

Elementary Band Theory for Extended Solids

Recipe for the construction of simple band structures

- 1) determine the valence-orbitals and the number of valence-electrons;
- 2) determine the relative energies of the valence-orbitals [using MO theory if necessary];
- 3) see how they depend on k [e.g., do the bands run uphill or downhill; are they steep or flat];
- 4) sketch the band structure (Fermi level!);
- 5) plot the projection onto the DOS.

Example: Krogman's salt

$K_2[Pt(CN)_4] \cdot 3H_2O$: white insulator, $\sigma = 10^{-7} \Omega^{-1}cm^{-1}$

$K_2[Pt(CN)_4]Cl_{0.3} \cdot 3H_2O$: bronze metal, $\sigma = 10^{+2} \Omega^{-1}cm^{-1}$

Comparison of specific conductivities

Semiconductors Si: $\sigma = 10^{-6} \Omega^{-1}cm^{-1}$

Ge: $\sigma = 10^{-2} \Omega^{-1}cm^{-1}$;

Metals

Cu: $\sigma = 10^{+6} \Omega^{-1}cm^{-1}$.

Krogman's salt: a quasi one-dimensional material

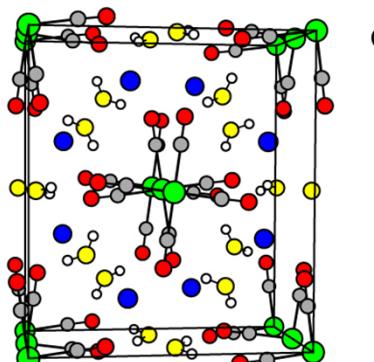
Step 1: valence-orbitals, electron-counting

$K_2[Pt(CN)_4] \cdot 3H_2O$: K^+ , CN^-

=> Pt^{+2} , d^8

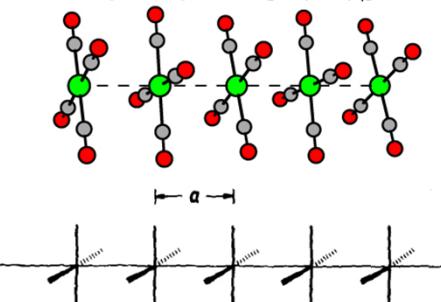
Step 2: relative energies of the valence-orbitals (here: d orbitals)

understanding of **the crystal structure** required!



Unit cell of $K_2[Pt(CN)_4] \cdot 3H_2O$

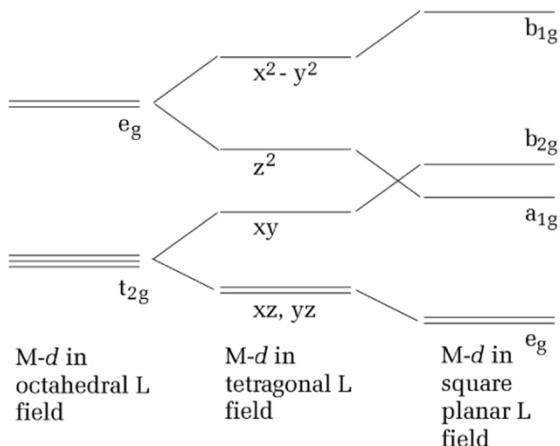
Chain of **square planar** $[Pt(CN)_4]^{2-}$ units



Krogman's salt: a quasi one-dimensional material

Step 2: continued

MO diagram of **square planar** $[\text{Pt}(\text{CN})_4]^{2-}$ (D_{4h} symmetry)

