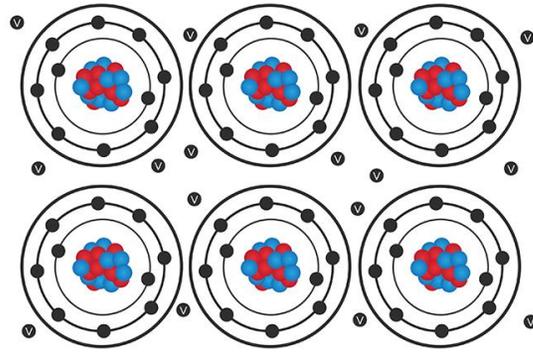
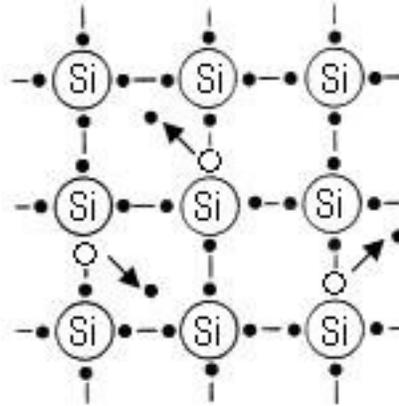


Solid State Physics

metal

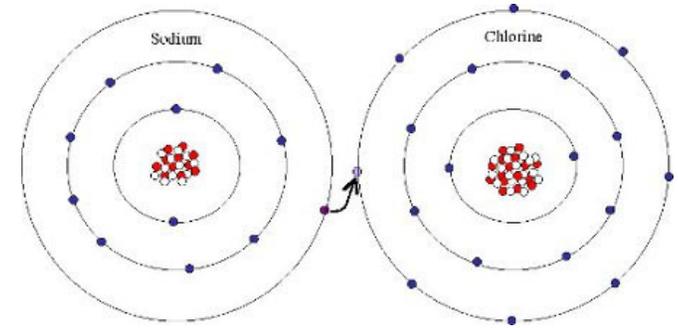


<https://infoq.am/how-does-bond-structure-affect-melting-point>



<https://keteresky.wordpress.com/2010/03/10/9-2-semiconductor-diod/>

NaCl



<http://knowledgebase.lookseek.com/Chemistry-Bonds-Ionic-Bonding.html>

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m_i} + \sum_j \frac{P_j^2}{2M_j} + \frac{1}{2} \sum_{j,j'}' \frac{Z_j Z_{j'} e^2}{4\pi\epsilon_0 |\mathbf{R}_j - \mathbf{R}_{j'}|} - \sum_{j,i} \frac{Z_j e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i,i'}' \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_{i'}|} \quad (2.1)$$

$$\mathbf{p}_i = -i\hbar\nabla_i$$

$$\mathbf{P}_j = -i\hbar\nabla_j$$

Each 3D.

$$i\hbar \frac{\partial}{\partial t} \psi(\{\mathbf{r}_i\}, \{\mathbf{R}_j\}, t) = \mathbf{H} + V_{\text{ext}}(\{\mathbf{r}_i\}, \{\mathbf{R}_j\}, t) \psi(\{\mathbf{r}_i\}, \{\mathbf{R}_j\}, t)$$

Without the possibly time variant external stimulus $V_{\text{ext}}(\{\mathbf{r}_i\}, \{\mathbf{R}_j\}, t)$, the **stationary** equation

$$\mathbf{H} \psi(\{\mathbf{r}_i\}, \{\mathbf{R}_j\}) = E \psi(\{\mathbf{r}_i\}, \{\mathbf{R}_j\})$$

5×10^{23} atoms/cm³ in Si. Cannot separate variables due to interaction terms.

Simply **hopeless** to solve the differential equation with $\sim 10^{23}$ variables.

Simplifying approximations

1. The Born-Oppenheimer approximation

Consider fixed nuclei. Solve Schrödinger equations for varied fixed nuclear positions, and then handle nuclear motion later.

Justification: proton to electron mass ratio = 1836

The electron Hamiltonian

$$\mathcal{H}_e = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i,i'}' \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i,j} \frac{Z_j e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_{j0}|}. \quad (2.3)$$

e-e interaction electron-nucleus Coulomb interaction

Still $\sim 10^{23}$ variables, unsolvable.

2. The mean-field (single-electron) approximation

Every electron experiences the same **average** potential $V(\mathbf{r})$ due to all nuclei and all other electrons.

$$\mathcal{H}_{1e} \Phi_n(\mathbf{r}) = \left(\frac{p^2}{2m} + V(\mathbf{r}) \right) \Phi_n(\mathbf{r}) = E_n \Phi_n(\mathbf{r}), \quad (2.4)$$

Discrete bound eigenstates confined in solid

Our choice of $V(\mathbf{r})$ determines eigenstates and eigenvalues.

3. Atomic core, effective Z , pseudopotential

Inner-shell electrons tightly bound. Consider nucleus & inner-shell electrons as the core.

$$\text{C: } Z = 6, 1s^2 2s^2 2p^2 \rightarrow Z_{\text{eff}} = 4, 2s^2 2p^2$$

$$\text{Al: } Z = 13, 1s^2 2s^2 2p^6 3s^2 3p^1, \rightarrow Z_{\text{eff}} = 3, 2s^2 2p^1$$

$$\text{Si: } Z = 14, 1s^2 2s^2 2p^6 3s^2 3p^2, \rightarrow Z_{\text{eff}} = 4, 2s^2 2p^2$$

But, the valence electrons wander into the core.

Use the pseudopotential instead of the Coulomb potential for each core.

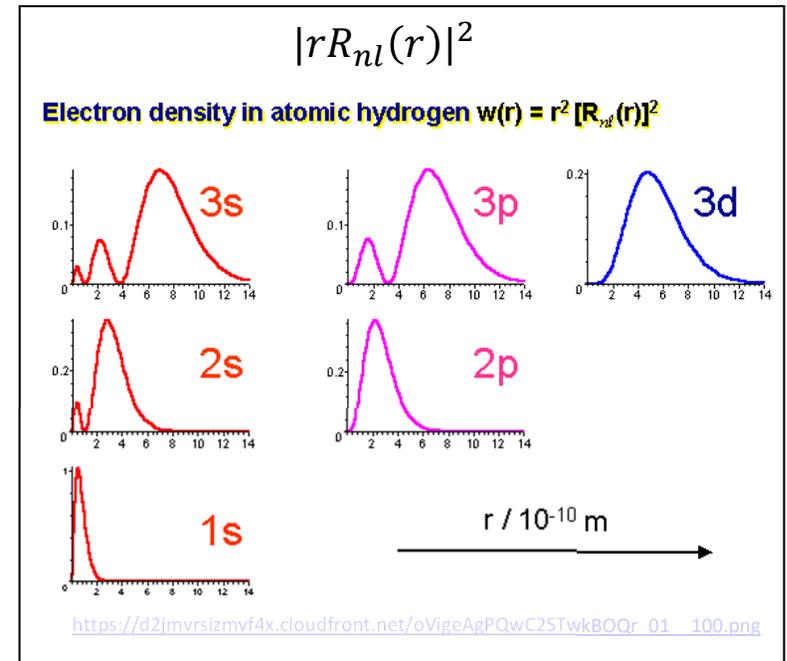
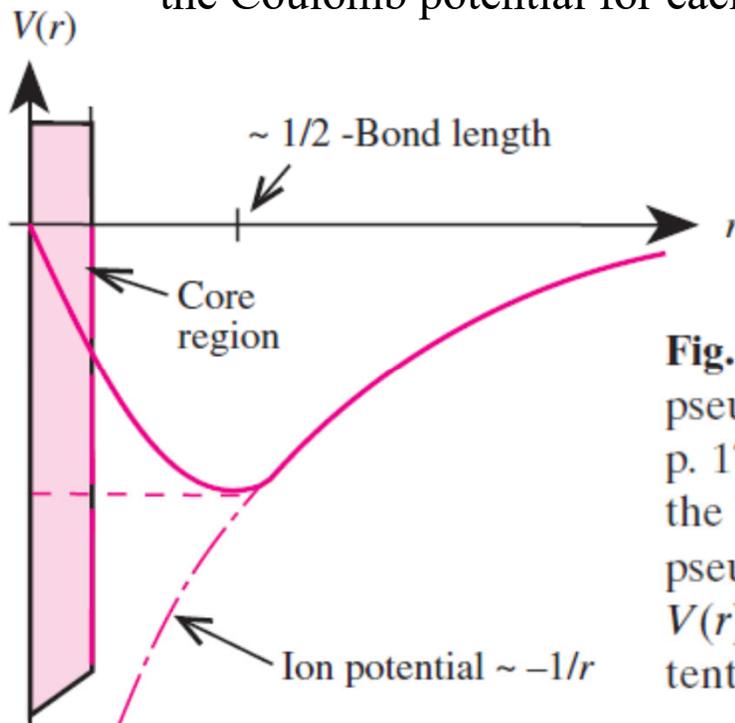
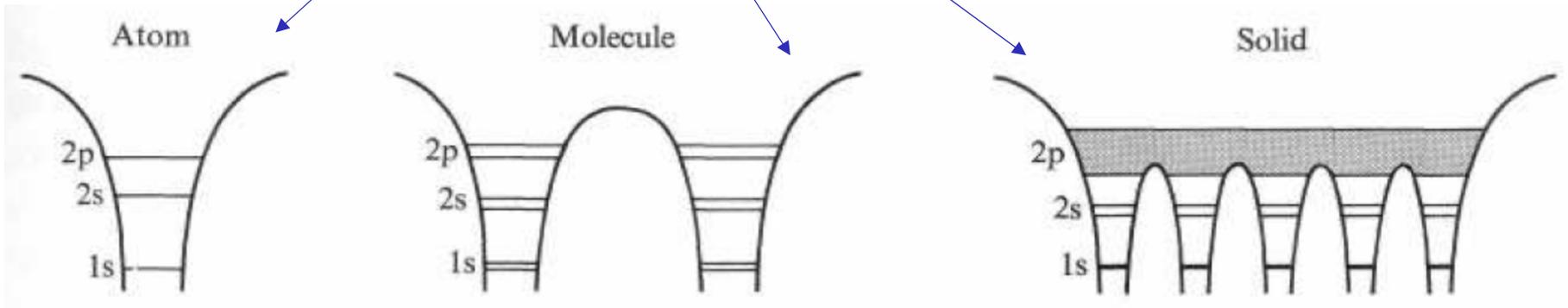
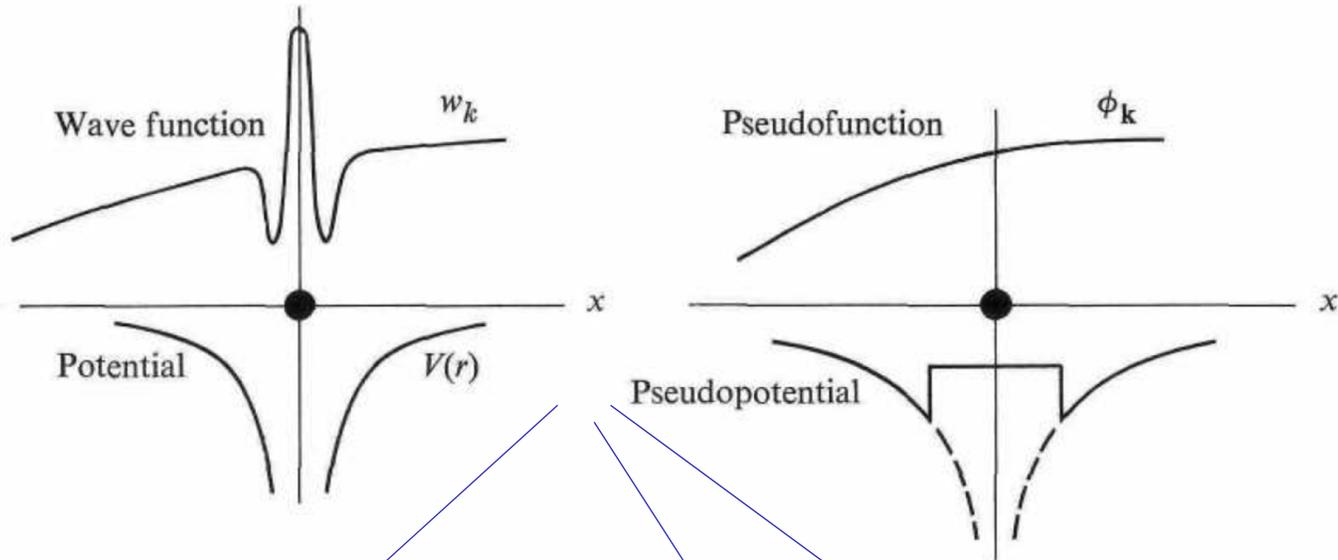


Fig. 2.11. Schematic plot of the atomic pseudopotential of Si in real space [Ref. 2.8, p. 17]. The *solid curve* in which $V(r) \rightarrow 0$ in the core region is said to be a “soft core” pseudopotential. The *broken curve* in which $V(r) \rightarrow \text{constant}$ is a “hard core” pseudopotential.



The simplest theory: Drude model

A **classical** theory proposed in 1900. Still widely used for metals.

In retrospect, we can justify the classical treatment with understanding of QM.

- Ion cores are fixed.
- Valence electrons are free inside the metal.
- Therefore, a **free electron gas** in a box.

$$1 \text{ mole} = 6.02 \times 10^{23} \text{ atoms} = M_A \text{ (atomic mass)}$$

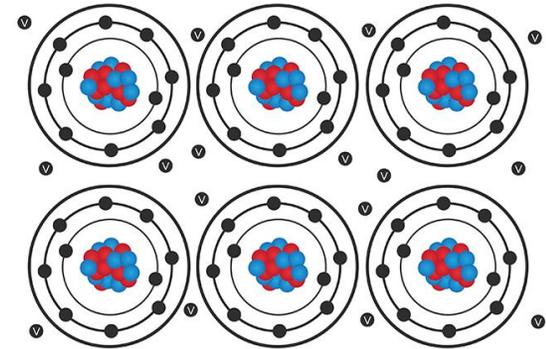
$$n = \frac{N}{V} = 6.02 \times 10^{23} \times \frac{\rho_m}{M_A} Z$$

← Mass density
← Charge of ion core
(i.e. # valence electrons per ion)

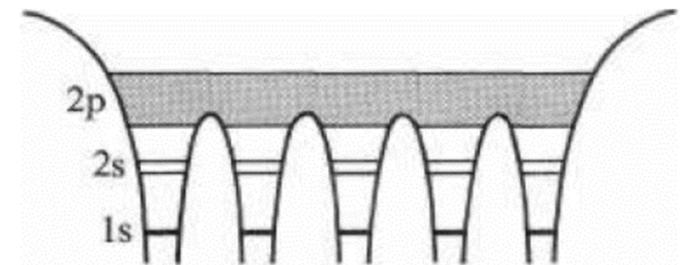
For Al,

$$n = \frac{N}{V} = 6.02 \times 10^{23} \times \frac{2.7 \text{ g/cm}^3}{27 \text{ g}} \times 3 = 1.8 \times 10^{23} / \text{cm}^3$$

- The **free electron gas** treated as an **ideal gas** (non-interacting)
- Thermal **speed** v_{th} at temperature T .
- Each electron collides with something in time τ **on average**, **thermalized**.



<https://infoqr.am/how-does-bond-structure-affect-melting-point>



In presence of applied electric field \mathbf{E} , each electron gains average net drift **velocity**

$$\mathbf{v}_d = -\frac{q\mathbf{E}\tau}{m}$$

$$\mathbf{J} = nq\mathbf{v}_d = -\frac{q^2n\tau}{m}\mathbf{E} \Rightarrow \frac{1}{\rho} = \sigma = \frac{q^2n\tau}{m} \Rightarrow \tau = \frac{m}{q^2n\rho}$$

A Homework 4 problem:

For Al, $\rho = 3 \times 10^{-7} \Omega \text{ cm}$. Use n we just found, to calculate τ .

Caution: Pay close attention to units.

You should get something around 10^{-14} s .

Sanity check of this model:

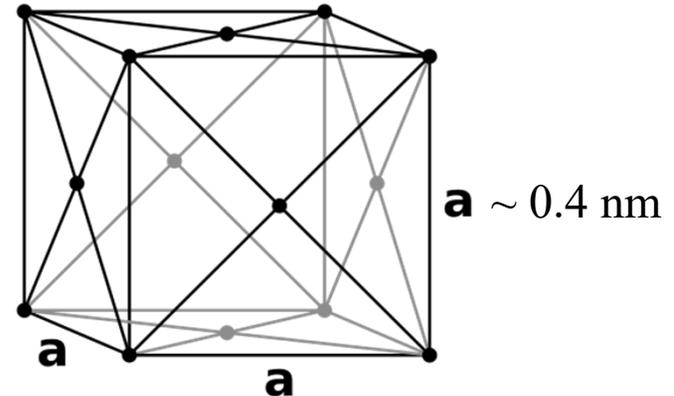
$$\frac{1}{2}mv_{th}^2 = \frac{3}{2}k_B T$$

At RT, $v_{th} \sim 10^7 \text{ cm/s}$.

The mean free path $v_{th}\tau \sim 10^{-7} \text{ cm} = 1 \text{ nm}$.

Drude thought electrons collided with ions.

This estimate made sense!



But, there's an issue:

If the mean free path $v_{th}\tau \sim \text{constant}$ (determined by structure), then

$$\rho \propto \frac{1}{\tau} \propto v_{th}.$$

$$\tau = -\frac{m}{q^2 n \rho}$$

$$\frac{1}{2} m v_{th}^2 = \frac{3}{2} k_B T \quad \Rightarrow \quad v_{th} \propto \sqrt{T} \quad \Rightarrow \quad \rho \propto \sqrt{T}$$

Experimental temperature dependence is different.

There are worse discrepancies with experiments, e.g. thermal conductivities.

Nevertheless, a useful model (when results independent of τ .)

Justification (in retrospect):

- Under the mean-field approximation, electrons are largely **independent**.
- With valence electrons wandering around fixed ion cores **in metals**, the charge-neutral environment experienced by each electron justifies the **free**-electron model.
 - The otherwise free electrons are confined in the interior – particles in a box
- Wave packets of free electrons can be treated as classical particles

The simplest theory improved: Drude–Sommerfeld model

Drude model assumes Boltzmann distribution – non-interacting electrons

Although nearly independent and free **on average**, electrons are much closer to each other than molecules in ideal gas.

Recall that $n \sim 10^{23}/\text{cm}^3$ for metals (e.g. $1.8 \times 10^{23}/\text{cm}^3$ for Al).

Exercise

The volume of 1 mole of ideal gas under ambient conditions is 22.4 l.

What is the density (molecules per cm^3) of the ideal gas?

What is the average distance between nearest molecules? Compare this to the free-electron gas in a metal.

Answers:

$$2.6 \times 10^{19}/\text{cm}^3.$$

$$(1/3) \times 10^{-6} \text{ cm} = 3.3 \text{ nm for the ideal gas.}$$

$$1.8 \times 10^{-8} \text{ cm} = 1.8 \text{ \AA} = 0.18 \text{ nm for a metal. 20 times smaller.}$$

We need to do better accounting of the free electrons.

Quasi-continuous (discrete) energy states of electrons

N independent, free electrons in a box of volume $V = L^3$

N is a large but finite number

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

Normalization in finite volume

de Broglie wavelength $\lambda = \frac{2\pi}{k}$

Small $k \Rightarrow$ large wavelength

Periodic boundary condition

$$k_x L = 2\pi n_x \quad k_y L = 2\pi n_y \quad k_z L = 2\pi n_z$$

Integers ($-, 0,$ or $+$)

$$k_x = \frac{2\pi}{L} n_x \quad k_y = \frac{2\pi}{L} n_y \quad k_z = \frac{2\pi}{L} n_z$$

For large (macroscopic) L , exact boundary condition not important.

Discreteness remains.

Momentum becomes good quantum number; \mathbf{k} and $-\mathbf{k}$ considered separate states.

Each state $|\mathbf{k}\rangle$ occupies a volume $(2\pi)^3/V$ in the wavevector space.

At $T = 0$, N electrons fill the lowest-energy states up to $|\mathbf{k}| = k_F$ Fermi wavevector

Why? $N = \frac{2 \left(\frac{4\pi}{3} k_F^3 \right)}{[(2\pi)^3/V]} \Rightarrow n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$

A Homework 4 problem:

For a 1D metal with N electrons in length L , find a similar relation between k_F and electron density $n = N/L$.

For a 2D metal with N electrons in area $A = L^2$, find a similar relation between k_F and electron density $n = N/A$.

The Fermi wavevector corresponds to the Fermi energy.

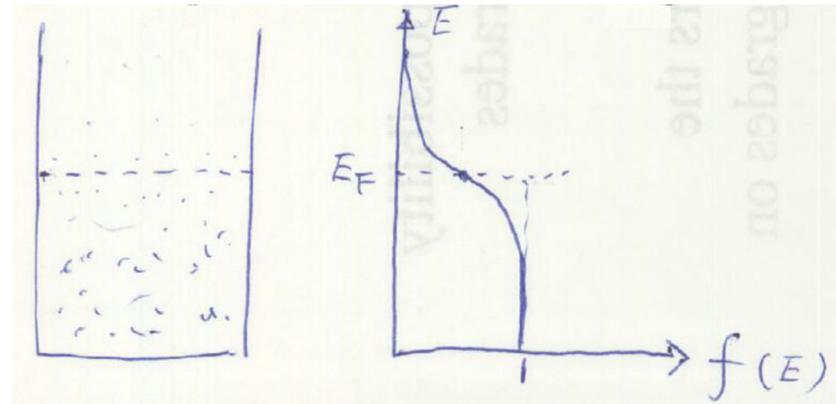
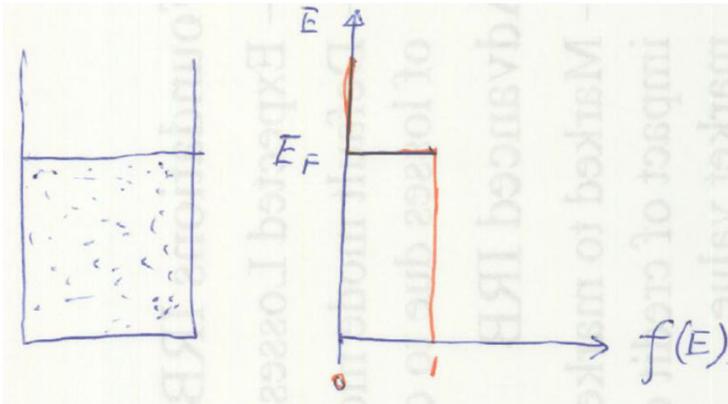
This state, where the N electrons fill the N lowest-energy states, is the **ground state** of the N -electron system.

Discreteness of \mathbf{k} is due to finite V .

Think about this with pictures of potential wells in mind.

When $T > 0$, some electrons are excited above the Fermi energy.
(Terminology: Fermi energy vs chemical potential)

$$f(E) = \frac{1}{e^{\frac{E - E_F}{k_B T}} + 1}$$



In general, the Fermi level (chemical potential) shifts with varying T .
For metals, the shift is very small (to be explained later).

Re-exam Drude model with the improved accounting of electrons

Only electrons near $k = k_F$ (Fermi surface) determine electrical transport behaviors.

Possible dependence of τ on energy does not have an effect.

This is one reason why the model works.

The electron **speed** at $k = k_F$ is called the Fermi velocity v_F : $\hbar k_F = m v_F$

Therefore, in the improved (Drude-Sommerfeld) model, the mean-free path is

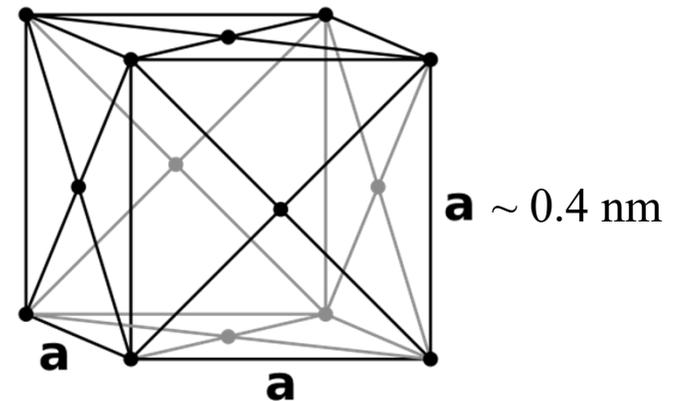
$$v_F \tau$$

A Homework 4 problem:

Find the electron mean free path for Al in ambient conditions
(using n and τ found earlier).

Answer: 16 nm.

Compare this to the original Drude model result (~ 1 nm).
Don't the electrons collide with ion cores?!



Merits and issues (partial list) of Drude and Drude–Sommerfeld models

Good phenomenological model for DC (meaning $\omega\tau \ll 1$)
conductivities of metals

The Fermi distribution changes little at T of interest from $T = 0$.

Only those electrons near Fermi energy matter, thus energy-independent τ are okay.

Working model for AC conductivities of metals

Works well especially for properties not dependent on exact τ values.

For example, optical frequencies usually satisfy $\omega\tau \gg 1$.

Once in this regime, the exact value does not matter.

Side note: Drude model is still widely used, e.g., in plasmonics.

A good book on this topic is

Stefan A. Maier, *Plasmonics: Fundamentals and Applications*

Cannot explain T dependence in DC conductivity.

What determines number of conduction electrons? Chemical valence?

Why are some elements not metals? (B not a metal while Al is)

What are the collision mechanisms? Electrons collide with what?

Band theory: independent electrons in periodic potential

To take advantage of the **periodic** structure of crystalline solids, let's review the math of periodic things.

