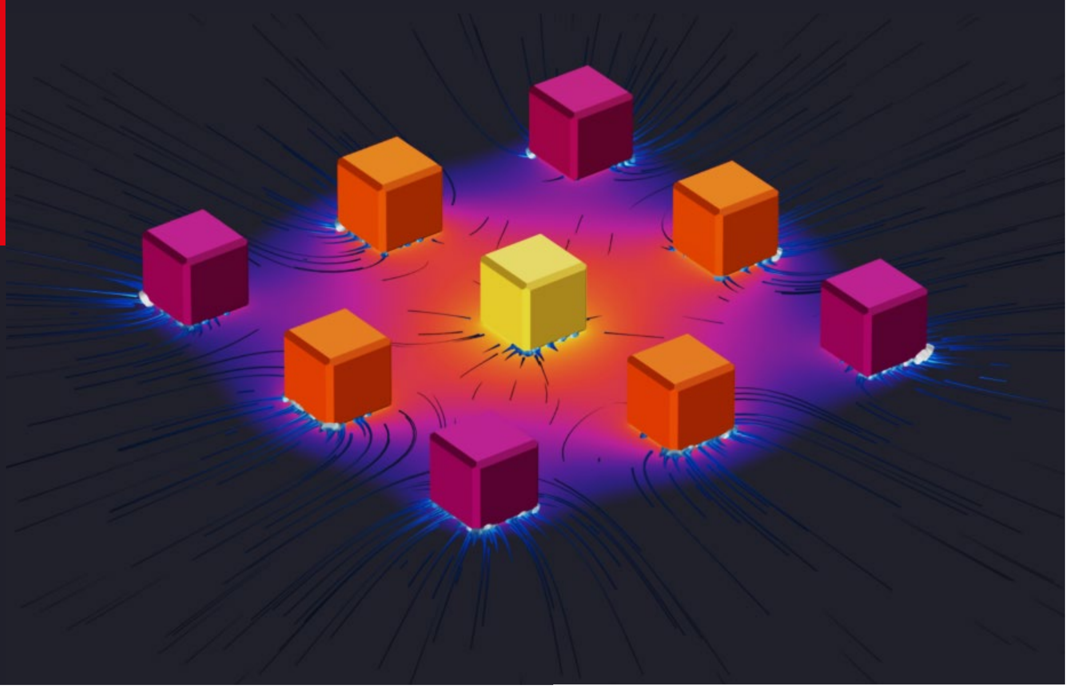
Nanoscale Heat Transfer (and Energy Conversion)

ME469

Instructor: Giulia Tagliabue



École
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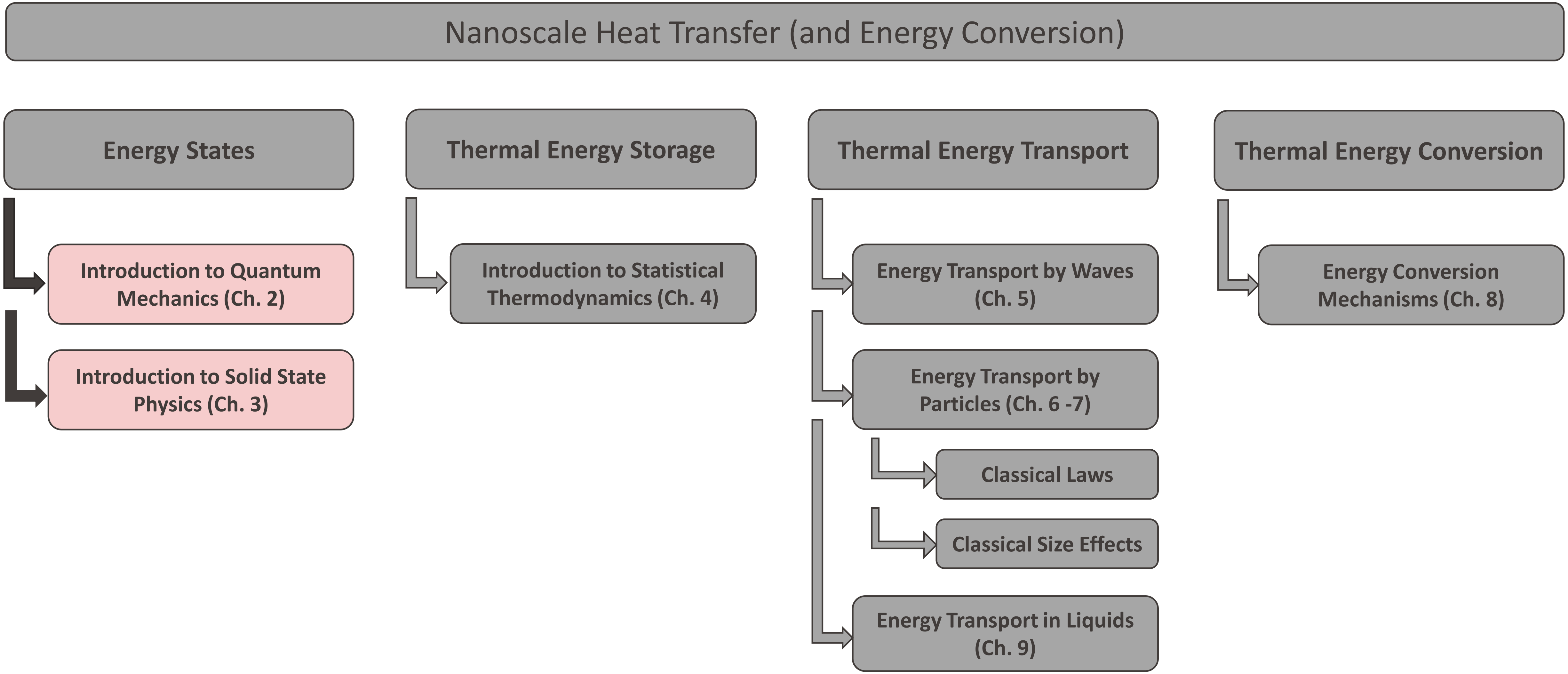
Spring Semester 2020

Last Week



Nanoscale Heat Transfer (and Energy Conversion)

Energy States
- Introduction to Quantum Mechanics (Ch. 2)
- Introduction to Solid State Physics (Ch. 3)

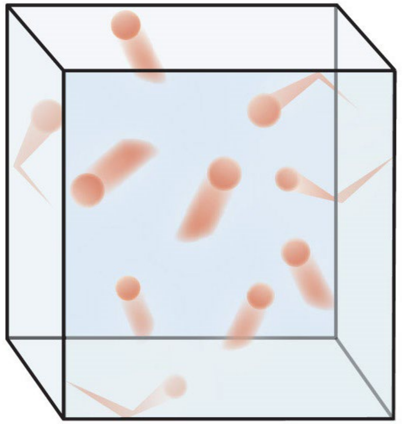
Thermal Energy Storage
- Introduction to Statistical Thermodynamics (Ch. 4)

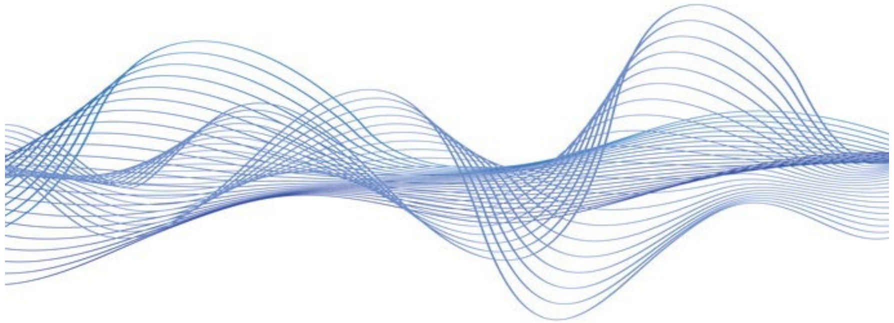
Thermal Energy Transport
- Energy Transport by Waves (Ch. 5)
- Energy Transport by Particles (Ch. 6 -7)
  - Classical Laws
  - Classical Size Effects
- Energy Transport in Liquids (Ch. 9)

Thermal Energy Conversion
- Energy Conversion Mechanisms (Ch. 8)

Wave-particle Duality

The wave nature of material particles gives rise to quantum mechanical effects!





