Bandstructures and Density of States

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Recap of Bloch's Theorem

Bloch's theorem: in a periodic potential, the density has the same periodicity. The possible wavefunctions are all 'quasi-periodic':

$$\psi_k(\mathbf{r}) \quad = \quad e^{i\mathbf{k}.\mathbf{r}} u_k(\mathbf{r}).$$

We write $u_k(\mathbf{r})$ in a plane-wave basis as:

$$u_k(\mathbf{r}) \quad = \quad \sum_G c_{Gk} e^{i\mathbf{G}.\mathbf{r}},$$

where $\mathbf{G}$ are the reciprocal lattice vectors, defined so that $\mathbf{G}.\mathbf{L} = 2\pi m$.

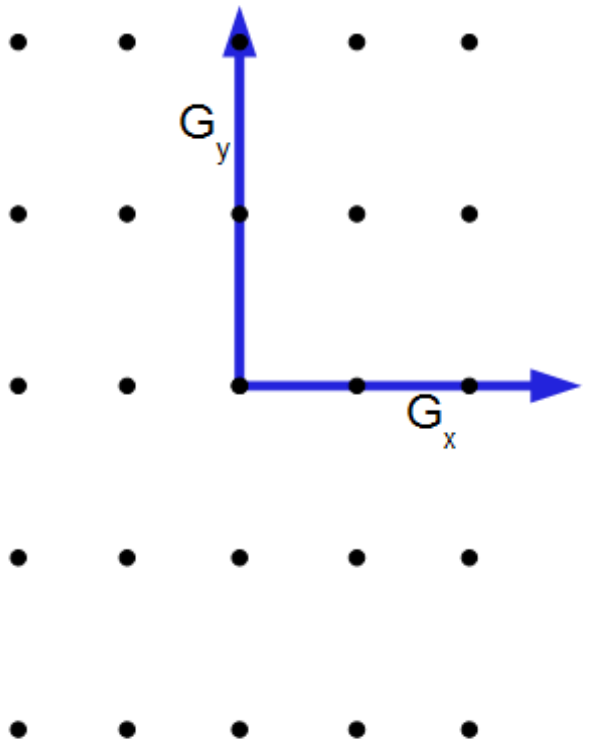
First Brillouin Zone

Adding or subtracting a reciprocal lattice vector **G** from **k** leaves the wavefunction unchanged – in other words our system is periodic in reciprocal-space too.

We only need to study the behaviour in the reciprocal-space unit cell, to know how it behaves everywhere. It is conventional to consider the unit cell surrounding the smallest vector, $\mathbf{G} = 0$ and this is called the first Brillouin zone.

First Brillouin Zone (2D)

The region of reciprocal space nearer to the origin than any other allowed wavevector is called the 1st Brillouin zone.



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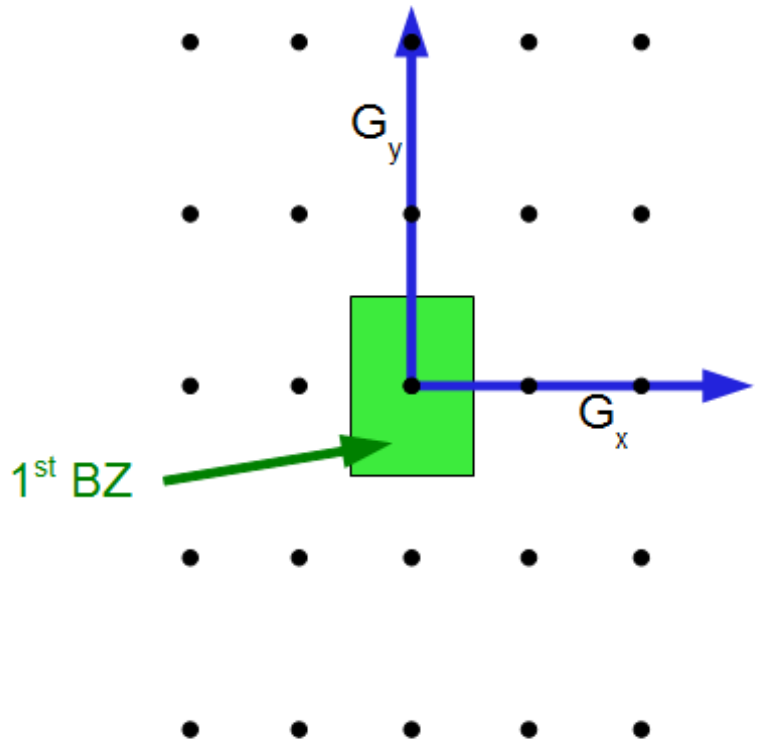


