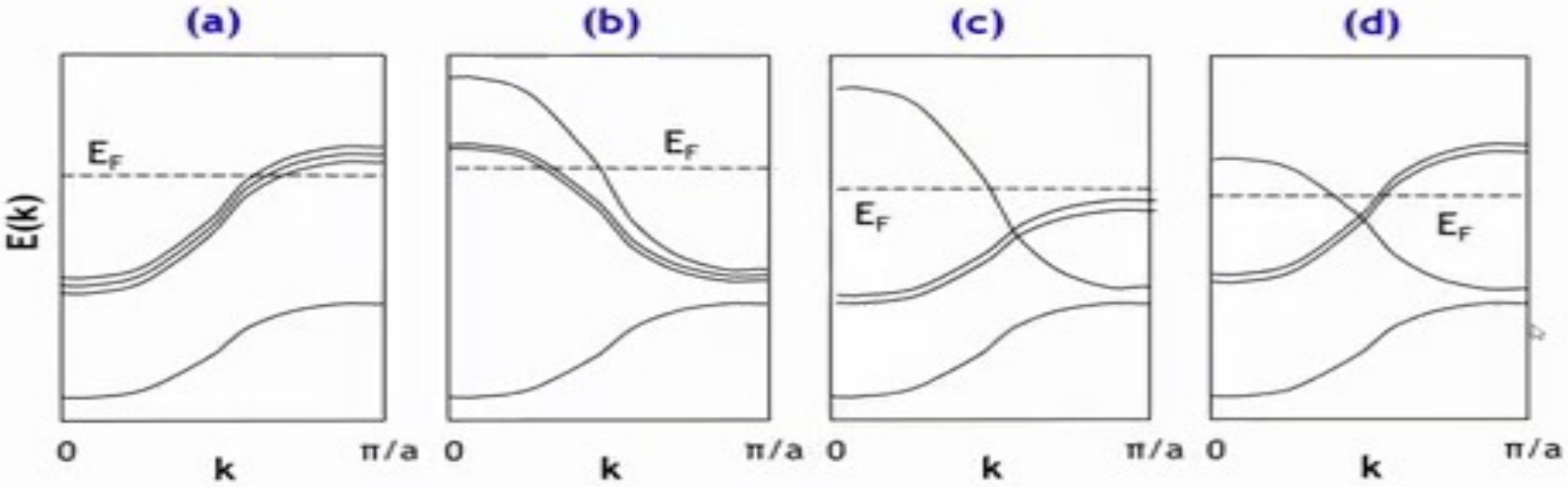
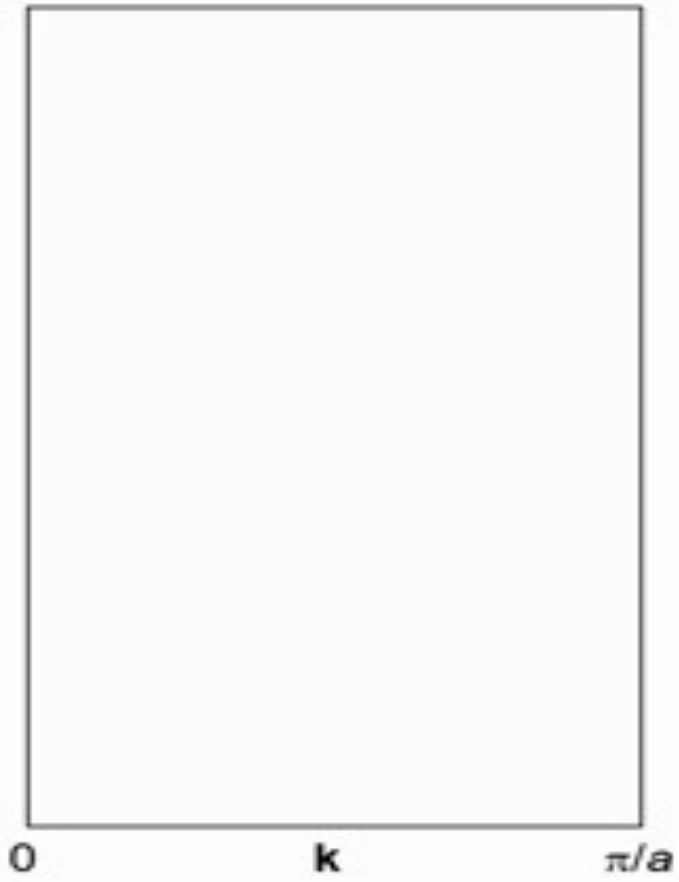
Band Structure: Linear F atom chain

F — F — F — F — F — F — F — F — F — F

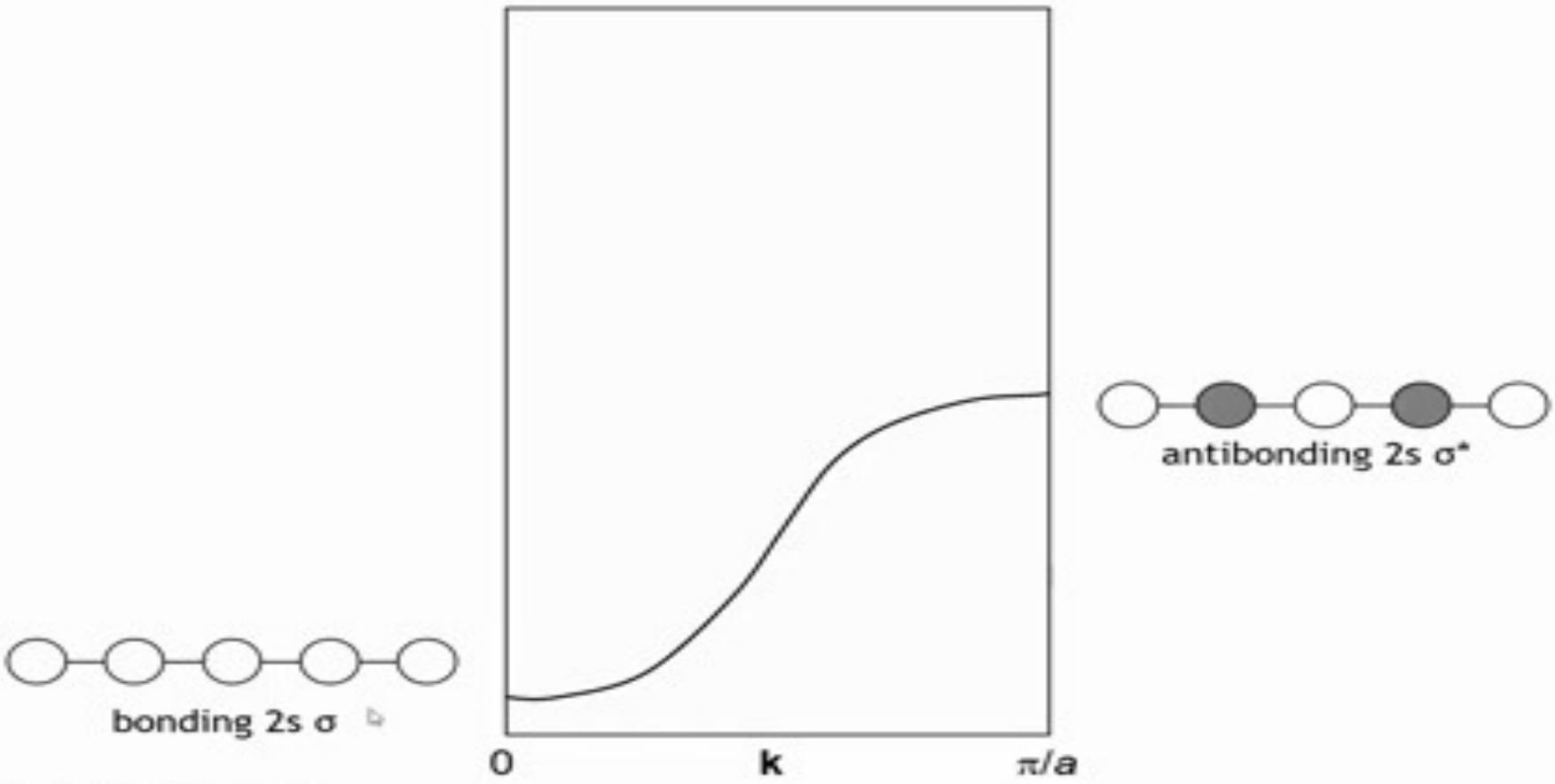


Which of the following is the correct band structure for a linear chain of F atoms?