Particle View | **Wave View**

Energy ↔ **Frequency, Amplitude**

Momentum ↔ **Wavevector**

$$p = \hbar k$$

Describing the Material Waves – The Schrodinger Equation*

To understand the dynamics of the material waves (and hence of the associated particles) we use the Schrodinger equation:

$$i\hbar\frac{\partial\Psi_t}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + U\right]\Psi_t$$

$U = potential\ energy\ landscape$

$\Psi_t(\vec{r},t) = wavefunction$

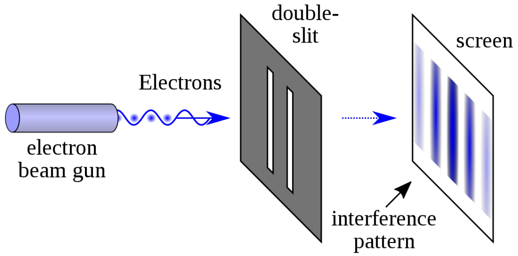
$$\int_{-\infty}^{+\infty}\Psi_t{\Psi_t}^{*}dx = 1$$

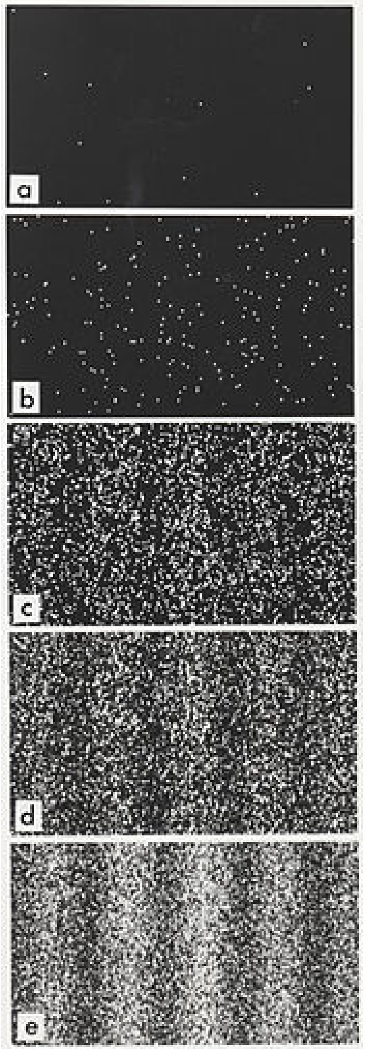
$\Psi_t{\Psi_t}^{*} = probability\ density\ function$

Steady-state Schrodinger equation (eigenvalue equation)

$$\left[-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + \boldsymbol{U}\Psi(\vec{r})\right] = E\Psi(\vec{r})$$

Together with the problem symmetry determines the energy levels and the wavefunctions



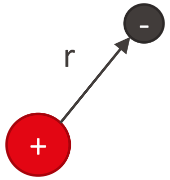


*Normally we would model the physics and derive the equations. Here we proceed in the opposite way.
We start from the equation and we show that the physics that follows corresponds to the observed physical phenomena

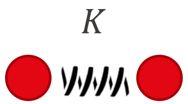
Summary of Solutions of Schrodinger Equation

	Potential	Wavefunction	Energy Levels	Quantum Numbers	Degeneracy
Free Particle	$\boldsymbol{U = 0}$	$\Psi_t = Ae^{-i(\omega t + kx)} + Be^{-i(\omega t - kx)}$ $k = \surd(2mE/\hbar \text{\textasciicircum} 2\ )$	$E = \frac{\hbar^2}{2m} k^2$	-	-
1D Infinite Potential Well	$\boldsymbol{U = 0}$ **for** $\boldsymbol{0 < x < L}$ $\boldsymbol{U = \infty}$ **for x** $<$ **0 and x** $\boldsymbol{> L}$	$\Psi_{n,t}(x,t) = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi x}{L}\right) e^{-i\omega t}$	$E_n = \frac{1}{2m}\left(\frac{\hbar n\pi}{L}\right)^2$	n	none
2D Infinite Potential Well		$\Psi_{n_x,n_y,t}(x,y,t) = \frac{2}{D} sin\left(\frac{n_x\pi}{L_x}x\right) sin\left(\frac{n_y\pi}{L_y}y\right) e^{-i\omega t}$	$E_{n_x,n_y} = \frac{(\hbar\pi)^2}{2m}\left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2\right]$	n_x , n_y	Depends on $n_{i,j}$
Harmonic Oscillator (1D)	$\boldsymbol{U = \frac{Kx^2}{2}}$	$\Psi_{n,t}(x,t) = \left[\sqrt{\frac{m\omega}{\pi\hbar}} \frac{1}{2^n n!}\right]^{1/2} H_n\left(\left[\frac{m\omega x^2}{\hbar}\right]^{1/2}\right) e^{-\frac{m\omega x^2}{2\hbar}} e^{-i\omega t}$	$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$	n	none
Rigid Rotor		$Y_l^m(\theta,\varphi) = \varepsilon i^l \left[\frac{(2l+1)(l-\|m\|)!}{4\pi(l+\|m\|)!}\right]^{1/2} P_l^{\|m\|} cos\theta e^{im\varphi}$	$E_l = \frac{\hbar^2}{2I} l(l+1)$	l, m	$2l + 1$
Hydrogen Atom (3D)	$U = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}$	$\Psi_{n,l,m}(r,\theta,\varphi) = R_{n,l}(r) Y_l^m(\theta,\varphi)$	$E_n = -\frac{Z^2 e^4 \mu}{8\epsilon_0^2 n^2 h^2}$	n, l, m	Depends on n

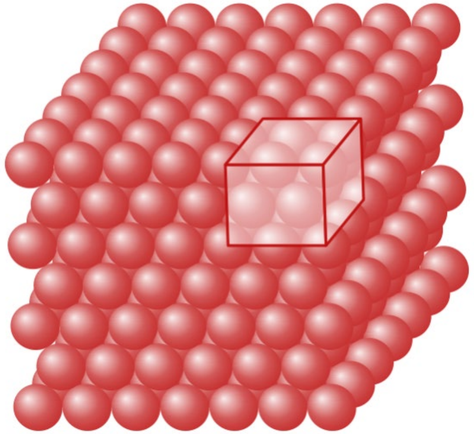
From Individual Elements to Periodic Arrangements



Individual Atom
(electron)



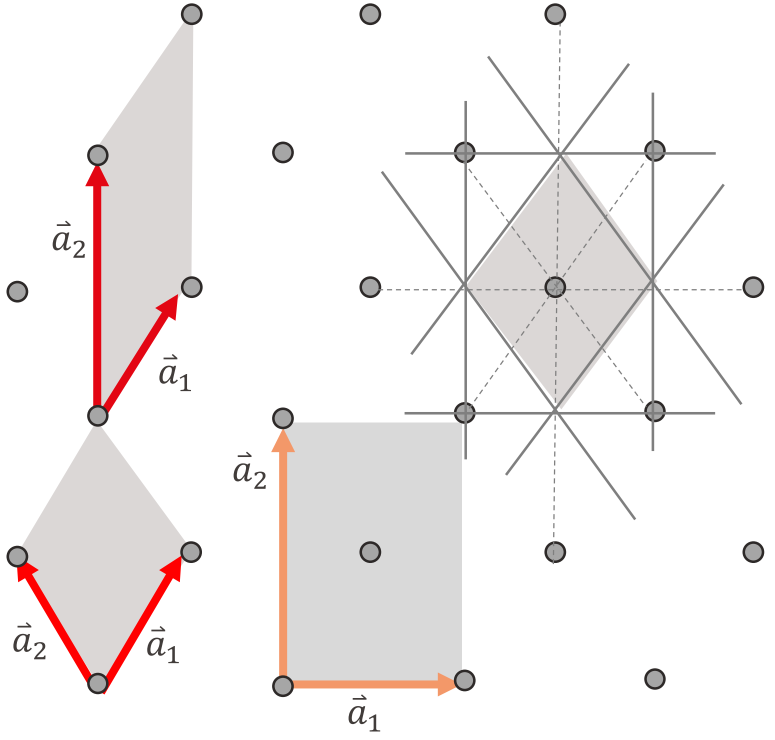
Individual Molecule
Single pair of Particles
(phonons)



3D Periodic Arrangement

Crystal Structure and the Real Lattice

Lattice



- A **Bravais lattice** is an infinite array of discrete points with an **arrangement AND orientation** that appears EXACTLY the same from whichever of the points the array is viewed
- A 3D Bravais lattice consists of all points with position vectors $\vec{R}$ of the form:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

We observe that the choice of the primitive lattice vectors (vectors connecting nearest neighbors in the lattice) entails a degree of arbitrariness.
We define a **primitive unit cell** as a parallelepiped defined by three primitive lattice vectors that contains only one lattice point.

