TYC Materials Modelling Course 2026
Periodicity and Energy

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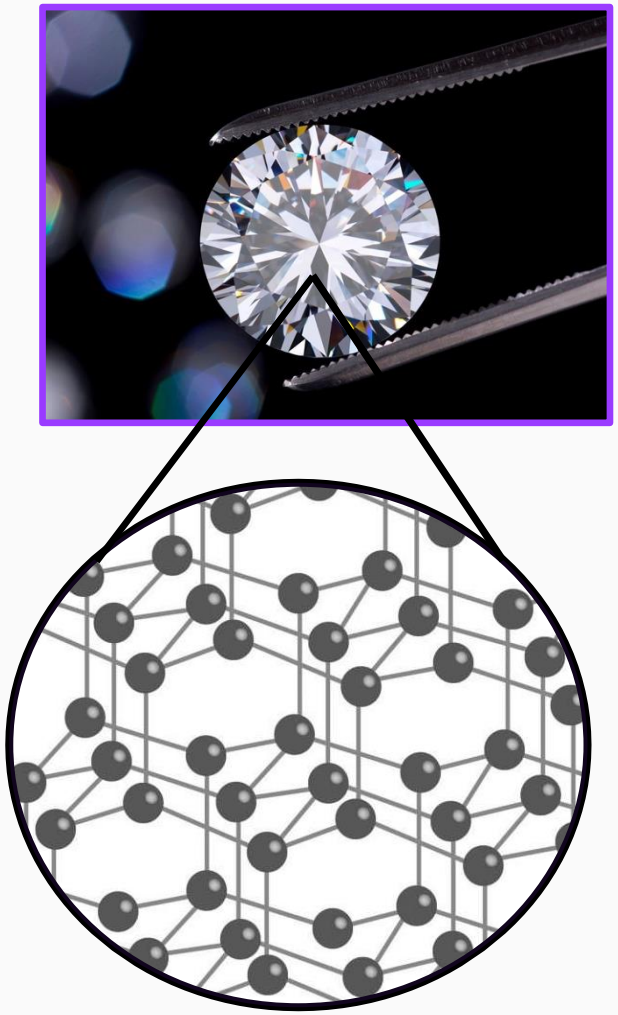
Periodic Boundary Conditions

What is crystal structure?

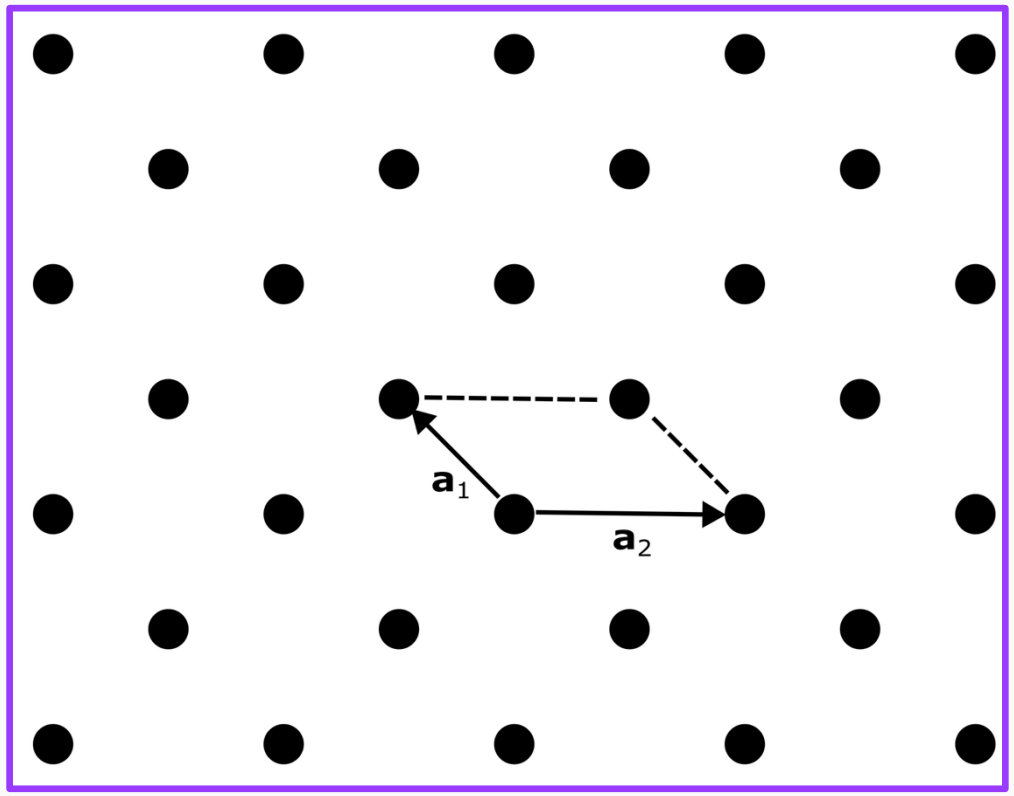


- In crystals, atoms are organised into repeating patterns.
- A crystal structure is a model of such a material, where the repeating pattern extends in all of space
- This is translational symmetry – we can translate the system a distinct value and return to the same crystal system.

Periodic Boundary Conditions

Mathematical Description of a Crystal Lattice

We represent the set of lattice points by giving the vectors which correspond to a symmetric translation of the system:



$$\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2$$

The lattice vectors together form the *unit cell*. The unit cell is a small periodic 'unit' of the lattice and fills all of space when repeated ad infinitum

3D Systems:

- Real Crystals are 3D, so the lattice is represented as

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

Periodic Boundary Conditions

Lattices and Bases

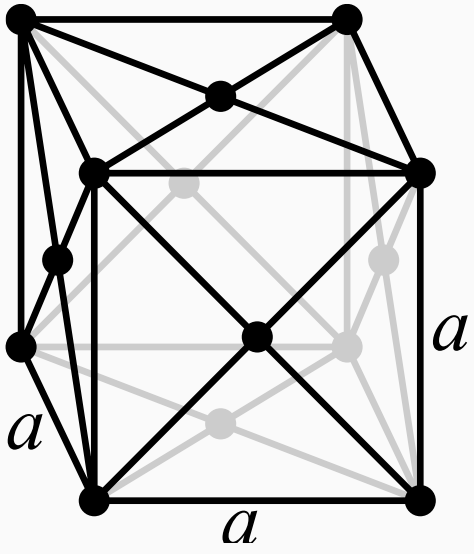
- A crystal structure is formed from a lattice and a basis
- A lattice is a set of periodically repeated ‘lattice points’ throughout space
- The ‘basis’ is a structure or arrangement of atoms placed at each lattice point.

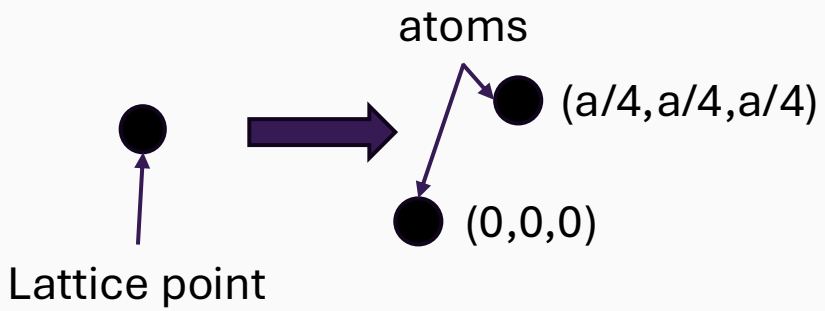
Periodic Boundary Conditions

Lattices and Bases – Example

- Diamond forms a ‘face-centered cubic’ lattice
- In diamond, each lattice point contains two atoms:

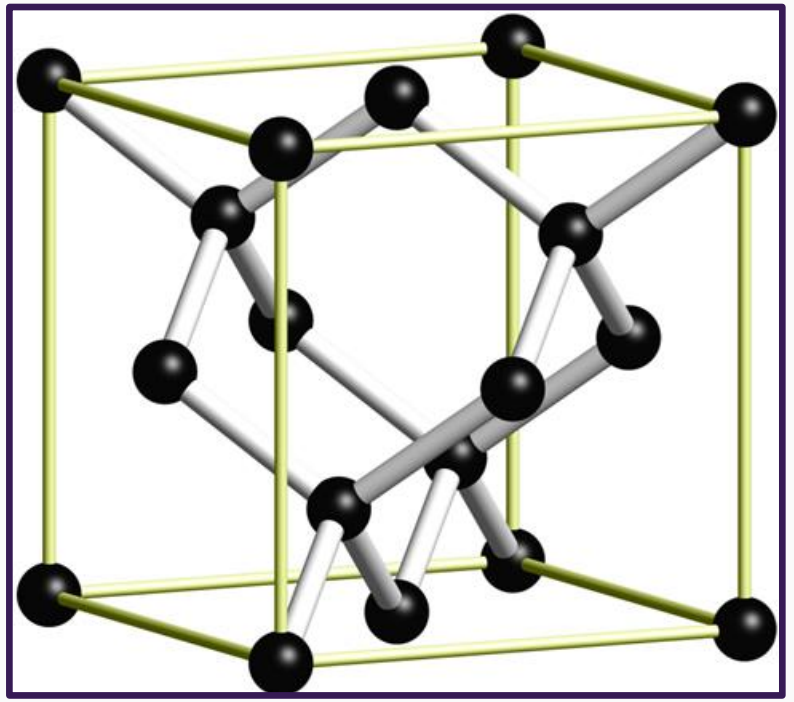
FCC lattice





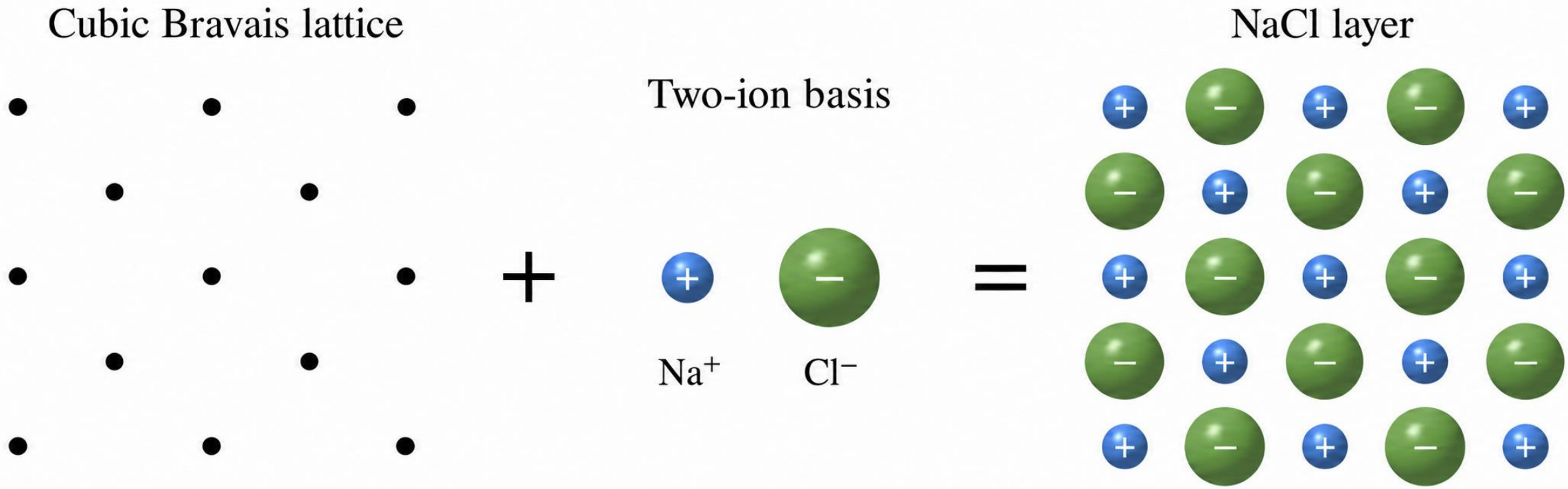
Each lattice point is composed of two atoms placed (0.25a,0.25a,0.25a) away from each other.

