Discover how easy it is to grasp the basics of band theory

Band Theory FOR DUMMIES

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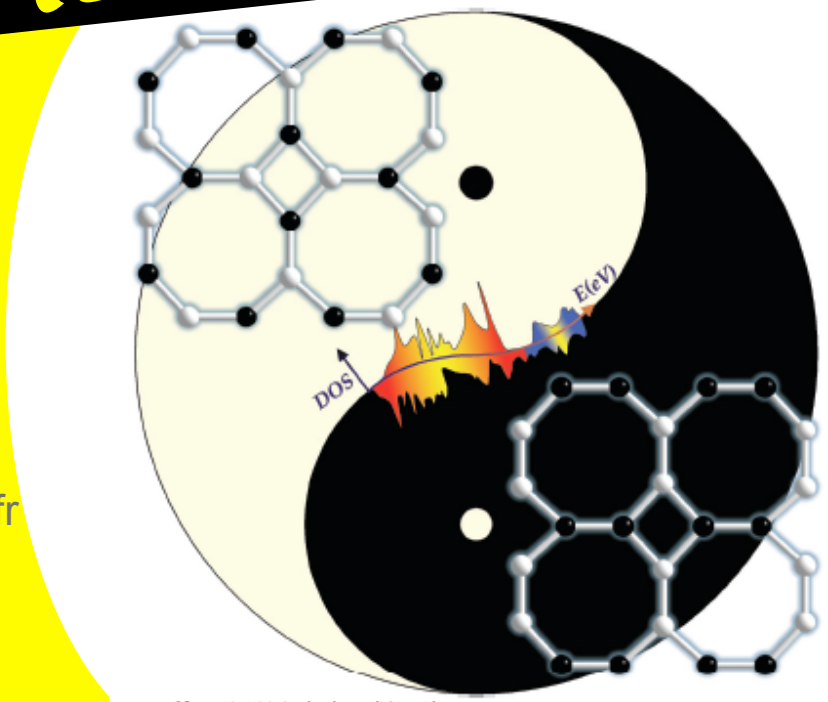


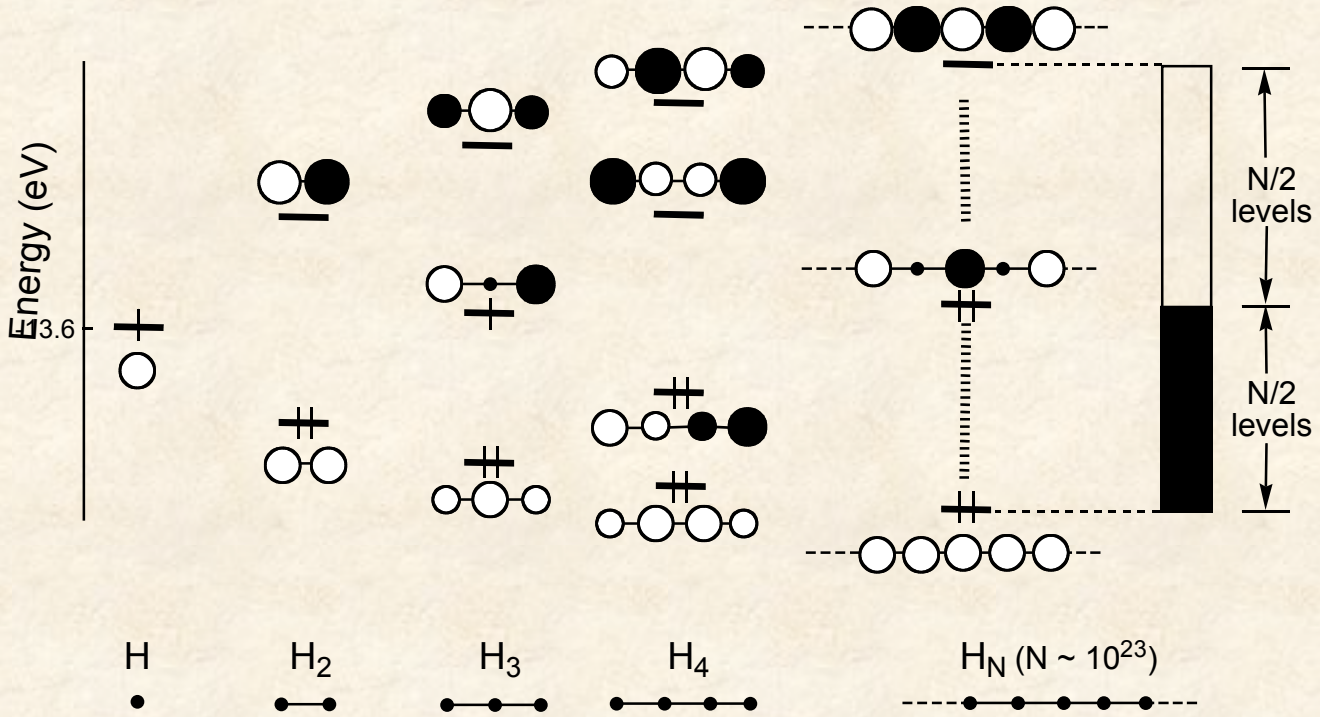
Electronic Structure of Solid Materials: Basic Concepts

Solid materials ≡ Periodic solids

The electronic structure of solids (1D, 2D or 3D)
is usually discussed in terms of band theory

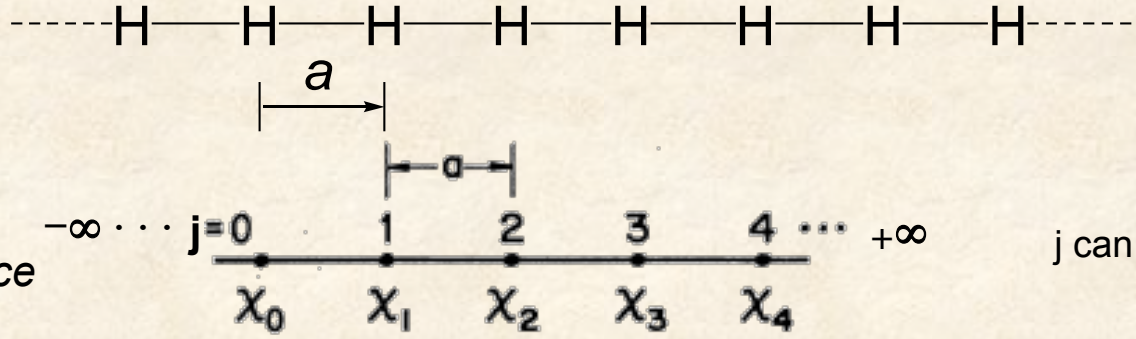
Orbitals and Bands in One Dimension

- The "molecular" approach: Linear H_n oligomers (n = 1, N ~ 10^{23})



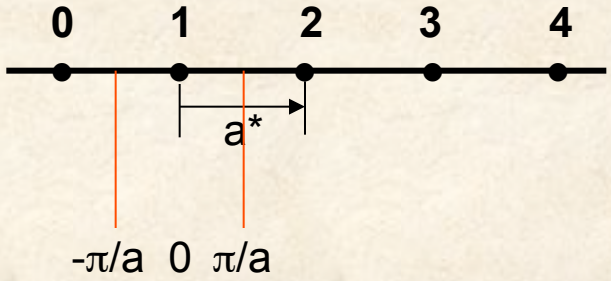
Bloch Functions, Crystal Orbitals and Band Structures

- The "solid state" approach: Infinite chain of equidistant H atoms



direct lattice

j can vary from -∞ to +∞



reciprocal lattice

$|a^*| = 2\pi/a$

Bloch orbital (function): $\phi(k) \; \alpha \; \sum_j [\exp(ikR_j) \; . \; \chi_j(r - R_j)]$

where: k = index (wave vector, vector belonging to the reciprocal lattice)

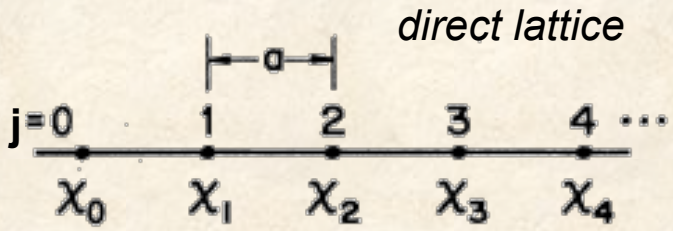
$R_j = ja$ (j, integer varying from -∞ to +∞)

$\chi_j = 1s(H_j)$

Bloch Functions, Crystal Orbitals and Band Structures

$$\phi(k) \propto \sum_j \exp(ikja)\,\chi_j$$

$$\phi(k) \longrightarrow E(k)$$



$E(k) = f(k)$

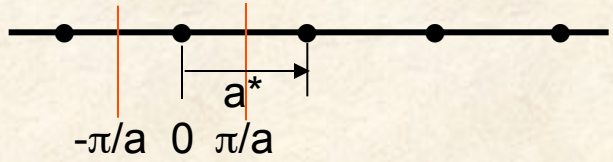
Periodical function in the reciprocal space (period = $2\pi/a$)

$\phi(k)$ and $\phi(-k)$ are degenerate, i.e. $E(k) = f(k)$ *is a centrosymmetrical function*

Thus, the study of the function $E(k) = f(k)$ *can be restricted to* the interval: $0 \leq k \leq \pi/a$

(Irreducible part of the first Brillouin zone)

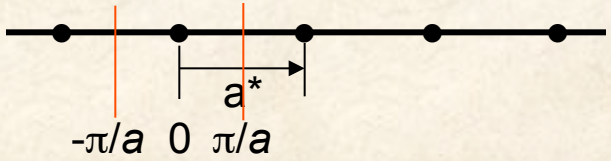
reciprocal lattice



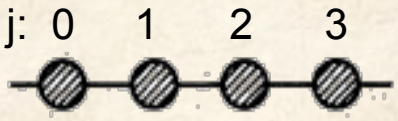
$|a^*| = 2\pi/a$

Bloch Functions, Crystal Orbitals and Band Structures

Bloch orbitals in the first Brillouin zone ($0 \leq k \leq \pi/a$)



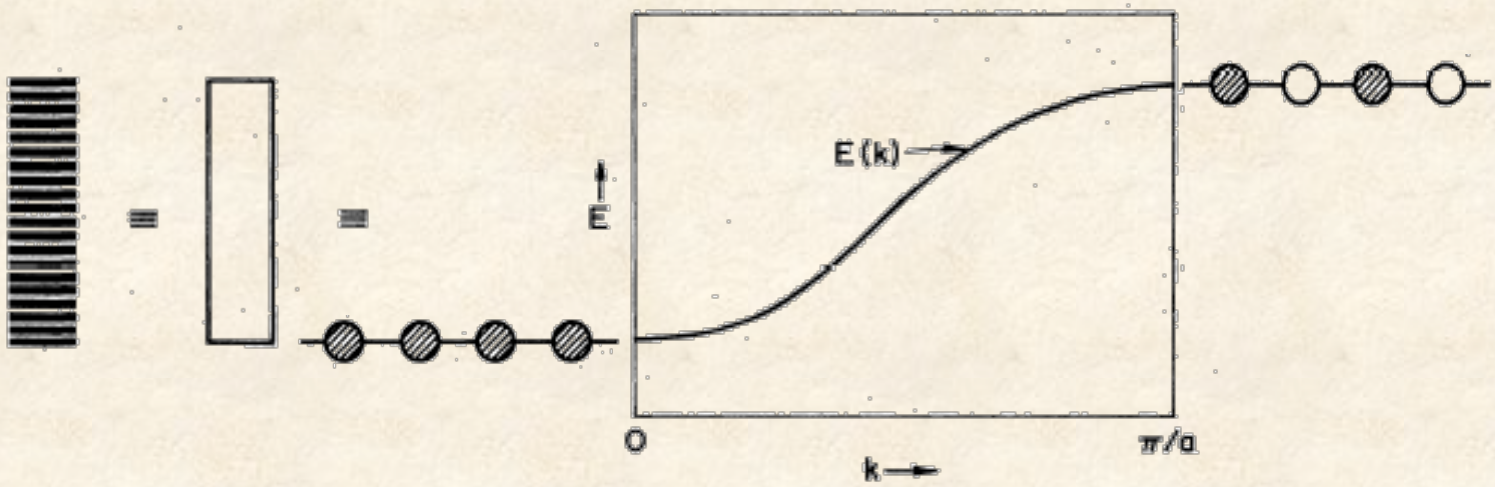
$k = 0$ $\quad \phi(0) \alpha \sum_j \exp(ikja)\, \chi_j = \sum_j \exp(0)\, \chi_j = \sum_j \chi_j = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$



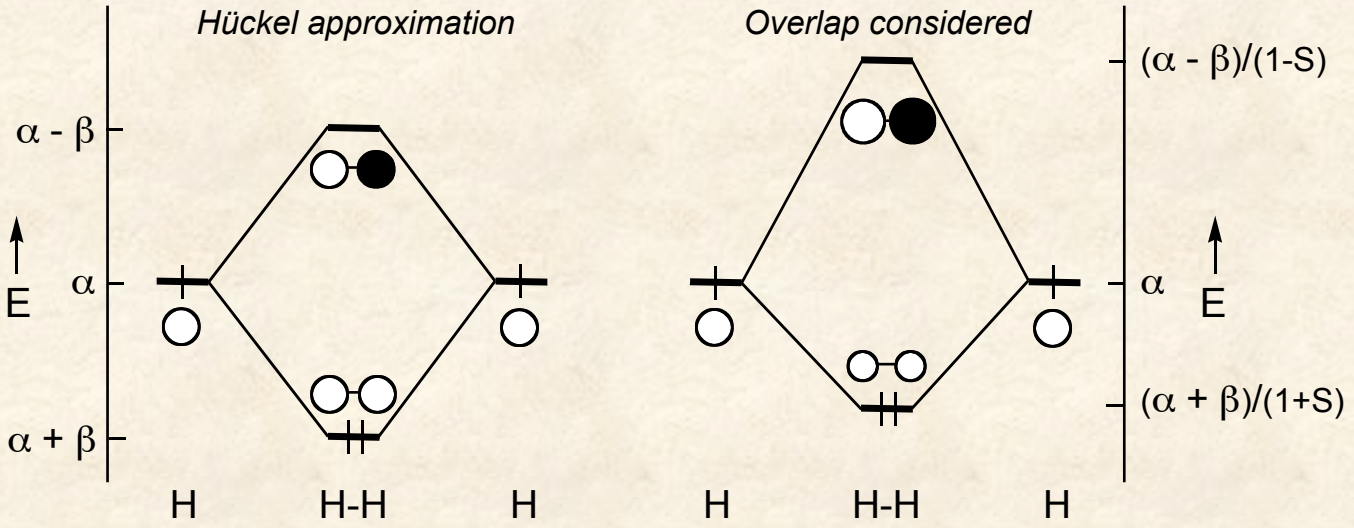
$k = \pi/a$ $\quad \phi(\pi/a) \alpha \sum_j \exp(ikja)\, \chi_j = \sum_j \exp(i\pi j)\, \chi_j = \sum_j (-1)^j \chi_j = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$

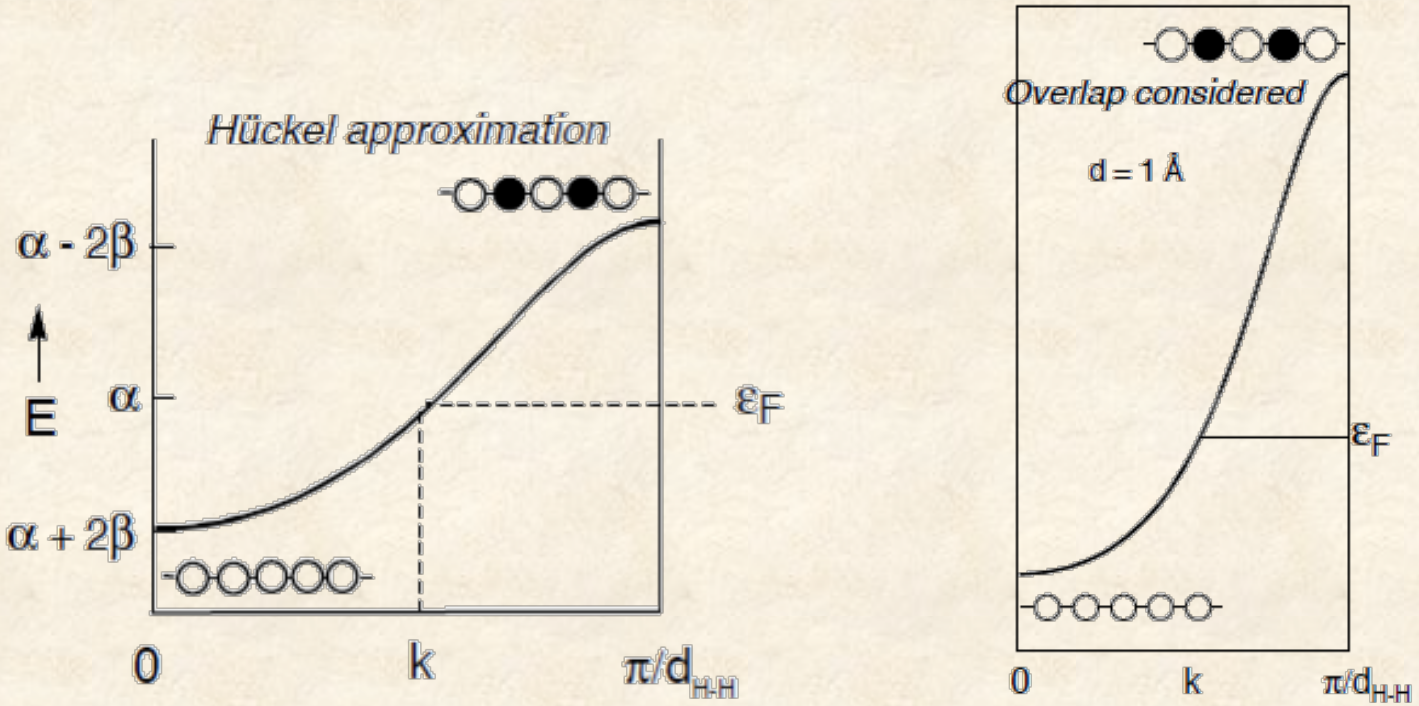
$\phi(k) \longrightarrow E(k)$ and $\phi(-k) \longrightarrow E(k)$

Band structure: $E(k) = f(k)$ for $0 \leq k \leq \pi/a$



Bloch Functions, Crystal Orbitals and Band Structures





Band Width

- Dispersive vs flat bands

  The band width *W* depends on the overlap between neighboring atoms, *i.e.* on the interatomic distance *a*.

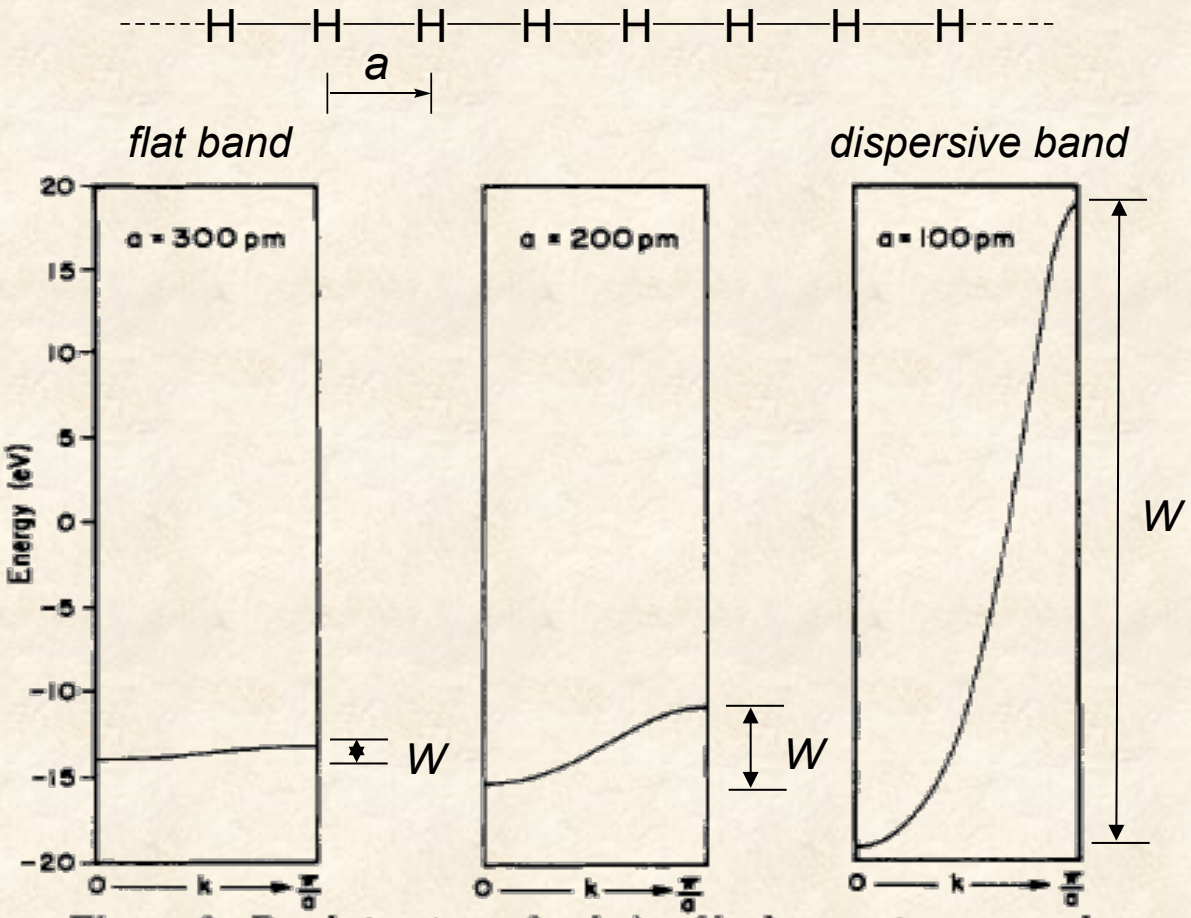
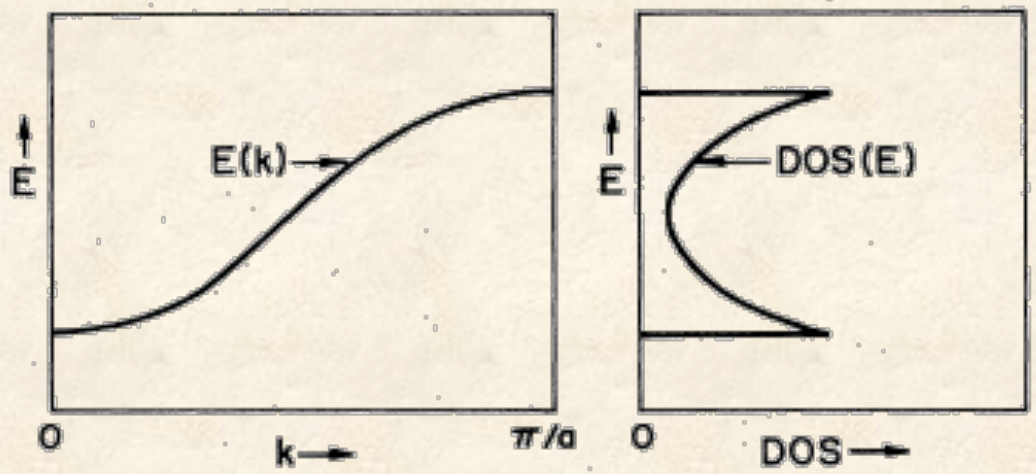


Figure 2. Band structure of a chain of hydrogen atoms spaced 300, 200, and 100 pm apart. The energy of an isolated H atom is −13.6 eV.

