Quantum Mechanics

Week 10

Mark Benazet Castells

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Exercise Material

Webpage

Week 10

Review

Exercises

Review of Last Week

- Any questions on last week's topics?
- Feedback on the previous session?

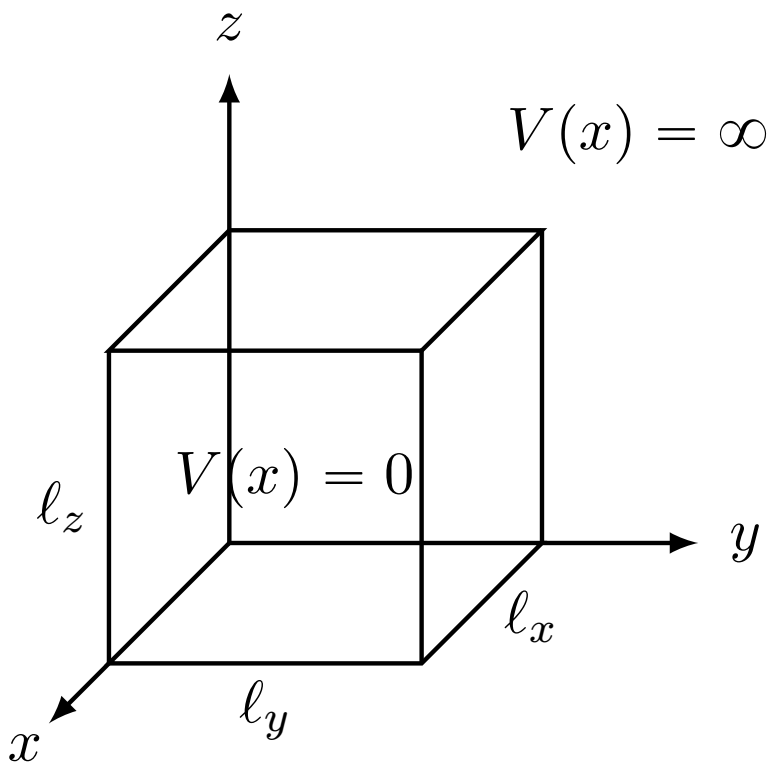
Review

Free Electron Model

- Simplifies electron-lattice interactions
- Approximates electrons as free particles in a 3D infinite potential well

Energy in a 3D Infinite Square Well

Electrons confined in a box



- Energy levels:

$$E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{\ell_x^2} + \frac{n_y^2}{\ell_y^2} + \frac{n_z^2}{\ell_z^2}\right) \tag{1}$$

- Wavefunctions:

$$\psi_{n_x,n_y,n_z} = \sqrt{\frac{8}{\ell_x\ell_y\ell_z}}\sin\left(\frac{n_x\pi}{\ell_x}x\right)\sin\left(\frac{n_y\pi}{\ell_y}y\right)\sin\left(\frac{n_z\pi}{\ell_z}z\right) \tag{2}$$

Remark: The free electron model is avoiding electron-electron interaction.

Transformation to k-space

- Wave vector $\mathbf{k}$:

$$\mathbf{k} = \frac{n_x \pi}{\ell_x}\hat{x} + \frac{n_y \pi}{\ell_y}\hat{y} + \frac{n_z \pi}{\ell_z}\hat{z} \tag{3}$$

- Components:

$$k_i = \frac{n_i \pi}{\ell_i}, \quad i \in \{x, y, z\} \tag{4}$$

- Magnitude:

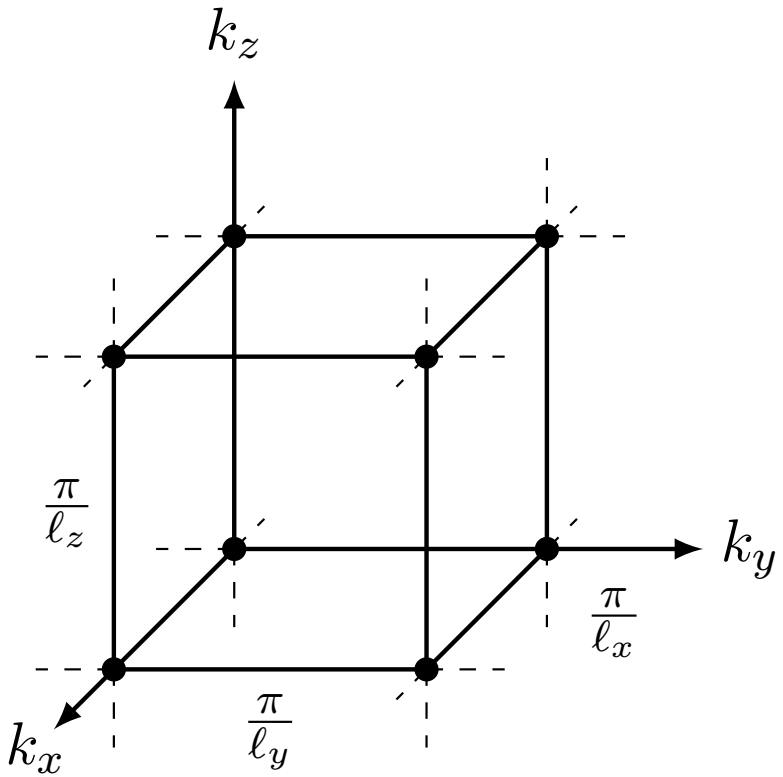
$$k^2 = k_x^2 + k_y^2 + k_z^2 \tag{5}$$

- Energy in k-space:

$$E(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} \tag{6}$$

k-space Lattice

Each node represents a quantized state



Volume of States in k-space

- Quantum states in k-space are distinct points
- Volume per state, V_k:

$$V_k = \frac{\pi^3}{V} \tag{7}$$

- $V = \ell_x \ell_y \ell_z$ is the volume of the box

Fermi Sphere

- Visualizes occupied states at absolute zero temperature
- Volume of the Fermi sphere:

$$V_{\text{Fermi sphere}} = \frac{1}{8} \cdot \frac{4}{3} \pi k_F^3 \tag{8}$$

- Relevant portion: Positive octant ($k_{x,y,z} > 0$) as the symmetric on each axis solutions are linearly dependent.

Linear Dependency of solutions

- Quantum numbers n_x, n_y, n_z map to k_x, k_y, k_z
- Only positive components k_x, k_y, k_z are relevant:

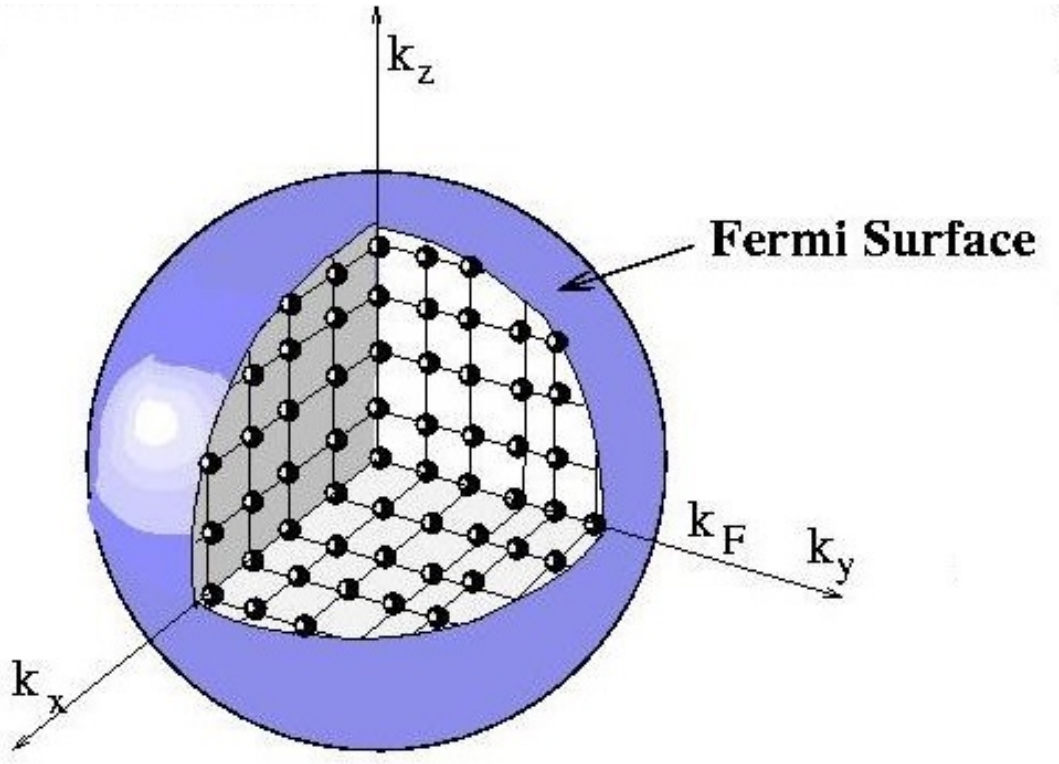
$$k_n = \frac{n\pi}{L}, \quad n > 0 \tag{9}$$

as the wave function $\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)$ is characterized by quantum number $n > 0$. Negative values of n lead to

$$\sin(-n\pi x/L) = -\sin(n\pi x/L),$$

indicating no new **independent** solutions.

- Ensures unique quantum state accounting in the positive octant


k_z
Fermi Surface
k_F
k_y
k_x

Fermi Energy

- The Fermi Energy is the highest occupied energy level.
- Electrons fill states up to k_F
- Fermi Level: Highest occupied energy state at absolute zero
- Each pair of electrons require a volume $\frac{\pi^3}{V}$

Determining k_F

- Total volume of occupied states in k-space:

$$\left\{\begin{array}{c}\text{Total Volume}\\ \text{of occupied}\\ \text{states in } k\text{-space}\end{array}\right\} = \left\{\begin{array}{c}\text{Total number}\\ \text{of electrons}\end{array}\right\} \cdot \frac{1}{2} \cdot \left\{\begin{array}{c}\text{Volume in}\\ k\text{-space per}\\ \text{electronic state}\end{array}\right\}$$

Calculating k_F and E_F

- Total number of atoms (N) times the free electrons per atom (q) :

$$N \cdot q$$

- Volume in k-space per state:

$$V_k = \frac{\pi^3}{V}$$

- Plugging in:

$$\frac{1}{8} \cdot \frac{4}{3} \pi k_F^3 = Nq \cdot \frac{\pi^3}{2V}$$

Remark: In practice N will be enormous (about the avogadro number magnitude)

Fermi Wavevector and Fermi Energy

- Fermi wavevector:

$$k_F = \left(\frac{3\pi^2 N q}{V}\right)^{1/3}$$

- Fermi energy (highest $\neq$ total energy):

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N q}{V}\right)^{2/3}$$

Therefore without electron-electron interaction we expect a continuous energy band which fills up until energy E_F

Potential Models

- Free Electron Model is not universally applicable
- Alternative models incorporate periodic potentials
- We include forces exerted on the electrons by the regularly spaced, positively charged, essentially stationary nuclei.