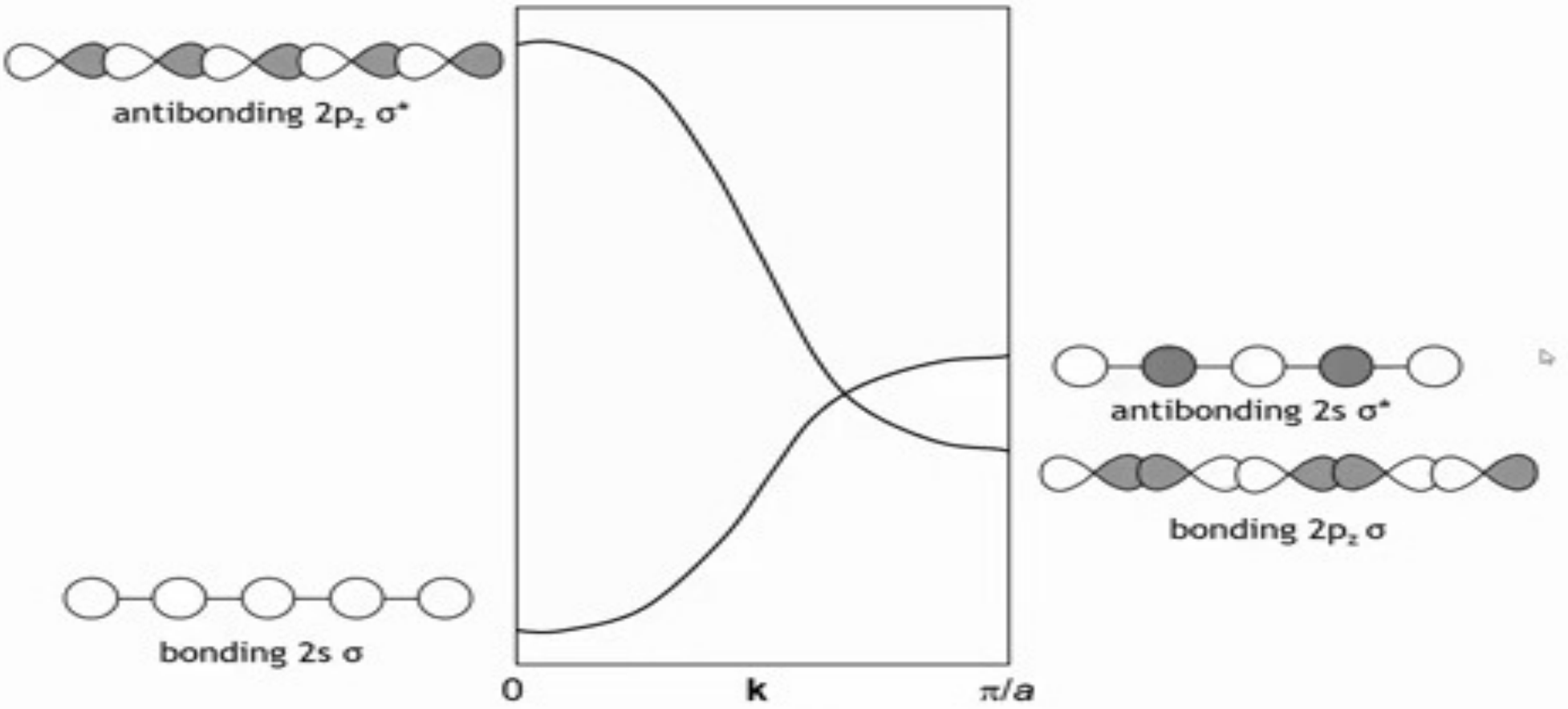
Band Structure: Linear F atom chain



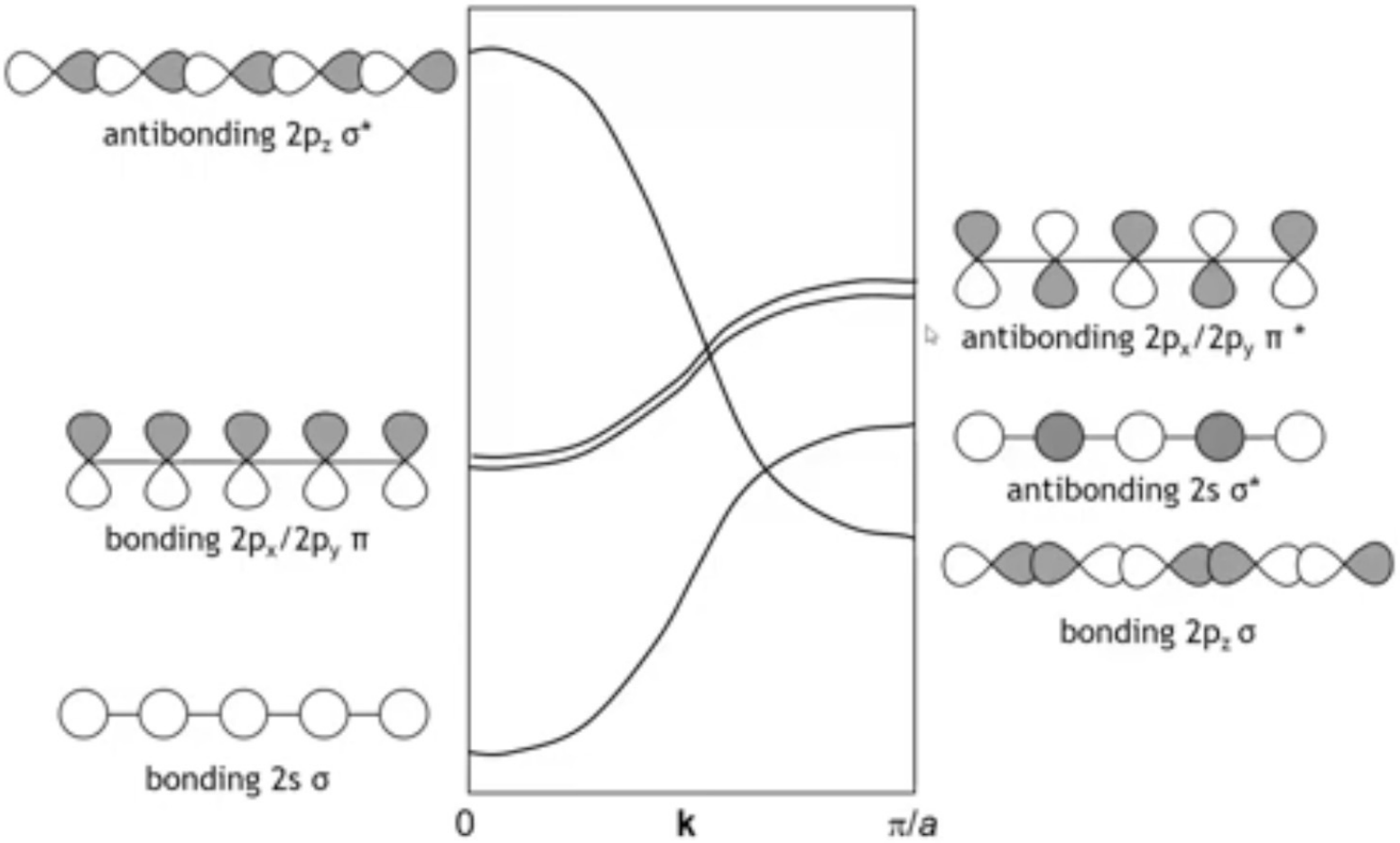
Band Structure: Linear F atom chain



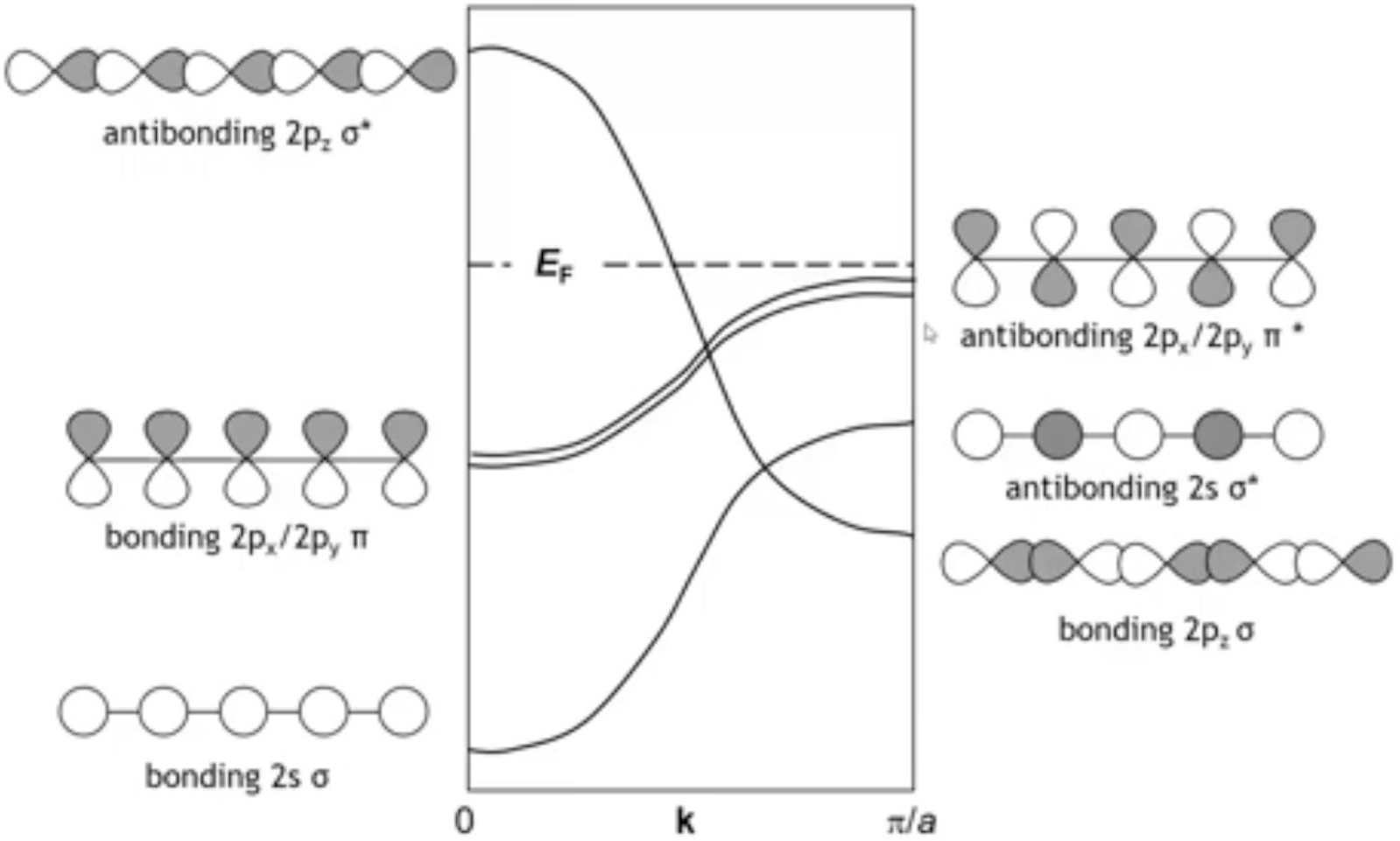
Band Structure: Linear F atom chain



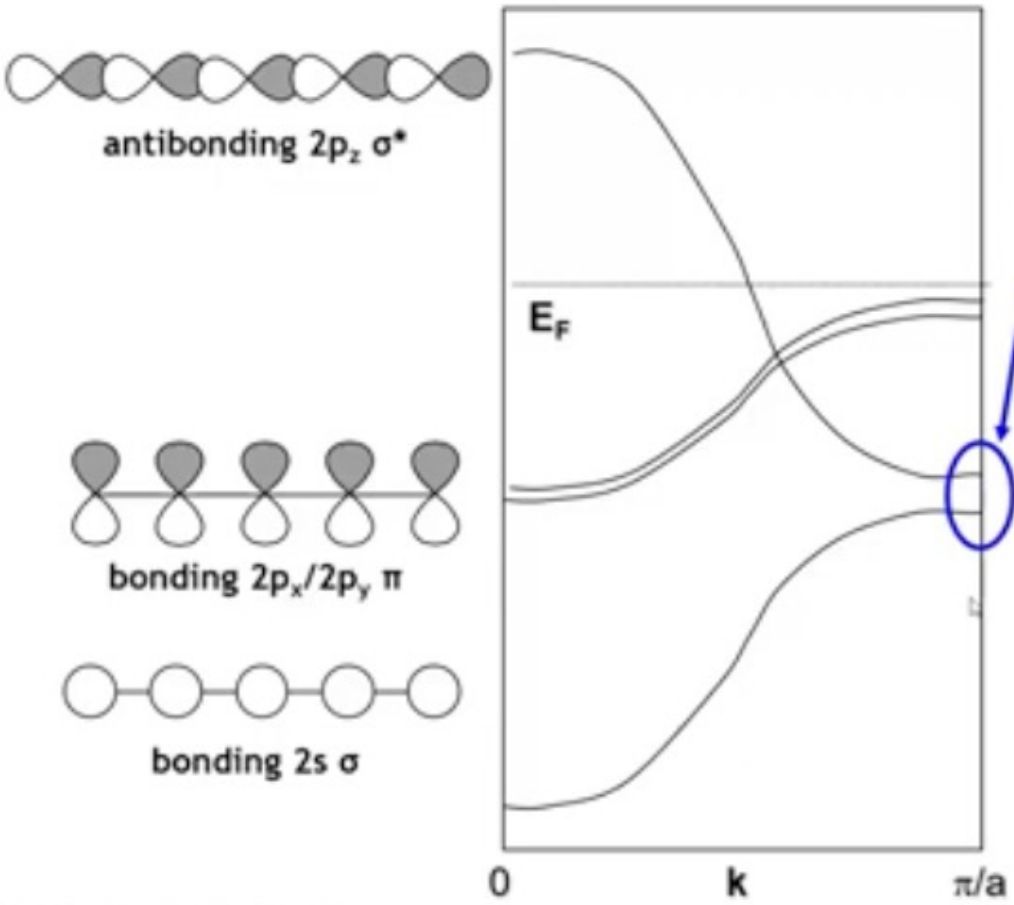
Band Structure: Linear F atom chain



Band Structure: Linear F atom chain



Band Structure: Linear Chain of F



A more accurate treatment of the band structure would show an avoided crossing between the 2p$_z$ σ and 2s σ* interactions at k=π/a. There would be mixing between these two bands (creating sp-hybrid like crystal orbitals).

Lessons from Linear F Chain

- There are now 4 orbitals in the unit cell (a single F atom with 1 *2s* + 3 *2p* orbitals) giving rise to 4 bands in the band structure.
- The fact that the 2p wavefunction changes sign at the nucleus causes the 2p σ band to run downhill (opposite of the 2s σ band).
- The reduced spatial overlap of the π interaction causes the π bands to be narrower than the σ bands.
- The 2p orbitals start out at a higher energy than the 2s orbitals (because of the atomic orbital energies)

Key Concepts

1D Band Structures Summary

Band Formation

- **Bloch functions:** $\psi = e \cdot u(x)$ determines phase relationships across unit cells
- **Zone boundaries:** $k = 0$ (uniform phase) vs $k = \pi/a$ (alternating phase via $e = -1$)
- **Orbital-band rule:** Number of orbitals in unit cell = number of bands
- **Peierls distortion:** Dimerization opens band gap by stabilizing filled states

Material Properties

- **Classification:** Fermi level cuts band (metal) vs between bands (semiconductor/insulator)
- **Direct gap:** VBM and CBM at same k → efficient optical transitions (LEDs)
- **Indirect gap:** Different k-points → requires phonon for momentum (Si solar cells)
- **Bandwidth:** σ orbitals wider than π orbitals due to stronger overlap

Homework

6.6-6.8, 6.12

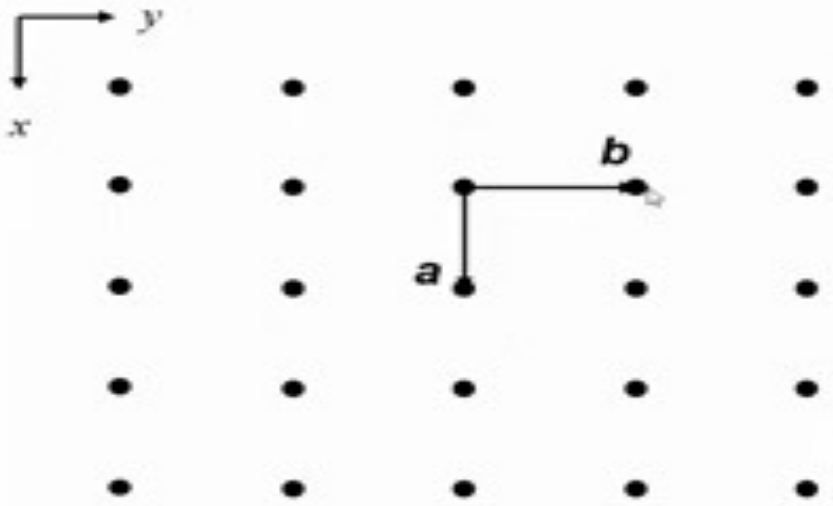
Learning Objectives

Electronic Band Structures in 2D Systems

By the end of this lecture, you will be able to:

- Construct reciprocal lattice vectors from real space lattice vectors using perpendicularity and length requirements
- Identify the first Brillouin zone as the Wigner-Seitz cell of reciprocal space
- Locate and interpret special k-points (Γ, X, M) in 2D square lattices
- Predict crystal orbital phase relationships at different k-points in two dimensions
- Read and construct band structure diagrams for 2D materials using cuts through reciprocal space