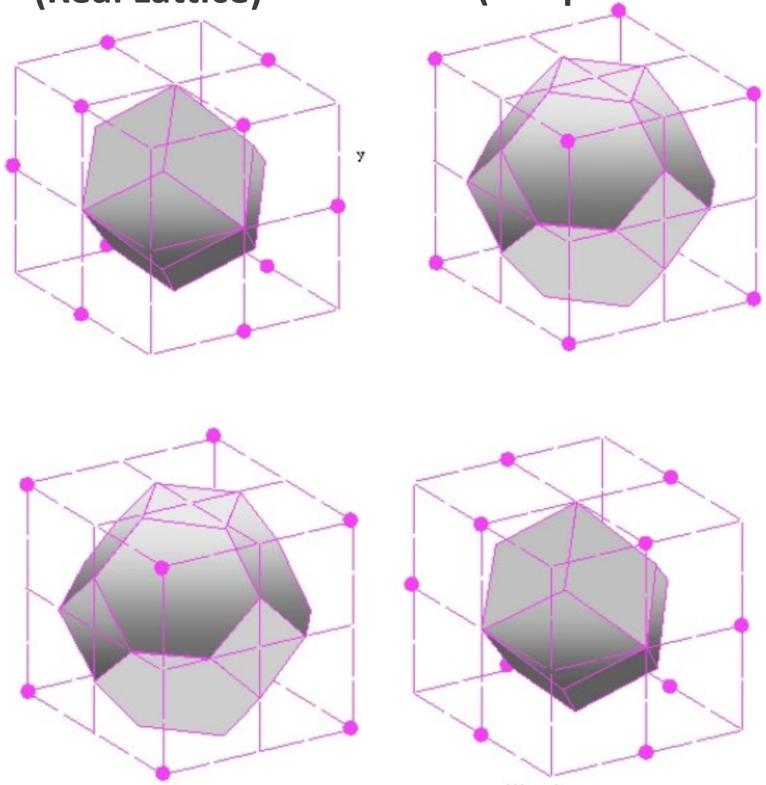
A construction that always ensures we have identified a primitive unit cell is the Wigner-Seitz construction. It consists in connecting all neighboring points surrounding an arbitrary lattice point and then to draw the bisecting plane perpendicular to each connection line.

Sometimes we describe the lattice by a conventional unit cell, that can contain more than one lattice point but has a more intuitive shape. It is important to recognize this is not a primitive unit cell.

Reciprocal Lattice and Brillouin Zone

Reciprocal lattice = the set of all wavevectors $\vec{G}$ that yield plane waves with the periodicity of a given Bravais lattice.

Like a real lattice the reciprocal lattice has a set of primitive vectors, $\vec{b}_1, \vec{b}_2, \vec{b}_3$ and it is possible to define its Wigner-Seitz cell, which is called **Brillouin zone**.



Wigner-Seitz Cell (Real Lattice)

Brillouin Zone (Reciprocal Lattice)

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$$

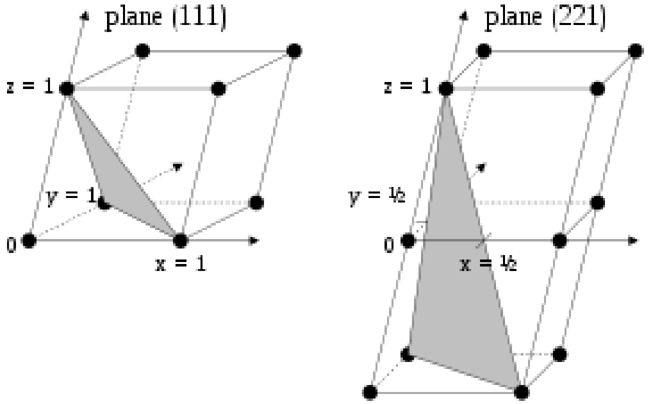
$$\vec{b}_1 = 2\pi\frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

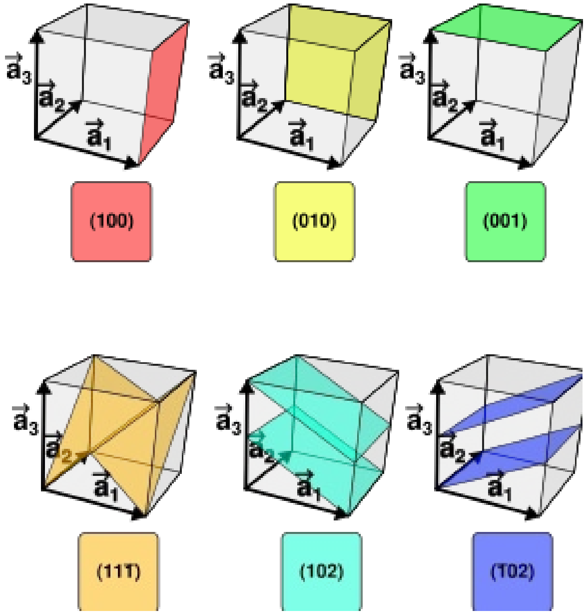
$$\vec{b}_2 = 2\pi\frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_3 = 2\pi\frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

Note: the wavevectors lying on the surface of the Brillouin zone define the Nyquist condition for the 3D crystal. This means that any wavevector larger than the Brillouin zone can be expressed with a wavevector inside the Brillouin zone.

Miller Indices





We use the following notations:

- Miller plane: $(\boldsymbol{hlk})$
- If one of the plane indices is negative we write $(-\boldsymbol{h}, \boldsymbol{l}, \boldsymbol{k}) = (\bar{\boldsymbol{h}}\boldsymbol{lk})$
- Based on the real lattice symmetries, planes along different directions can exhibit the same atom arrangement. We call these **equivalent planes** and indicate them as $\{\boldsymbol{hkl}\}$
    - E.g. in a cubic lattice the planes (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$
- Direction perpendicular to a Miller plane: $[\boldsymbol{hkl}]$
- All equivalent directions in a crystal are indicated as $\langle\boldsymbol{hkl}\rangle$

In This Lecture…

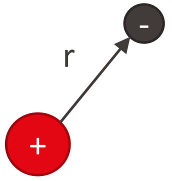
- **Electron Energy States in Periodic Lattices**
  - Band Structure and Material Properties

Summary of Solutions of Schrodinger Equation (electrons)

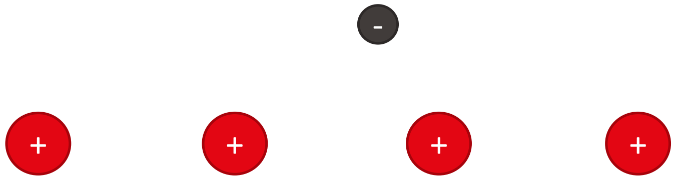
	Potential	Wavefunction	Energy Levels	Quantum Numbers	Degeneracy
Free Particle	$U = 0$	$\Psi_t = Ae^{-i(\omega t+kx)} + Be^{-i(\omega t-kx)}$ $k = \sqrt{}(2mE/\hbar\text{^}2\,)$	$E = \frac{\hbar^2}{2m}k^2$	-	-
1D Infinite Potential Well	$U = 0$ for $0 < x < L$ $U = \infty$ for $x < 0$ and $x > L$	$\Psi_{n,t}(x,t) = \sqrt{\frac{2}{L}}\,sin\left(\frac{n\pi x}{L}\right)e^{-i\omega t}$	$E_n = \frac{1}{2m}\left(\frac{\hbar n\pi}{L}\right)^2$	n	none
2D Infinite Potential Well		$\Psi_{n_x,n_y,t}(x,y,t) = \frac{2}{D}\,sin\left(\frac{n_x\pi}{L_x}x\right)sin\left(\frac{n_y\pi}{L_y}y\right)e^{-i\omega t}$	$E_{n_x,n_y} = \frac{(\hbar\pi)^2}{2m}\left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2\right]$	$n_x\,, n_y$	Depends on $n_{i,j}$
Harmonic Oscillator (1D)	$U = \frac{Kx^2}{2}$	$\Psi_{n,t}(x,t) = \left[\sqrt{\frac{m\omega}{\pi\hbar}}\frac{1}{2^n n!}\right]^{1/2} H_n\left(\left[\frac{m\omega x^2}{\hbar}\right]^{1/2}\right)e^{-\frac{m\omega x^2}{2\hbar}}e^{-i\omega t}$	$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$	n	none
Rigid Rotor		$Y_l^m(\theta,\varphi) = \varepsilon i^l\left[\frac{(2l+1)(l-\lvert m\rvert)!}{4\pi(l+\lvert m\rvert)!}\right]^{1/2} P_l^{\lvert m\rvert}cos\theta e^{im\varphi}$	$E_l = \frac{\hbar^2}{2I}l(l+1)$	l, m	$2l + 1$
Hydrogen Atom (3D)	$U = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}$	$\Psi_{n,l,m}\,(r,\theta,\varphi) = R_{n,l}(r)Y_l^m(\theta,\varphi)$	$E_n = -\frac{Z^2e^4\mu}{8\epsilon_0^2n^2h^2}$	n, l, m	Depends on n

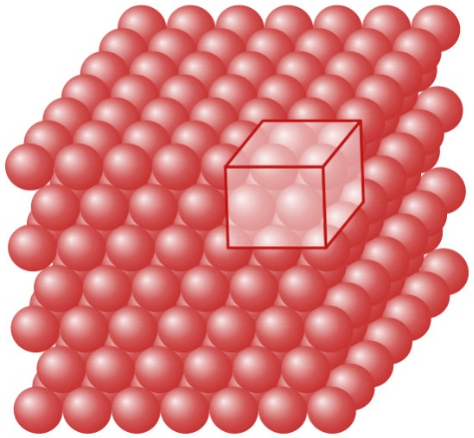
The potential defines the wavefunctions and the energy states. In a crystal we will have a periodic potential.

