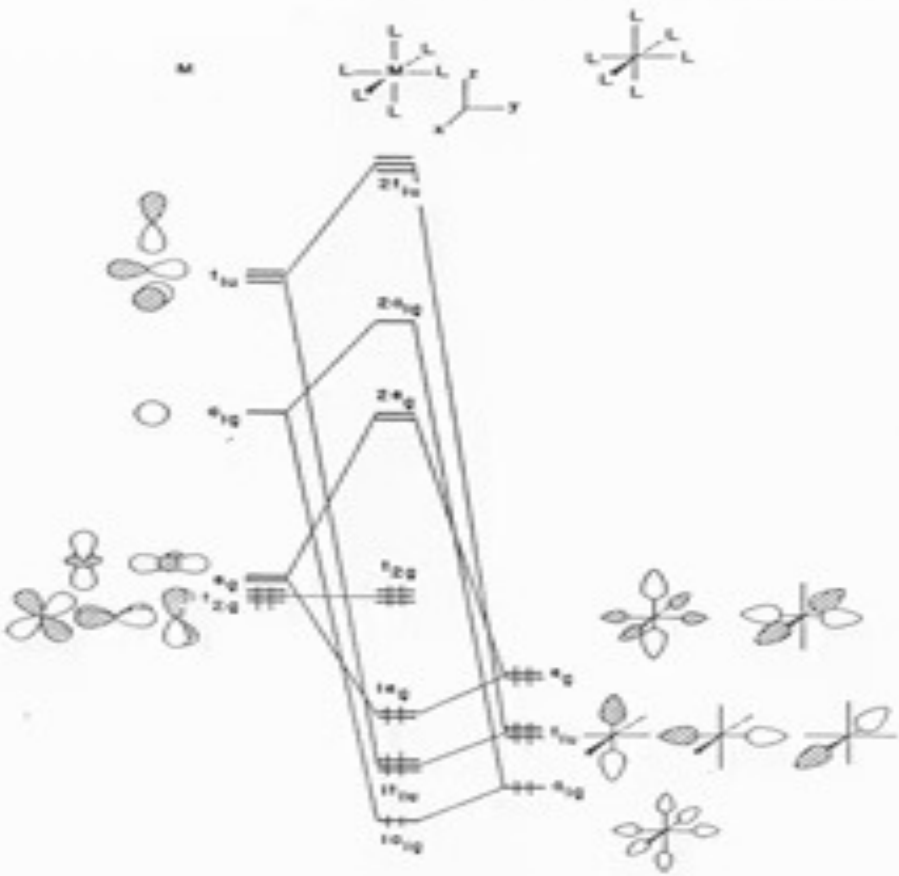
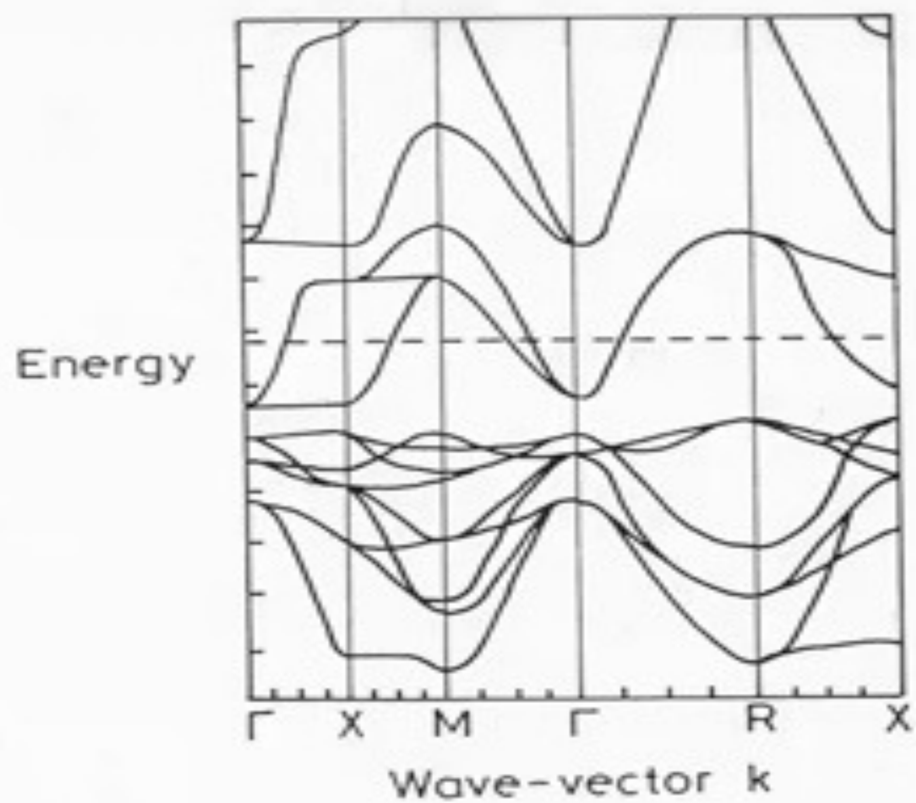
Learning Objectives — Intro to Band Theory (1D Hydrogen Chain)

- Understand **why crystals require band structures** instead of molecular orbitals.
- Define a **crystal orbital** as a **Bloch function** (periodic basis × lattice phase term).
- Interpret **k** as both a **wavevector** and **crystal momentum**.
- Identify **bonding (k=0)** and **antibonding (k=π/a)** limits in the **1st Brillouin zone**.
- Relate **band width** to **orbital overlap** (wide = delocalized, narrow = localized).
- Recognize **density of states (DOS)** as a summary of orbital distribution vs. energy.

