

Bands and Bandstructure

Lecture 7

Electrons in a Periodic Potential

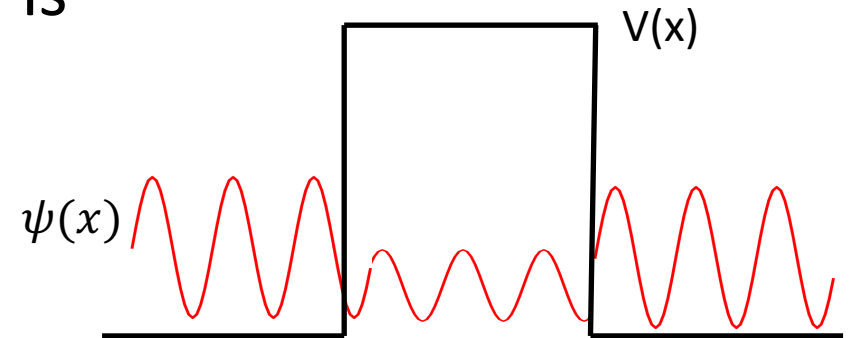
- Bloch's theorem:

If the potential is periodic, the wave function solution to the Schrodinger's equation is modulated by a function with the same periodicity

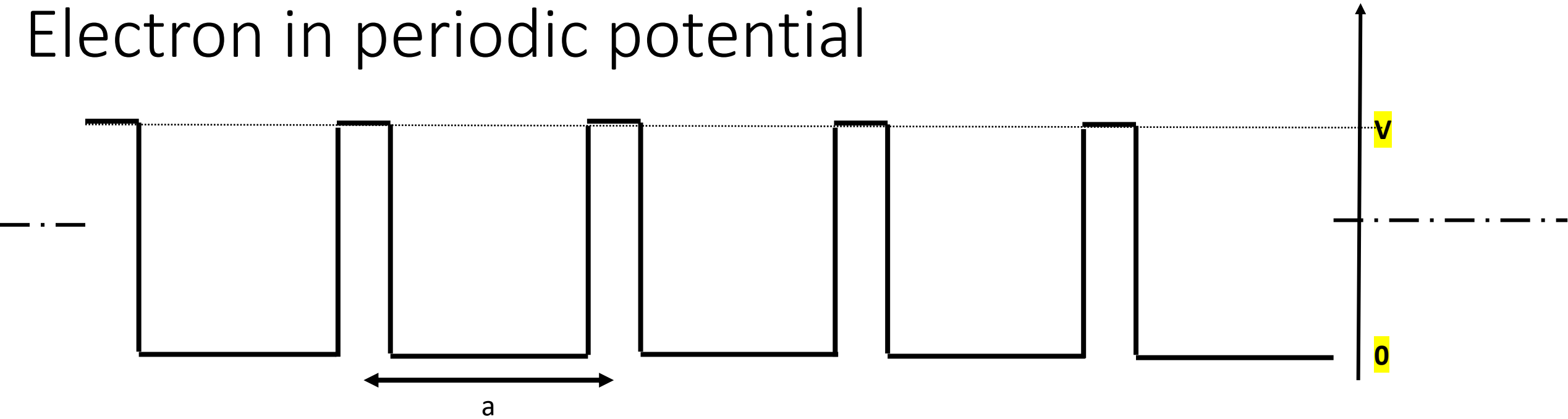
Therefore, the solution to the periodic potential is

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

Where $u(x + a) = u(x)$



Electron in periodic potential



How do we solve the Schrodinger's equation for such a potential profile ?

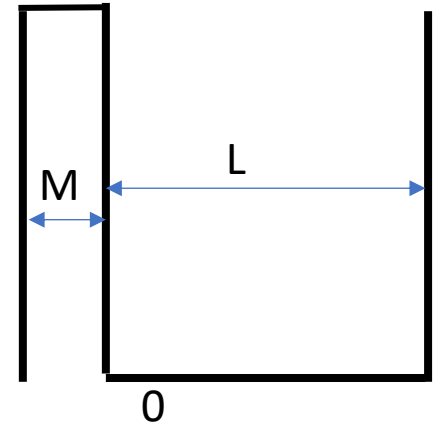
We use the oldest of tricks: Divide and conquer. We divide the space into two regions A and B.

$$V(x) = \begin{cases} 0 & 0 < x < L \\ V & -M < x < 0 \end{cases}$$

$$\text{And } a = L + M$$

In a crystal lattice:

Any function should have the lattice periodicity!



In region A, $0 < x < L$ where $V(x) = 0$

The Schrodinger's equation is $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$

Solution $\psi_k^R(x) = Ae^{ikx} + Be^{-ikx}$

In region A, $-M < x < 0$ where $V(x) = V$

The Schrodinger's equation is $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$

Solution $\psi_q^L(x) = Ce^{qx} + De^{-qx}$

Boundary conditions: $\psi_k^L(x=0) = \psi_k^R(x=0)$ and $\psi_k^R(x=L) = \psi_k^L(x=-M) * e^{ika}$
 $\psi_k^{L'}(x=0) = \psi_k^{R'}(x=0)$ and $\psi_k^{R'}(x=L) = \psi_k^{L'}(x=-M) * e^{ika}$

Four equations, Four unknowns A, B, C, D

Substituting: At $x = 0$

$$\begin{aligned} A + B &= C + D \\ ik(A - B) &= q(C - D) \end{aligned}$$

At $x = L$

$$\begin{aligned} Ae^{ikL} + Be^{-ikL} &= [Ce^{-qM} + De^{qM}]e^{ika} \\ ik[Ae^{ikL} - Be^{-ikL}] &= q[Ce^{-qM} - De^{qM}]e^{ika} \end{aligned}$$

Solution is obtained when

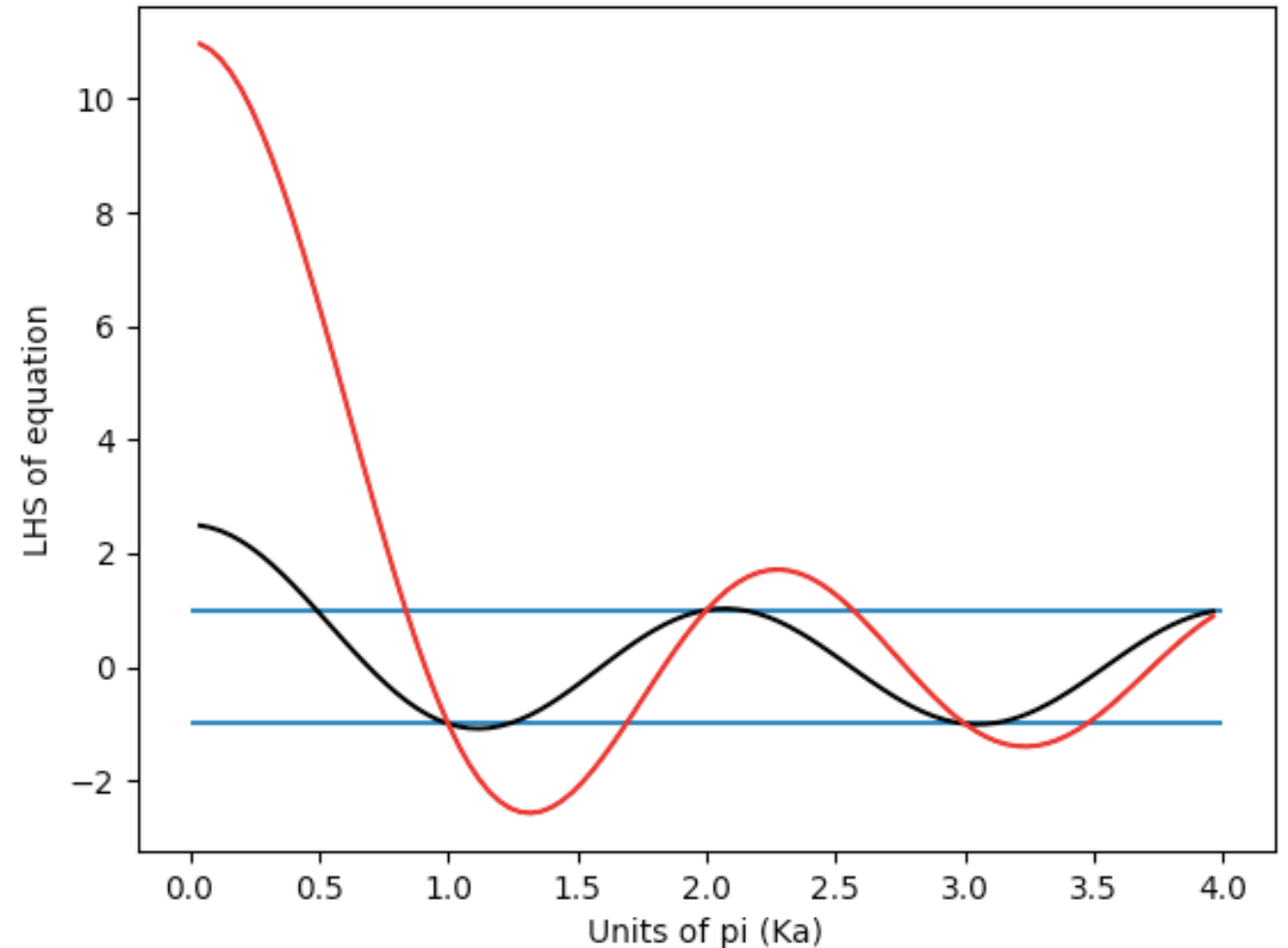
$$\begin{vmatrix} 1 & 1 & -1 & -1 \\ e^{ikL} & e^{-ikL} & -e^{-qM+ika} & -e^{qM+ika} \\ ik & -ik & q & -q \\ ike^{ikL} & -ike^{-ikL} & -qe^{-qM+ika} & qe^{qM+ika} \end{vmatrix} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = 0$$