From Individuals to Crystals

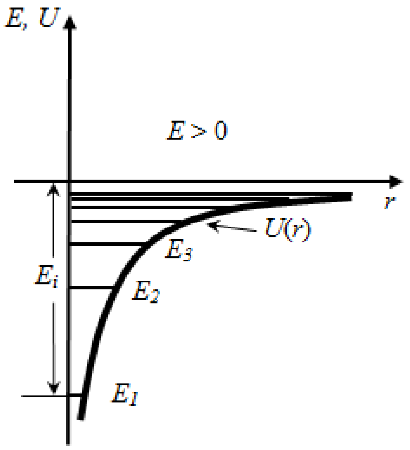


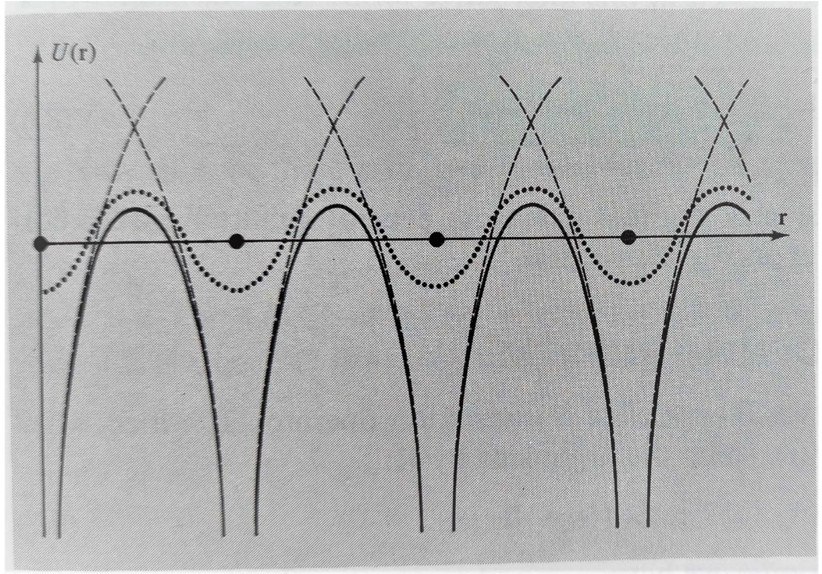
Individual Atom
(electron)





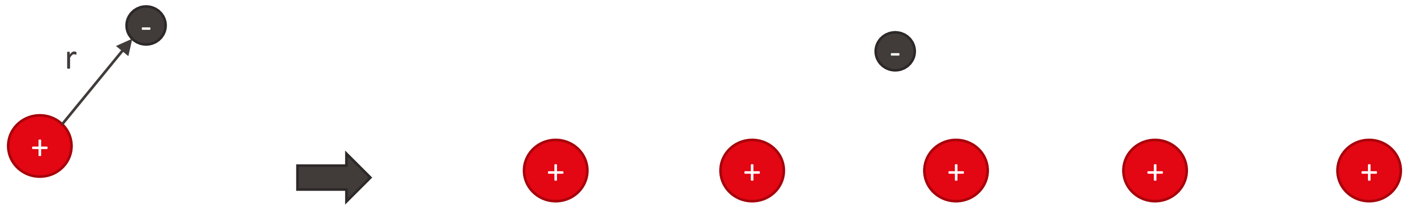
3D Periodic Arrangement



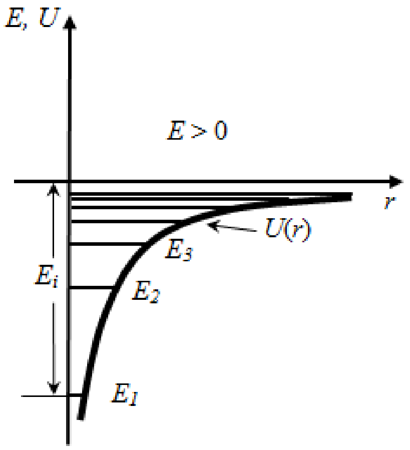


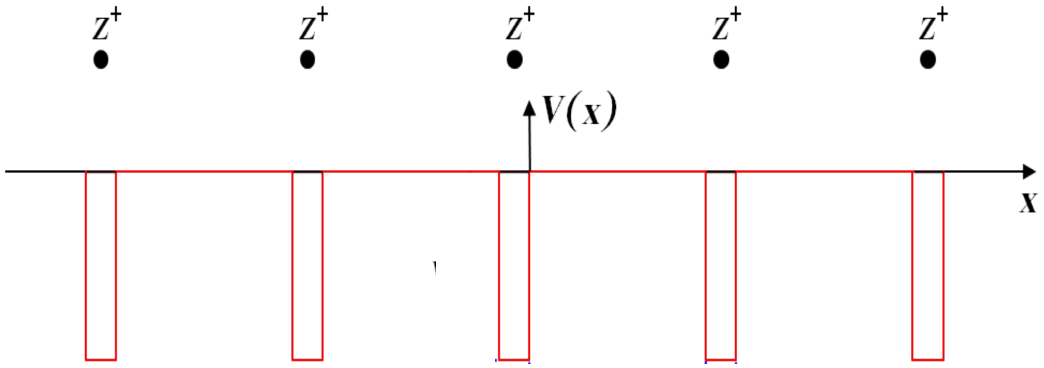
What are the electronic energy levels and wavefunctions in a periodic potential?

From Individuals to Crystals



Individual Atom
(electron)

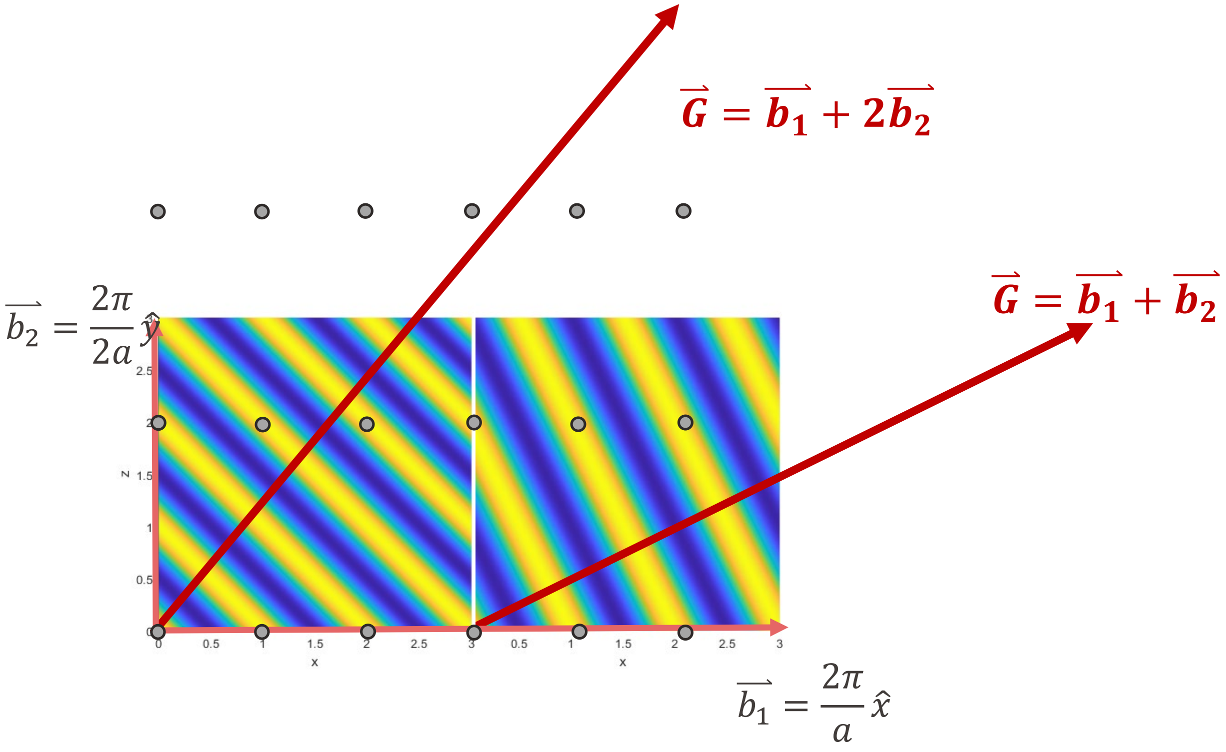




Kronig-Penney Potential

➡ **What are the electronic energy levels and wavefunctions in a periodic potential?**

From Individuals to Crystals



Reciprocal lattice vectors identify waves with periodicity equal to that of the lattice along different spatial directions.

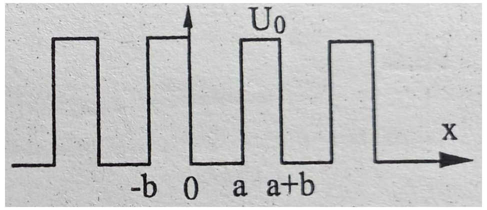
The spacing between lattice points along different spatial directions is different.