E versus **k**

How does the energy of states vary across the Brillouin zone? Let's consider one particular wavefunction:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u(\mathbf{r})$$

We'll look at two different limits – electrons with high potential energy, and electrons with high kinetic energy.

Very localised electrons

If an electron is trapped in a very strong potential, then we can neglect the kinetic energy and write:

$$\hat{H} = \hat{V}$$

The energy of our wavefunction is then

$$\begin{aligned} E(k) &= \int \psi^\star(\mathbf{r}) V(\mathbf{r}) \psi(\mathbf{r}) d^3\mathbf{r} \\ &= \int V(\mathbf{r}) |\psi(\mathbf{r})|^2 d^3\mathbf{r} \\ &= \int V(\mathbf{r}) |u(\mathbf{r})|^2 d^3\mathbf{r} \end{aligned}$$

It doesn't depend on $\mathbf{k}$ at all! We may as well do all calculations at $\mathbf{k} = 0$.

Free Electrons

For an electron moving freely in space there is no potential, so the Hamiltonian is just the kinetic energy operator:

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

The eigenstates of the Hamiltonian are just plane-waves – i.e. $c_{Gk} = 0$ except for one particular $\mathbf{G}$.

Our wavefunction is now

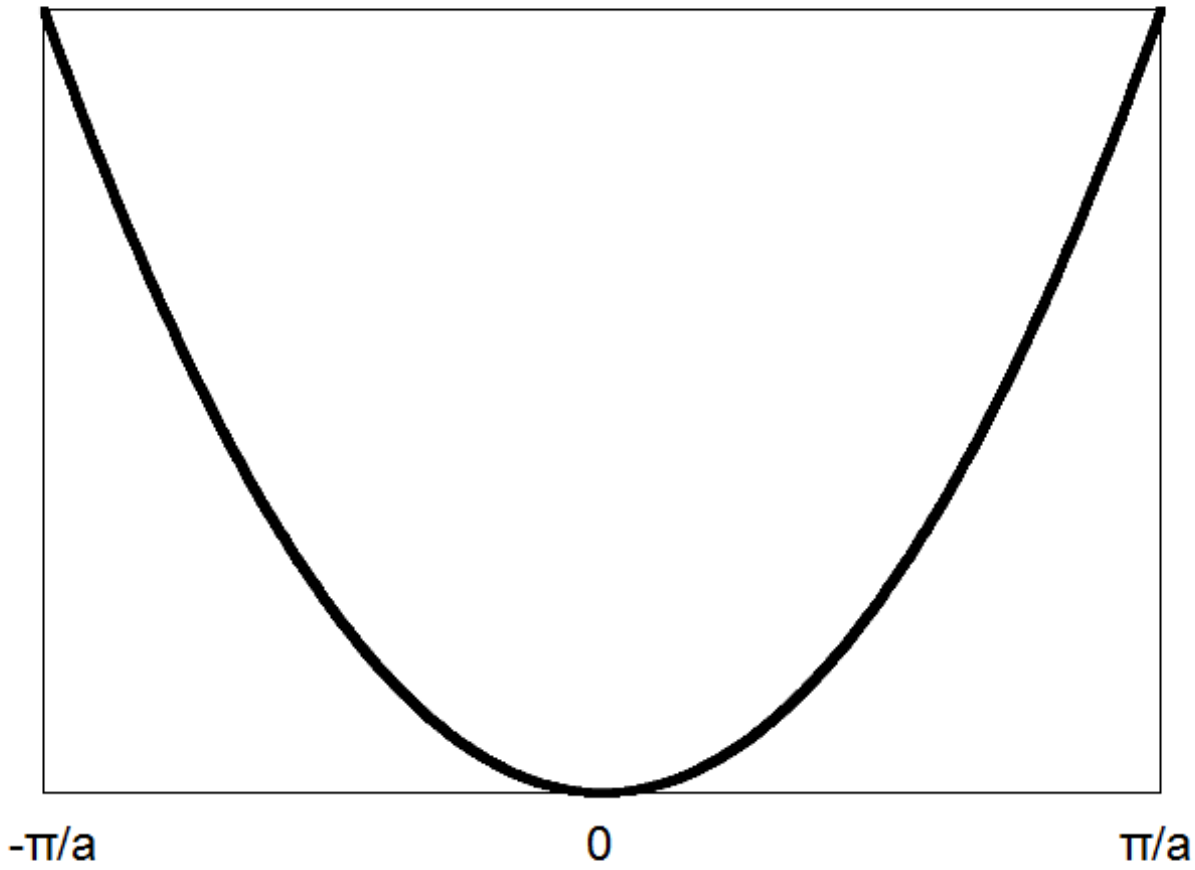
$$\begin{aligned} \psi(\mathbf{r}) &= c_G e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}} \\ \Rightarrow \nabla^2\psi(\mathbf{r}) &= -(\mathbf{k}+\mathbf{G})^2\psi(\mathbf{r}) \end{aligned}$$