$$\frac{q^2 - k^2}{2qk} \sinh qM \sin kL + \cosh qM \cos kL = \cos k(L + M)$$

$$\frac{q^2 - k^2}{2qk} \sinh qM \sin kL + \cosh qM \cos kL = \cos k(a)$$

Plot the function for different values of L,M and k. See that there can be solutions only for certain k

This means that for certain k values, there are no plane wave solutions!



Bands and Dispersion

A lot of information can be obtained from the relationship between energy (E) and wavevector (k) for a wave

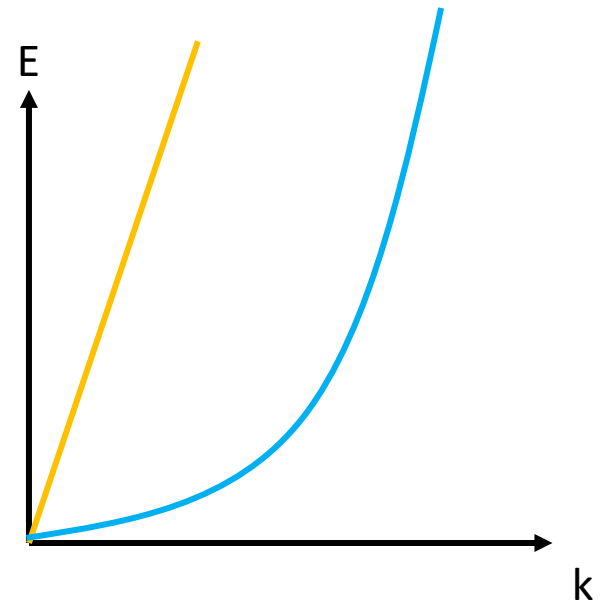
For an electromagnetic radiation $E = h\nu = \frac{hc}{\lambda} = \frac{c\hbar 2\pi}{\lambda} = c\hbar k$

Therefore, for light, the dispersion relation is linear.

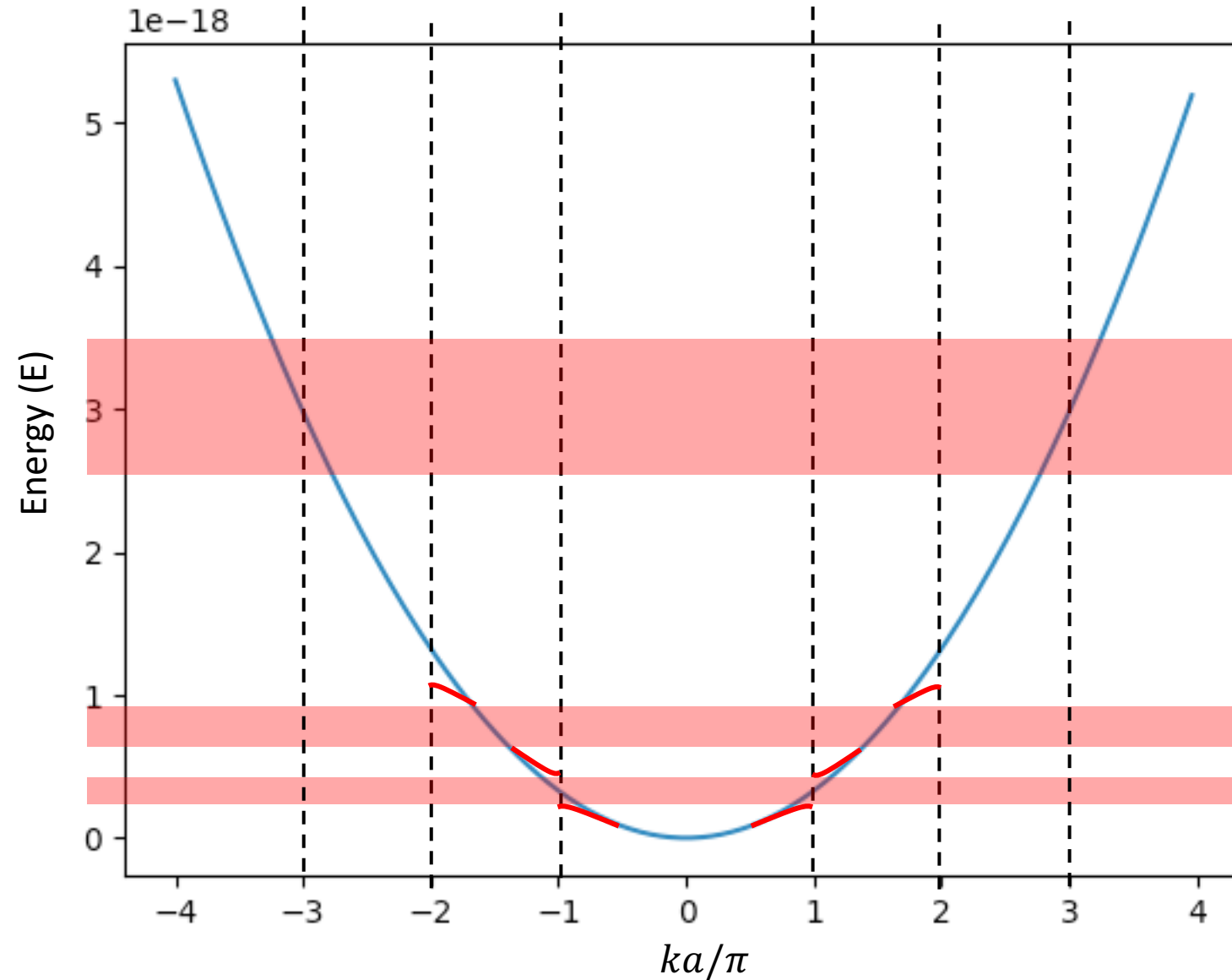
For a free electron, the wave solutions are plane waves

The energy turned out to be quadratic $E = \frac{\hbar^2 k^2}{2m}$

So we were interested in knowing what happens to the electron solutions when the potential is periodic!