Real and Reciprocal Lattices in 2D

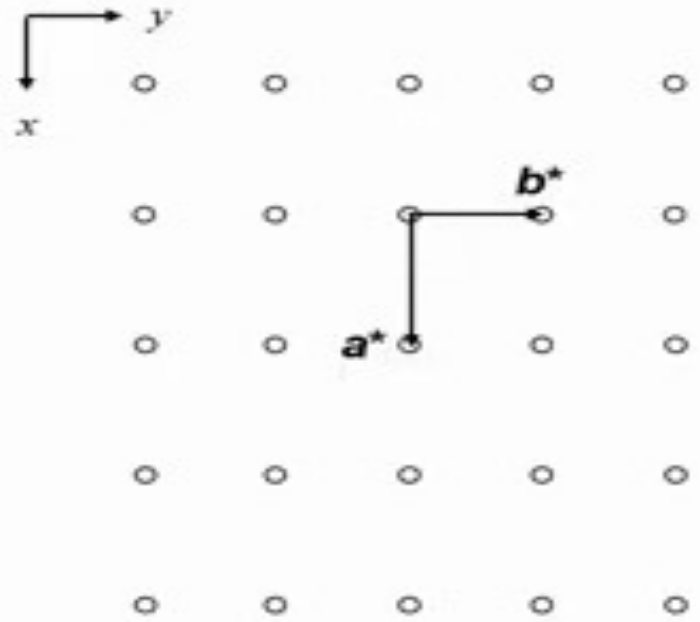


real-space lattice

$$\boldsymbol{T} = u\boldsymbol{a} + v\boldsymbol{b}$$

a, **b** = lattice vectors

u, *v* = integers



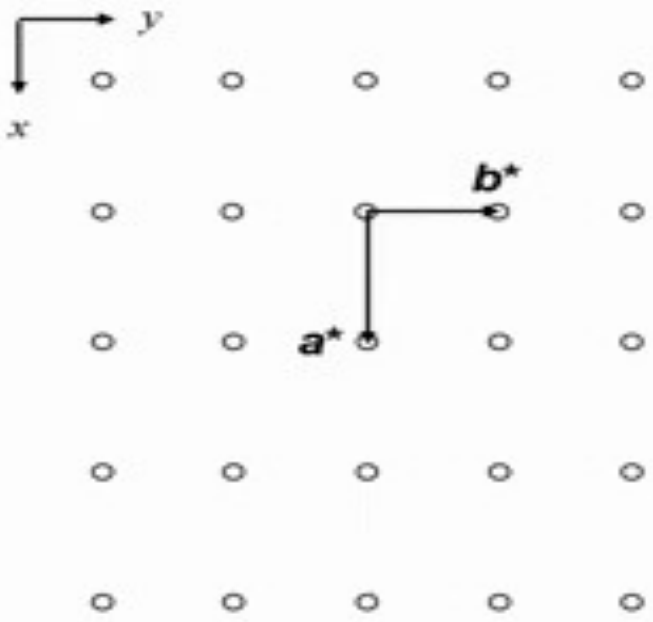
reciprocal-space lattice

$$\boldsymbol{G} = h\boldsymbol{a}^* + k\boldsymbol{b}^*$$

a*, **b*** = lattice vectors

h, *k* = integers

Real and Reciprocal Lattices in 2D



reciprocal-space lattice

$$\boldsymbol{G} = h\boldsymbol{a}^* + k\boldsymbol{b}^*$$

$\boldsymbol{a}^*$ $\boldsymbol{b}^*$ = lattice vectors

h, k = integers

Reciprocal space lattice vectors

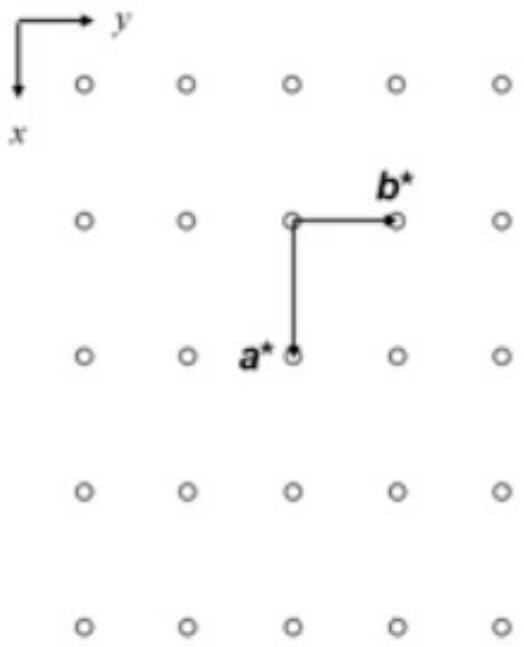
$\boldsymbol{a}^*$ perpendicular to $\boldsymbol{b}$

$\boldsymbol{a}^* \cdot \boldsymbol{a} = 2\pi$

$\boldsymbol{b}^*$ perpendicular to $\boldsymbol{a}$

$\boldsymbol{b}^* \cdot \boldsymbol{b} = 2\pi$

Real and Reciprocal Lattices in 2D



reciprocal-space lattice

$$\boldsymbol{G} = h\boldsymbol{a}^* + k\boldsymbol{b}^*$$

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Reciprocal space lattice vectors

$\boldsymbol{a}^*$ perpendicular to $\boldsymbol{b}$

$\boldsymbol{a}^* \cdot \boldsymbol{a} = 2\pi$

$\boldsymbol{b}^*$ perpendicular to $\boldsymbol{a}$

$\boldsymbol{b}^* \cdot \boldsymbol{b} = 2\pi$

Reciprocal space rectangular lattice

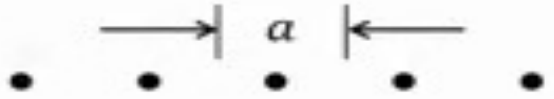
$$\boldsymbol{a}^* = \frac{2\pi}{a}\hat{x}$$

$$\boldsymbol{b}^* = \frac{2\pi}{b}\hat{y}$$

Reciprocal Space in 1D

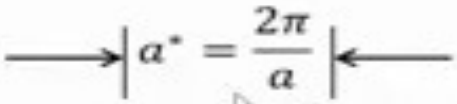
real-space lattice

$\boldsymbol{T} = u\boldsymbol{a}$



reciprocal-space lattice

$\boldsymbol{G} = h\boldsymbol{a}^*$



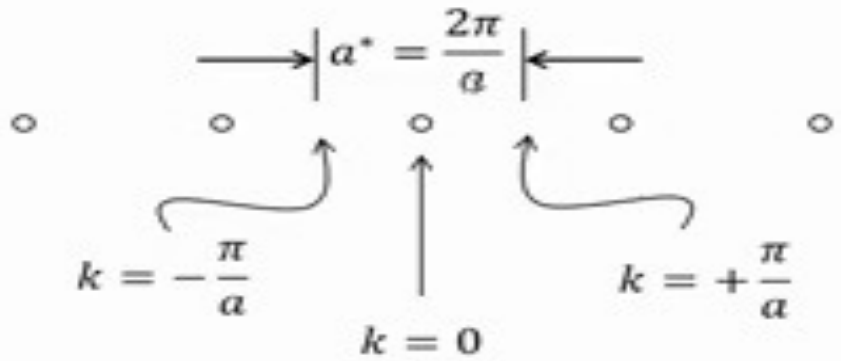
Reciprocal Space in 1D

real-space lattice

$\boldsymbol{T} = u\boldsymbol{a}$

reciprocal-space lattice

$\boldsymbol{G} = h\boldsymbol{a}^*$



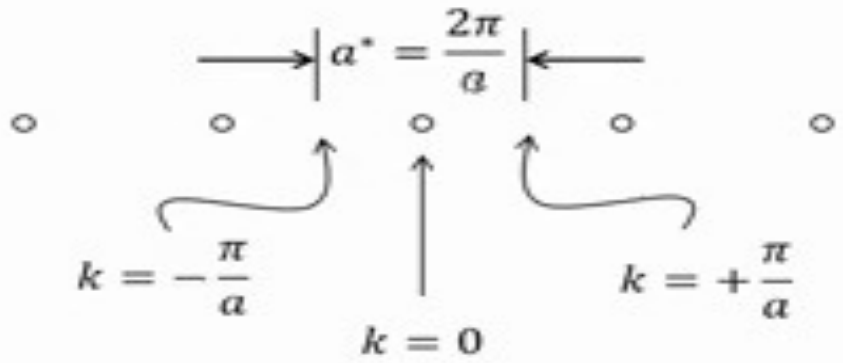
Reciprocal Space in 1D

real-space lattice

$\boldsymbol{T = ua}$

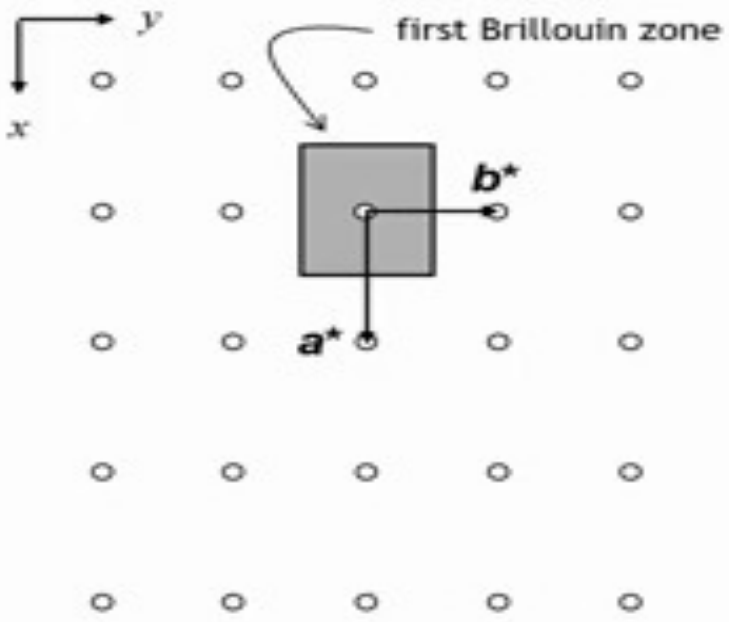
reciprocal-space lattice

$\boldsymbol{G = ha^*}$



The boundaries of the first Brillouin zone are ½ a^* toward each of the neighboring reciprocal-space lattice points.

The First Brillouin Zone in 2D



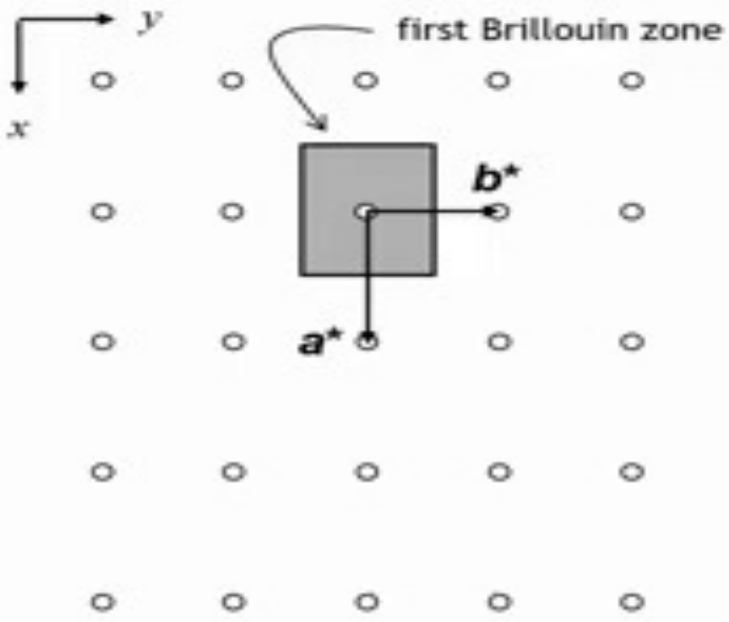
reciprocal-space lattice

$$\boldsymbol{G} = h\boldsymbol{a}^* + k\boldsymbol{b}^*$$

$\boldsymbol{a}^*$ $\boldsymbol{b}^*$ = lattice vectors

h, k = integers

The First Brillouin Zone in 2D



reciprocal-space lattice

$$\boldsymbol{G} = h\boldsymbol{a}^* + k\boldsymbol{b}^*$$

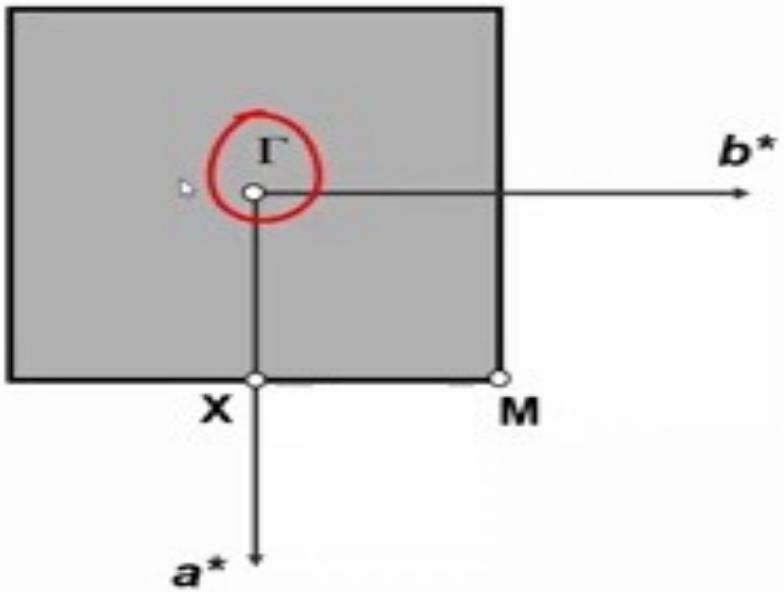
$\boldsymbol{a}^*$ $\boldsymbol{b}^*$ = lattice vectors

h, k = integers

The first Brillouin zone is the area in reciprocal space that contains all k points closer to the lattice point it surrounds than to any other reciprocal space lattice point.

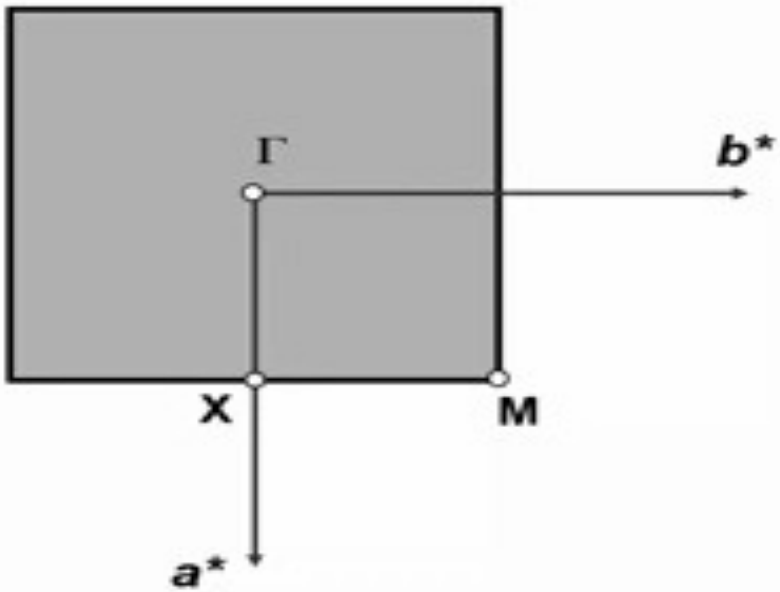
In crystallography we call this type of cell a Wigner-Seitz cell.

