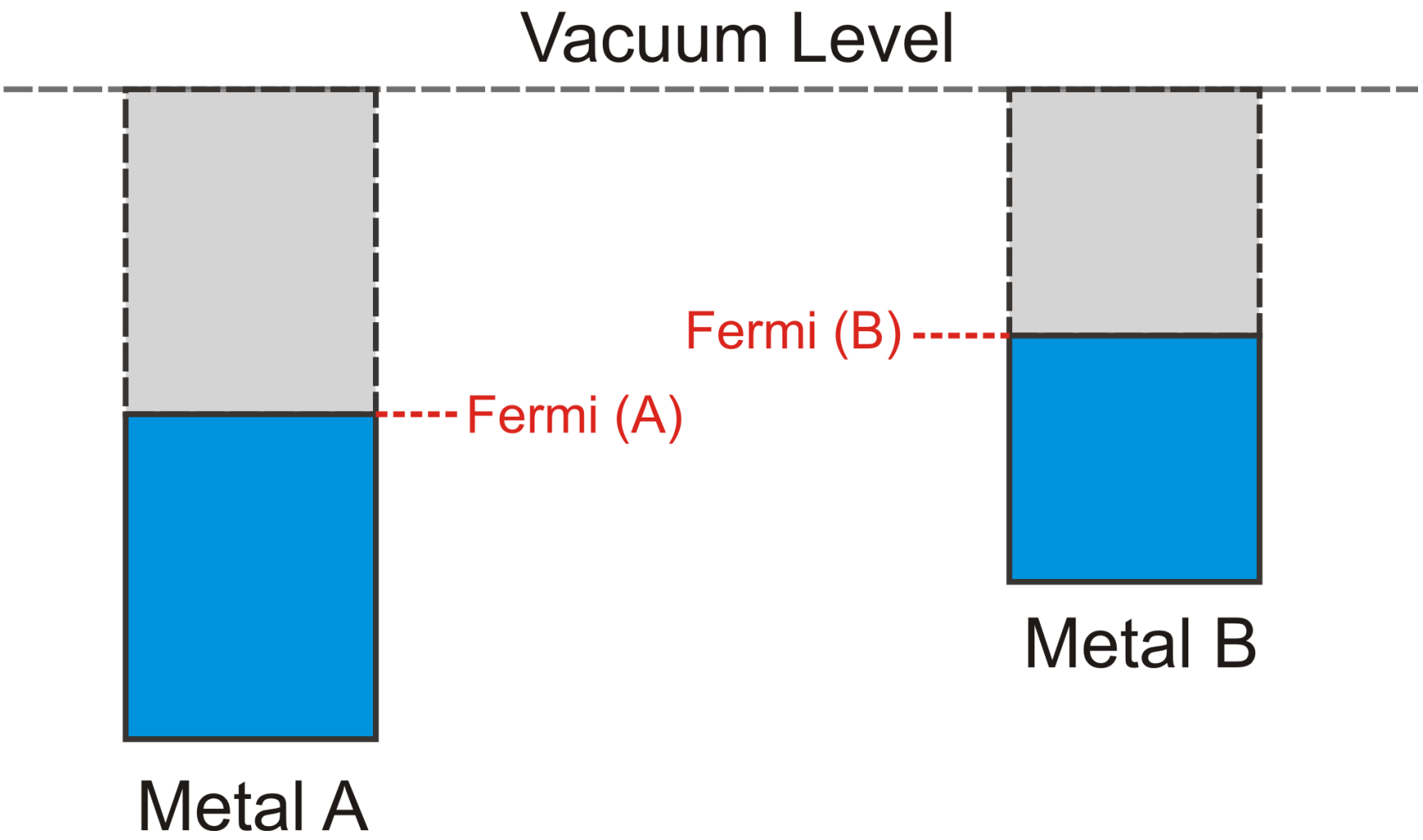
2.1 Work Function, Fermi Level and XPS Binding Energies




(a)
(b)
(c)
(d)
Normalized Intensity (Arb. Units)
Work Function (eV)
Binding Energy (eV)
0.83 eV
Work Function (eV)
Defect Intensity (counts/sec.)
(e)
(f)
(g)
O 1s
0.49 eV
Ti 2p3/2
0.54 eV
0 eV
Change in Binding Energy (eV)
Ti4+ 2p3/2
O 1s
Ti0 2p3/2
Defect Intensity (counts/sec.)

2.2 Equalizing Fermi Levels

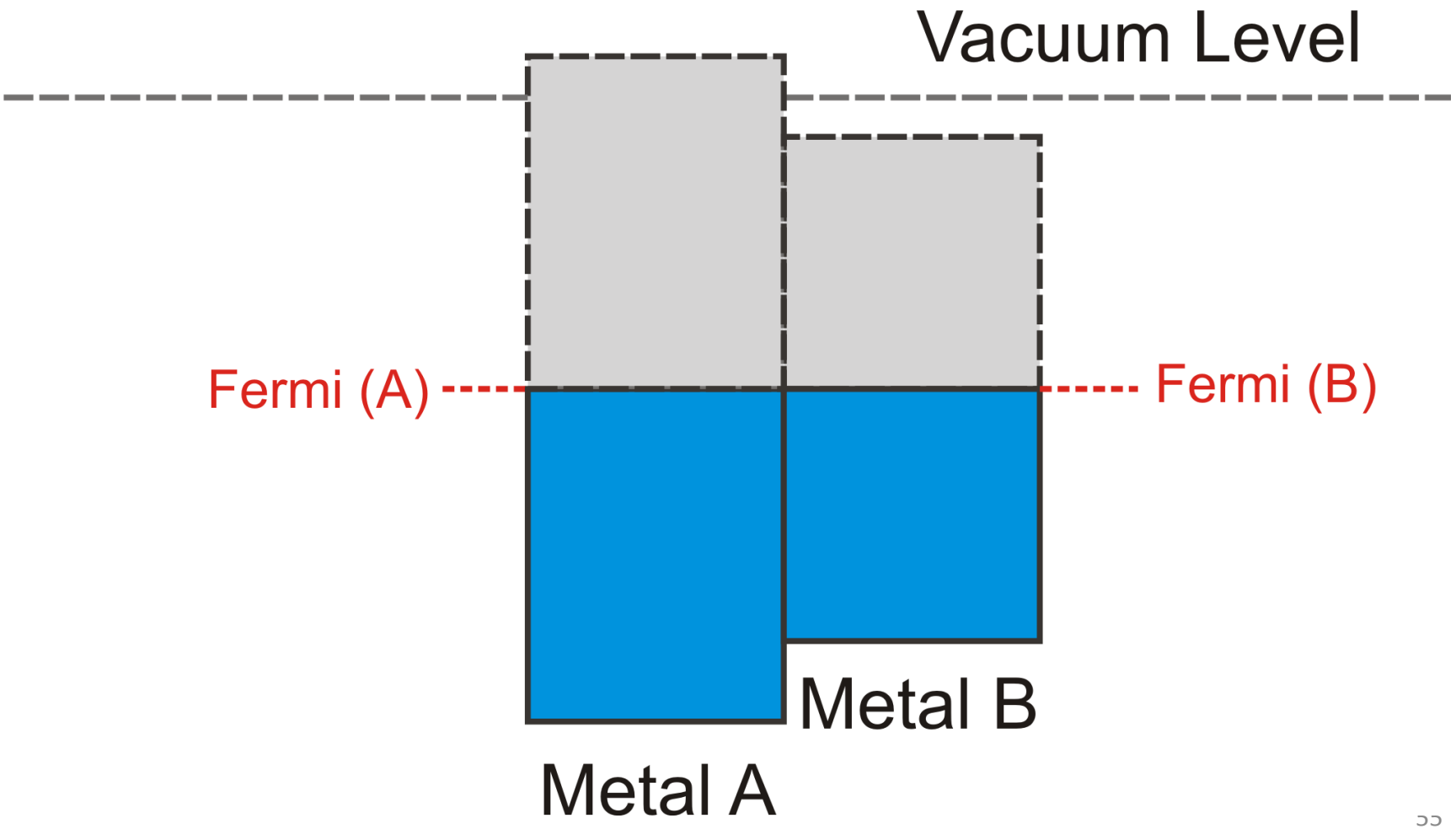
Two metals with different Fermi levels at infinite distance