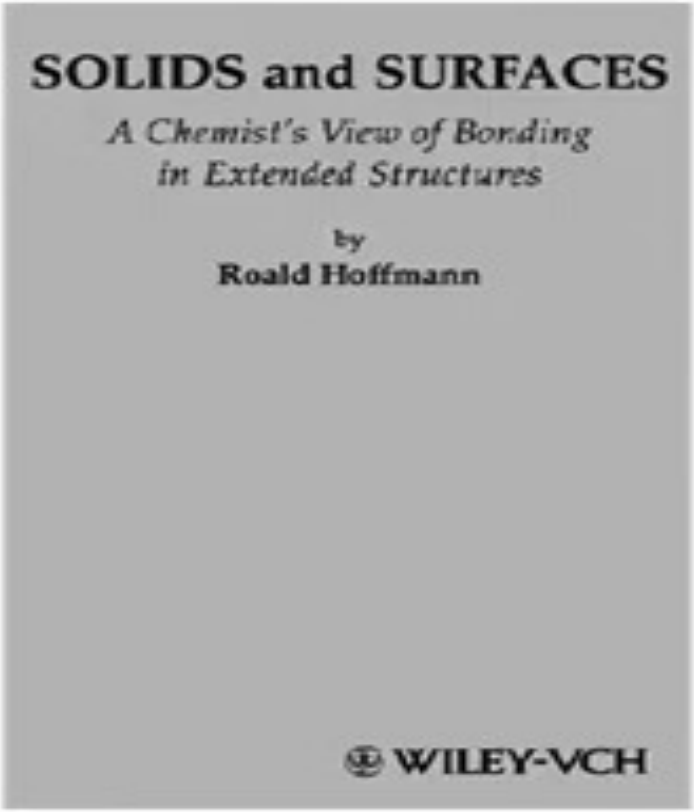
Electronic Band Structure

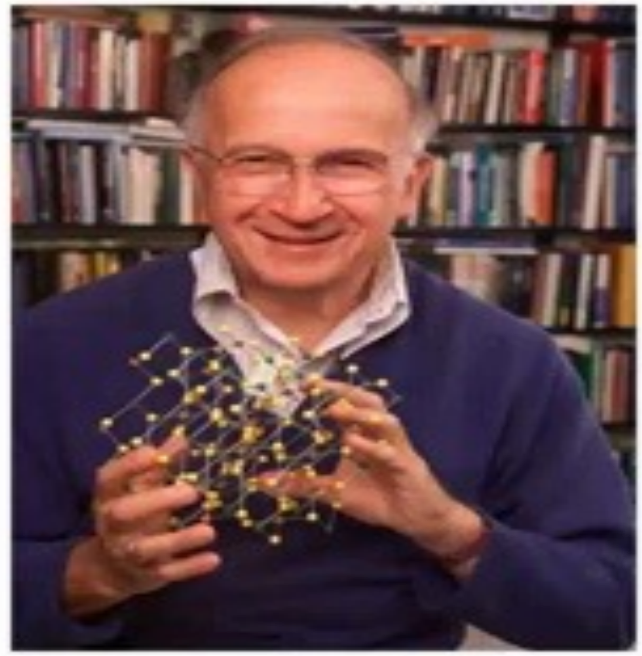


MO diagram for finite sized molecule



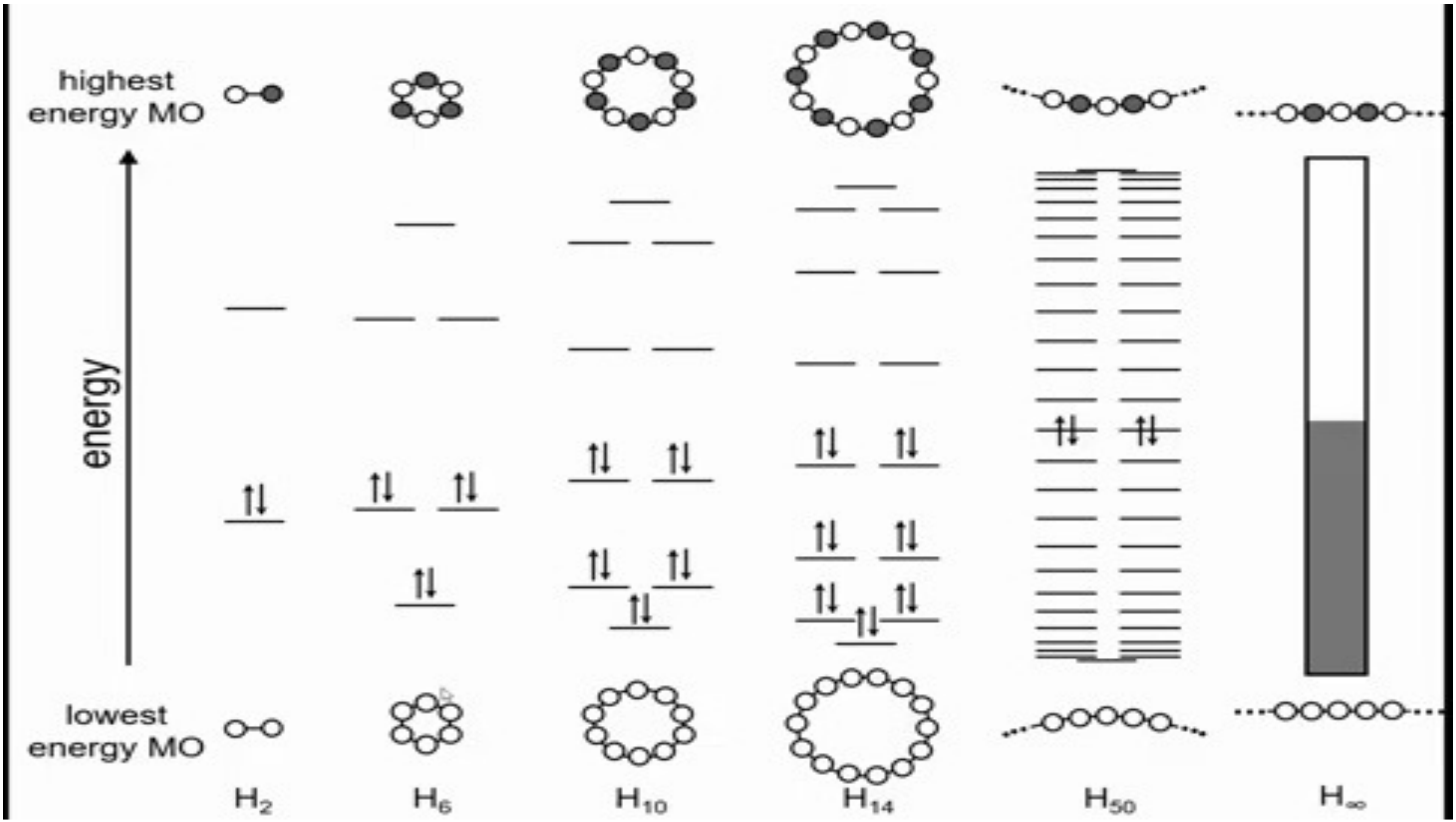
Band structure diagram for infinite crystal





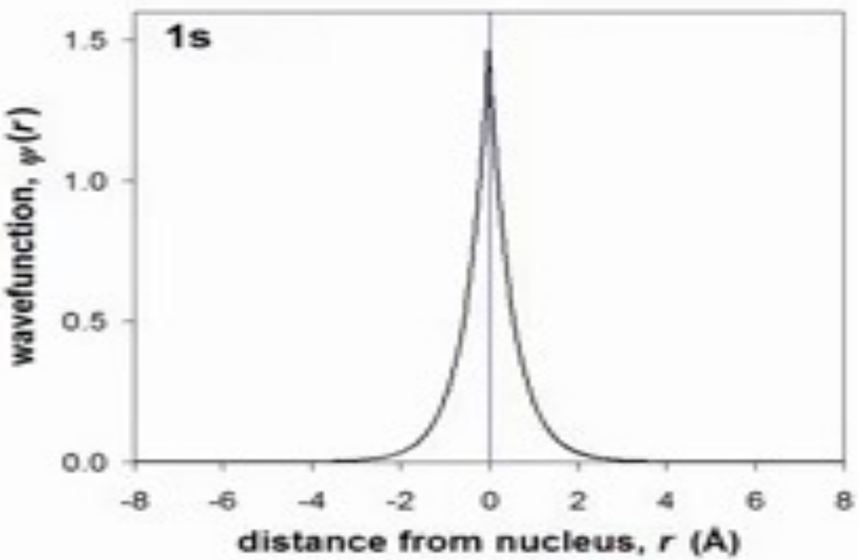
Roald Hoffmann
(Cornell)

Published in 1989

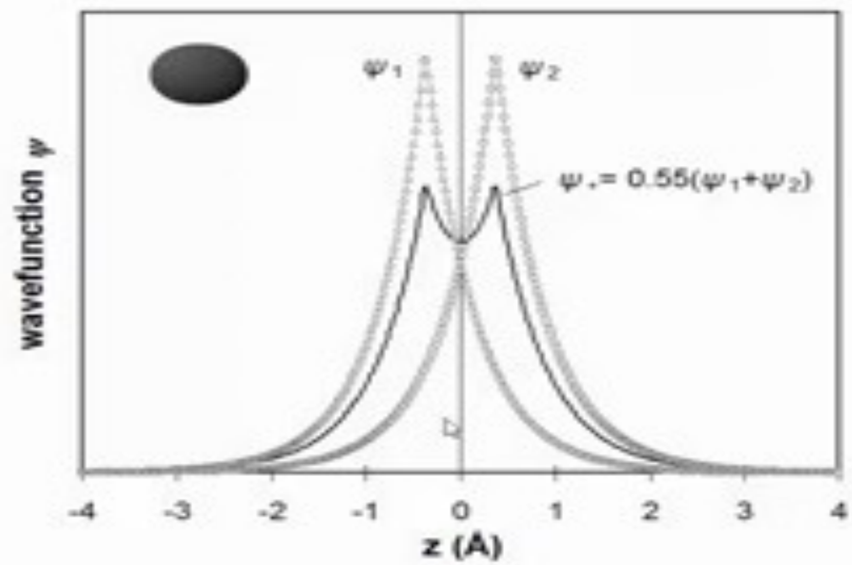


highest energy MO
energy
lowest energy MO
H2
H6
H10
H14
H50
H∞

Atomic and Molecular Orbitals



Atomic orbital



Molecular orbital

To describe the structures of molecules we approximated MOs as linear combinations of atomic orbitals.

Crystal Orbitals
(Bloch Functions)

$$\psi(x) = e^{ikx} u(x)$$

Wavefunction

(x is the position along the chain)

Imposes the periodicity of the lattice

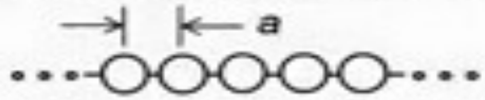
$$e^{ikx} = \cos(kx) + i\sin(kx)$$

Basis set

Represents the molecular orbitals inside the unit cell (repeats exactly from one unit cell to the next)

First Brillouin Zone

What is k? What is its physical significance? What are it's allowed values?



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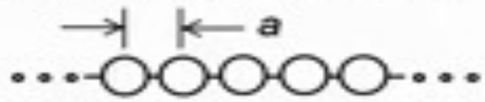

Consider a ring of *N* hydrogen atoms, with *N* large enough that we can neglect curvature. If we start at any point on the chain, x, and go all the way around the chain to the same point, x + *Na*, the wavefunction must repeat (periodic boundary conditions).

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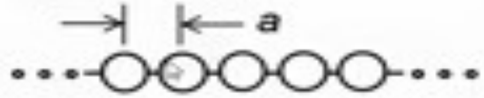

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$$\psi(x) = \psi(x + Na)$$

$$e^{ikx}u(x) = e^{ik(x+Na)}u(x + Na)$$

But *u(x)* is periodic. That is it repeats identically from one unit cell to the next. So, $u(x) = u(x + Na)$ and

$$e^{ikx} = e^{ik(x+Na)} = e^{ikx}e^{ikNa}$$

First Brillouin Zone (cont)

Applying Euler's relationship

$$e^{ikx} = e^{ikx} e^{ikNa} = e^{ikx}\left[\cos(kNa) + i\sin(kNa)\right]$$

First Brillouin Zone (cont)

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Obviously, the term in brackets must be equal to 1. That will only happen when $kNa = n(2\pi)$ (where n is an integer) because $\cos(n2\pi) = 1$ and $\sin(n2\pi) = 0$. So

First Brillouin Zone (cont)

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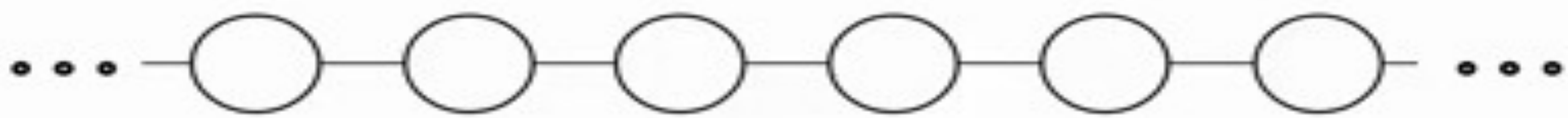
$$kNa = n(2\pi)$$

Rearranging we get

$$k = n\frac{(2\pi)}{Na} = \pm\frac{2\pi}{Na}, \pm\frac{4\pi}{Na}, \pm\frac{6\pi}{Na}, \ldots \pm(N/2)\frac{2\pi}{Na}$$

Notice that even as the length of the chain (N) goes to infinity the relevant values of k are limited to the range $-\pi/a$ to $+\pi/a$. This range is called the **First Brillouin Zone.**

1D Chain of H atoms



Visualizing Crystal Orbitals

What does the crystal orbital look like when k = 0 (at the center of the Brillouin zone)?

$$\psi_k = e^{ikx}u(x)$$

$$\psi_{k=0} = e^0\,\psi_{1s(0)} + e^0\,\psi_{1s(1)} + e^0\,\psi_{1s(2)} + e^0\,\psi_{1s(3)} + e^0\,\psi_{1s(4)} + e^0\,\psi_{1s(5)} + \ldots$$