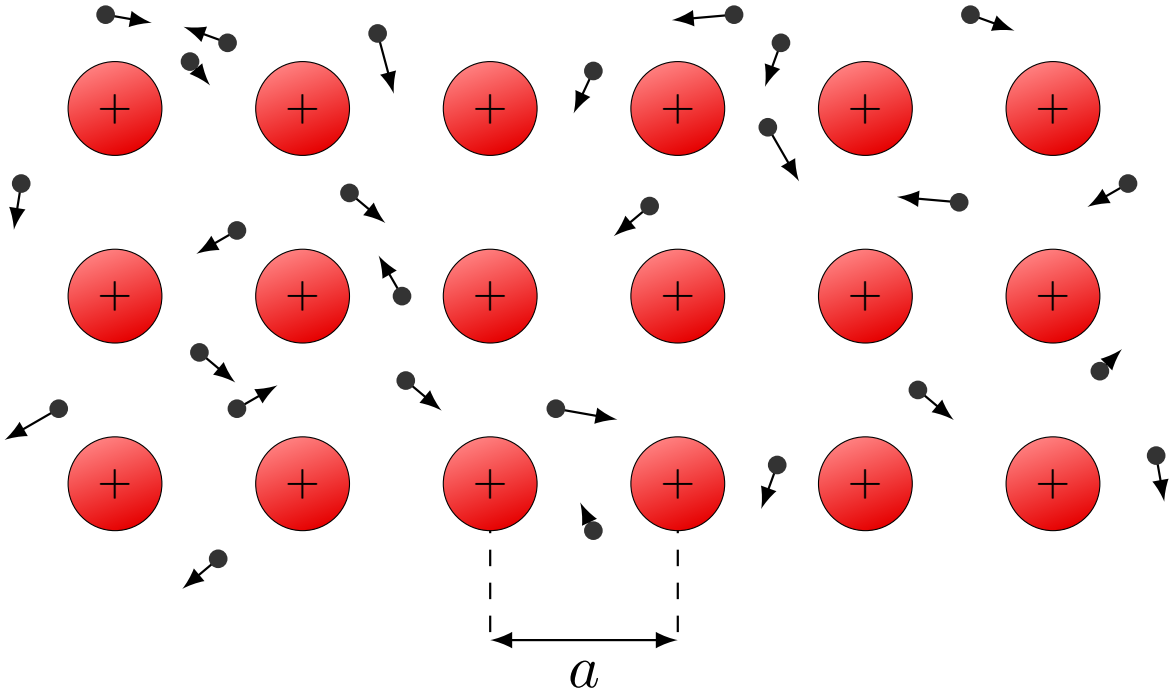
Periodic Potential

- Electronic properties of crystals determined by periodic potential
- Mathematically represented as:

$$V(x) = V(x + a) \tag{10}$$

- a denotes the lattice constant

Periodic Potential (cont.)



Bloch's Theorem

- Describes electron wavefunctions in a periodic potential $V(x) = V(x + a)$
- Bloch functions form:

$$\psi(x + a) = e^{iKa}\psi(x), \quad K \in \mathbb{R} \tag{11}$$

- Solutions to the Time-Independent Schrödinger Equation (TISE)
- Moving one lattice spacing results in the same wavefunction, except for a phase factor e^{iKa}, where a is the lattice distance and K is a real variable wich depends on the energy.

Periodic Boundary Conditions

- Real solids have finite size
- Periodic potential $V(x)$ cannot extend indefinitely
- Introduce periodic boundary conditions (start and end from finite size):

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

- N is the number of unit cells, a is the lattice constant

Bloch's Theorem with Periodic Boundary Conditions

- Modified Bloch's theorem:

$$\psi(x) = e^{iKNa}\psi(x) \tag{12}$$

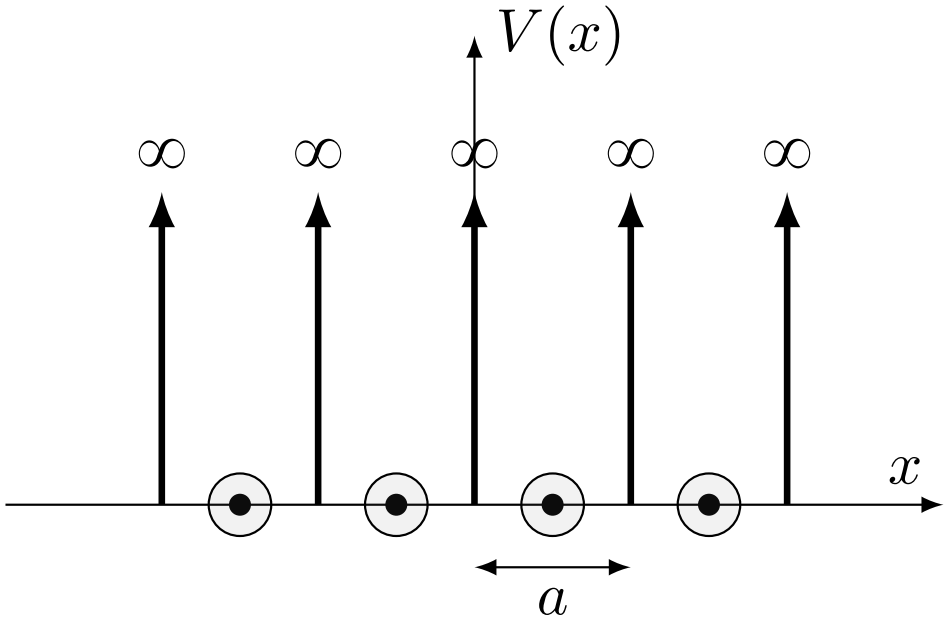
- Leads to the condition $e^{iKNa} = 1 \rightarrow KNa = 2\pi n$ and hence $K = \frac{2\pi n}{Na}$ with $n = 0, \pm 1, \pm 2, ...$

One-Dimensional Dirac-Comb Model

- Models periodic potential in the crystal:

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja) \tag{13}$$

- α is a strength constant


$V(x)$
∞
∞
∞
∞
∞
x
a

Time-Independent Schrödinger Equation (TISE)

- In regions where $V(x)$ is zero (for example $0 < x < a$):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{14}$$

- General solution (we know from 1D infinite square well):

$$\psi_1(x) = A\sin(kx) + B\cos(kx) \tag{15}$$

- Wave number k:

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{16}$$

Boundary Conditions and Discontinuity

- For a cell to the left of the origin $(-a < x < 0)$:

$$\psi_2(x) = e^{-iKa}\left[A\sin(k(x+a)) + B\cos(k(x+a))\right] \tag{17}$$

- #1 Continuity at the crystal boundary $\psi_1(0) = \psi_2(0)$:

$$B = e^{-iKa}\left[A\sin(ka) + B\cos(ka)\right] \tag{18}$$

- #2 Derivative discontinuity due to delta function:

$$kA - e^{-iKa}kA\cos(ka) - B\sin(ka) = \frac{2m\alpha}{\hbar^2}B \tag{19}$$

- Solving for $A\sin(ka)$:

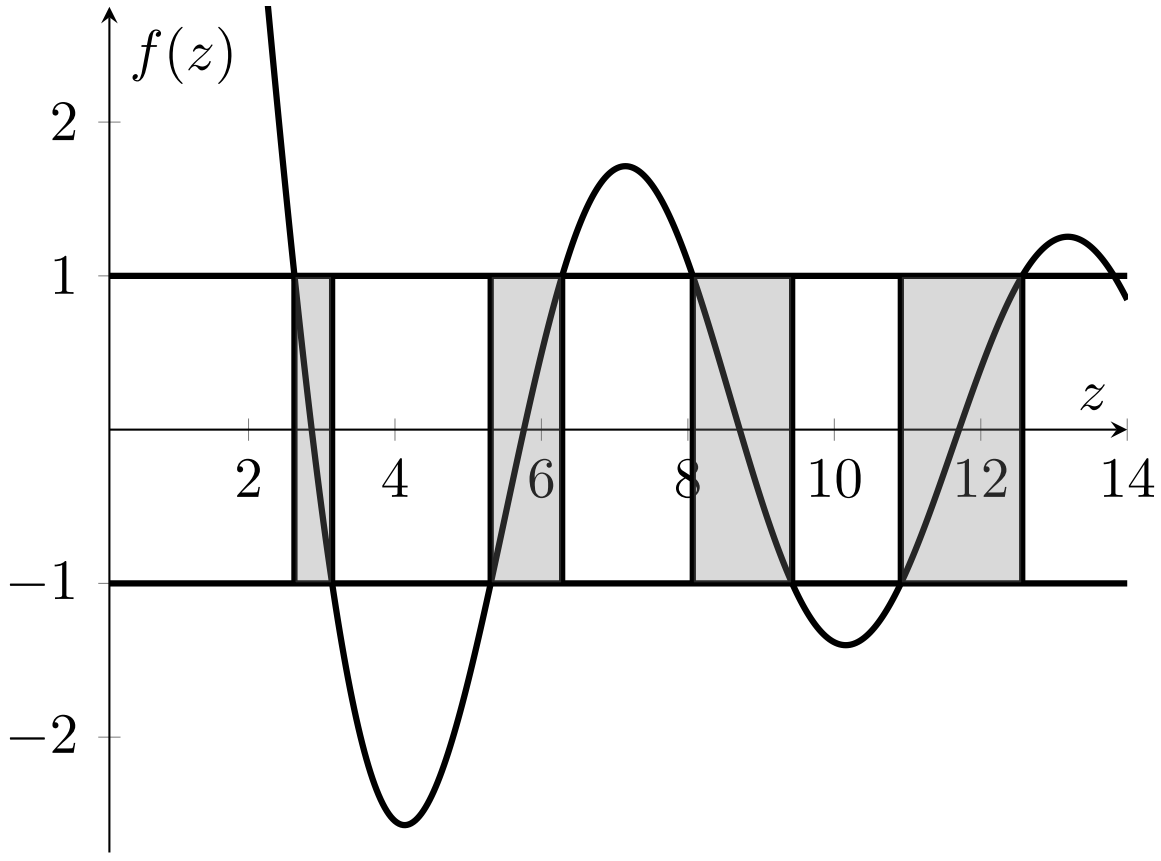
$$A\sin(ka) = \left[e^{iKa} - \cos(ka)\right]B \tag{20}$$

Crystalline Energy Bands Condition

- Relates K to k:

$$\underbrace{\cos(Ka)}_{\text{LHS } \in[-1,1]} = \underbrace{\cos(ka) + \frac{m\alpha}{\hbar k} \cdot \sin(ka)}_{\text{RHS exceeds the range } [-1,1]} \tag{21}$$

- Illustrates conditions for allowed energy states (bands) and forbidden energy states (gaps)


$f(z)$
2
1
-1
-2
z
2
4
6
8
10
12
14

Energy Bands and Band Gaps

- In solids, solutions to the TISE reflect the periodic nature of the potential.
- Not all energy levels are permissible; solutions result in specific allowed and forbidden energy ranges (as $k \propto E$)
- Instances where the RHS of the solution exceeds the LHS lead to distinct energy bands (allowed energy ranges) and band gaps (forbidden energy ranges).
- Therefore only certain ka are allowed in order to solve the T.I.S.E.

Types of Materials

Conductors:

- Valence band overlaps with conduction band.
- Electrons flow freely, minimal band gaps, excellent conductivity.