Periodic functions of time
(we are familiar with as electrical engineers)

$$f(t + T) = f(t)$$

$$\omega_0 = 2\pi/T \quad \text{Fundamental frequency}$$

$$f(t) = \sum_n F(n\omega_0) \boxed{e^{jn\omega_0 t}}$$

Basis functions

$$F(n\omega_0) = \frac{1}{T} \int_{t'}^{t'+T} e^{-jn\omega_0 t} f(t) dt$$

Periodic functions in 1D space

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

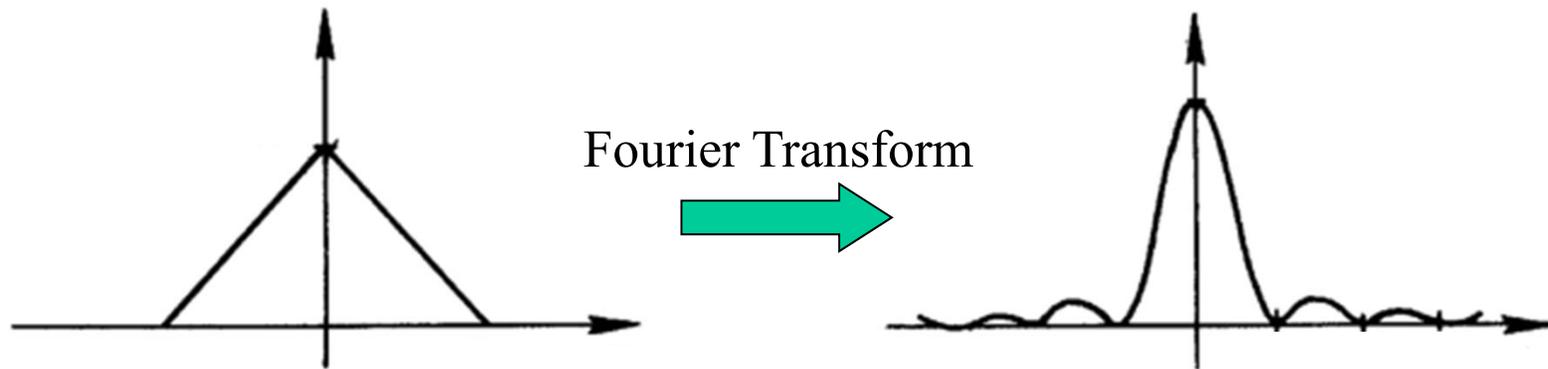
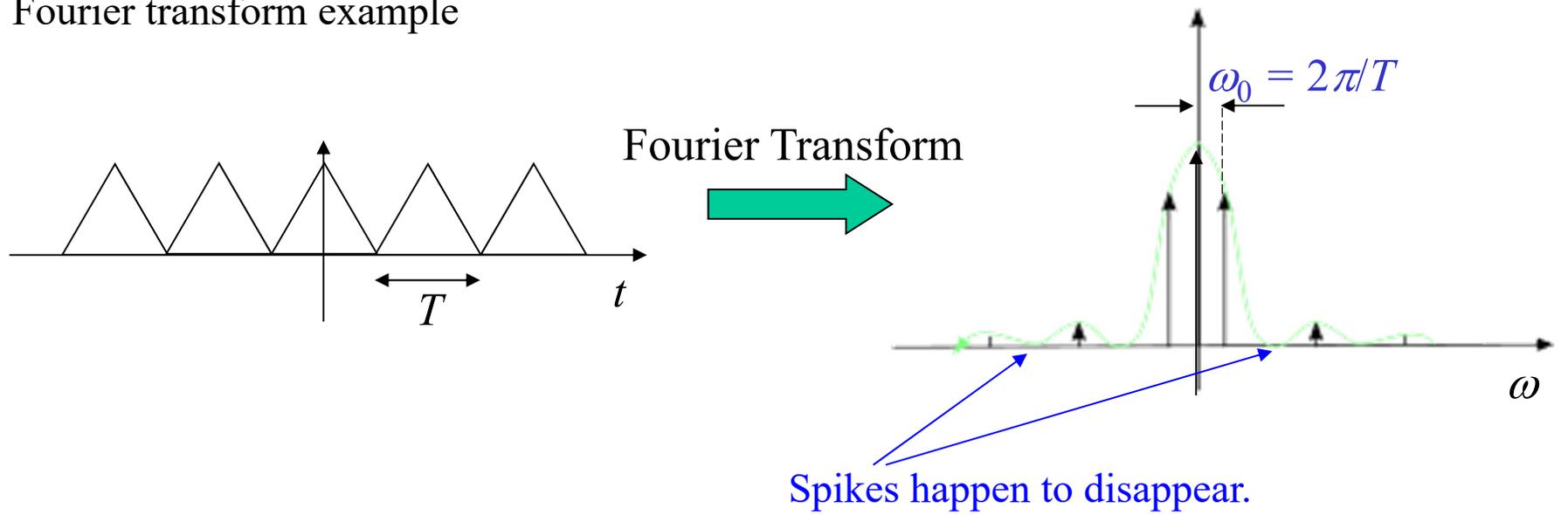
$$k_0 = 2\pi/L$$

$$\psi(x) = \sum_n \Psi\left(n\frac{2\pi}{L}\right) e^{in\frac{2\pi}{L}x}$$

Any wave function that satisfies the periodic boundary condition can be written in this form.

$$\Psi\left(n\frac{2\pi}{L}\right) = \frac{1}{L} \int_{x'}^{x'+L} e^{-in\frac{2\pi}{L}x} \psi(x) dx$$

Fourier transform example



One-electron Schrödinger equations in a 1D periodic potential

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x) = E \psi(x)$$

Periodic boundary condition $\psi(x + L) = \psi(x)$

$$\Rightarrow \psi(x) = \sum_{n_q} \Psi(n_q \frac{2\pi}{L}) e^{in_q \frac{2\pi}{L} x} \equiv \sum_q \Psi(q) e^{iqx}$$

Large period L , small fundamental spatial frequency $2\pi/L$.

Periodic potential $V(x + a) = V(x)$ due to periodic structure

$L = Na$; a is unit cell size. N is the number of atomic periods (unit cells)

$$V(x) = \sum_{l_x} \tilde{V}(l_x \frac{2\pi}{a}) e^{il_x \frac{2\pi}{a} x} \equiv \sum_K \tilde{V}(K) e^{iKx}$$

Small period a , large fundamental spatial frequency $2\pi/a$.

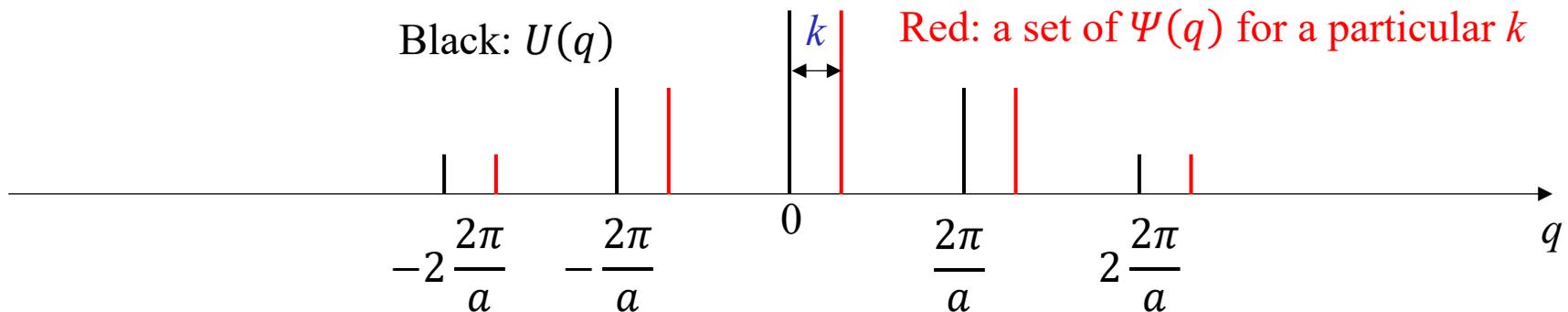
Insert these two Fourier expansions into the Schrödinger equation, and solve it for each q .

$$\psi(x) = \sum_{n_q} \Psi\left(n_q \frac{2\pi}{L}\right) e^{in_q \frac{2\pi}{L}x} \equiv \sum_q \Psi(q) e^{iqx}$$

Solving the Schrödinger equation for each q , it is shown that

$$\Psi(q) = U(q - k), \text{ where}$$

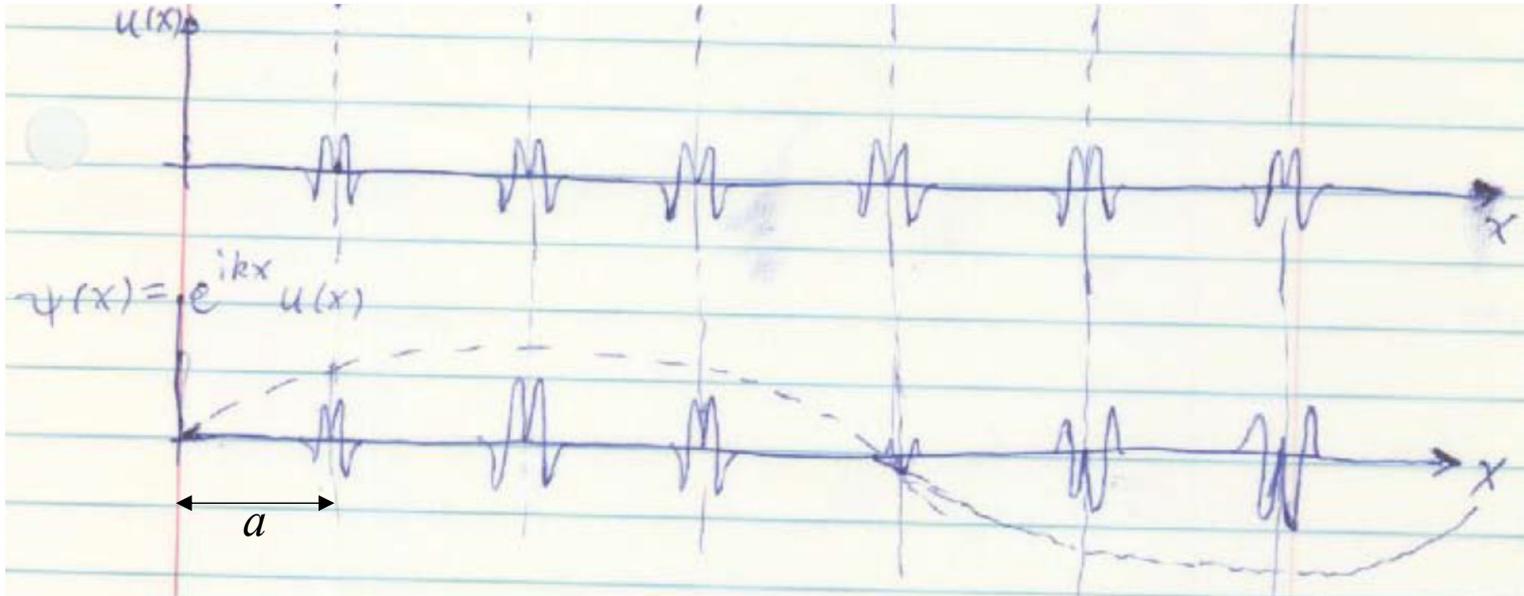
$U(q) \neq 0$ only for $q = K = l_K \frac{2\pi}{a}$, where l_K are integers,
and there are N distinct values of k , with interval $2\pi/L$, in every $2\pi/a$ -long zone.



With our knowledge of signals and systems, we immediately see that $\psi(x)$, with a spectrum $\Psi(q)$, is the plane wave e^{ikx} sampled by a “pulse train” $u(x)$:

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

$u(x)$ is a **periodic** function (“pulse train”): $u(x + a) = u(x)$



$U(K)$ is the Fourier transform of $u(x)$: $u(x) = \sum_{l_K} U(l_K \frac{2\pi}{a}) e^{il_K \frac{2\pi}{a} x} \equiv \sum_K U(K) e^{iKx}$

You see, a single-frequency “signal” e^{ikx} with “frequency” $k = n_x \frac{2\pi}{L}$ is sampled by $u(x)$ at a higher “sampling frequency” $2\pi/a$.

With such “sampling”, “single-frequency signals” with “frequencies” k and

$$k + l_K \frac{2\pi}{a} = k + K$$

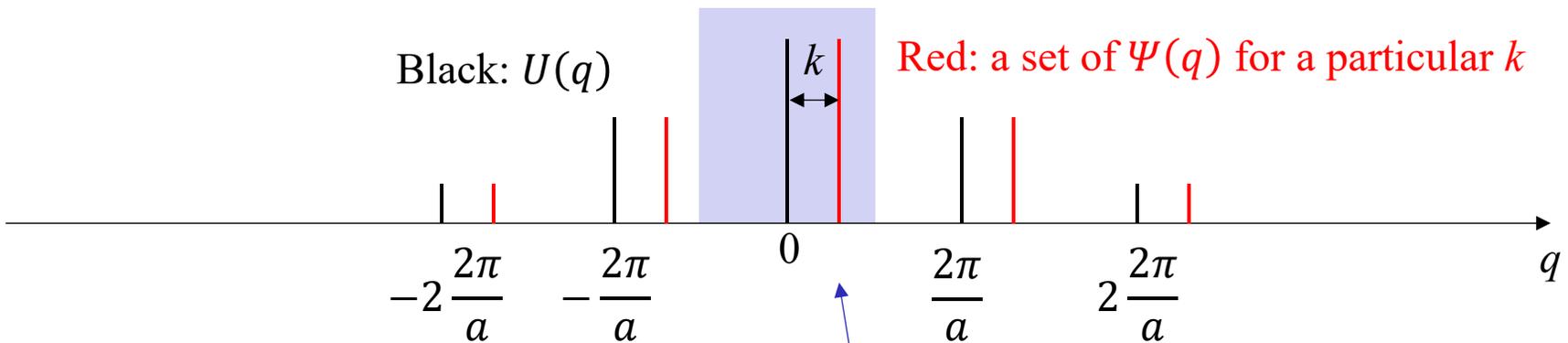
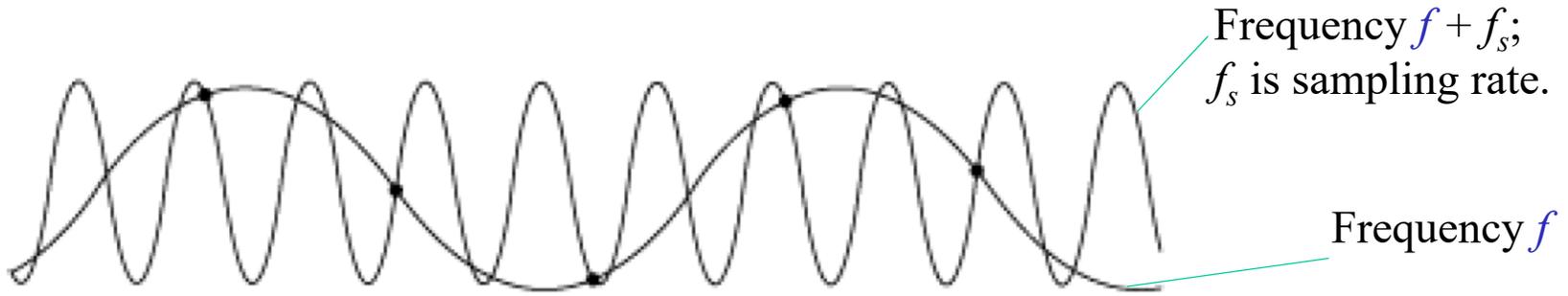
are **not distinguishable**.

“Sampled” at “sampling frequency” $2\pi/a$,
 “single-frequency signals” with “frequencies” k and

$$k + l_K \frac{2\pi}{a} = k + K$$

are not distinguishable.

“Aliasing” in signals and systems.

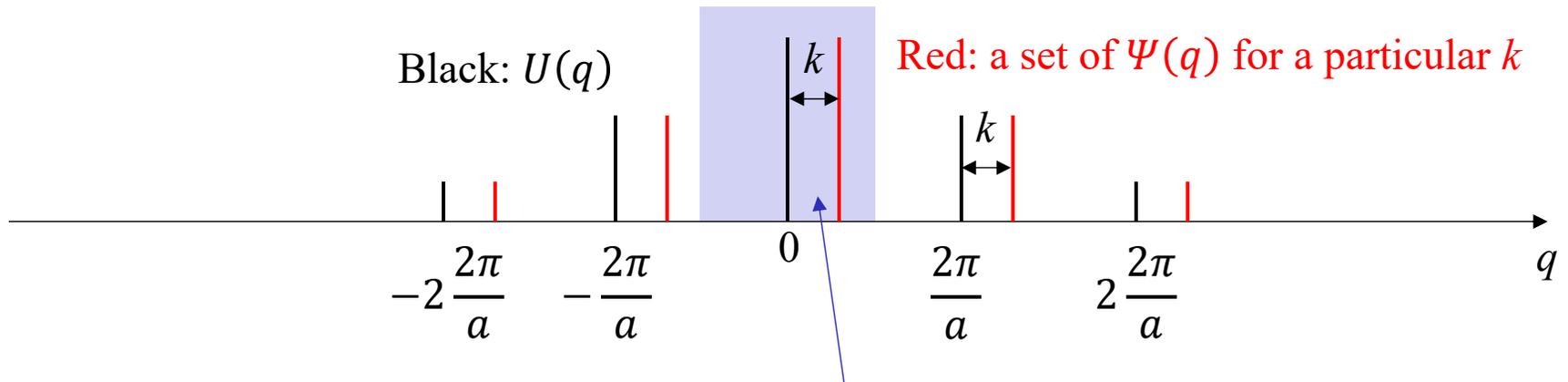


We define all k in one $2\pi/a$ -long zone : $-\pi/a$ to π/a , the first Brillouin zone.

$$k = \frac{2\pi}{L} n_x$$

$$n_x = 0, \pm 1, \pm 2, \dots, \pm \frac{N}{2}$$

N is # of unit cells,
 not # of electrons.



The “single-frequency signal” e^{ikx} in the 1st Brillouin zone and those e^{iqx} in higher Brillouin zones, where

$$q = k + l_K \frac{2\pi}{a} = k + K$$

are not distinguishable.

Therefore, $\Psi(q)e^{iqx}$ can be “aliased” into the 1st Brillouin zone by shifting

$$-K = -l_K \frac{2\pi}{a}$$

Thus, for a particular k ,

$$\psi_k(x) \equiv \psi(x) = \sum_q \Psi(q) e^{iqx} = \sum_q U(q - k) e^{i(K+k)x} = e^{ikx} \sum_K U(K) e^{iKx}$$

$$\therefore \sum_K U(K) e^{iKx} = u(x) \quad \therefore \psi_k(x) = u(x) e^{ikx}$$

Keep in mind that $u(x)$ is a periodic function: $u(x + a) = u(x)$

First, we consider $V(x) \approx 0$ but periodic.

$$V(x) \approx 0 \Rightarrow E = \hbar^2 k^2 / 2m$$

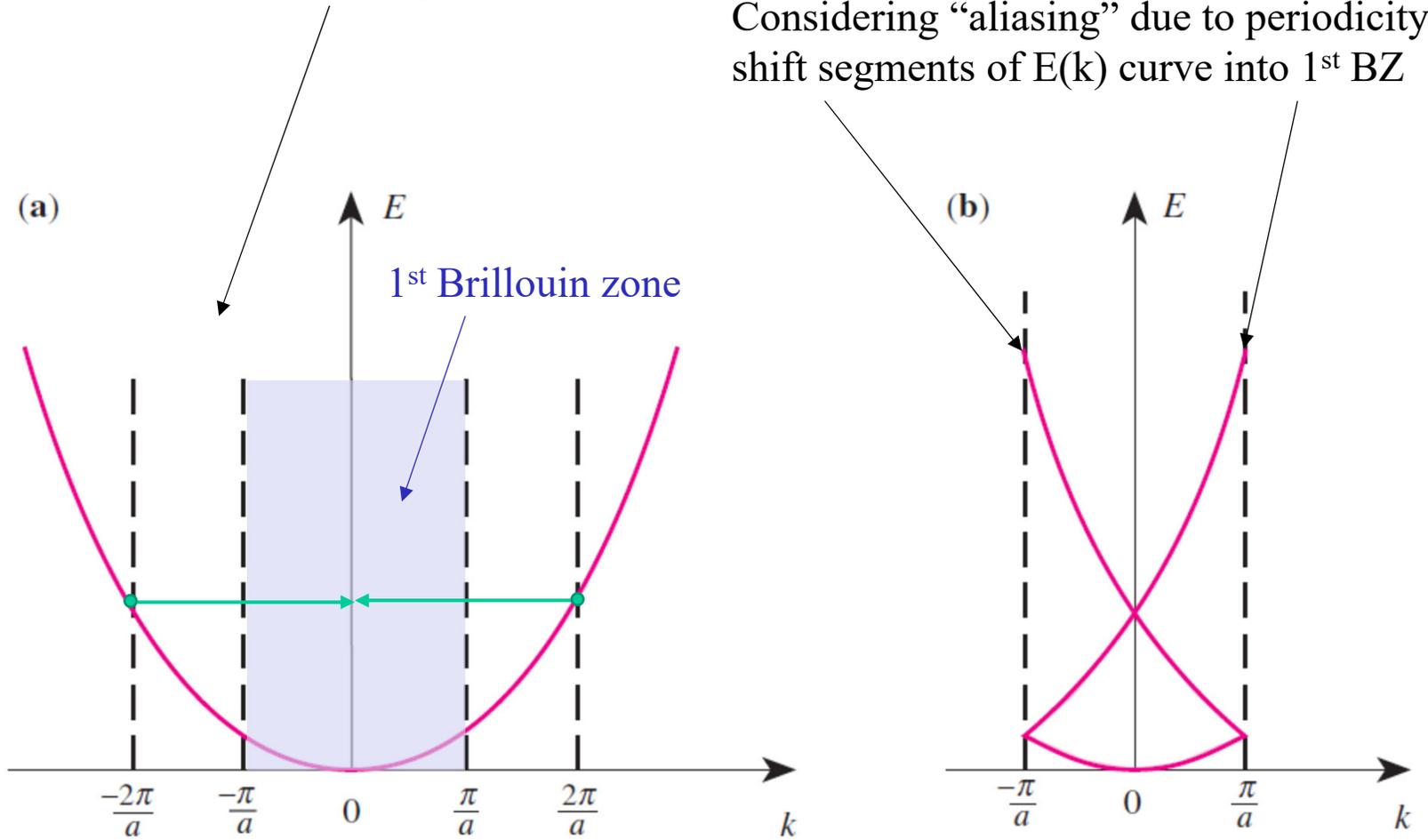


Fig. 2.1. The band structure of a free particle shown in (a) the extended zone scheme and (b) the reduced zone scheme

Now, we consider **weak** periodic $V(x) = \sum_{l_x} \tilde{V}(l_x \frac{2\pi}{a}) e^{il_x \frac{2\pi}{a} x} \equiv \sum_K \tilde{V}(K) e^{iKx}$

Small period a , large fundamental spatial frequency $2\pi/a$.

Solve Schrödinger equation for each k

$$\Rightarrow E(k) \approx E^{(0)}(k) \text{ away from } k \approx K/2, \quad E\left(\frac{K}{2}\right) \approx E^{(0)}\left(\frac{K}{2}\right) \pm |\tilde{V}(K)|$$

6.2 Electrons in a Periodic Potential

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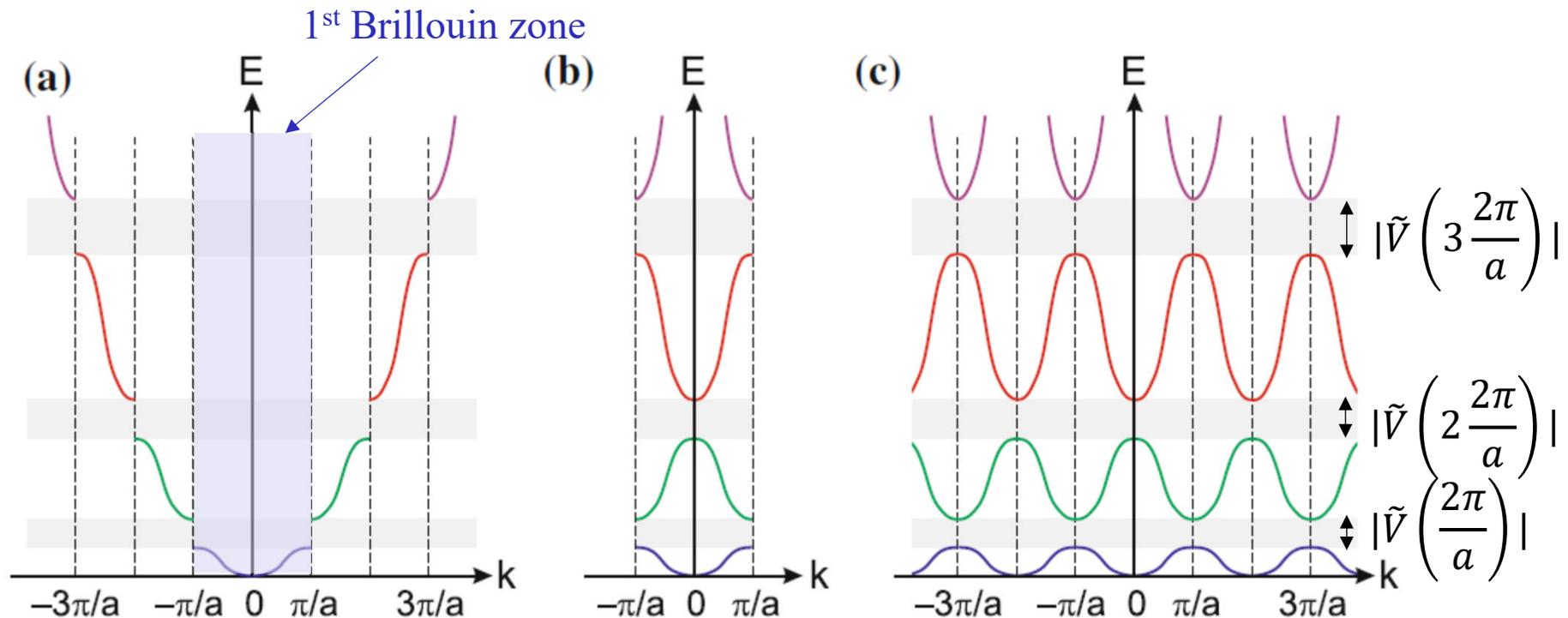


Fig. 6.1 Zone schemes for a band structure: (a) extended, (b) reduced and (c) repetitive zone scheme

We just discovered energy bands!

N distinct k values in 1st BZ

Assuming one atom in each unit cell (size a), we have N single-electron states each band.

If the element is valence 1, only half of the states of the lowest band are occupied.

If the element is valence 2, the lowest band is filled.

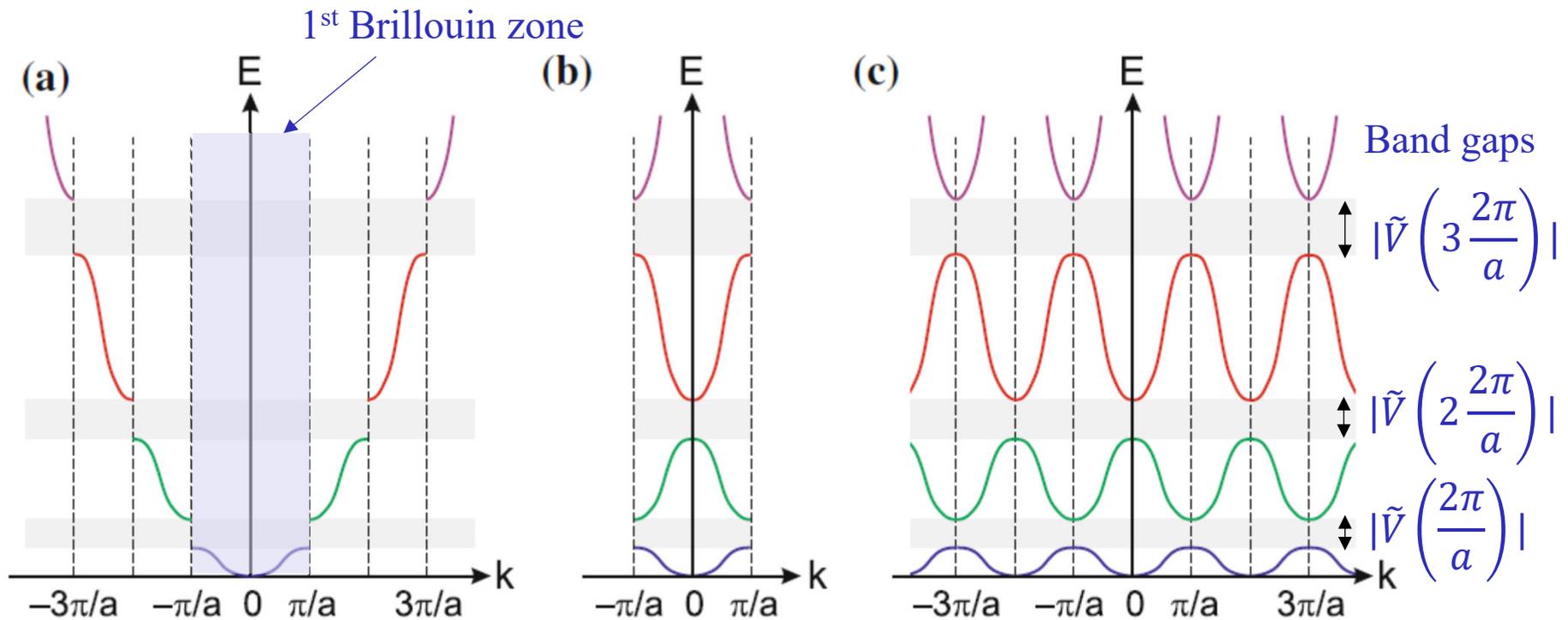
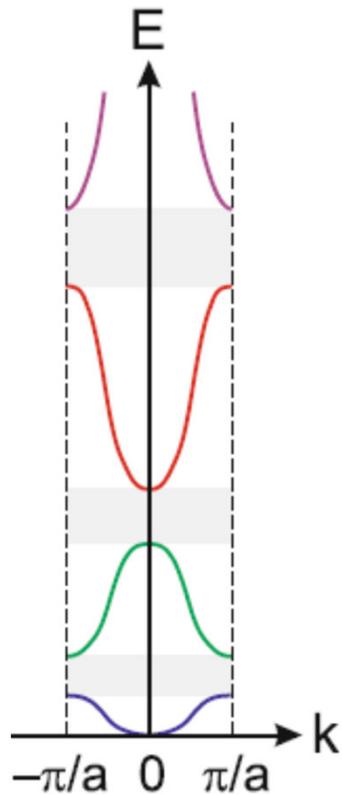


Fig. 6.1 Zone schemes for a band structure: (a) extended, (b) reduced and (c) repetitive zone scheme



For each band, the two states at the 2 edges of the 1st BZ, $k = -\pi/a$ and $k = \pi/a$, are **the same state**.