Diamond



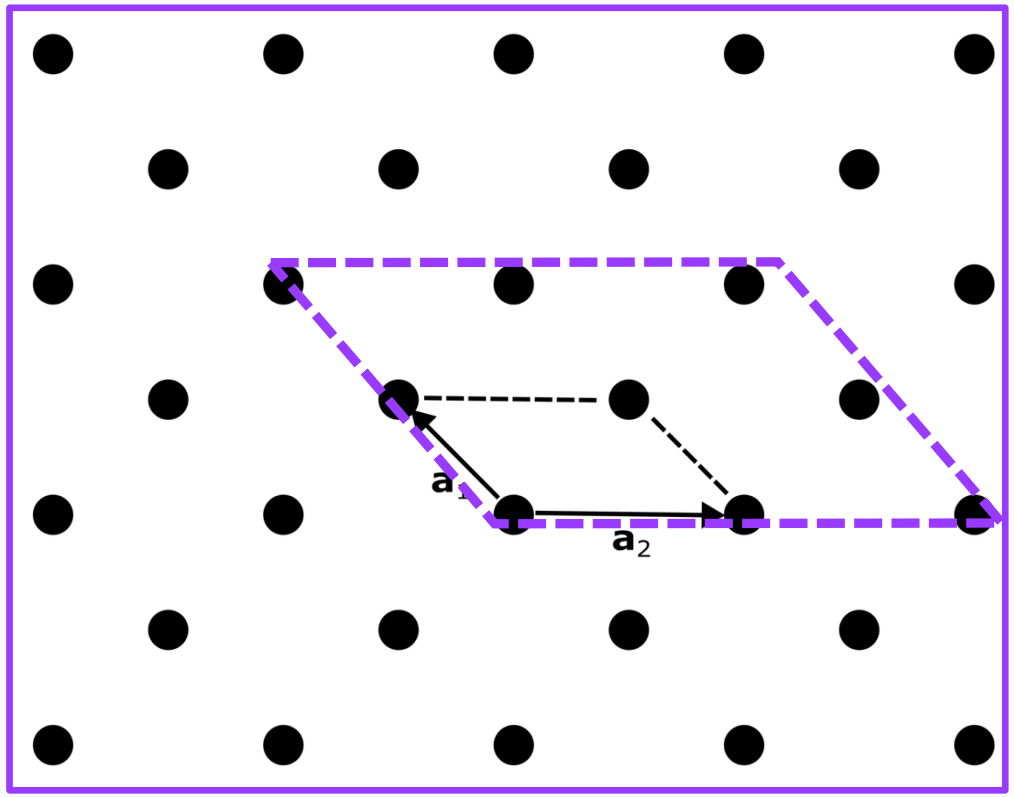
Periodic Boundary Conditions

Lattices and Bases – Another Example



Periodic Boundary Conditions

Unit Cells and Supercells



- Unit cells are not unique: One can also define a *supercell* by combining multiple unit cells
- For example, in our 2D example (left) one can instead define the periodic cell to be the unit cell with sides $2\mathbf{a}_1$ and $2\mathbf{a}_2$

Periodic Boundary Conditions

Bravais Lattices – How many lattices are possible

- In total, there are fourteen possible lattice systems (next slide).

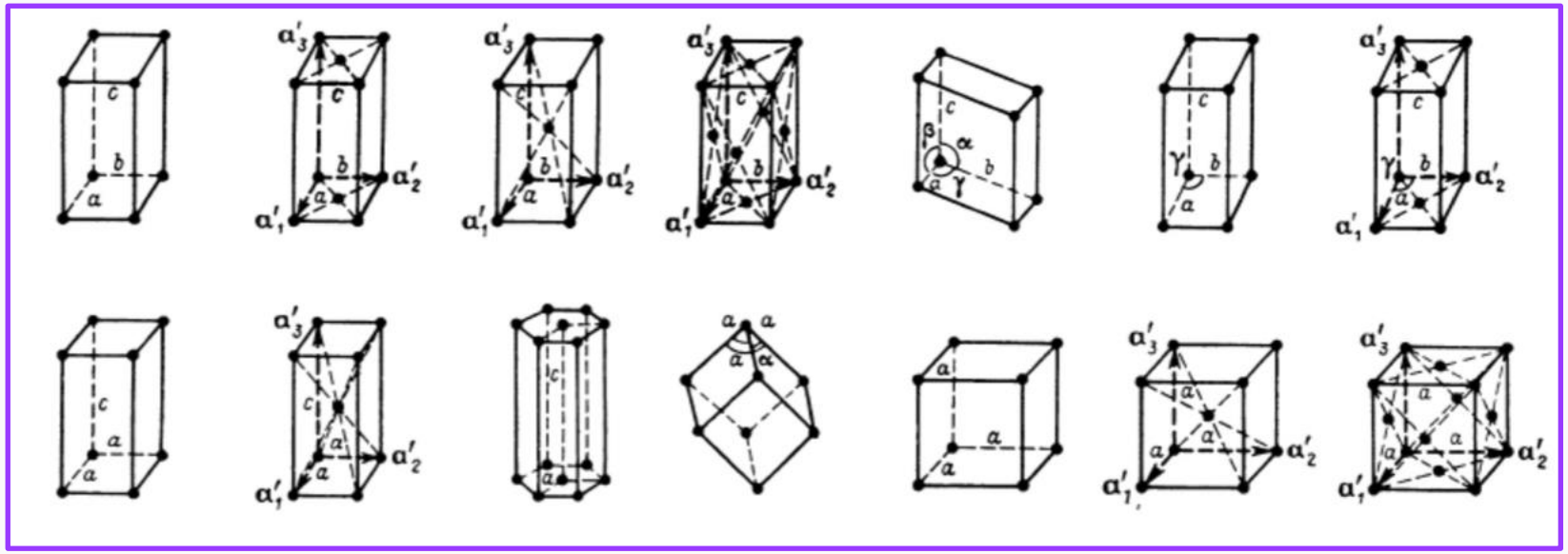
- Note, that this does not mean there are only 14 crystal structures – the basis still needs to be considered.

- These are known as the Bravais lattices.

Periodic Boundary Conditions

The Bravais lattices

- The fourteen systems are formed from 7 lattice systems and then a number of different ‘centering’ types



- Triclinic, Monoclinic, orthorhombic, tetragonal, hexagonal, cubic.
- Centering: Primitive, base-centered, body-centered, face-centered

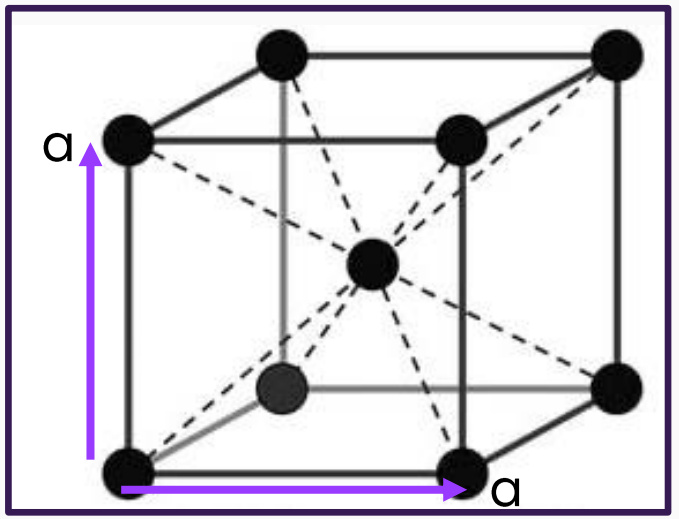
Periodic Boundary Conditions

The Bravais lattices

- Example: Cubic System
  - All lattice vectors have same length **a**=**b**=**c**=|**a**|=a
  - All lattice vectors at right angles to each other
  - Unit cell forms a cube!

- Centering Examples: Body-Centered vs Face-Centered
  - Atom placed at the face of each side of the unit cell
  - Atom places at the center of the unit cell

BCC



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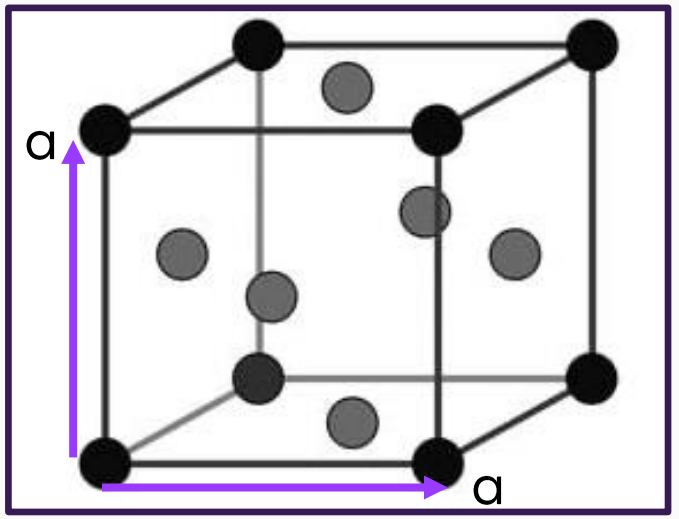
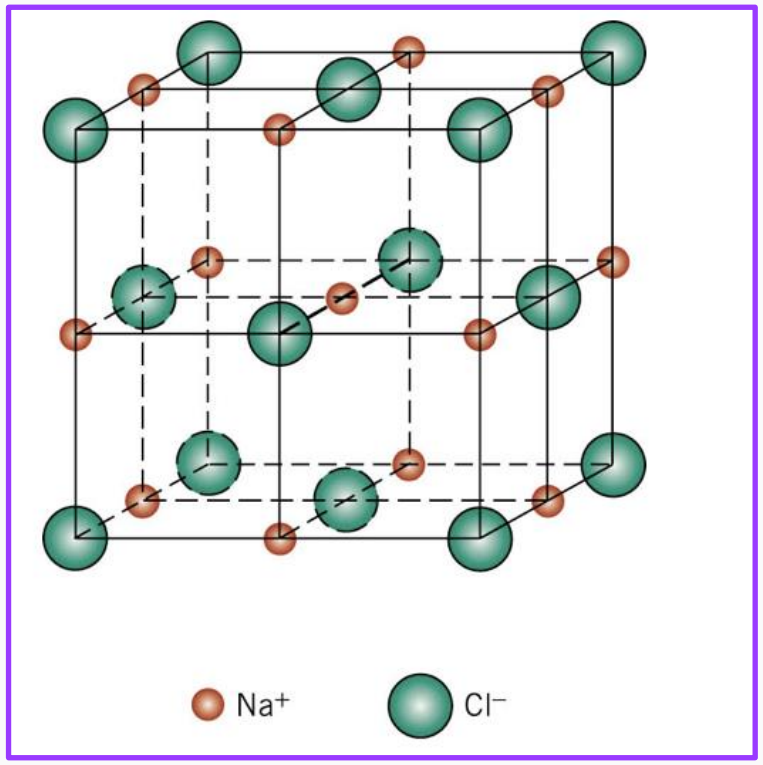
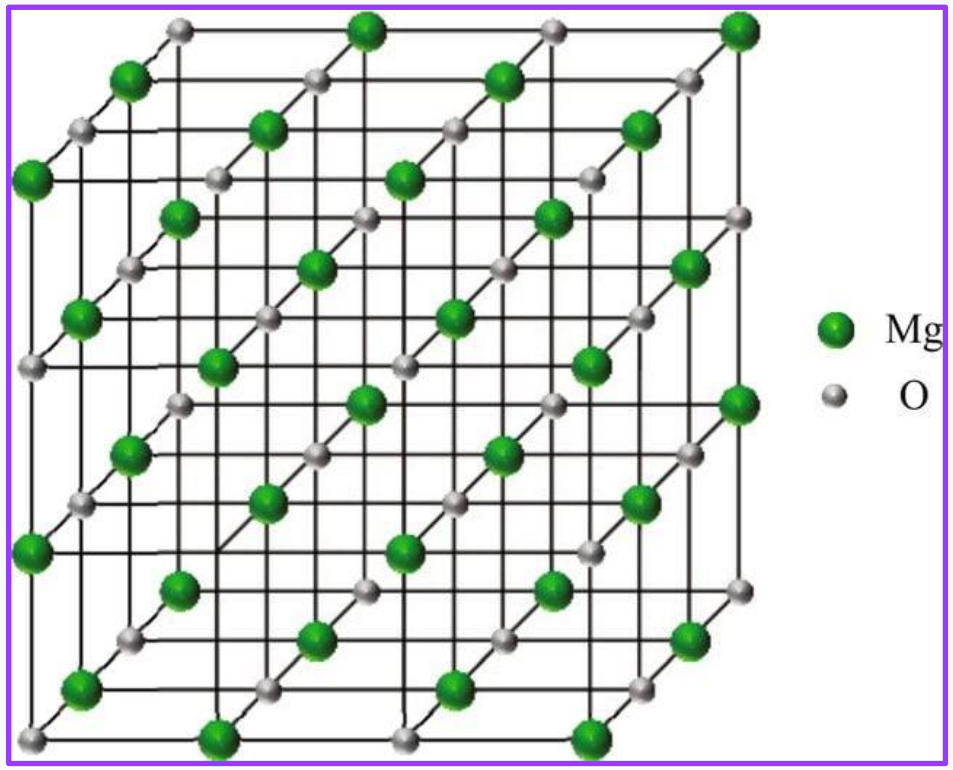