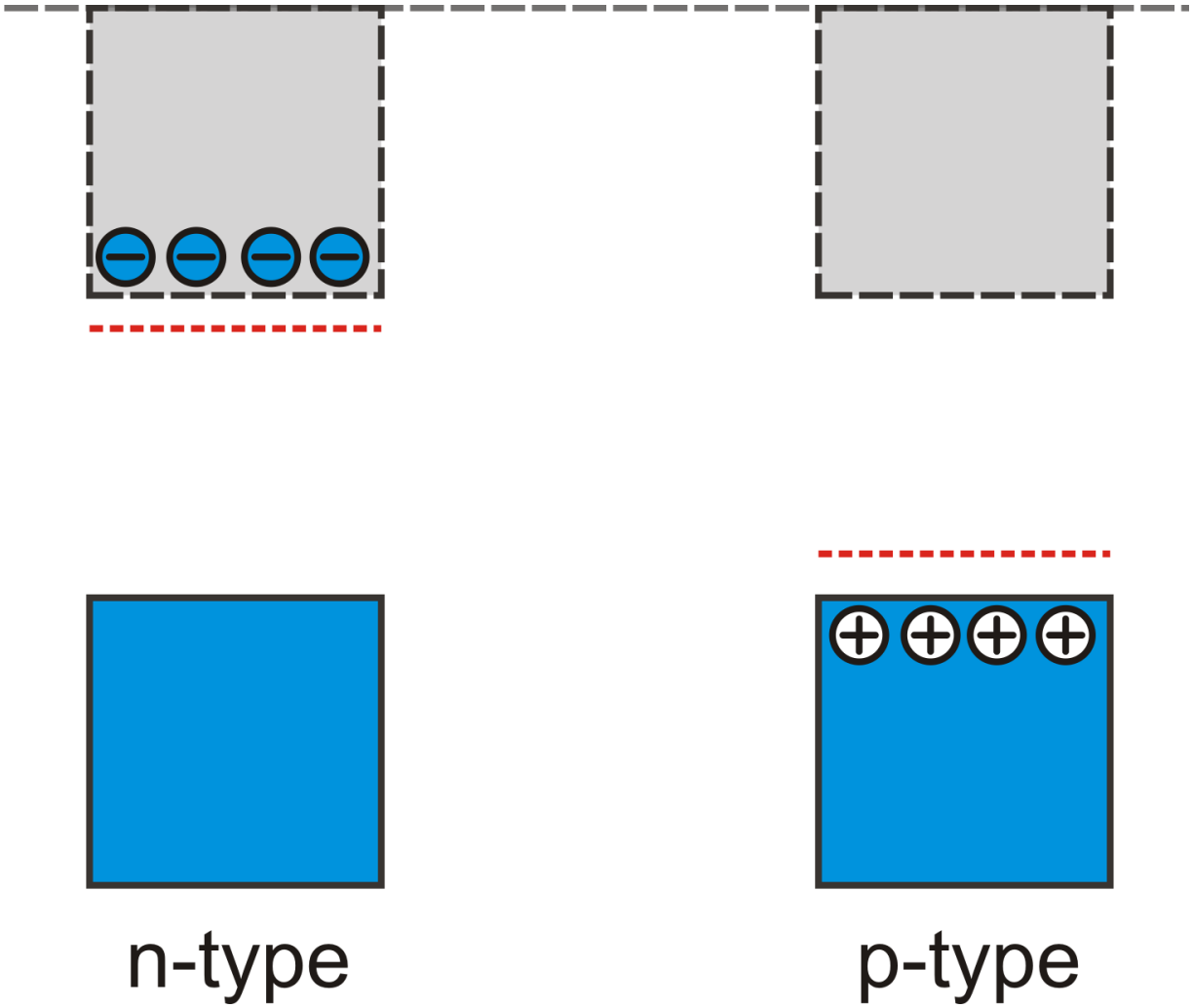
2.2 Equalizing Fermi Levels

Two metals with different Fermi levels in contact

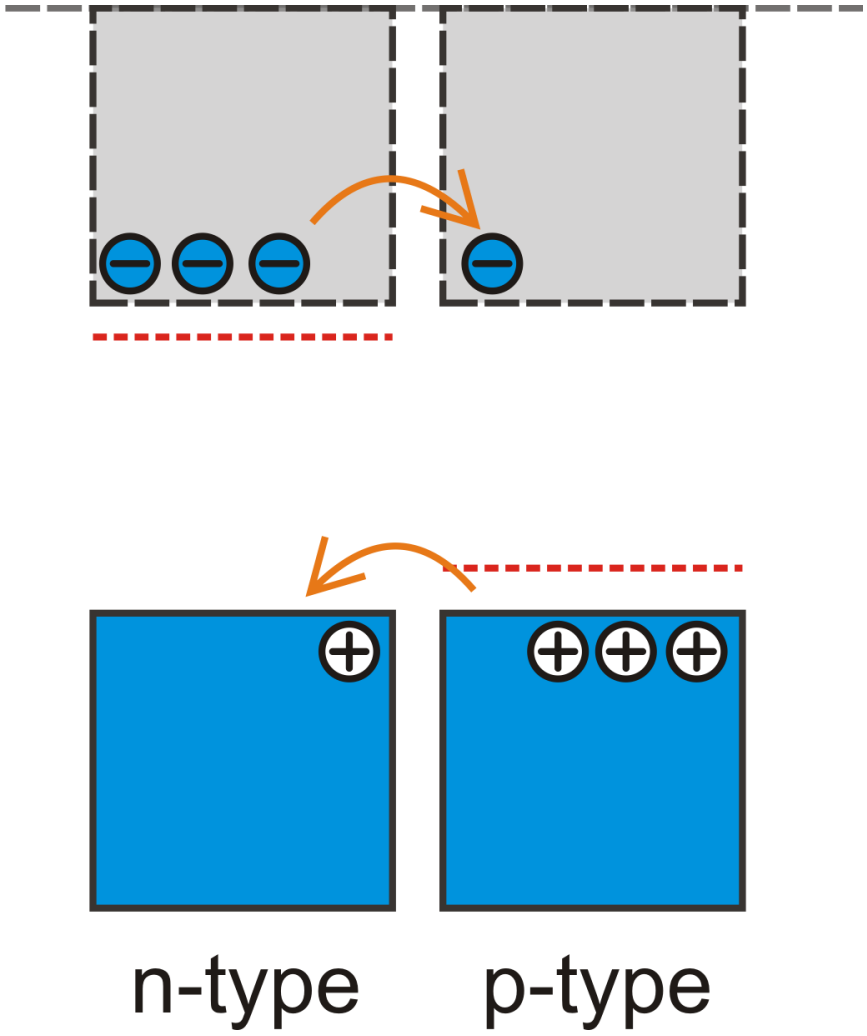
- Fermi levels equilibrate
- Electrons move from low work function to high work function