Special Points in a 2D Square Lattice



label	coordinates
Γ	0 a^* + 0 b^*
X	(1/2) a^* + 0 b^*
M	(1/2) a^* + (1/2) b^*

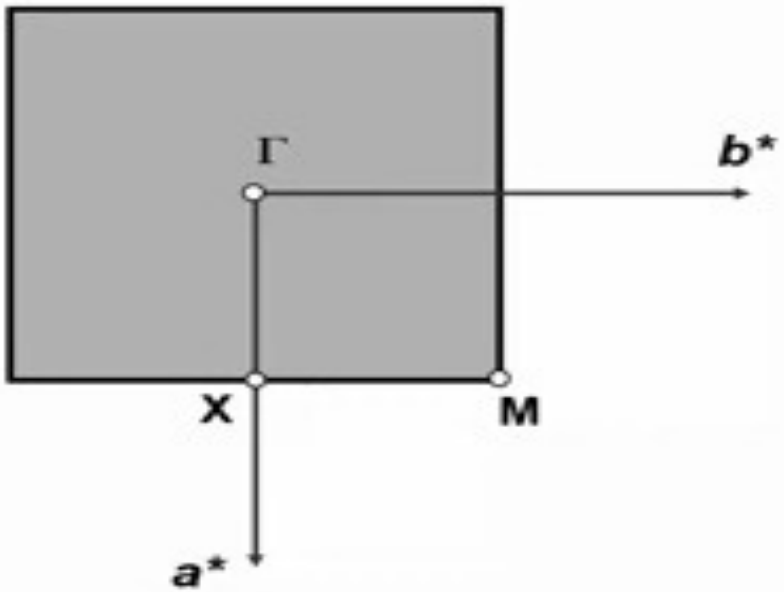
Special Points in a 2D Square Lattice



label	coordinates
Γ	0 $\boldsymbol{a}^*$ + 0 $\boldsymbol{b}^*$
X	(1/2) $\boldsymbol{a}^*$ + 0 $\boldsymbol{b}^*$
M	(1/2) $\boldsymbol{a}^*$ + (1/2) $\boldsymbol{b}^*$

$$\boldsymbol{a}^* = \frac{2\pi}{a}\hat{x} \qquad \boldsymbol{b}^* = \frac{2\pi}{b}\hat{y}$$

Special Points in a 2D Square Lattice

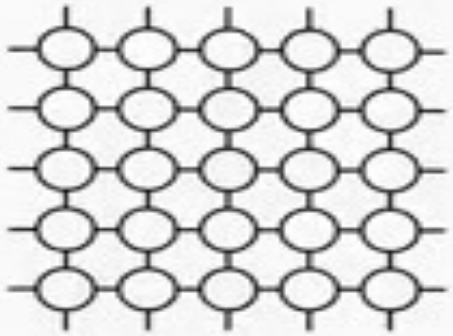


label	coordinates
Γ	0 $\boldsymbol{a}^*$ + 0 $\boldsymbol{b}^*$
X	(1/2) $\boldsymbol{a}^*$ + 0 $\boldsymbol{b}^*$
M	(1/2) $\boldsymbol{a}^*$ + (1/2) $\boldsymbol{b}^*$

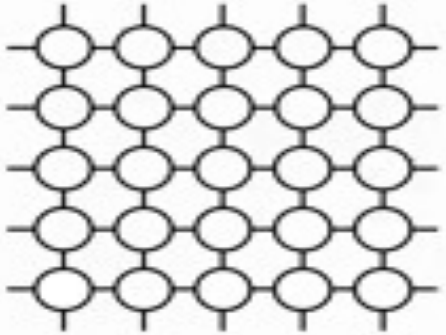
$$\boldsymbol{a}^* = \frac{2\pi}{a}\hat{x} \qquad \boldsymbol{b}^* = \frac{2\pi}{b}\hat{y}$$

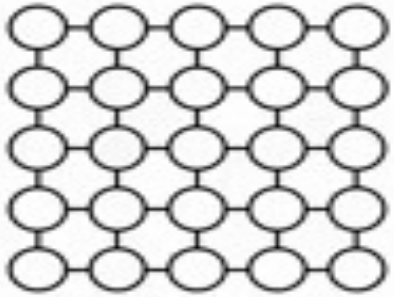
label	wave vector (Cartesian)
Γ	$0\,\boldsymbol{k}_x + 0\,\boldsymbol{k}_y$
X	$(\pi/a)\,\boldsymbol{k}_x + 0\,\boldsymbol{k}_y$
M	$(\pi/a)\,\boldsymbol{k}_x + (\pi/a)\,\boldsymbol{k}_y$

Band Structure 2D H atom Sheet



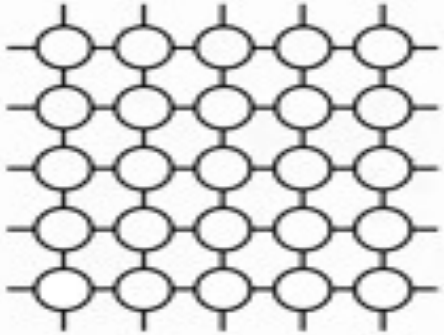
Band Structure 2D H atom Sheet

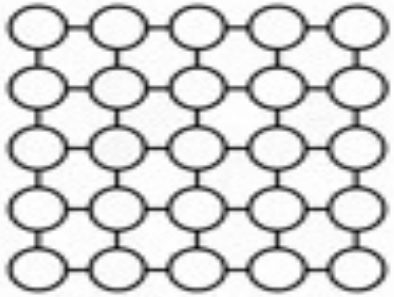




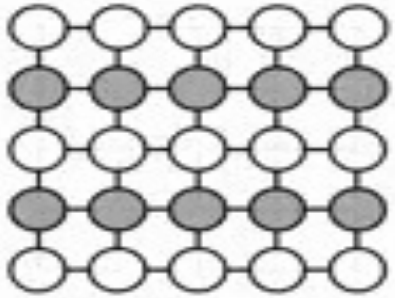
Γ point
$k_x = k_y = 0$
bonding

Band Structure 2D H atom Sheet



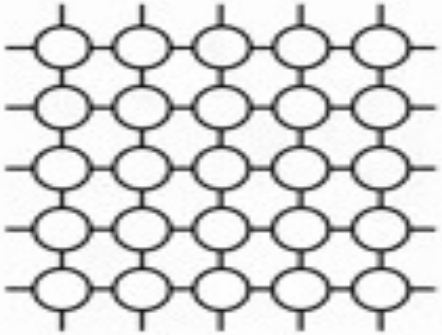


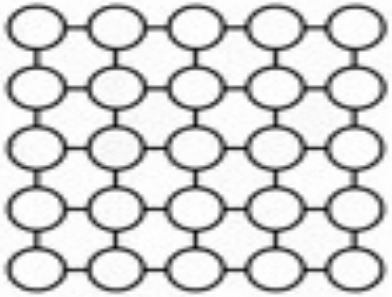
Γ point
$k_x = k_y = 0$
bonding



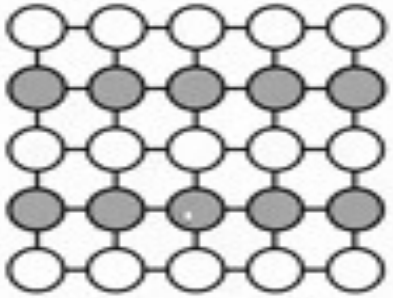
X point
$k_x = \pi/a$ $k_y = 0$
nonbonding

Band Structure 2D H atom Sheet

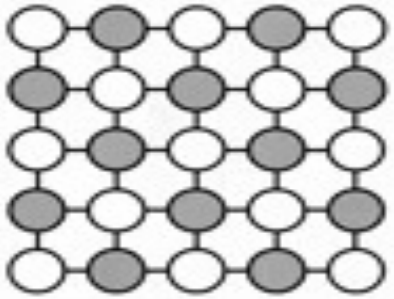




Γ point
$k_x = k_y = 0$
bonding

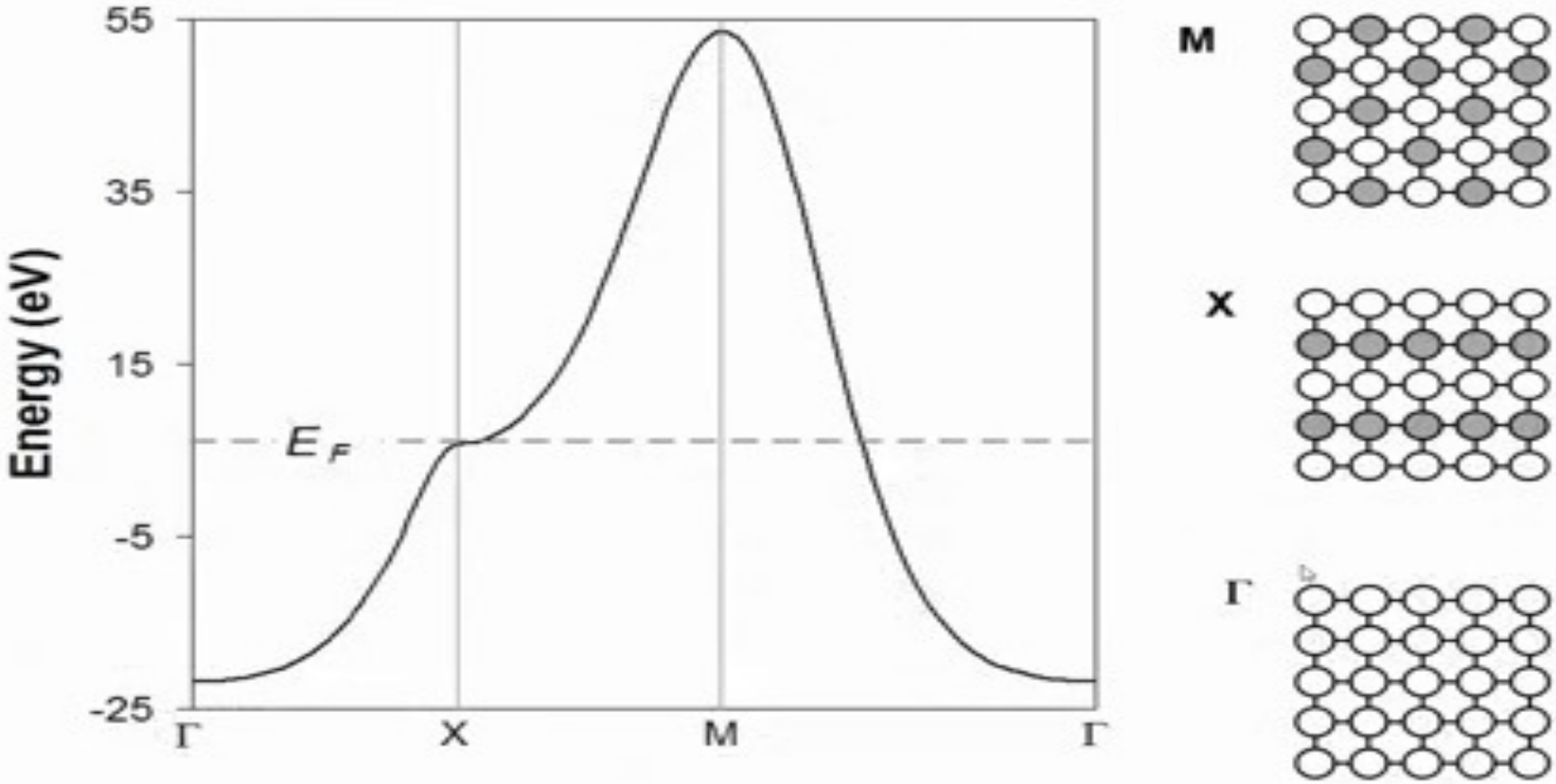


X point
$k_x = \pi/a$ $k_y = 0$
nonbonding



M point
$k_x = k_y = \pi/a$
antibonding

Band Structure 2D H atom Sheet



1. In a 2D real space lattice defined by vectors A and B, what is the fundamental defining relationship for the reciprocal space lattice vector A^*?

A. A^* is parallel to A, and $|A^*| = 2\pi/|A|$.

B. A^* is parallel to B, and $A^* \cdot B = 2\pi$.

C. A^* is perpendicular to A, and $A^* \cdot A = 1$.

D. A^* is perpendicular to B, and $A^* \cdot A = 2\pi$.

D. A^* is perpendicular to B, and $A^* \cdot A = 2\pi$.

✓ **Right answer**

This is the correct general definition. A^* must be perpendicular to the *other* real space vector (B) and its dot product with its corresponding real vector (A) is 2π.

2. What is the First Brillouin Zone (B1 zone) in reciprocal space?

A. The Wigner-Seitz cell of the reciprocal space lattice.

B. The unit cell of the real space lattice, just inverted.

C. The largest possible unit cell that can be drawn in reciprocal space.

D. A square area centered at the origin, regardless of lattice type.

A. The Wigner-Seitz cell of the reciprocal space lattice.

✓ **That's right!**

This is the correct definition. The B1 zone is the Wigner-Seitz cell centered on a reciprocal lattice point (the origin), containing all k-points closer to that point than to any other.

3. In a 2D band structure, what does the special k-point Gamma (Γ) represent?

A. The center of the First Brillouin Zone, where $k_x = 0$ and $k_y = 0$.

B. The energy level of the highest occupied orbital.

C. The center of the edge of the First Brillouin Zone.

D. The corner of the First Brillouin Zone.

A. The center of the First Brillouin Zone, where $k_x = 0$ and $k_y = 0$.

✓ **Right answer**

This is correct. The Gamma point is the origin of the reciprocal space lattice and represents the crystal orbital with $k = 0$ (all unit cells in-phase).

4. For the 2D square lattice of hydrogen atoms, what is the nature of the crystal orbital at the M-point ($k_x = \pi/A, k_y = \pi/A$)?

A. All orbitals are in-phase (all-bonding).

B. Orbitals alternate phase in both x and y directions (all-antibonding).

C. The orbitals are randomly phased and have zero net overlap.

D. Orbitals alternate phase in the x-direction but are in-phase in the y-direction.

B. Orbitals alternate phase in both x and y directions (all-antibonding).

✓ That's right!

This is correct. At the M point, the phase reverses in both directions, creating a 'checkerboard' pattern where every orbital is out-of-phase with all its neighbors, resulting in the highest energy, all-antibonding orbital.

5. If the real space lattice vector A in a rectangular lattice is made *shorter*, what happens to the length of the corresponding reciprocal space lattice vector $|A^*|$?

A. It becomes shorter.

B. It stays the same length.

C. It becomes longer.

D. It depends on the length of B.

C. It becomes longer.

✓ **That's right!**

This is correct. For an orthogonal lattice, $|A^*| = 2\pi/|A|$. If the denominator $|A|$ decreases (gets shorter), the total value $|A^*|$ must increase (get longer).

