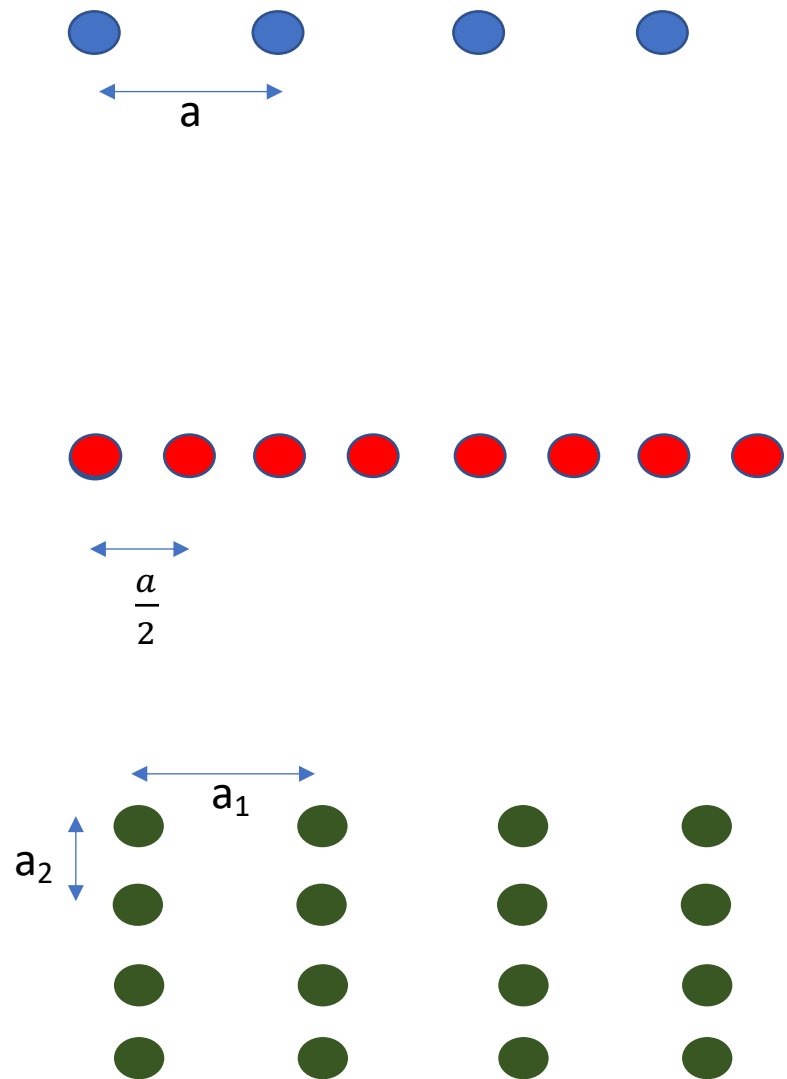


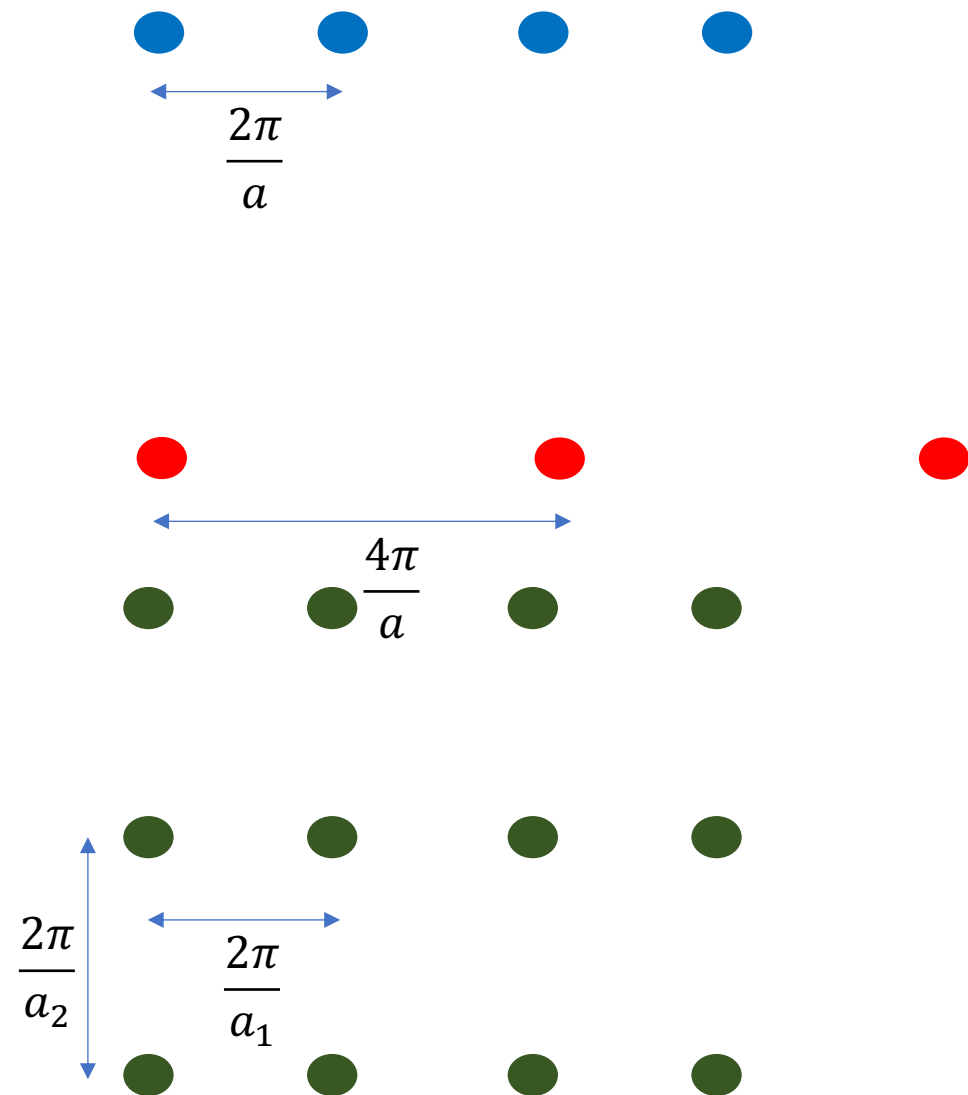
Lecture 6

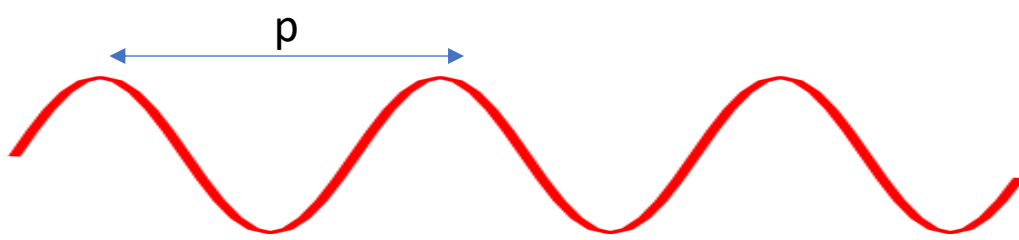
Reciprocal lattice and BandStructure

Real Space



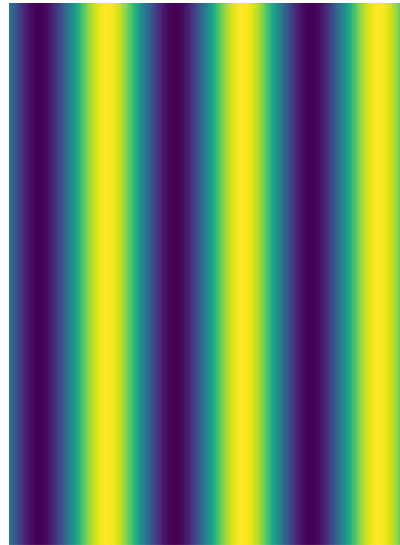
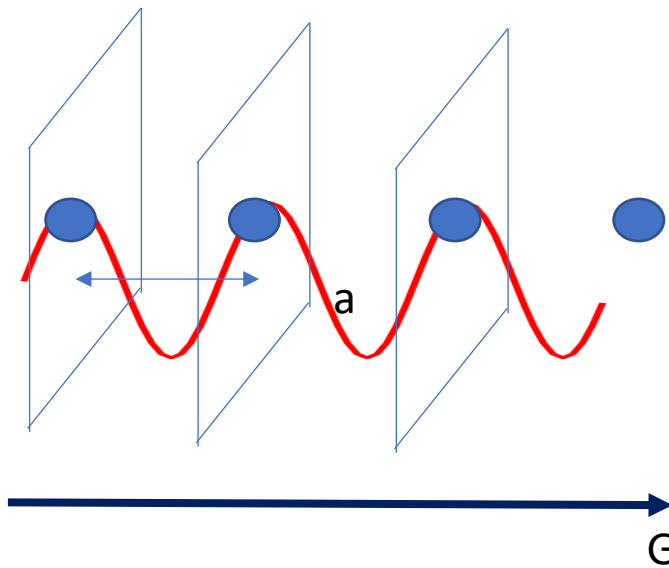
Reciprocal Space