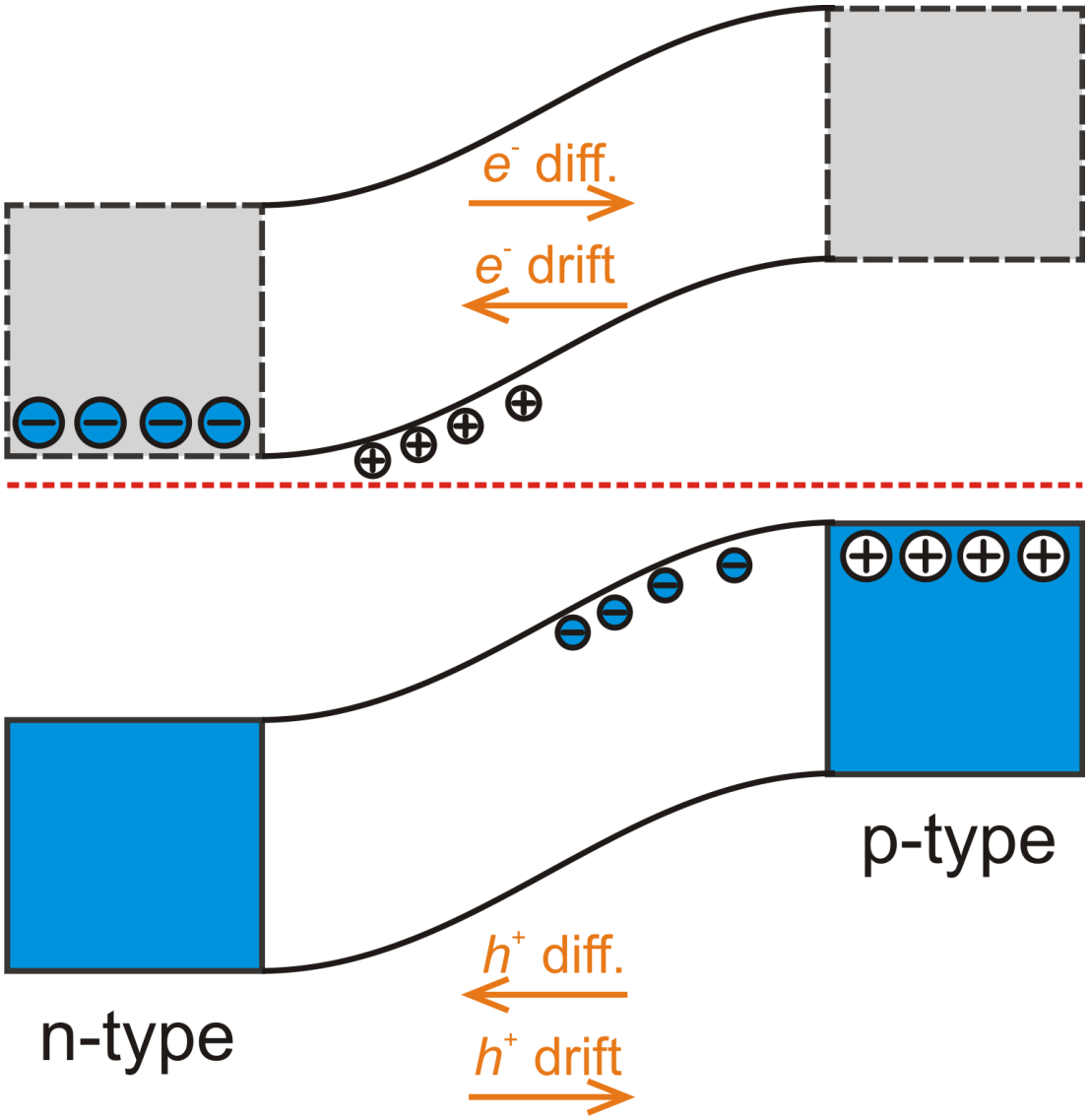
2.3 Band Bending at p-n Junction



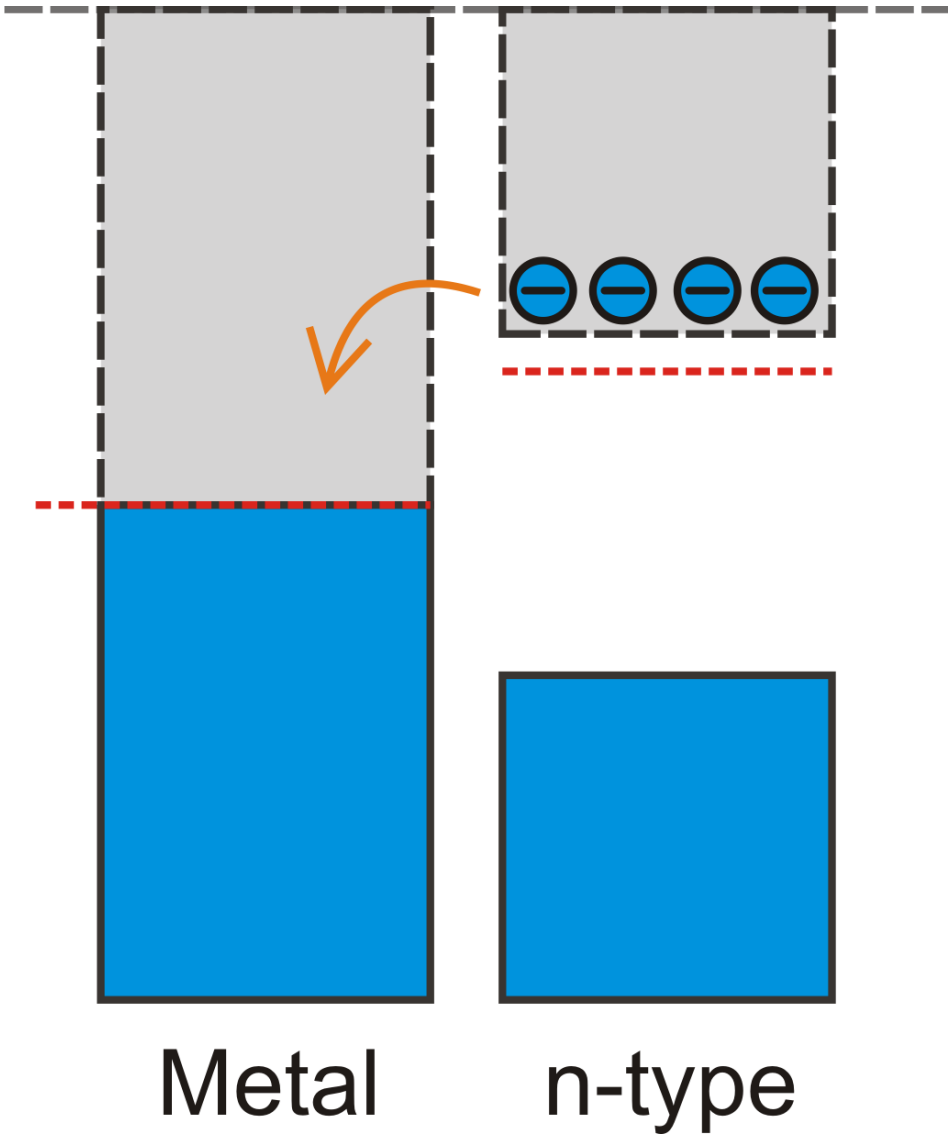
2.3 Band Bending at p-n Junction



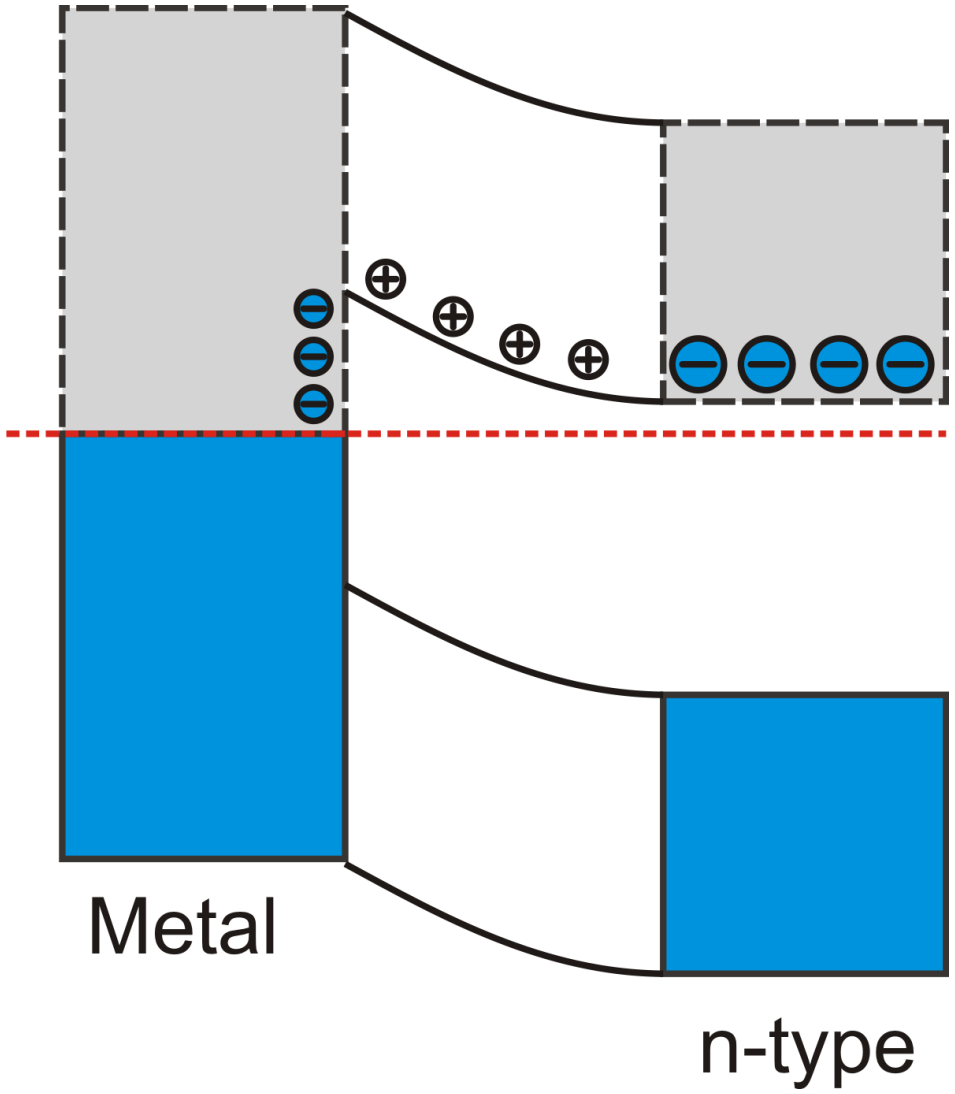
2.3 Band Bending at p-n Junction



2.4 Band Bending at Metal-SC Junction