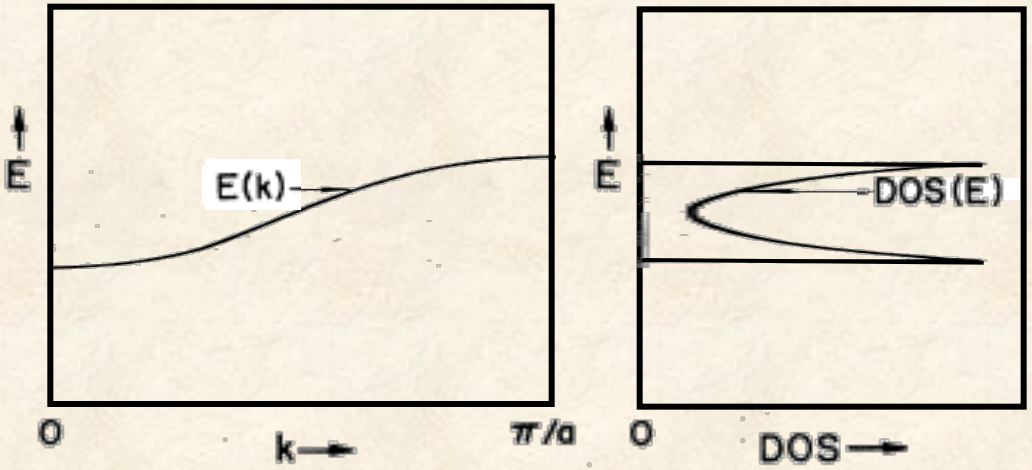
Density of States (DOS)

DOS (E)*dE* = Number of states (levels), *n*, between E and E + *dE*

$a = d_{H\text{-}H}$ short
Dispersive band



$a = d_{H\text{-}H}$ long
Flat band

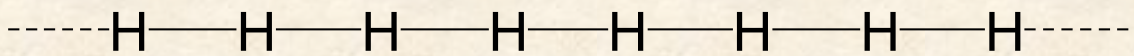


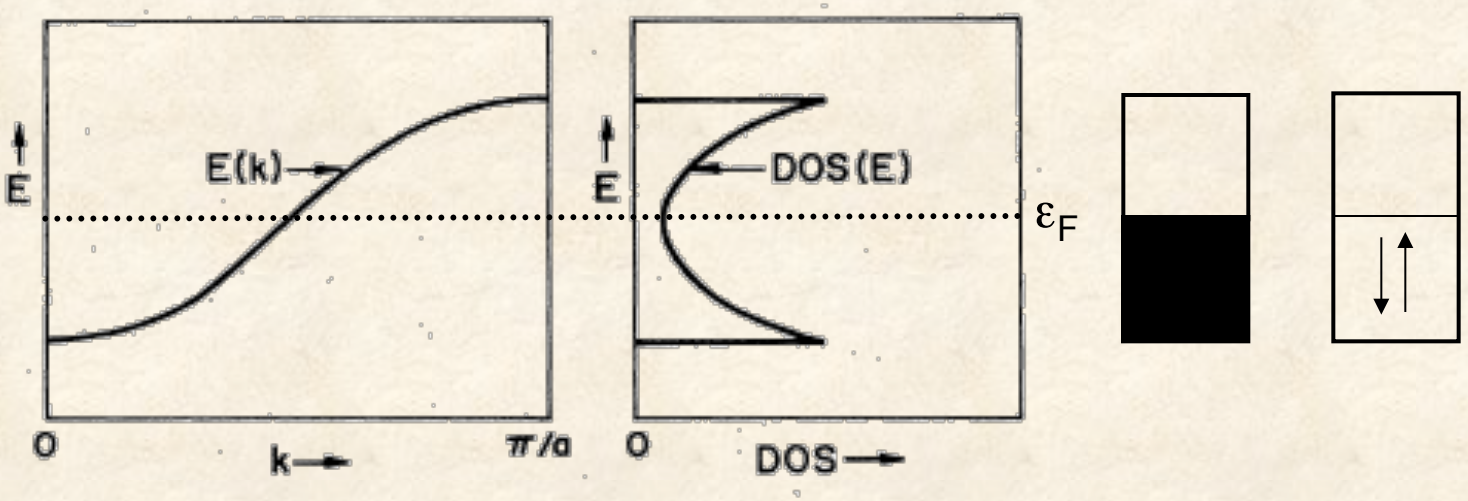
$n\,(E) \propto (\delta E(k)/\delta k)^{-1}$

NB: The area of the surface delimited by the curve DOS(E) = f(E) is constant when a varies

The Fermi Level (ε_F)

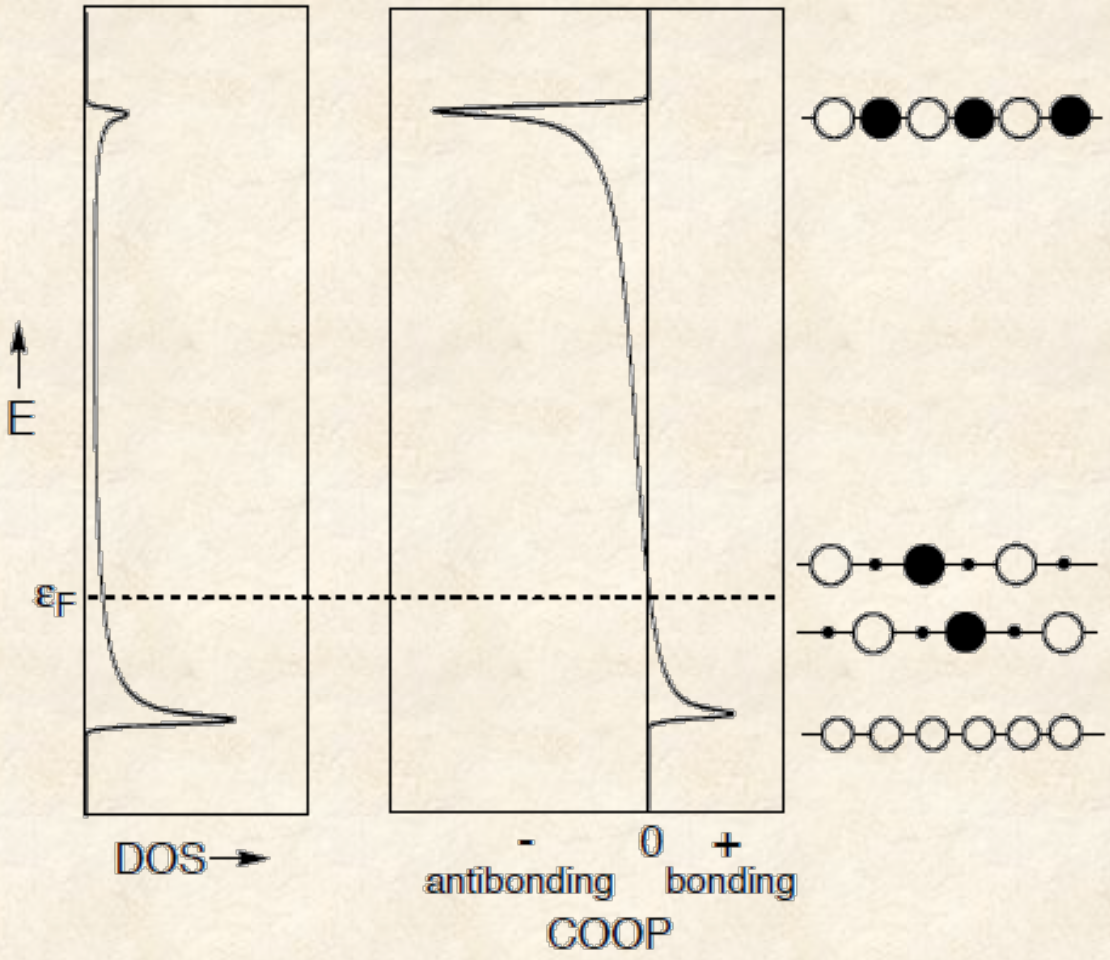
Fermi level (ε_F) (solid) ≡ HOMO (molecule)





The Crystal Orbital Overlap Population (COOP) curve

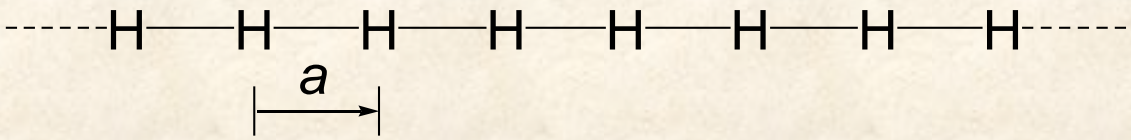
Mulliken overlap population *vs. energy*



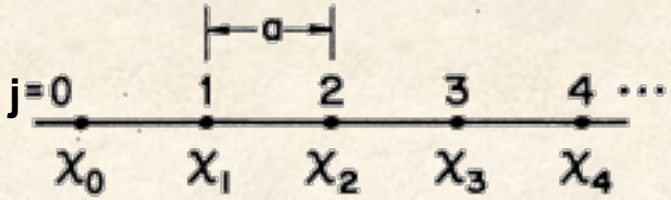
Mulliken overlap population:

$\Psi = c_1\chi_1 + c_2\chi_2$ ED (MO): $1 = {c_1}^2 + {c_2}^2 + 2c_1c_2S_{12}$

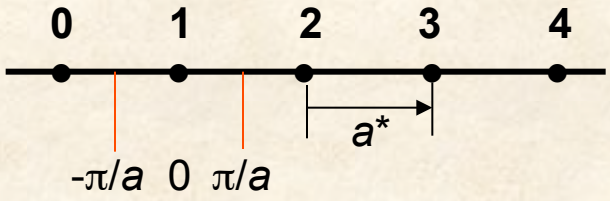
More than One Elementary Unit in the Unit Cell: Folding Bands



$a = d_{H\text{-}H}$

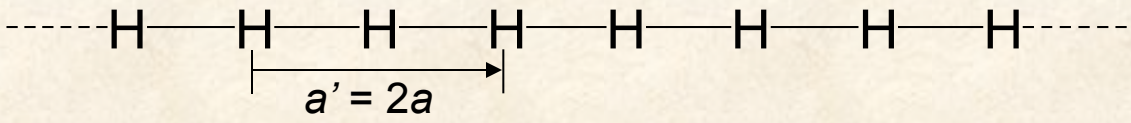


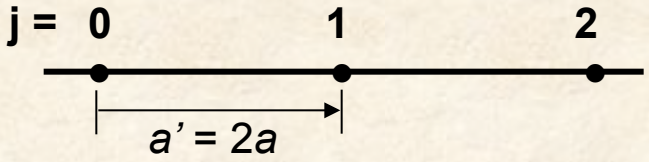
direct lattice



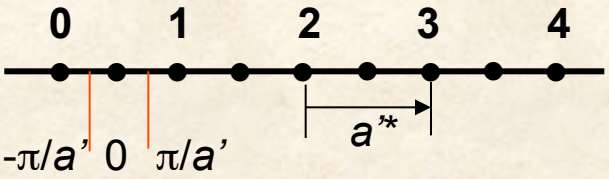
reciprocal lattice

$|a^*| = 2\pi/a$





direct lattice

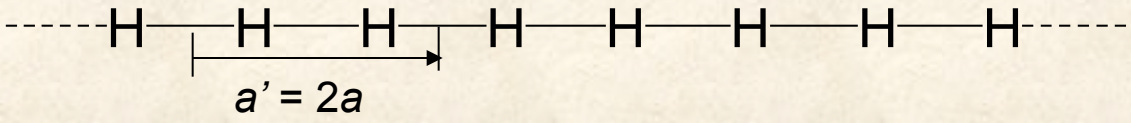


reciprocal lattice

$|a'^*| = 2\pi/a' = \pi/a$

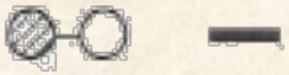
More than One Elementary Unit in the Unit Cell: Folding Bands

$a = d_{H\text{-}H}$



direct lattice

2 H per unit cell, thus 2 χ_j orbitals : χ_j^{σ} and $\chi_j^{\sigma*}$



$\chi^{\sigma*}$ (vacant)

χ^{σ} (occupied)

Bloch orbitals in the irreducible part of the first Brillouin zone ($0 \leq k \leq \pi/a'$):

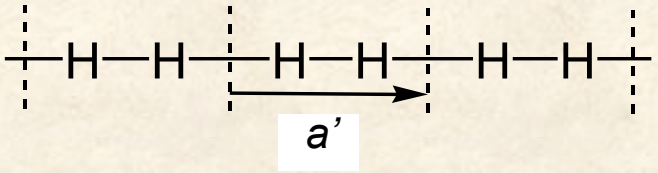
$\phi(k) \alpha \sum_j [\exp(ikR_j) \cdot \chi_j]$, with $R_j = j.a$ *and* $\chi_j = \chi_j^{\sigma}$ or $\chi_j^{\sigma*}$

$k = 0$ $\quad \phi_{\sigma}(0) \alpha \sum_j \exp(0)\, \chi_j^{\sigma}$ and $\phi_{\sigma*}(0) \alpha \sum_j \exp(0)\, \chi_j^{\sigma*}$

$k = \pi/a' = \pi/2a$ $\quad \phi_{\sigma}(\pi/a') \alpha \sum_j \exp(i\pi j)\, \chi_j^{\sigma}$ and $\phi_{\sigma*}(\pi/a') \alpha \sum_j \exp(i\pi j)\, \chi_j^{\sigma*}$

More than One Elementary Unit in the Unit Cell: Folding Bands

$a' = 2d_{H\text{-}H}$

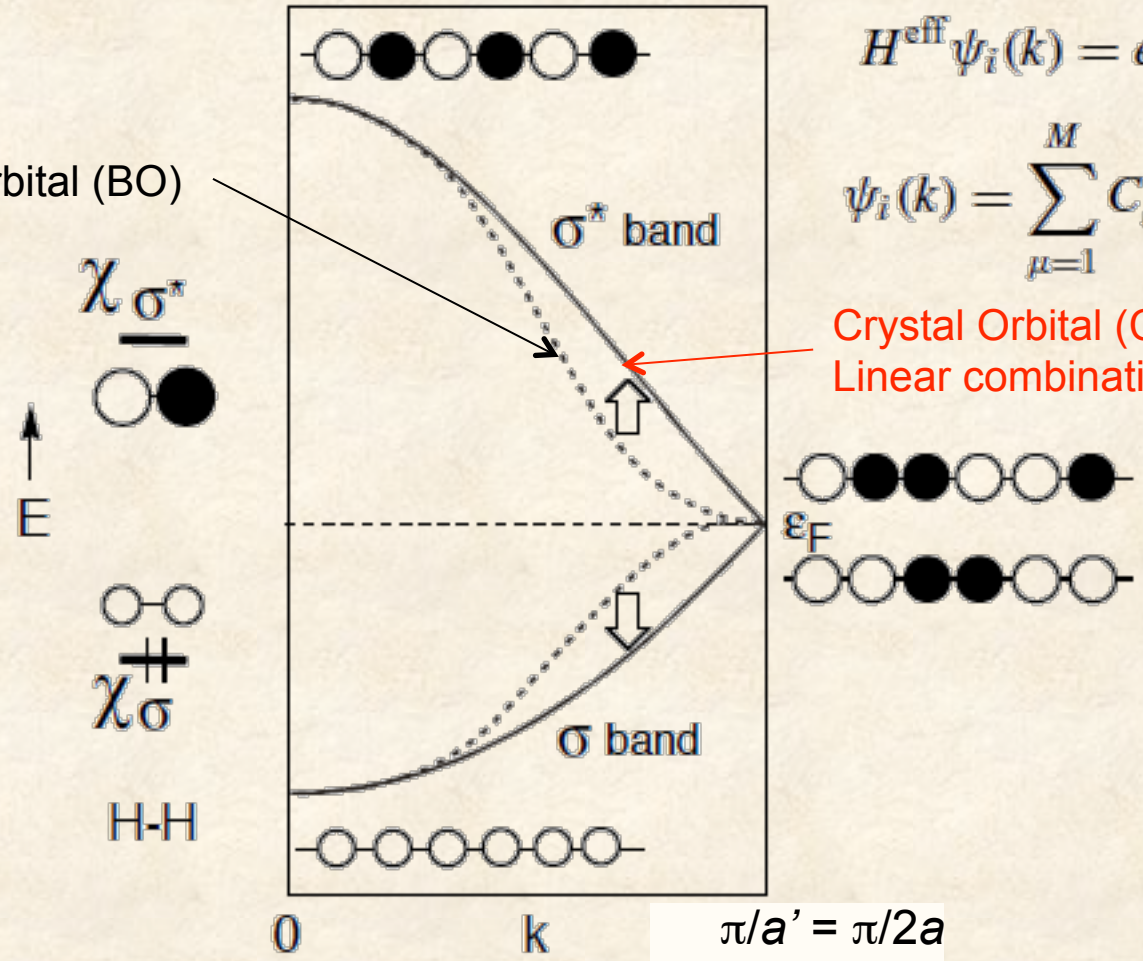


$$H^{\text{eff}}\psi_i(k) = e_i(k)\psi_i(k)$$

$$\psi_i(k) = \sum_{\mu=1}^{M} C_{\mu i}(k)\phi_\mu(k)$$

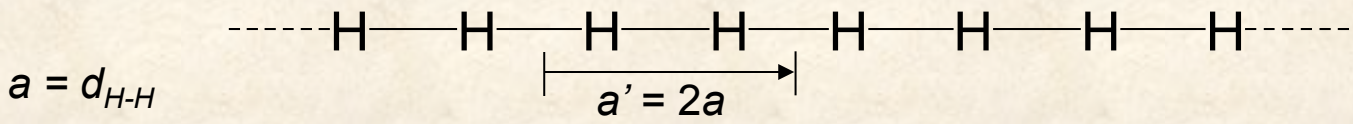
Bloch Orbital (BO)

Crystal Orbital (CO) = Linear combination of BO

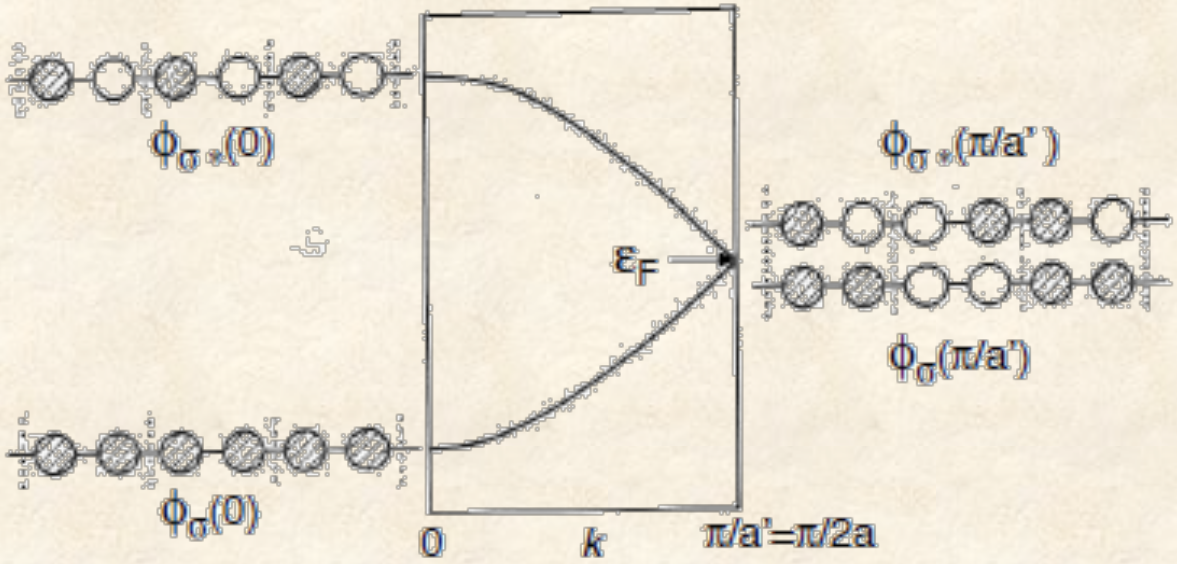


$\pi/a' = \pi/2a$

More than One Elementary Unit in the Unit Cell: Folding Bands

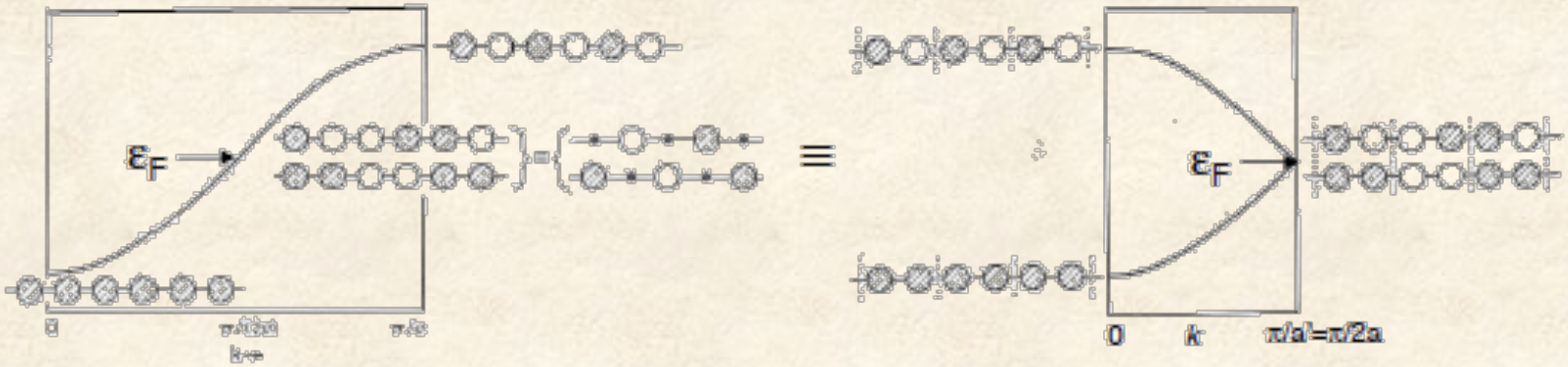


Band structure: E(*k*) = f(*k*)

