

# Electronic Structure

- Drude theory
- Free electron gas
- Nearly free electron model
- Tight-binding model
- Semiconductors

*Reading: A/M 1-3,8-10*

*G/S 7,11*

*Hoffmann p. 1-20*

# DC ELECTRICAL CONDUCTIVITY

A constant electric field  $\mathbf{E}$  results in an electrical current per unit area  $\mathbf{J}$ :

$$\mathbf{J}(\mathbf{r}) = \sigma \mathbf{E}(\mathbf{r})$$

where the proportionality constant  $\sigma$  is the **electrical conductivity**

$J$  (current density):  $A \text{ cm}^{-2}$

$E$  (field):  $V \text{ cm}^{-1}$

$\sigma$  (conductivity):  $A \text{ V}^{-1} \text{ cm}^{-1}$  (or  $\Omega^{-1} \text{ cm}^{-1}$ )

if the conductivity is a constant (field-independent), we have **Ohm's Law**

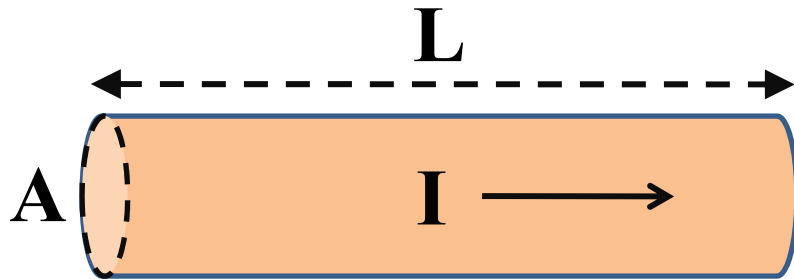
large  $\sigma$  = conductor (metal)  
moderate  $\sigma$  = semiconductor  
small  $\sigma$  = insulator

$$V = IR$$

the inverse of the conductivity is the **resistivity**,  $\rho$

$$\rho = \frac{1}{\sigma}$$

# RESISTIVITY FORMULA



$I$  = current

$A$  = x-sectional area of wire

$L$  = length of wire

$$\mathbf{J} = \sigma \mathbf{E}$$

$$\mathbf{E} = \rho \mathbf{J}$$

$$\mathbf{E} = \rho I/A$$

voltage drop:  $V = EL$

$$V/L = \rho I/A$$

$$\mathbf{R} = \rho L/A$$

$\rho$  is a material property, independent of geometry,  
with units of ohm·cm

# Resistivities of Real Materials

Compound	Resistivity ( $\Omega\text{-cm}$ )	Compound	Resistivity ( $\Omega\text{-cm}$ )
<i>Ca</i>	$3.9 \times 10^{-6}$	<i>Si</i>	$\sim 0.1$
<i>Ti</i>	$42 \times 10^{-6}$	<i>Ge</i>	$\sim 0.05$
<i>Mn</i>	$185 \times 10^{-6}$	<i>ReO<sub>3</sub></i>	$36 \times 10^{-6}$
<i>Zn</i>	$5.9 \times 10^{-6}$	<i>Fe<sub>3</sub>O<sub>4</sub></i>	$52 \times 10^{-6}$
<i>Cu</i>	$1.7 \times 10^{-6}$	<i>TiO<sub>2</sub></i>	$9 \times 10^4$
<i>Ag</i>	$1.6 \times 10^{-6}$	<i>ZrO<sub>2</sub></i>	$1 \times 10^9$
<i>Pb</i>	$21 \times 10^{-6}$	<i>Al<sub>2</sub>O<sub>3</sub></i>	$1 \times 10^{19}$

Most semiconductors in their pure form are not good conductors, they need to be doped to become conducting.

Not all so called "ionic" materials like oxides are insulators.



# DRUDE MODEL (1900)

classical (Newtonian) theory of electrical conductivity in metals

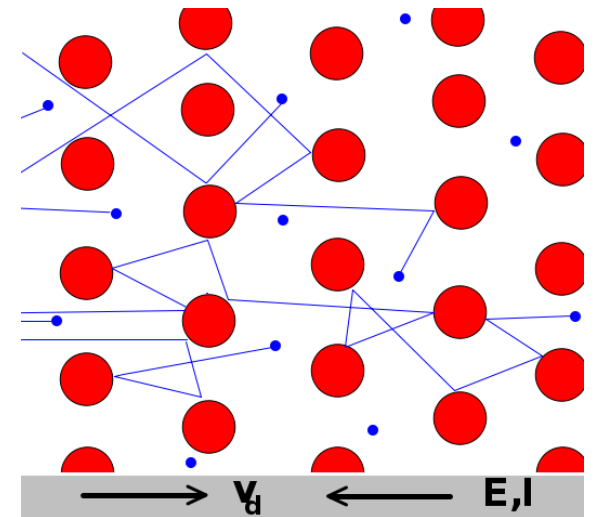
Kinetic theory of gases applied to electrons in a metal. Metal treated as a “gas” of mobile valence electrons moving against a background of immobile ions.

Conductivity is determined by electrons colliding with “scatterers”. Assumptions:

1. no electron-electron forces (**independent electron approximation**)
2. between collisions, no electron-ion forces (**free electron approx.**)
3. collisions are instantaneous, leading to abrupt changes in  $e^-$  velocity
4. collisions randomize the  $e^-$  velocity to a thermal distribution
5. there is a mean time between collisions of  $\tau$  (**collision time**)

$$P = \frac{dt}{\tau}$$

Probability of an electron undergoing a collision during time interval  $dt$



If  $n$  electrons per unit volume move with velocity  $\mathbf{v}$  across an area  $A$  in time  $dt$ , the charge crossing this area in time  $dt$  is  $-nevAdt$

$$\mathbf{J} = -nev$$

This is the *net* current density (the net **drift current**)

Let's find an expression for the average electron velocity (the **drift velocity**). Without a field,  $\langle \mathbf{v} \rangle = 0$ . But with a field  $\mathbf{E}$ ,

$$\mathbf{v} = \mathbf{a}t = \mathbf{F}t/m = -e\mathbf{E}t/m$$

average time between collisions is  $\tau$ , so:  $\mathbf{v}_{\text{drift}} = -e\mathbf{E}\tau/m$

$$\mathbf{J} = -nev = \left( \frac{ne^2\tau}{m} \right) \mathbf{E} = \sigma \mathbf{E} ; \quad \sigma = \frac{ne^2\tau}{m}$$

# CARRIER MOBILITY

The proportionality constant between the absolute drift velocity and the electric field is called the **electron mobility**,  $\mu$ :


$$|\mathbf{v}_{\text{drift}}| = \left( \frac{e\tau}{m} \right) \mathbf{E} = \mu \mathbf{E} \quad ; \quad \mu = \frac{e\tau}{m} \quad ; \quad \sigma = ne\mu$$


Note:  $\tau$  is the collision time, not the electron lifetime!

TABLE 7.1 Parameters of Some Metals at  $T = 295 \text{ K}$

Metal	Atomic Number $A$	Valence $z$	Mass Density $\rho_m$ ( $10^3 \text{ kg/m}^3$ )	Electron Density $n$ ( $10^{29} \text{ m}^{-3}$ )	Conductivity $\sigma$ [ $10^6(\Omega \cdot \text{m})^{-1}$ ]	Collision Time $\tau$ ( $10^{-15} \text{ s}$ )
Ag	107.9	1	10.5	0.585	62.1	37.6
Al	26.98	3	2.70	1.81	36.5	7.17
Ba	137.3	2	3.59	0.315	2.6	2.93
Be	9.012	2	1.82	2.43	30.8	4.50
Ca	40.08	2	1.53	0.460	27.8	21.5
Cd	112.4	2	8.65	0.927	13.8	5.29
Cs	132.3	1	2.00	0.091	5.0	19.5
Cu	63.55	1	8.93	0.846	58.8	24.7
In	114.8	3	7.29	1.15	11.4	3.53
K	39.10	1	0.91	0.140	13.9	35.2
Li	6.939	1	0.54	0.469	10.7	8.11
Mg	24.31	2	1.74	0.862	22.3	9.18

# PREDICTIONS OF DRUDE THEORY

predicted collision time:  $\tau = \frac{\sigma m}{ne^2}$    $10^{-15} - 10^{-14}$  sec

predicted **mean free path**:  $l = v_0 \tau$    $1 - 10$  Å

↑

average electronic speed:  $\sim 10^5$  m/s from equipartition theory

but experimental mean free paths can be  $10^3 - 10^8$  Å

**→ electrons do not simply bounce off the ions!**

Drude model provides good explanations of:

1. DC and AC conductivity of metals
2. Hall effect (magnitude, but not sign)
3. Wiedemann-Franz Law ( $\kappa / \sigma = LT$ )
4. thermal conductivity due to electrons near room temperature

but, since it uses classical statistical mechanics (Maxwell-Boltzmann), it gets most other quantities wrong (heat capacity, thermopower, etc.).

# SOMMERFELD THEORY

the simplest quantum mechanical theory of electrons in metals

**Applies Pauli Exclusion Principle to kinetic gas theory.** Ignores *all* forces except the confining surfaces of the solid, treating electrons as free & indy particles in a box.

The quantum mechanical (QM) treatment has two major effects:

1. only electrons with certain wave vectors (energies) are allowed
2. quantum statistical mechanics (**Fermi-Dirac distribution**)  
→ the Pauli exclusion principle must be obeyed (one e<sup>-</sup> per state)

The allowed energy levels for an electron in a 3D box of volume  $V$  are found by solving the (time-independent) **Schrödinger equation**

$$H\psi = E\psi$$

where the **Hamiltonian**,  
(the energy operator) is:

$$H = \frac{p^2}{2m} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2$$

the Schrödinger equation becomes:  $-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi$

the general solution is a plane wave:  $\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}$

with energy:  $E(\mathbf{k}) = \frac{1}{2} m v^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

electrons in the metal behave as plane waves of wave vector  $\mathbf{k}$

$$\mathbf{p} = m\mathbf{v} = \hbar\mathbf{k} \quad ; \quad k = \frac{2\pi}{\lambda}$$

we next see that the boundary conditions restrict  $k$  to discrete values

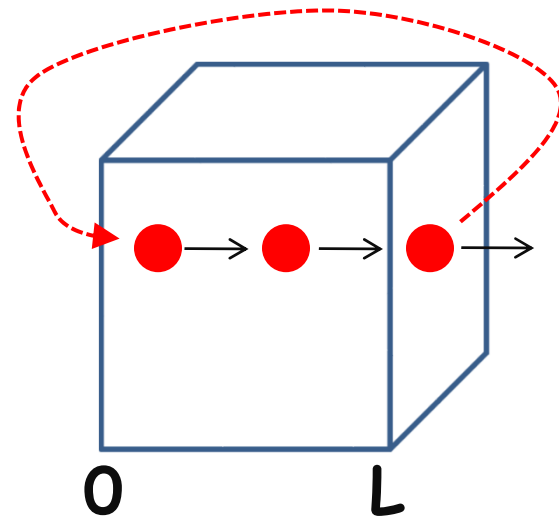
we require that the electrons stay in the crystal, and this places a constraint on the allowed values of  $k$

we apply **Born-von Karman (periodic) boundary conditions** to keep the electrons in the metal. For a cubic crystal of edge length  $L$ ,

$$\psi(x + L, y, z) = \psi(x, y, z)$$

$$\psi(x, y + L, z) = \psi(x, y, z)$$

$$\psi(x, y, z + L) = \psi(x, y, z)$$



this condition is met only when:  $e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$

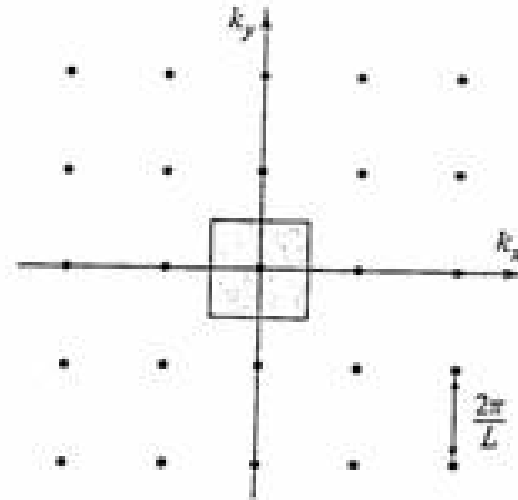
in other words:  $k_x = \frac{2\pi n_x}{L}$ ;  $k_y = \frac{2\pi n_y}{L}$ ;  $k_z = \frac{2\pi n_z}{L}$

where  $n_x, n_y, n_z$  are integers

# DENSITY OF $k$ -SPACE POINTS in 2D

Figure 2.2

Points in a two-dimensional  $k$ -space of the form  $k_x = 2\pi n_x/L$ ,  $k_y = 2\pi n_y/L$ . Note that the area per point is just  $(2\pi/L)^2$ . In  $d$  dimensions the volume per point is  $(2\pi/L)^d$ .



each electron level occupies an area in  $k$ -space of:

$$\left(\frac{2\pi}{L}\right)^2$$

the number of levels in a large area of  $k$ -space  $\Omega$  is:

$$\frac{\text{total area}}{\text{area per k-point}} = \frac{\Omega}{(4\pi^2 / L^2)} = \frac{\Omega A}{4\pi^2}$$

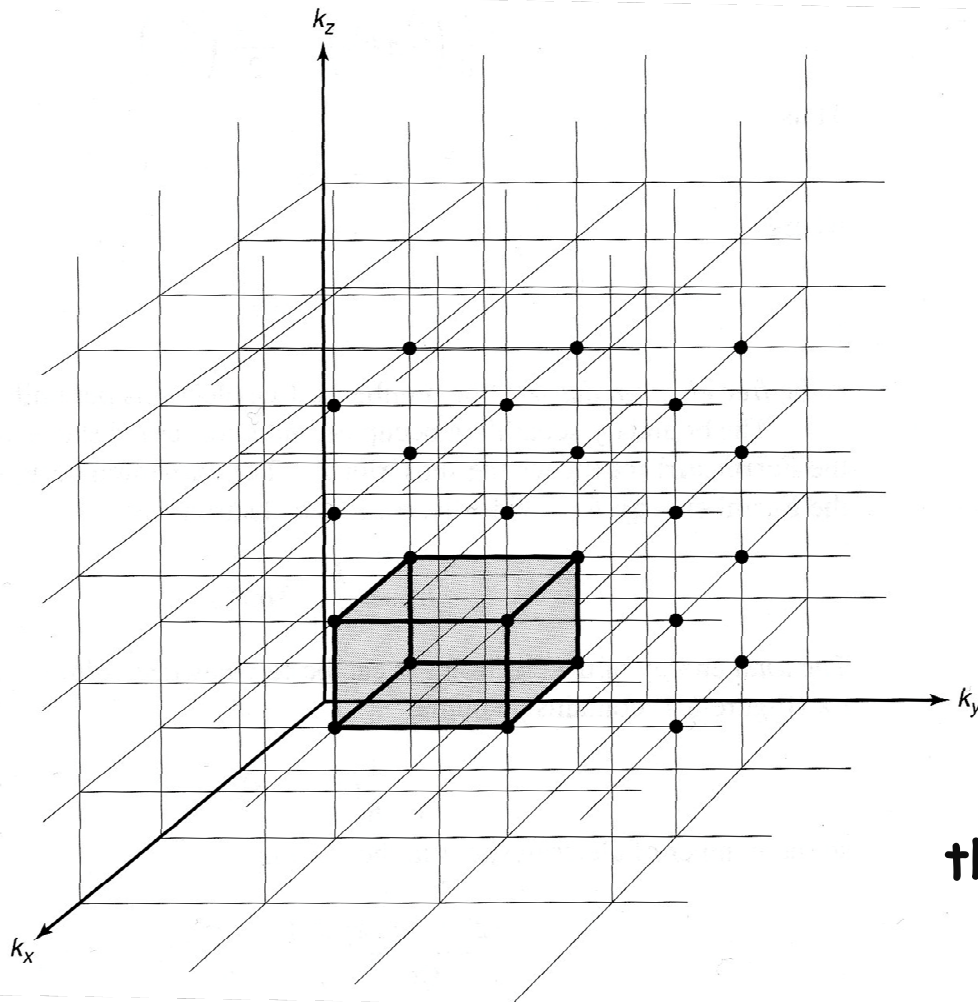
the density of  $k$ -space points per unit area is:

$$\frac{A}{4\pi^2}$$



# 3D CASE

the allowed wave vectors are those whose Cartesian coordinates in  $k$ -space are integral multiples of  $2\pi/L$



each electron level occupies a volume in  $k$ -space of:

$$\left(\frac{2\pi}{L}\right)^3$$

the number of levels in a large volume of  $k$ -space  $\Omega$  is:

$$\frac{\Omega}{(8\pi^3 / L^3)} = \frac{\Omega V}{8\pi^3}$$

the  $k$ -space density of levels is:

$$\frac{V}{8\pi^3}$$

Assume that we have  $N$  electrons in our solid. To build up the ground state of the solid (0 K), we add the electrons one by one into the allowed levels according to the Pauli exclusion principle:

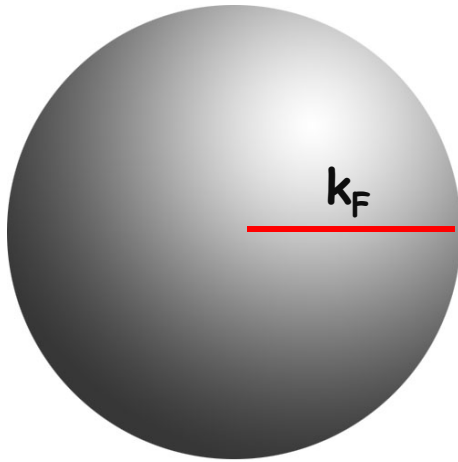
- each allowed wave vector (level) has two electronic states, spin up and spin down

since energy is quadratic in wave vector: 
$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

the lowest energy level corresponds to  $k = 0$  (2 electrons)  
the next lowest is  $|k| = 2\pi/L$  (6 levels, 12 electrons total), etc.

when  $N$  is enormous, the occupied region of  $k$ -space will look like a sphere (the **Fermi sphere**). The radius of this sphere is labeled  $k_F$ :

volume of the Fermi sphere: 
$$\Omega_F = \frac{4}{3} \pi k_F^3$$



at 0 Kelvin, the ground state of the N-electron system is formed by occupying all single-particle levels with k less than  $k_F$

the number of allowed values of k is:  $\left(\frac{4}{3}\pi k_F^3\right)\left(\frac{V}{8\pi^3}\right) = \frac{k_F^3}{6\pi^2}V$

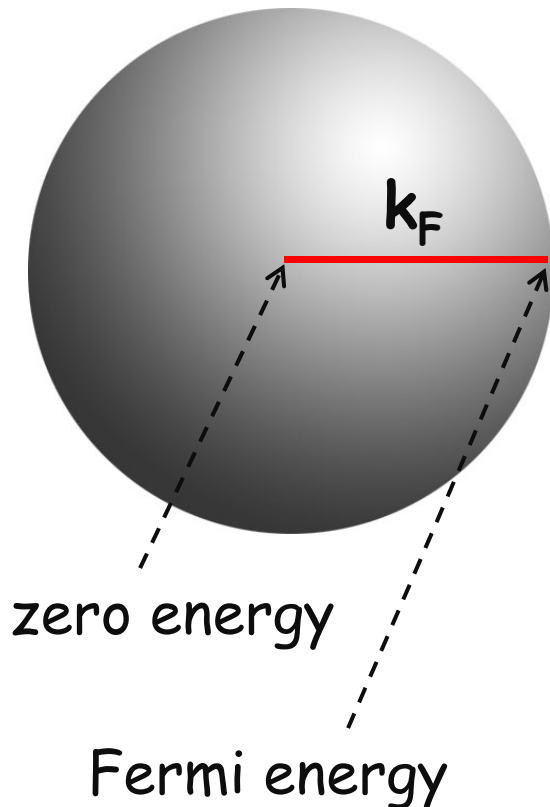
the total number of electrons is twice this:  $N = \frac{k_F^3}{3\pi^2}V$

the free electron density  $n$  is then:  $n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$

# FERMI SPHERE

The surface of the Fermi sphere separates occupied and unoccupied states in k-space.

$$k_F = (3\pi^2 n)^{1/3}$$



- bounded by **Fermi surface**
- radius is **Fermi wave vector**
- **Fermi energy**:  $E_F = \hbar^2 k_F^2 / 2m$
- **Fermi momentum**:  $p_F = \hbar k_F$
- **Fermi velocity**:  $v_F = \hbar k_F / m$
- **Fermi temperature**:  $T_F = E_F / k_B$

**TABLE 7.3 Free-Electron Parameters for Various Metals**

Metal	$k_F$ ( $10^{10} \text{ m}^{-1}$ )	$v_F$ ( $10^6 \text{ m/s}$ )	$E_F$ (eV)	$T_F$ ( $10^3 \text{ K}$ )
Ag	1.20	1.39	5.49	63.7
Al	1.75	2.03	11.7	135
Ba	0.977	1.13	3.64	42.2
Be	1.93	2.23	14.2	165
Ca	1.11	1.28	4.68	54.3
Cd	1.40	1.62	7.47	86.6
Cs	0.646	0.748	1.59	18.4
Cu	1.36	1.57	7.03	81.5
In	1.50	1.74	8.63	100
K	0.745	0.863	2.12	24.6
Li	1.12	1.29	4.74	55.0
Mg	1.37	1.58	7.11	82.5
Na	0.922	1.07	3.24	37.6
Rb	0.698	0.808	1.86	21.5
Sr	1.02	1.18	3.94	45.7
Zn	1.57	1.82	9.40	109

in terms of the free electron density, the energy of the most energetic electrons is:

$$E_F = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m}$$

the total energy of the ground-state electron gas is found by adding up the energies of all the levels within the Fermi sphere.

it's easiest to integrate over concentric shells:

$$E_{tot} = \int_0^{k_F} \underset{\substack{\uparrow \\ \text{spin}}}{2} \cdot \underset{\substack{\uparrow \\ \text{volume of shell of width } dk}}{(4\pi k^2 dk)} \cdot \underset{\substack{\uparrow \\ \text{density of levels}}}{\left(\frac{V}{8\pi^3}\right)} \cdot \underset{\substack{\uparrow \\ \text{energy of levels in this shell}}}{\left(\frac{\hbar^2 k^2}{2m}\right)}$$

$$E_{tot} = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_F} k^4 dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m}$$

by substituting for the volume in terms of N:  $V = \frac{3\pi^2 N}{k_F^3}$  .

we can find the average energy per electron:

$$\frac{E_{tot}}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} E_F$$

The average electron energy at 0 K is 60% of the Fermi energy.

we can also write this result as:  $\frac{E_{tot}}{N} = \frac{3}{5} k_B T_F$

Typically,  $T_F \approx 5 \times 10^4$  K, while the energy per electron in a classical electron gas ( $1.5k_B T$ ) vanishes (= zero) at 0 K.

a classical gas achieves this E/N only at  $T = (2/5)T_F$

# QUANTUM DEGENERACY PRESSURE

the electron gas exerts a quantum mechanical pressure (called the **degeneracy pressure**) that keeps the free electron gas from collapsing at 0 K:

$$P = - \left( \frac{\partial E_{tot}}{\partial V} \right)_N$$

$$E_{tot} = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2 (3\pi^2 N)^{5/3}}{10\pi^2 m} V^{-2/3}$$

$$P = \frac{2}{3} \frac{\hbar^2 (3\pi^2 N)^{5/3}}{10\pi^2 m} V^{-5/3} = \frac{2}{3} \frac{E_{tot}}{V}$$

The degeneracy pressure is a consequence of the **Pauli principle**. White dwarfs and neutron stars are stabilized by this pressure.



# 3D DENSITY OF STATES

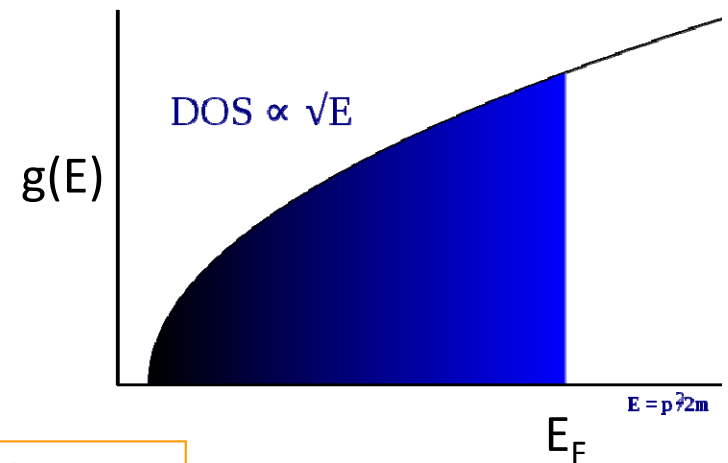
the **density of states**  $g(E)$  is the number of one-electron states (including spin multiplicity) per unit energy and volume

$$g(E)_{3D} \equiv \frac{1}{V} \frac{dN}{dE}$$

$N = 2 \times \text{Fermi sphere volume} \times \# \text{ levels per unit volume}$

$$N = 2 \times \frac{4\pi}{3} k^3 \times \frac{V}{8\pi^3}$$

$$N = \frac{V}{3\pi^2 \hbar^3} (2m^* E)^{3/2}$$



$$g(E)_{3D} = \frac{1}{V} \frac{dN}{dE} = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} E^{1/2}$$

# EFFECT OF REDUCED DIMENSIONALITY ON DOS

2D sheet - quantum well



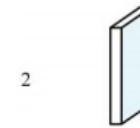
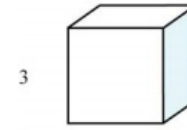
$$g(E) = \frac{m^*}{\pi \hbar^2 L_z}$$

1D quantum wire

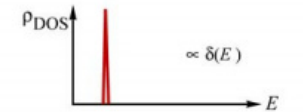


$$g(E) = \frac{\sqrt{2m_e^*}}{\pi \hbar L_x L_y} E^{-1/2}$$

Degrees of freedom



Density of states



0D quantum dot



$$g(E) = \text{discrete}$$

3D

$$\psi = Ae^{i(k_x x + k_y y + k_z z)}$$

$$E = \frac{\hbar^2}{2m_e^*} (k_x^2 + k_y^2 + k_z^2)$$



Well

$$\psi = A \sin k_z z \cdot e^{i(k_x x + k_y y)}$$

$$E = \frac{\hbar^2 n_z^2}{8m_e^* L_z^2} + \frac{\hbar^2}{2m_e^*} (k_x^2 + k_y^2)$$



$$\psi = A \sin k_x x \cdot \sin k_y y \cdot e^{ik_z z}$$

$$E = \frac{\hbar^2}{8m_e^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) + \frac{\hbar^2}{2m_e^*} k_z^2$$

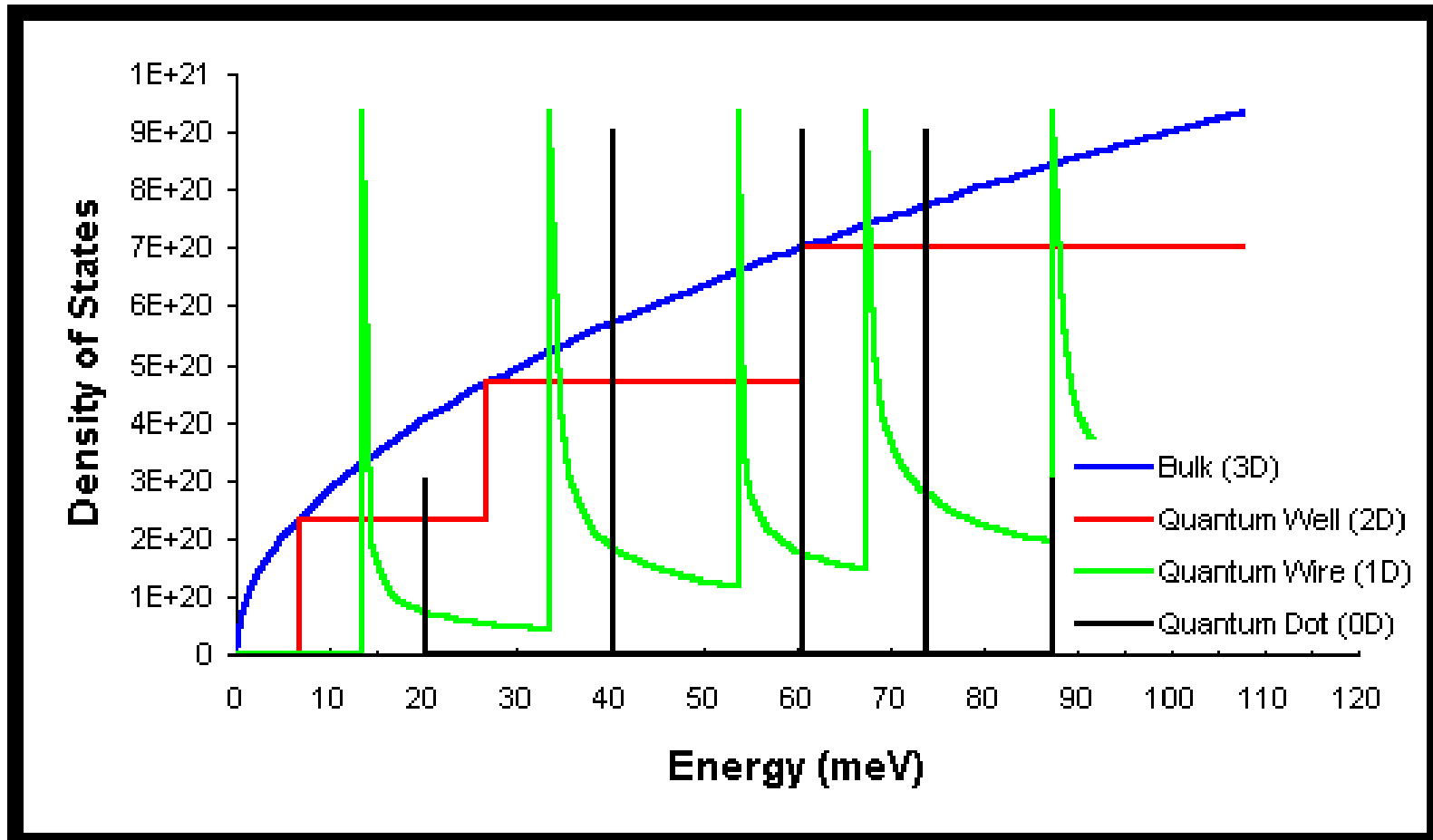


$$\psi = A \sin k_x x \cdot \sin k_y y \cdot \sin k_z z$$

Dot

$$E = \frac{\hbar^2}{8m_e^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

# Quantum Confinement and Dimensionality



# FERMI-DIRAC DISTRIBUTION FUNCTION

At absolute zero the occupancy of states is 1 for  $E \leq E_F$  and 0 for  $E > E_F$ . At finite temperatures, some electrons near  $E_F$  have enough thermal energy to be excited to empty states above  $E_F$ , with the occupancy  $f(E_k, T)$  given by the **Fermi-Dirac distribution function**.