Periodic Boundary Conditions

Example Systems

MgO, NaCl and rock-salt structure:





NaCl and MgO share the same kind of crystal structure known as the ‘rock-salt’ crystal structure

The Reciprocal Lattice

Representing Periodic Functions

- Generally, we can represent periodic functions as Fourier series.
  E.g. in one dimension if $l = l_1 a$ (a=period) :

$$f(x + l) = f(x)$$

$$f(x) = \sum_n A_n e^{\frac{2\pi i n x}{a}} \qquad n = \text{integer}$$

- We can write this in the form

$$f(x) = \sum_{\boldsymbol{g}} A_{\boldsymbol{g}} e^{i\boldsymbol{g}x}$$

where g are said to belong to a set of "reciprocal lattice lengths"

$$g_n = n\frac{2\pi}{a}$$

The Reciprocal Lattice

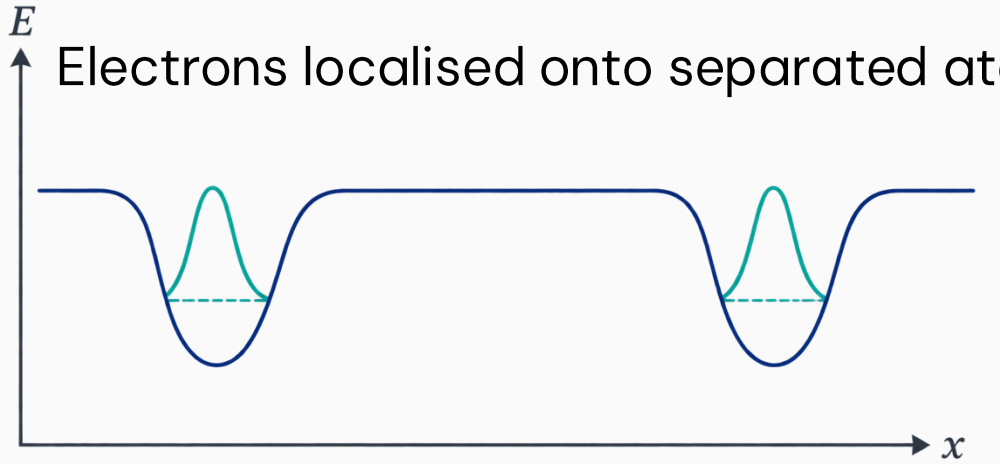
3D Crystals

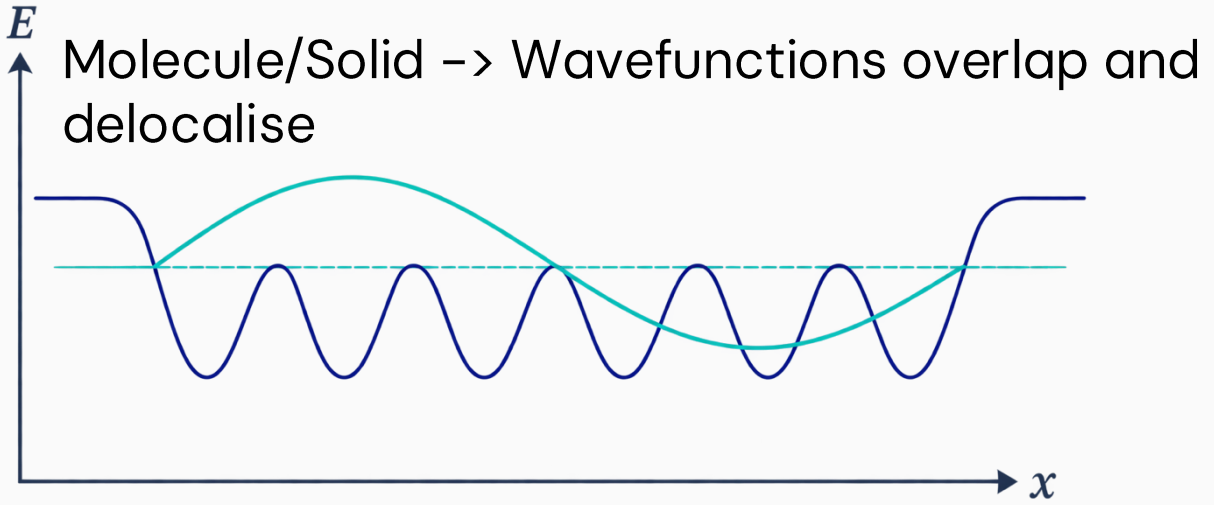
- Coeficients in $f(x) = \sum_g A_g e^{igx}$ defined by $A_g = \frac{1}{a}\int_{\text{Cell}} f(x)e^{-igx}dx$
- $f(x+l) = \sum_g A_g e^{ig(x+l)} = f(x) \Rightarrow e^{igl} = 1$
- Extension to 3D: $\boldsymbol{R}\cdot\mathbf{G} = 2\pi m$, or $e^{i\mathbf{G}\cdot\boldsymbol{R}} = 1$
- We define $\boldsymbol{G} = m_1\boldsymbol{b}_1 + m_2\boldsymbol{b}_2 + m_3\boldsymbol{b}_3$ as the reciprocal lattice vectors (analogous to $\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$, the "direct lattice"):

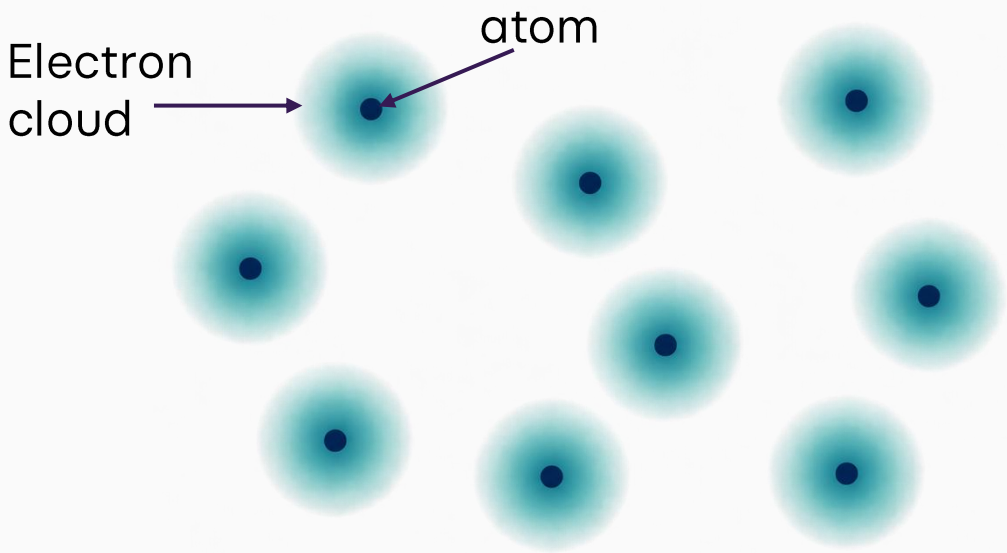
$$\boldsymbol{b}_1 = 2\pi\frac{\boldsymbol{a}_2\times\boldsymbol{a}_3}{\boldsymbol{a}_1\cdot(\boldsymbol{a}_2\times\boldsymbol{a}_3)} \qquad \boldsymbol{b}_2 = 2\pi\frac{\boldsymbol{a}_3\times\boldsymbol{a}_1}{\boldsymbol{a}_1\cdot(\boldsymbol{a}_2\times\boldsymbol{a}_3)} \qquad \boldsymbol{b}_3 = 2\pi\frac{\boldsymbol{a}_1\times\boldsymbol{a}_2}{\boldsymbol{a}_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

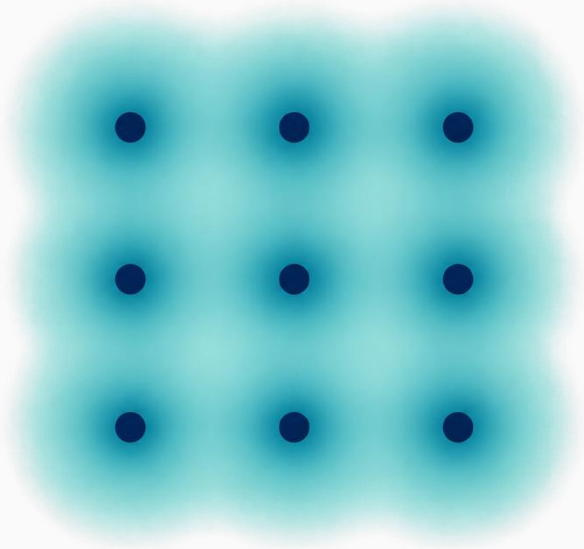
Electrons in Solids

Delocalisation of electrons over molecules and solids









Electrons in Solids

Electron Waves

- Solids have are built from nuclei, cohered together by delocalised electrons in the material.

- What is the wavefunction of these electrons?
    - You have seen electron waves before – e.g. free electrons
    - Free electrons may be too rough of an approximation, however.
    - We have significant sources of potential (i.e. ions) which are periodically arranged

- What effect does the translational symmetry of the potential have on the form of the electron wavefunctions?

Bloch's Theorem

Electrons in Crystals

- Schrodinger Eqn for a single electron:

$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\boldsymbol{r})\right)\psi = \epsilon\psi$$

- Potential is periodic, i.e. it is translationally invariant

$$U(\boldsymbol{r} + \boldsymbol{R}) = U(\boldsymbol{r})$$

- As the potential is periodic, the Hamiltonian is also periodic

$$H(\boldsymbol{r} + \boldsymbol{R}) = H(\boldsymbol{r})$$

Bloch's Theorem

- Define translation operator

$$T_{\boldsymbol{R}} f(\boldsymbol{r}) = f(\boldsymbol{r} + \boldsymbol{R})$$

- We have

$$T_{\boldsymbol{R}} H\psi = H(\boldsymbol{r} + \boldsymbol{R})\psi(\boldsymbol{r} + \boldsymbol{R}) = H(\boldsymbol{r})\psi(\boldsymbol{r} + \boldsymbol{R}) = HT_{\boldsymbol{R}}\psi$$
$$\Rightarrow T_{\boldsymbol{R}} H = HT_{\boldsymbol{R}} \qquad \text{(A)}$$

- We also know that consecutive applications of T_R should go as

$$T_{\boldsymbol{R}} T_{\boldsymbol{R}'}\psi(r) = \mathrm{T}_{\mathbf{R}'}\mathrm{T}_{\mathbf{R}}\psi(r) = \psi(\boldsymbol{r} + \boldsymbol{R} + \boldsymbol{R}')$$
$$\Rightarrow T_{\boldsymbol{R}} T_{\boldsymbol{R}'} = T_{\boldsymbol{R}'} T_{\boldsymbol{R}} = T_{\boldsymbol{R}+\boldsymbol{R}'}$$

- (A) is a commutation relation – From formal QM this implies that these two operators should share eigenstates.

$$H\psi = \epsilon\psi$$
$$T_{\boldsymbol{R}}\psi = c(\boldsymbol{R})\psi$$

Periodic Boundary Conditions

$$H\psi = \epsilon\psi$$
$$T_{\boldsymbol{R}}\psi = c(\boldsymbol{R})\psi$$

- So we have the effect of T_R acting on ψ, but what are the eigenvalues, $c(R)$?