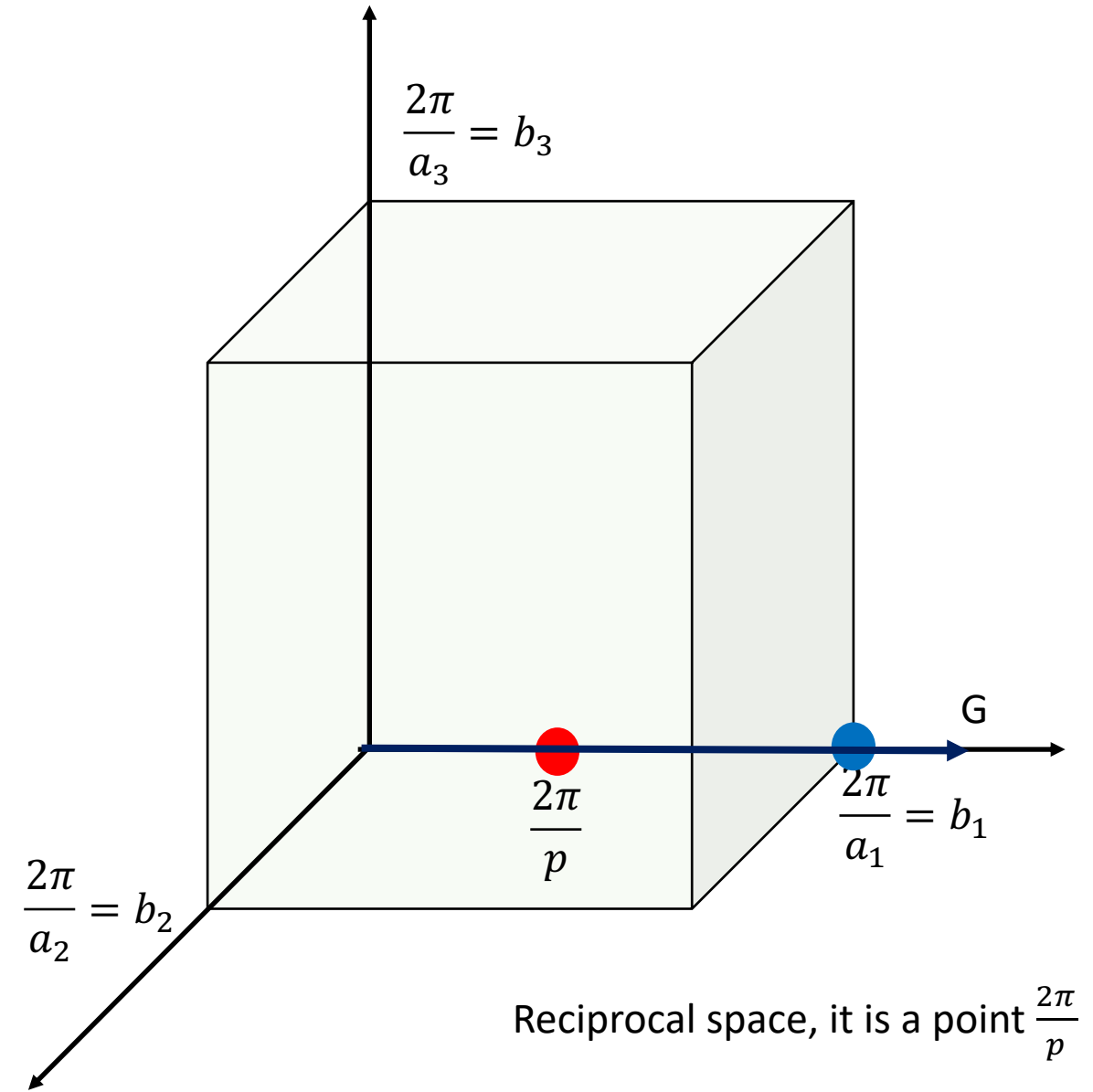


Function with a known periodicity p

Function with the periodicity of a crystal



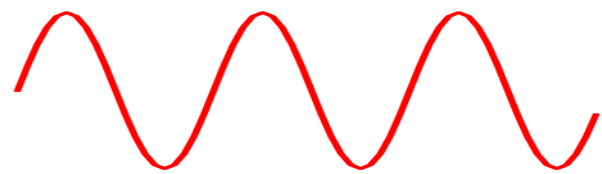
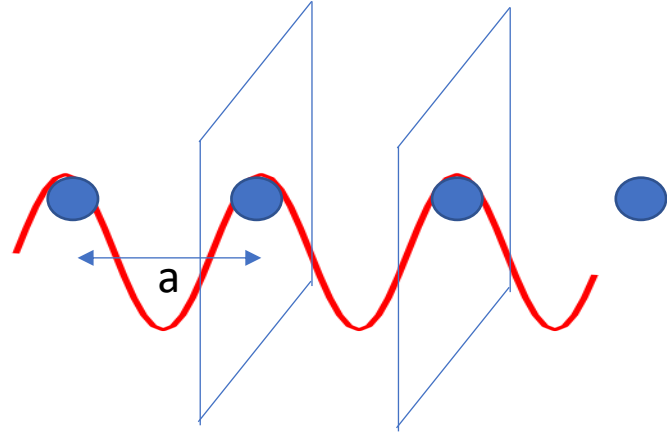
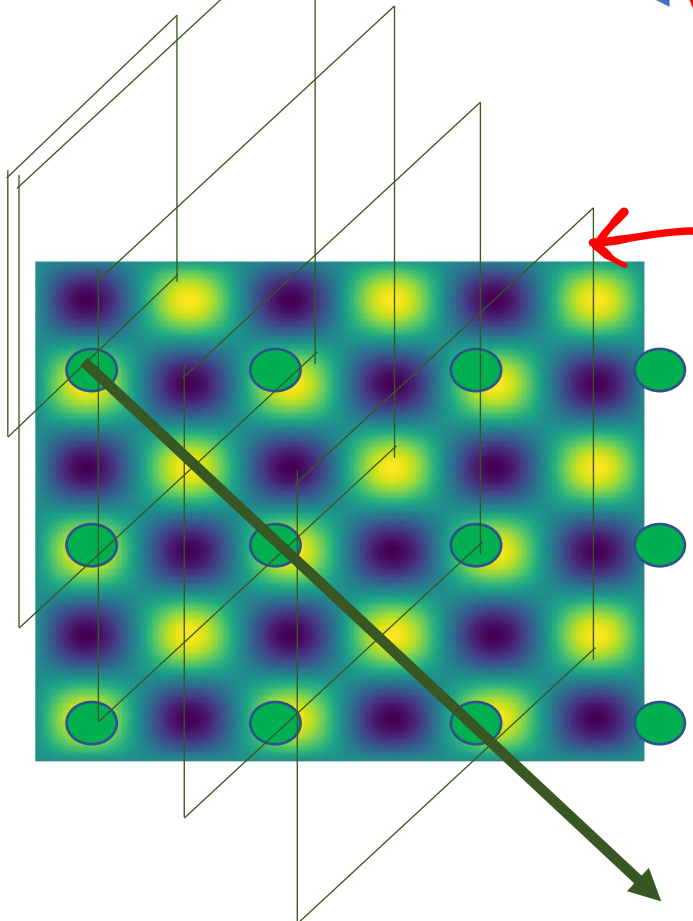
Imagine the function extends in the Y plane. No change.
 You can think about constant value planes.
 Reciprocal vector is perpendicular to those constant value planes