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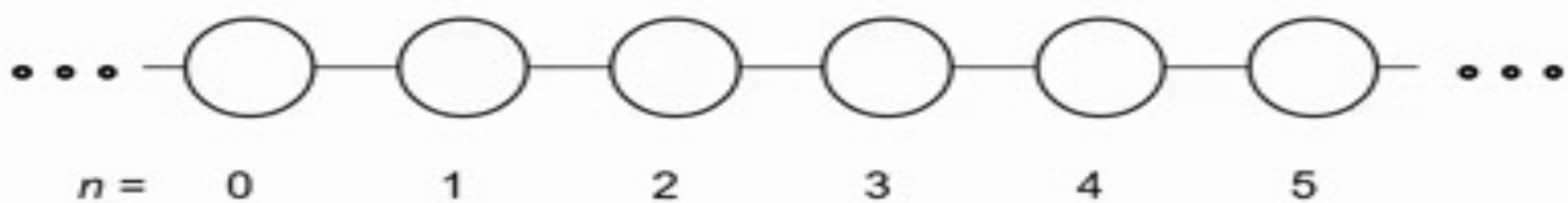
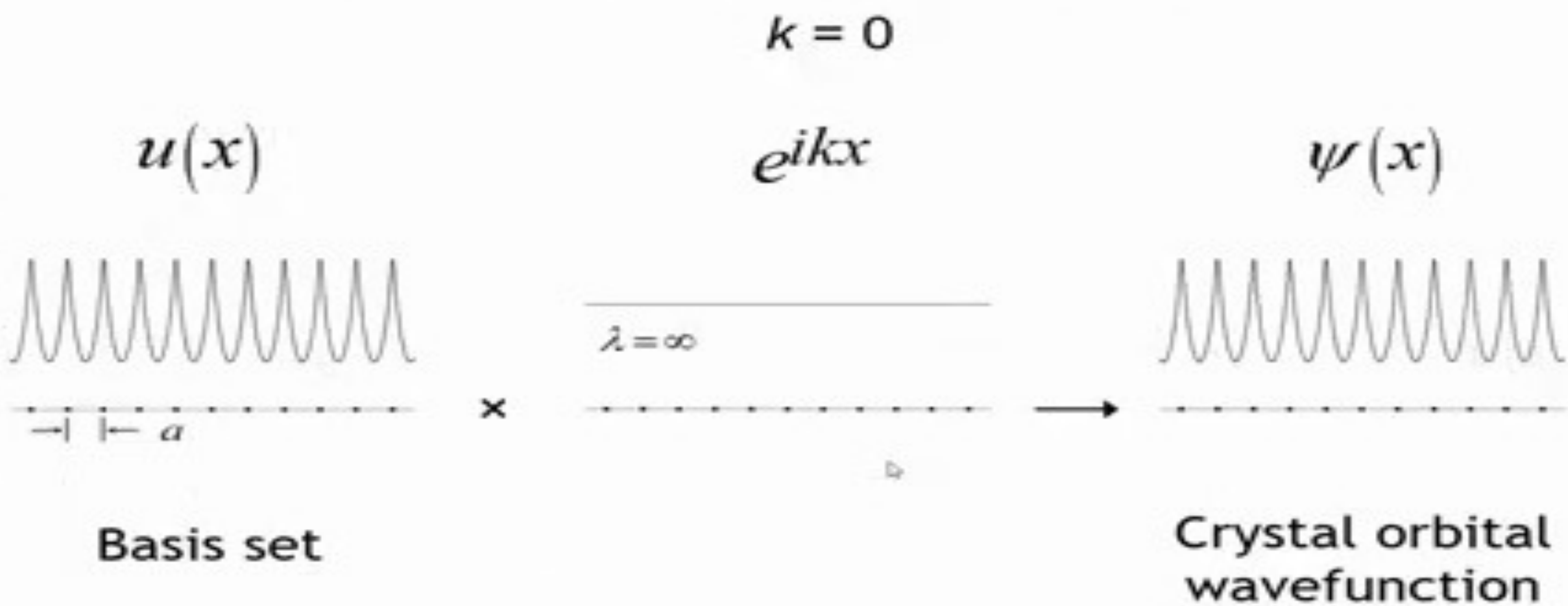


All H-H interactions are bonding, this is the lowest energy crystal orbital


k = 0
u(x)
e^{ikx}
ψ(x)
λ = ∞
a
Basis set
Crystal orbital wavefunction

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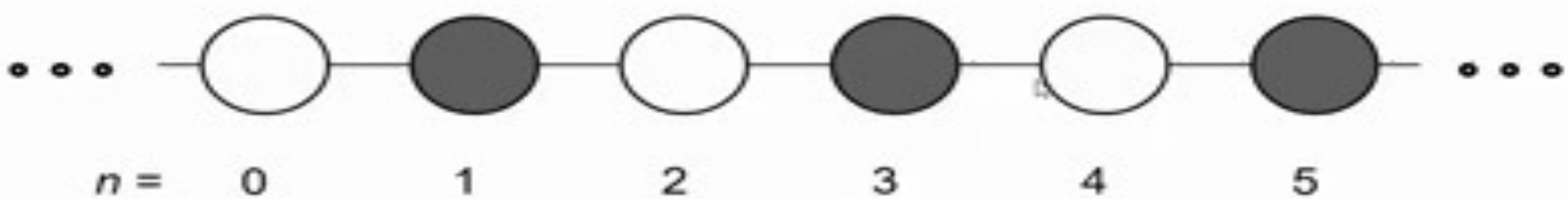
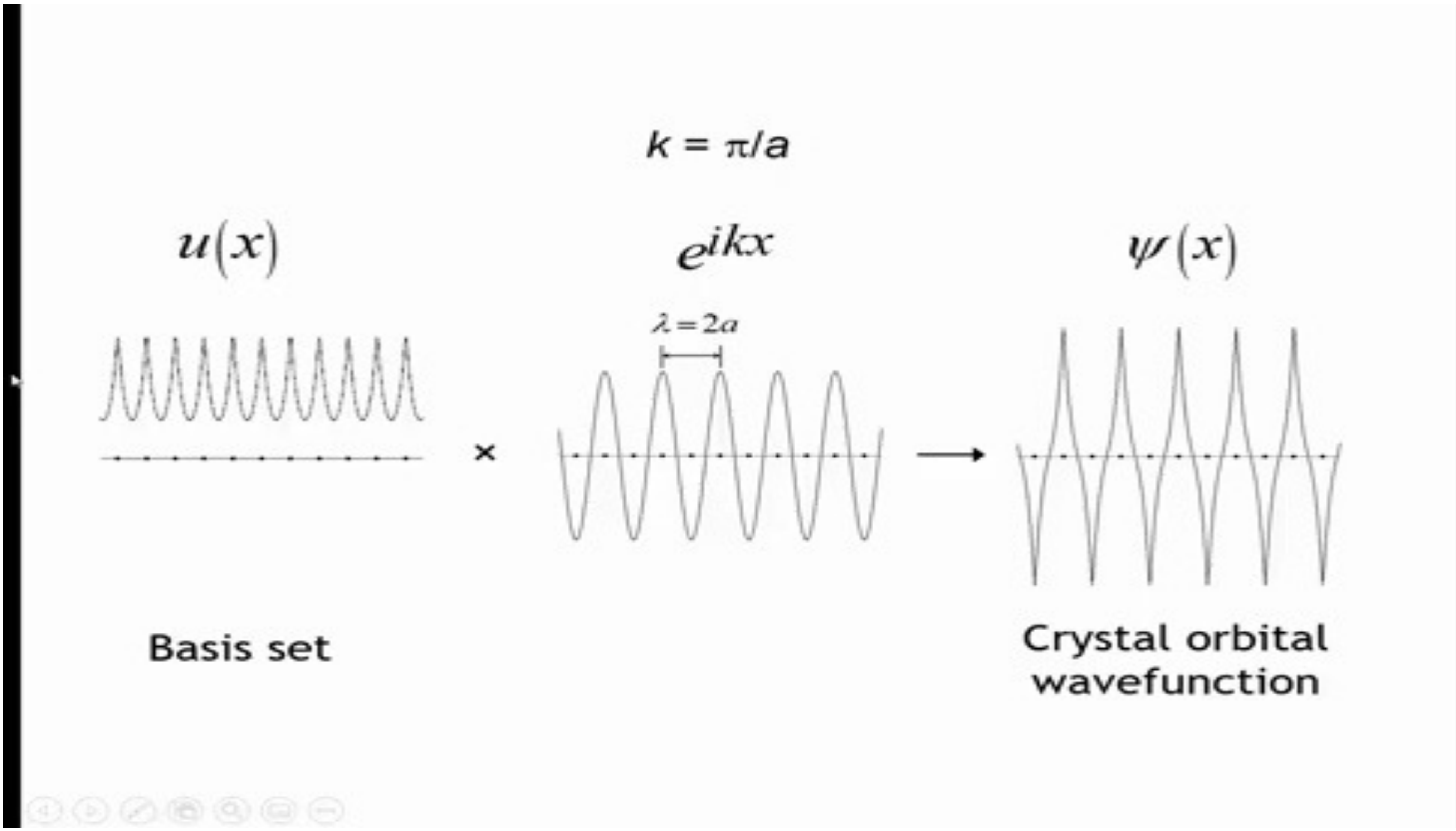
$$\psi_{k=\pi/a} = e^{0}\psi_{1s(0)} + e^{i\pi}\psi_{1s(1)} + e^{i2\pi}\psi_{1s(2)} + e^{i3\pi}\psi_{1s(3)} +$$