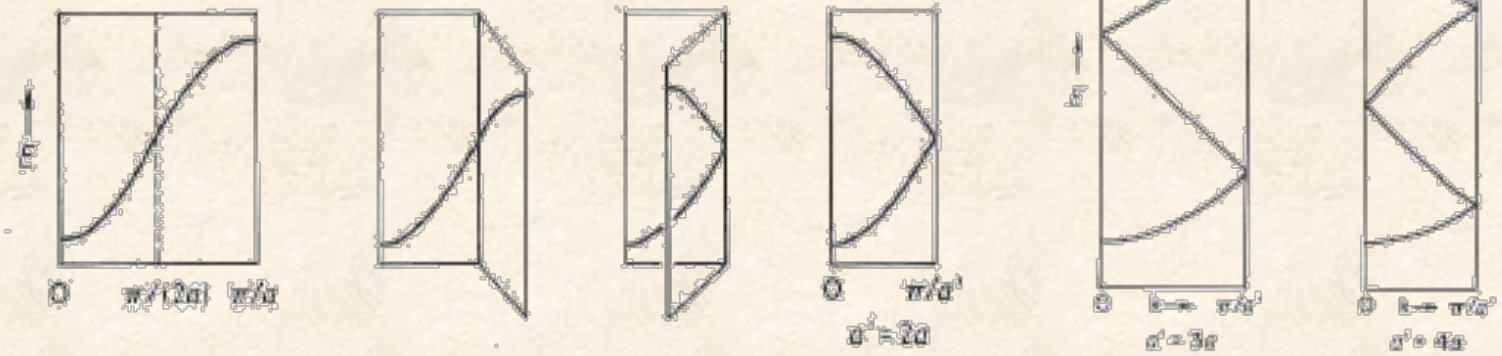


More than One Elementary Unit in the Unit Cell: Folding Bands

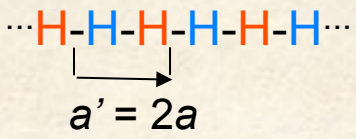
$a = d_{H\text{-}H}$



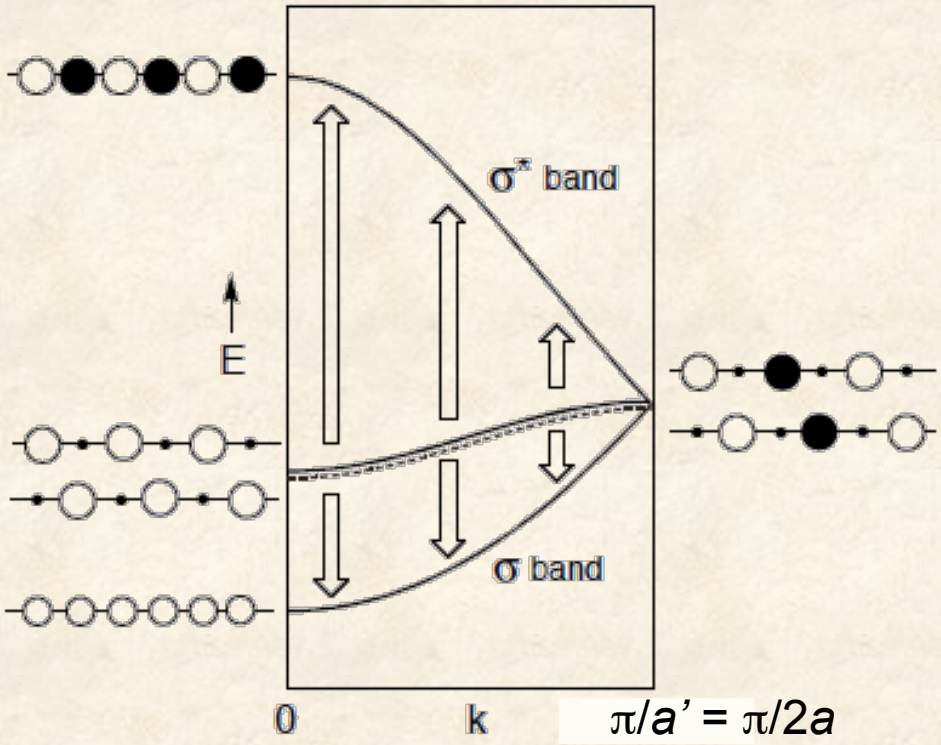
Band folding:



Exercise: Generate the band structure of the double cell ($a' = 2a$) by considering the interaction between two interpenetrating H networks

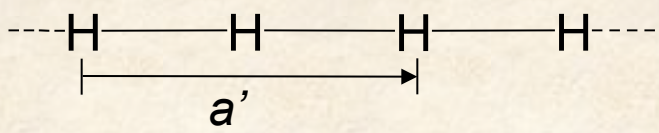


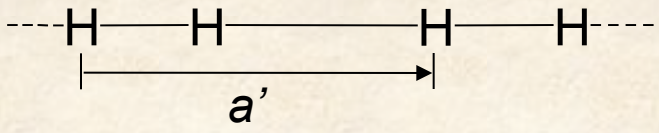
The ···H·····H··· network generates a flat band (very weak overlap between red atoms).
Similarly, the ···H·····H··· network generates a flat band.
Both flat bands interact and repel each other.
They interact strongly at $k = 0$ (S is maximum)
They do no interact by symmetry at $k = \pi/a'$ (S = 0)

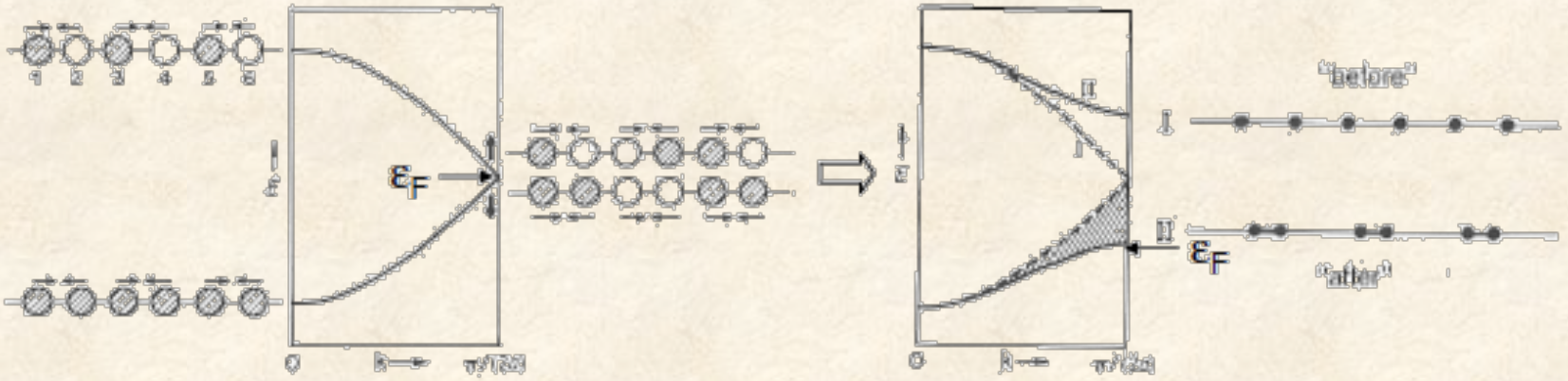


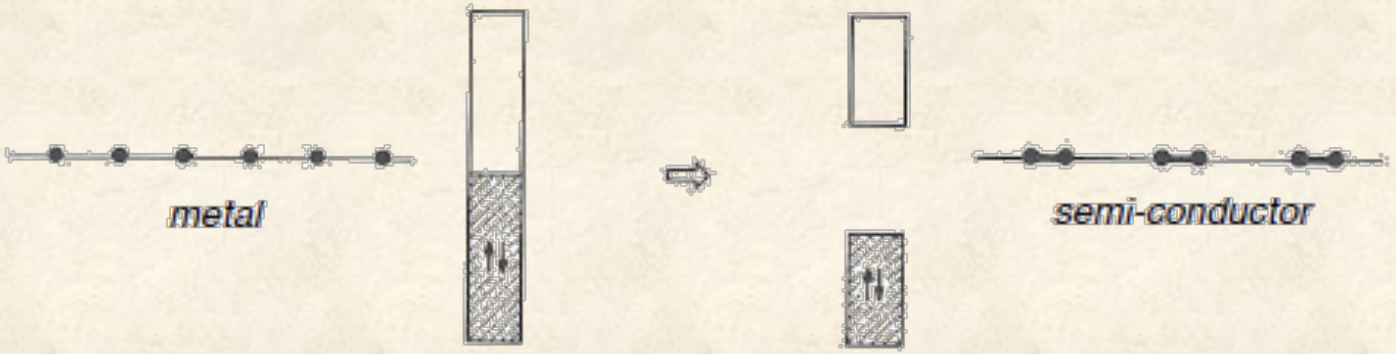
The Peierls Distortion

Peierls distortion (solid) ≡ Jahn-Teller distortion (molecule)



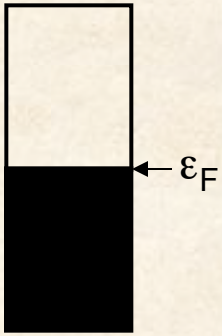




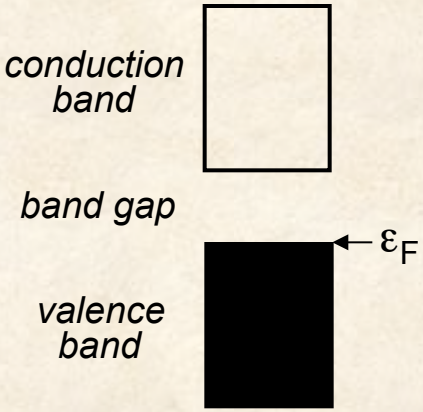


Metal, Semi-conductor or Insulator?

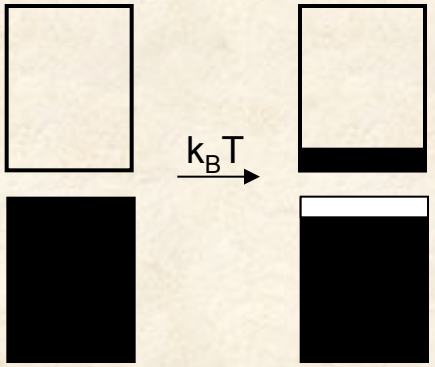
- At the "atomic" level



conductor (metal)

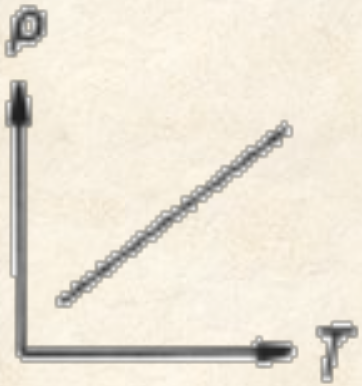


semi-conductor or insulator

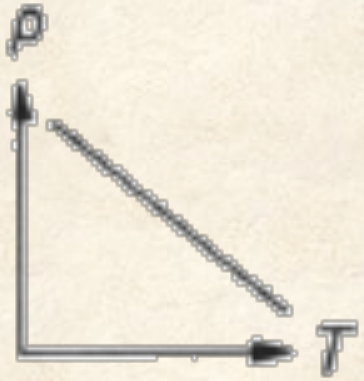


semi-conductor ⟶ metal

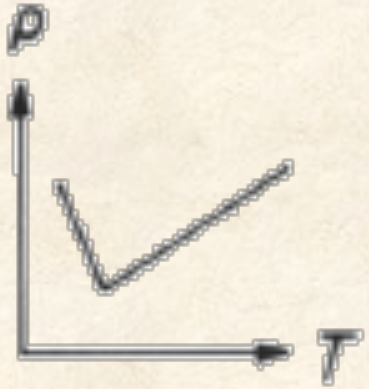
- At the macroscopic level (ρ = resistivity)



conductor (metal)
$\rho \sim 10^{-6}\ \Omega.cm$



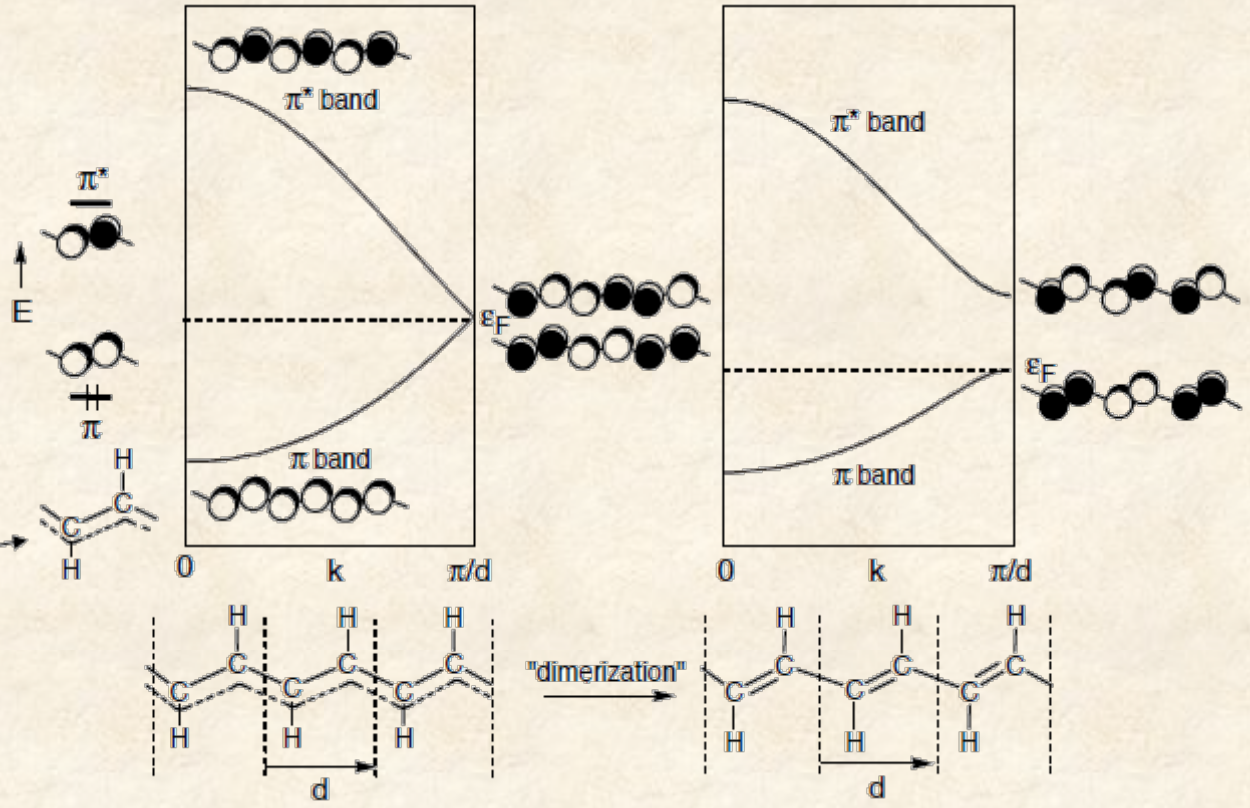
semi-conductor ($\rho \sim 10^{5}\ \Omega.cm$)
or insulator ($\rho \sim 10^{15}\ \Omega.cm$)



semi-conductor ⟶ metal
($\rho \sim 10^{5}\ \Omega.cm$) ($\rho \sim 10^{-3}\ \Omega.cm$)

ρ (resistivity) inversely proportional to DOS n(e) at ε_F

Exercise: Generate the π-type band structure of a regular zigzag polyacetylene chain and show that it is Peierls unstable



The unit cell contains 2 (not 1) carbon atoms

NB. The Peierls distortion is not associated with a doubling of the unit cell, but with the loss of an helicoidal axis.

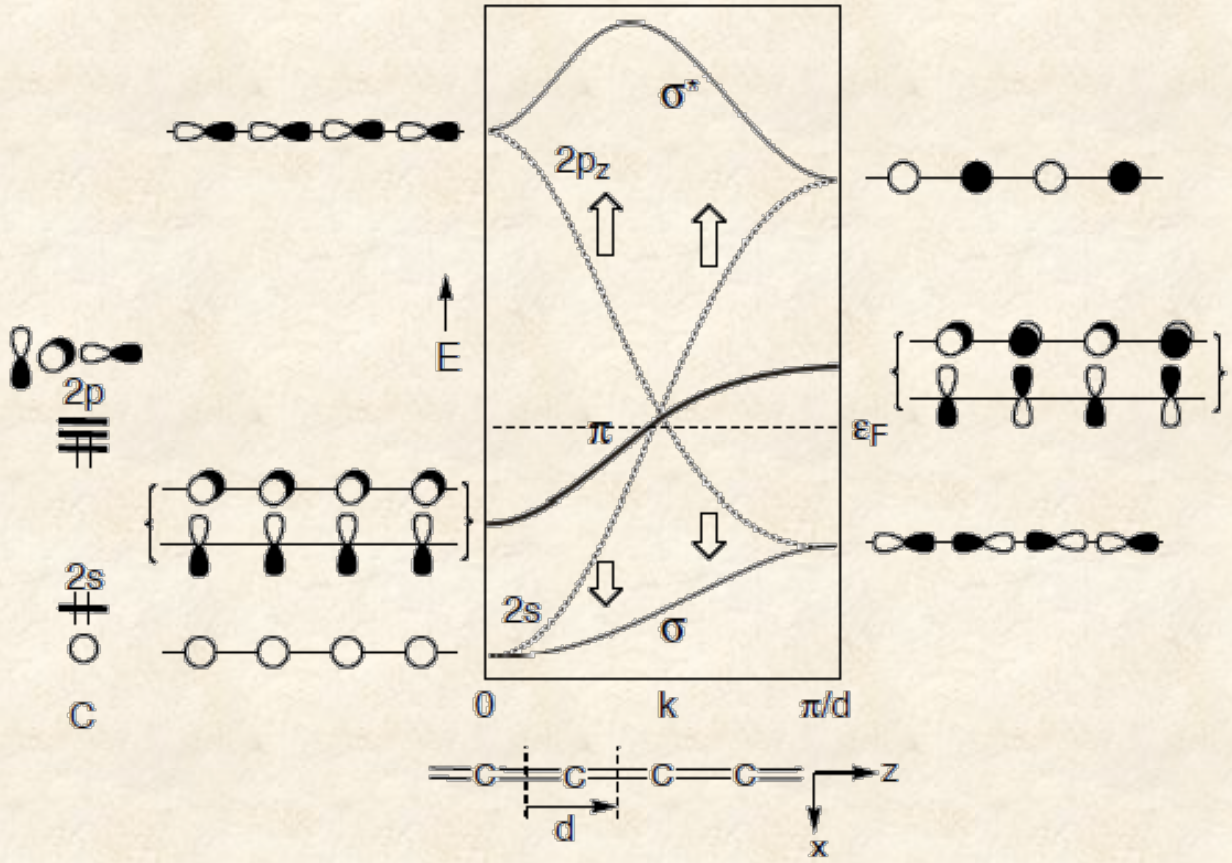
Exercise: Generate the band structure of a chain made of equidistant carbon atoms

$\cdots$=C=C=C=C=C$\cdots$

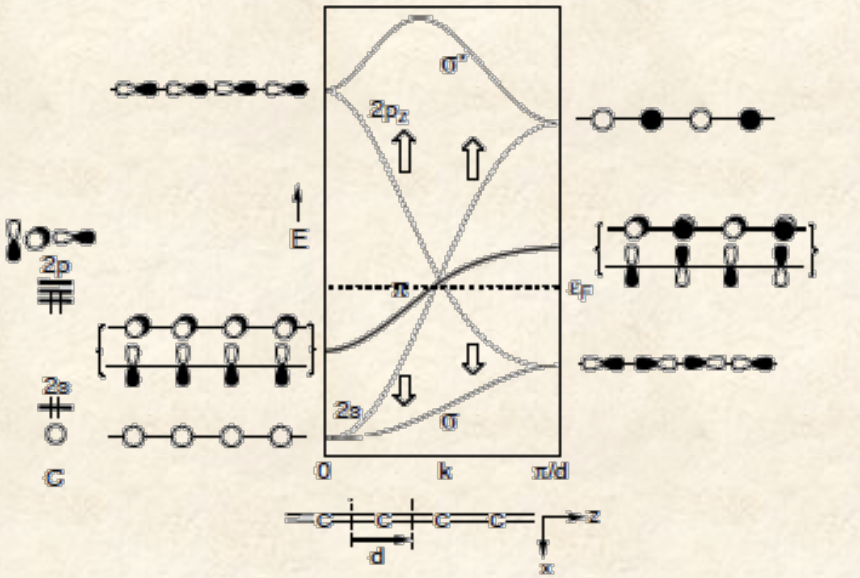
a) Each carbon AO generates a Bloch function.