- We have the following relations between the $C(\boldsymbol{R})$

$$T_{\boldsymbol{R}}T_{\boldsymbol{R'}} = c(\boldsymbol{R})T_{\boldsymbol{R'}}\psi = c(\boldsymbol{R})c(\boldsymbol{R'})\psi$$
$$\mathrm{T}_{\mathbf{R}'}T_{\boldsymbol{R}}\psi = T_{\boldsymbol{R}+\boldsymbol{R'}}\psi = c(\boldsymbol{R}+\boldsymbol{R'})$$

  which implies

$$c(\boldsymbol{R}+\boldsymbol{R'}) = c(\boldsymbol{R})c(\boldsymbol{R'})$$

  and we can write

$$c(\boldsymbol{a}_i) = e^{2\pi i x_i}$$

  apply $c(\boldsymbol{a}_1)c(\boldsymbol{a}_2)c(\boldsymbol{a}_3)$ n_1, n_2, n_3 times

$$c(\boldsymbol{R}) = c(\boldsymbol{a}_1)^{n_1}c(\boldsymbol{a}_2)^{n_2}c(\boldsymbol{a}_3)^{n_3}$$

Periodic Boundary Conditions

Proof of Bloch's Theorem

$$c(\boldsymbol{R}) = c(\boldsymbol{a}_1)^{n_1} c(\boldsymbol{a}_2)^{n_2} c(\boldsymbol{a}_3)^{n_3}$$

- This is equivalent to

$$c(\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}$$

where $\boldsymbol{k} = x_1\boldsymbol{b}_1 + x_2\boldsymbol{b}_2 + x_3\boldsymbol{b}_3$

- and so

$$T_{\boldsymbol{R}}\psi = \psi(\boldsymbol{r} + \boldsymbol{R}) = c(\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi(\boldsymbol{r})$$

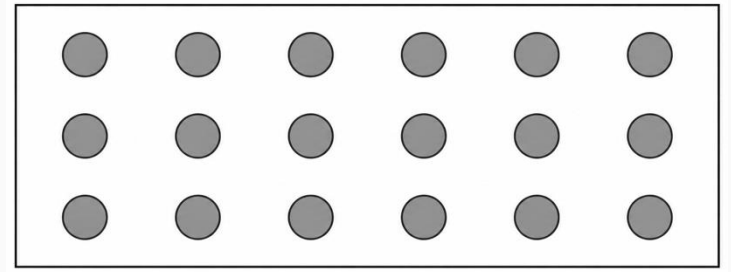
- let $u_{\boldsymbol{k}}(\boldsymbol{r}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\psi_{\boldsymbol{k}}(\boldsymbol{r})$

$$u_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{R}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \psi_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{R}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\psi_{\boldsymbol{k}}(\boldsymbol{r}) = u_{\boldsymbol{k}}(\boldsymbol{r})$$

$$\Rightarrow \psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r}) \text{ where } u_{\boldsymbol{k}}(\boldsymbol{r}) \text{ is periodic.}$$

What is k?

Born–von Karman Boundary Conditions



We apply a periodic boundary condition to our *whole* solid – imagine 'connecting the ends up'.

$$\psi(\boldsymbol{r} + N_i \boldsymbol{a}_i) = \psi(\boldsymbol{r}), \qquad i = 1,2,3$$

N_i is the number of times the primitive unit cell is repeated along the i direction (1=x, 2=y, 3=z). $N = N_1 N_2 N_3$ is the total number of primitive cells in the solid.

What is k?

Born–von Karman Boundary Conditions

$$\psi(\boldsymbol{r} + N_i \boldsymbol{a}_i) = \psi(\boldsymbol{r}), \qquad i = 1,2,3$$

Apply to Bloch state:

$$\psi_{\boldsymbol{k}}(\boldsymbol{r} + N_i \boldsymbol{a}_i) = e^{iN_i \boldsymbol{k}\cdot\boldsymbol{a}_i}\psi_{\boldsymbol{k}}(\boldsymbol{r})$$

$$\Rightarrow e^{iN_i \boldsymbol{k}\cdot\boldsymbol{a}_i} = 1$$

from $\boldsymbol{k} = x_1\boldsymbol{b}_1 + x_2\boldsymbol{b}_2 + x_3\boldsymbol{b}_3$ we then get

$$\boldsymbol{e}^{2\pi i N_i x_i} = 1$$

$$\Rightarrow 2\pi i N_i x_i = 2\pi \times \text{int.}$$

$$\Rightarrow x_i = \frac{m_i}{N_i} \quad \text{where } m_i = \text{int.}$$

As many allowed k-values as there are primitive cells in the crystal!

What is k?

Interpretation of **k**

$$\psi(\boldsymbol{r}) = \psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} U_{\boldsymbol{k}}(\boldsymbol{r})$$

- $\hbar\boldsymbol{k}$ plays a similar role to momentum
- However, it is not the *real* momentum (it is not the eigenvalue of $-i\hbar\nabla$)
- **k** is expressed in terms of the reciprocal lattice vectors

$$\boldsymbol{k} = x_1\boldsymbol{b}_1 + x_2\boldsymbol{b}_2 + x_3\boldsymbol{b}_3$$

but is not necessarily a reciprocal lattice vector (**G**). x_1, x_2, x_3 are not required to be integers.

- **k** is in reciprocal space, also known as k-space.

What is k?

Example: Free Electron model

- Use the free-electron model as a first, very simple approach

  Kinetic Energy : $T = -\frac{\hbar\nabla^2}{2m}$. Potential Energy: $U =$ Constant

  (equivalent to U=0)

- Because $V(r) = \text{Constant}$, the potential is trivially 'periodic'

- Take R as a lattice vector (any value of R will do)

What is k?

Example: Free Electron model

Kinetic Energy : $T = -\frac{\hbar\nabla^2}{2m}$. Potential Energy: $U = 0$ (Electrons are free)

- All energy is kinetic. Wavefunctions are planewaves
- Kinetic energy operator:

$$-\frac{\hbar}{2m}\nabla^2\psi_{\boldsymbol{q}}(\boldsymbol{r}) = -\frac{\hbar}{2m}\nabla^2 e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$$
$$= \frac{\hbar q^2}{2m} e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$$
$$\text{Kinetic Energy} = \frac{\hbar q^2}{2m}$$

What is k?

Example: Free Electron model

$$\psi_{\boldsymbol{k}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r})$$

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

Constant potential is a trivially periodic system:

The free-electron wave function: $\psi_{\boldsymbol{q}}(\boldsymbol{r}+\boldsymbol{R}) = \mathrm{e}^{i\boldsymbol{q}\cdot(\boldsymbol{r}+\boldsymbol{R})} = e^{i\boldsymbol{q}\cdot\boldsymbol{R}} \psi_{\boldsymbol{q}}(\boldsymbol{r})$

$$\Rightarrow e^{i\boldsymbol{q}\cdot\boldsymbol{r}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

so … $e^{i(\boldsymbol{q}-\boldsymbol{k})\cdot\boldsymbol{r}} = 1 \Rightarrow \boldsymbol{q}-\boldsymbol{k} = \boldsymbol{G}_n$

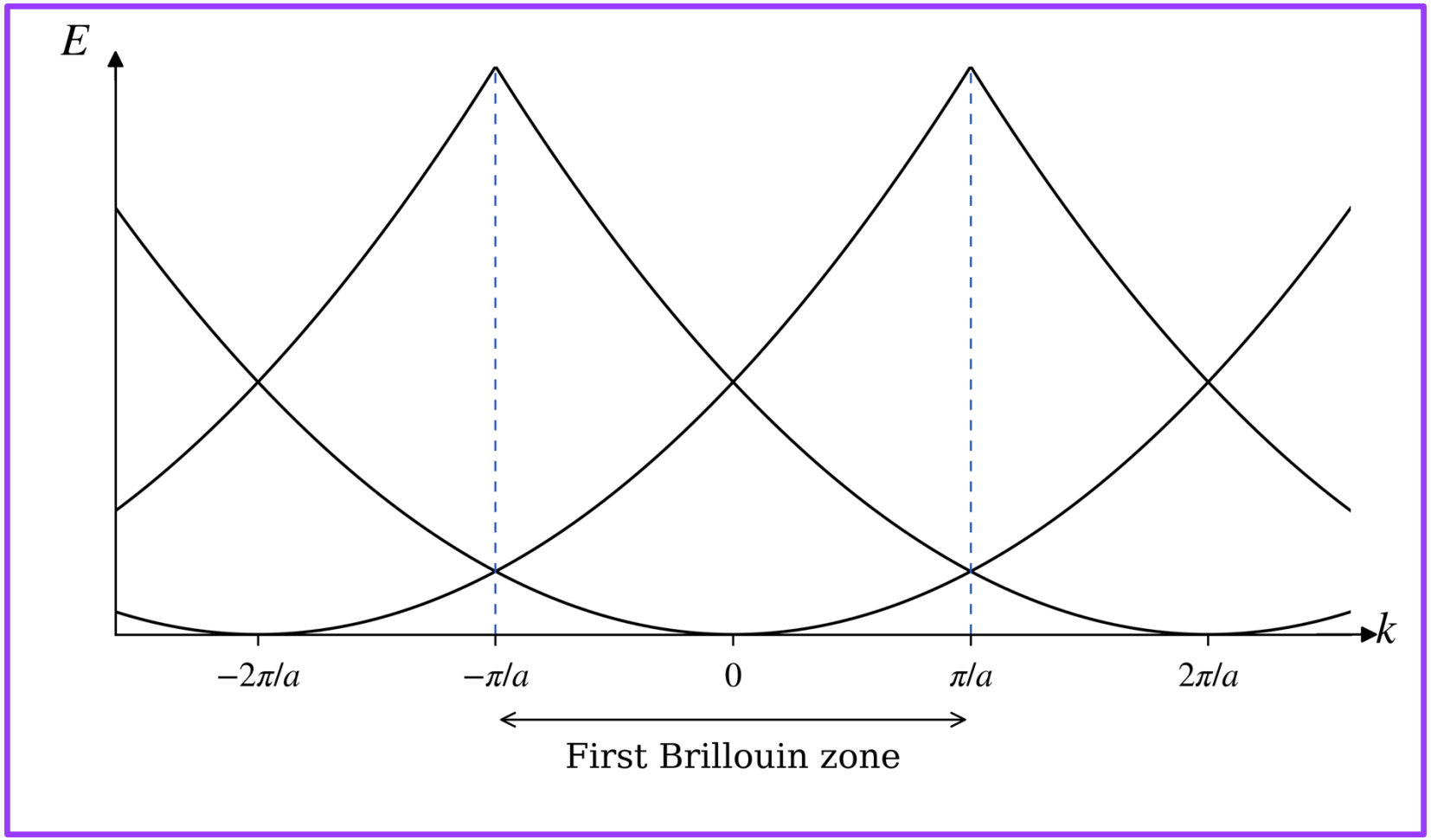
This means that many different states (with different **q**) have the same Bloch translation phase:

$$\boldsymbol{q} = \boldsymbol{k} + \boldsymbol{G}_n$$

What is k?

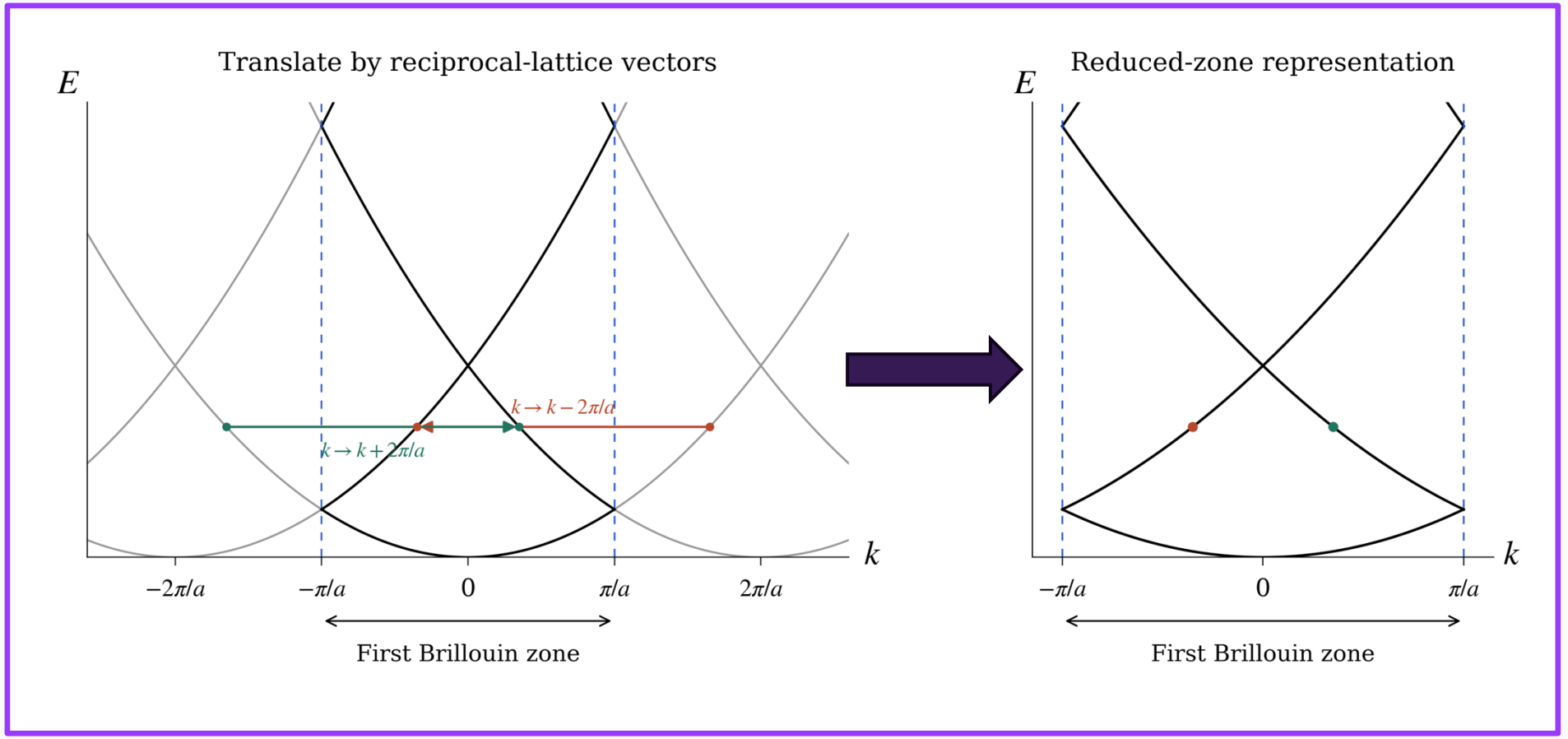
Back to the energy: $\frac{\hbar^2 q^2}{2m} = \frac{\hbar^2}{2m}(|\boldsymbol{k} + \boldsymbol{G}_n|)^2$