In electric field \mathcal{E} , $\hbar\Delta k = q\mathcal{E}\tau$, and $mv_d = \hbar\Delta k$ for a **partially filled band**.

A fully occupied band does not conduct.

For our 1D examples:

Assuming one atom in each unit cell, we have N single-electron states each **band**.

If the element is valence 1, only half of the states of the lowest band are occupied.

⇒ **conductor**

If the element is valence 2, the lowest band is filled.

⇒ **Insulator/semiconductor**

What about valence 3 and 4?

The band states are **eigenstates of the Hamiltonian (energy)**.

Half filled \Rightarrow metal.

Electron occupancy of band states at ambient temperatures not too different from that at $T = 0$.

In electric field \mathcal{E} , $\hbar\Delta k = q\mathcal{E}\tau$, and $mv_d = \hbar\Delta k$.

Assuming energy-independent τ , each electron is shifted by Δk .

Therefore, $mv_d = \hbar\Delta k$.

Fully filled \Rightarrow insulator/semiconductor.

No conduction at $T = 0$.

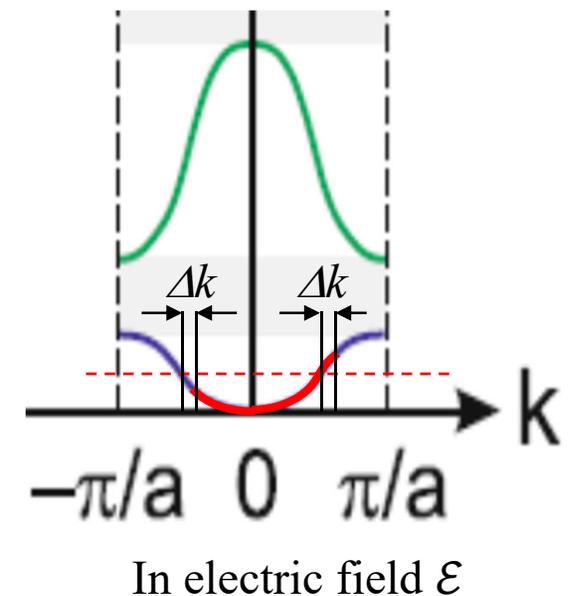
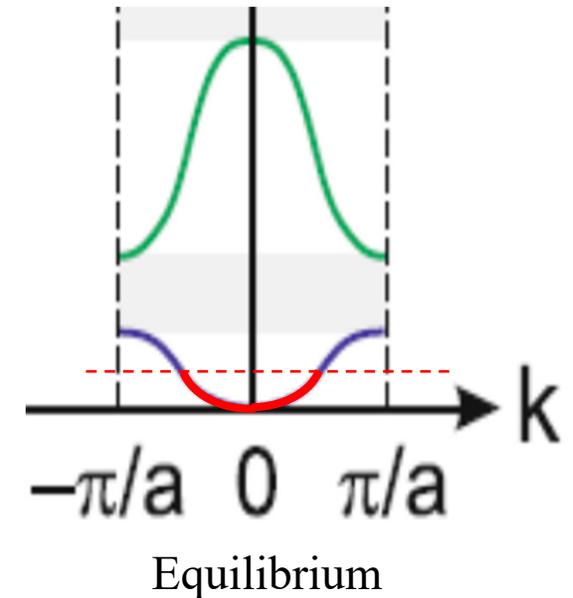
At $T > 0$, thermal excitation \Rightarrow

A few vacancies in the previously empty band, and same # of electrons in the band immediately above.

Electron occupancy of band states sensitive to T .

\Rightarrow conduction electrons, holes to be discussed later

Half-filled band



Bloch's Theorem

(Notice it's a **theorem, not a law**. Mathematically derived)

$$\psi_k(x) = u(x)e^{ikx} \quad u(x) \text{ is a } \mathbf{periodic}: u(x + a) = u(x)$$

Extended to 3D, this is the **Bloch's Theorem**:

The eigenstates $\psi(\mathbf{r})$ of the **one-electron** Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \underbrace{V(\mathbf{r})}_{\text{lattice vectors}} \leftarrow \text{including contributions from all other e's}$$

To be explained

where $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$ for all \mathbf{R} in a **Bravais lattice** can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r})$$

where $u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n,\mathbf{k}}(\mathbf{r})$.

Equivalently,

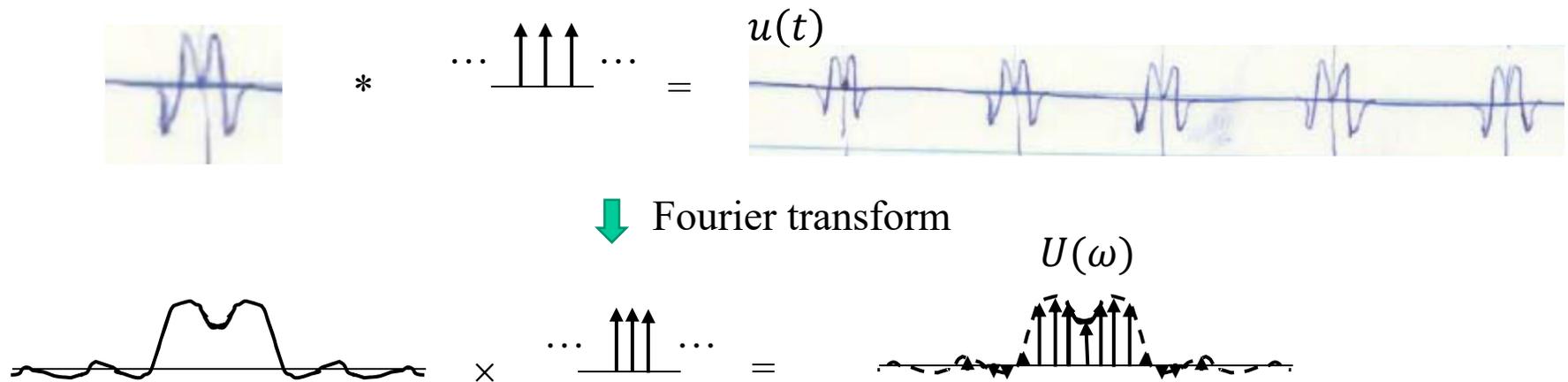
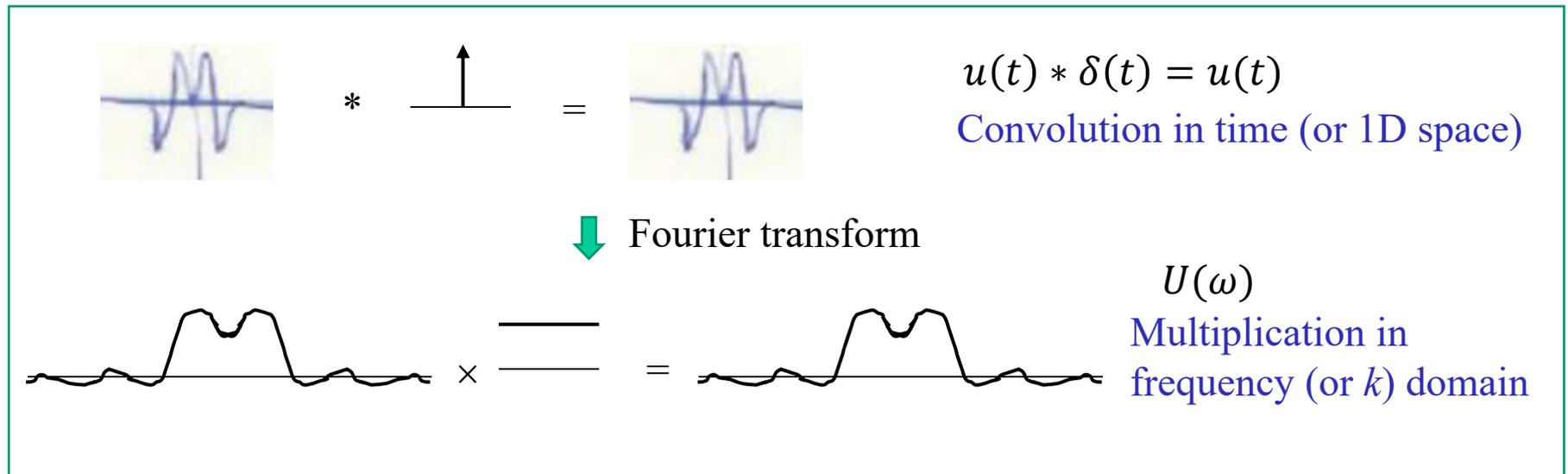
$$\psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n,\mathbf{k}}(\mathbf{r})$$

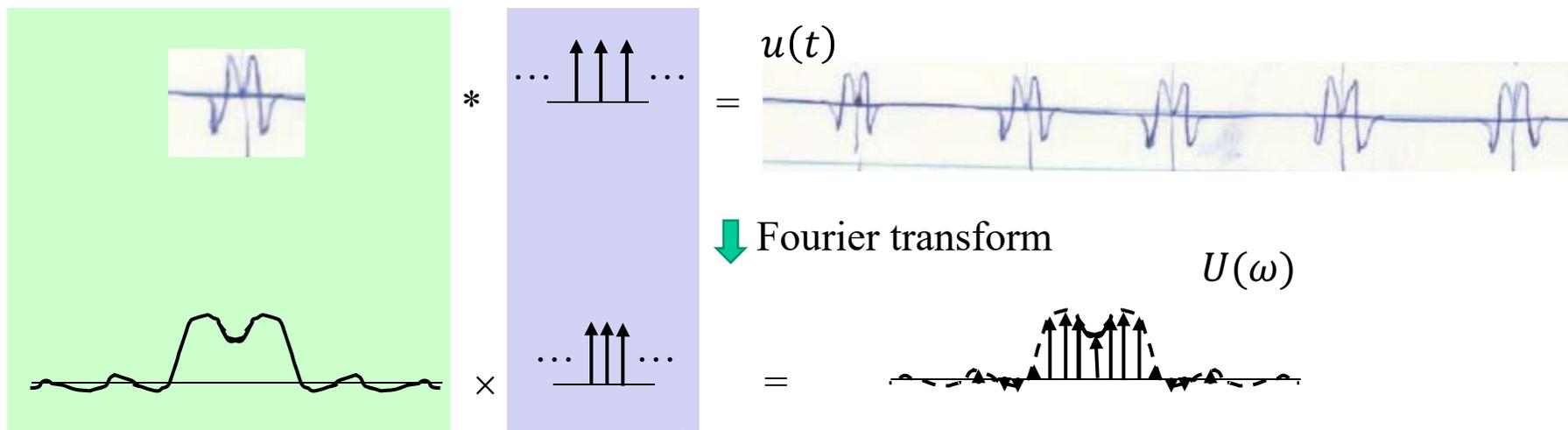
Here, n is the **band index**.

A periodic function $u(\mathbf{r})$ is a solution to the Schrödinger Eq (with $\mathbf{k} = 0$), but the Bloch function is general.

We understood Bloch's theorem in 1D space by using time-domain signal analogy.

We need to better understand 3D periodicity.



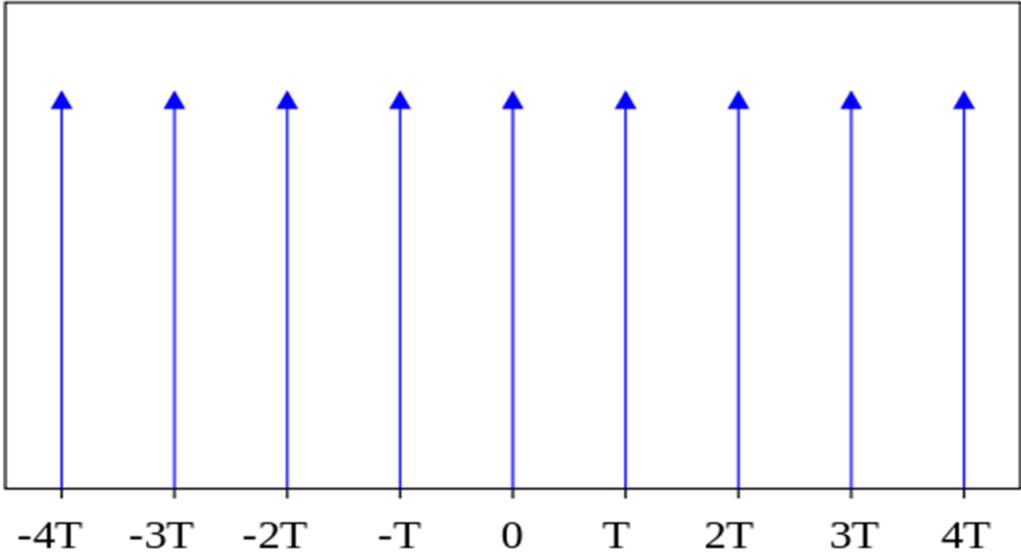


For **whatever we are to study**, the δ impulse comb captures the periodicity.

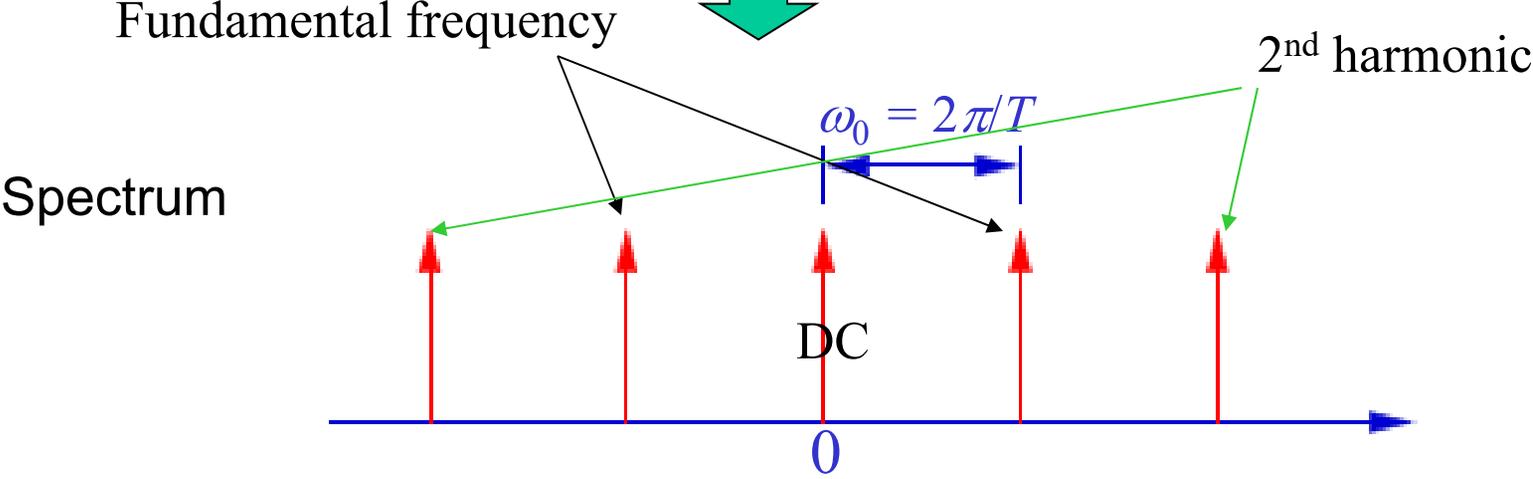
We now examine the **periodicity**, which can be applied to **whatever we are to study**.

Infinitely long impulse comb

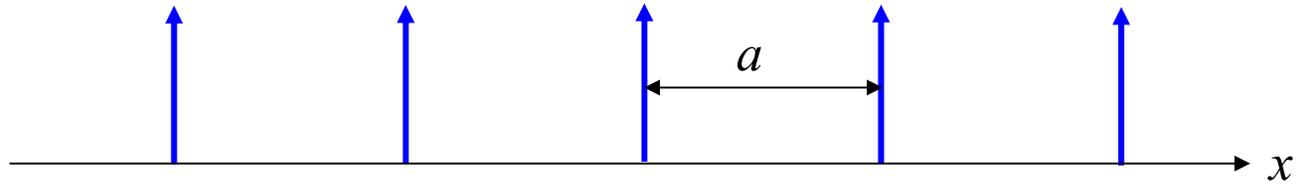
Time-domain signal



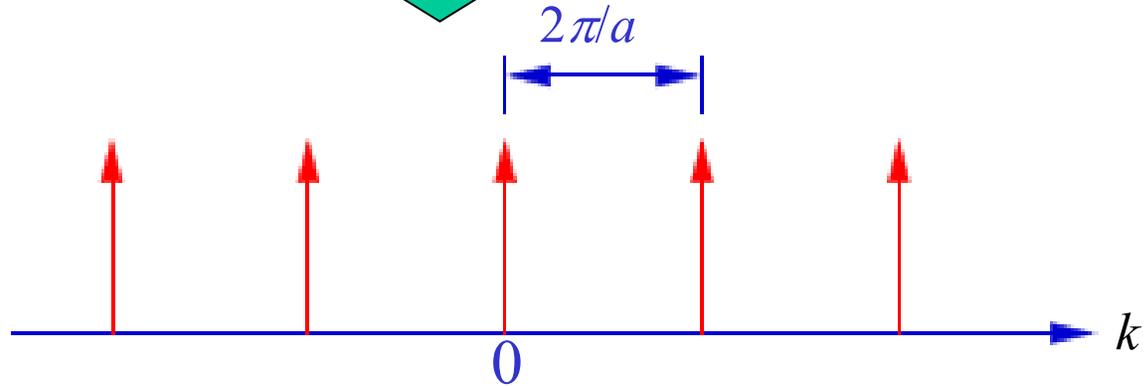
Fourier transform



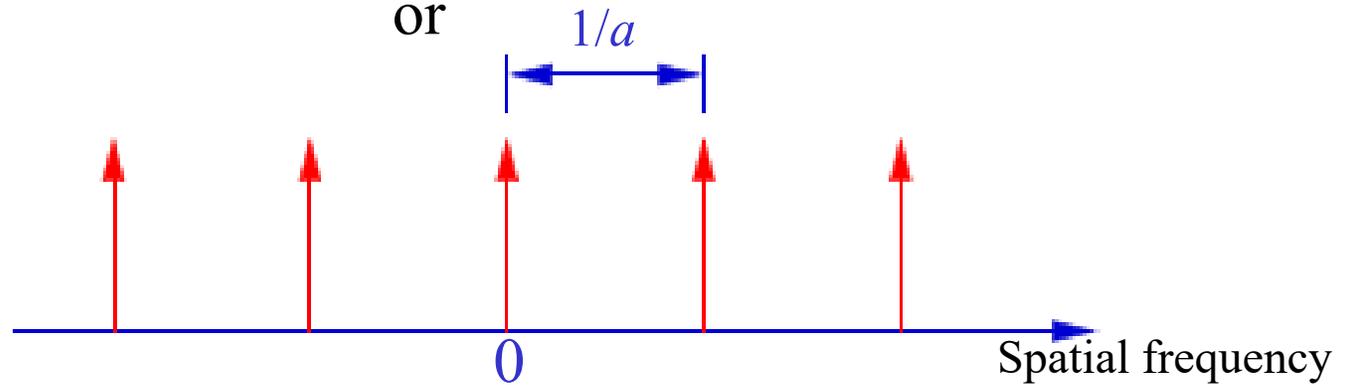
The math is the same for space (as for time)



Fourier transform

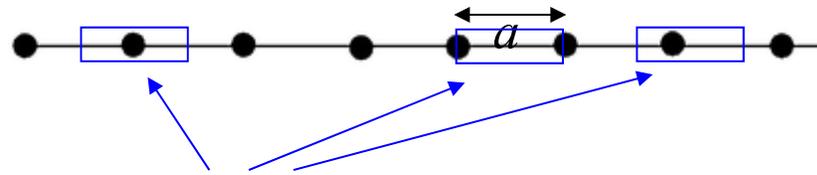


or



You may replace the spikes with points

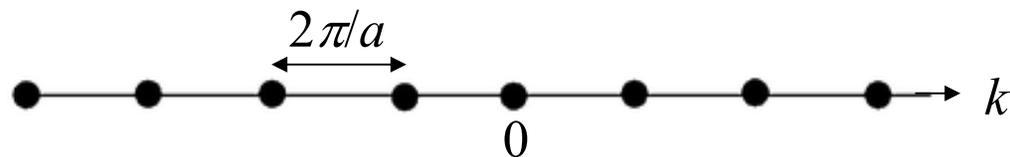
In real space:



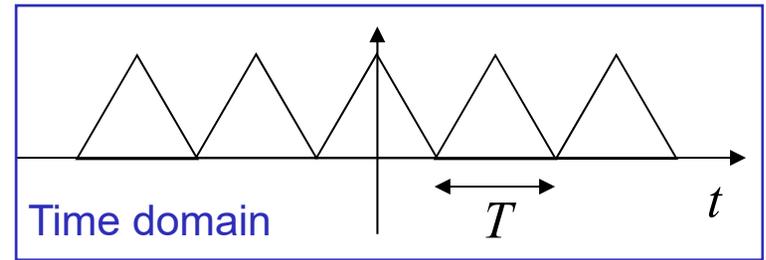
We call a period a “unit cell.” Infinite choices for the unit cell.



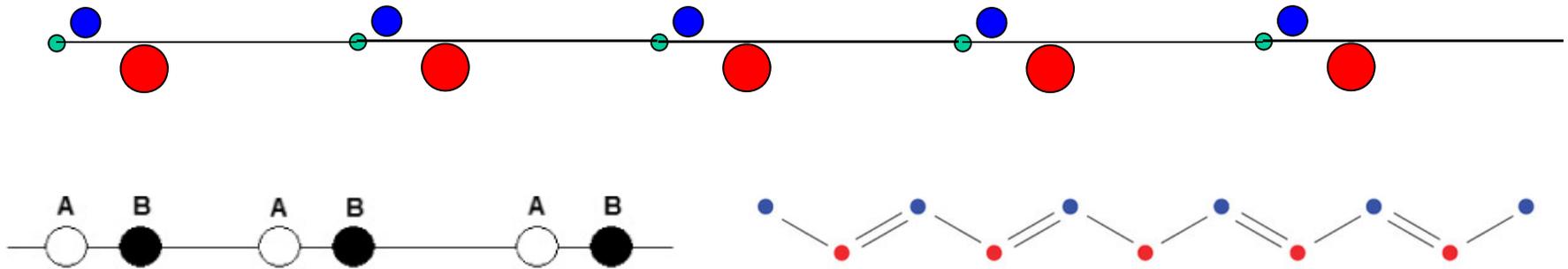
In reciprocal (or k -) space:



Just like you can have a pulse train in **time domain**

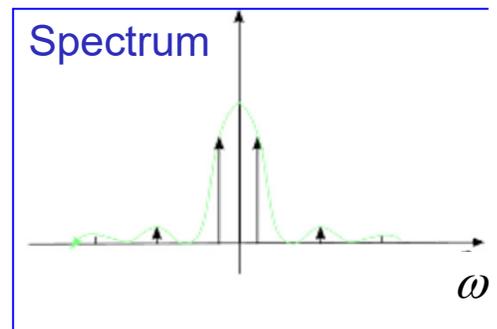
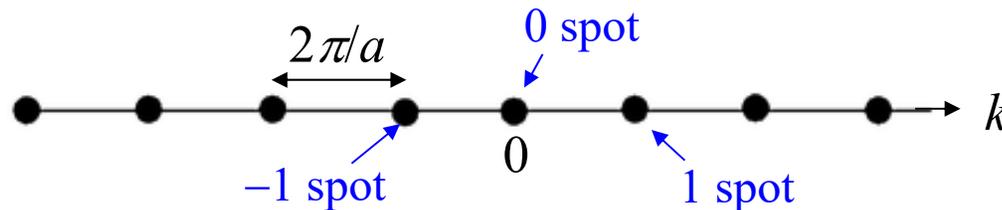


the unit cell can have an **internal structure**



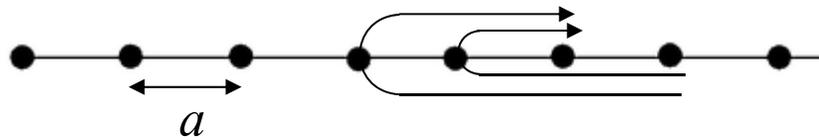
Again, you have infinite choices defining the unit cell, but the **periodicity** remains the same for all choices.