Origin of bands in periodic Potential

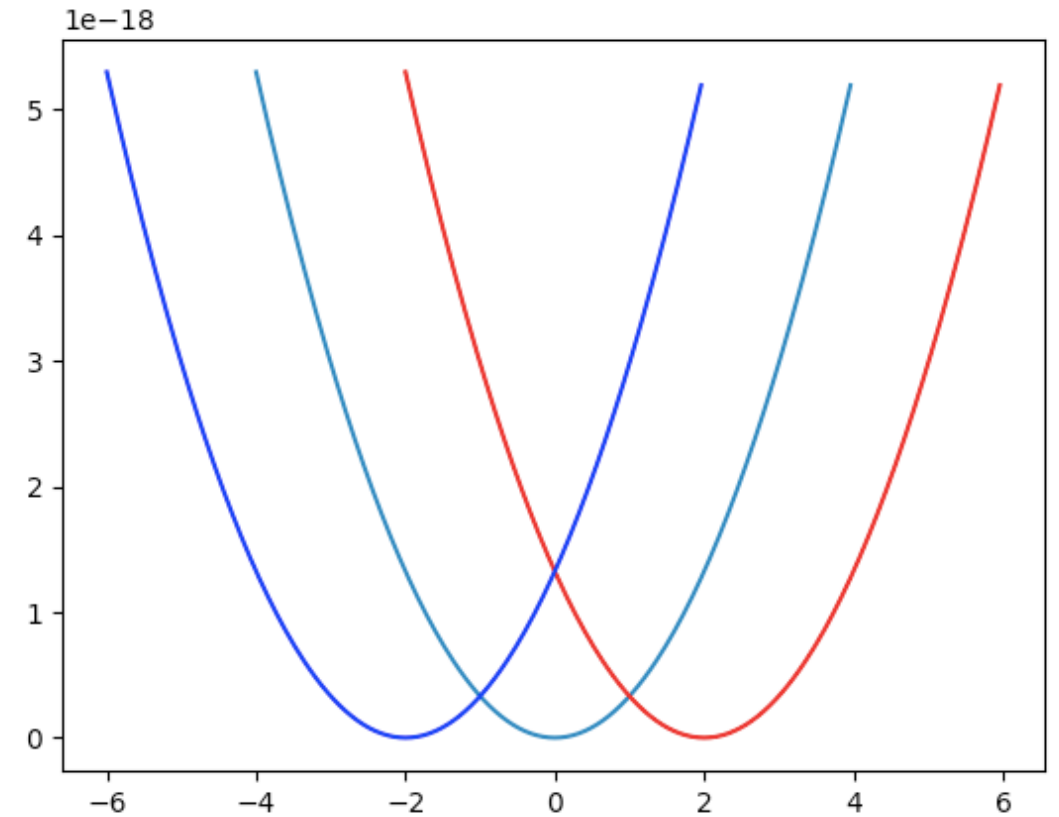
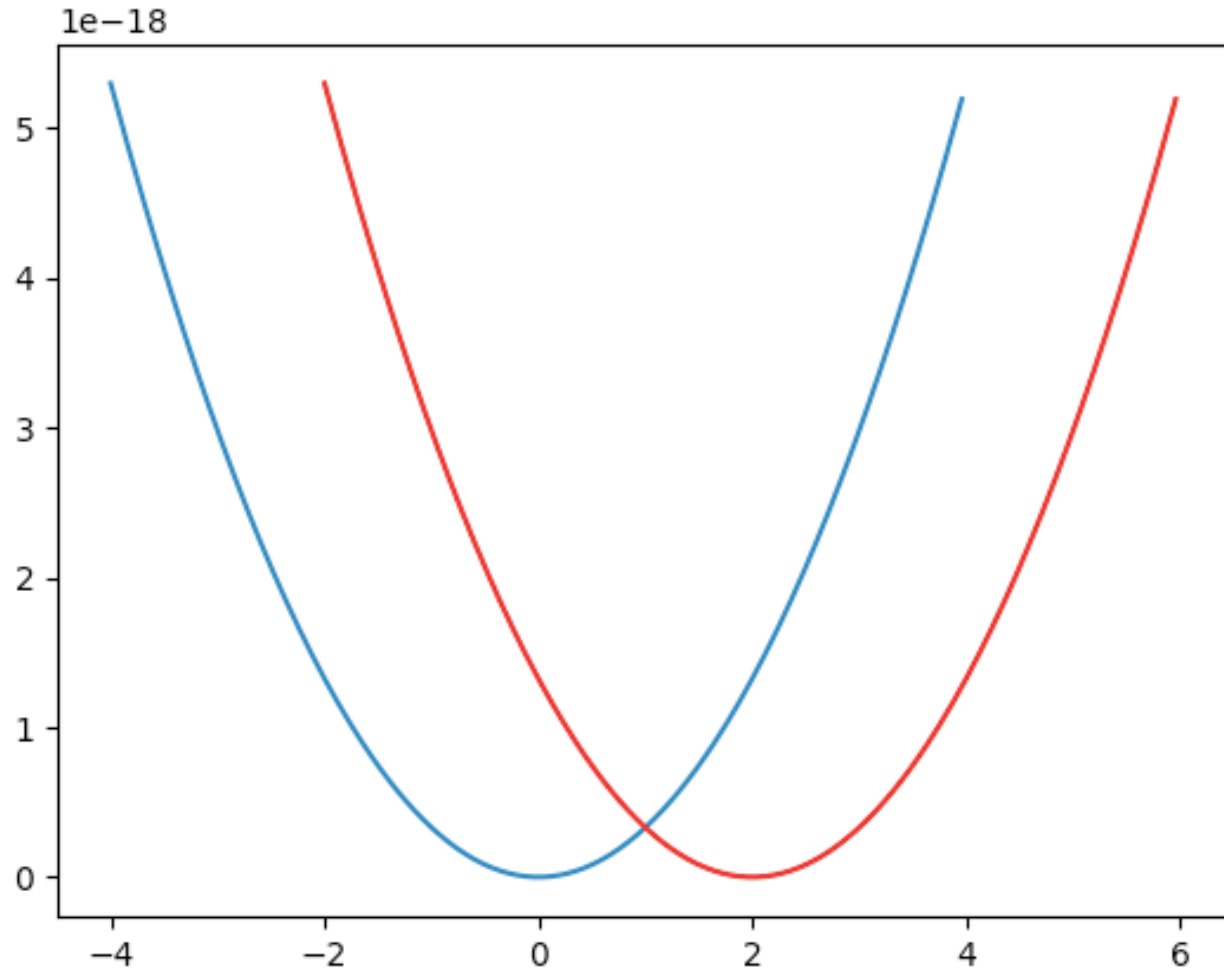


The free electron solutions are also solutions to the periodic potentials for certain energies

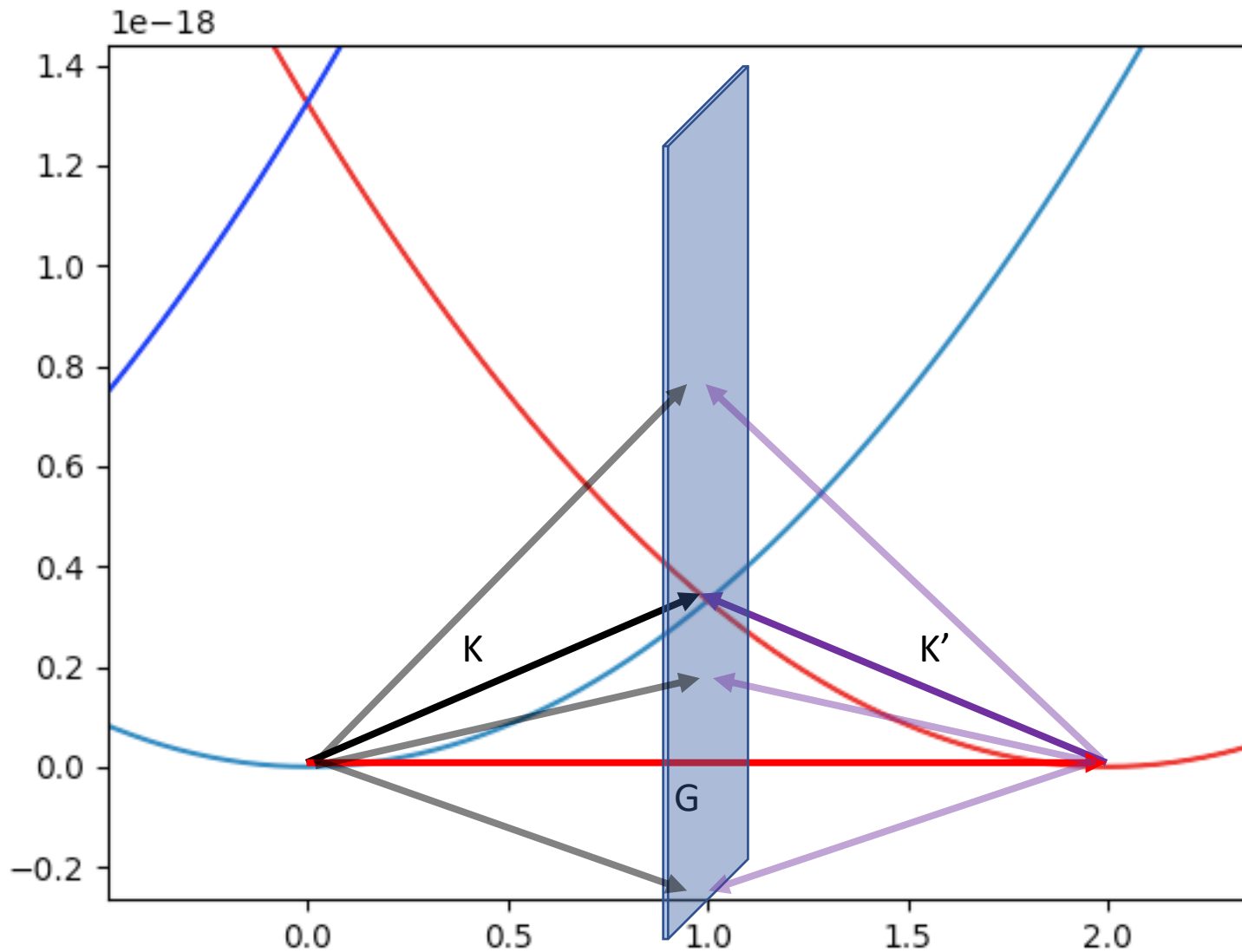
For a certain band of energies, denoted by red bands in the figure, there are no plane wave solutions of the Bloch form.