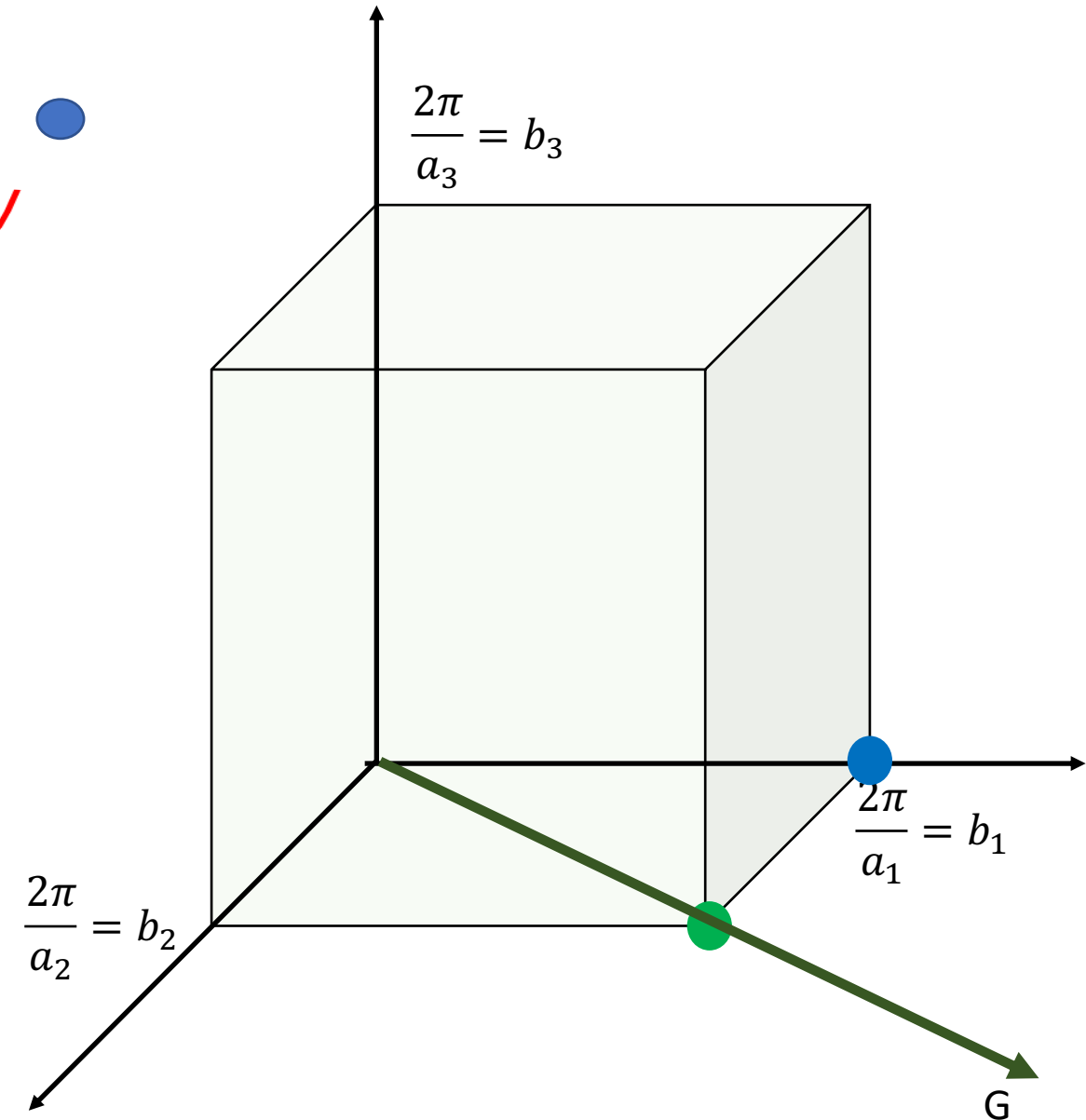
You get reciprocal lattice vector b_1

Two-dimensional periodicity

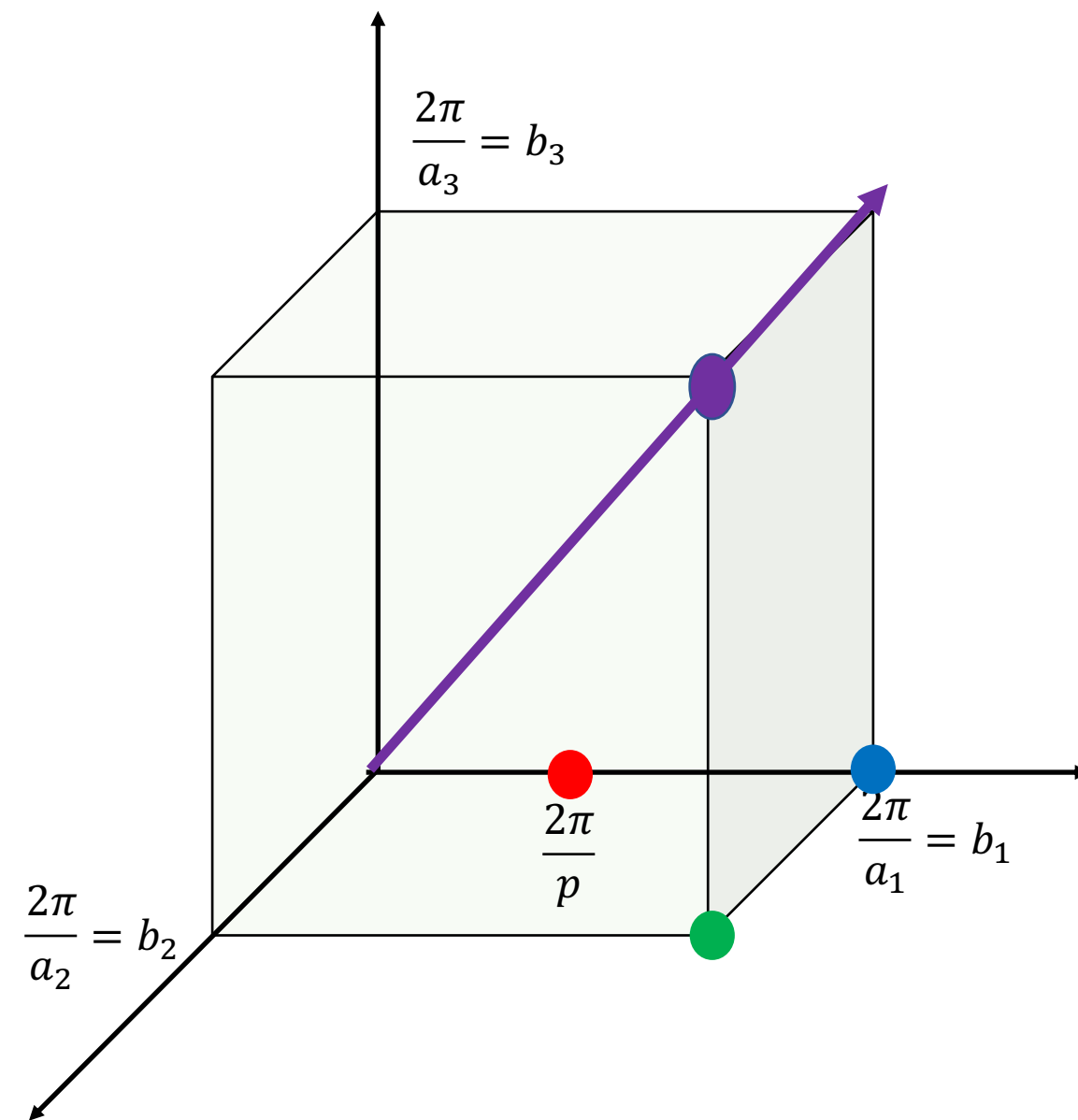
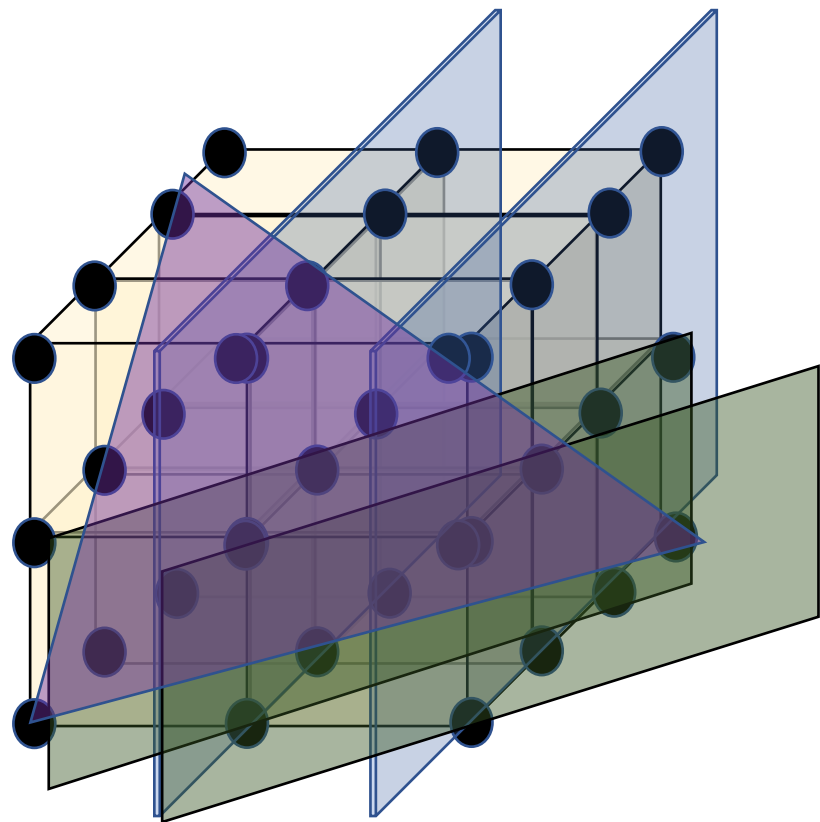
Instead, if constant value in y
The function goes sinusoid!



Constant values are observed in direction



This has periodicity in three dimensions

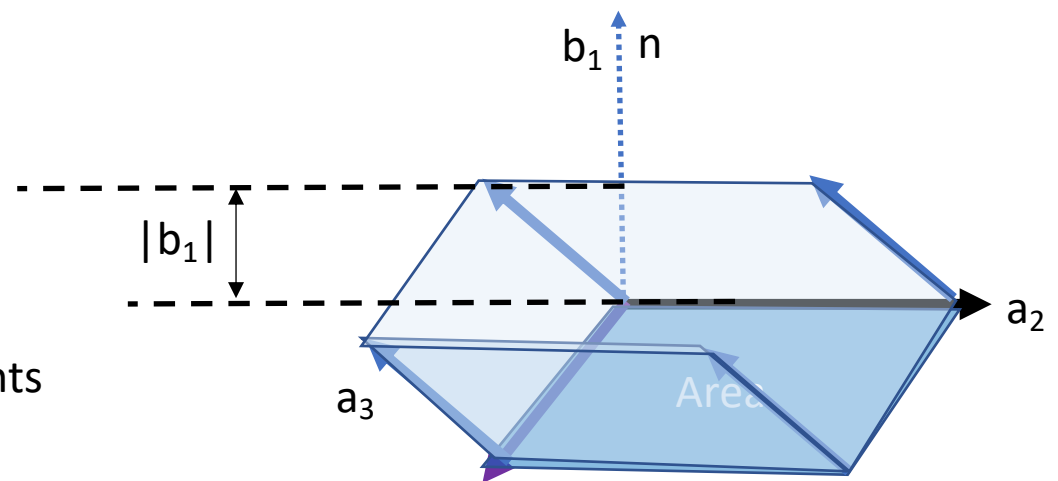


Properties of Reciprocal lattice

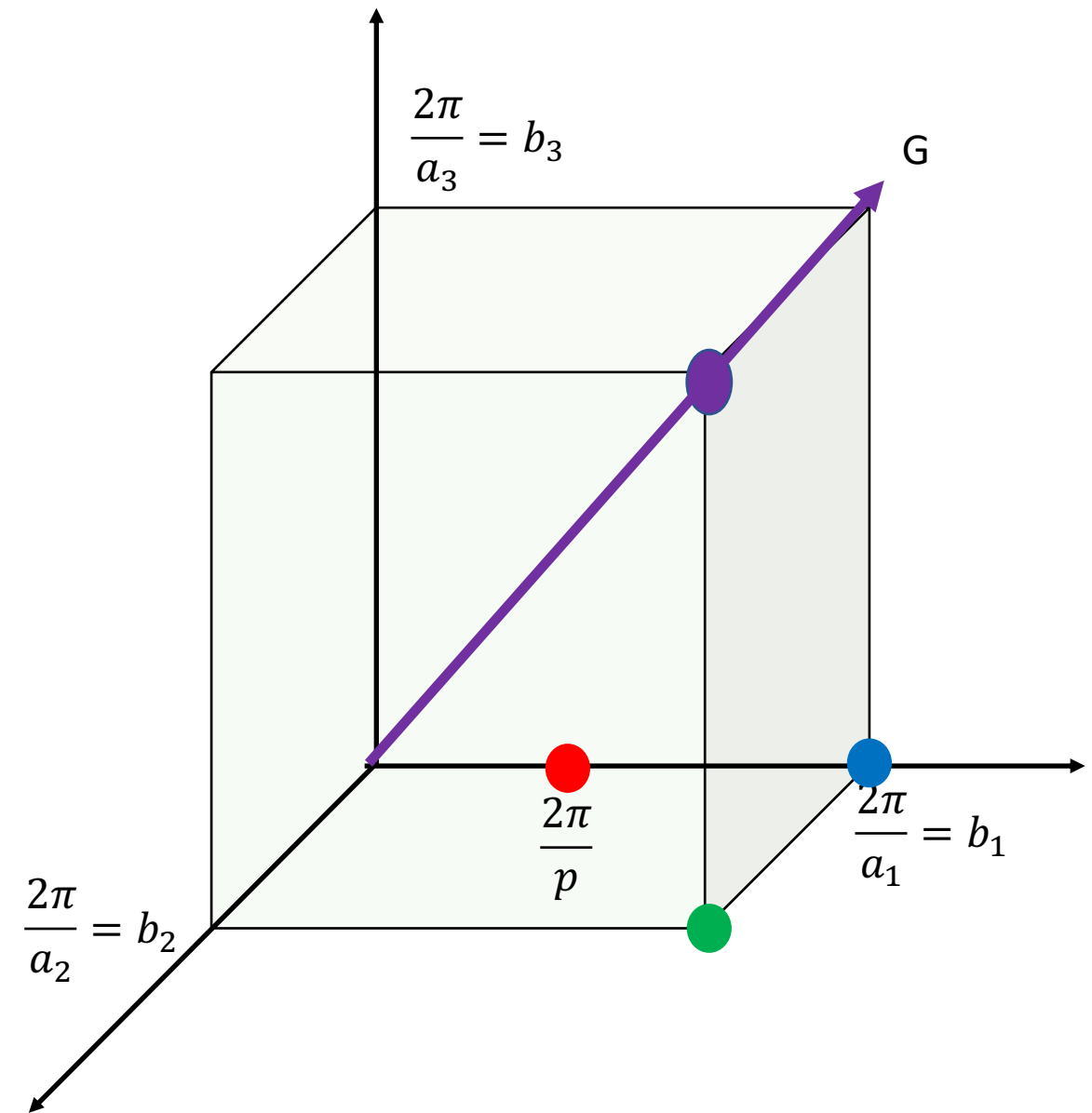
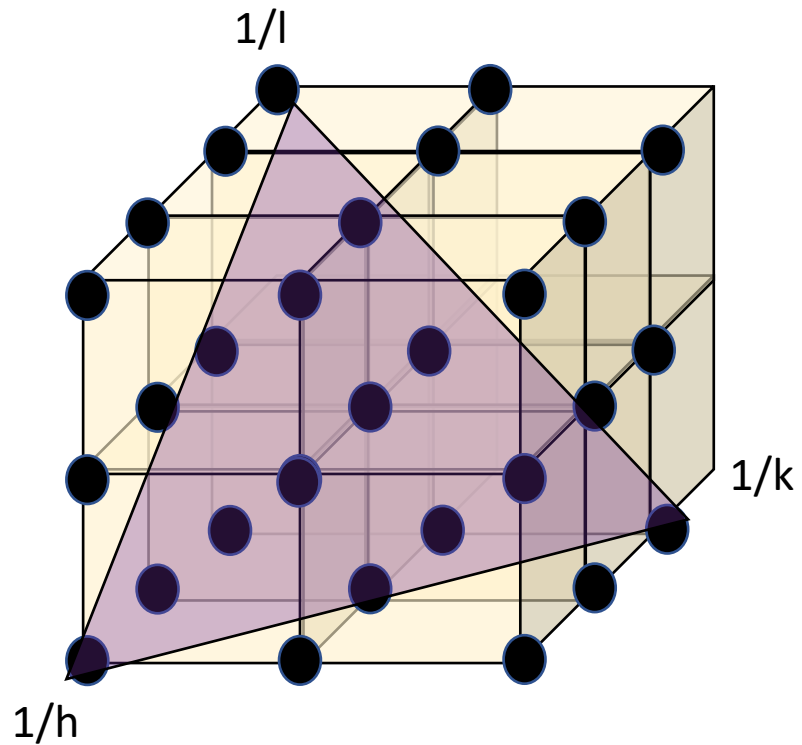
- Any point in RS represents a function with periodicity inverse of its length
- Any point in RL, presents a function with periodicity of real space lattice
- RL vector is perpendicular to the family of planes in the real space

$$b_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

Magnitude of the reciprocal lattice vector
Is equal to the spacing between the family of planes it represents



Let us look at one plane that is perpendicular to G



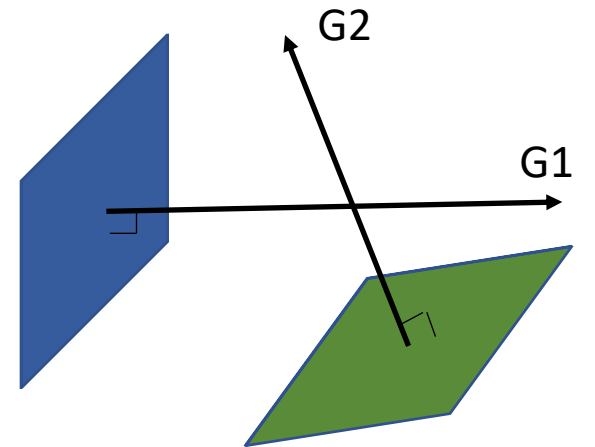
The coordinates of the reciprocal lattice vector is the Miller indices of the planes it represents!