Fourier transform
(A computer can do FFT)



The intensities of the spots vary due to the **unit cell** internal structure, just like in the spectrum of a time-domain pulse train:

Nature's way of doing Fourier transform: Diffraction



← Shine a beam (X-ray) with many wavelengths (broadband)

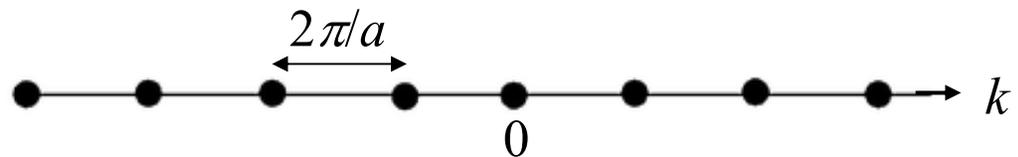
To have constructive interference between reflections by all atoms/unit cells:

$$a = \frac{\lambda}{2} n \quad \Rightarrow \quad \frac{2\pi}{k} = \lambda = \frac{2a}{n} \quad \Rightarrow \quad \boxed{k = n \frac{2\pi}{2a}}$$

← The k of the photon

The k (vector, proportional to its momentum) of the photon is changed upon reflection by

$$|\Delta k| = |k_f - k_i| = 2 \left(n \frac{2\pi}{2a} \right) = n \frac{2\pi}{a}$$

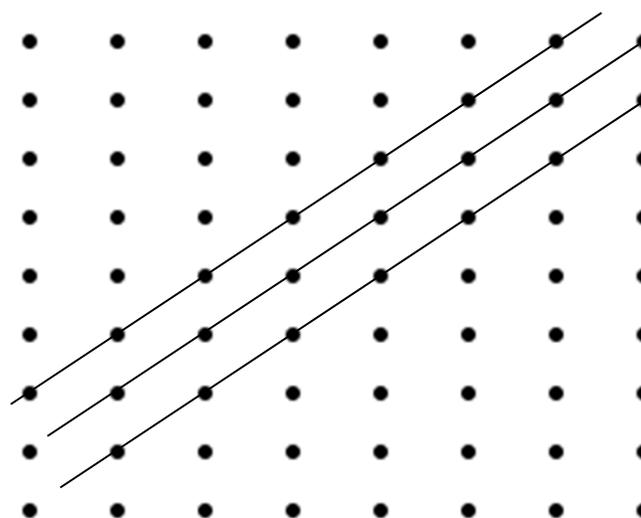
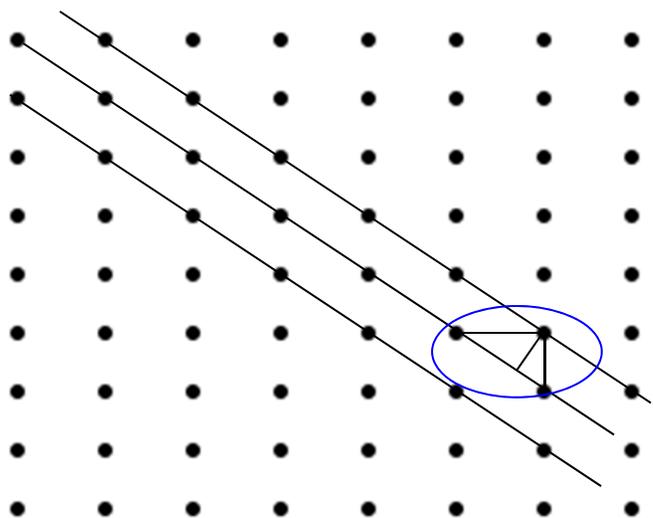
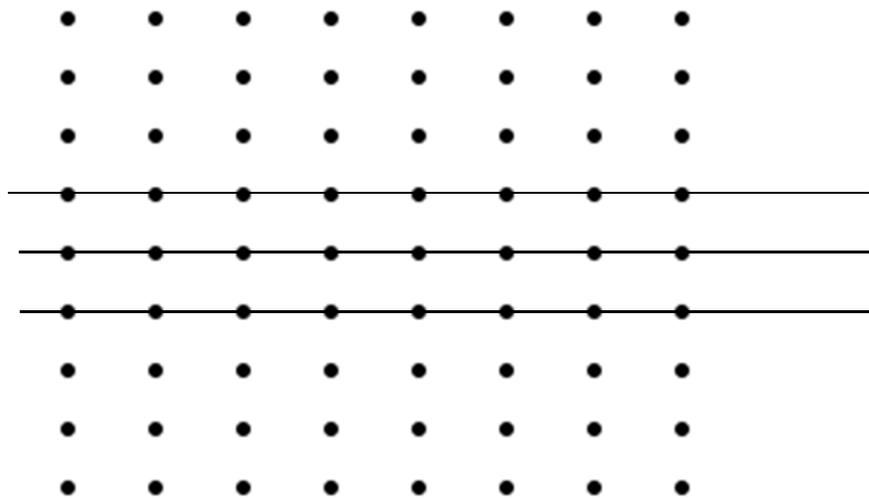
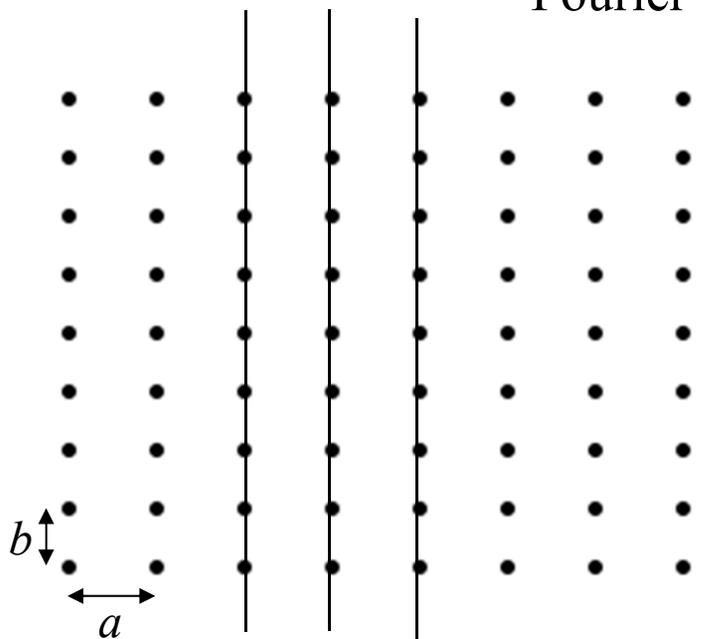


You see, the Fourier transform is just a “spectrum” of Δk .

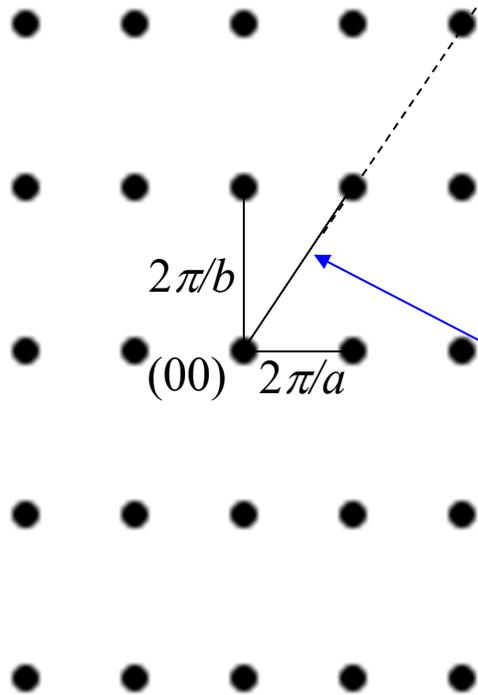
It feels like the lattice gives the photons momenta $n(2\pi/a)$.

You have a kind of “**momentum conservation.**”

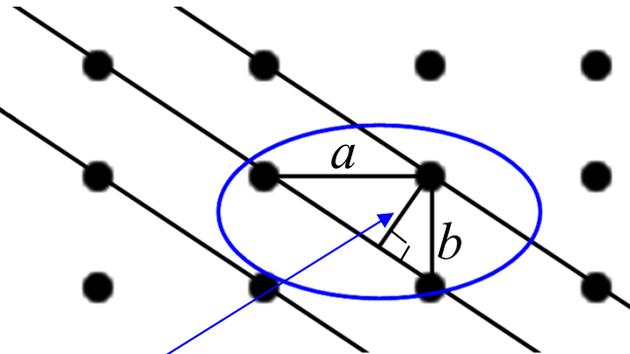
Fourier transform in 2D



Reciprocal

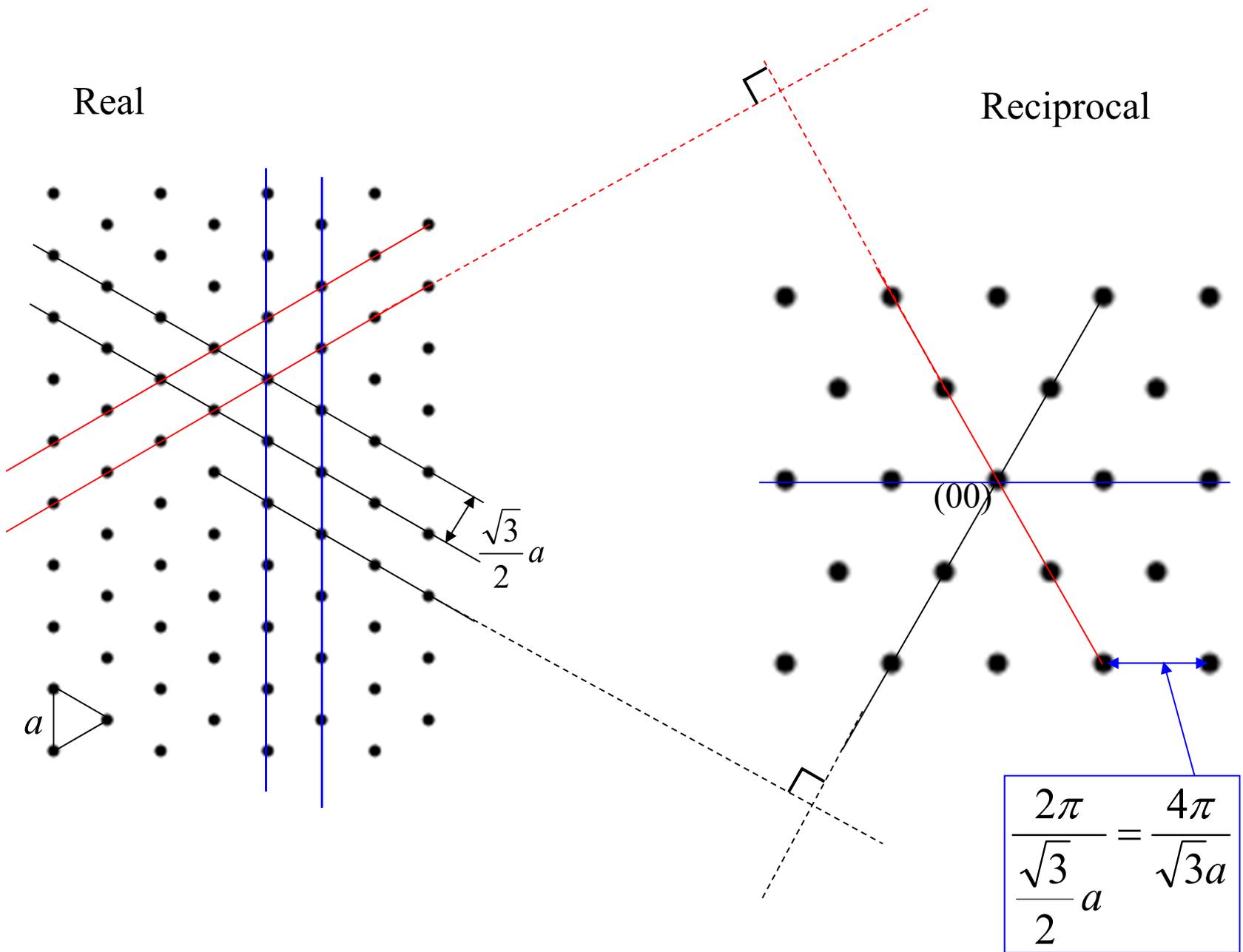


Real

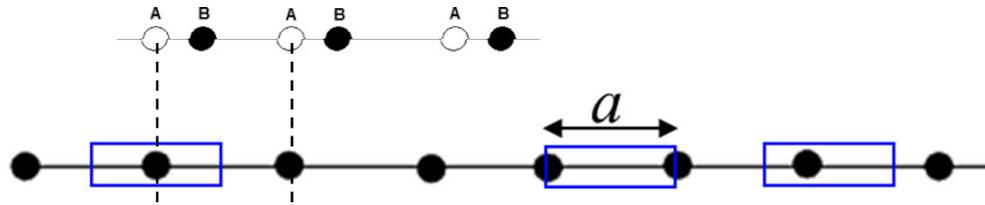


$$\frac{ab}{\sqrt{a^2 + b^2}}$$

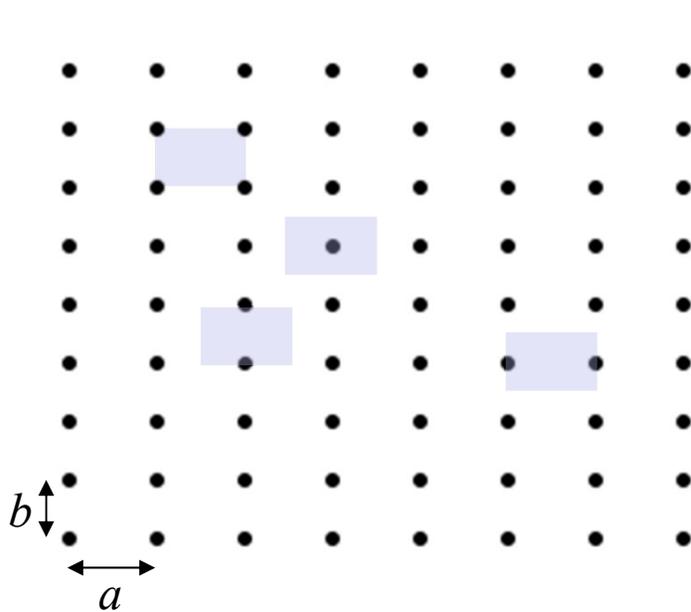
$$\frac{2\pi\sqrt{a^2 + b^2}}{ab}$$



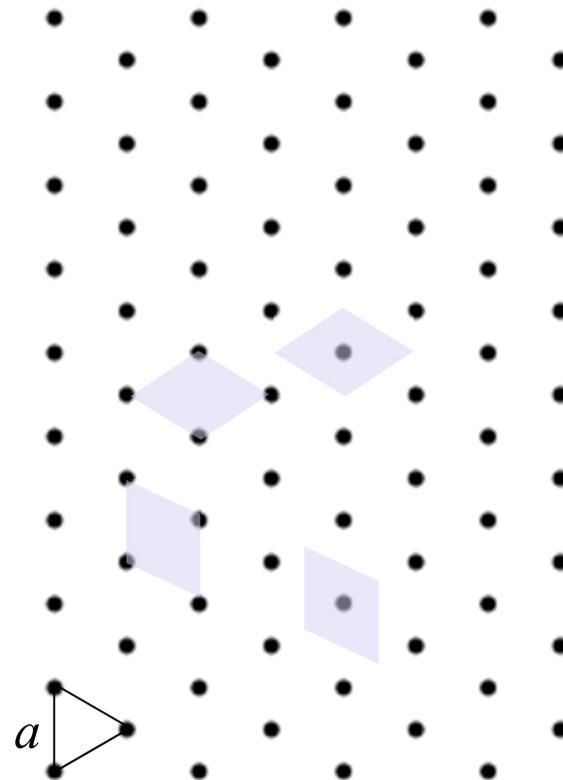
The periodic structure with out an internal structure of the unit cell is the Bravais lattice.



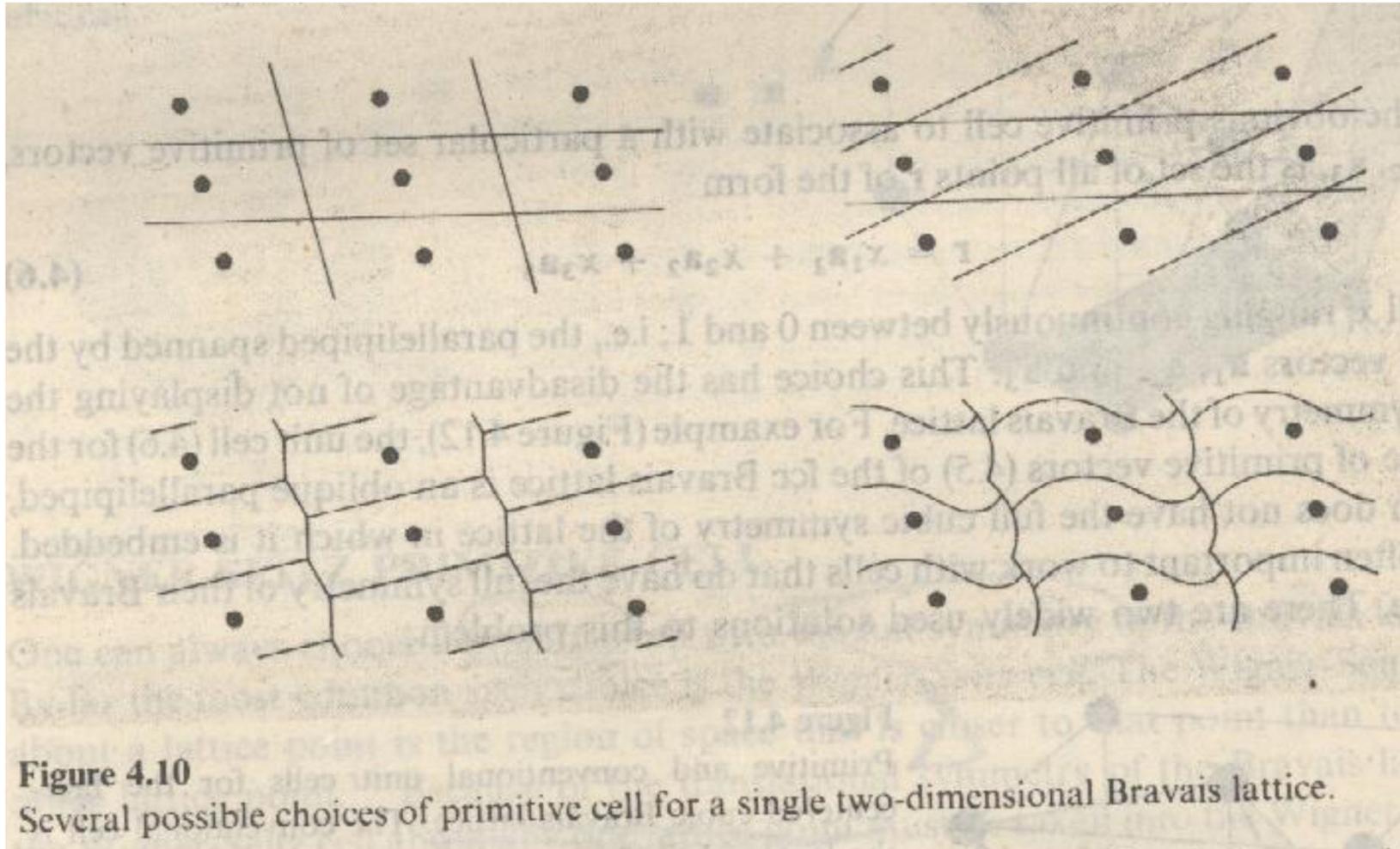
The **periodic structure** without an internal structure of the **unit cell** is the **Bravais lattice**.



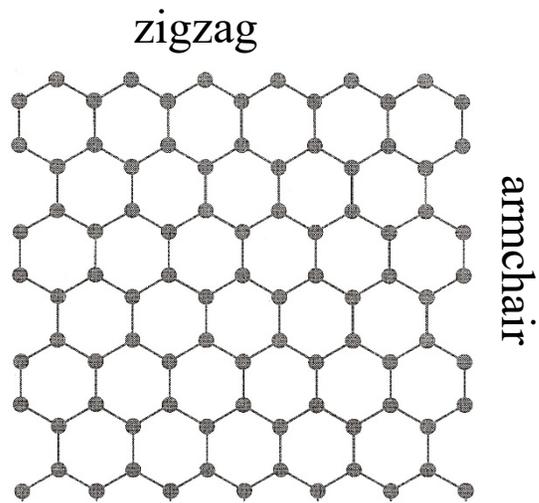
Infinite choices defining the unit cell.
Periodicity remains the same for all choices.



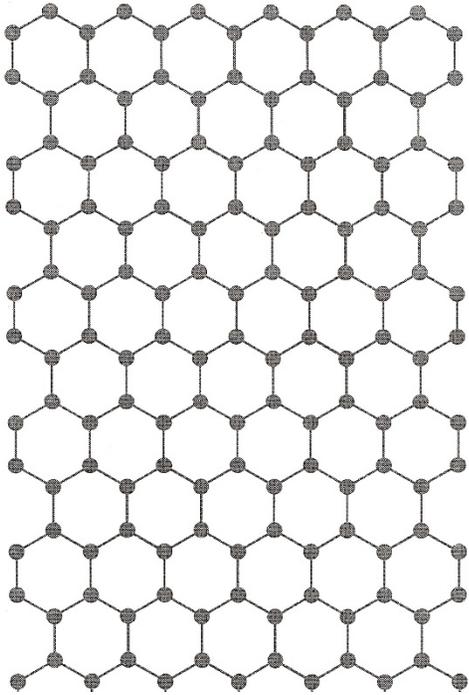
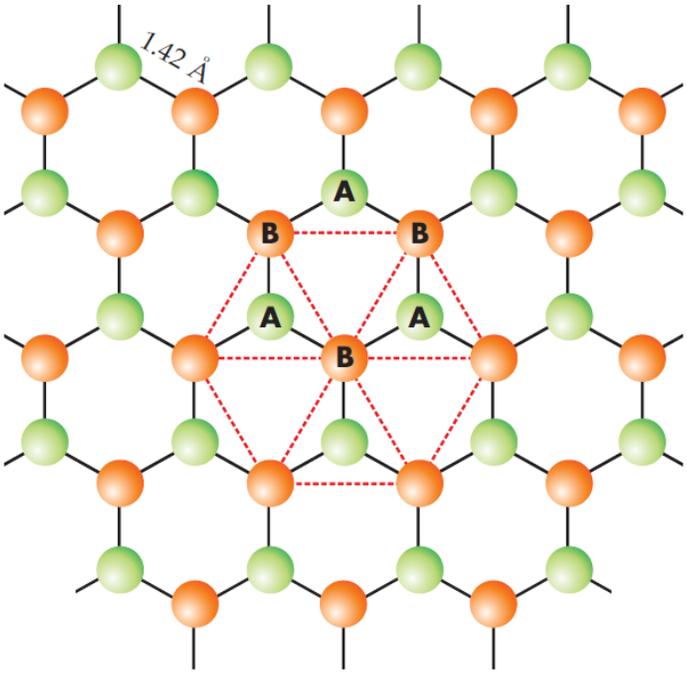
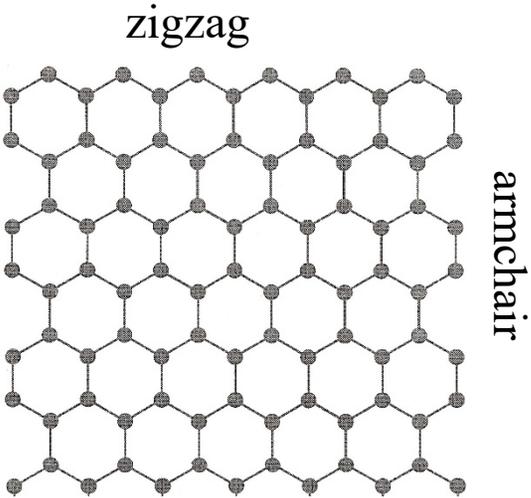
Infinite choices to define the unit cell.
Periodicity remains the same for all choices.



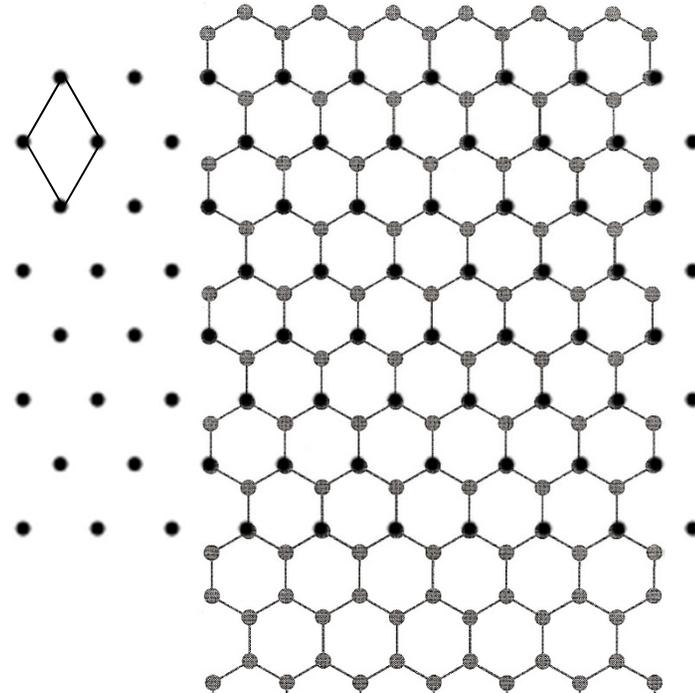
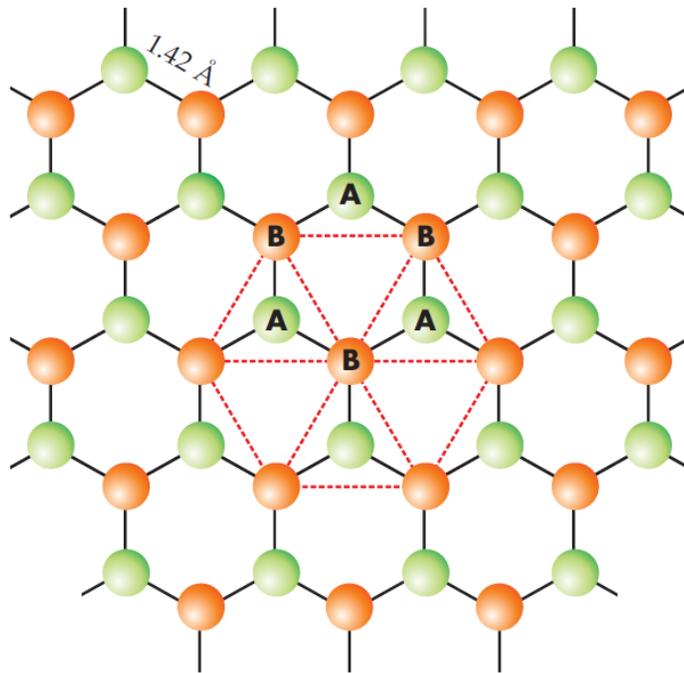
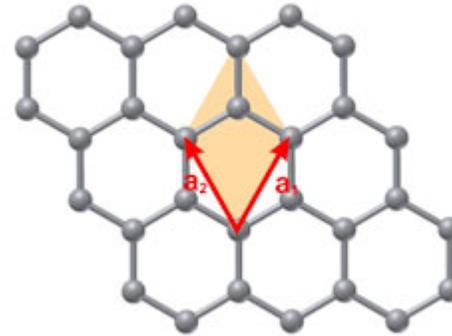
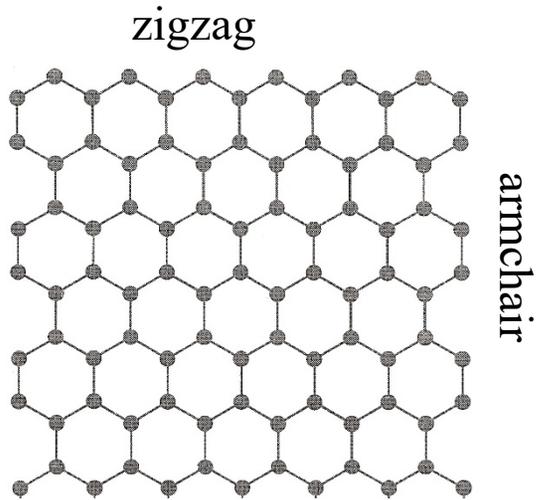
Is the graphene “lattice” a (Bravais) lattice?



Wait a minute, is the graphene “lattice” a lattice?