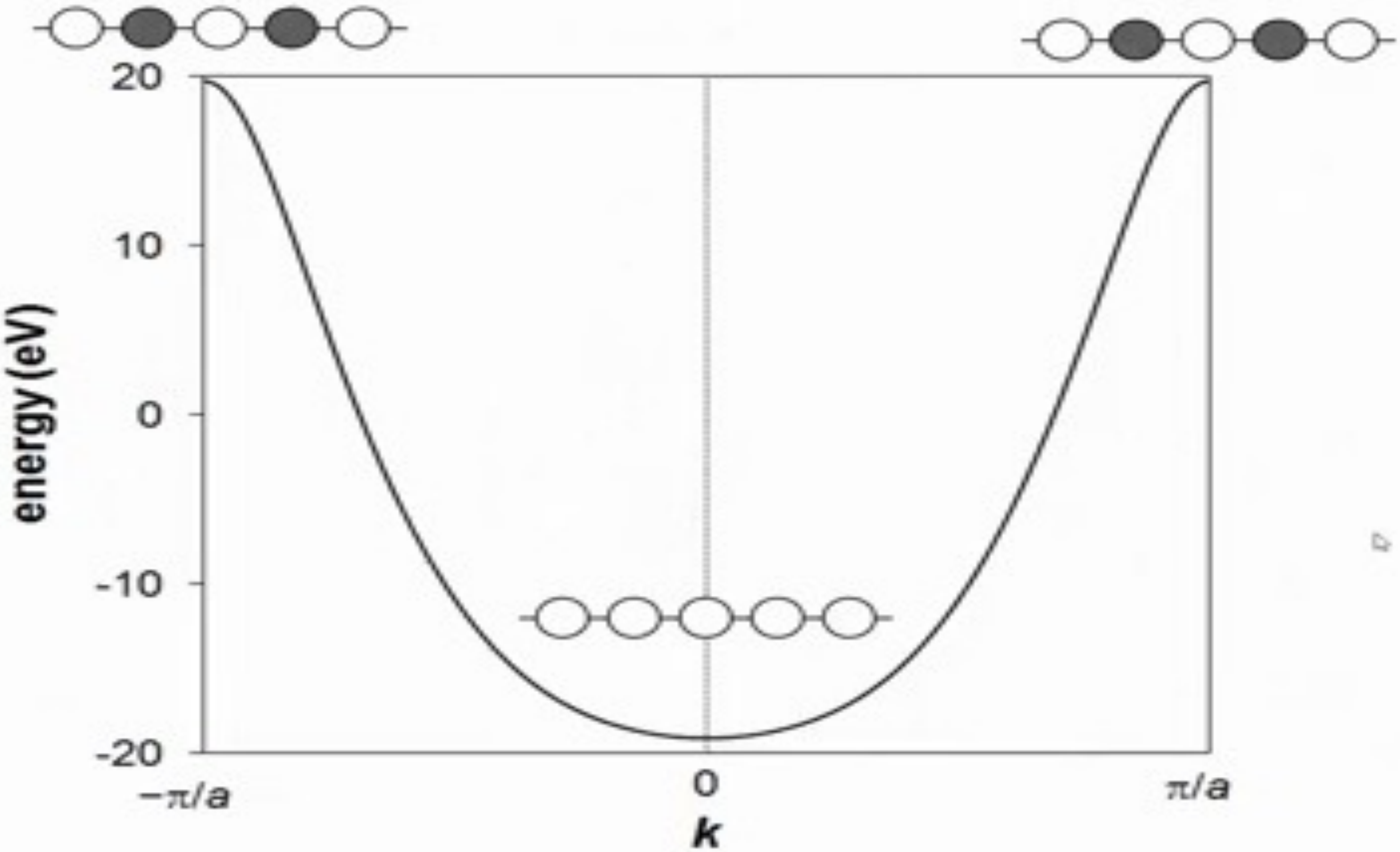
$$\psi_{k=\pi/a} = \psi_{1s(0)} - \psi_{1s(1)} + \psi_{1s(2)} - \psi_{1s(3)} + \psi_{1s(4)} - \psi_{1s(5)} + \cdots$$



All H-H interactions are antibonding, this is the highest energy crystal orbital

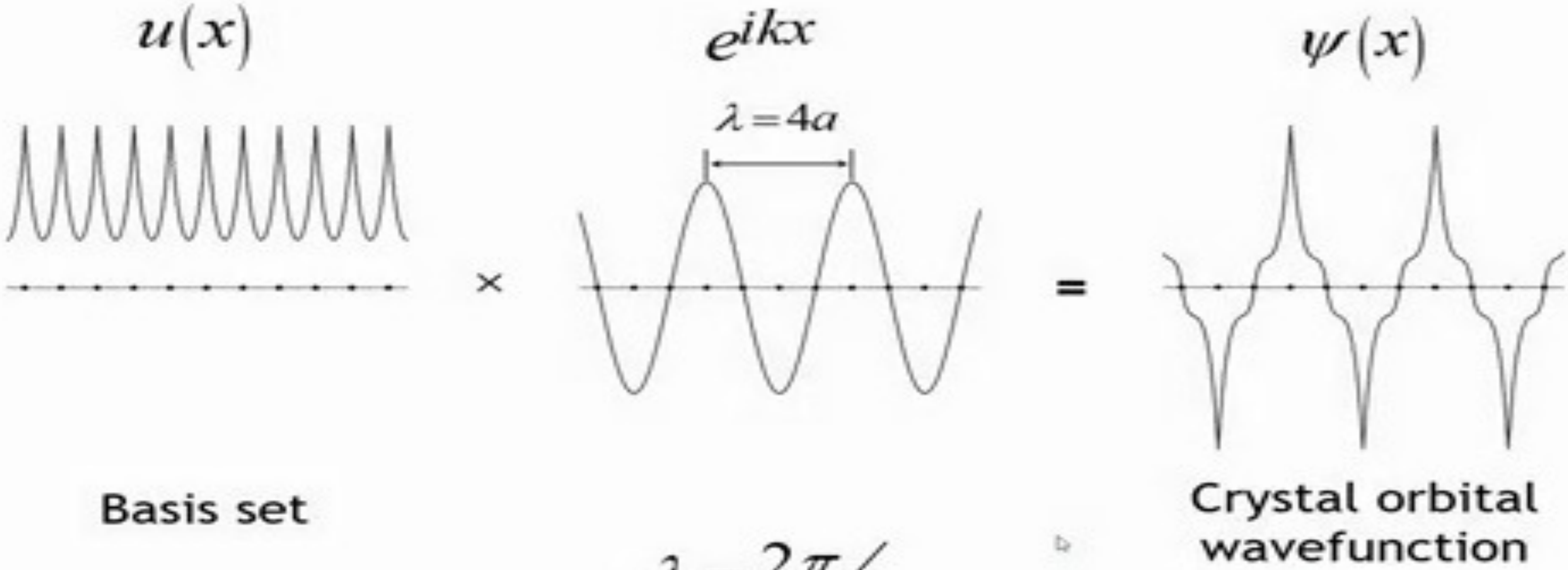

$k = \pi/a$
$u(x)$
e^{ikx}
$\psi(x)$
$\lambda = 2a$
×
Basis set
Crystal orbital wavefunction

Band Structure Linear H atom chain



Intermediate values of k

$k = \pi/2a$



$$\lambda = 2\pi/k$$

What is k?

- *k* is a quantum number that "labels" wave functions (analogous to SALCs) generated by the translational symmetry of the crystal (it determines the coefficients of the basis set)

- Reciprocal space wavevector. It tells us how rapidly the crystal orbital changes phase