Angle between planes

- If $\vec{G_1} = h_1\vec{b_1} + k_1\vec{b_2} + l_1\vec{b_3}$ represents a plane 1 and $\vec{G_2} = h_2\vec{b_1} + k_2\vec{b_2} + l_2\vec{b_3}$ represents second plane

The angle between the two planes is the angle between the two normal

$$\cos \theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}}$$

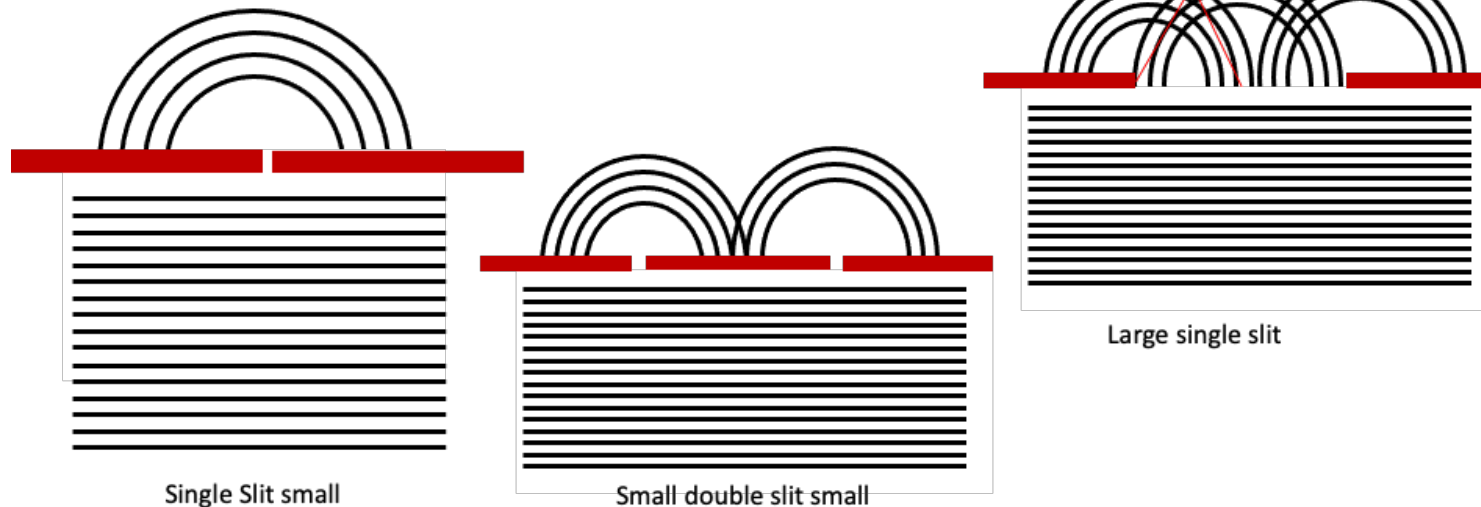


Relation Between RS and Diffraction

Diffraction in Solids

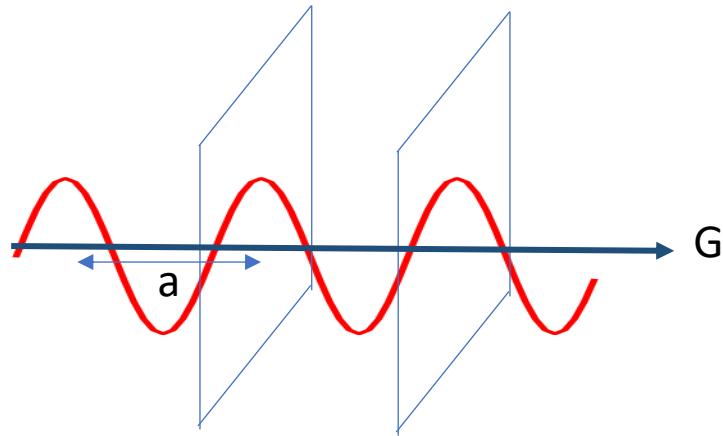
- Typical inter-atomic distance in solids – 1 – 3 Å
- For a wave to diffract, the wavelength should be smaller than the inter-atomic distance
- Energy of photon $E = h\nu = \frac{hc}{\lambda}$
- For $\lambda < 1 \text{ Å}$, $E > 12 \text{ keV}$ is necessary!
- Wave vector $k = \frac{2\pi}{\lambda}$ is the vector direction of the propagation of radiation

Diffraction



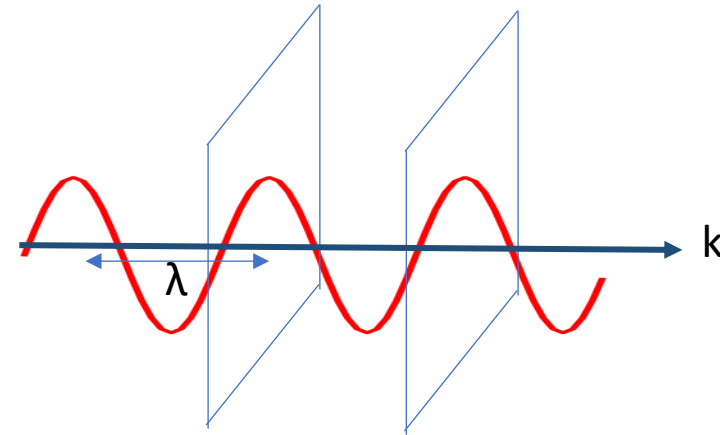
Destructive interference if $\sin\theta \frac{d}{2} = \frac{\lambda}{2}$

Remember the 1D wave and the reciprocal vector



$$G = \frac{2\pi}{a}$$

Wave propagation in free space



$$k = \frac{2\pi}{\lambda}$$

So, both G and k have inverse length units, Both live in reciprocal space!

Both G and K are vectors.

$$G = \frac{2\pi}{d} \hat{G} \text{ and } k = \frac{2\pi}{\lambda} \hat{n}$$

Where $\hat{G}$ and $\hat{n}$ are unit normals

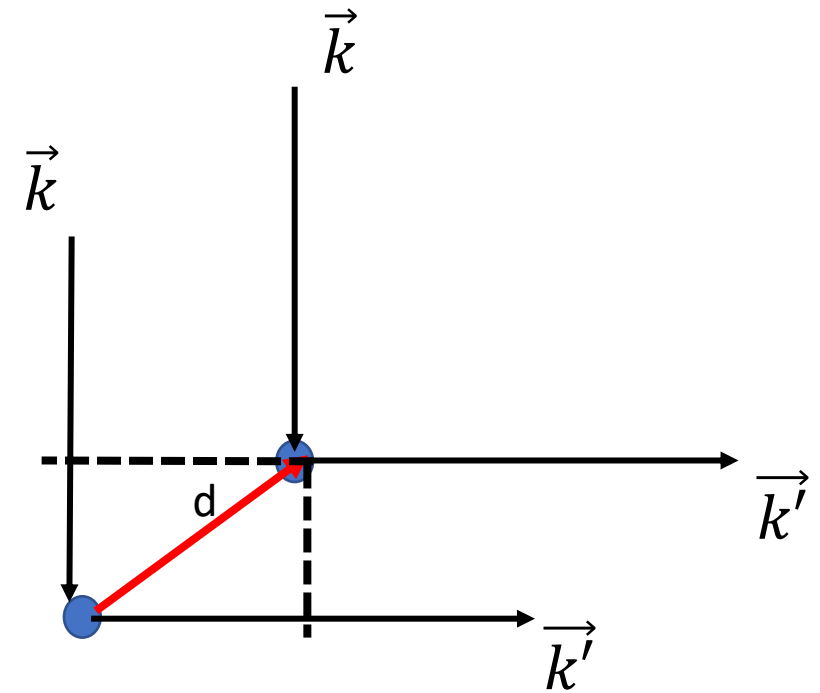
Von Laue Formalism

Consider an X-ray (any wave) of wave vector $\vec{k}$,
Incident on an atom in a crystal.

The wave gets scattered elastically to another wave $\vec{k}'$.

Elastic scattering means $|\vec{k}| = |\vec{k}'| = 2\pi/\lambda$

The wavelength doesn't change. But the direction changes.



A second wave gets scattered from another atom at a distance d from the first one

A constructive interference is observed when the path difference is an integer multiple of λ

Von Laue Formalism

Path difference = AO + OB

$$\overrightarrow{OA} = -\overrightarrow{a_1} \cdot \vec{k}$$

$$\overrightarrow{OB} = \overrightarrow{a_1} \cdot \vec{k}'$$

Total path difference = $\overrightarrow{a_1} \cdot (\hat{n}' - \hat{n})$

For constructive interference

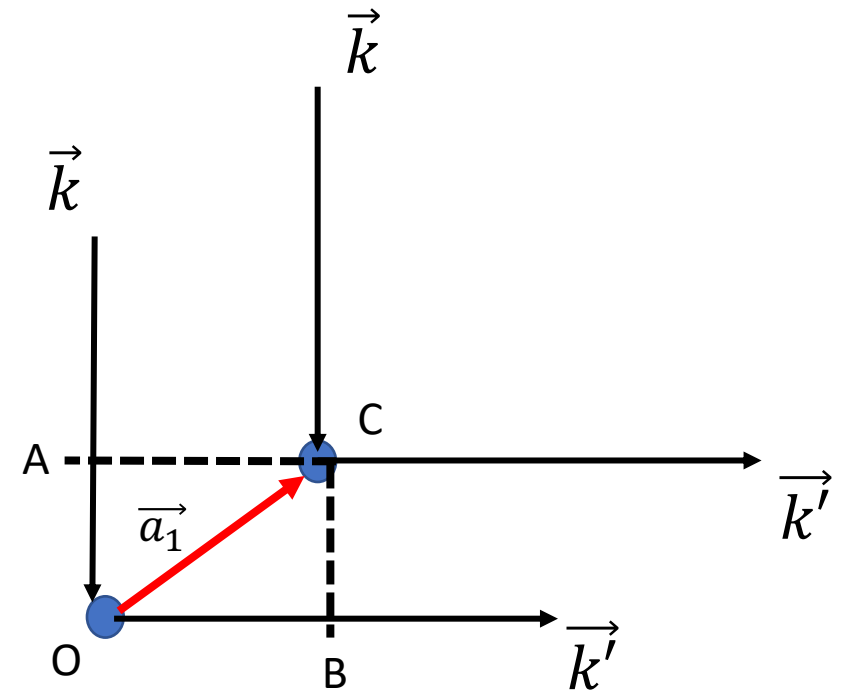
$$\overrightarrow{a_1} \cdot (\hat{n}' - \hat{n}) = m\lambda$$

