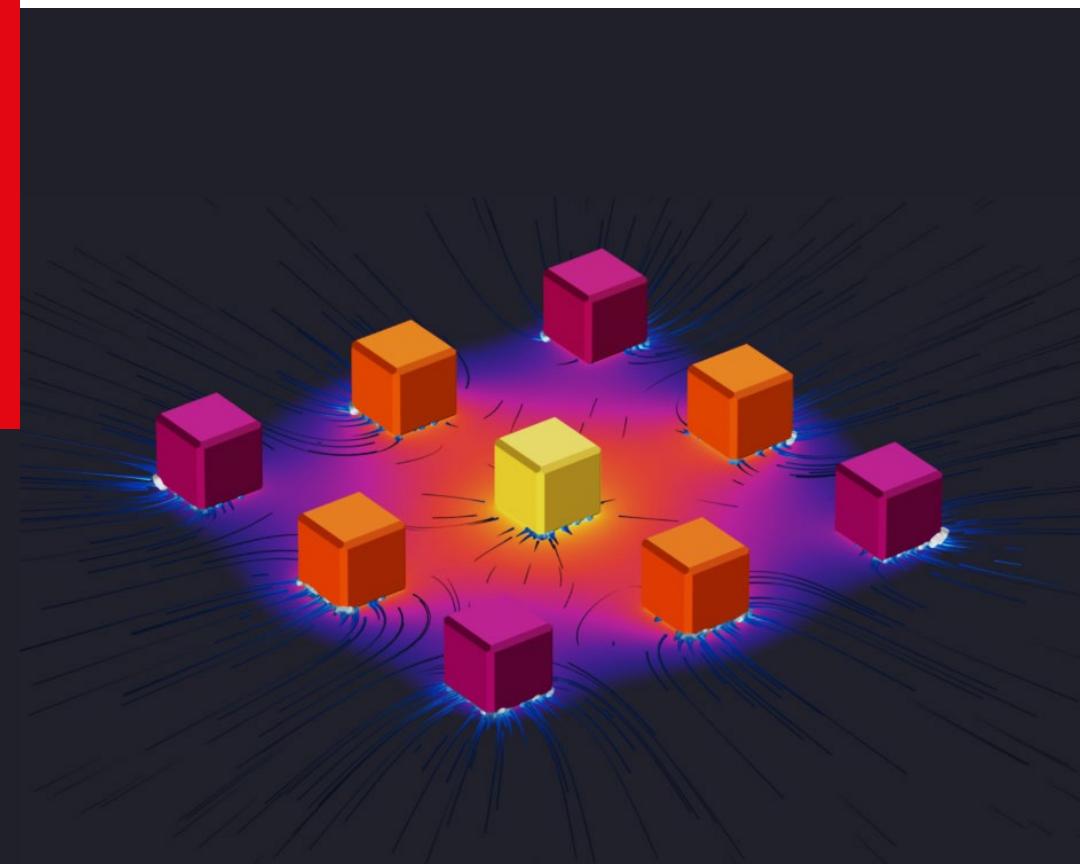


# Nanoscale Heat Transfer (and Energy Conversion)

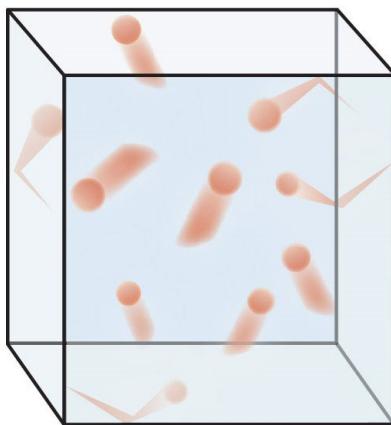
## ME469

*Instructor:* Giulia Tagliabue

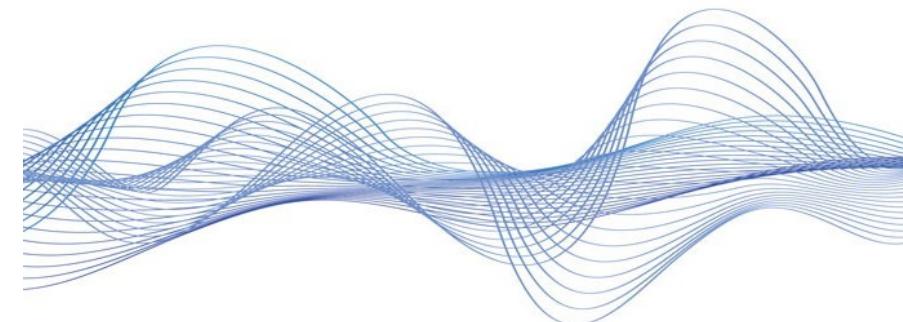


# Wave-particle Duality

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



Particle View



Wave View

Energy



$$E = h\nu = \hbar\omega$$



Frequency, Amplitude

Momentum



$$p = \hbar k = \frac{h}{\lambda}$$



Wavevector

$$h = 6.6 \cdot 10^{-34} \text{ Js}$$

$$\hbar = h/2\pi$$

# Describing the Material Waves – The Schrodinger Equation\* **EPFL**

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

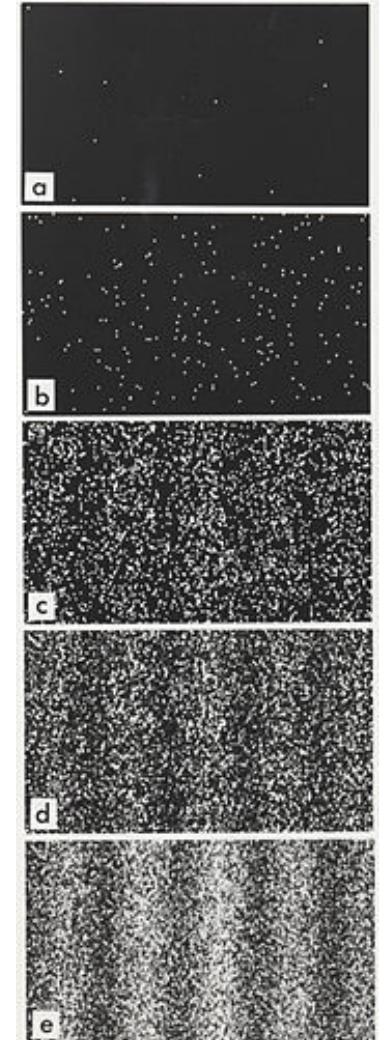
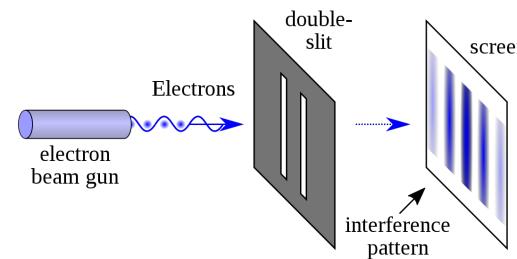
$$\int_{-\infty}^{+\infty} \Psi_t \Psi_t^* dx = 1$$

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

Steady-state Schrodinger equation (eigenvalue equation)

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

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



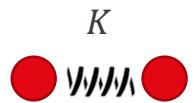
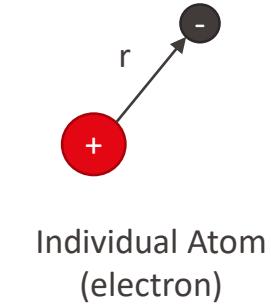
\*Normally we would model the physics and derive the equations. Here we proceed in the opposite way.

We start from the equation and we show that the physics that follows corresponds to the observed physical phenomena

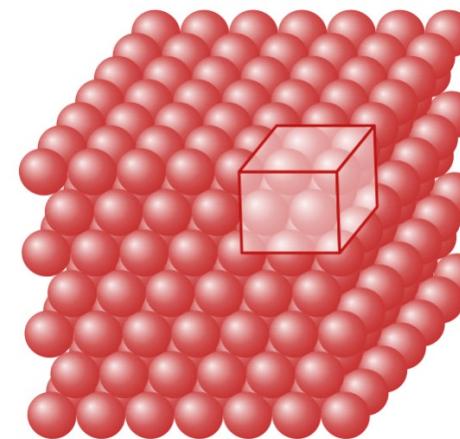
# Summary of Solutions of Schrodinger Equation

|                            | Potential   | Wavefunction  | Energy Levels   | Quantum Numbers | Degeneracy           |
|----------------------------|---|---|---|-----------------|----------------------|
| Free Particle              | $U = 0$   | $\Psi_t = Ae^{-i(\omega t+kx)} + Be^{-i(\omega t-kx)}$<br>$k = \sqrt{(2mE/\hbar^2)}$  | $E = \frac{\hbar^2}{2m} k^2$  | -               | -                    |
| 1D Infinite Potential Well | $U = 0$ for $0 < x < L$<br>$U = \infty$ 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                |   | $Y_l^m(\theta, \varphi) = \varepsilon i^l \left[ \frac{(2l+1)(l- m )!}{4\pi(l+ m )!} \right]^{1/2} P_l^{ m } \cos\theta e^{im\varphi}$  | $E_l = \frac{\hbar^2}{2I} l(l+1)$   | $l, m$          | $2l+1$               |
| Hydrogen Atom (3D)         | $U = -\frac{Ze^2}{4\pi\epsilon_0 r}$                            | $\Psi_{n,l,m}(r, \theta, \varphi) = R_{n,l}(r) Y_l^m(\theta, \varphi)$  | $E_n = -\frac{Z^2 e^4 \mu}{8\epsilon_0^2 n^2 \hbar^2}$  | $n, l, m$       | Depends on n         |