So, there are no electron states at the onset of certain points $k = \frac{m\pi}{a}$
Where m is any integer.

Physical picture of existence of a gap



If we have a parabolic dispersion at one RL point,
Periodicity demands the same at all lattice points



Criteria for constructive interference

If an electron at 0th unit cell has wave vector k

And the other one from the second unit cell has wave vector k'

The two electrons can have constructive interference when

$$k - k' = G$$

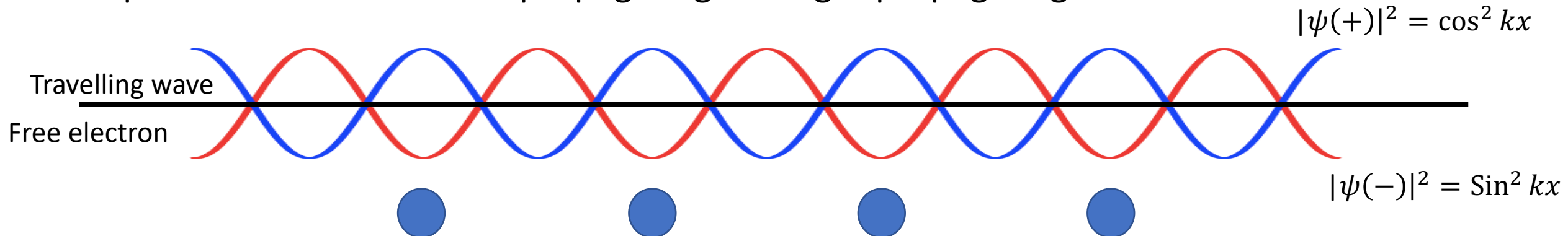
In fact constructive interference is obtained in a whole range of vector lying on the Bragg's plane

Crystal Interference

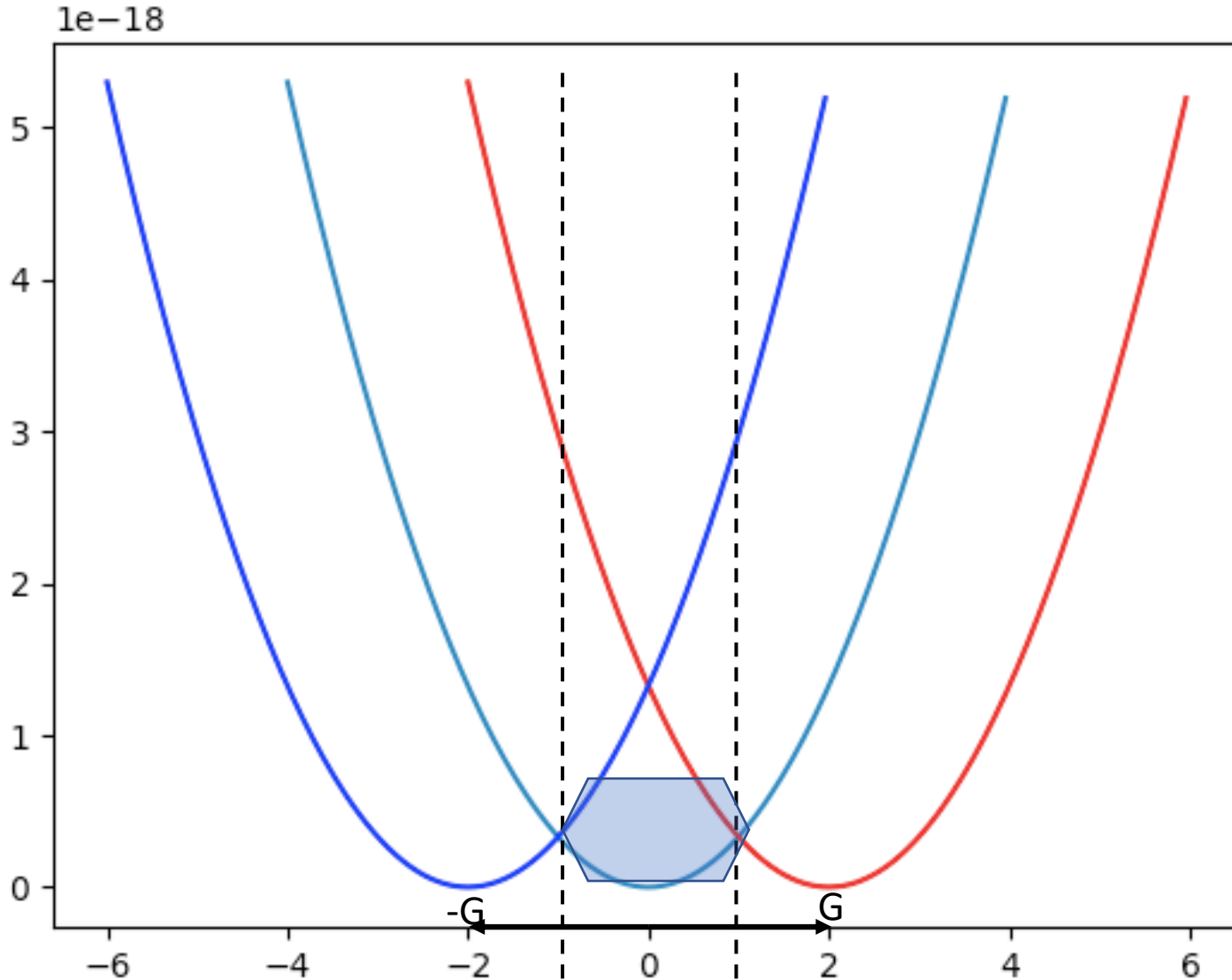
- At the Bragg's plane $\psi(+) = \psi_k(x) + \psi_{(K-k)}(x)$
$$\psi_k(x) + \psi_{-k}(x) = e^{ikx} + e^{-ikx}$$
$$\psi(+) = 2 \cos \frac{\pi x}{a}$$

- The same two waves can also interact as
$$\psi(-) = \psi_k(x) - \psi_{(K-k)}(x)$$
$$\psi_k(x) - \psi_{-k}(x) = e^{ikx} - e^{-ikx}$$
$$\psi(-) = -2 \sin \frac{\pi x}{a}$$

Thus, the interaction leads to the formation of two standing waves, each having equal contributions of left propagating and right propagating waves



First Brillouin Zone Representation



The Bragg planes are present at the Brillouin zone edges.

Thus band is continuous inside the Brillouin zone, and there is a discontinuity at the zone edge.

Any vector outside the Brillouin zone can be presented by a wave inside the zone – Reduced Zone.

If there exists an electron with k' outside the first BZ.
we write $k' = k + G$ where G is the RL vector

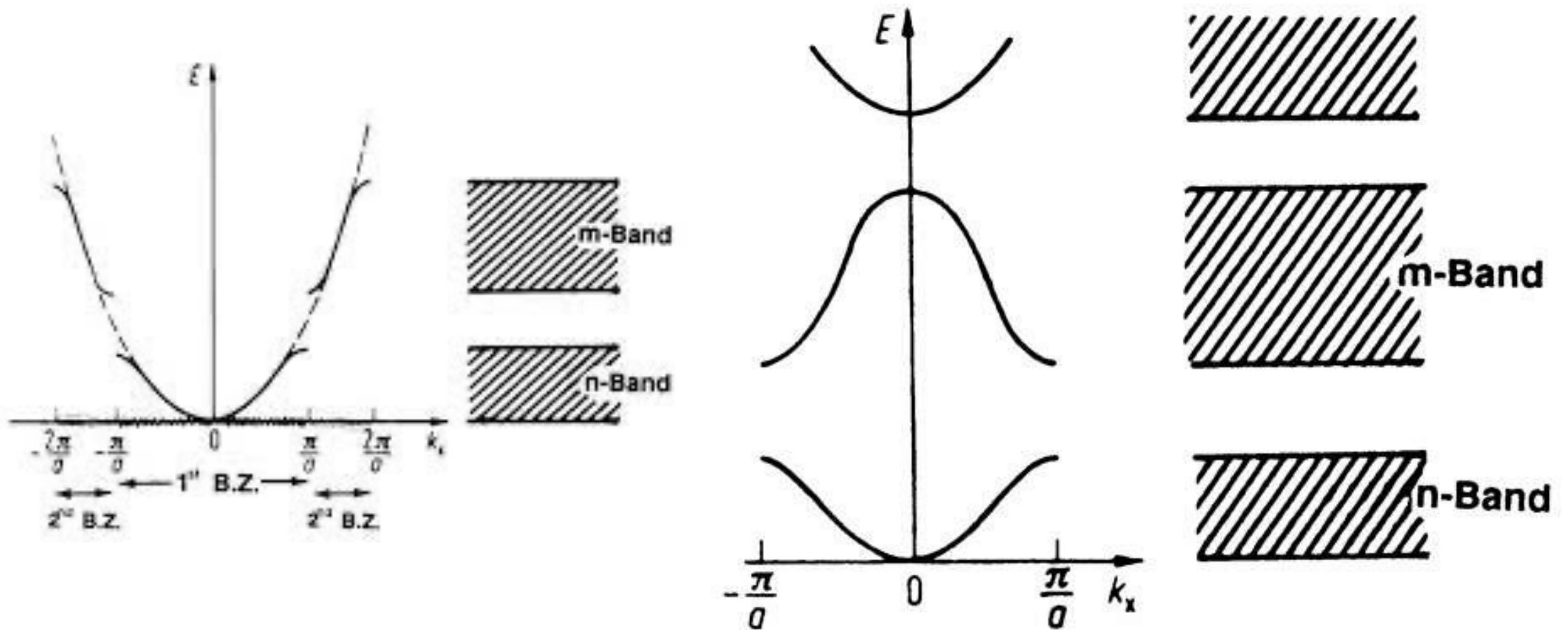
$\psi_{k'}(r + R) = e^{ik'.R}\psi(r)$ is the Bloch's form.