Where m is any integer

Multiply both sides by $\frac{2\pi}{\lambda}$

$$\overrightarrow{a_1} \cdot \left(\frac{2\pi}{\lambda} \hat{n} - \frac{2\pi}{\lambda} \hat{n}' \right) = 2\pi m$$

$$\overrightarrow{a_1} \cdot (\vec{k}' - \vec{k}) = 2\pi m$$



The same can be extended to 3D array of atoms.
Instead of a single x, now we have R

$$\vec{R} \cdot (\vec{k}' - \vec{k}) = 2\pi m$$

$$\vec{R} \cdot (\vec{k}' - \vec{k}) = 2\pi m$$

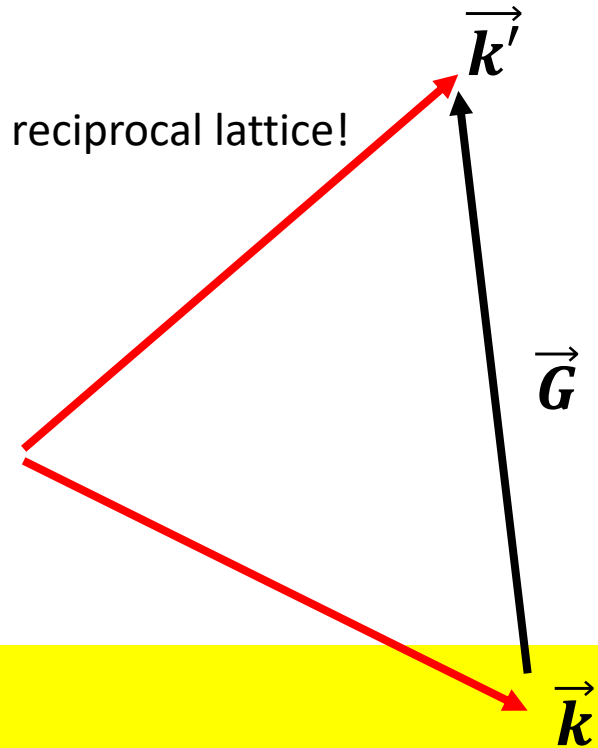
Rise the entire equation to an exponent

$$e^{\vec{R} \cdot (\vec{k}' - \vec{k})} = e^{2\pi m}$$

This equation should now be familiar to you! This is the definition of the reciprocal lattice!

$$e^{\vec{R} \cdot (\vec{k}' - \vec{k})} = e^{\vec{R} \cdot \vec{G}} = 1$$

Where $\vec{G}$ is any reciprocal lattice vector!



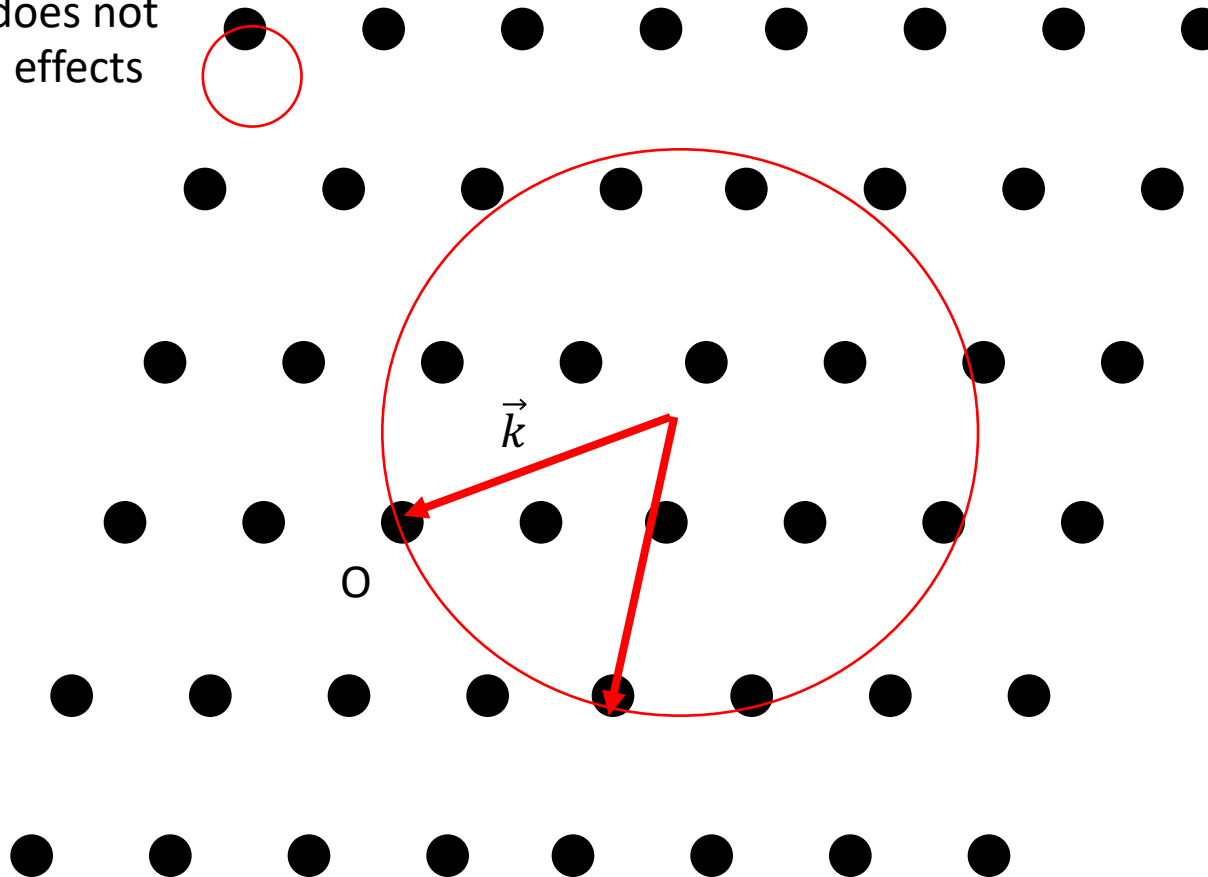
Therefore the condition for constructive interference is

$$(\vec{k}' - \vec{k}) = \vec{G}$$

ie. The difference between the scattered wavevector and the incident wave vector should be a reciprocal lattice vector

Condition for diffraction

Small k , large λ does not show diffraction effects



1. Draw the reciprocal lattice
2. Draw a sphere with radius $=2\pi/\lambda$ of the incident radiation
3. Ensure the sphere touches at least one lattice point. Mark that point as the origin.

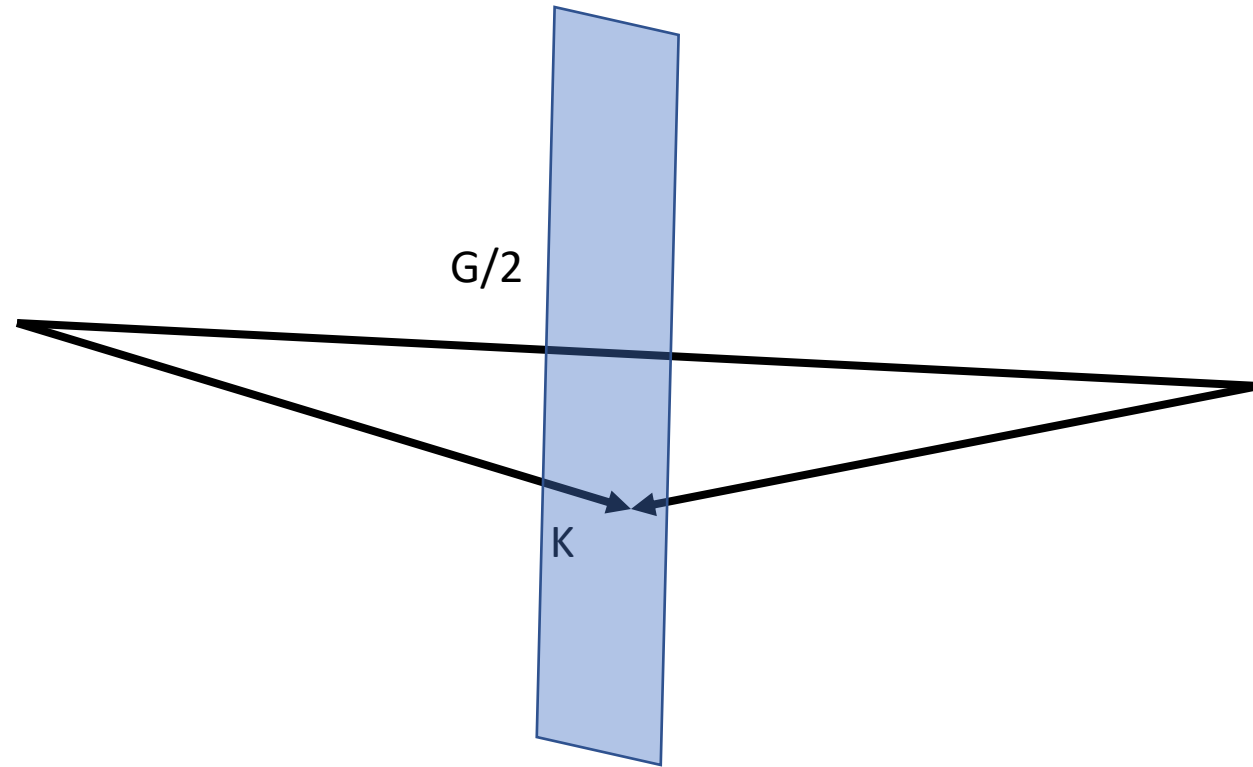
Diffraction condition is met only when the sphere touches any other lattice point.

The vector joining the two touching points gives the family of planes diffracting!

Incident radiation with very small λ (Electron beam in TEM)
Has very large k , and can have multiple simultaneous diffraction.

Homework: 1. Reconcile the Von Laue formalism with Bragg's law.

2. Show that interference is observed when $\vec{k} \cdot \vec{G} = \frac{1}{2} |G|$



Now what happens to atoms in lattices ?