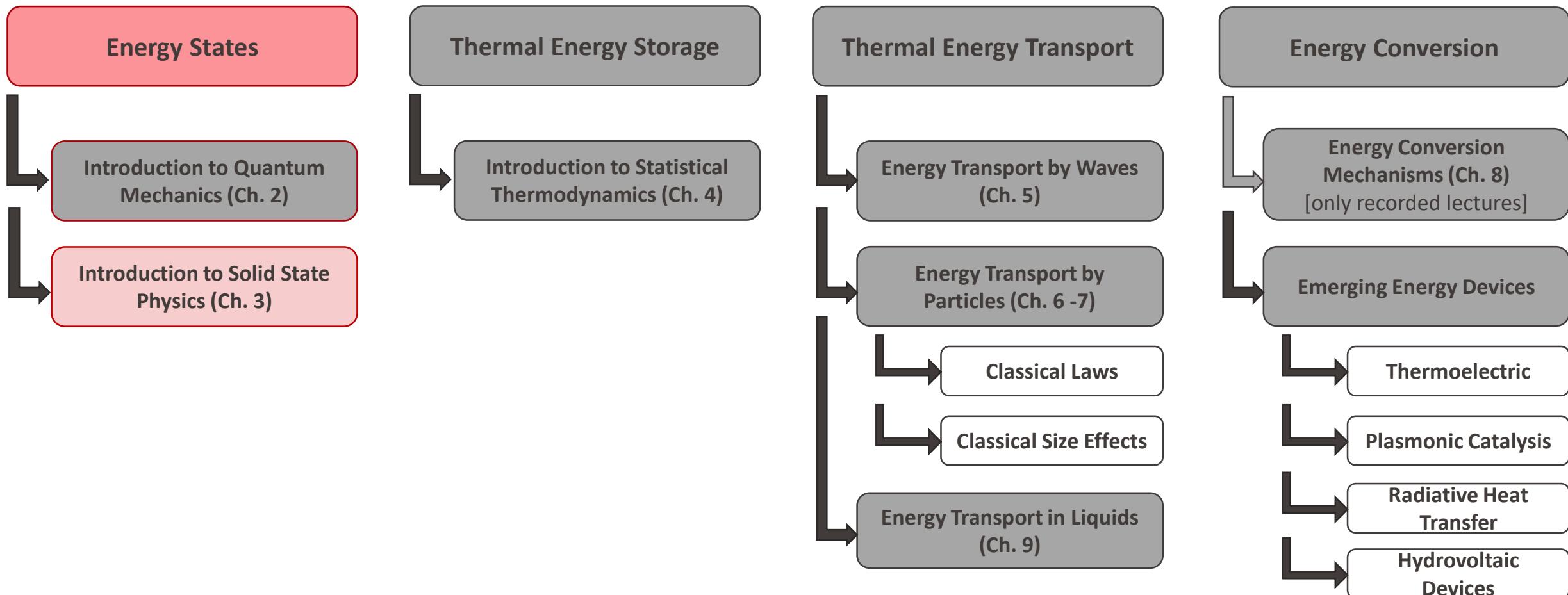
# From Individual Elements to Periodic Arrangements



Individual Molecule  
Single pair of Particles  
(phonons)



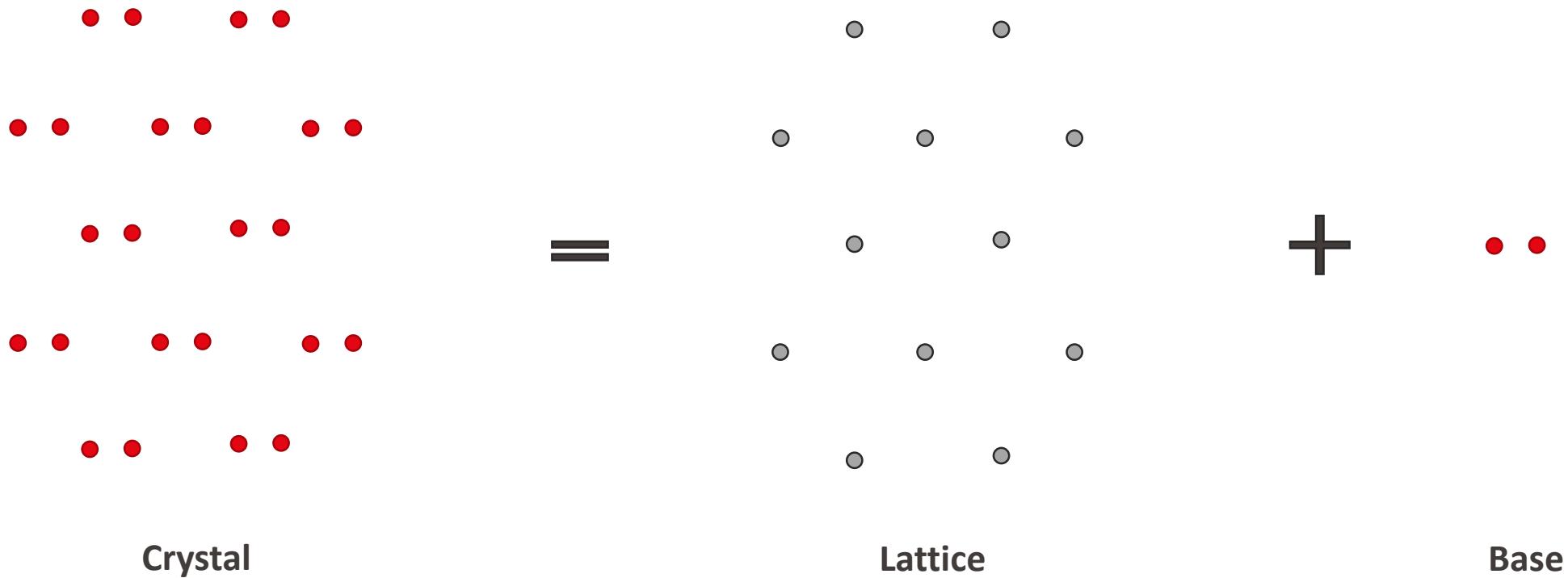
## Nanoscale Heat Transfer (and Energy Conversion)



# In This Lecture...

- **Crystal Structure, the Real and Reciprocal Lattice, Miller Indices**
- Electron Energy States in Periodic Lattices – Intro to Periodic Potential

# Crystal Structure and the Real Lattice



A crystal is a 3D periodic arrangement of atoms.

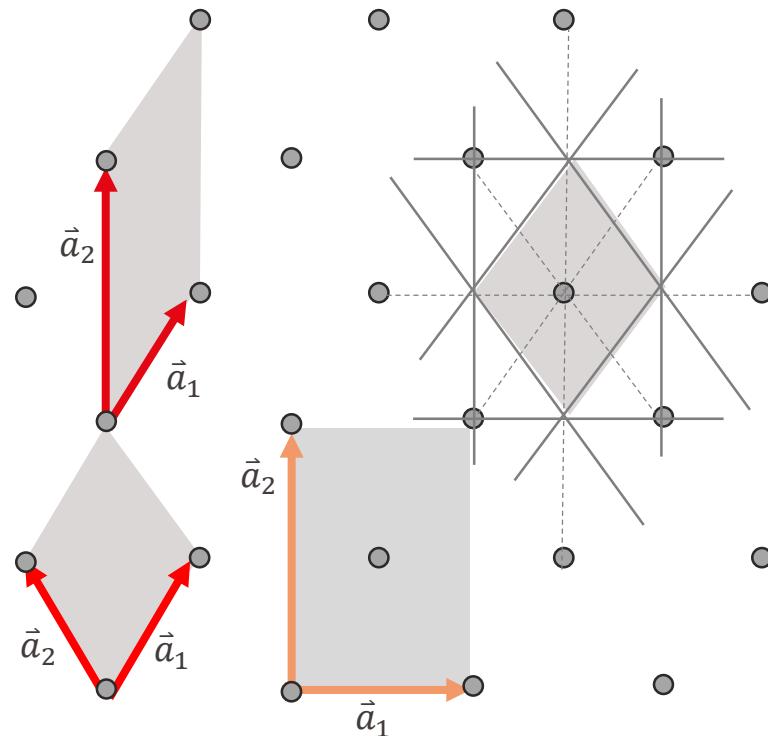
To describe it we use a **lattice**, i.e. a periodic array of points that replicates the periodicity.

Importantly, the periodicity of the crystal structure might become apparent only if we consider the regular repetition of a group of more than one atom. This is called the **base**.

Crystal = lattice + base

# 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:

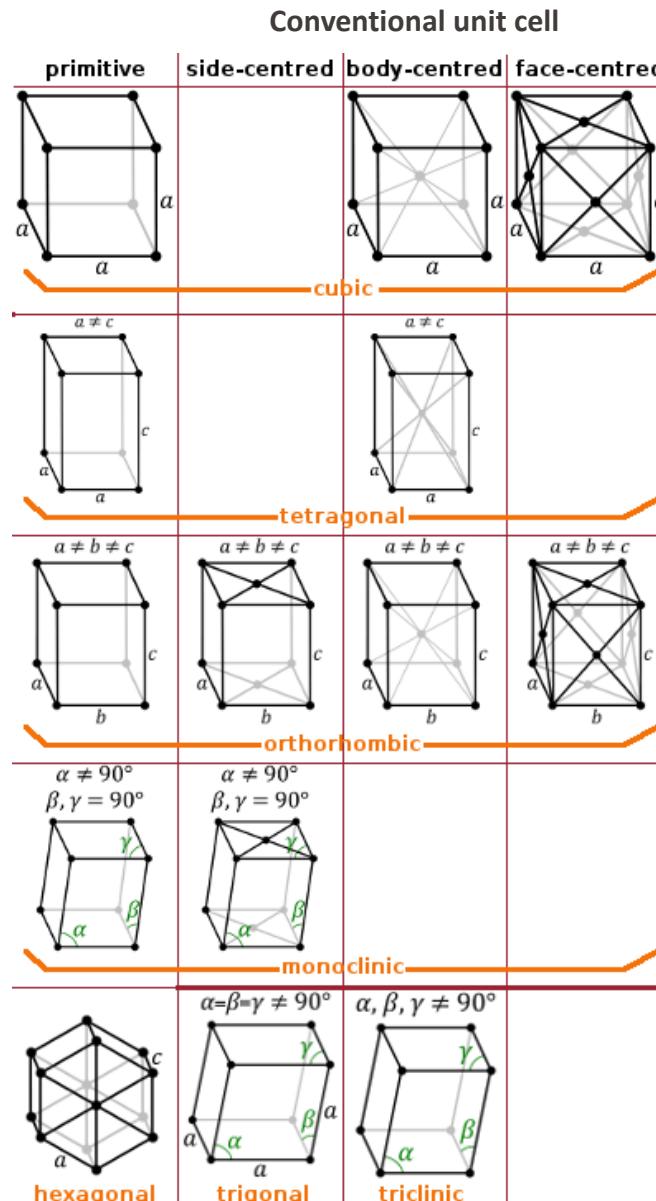
$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

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.