➡ **Different directions in the lattice have different periodic potentials!**

In This Lecture…

- Electron Energy States in Periodic Lattices
  - **Band Structure and Material Properties**
  - Density of States

Electron Energy States in a Periodic Potential



We consider a 1D periodic (Kronig-Penney) potential:

$$U = \begin{cases} 0 & 0 < x \leq a \\ U_0 & -b < x \leq 0 \end{cases}$$

We therefore obtain the following Schrodinger eqns:

$$\begin{cases} -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}\Psi(x) - E\Psi(x) = 0 & 0 < x \leq a \\ -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}\Psi(x) + (U_0 - E)\Psi(x) = 0 & -b < x \leq 0 \end{cases}$$

Considering the solutions inside the periodic potential we recognize that $(U_0 - E) > 0$ and therefore we have the following two solutions*:

$$\begin{cases} \Psi_1(x) = Ae^{iKx} + Be^{-iKx} & 0 < x \leq a \\ \Psi_2(x) = Ce^{Qx} + De^{-Qx} & -b < x \leq 0 \end{cases}$$

where

$$E = \frac{\hbar^2 K^2}{2m} \qquad U_0 - E = \frac{\hbar^2 Q^2}{2m}$$

To find the coefficients and solve the problem we need to apply the continuity of the wavefunction and its derivative.

We first set these two conditions at $x = 0$:

$$\begin{cases} \Psi_1(0) = \Psi_2(0) \\ \left.\dfrac{\partial \Psi_1}{\partial x}\right|_{x=0} = \left.\dfrac{\partial \Psi_2}{\partial x}\right|_{x=0} \end{cases} \Rightarrow \begin{cases} A + B = C + D \\ iK(A - B) = C - D \end{cases}$$

To find a second boundary condition we must use the periodicity of the potential function.

---

* if $(U_0 - E) > 0$ the characteristic equation of the differential equation has real solutions. When $U_0 = 0$, instead, the solutions are imaginary.

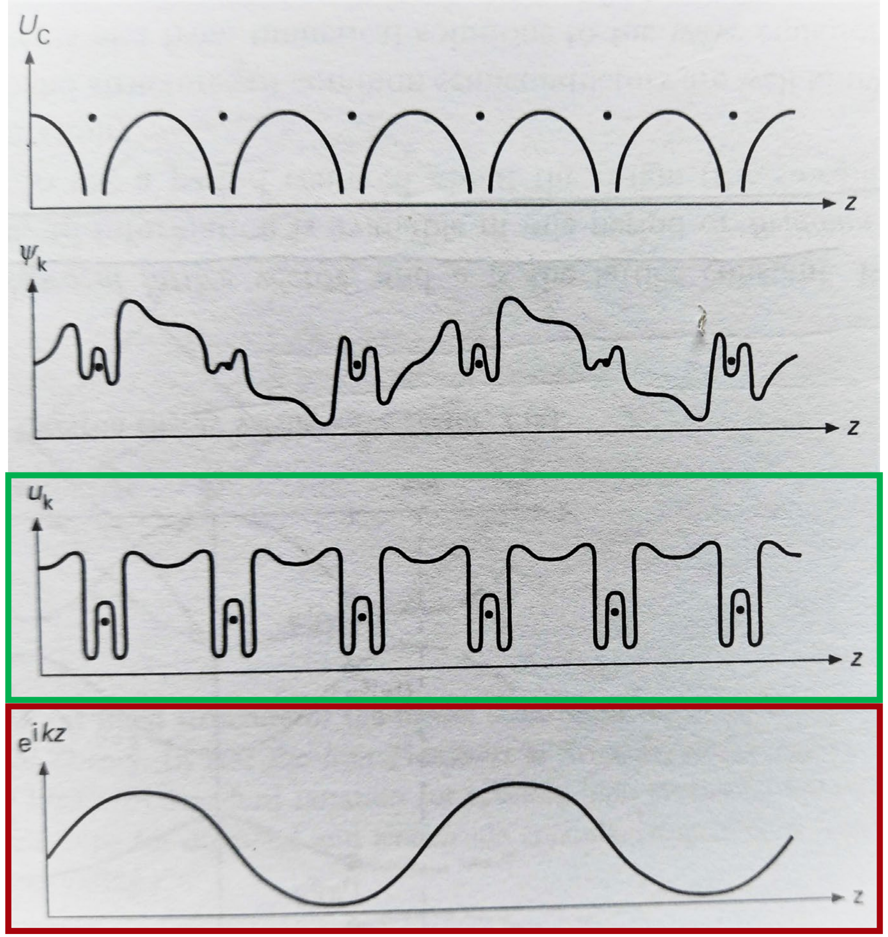
Electron Energy States in a Periodic Potential

Bloch's Theorem demonstrates that we can write a wavefunction in a periodic potential as follows:

$$\Psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}} \qquad \text{where} \qquad u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r}) \qquad \forall\vec{R}$$

Plane wave (phase factor)

Function with the periodicity of the lattice



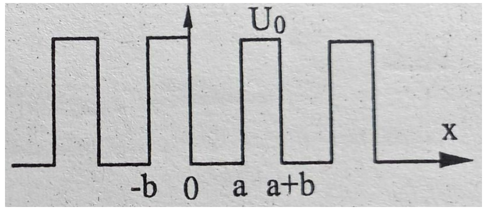
Indeed it is straightforward to show that if the wavefunction has this structure, then:

$$\Psi_{n\vec{k}}(\vec{r}+\vec{R}) = \Psi_{n\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{R}}$$

It is important to recognize that:

- $\vec{k} \neq K$
- While in the case of a free particle with wavefunction $\Psi \propto e^{i\vec{k}\cdot\vec{r}}$, $\vec{k}$ was proportional to the electron momentum, in a periodic potential this is not the case. Yet, the quantity $\hbar\vec{k}$ is known as ***crystal momentum*** and plays an important role in the dynamics of electrons in a solid.
- For every value of $\vec{k}$ there are infinite solutions $u_{n\vec{k}}(\vec{r})$, this is why we have introduced the index n to distinguish different wavefunctions with the same $\vec{k}$.

Electron Energy States in a Periodic Potential



Let's now go back to our 1D lattice and Kronig-Penney potential.

We observe that our period is equal to $(a+b)$. Therefore, using Bloch's Theorem we can write:

$$\Psi(x+(a+b)) = \Psi(x)e^{ik(a+b)}$$

To determine more equations and solve the problem, we need to apply the continuity of the wavefunction and its derivative in a second point.

We note that the region $-b < x \le 0$ is equivalent to a $< x \le a+b$. Hence we want to define these conditions at $x = a$.

Using Bloch's theorem, we can write: $$\Psi_2(a) = \Psi_2(-b+(a+b)) = \Psi_2(-b)e^{ik(a+b)}$$

It follows that at $x = a$:

$$\begin{cases} \Psi_1(a) = \Psi_2(a) \\ \left.\dfrac{\partial \Psi_1}{\partial x}\right|_{x=a} = \left.\dfrac{\partial \Psi_2}{\partial x}\right|_{x=a} \end{cases} \qquad \begin{cases} \Psi_1(a) = \Psi_2(-b)e^{ik(a+b)} \\ \left.\dfrac{\partial \Psi_1}{\partial x}\right|_{x=a} = \left.\dfrac{\partial \Psi_2}{\partial x}\right|_{x=-b} e^{ik(a+b)} \end{cases} \Rightarrow \begin{cases} Ae^{iKa} + Be^{-iKa} = \left(Ce^{-Qb} + De^{Qb}\right)e^{ik(a+b)} \\ iK\left(Ae^{iKa} - Be^{-iKa}\right) = Q\left(Ce^{-Qb} - De^{Qb}\right)e^{ik(a+b)} \end{cases}$$

We can now put all four conditions together to solve for the wavefunction coefficients.

Electron Energy States in a Periodic Potential

$$\begin{cases} A + B - C - D = 0 \\ iKA - iKB - C - D = 0 \\ e^{iKa}A + e^{-iKa}B - e^{ik(a+b)-Qb}C - e^{ik(a+b)+Qb}D = 0 \\ iKe^{iKa}A - iKe^{-iKa}B - Qe^{ik(a+b)-Qb}C + Qe^{ik(a+b)+Qb}D = 0 \end{cases} \Rightarrow \begin{bmatrix} 1 & 1 & -1 & -1 \\ iKA & -iKB & -1 & -1 \\ e^{iKa} & e^{-iKa} & -e^{ik(a+b)-Qb} & -e^{ik(a+b)+Qb} \\ iKe^{iKa} & -iKe^{-iKa} & -Qe^{ik(a+b)-Qb} & Qe^{ik(a+b)+Qb} \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = 0$$

The system can be solved only if $det\overline{\overline{M}} = 0$ where $\overline{\overline{M}}$ is the matrix of the coefficients of the system. The resulting equation is:

$$\frac{Q^2 - K^2}{2Ka} \sinh(Qb) \sin(Ka) + \cosh(Qb) \cos(Ka) = \cos(k(a+b)) \qquad \text{where} \qquad K = \sqrt{\frac{2mE}{\hbar^2}} \qquad Q = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

By solving this equation it is possible to obtain the dispersion relation $E(k)$.

It is interesting to observe that the right hand side of the above equation is limited to $[-1,1]$. Instead the left-hand side of the equation can assume values on a much larger range. Therefore, there might be values of E for which it is NOT possible to satisfy the above constraint and a solution does not exist.

