# Lecture 3 – Density Functional Theory for Solids

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TYC Materials Modeling Course

# How can we use DFT to simulate materials?

- **1964** Inhomogeneous electron gas, P. Hohenberg and W. Kohn, *Phys. Rev.*

As we saw in the last lecture, we can use density functional theory to solve many electron problems.

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- **1979** Momentum-space formalism for the total energy of solids, J. Ihm, A. Zunger, M. L. Cohen, *J. Phys. Condens. Matter*

It took 15 years to work out how to use computers to do DFT calculations for solids.

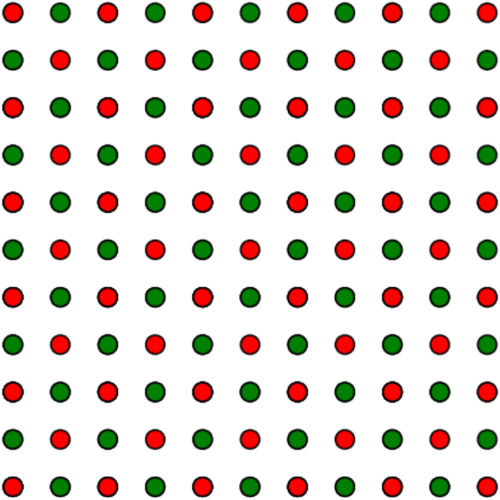
# Overview

1. Crystallography
2. Bloch's theorem
3. Bandstructure

# Crystallography

# What are crystals?

In crystals, the atoms form a pattern that is infinitely repeated.



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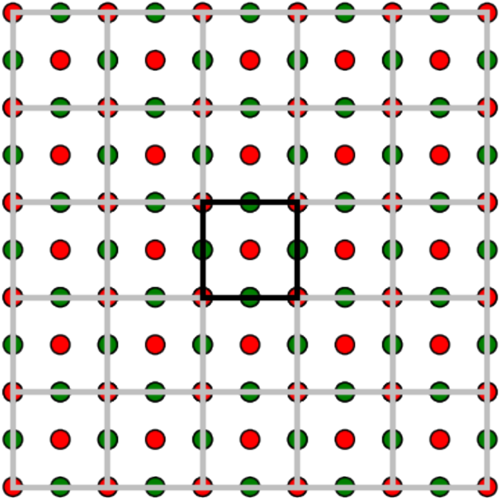
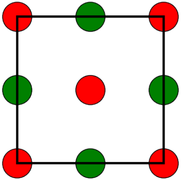
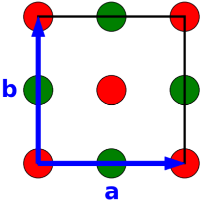


# The unit cell



- One unit cell represents the whole infinite crystal.
- Unit cells are not unique (could use a smaller or larger cell)
- If we calculate a property everywhere in the unit cell, we know its value everywhere in the infinite crystal.
- Larger cells are more expensive computationally

# The cell vectors



- The shape of the cell is defined by its cell vectors (**a**, **b**, **c**).
- If we move an integer number of lattice vectors we end up where we started (just in anther cell)
- Let us define $\mathbf{R} = n_a\mathbf{a} + n_b\mathbf{b} + n_c\mathbf{c}$

# Bravais lattices

Given our definition $\mathbf{R} = n_a\mathbf{a} + n_b\mathbf{b} + n_c\mathbf{c}$, how many unique 3D patterns can we make?