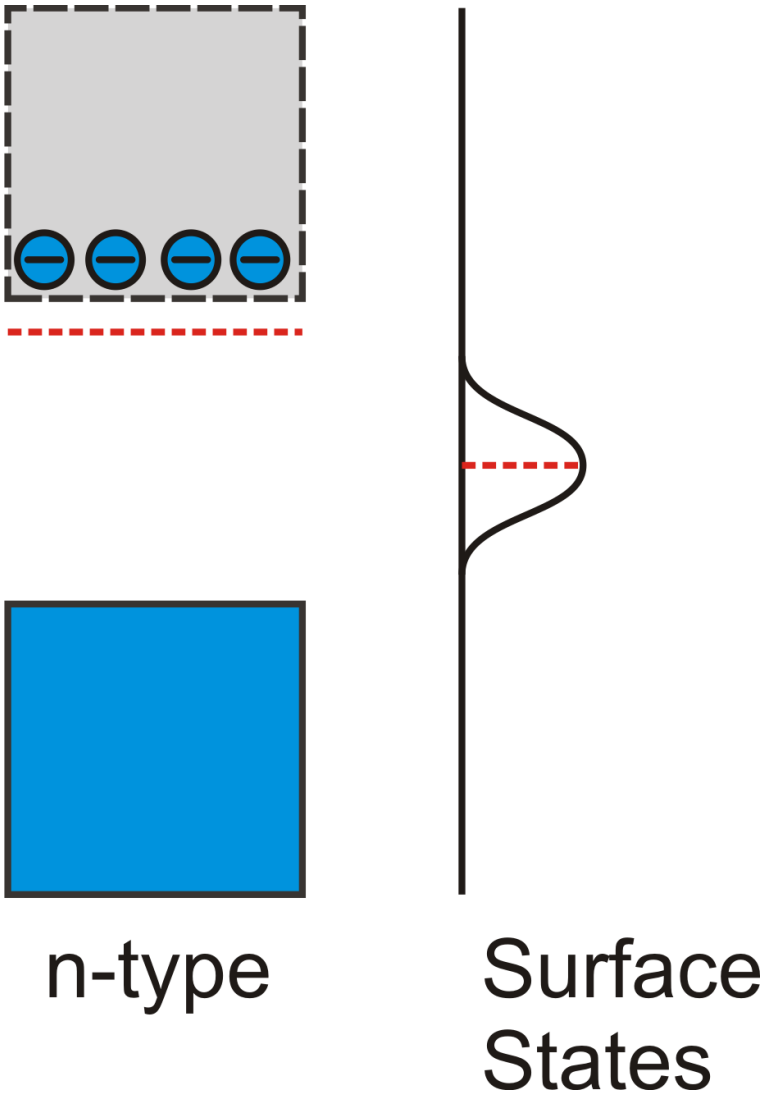
2.4 Band Bending at Metal-SC Junction



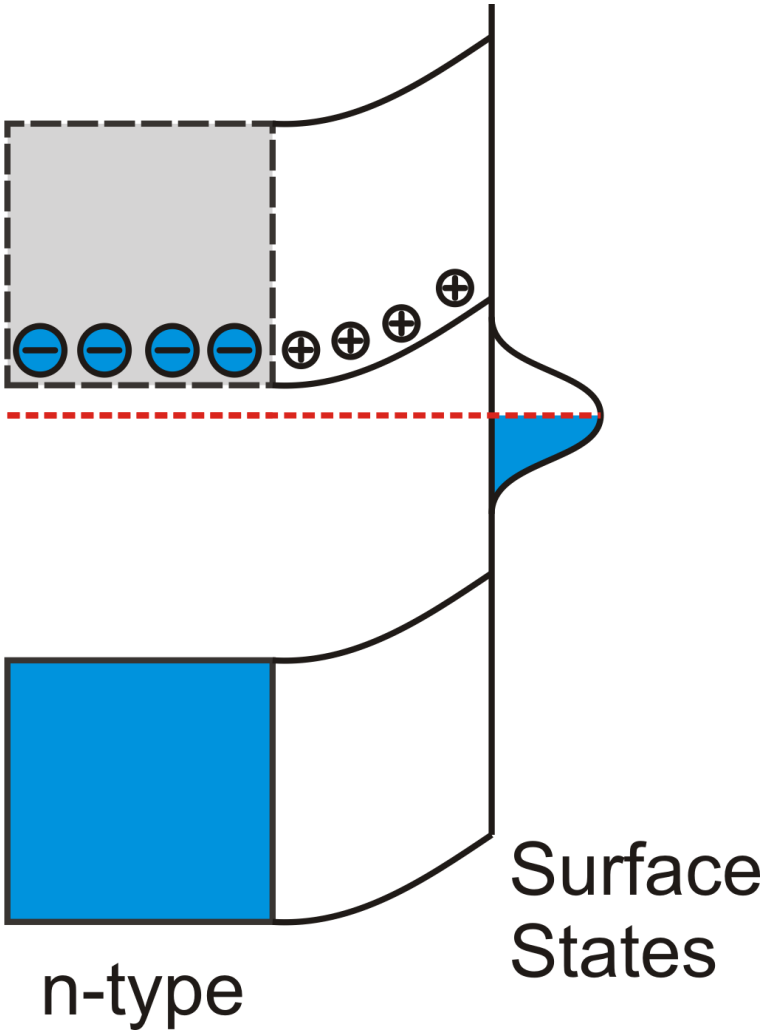
Note:

- Metals have carrier densities of ~10^{22} cm^{-3}
- Screening lengths of ca. 0.1 nm
- Semi-cond. have carrier densities ~10^{17} cm^{-3}
- Screening lengths of ca. 10 nm