$$\psi_{k'}(r + R) = e^{i(k+G).R}\psi(r) = e^{i(k.R)}\psi(r)$$

Thus the Bloch's form is obtained for any k' , by its representation inside the first zone.

However, the energy of the wave outside the first zone would be different.

Extended, Reduced, and Bands in Brillouin

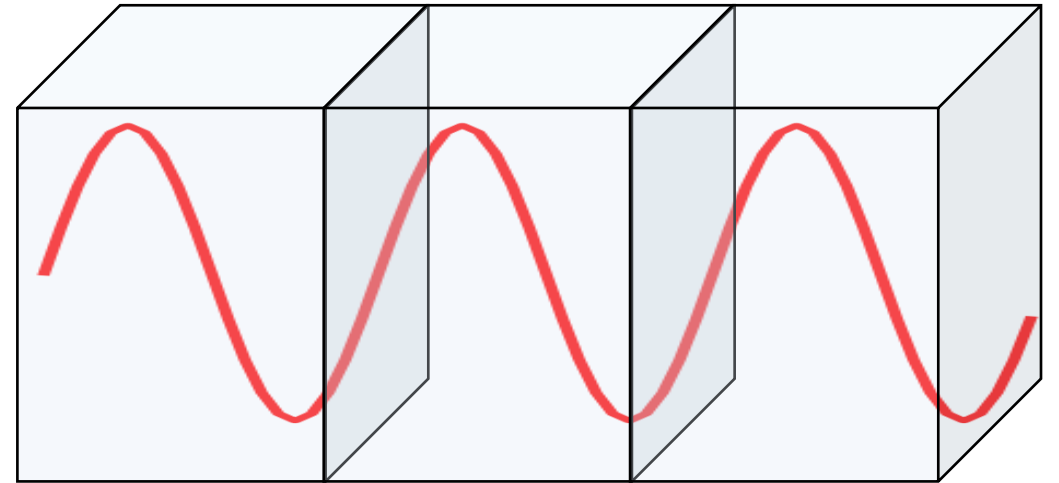


Each k point in the BZ now has several solutions, each of which is called with a band index n .

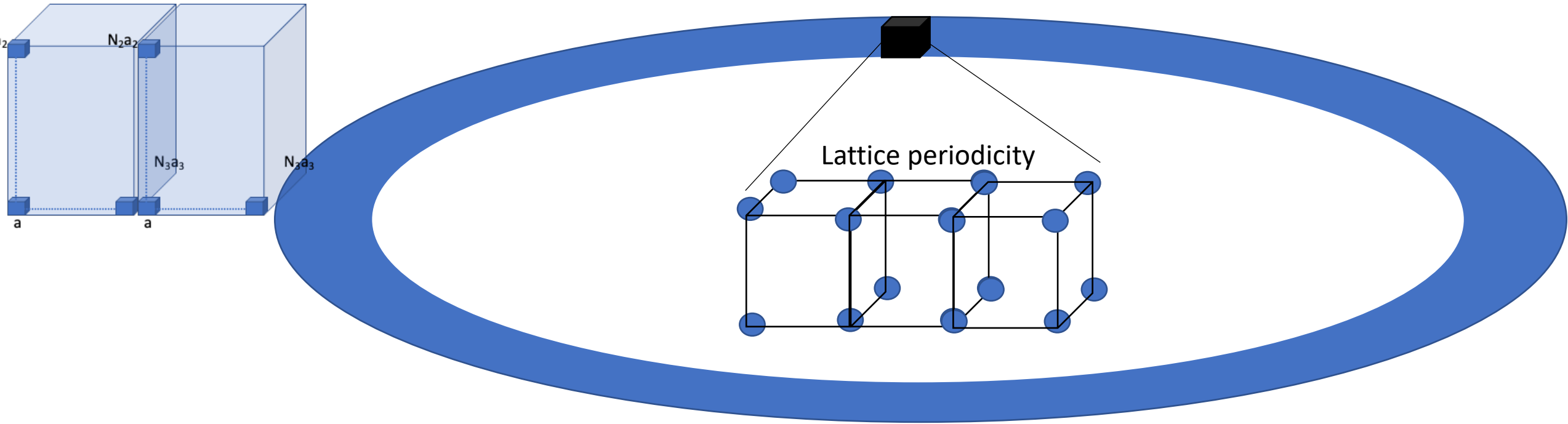
How many electrons ?

- Since, each energy level can have only two electrons (Pauli's exclusion), the question then is how many discrete energy levels are there in a band, hence in a crystal
- So, what is the smallest K there is ? Since energy and wave vector are related. A different wave of asking this question is , what is the length of the largest wave in the crystal ?

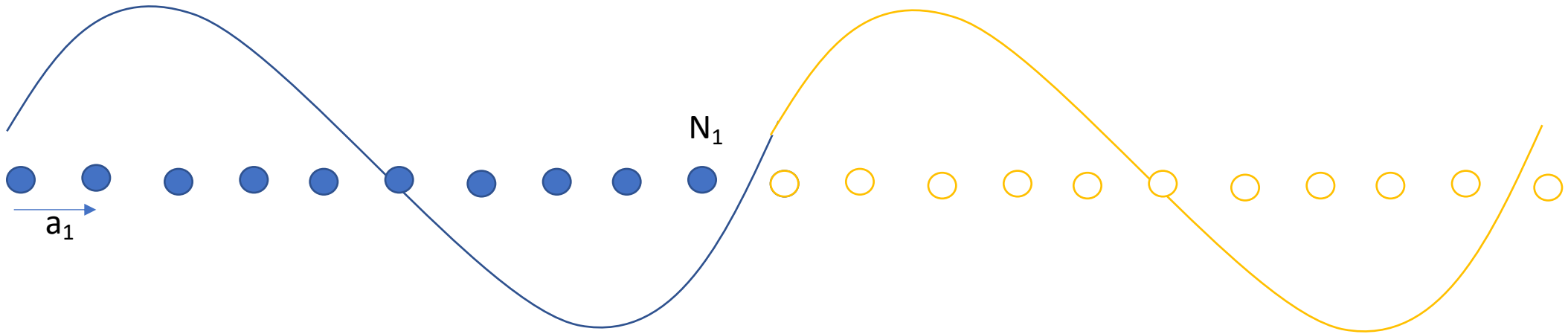
The answer is simple: It should end at where it begins in a crystal!
Else, there will be reflections.



Periodic Lattice in a Loop (Born Von Karman)



- If we take a crystal whose lateral dimensions are $L \times L \times L$ (a cube of dimension L), such that its total volume is L^3
- If can take the number of unit cells in each direction to be N_i , then
 - $\psi(r + N_i a_i) = \psi(r)$



- Which according to Bloch's equation

$$\psi_k(r + N_i a_i) = e^{i(k \cdot N_i a_i)} \psi_k(r)$$

$$N_i(k \cdot a_i) = 2\pi * integer$$

Smallest k-value

$$\Delta k_i = \frac{2\pi \vec{b}_i}{N_i}$$

- This makes k values to be discrete and have a form

$$k = \frac{2\pi m_1}{N_1} \vec{b}_1 + \frac{2\pi m_2}{N_2} \vec{b}_2 + \frac{2\pi m_3}{N_3} \vec{b}_3$$

Where m's are integers.