Simple 1D illustration (R=2a) :



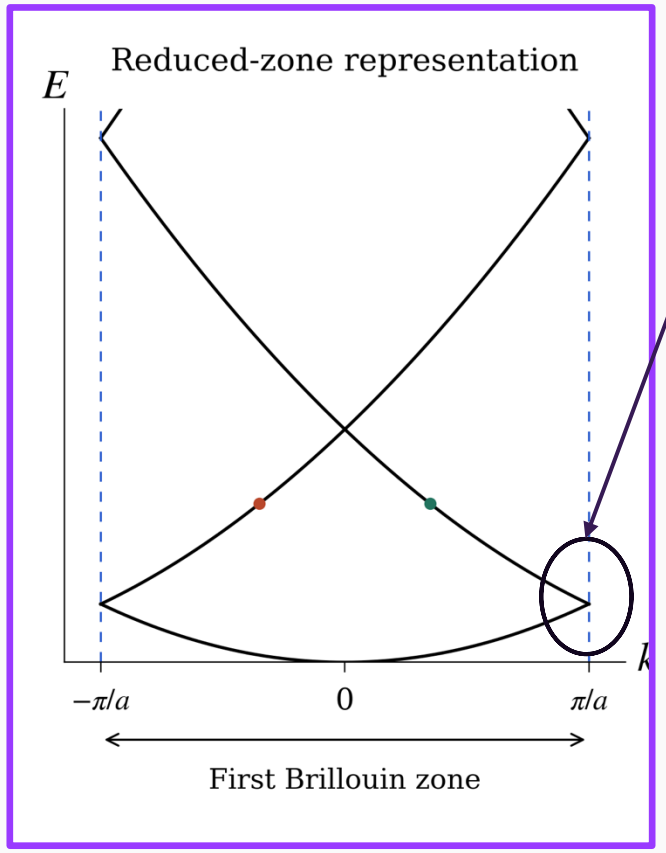
What is k?

- **k** separated by **G** are equivalent – collapse everything into first Brillouin zone by adding/subtracting **G** appropriately:



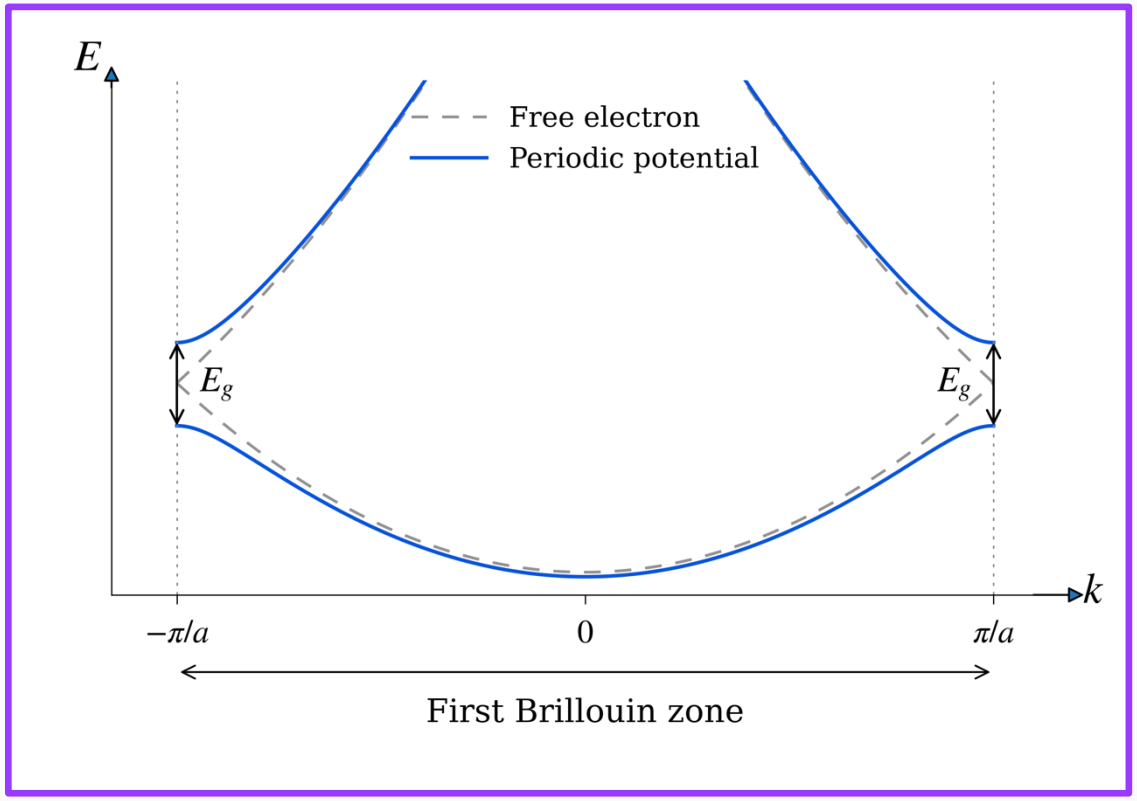
Bandstructure and Band-gap

“Weak” periodic potential



- Introduction of periodic potential can be shown to perturb states, strongly at degeneracies, where states get mixed.
- This can be called the ‘nearly free electron model’ – Electrons are *almost* free, if not for that periodic potential
- Derivations found in standard textbooks (Ashcroft-Mermin *Solid State Physics,* Ziman *Theory of Solids)*. Here we are mainly interested in the results.

Band-structure and Band-gap



- The periodic potential mixes the degenerate free-electron states $\psi_{\boldsymbol{k}}$ and $\psi_{\boldsymbol{k-G}}$ at the Brillouin-zone boundary, splitting their energies and opening a band gap.

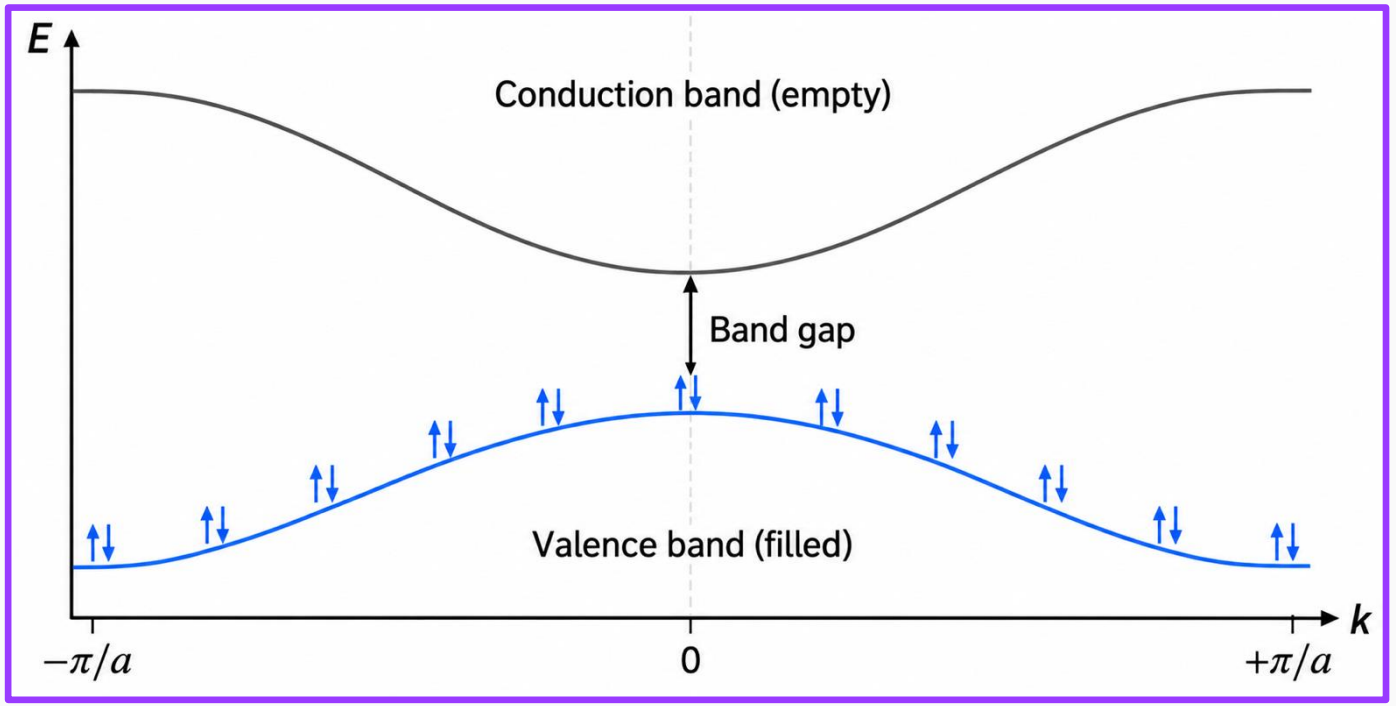
- This result is *general*. However, this simple 1D model is very simplified. It offers some illustrative insights however….

Nearly free electron model

The band gap

- Sudden jump in E(k) referred to as the band gap

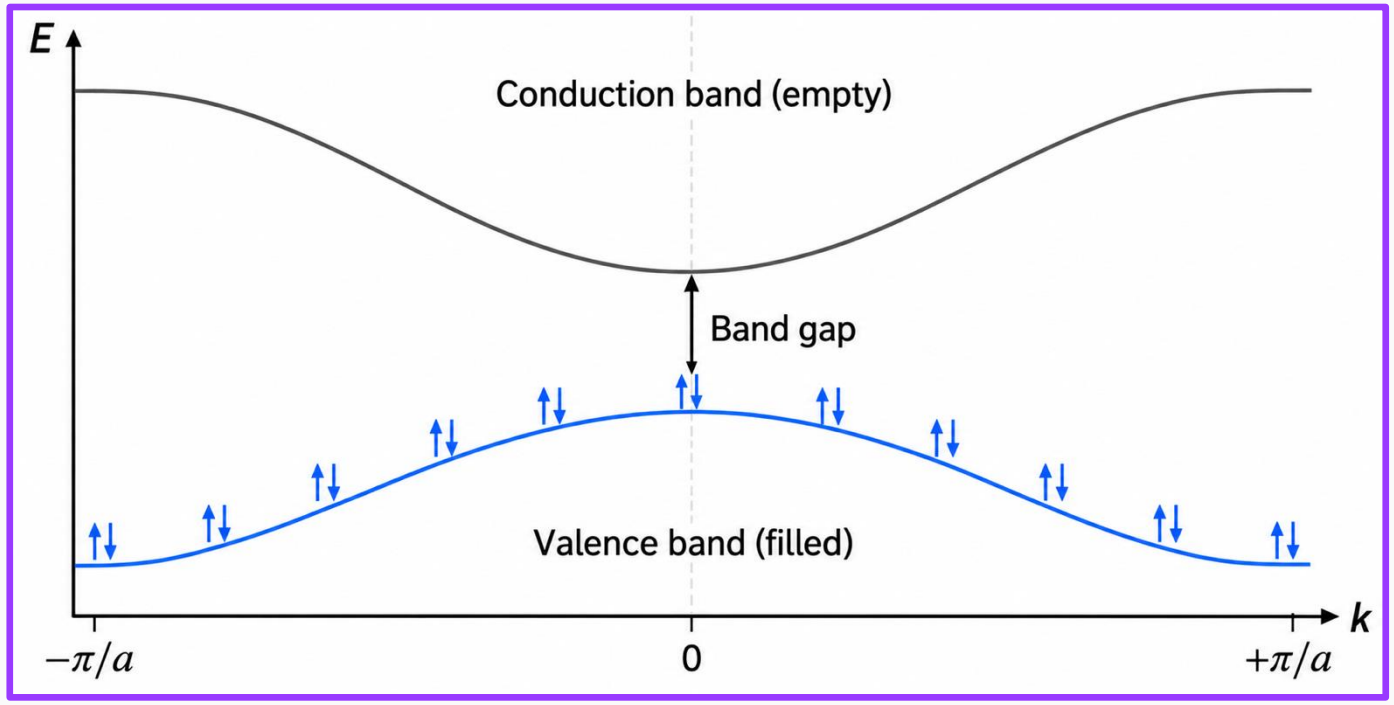
- When we fill electron states, start at lowest energy and move up. 2 electrons allowed per k-state (Pauli exclusion principle!)