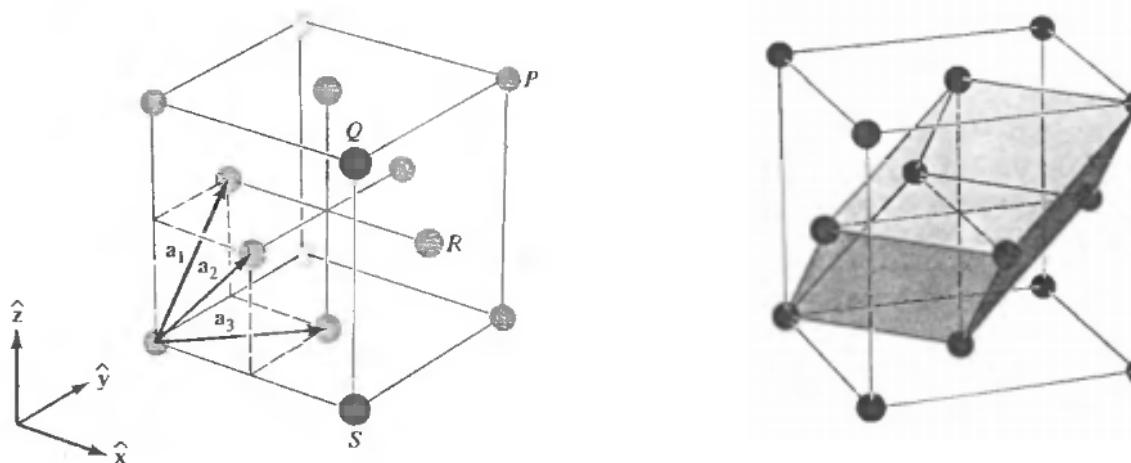
A construction that always ensures we have identified a primitive unit cell is the Wigner-Seitz construction. It consists in connecting all neighboring points surrounding an arbitrary lattice point and then to draw the bisecting plane perpendicular to each connection line.

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.

# Crystal Structure and the Real Lattice



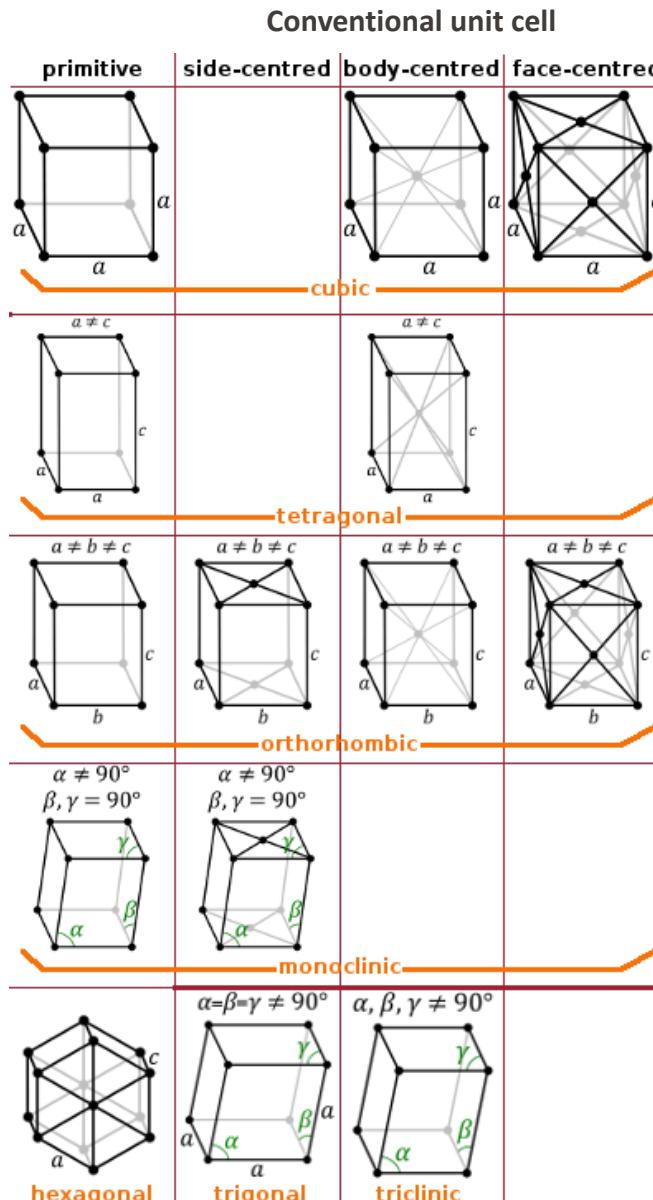
- There are **14 types of Bravais lattice** with varying degrees of symmetry (side lengths and angles)
- The fundamental requirements that the primitive cell can fill the **ENTIRE** space limits the rotational symmetries to  $2\pi, \pi, 2\pi/3, \pi/2$  and  $\pi/3$
- For each lattice we can identify the primitive vectors and the Wigner-Seitz Primitive cell.
  - E.g. for the face centered cubic (FCC) lattice



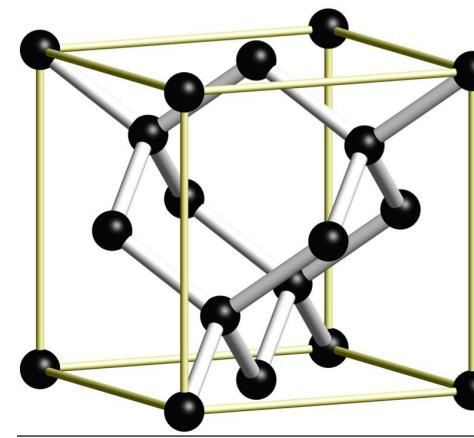
$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}).$$

- Elements such as Ag, Au, Al, Cu crystallize with FCC structure

# Crystal Structure and the Real Lattice



- There are **14 types of Bravais lattice** with varying degrees of symmetry (side lengths and angles)
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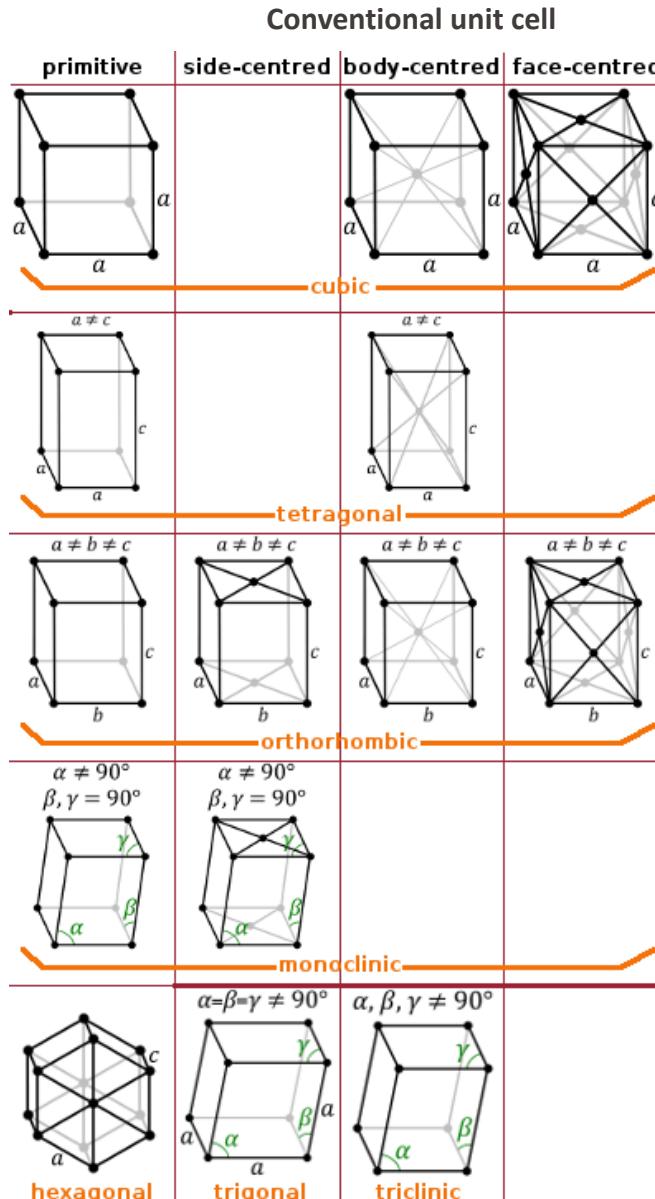
$$\mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y}).$$

Base atoms : 0 and  $a/4(\hat{x} + \hat{y} + \hat{z})$

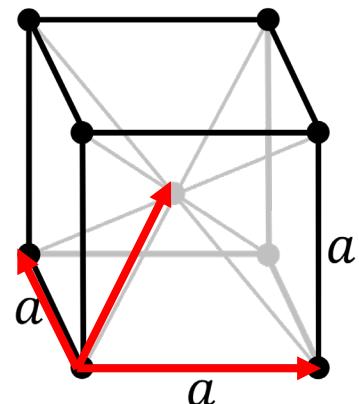
→ Zincblende structure

- Elements such as Ag, Au, Al, Cu, Pd, Pt, Rh crystallize with FCC structure
- A diamond structure is an FCC with a 2-atom base whose coordinates
- Elements such as C, Si, Ge crystallize with diamond structure
- A Zincblende structure is like a diamond structure but the two atom forming the base are different
- Elements such as GaAs, GaP, SiC, CdS, crystallize with Zincblende structure