Electron Filling:

- The smallest $\Delta k = \frac{2\pi}{L}$, Brillouin Zone width are $\frac{2\pi}{a}$
- Total length of sample $L = Na$, N – number of unit cells
- Hence each band in the first Brillouin zone contains N states
- Each state can have two electrons of opposite spins and hence, there are $2N$ independent states (orbitals) in each band
- If each primitive cell has 1 valence electron, then atleast one band is half empty! Thus materials with one valence electron per atom in the primitive cells have partially empty bands.

Electron contributions:

- If each atom in the primitive cell has two electrons, the bands can be exactly filled.
- If each primitive cell has a basis of two atoms, it will always have an even number of electrons per primitive cell. This will have a very high probability to have filled bands!

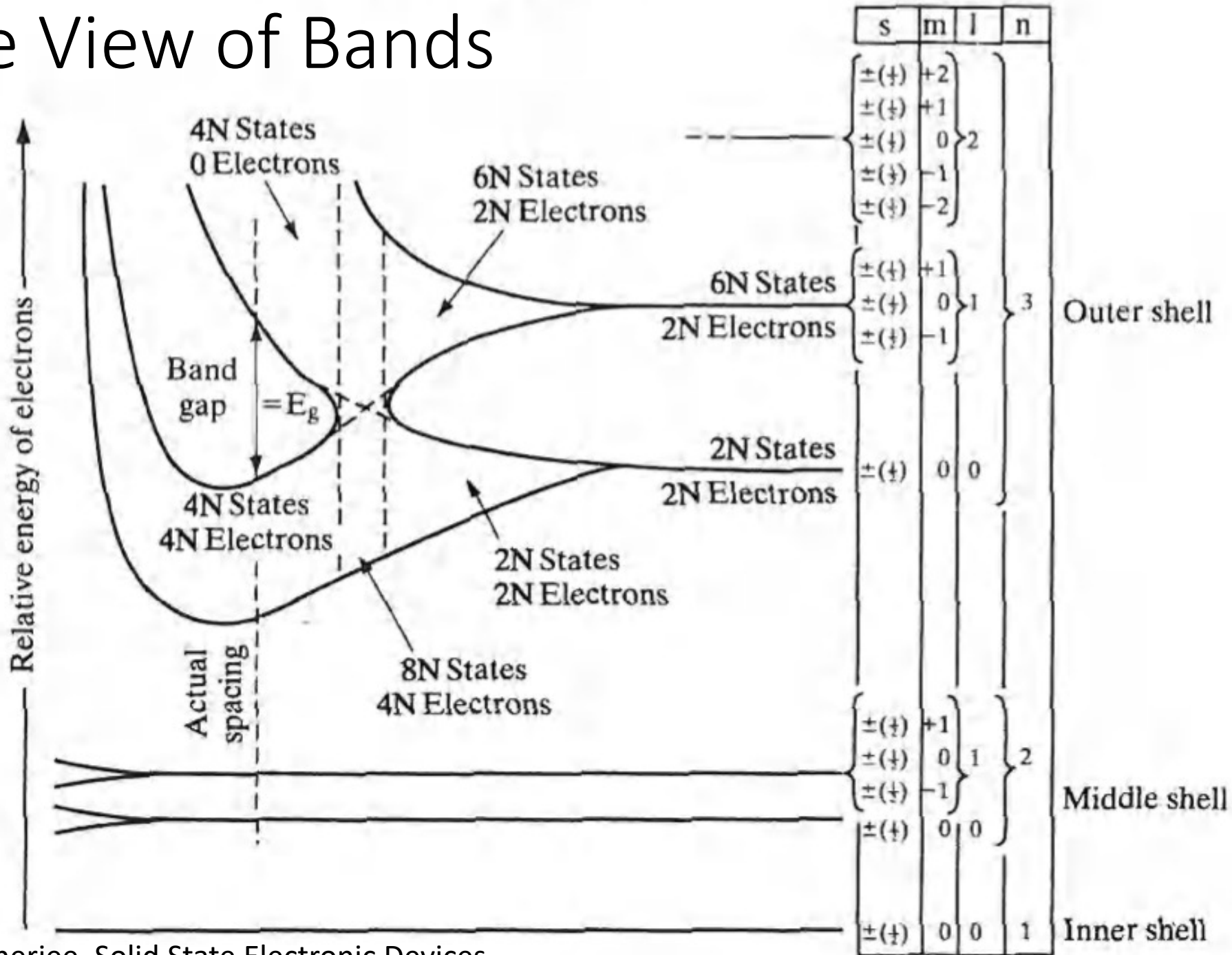
Bands and types of materials

- All materials have electronic bands and bandgaps at some point in the reciprocal space
- If the valence electrons fill one or more bands leaving others empty, you have an insulator/semiconductor depending on the gap between the bands. If the gap is in the range of the thermal energy, you have a semiconductor and if its larger, you have an insulator. This distinction is fast becoming blurred, with large gap semiconductors such as AlN, GaN, and SiC being used extensively
- A filled band is an insulator because, an applied electric field cannot change the electronic distribution in the material as no empty state is available.

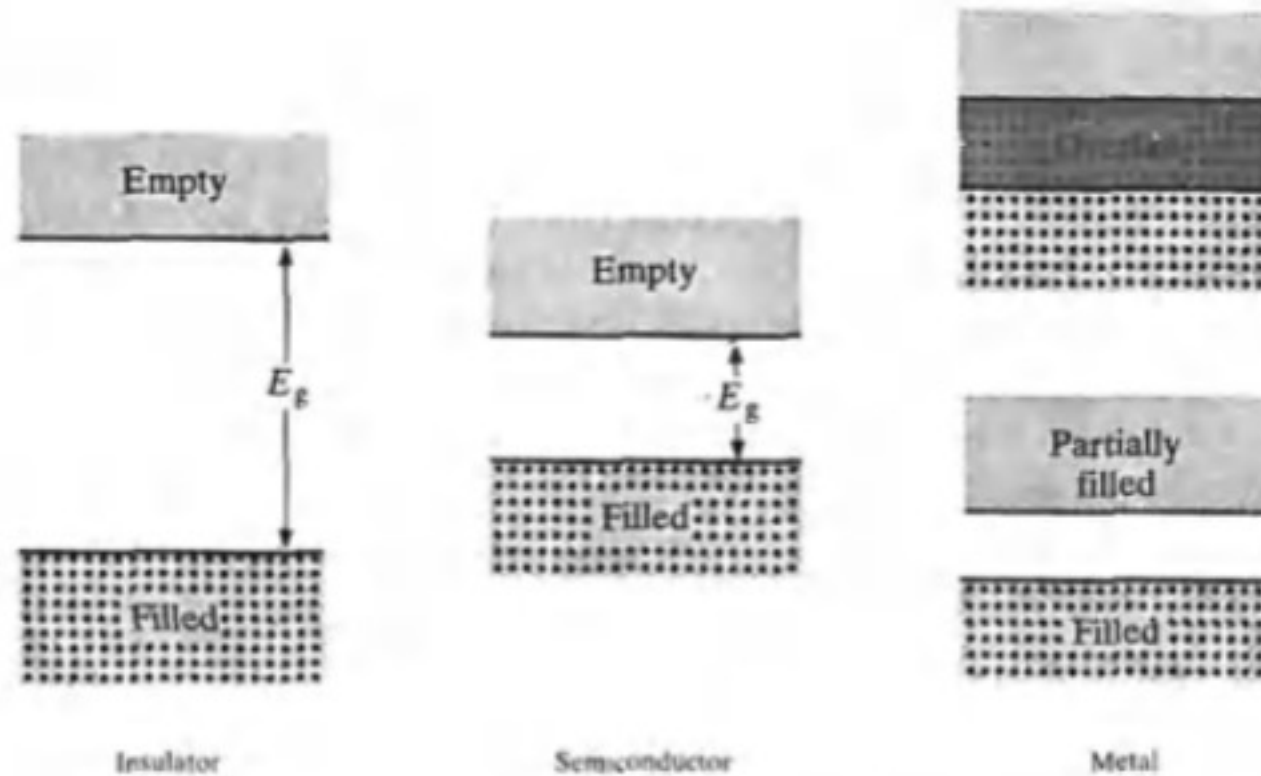
Bands and types of materials

- However, a primitive cell with even number of electrons can be a metal! If the bands overlap.
- All alkali earth elements are metals
- All alkaline earth elements have two electrons, however, the bands overlap giving them also metals.
- Diamond, Si, Ge all have even number of electrons and hence have filled bands at 0K.