Homework

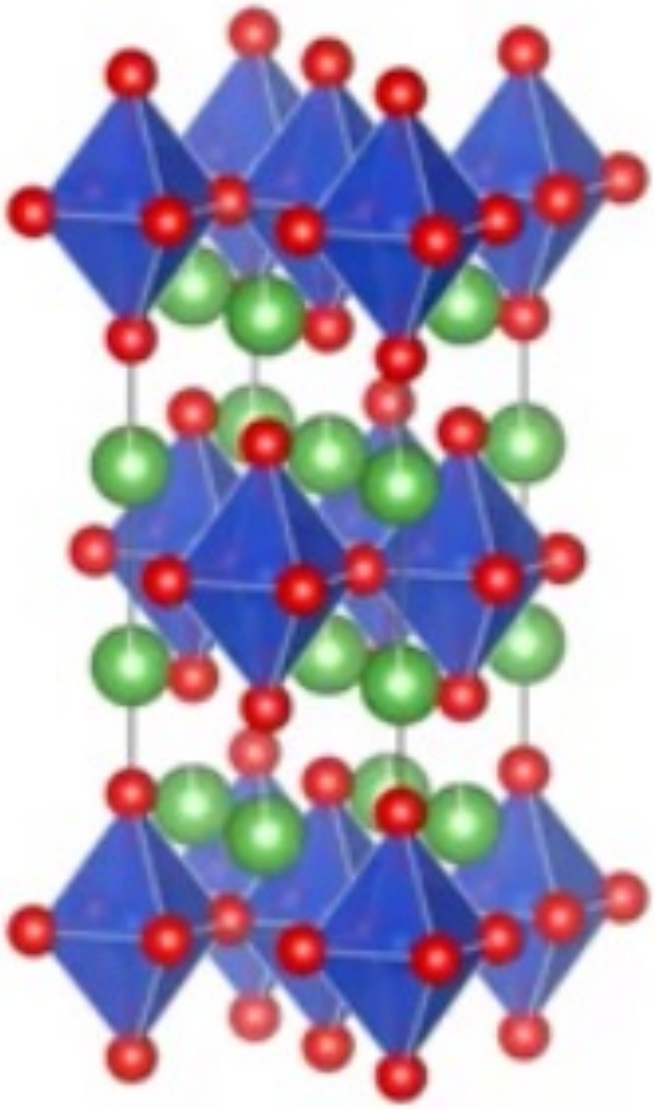
6.13, 6.14

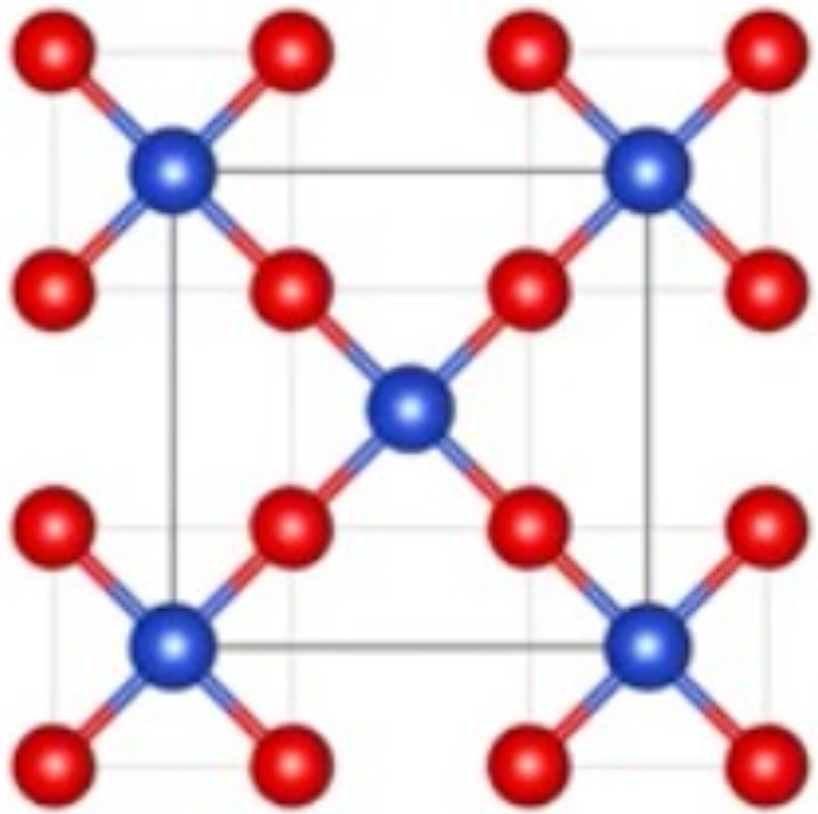
Learning Objectives

Band Structure of the CuO_2^{2-} Layer

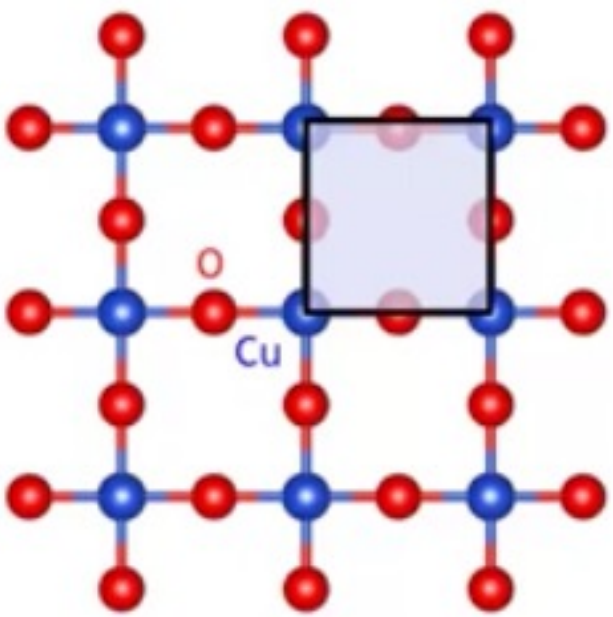
By the end of this lecture, you will be able to:

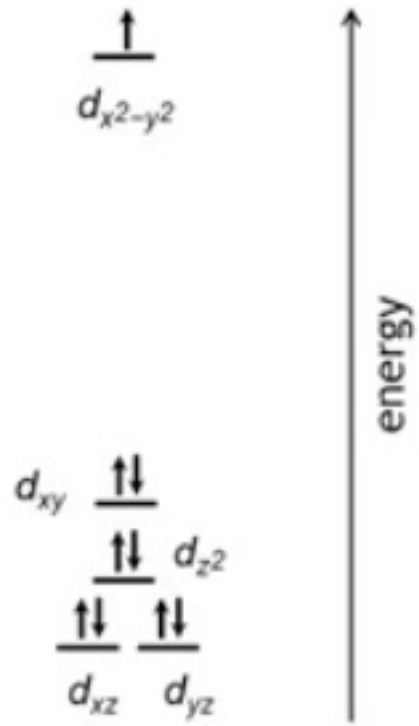
- Construct band structures for multi-atom unit cells from molecular orbital diagrams
- Interpret density of states (DOS) and partial DOS diagrams to identify orbital contributions
- Predict orbital overlap patterns and symmetry-allowed interactions at different k-points
- Relate band width to orbital overlap strength and electron delocalization
- Extract key properties from band structure diagrams: metallic vs semiconducting behavior, localized vs delocalized electrons