# Crystal Structure and the Real Lattice



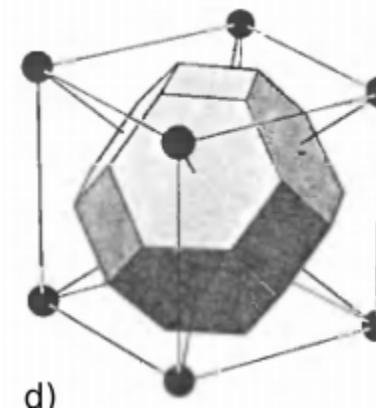
- There are **14 types of Bravais lattice** with varying degrees of symmetry (side lengths and angles)
- The fundamental requirements that the primitive cell can fill the ENTIRE space limits the rotational symmetries to  $2\pi, \pi, 2\pi/3, \pi/2$  and  $\pi/3$
- For each lattice we can identify the primitive vectors and the Wigner-Seitz Primitive cell.
  - For the **body centered cubic (BCC)** lattice



$$\vec{a}_1 = a \hat{x}$$

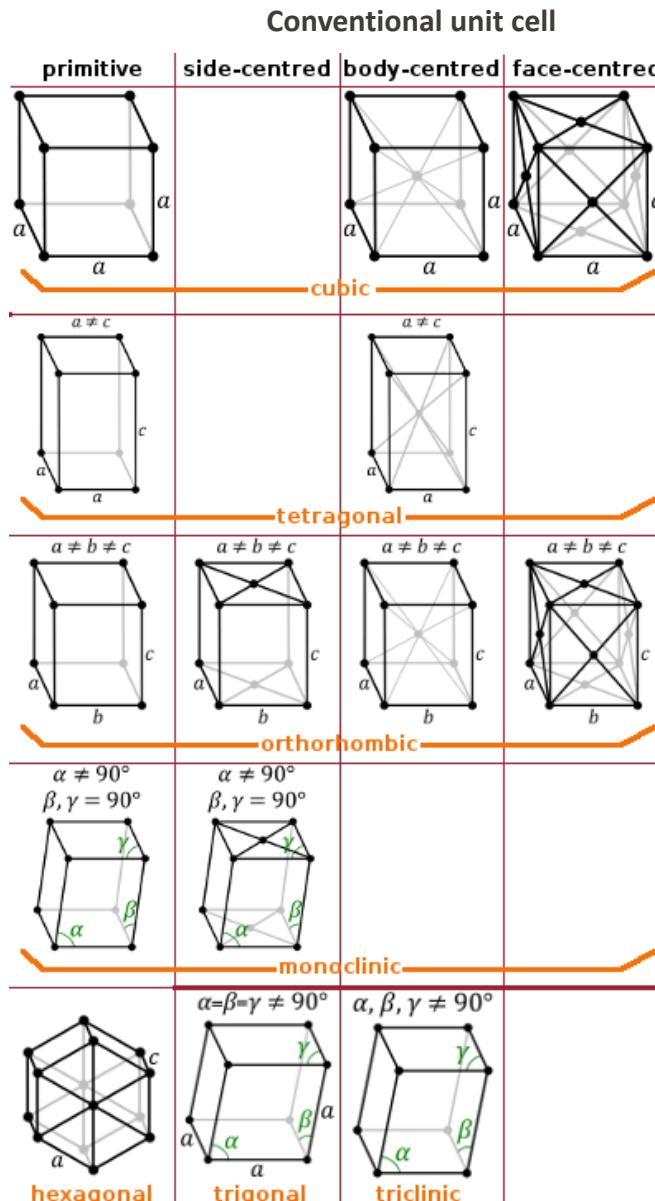
$$\vec{a}_2 = a \hat{y}$$

$$\vec{a}_3 = \frac{a}{2} (\hat{x} + \hat{y} + \hat{z})$$

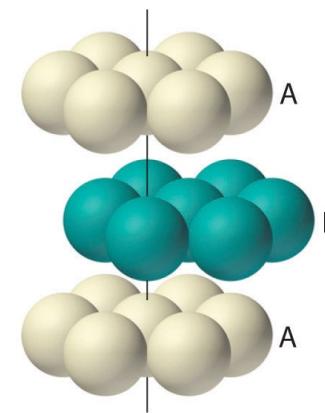


- Elements such as Cr, Fe, K, Li, Mo, Na, W crystallize with body centered cubic (BCC)

# Crystal Structure and the Real Lattice

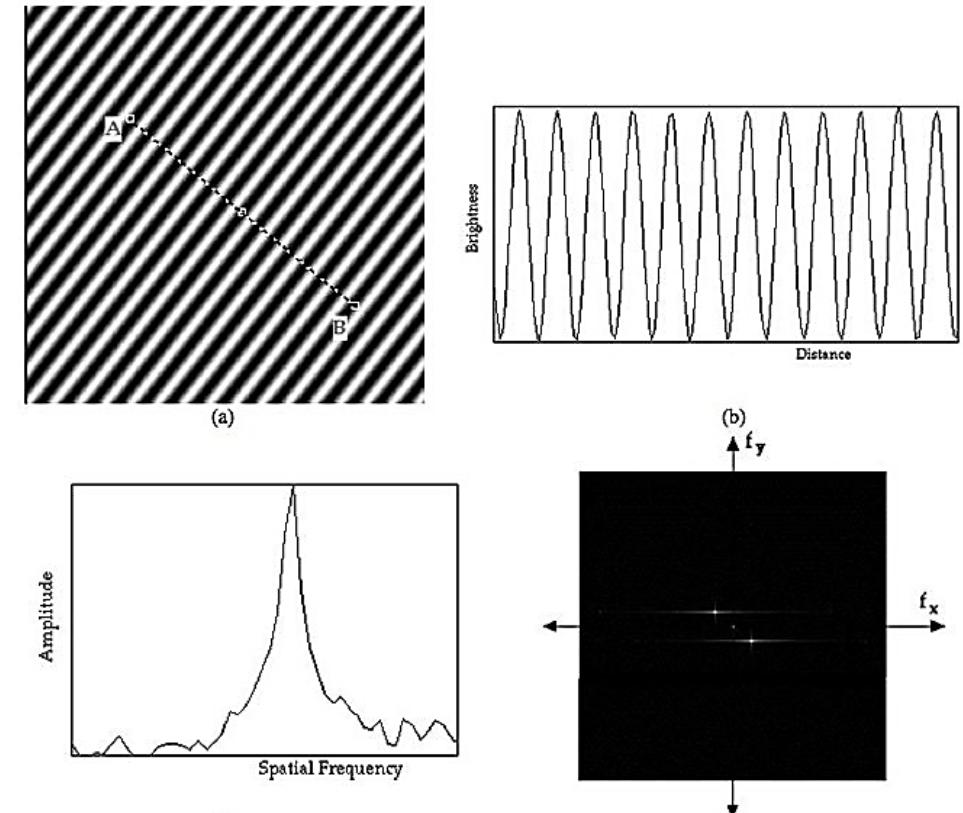
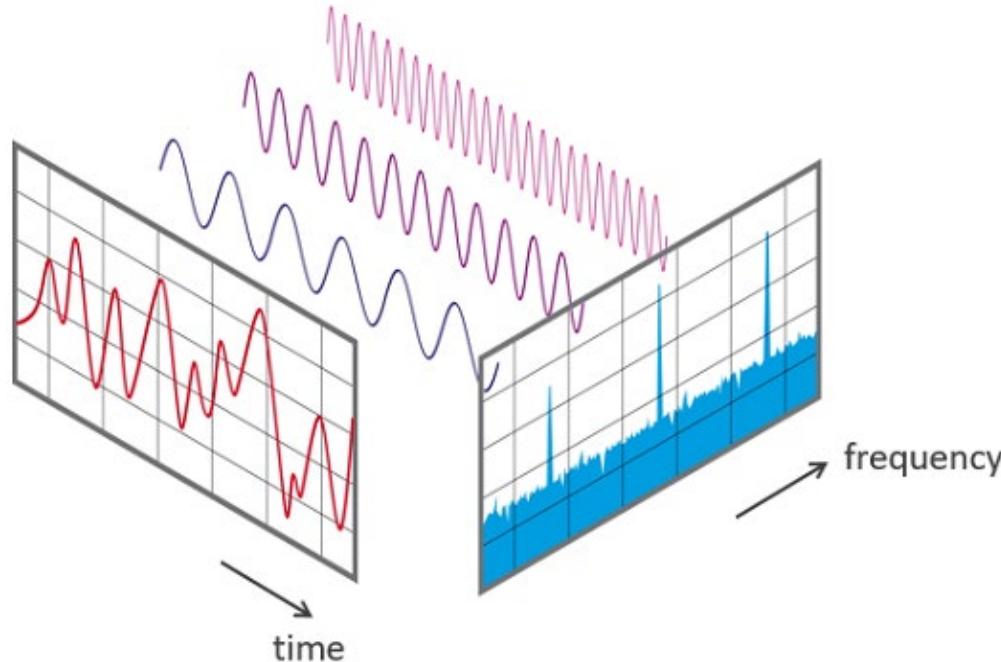


- There are **14 types of Bravais lattice** with varying degrees of symmetry (side lengths and angles)
- The fundamental requirements that the primitive cell can fill the **ENTIRE** space limits the rotational symmetries to  $2\pi, \pi, 2\pi/3, \pi/2$  and  $\pi/3$
- Another important lattice structure is the hexagonal closed-pack structure. This is **NOT** a Bravais lattice but can be obtained as two interpenetrating simple hexagonal Bravais lattices.



- Elements such as Mg, Hf, Ru, Ti, Zn crystallize with hexagonal closed-packed structure

# Fourier Transforms and the Reciprocal Lattice



- It is often convenient to calculate the Fourier transform of a signal (temporal or spatial) to identify the frequencies contained in it.
- Considering that a lattice is a periodic structure, by calculating its Fourier transform we can identify the fundamental frequencies that compose it

# Fourier Transforms and the Reciprocal Lattice

We remember that a periodic function  $f(x)$  with spatial period  $a$  can be expressed as:

$$f(x) = \sum_{n=-\infty}^{\infty} (a_n \sin \frac{2\pi n}{a} x + b_n \cos \frac{2\pi n}{a} x) = \sum_{n=-\infty}^{\infty} (a'_n e^{ink_x} + b'_n e^{-ink_x}) = \sum_{n=-\infty}^{\infty} (a'_n - i b'_n) e^{ink_x}$$

where  $k_x = \frac{2\pi}{a}$

If we now consider a 3D function that is invariant with any translational lattice vector  $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$

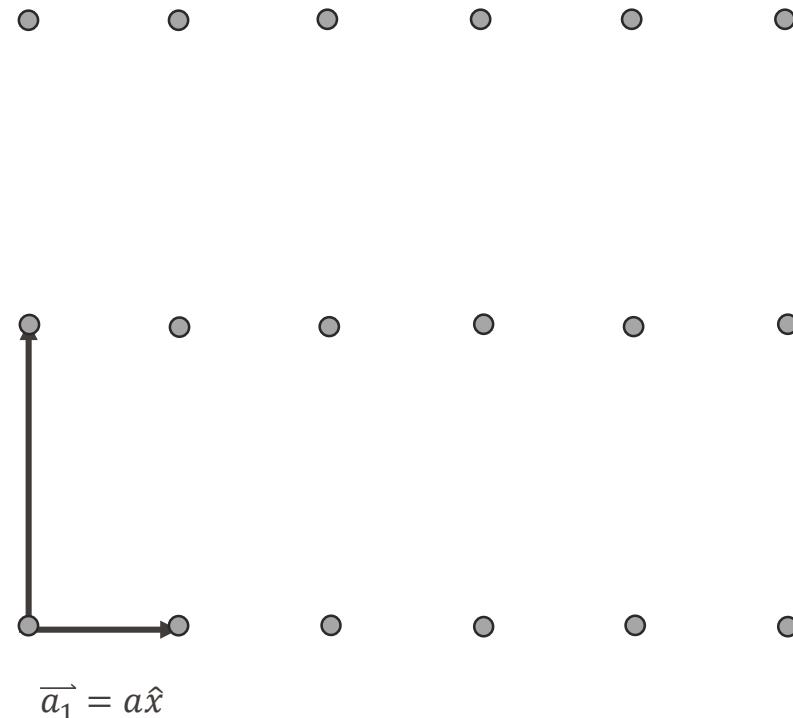
$$f(\vec{r}) = \sum_{\vec{G}} f_G e^{i\vec{r} \cdot \vec{G}} \quad \text{where} \quad \vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \quad f_G = \frac{1}{V} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{r} \cdot \vec{G}}$$