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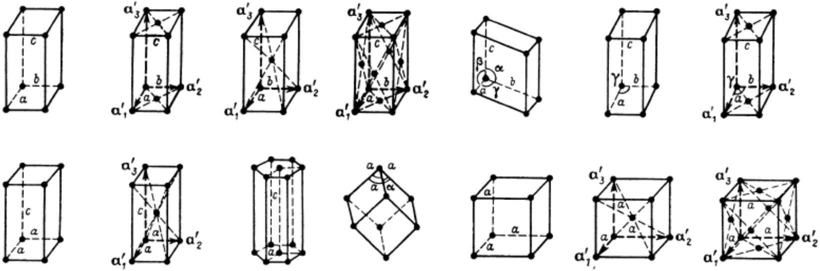
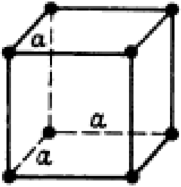


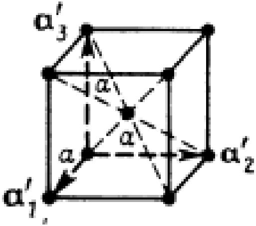
Only 14, the 3D Bravais lattices.

# Bravais lattices

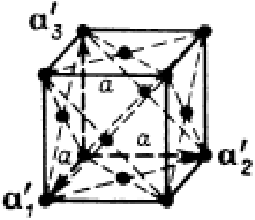
The three simplest Bravais lattices are:



Simple cubic (SC)



Body centered cubic (BCC)



Face centered cubic (FCC)

These cubic cells have $a=b=c$

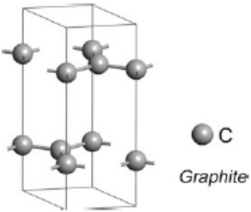
# Crystal structure

$$\boxed{\text{crystal structure} = \text{lattice} + \text{motif}}$$

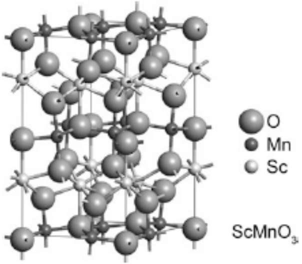
Lattice – the shape and size of the unit cell

Motif – the atoms within the unit cell

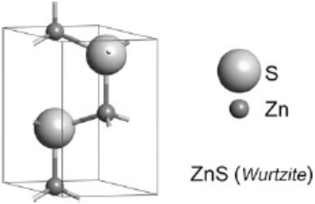
# Some example crystal structures



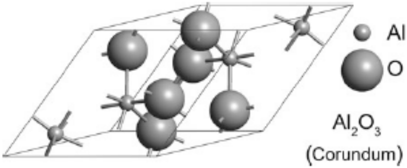
Graphite



$ScMnO_3$



ZnS (*Wurtzite*)



$Al_2O_3$
(Corundum)

# Bloch’s theorem

# A periodic potential

In a crystal, the potential generated by the atoms will be periodic:

**Periodic potential**

$$V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r})$$

Adding any possible **R** doesn't change the value of $V$. This is the case for all observables of the system.

# Bloch's theorem

Bloch proved that solutions of the Schrödinger equation in a periodic potential are only "quasi-periodic", with the following form,

## Bloch's theorem

$$\psi_k(\mathbf{r}) = U_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \tag{1}$$

The wavefunction does contain a periodic part,

$$U_k(\mathbf{r}) = U_k(\mathbf{r} + \mathbf{R}) \tag{2}$$

And a non-periodic part,

$$\exp(i\mathbf{k} \cdot \mathbf{r}) \tag{3}$$

# Proof of Bloch’s theorem

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Consider the Schrödinger equation,

$$\hat{H}(\mathbf{r})\,\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) \tag{4}$$

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How does $\hat{H}(\mathbf{r})$ change as we add **R**?

$$\hat{H}(\mathbf{r}+\mathbf{R}) = -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}+\mathbf{R}} + V(\mathbf{r}+\mathbf{R}) \tag{5}$$

We can see that the Hamiltonian operator is a periodic operator too,

$$\therefore \hat{H}(\mathbf{r}+\mathbf{R}) \equiv \hat{H}(\mathbf{r}) \tag{6}$$

# Proof of Bloch's theorem

As both $\psi\left(\mathbf{r}\right)$ and $\psi\left(\mathbf{r}+\mathbf{R}\right)$ are solutions of exactly the same equation, they can only differ by a multiple,

$$\psi\left(\mathbf{r}\right)=\zeta\left(\mathbf{R}\right)\psi\left(\mathbf{r}+\mathbf{R}\right) \tag{7}$$