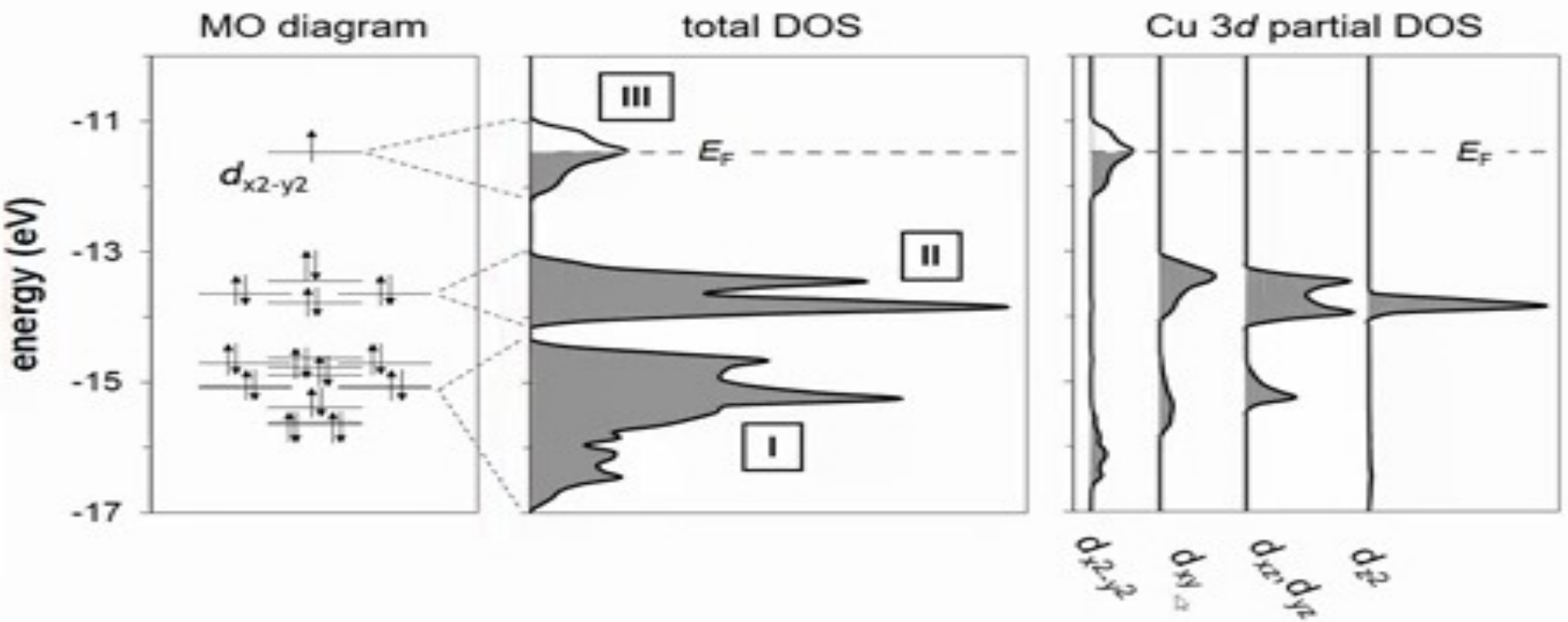
CuO_2^{2-} Sheet





d-orbital energies
square planar Cu^{2+}

MO Diagram → DOS Plot

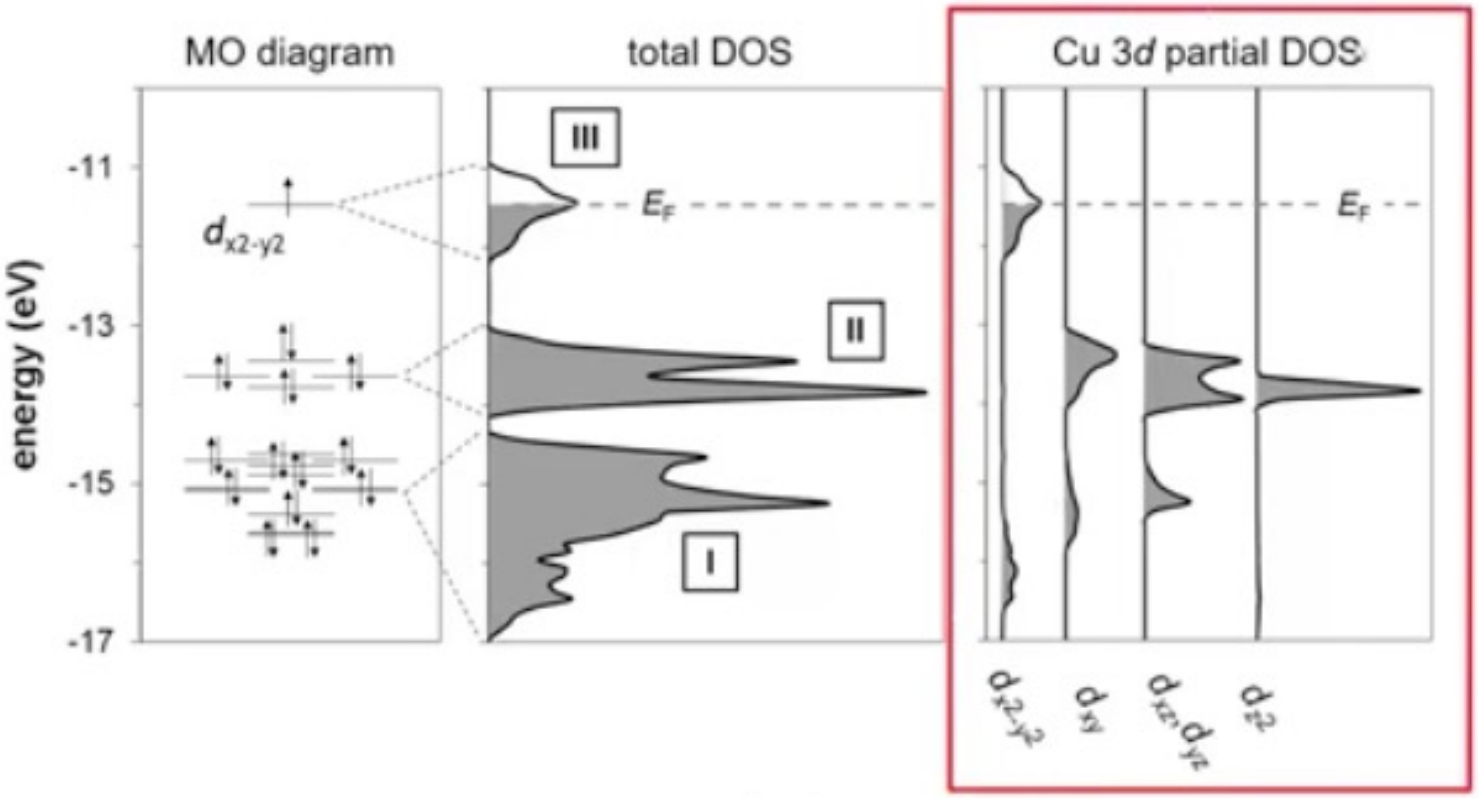


I — O 2p nonbonding and Cu-O bonding

II — Cu 3d-O 2p π antibonding

III — Cu 3d-O 2p σ antibonding

MO Diagram → DOS Plot



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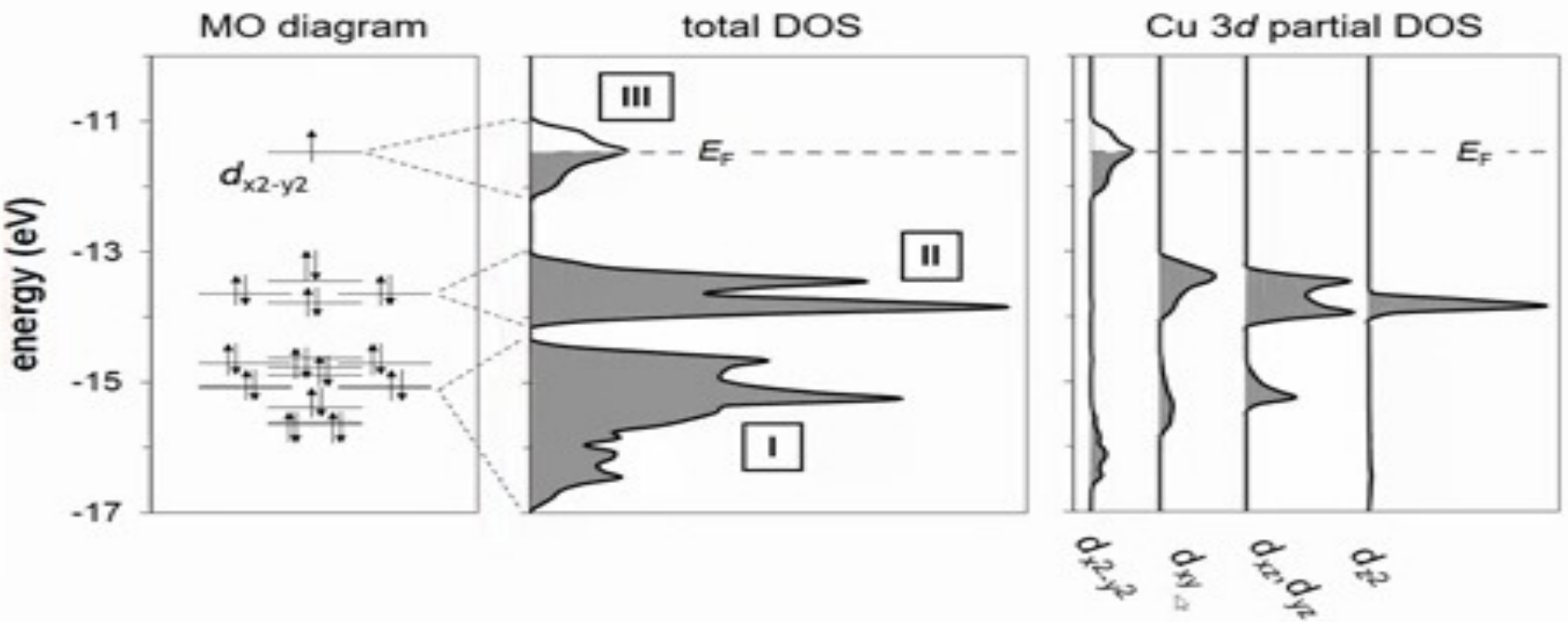
MO Diagram → DOS Plot

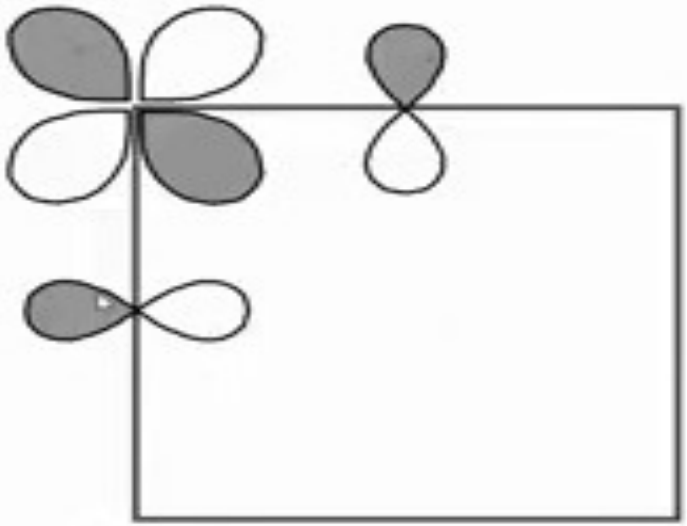


I — O 2p nonbonding and Cu-O bonding

II — Cu 3d-O 2p π antibonding

III — Cu 3d-O 2p σ antibonding

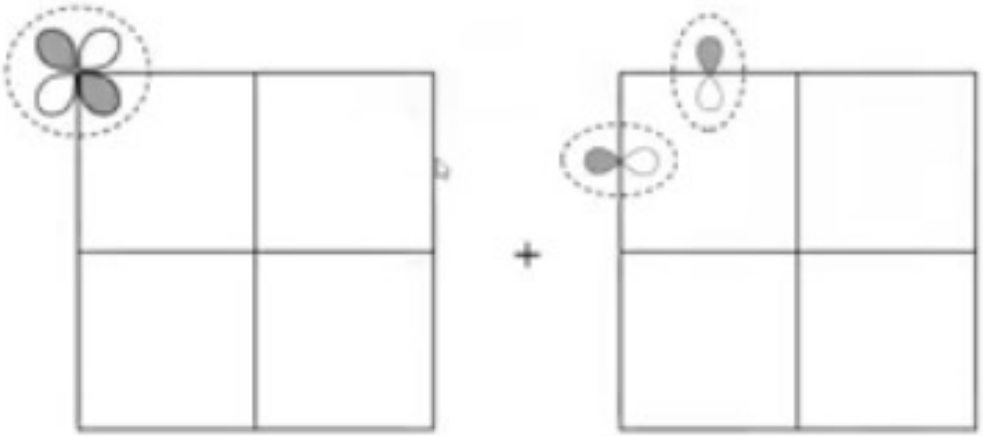
Basis set orbitals (d_{xy} band)



Cu $3d_{xy}$ – O $2p\ \pi^*$

d_{xy} band

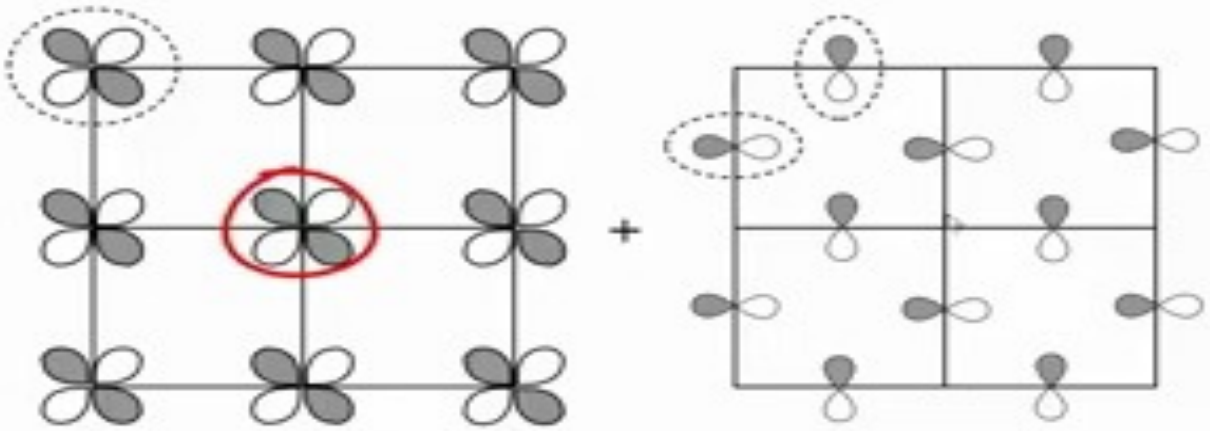
Γ ($k_x = 0$, $k_y = 0$)



Cu $3d_{xy}$ O $2p$

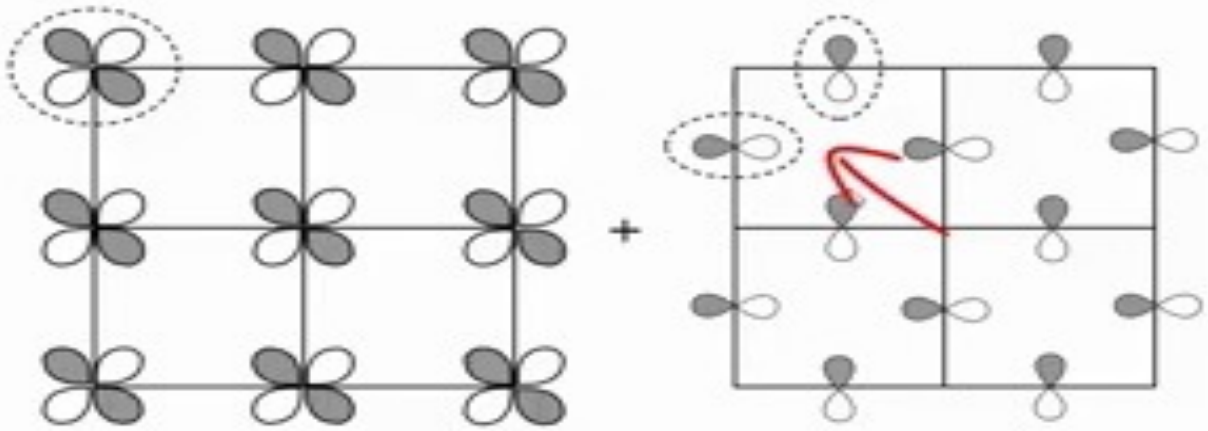
d_{xy} band

Γ ($k_x = 0$, $k_y = 0$)



d_{xy} band

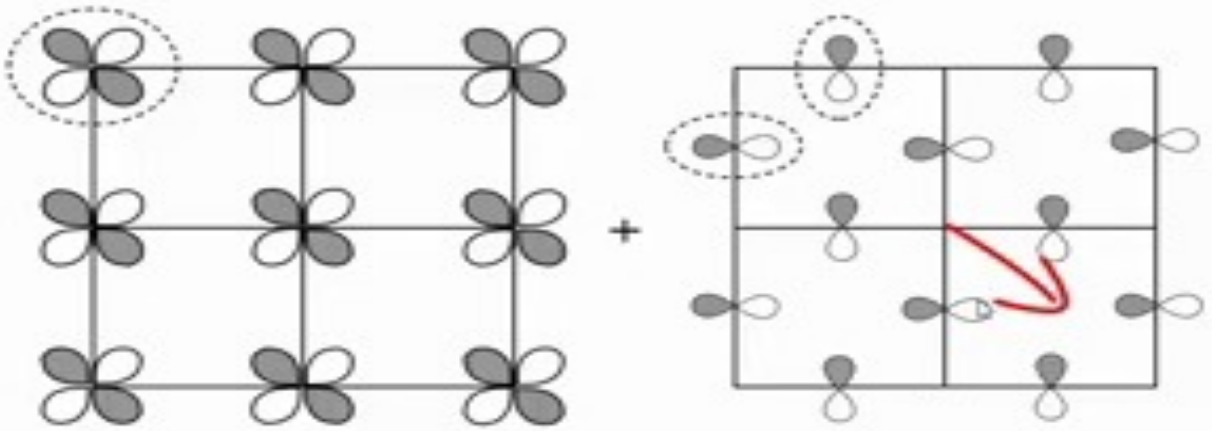
Γ ($k_x = 0$, $k_y = 0$)



Cu $3d_{xy}$ + O $2p$

d_{xy} band

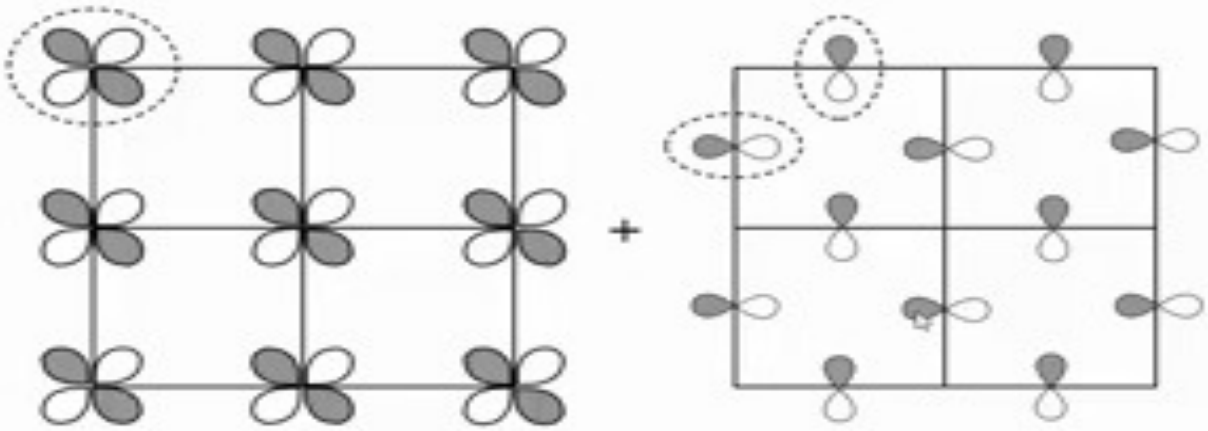
Γ ($k_x = 0$, $k_y = 0$)



Cu $3d_{xy}$ O $2p$

d_{xy} band

Γ ($k_x = 0$, $k_y = 0$)