We conclude that **periodicity restricts the allowed energy levels** similarly to the energy quantization effect caused by the potential of an isolated atom/molecule**.**

Electron Energy States in a Periodic Potential

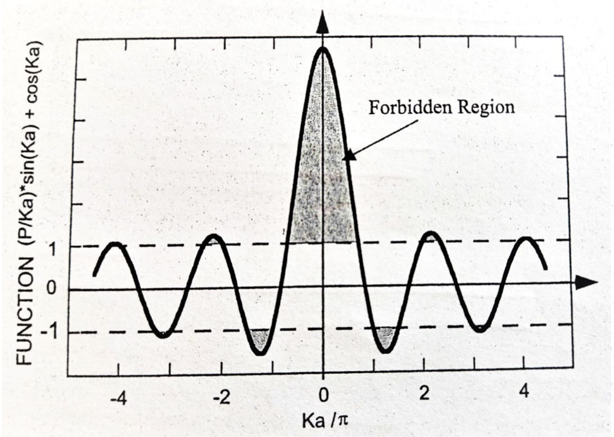
In order to gain deeper insight into this effect, we simplify the above equation by assuming that $b \rightarrow 0$ and $U_0 \rightarrow \infty$ while $\frac{Q^2ba}{2} = constant$.

We thus get:

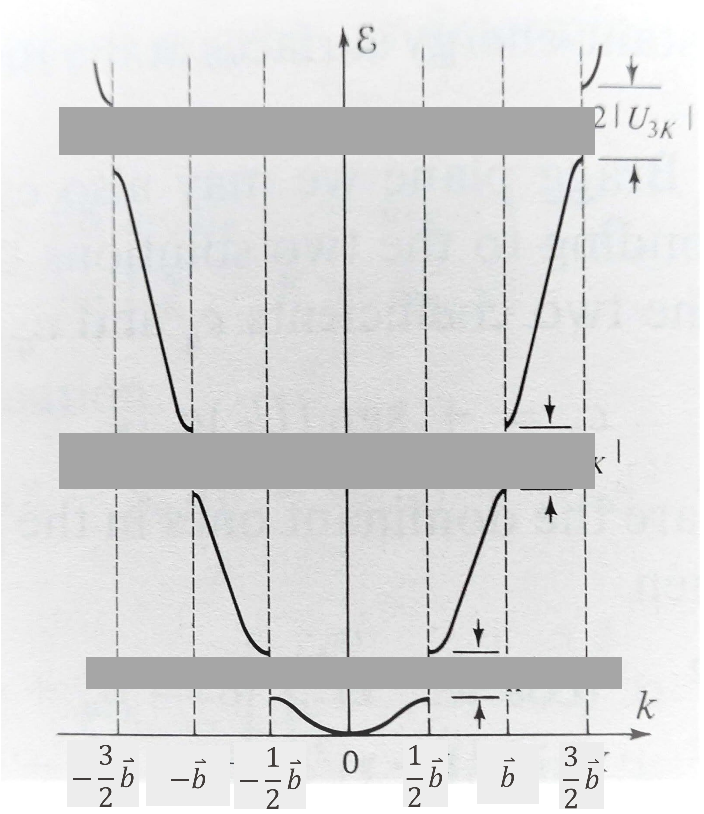
$$\frac{Q^2b}{2K} sinKa + cosKa = coska$$

There exist a value of K, and hence E, that satisfies this equation if

$$y = \frac{Q^2b}{2K} sinKa + cosKa \in [-1,1]$$

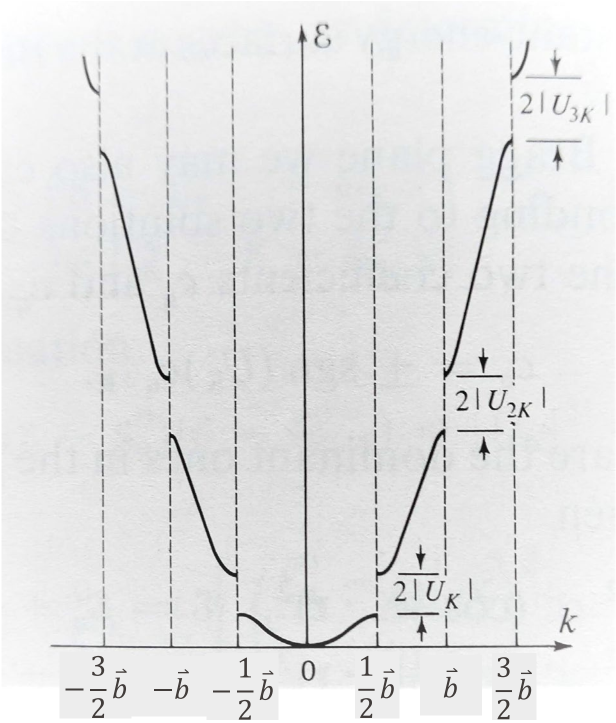


Thus we observe that we obtain bands of allowed K values and bands of forbidden K values. Therefore, the periodicity creates energy bands and energy band-gaps.
Also, for every value of k we have many K (i.e. energy) values)

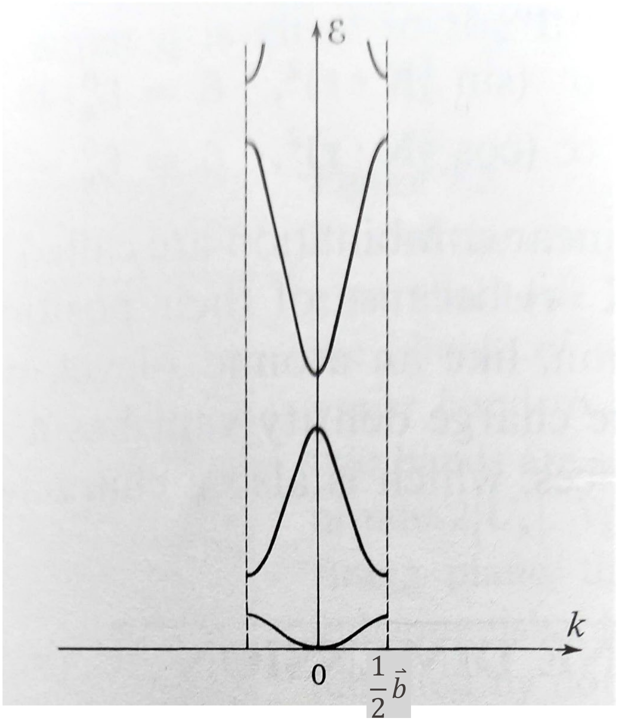


It can be demonstrated that **the band-gaps occur at the edges of the Brillouin zone**, i.e. for values of k equal to half the reciprocal lattice vector $\vec{b} = 2\pi/a$. This is due to interference effects of electrons in the periodic structure.

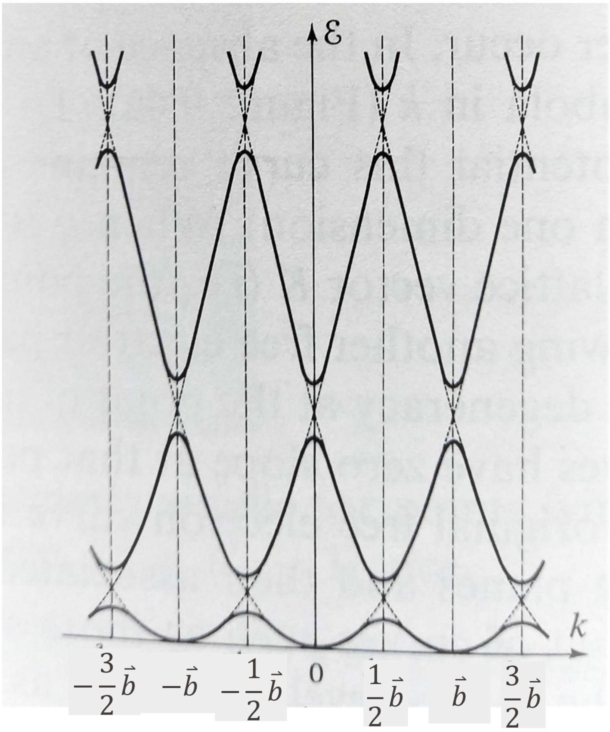
Electron Energy States in a Periodic Potential



Extended Zone Scheme representation



Reduced Zone Scheme representation



Repeated Zone Scheme representation

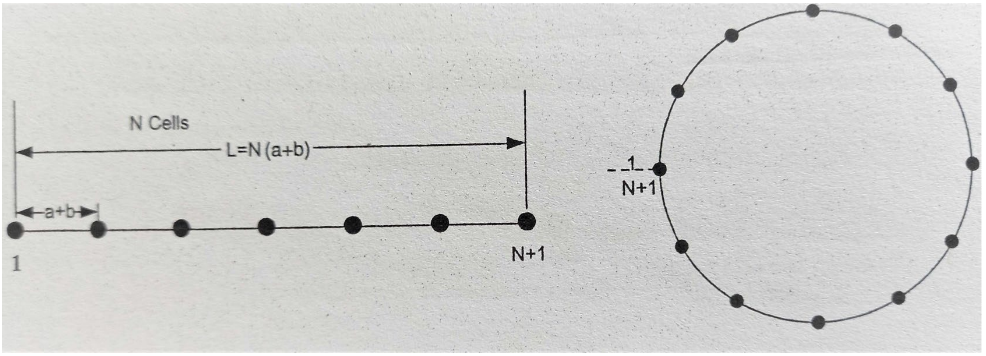
Observe that in a periodic 1D structure we have a parabolic-like distribution of energy states that is interrupted close to the edges of the Brillouin zone. In addition we observe that, once we have constructed the reduced-scheme representation, for a given value of $\vec{k}$ there is a discrete and infinite set of values of E_{nk} similar to the case of an infinite potential well. However, as $\vec{k}$ increase, the values of E_{nk} change almost continuously until the Brillouin zone, hence forming a band n of energies.