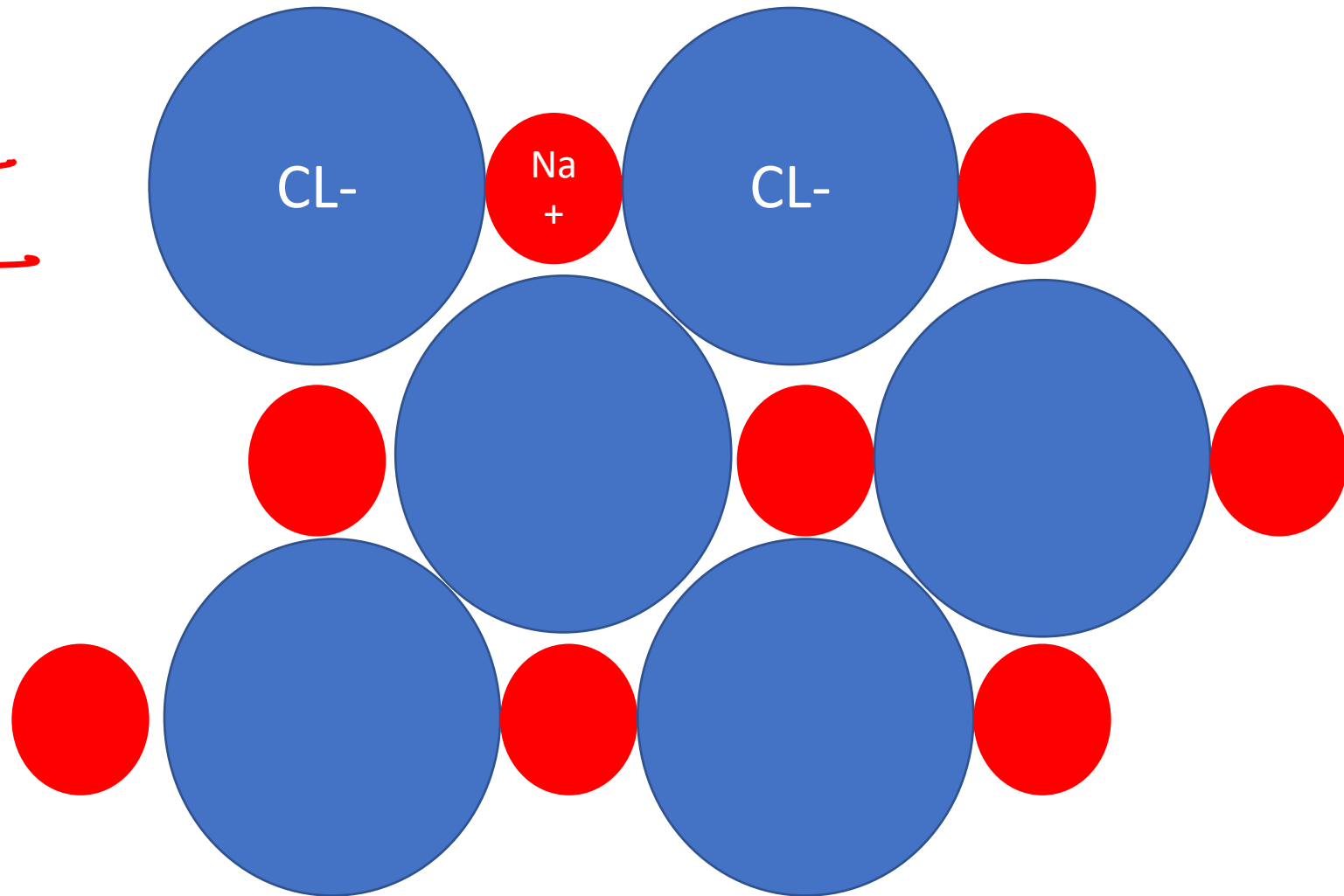
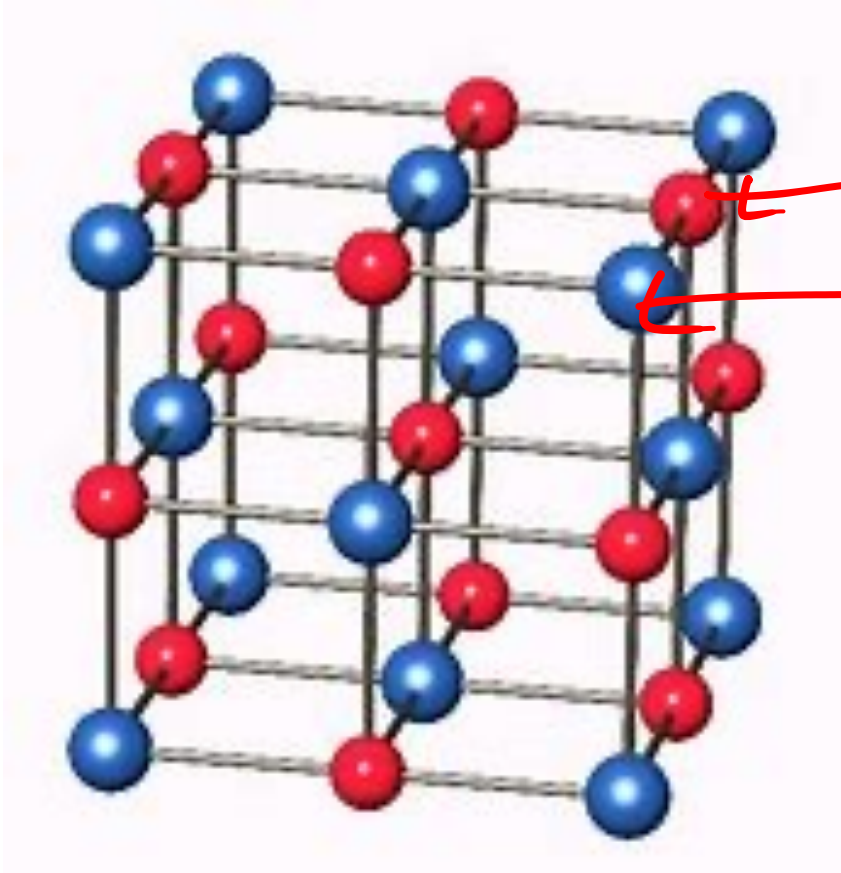
All materials are made up of atoms.

Atoms in crystals have periodicity

So now, what happens in such periodic arrangement of atoms ?

Atoms in periodic lattice

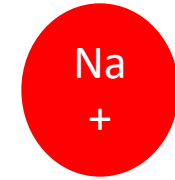
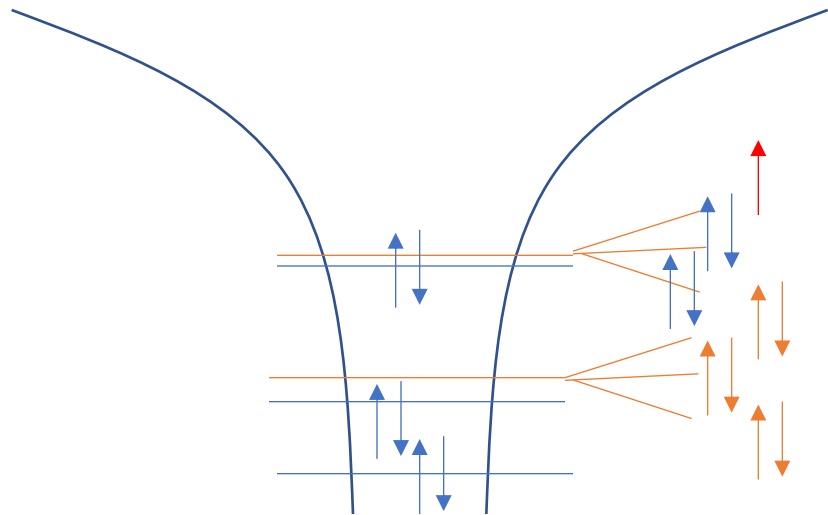
- Structure of NaCl





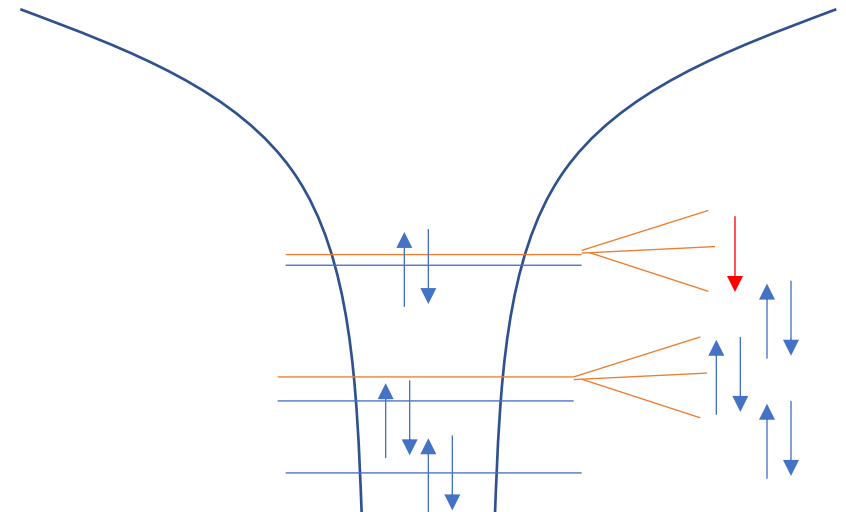
- Chlorine atom has the following atomic configuration for 17 electrons:

$1S^2, 2S^2, 2P^6, 3S^2, 3P^5$

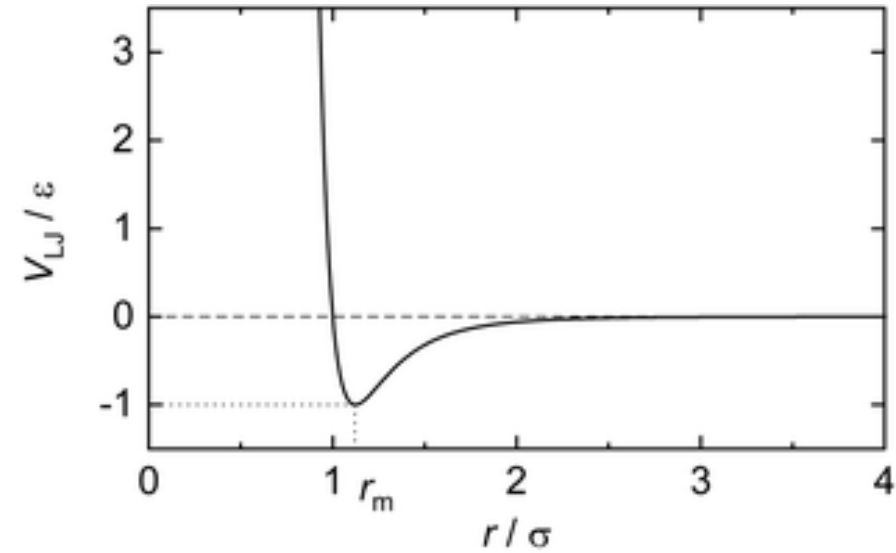
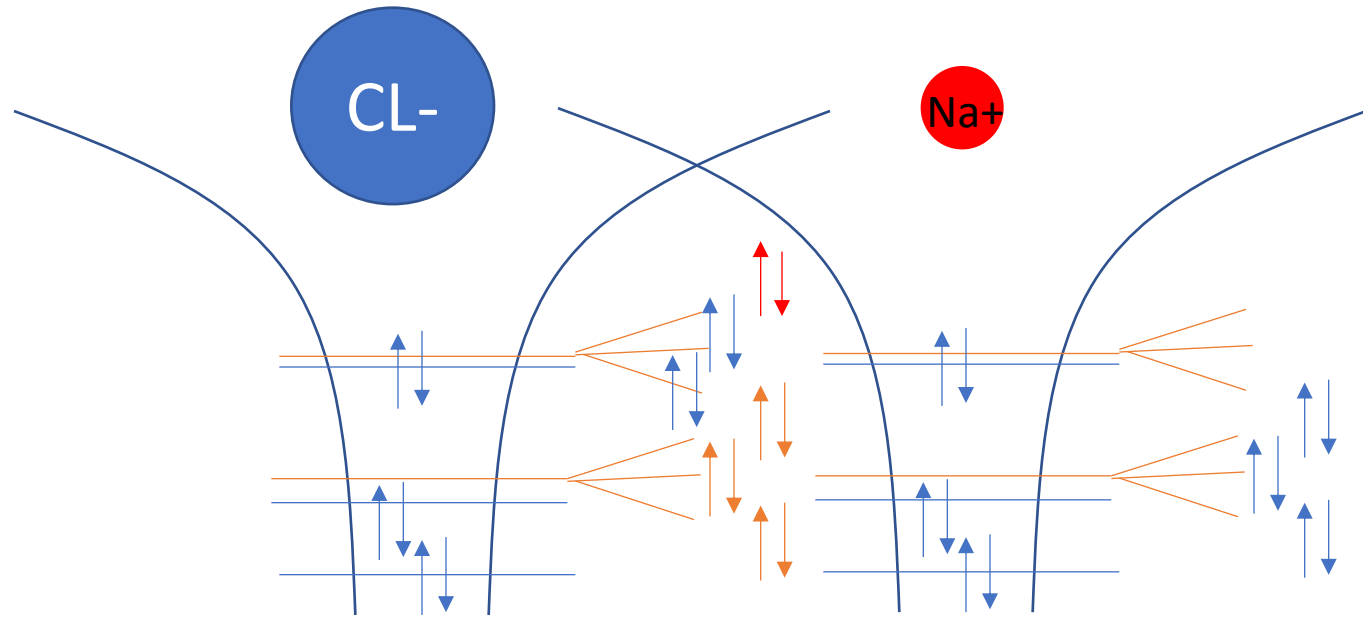