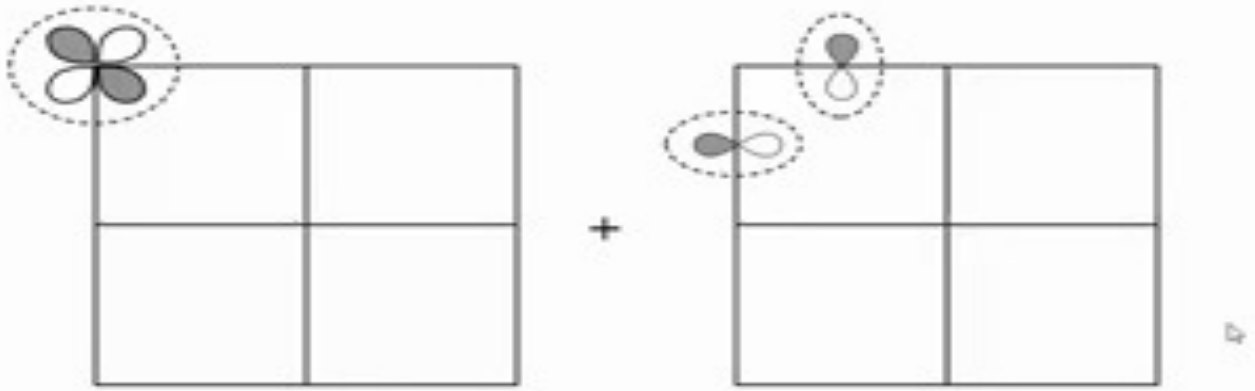


Mixing is symmetry forbidden

Cu $3d_{xy}$ and O $2p$ remain nonbonding

d_{xy} band

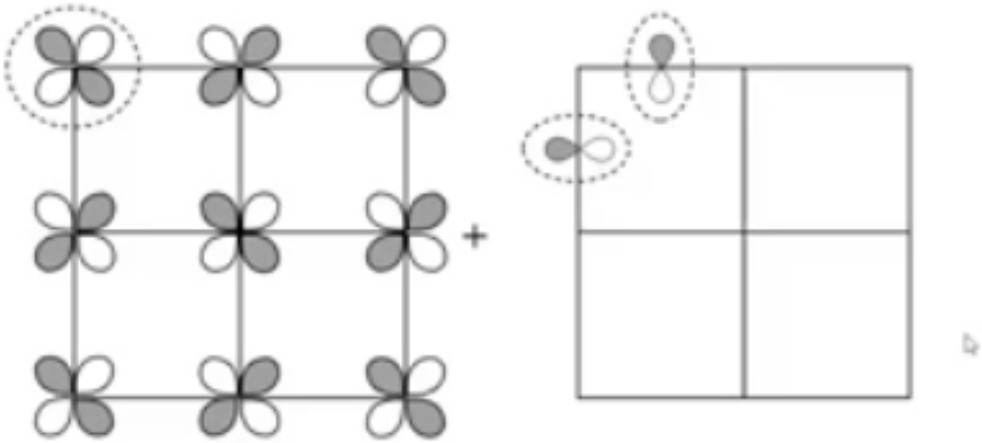
M ($k_x = \pi/a$, $k_y = \pi/a$)



Cu $3d_{xy}$ O $2p$

d_{xy} band

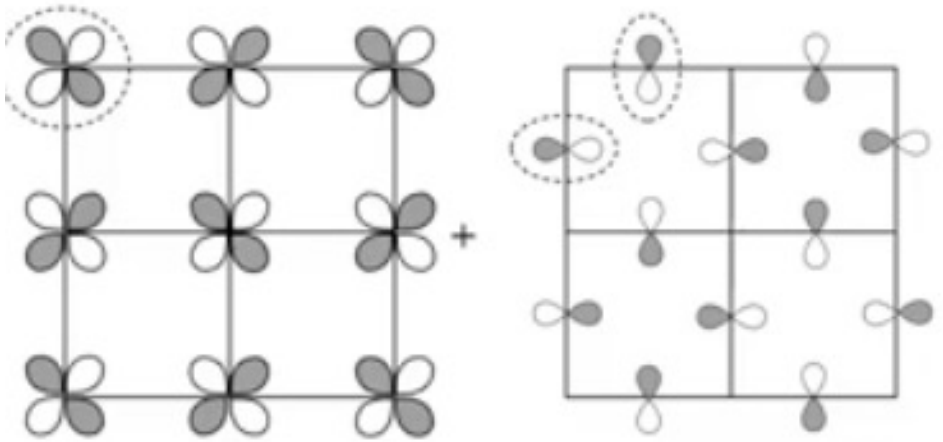
M ($k_x = \pi/a,\ k_y = \pi/a$)



Cu $3d_{xy}$ O $2p$

d_{xy} band

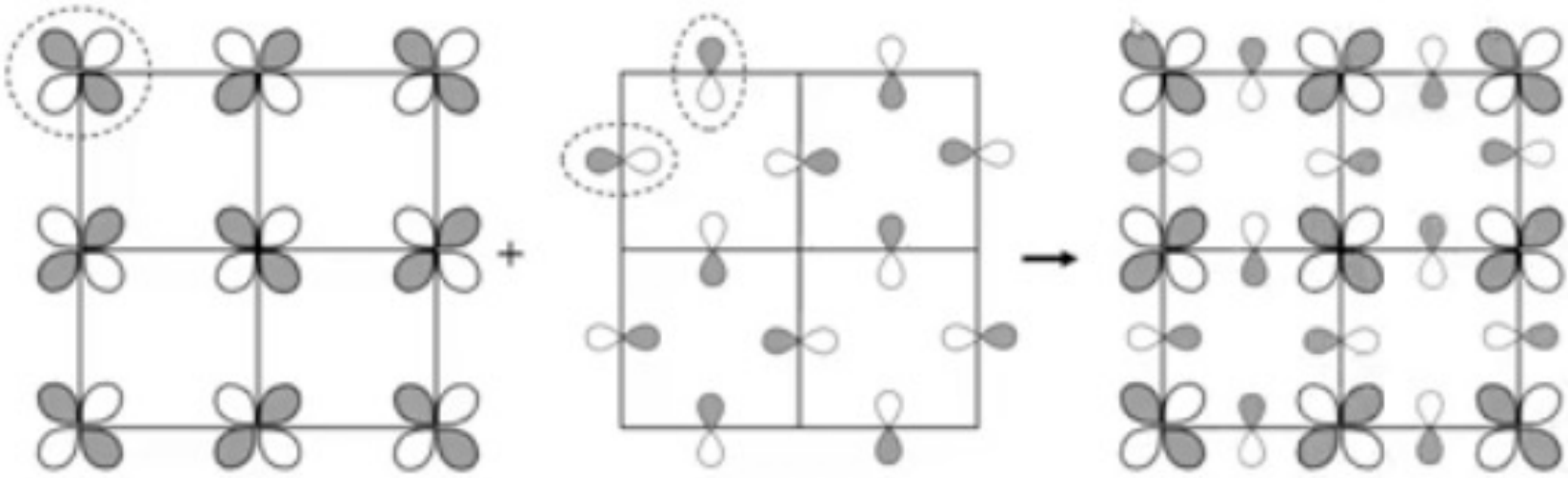
M ($k_x = \pi/a$, $k_y = \pi/a$)



Cu $3d_{xy}$ O $2p$

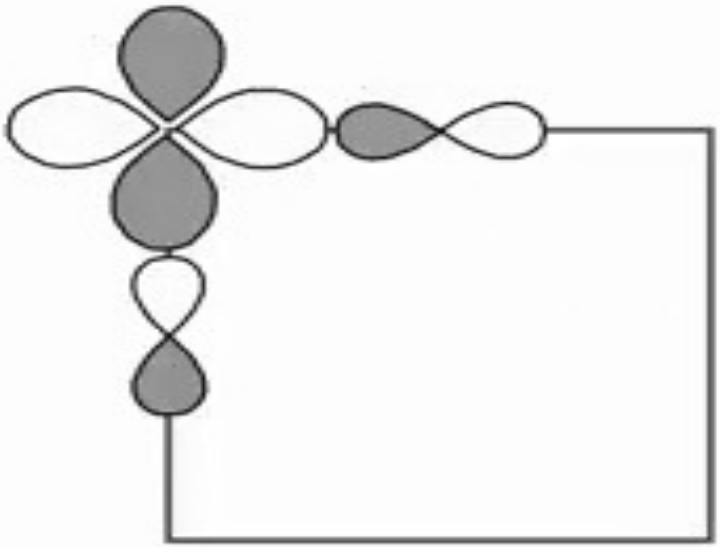
d_{xy} band

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



Cu $3d_{xy}$ O $2p$ π^* crystal orbital

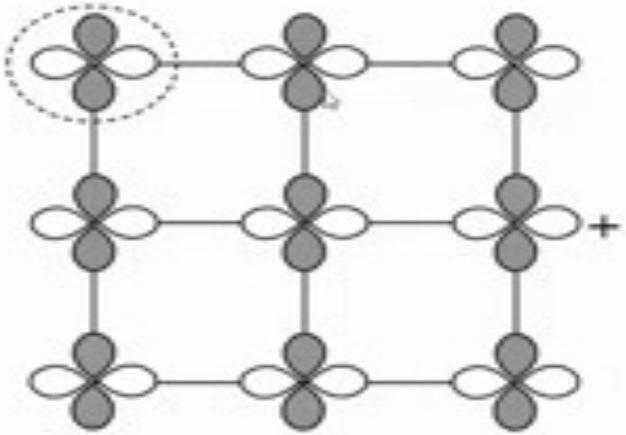
Basis set orbitals (d_{x2-y2} band)



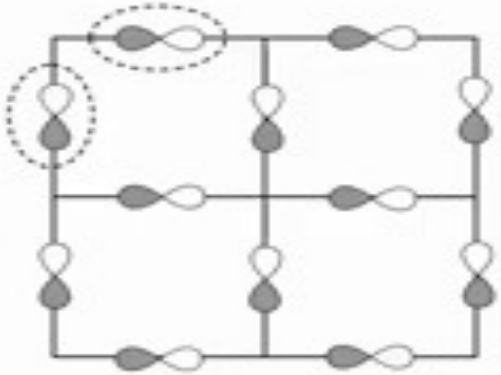
Cu $3d_{x^2-y^2}$ – O $2p\ \sigma^*$

d_{x2-y2} band

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



Cu $3d_{x2-y2}$



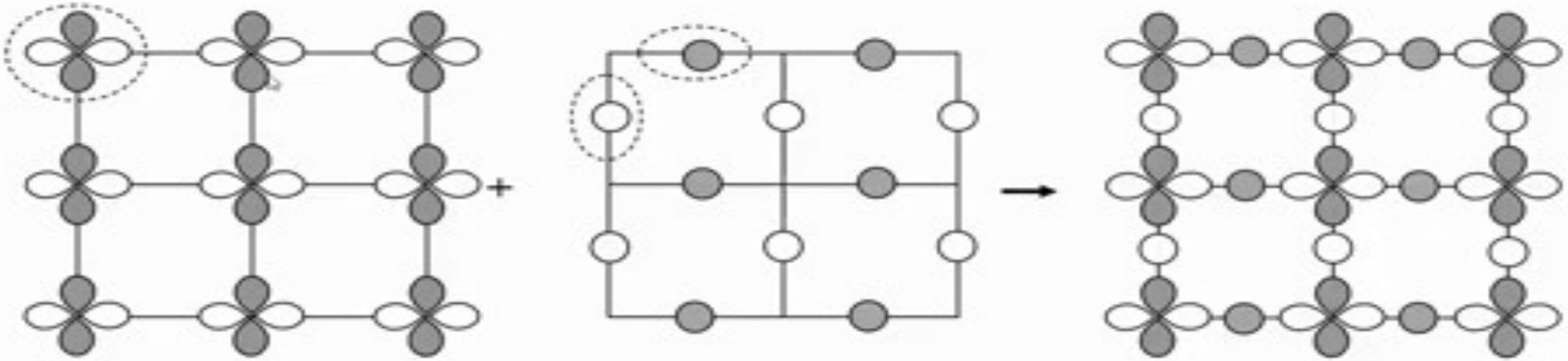
O $2p$

Mixing is symmetry forbidden

No O 2p character in the Cu $3d_{x2-y2}$ band at Γ.

d_{x2-y2} band

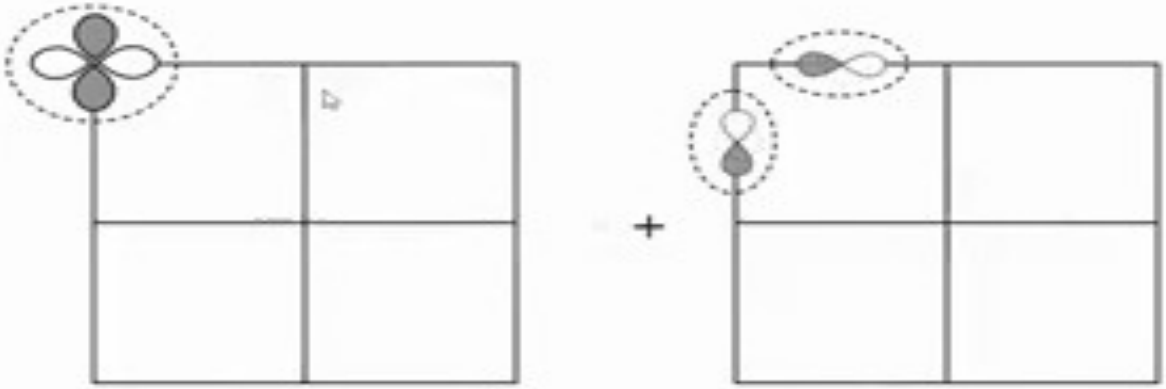
$\Gamma\ (k_x = 0, k_y = 0)$



Cu $3d_{x2-y2}$ O $2s$ σ^* crystal orbital

d_{x2-y2} band

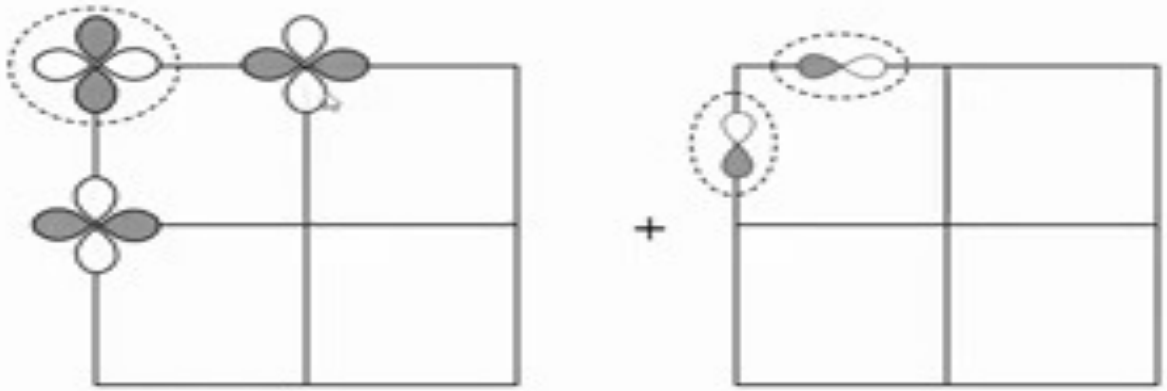
M ($k_x = \pi/a$, $k_y = \pi/a$)