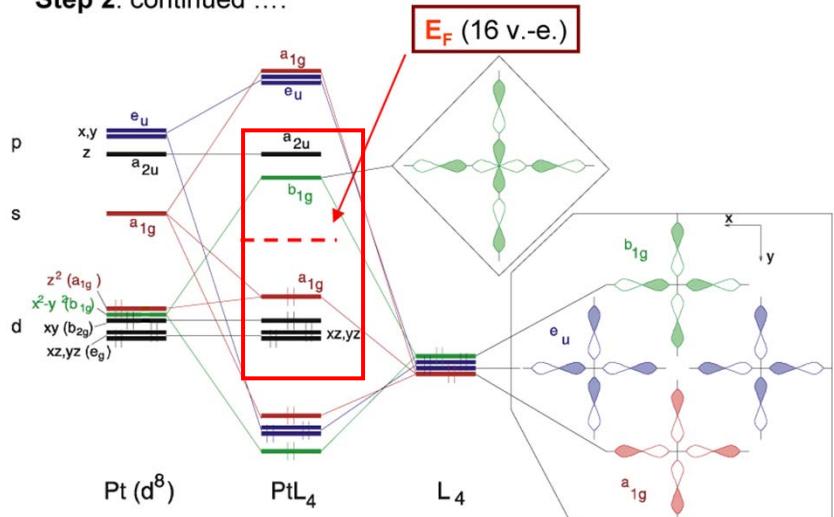


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D_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2; z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	$(R_x; R_y)$	$(xz; yz)$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	$(x; y)$	

Krogman's salt: a quasi one-dimensional material

Step 2: continued



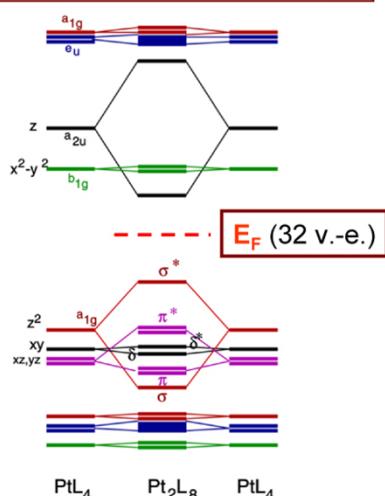
The complete MO of PtL_4

DeKock and Gray, *Chemical Structure and Bonding*, 2nd Ed., University Science Books, 1989

Krogman's salt: a quasi one-dimensional material

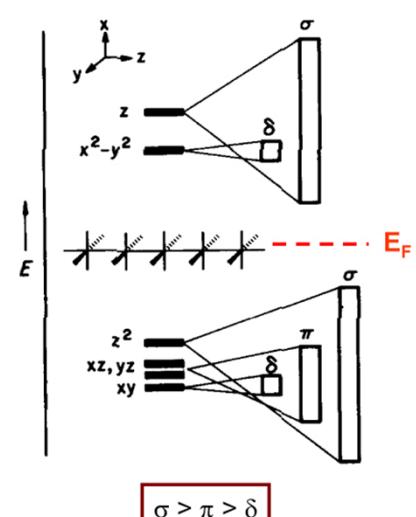
Step 2: continued

Relative height of p_z vs. $d_{x^2-y^2}$?



Formation of PtL_4 pairs

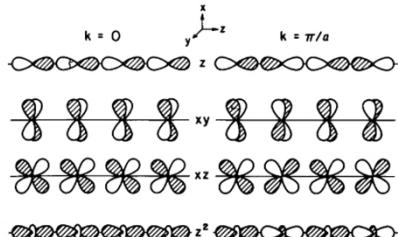
Step 3: determine how the bands run
? Bandwidths ?



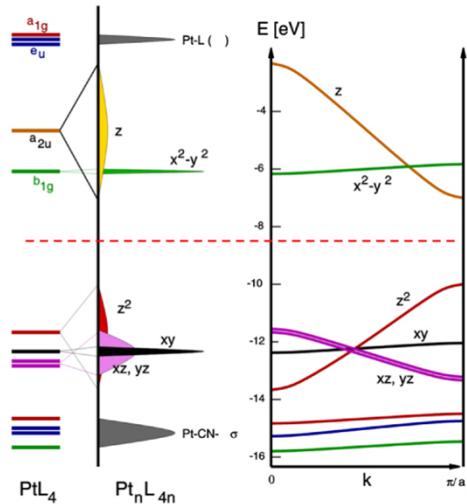
Krogman's salt: a quasi one-dimensional material