2.5 Band Bending at Surfaces



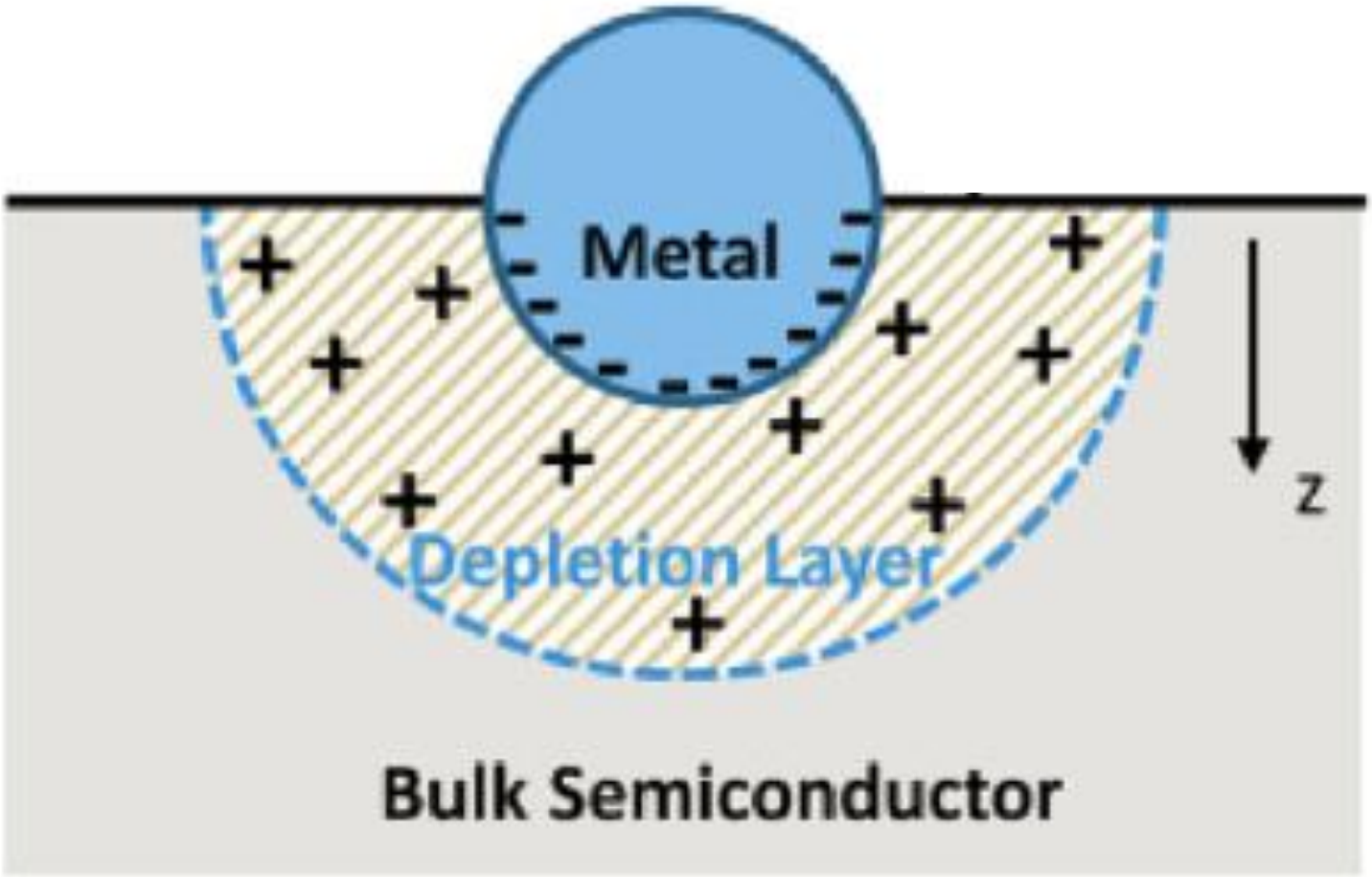
2.5 Band Bending at Surfaces



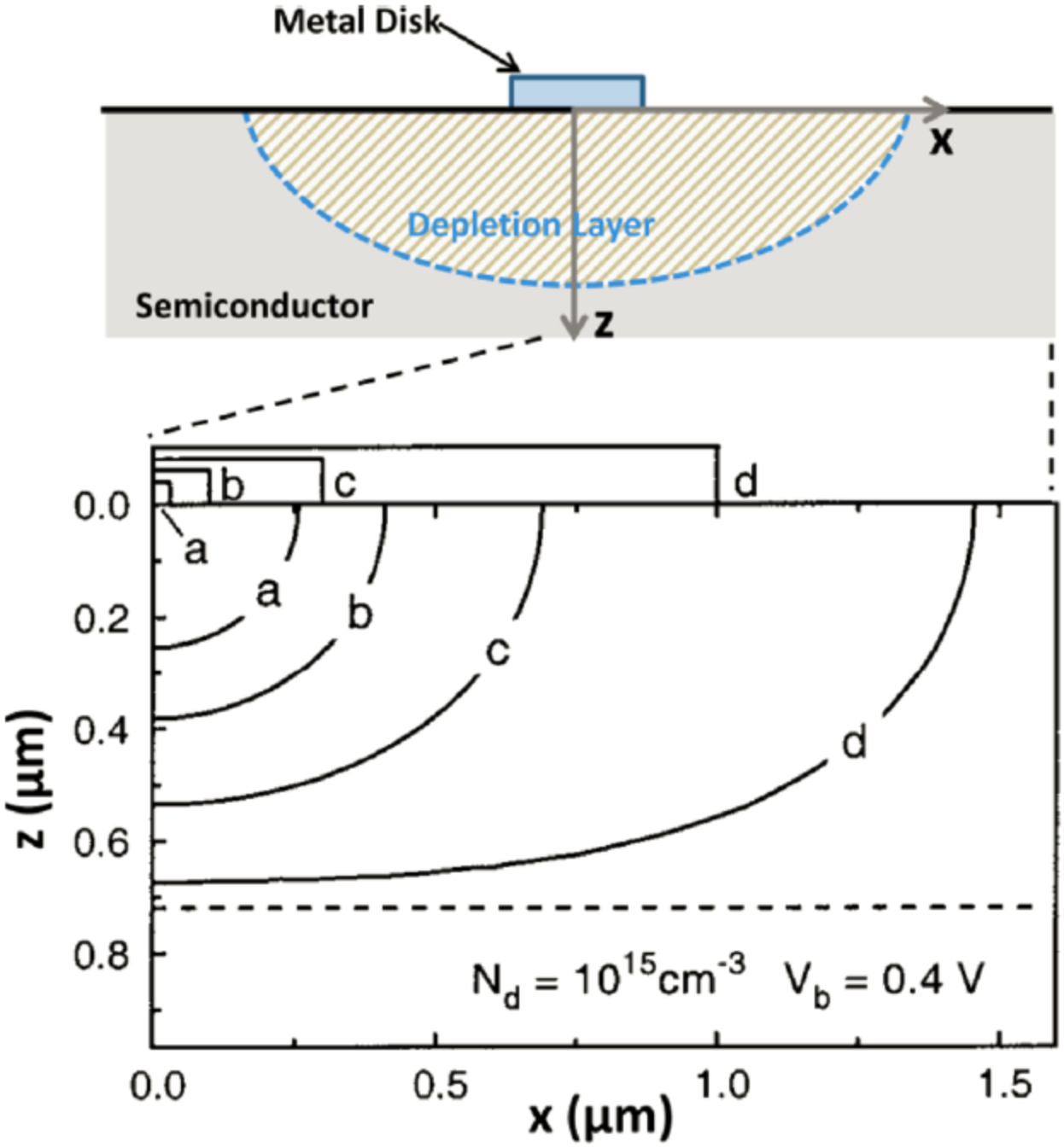
What does all this have to do with catalysis?

- Surfaces can have significantly different energy levels than expected from bulk considerations.
- This will affect interactions and charge transfer with adsorbed molecules.
- Adsorbed molecules can also change the surface band bending.