Because of the periodicity:  $f(\vec{r}) = \sum_{\vec{G}} f_G e^{i\vec{r} \cdot \vec{G}} = \sum_{\vec{G}} f_G e^{i(\vec{r} + \vec{R}) \cdot \vec{G}} = f(\vec{r} + \vec{R}) \quad \Rightarrow \quad e^{i\vec{R} \cdot \vec{G}} = 1 \quad \Rightarrow \quad \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

Thus we have:  $\vec{a}_2 \cdot \vec{b}_1 = 0 \quad \Rightarrow \quad \vec{b}_1 = c \vec{a}_2 \times \vec{a}_3$       In addition:  $\vec{a}_1 \cdot \vec{b}_1 = 2\pi \quad \Rightarrow \quad c = \frac{2\pi}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$

We can thus define:  $\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$        $\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$        $\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$       where  $V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$

# Fourier Transforms and the Reciprocal Lattice

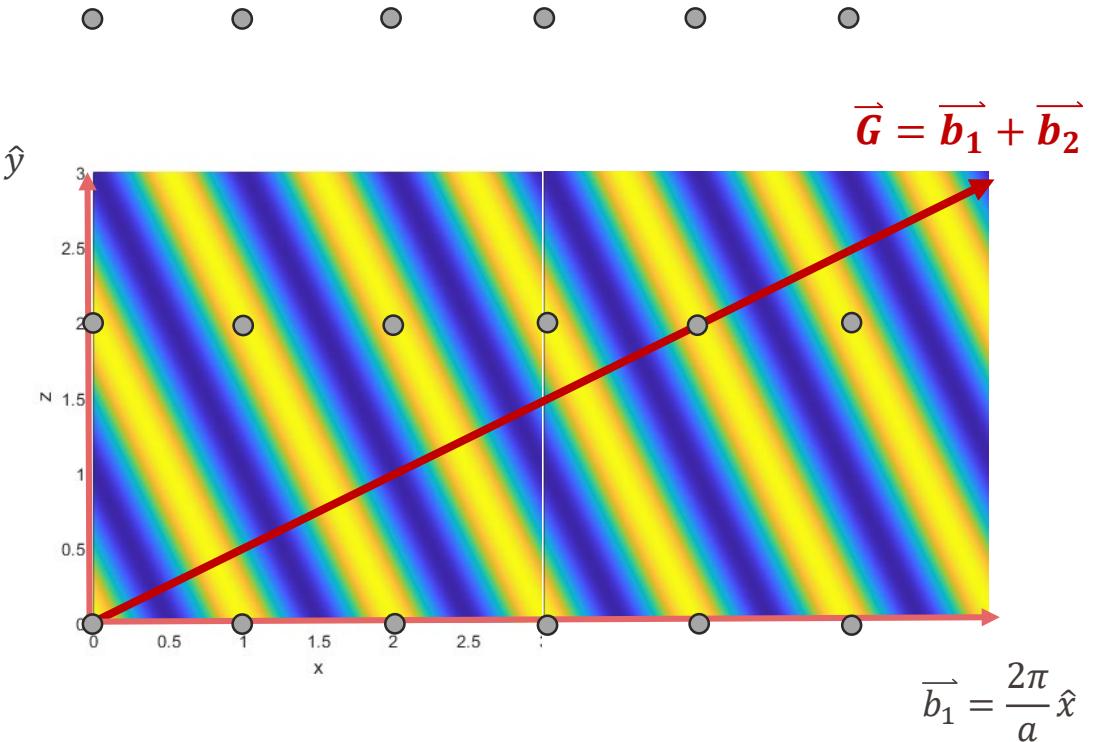


$$\vec{b}_2 = \frac{2\pi}{2a} \hat{y}$$

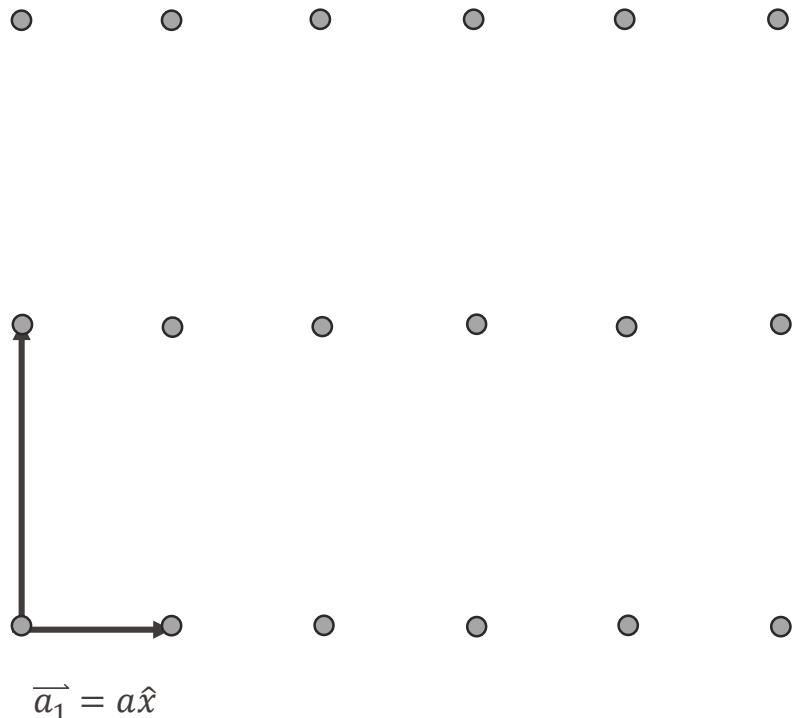
$$\vec{a}_1 \cdot \vec{b}_1 = 2\pi \rightarrow \vec{b}_1 = \frac{2\pi}{a} \hat{x}$$

In 2D we simply have :

$$\vec{a}_2 \cdot \vec{b}_2 = 2\pi \rightarrow \vec{b}_2 = \frac{2\pi}{2a} \hat{y}$$