$$\lambda = 2\pi / k$$

- It determines the crystal momentum of an electron

$$p = h / \lambda$$

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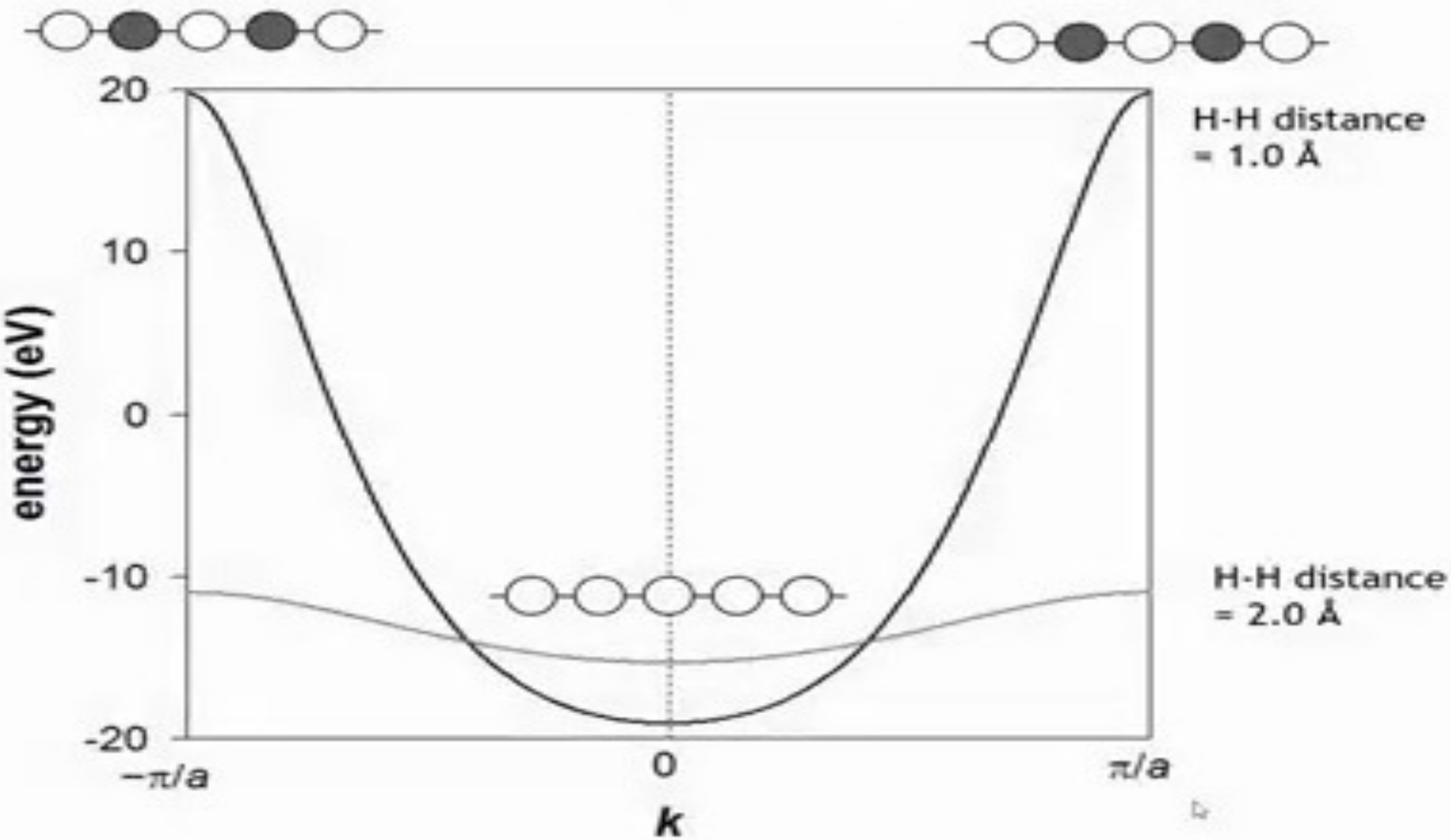
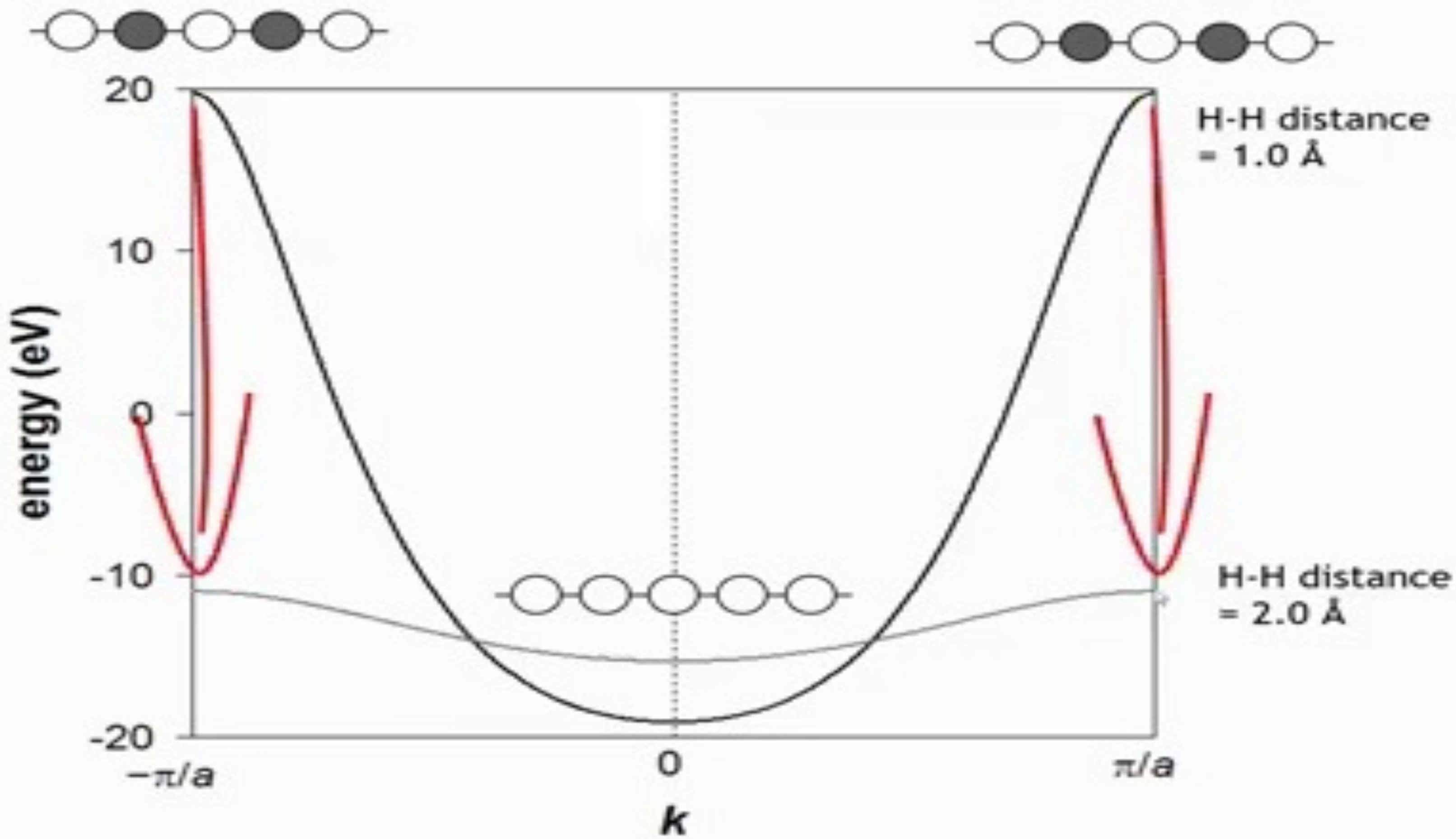
$$p = h / \lambda \longrightarrow p = hk / 2\pi = \hbar k$$

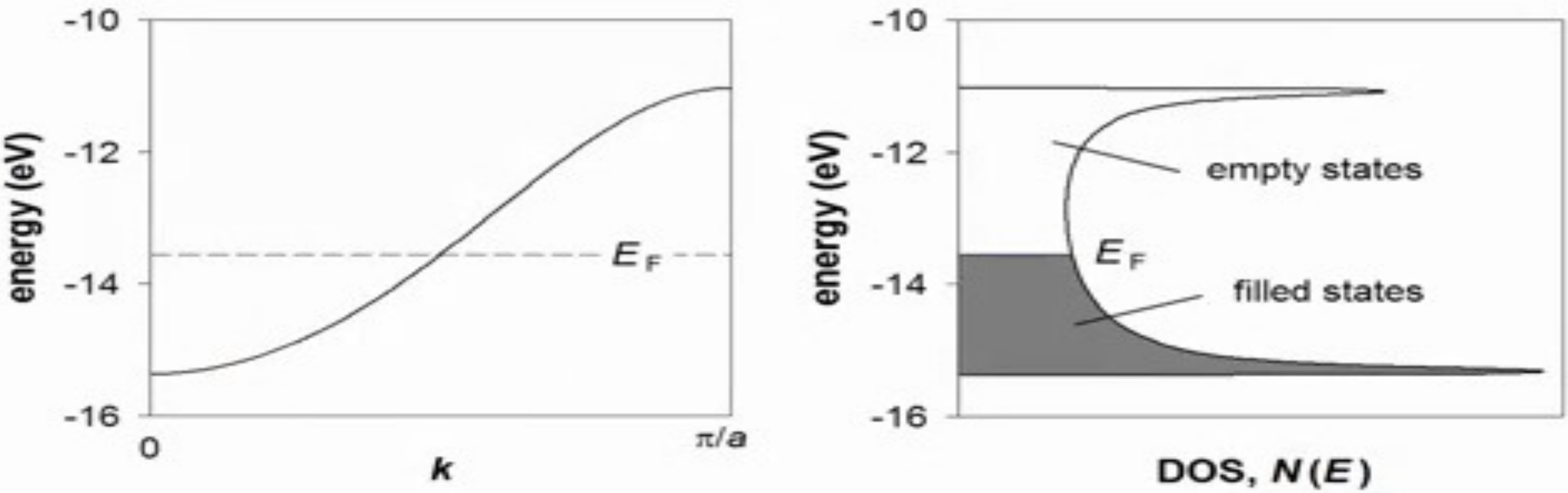
Bandwidth and orbital overlap



Bandwidth and orbital overlap



Density of States



Density of states, $N(E)$, which is the number of allowed energy levels per unit volume of the solid over the energy range E to $E + dE$, as dE goes to zero.

Flat bands give sharp peaks in the DOS, wide bands give shallow features in the DOS.

- **Goal:** Bridge from molecular orbitals → crystal band structure.
- **Approach:** Extend MO theory to infinite periodic solids using **Bloch functions:**
  $\psi(x) = u(x) \cdot e^{ikx}$
  - $u(x)$: periodic basis (hydrogen 1s) • e^{ikx}: imposes lattice periodicity
- **k ("crystal momentum"):**
  - Labels distinct crystal orbitals
  - Determines wavelength $\lambda = 2\pi/k$ → momentum $p = \hbar k$
  - Allowed range: $-\pi/a \le k \le +\pi/a$ (1st Brillouin zone)
- **Extremes:**
  $k = 0$ → all bonding (ψ in-phase) lowest energy
  $k = \pi/a$ → all antibonding (ψ alternating $\pm$) highest energy
- **Bandwidth:** $\Delta E \approx E(\pi/a) - E(0) \propto$ orbital overlap
  - Large overlap → wide band → delocalized electrons
  - Small overlap → narrow band → localized electrons
- **Density of States (DOS):** number of states per energy interval dE
  - Peaks where bands are flat (bottom/top)
  - Minima where bands steep (midband)
- **Essence:** Infinite chain → continuous bands; k maps real-space bonding to energy-momentum space.

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Answer: The basis set *u(x)* represents the repeating local wavefunction within each unit cell. For the hydrogen chain, it's the **1s atomic orbital** of hydrogen, repeated periodically along the lattice. It captures the local bonding environment while e^{ikx} imposes long-range periodicity.

How does the value of k determine whether a crystal orbital is bonding or antibonding?

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The value of **k** determines how the phases of the atomic orbitals vary along the crystal.

- When **k = 0**, all orbitals are **in phase**, so all overlaps are **constructive → maximum bonding → lowest energy**.
- When **k = π/a**, adjacent orbitals alternate in sign (**+ − + −**) → **complete destructive overlap → maximum antibonding → highest energy**.
- Intermediate k values produce partial phase alternation, giving orbitals with **mixed bonding/antibonding** character and **intermediate energies**.