Fermi function:

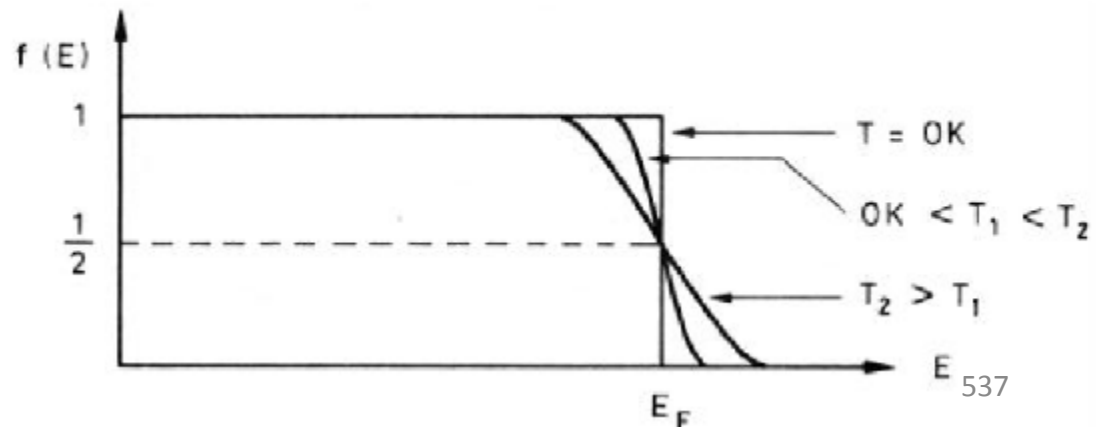
$$f(E_k, T) = \frac{1}{e^{(E_k - \mu)/k_B T} + 1}$$

- consequence of Pauli exclusion principle
- plays central role in solid state physics
- $\mu$  is the chemical potential ( $\mu = E_F$  @ 0 K)

## Energy distribution of electrons

$$f(E) = \frac{1}{e^{(E - E_F)/k_B T} + 1}$$

\*  $f = 0.5$  at  $E = E_F$



# STATISTICAL DISTRIBUTION FUNCTIONS

## Boltzmann distribution:

- for independent, distinguishable classical particles (high  $T$ , low density, so quantum effects negligible)

$$f_B(E) = \frac{1}{\exp[(E - \mu) / k_B T]}$$

$$0 < f(E) < N$$

## Fermi-Dirac distribution:

- for independent, identical Fermions (particles of half-integer spin)

$$f_{FD}(E) = \frac{1}{\exp[(E - \mu) / k_B T] + 1}$$

$$0 < f(E) < 1$$

## Bose-Einstein distribution:

- for independent, identical Bosons (particles of integer spin)

$$f_{BE}(E) = \frac{1}{\exp[(E - \mu) / k_B T] - 1}$$

$$0 < f(E) < N$$

# Fermi-Dirac Function

The Fermi-Dirac function gives the fraction of allowed states,  $f(E)$ , at an energy level  $E$ , that are populated at a given temperature.

$$f(E) = 1/[1 + \exp\{(E-E_F)/kT\}]$$

where the Fermi Energy,  $E_F$ , is defined as the energy where  $f(E) = 1/2$ . That is to say one half of the available states are occupied.  $T$  is the temperature (in K) and  $k$  is the Boltzmann constant ( $k = 8.62 \times 10^{-5}$  eV/K)

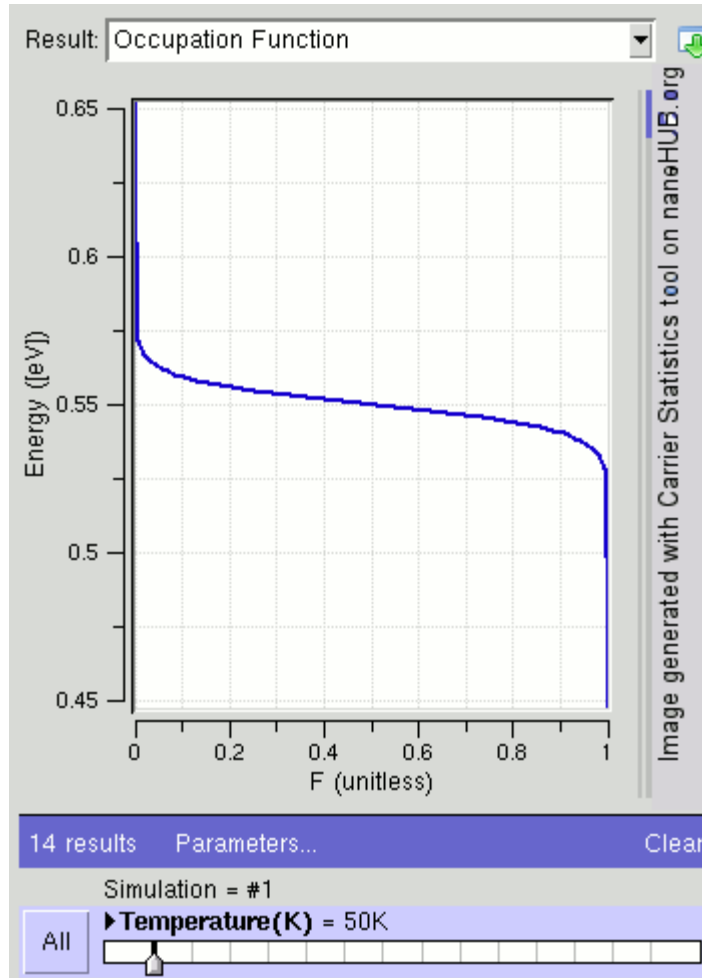
As an example consider  $f(E)$  for  $T = 300$  K and a state 0.1 eV above  $E_F$ :

$$f(E) = 1/[1 + \exp\{(0.1 \text{ eV})/((300\text{K})(8.62 \times 10^{-5} \text{ eV/K}))\}]$$
$$f(E) = 0.02 = 2\%$$

Consider a band gap of 1 eV.

$$f(1 \text{ eV}) = 1.6 \times 10^{-17}$$

See that for even a moderate band gap (Silicon has a band gap of 1.1 eV) the intrinsic concentration of electrons that can be thermally excited to move about the crystal is tiny. Thus pure Silicon (if you could make it) would be quite insulating.



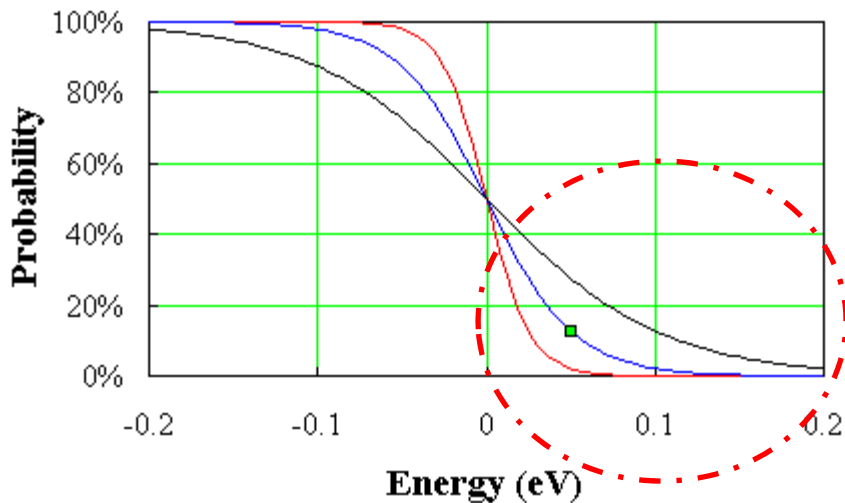
Fermi function  $f(E)$  vs. energy, with  $E_F = 0.55$  eV and for various temperatures in the range  $50\text{K} \leq T \leq 375\text{K}$ .



$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

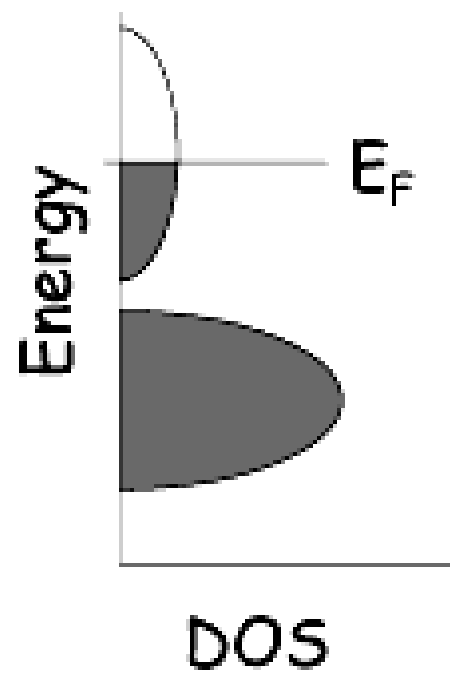
For  $E-E_F \gg kT$ ,  $f(E)$  reduces to the classical Boltzmann function:

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \approx \frac{1}{e^{(E-E_F)/k_B T}} = e^{-(E-E_F)/k_B T} = e^{-\Delta E/k_B T}$$

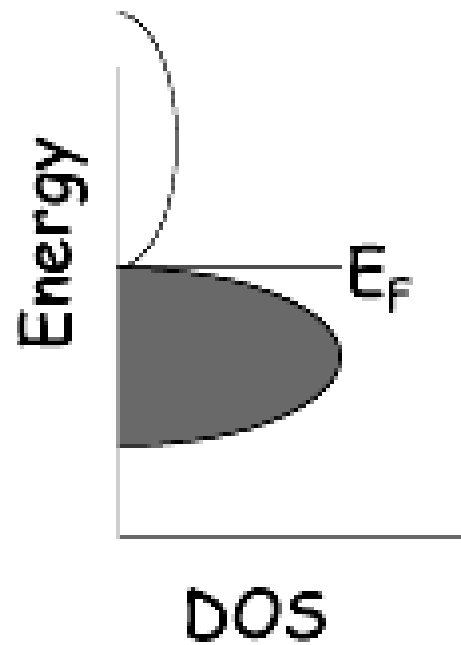


The "Boltzmann tail" of the distribution

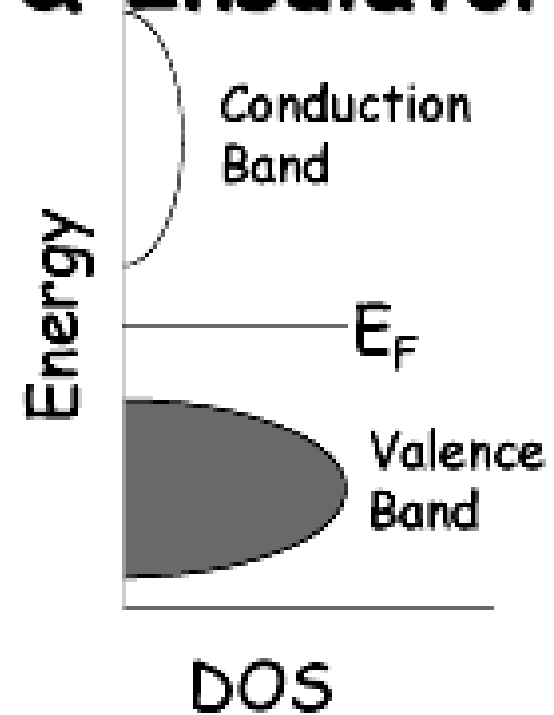
# Metals, Semiconductors & Insulators



**Metal**



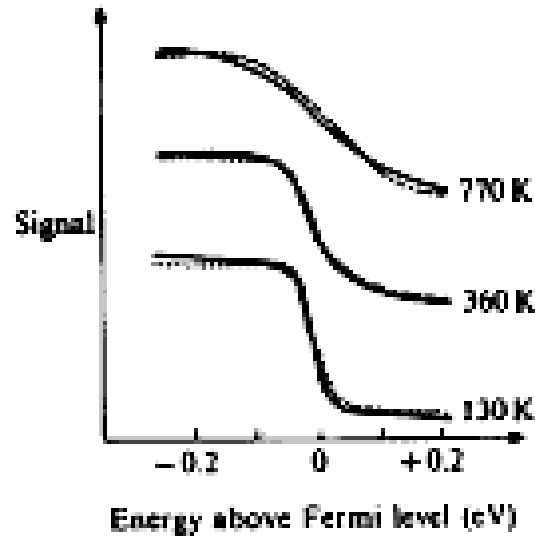
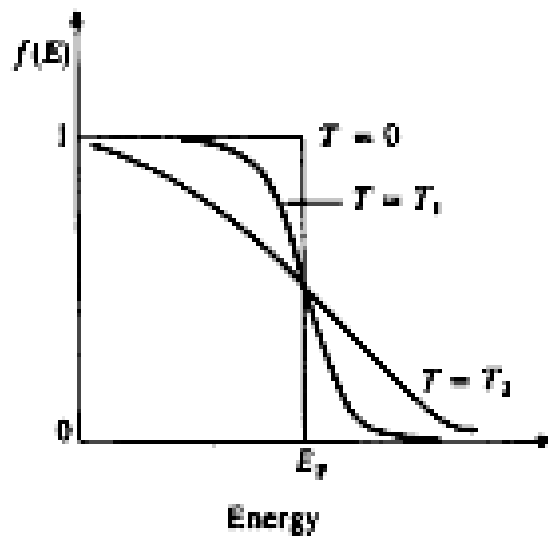
**Semimetal**



**Semiconductor  
/Insulator**

In a metal the Fermi level cuts through a band to produce a partially filled band. In a semiconductor/insulator there is an energy gap between the filled bands and the empty bands. The distinction between a semiconductor and an insulator is artificial, but as the gap becomes large the material usually becomes a poor conductor of electricity. A semimetal results when the band gap goes to zero.

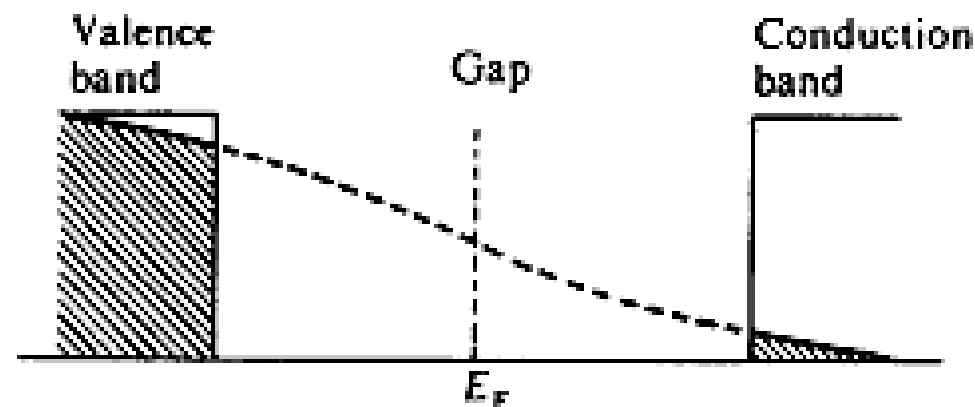
# Fermi Dirac Function Metals and Semiconductors



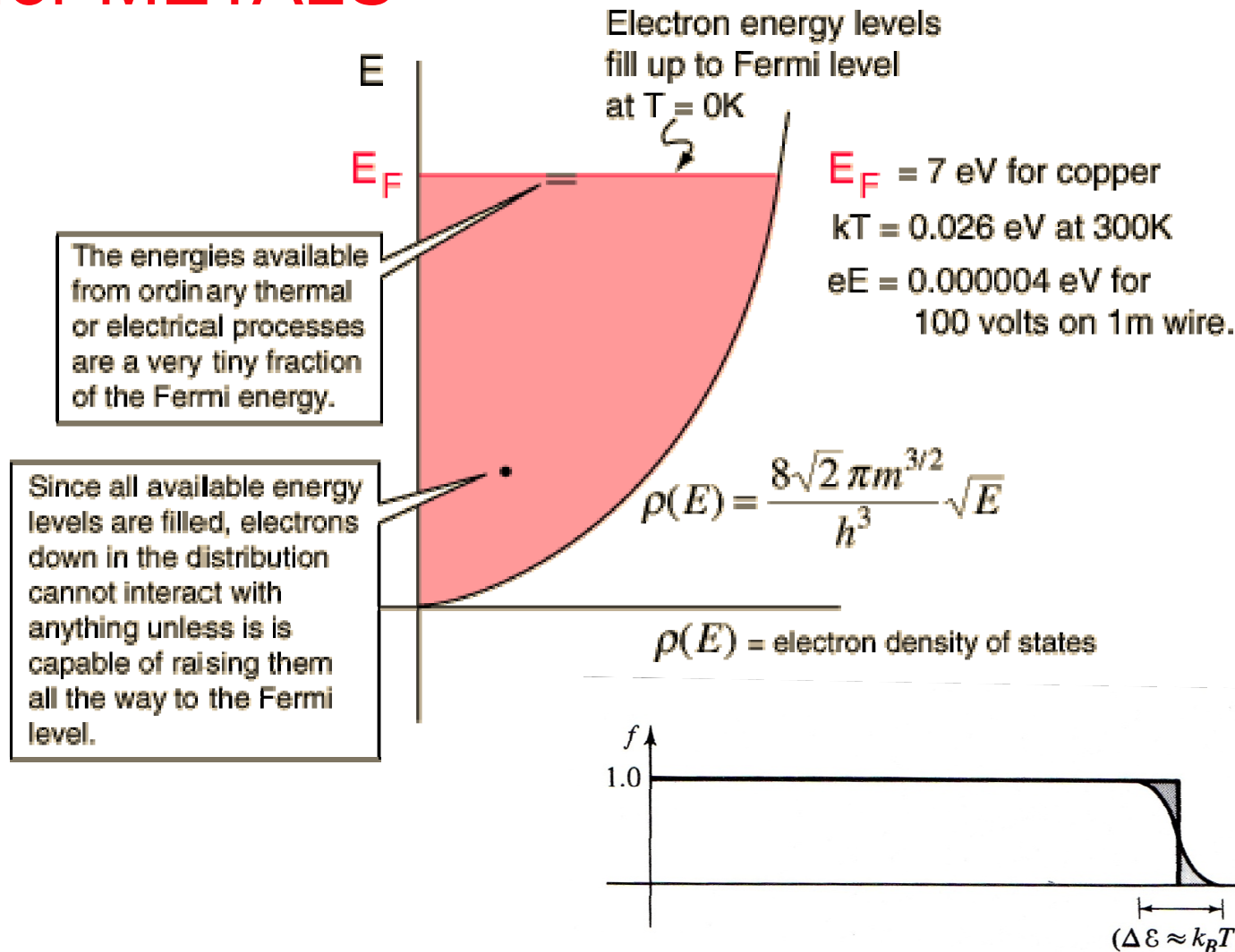
$f(E)$  as determined experimentally for Ru metal (note the energy scale)



$f(E)$  for a semiconductor

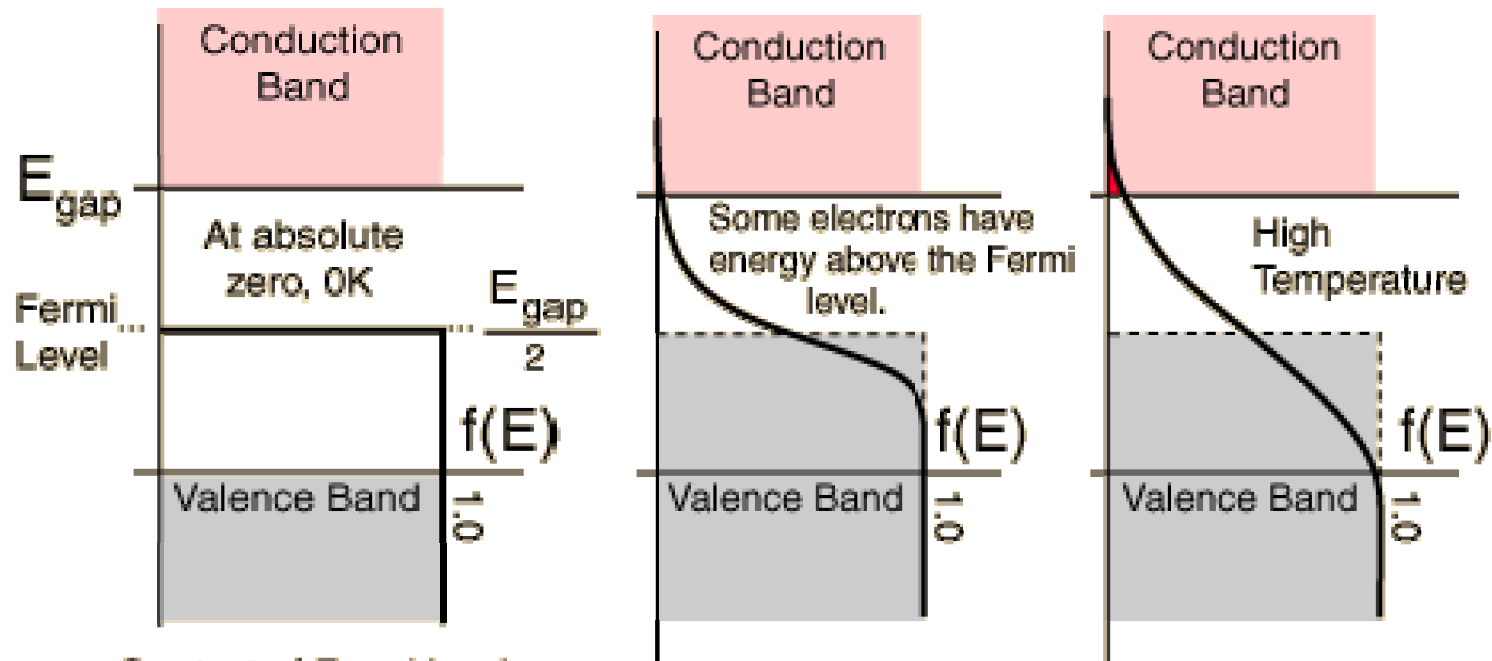


# $f(E)$ for METALS



At normal temperatures,  $kT$  is small compared with  $E_F$ . Since only those electrons within  $\sim kT$  of  $E_F$  can be thermally promoted or participate in electrical conduction, most of the electrons are "frozen out".

# $f(E)$ for SEMICONDUCTORS



Context of Fermi level for a semiconductor

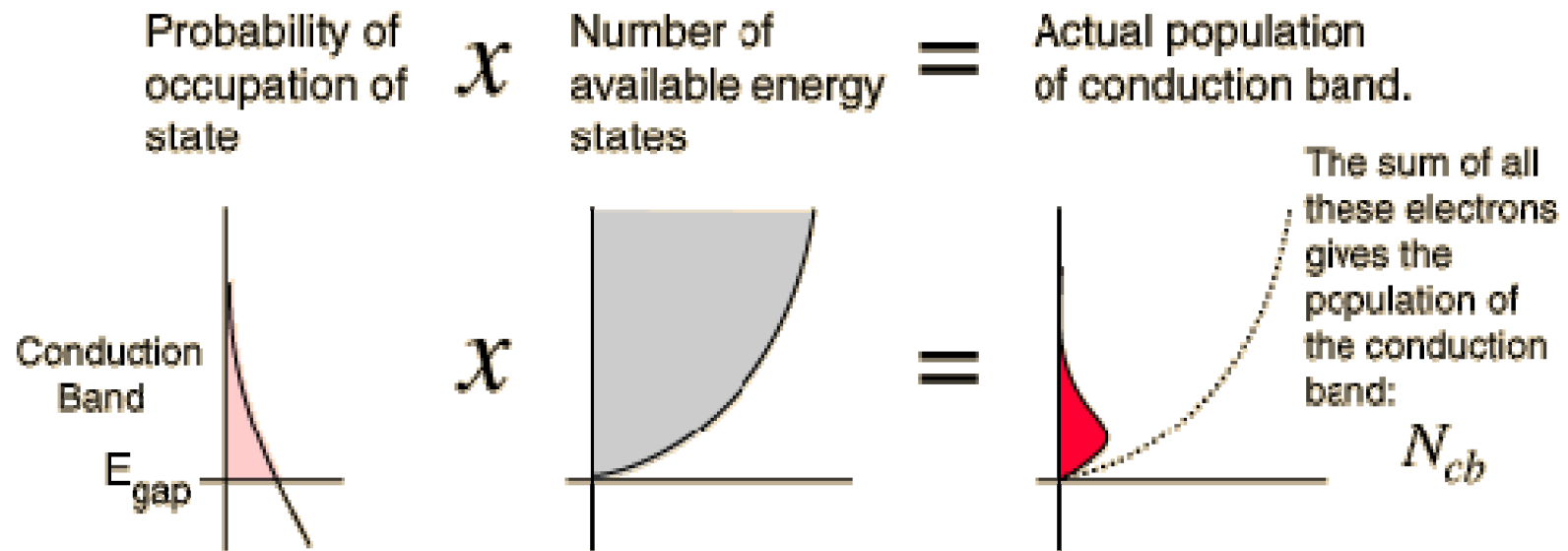
No electrons can be above the valence band at 0K, since none have energy above the Fermi level and there are no available energy states in the band gap.

At high temperatures, some electrons can reach the conduction band and contribute to electric current.

[www.hyperphysics.edu](http://www.hyperphysics.edu)

# CARRIER DENSITY in SEMICONDUCTORS

$$n = \int_{-\infty}^{\infty} f(E)g(E)dE$$



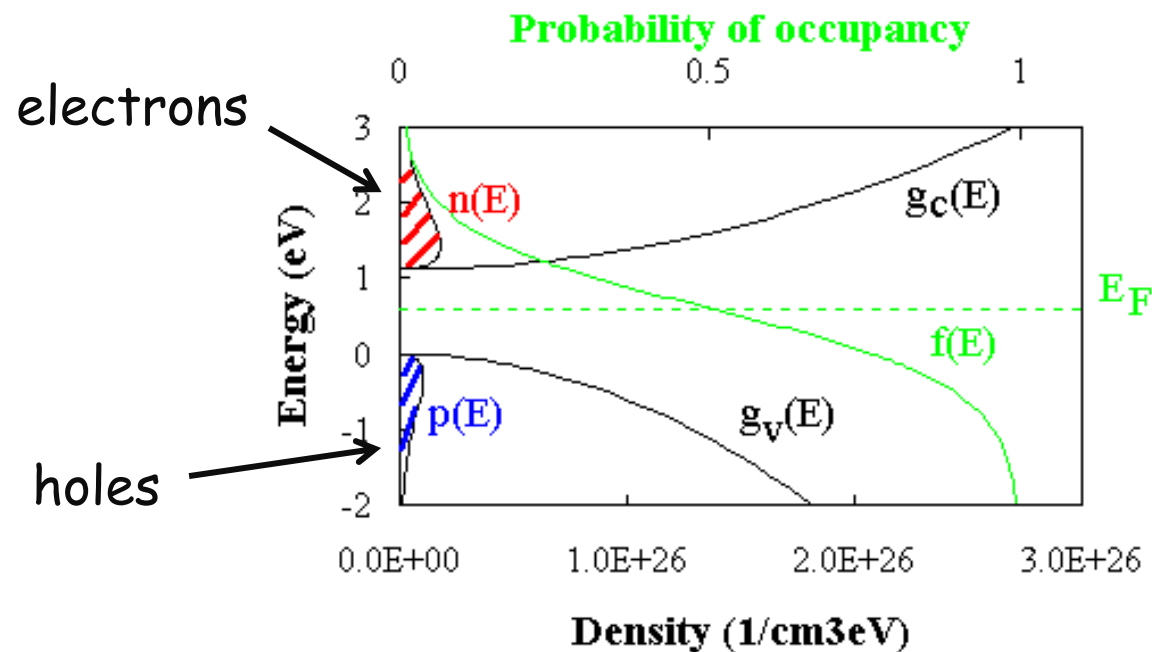
# IMPORTANCE OF $g(E)$ and $f(E)$

$$U = \int E f(E) g(E) dE$$

$$n = \int f(E) g(E) dE$$

$$C = \frac{\partial}{\partial T} \int E f(E) g(E) dE$$

$$k = \frac{1}{d} \frac{\partial}{\partial T} \int E f(E) g(E) \nu(E) \Lambda(E) dE$$



$f(E)g(E)$  product for a bulk semiconductor, showing the "pools" of free electrons and holes at the band edges

# NEARLY-FREE ELECTRON MODEL

Starts from the free electron perspective ( $V = 0$ ) and adds a very weak periodic potential to represent the ions. Electrons still independent.

- since the potential is very weak, we can use perturbation theory to calculate how the free electron wavefunction and energies are changed.

**Bloch's Theorem:** The wavefunction of an electron in a periodic potential can be written as a plane wave times a function with the periodicity of the Bravais lattice.

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

with:  $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$

**main result:** The periodic potential deforms the parabolic  $E(k)$  of free electrons only near the edge of the Brillouin zone; this results in an energy gap at the Brillouin zone boundary (i.e., when  $k \approx 2\pi/a$ ).

- most useful for  $s$ - and  $p$ -block metals (e.g., alkali metals)



# ELECTRONIC STRUCTURE METHODS

## **Tight binding**

Nearly-free electron model

Hartree–Fock

Modern valence bond

Generalized valence bond

Møller–Plesset perturbation theory

Configuration interaction

Coupled cluster

Multi-configurational self-consistent field

Density functional theory

Quantum chemistry composite methods

Quantum Monte Carlo

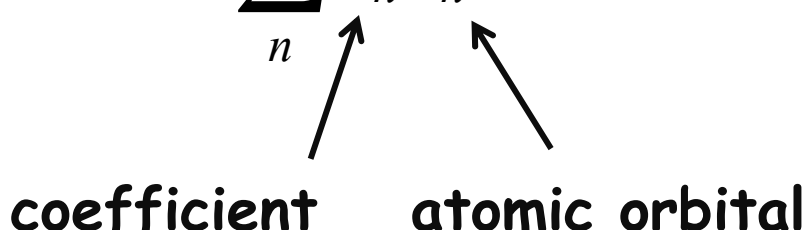
k·p perturbation theory

Muffin-tin approximation

# TIGHT-BINDING MODEL

Molecular orbital (“chemical”) approach to the electronic structure of infinite 3D solids.

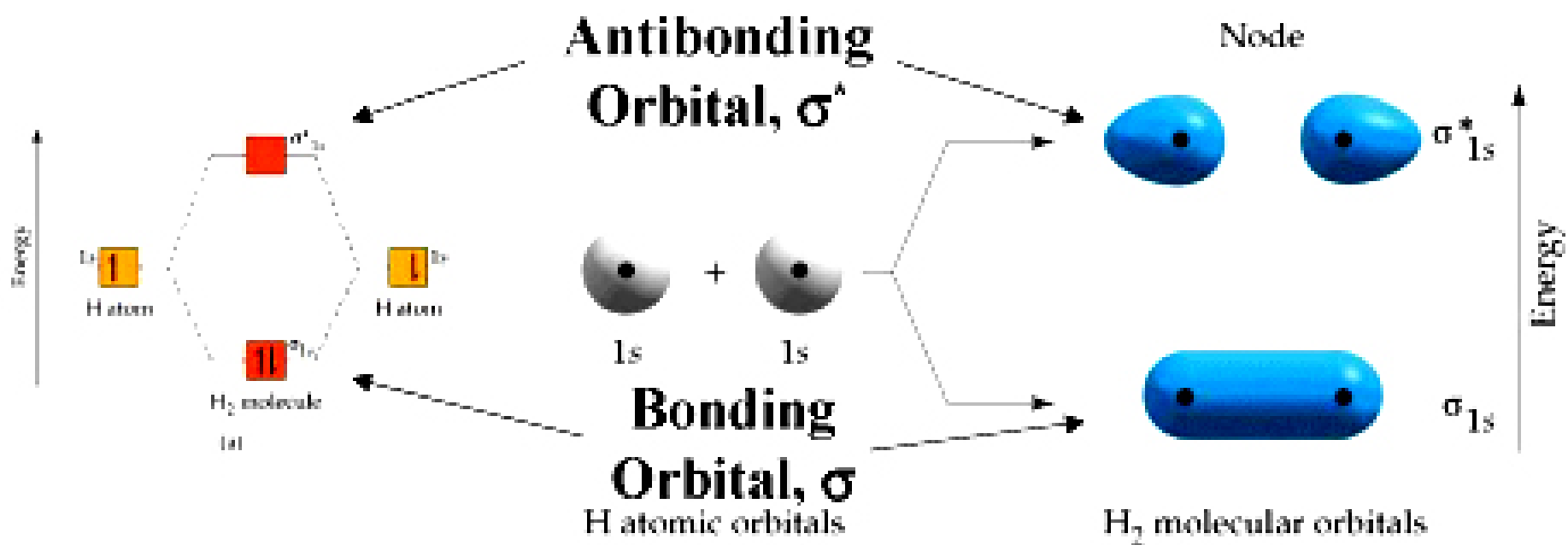
- starts from basis of **linear combinations of atomic orbitals** (LCAOs), and considers interactions between atomic sites as perturbations
- opposite simplification of the free electron models