# Fourier Transforms and the Reciprocal Lattice

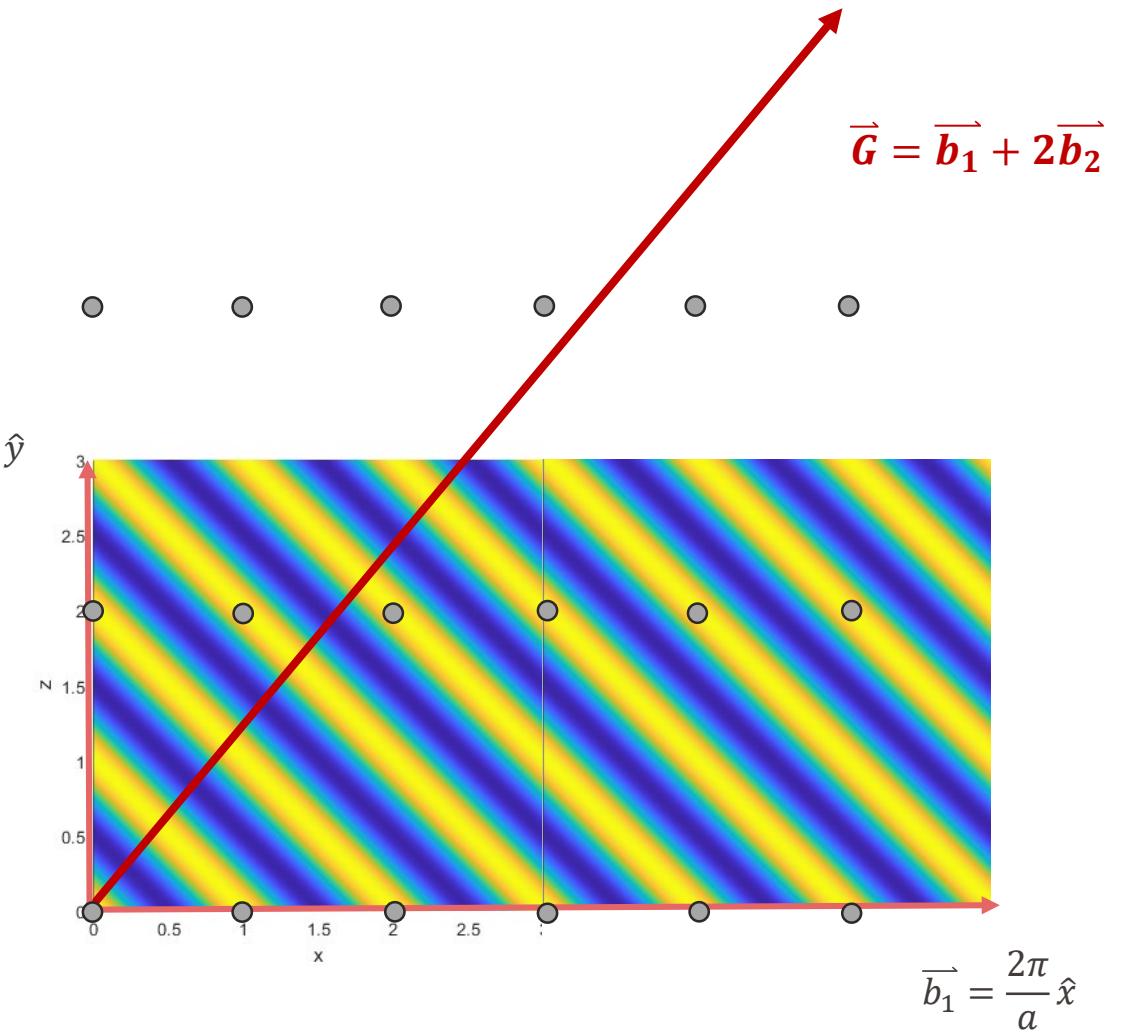


$$\vec{b}_2 = \frac{2\pi}{2a} \hat{y}$$

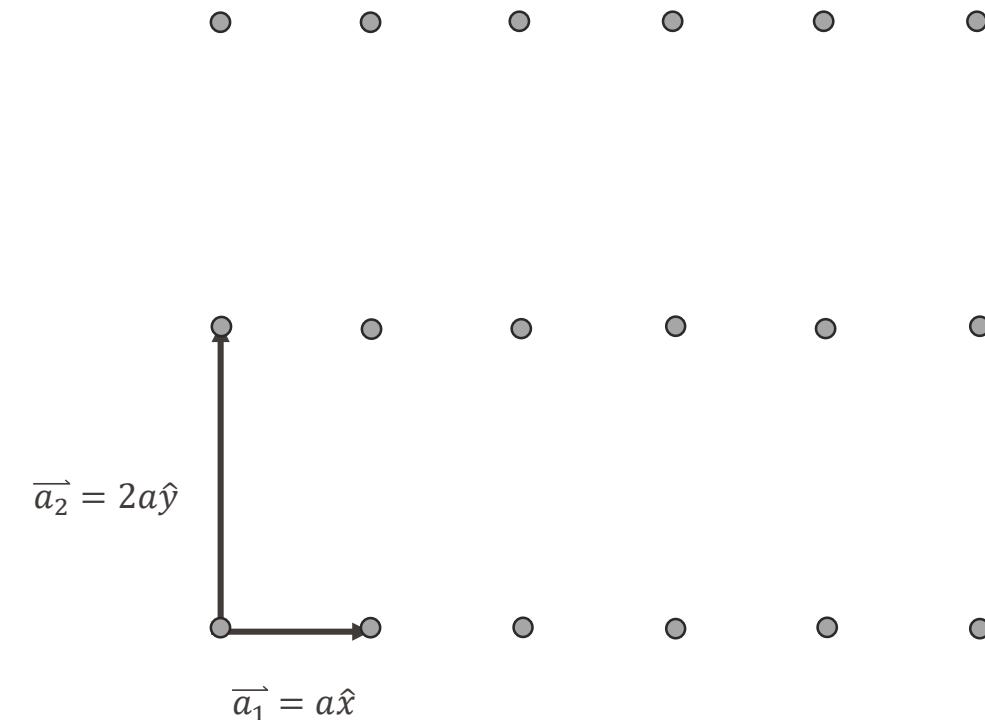
$$\vec{a}_1 \cdot \vec{b}_1 = 2\pi \rightarrow \vec{b}_1 = \frac{2\pi}{a} \hat{x}$$

In 2D we simply have :

$$\vec{a}_2 \cdot \vec{b}_2 = 2\pi \rightarrow \vec{b}_2 = \frac{2\pi}{2a} \hat{y}$$



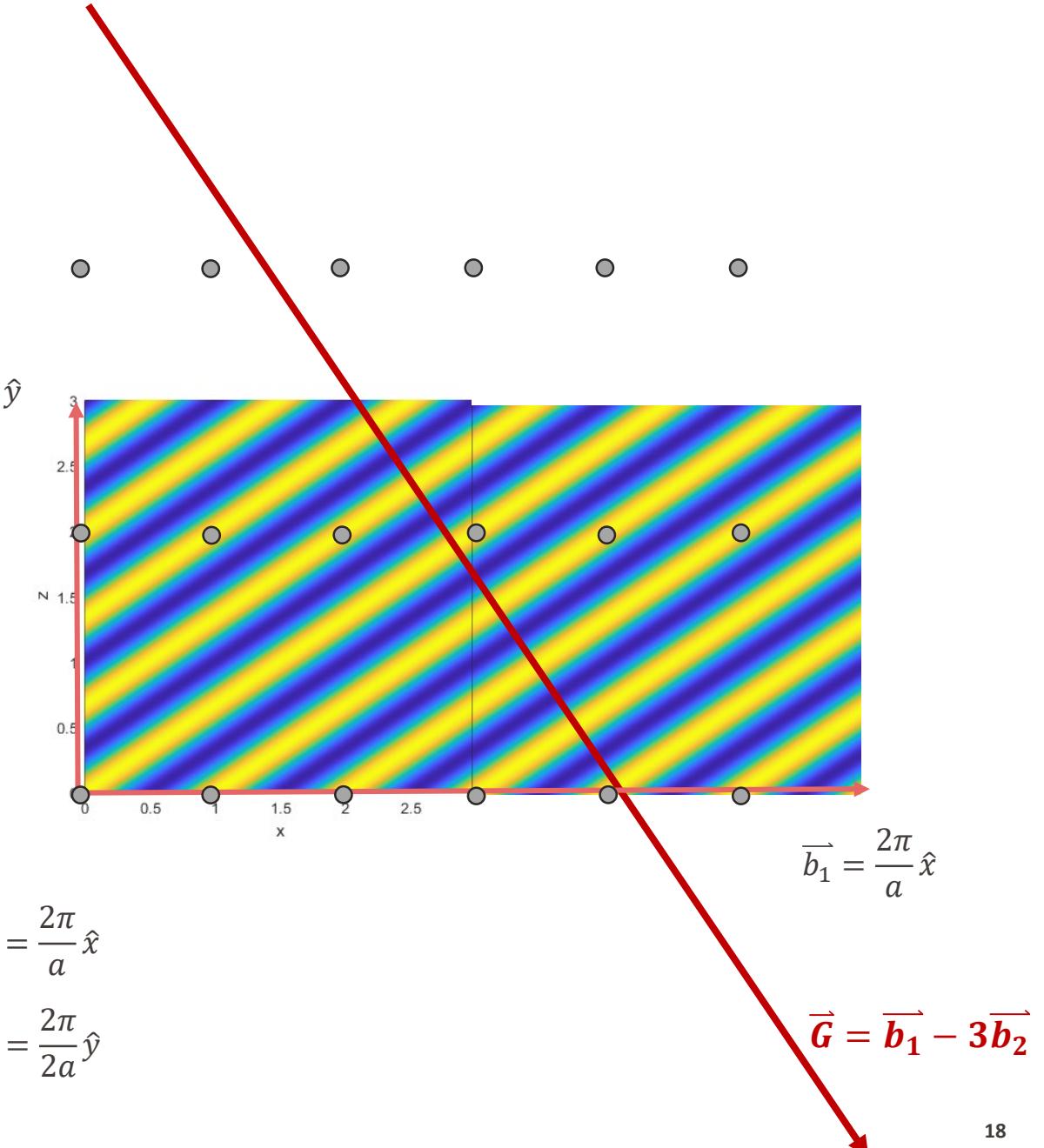
# Fourier Transforms and the Reciprocal Lattice



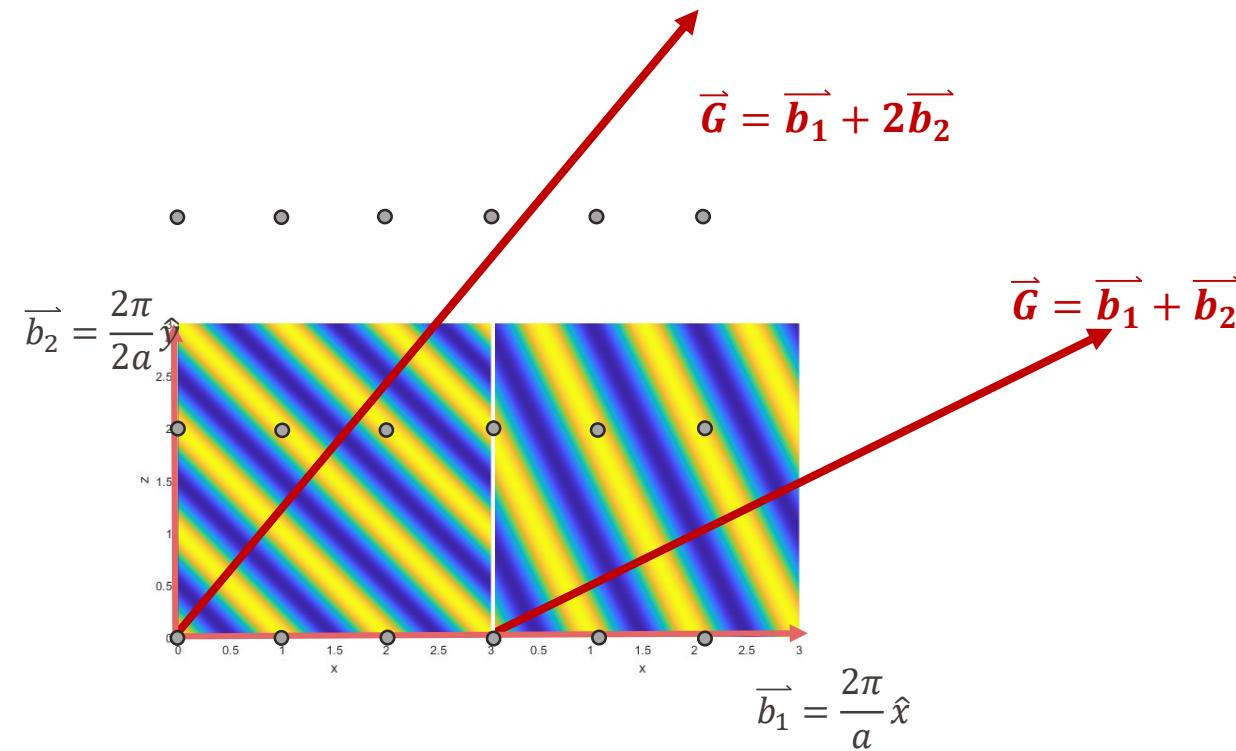
$$\vec{a}_1 \cdot \vec{b}_1 = 2\pi \rightarrow \vec{b}_1 = \frac{2\pi}{a} \hat{x}$$

$$\vec{a}_2 \cdot \vec{b}_2 = 2\pi \rightarrow \vec{b}_2 = \frac{2\pi}{2a} \hat{y}$$

In 2D we simply have :