Step 3: continued

? Uphill or downhill ?
Zone center vs. zone border,

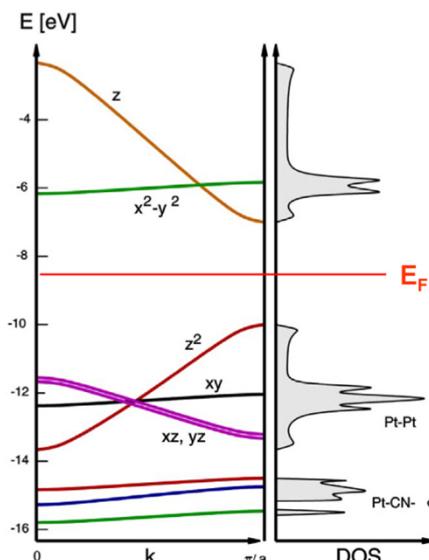


Step 4: sketch the band structure



Krogman's salt: a quasi one-dimensional material

Step 5: sketch the DOS



Large bandgap (> 3 eV) => white insulator

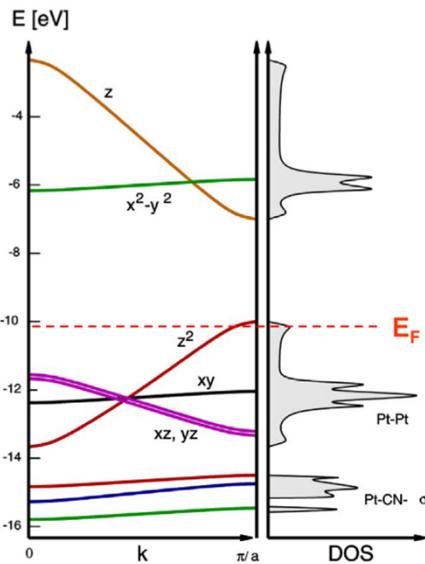
Krogman's salt: a quasi one-dimensional material

$\text{K}_2[\text{Pt}(\text{CN})_4]$ vs. $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.3}$: what are the differences?

Assuming the same band structure (the same crystal structure):
 Fermi level will be lower ($d^{7.7}$ instead of d^8)

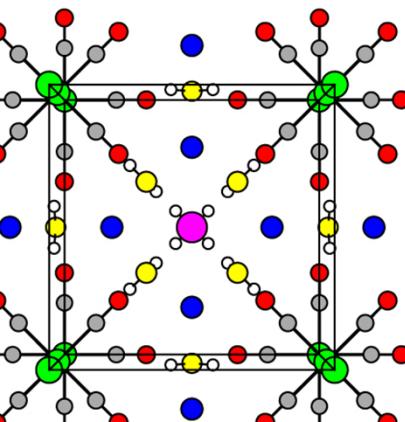
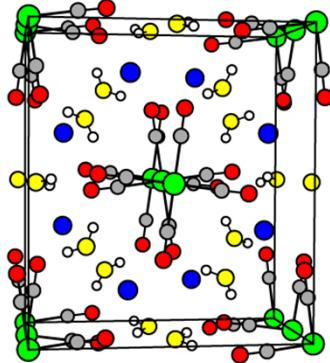
Partly filled d_{z^2} band
 \Rightarrow itinerant electrons along the c^* direction
 \Rightarrow **metallic conductivity** along c^*

BUT is the crystal structure the same?