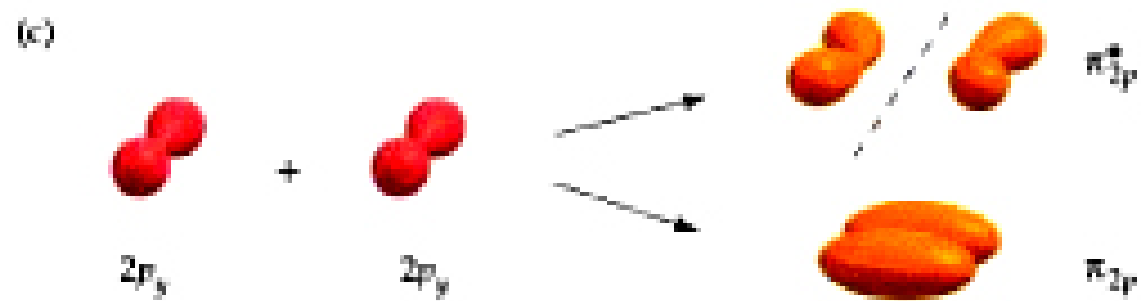
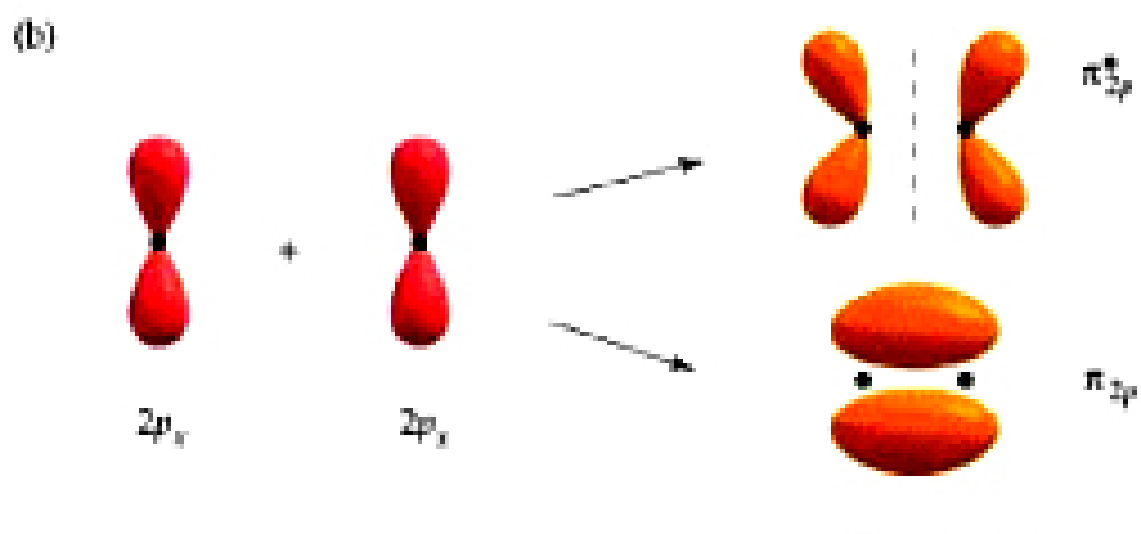
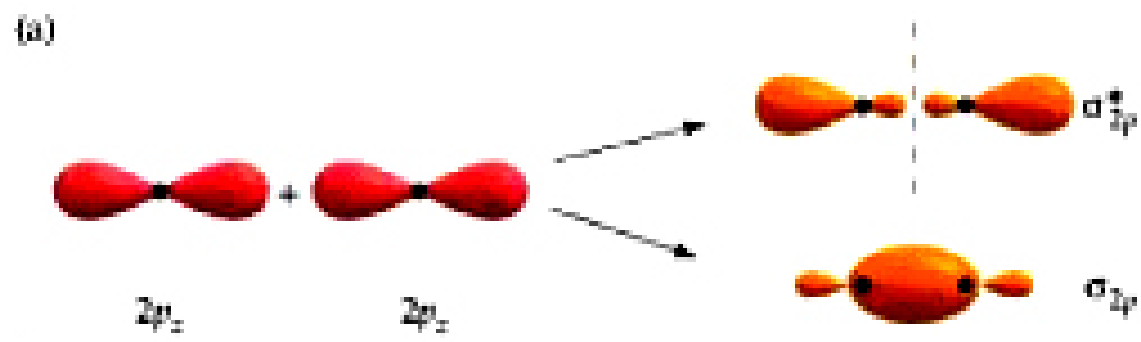
$$\psi(\mathbf{r}) = \sum_n c_n \phi_n(\mathbf{r})$$


coefficient      atomic orbital

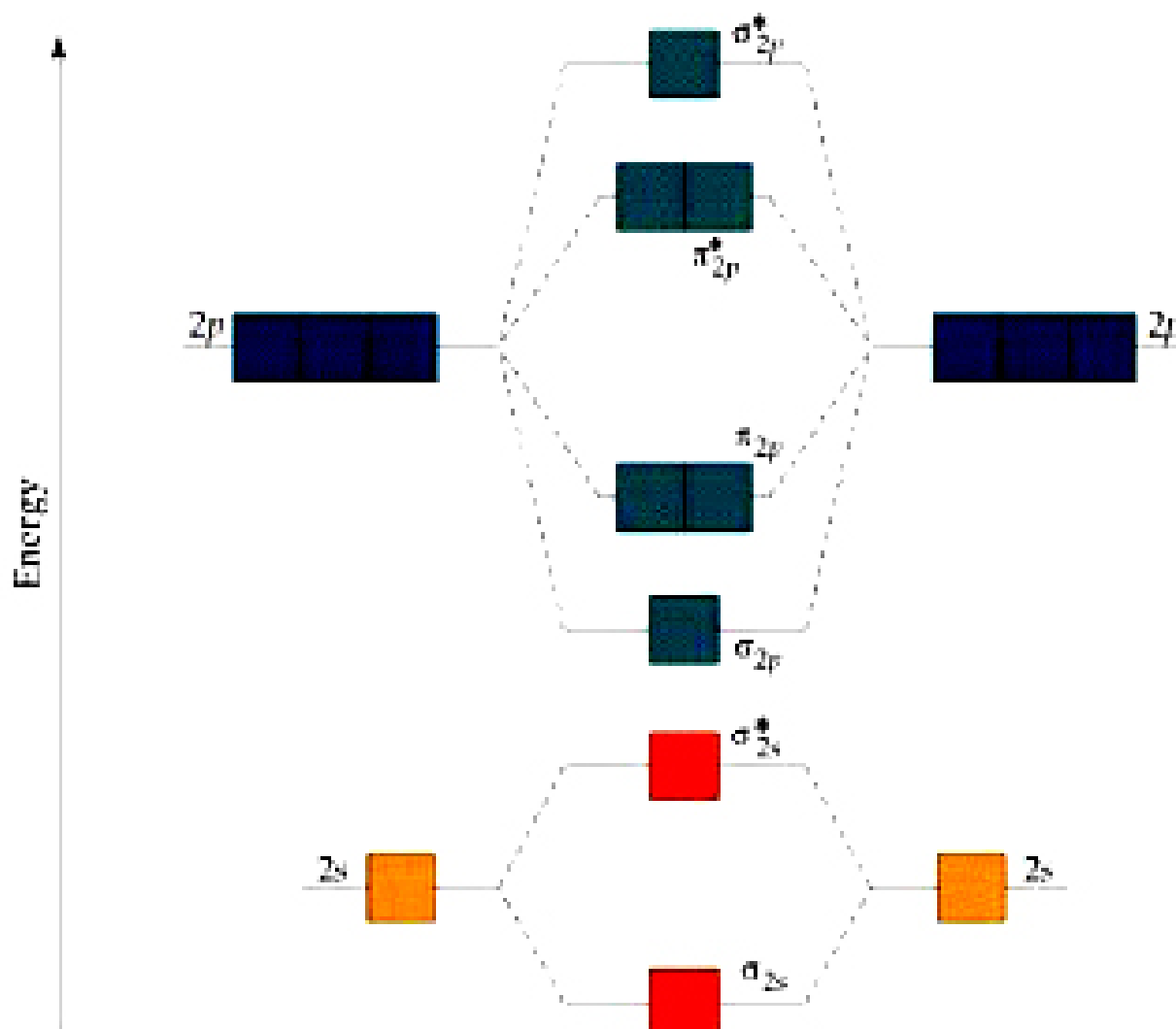
- particularly useful for insulators, d bands of transition metals, polymers, some semiconductors, and other “tightly-bound” systems

# Molecular Orbital Theory



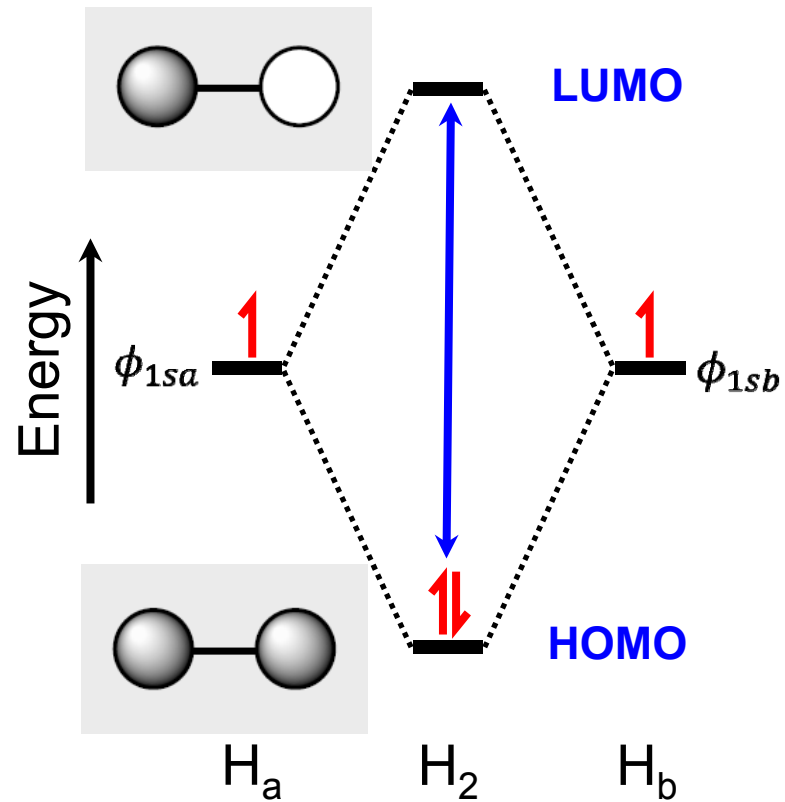


# Diatomic Molecules



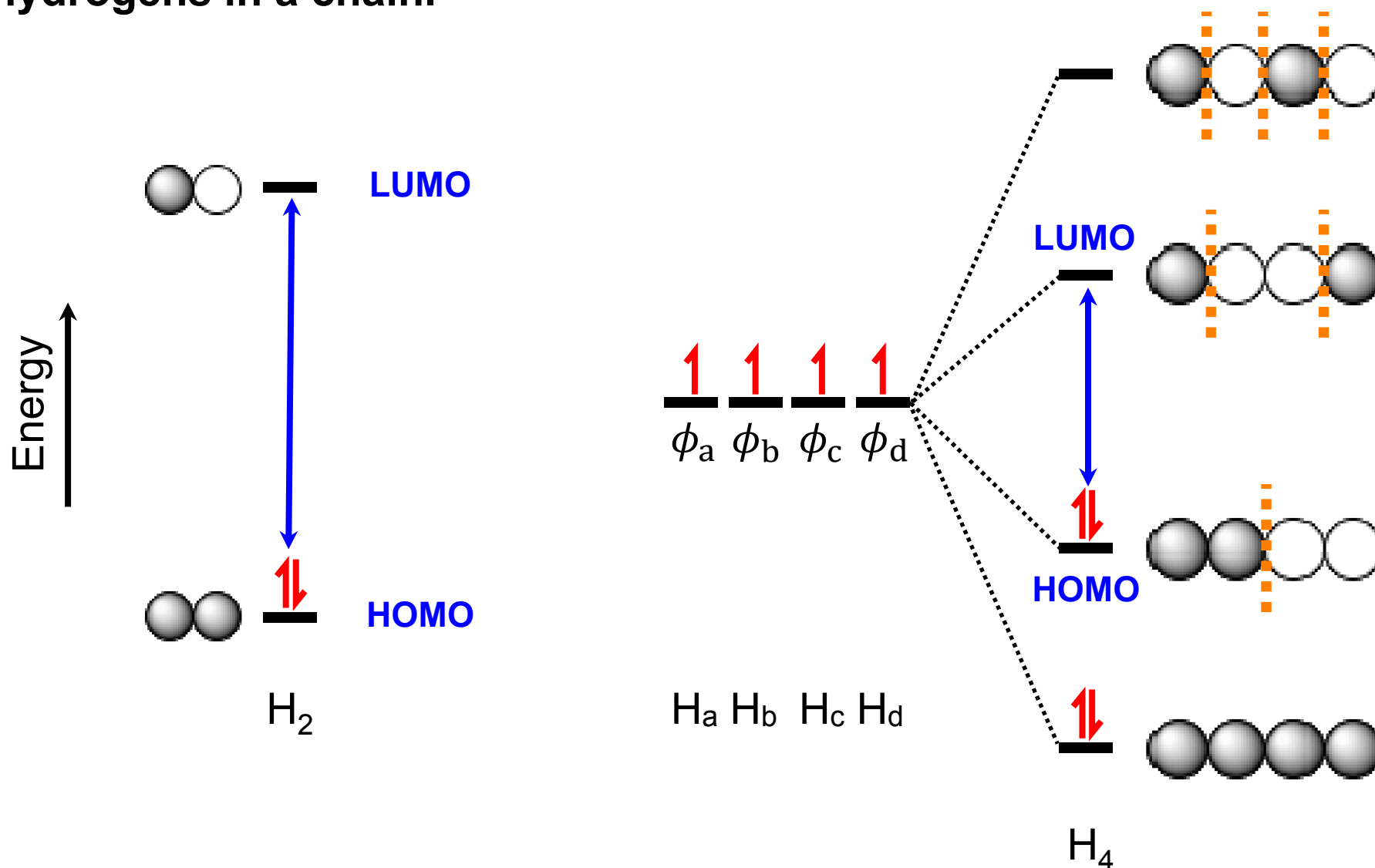
# From MOs to Band Theory

MO diagram for H<sub>2</sub>.



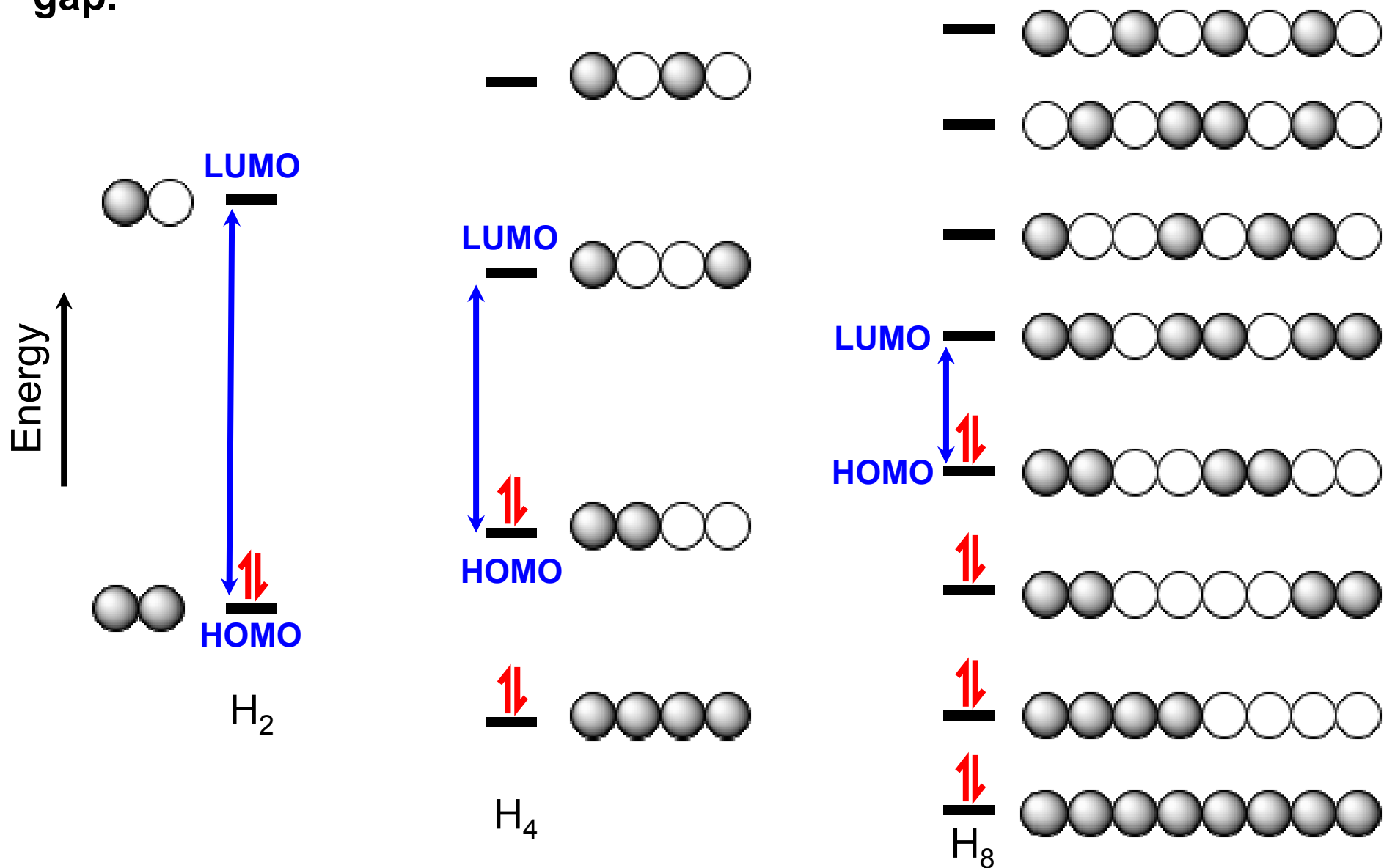
# From MOs to Band Theory

Look at what happens when we move from two hydrogens to four hydrogens in a chain.



# From MOs to Band Theory

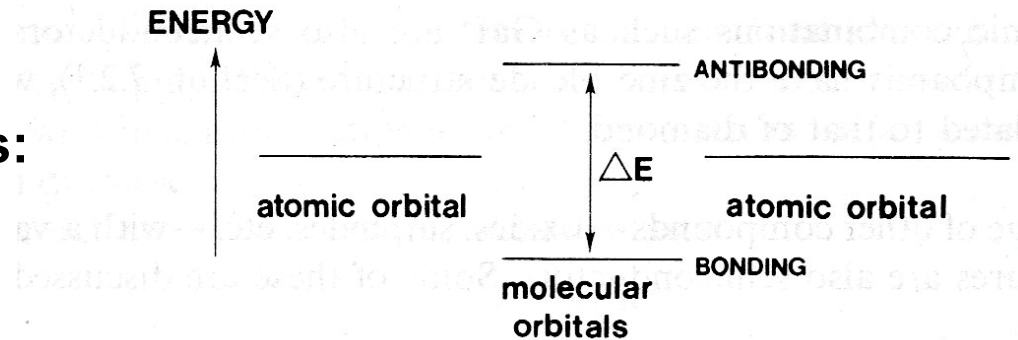
Eight hydrogens gives eight MOs and an even smaller HOMO-LUMO gap.



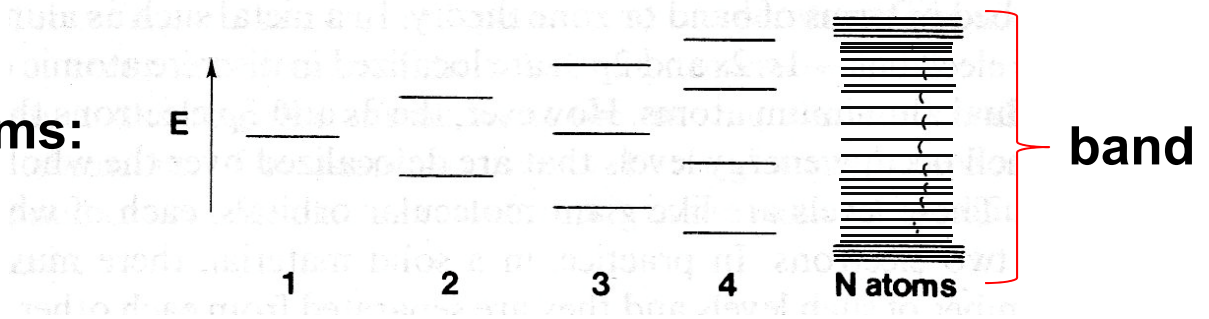


# MO Theory for Solids – Qualitative Expectations

Interaction of two atoms:



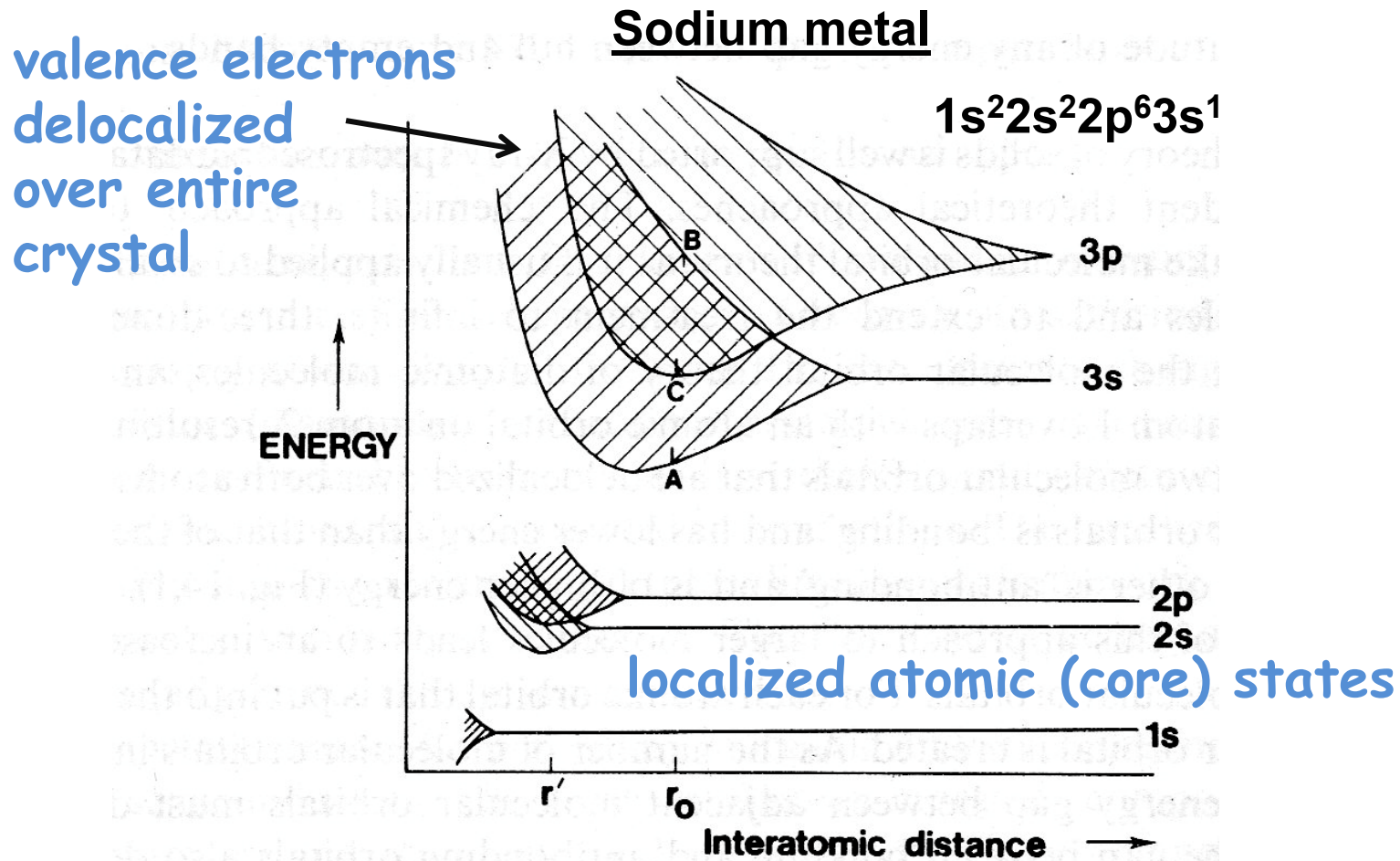
Interaction of many atoms:



N atomic orbitals give N molecular orbitals.

when N is enormous, the MOs form **bands** ( $\Delta E \ll kT$ )

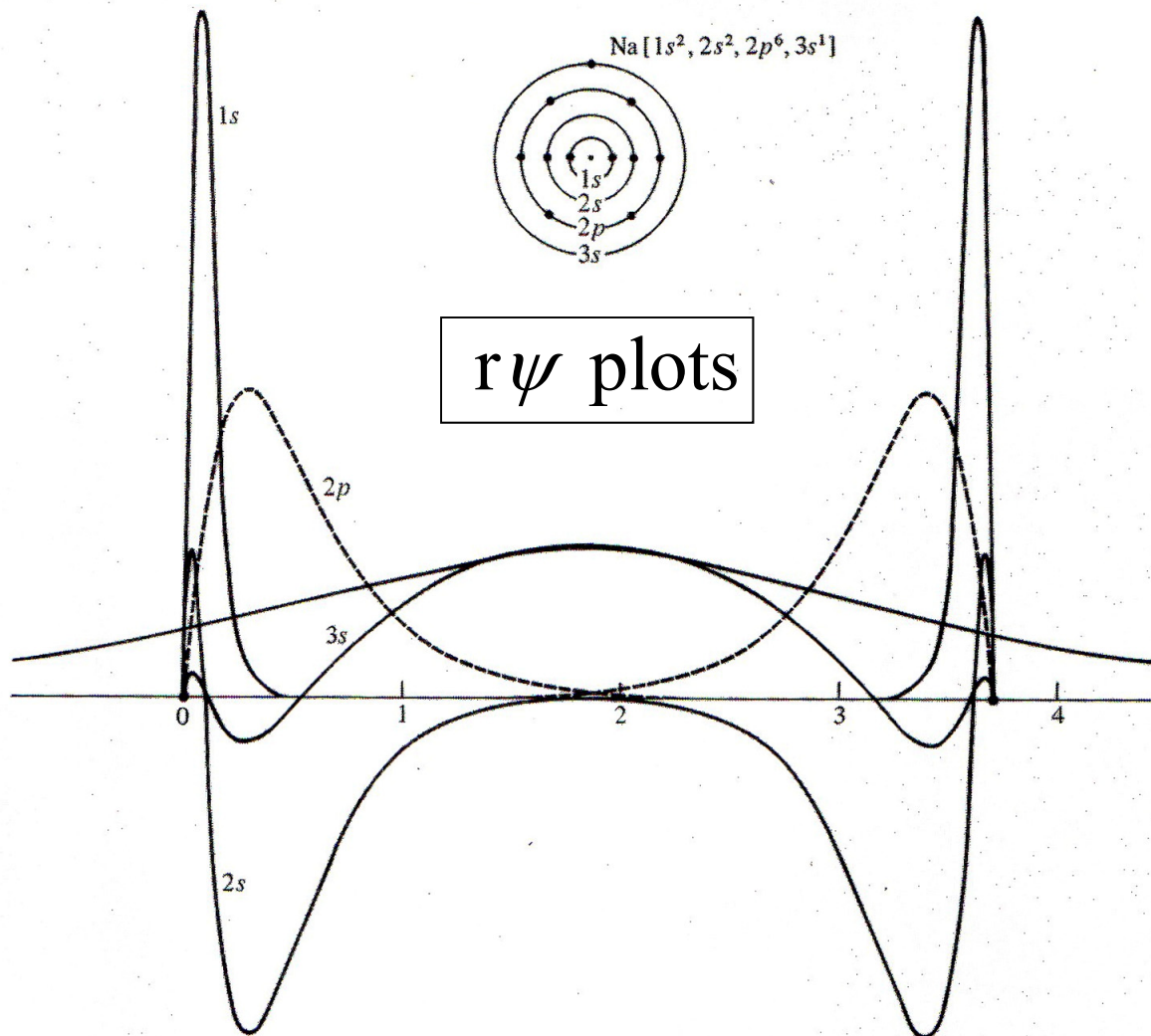
bands form only when there is sufficient spatial overlap between atomic orbitals to form delocalized states ... **depends on interatomic distance**



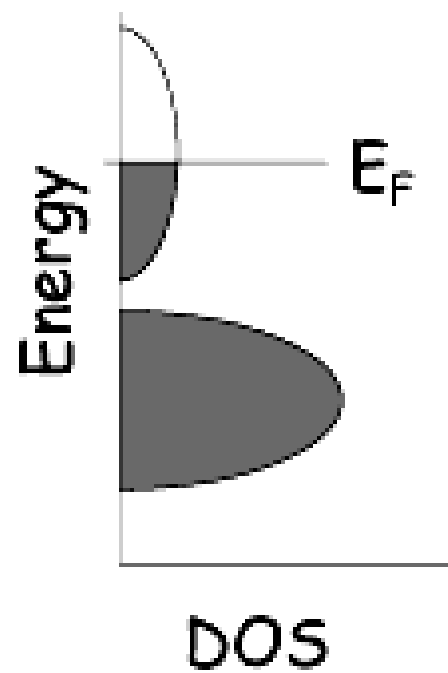
**greater orbital overlap → wider bands**

at high enough pressures, many solids become metallic<sup>58</sup>

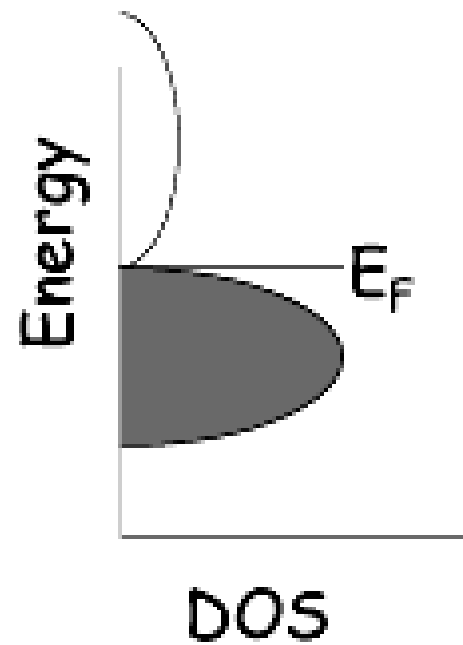
# Orbital overlaps for sodium:



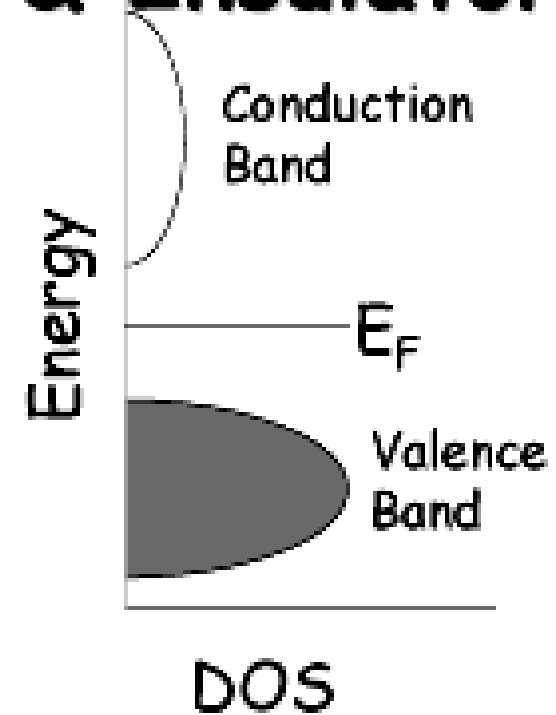
# Metals, Semiconductors & Insulators



**Metal**



**Semimetal**



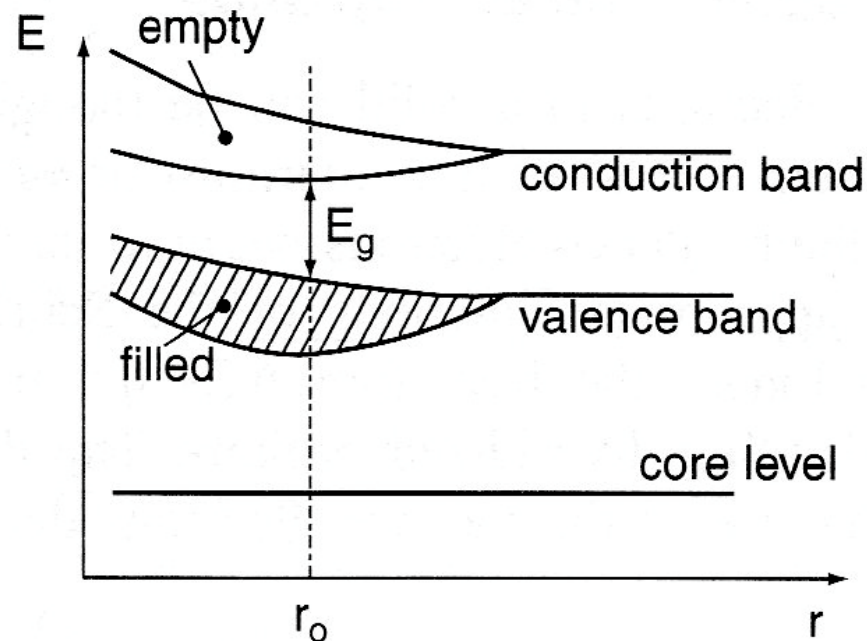
**Semiconductor  
/Insulator**

In a metal the Fermi level cuts through a band to produce a partially filled band. In a semiconductor/insulator there is an energy gap between the filled bands and the empty bands. The distinction between a semiconductor and an insulator is artificial, but as the gap becomes large the material usually becomes a poor conductor of electricity. A semimetal results when the band gap goes to zero.