Free Electrons

$$\begin{aligned} E(\mathbf{k}) &= -\frac{\hbar^2}{2m}\int \psi^\star(\mathbf{r})\nabla^2\psi(\mathbf{r})d^3\mathbf{r} \\ &= \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2\int \psi^\star(\mathbf{r})\psi(\mathbf{r})d^3\mathbf{r} \\ &= \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2 \end{aligned}$$

So $E(\mathbf{k})$ is quadratic in $\mathbf{k}$, with the lowest energy state $\mathbf{G} = 0$.

Free Electrons

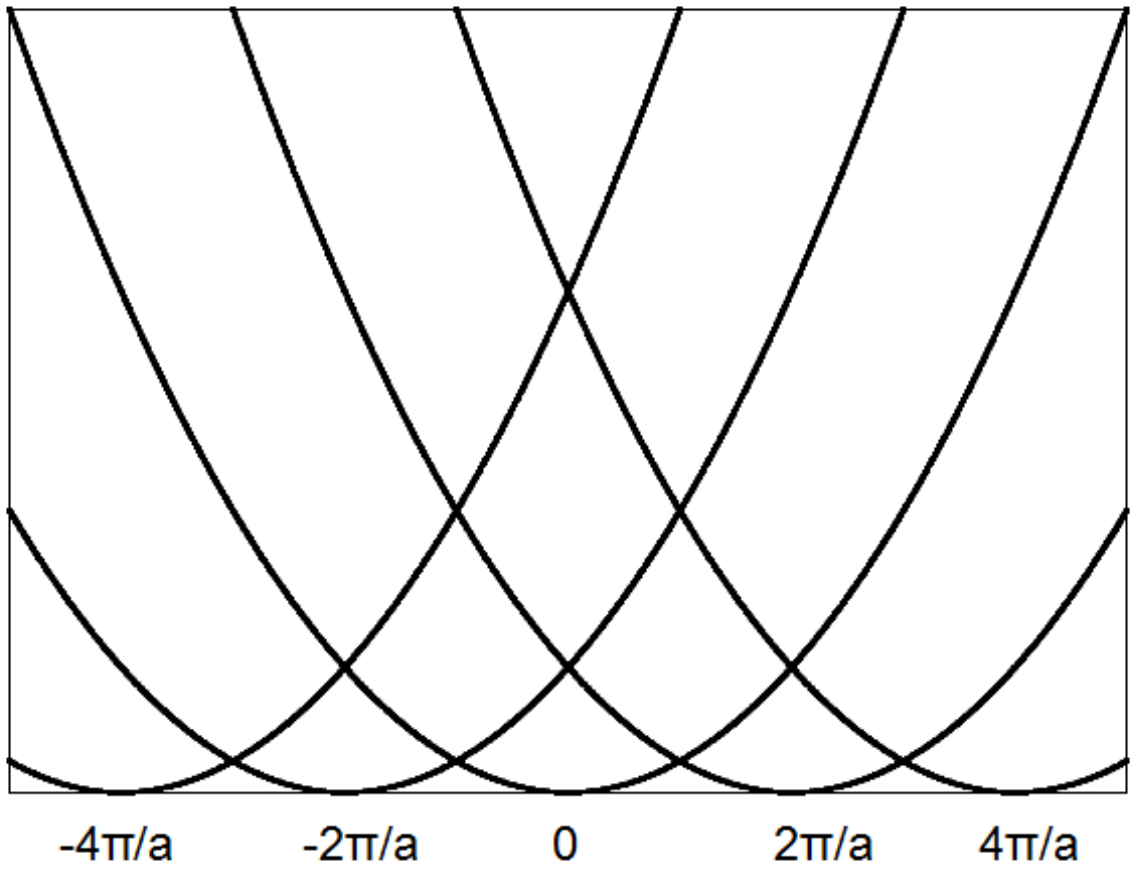


Free Electrons

Each state has an energy that changes with **k** – they form energy bands in reciprocal space.

Recall that the energies are periodic in reciprocal-space – there are parabolae centred on each of the reciprocal lattice points.