Also, we know that both wavefunctions have to be normalised,

$$\left|\zeta\left(\mathbf{R}\right)\right|^{2}=1 \tag{8}$$

Complex maths (the Euler identity) tells us that the solution of this is,

$$\zeta\left(\mathbf{R}\right)=\exp\left[i\chi\left(\mathbf{R}\right)\right] \tag{9}$$

# Proof of Bloch's theorem

We can consider adding $\mathbf{R}+\mathbf{R}'$ as well. We have to get the same answer if we add the whole vector at once, or do it in steps. Hence,

$$\zeta\left(\mathbf{R}+\mathbf{R}'\right)=\zeta\left(\mathbf{R}\right)\zeta\left(\mathbf{R}'\right) \tag{10}$$

The equation above is a linear equation, which has only one possible solution

$$\chi\left(\mathbf{r}+\mathbf{R}\right)=\mathbf{k}\cdot\mathbf{R} \tag{11}$$

where *k* is an arbitrary vector in the reciprocal space. All together, this means,

$$\psi\left(\mathbf{r}+\mathbf{R}\right)=e^{i\mathbf{kR}}\psi\left(\mathbf{r}\right) \tag{12}$$

This directly implies the required result.

# Reciprocal Brillouin zone

What values can this *K*-vector we have introduced through Bloch's theorem have?

**Bloch's theorem**

$$\psi_k\left(\mathbf{r}\right) = U_k\left(\mathbf{r}\right)\exp\left(i\mathbf{k}\cdot\mathbf{r}\right) \tag{13}$$

This complex exponent is itself a periodic function

$$\pm\exp i\theta = \cos\left(\theta\right) \pm i\sin\left(\theta\right) \tag{14}$$

So,

$$\exp\left(\theta + 2\pi\right) = \exp\left(\theta\right) \tag{15}$$

## Reciprocal Brillouin zone

The maths is a bit more complex in 3D, but we end up with three reciprocal lattice vectors.

$$\mathbf{G}_x = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \tag{16}$$

$$\mathbf{G}_y = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot (\mathbf{c} \times \mathbf{a})} \tag{17}$$

$$\mathbf{G}_z = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})} \tag{18}$$

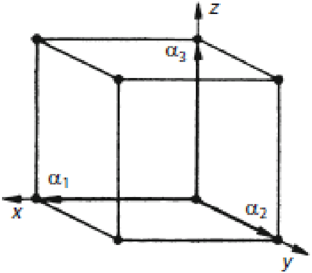
Our Bloch wave is identical for **k** values that have this periodicity.

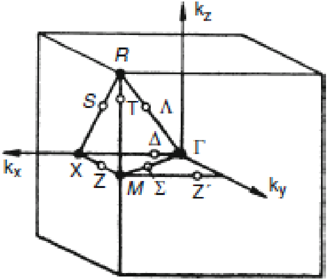
$$\psi_k (\mathbf{r}, \mathbf{k} + \mathbf{G}) = \psi_k (\mathbf{r}, \mathbf{k}) \tag{19}$$

Most important property of these definition is that as realspace unit cell gets larger, the reciprocal unit cell gets smaller.

# Reciprocal Brillouin zone - SC

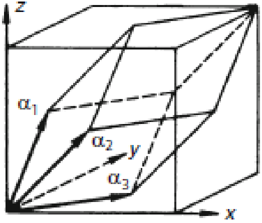
The reciprocal lattice of a simple cubic lattice is also a simple cubic lattice.