Thus, **k controls the bonding character and energy** of each crystal orbital across the band.

Homework

6.1-6.5

Learning Objectives

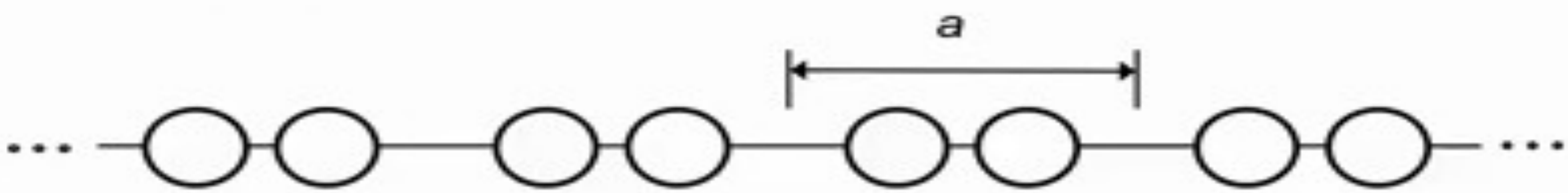
Electronic Band Structures in 1D Systems

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

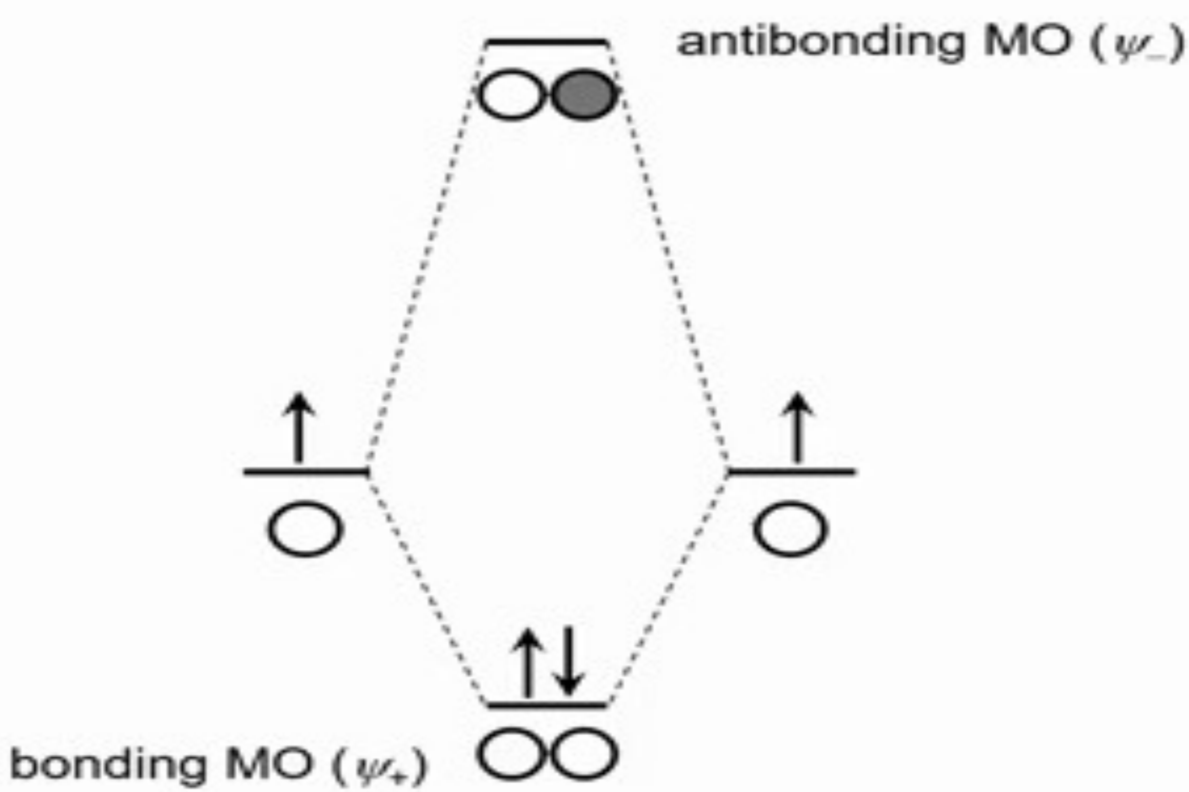
- Construct band structures for one-dimensional molecular chains and understand how dimerization creates band gaps
- Predict the number of bands from the number of atomic orbitals in the unit cell
- Distinguish between direct and indirect band gaps and explain their impact on optical properties
- Classify materials as metals, semiconductors, or insulators based on band structure and Fermi level position
- Analyze how different atomic orbitals (s, p-sigma, p-pi) contribute to band formation and dispersion

Linear Chain of H_2 Molecules

Let's see what happens to the band structure of our H atom chain if we let the atoms dimerize into H_2molecules.



Now there are two H-H distances, a short intramolecular distance and a longer intermolecular distance.



The unit cell now contains two atoms (each with one orbital), so there are two molecular orbitals per unit cell and there will be two bands in the band structure diagram.

Bonding MO Band

$$\psi(x) = e^{ikx}u(x)$$

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$k = 0,\ u = \psi_+$

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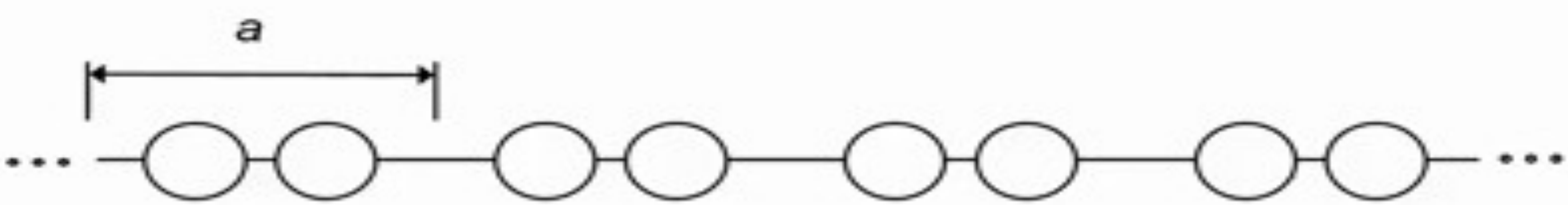

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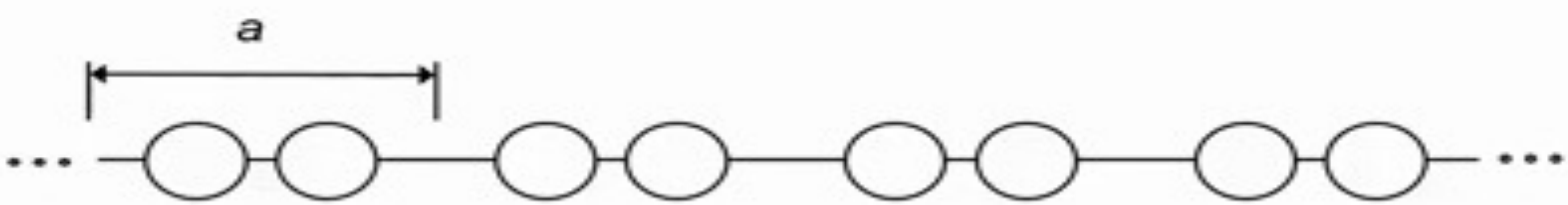

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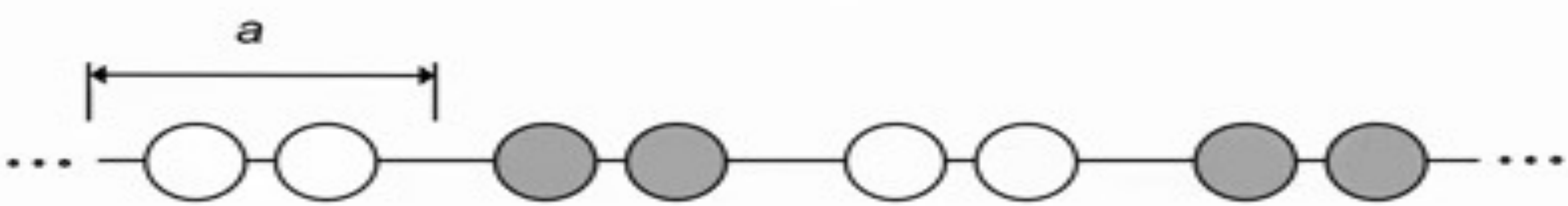

Antibonding MO Band

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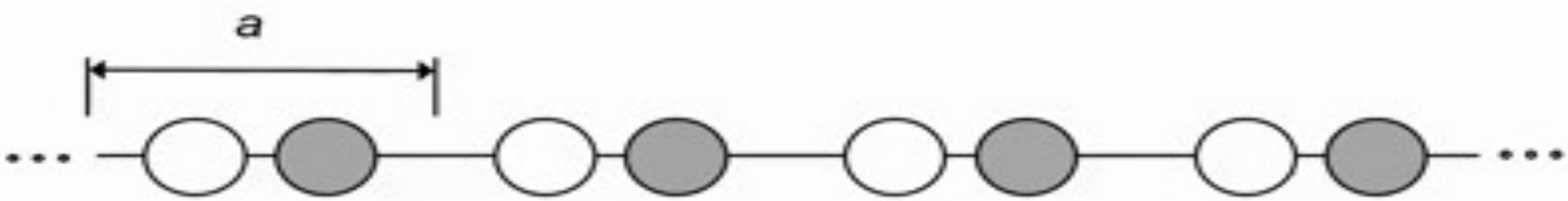
$k = 0$, $u = \psi_-$