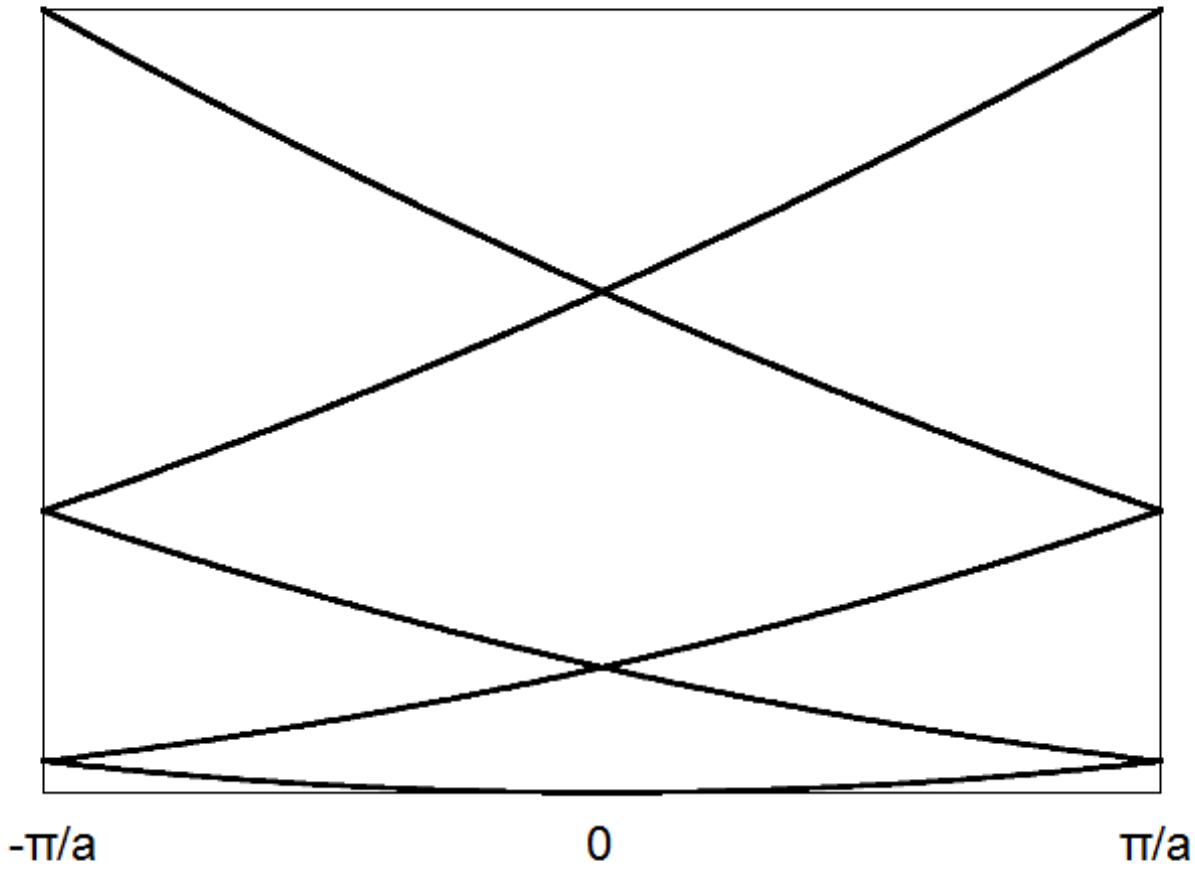
Free Electrons



Free Electrons

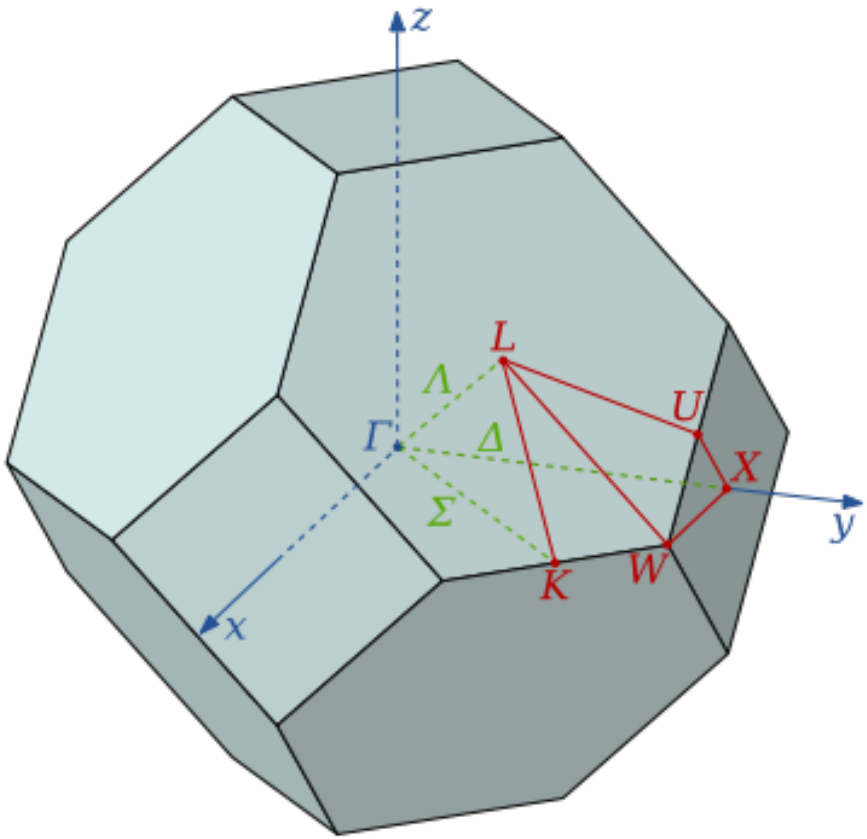
All of the information we need is actually in the first Brillouin zone, so it is conventional to concentrate on that.

Free Electrons



3D

In 3D things get complicated. In general the reciprocal lattice vectors do not form a simple cubic lattice, and the Brillouin zone can have all kinds of shapes.