Electron Energy States in a Periodic Potential

From the previous representation we might have the impression that $\vec{k}$ is a continuous value.

However, we need to remember that $\vec{k}$ is the wavevector of a plane-wave that extends over the entire crystal. To understand what values of $\vec{k}$ are allowed, we thus have to consider the crystal in its entirety.

To mimic a truly infinite periodic lattice, it is common to apply the Born-Von Karmann boundary condition that loops the crystal onto itself. This is easy to define and represent for a 1D lattice.



We thus impose the following constraint on the wavefunction:

$$\Psi(x + N(a+b)) = \Psi(x)$$

Using Bloch's theorem:

$$\Psi\big(x + N(a+b)\big) = \Psi(x)e^{ikN(a+b)} = \Psi(x)$$

Therefore it follows: $kN(a+b) = 2\pi n$ ➡ $k = \dfrac{2\pi n}{L}$ Where L is the size of the crystal and n is an integer value.

Thus the values of k are discrete but their separation is relatively small due to the large size of a typical crystal. As a result **the energy states are always discrete.**

Furthermore we observe that for a crystal with periodicity $(a+b)$ with *N* lattice points*:

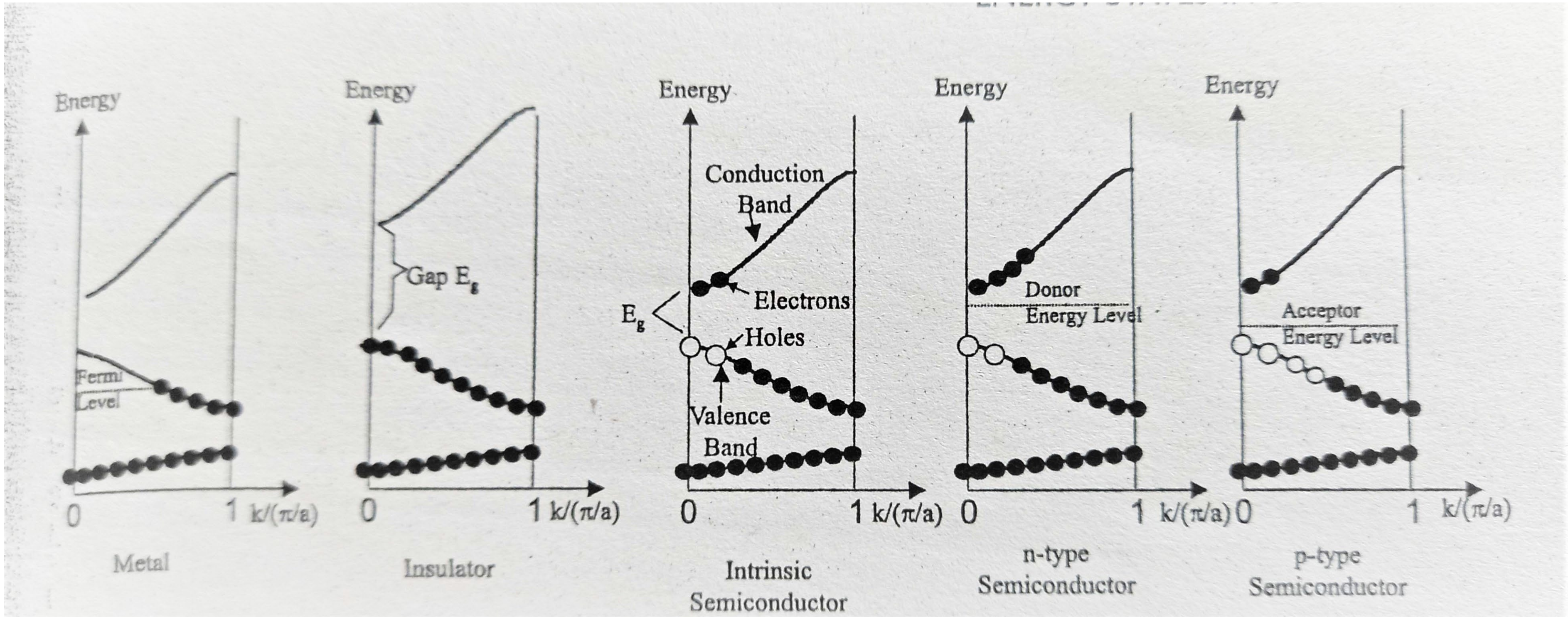
$$\left[\begin{array}{l} \vec{b} = 2\pi/(a+b) \\ \\ k = \dfrac{2\pi n}{N(a+b)} = \dfrac{\vec{b}}{N}n \end{array}\right.$$

And therefore when $\boldsymbol{n = N}$ ➡ $\boldsymbol{k = \vec{b}}$

Within the first Brillouin zone,
in each energy band
there are *N* available energy states

*remember that the lattice can have a base and also every atom can have multiple electrons. Therefore the number of lattice points is different to the electron values

Band Structure and Material Properties

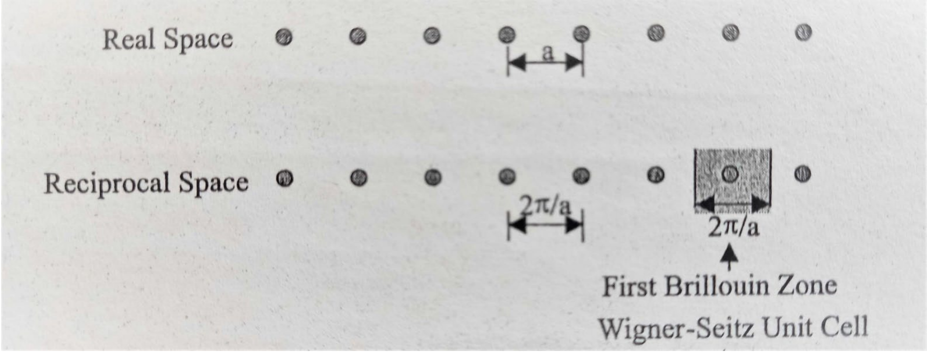


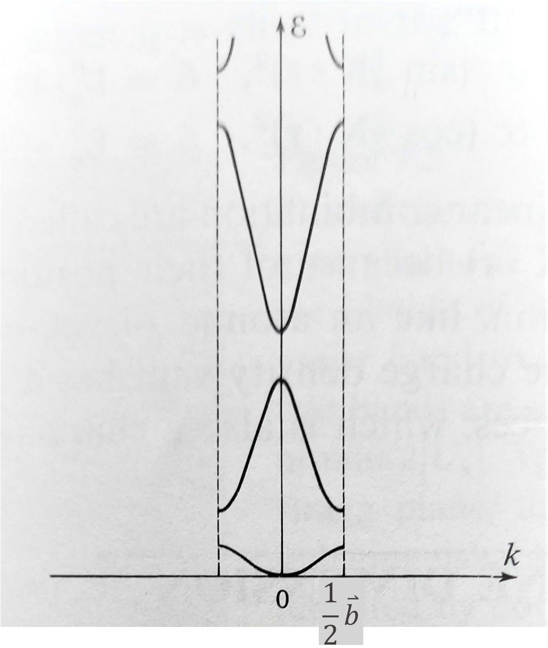
- Each available state can have 2 electrons, one with spin up and one with spin down. Thus, in each band, for a lattice with *N* points, there are *N* available energy states and *2N* electrons. Electrons fills the energy bands starting from the lowest energy state. Depending on the number of electrons per atom we can have different degrees of filling of the energy bands. In metals, the highest occupied energy band is only partially filled. Thus electrons can be easily excited by thermal effects in unoccupied states within the same band. In semiconductor and insulators, the highest occupied energy band is completely filled. Temperature and dopants can create some vacancies in the filled bands.
- The highest filled energy state is called ***Fermi Level.***
- Collisions between different particles must conserve the crystal momentum: $\sum_i \hbar \vec{k}_i = \sum_f \hbar(\vec{k}_f + \vec{G})$