The differences between metals, semimetals, semiconductors, and insulators depend on:

- the band structure
- whether the valence band is full or only partly full
- the magnitude of any energy gap between full and empty bands

**filled valence band, empty conduction band → semiconductor/insulator**



# Orbital Interactions: Key Points

- **The overlap of two atomic orbitals is dependent upon:**
  - symmetry of the orbitals
  - distance between the orbitals
  - spatial extent of the orbitals
  - the energy difference between orbitals
- **Increasing the overlap (spatial and energetic) leads to the following:**
  - Stabilization of the bonding MO
  - Destabilization of the antibonding MO
  - The antibonding MO is destabilized to a greater extent than the bonding MO is stabilized
- **The spatial overlap in a bond depends upon symmetry**
  - It decreases as the number of nodal planes increases,  $\sigma > \pi > \delta$
  - $\pi$  and particularly  $\delta$  bonds are more sensitive to changes in bond angle

# Elementary Band Theory for Molecules

## Schrödinger equation

$$\hat{H}\psi = E\psi$$

Solving the Schrödinger equation  
after applying simplifications

tight binding approach

**LCAO**: linear combination of atomic wavefunctions, the Atomic Orbitals  $\phi$

$$\psi = \sum_i c_i \phi_i$$

$\phi$  is normalized, thus  $\int \phi_i^2 d\tau = 1$

with  $d\tau = \partial x \partial y \partial z$

Calculate the expectation value of  $\hat{H}$ :

$$E = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau}$$

$c_i$ : coefficients  
AO's: basis set

For a minimal E:  $\partial E / \partial c_i = 0$

# Elementary Band Theory for Molecules

**Case studies:** 1) the diatomic case

$$\psi = \sum_i c_i \phi_i = c_1 \phi_1 + c_2 \phi_2$$

For a minimal E:  $\partial E / \partial c_i = 0$ , i.e.

$$\partial E / \partial c_1 = 0 \text{ and } \partial E / \partial c_2 = 0$$

**=> two solutions**

$E = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau}$	$\longrightarrow$ numerator (I)
	$\longrightarrow$ denominator (II)

$$\int \psi \hat{H} \psi d\tau = \int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2) d\tau$$

$$= \int (c_1^2 \phi_1 \hat{H} \phi_1 + 2c_1 c_2 \phi_1 \hat{H} \phi_2 + c_2^2 \phi_2 \hat{H} \phi_2) d\tau$$

$$= c_1^2 \int \phi_1 \hat{H} \phi_1 d\tau + 2c_1 c_2 \int \phi_1 \hat{H} \phi_2 d\tau + c_2^2 \int \phi_2 \hat{H} \phi_2 d\tau$$

**Coulomb-integral**

$$\alpha_1 < 0$$

**resonance-integral**

$$\beta_{12} < 0 \text{ if bonding}$$

**Coulomb-integral**

$$\alpha_2 < 0$$



## Case studies: the diatomic case, continued

$$\psi = \sum_i c_i \phi_i = c_1 \phi_1 + c_2 \phi_2$$

Numerator (I):  $\int \psi \hat{H} \psi d\tau = c_1^2 \alpha_1 + 2c_1 c_2 \beta_{12} + c_2^2 \alpha_2$

Denominator (II):  $\int \psi^2 d\tau = \int (c_1 \phi_1 + c_2 \phi_2)^2 d\tau$

$$= \int (c_1^2 \phi_1^2 + 2c_1 c_2 \phi_1 \phi_2 + c_2^2 \phi_2^2) d\tau$$

$$= c_1^2 \int \phi_1^2 d\tau + 2c_1 c_2 \int \phi_1 \phi_2 d\tau + c_2^2 \int \phi_2^2 d\tau$$

=1

overlap

=1

$S_{12} \geq 0$  if bonding

$$\Rightarrow \int \psi^2 d\tau = c_1^2 + 2c_1 c_2 S_{12} + c_2^2$$

$$\partial E / \partial c_1 = 0$$

$$\frac{\partial E}{\partial c_1} = \frac{\partial}{\partial c_1} \frac{c_1^2 \alpha_1 + 2c_1 c_2 \beta_{12} + c_2^2 \alpha_2}{c_1^2 + 2c_1 c_2 S_{12} + c_2^2} = 0$$

Use quotient rule!

$$D\left\{\frac{f(x)}{g(x)}\right\} = \frac{g(x)f'(x) - f(x)g'(x)}{[g(x)]^2}$$

Minimization with respect to coefficients  $c_1$  and  $c_2$  gives a system of two simultaneous equations

## Case studies: the diatomic case, continued

$$(\alpha_1 - E)c_1 + (\beta_{12} - ES_{12})c_2 = 0$$

$$(\beta_{12} - ES_{12})c_1 + (\alpha_2 - E)c_2 = 0$$

Secular determinant = 0

$$0 = \begin{vmatrix} \alpha_1 - E & \beta_{12} - ES_{12} \\ \beta_{12} - ES_{12} & \alpha_2 - E \end{vmatrix}$$

General rule:

$$0 = \begin{vmatrix} A & B \\ C & D \end{vmatrix} = AD - BC$$

$$0 = (\alpha_1 - E) (\alpha_2 - E) - (\beta_{12} - ES_{12}) (\beta_{12} - ES_{12})$$

**Case studies:** 1a) the diatomic homoatomic case, e.g.  $H_2$

$$\alpha_1 = \alpha_2 = \alpha$$

$$0 = (\alpha - E) (\alpha - E) - (\beta - ES) (\beta - ES) = (\alpha - E)^2 - (\beta - ES)^2$$

$$\Rightarrow (\alpha - E) = \pm (\beta - ES)$$

## Case studies: the diatomic homoatomic case, e.g. $H_2$

$\alpha - E = \pm (\beta - ES)$ : two solutions, A and B

**A**

$$\alpha - E = -(\beta - ES)$$

$$\alpha + \beta = E(1 + S)$$

$$E = (\alpha + \beta)/(1+S)$$

$$c_1 = 1/\sqrt{2(1 + S)} = c_2$$

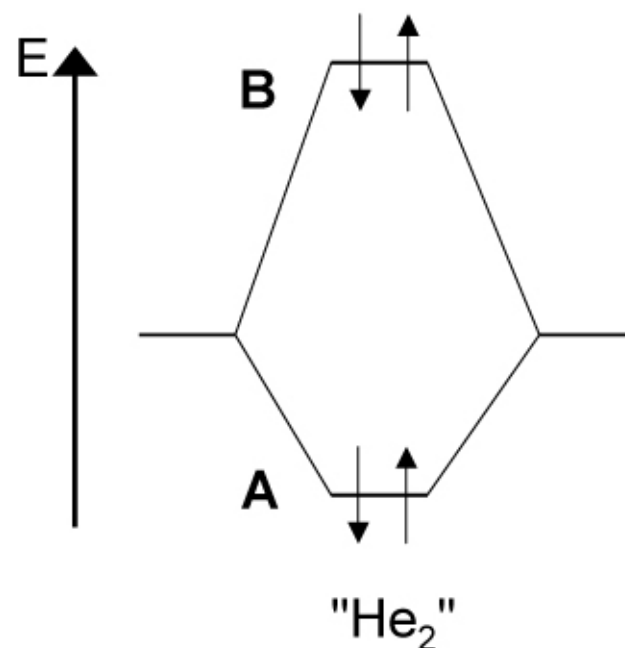
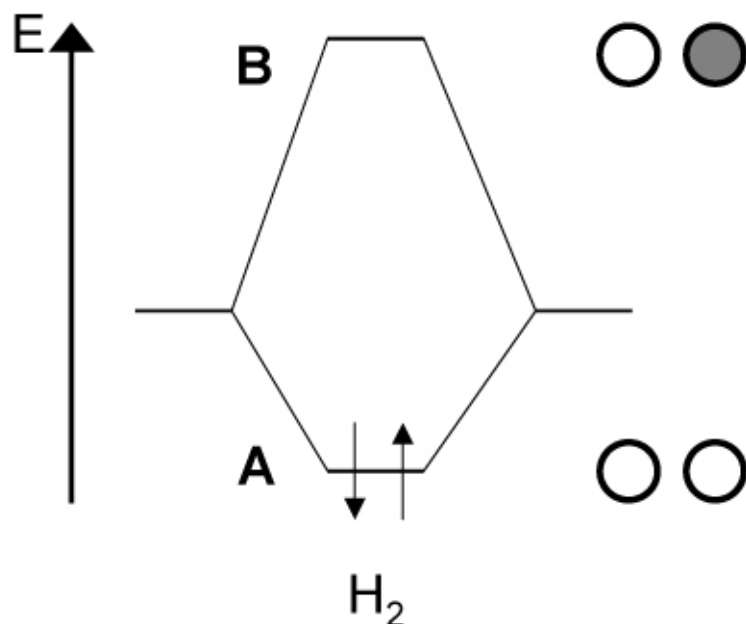
**B**

$$\alpha - E = \beta - ES$$

$$\alpha - \beta = E(1 - S)$$

$$E = (\alpha - \beta)/(1-S)$$

$$c_1 = 1/\sqrt{2(1 - S)} = -c_2$$



Calculated without any approximation

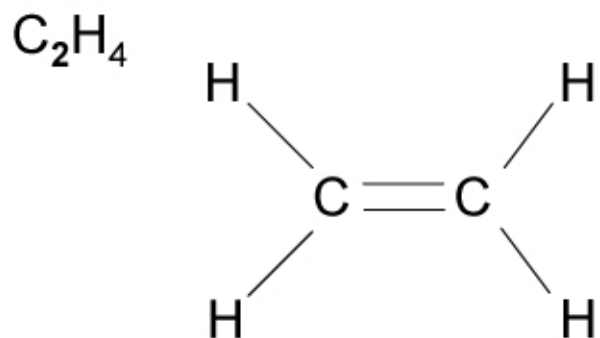
**Overlap Integral  $S$ :** proportional to degree of spatial overlap between two orbitals. It is the product of wave functions centered on different lattice sites. Varies from 0 (no overlap) to 1 (perfect overlap).

**Coulomb Integral  $\alpha$ :** It is the kinetic and potential energy of an electron in an atomic orbital experiencing interactions with all the other electrons and all the positive nuclei

**Resonance Integral  $\beta_{12}$ :** Gives the energy of an electron in the region of space where orbitals 1 and 2 overlap. The value is finite for orbitals on adjacent atoms, and often assumed to be zero otherwise.

## Case studies: more complex molecules

Conjugated molecules, e.g. ethene,  $C_2H_4$ , and butadiene,  $C_4H_6$



VB:  $sp^2$  for each C atom

Consider only the  $\pi$  bonds:

$$\psi = \sum_i c_i \phi_i = c_1 \phi_1 + c_2 \phi_2$$

Problem solved by analogy:

$$E_1 = (\alpha + \beta)/(1+S), E_2 = (\alpha - \beta)/(1-S)$$

$C_4H_6$       $\psi = \sum_i c_i \phi_i = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + c_4 \phi_4$

Secular determinant = 0

$$0 = \begin{vmatrix} \alpha_1 - E & \beta_{12} - ES_{12} & \beta_{13} - ES_{13} & \beta_{14} - ES_{14} \\ \beta_{21} - ES_{21} & \alpha_2 - E & \beta_{23} - ES_{23} & \beta_{24} - ES_{24} \\ \beta_{31} - ES_{31} & \beta_{32} - ES_{32} & \alpha_3 - E & \beta_{34} - ES_{34} \\ \beta_{41} - ES_{41} & \beta_{42} - ES_{42} & \beta_{43} - ES_{43} & \alpha_4 - E \end{vmatrix}$$

## C<sub>4</sub>H<sub>6</sub>, continued ....

Problem 'solution' by approximation(s):

1. approx.: set  $\beta_{ij} = 0$  unless adjacent atoms → **Extended Hückel**
2. approx.: set  $S_{ij} = 0$  → **Simple Hückel**

Hückel determinant:

$$| H_{ij} - E | = 0$$

Extended Hückel determinant:

$$| H_{ij} - S_{ij}E | = 0$$

$$H_{ii} = \alpha_i = \int \phi_i \hat{H} \phi_i d\tau \quad \text{Coulomb integral} \equiv - \text{ionization potential}$$

$$H_{ii} = -I_i$$

$$H_{ij} = \beta_{ij} = \int \phi_i \hat{H} \phi_j d\tau \quad \text{resonance integral}$$

$H_{ij}$  is proportional to the average of  $H_{ii}$  and  $H_{jj}$

C<sub>4</sub>H<sub>6</sub>, secular determinant in the **Simple Hückel** approximation

$$0 = \begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

## $C_4H_6$ , continued ....

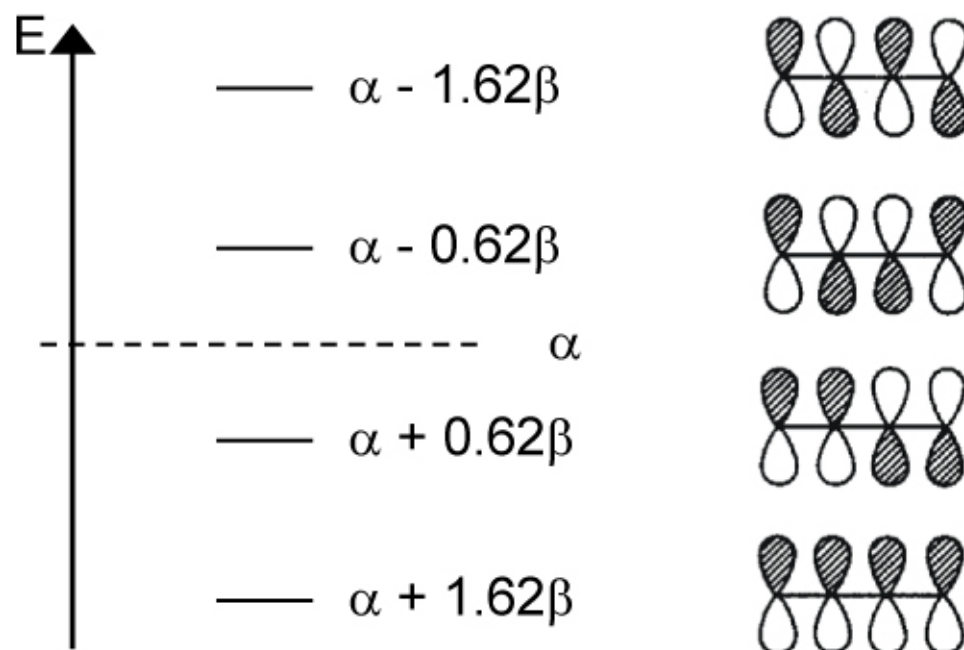
$$0 = (\alpha - E)^4 - 3(\alpha - E)^2\beta^2 + \beta^4$$

solve in analogy to

$$ax^4 + bx^2 + c = 0, \text{ with } u = x^2:$$

$$au^2 + bu + c = 0$$

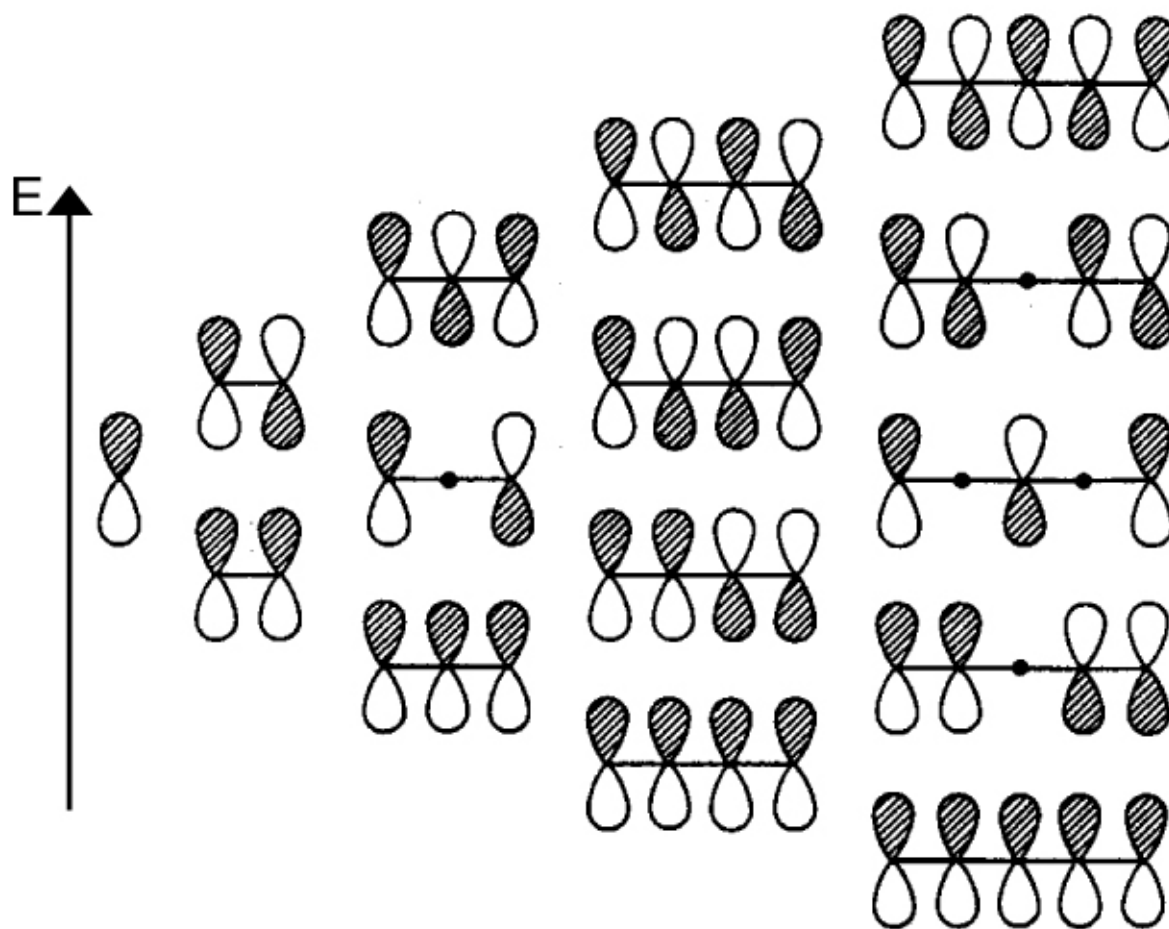
$$\Rightarrow E = \alpha \pm 1.62\beta, E = \alpha \pm 0.62\beta$$



**Simple Hückel**

# General scheme for 'linear' polyenes

## Simple Hückel



$$\text{C}_2\text{H}_4: E = \alpha \pm \beta; \text{C}_3\text{H}_5: E = \alpha \pm \sqrt{2}\beta, \alpha;$$

$$\text{C}_4\text{H}_6: \alpha \pm 1.6\beta, \alpha \pm 0.6\beta; \text{C}_n\text{H}_{n+2}: E = \alpha \pm 2\beta, \dots$$



## General scheme for 'linear' polyenes

$C_nH_{n+2}$ :  $n$  atoms,  $n$   $\pi$  orbitals,  $j$  energy levels with  $j = 1, 2, 3, \dots, n$

$$E_j = \alpha + 2\beta \cos(j\pi)/(n+1)$$

Examples:

ethene,  $C_2H_4$ ,  $n = 2$ :

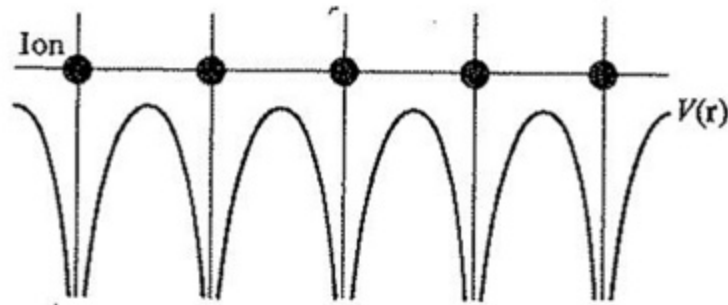
$$E_1 = \alpha + 2\beta \cos\pi/3 = \alpha + \beta$$

$$E_2 = \alpha + 2\beta \cos(2\pi)/3 = \alpha - \beta$$

allyl,  $C_3H_5$ ,  $n = 3$ :

$$E_1 = \alpha + 2\beta \cos\pi/4 = \alpha + \sqrt{2}\beta \dots$$

# EFFECT of PERIODIC POTENTIAL - BLOCH WAVEFUNCTIONS



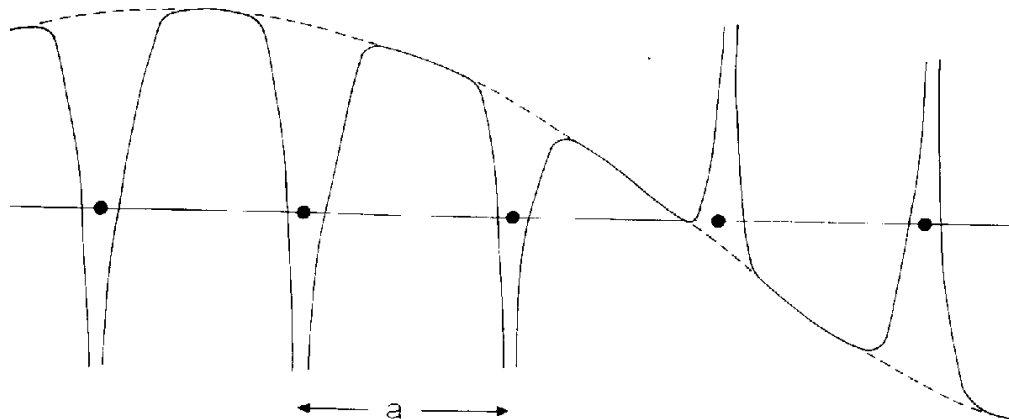
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$$

**Bloch's Theorem:** The wavefunction of an electron in a periodic potential can be written as a plane wave times a function with the periodicity of the Bravais lattice.

$$\psi_{\mathbf{k}}(\mathbf{x}) = u_{\mathbf{k}}(\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$



with:  $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$

# Elementary Band Theory for Extended Solids

Energy bands in solids arise from overlapping

**atomic orbitals** => **crystal orbitals** (that make up the bands)

Recipe: use **LCAO (tight binding) approach**

Crystal = regular periodic array => translational symmetry

**Periodic boundary condition requires:**  $\psi(\mathbf{x}+N\mathbf{a}) = \psi(\mathbf{x})$ .

I.e. each wavefunction must be **symmetry equivalent** to the one in the neighboring cells.

For a 1D solid with lattice constant  $a$  and  $n =$  atom index:

## **Bloch's theorem**

$$\psi_{\mathbf{k}} = \sum_n e^{i\mathbf{k}n\mathbf{a}} \phi_n \quad (\text{a solution of the Schrödinger equation})$$

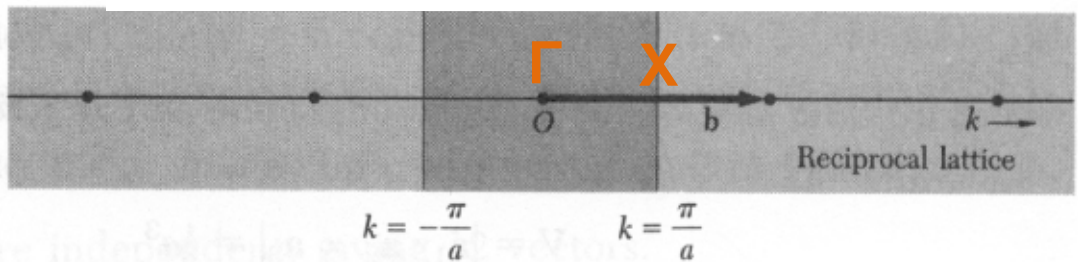
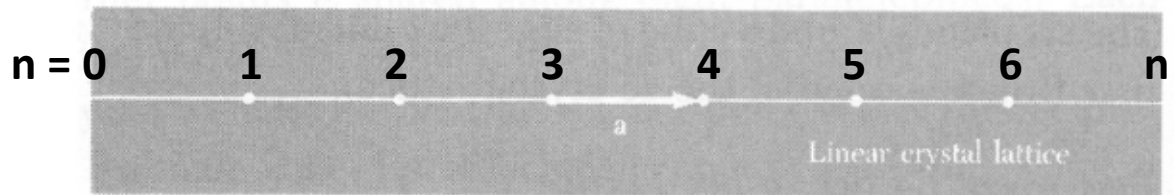
$$\psi_{\mathbf{k}} = \sum_n \{(\cos kna + i\sin kna)\phi_n\}$$

$$\psi_k = \sum_n \{(\cos kna + i \sin kna) \phi_n\}$$



$$\psi_k = \sum_n e^{inka} \phi_n$$

**1-dimensional case**



$$-\pi/a \leq k \leq \pi/a$$

**range of unique k**

**Consider k = 0: zone center  $\Gamma$**

$$\cos(kna) = \cos(0) = 1$$

$$\sin(kna) = \sin(0) = 0$$

$$e^{i0na} = 1$$

$$\psi = \sum \phi_n = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \dots$$

**Consider k =  $\pi/a$ : zone border X**

$$\cos(kna) = \cos(\pi n) = (-1)^n$$

$$\sin(kna) = \sin(\pi n) = 0$$

$$\psi = \sum (-1)^n \phi_n = \phi_0 - \phi_1 + \phi_2 - \phi_3 + \dots$$

$$e^{i\pi n} = (-1)^n$$

# Elementary Band Theory for Extended Solids

Example: linear infinite chain of equidistant H atoms

**Zone center  $\Gamma$**

$$\psi = \sum \phi_n = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \dots$$



**all in phase;**  
**all bonding ( $\sigma$ )**

**Zone border X**

$$\psi = \sum (-1)^n \phi_n = \phi_0 - \phi_1 + \phi_2 - \phi_3 + \dots$$



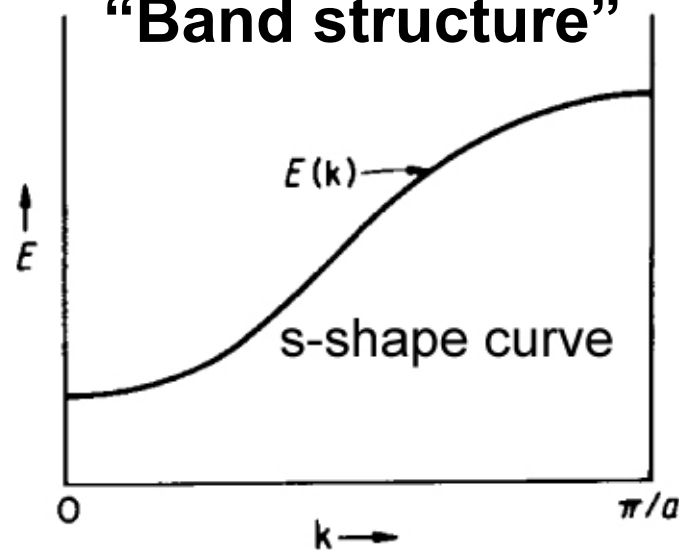
**all out of phase;**  
**all antibonding ( $\sigma^*$ )**

large number of MOs  
form band of states



Plot E as a function of k:

**“Band structure”**



$$-\pi/a \leq k \leq \pi/a;$$

$$E(k) = E(-k)$$

$$E(k) = \alpha + 2\beta \cos(ka)$$

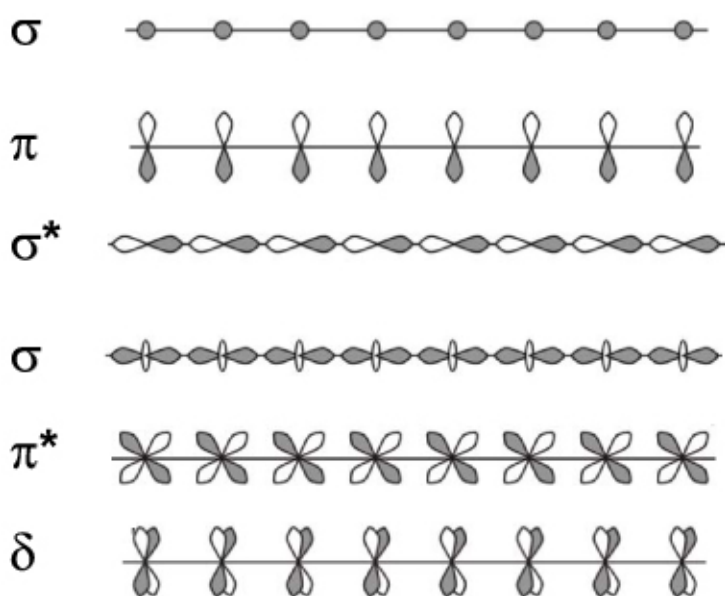
**Other case:** s, p and d orbitals in an infinite chain.

Let z be in the chain direction. Then,  $p_x$  will be analog to  $p_y$ , and  $d_{xy}$  to  $d_{x^2-y^2}$ , and  $d_{xz}$  to  $d_{yz}$ .

### Zone center $\Gamma$

$$\psi = \sum \phi_n = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \dots$$

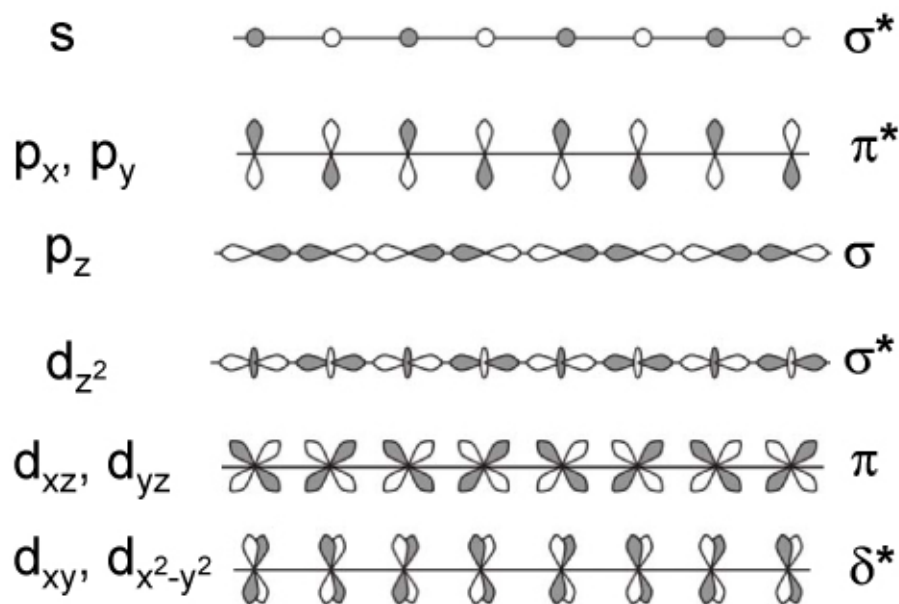
**all in phase; but ? bonding ?**



### Zone border X

$$\psi = \sum (-1)^n \phi_n = \phi_0 - \phi_1 + \phi_2 - \phi_3 + \dots$$

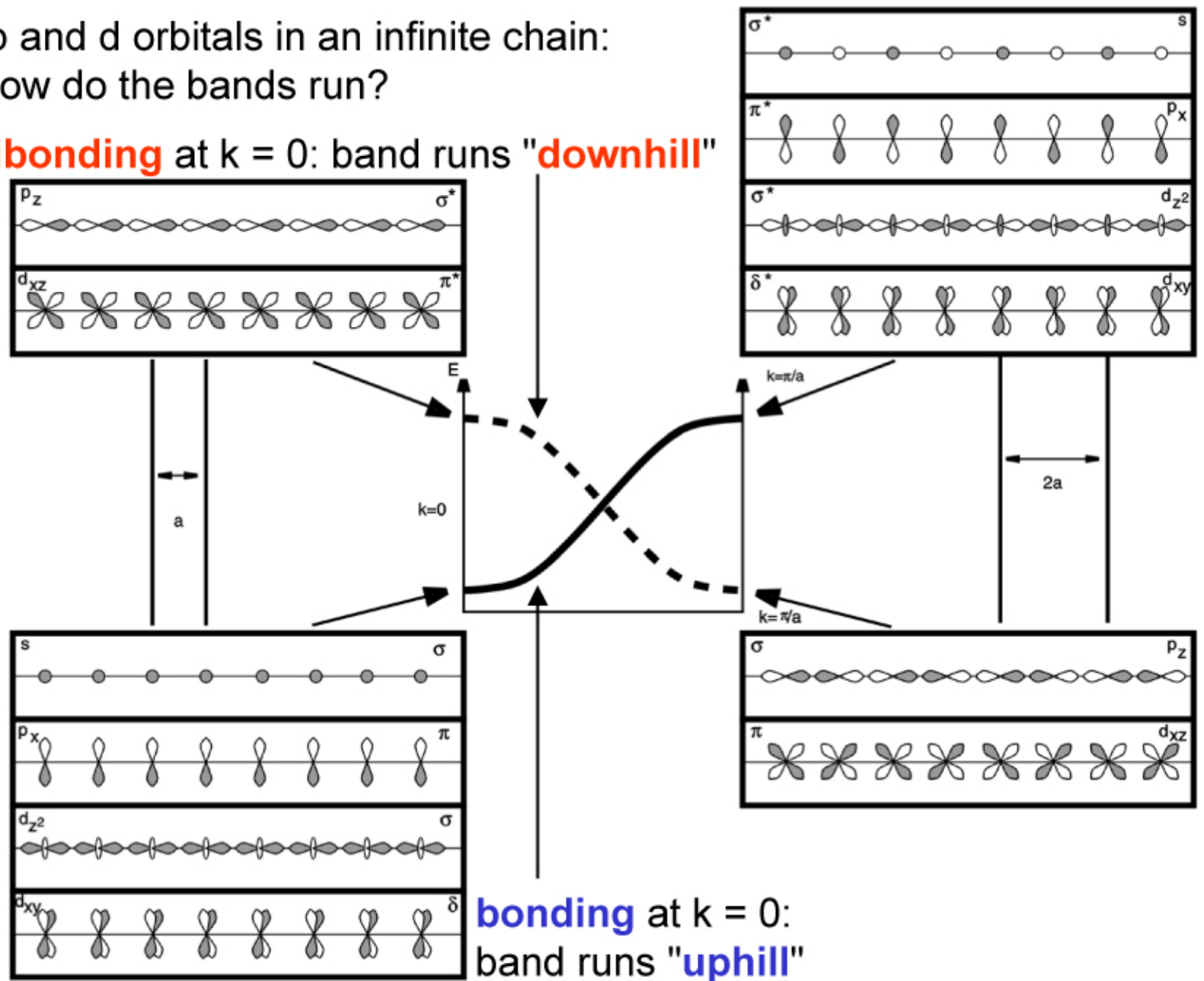
**all out of phase; but ? bonding ?**



Bonding/antibonding: depends on in phase/out of phase AND orientation

s, p and d orbitals in an infinite chain:  
how do the bands run?

**antibonding** at  $k = 0$ : band runs "downhill"



**bonding** at  $k = 0$ :  
band runs "uphill"



# WIDTH OF THE BANDS

## Bandwidth (**dispersion**)

The difference between highest and lowest level of one band.