Krogman's salt: a quasi one-dimensional material

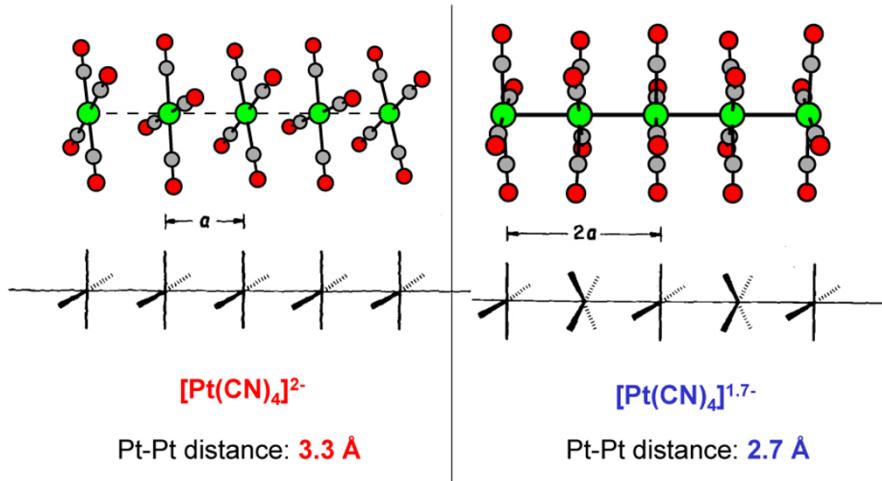
$\text{K}_2[\text{Pt}(\text{CN})_4]$ vs. $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.3}$: what are the differences?



Krogman's salt: a quasi one-dimensional material

$\text{K}_2[\text{Pt}(\text{CN})_4]$ vs. $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.3}$: what are the differences?

Chains of **square planar** $[\text{Pt}(\text{CN})_4]^{x-}$ units: "eclipsed" vs. staggered

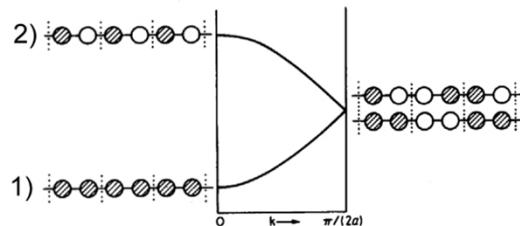


Why is the Pt-Pt distance shorter? Why staggered conformation?

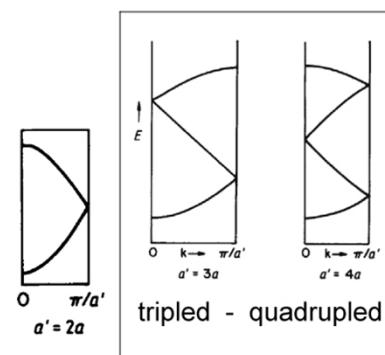
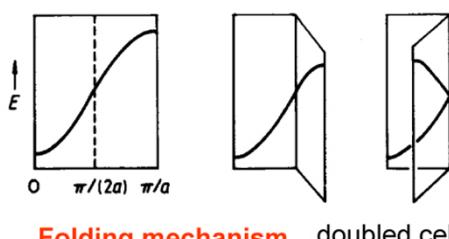
Krogman's salt: a quasi one-dimensional material

1) What are the consequences of the cell doubling?

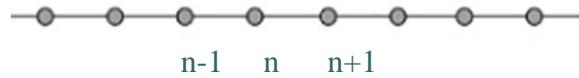
Doubled direct cell \Rightarrow half reciprocal cell



2 basis orbitals:
1) 2)

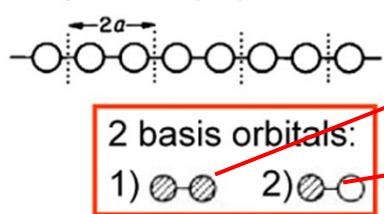
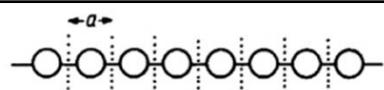


Folding mechanism doubled cell



$$E(k) = \langle e^{-ikna} \phi_n | \hat{H} | \{ e^{ik(n-1)a} \phi_{n-1} + e^{ikna} \phi_n + e^{ik(n+1)a} \phi_{n+1} \} \rangle$$

$$\dots = \alpha + 2\beta \cos ka$$



$$\psi_1(k) = \sum_n e^{ink \cdot 2a} (\phi_{2n} + \phi_{2n+1})$$

$$\psi_2(k) = \sum_n e^{ink \cdot 2a} (\phi_{2n} - \phi_{2n+1})$$

$$E_1(k)(2\text{-atom\,-basis}) =$$

$$e^{-ikn \cdot 2a} \cdot e^{ik(n-1) \cdot 2a} \langle (\phi_{2n} + \phi_{2n+1}) | \hat{H} | (\phi_{2n-2} + \phi_{2n-1}) \rangle$$