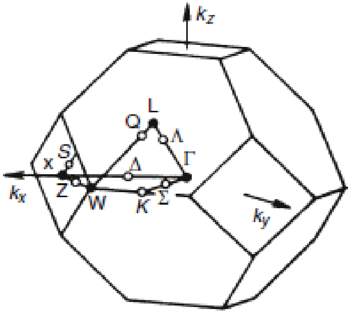




# Reciprocal Brillouin zone - FCC

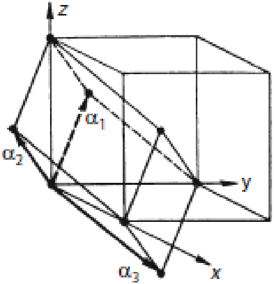
The reciprocal lattice of a face centered cubic lattice is a body centered cubic lattice.

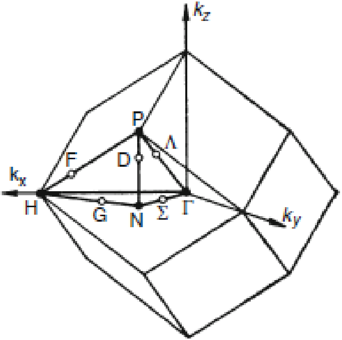




# Reciprocal Brillouin zone - BCC

The reciprocal lattice of a body centered cubic lattice is a face centered cubic lattice.





# What does this mean?

So what does all this abstract maths tell us about quantum systems?

$$E = \int_{\Omega} \psi^* \hat{H} \psi \, d\Omega = \int_{\Omega} \psi^* \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) \, d\Omega \qquad (20)$$

Let's consider two extreme limits:

1. Potential energy dominated
2. Kinetic energy dominated

Real examples are going to be somewhere in the middle.

# Potential energy dominated

Let $\hat{H}(\mathbf{r}) = V(\mathbf{r})$ and remember Bloch's theorem:

**Bloch's theorem**

$$\psi_k(\mathbf{r}) = U_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \tag{21}$$

# Potential energy dominated

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**Bloch's theorem**

$$\psi_k(\mathbf{r}) = U_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \tag{21}$$

Consider,

$$E = \int_\Omega \psi^*(\mathbf{r})\, V(\mathbf{r})\, \psi(\mathbf{r})\, d\Omega \tag{22}$$

$$= \int_\Omega V(\mathbf{r})\, |\psi(\mathbf{r})|^2 d\Omega \tag{23}$$

# Potential energy dominated

$$E = \int_{\Omega} V(\mathbf{r}) \, |v_k(\mathbf{r})|^2 \exp(i\mathbf{k} \cdot \mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\Omega \tag{24}$$

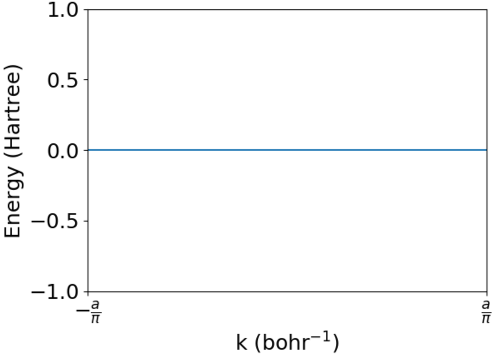
$$= \int_{\Omega} V(\mathbf{r}) \, |V_K(\mathbf{r})|^2 \exp 1 d\Omega \tag{25}$$

$$= \int_{\Omega} V(\mathbf{r}) \, |V_K(\mathbf{r})|^2 d\Omega \tag{26}$$

so the energy has no **k**-dependence in this case!

## Example: Isolated Hydrogen

If we looked at isolated hydrogen in a periodic DFT code, we would see this absence of **k**-dependence:



For systems like this, **k**-space isn't adding anything to the description.