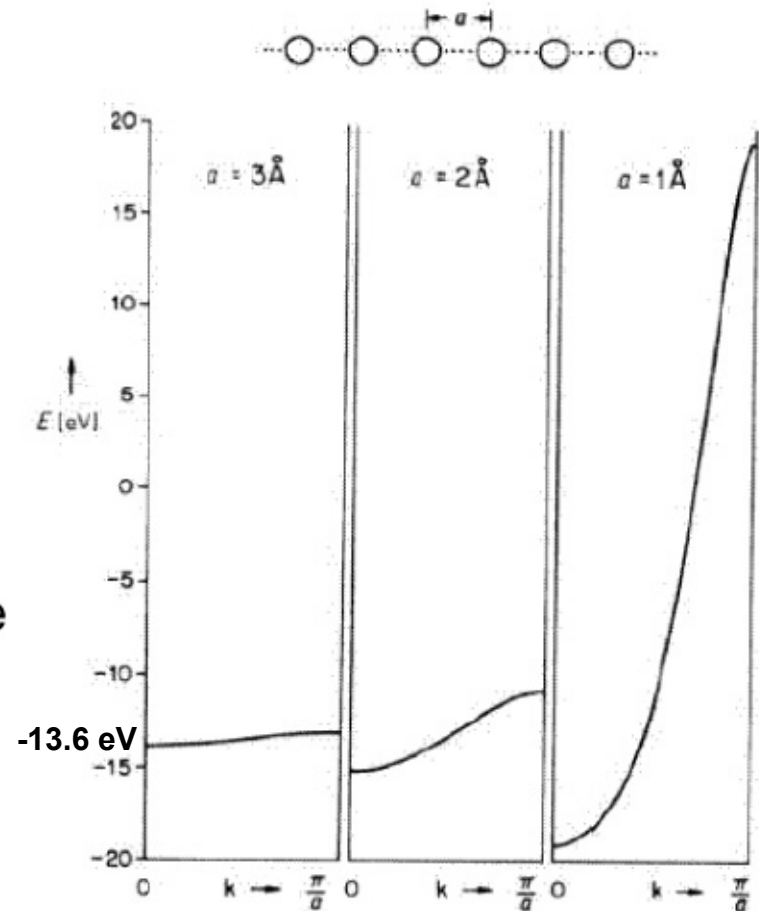
The bandwidth is determined by the **overlap** between the interacting orbitals.

The smaller the distance between the atoms, the larger the bandwidth.

**Note:** as always, the bonding orbitals are less stabilized than the antibonding orbitals are destabilized

a consequence of **overlap**: e.g., for a dimer,

$$E_{+/-} = \frac{\alpha \pm \beta}{1 \pm S}$$



Infinite chain of H atoms



# CALCULATION OF 1-D BAND STRUCTURE

N atoms  $\psi_k = \sum_{n=0}^N e^{inka} \phi_n$

Crystal Schrodinger Equation:  $H\psi(k) = E(k)\psi(k)$

Electronic energies:  $E(k) = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$

Dirac bra-ket notation:

$$\langle \psi | \hat{H} | \psi \rangle \equiv \int \psi^* \hat{H} \psi d\tau$$

for **normalized** atomic orbitals  
and ignoring overlap integrals:

$$\begin{aligned} \langle \phi_m | \phi_n \rangle &= 1 \text{ if } m = n \\ \langle \phi_m | \phi_n \rangle &= 0 \text{ if } m \neq n \end{aligned}$$

$$\langle \psi | \psi \rangle = \sum_{m,n} e^{i(n-m)ka} \langle \phi_m | \phi_n \rangle = N$$

$$\langle \psi | \hat{H} | \psi \rangle$$

$$\psi_k = \sum_n e^{inka} \phi_n$$

1. for on-site ( $m = n$ ):  $\langle \psi(k) | \hat{H} | \psi(k) \rangle = \sum_n \langle \phi_n | \hat{H} | \phi_n \rangle = N\alpha$
2. for resonance ( $m \neq n$ ), consider only the nearest neighbors (2)



$$\langle e^{-inka} \phi_n | \hat{H} | e^{i(n\pm 1)ka} \phi_{n\pm 1} \rangle = \beta e^{\pm ika}$$

$$E(k) = \frac{\langle \psi(k) | \hat{H} | \psi(k) \rangle}{\langle \psi(k) | \psi(k) \rangle} = \frac{N\alpha + N\beta(e^{ika} + e^{-ika})}{N}$$

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



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

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

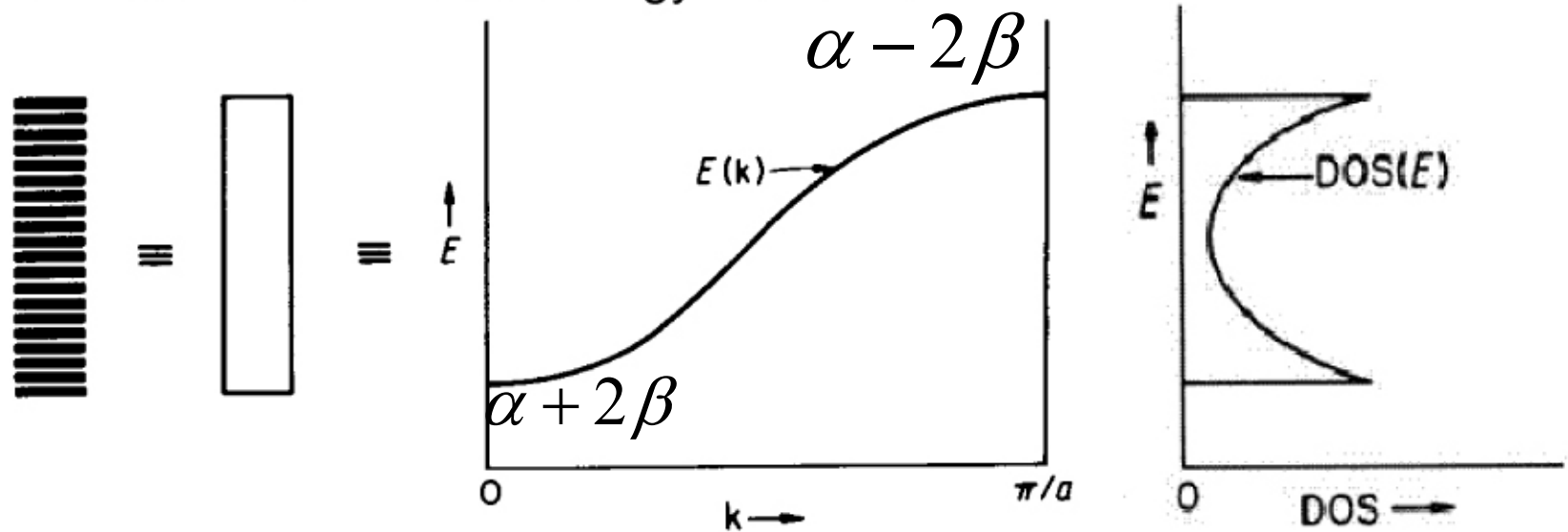
**Bandwidth** in 1D is  $4\beta$  (this result ignores overlap (S integrals))

in  $Z$  dimensions:  $W = 4Z\beta$

# SLOPE OF THE BANDS – DENSITY OF STATES

Densities of states (DOS)

≡ number of levels in the energy interval  $\Delta E$



DOS is proportional to the inverse slope of the band;

steep bands (large overlap)  $\Rightarrow$  small DOS

flat bands (small overlap)  $\Rightarrow$  large DOS

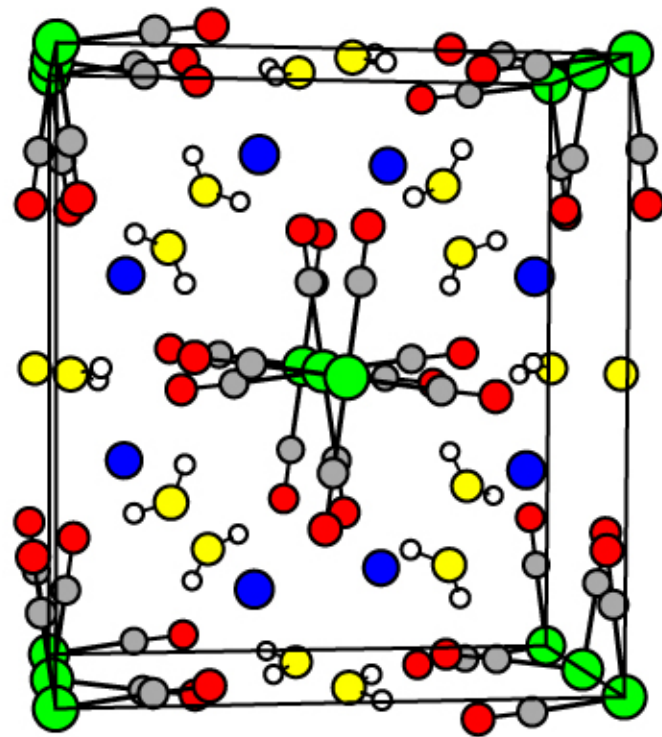
**DOS( $E_F$ ) determines properties**

e.g., electrical conductivity, magnetic susceptibility, specific heat ...

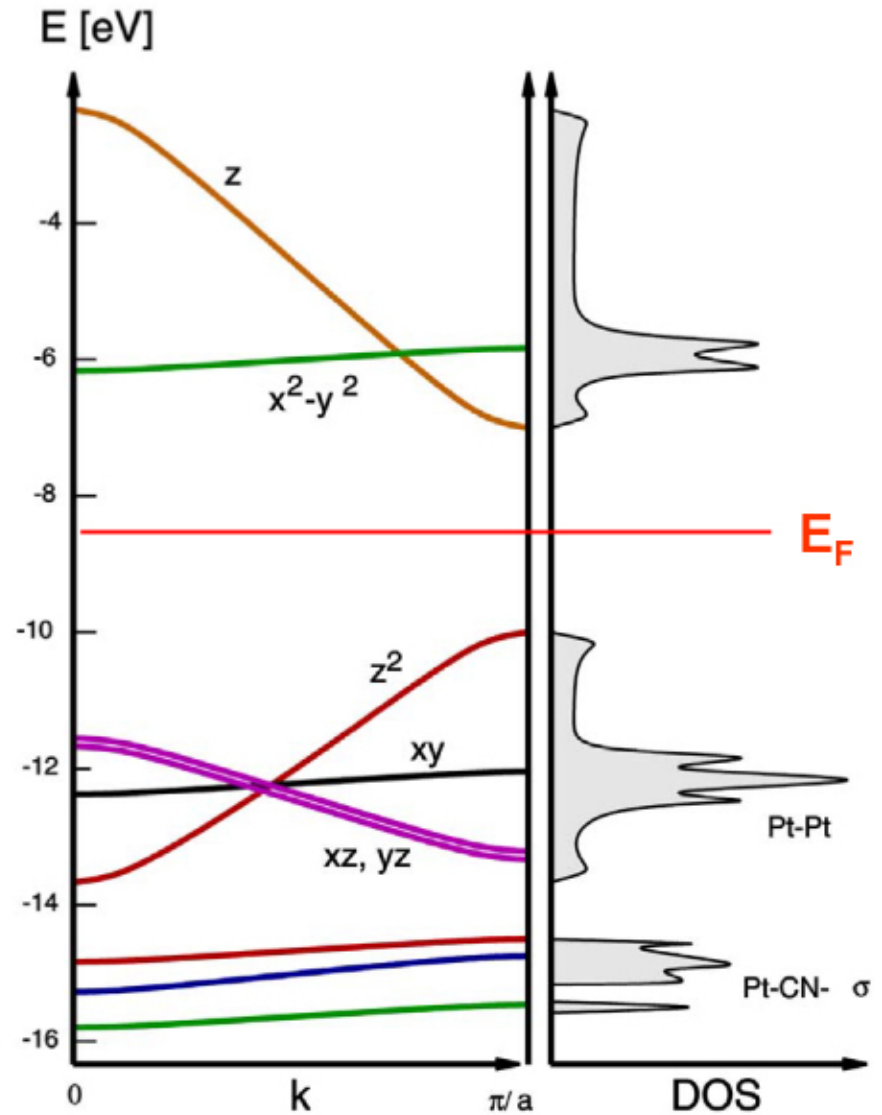
DOS( $E_F$ ) = 0: always nonmetallic

DOS( $E_F$ ) > 0: often metallic

## Example: Krogman's salt



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

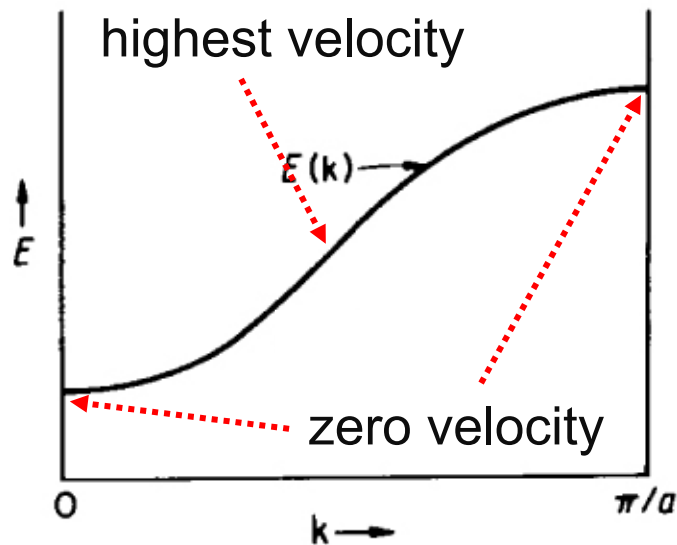


the DOS counts levels – the integral of the DOS up to  $E_F$  is the total number of occupied MOs

# SLOPE OF THE BANDS – CARRIER VELOCITY

the mean velocity of an electron described by energy  $E$  and wave vector  $\mathbf{k}$  is

$$\mathbf{v}(\mathbf{k}) = \left( \frac{1}{\hbar} \right) \frac{\partial E}{\partial \mathbf{k}}$$



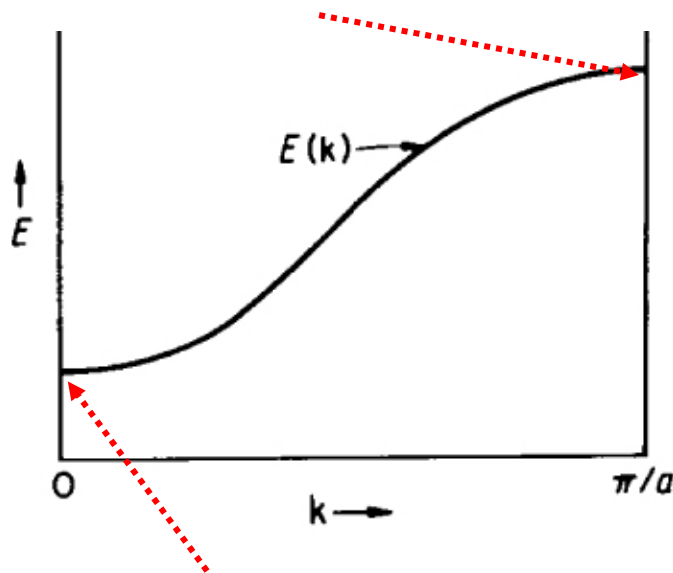
- General result. Electrons move forever with constant velocity (in ideal crystals).
- Zero velocity for electrons in isolated atomic levels (zero bandwidth)
- less overlap  $\rightarrow$  lower tunneling probability  $\rightarrow$  lower velocity

# CURVATURE OF THE BANDS – CARRIER MASS

the **effective mass** of a charge carrier near a band minimum or maximum is inversely proportional to the curvature of the band:

$$\frac{1}{m^*} = \left( \frac{1}{\hbar^2} \right) \frac{\partial^2 E}{\partial \mathbf{k}^2}$$

negative  
effective mass! → hole!



positive effective mass

**Parabolic approximation** near  
minimum/maximum:

$$E(k) = E_0 + \frac{\hbar^2 k^2}{2m^*}$$

$$\Rightarrow \frac{\partial^2 E}{\partial k^2} = \frac{\hbar^2}{m^*}$$

# 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

$\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ : 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,  $\sigma = 10^{+2} \Omega^{-1}\text{cm}^{-1}$

### Comparison of specific conductivities

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

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

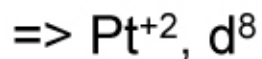
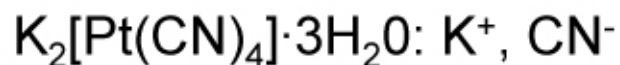
**Metals**

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

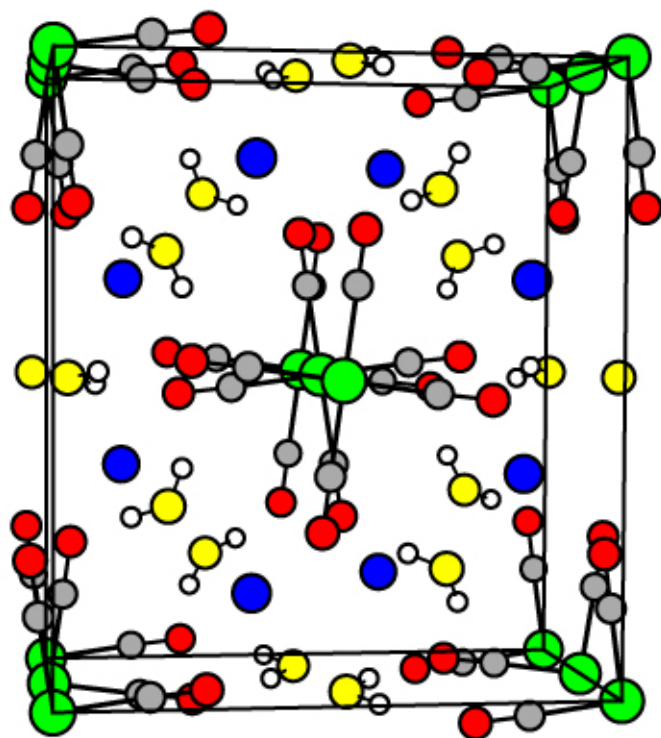


# Krogman's salt: a quasi one-dimensional material

**Step 1:** valence-orbitals, electron-counting

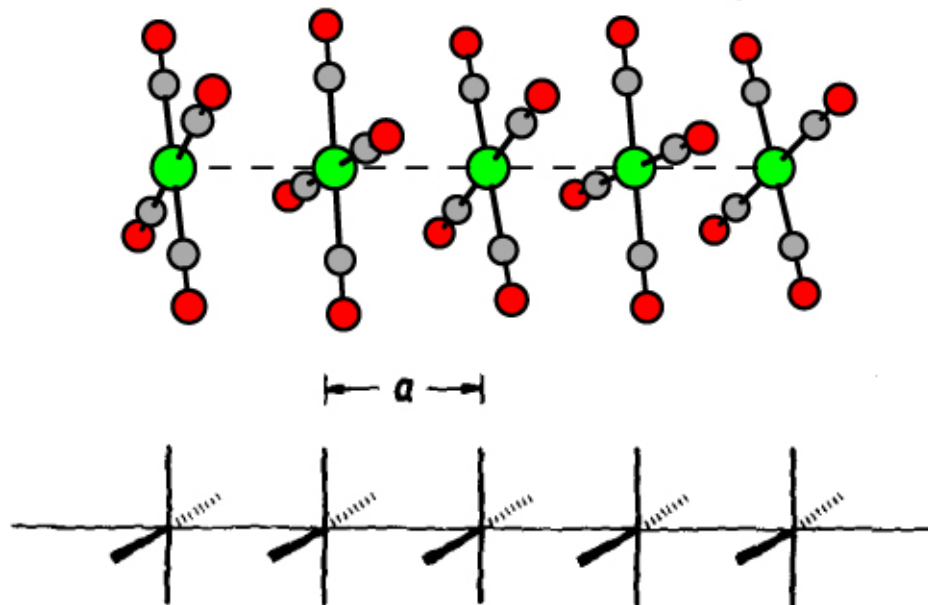


**Step 2:** relative energies of the valence-orbitals (here: **d** orbitals)  
understanding of **the crystal structure** required!



Unit cell of  $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$

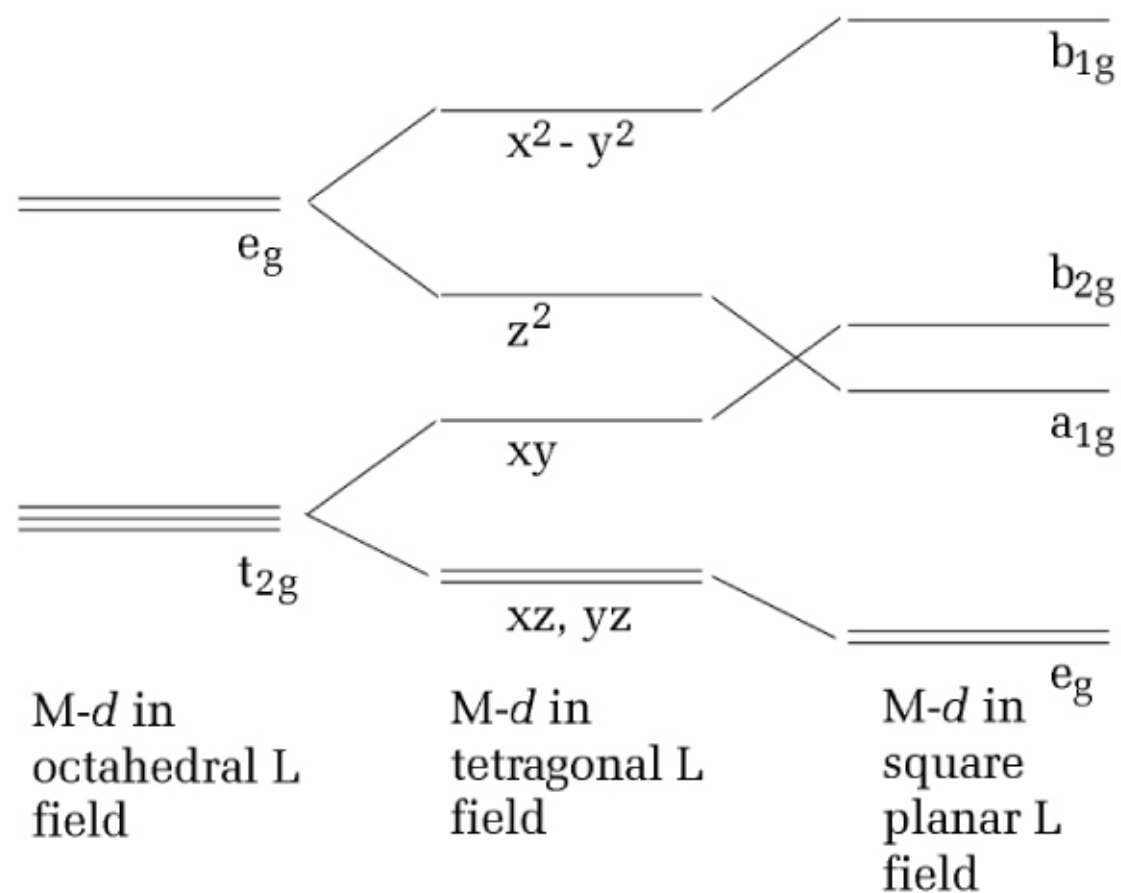
Chain of **square planar**  $[\text{Pt}(\text{CN})_4]^{2-}$  units



# Krogman's salt: a quasi one-dimensional material

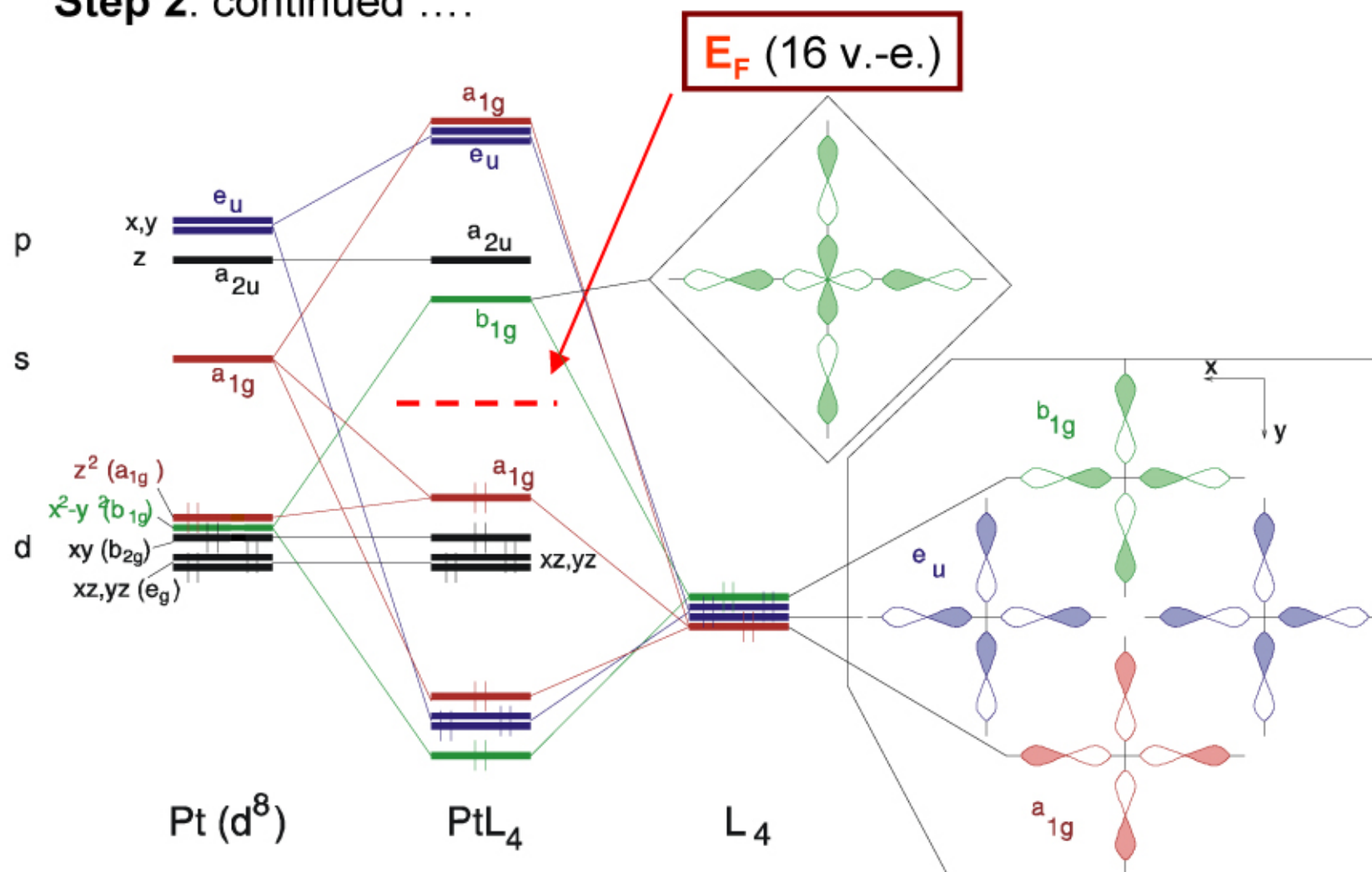
Step 2: continued ....

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



# Krogman's salt: a quasi one-dimensional material

Step 2: continued ....

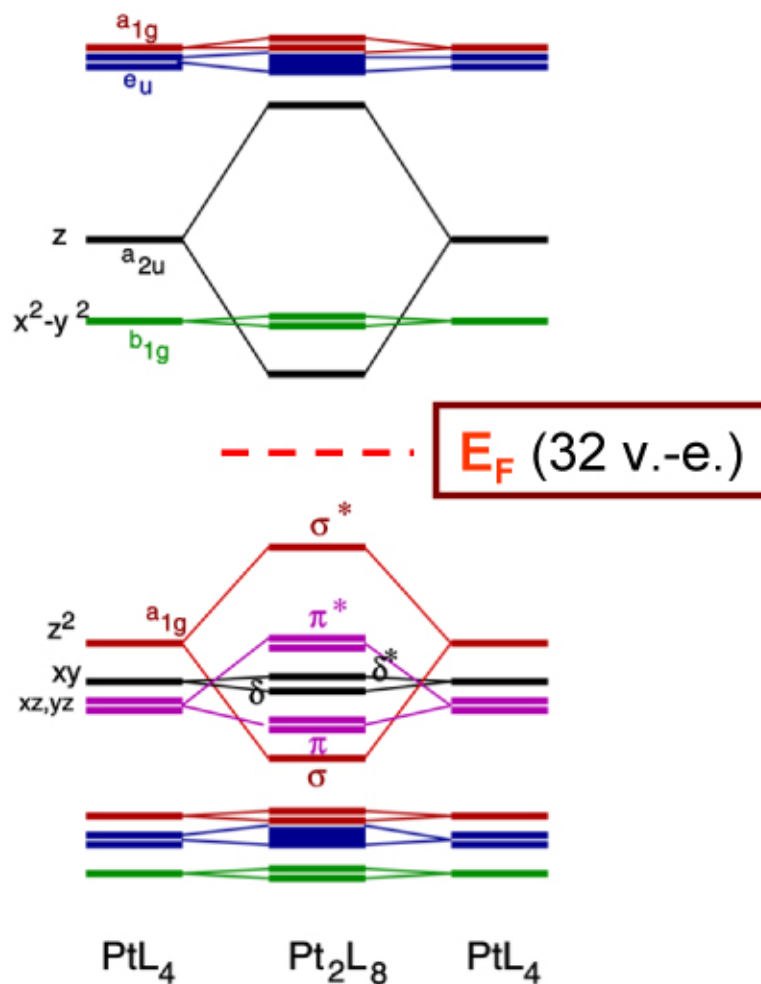


The complete MO of  $\text{PtL}_4$

# Krogman's salt: a quasi one-dimensional material

Step 2: continued ....

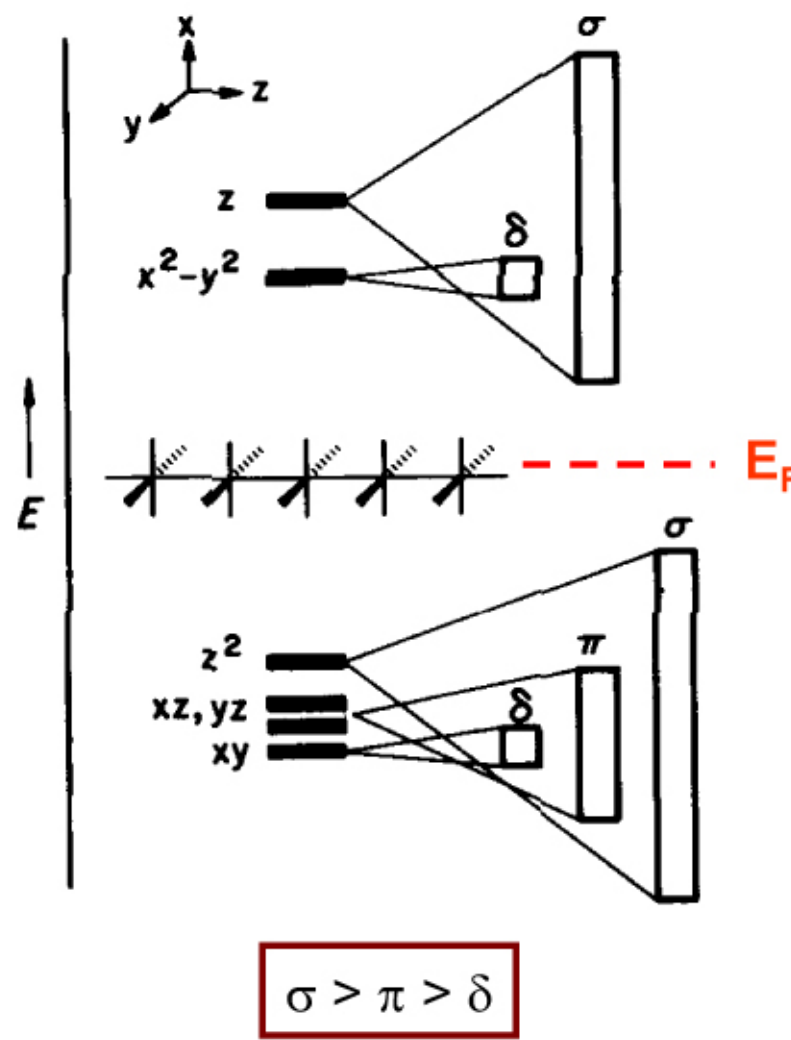
Relative height of  $p_z$  vs.  $d_{x^2-y^2}$ ?



Formation of PtL<sub>4</sub> pairs

Step 3: determine how the bands run

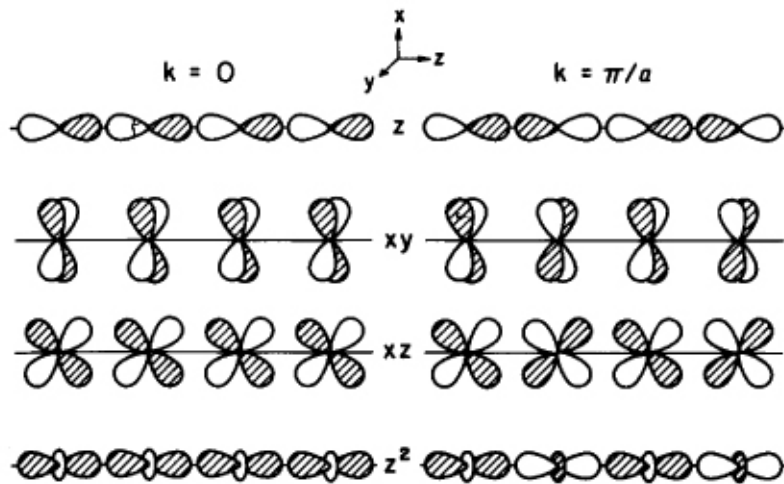
? Bandwidths ?