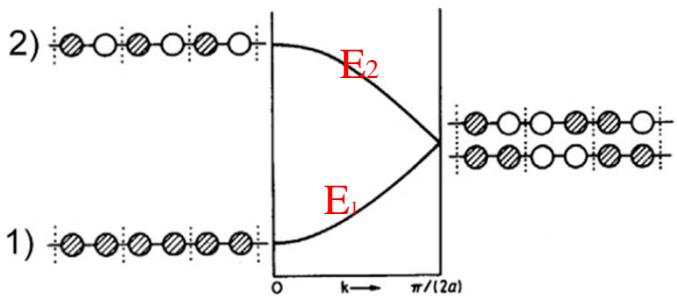
$$+ e^{-ikn \cdot 2a} \cdot e^{ik(n+1) \cdot 2a} \langle (\phi_{2n} + \phi_{2n+1}) | \hat{H} | (\phi_{2n+2} + \phi_{2n+3}) \rangle$$

$$= e^{-ik \cdot 2a} \beta + 2\alpha + 2\beta + e^{ik \cdot 2a} \beta$$

$$= 2\alpha + 2\beta + 2\beta \cos 2ka$$

Similarly:

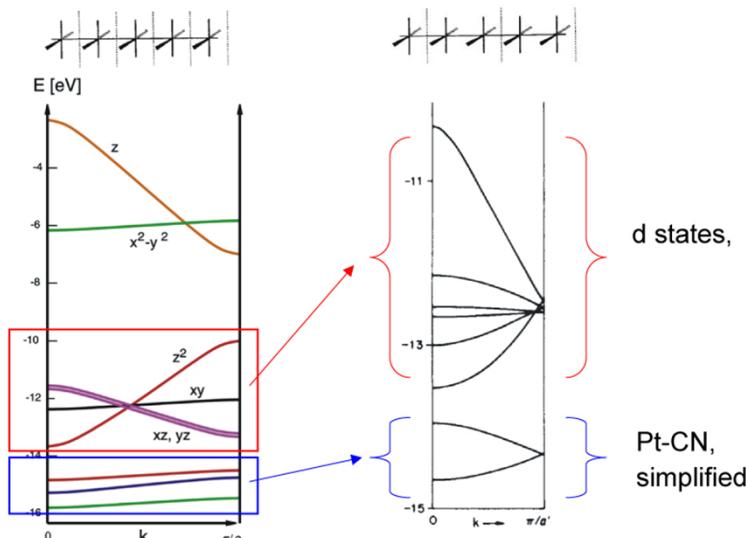
$$\begin{aligned}
 E_2(k)(2\text{-atom-basis}) &= \\
 e^{-ikn\cdot 2a} \cdot e^{ik(n-1)\cdot 2a} &\langle (\phi_{2n} - \phi_{2n+1}) | \hat{H} | (\phi_{2n-2} - \phi_{2n-1}) \rangle \\
 + e^{-ikn\cdot 2a} \cdot e^{ikn\cdot 2a} &\langle (\phi_{2n} - \phi_{2n+1}) | \hat{H} | (\phi_{2n} - \phi_{2n+1}) \rangle \\
 + e^{-ikn\cdot 2a} \cdot e^{ik(n+1)\cdot 2a} &\langle (\phi_{2n} - \phi_{2n+1}) | \hat{H} | (\phi_{2n+2} - \phi_{2n+3}) \rangle \\
 = -e^{-ik\cdot 2a} \beta + 2\alpha - 2\beta - e^{ik\cdot 2a} \beta \\
 = 2\alpha - 2\beta - 2\beta \cos 2ka
 \end{aligned}$$



Krogman's salt: a quasi one-dimensional material

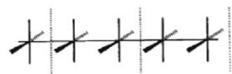
1) What are the consequences of the cell doubling?