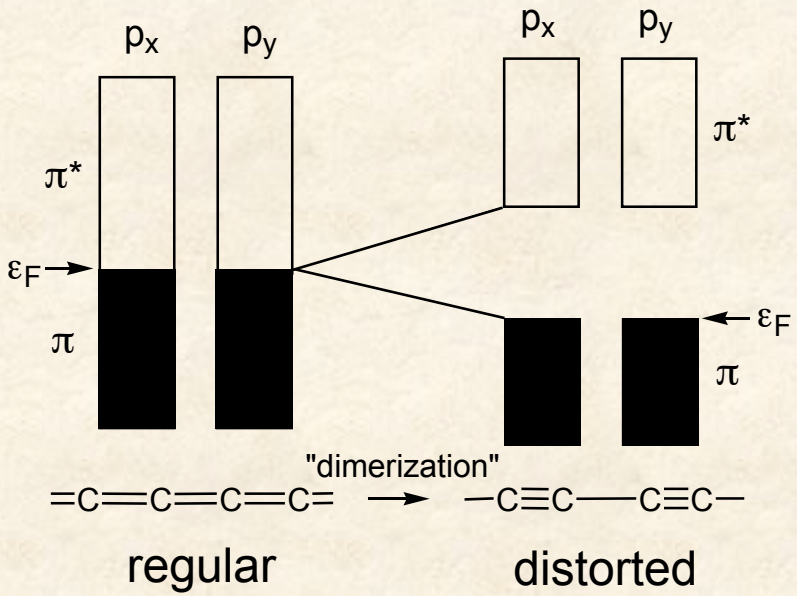
b) The σ-type 2s and $2p_z$ Bloch bands interact and strongly repel each other. The resulting σ and σ* bands have no particular shapes and are rather flat.

c) The π band is doubly degenerate.



A chain of equidistant carbon atoms… Peierls Instability…





To summarize

a) Identify the repeat unit (unit cell)

b) Consider the content of the repeat unit as a molecular fragment

c) Consider the MO diagram of this repeat unit (AOs if single atom). It contains the interactions between all the AOs inside one individual unit cell

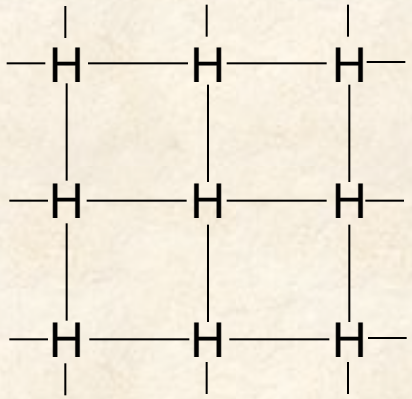
d) Generate the Bloch functions developed on each MO. A Bloch function developed on one particular χ MO of the unit cell describes the interactions between all the χ_j MOs of different unit cells

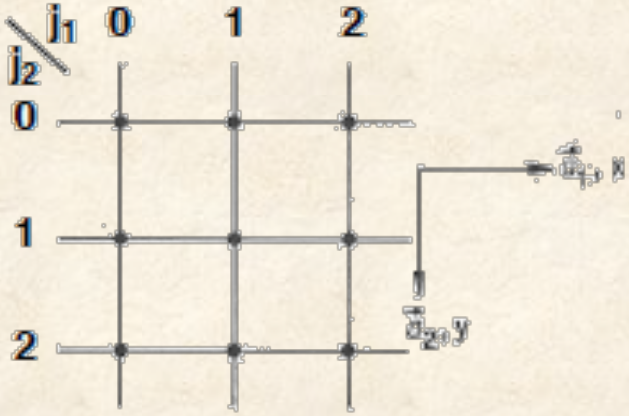
e) Allow the Bloch orbitals to interact at each *k*-point if symmetry allows it to get the crystal orbitals (CO). The final band structure will arise

More Dimensions

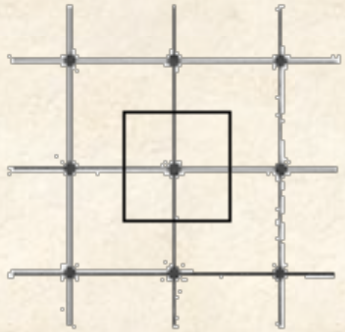
Two Dimensions

Square lattice of H atoms
(1 H per unit cell)

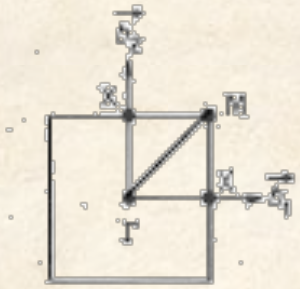




direct lattice



reciprocal lattice



Brillouin zone

Bloch orbitals: $\phi(k) \; \alpha \sum_{j_1} \sum_{j_2} \exp(ikR_j) \; \chi_j$

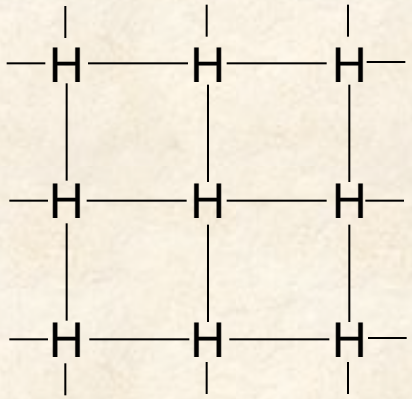
where $k = (k_x, k_y)$

$R_j = j_1 a_1 + j_2 a_2$ (j_1 and $j_2 = 0, \infty$)

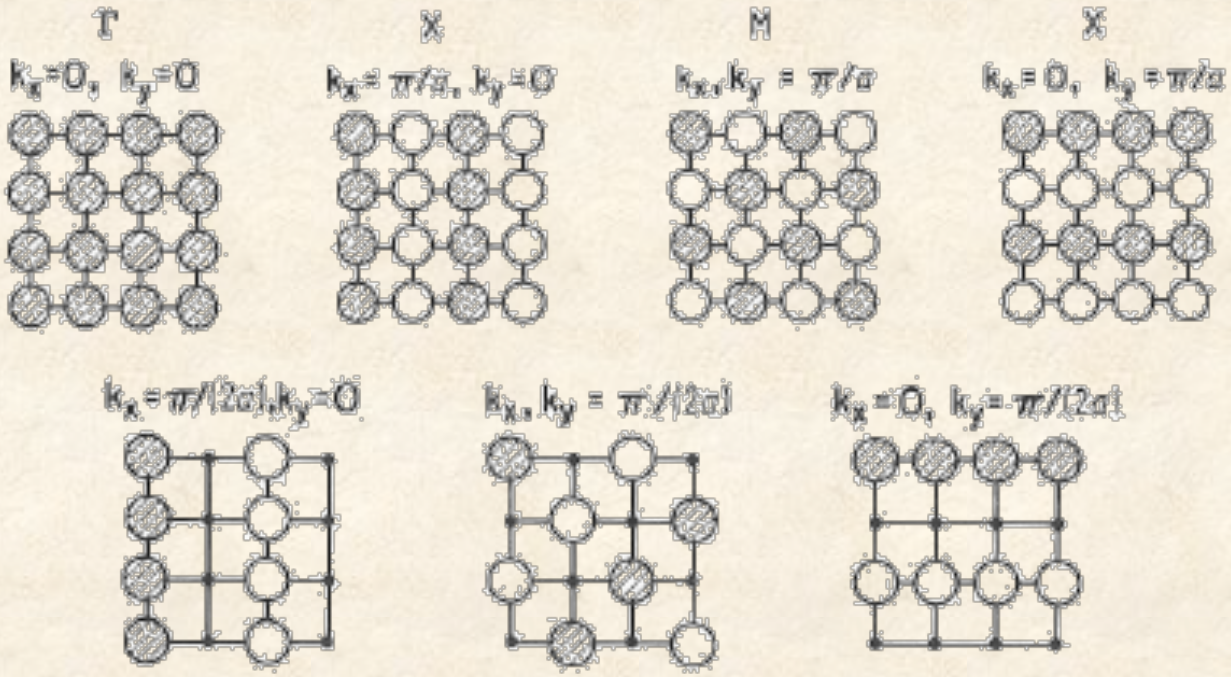
χ_j = 1s(H)

Two dimensions

Square lattice of H atoms
(1 H per unit cell)

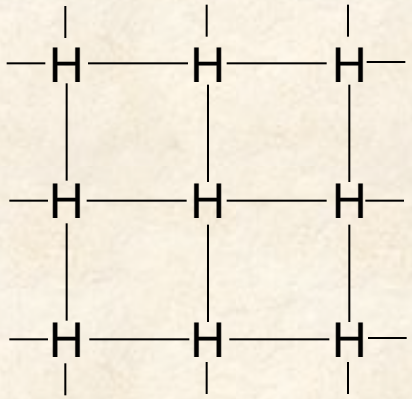


Bloch orbitals:



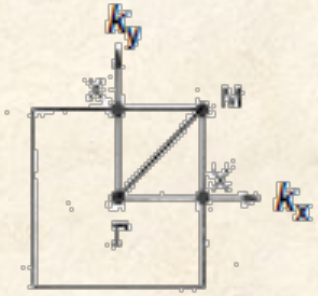
Two dimensions

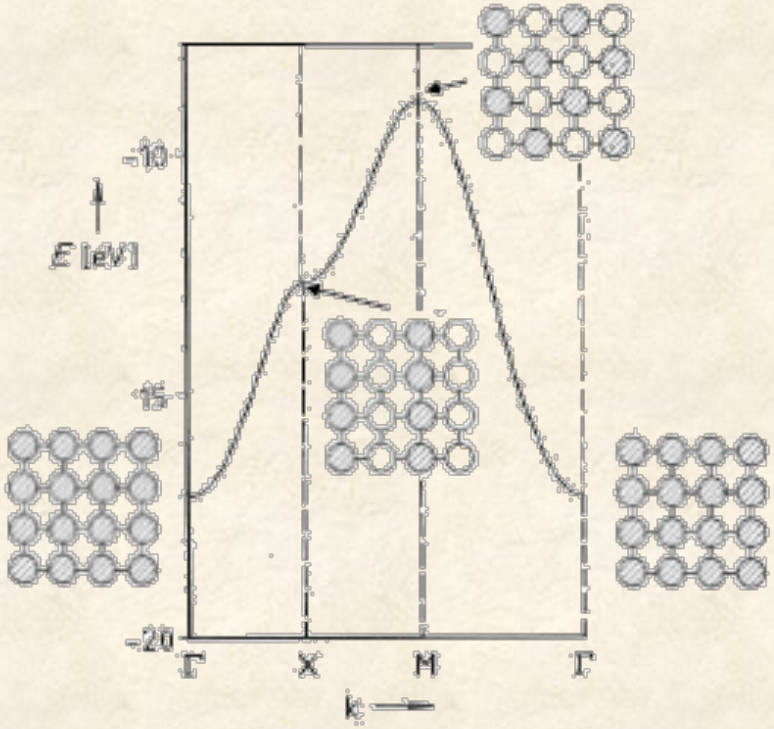
Square lattice of H atoms
(1 H per unit cell)



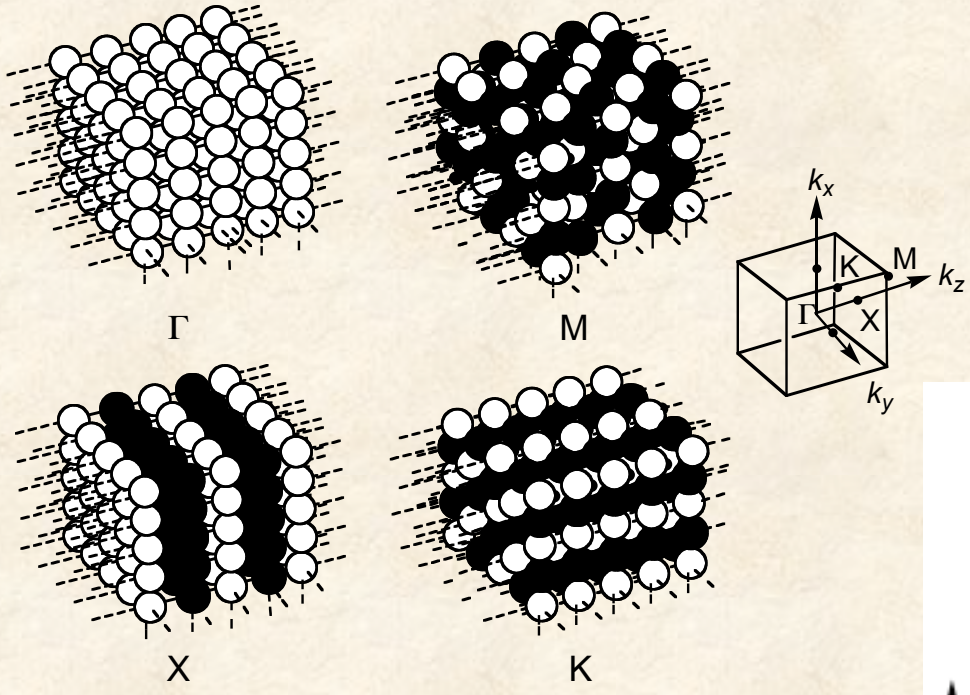
$\phi(k) \longrightarrow E(k)$

Band structure: $E(k) = f(k)$



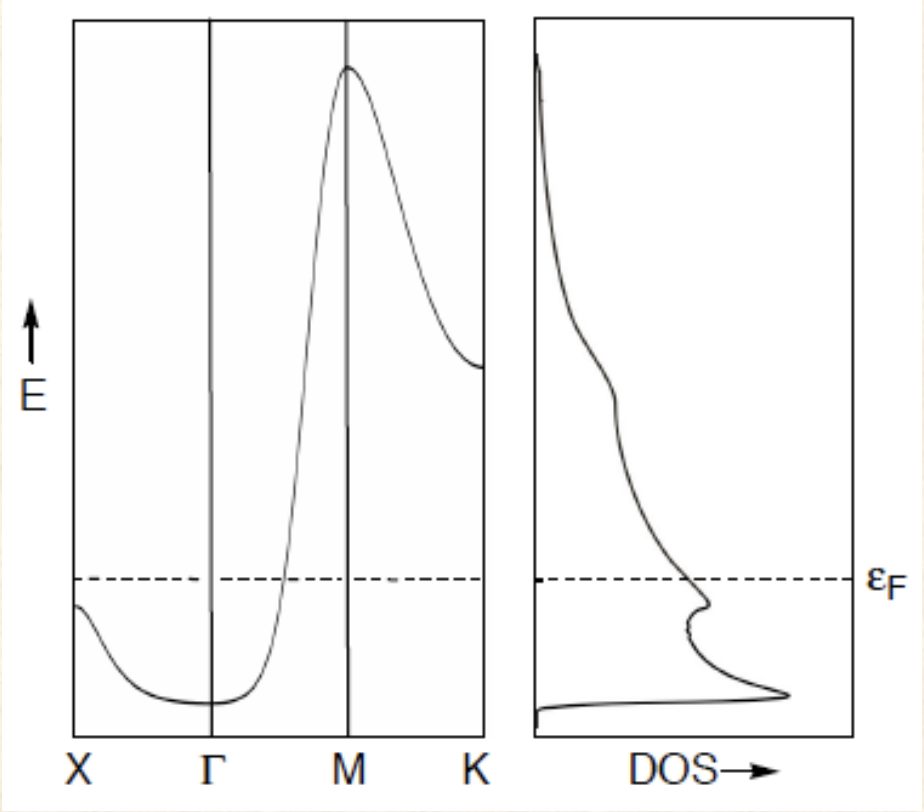


Three dimensions

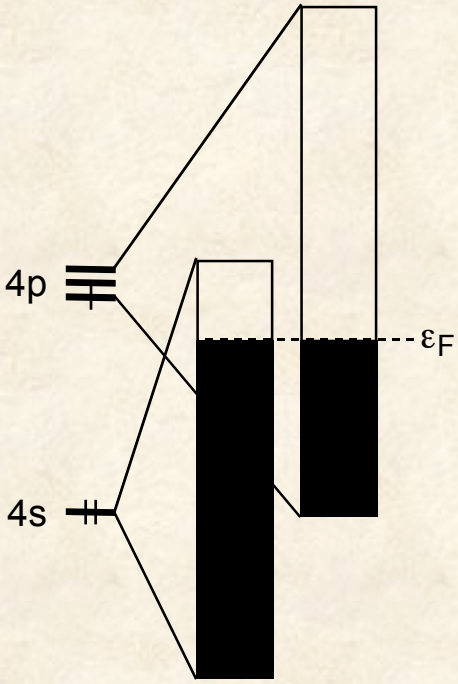


Bloch orbitals

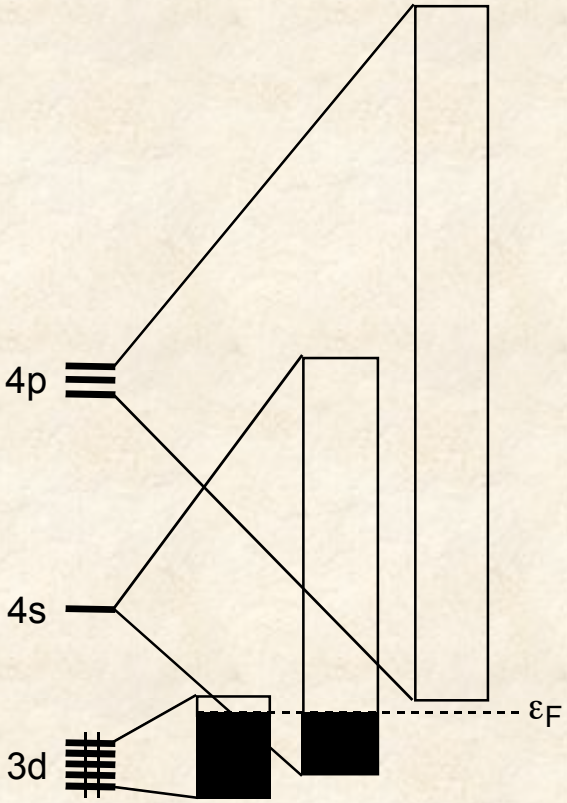
Simple cubic lattice of H atoms
(1 H per unit cell)



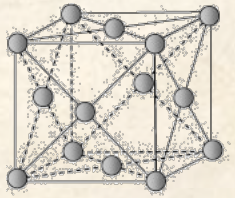
Three dimensions



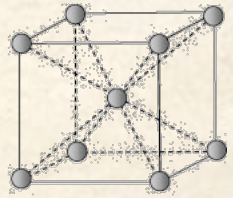
Al bulk fcc Al



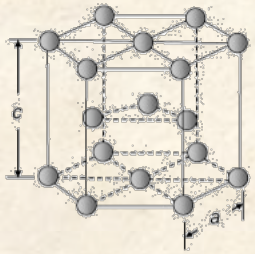
Ni bulk fcc Ni



Face centered cubic (fcc)



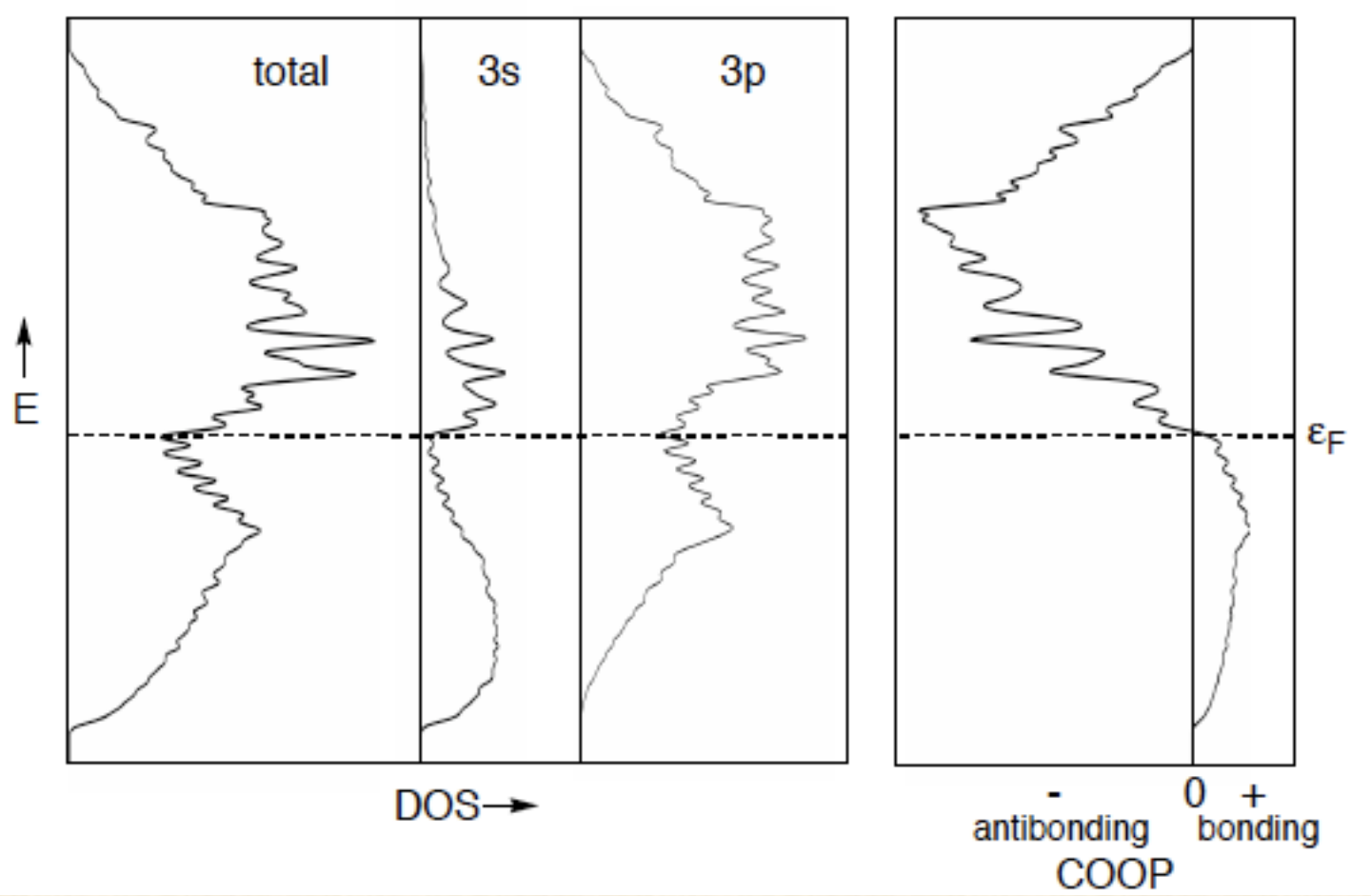
Body centered cubic (bcc)