# Kinetic energy dominated

For the opposite case, we set $V(\mathbf{r}) = 0$, ie free electron

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 \tag{27}$$

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So consider,

$$\nabla^2\psi(\mathbf{r}) = \nabla^2 v_k \exp\left(i\left(\mathbf{k}+\mathbf{G}\right)\cdot\mathbf{r}\right) \tag{28}$$

$$= -\left(\mathbf{k}+\mathbf{G}\right)^2 v_k\left(\mathbf{r}\right) \tag{29}$$

# Kinetic energy dominated

In terms of energy,

$$E = -\frac{\hbar^2}{2m}\int_\Omega \psi^*(\mathbf{r})\,\nabla^2\psi(\mathbf{r})\,d\Omega \tag{30}$$

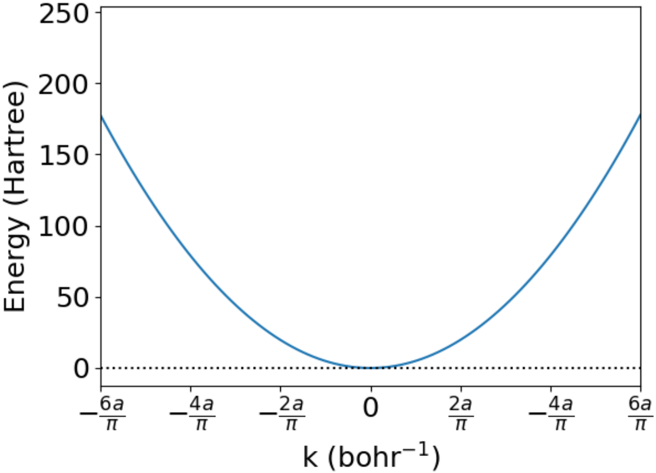
$$= \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2\int_\Omega U_k^*(\mathbf{r})\,U_k(\mathbf{r})\,d\Omega \tag{31}$$

$$= \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2 \tag{32}$$

We have a parabolic **k**-point dependence, around each reciprocal lattice vector.

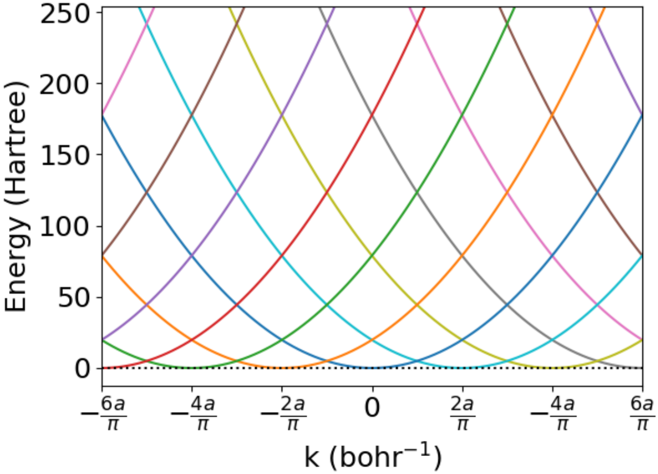
# Free electron gas

We have a parabola centered on the Γ-point.



# Free electron gas

But there is also a parabola centered on each reciprocal lattice point.