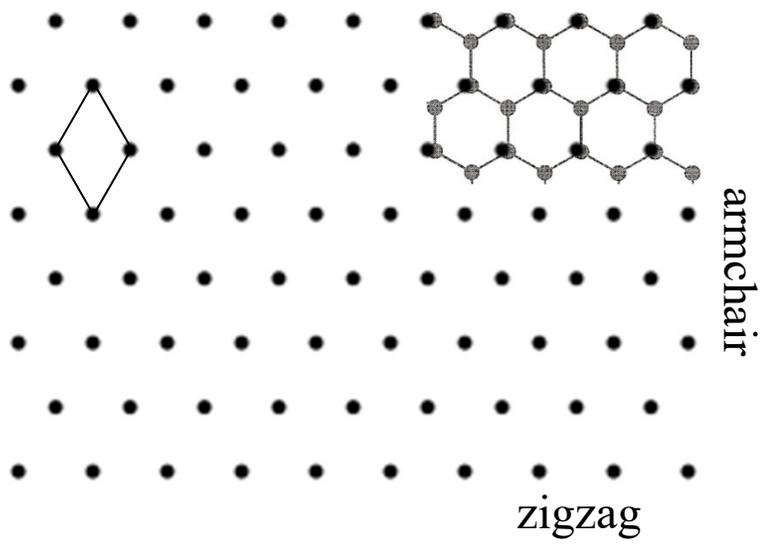


Wait a minute, is the graphene “lattice” a lattice?

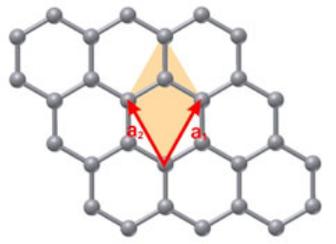
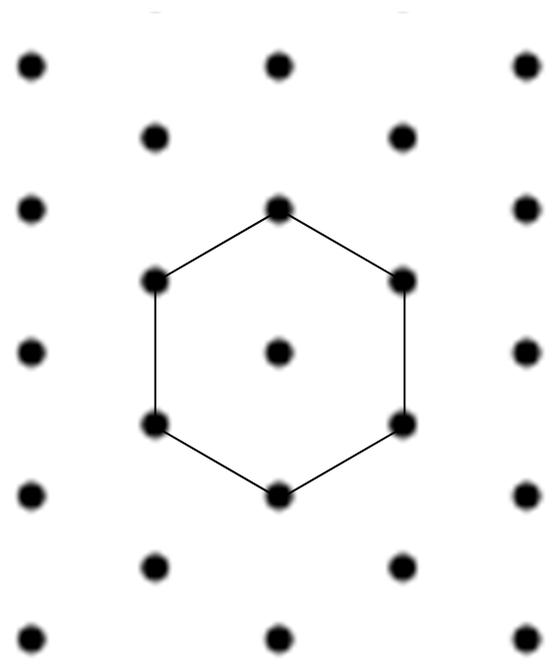


Crystal structure = lattice + basis

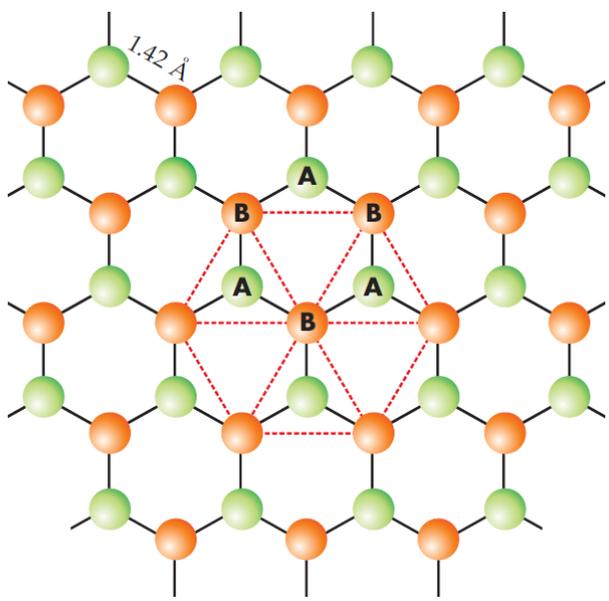
Real



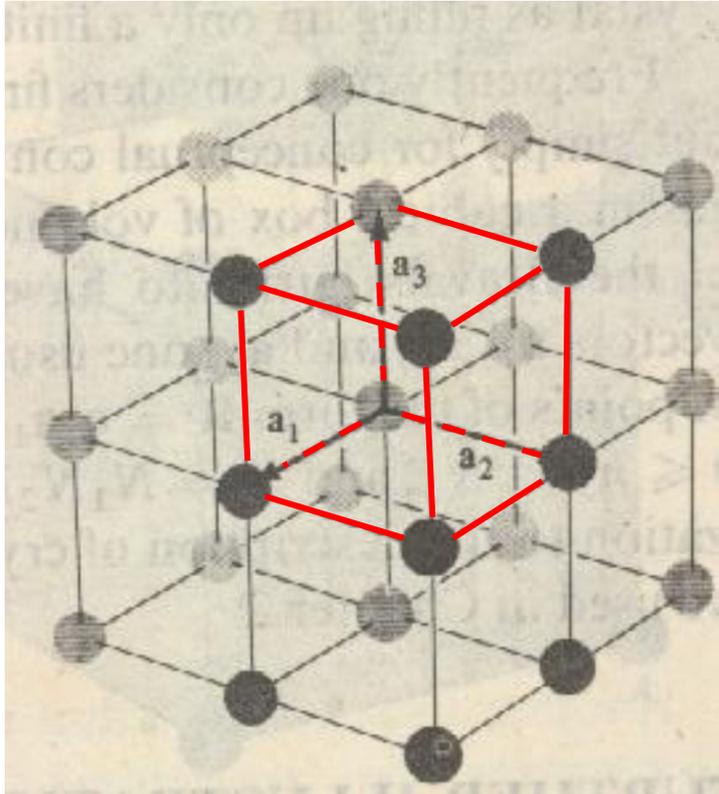
Reciprocal



2 atoms per unit cell



The simplest 3D Bravais lattice



Simple cubic

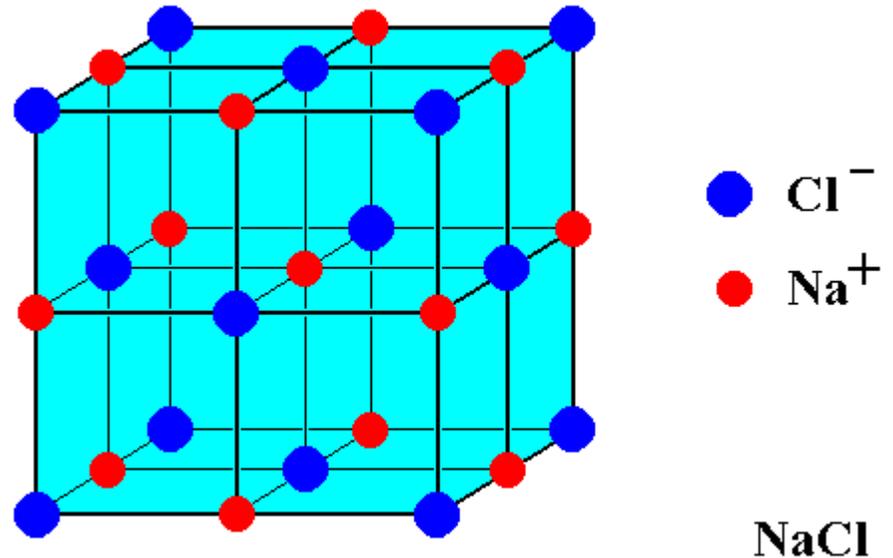
\mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 , are primitive vectors

In a 3D Bravais lattice, each lattice point is represented by a position vector

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

How many lattice points per unit cell?

Question

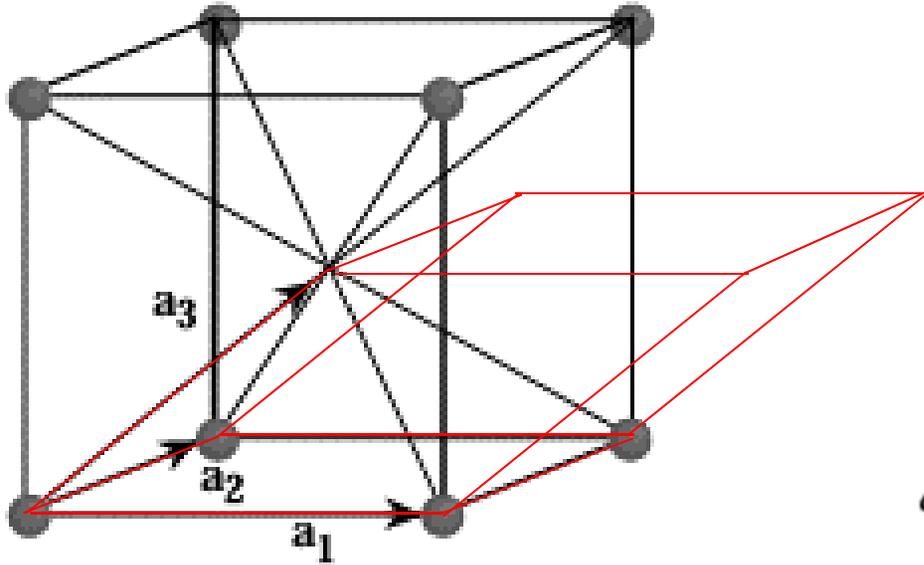


<https://chemistry.stackexchange.com/questions/34119/number-of-atoms-in-nacl-unit-cell>

Is the NaCl structure a simple cubic lattice?

Other frequently seen lattices

Conventional vs. primitive unit cells



BCC (body-centered cubic)

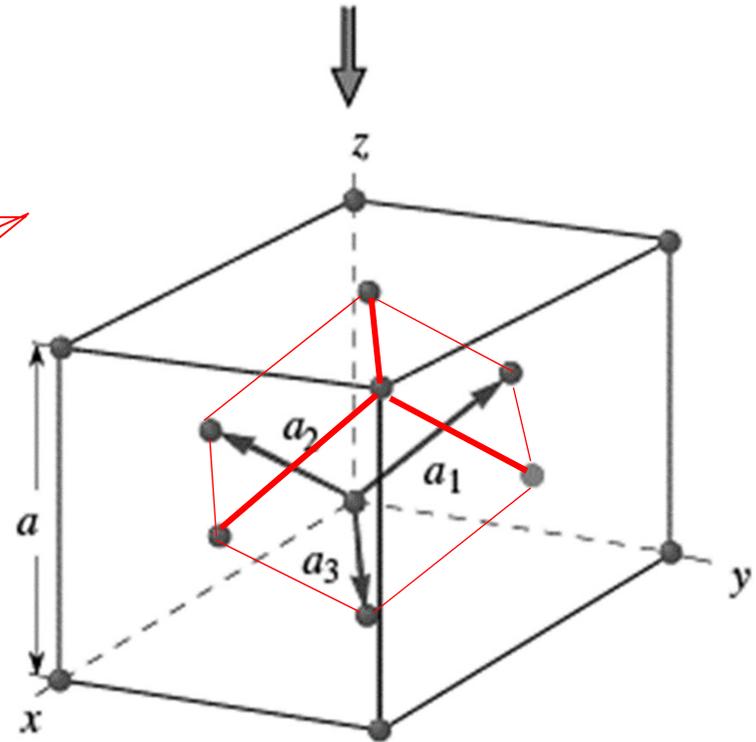


Figure 1.3: Primitive basis vectors for the face centered cubic lattice.

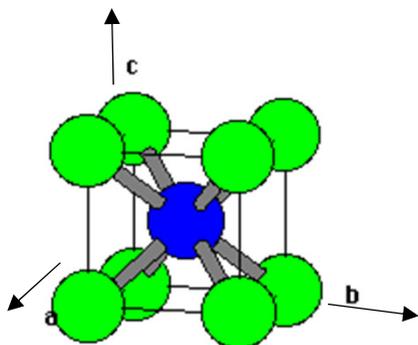
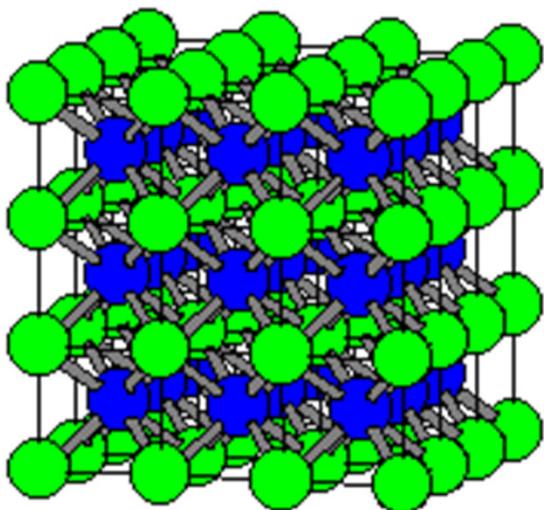
FCC (face-centered cubic)

BCC & FCC are Bravais Lattices.

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

How many lattice points in the conventional unit cells?

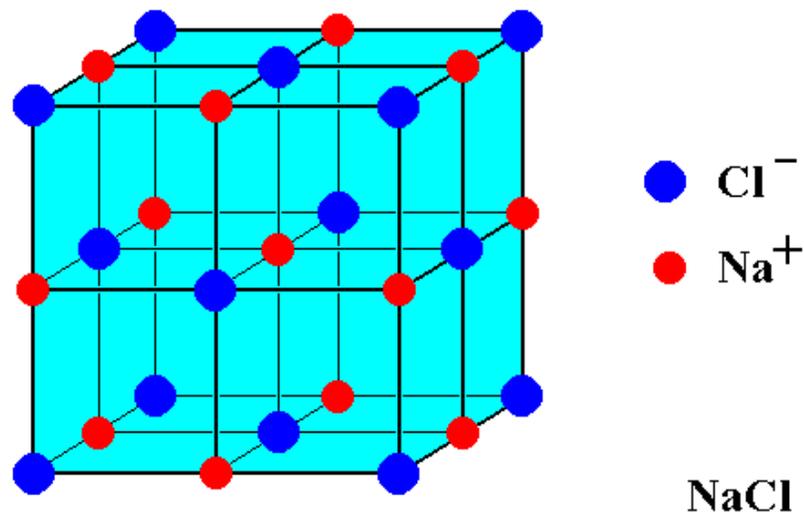
CsCl structure



<http://www.ilpi.com/inorganic/structures/cscl/index.html>

Is the CsCl structure a BCC lattice?

NaCl structure



<https://chemistry.stackexchange.com/questions/34119/number-of-atoms-in-nacl-unit-cell>

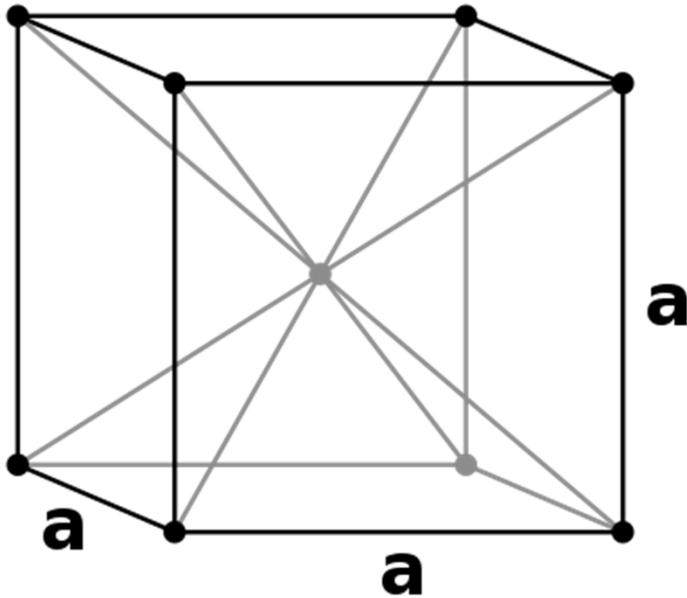
What's the underlying Bravais lattice of the NaCl structure?

How many atoms per primitive unit cell?

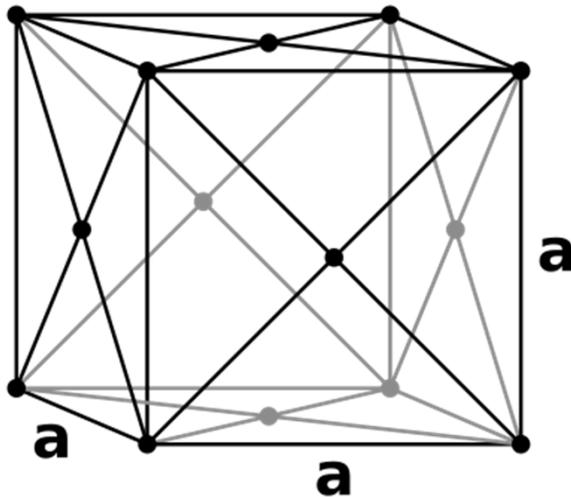
How many atoms per conventional unit cell?

Homework 4 problems:

The lattice parameter of a BCC lattice is a is the edge length of the **conventional unit cell**.
What is the volume of the **primitive unit cell**?
What is the volume per lattice point?

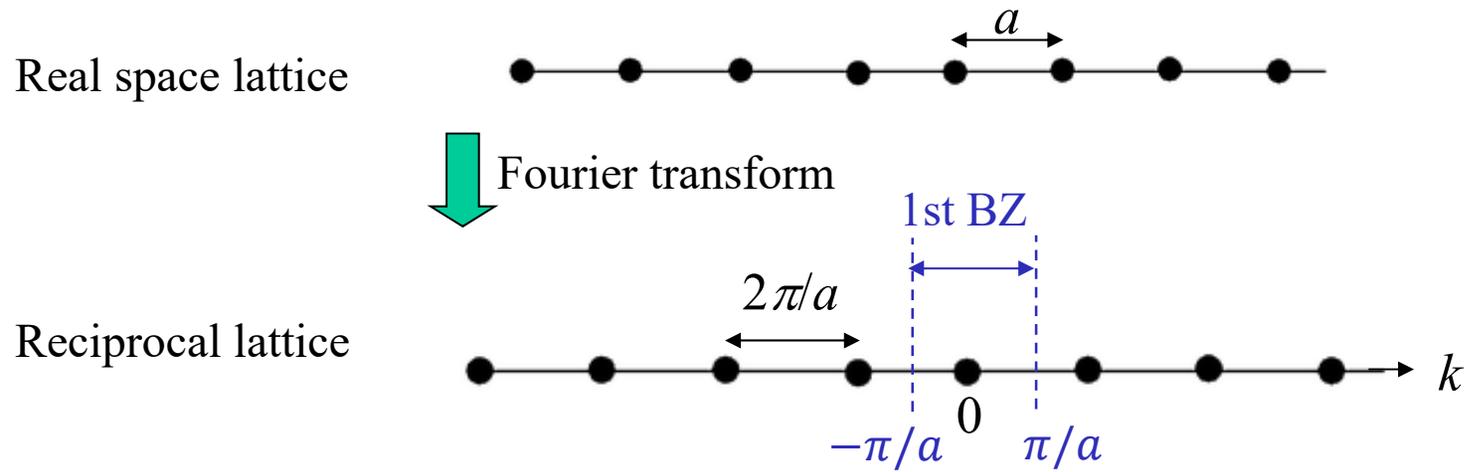


The lattice parameter of an FCC lattice is a is the edge length of the **conventional unit cell**.
What is the volume of the **primitive unit cell**?
What is the volume per lattice point?



Reciprocal lattice and first Brillouin zone

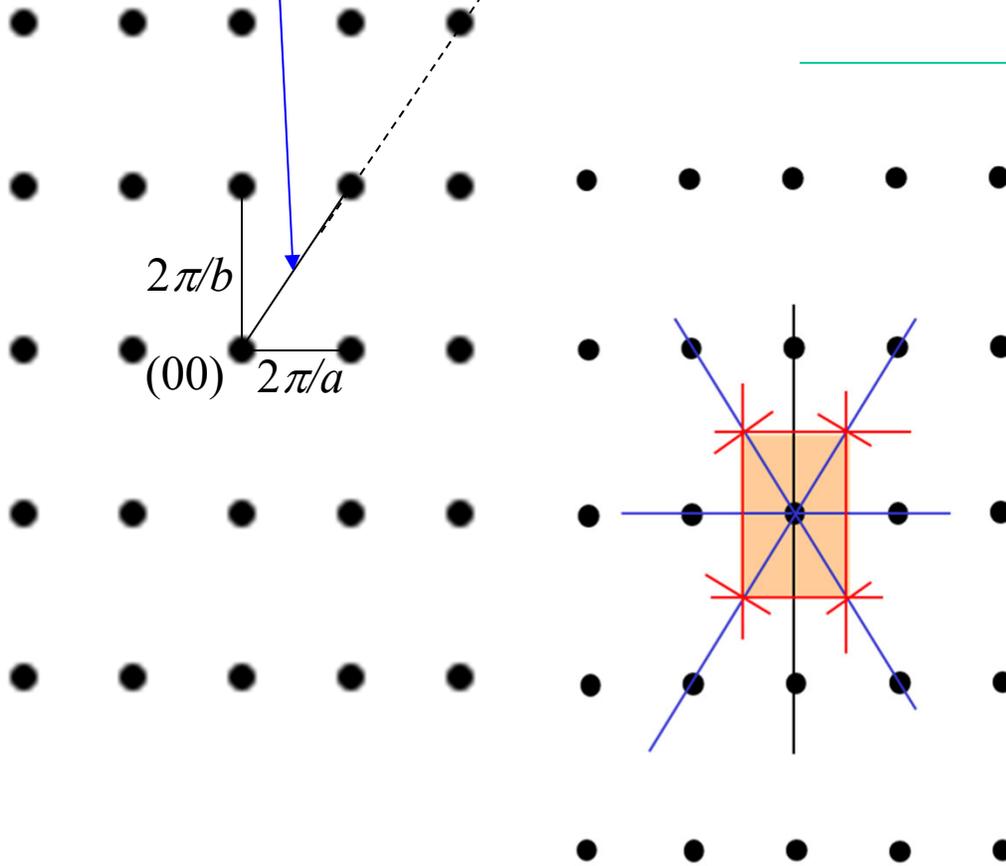
1D



2D

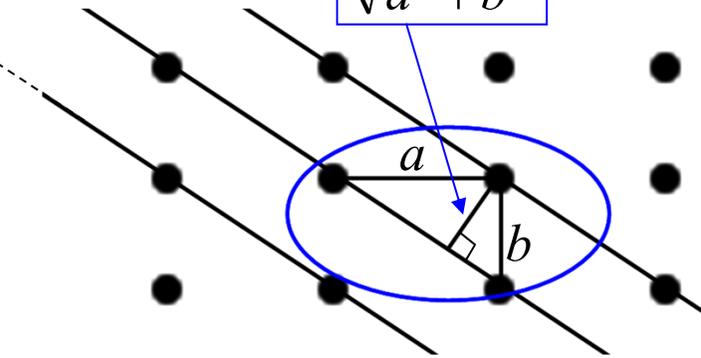
Reciprocal

$$\frac{2\pi\sqrt{a^2 + b^2}}{ab}$$

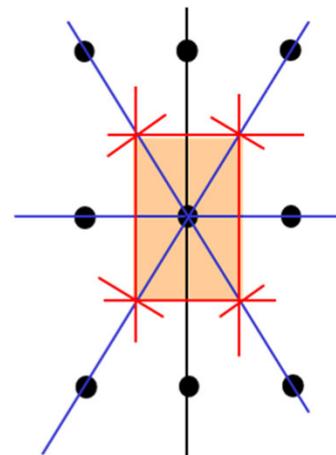


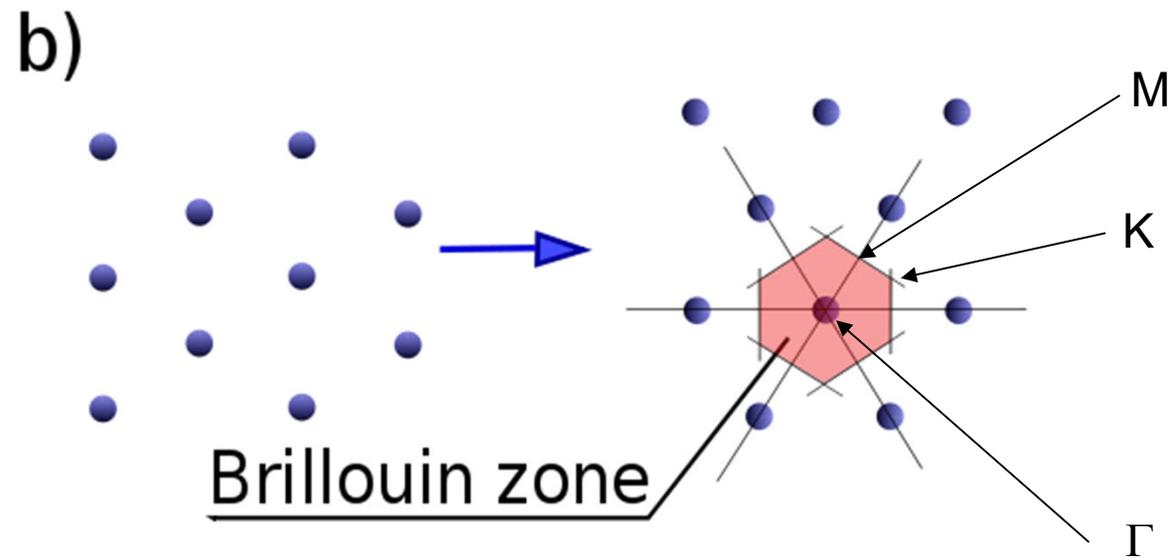
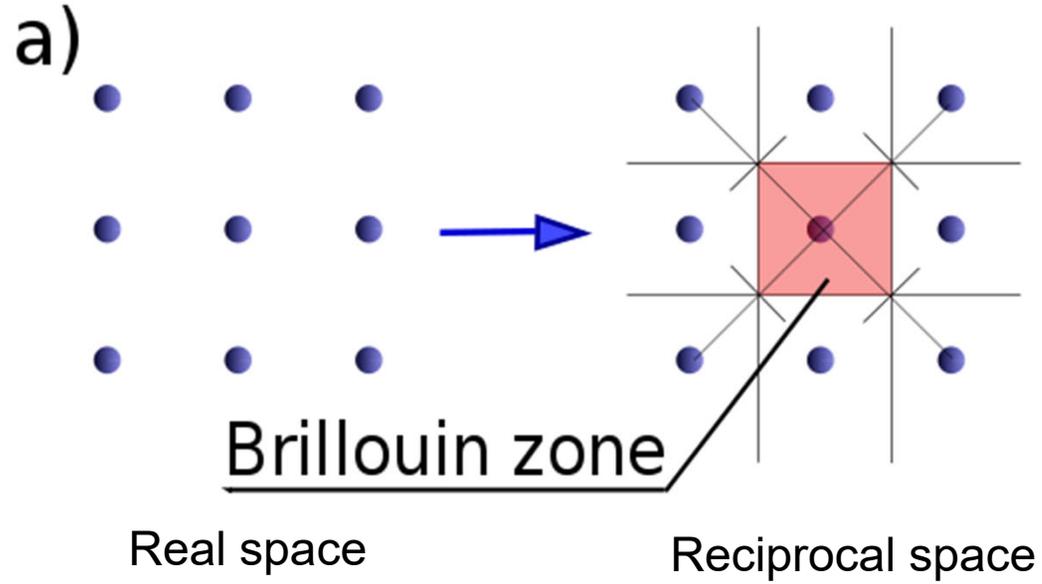
Real

$$\frac{ab}{\sqrt{a^2 + b^2}}$$



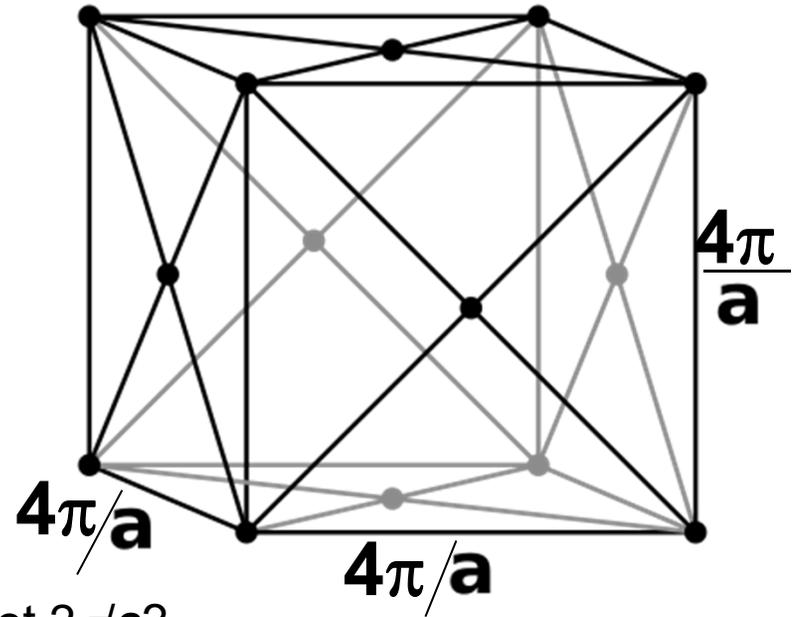
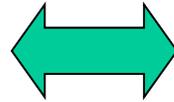
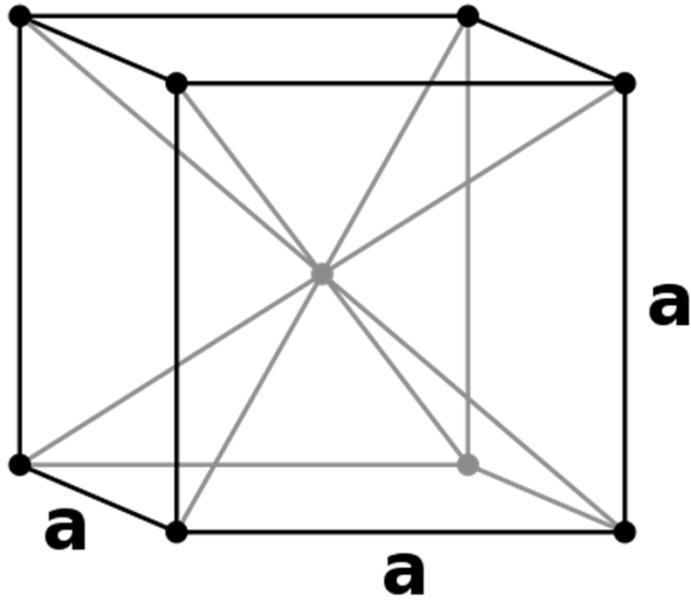
Construct the 1st BZ:
Connect point (00) to nearest neighbors.
Draw bisectors.
Area enclosed by all bisectors is the 1st BZ.