Alternate View of Bands



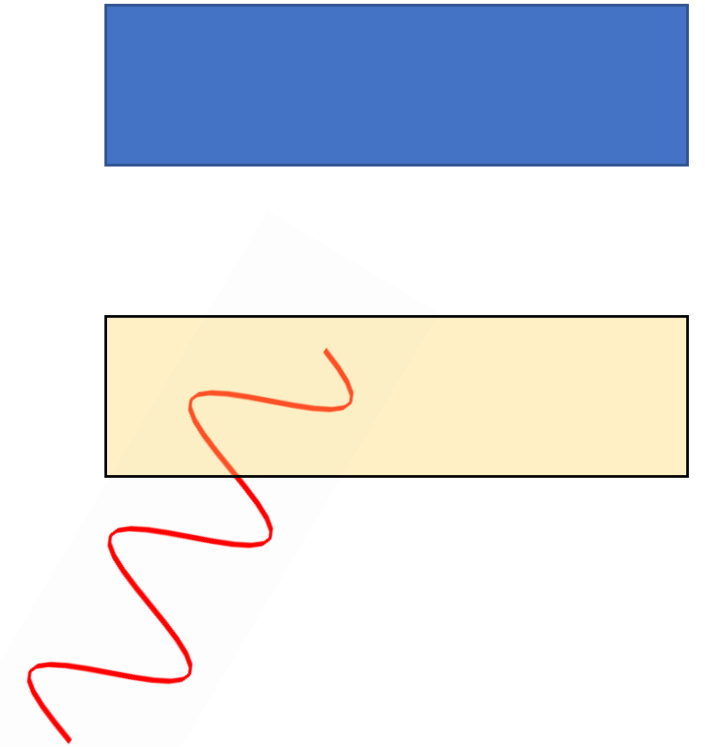
Difference between different materials



How do we measure bandgap ?

Optical Absorption

- It is based on the fact that filled states and empty states are separated by a gap in energy called as band gap
- If the separation in the gap is more than the thermal energy, then external energy source can be supplied to excite the electrons from one band to another
- If the electron concentration in the nearly empty band be calculated, then the correlation between the energy supplied and the electron concentration will give a measure of the bandgap!



Direct Optical Absorption

- Bands are Parabolic with sharp end points.
- Say an electron in the topmost filled band, called as the valence band has a wave vector k . It is written in the Bloch form

$$\psi_k = U_k(r)e^{ik \cdot r}$$

- If the electron were to be excited to the unoccupied band with form

$$\psi_{k'} = U_{k'}(r)e^{ik' \cdot r}$$

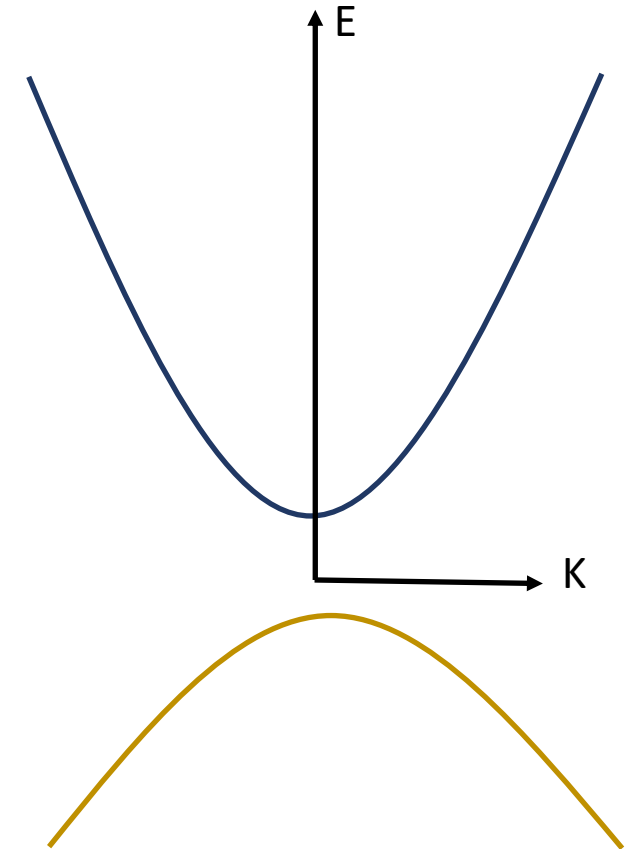
There are two conditions:

1. Energy conservation $E_{k'} = E_k \pm h\nu$
2. Momentum conservation $k' = k + q$

A point to remember: $k = 2\pi/\lambda$, and $\lambda \leq 1 - 4\text{\AA}$ for an electron in crystal and $\lambda \sim 300 - 800 \text{ nm}$ for a visible radiation of light. So, q is much smaller than k and k' . Which gives the selection rule for photons