Nearly free electron model

Metals and Insulators

- To conduct, we need a *net* **k**
- Filled valence band has no net **k**
- To conduct, an electron needs to jump into an appropriate **k**-state in the conduction band.
- Large band-gap => Too hard to jump => no conduction => Insulator!

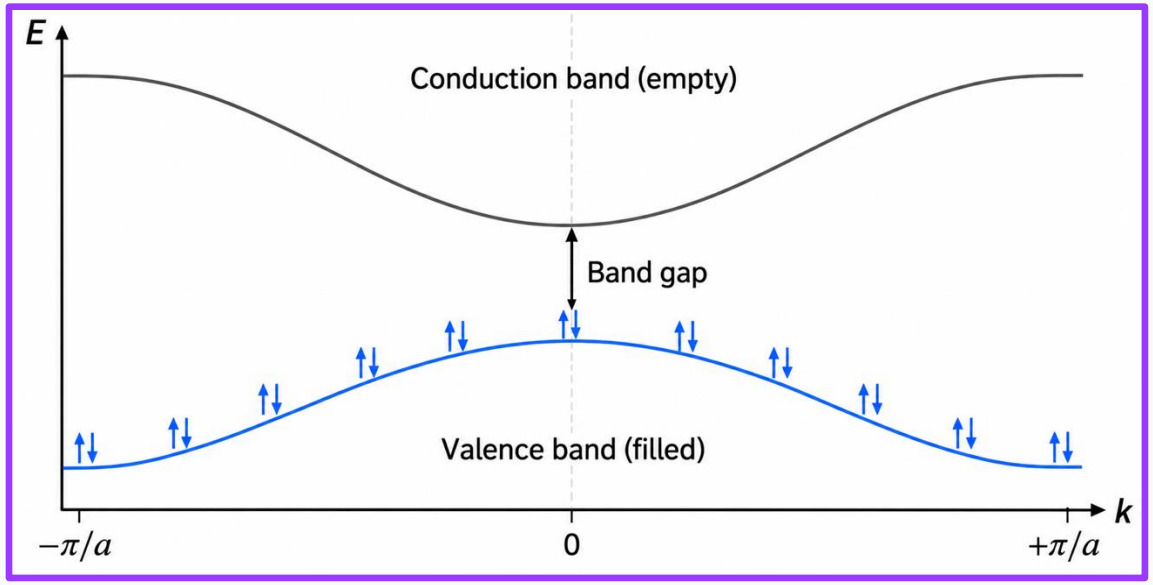


Nearly free electron model

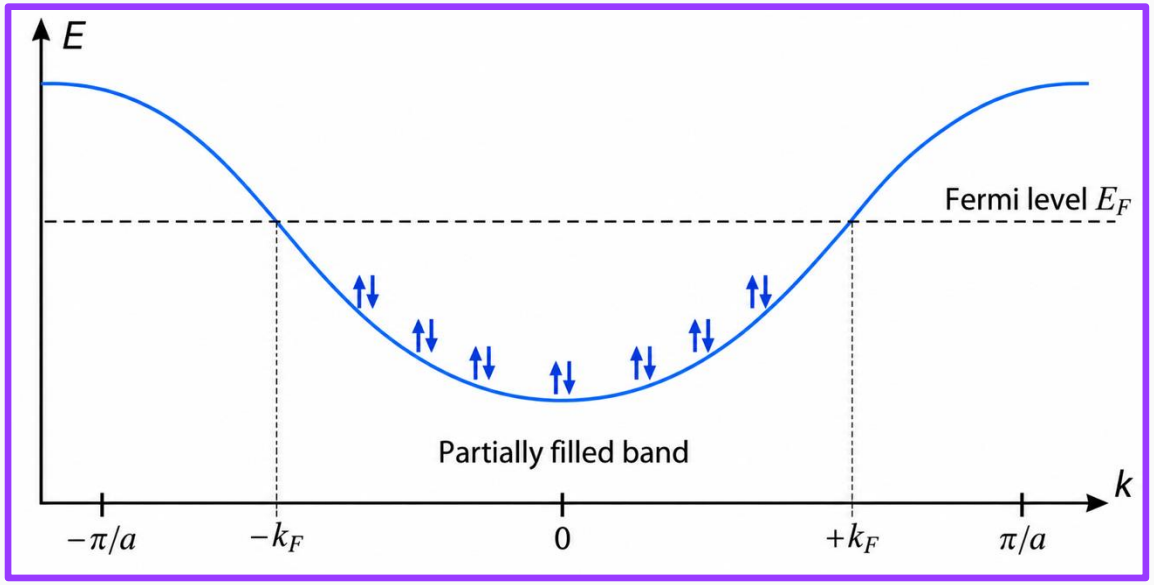
Metals and Insulators

Generally, this is the distinction:

Insulator – Band gap at the Fermi level



Band gap – Continuity in E(k) Fermi level



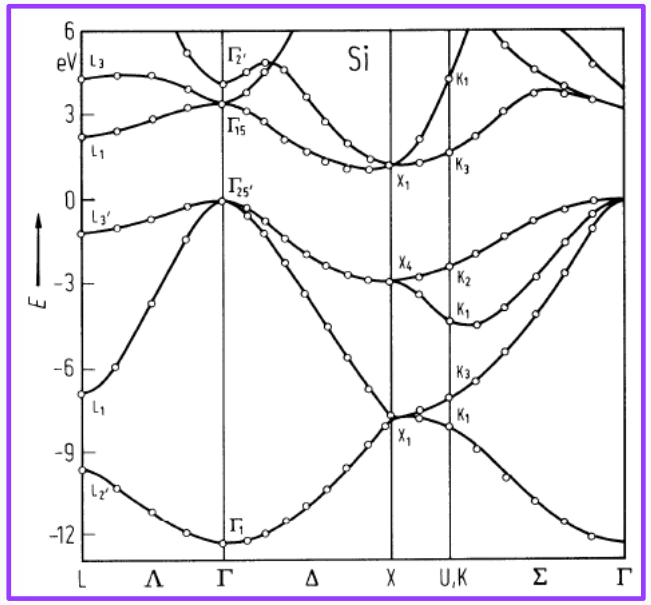
Semiconductors have a band gap, but a *small* one. Gives them some enhanced conductivity at RT. (e.g. Si bandgap is ~1.1 eV)

Nearly free electron model

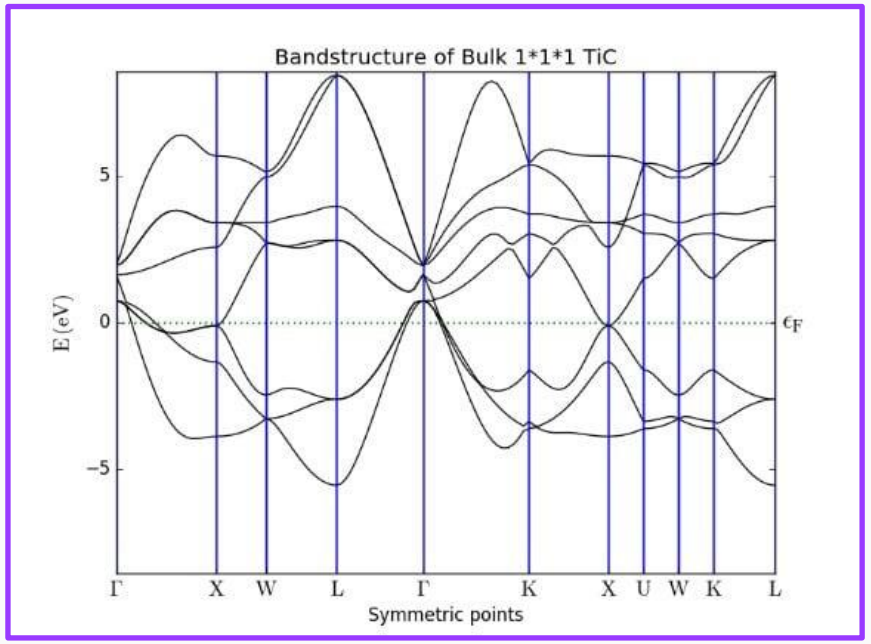
Real Band Structures

- Real crystals are 3D, giving a wide range of possible structures. Also multi-electron systems, giving complexity.

- Real band-structures are more complicated than the simple ones we have been considering:



Band Structure of Si



Band Structure of Ti

Summary and Take-Homes

- Periodicity of crystals allows us to represent the whole, infinite system using just a finite unit cell which is repeated through all space

- Periodicity also gives us a particular mathematical form of electron states:

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}u_{\boldsymbol{k}}(\boldsymbol{r}) \text{ where } u_{\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = u_{\boldsymbol{k}}(\boldsymbol{r})$$

$$\text{equivalently } \psi_{\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_{\boldsymbol{k}}(\boldsymbol{r})$$

- In crystals, energy levels of electrons form ‘bands’ which are separated by ‘band gaps’

- Insulators vs Metal is decided by where the electrons ‘fill up to’.

Quick Break

Questions?

Total Energy

Back to DFT

Total energy in DFT calculations:

$$E_{\mathrm{Tot}} = \int \rho(\boldsymbol{r}) V_{\mathrm{Nuc}}(\boldsymbol{r}) d^3r + T_{\mathrm{KS}} + E_{\mathrm{XC}} + E_{\mathrm{Har}} + E_{\mathrm{Nuc-Nuc}}$$

- T_{KS} is the kinetic energy of the noninteracting electrons in the fictitious KS system. It is **not** the real, many-body kinetic energy.

- E_{XC} is the exchange—correlation energy. It provides the energy difference between a noninteracting system and an interacting, many-electron system.
    - E_{XC} contains a term which corrects the T_{KS} kinetic energy to give the correct many-body kinetic energy.
    - It also contains the correction to the self-interaction error of the Hartree term.

Total Energy

Real Band Structures

$$E_{\mathrm{Tot}} = \int \rho(\boldsymbol{r}) V_{\mathrm{Nuc}}(\boldsymbol{r}) d^3 r + T_{\mathrm{KS}} + E_{\mathrm{XC}} + E_{\mathrm{Har}} + E_{\mathrm{Nuc-Nuc}}$$

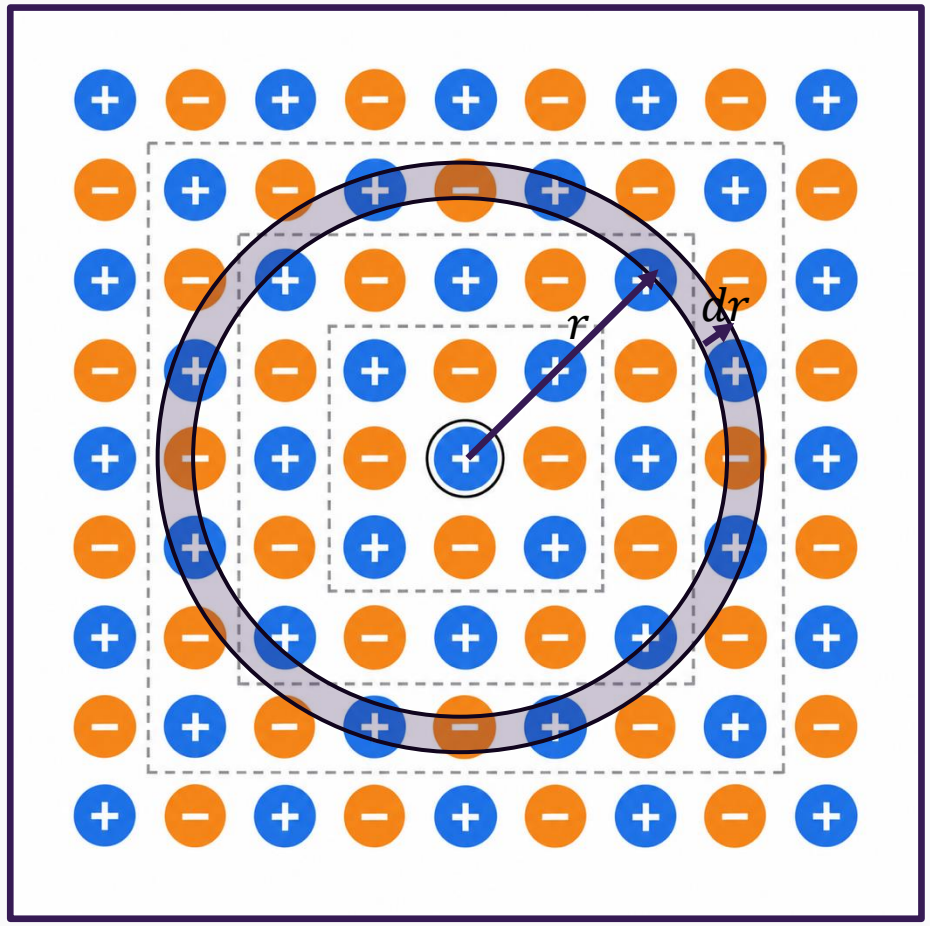
- Nuclei are included as point charges:

$$V_{\mathrm{Nuc}} = \sum_i \frac{1}{4\pi\epsilon_0} \frac{Z_i}{r_i}$$

Total Energy

Ion–Ion Interaction

Say we had a perfectly ionic system:



Sum the total contribution by summing total number of ions in each spherical shell, (volume integral):

$$\text{Shell volume} \sim 4\pi r^2 dr$$

$$\text{Potential} \sim \frac{1}{r}$$

$$\Rightarrow V(R) \sim \int^{R} r dr = R^2$$

So the contribution to the potential up to distance R increases by the square!