Hexagonal close-packed (hcp)

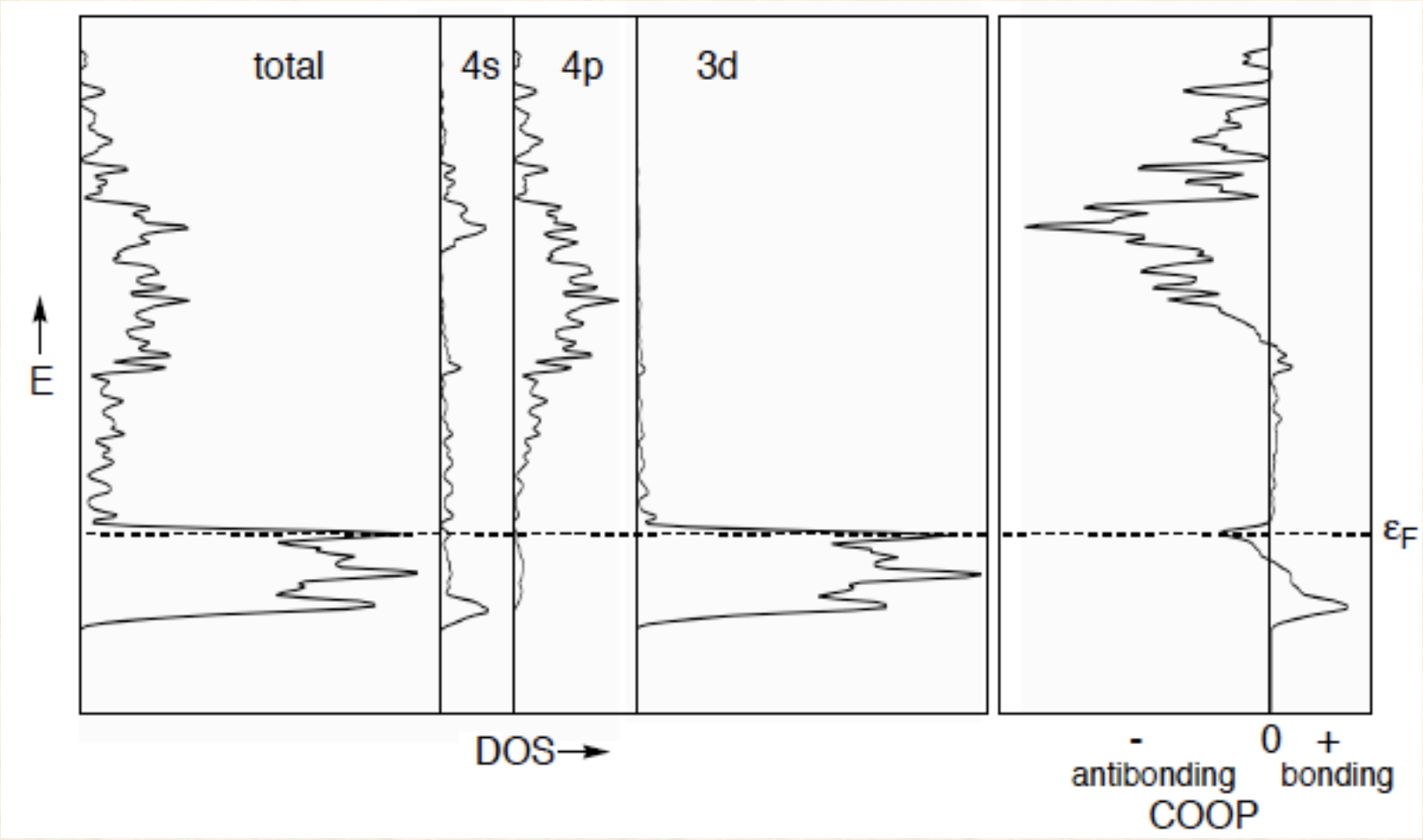
Three dimensions

Bulk fcc Al

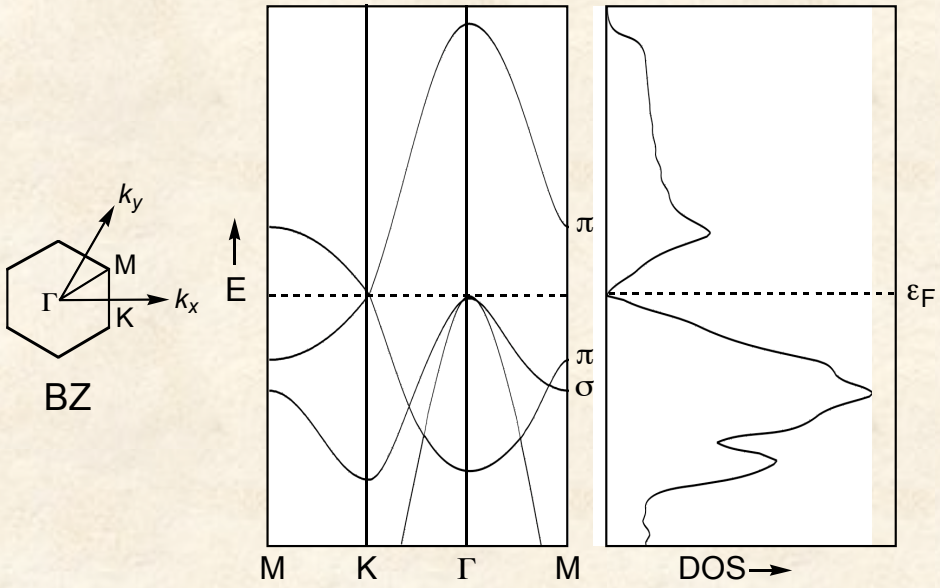


Three dimensions

Bulk fcc Ni



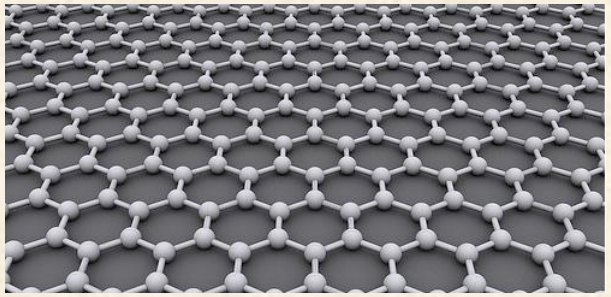
More examples: graphite and diamond



Graphite (graphene) (2-D)

DOS = 0 at ε_F and only at this point

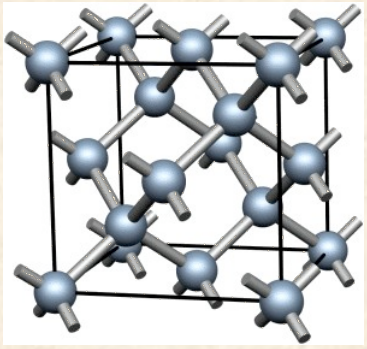
Semi-metal

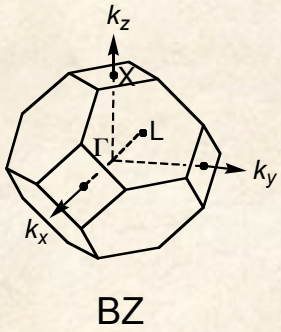


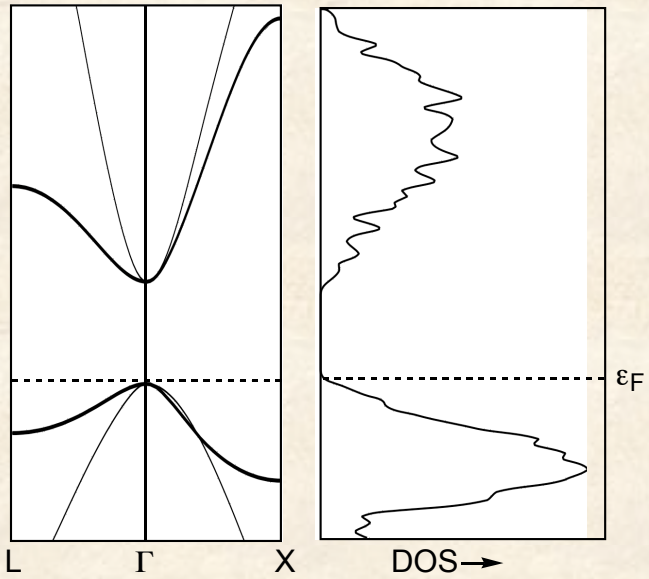
Diamond (3-D)

Large forbidden energy gap above ε_F

Insulator



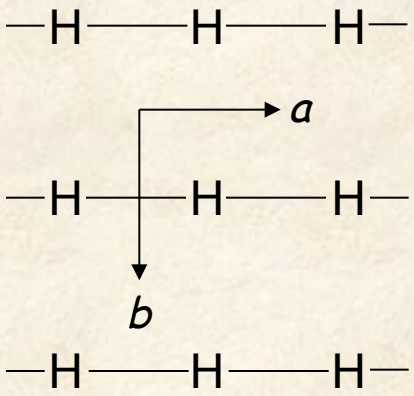


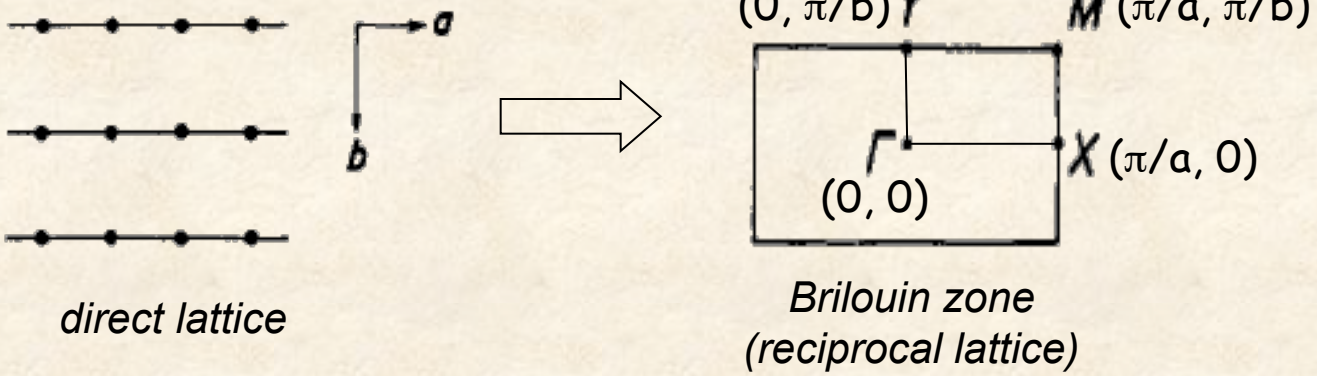


Partially Filled Bands: The Fermi Surface

Partially Filled Bands: The Fermi Surface

Rectangular lattice of H atoms
(1 H per unit cell)





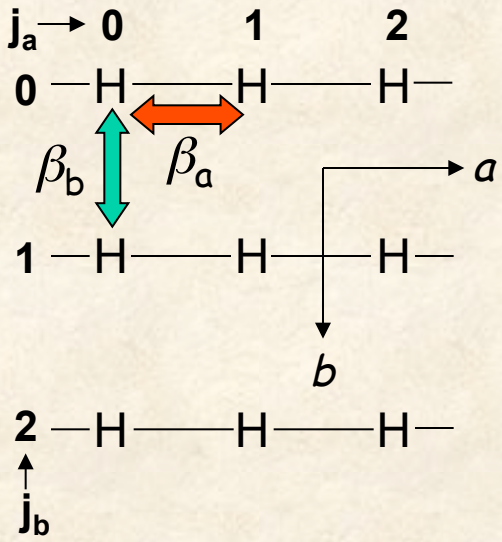
direct lattice

Brilouin zone
(reciprocal lattice)

Construction of BOs, $\phi(k)$ $\Longrightarrow$ Band structure, E(k) = f(k)

Partially Filled Bands: The Fermi Surface

Rectangular lattice of H atoms
(1 H per unit cell)

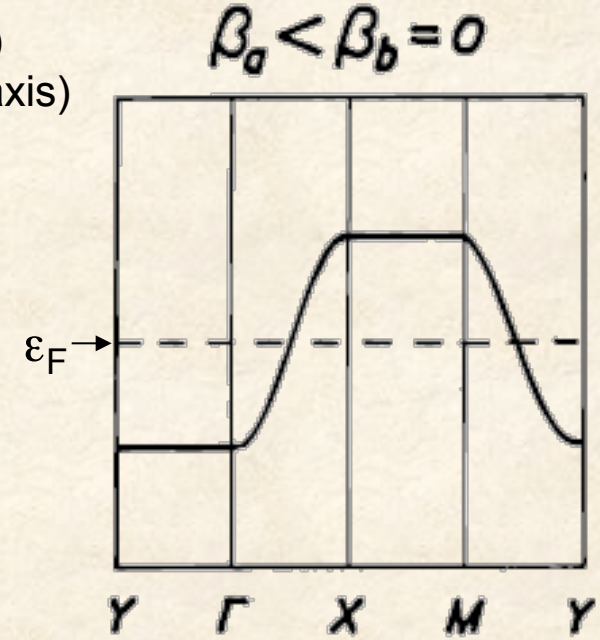


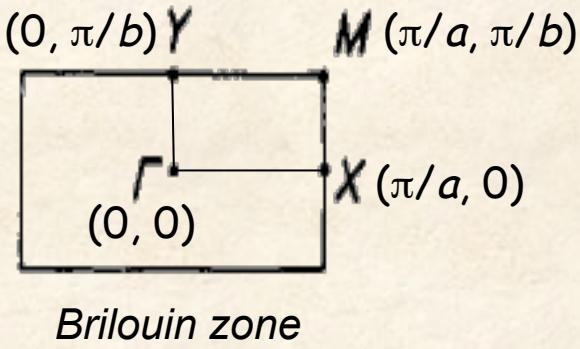
β_a and β_b: resonance integrals
(transfer integrals)

$$\beta_a = \langle \chi_{ja} \mid H^{eff} \mid \chi_{ja+1} \rangle$$

$$\beta_b = \langle \chi_{jb} \mid H^{eff} \mid \chi_{jb+1} \rangle$$

Band structure, E(k) = f(k)
(if no interaction along b axis)

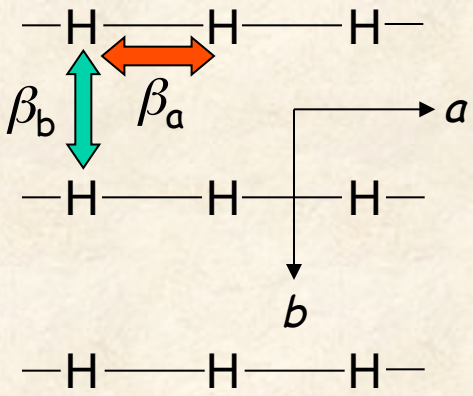




Brilouin zone

Partially Filled Bands: The Fermi Surface

Rectangular lattice of H atoms
(1 H per unit cell)

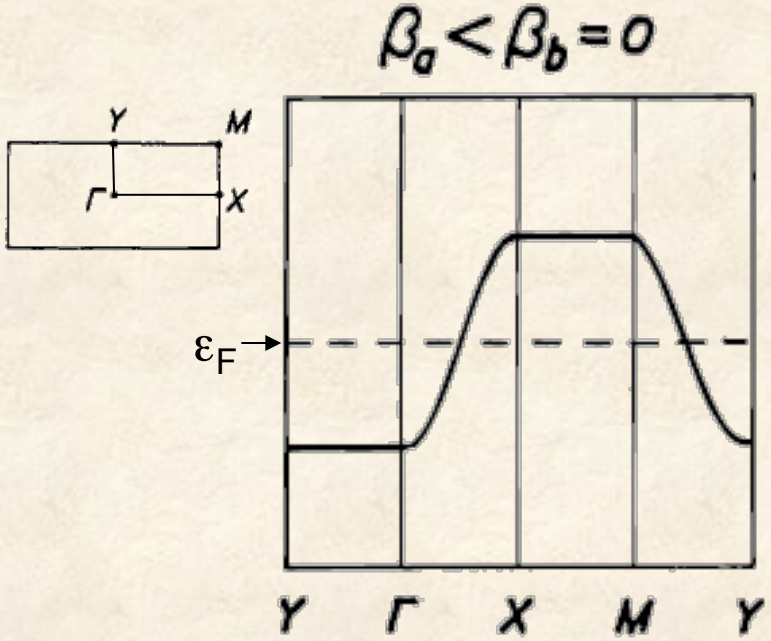


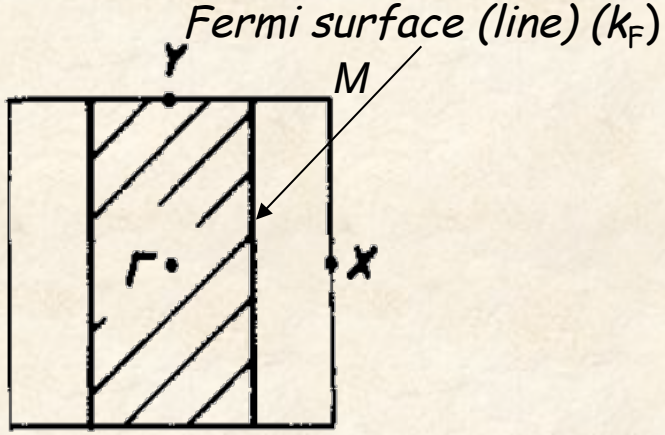
β_a and β_b: resonance integrals (transfer integrals)

$$\beta_a = \langle \chi_{ja} \mid H^{eff} \mid \chi_{ja+1} \rangle$$

$$\beta_b = \langle \chi_{jb} \mid H^{eff} \mid \chi_{jb+1} \rangle$$

Partially filled bands ⇨ Fermi surface

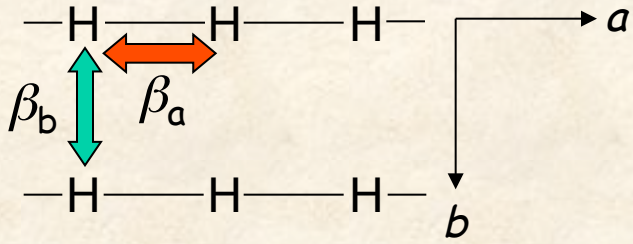




Fermi surface: boundary surface separating the "occupied" and "unoccupied" wave vectors: a point (1D), a line (2D) or a surface (3D)

Partially Filled Bands: The Fermi Surface

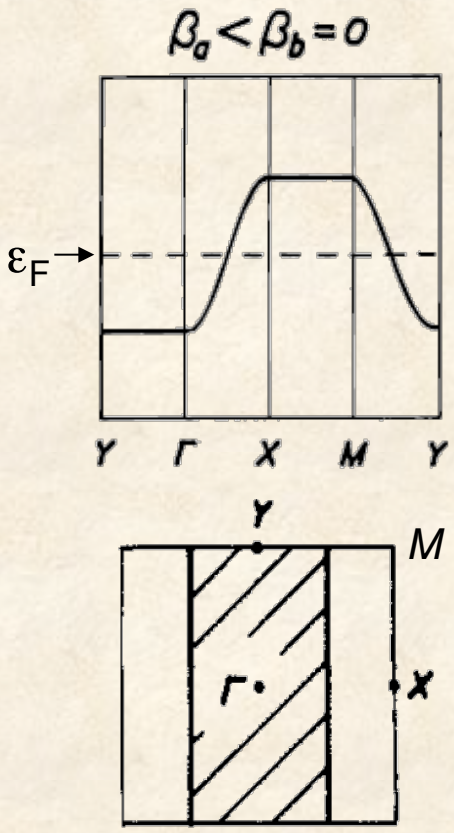
Rectangular lattice of H atoms
(1 H per unit cell)