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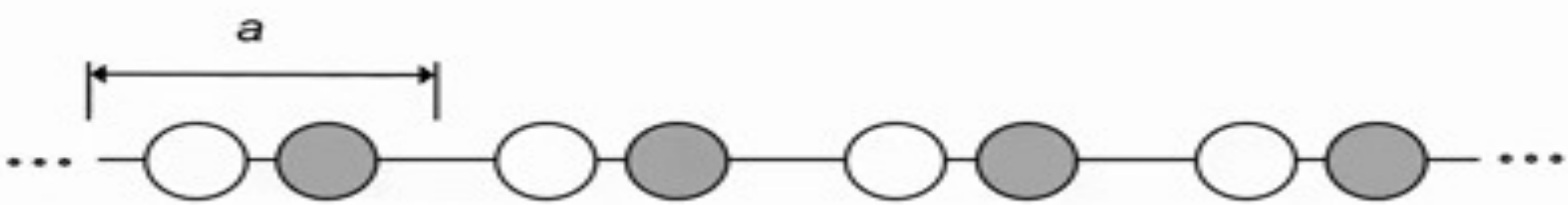

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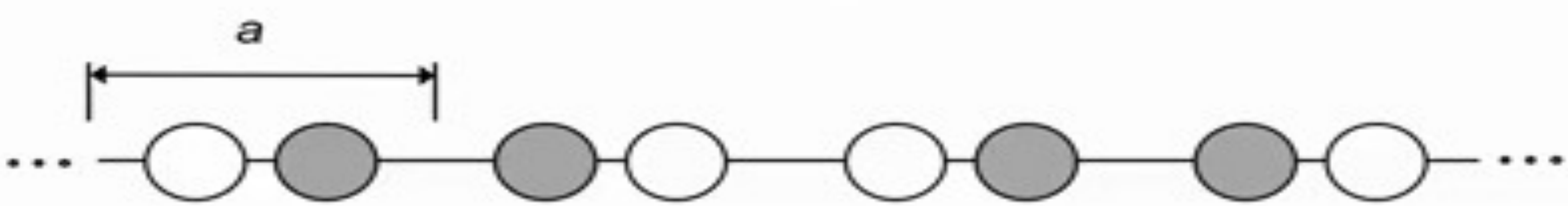


$k = \pi/a$, $u = \psi_+ \rightarrow$ intramolecular = bonding; intermolecular = antibonding

$k = 0$, $u = \psi_+ \rightarrow$ intramolecular = bonding; intermolecular = bonding

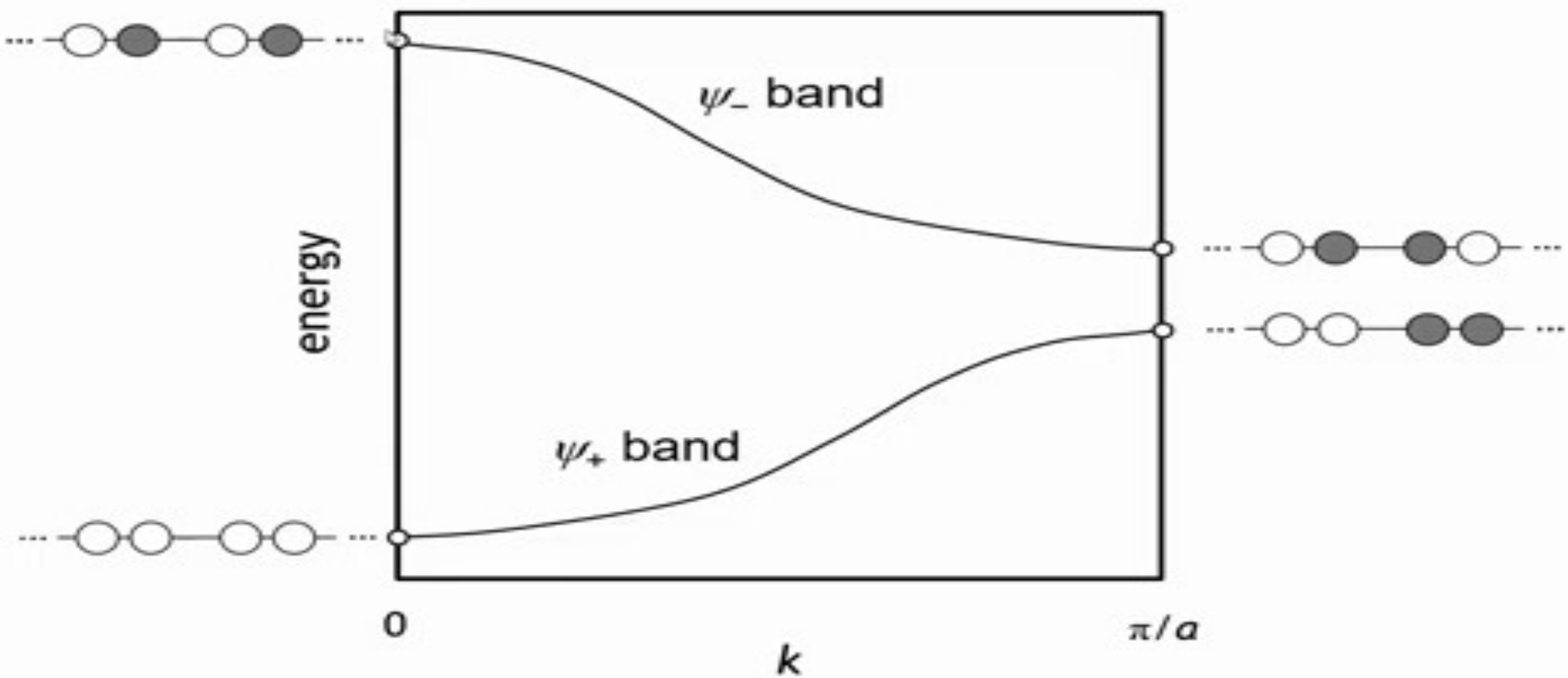
$k = 0$, $u = \psi_- \rightarrow$ intramolecular = antibonding; intermolecular = antibonding

$k = \pi/a$, $u = \psi_- \rightarrow$ intramolecular = antibonding; intermolecular = bonding

$k = \pi/a$, $u = \psi_+ \rightarrow$ intramolecular = bonding; intermolecular = antibonding

$k = 0$, $u = \psi_+ \rightarrow$ intramolecular = bonding; intermolecular = bonding

Band Structure Linear H_2 chain



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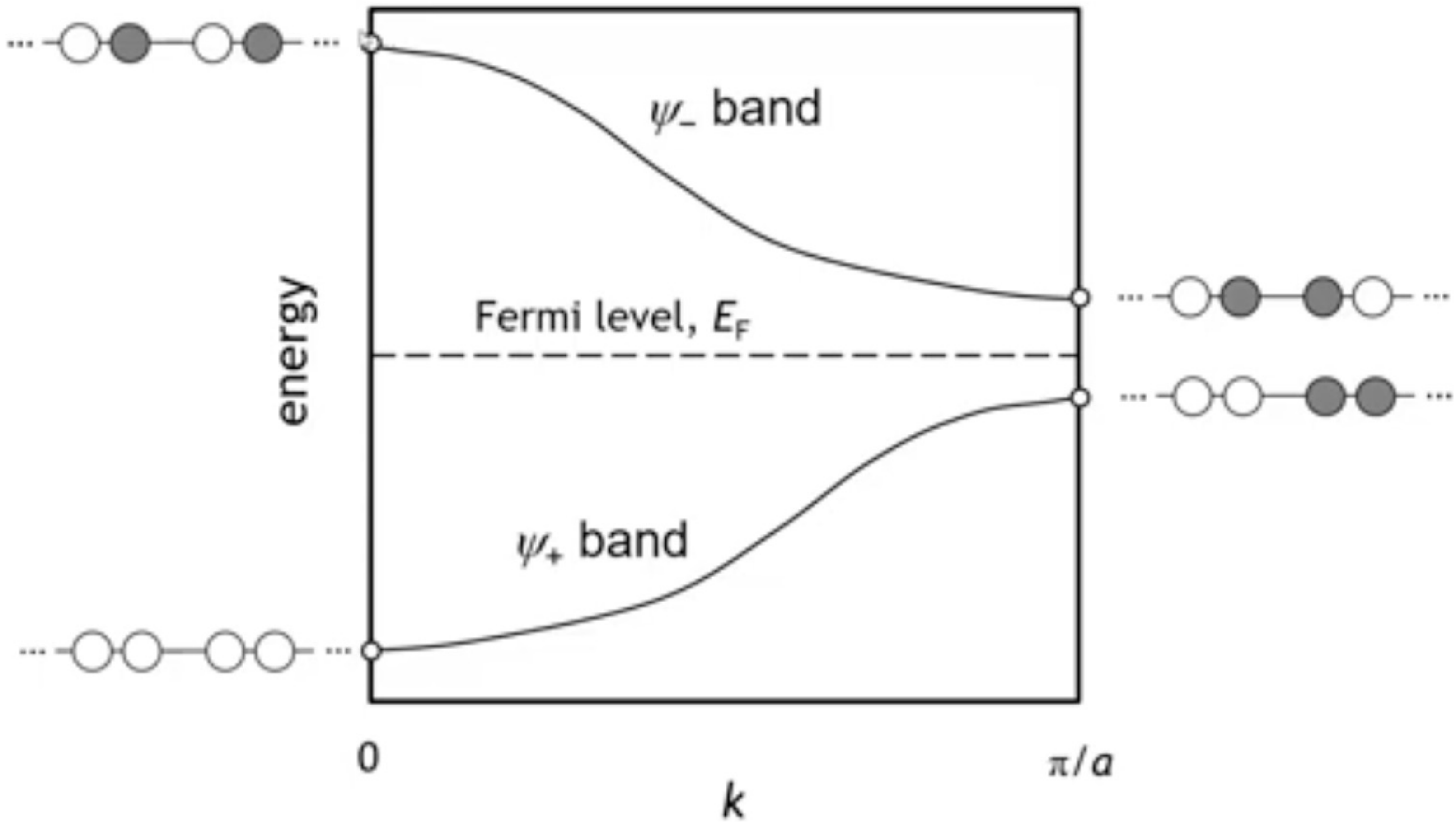