Influence on Metal-Support Interaction

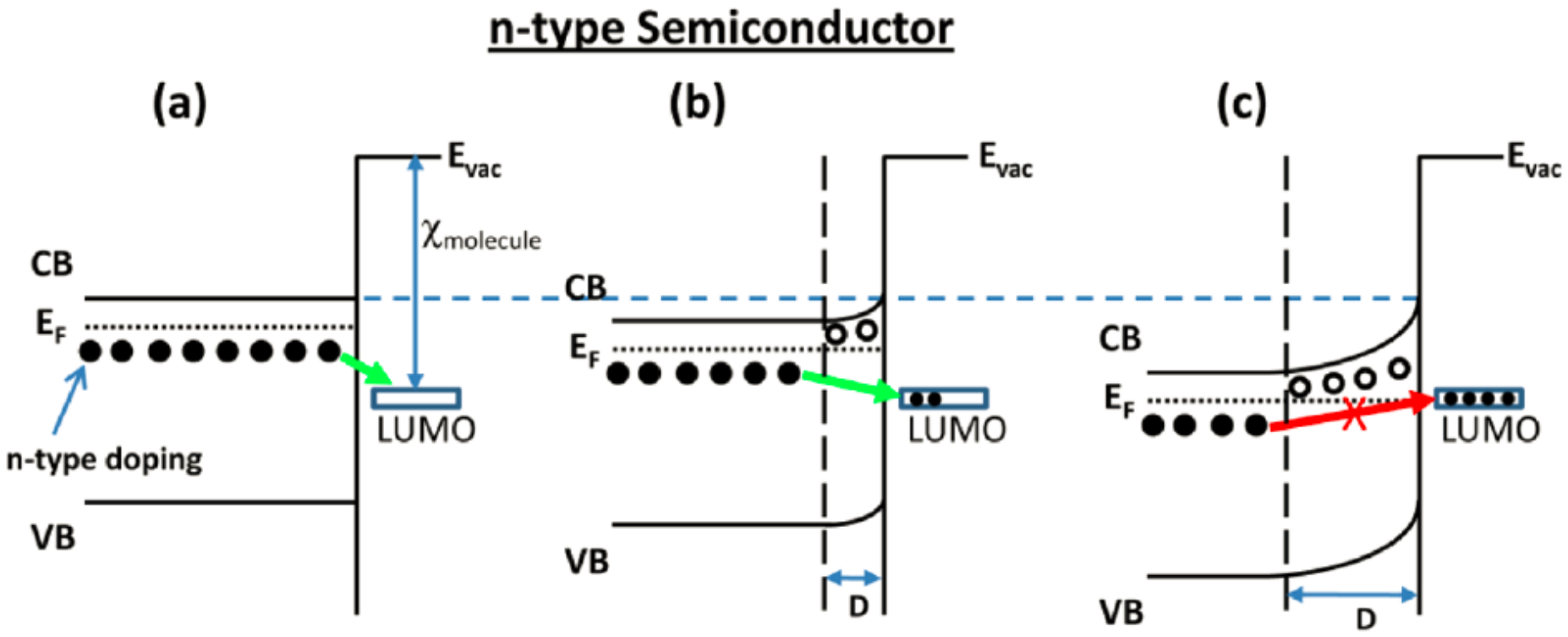


Zhang, Yates, *Chem. Rev*. 2012, 112, 5520−5551



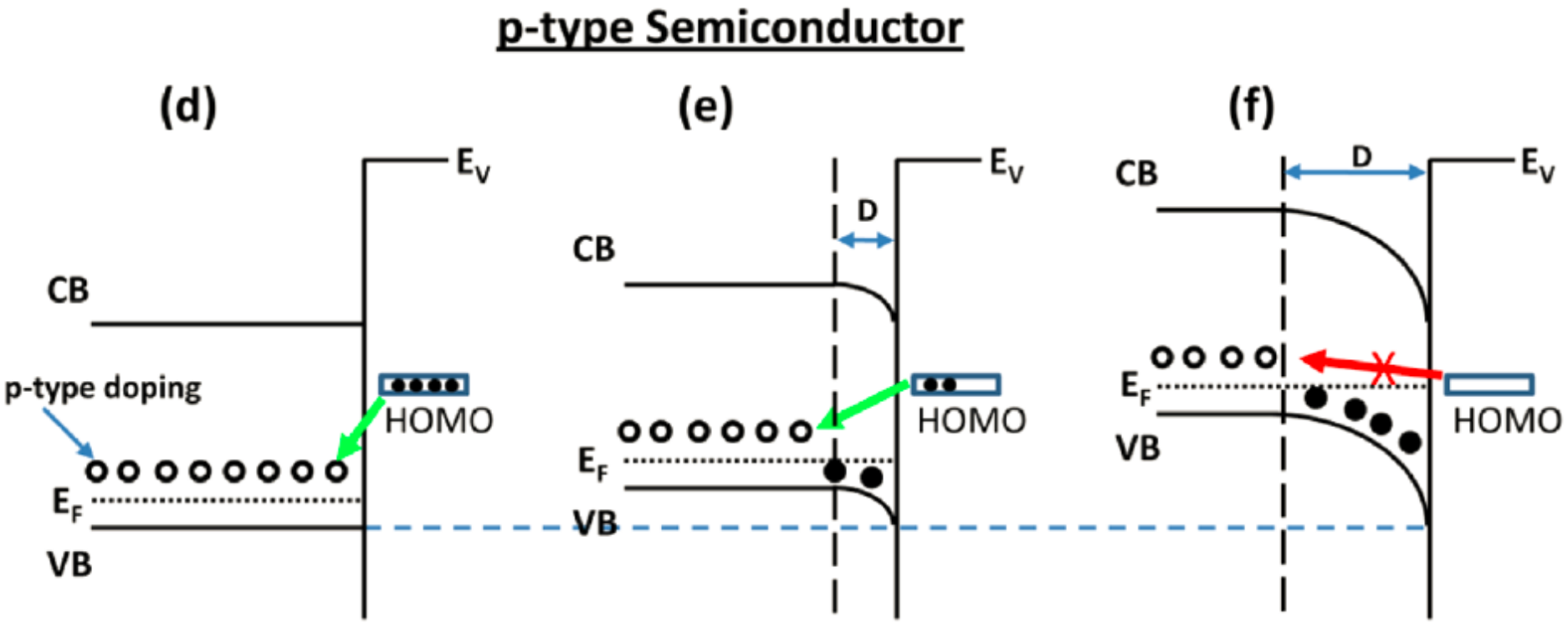