Cu $3d_{x2-y2}$ O $2p$

d_{x2-y2} band

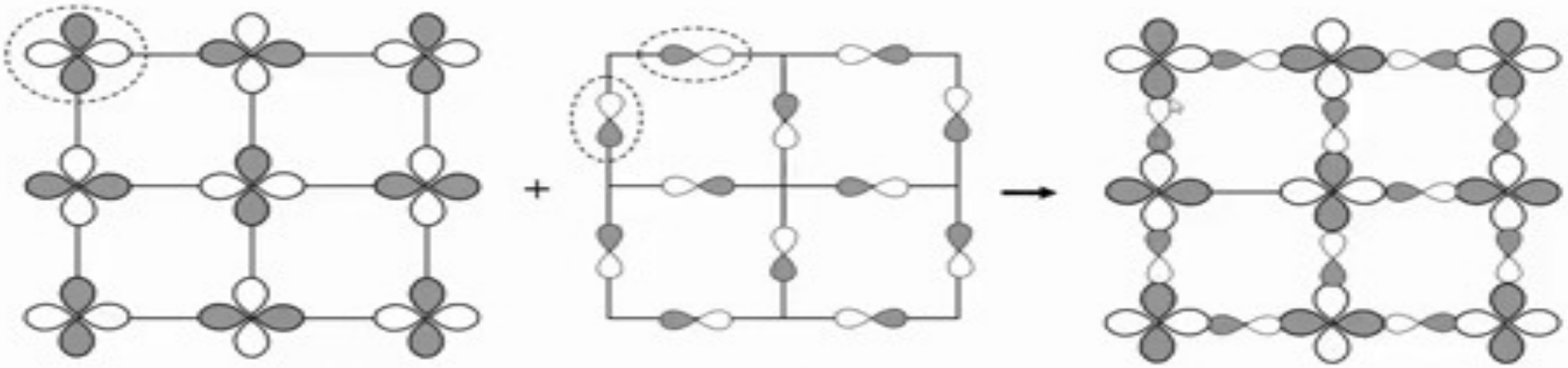
M ($k_x = \pi/a$, $k_y = \pi/a$)



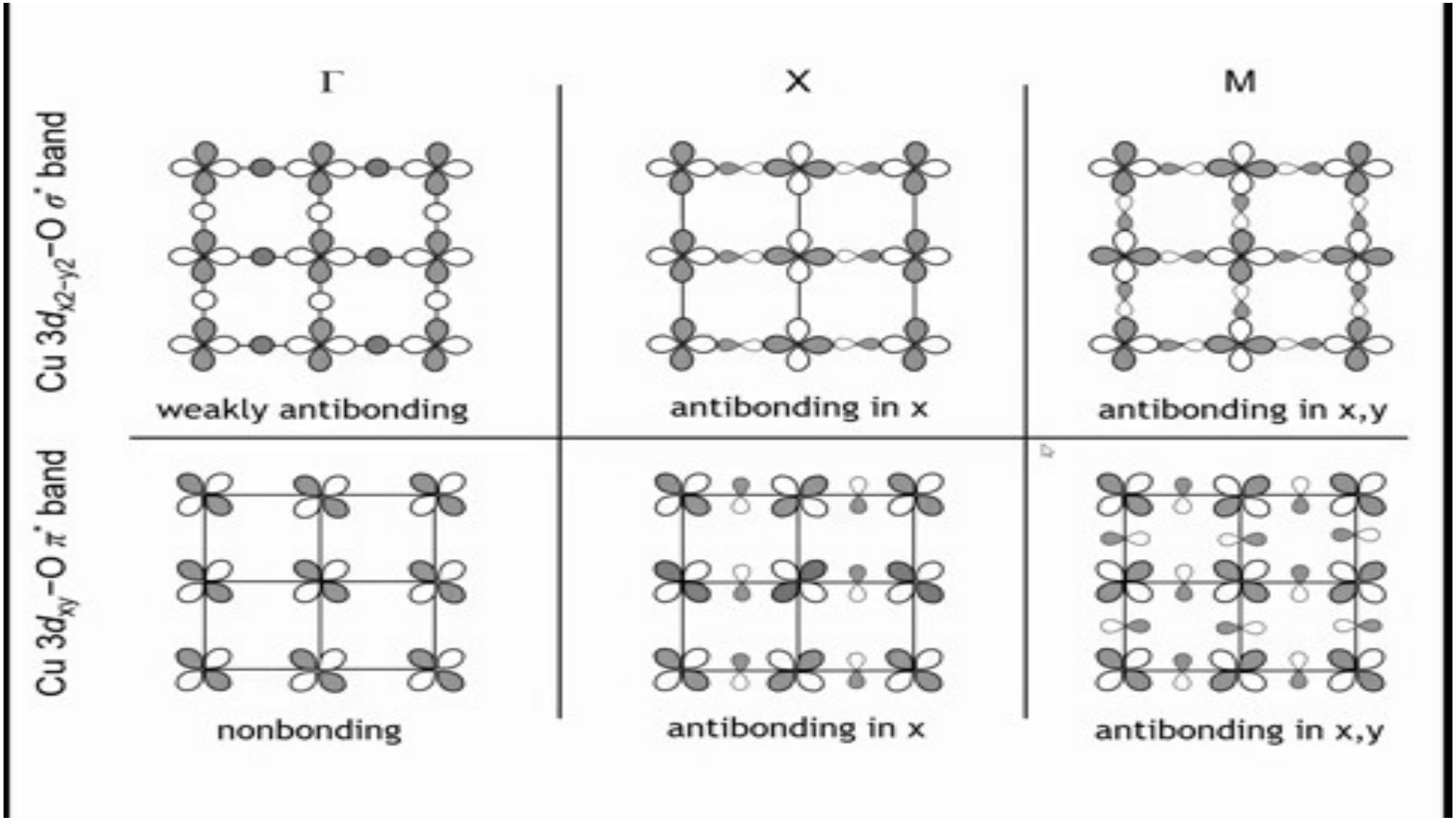
Cu $3d_{x2-y2}$ O $2p$

d_{x2-y2} band

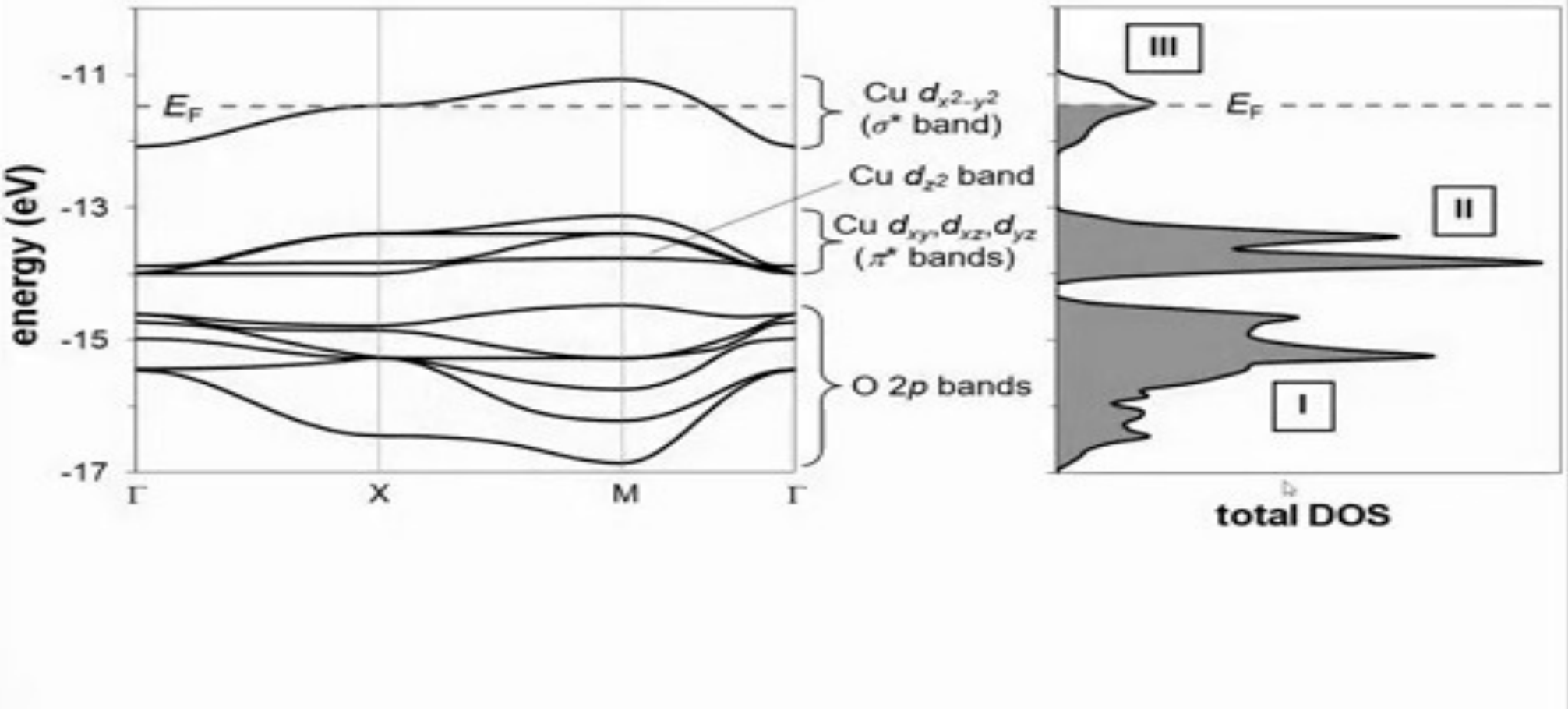
M ($k_x = \pi/a$, $k_y = \pi/a$)



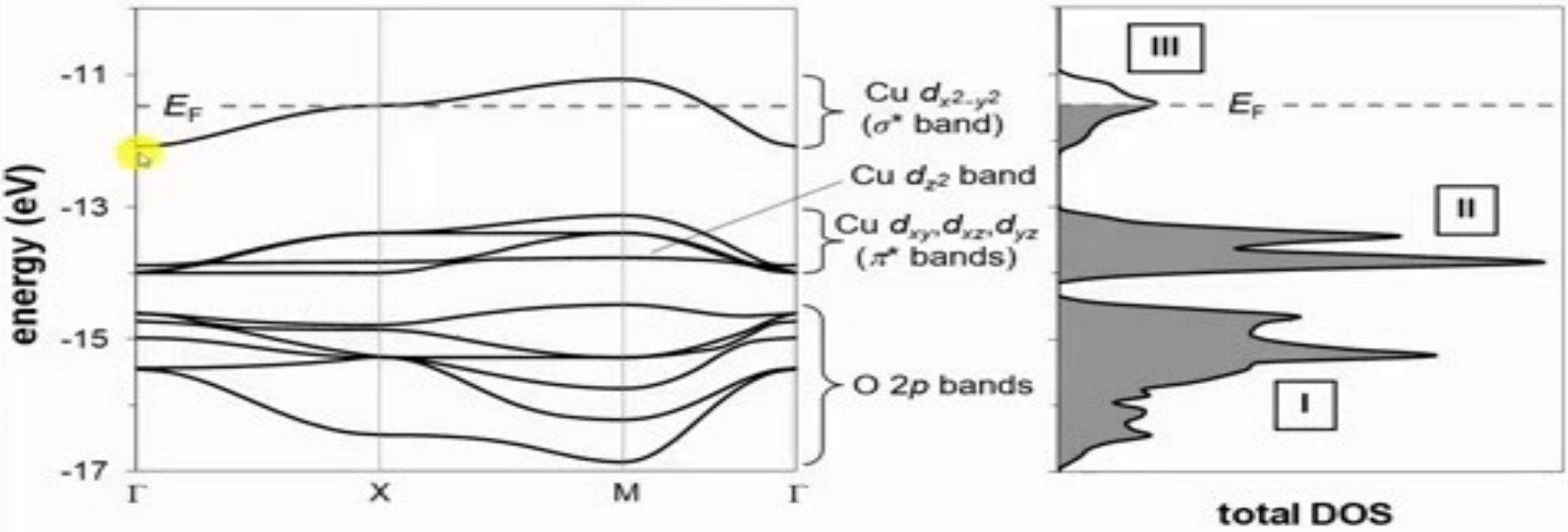
Cu $3d_{x2-y2}$ + O $2p$ → σ^* crystal orbital


Γ
X
M
Cu 3d$_{x2-y2}$–O σ* band
weakly antibonding
antibonding in x
antibonding in x,y
Cu 3d$_{xy}$–O π* band
nonbonding
antibonding in x
antibonding in x,y

Band Structure CuO_2^{2-} Sheet



Band Structure CuO_2^{2-} Sheet



Key Concepts: Band Structure

What is being plotted? Energy vs. k, where k is the wavevector that gives the phase of the MO's on moving from one unit cell to the next (as well as the crystal momentum of the electron).

How many lines are there in a band structure diagram? As many as there are atomic orbitals in the unit cell.

How is the center of gravity energy level of each band determined? It usually follows from the MO diagram.

How do we determine whether a band runs uphill or downhill? By comparing the orbital overlap at k=0 and k=π/a.

How do we distinguish metals from semiconductors and insulators? The Fermi level cuts a band in a metal, whereas there is a gap between the filled and empty states in a semiconductor.

Why are some bands flat and others steep? This depends on the degree of orbital overlap between building units.

Wide bands $\rightarrow$ Large intermolecular overlap $\rightarrow$ delocalized e^-
Narrow bands $\rightarrow$ Weak intermolecular overlap $\rightarrow$ localized e^-

Homework:

- 6.9
- 6.10
- 6.11
- 6.13
- 6.14
- 6.15
- 6.16