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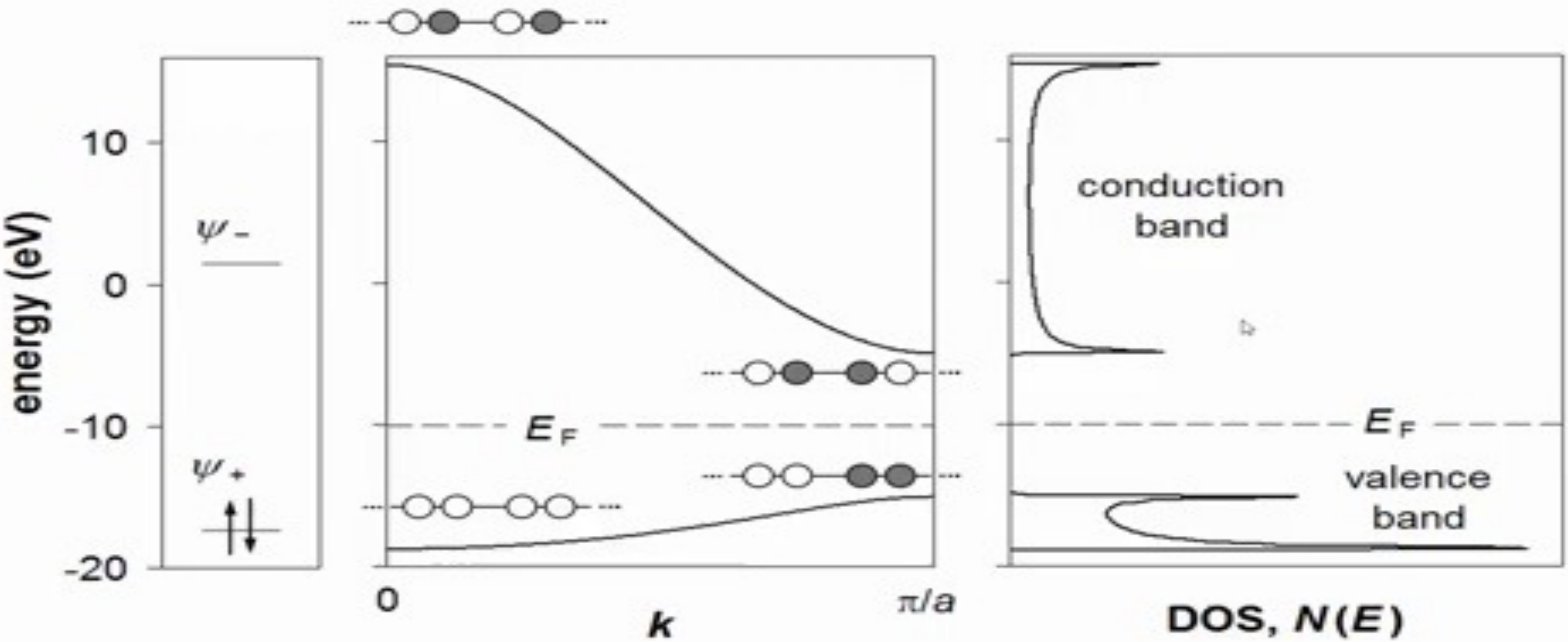

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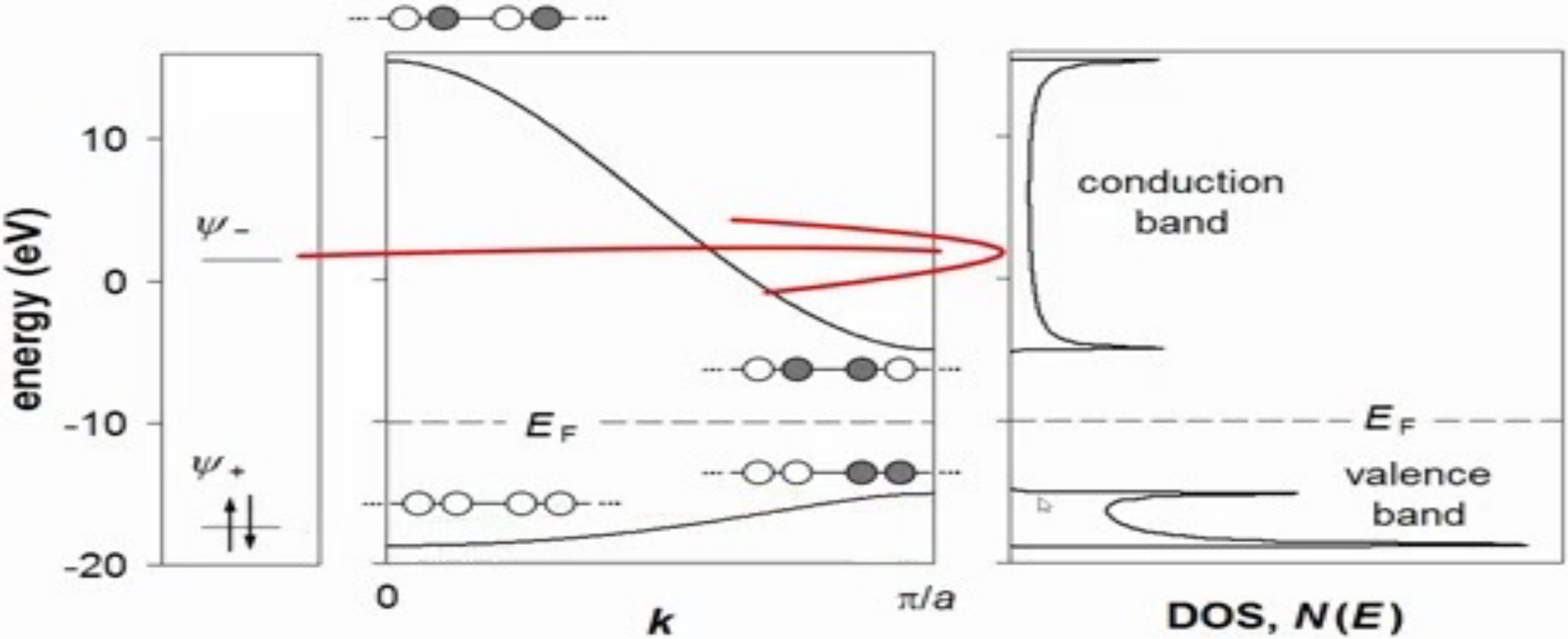
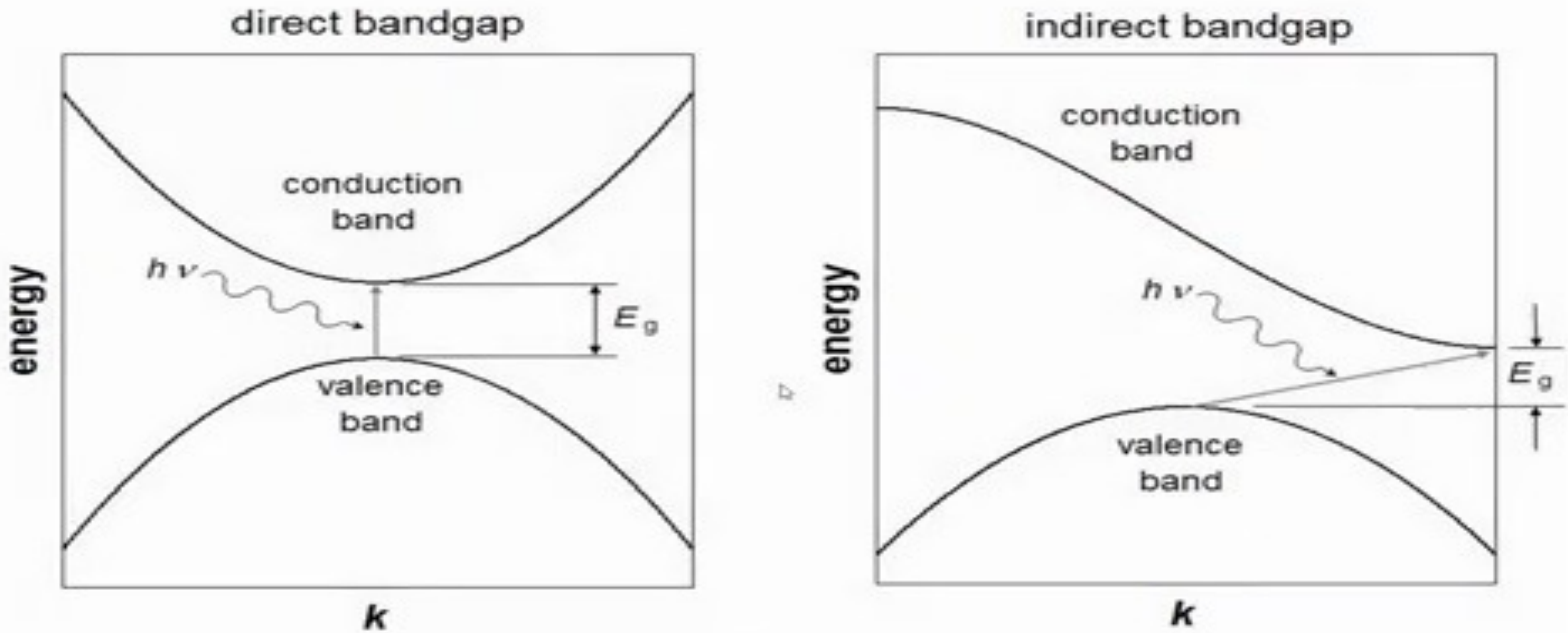


Indirect vs. Direct Gap Semiconductor



For an indirect transition electron momentum (k) must change, this requires a lattice vibration (phonon). Hence less efficient absorber.