Zhang, Yates, *Chem. Rev*. 2012, 112, 5520−5551

Band Bending and Adsorption



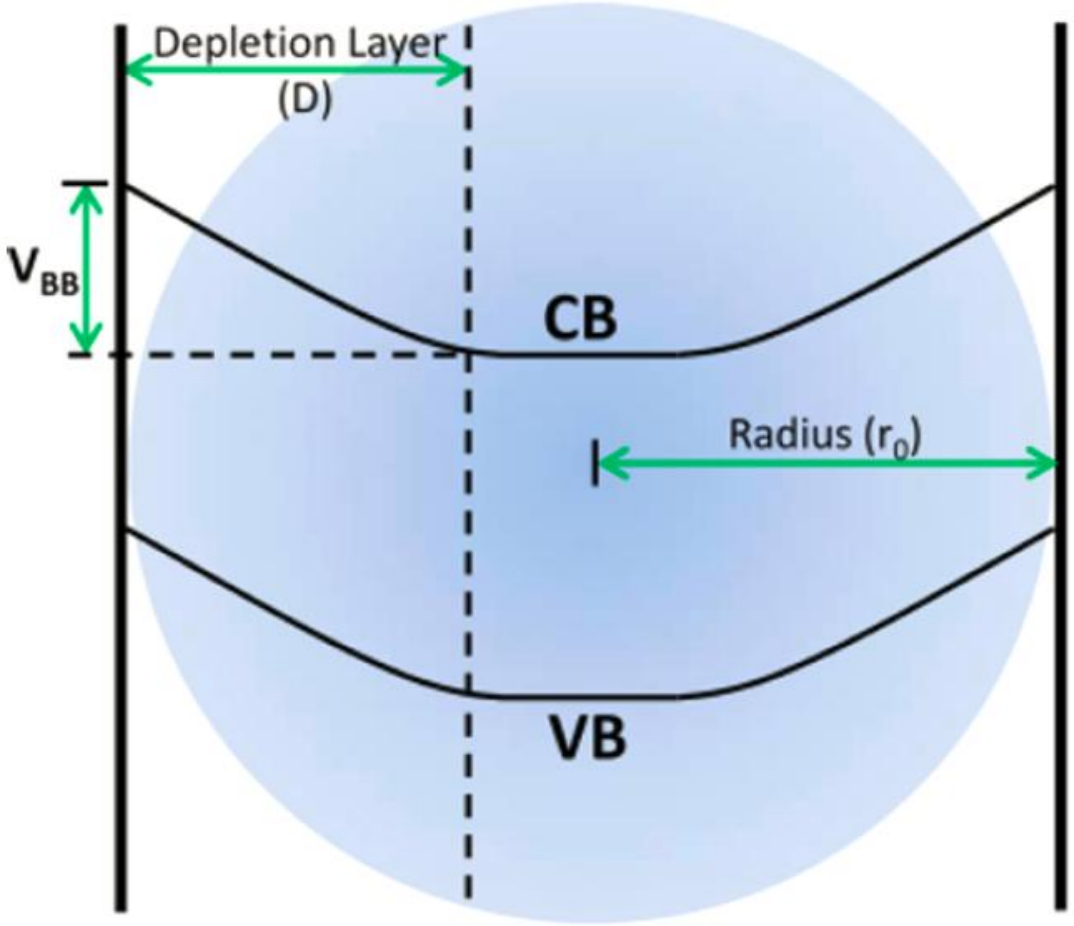
Zhang, Yates, *Chem. Rev*. 2012, 112, 5520−5551