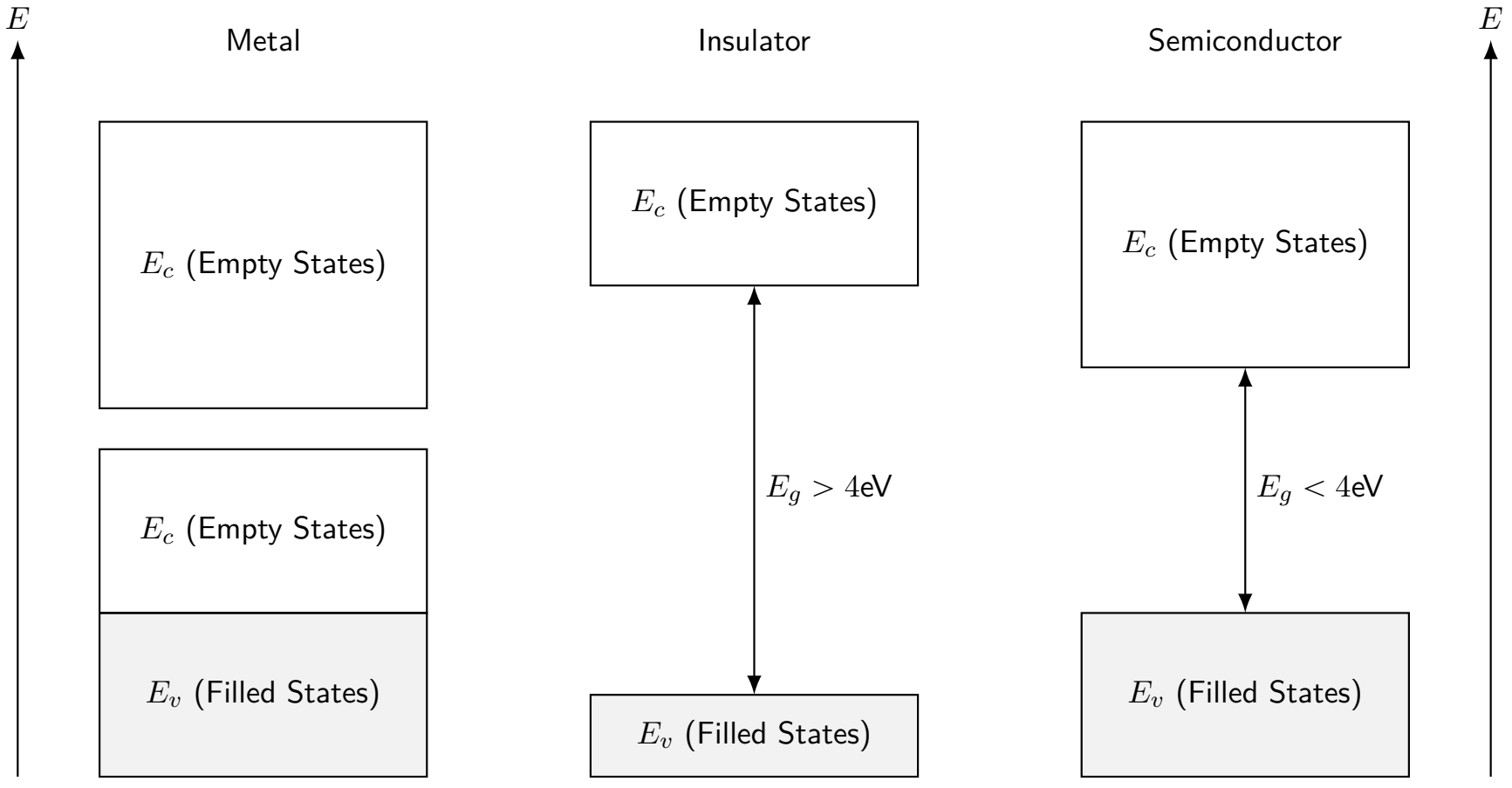
Semiconductors:

- Small but finite band gap.
- At absolute zero, the valence band is full, and the conduction band is empty.
- Room temperature thermal energy ($k_B T$) can excite electrons to the conduction band.

Insulators:

- Large band gap.
- Require substantial energy to transition electrons from the valence to the conduction band.
- Poor conductivity under normal conditions.

Type of materials



Exercises

Exercise 1

Really important, must do!

Exercise 2

Really important, must do!

Exercise 5

Nice exercise if you are interested in solid state physics.