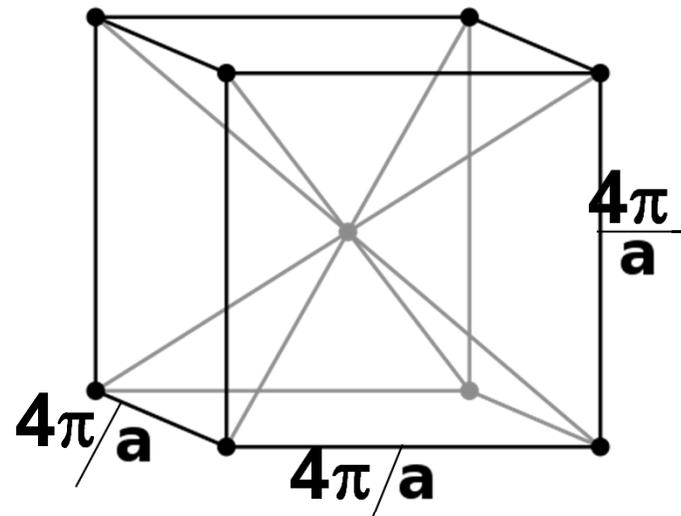
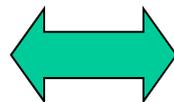
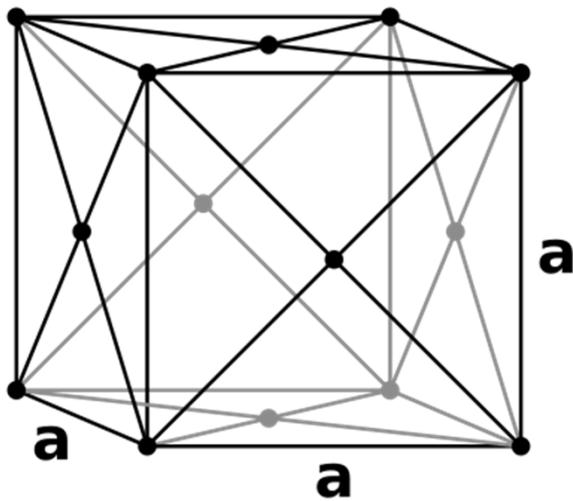


Names are given to
high-symmetry points

3D: BCC & FCC are reciprocal lattices of each other



Why not $2\pi a$?
(a Homework 4 problem)

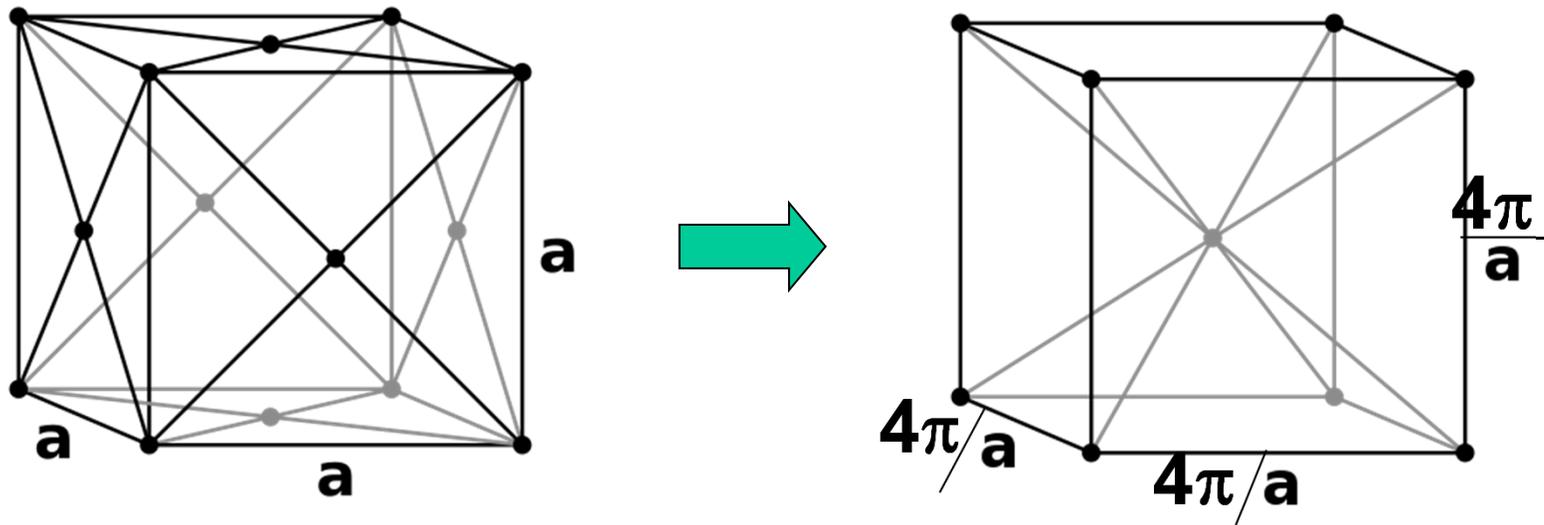


Homework 4 problems:

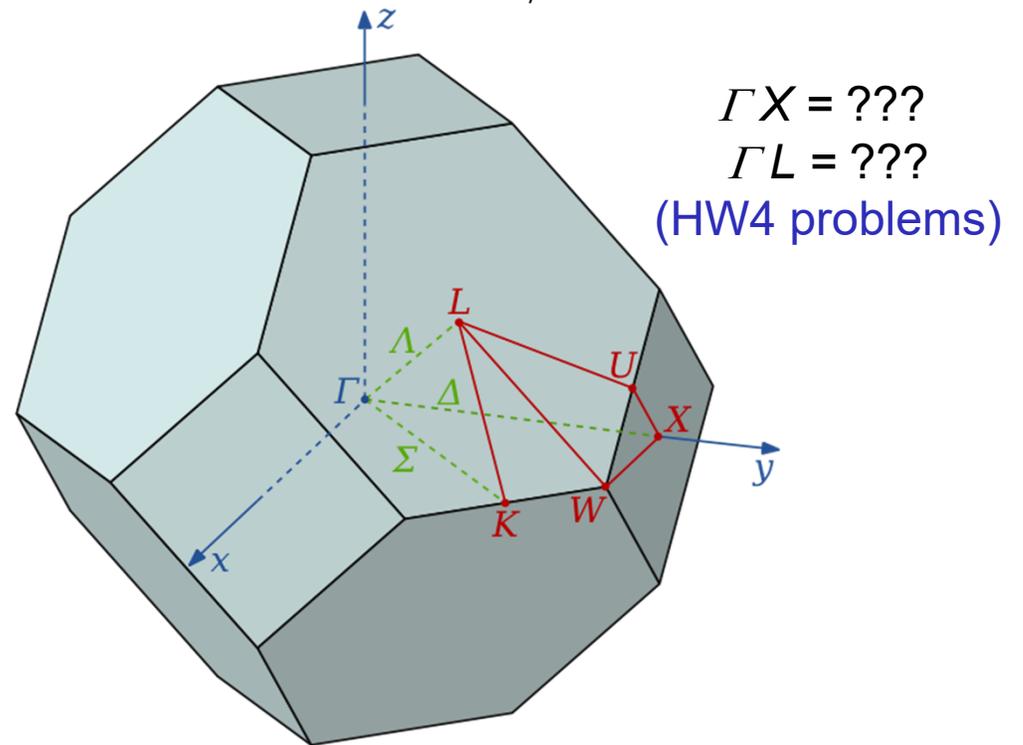
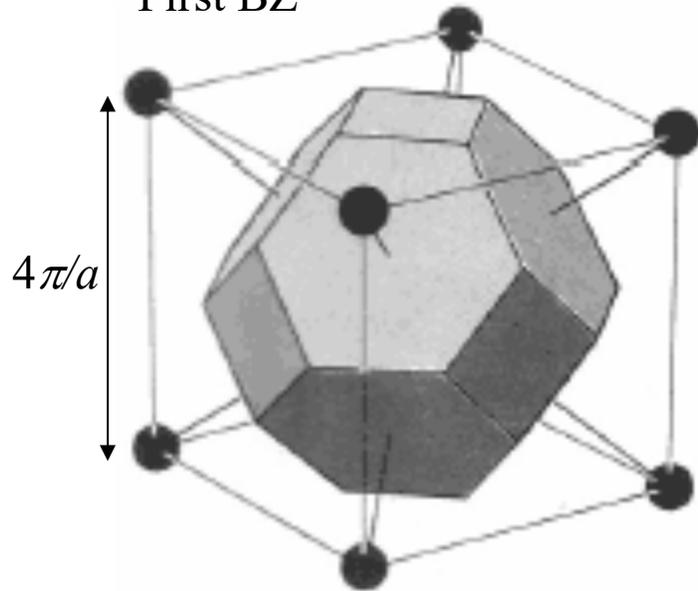
What is the reciprocal lattice of a simple cubic lattice of lattice parameter a ?

Given the fact that BCC & FCC are reciprocal lattices of each other (no need to prove it), show that the edge lengths of the FCC & BCC unit cells of the reciprocal lattices are $4\pi/a$.

The reciprocal lattice of FCC is BCC.



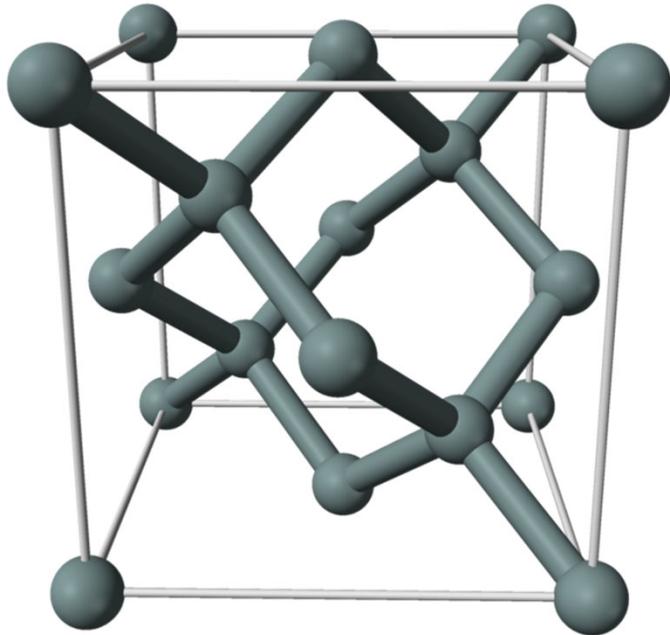
First BZ



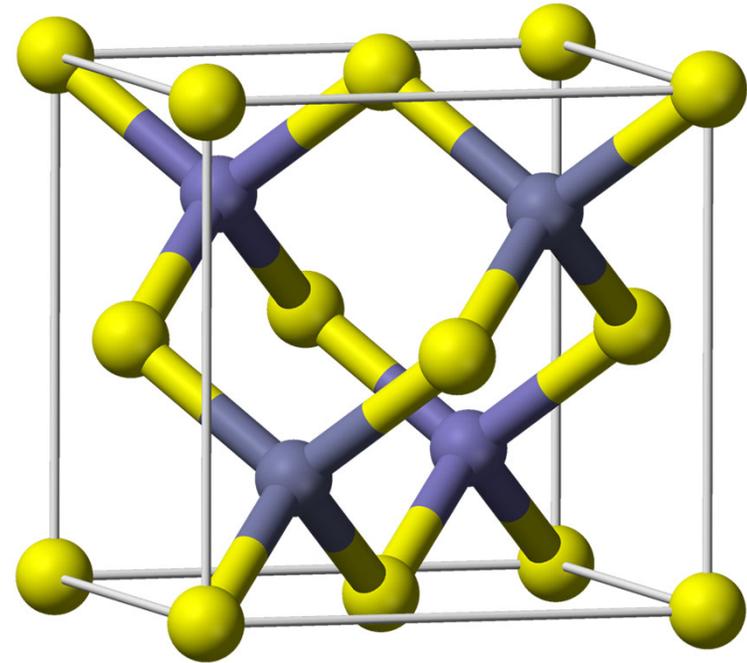
Why is FCC so important?

Why is FCC so important?

It's the underlying Bravais lattice of mainstream semiconductors (Si and many III-V).



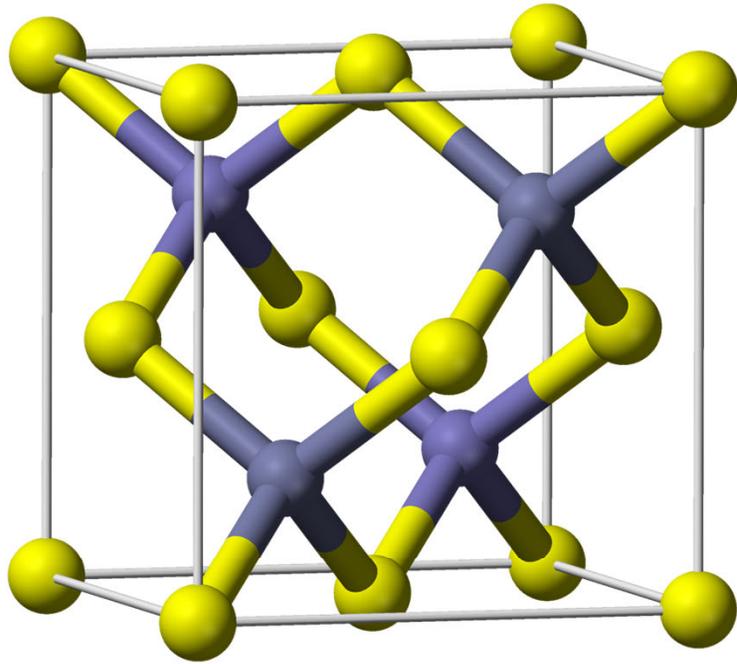
<https://fr.m.wikipedia.org/wiki/Fichier:Silicon-unit-cell-3D-balls.png>



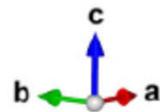
https://en.wikipedia.org/wiki/Cubic_crystal_system#Zincblende_structure

Si: diamond, $a = 5.4 \text{ \AA}$. GaAs: zincblende

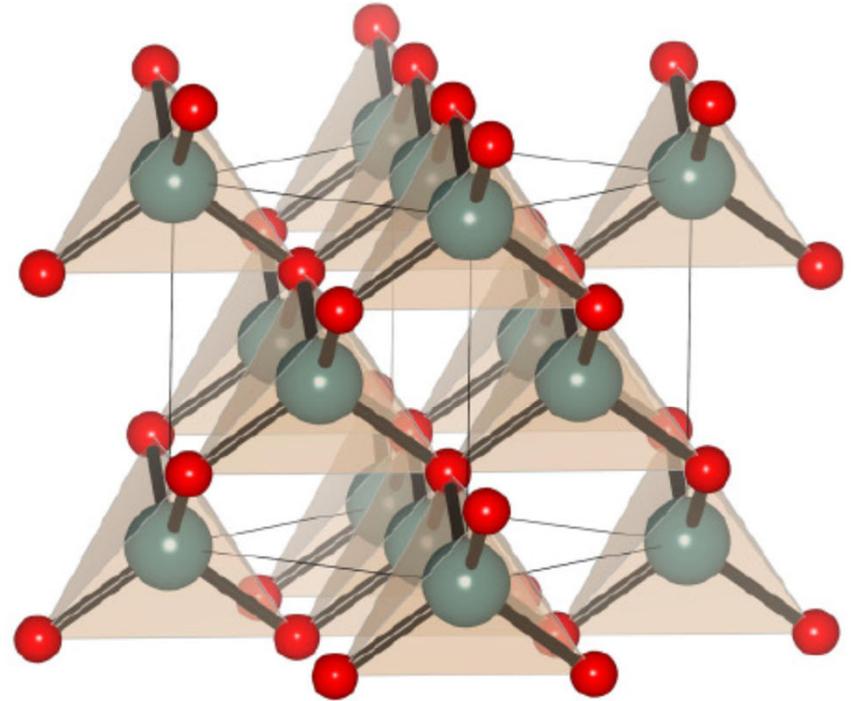
Crystal structure = lattice + basis (unit cell)



(c)



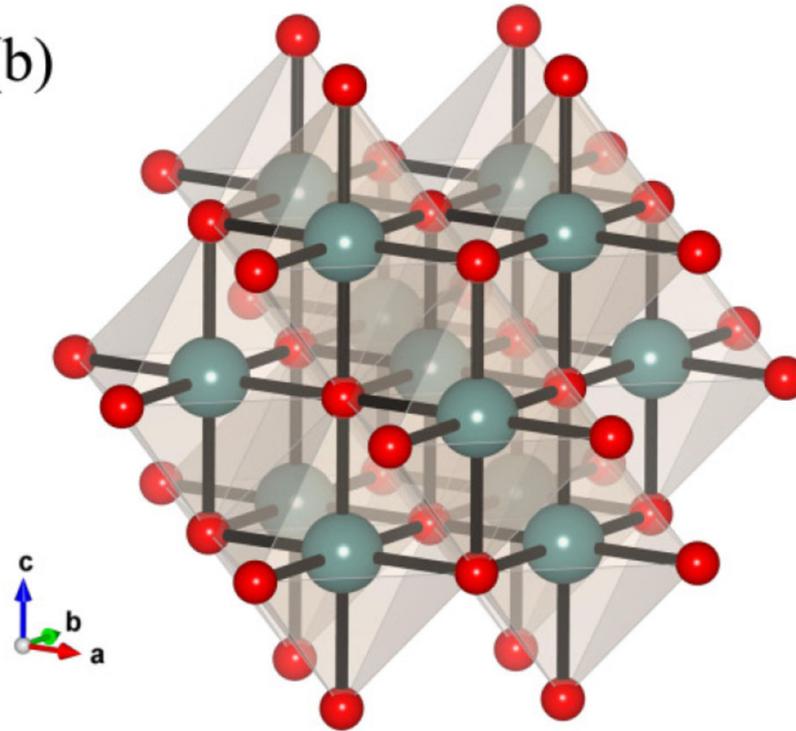
Zincblende: show the pyramid cages



Zagorac, PHYSICAL REVIEW B **89**, 075201 (2014)

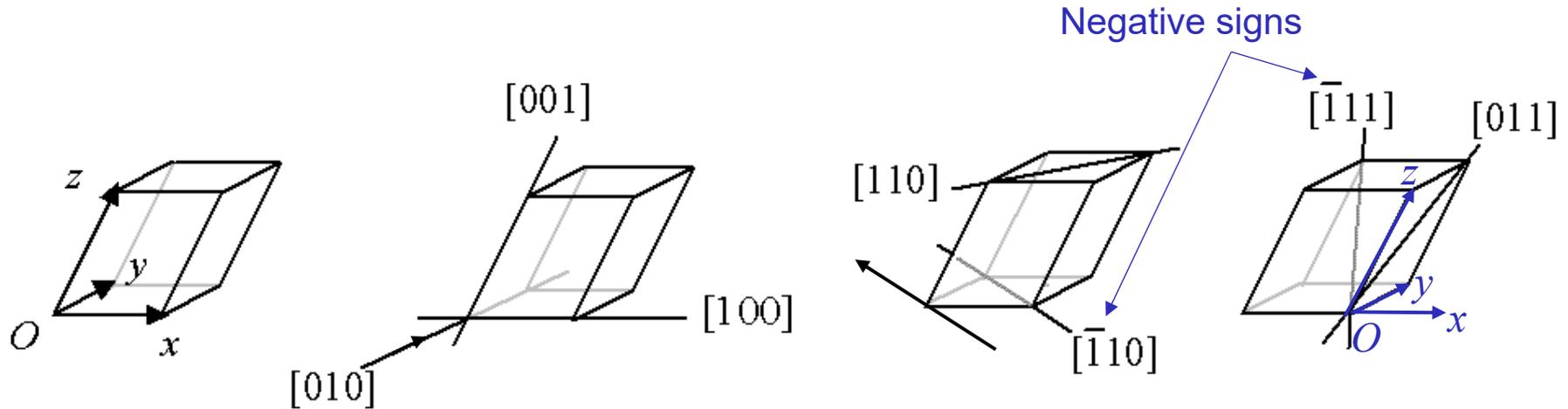
NaCl structure: show the octahedral cages

(b)



Crystallographic direction index

The related notation $[hkl]$ denotes the direction $h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3$



https://en.wikipedia.org/wiki/Miller_index

Cubic systems

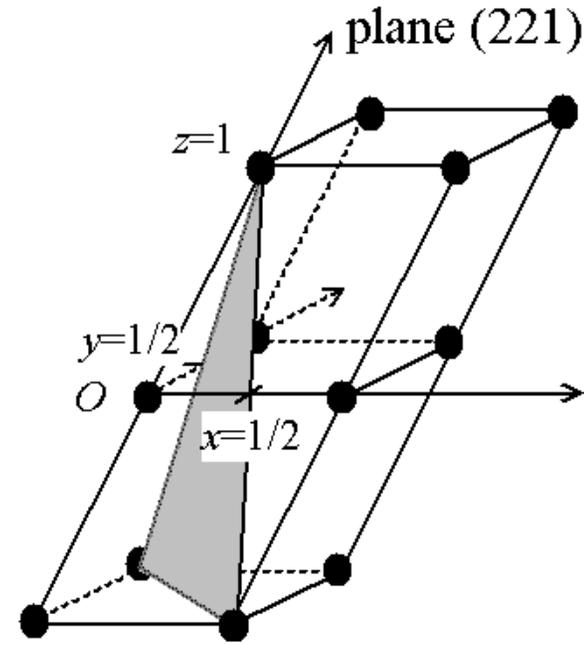
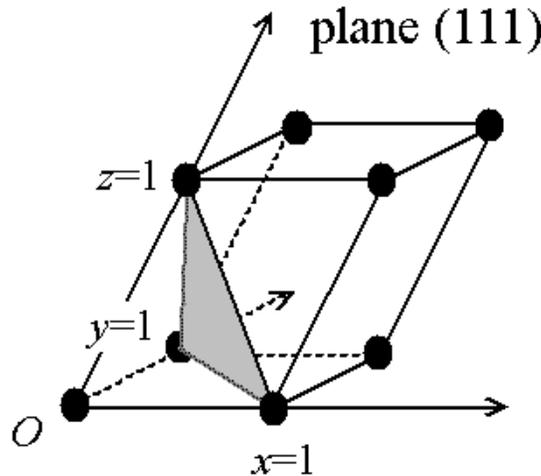
Indices in angle brackets such as $\langle 100 \rangle$ denote a family of directions that are equivalent due to symmetry operations, such as $[100]$, $[010]$, $[001]$.

Miller indices for crystallographic planes

(hkl) denotes planes orthogonal to the reciprocal lattice vector three Miller indices h, k, ℓ

$$\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3$$

Equivalently, (hkl) denotes a plane that **intercepts** the three points \mathbf{a}_1/h , \mathbf{a}_2/k , and \mathbf{a}_3/ℓ , or some multiple thereof.



https://en.wikipedia.org/wiki/Miller_index

This is an easier way to get the indices:

Reciprocals of the intercepts in real space;

No need to find the reciprocal primitive vectors.

If one of the indices is zero, it means that the planes do not intersect that axis (the intercept is "at infinity").

Different conventions in naming the real and reciprocal primitive vectors

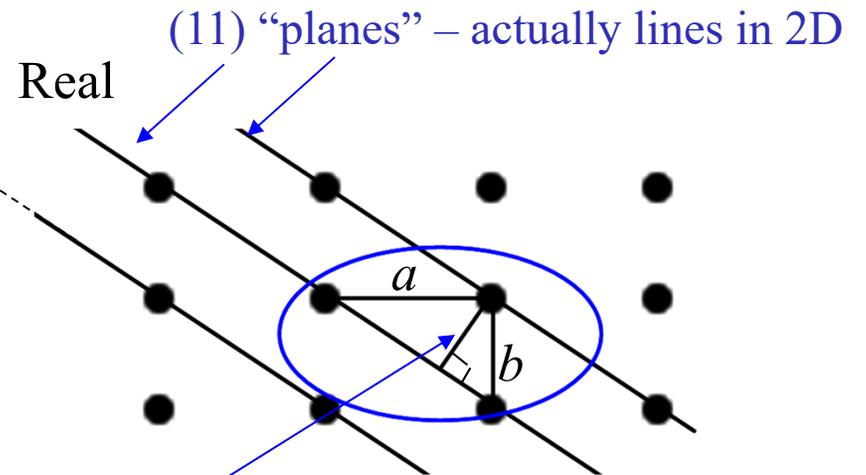
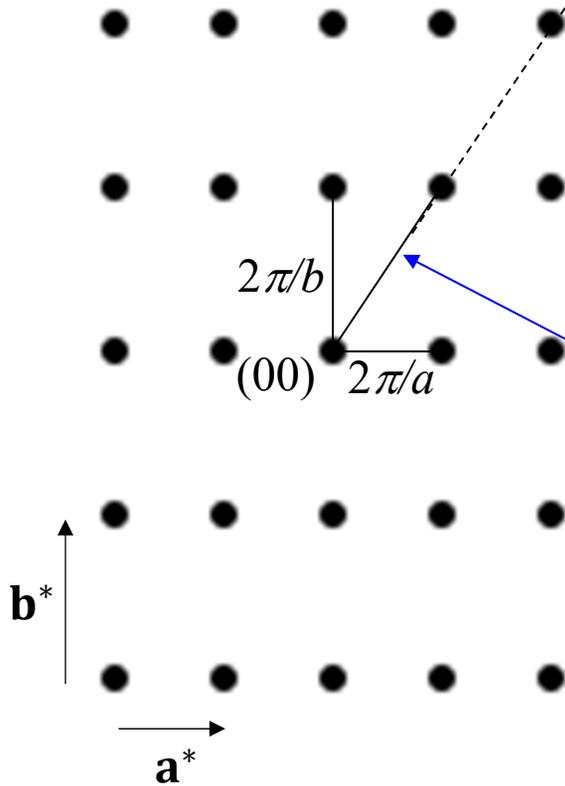
Real: $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$; reciprocal $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$

Real: $\mathbf{a}, \mathbf{b}, \mathbf{c}$; reciprocal $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$

An easier way to get the indices:
Reciprocals of the intercepts in real space.