Band Bending and Adsorption

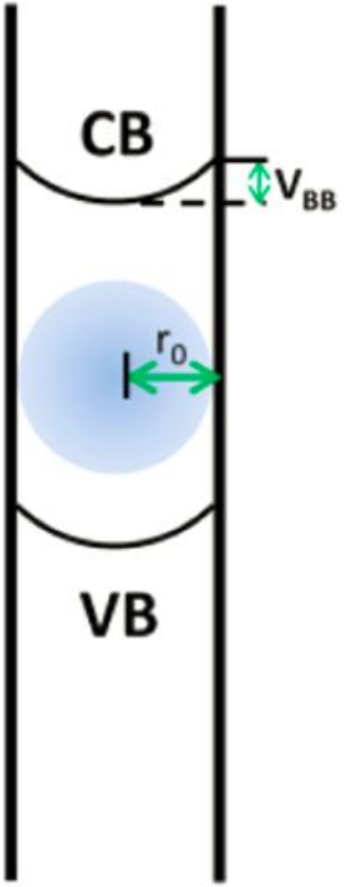


Zhang, Yates, *Chem. Rev*. 2012, 112, 5520−5551

Band Bending and Particle Size

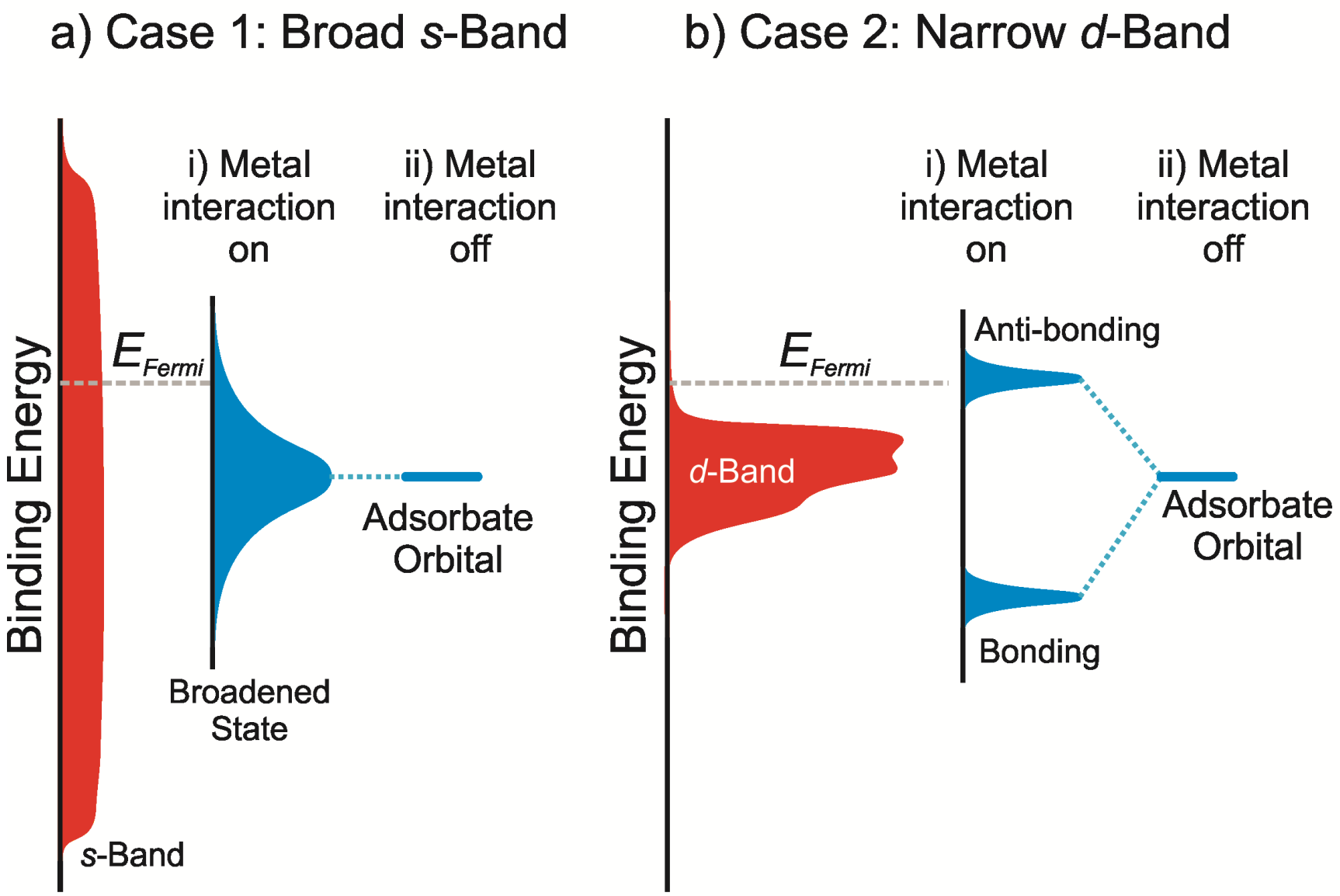


Big Particle



Small Particle

Zhang, Yates, *Chem. Rev*. 2012, 112, 5520−5551


a) Case 1: Broad s-Band
b) Case 2: Narrow d-Band
i) Metal interaction on
ii) Metal interaction off
Binding Energy
E Fermi
Adsorbate Orbital
Broadened State
s-Band
d-Band
Anti-bonding
Bonding

Further Reading

- “Solids and Surfaces: A Chemist’s View of Bonding in Extended Structures” R. Hoffmann
- “Electronic Properties of Materials” D. Jiles
- “Solid Surfaces, Interfaces and Thin Films” H. Lüth
- “Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces” Zhang, Yates: *Chem. Reviews* (2012)

Any Questions?

Doping with defects