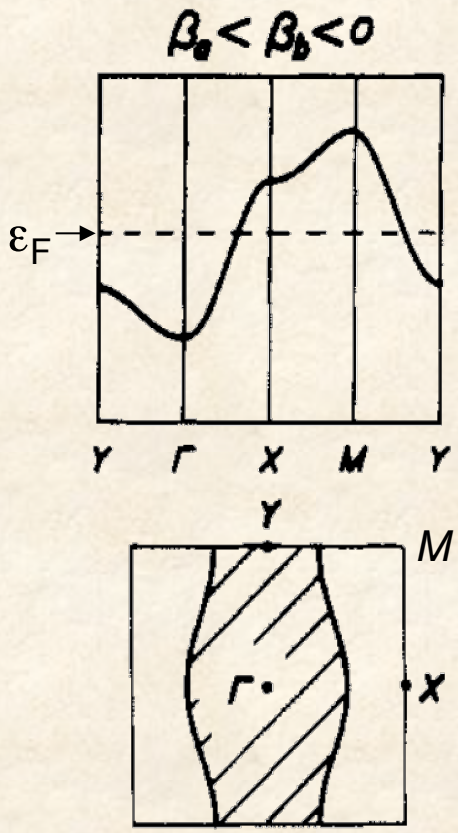


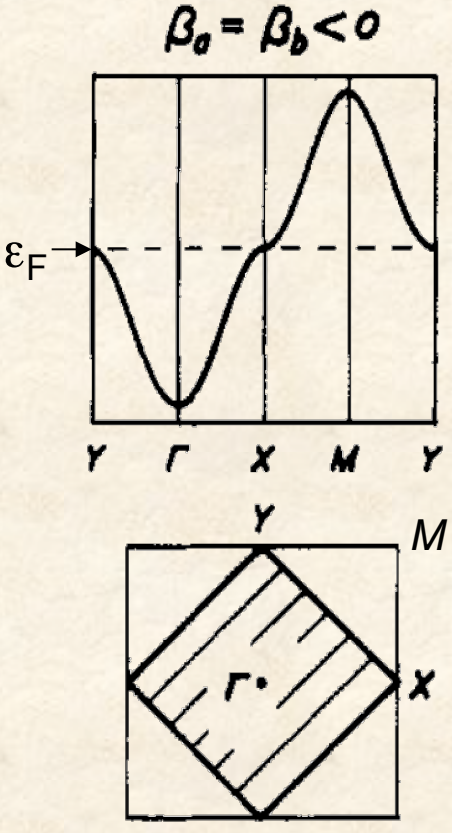
$$\beta_a = \langle \chi_{ja} \mid H^{eff} \mid \chi_{ja+1} \rangle$$

$$\beta_b = \langle \chi_{jb} \mid H^{eff} \mid \chi_{jb+1} \rangle$$

Band structures and Fermi surfaces

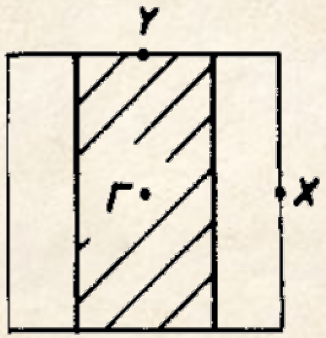




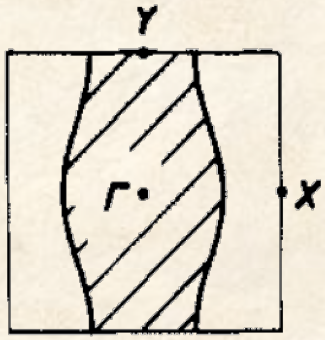


Partially Filled Bands: The Fermi Surface

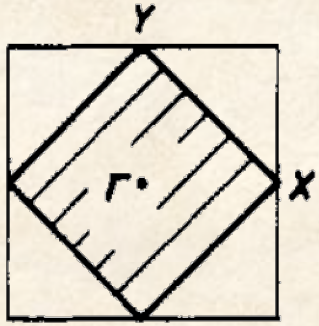
Fermi surfaces explain the dimensionality of metallic properties



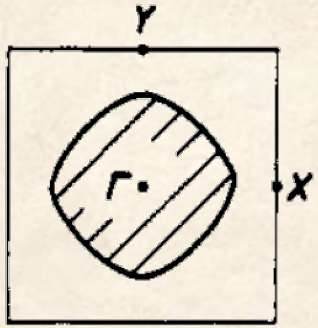
1D metal
(along *a* axis)



pseudo-1D metal
(along *a* axis)



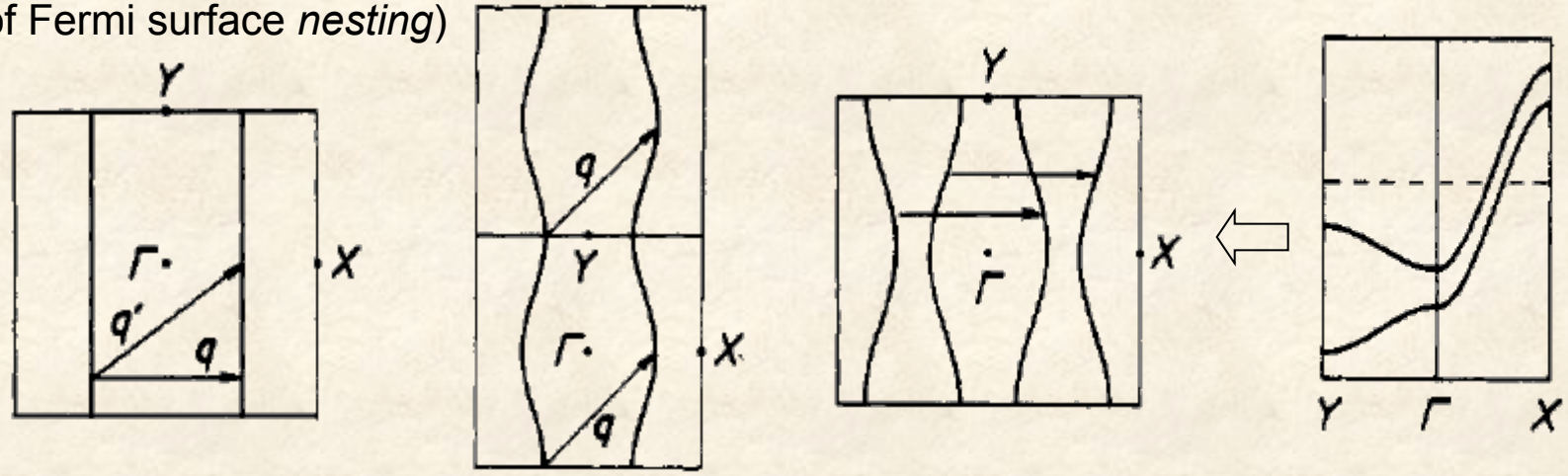
2D (anisotropic) metal
(along *a+b* and *a-b* axis)



2D (isotropic) metal
(close loop)

Partially Filled Bands: The Fermi Surface

Fermi surfaces explain distortions in solids due to electronic instabilities
(concept of Fermi surface *nesting*)

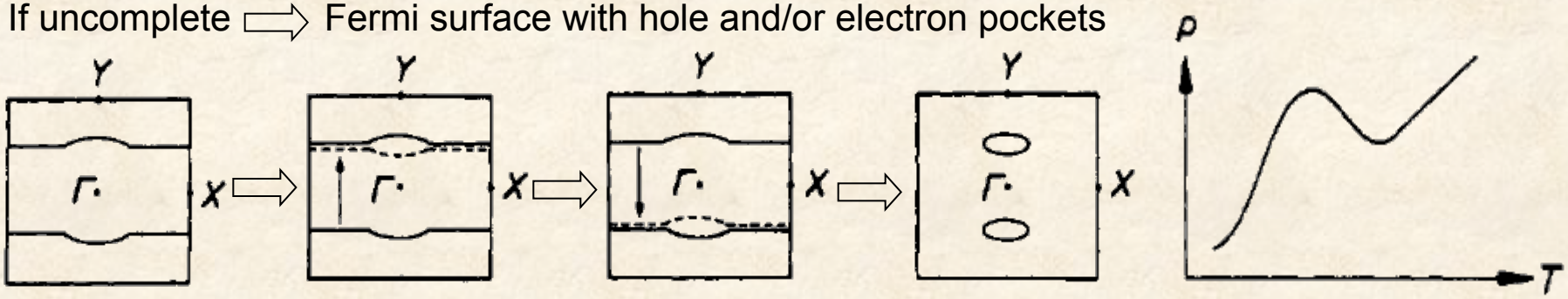


A Fermi surface is nested by a vector *q* when a section can be moved by such a vector to be superimposed on another section

A metallic system with a *nested* Fermi surface is subject to a metal-insulator phase transition (interaction of occupied and vacant crystal orbitals of same symmetry of $E = E(k_F)$ related by *q*)

If complete ⇨ destruction of the Fermi surface

If uncomplete ⇨ Fermi surface with hole and/or electron pockets



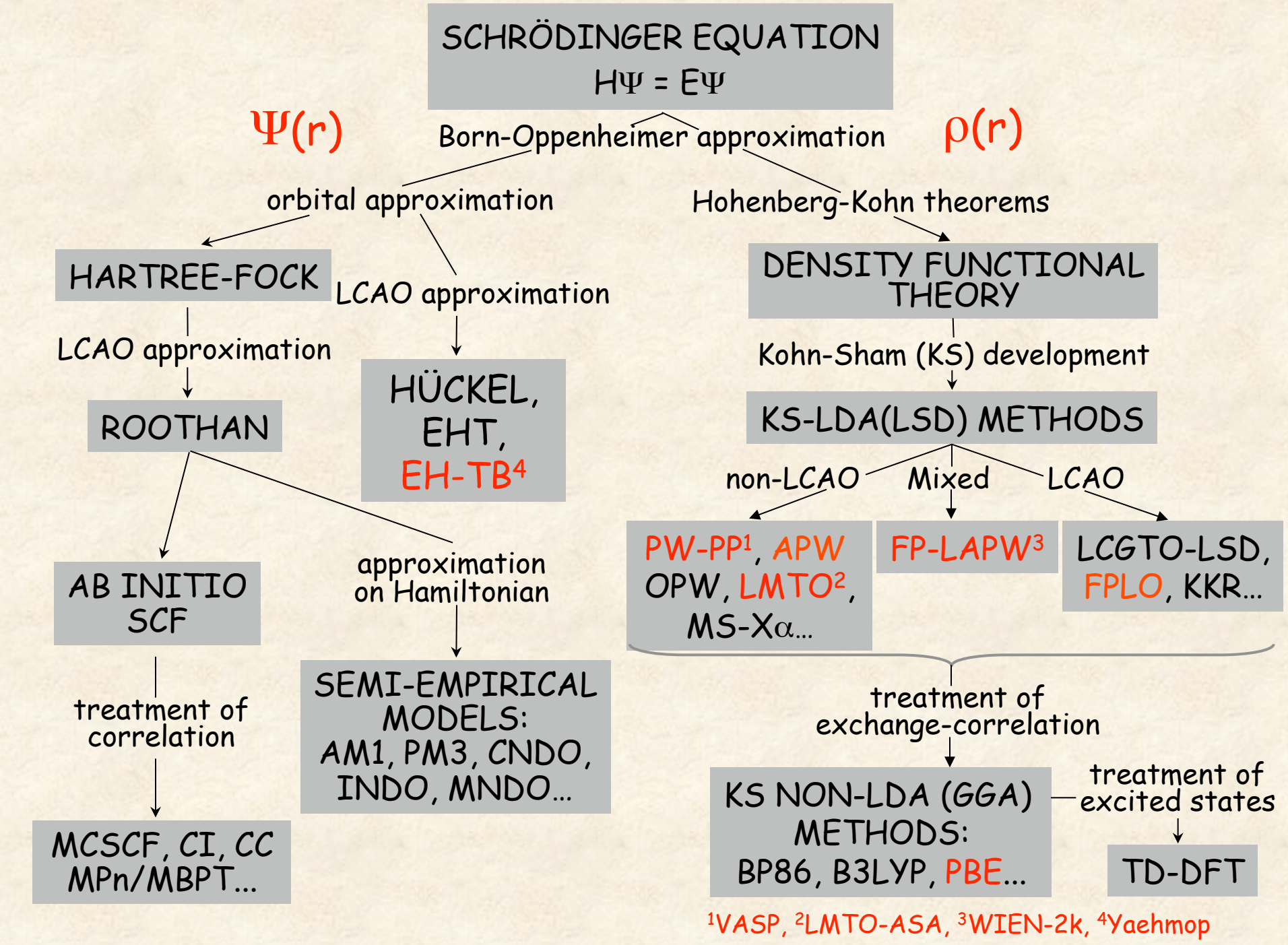
Computational Aspects

Computational Aspects

- Quantum chemical methods

There are different ways to solve the Schrödinger equation for periodic systems

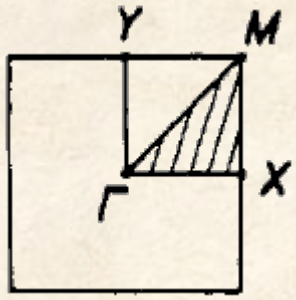
Crystal orbitals $\Psi_n(k)$


SCHRÖDINGER EQUATION
HΨ = EΨ
Ψ(r)
Born-Oppenheimer approximation
ρ(r)
orbital approximation
Hohenberg-Kohn theorems
HARTREE-FOCK
LCAO approximation
DENSITY FUNCTIONAL THEORY
LCAO approximation
Kohn-Sham (KS) development
ROOTHAN
HÜCKEL, EHT, EH-TB4
KS-LDA(LSD) METHODS
non-LCAO
Mixed
LCAO
AB INITIO SCF
approximation on Hamiltonian
PW-PP1, APW OPW, LMTO2, MS-Xα...
FP-LAPW3
LCGTO-LSD, FPLO, KKR...
treatment of correlation
SEMI-EMPIRICAL MODELS: AM1, PM3, CNDO, INDO, MNDO...
treatment of exchange-correlation
KS NON-LDA (GGA) METHODS: BP86, B3LYP, PBE...
treatment of excited states
TD-DFT
MCSCF, CI, CC MPn/MBPT...
1VASP, 2LMTO-ASA, 3WIEN-2k, 4Yaehmop

Computational Aspects

Crystal orbitals $\Psi_n(k) \Longrightarrow e_n(k)$
for specific *k* wave vectors along symmetry lines
of the irreducible part of Brillouin zone

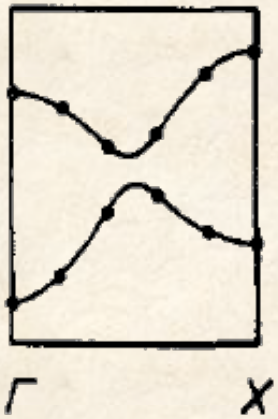
- Band dispersion relation, $E(k) = f(k)$



Brillouin zone

one band

two bands with different symmetry

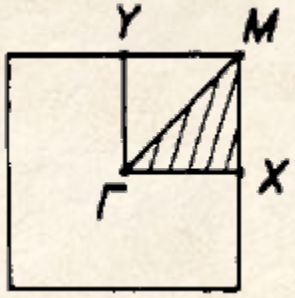


two bands with identical symmetry

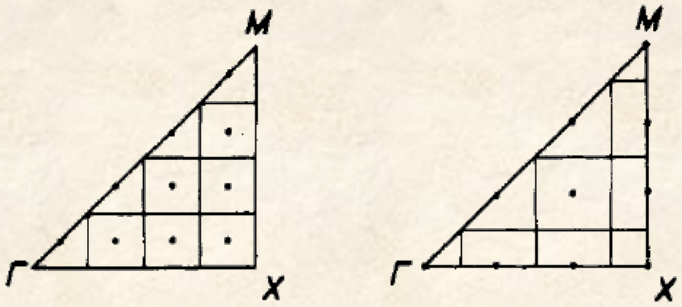
Computational Aspects

M crystal orbitals $\Psi_n(k) \Longrightarrow e_n(k)$

for *L* k wave vectors "inside" the irreducible part of Brillouin zone (sampling)

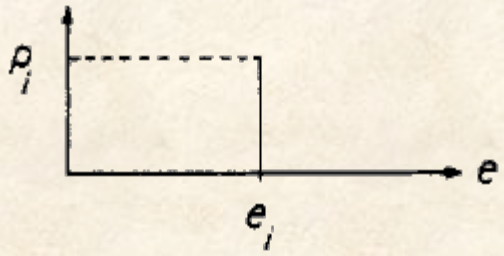


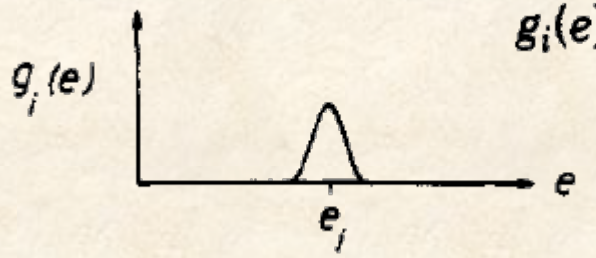
Brillouin zone



two sets of 10 *k* "points" of weight w_i

- Density of states, Fermi level, and electronic energy





$$g_i(e) = \frac{1}{\sqrt{\pi}\delta} p_i \exp\left[-\left(\frac{e - e_i}{\delta}\right)^2\right]$$

$$\int_{-\infty}^{\infty} g_i(e)\, de = p_i$$

Total DOS: $n(e) = \sum_{i=1}^{M \times L} 2g_i(e)$ Fermi level: $\sum_{i=1}^{\max} 2p_i = N_{tot}$ (e^-/unit cell) $\Longrightarrow$ $e_{max} = e_F$

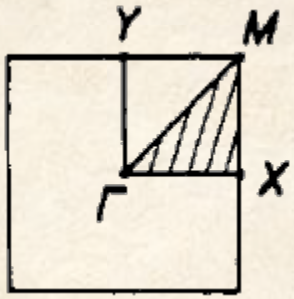
Total electronic energy of the system: $E_{elec} = \int_{-\infty}^{e_f} n(e) e\, de$

Computational Aspects

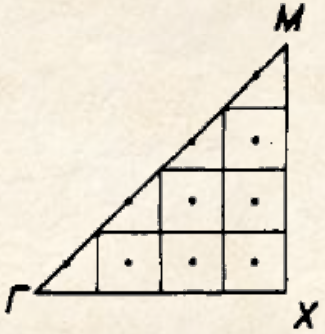
M crystal orbitals $\Psi_n(k) \Longrightarrow e_n(k)$

for *L* k wave vectors "inside" the irreducible part of Brillouin zone

2D square system ⟹



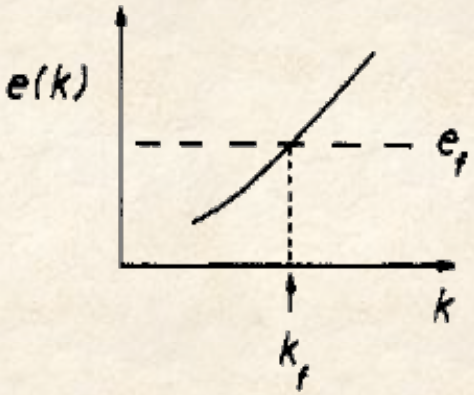
Brillouin zone



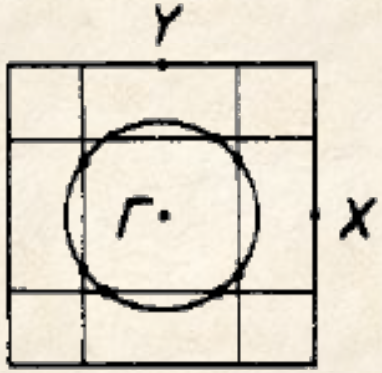
mesh of *L k* "points"

- Fermi surface

$e_n(k_i) \Longrightarrow e_n(k_F) = e_F$ (constant energy surface)



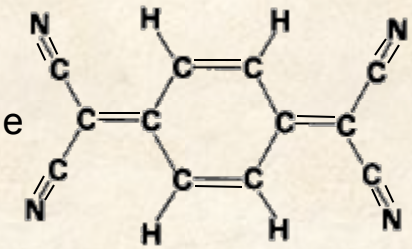
⟹



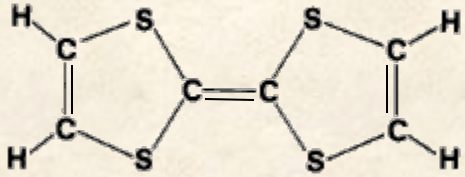
The Theoretical Machinery at Work…

Application to the Texbook Example of TTF-TCNQ, the First Organic Molecular Metal

Tetracyanoquinomethane
(TCNQ)



Tetrathiafulvalene
(TTF)



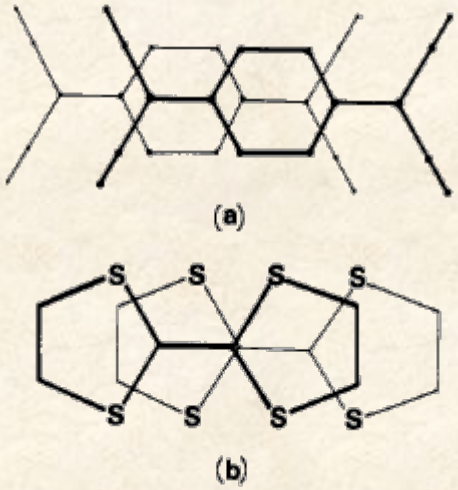


Figure 2. Arrangements found for neighboring molecules in stacks of (a) TCNQ, (b) TTF in TTF-TCNQ crystals.

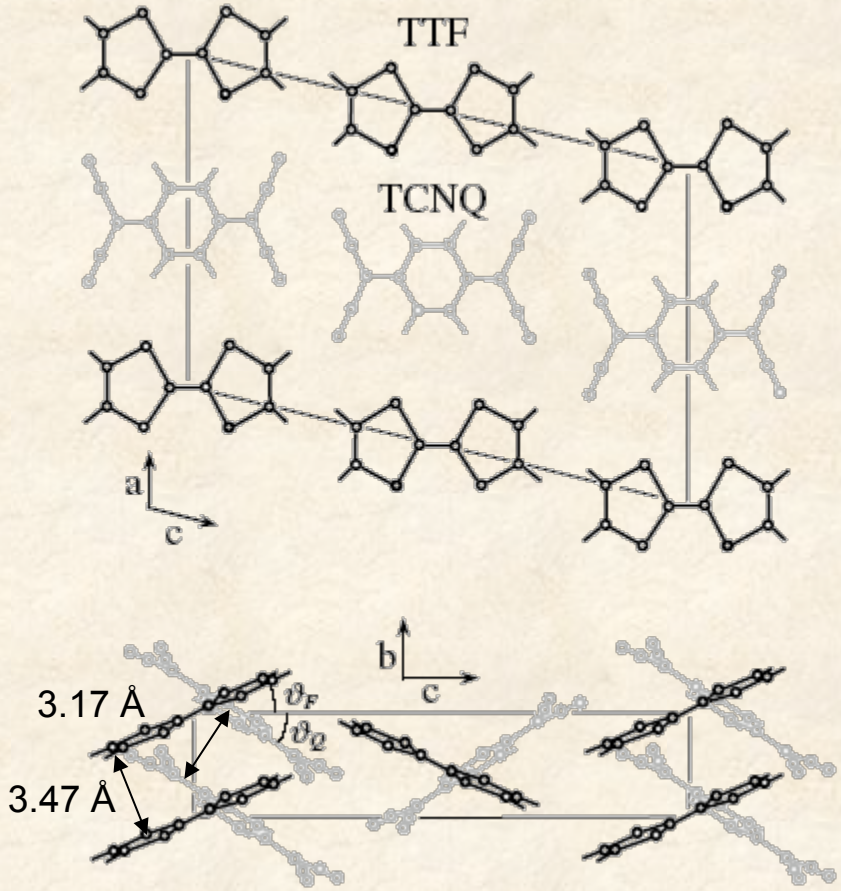


FIG. 1. Crystal structure of TTF-TCNQ.