More easily visualized in 2D.

Reciprocal



$$\frac{ab}{\sqrt{a^2 + b^2}}$$

(11) Line intercept **a** and **b** axis at 1 and 1.

real reciprocal
 (11) line \perp (**a*** + **b***)

$$\frac{2\pi\sqrt{a^2 + b^2}}{ab}$$

Distance between neighboring lines

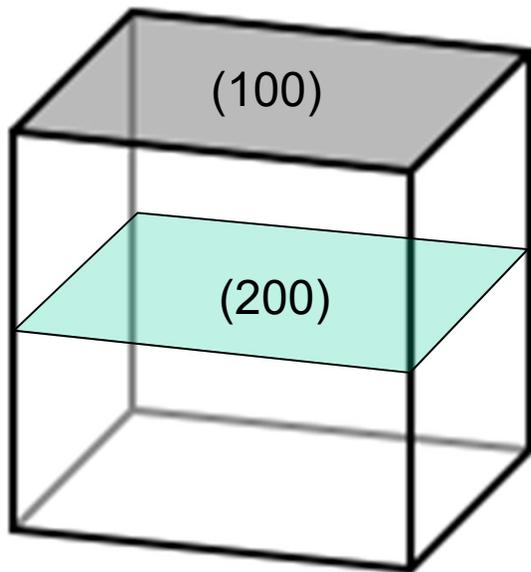
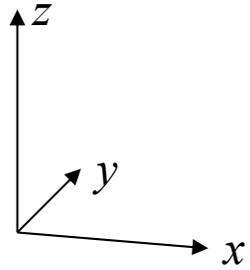
$$d = \frac{2\pi}{|\mathbf{a}^* + \mathbf{b}^*|}$$

Convention used:

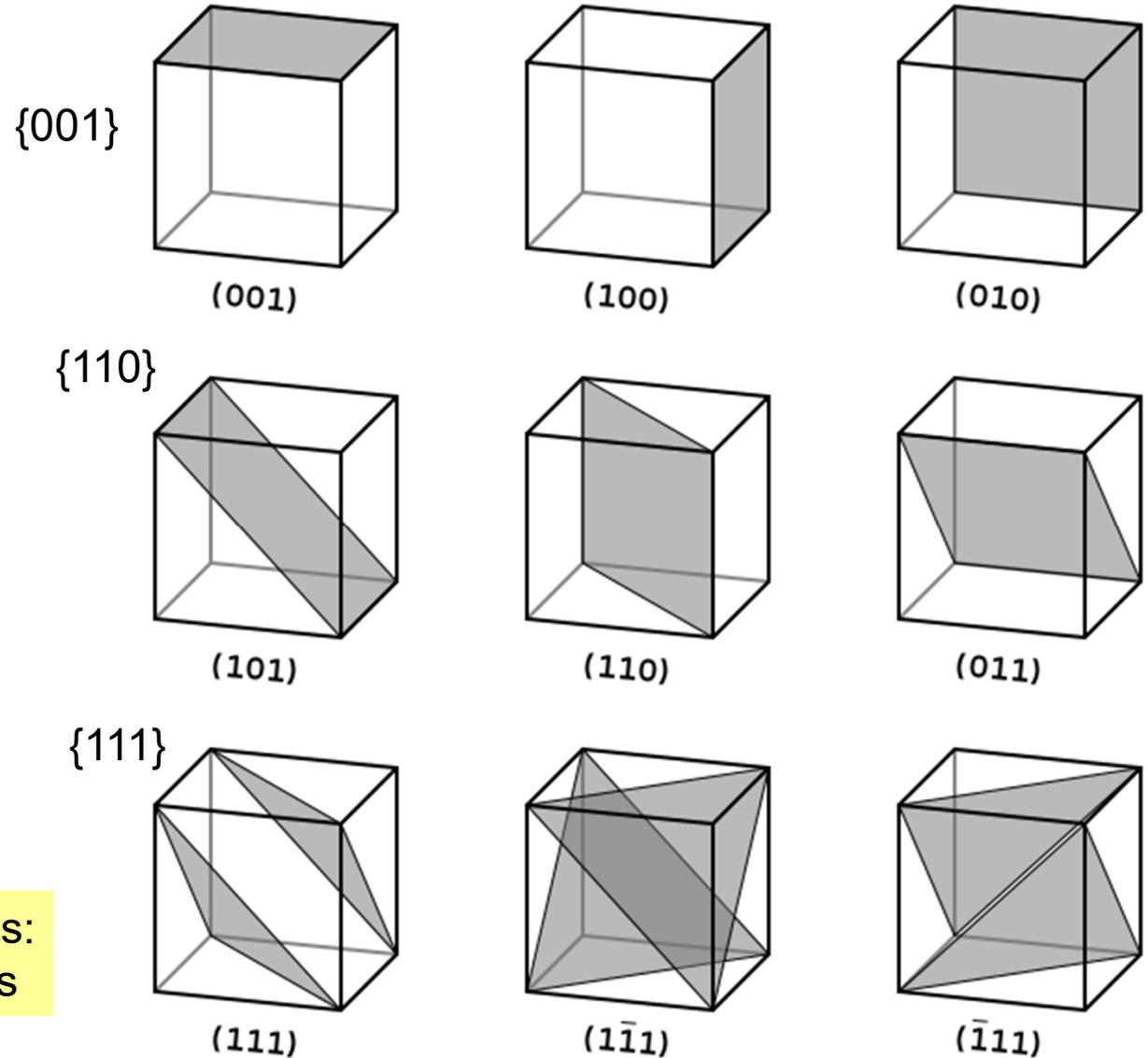
Real: **a**, **b**; reciprocal **a***, **b***

Cubic systems

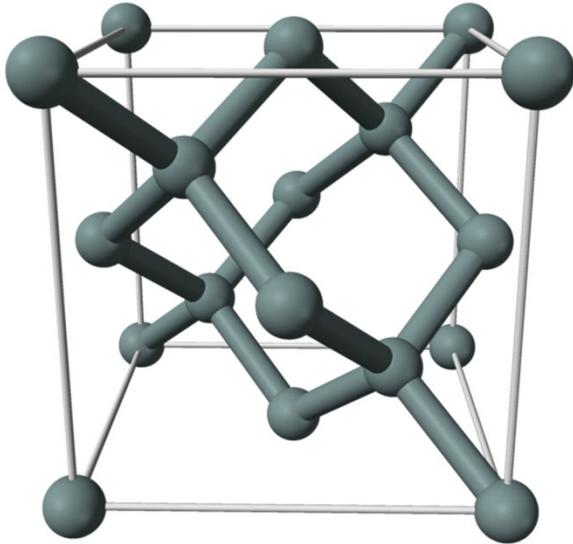
Indices in curly brackets or braces such as $\{100\}$ denote a family of planes that are equivalent due to symmetry operations.



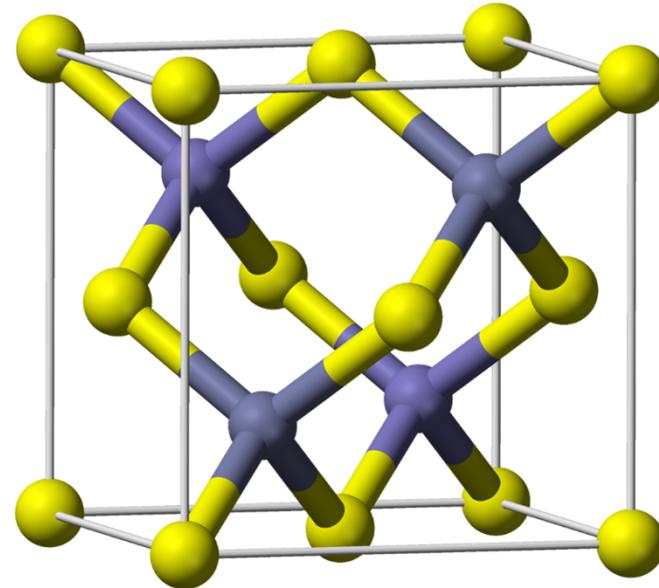
Easier way to get the indices:
Reciprocals of the intercepts



Crystallographic direction and plane indices are usually defined with regard to conventional unit cells, due to their high symmetry.



<https://fr.m.wikipedia.org/wiki/Fichier:Silicon-unit-cell-3D-balls.png>



https://en.wikipedia.org/wiki/Cubic_crystal_system#Zincblende_structure

CMOS technology uses the (100) surface of Si.

Homework 4 problems:

Schematically illustrate the 1D atomic lines in the $\langle 100 \rangle$ direction of Si (diamond structure). Specify distances between neighboring atoms. Define the 1D periodic structures of these lines by defining a unit cell and a Bravais lattice for each (if different). Are all these atomic lines equivalent to each other? Repeat for $\langle 110 \rangle$ and $\langle 111 \rangle$.

Repeat the above for GaAs (zincblende structure).

Homework 4 problems:

Schematically illustrate the 2D atomic planes parallel to $\{100\}$ planes of Si. Specify distances between neighboring atoms. Define the 2D periodic structures of these atomic planes by defining a unit cell and a Bravais lattice for each (if different). Are all the lines equivalent to each other? Repeat for $\{110\}$ and $\{111\}$.

Repeat the above for GaAs.

Crystallography highlights

Primitive unit cells are the smallest unit that repeats itself.

Bravais Lattices

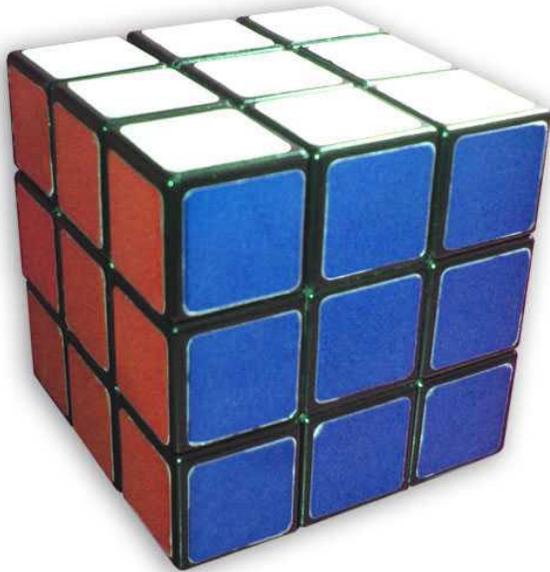
A mathematical concept that captures (only) the periodicity of crystal structures:

- No boundaries or surfaces
- No real (physical) thing – just points, hence no defects
- No motion

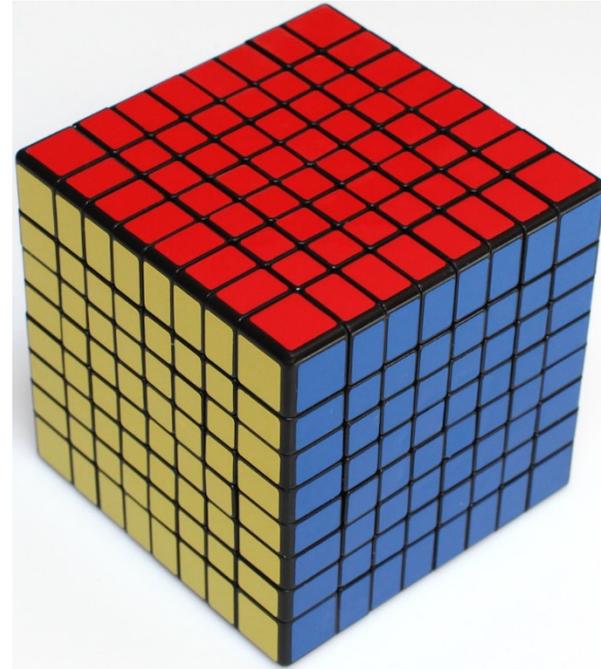
What do you mean by “infinitely large”?

A big cube is made of $10 \times 10 \times 10$ small cubes. How many of them are on the faces?

A big cube is made of 10 X 10 X 10 small cubes. How many of them are on the faces?



$$3^3 = 27$$
$$(3-2)^3 = 1$$



$$10^3 = 1000$$
$$(10-2)^3 = 512$$

Half of the small cubes are on surfaces!

Surfaces are usually different in structure from crystallographic planes – [reconstruction](#).

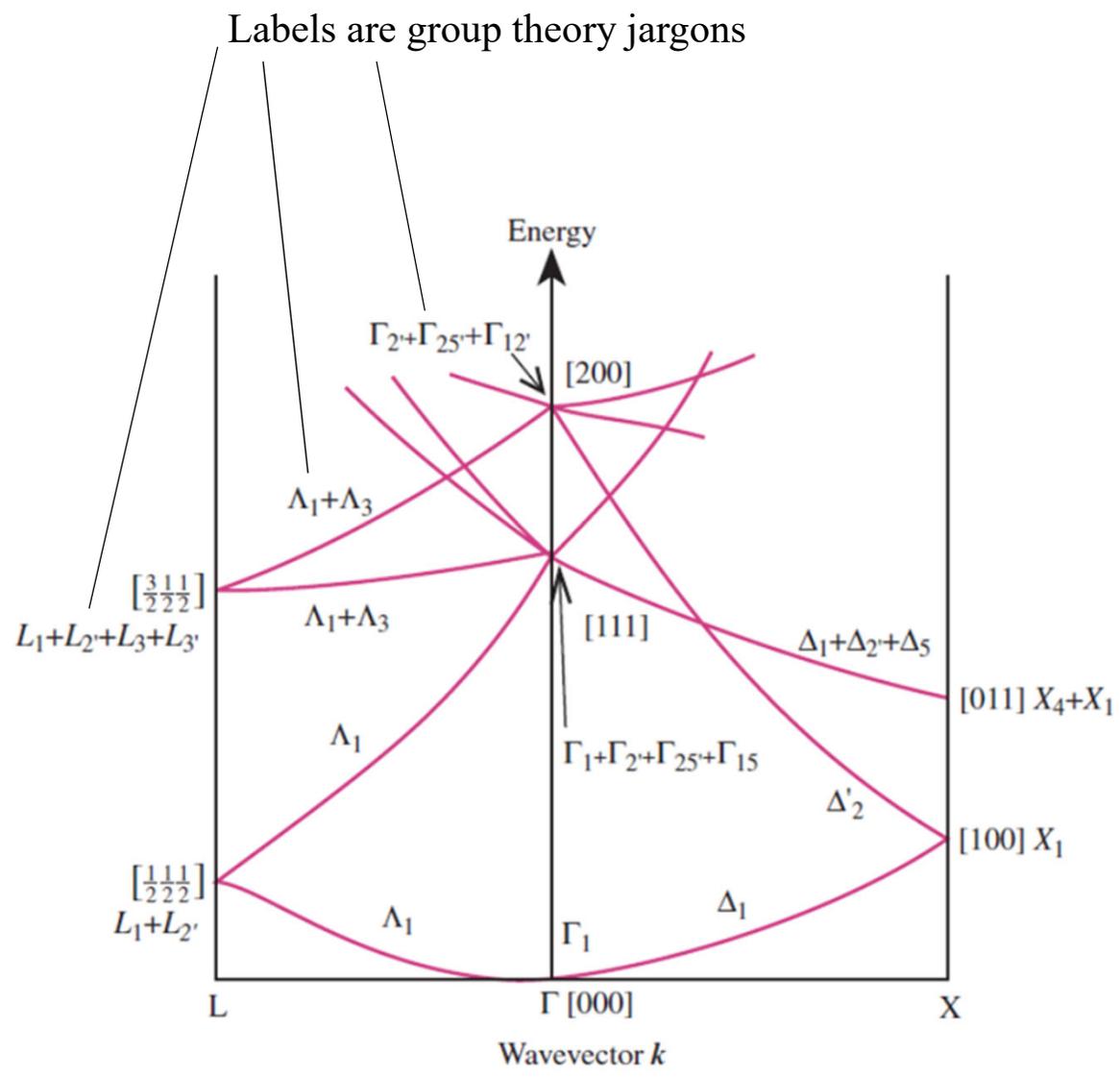
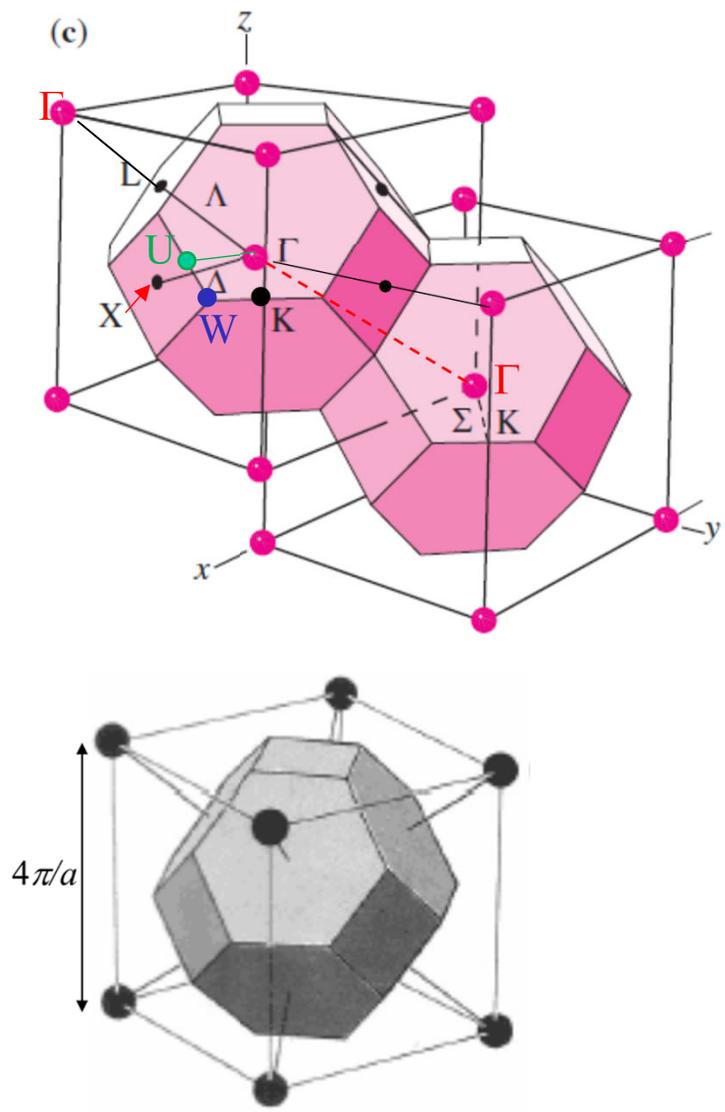
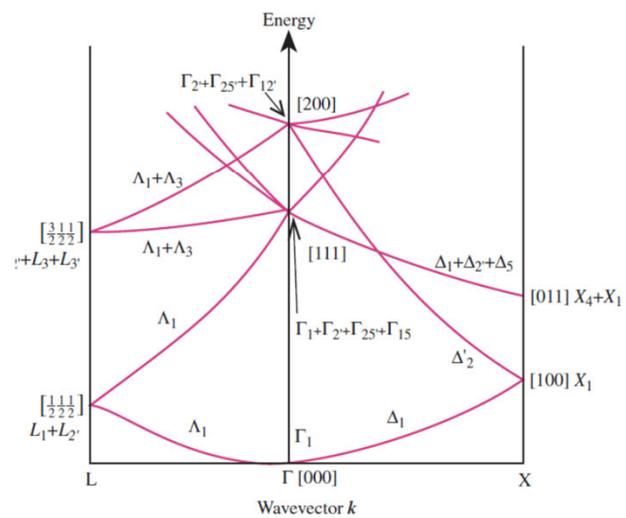
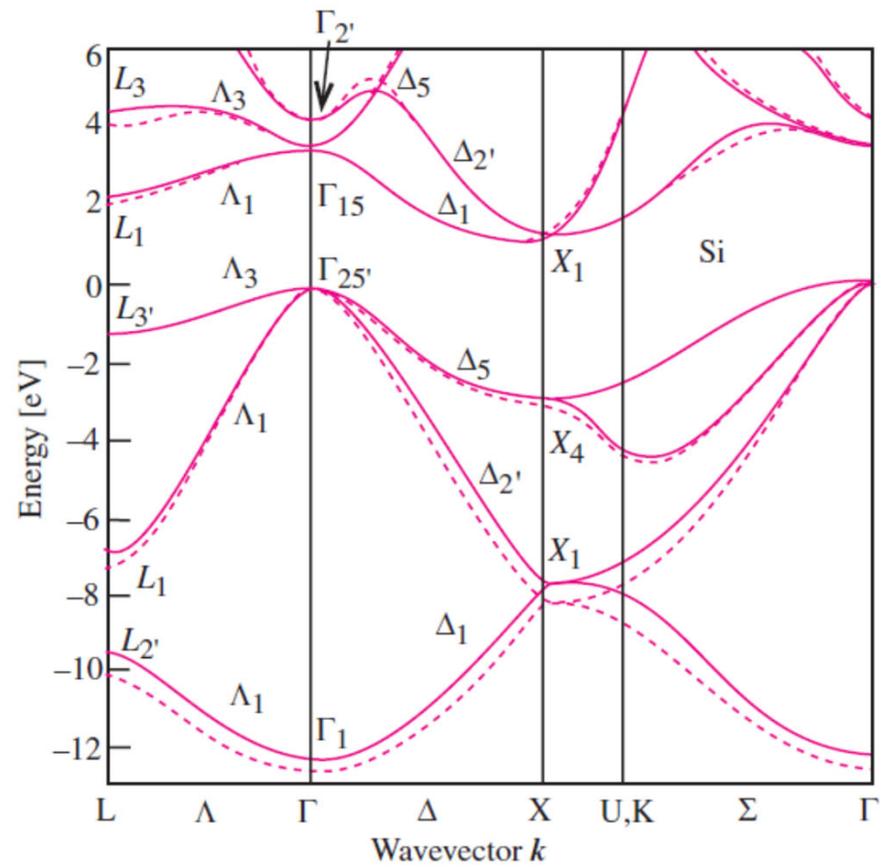
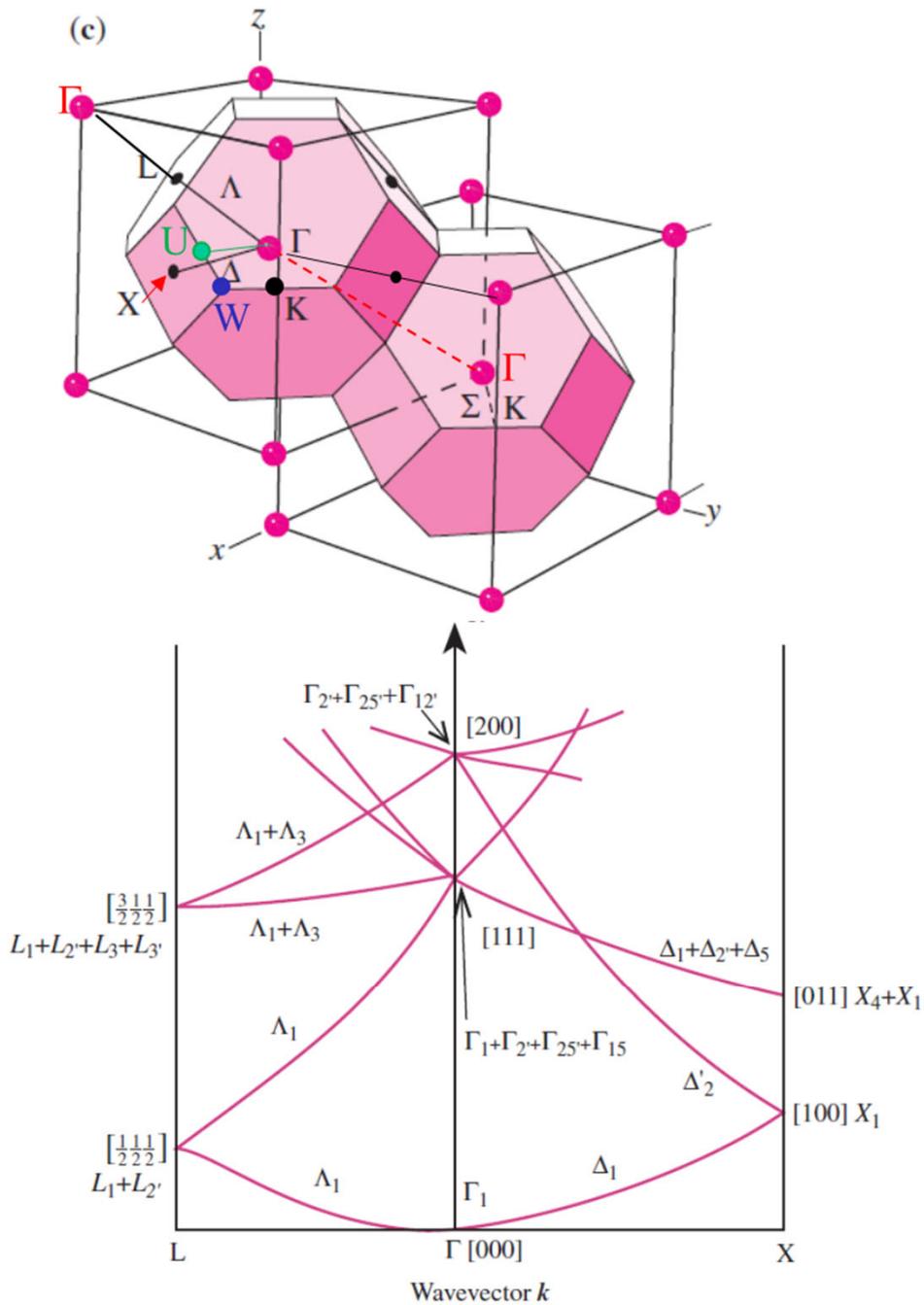
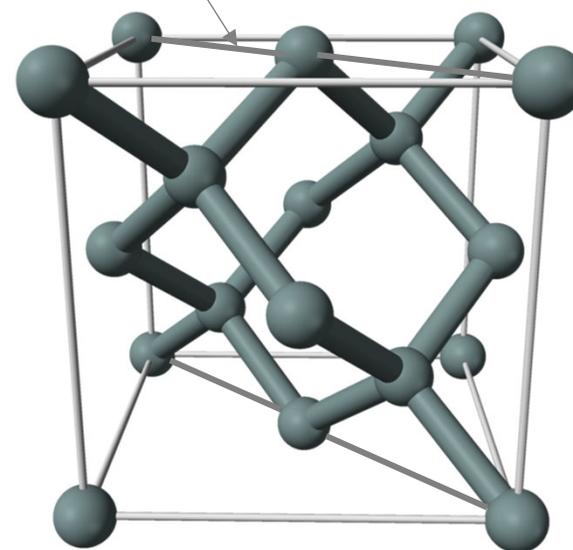
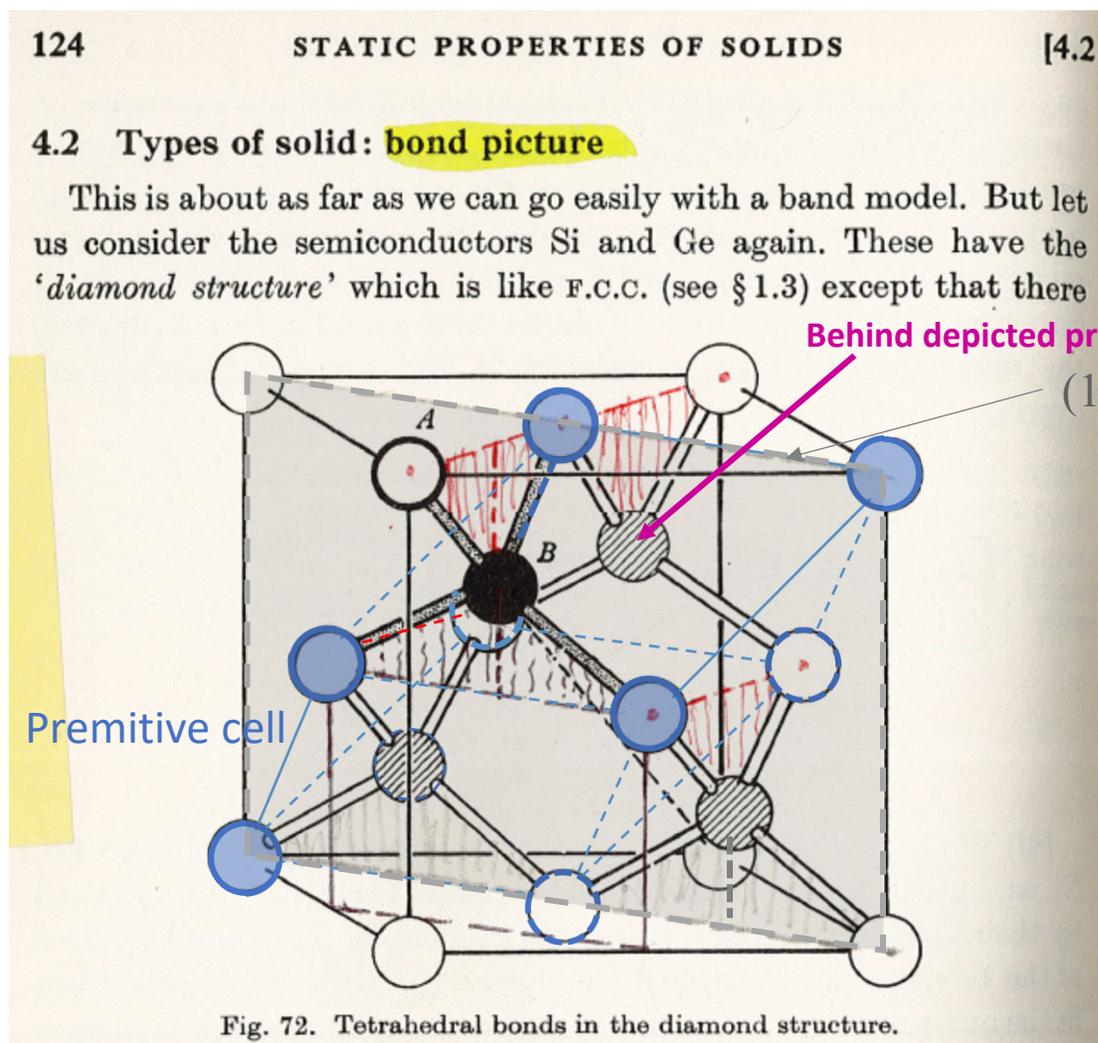