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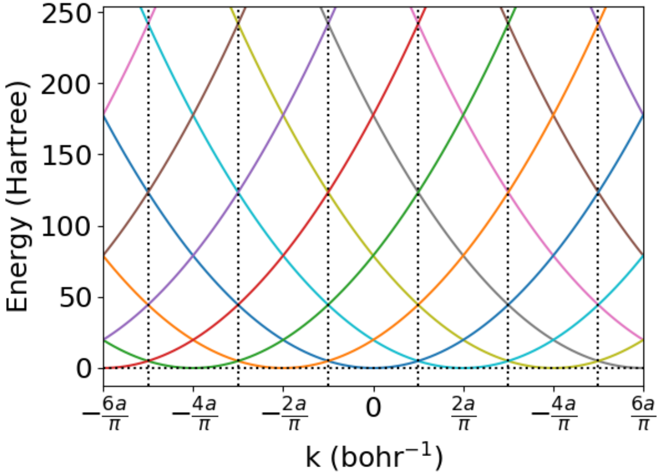
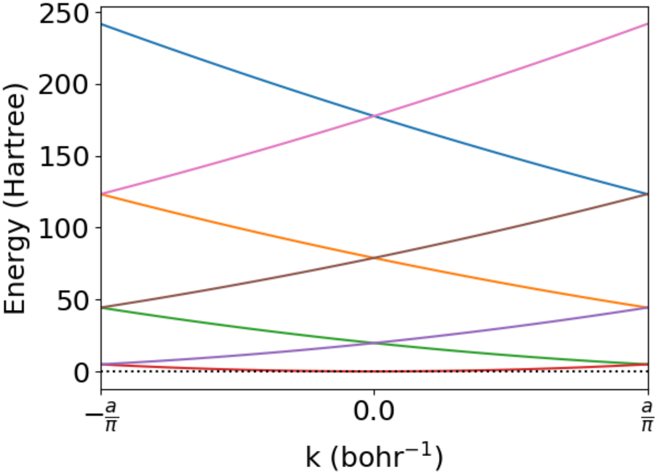
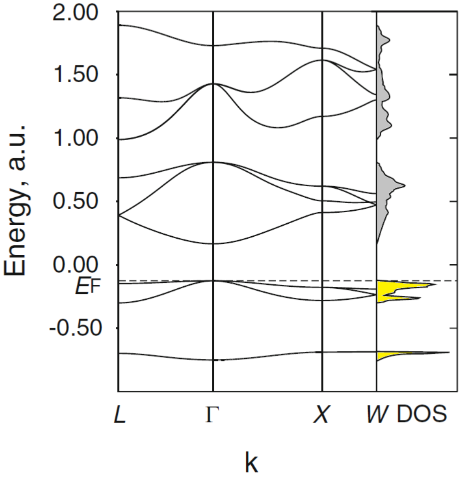


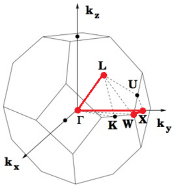
# Free electron gas

All unique information can be contained in the $1^{\text{st}}$ Brillouin zone.



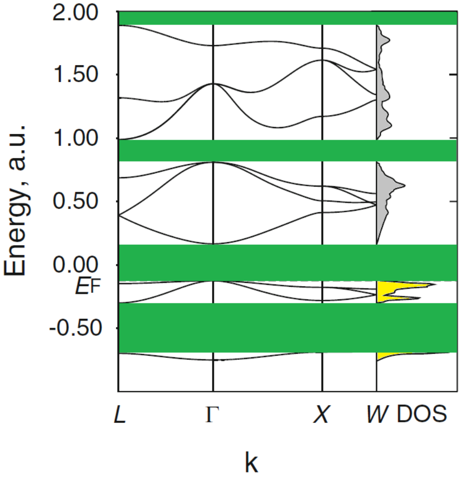
# Real example: MgO

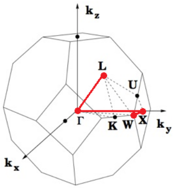




This is the LDA bandstructure of MgO.

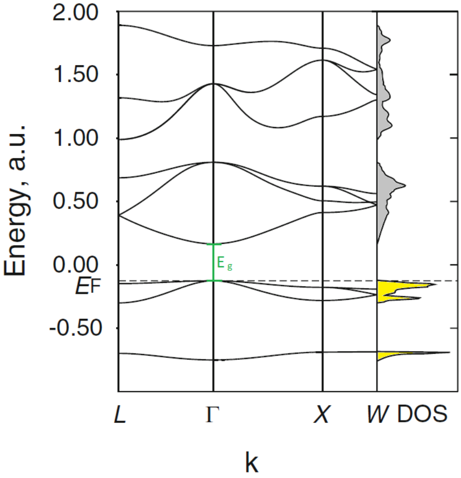
# Real example: MgO

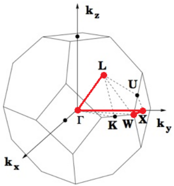




There are forbidden energy regions, called band gaps.