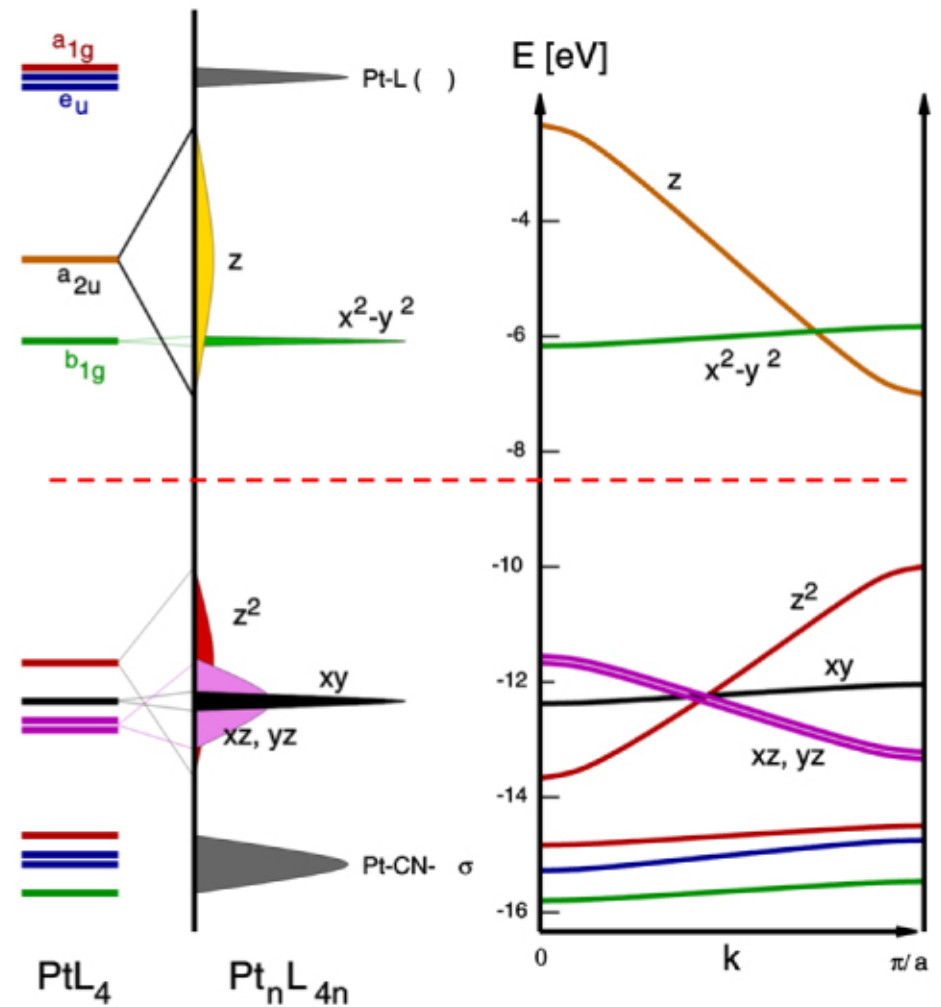
# Krogman's salt: a quasi one-dimensional material

Step 3: continued ....

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

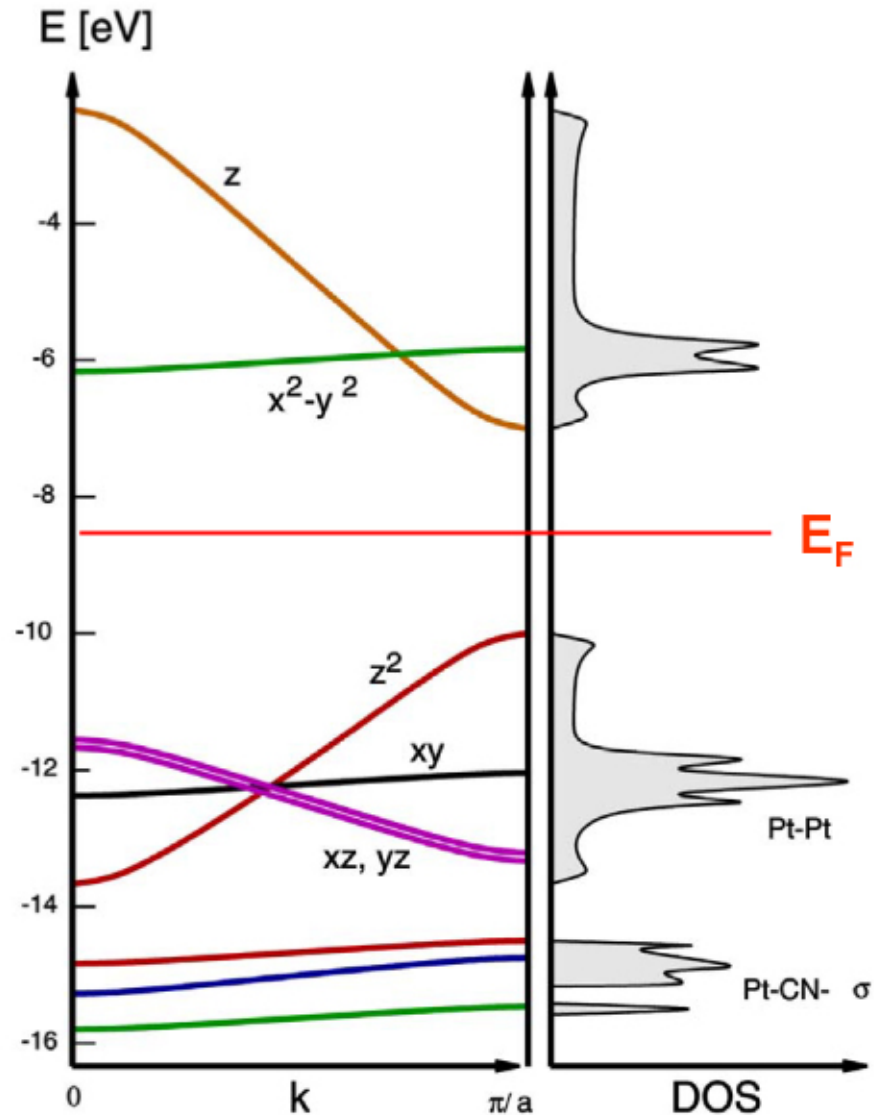


Step 4: sketch the band structure



# Krogman's salt: a quasi one-dimensional material

Step 5: sketch the DOS



Large bandgap ( $> 3$  eV)  $\Rightarrow$  white insulator

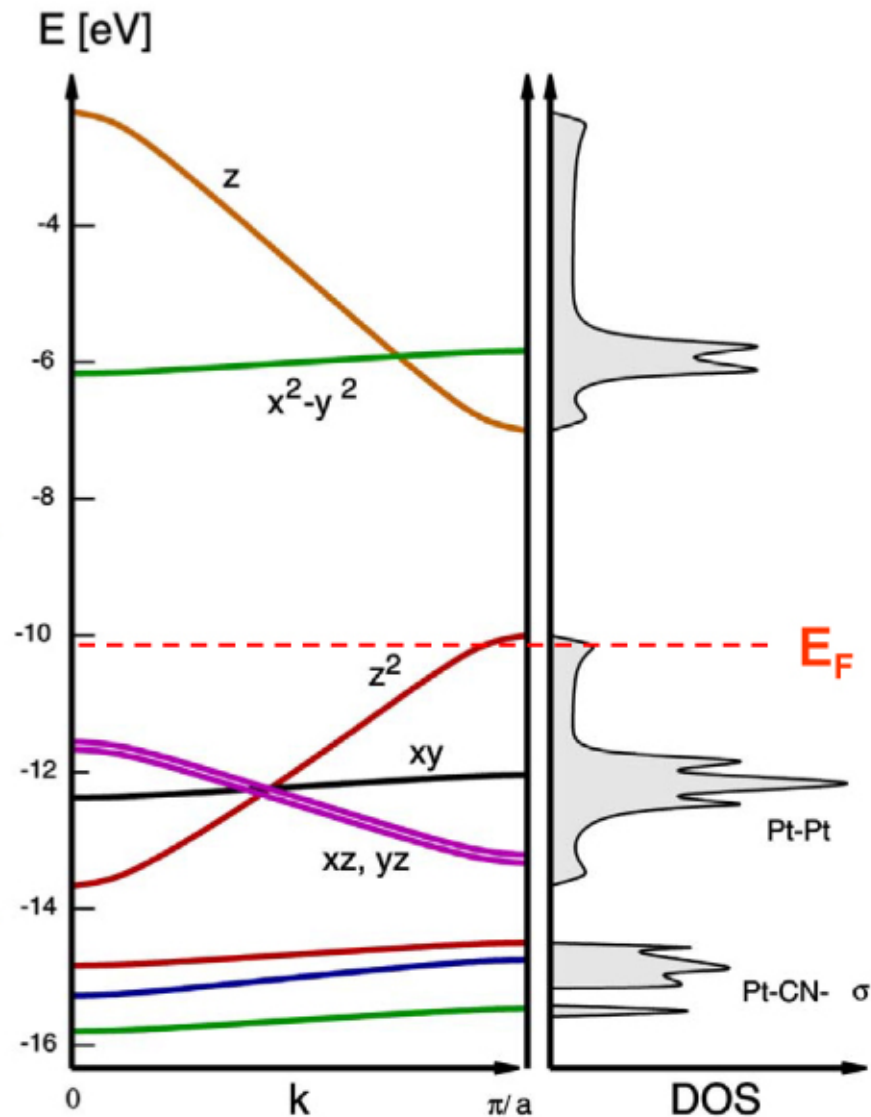
# Krogman's salt: a quasi one-dimensional material

$K_2[Pt(CN)_4]$  vs.  $K_2[Pt(CN)_4]Cl_{0.3}$ : 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  
=> itinerant electrons along the  $c^*$  direction  
=> **metallic conductivity** along  $c^*$

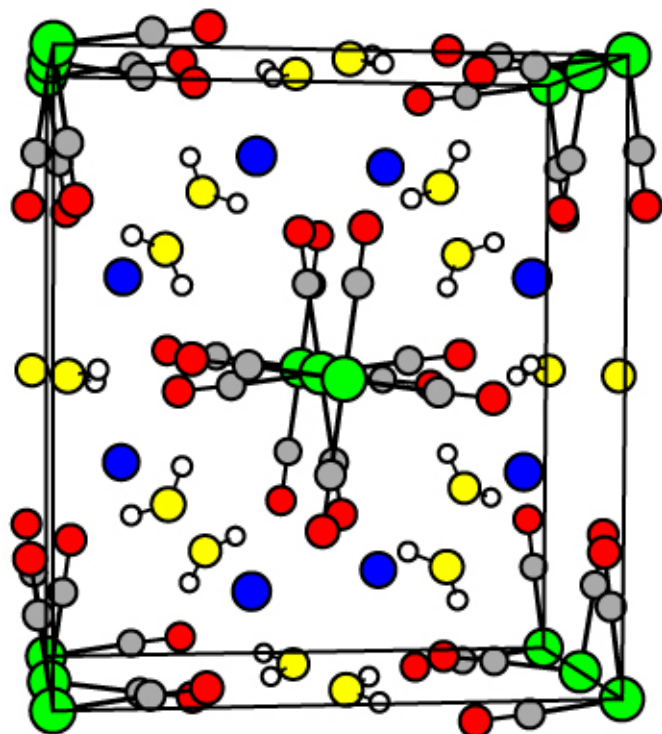
BUT is the crystal structure the same?



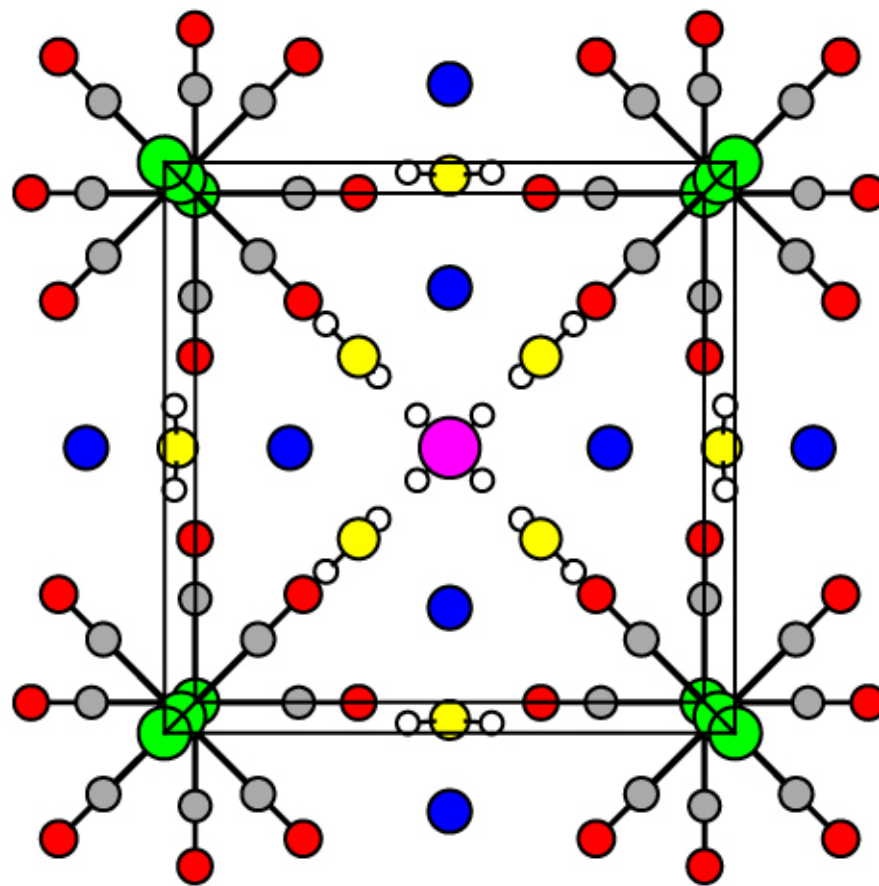


# Krogman's salt: a quasi one-dimensional material

$K_2[Pt(CN)_4]$  vs.  $K_2[Pt(CN)_4]Cl_{0.3}$ : what are the differences?



Structure of  $K_2[Pt(CN)_4]$



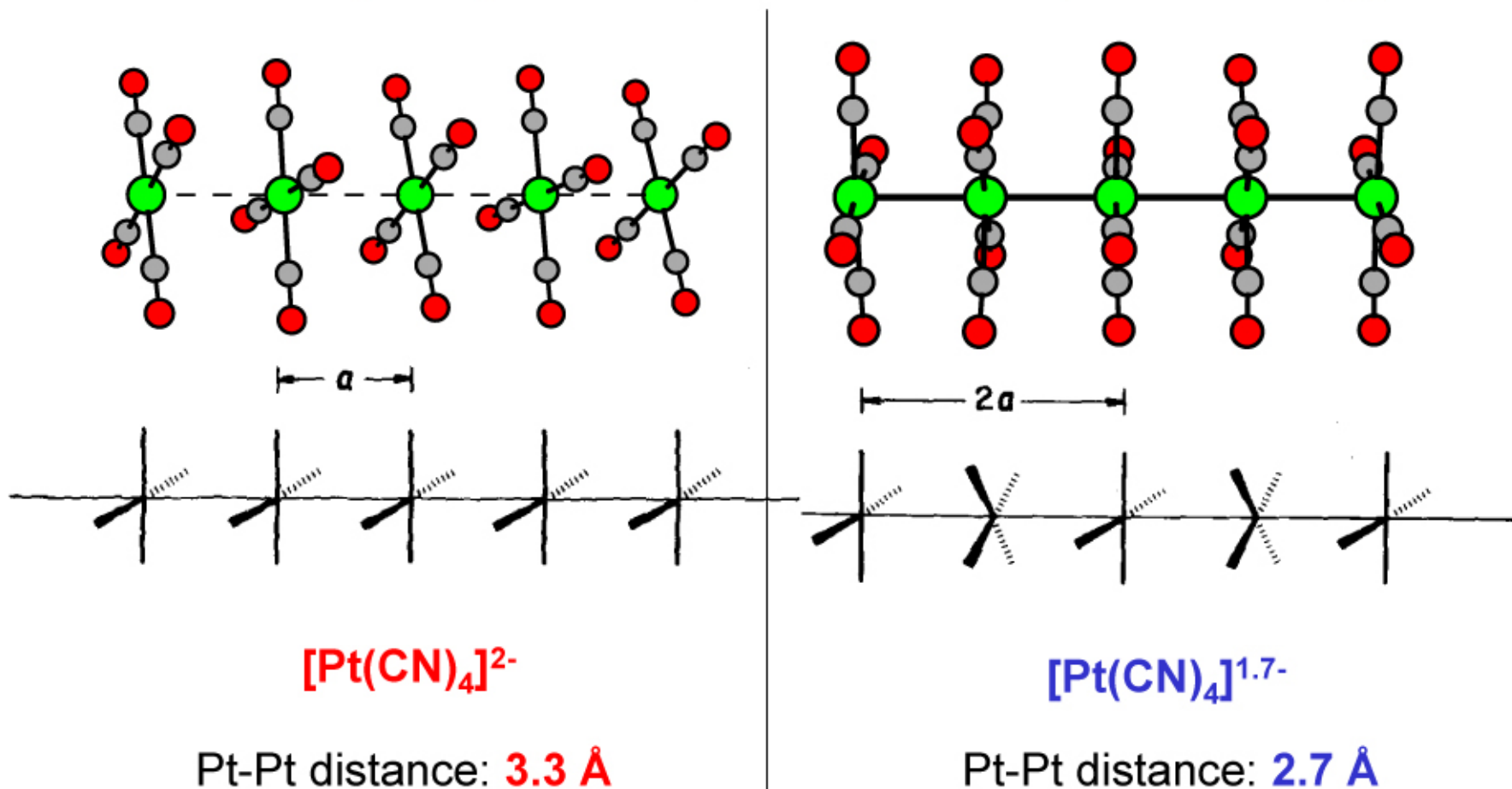
Structure of  $K_2[Pt(CN)_4]Cl_{0.3}$



# Krogman's salt: a quasi one-dimensional material

$K_2[Pt(CN)_4]$  vs.  $K_2[Pt(CN)_4]Cl_{0.3}$ : what are the differences?

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

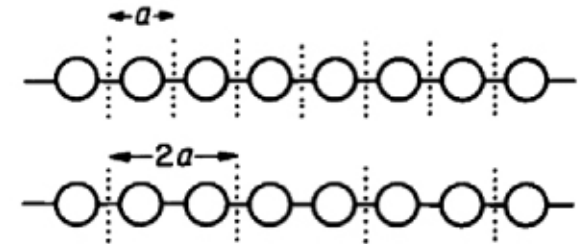


Why is the Pt-Pt distance shorter? Why staggered conformation?

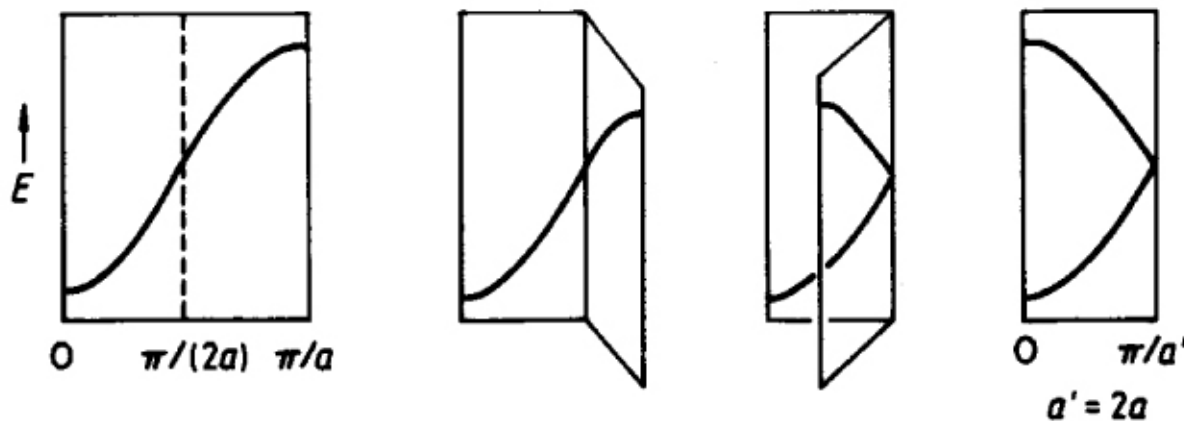
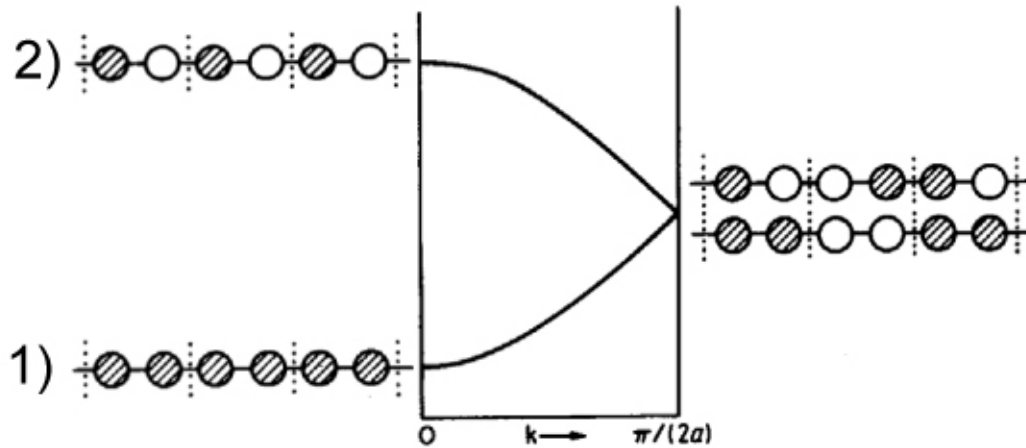
# Krogman's salt: a quasi one-dimensional material

1) What are the consequences of the cell doubling?

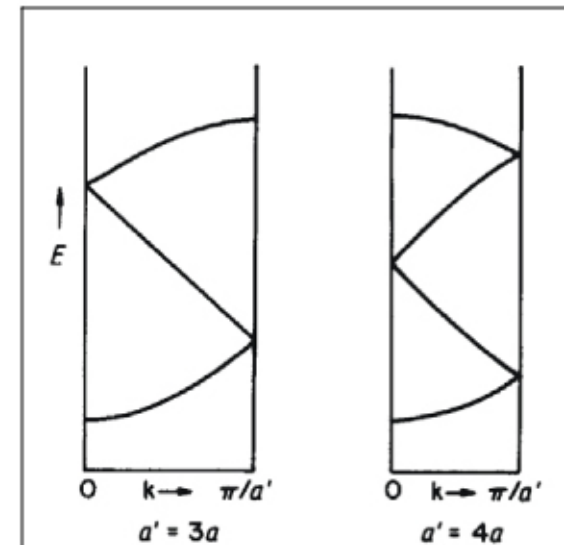
Doubled direct cell => half reciprocal cell



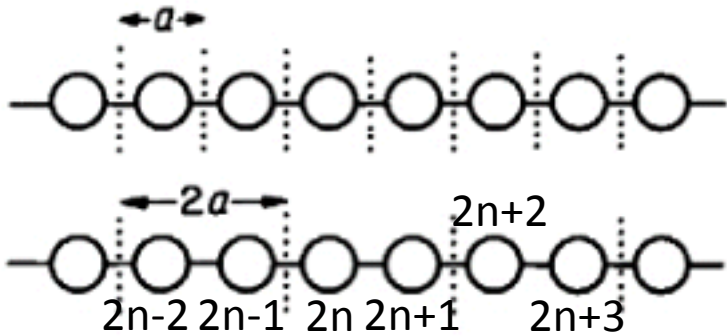
2 basis orbitals:  
1) 2)





Folding mechanism      doubled cell



tripled - quadrupled



2 basis orbitals:  
 1)  2) 

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

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

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

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

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

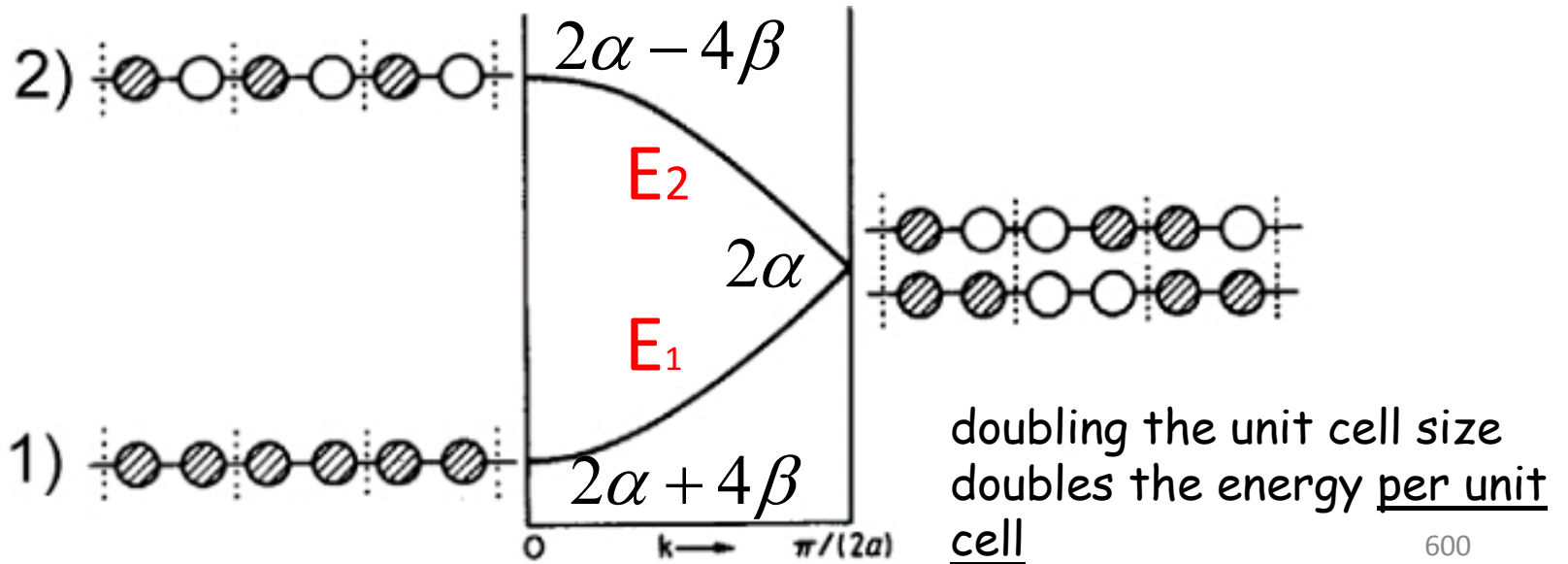
$$+ e^{-ikn \cdot 2a} \cdot e^{ik(n+1) \cdot 2a} \langle (\phi_{2n} + \phi_{2n+1}) | \hat{H} | (\phi_{2n+2} + \phi_{2n+3}) \rangle$$

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

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

Similarly:

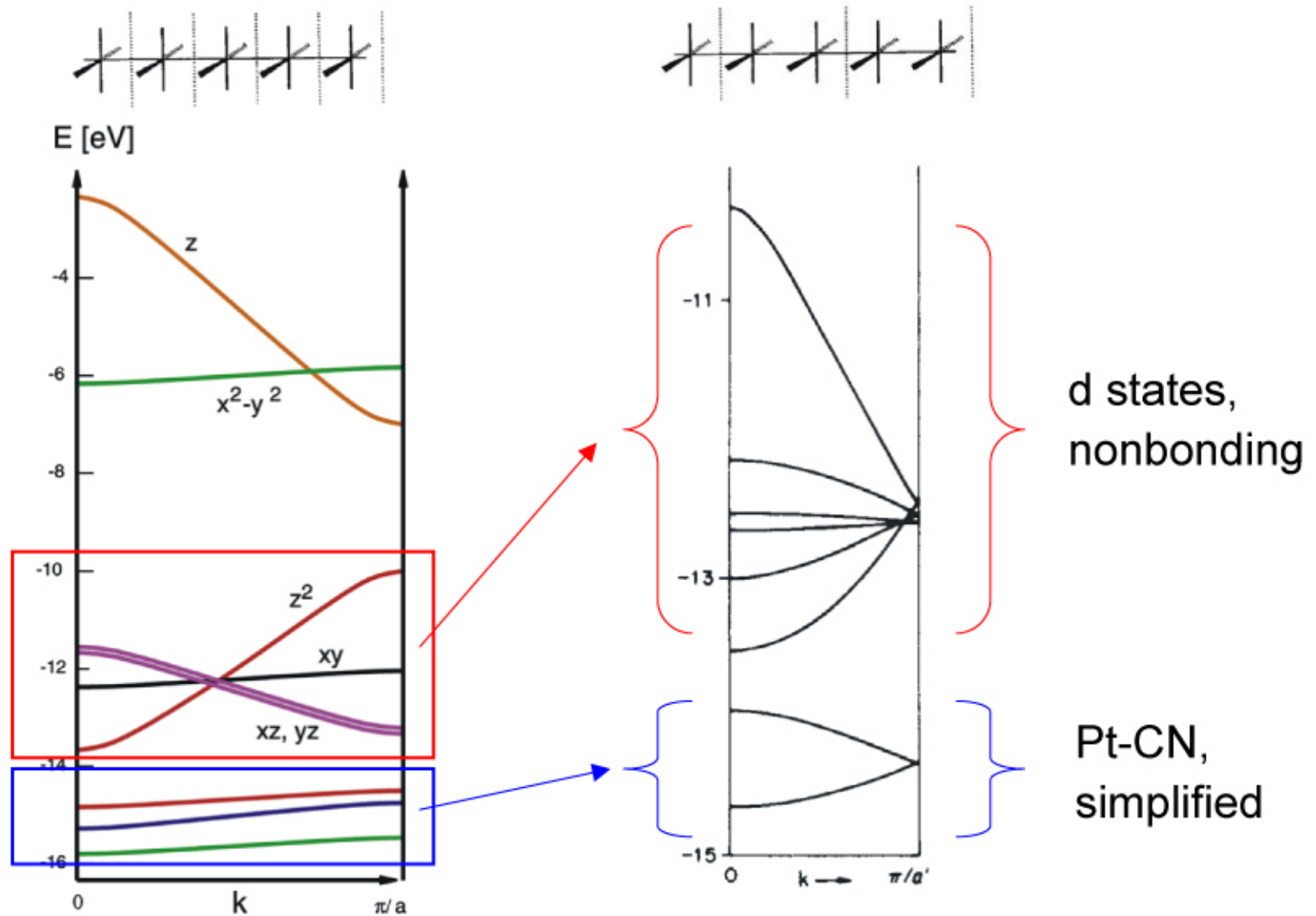
$$\begin{aligned}
 E_2(k)(2\text{-atom-basis}) &= \\
 & e^{-ikn \cdot 2a} \cdot e^{ik(n-1) \cdot 2a} \langle (\phi_{2n} - \phi_{2n+1}) | \hat{H} | (\phi_{2n-2} - \phi_{2n-1}) \rangle \\
 & + e^{-ikn \cdot 2a} \cdot e^{ikn \cdot 2a} \langle (\phi_{2n} - \phi_{2n+1}) | \hat{H} | (\phi_{2n} - \phi_{2n+1})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



# Krogman's salt: a quasi one-dimensional material

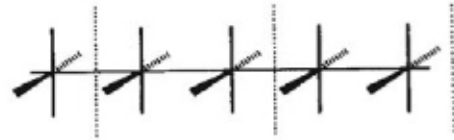
1) What are the consequences of the cell doubling?

=> apply the folding mechanism

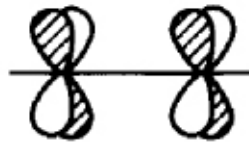


# Krogman's salt: a quasi one-dimensional material

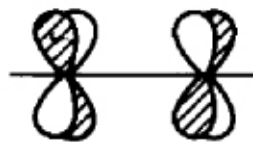
2) What are the consequences of the staggering?