$$k = k'$$

For a direct absorption case

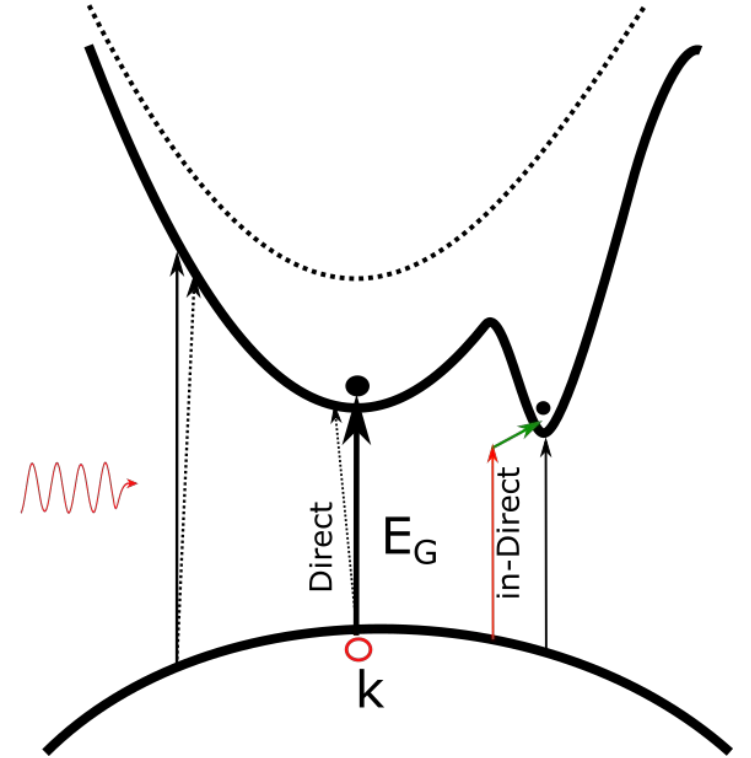


In-Direct Optical Absorption

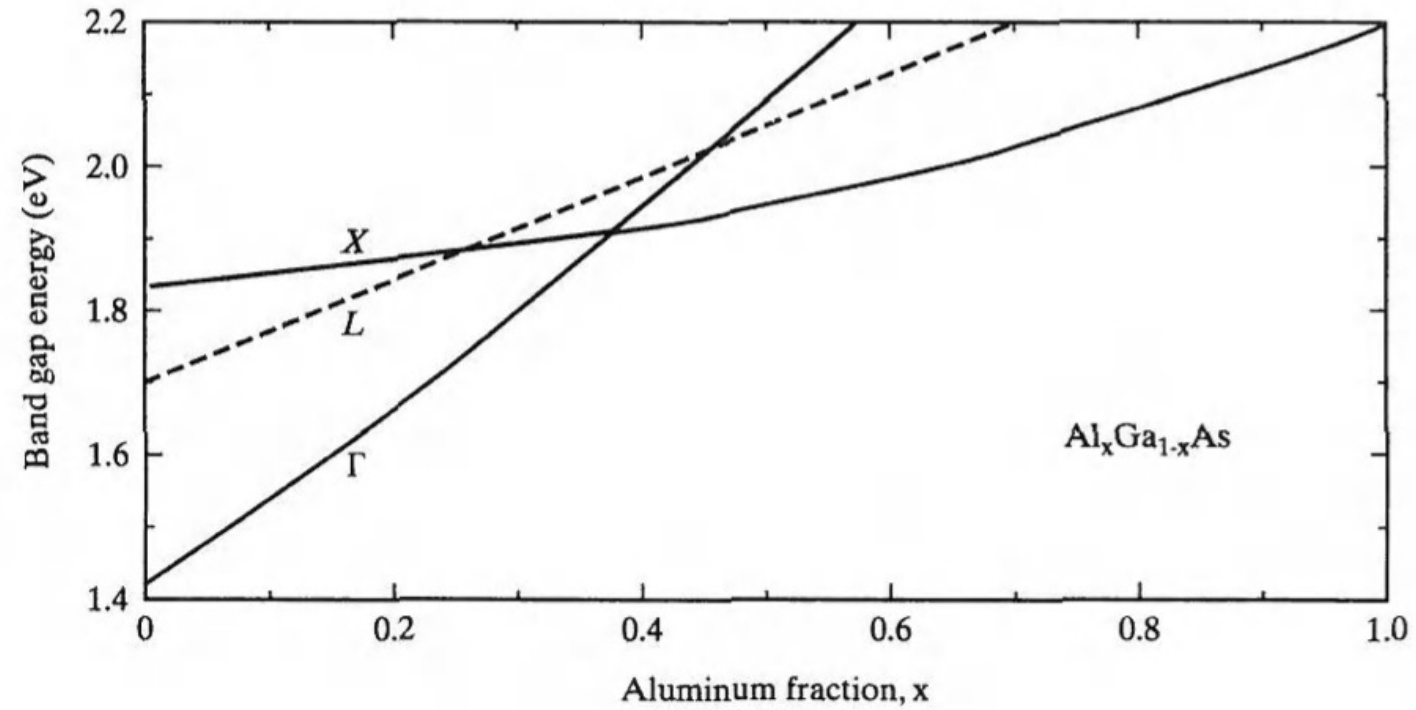
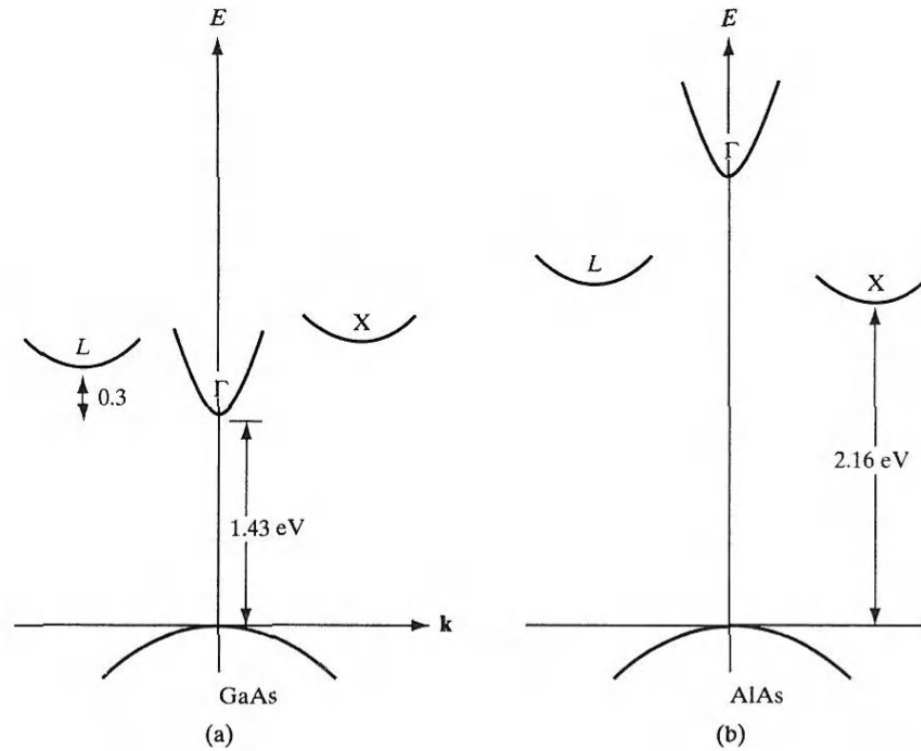
$$k \neq k'$$

For a direct absorption case

- What happens if the bottom of conduction band and bottom of valence band are not aligned in K-space. One example of this is Silicon.
- In this case, $k \neq k'$. The transition cannot happen directly and needs assistance
 - Either with the help of a defect/phonons.
 - It is a two step process which involves a third species
 - Orders of magnitude less efficient than the first order process in direct bands



Direct to Indirect transition



Electromagnetic Interaction

- If c is the velocity of light in free space, and v the velocity of light in material M ,

$$n = \frac{c}{v} = \frac{\lambda_0}{\lambda}$$

Is called as the refractive index of the material M

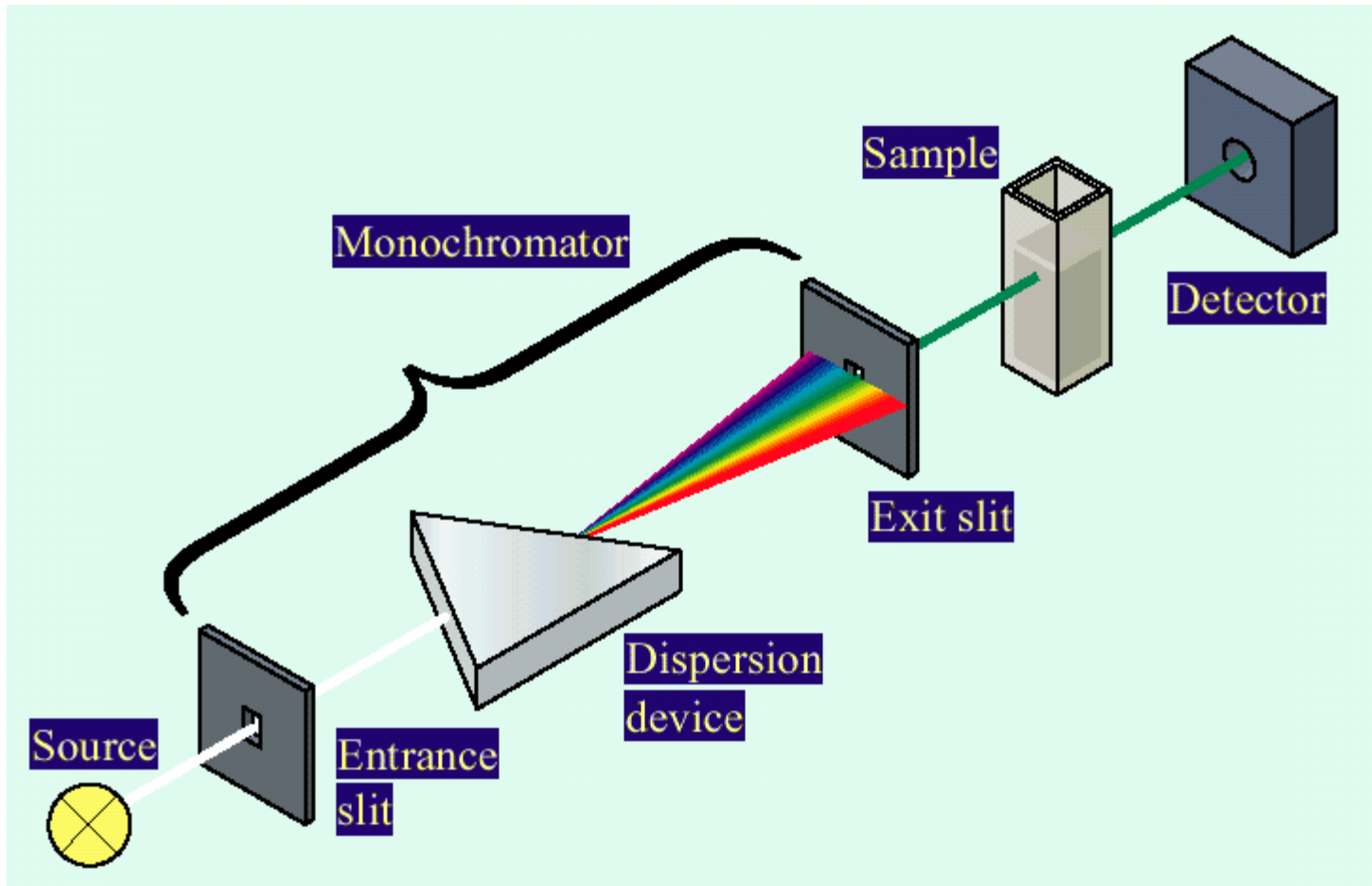
The complex refractive index $\hat{n} = n - ik$

Where k is called as the extinction coefficient $k = \frac{\alpha\lambda}{4\pi}$

α is the absorption in the material.

α is an important experimental value. It can be easily measured as a function of different wavelength of the incident light.

Typical measurement scheme



- When light is incident on the sample normally (perpendicular) the transmission

$$T = \frac{(1 - R^2)e^{-\frac{4\pi x}{\lambda}}}{1 - R^2e^{-8\pi x/\lambda}}$$

And Reflection

$$R = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2}$$

n and k of semiconductors are typically measured by measuring the transmission and reflection at interfaces. The tool used is called as ellipsometer.

- In a direct band gap semiconductor

If the incident radiation energy $E = h\nu$ is close to the bandgap E_g a sharp increase in the optical absorption is observed

The absorption $\alpha = \frac{A}{h\nu} (h\nu - E_g)^\gamma$

The constant $\gamma = 0.5$ for direct band – band transition

$\gamma = 2$ for indirect transitions.

This means the term $(\alpha h\nu)^{2(0.5)}$ should be linear with the photon energy and the x-intercept gives the bandgap! The $(\alpha h\nu)^{2(0.5)}$ is called as the Tauc coefficients.