# Real example: MgO

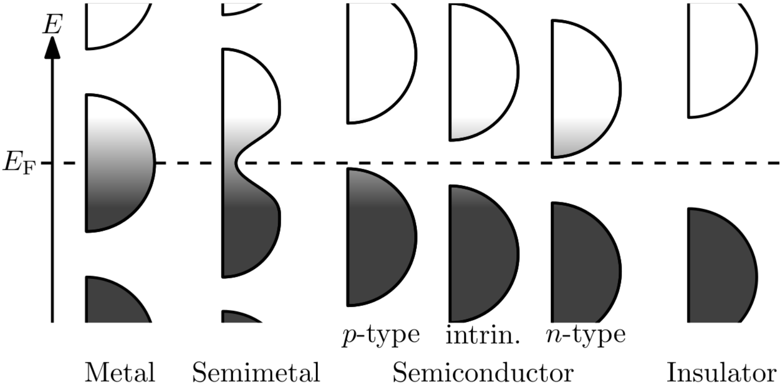




The most important parameter is the band gap.

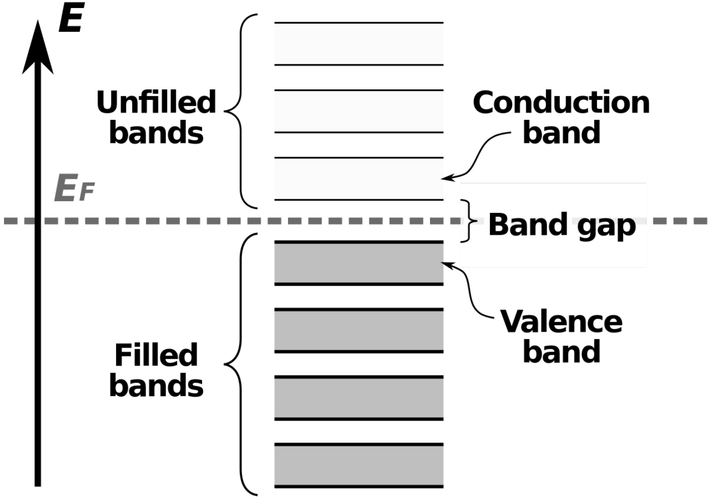
# The band gap

Size of the band gap tells us what kind of material we have.



# The bandstructure

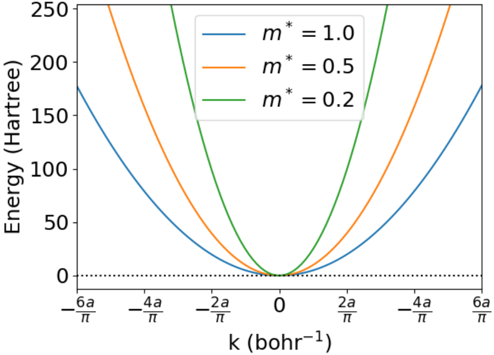
The conduction band and valance band are the most important.



# The bandstructure

The curvature of the conduction band and valance band is related to how easily charge can flow through them (i.e. how good a conductor the material is.)

$$E\left(\mathbf{r}\right) = \frac{\hbar^2 k^2}{2m^*} \tag{33}$$



# Effective mass

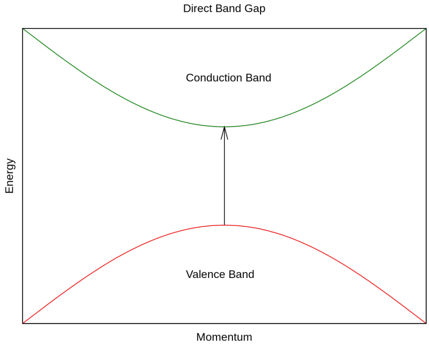
For semiconductors the effective mass is often lower than one.