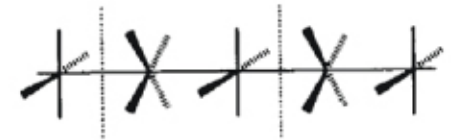
$d_{xy}$  states:



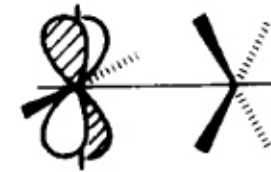
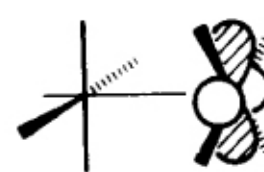
$\delta$  bonding



$\delta$  antibonding



$d_{xy}$  states:

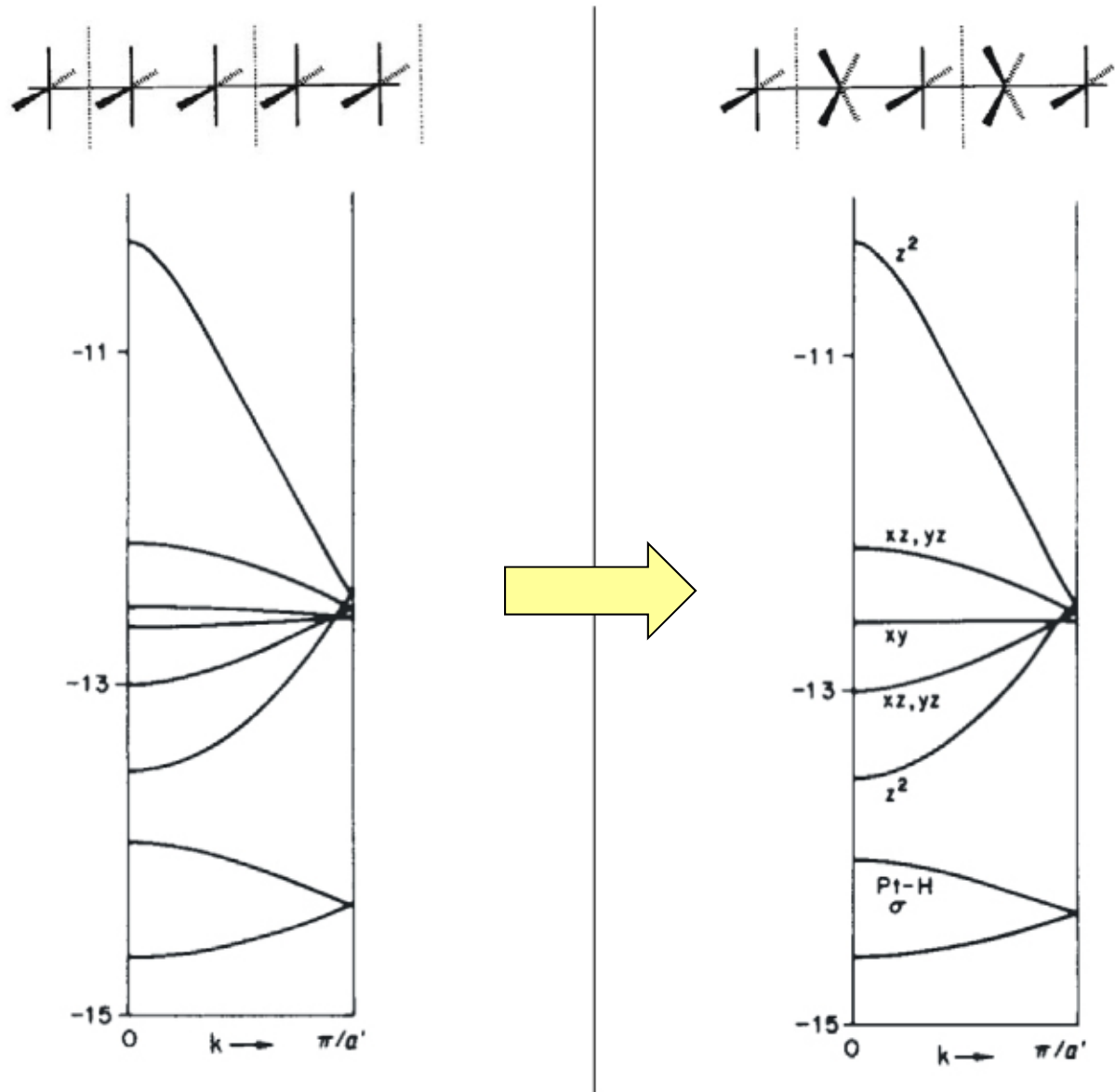


**nonbonding**

=> does not depend on  $k$

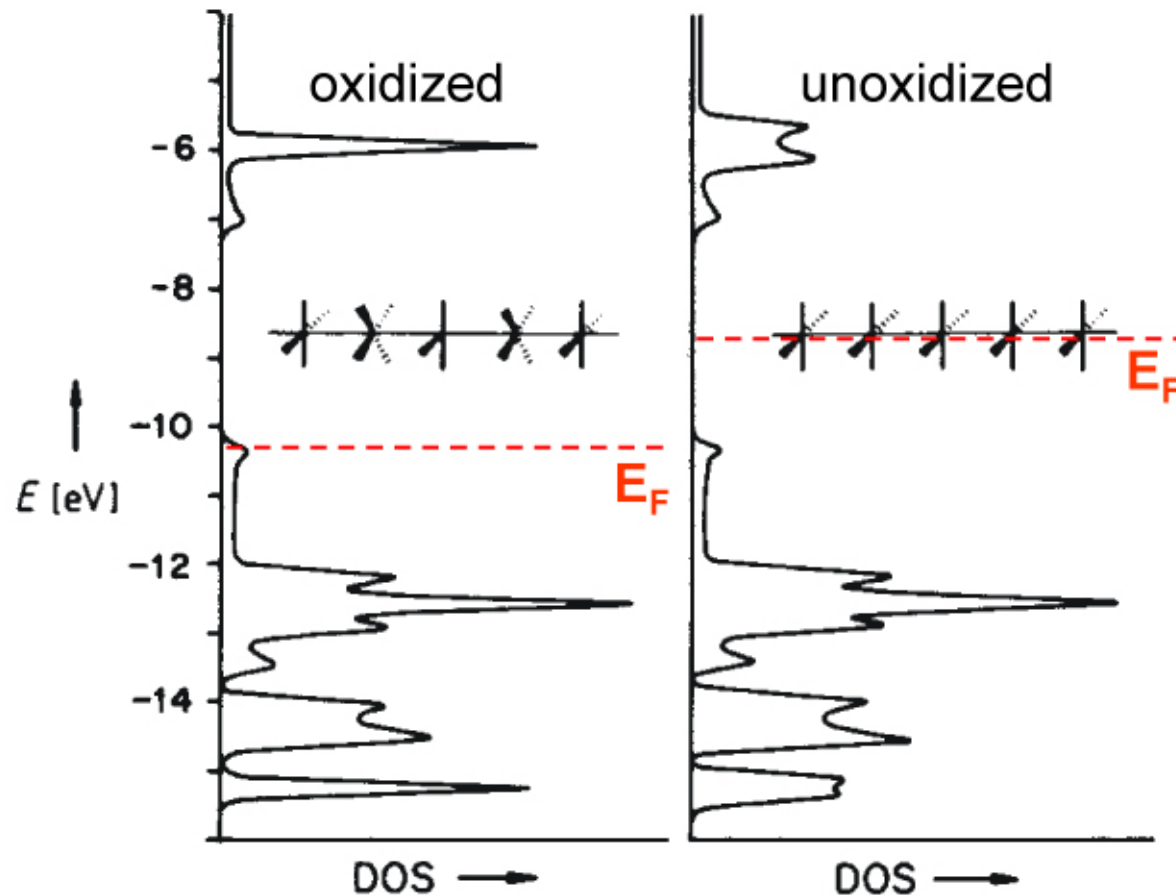
# Krogman's salt: a quasi one-dimensional material

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:

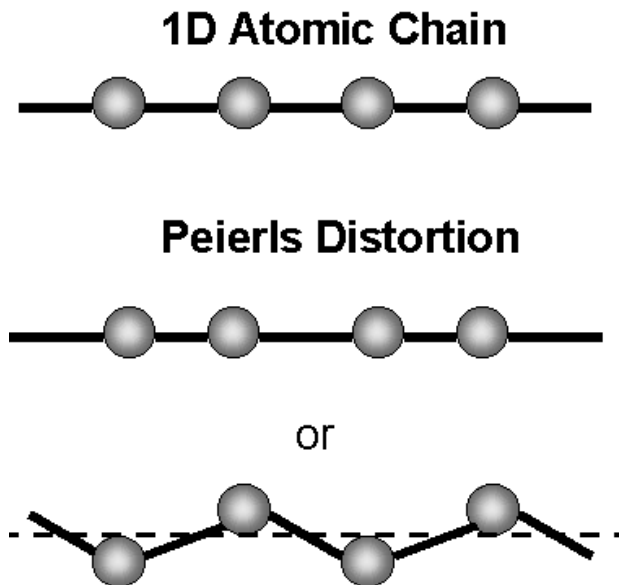
$K_2[Pt(CN)_4] \cdot 3H_2O$ : white insulator,  $\sigma = 10^{-7} \Omega^{-1}cm^{-1}$   
 $K_2[Pt(CN)_4]Cl_{0.3} \cdot 3H_2O$ : bronze metal,  $\sigma = 10^{+2} \Omega^{-1}cm^{-1}$



# PEIERLS (pay-earls) DISTORTION

*"1D equally spaced chains with one electron per ion are unstable"*

such a system can lower its energy by distorting so as to remove an electronic degeneracy.

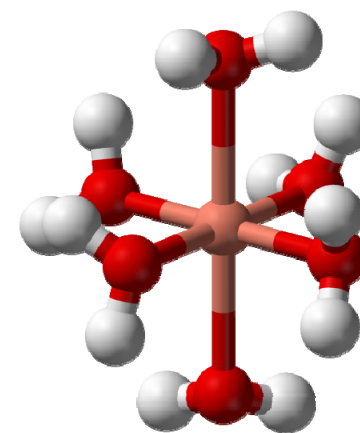
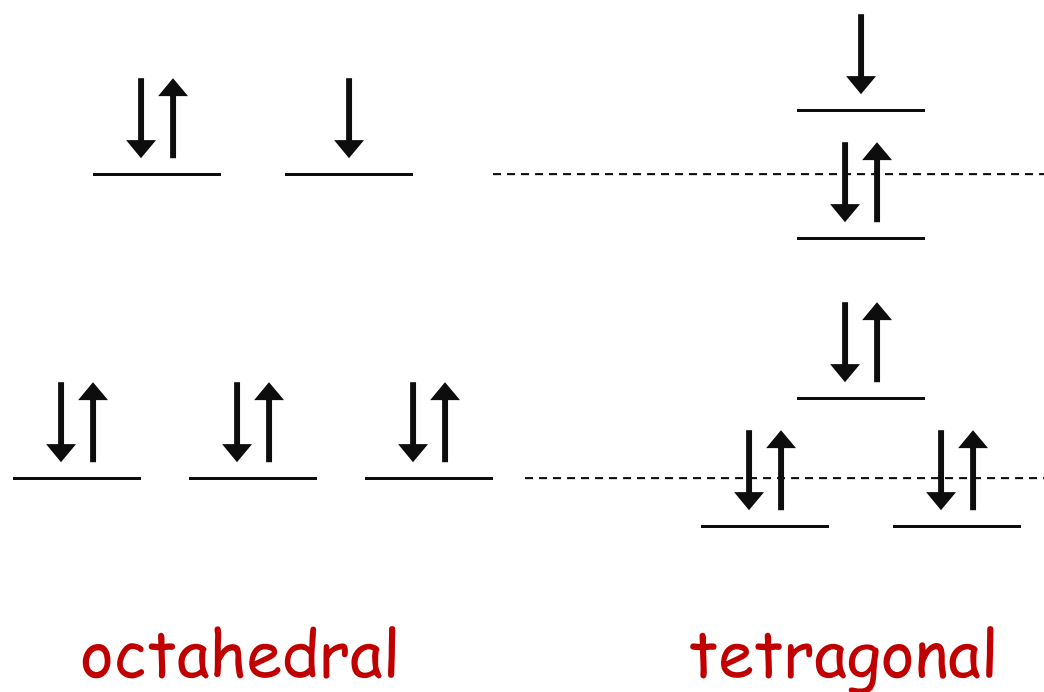


This is the solid state analogue of the Jahn-Teller effect.  
- symmetry breaking lifts a degeneracy

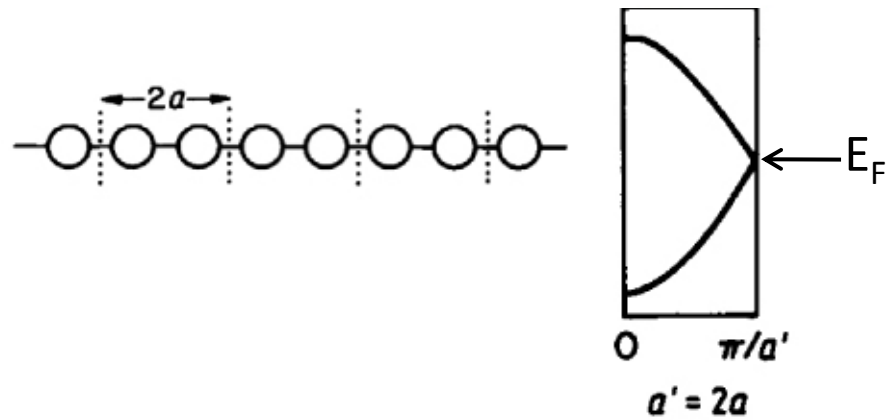
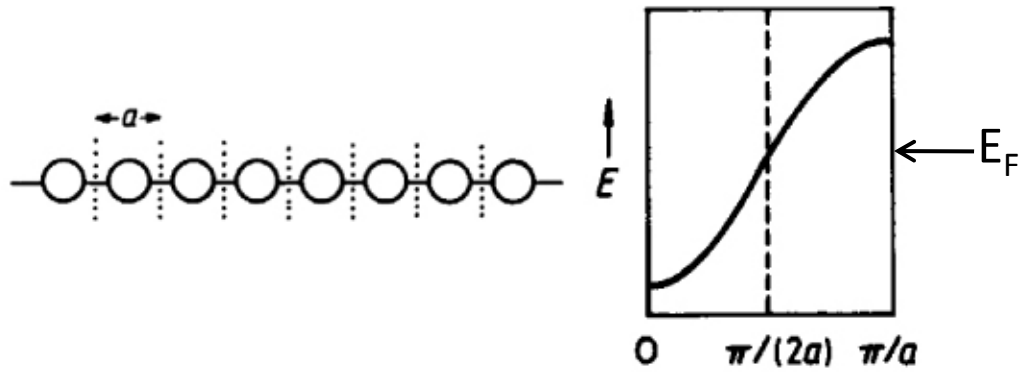
# JAHN-TELLER EFFECT

a non-linear molecule with unequally-occupied degenerate orbitals will undergo a symmetry-lowering deformation that breaks the degeneracy, stabilizing the system.

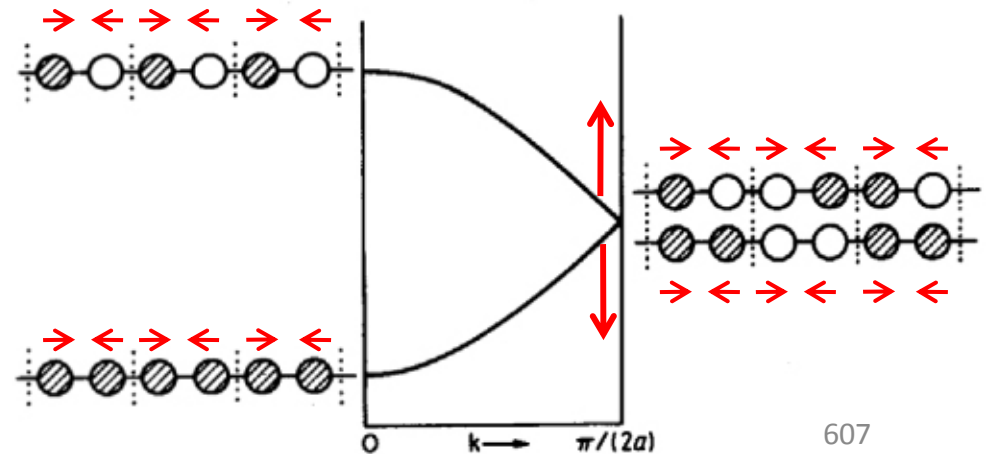
e.g. tetragonal distortion lowers the energy of a  $d^9$  complex

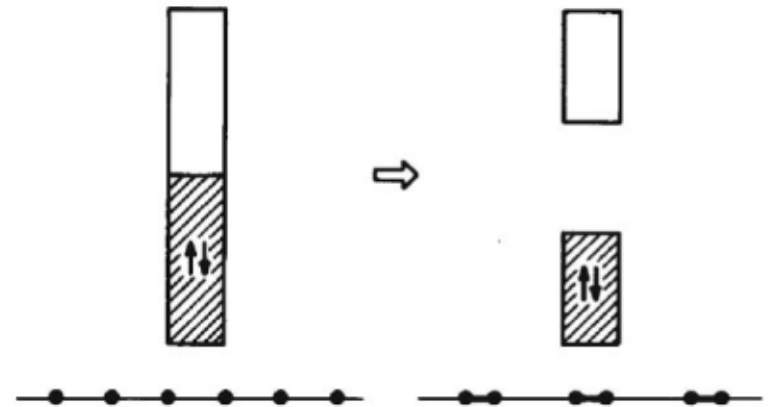
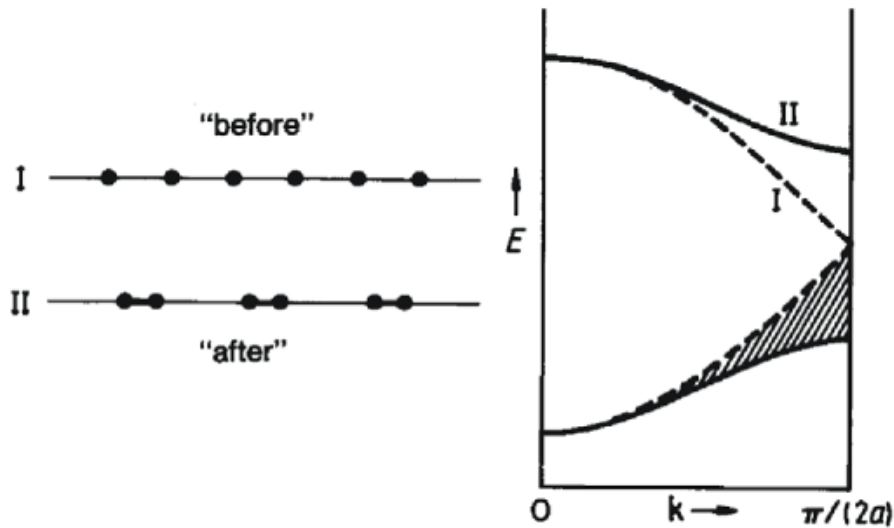


# PEIERLS DISTORTION OF H ATOM CHAIN



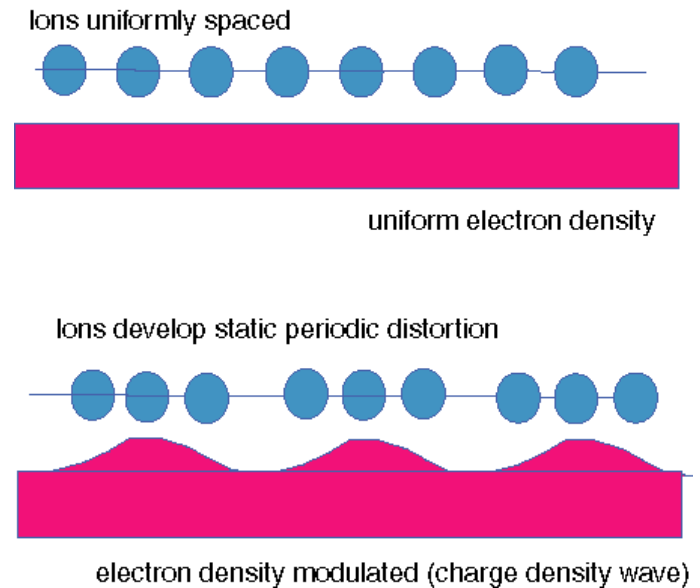
symmetric pairing distortion opens a band gap at the Fermi level.



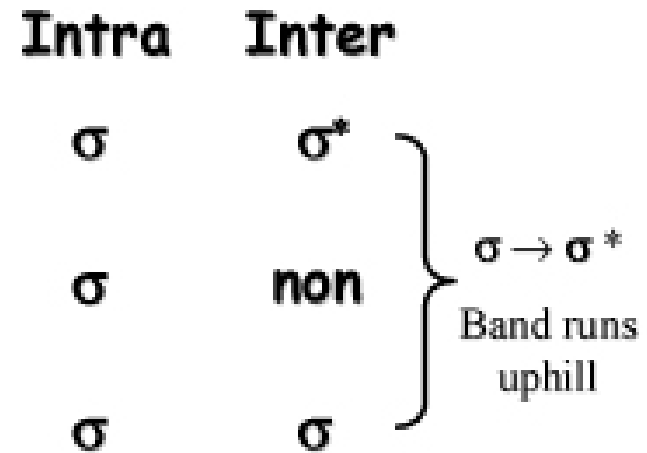
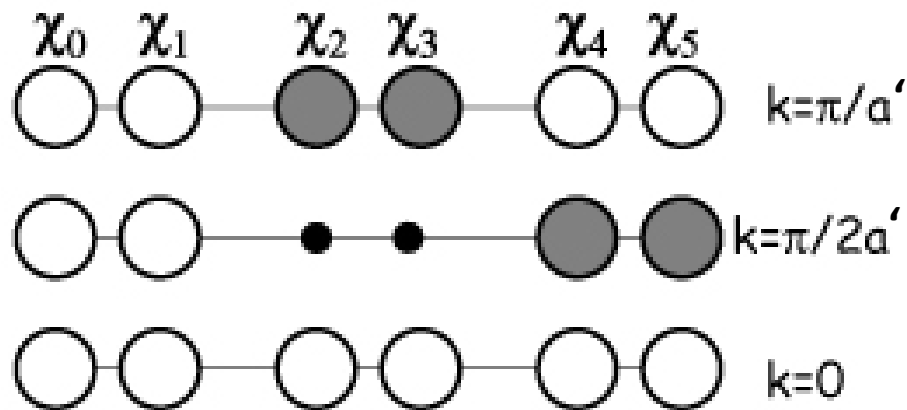


- distortion stabilizes the system
- effect is largest for  $\frac{1}{2}$  filled band
  - band gap forms
  - $H_2$  molecules more stable than H chain

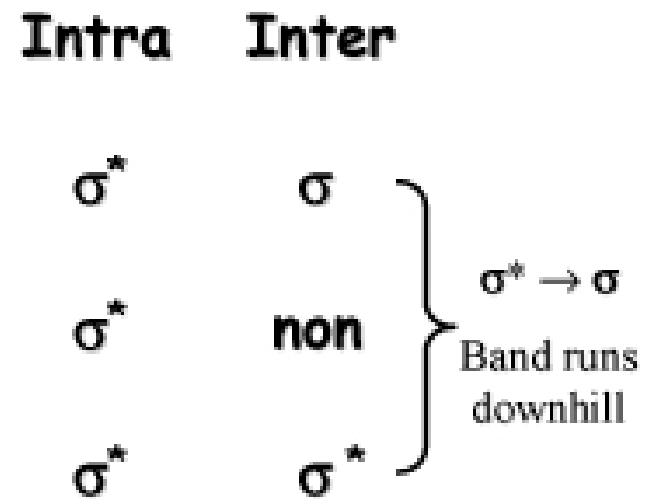
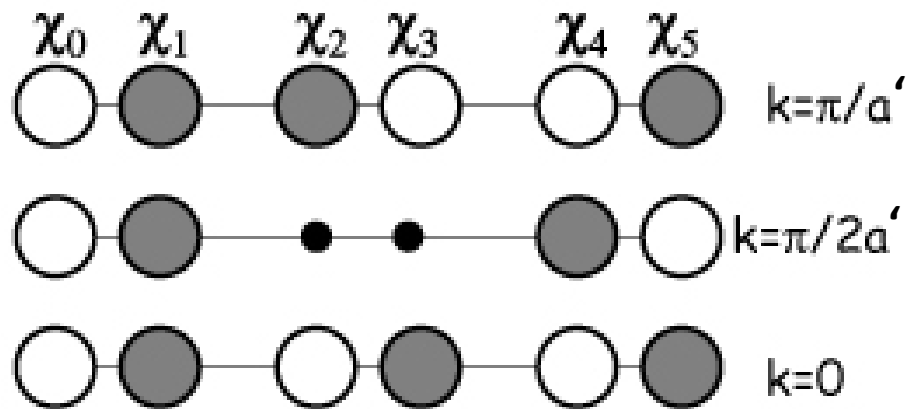
→ charge density waves



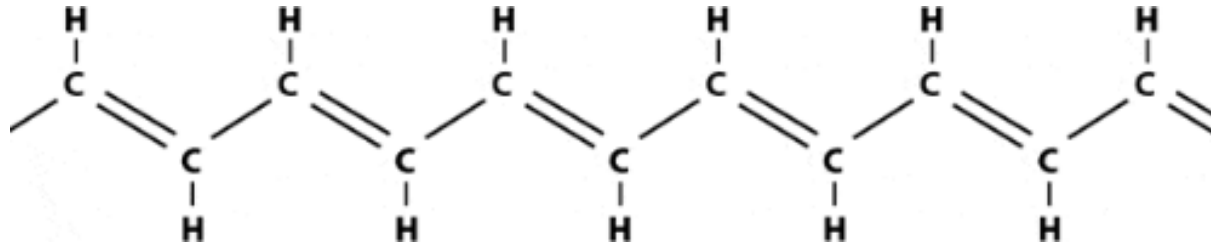
### Valence Band (HOMO $\sigma$ )



### Conduction Band (LUMO $\sigma^*$ )



# POLYACETYLENE



another 1D Peierls distortion  $\rightarrow$  localization of pi electrons



Reduction with alkali metal (*n*-doping):  
 $[\text{CH}]_n + x \text{Na} \rightarrow [\text{CH}]_n^{x-} + x \text{Na}^+$



Oxidation with halogen (*p*-doping):  
 $[\text{CH}]_n + 3x/2 \text{I}_2 \rightarrow [\text{CH}]_n^{x+} + x \text{I}_3^-$

pure PA = insulator

doped PA = conductor

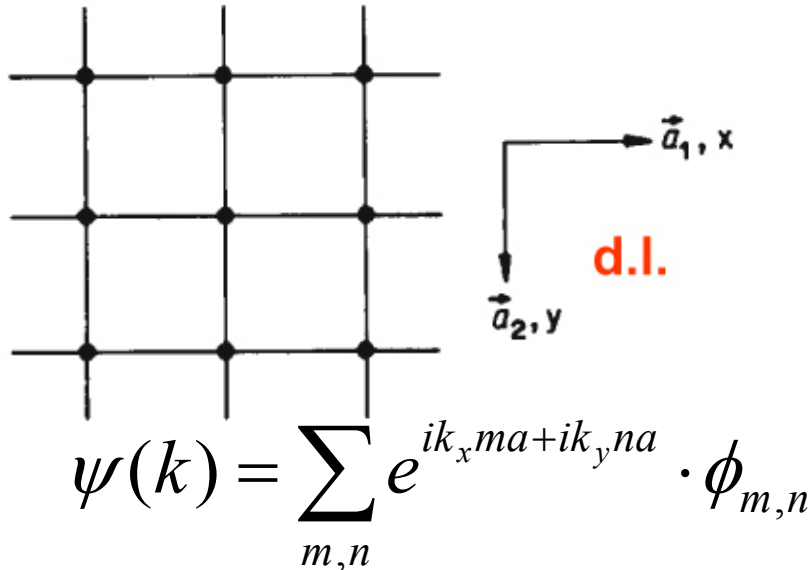
*Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa*  
*Nobel Prize in Chemistry 2000, organic semiconductors*

2D and 3D Peierls distortions also occur, sometimes forming band gaps

# 2D BAND STRUCTURE

a two-dimensional square net [s orbitals only (or  $p_z$ )]

## Simple Hückel



Consider the **crystal orbitals** at **special k points** (high symmetry)

$$\Gamma = (k_x=0, k_y=0, k_z=0)$$

$$M = (\pi/a, \pi/a, 0)$$

$$R = (\pi/a, \pi/a, \pi/a)$$

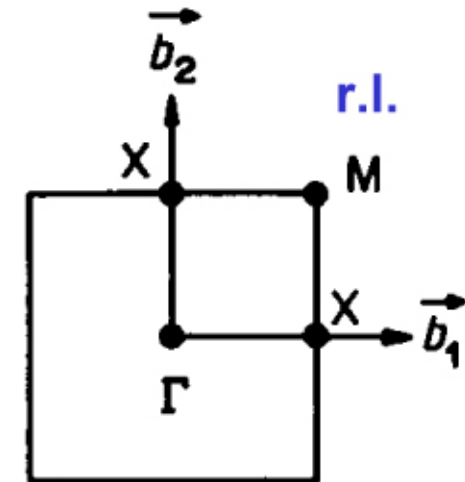
$$X = (\pi/a, 0, 0)$$

$$Y = (0, \pi/a, 0)$$

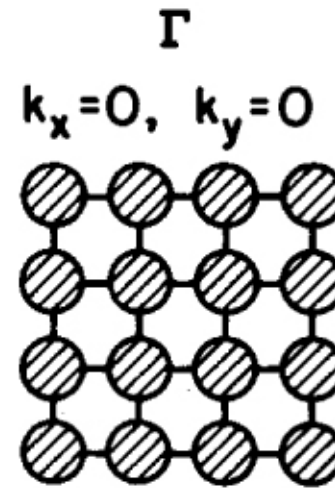
$$Z = (0, 0, \pi/a)$$

**zone center  $\Gamma$**

all a.o. in phase

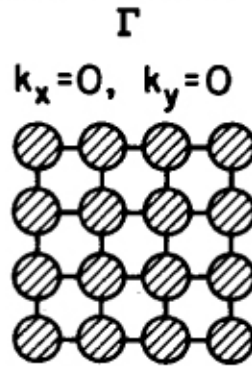
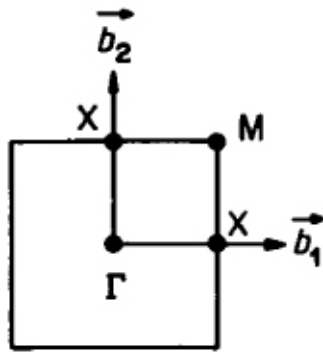


**Brillouin zone**



# Elementary Band Theory for Extended Solids

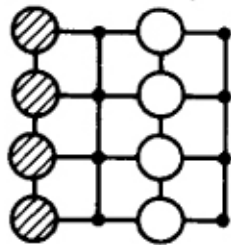
More dimensions: a two-dimensional square net [s orbitals only (or  $p_z$ )]