=> apply the folding mechanism

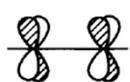


Krogman's salt: a quasi one-dimensional material

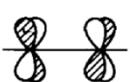
2) What are the consequences of the staggering?



d_{xy} states:



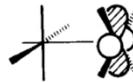
δ bonding



δ antibonding



d_{xy} states:

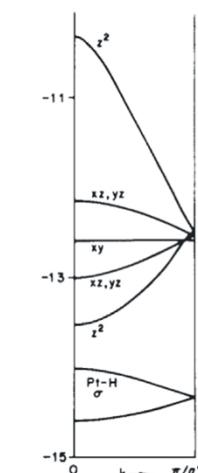
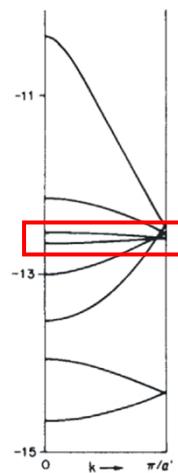


nonbonding

=> does not depend on k

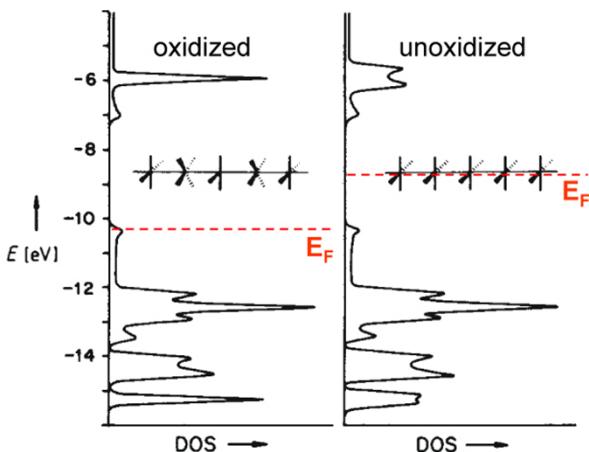
Krogman's salt: a quasi one-dimensional material

2) What are the consequences of the staggering?



Krogman's salt: a quasi one-dimensional material

Comparison of the densities of states

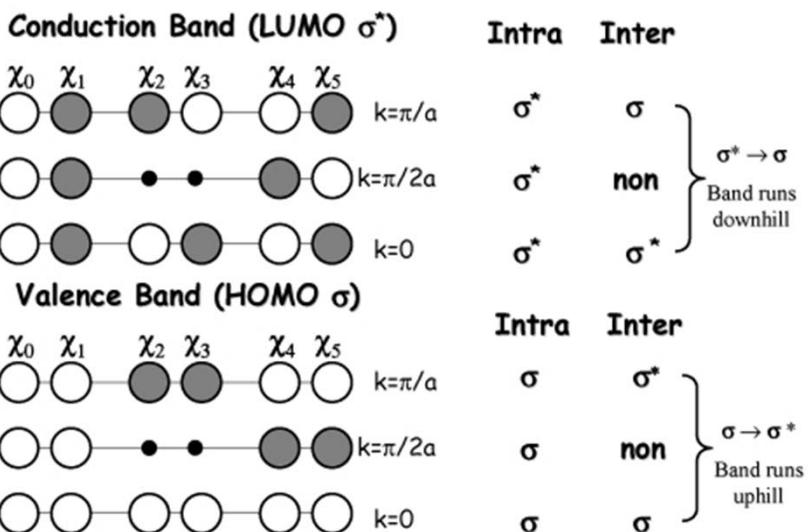


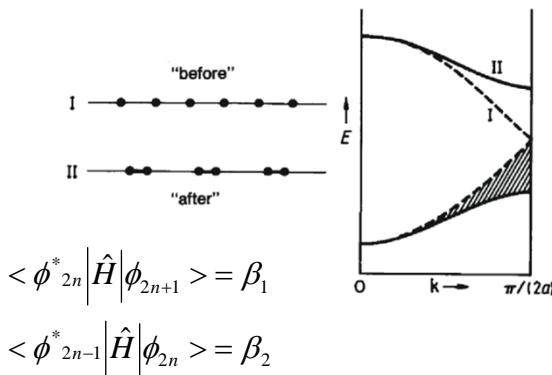
Calculations **in agreement with** the observations:

$\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$:	white insulator, $\sigma = 10^{-7} \Omega^{-1}\text{cm}^{-1}$
$\text{K}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.3} \cdot 3\text{H}_2\text{O}$:	bronze metal, $\sigma = 10^{+2} \Omega^{-1}\text{cm}^{-1}$

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Peierls Distortion (H_2 Chain)



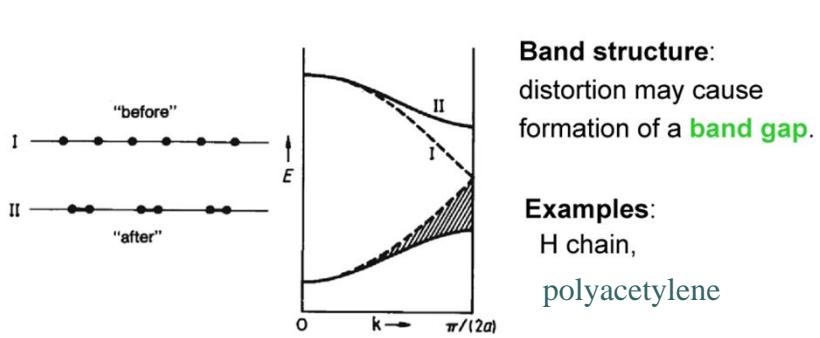
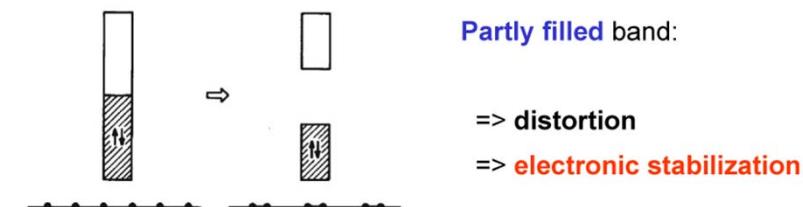


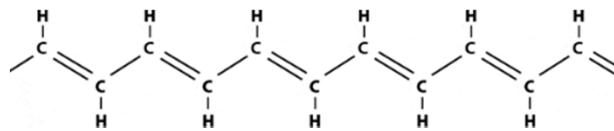
$$E_1 = \alpha + \beta_1 + \beta_2 \cos 2ka$$

$$E_2 = \alpha - \beta_1 - \beta_2 \cos 2ka$$

Elementary Band Theory for Extended Solids

Distortions: in solids (charge density waves/Peierls)





*Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa
Nobel Prize in Chemistry 2000.*

Oxidation with halogen (*p*-doping):



Reduction with alkali metal (*n*-doping):

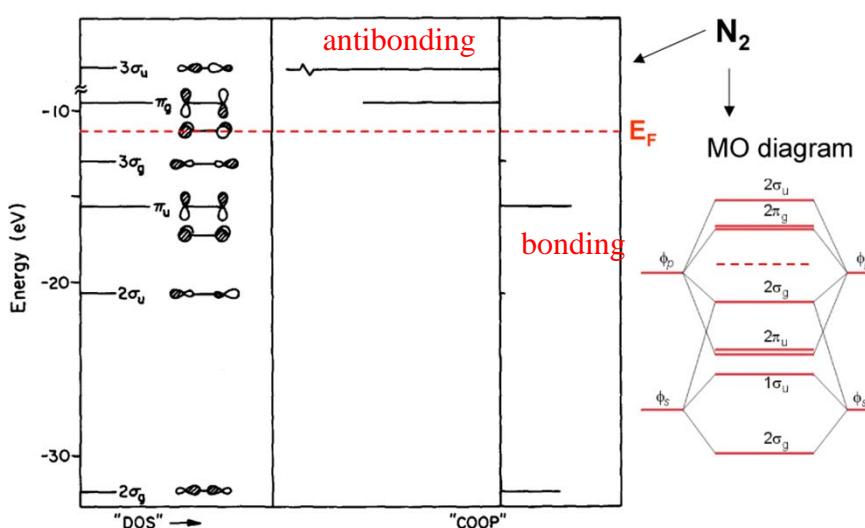


Elementary Band Theory for Extended Solids

Analysis of the bonding situation:

COOP = Crystal Orbital Overlap Population;

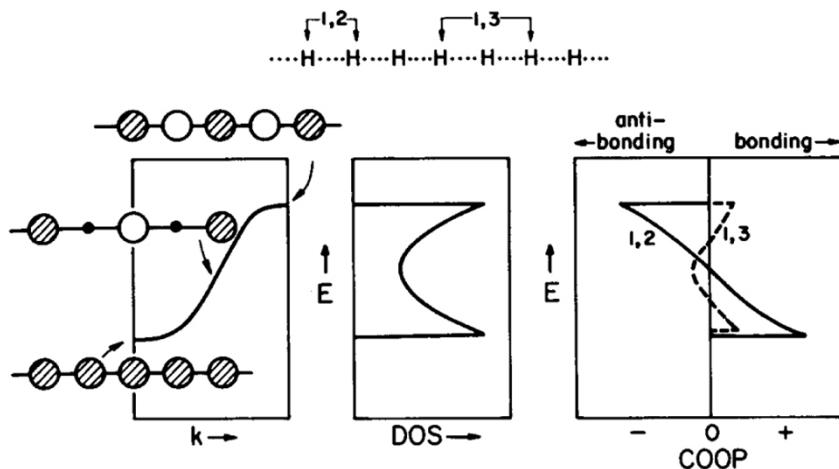
obtained by weighing the DOS
according to bonding/antibonding



Elementary Band Theory for Extended Solids

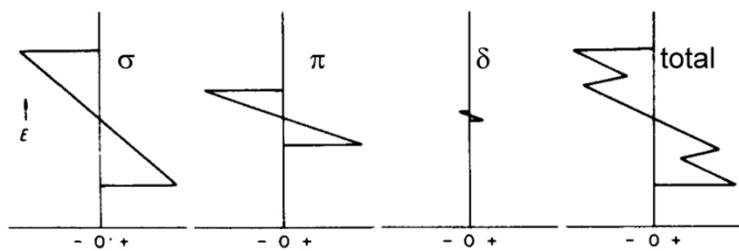
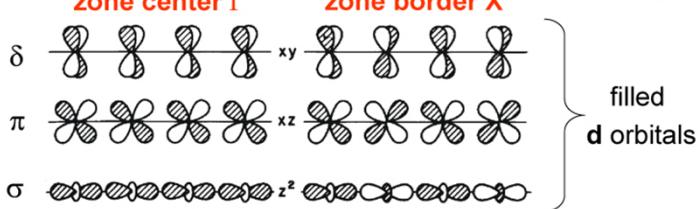
COOP = Crystal Orbital Overlap Population

Simple Hückel



Krogman's salt: a quasi one-dimensional material

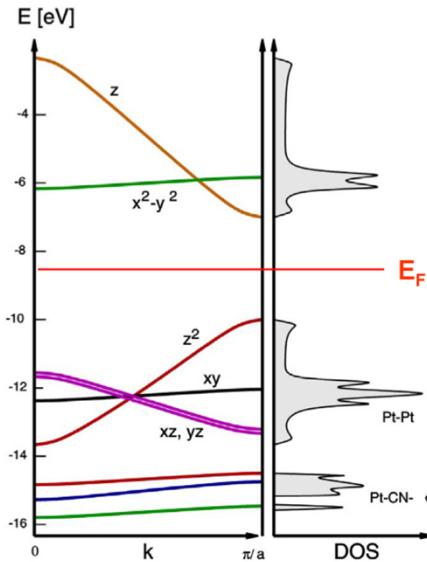
Simple Hückel



Strength of the interactions: $\sigma > \pi > \delta$

Krogman's salt: a quasi one-dimensional material

Step 5: sketch the DOS



Large bandgap (> 3 eV) => white insulator

Krogman's salt: a quasi one-dimensional material

Complete calculated DOS and COOP