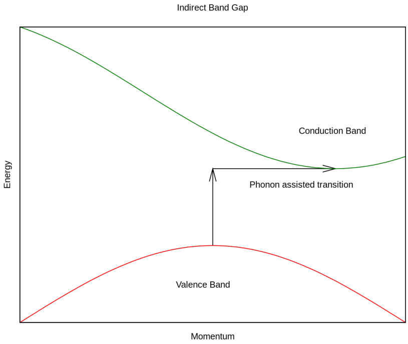
| $m^*$ | Ge | Si | GaAs |
|---|---|---|---|
| Electrons | $0.55\ m_e$ | $1.1\ m_e$ | $0.067\ m_e$ |
| Holes | $0.37\ m_e$ | $0.56\ m_e$ | $0.48\ m_e$ |

Easier to move electrons in a semiconductor with an electric field than in free space!

# Type of band gap

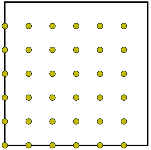
If the band gap is direct or indirect tells us about the interaction of the material with light.



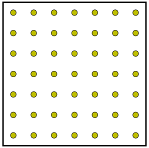


# **k**-point sampling

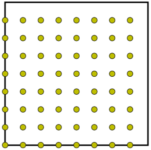
Rather than calculating the wavefunction ψ for every value of **k**, we just pick some **k**-points and average over them.



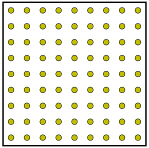
6×6×6



7×7×7



8×8×8



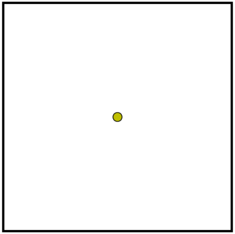
9×9×9

The simplest (and most common choice) is to uniformly sample the reciprocal Brillouin zone.

This is called Mohnhorst-Pack sampling.

# **k**-point sampling

The simplest thing we can do is to use only one **k**-point.

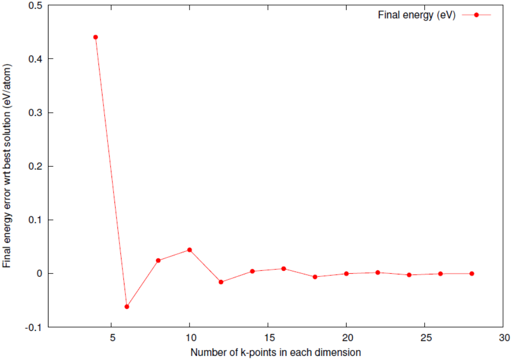


- As the reciprocal Brillouin zone is smaller the larger the unit cell is, this will only work for large unit cells.
- However, this makes calculations a lot cheaper because the wavefunction becomes real everywhere.
- A downside is that we don't know the bandstructure

This is called Γ-point sampling.

## **k**-point convergence

It is always important to check that enough k-points where used to calculate a good average.

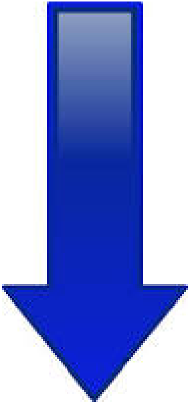


This is the energy dependence on **k**-point sampling for a unit cell of diamond.

## How many k-points?

As a (very) rough guideline

less



more

- $\sim 1$
  Low symmetry systems
  (atoms, molecules)
- $\sim 100$
  Semiconductors, insulators
- $\sim 1000$
  Metals

# Conclusions

- The solutions of the Schrödinger equation in a periodic potential (a crystal) are Bloch waves.
- These Bloch waves introduce **k**-point dependence and bandstructure for materials.
- Practical DFT calculations always need enough **k**-points to well reproduce the material being studied.