Total Energy

Ewald Summation

- This sum is actually *conditionally convergent*.
- The terms $E_{\mathrm{Ion-Ion}}$ and $E_{\mathrm{electron-electron}}$ and individually infinite. There are infinitely many positive charges, and infinitely many electrons – but together they cancel out and give a neutral system!
- In practice, the sum is found using a technique called an Ewald summation.
- Exact formulas for electrostatic terms will vary between different codes.

Total Energy

Ewald Summation

- Ewald summation splits the Coulomb interaction into a short-range contribution, evaluated in direct space, and a smooth long-range contribution, evaluated in reciprocal space.

- The splitting is chosen so that both sums converge rapidly in their respective representations.

$$E_{\text{ion}-\text{ion}} = \frac{1}{2}\sum_{I,J} Z_I Z_J e^2 \left\{ \sum_i \frac{\operatorname{erfc}\left(\eta|\mathbf{r}_I + \mathbf{R} - \mathbf{r}_J|\right)}{|\mathbf{r}_I + \mathbf{R} - \mathbf{R}_J|} - \frac{2\eta}{\sqrt{\rho}}\delta_{IJ} \right.$$
$$\left. + \frac{4\pi}{\Omega}\sum_{\mathbf{G}\neq 0} \frac{1}{|\mathbf{G}|^2} \exp\left(-\frac{|\mathbf{G}|^2}{4\eta^2}\right) \cos\left[(\mathbf{r}_I - \mathbf{r}_J)\cdot\mathbf{G}\right] - \frac{\pi}{\eta^2\Omega} \right\}$$

https://micro.stanford.edu/mediawiki/images/4/46/Ewald_notes.pdf

Planewave Basis

Representing Functions

- We need to represent our ϕ_{KS} somehow – We do this computationally using a basis set.
- Simplest of these is a planewave basis set
- We have done this quite a lot already, every time write a function as something like:

$$f(r) = \sum_i f_i e^{i\boldsymbol{k_i}\cdot\boldsymbol{r}}$$

- Basis sets will be covered in more detail in later lectures, for now we will just look at planewaves

Planewave Basis

Representing Electron Orbitals

- We represent a KS orbital as

$$\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$$

$$u_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}}^{\boldsymbol{G}_{\max}} c_{n\boldsymbol{k}}(\boldsymbol{G}) e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$

where $\boldsymbol{G}$ are the reciprocal lattice vectors, and $\boldsymbol{G}_{\max}$ is selected according to a 'cutoff energy'

$$\frac{\hbar^2 |k^2 + G^2|}{2m_e} \leq E_{\text{Cutoff}}$$

Warning! – Planewaves used in expansion not the same as Bloch theorem. **k** is a physical variable, planewave basis is *our* way of representing functions.

Planewave Basis

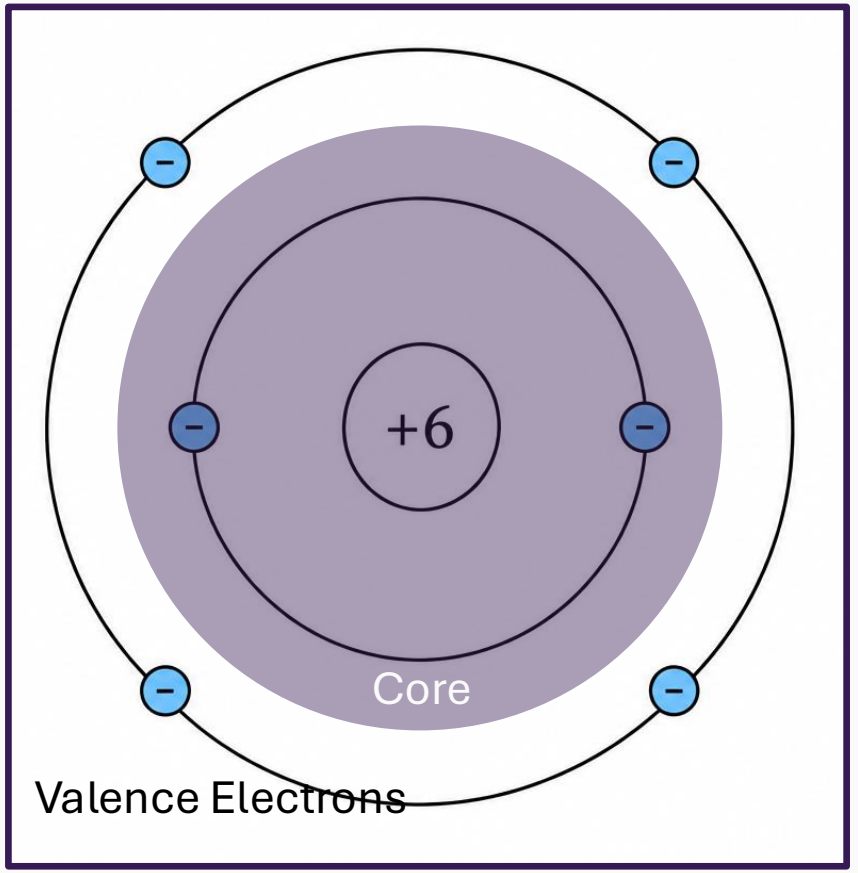
Representing Electron Orbital

- The higher our energy cutoff, the *more* planewaves we are using to represent our functions → Higher accuracy.
- However, higher number of planewaves → → More computationally demanding.
- Typically, calculations will require testing to find optimal E_{cutoff} – more on this in later lectures.
- There are other, very common, tricks used to reduce basis set size…..

Pseudopotentials

Core and Valence Electrons

- In practice, we separate electrons into ‘core’ and ‘valence’ electrons
- e.g. Can separate C into an inner core of Q=+4, (6 protons + 2 electrons) and 4 outer valence electrons
- Most chemistry and important bonding happens due to the valence electrons – core electrons not important to model *explicitly*.



Pseudopotentials

Basic Idea Pseudopotentials

- We could replace the nucleus + core electrons with something representing their collective effect.

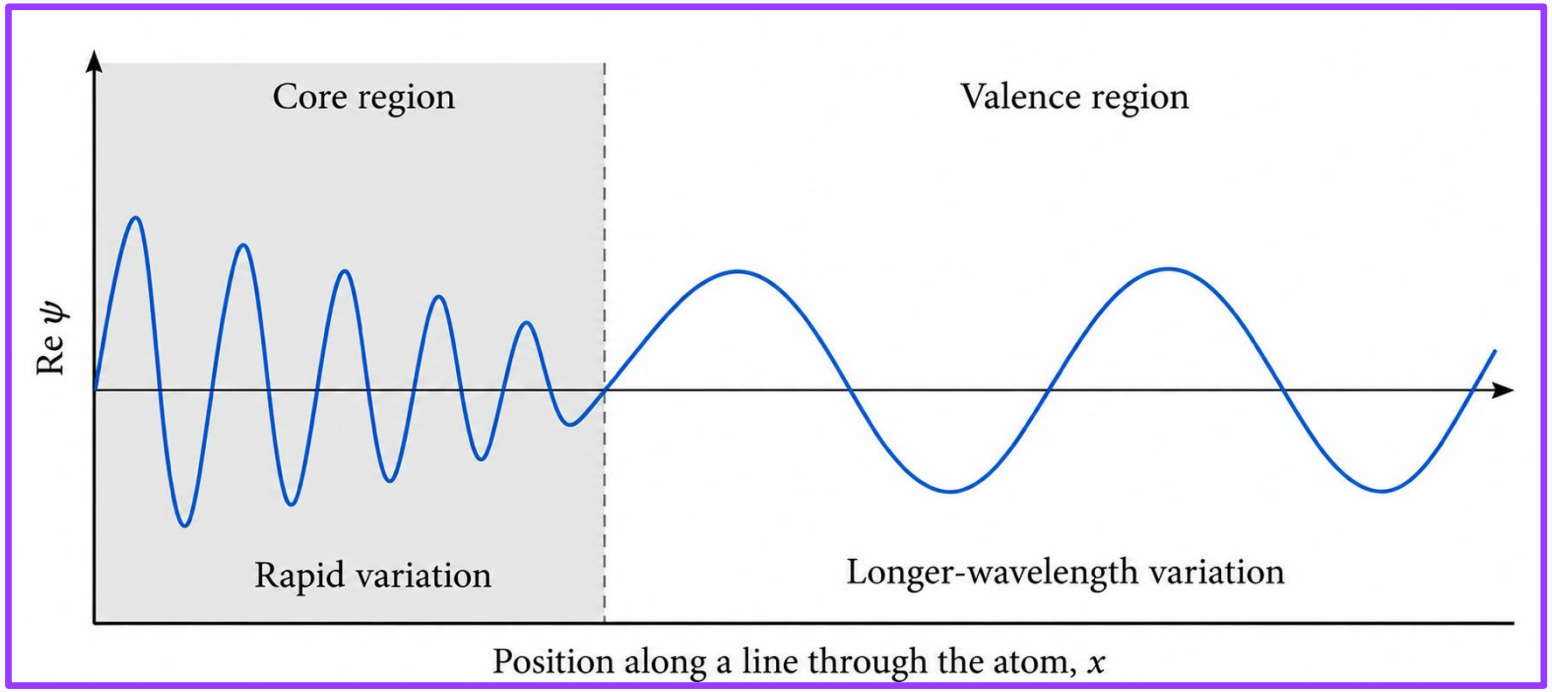
- This would reduce the number of electrons we need to model computationally – improving efficiency of calculations.

- But, also, we can reduce the energy cutoff of our planewave basis….but why?

Pseudopotentials

Wavefunctions in the core region

- In the core region, electrons are close to the nucleus – this increases the kinetic energy of the electron.