The Texbook Example of TTF-TCNQ

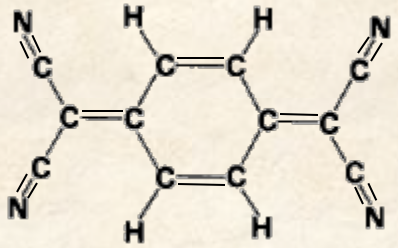
TTF-TCNQ: A truly organic molecular metal

$\sigma \sim 5.10^3\ \Omega^{-1}.cm^{-1}$ at 80 K (-210 °C) (10^6 for Cu)

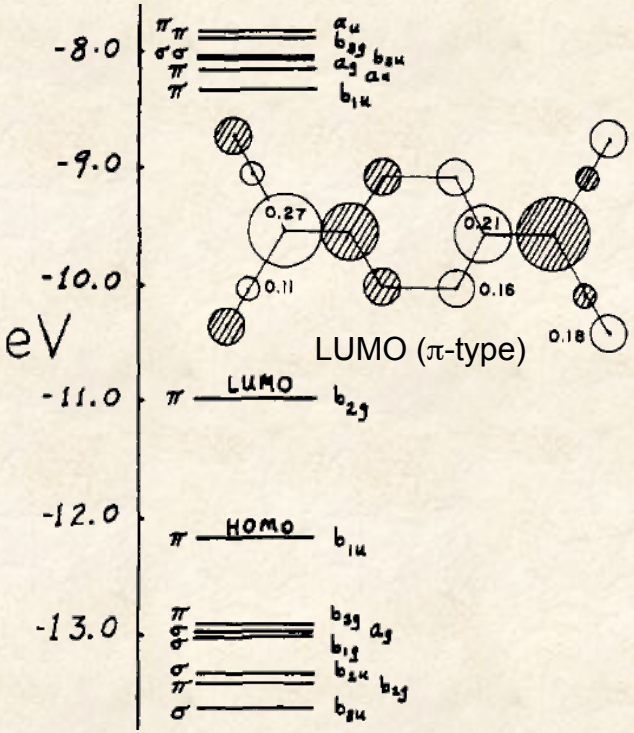
What's special for TTF-TCNQ?

The Texbook Example of TTF-TCNQ

TCNQ: *A good acceptor*



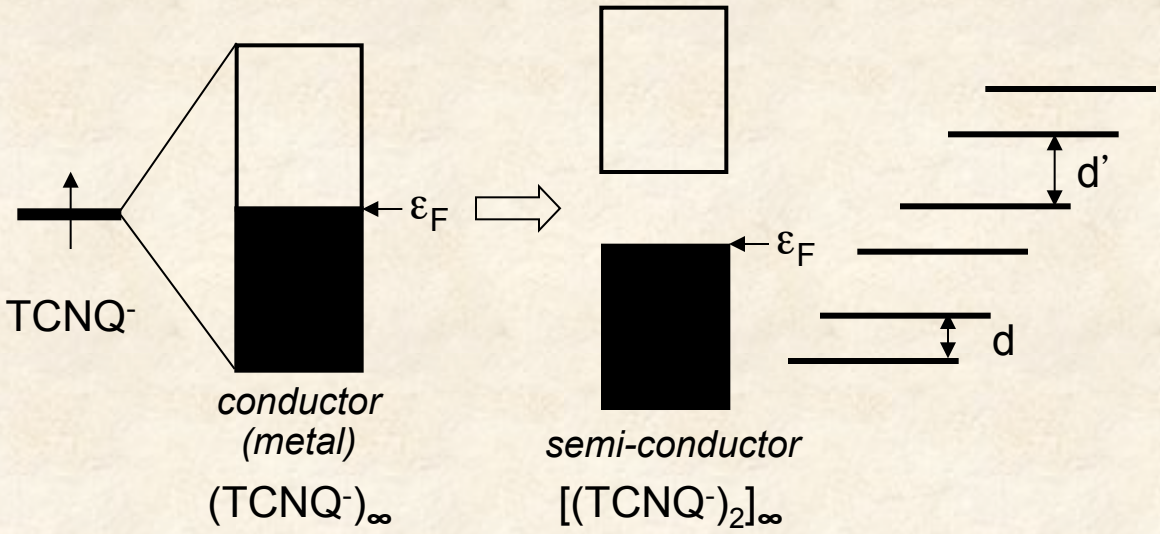
Tetracyanoquinomethane
(TCNQ) - 16 π e⁻



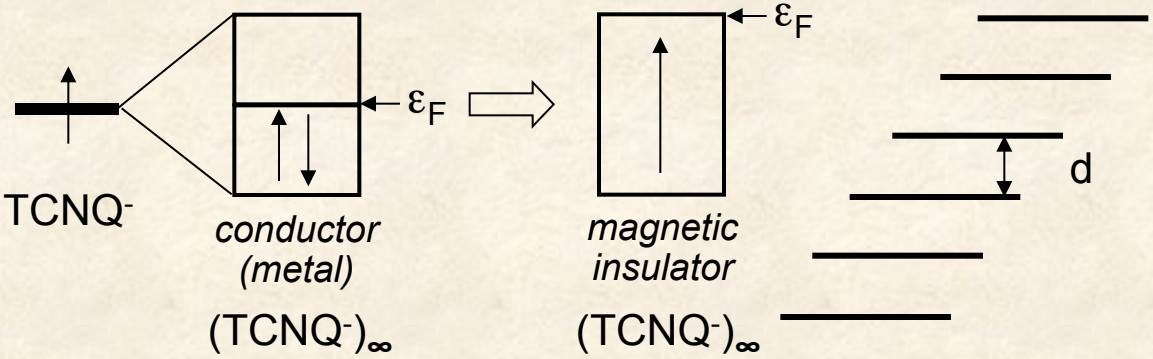
Some EHMO energy levels and
MO symmetries for TCNQ.

weakly antibonding
LUMO (π-type) ⇨ acceptor character ⇨ $TCNQ^-$

(structural change upon reduction)



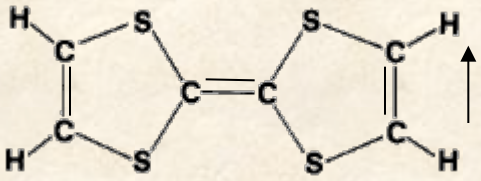
or alternatively, if U (e^--e^- repulsion) > W (bandwith)



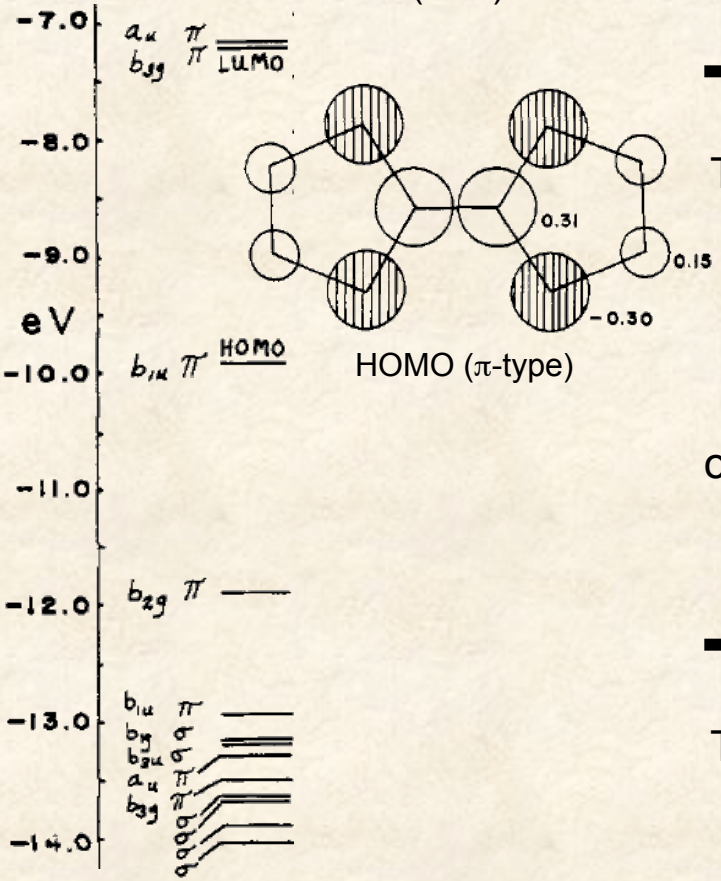
J. P. Lowe, *J. Am. Chem. Soc.* **1980**, *102*, 1262

The Texbook Example of TTF-TCNQ

TTF: A good donor



Tetrathiafulvalene (TTF) - 14 π e⁻

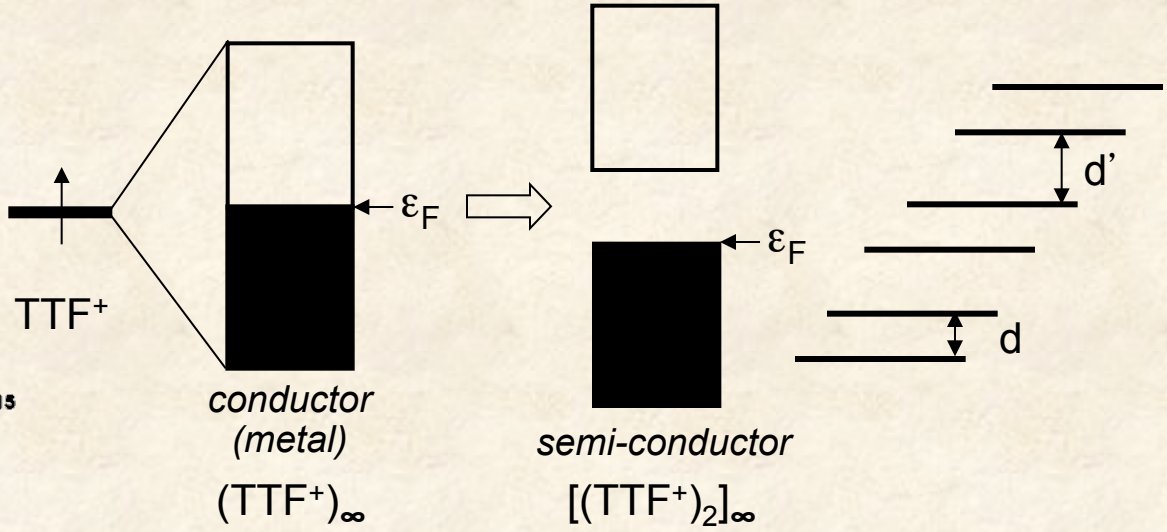


HOMO (π-type)

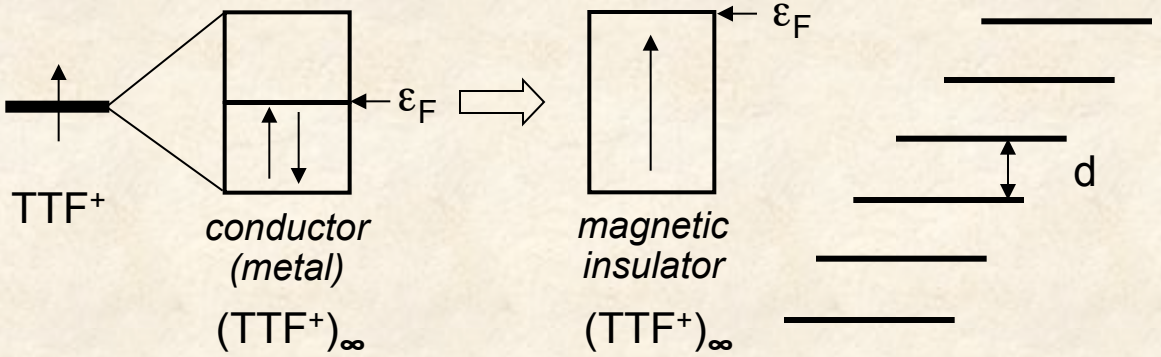
Some EHMO energy levels and MO symmetries for TTF.

weakly bonding HOMO (π-type) ⇒ donor character ⇒ TTF^+

(structural change upon oxidation)



or alternatively, if U (e^--e^- repulsion) > W (bandwith)



J. P. Lowe, *J. Am. Chem. Soc.* **1980**, *102*, 1262

The Texbook Example of TTF-TCNQ

TCNQ salts are generally semi-conductors

$Na(TCNQ) \Rightarrow (TCNQ_2)^{2-}$ dimers

$K(TCNQ) \Rightarrow (TCNQ_2)^{2-}$ dimers

$Cs_2(TCNQ) \Rightarrow (TCNQ_3)^{2-}$ trimers

$NEt_4(TCNQ)_2 \Rightarrow (TCNQ_4)^{-}$ tetramers

TTF salts as well…

The Electronic Structure of TTF-TCNQ

What's special for TTF-TCNQ?

DFT band structure (two TCNQ and two TTF molecules per unit cell):

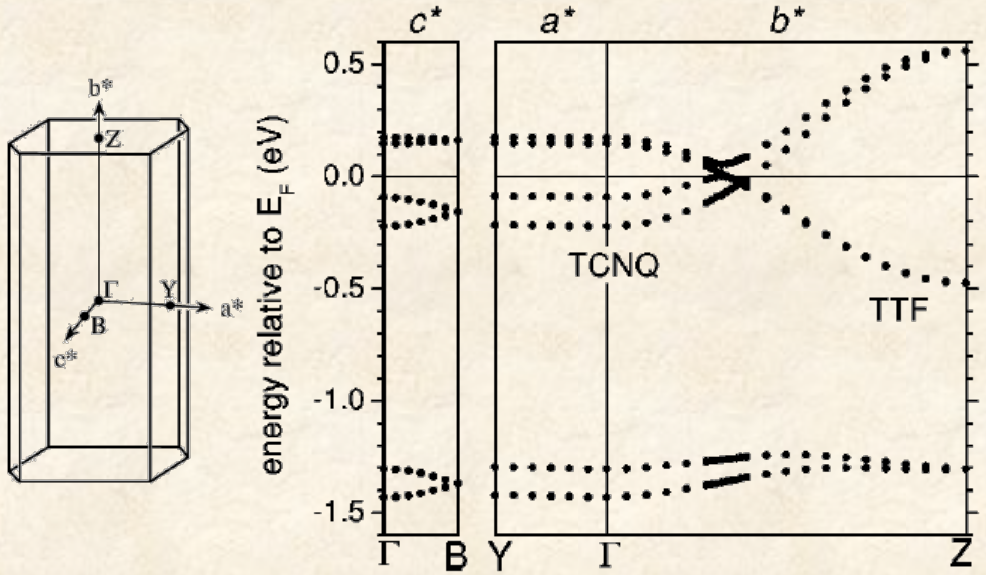


FIG. 2. DFT band structure near the Fermi level along the three major high-symmetry lines of the Brillouin zone of TTF-TCNQ.

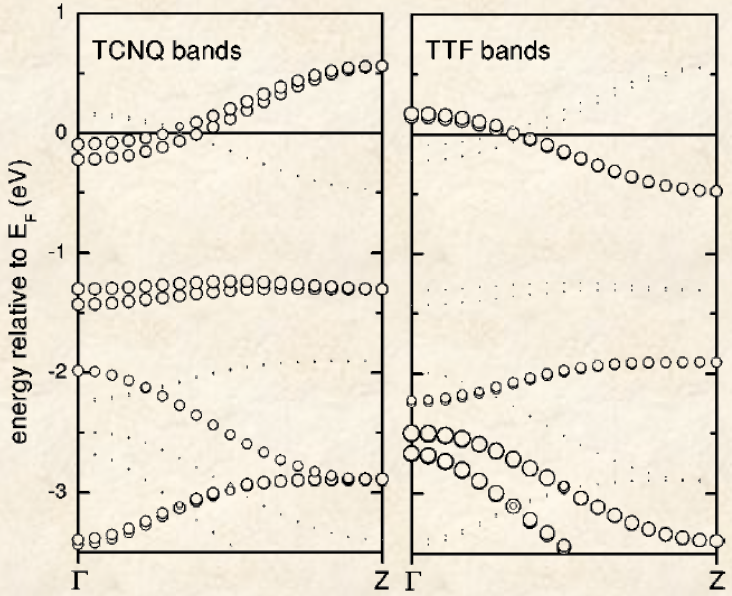


FIG. 3. Theoretical band dispersions along ΓZ showing the molecular origin of the bands. The size of the symbols represents the charge of each state residing on the TCNQ (left panel) and TTF (right panel) molecules.

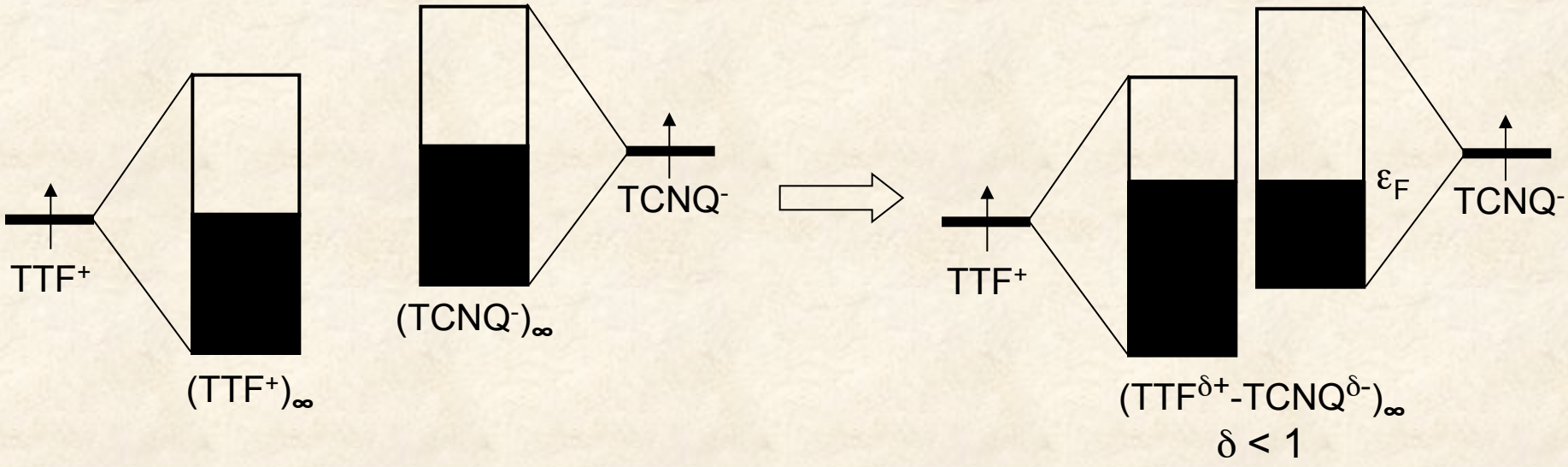
The TTF and TCNQ bands overlap at the Fermi level (1D metal)

M. Sing, *Phys. Rev. B.* **2003**, *68*, 125111

The Electronic Structure of TTF-TCNQ

What's special for TTF-TCNQ?

The TTF and TCNQ bands overlap at the Fermi level

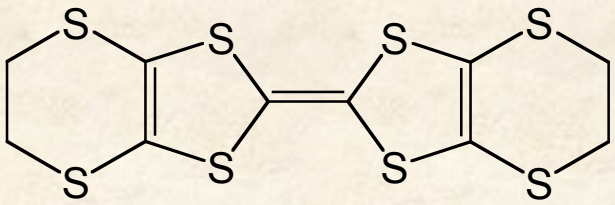


No distortion (at room temperature)

TTF-TCNQ is a 1D metal

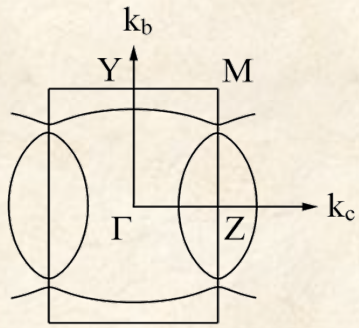
Examples of Molecular Materials and their Electronic Structure

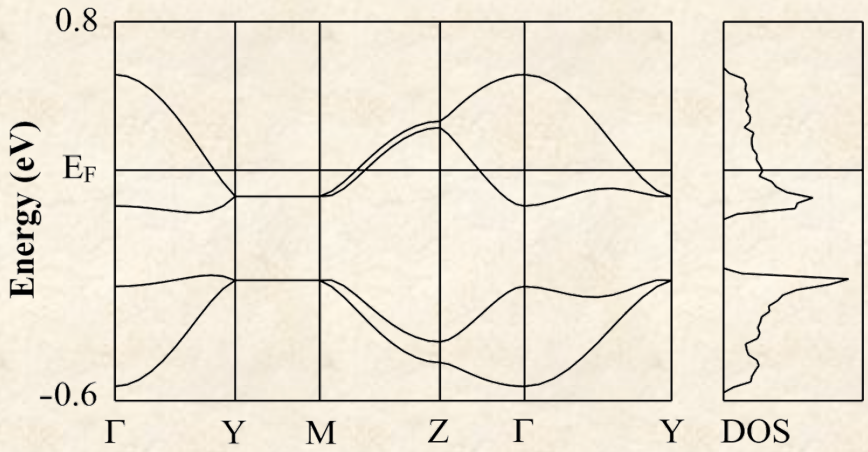
The superconductor κ-$(ET)_2Cu(NCS)_2$ (T_c = 11 K)



BEDT-TTF (ET)

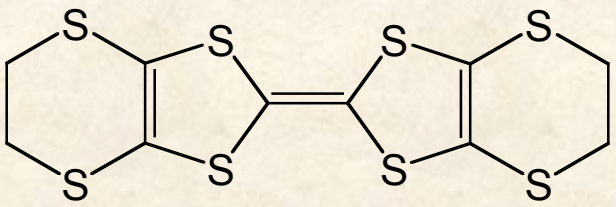
… An extensive work to shift the Fermi level by replacing part of Cu(I) with Cu(II) has so far been unsuccessful for κ-$(ET)_2Cu(NCS)_2$, however, successful in a very limited range in κ-$(ET)_2(Cu^I_{2-x-y}Cu^{II}_x)\{(CN)_{3-2y}[N(CN)_2]_y\}$ [24]. A uni-axial strain of 1 kbar applied along the c-axis of κ-$(ET)_2Cu(NCS)_2$ increases T_c by 1 K [25] owing to the much flattened 1D like Fermi surface under pressure as expected from the band calculation giving rise to an enhancement of electron correlation. A uni-axial strain along the b-axis monotonically decreases T_c, probably due to the increase of the bandwidth and hence the decrease of $D(\varepsilon_F)$.