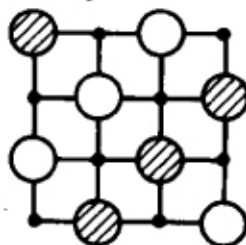
schematic  
band structure

Crystal orbitals at special k points

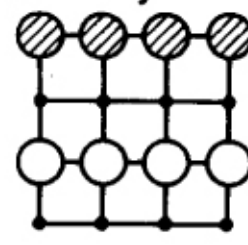
$k_x = \pi/(2a), k_y = 0$



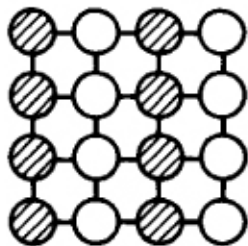
$k_x, k_y = \pi/(2a)$



$k_x = 0, k_y = \pi/(2a)$

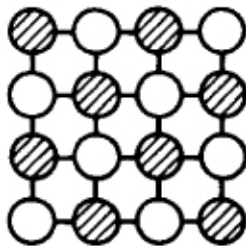


$k_x = \pi/a, k_y = 0$



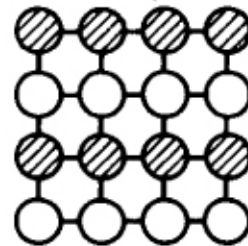
X

$k_x, k_y = \pi/a$

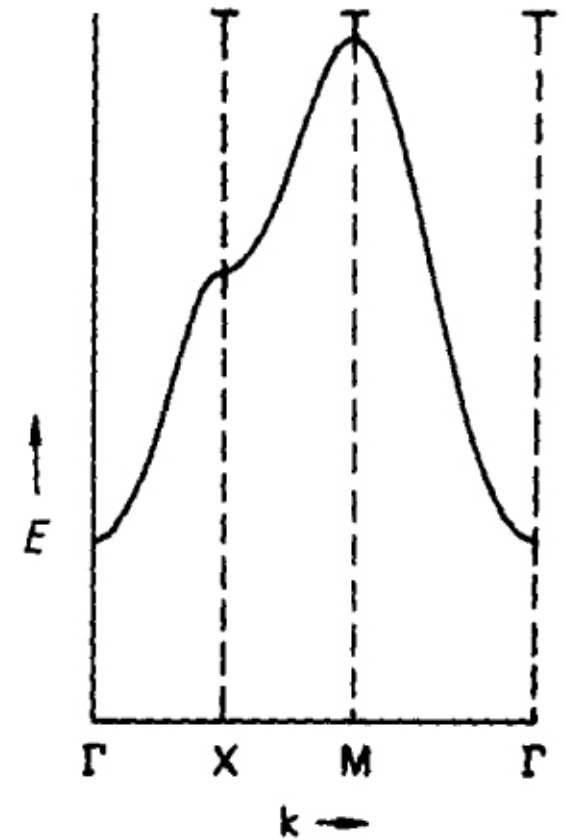


M

$k_x = 0, k_y = \pi/a$



X





## How to calculate $E(k)$ ?

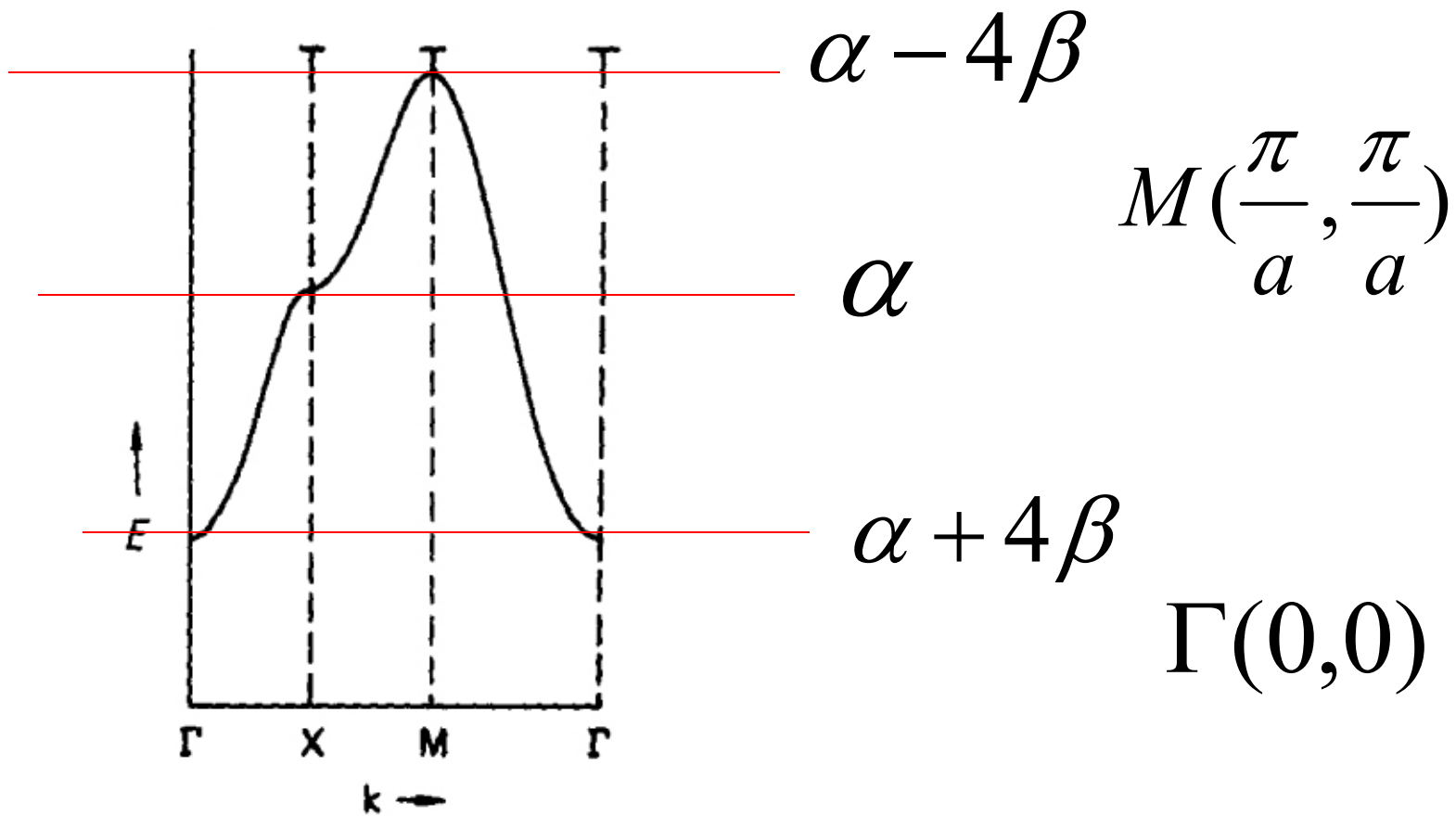
$$\psi(k) = \sum_{m,n} e^{ik_x ma + ik_y na} \cdot \phi_{m,n}$$

Crystal Schrodinger Equation:

$$H\psi(k) = E(k)\psi(k)$$

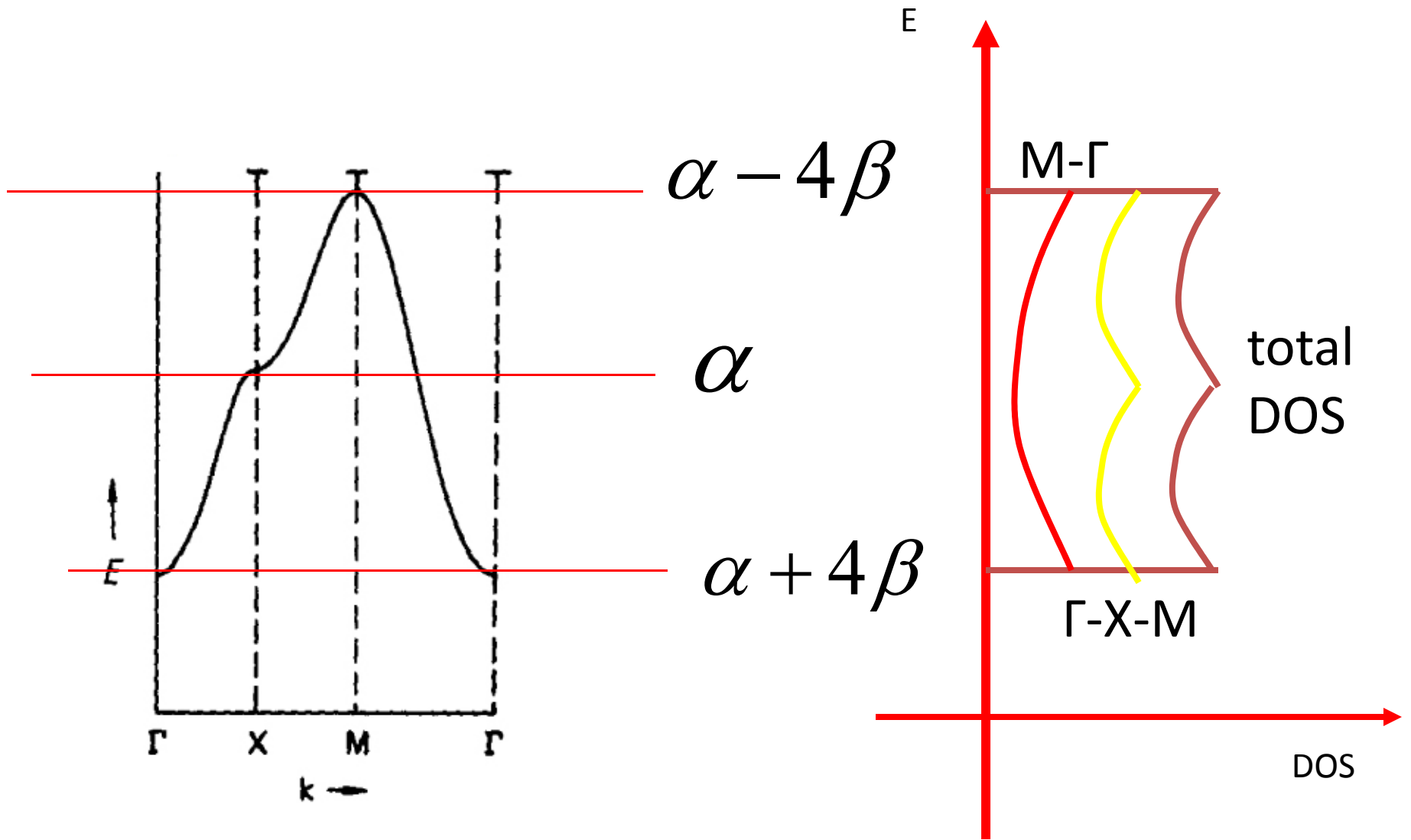
$$E(k) = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$E(k) = \alpha + 2\beta(\cos k_x a + \cos k_y a)$$



$$E(k) = \alpha + 2\beta(\cos k_x a + \cos k_y a)$$

$$W = 4Z\beta$$

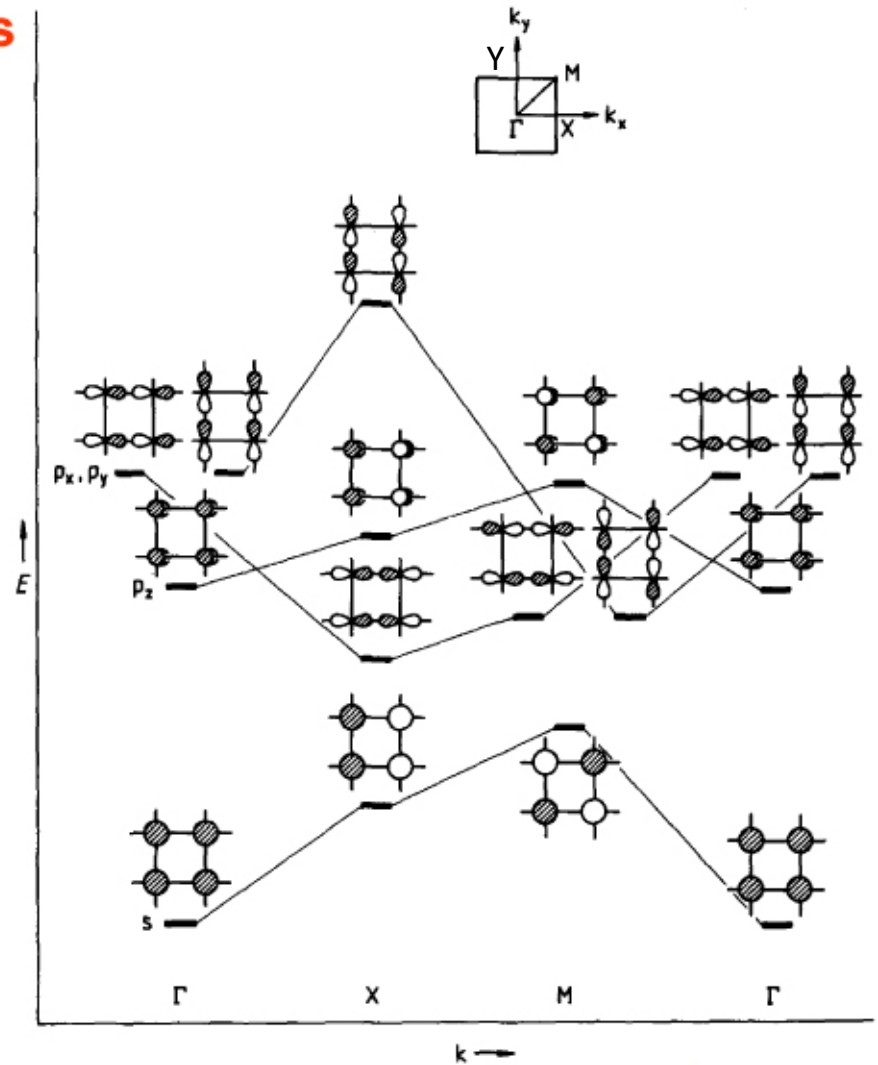
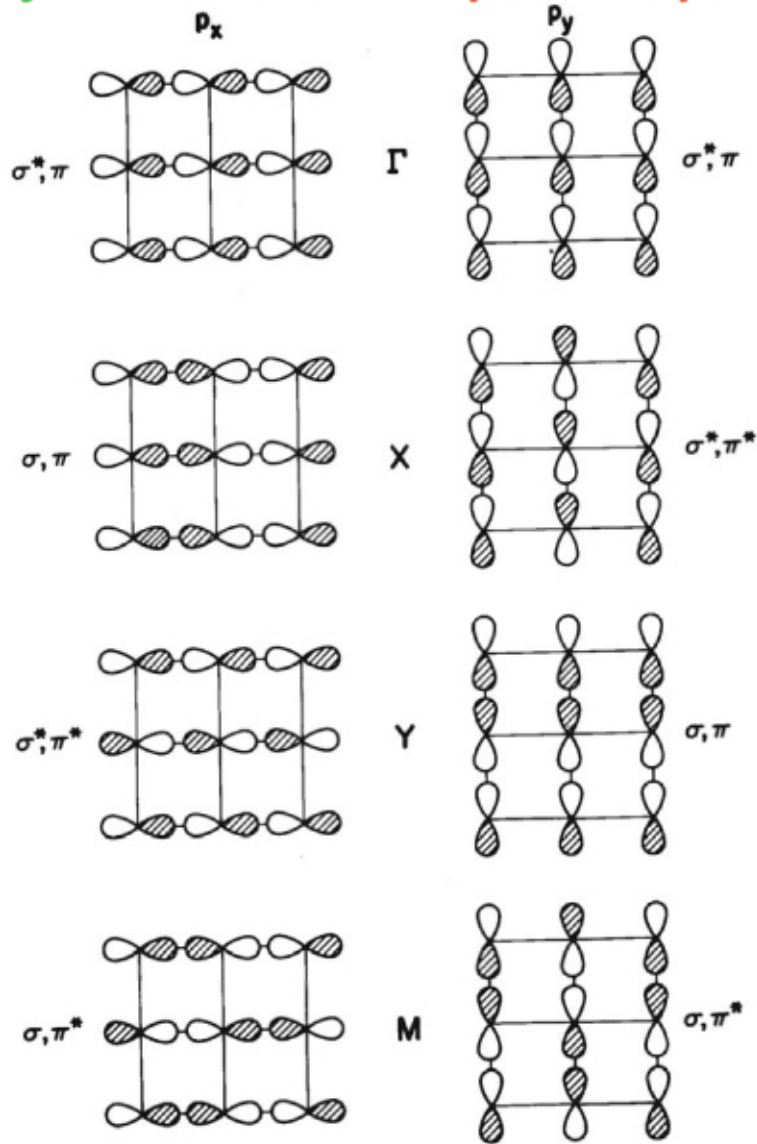


$$E(k) = \alpha + 2\beta(\cos k_x a + \cos k_y a)$$

# Elementary Band Theory for Extended Solids

More dimensions: a two-dimensional square net [s and p orbitals]

Crystal orbitals at special k points



schematic band structure

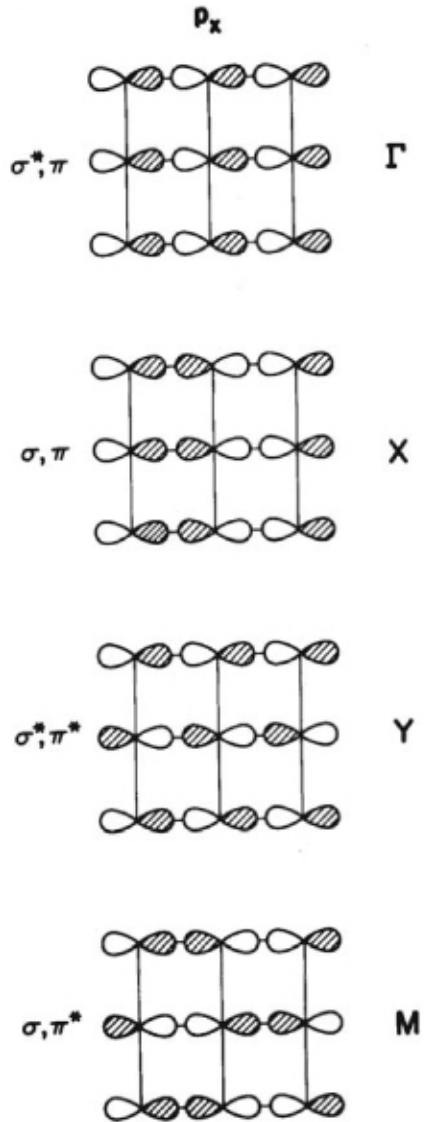
# EFFECT OF LATTICE SPACING

$$\beta_a > 0$$

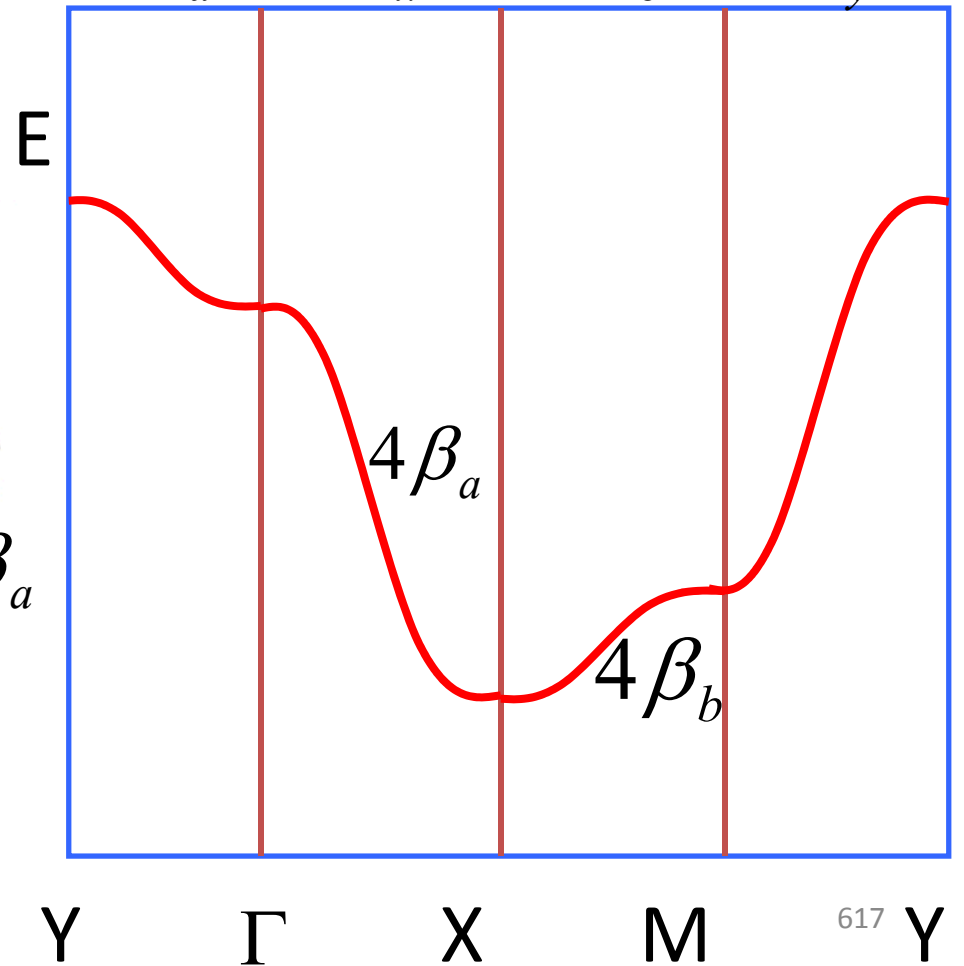
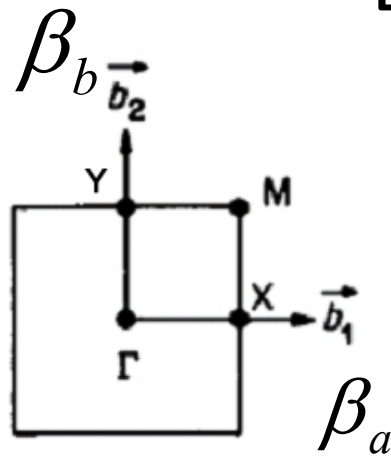
$$\beta_b < 0$$

$$|\beta_a| > |\beta_b|$$

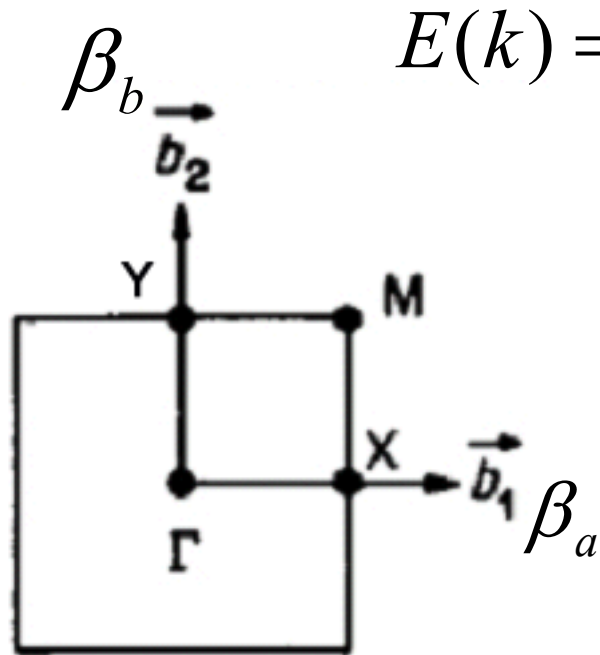
consider the  $p_x$  orbitals. For a square lattice:



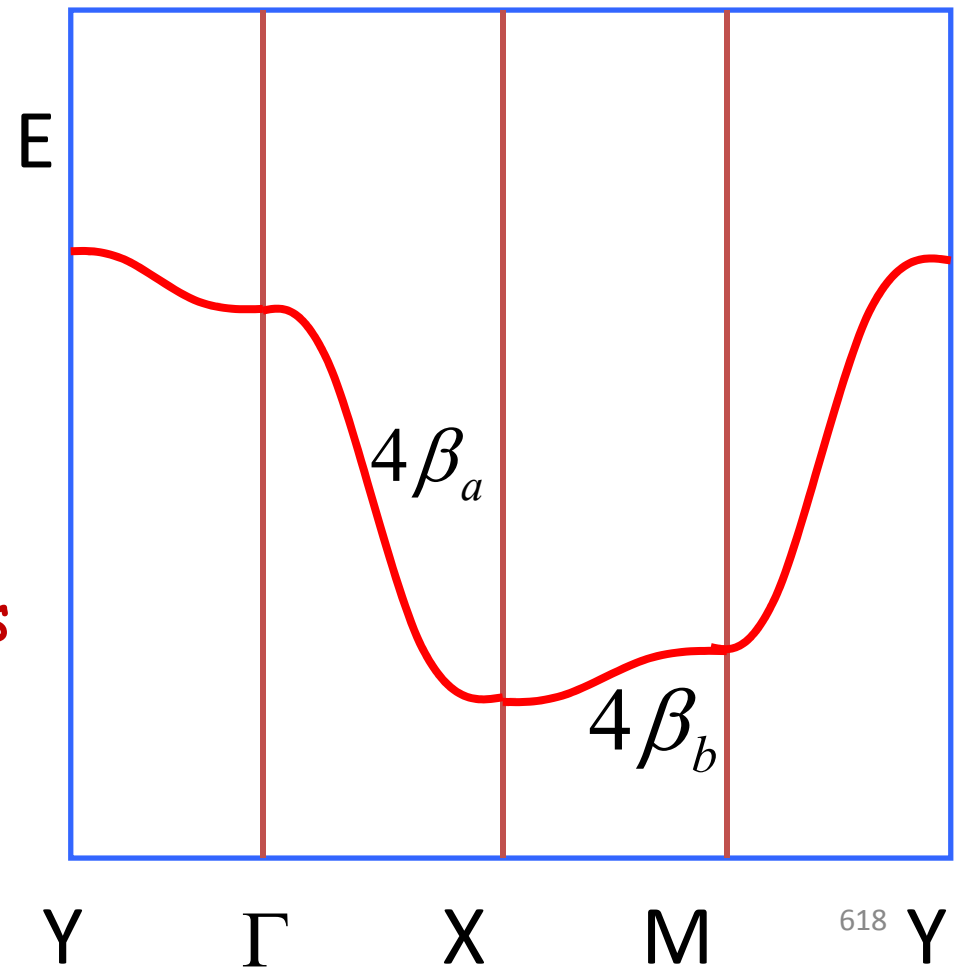
$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$



For rectangular lattice with increased lattice constant in the y-direction,  $\beta_b$  is smaller than before:



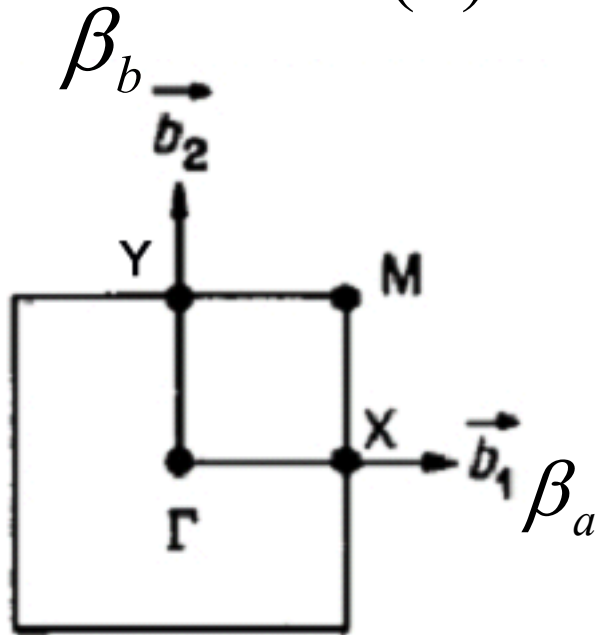
$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$



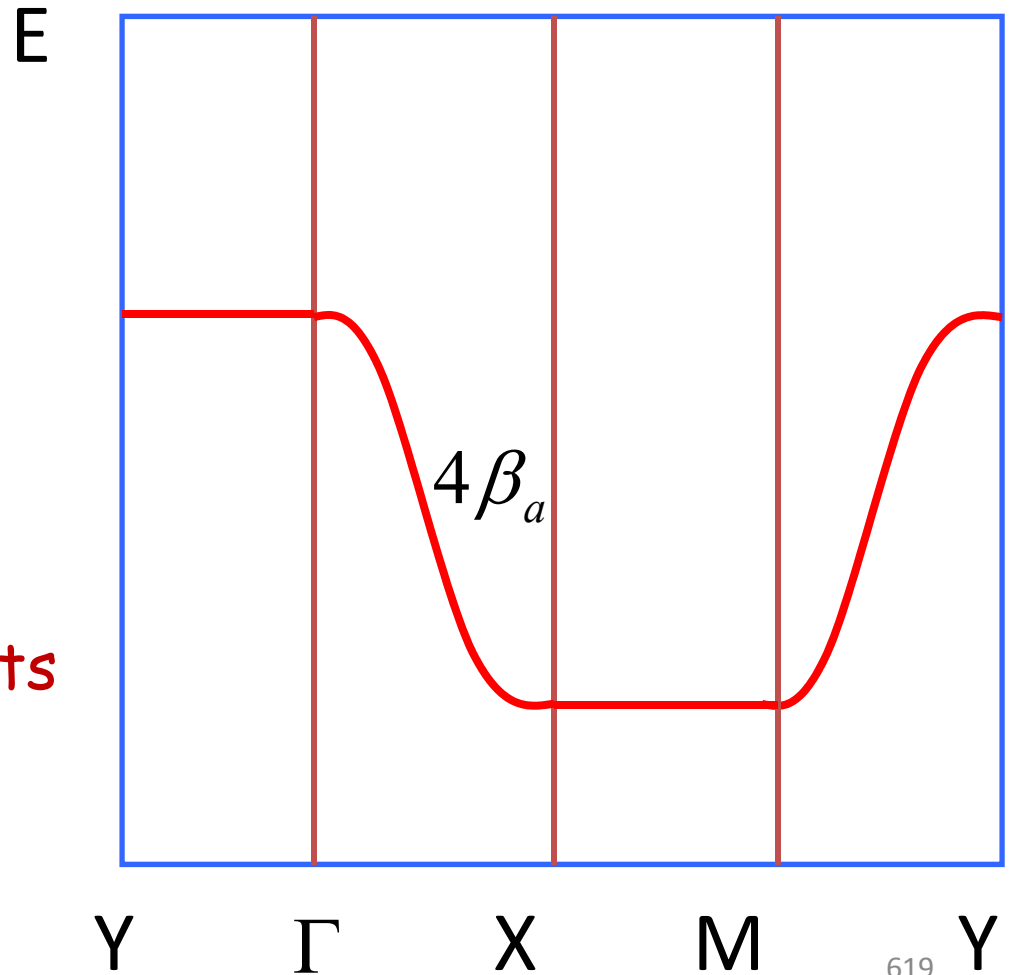
- X, Y not equivalent k-points
- less overlap in y-direction than for square lattice

For rectangular lattice with very large lattice constant in y-direction,  $\beta_b$  is almost zero:

$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$

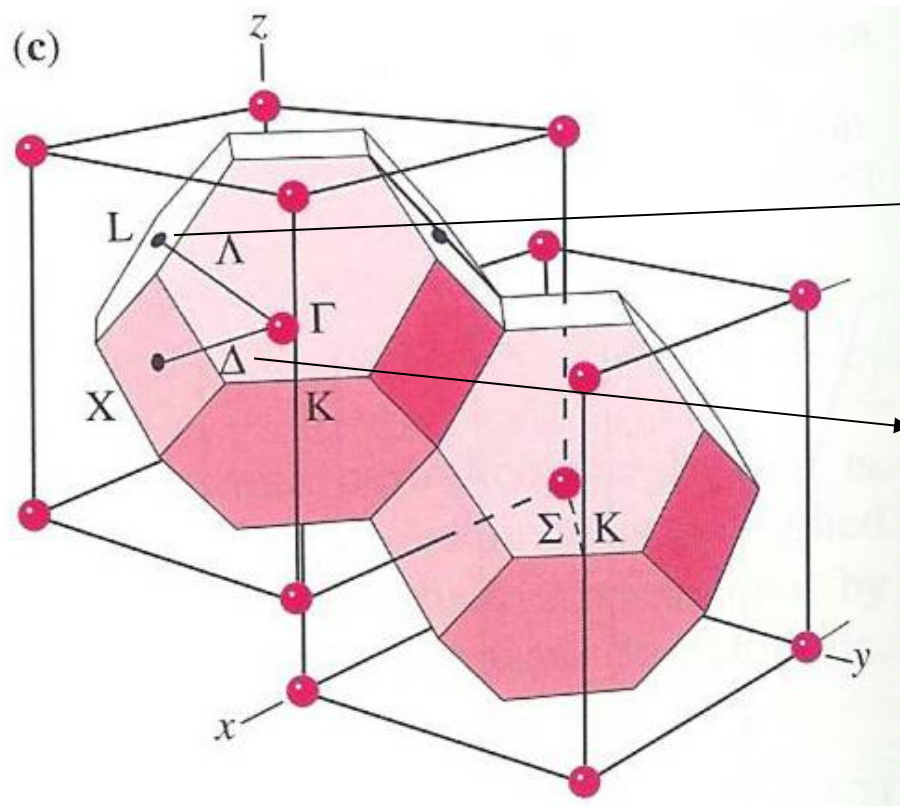


- $X, Y$  not equivalent k-points
- no overlap in y-direction, so identical to 1D band structure!



# 3D BAND STRUCTURE

## Brillouin Zone of Diamond and Zincblende Structure (FCC Lattice)



Notation:

- Zone Edge or surface : Roman alphabet
- Interior of Zone: Greek alphabet
- Center of Zone or origin:  $\Gamma$

Notation:

$\Delta \Leftrightarrow [100]$   
direction

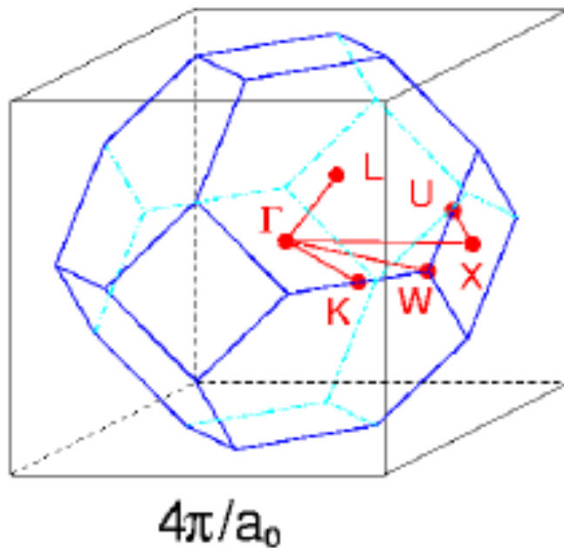
$X \Leftrightarrow$  BZ edge  
along  $[100]$   
direction

$\Lambda \Leftrightarrow [111]$   
direction

$L \Leftrightarrow$  BZ edge  
along  $[111]$   
direction<sup>620</sup>



### The first Brillouin zone



### High symmetry points and directions

$$\Gamma = 2\pi/a_0[0, 0, 0]$$

$$X = 2\pi/a_0[1, 0, 0]$$

$$L = 2\pi/a_0[1/2, 1/2, 1/2]$$

$$U = 2\pi/a_0[1, 1/4, 1/4]$$

$$W = 2\pi/a_0[1, 1/2, 0]$$

$$K = 2\pi/a_0[3/4, 3/4, 0]$$

$$\Delta = 2\pi/a_0[\xi, 0, 0], \quad 0 \leq \xi \leq 1$$

$$\Lambda = 2\pi/a_0[\xi, \xi, \xi], \quad 0 \leq \xi \leq 1/2$$

$$\Sigma = 2\pi/a_0[\xi, \xi, 0], \quad 0 \leq \xi \leq 3/4$$

$$Z = 2\pi/a_0[1, \xi, 0], \quad 0 \leq \xi \leq 1/2$$

$$Q = 2\pi/a_0[1-\xi, 1/2, \xi], \quad 0 \leq \xi \leq 1/2$$

$$S = 2\pi/a_0[1, \xi, \xi], \quad 0 \leq \xi \leq 1/4$$

# Electronic Band Structure of Si