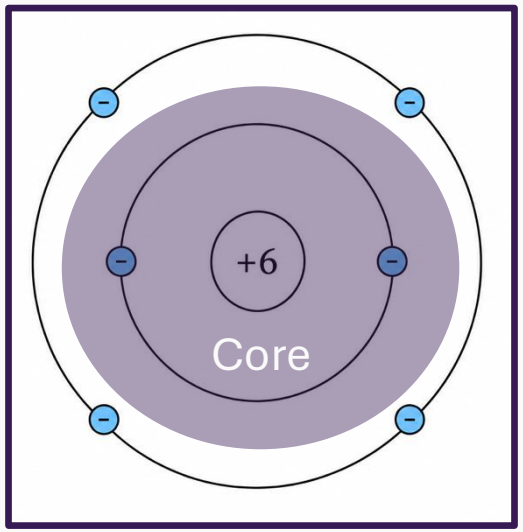
- High KE = Rapid oscillations in the wavefunction (Think de Broglie relation: $\lambda = \frac{h}{p}$)

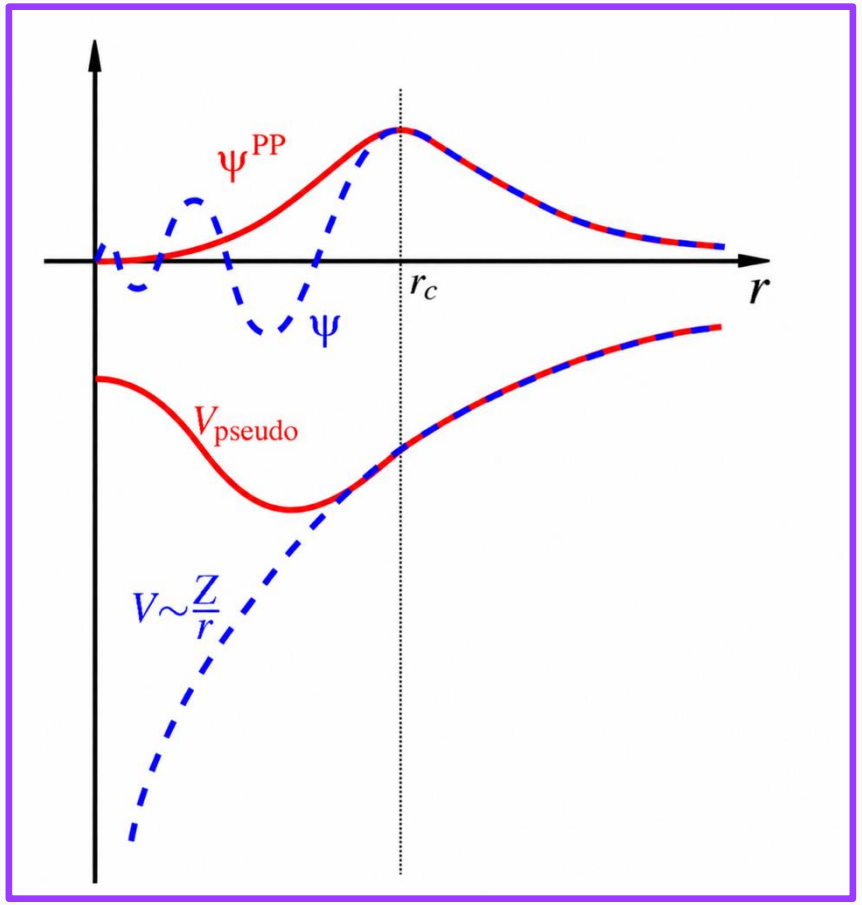
- If we have very rapid oscillations in ψ, we need E_{cutoff} to be high also (to contain rapidly oscillating planewaves in the basis).

Pseudopotentials

Replacing core region with Pseudopotentials

- Strategy: Replace the nucleus + core electrons with a ‘pseudo-potential’ and instead find ‘pseudo-wavefunctions’





- The pseudopotential is fitted so-as to make the electron wavefunctions smooth in the core region.

Pseudopotentials

Replacing core region with Pseudopotentials

- Strategy: Replace the nucleus + core electrons with a ‘pseudo-potential’ and instead find ‘pseudo-wavefunctions’

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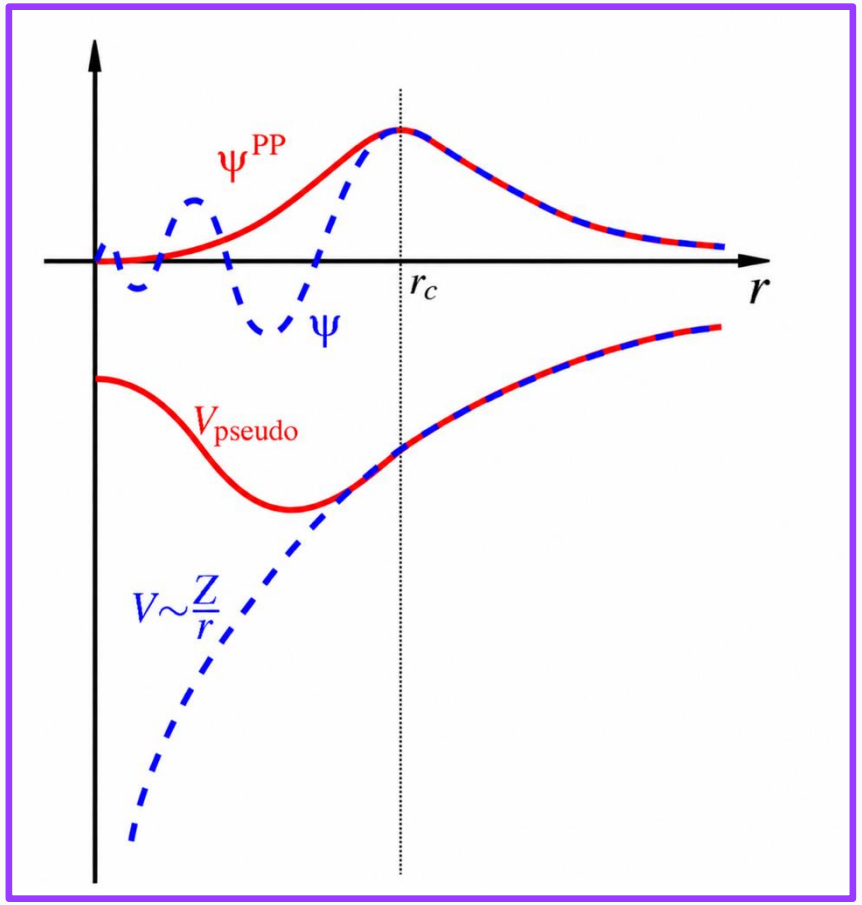


Pseudopotentials

Conditions of Pseudopotentials

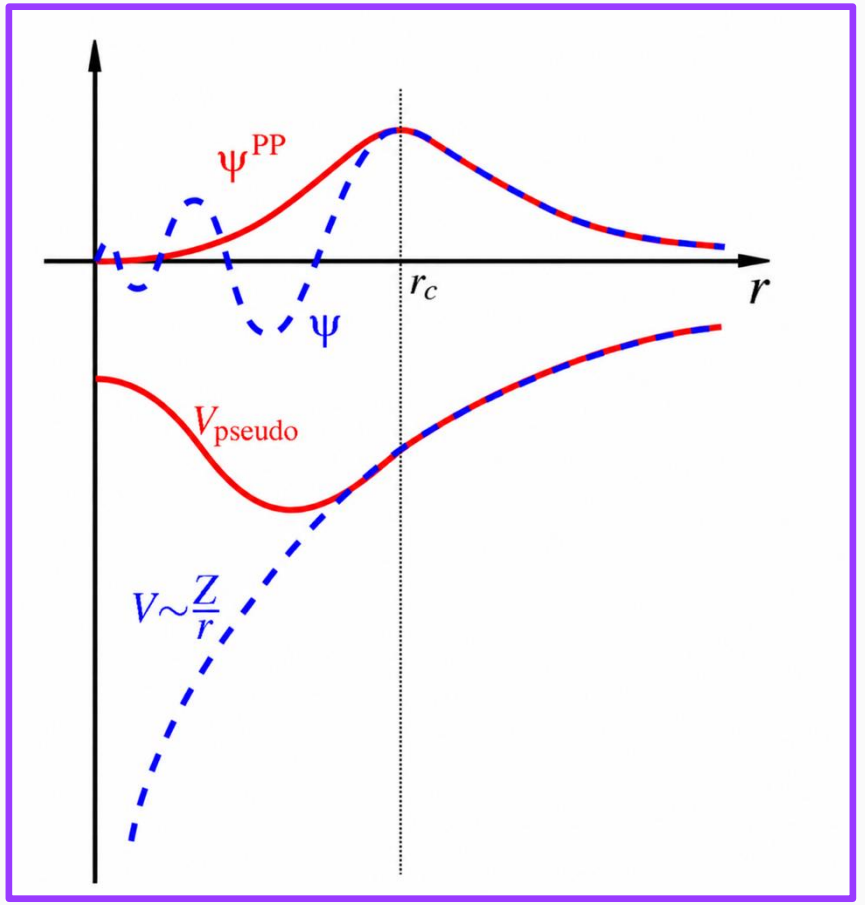
- Beyond core region, the pseudo-wavefunction should be equal to the 'real' wavefunction

$$\psi^{PP}(r > r_c) = \psi(r > r_c)$$

- Same eigenvalues: $\epsilon_i^{PP} = \epsilon_i$

- "Norm-conserving" pseudopotentials are often used (not always) . Here, the total probability density of the pseudo-wavefunction inside the core region remains the same:

$$\int_{r<r_C} |\psi^{PP}(\boldsymbol{r})|^2 d^3r = \int_{r<r_c} |\psi(\boldsymbol{r})|^2 d^3r$$



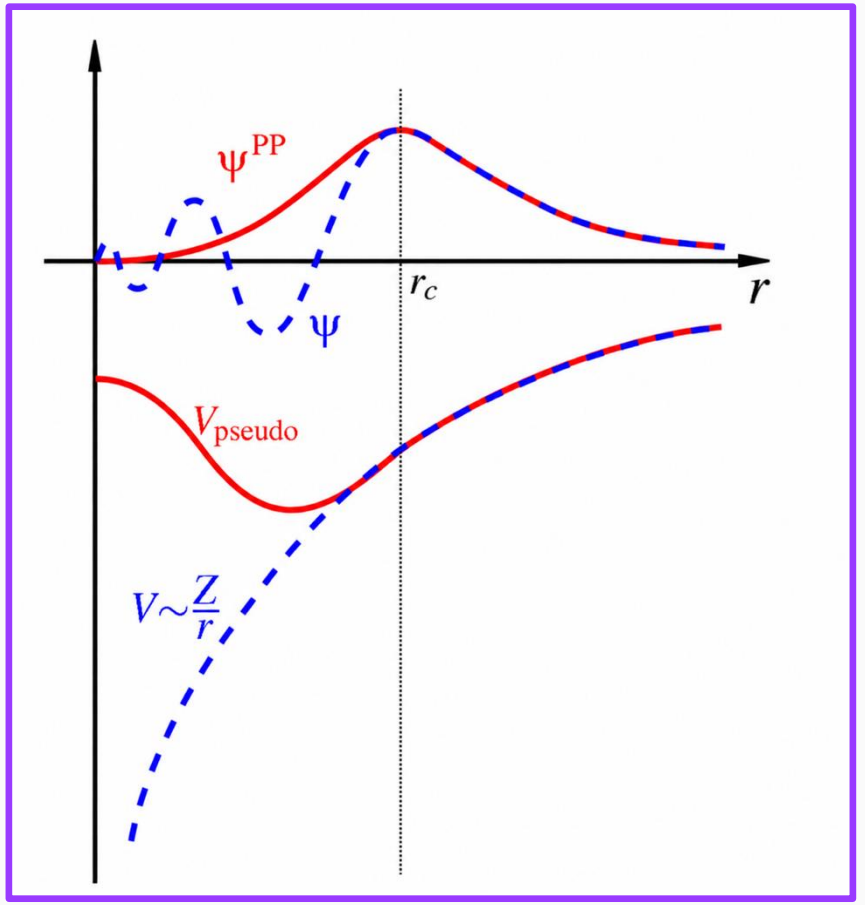
Pseudopotentials

Properties of Pseudopotentials

- **Hardness:** *Hard* pseudopotentials still require a large planewave cutoff. *Soft* pseudopotentials benefit from a very low planewave cutoff.

- **Transferability:** *Transferable* pseudopotentials work well in many different chemical environments

Pseudopotentials are often a balance between these two properties!



Pseudopotentials

Calculation Types

- **Pseudopotential Calculations:** Absorb some electrons and nucleus into a core with the manufactured potential. Gives smooth (pseudo)wavefunctions in the core region. **Most calculations on materials and molecules use this approach**.

- **All electron calculations:** All core electrons explicitly considered. *Much* more computationally expensive this way. But necessary for some situations.

Summary and Take-Homes

- Electrostatics has to be done carefully in periodic systems – Ewald summations employed by most electronic structure codes

- Electron wavefunctions can be represented by linear sums of planewaves.
    - Not the only way of representing wavefunctions (other methods discussed in later lectures)
    - Quality of planewave basis decided by value of E_{cutoff}

- Pseudopotentials are used to represent core-region electrons + the nucleus
    - Reduces the number of electrons we need to simulate
    - Smooths the wavefunctions in the core-region, reducing the E_{cutoff} necessary for calculations

Further Reading

- I have use *Solid State Physics* by Aschroft and Mermin for compiling much of the first hour of this lecture.
- Have also used *Theory of Solids* by Ziman, however this is a little old-fashioned and Ashcroft–Mermin is considered *the* text of the field.

- Other materials on more computational stuff such as Ewald summations and pseudopotentials are varied, often a DFT software manual is a good place to start, e.g:

    - The VASP Manual https://vasp.at/wiki/The_VASP_Manual

    - CP2K ”Quickstep Paper”: Kühne, Thomas D., et al. *The Journal of Chemical Physics* 152.19 (2020).

Questions?