- Na atom has the following atomic configuration for 11 electrons:

$1S^2, 2S^2, 2P^6, 3S^1$

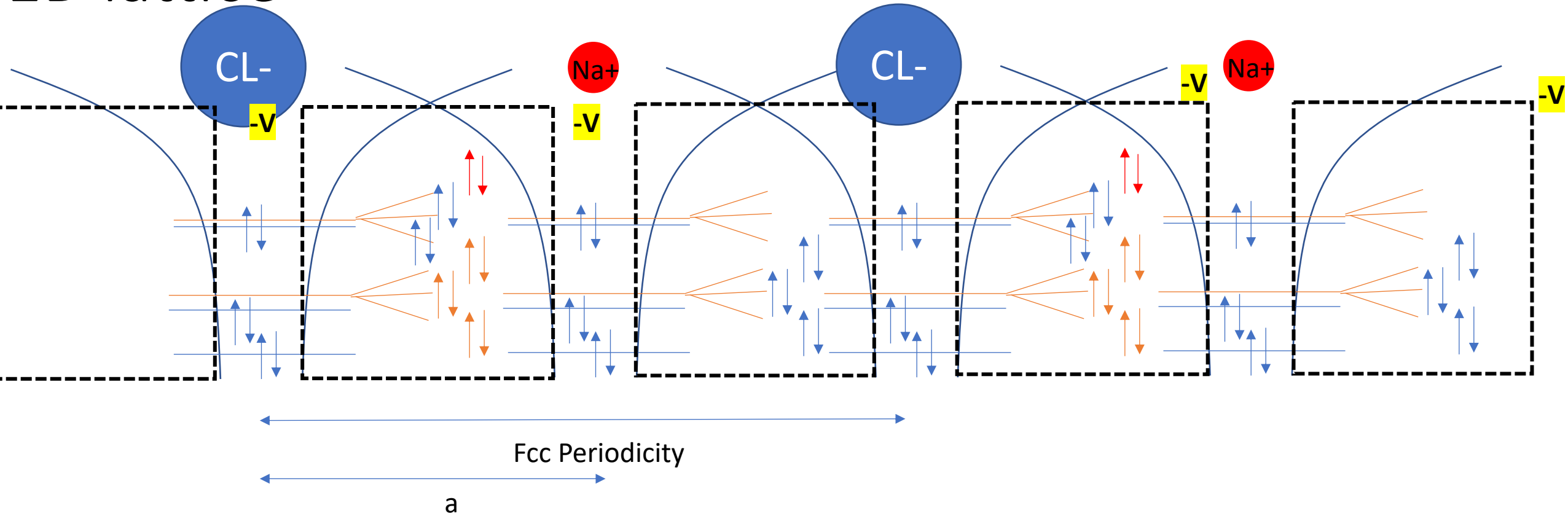


So what happens when they are brought together?



- Sodium donates an electron to reach a stable orbital configuration, but carries a positive charge
- Chlorine takes an electron to form a stable configuration, taking an overall negative charge
- Strong Coulomb attraction is felt by the two atoms with opposite charges
- Electron – Electron repulsion between the outer-most electronic orbitals, ion core – ion core repulsion also works to increase the interatomic distance
- Lennard Jones potential $V = C \left[\frac{1}{r^{12}} - \frac{1}{r^6} \right]$. The minimum determines the atomic separation

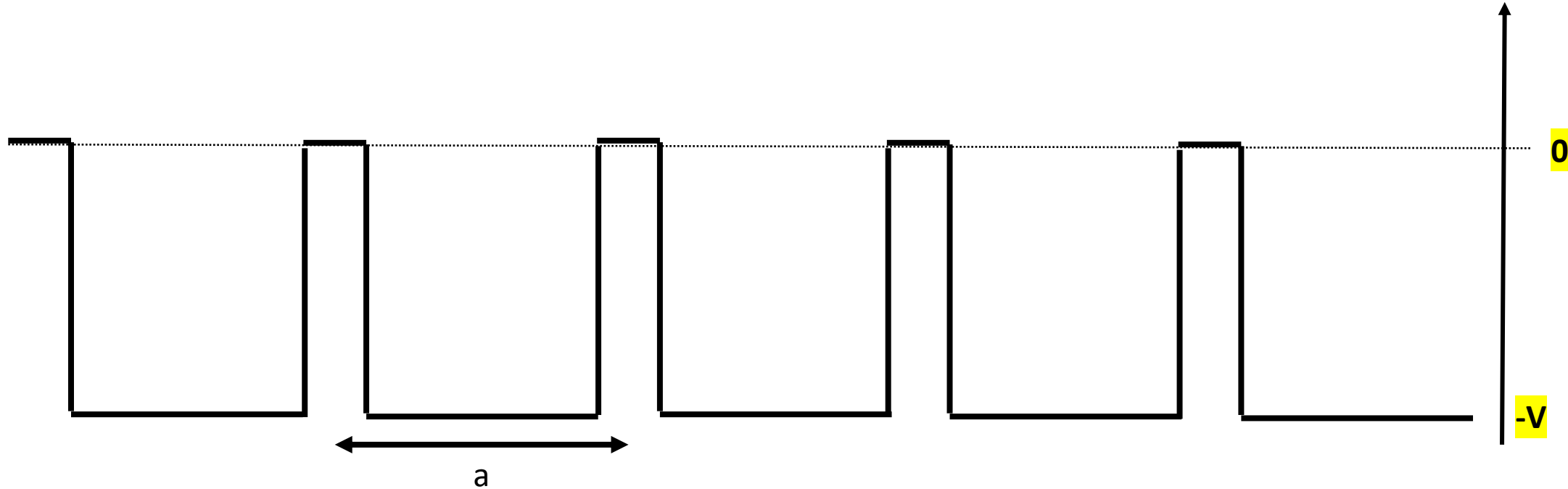
1D lattice



Atom with a motif at each lattice point

- At the center of the atom core, the electrons experience an attractive force with negative potential ($-V$)
- Between the atoms, the potential is significantly reduced and the electrons behave as it is almost free.
- The potential profile can be approximated to a train of rectangles

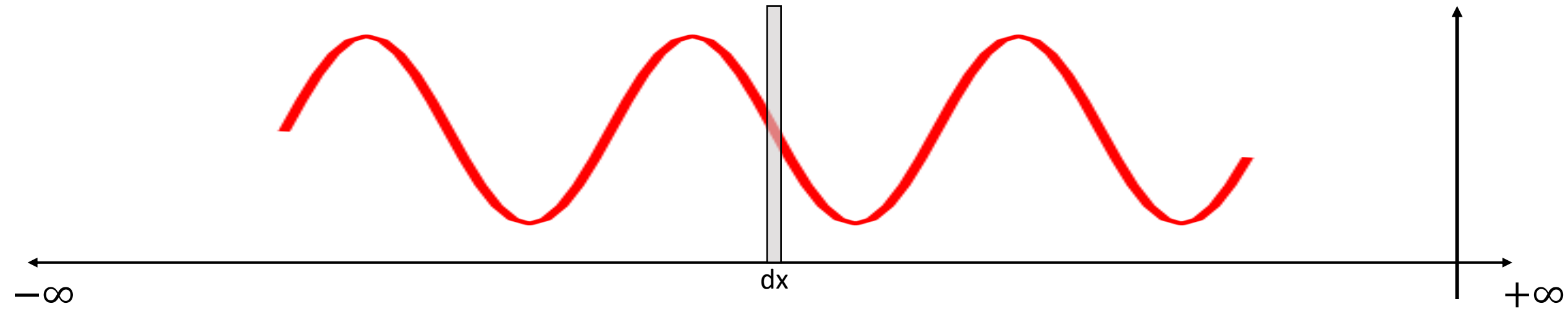
Approximated potential profile in a 1D lattice



- The approximated potential profile is a linear chain
- Potential energies are relative. A fixed value can be added to all potential values. So, for sake of convenience, the scales are shifted by V
- The behavior of an electron in a potential profile is determined by Quantum mechanics.
- As per de Broglie, electrons must be considered to be a wave as well as a particle

Electron wave which is free

What is the ordinate/Y axis ?



In quantum mechanics, all properties of an electron is determined by a function: Wave function

Wave function, represented by $|\psi(x, t)\rangle$, is a complex function such that $|\psi^2(x, t)|dx$ is the probability to find the electron at $x - (x+dx)$, and at time t

Equation that governs the electron wavefunction is the Schrodinger's equation

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi = -\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi$$

A case of free electron

- Let us consider a totally free electron. No potentials!

$$V(x) = 0 \text{ everywhere}$$

Substituting the potential in the S.E.

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi = -\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} + (0)\psi$$

Splitting the time dependence and spatial dependence

$$\psi(x, t) = \psi(x)\psi(t)$$

Now you have two equation

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi$$

and

$$-\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$$

Where E is the total energy

Solutions are obtained by guessing and substitution

$$\psi(t) = Ae^{-\frac{iEt}{\hbar}}$$

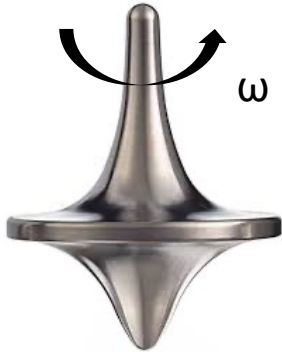
$$\psi(x) = Ce^{-ikx}$$

What is the physical significance ?

$$\psi(t) = Ae^{-\frac{iEt}{\hbar}}$$

$$\psi(t) = Ae^{-i\omega t} \text{ where } \omega = \frac{E}{\hbar}$$

A top with higher Energy spins faster



Sinusoids in time. Repeats every T secs

So we represent $\omega = \frac{2\pi}{T}$, where T is the period of rotation.
And ω is called as frequency.

$$\psi(x) = Ce^{ikx}$$

See the similarity ?