# Fourier Transforms and the Reciprocal Lattice



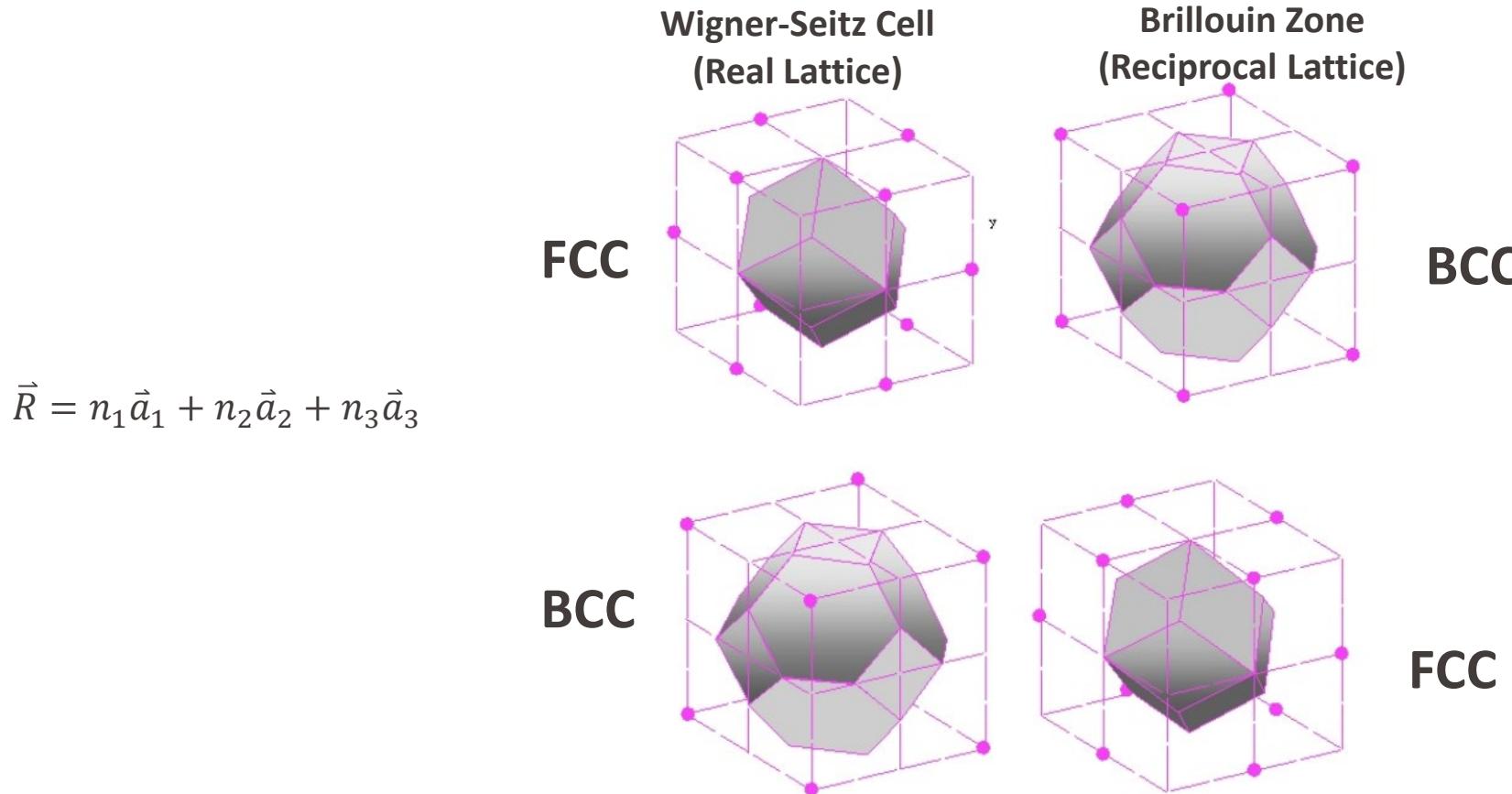
Reciprocal lattice vectors identify waves with periodicity equal to that of the lattice along different spatial directions.

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

# 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**.



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

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

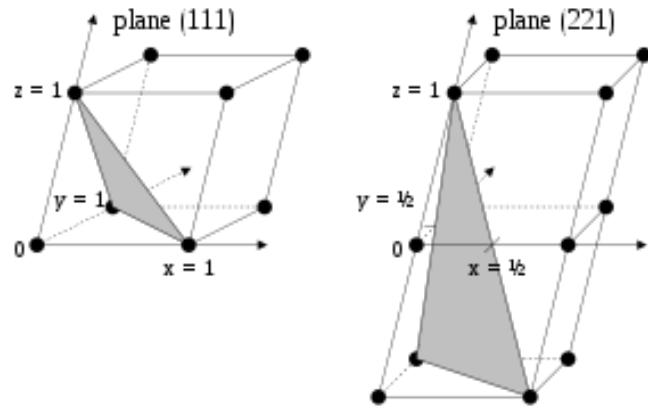
$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

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

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

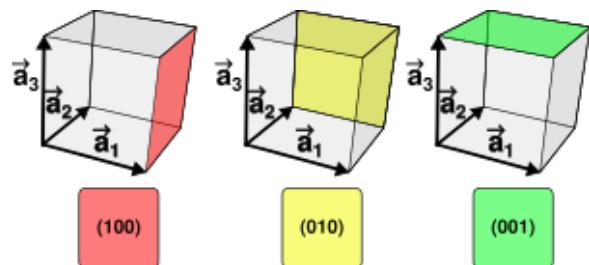
*Note:* the wavevectors lying on the surface of the Brillouin zone define the Nyquist condition for the 3D crystal. This means that any wavevector larger than the Brillouin zone can be expressed with a wavevector inside the Brillouin zone.

# Miller Indices



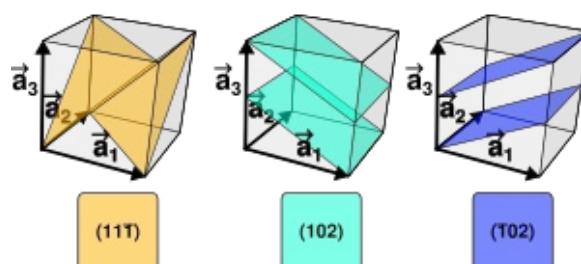
For any family of lattice planes separated by a distance  $d$ , there are reciprocal lattice vectors perpendicular to the planes, the shortest of which have a length of  $2\pi/d$ .

The *Miller Indices* of a lattice plane are the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a specified set of reciprocal lattice vectors. Thus a **Miller plane with indices  $h, l, k$  is normal to the reciprocal lattice vector  $\vec{G} = h\vec{b}_1 + l\vec{b}_2 + k\vec{b}_3$**  (see slide 17)

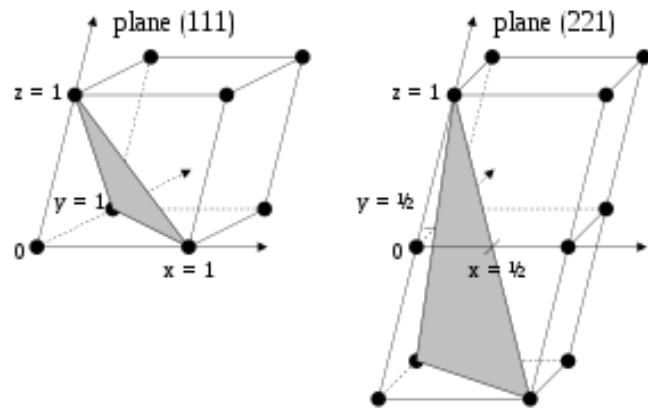


To obtain the Miller indices of a plane (see image on the top right):

- Consider the real lattice and identify the intercepts of the desired plane with the axes formed by the primitive vectors  $\vec{a}_i$ 
  - E.g.  $1\vec{a}_1, 1\vec{a}_2, 2\vec{a}_3$  (or  $1/2\vec{a}_1, 1/2\vec{a}_2, 1\vec{a}_3$ )
- Take the reciprocal of the intercepts and reduce them to the three smallest integers that have the same ratio as the original set
  - E.g.  $\left(\frac{1}{1}, \frac{1}{1}, \frac{1}{2}\right) \rightarrow \left(\frac{2}{2}, \frac{2}{2}, \frac{1}{2}\right) \rightarrow (2,2,1)$

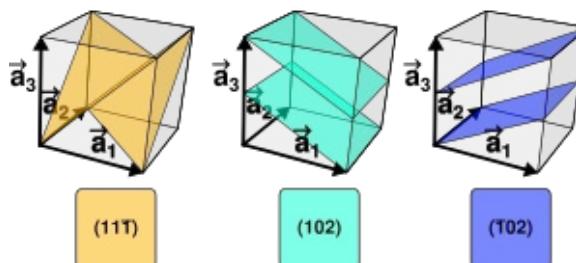
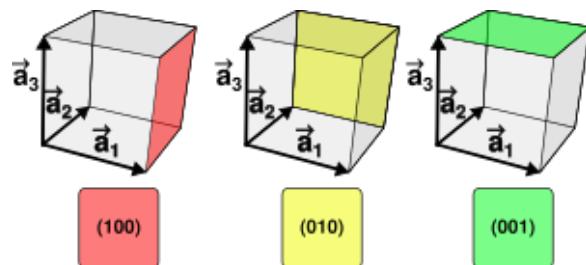


# Miller Indices



We use the following notations:

- Miller plane:  $(hkl)$
- If one of the plane indices is negative we write  $(-h, l, k) = (\bar{h}lk)$
- 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  $\{hkl\}$ 
  - 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:  $[hkl]$
- All equivalent directions in a crystal are indicated as  $\langle hkl \rangle$