Calculated Fermi surface (top), energy dispersion (bottom left) and density of states $D(\varepsilon)$ (bottom right) of the organic network of κ-$(ET)_2Cu(NCS)_2$

Electronic Structure of the Superconductor κ-$(ET)_2Cu(NCS)_2$



BEDT-TTF (ET)

4 molecules per unit cell

⇩

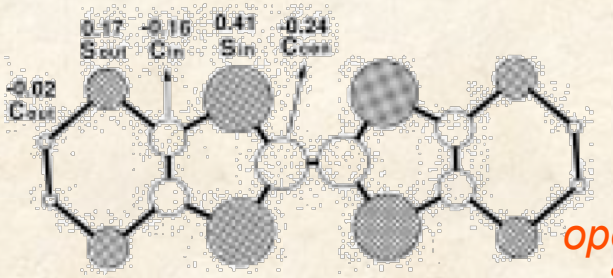
4 HOMOs (basis set)

⇩

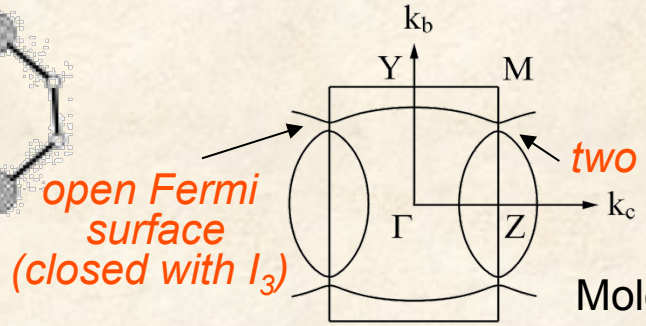
4 crystal orbitals (k)

⇩

4 bands (E(k))

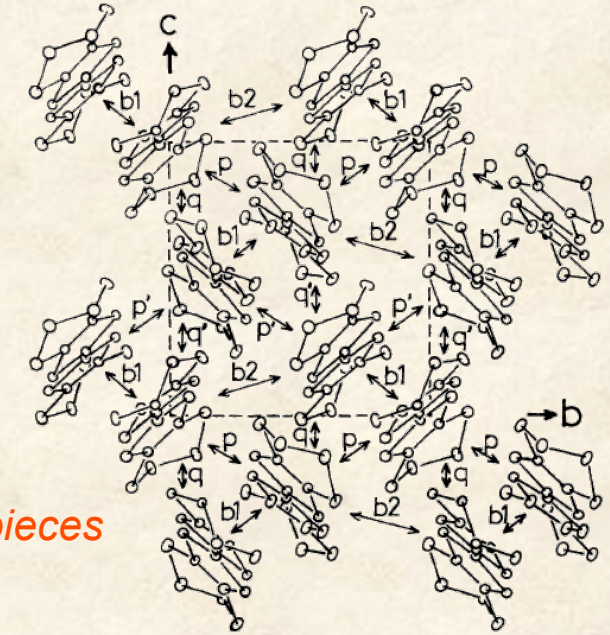


HOMO of BEDT-TTF

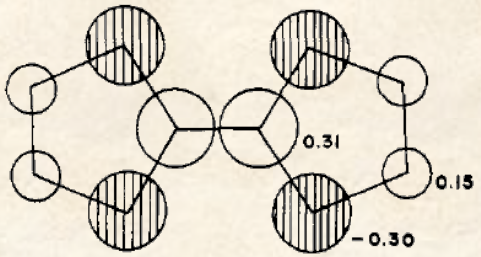


open Fermi surface (closed with I_3)

two pieces

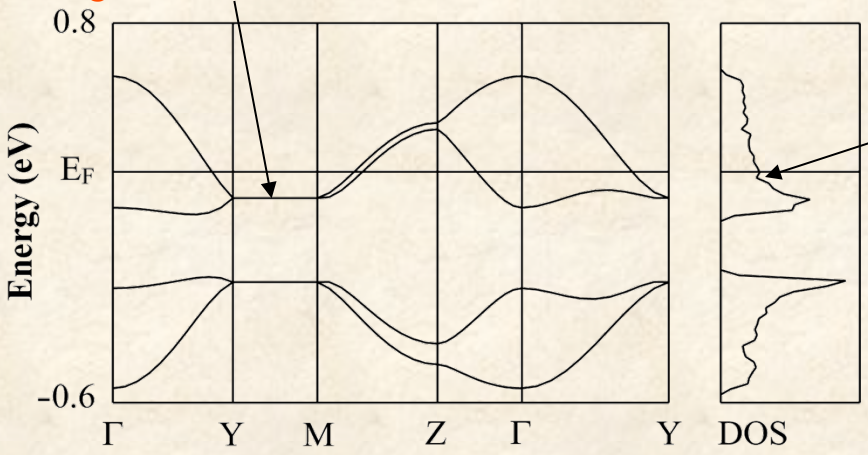


Molecular arrangement of ET molecules



HOMO of TTF

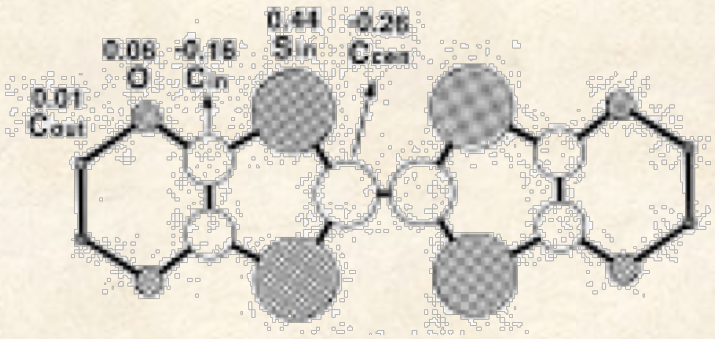
degenerate bands



metal character

Calculated Fermi surface (top), energy dispersion (bottom left) and density of states $D(\varepsilon)$ (bottom right) of the organic network of κ-$(ET)_2Cu(NCS)_2$

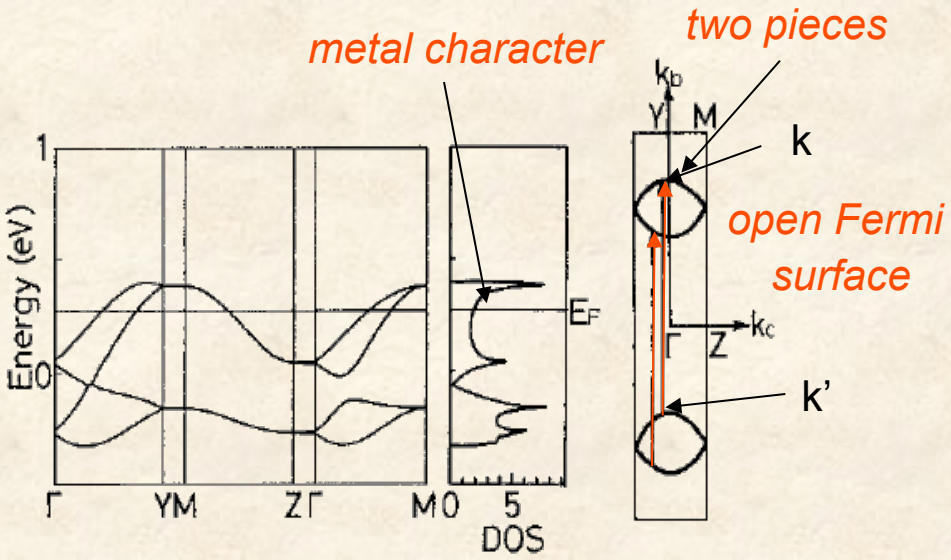
Electronic Structure of some (BEDO-TTF) Complexes



HOMO of BEDO-TTF

4 BEDO-TTF per unit cell

(d)

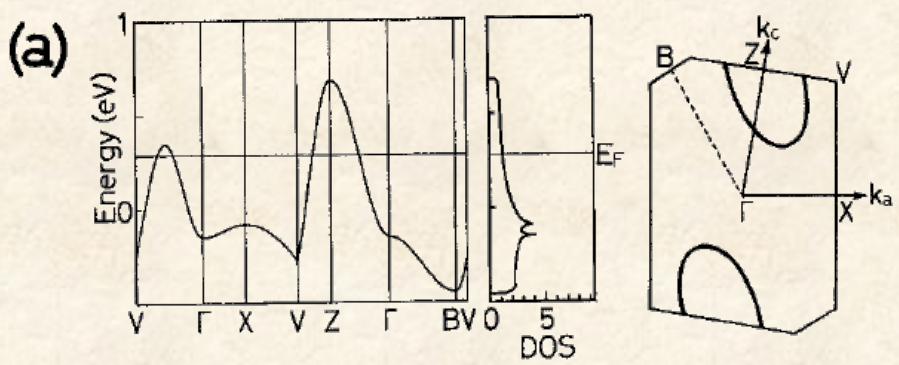


$(BEDO\text{-}TTF)_5(HCP)(PhCN)_{0.2}$

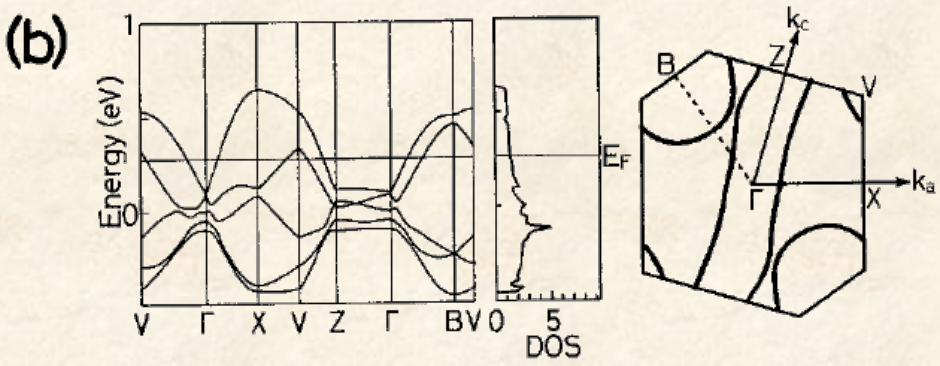
Calculated band structures, density of states (DOS), and Fermi surface of (d) $(BEDO\text{-}TTF)_5(HCP)(PhCN)_{0.2}$. The nesting vector **q** is represented by arrows in d.

Two Fermi surfaces superposed to each other by translation vector **q** = 3/5 *b**(**q** = k - k' (k = 0.3 π/b)) (arrows in Figure). This nesting of the Fermi surface (often seen in the quasi-1D materials) typically causes a CDW- or SDW-associated metal-insulator transition.

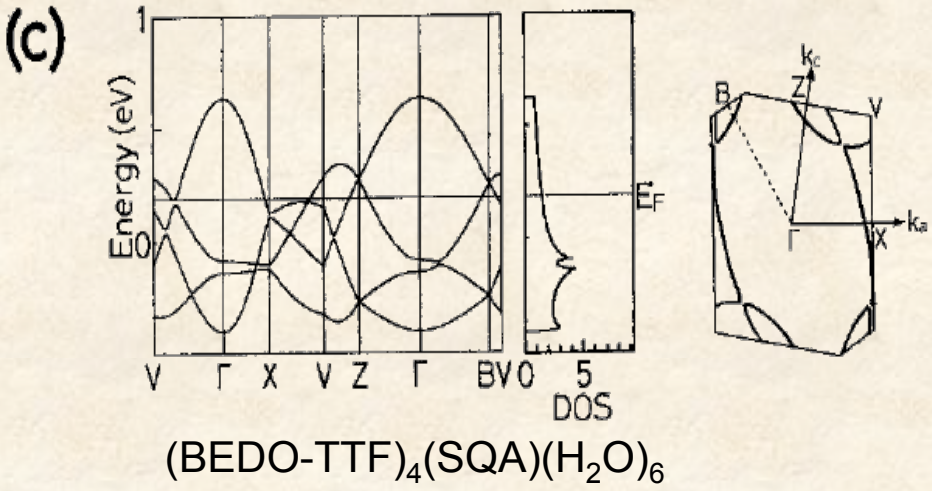
Electronic Structure of some (BEDO-TTF) Complexes



$(BEDO\text{-}TTF)_{10}(CF)_4(H_2O)_3$



$(BEDOTTF)_5(HCTMM)(PhCN)_2$



$(BEDO\text{-}TTF)_4(SQA)(H_2O)_6$

hole pocket around X (band nearly empty)
electron pockets around B and Z (band nearly full)

Calculated band structures, densities of states (DOS), and Fermi surfaces of (a) $(BEDO\text{-}TTF)_{10}(CF)_4(H_2O)_3$, (b) $(BEDO\text{-}TTF)_5(HCTMM)(PhCN)_2$, and (c) $(BEDO\text{-}TTF)_4(SQA)(H_2O)_6$.

⇨ *2D-metals*

Home Work: What is the Band Structure of $(EDO\text{-}TTF)_2PF_6$?

Gigantic Photoresponse in ¼-Filled-Band Organic Salt $(EDO\text{-}TTF)_2PF_6$

Matthieu Chollet,[1] Laurent Guerin,[1,2] Naoki Uchida,[3] Souichi Fukaya,[1] Hiroaki Shimoda,[1] Tadahiko Ishikawa,[1] Kazunari Matsuda,[3] Takumi Hasegawa,[4] Akira Ota,[5] Hideki Yamochi,[5,6] Gunzi Saito,[5] Ryoko Tazaki,[7,8,9] Shin-ichi Adachi,[7,8] Shin-ya Koshihara[1,7,8]*

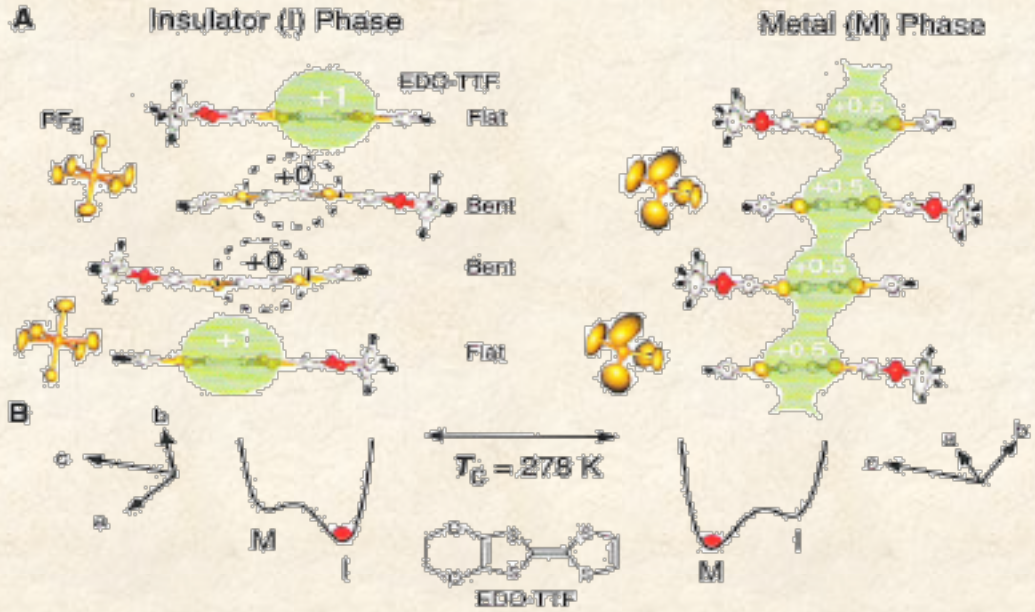
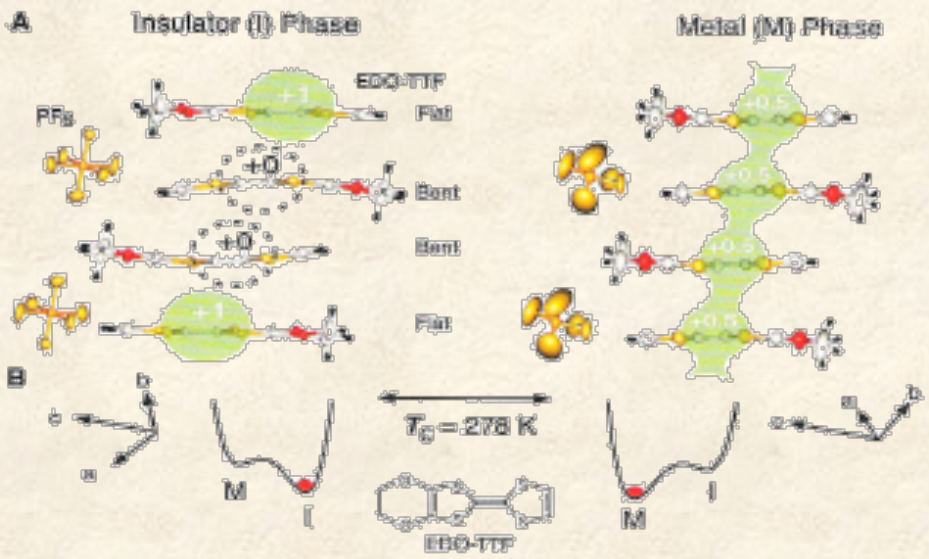


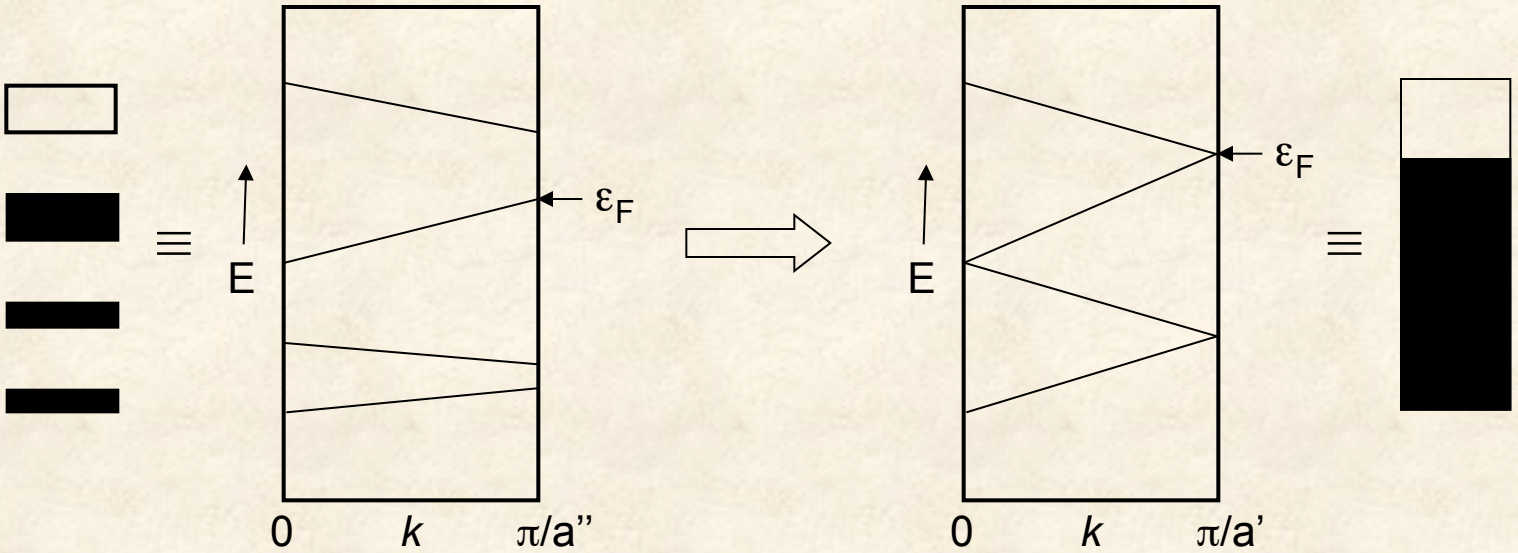
Fig. 1. (A) Schematic views of the lattice and electronic structural changes accompanying the M-I phase transition in $(EDO\text{-}TTF)_2PF_6$. A side view of an EDO-TTF molecule is shown. The unit cell includes two and four EDO-TTF molecules in M and I phases, respectively (15). In the I phase, holes are localized on EDO-TTF molecules with a flat structure due to CO_2 and quasi-neutral molecules show a bent structure. In the M phase, charges (holes) are delocalized and PF_6 (acceptor) molecules exhibit disorder (15–18). (B) Schematics for free energy change accompanying M-I transition and the structure of the EDO-TTF molecule.

Science **2005**, *307*, 86-89

Home Work: What is the Band Structure of $(EDO\text{-}TTF)_2PF_6$?



Expected band structure (four EDO-TTF molecules per unit cell):



Additional Reading

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