Fig. 2.9. Band structure of nearly free electrons for a diamond-type crystal in the reduced zone scheme



A look at the bond picture



From Ziman, Principles of the Theory of Solids

4.2 Types of solid: **bond picture**

This is about as far as we can go easily with a band model. But let us consider the semiconductors Si and Ge again. These have the 'diamond structure' which is like F.C.C. (see § 1.3) except that there

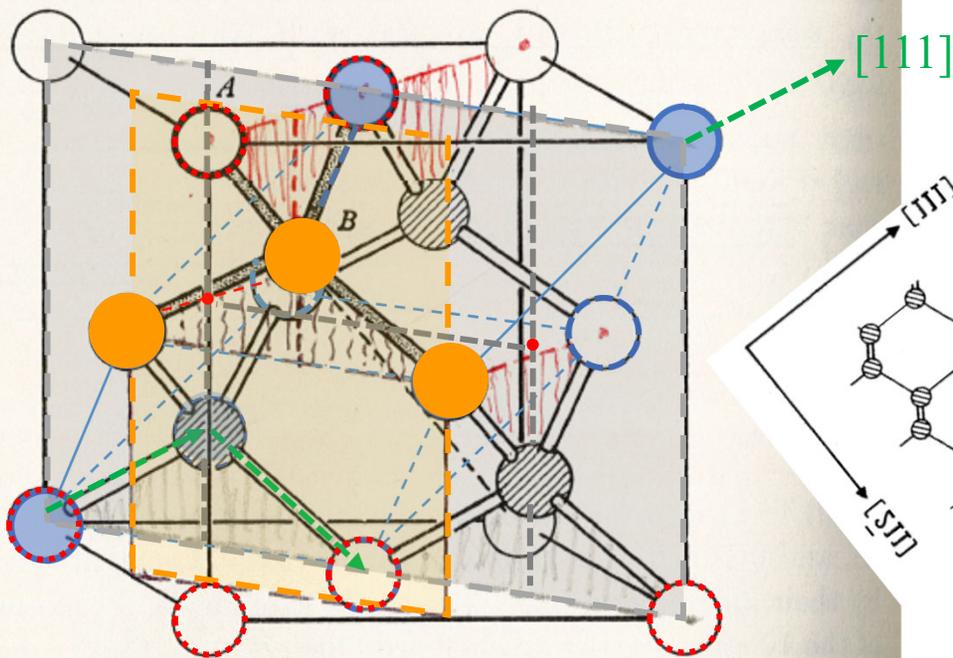
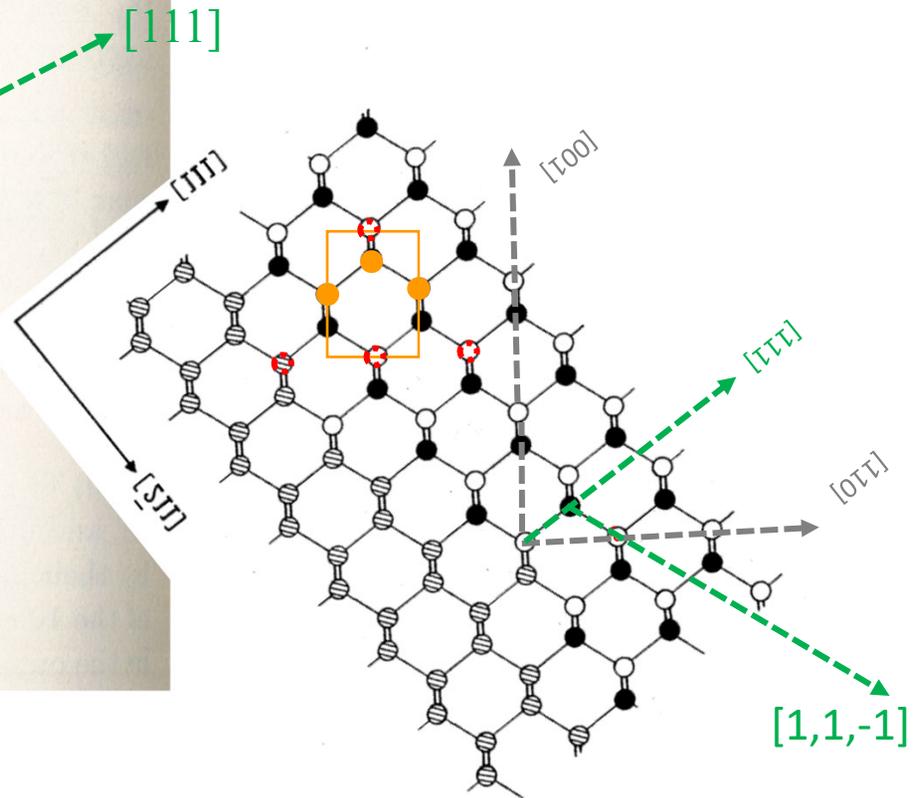


Fig. 72. Tetrahedral bonds in the diamond structure.



From Ziman, Principles of the Theory of Solids

4.2 Types of solid: bond picture

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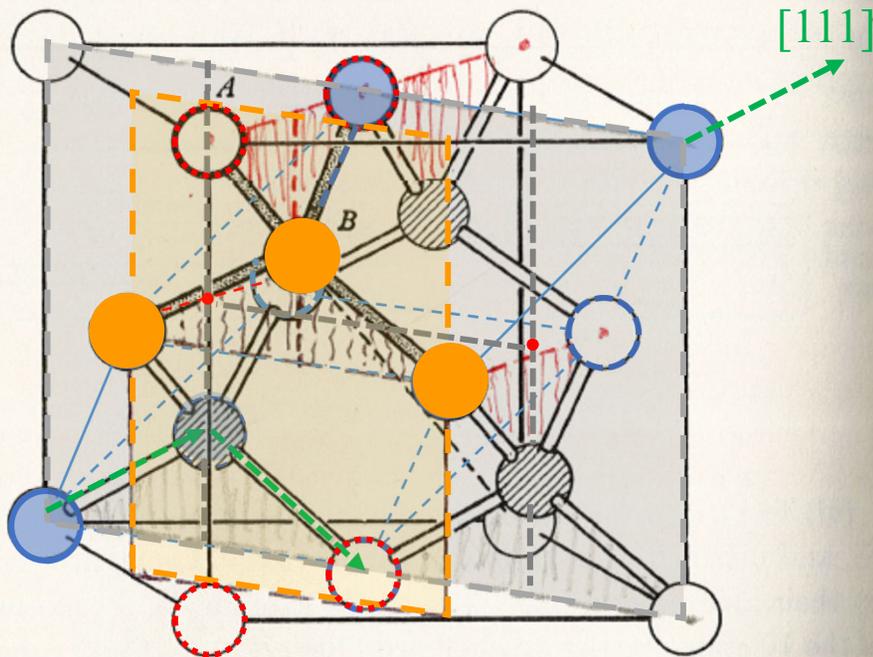
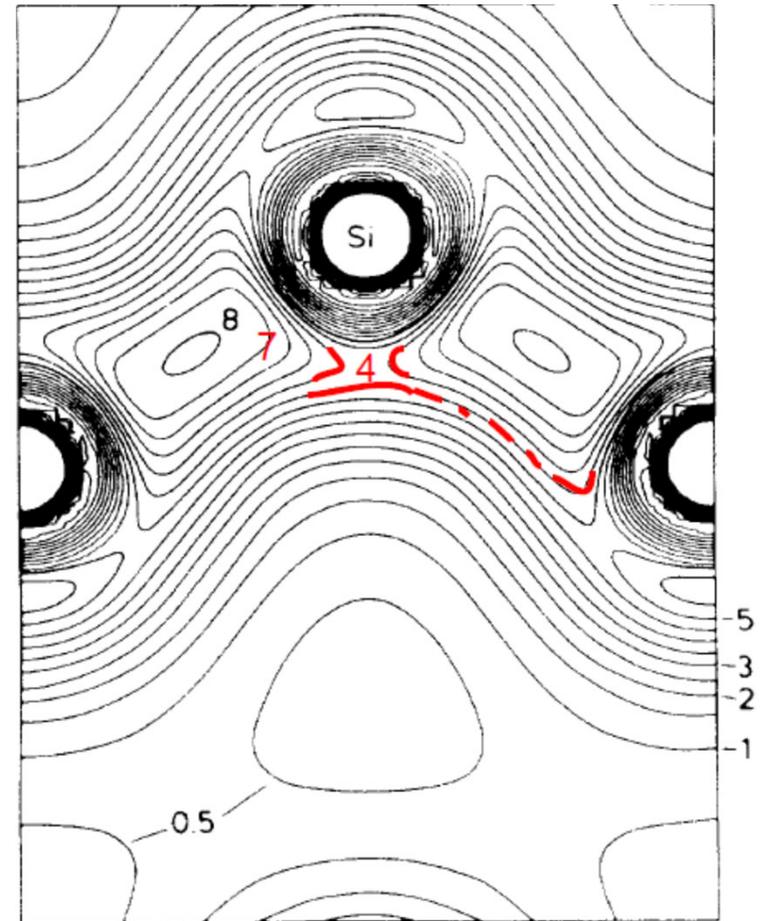
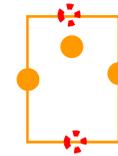


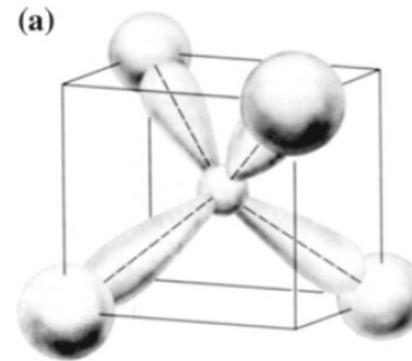
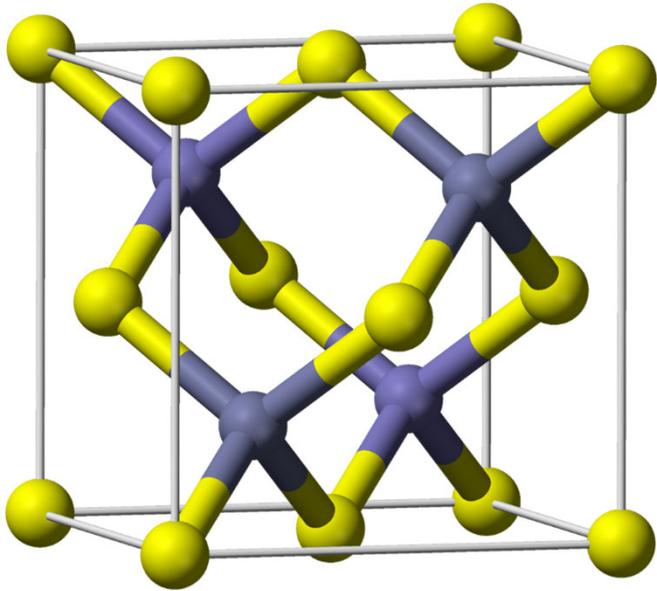
Fig. 72. Tetrahedral bonds in the diamond structure.

From Ziman, *Principles of the Theory of Solids*

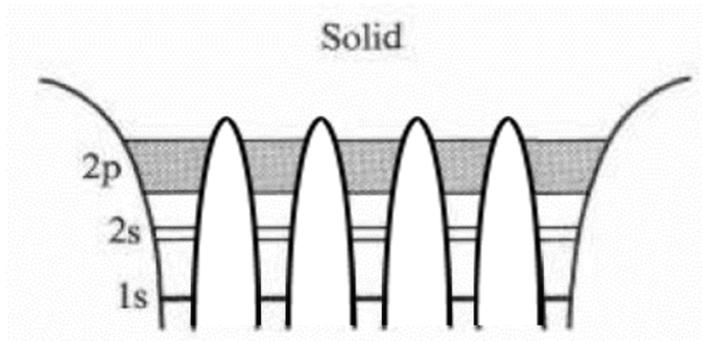


Christensen, *Phys. Rev. B* **36**,1032 (1987)

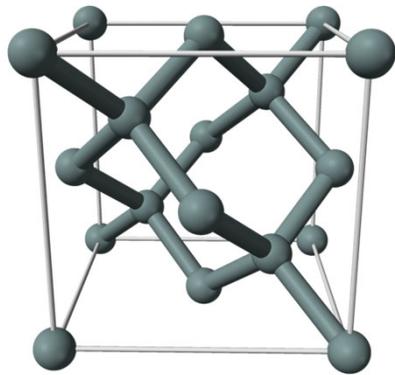
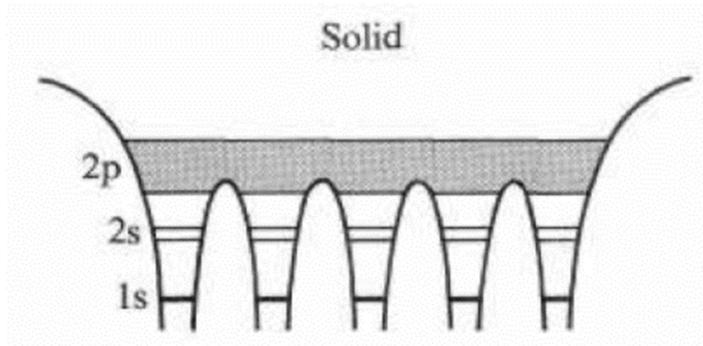
Electron probability density concentrates between neighboring Si atoms, as expected from sp^3 bonding.



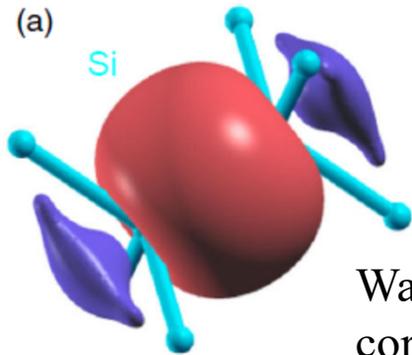
Electron probability density concentrates between neighboring Si atoms, as expected from sp^3 bonding. For zincblende, higher density towards the anion (group V atom in III-V).



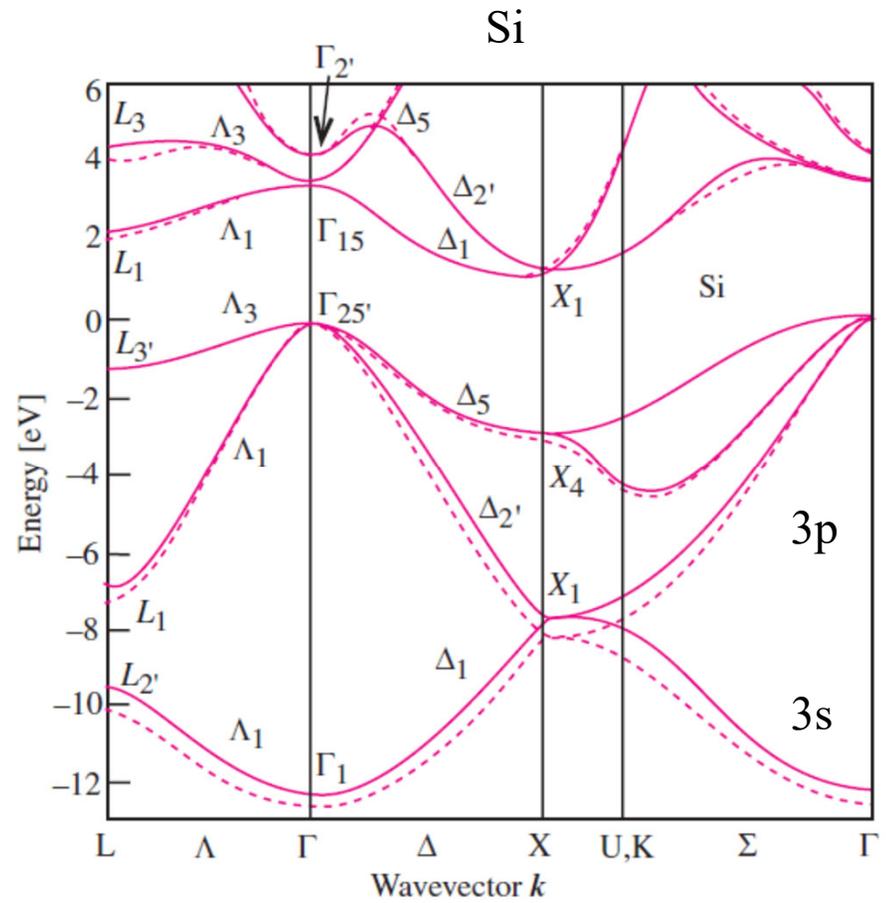
The bond orbitals form a 3D network.



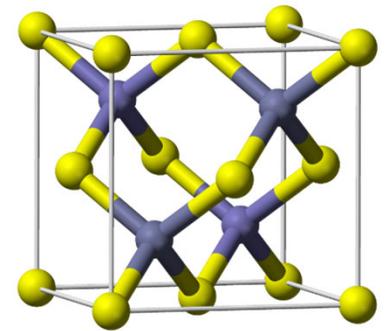
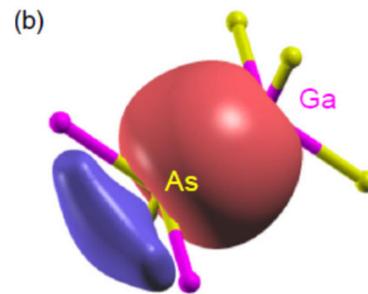
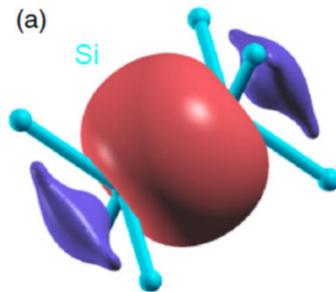
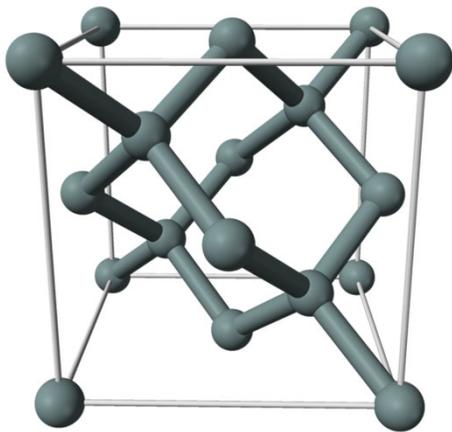
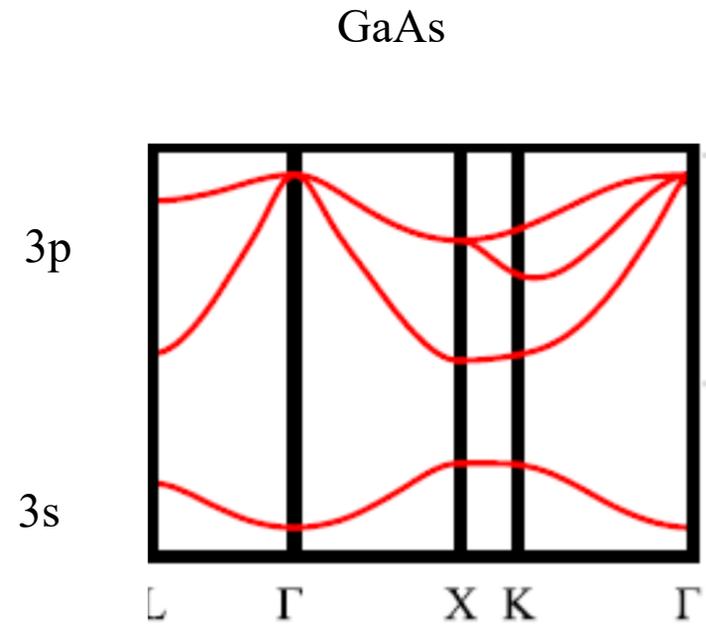
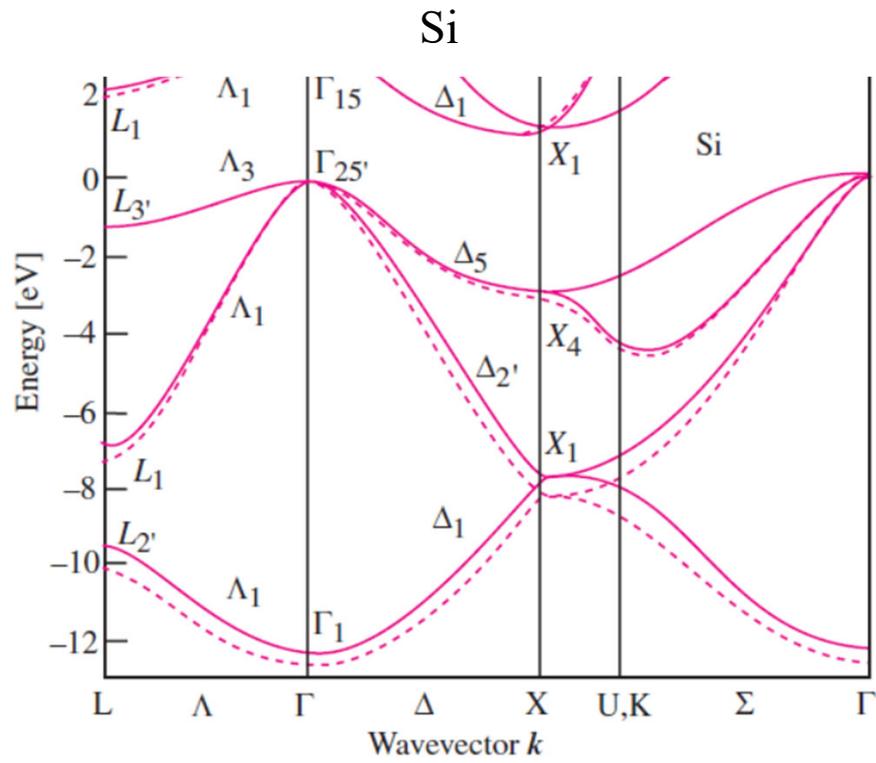
(a)



Wave function (not electron density as shown in previous slides) corresponding to the sp^3 - σ bond.



Bands have atomic orbital characters.



Marzari, Rev. Mod. Phys. 84,1419 (2012)

The band and bond pictures of solids

A band state (identified by a wavevector k and an energy E) is an **extended** eigenstate of the Hamiltonian of the crystal.

A bond orbital is a localized state corresponding to a chemical bond.

The two pictures are different perspectives of the same electrons of a crystal.

The band states and the bond orbitals are two different basis sets.

Chemical bonds are not strictly defined, but a set of localized orbitals can be found that are orthogonal and complete to serve as a basis set.

These localized bond orbitals are not eigenstates of the Hamiltonian, thus does not have definitive energies.

The band picture is more useful when studying the macroscopic properties of a semiconductor, e.g., light absorption and emission, electrical transport

The bond picture is more useful when we think about the chemistry and atomic-scale structure: surfaces and interfaces, epitaxial growth, defects

Closing Remarks & Recommended Reading

By now we have laid down the cornerstones for the understanding of semiconductors: Quantum mechanics and Solid state physics.

These are vast fields of physics on their own. We have to pick a limited subset of topics to cover in this course. So do any instructors and [textbooks](#) of a similar course.

Therefore, textbooks on semiconductor fundamentals are often very dense, not easy reads.

Now you have learned enough to [start](#) reading some of these books.

[Recommended reading](#)

Peter Y. Yu & Manuel Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties*, 4th Edition.

[Available as e-book and paper book at UT Library.](#)

Ch. 2, p. 17-18

2.1 Quantum Mechanics, p. 18-20

2.2 Translational Symmetry and Brillouin Zones, p. 20-25

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2.5 Band Structure Calculations by Pseudopotential Methods: Read p. 58-59. It's okay if you don't understand everything.

2.7 Tight-Binding or LCAO Approach to the Band Structure of Semiconductors, p. 83-96: I talked about the bond and band pictures from a different perspective. Try to understand this section as much as you can.