# In This Lecture...

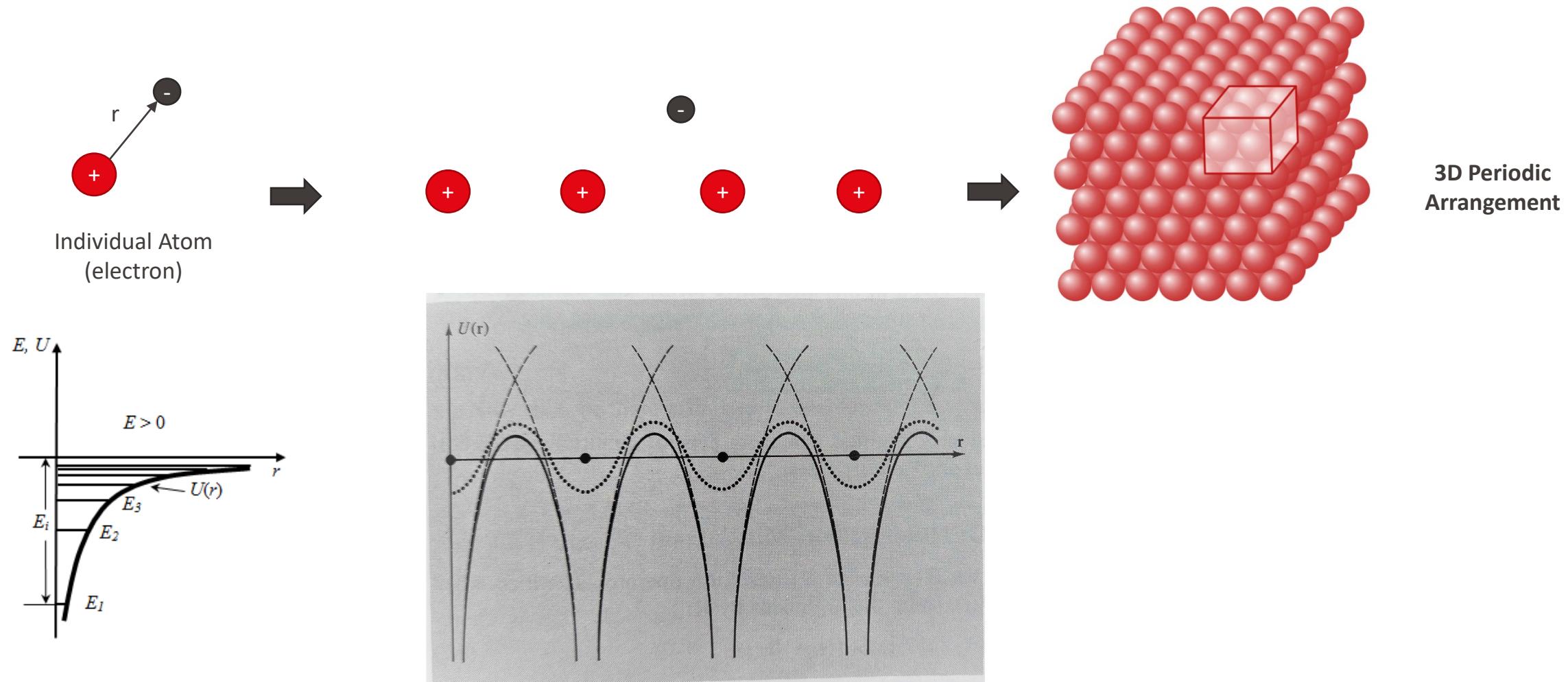
- Crystal Structure, the Real and Reciprocal Lattice, Miller Indices
- **Electron Energy States in Periodic Lattices – Intro to Periodic Potential**

# Summary of Solutions of Schrodinger Equation (electrons)

|                            | Potential  | Wavefunction  | Energy Levels   | Quantum Numbers | Degeneracy           |
|----------------------------|--|---|---|-----------------|----------------------|
| Free Particle              | $U = 0$  | $\Psi_t = Ae^{-i(\omega t+kx)} + Be^{-i(\omega t-kx)}$<br>$k = \sqrt{(2mE/\hbar^2)}$  | $E = \frac{\hbar^2}{2m} k^2$  | -               | -                    |
| 1D Infinite Potential Well | $U = 0 \text{ for } 0 < x < L$<br>$U = \infty \text{ for } x < 0 \text{ and } x > L$ | $\Psi_{n,t}(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-i\omega t}$   | $E_n = \frac{1}{2m} \left(\frac{\hbar n \pi}{L}\right)^2$   | $n$             | 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                |  | $Y_l^m(\theta, \varphi) = \varepsilon i^l \left[ \frac{(2l+1)(l- m )!}{4\pi(l+ m )!} \right]^{1/2} P_l^{ m } \cos\theta e^{im\varphi}$  | $E_l = \frac{\hbar^2}{2I} l(l+1)$   | $l, m$          | $2l+1$               |
| Hydrogen Atom (3D)         | $U = -\frac{Ze^2}{4\pi\epsilon_0 r}$   | $\Psi_{n,l,m}(r, \theta, \varphi) = R_{n,l}(r) Y_l^m(\theta, \varphi)$  | $E_n = -\frac{Z^2 e^4 \mu}{8\epsilon_0^2 n^2 \hbar^2}$  | $n, l, m$       | Depends on n         |

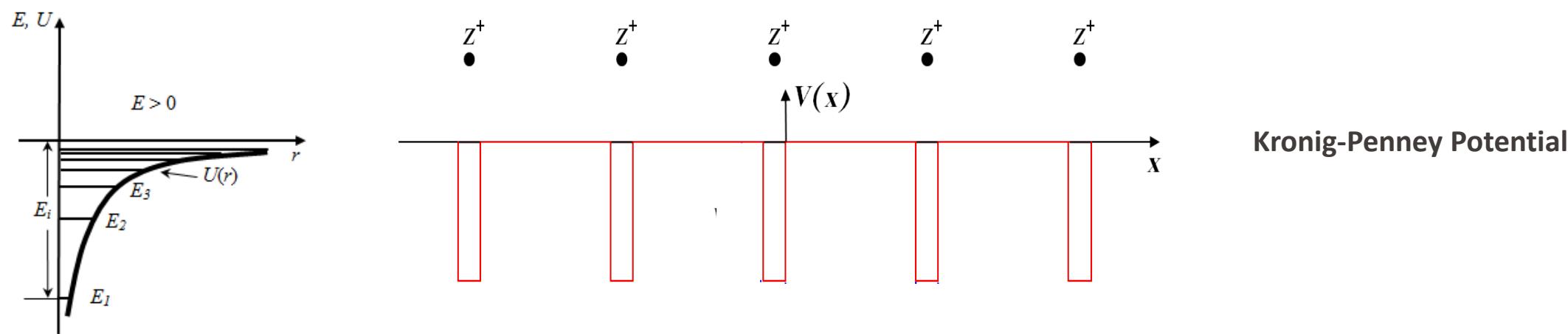
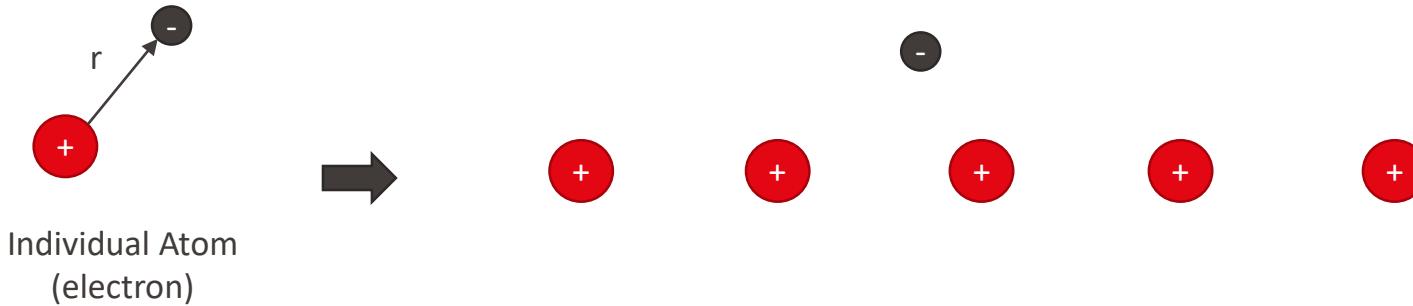
→ The potential defines the wavefunctions and the energy states. In a crystal we will have a periodic potential.

# From Individuals to Crystals



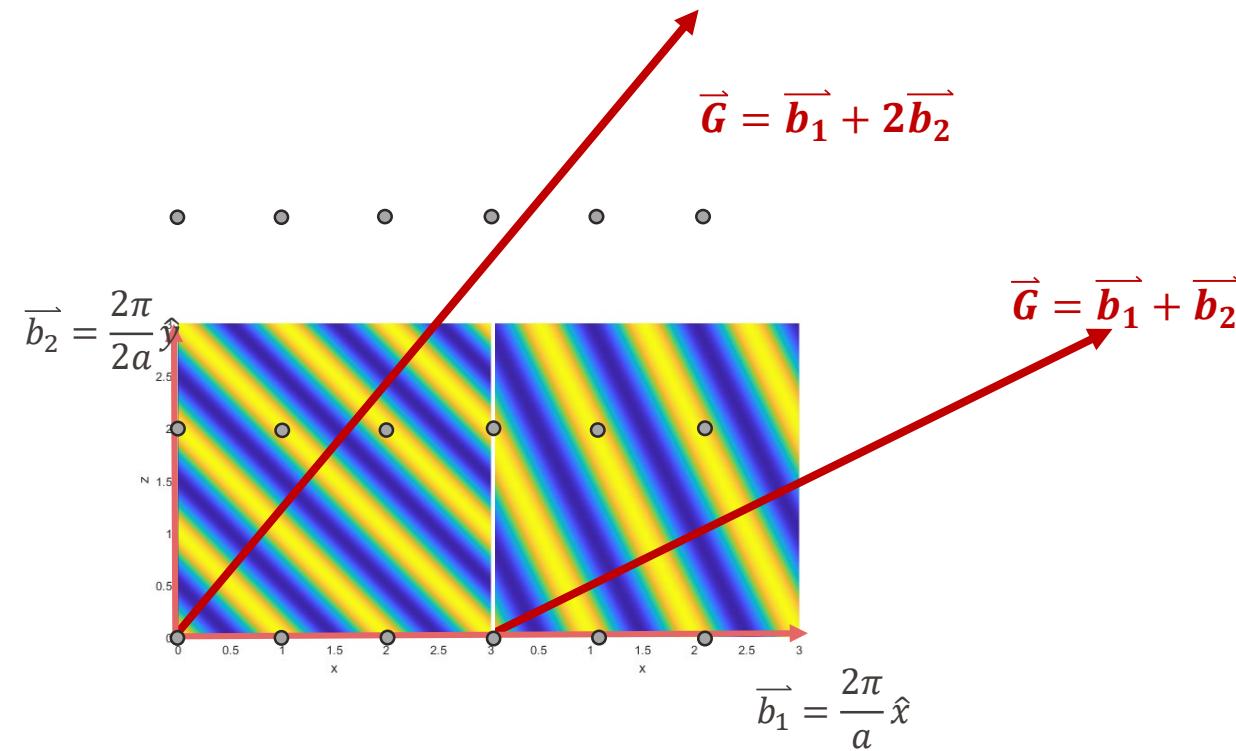
→ What are the electronic energy levels and wavefunctions in a periodic potential?

# From Individuals to Crystals



→ 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 the Next Lecture...

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