$i = initial\ state$
$f = final\ state$

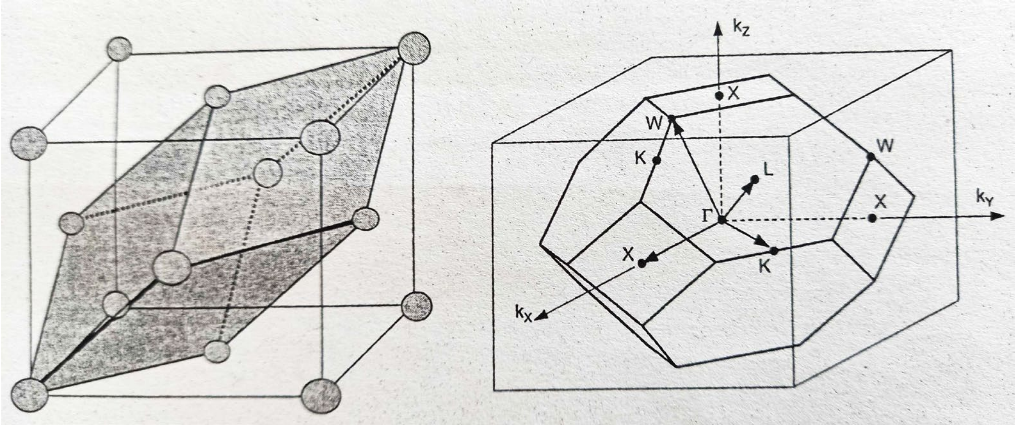
Band Structure and Material Properties

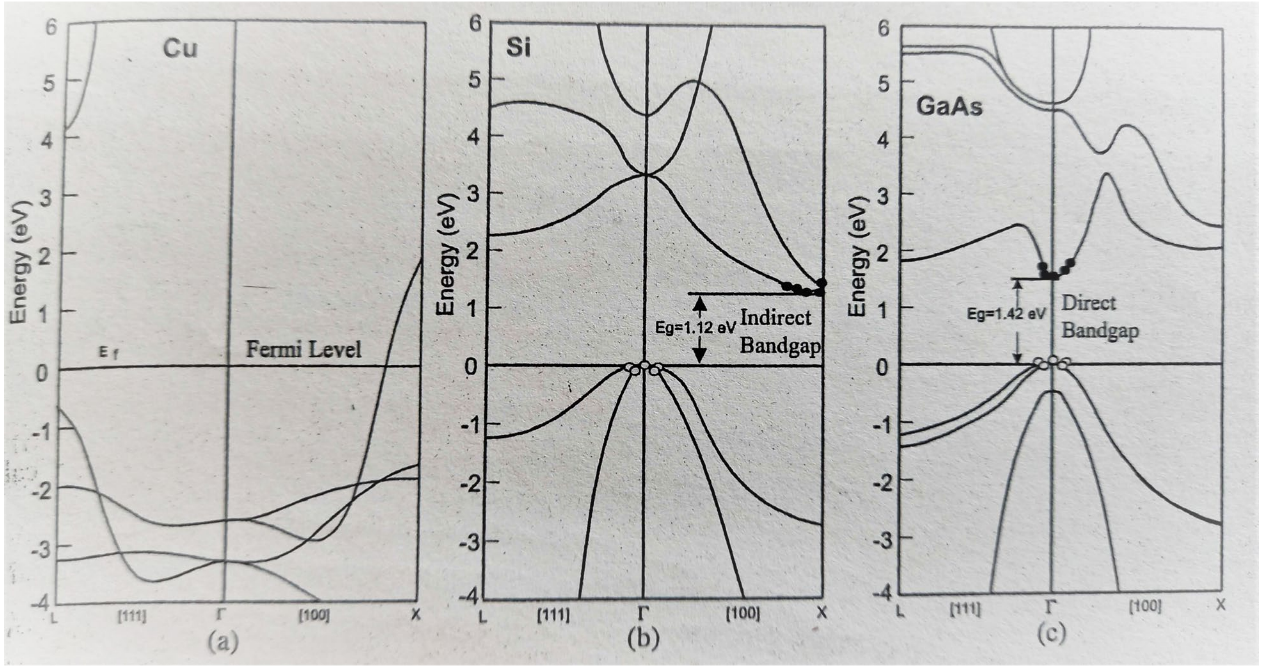
1D Lattice





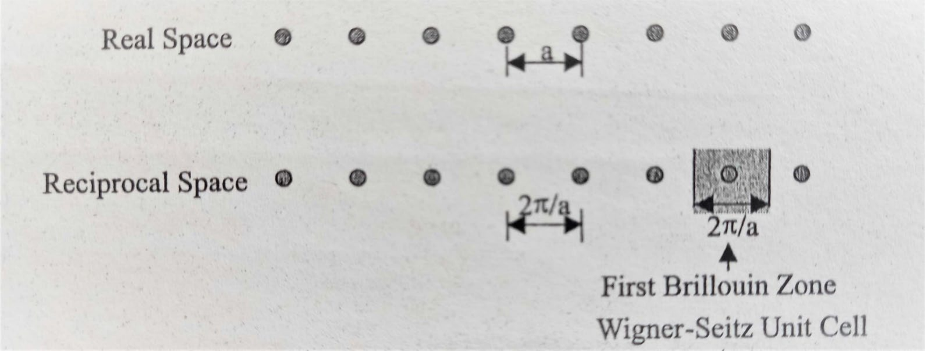
3D Lattice

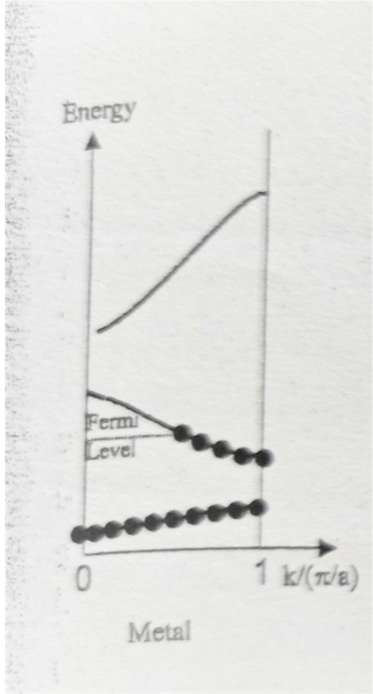




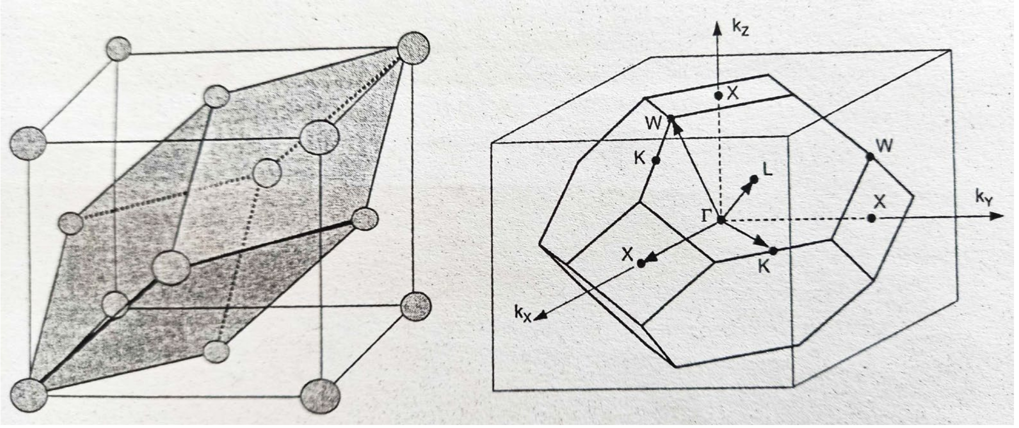
Band Structure and Material Properties

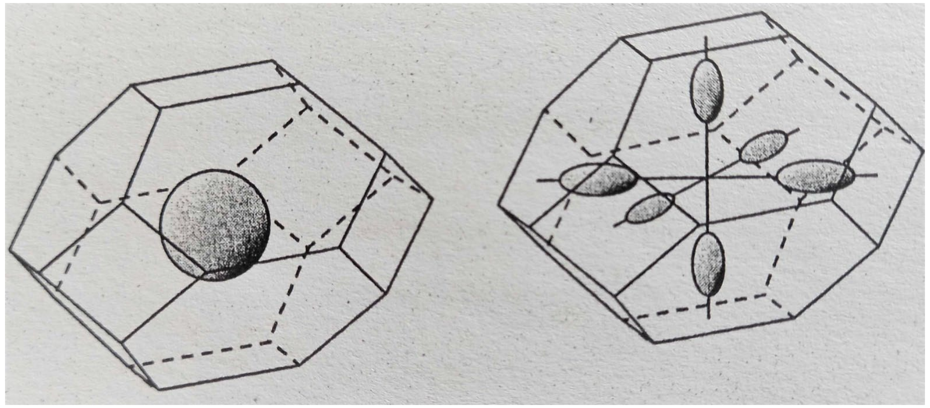
1D Lattice





3D Lattice





Fermi Surfaces (constant energy surface corresponding to the energy of the highest occupied level)

Supplementary Slides