K is called as spatial frequency

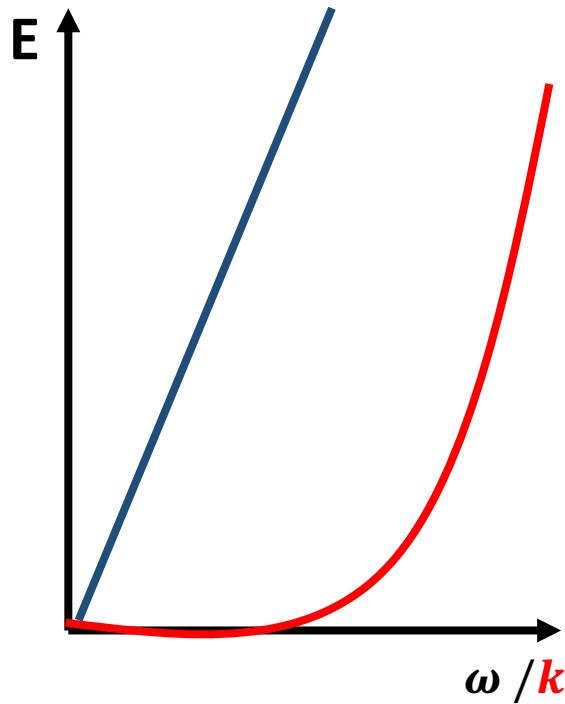
Substitute the solution in Schrodinger's equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = \frac{\hbar^2 k^2}{2m} (Ce^{ikx})$$

Comparing this with the Eigen equation

$$H\psi = E\psi$$

$$\text{We get the energy } E = \frac{\hbar^2 k^2}{2m}$$



- The relationship between energy and ω is linear because of the first order differential in time
- The relationship between energy and k is quadratic because of the second order differential in space

This is the consequence of the Schrodinger's wave equation

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi = -\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi$$

Therefore, a total free electron has the form $\psi(x, t) = A e^{ikx} e^{-i\omega t}$

From our previous argument, $P(x) = |\psi(x, t)|^2$ gives the probability to find an electron at time t

$P(x) = A^2$ is the probability to find an electron in space.

This is a constant! So, you have equal probability to find an electron in all of space

Wavefunctions in 3D

$$\psi(r) = e^{iK \cdot r}$$

$$K = \{k_x, k_y, k_z\} \text{ and } r = \{x, y, z\}$$

$$\psi(x, y, z, t) = e^{ixk_x} \cdot e^{iyk_y} \cdot e^{izk_z} \cdot e^{-i\omega t}$$

Energy of a free electron in 3D space

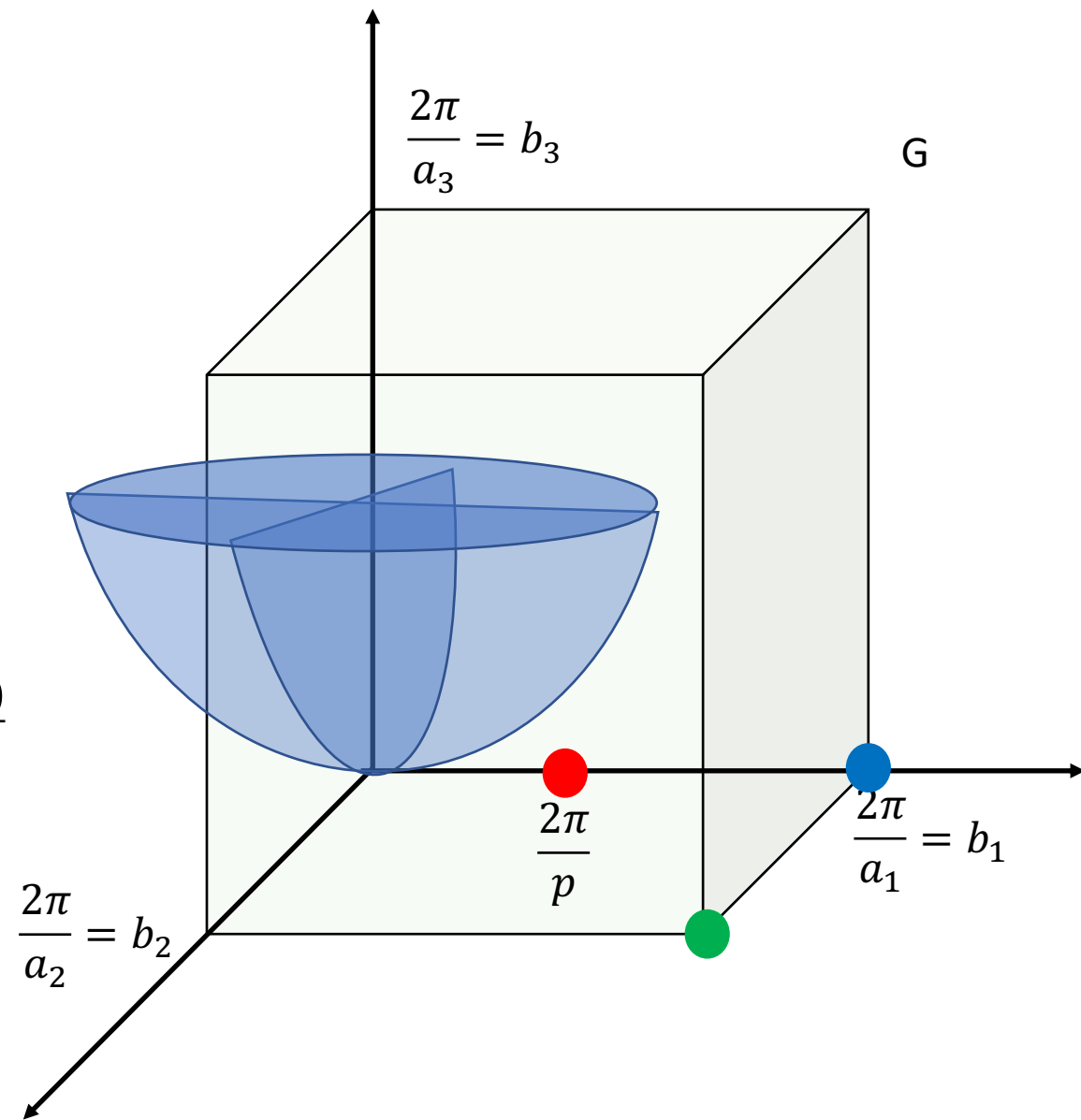
$$\text{Energy } E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m}$$

A free electron can have any energy from 0 to infinity and the corresponding wave vectors.

There are infinite solutions to the Schrodinger's equation.

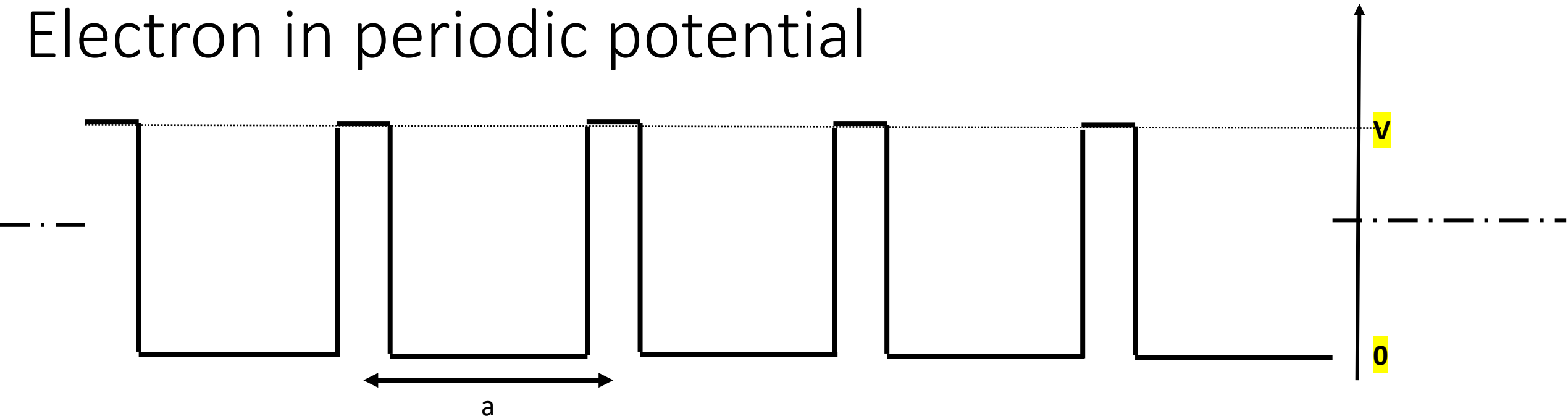
All of them being plane waves!

The energy is related to the wavevector squared!



k, K lives in Reciprocal space!

Electron in periodic potential



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

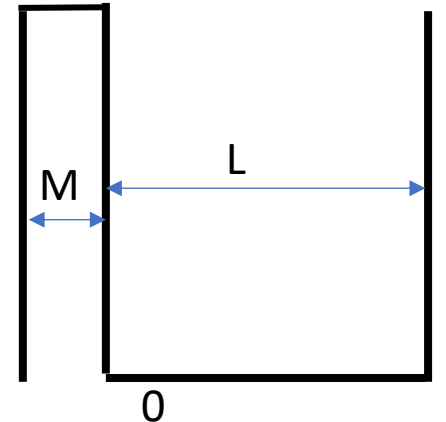
We use the oldest of tricks: Divide and conquer. We divide the space into two regions A and B.

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

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

In a crystal lattice:

Any function should have the lattice periodicity!



Kronig - Penney Model

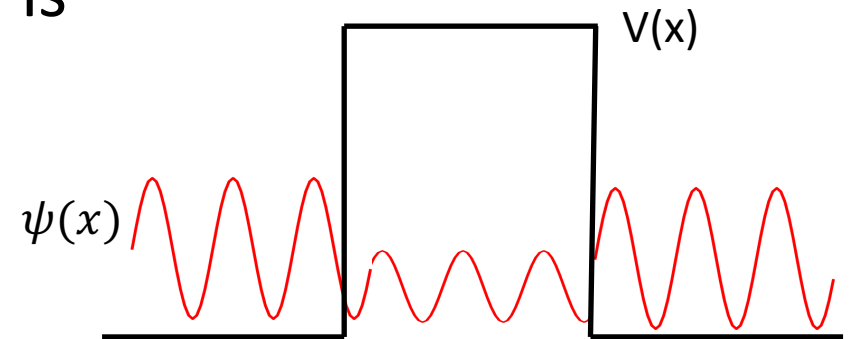
- Bloch's theorem:

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



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

$$u_k'' + 2iku_k' + (\alpha^2 - k^2)u_k = 0$$

$$\alpha^2 = \frac{2mE}{\hbar^2}$$

Substitute $u_k(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$

Boundary conditions: $u_k(x=0) = u_k(x=0)$ and $u_k(x=L) = u_k(x=-M)$

$u_k'(x=0) = u_k'(x=0)$ and $u_k'(x=L) = u_k'(x=-M)$

Four equations and four unknowns:

Solution is obtained when

$$\begin{vmatrix} 1 & 1 & -1 & -1 \\ e^{i(\alpha-k)L} & e^{-i(\alpha+k)L} & -e^{-i(\beta-ik)M} & -e^{i(\beta+ik)M} \\ i(\alpha-k) & -i(\alpha+k) & -i(\beta-ik) & i(\beta+ik) \\ i(\alpha-k)e^{i(\alpha-k)L} & -i(\alpha+k)e^{-i(\alpha+k)L} & -i(\beta-ik)e^{-i(\beta-ik)M} & i(\beta+ik)e^{i(\beta+ik)M} \end{vmatrix} = 0$$

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

$$u_k'' + 2iku_k' - (\beta^2 + k^2)u_k = 0$$

$$\beta^2 = \frac{2m(V-E)}{\hbar^2}$$

Substitute $u_k(x) = Ce^{i\beta x} + Be^{-i\beta x}$

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta M \sin \alpha L + \cosh \beta M \cos \alpha L = \cos k(L + M)$$

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta M \sin \alpha L + \cosh \beta M \cos \alpha L = \cos k(a)$$

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