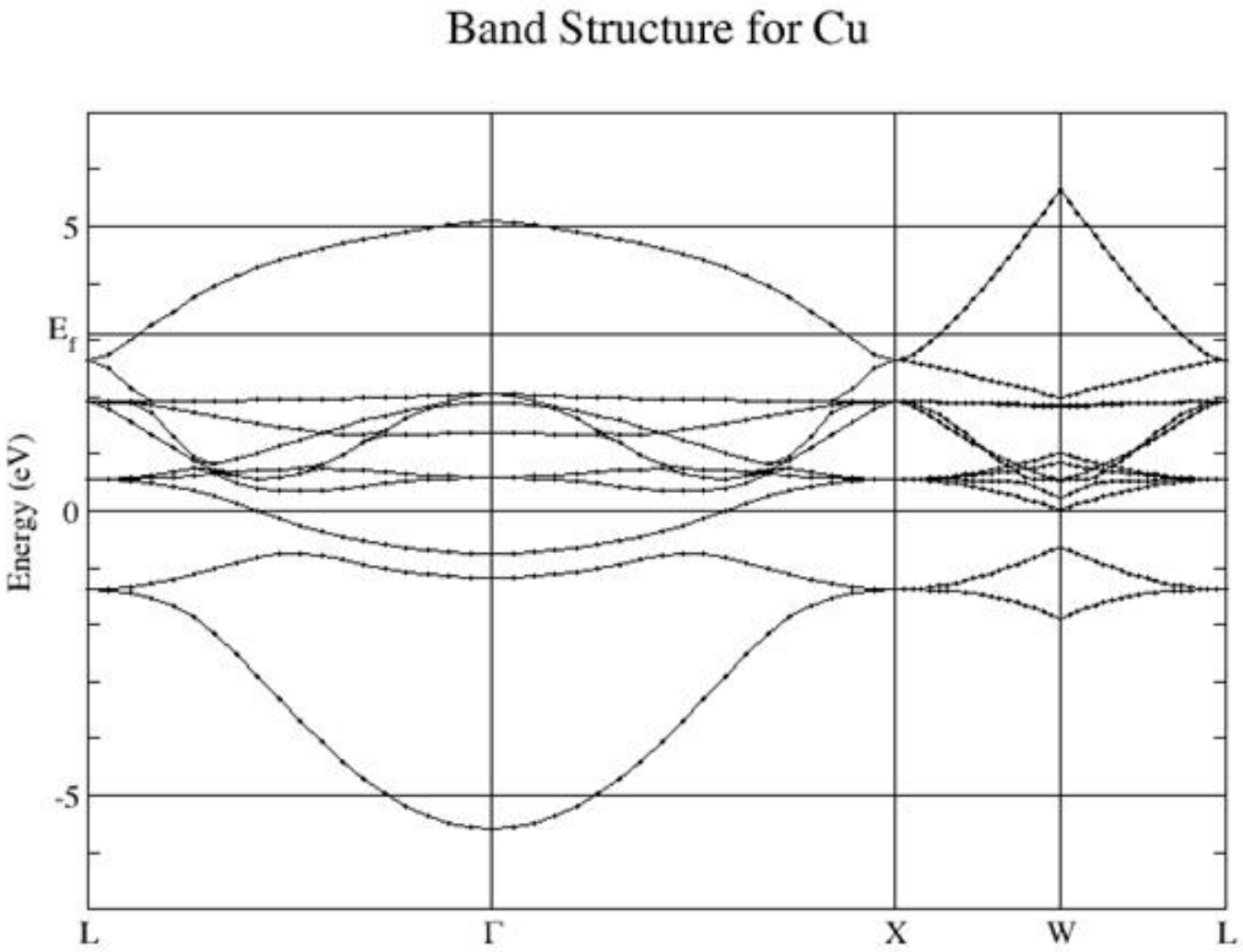
Band structure

The way the energies of all of the states changes with **k** is called the band structure.

Because **k** is a 3D vector, it is common just to plot the energies along special high-symmetry directions. The energies along these lines represent either maximum or minimum energies for the bands across the whole Brillouin zone.

Naturally, in real materials electrons are neither completely localised nor completely free, but you can still see those characteristics in genuine band structures.

Band structure

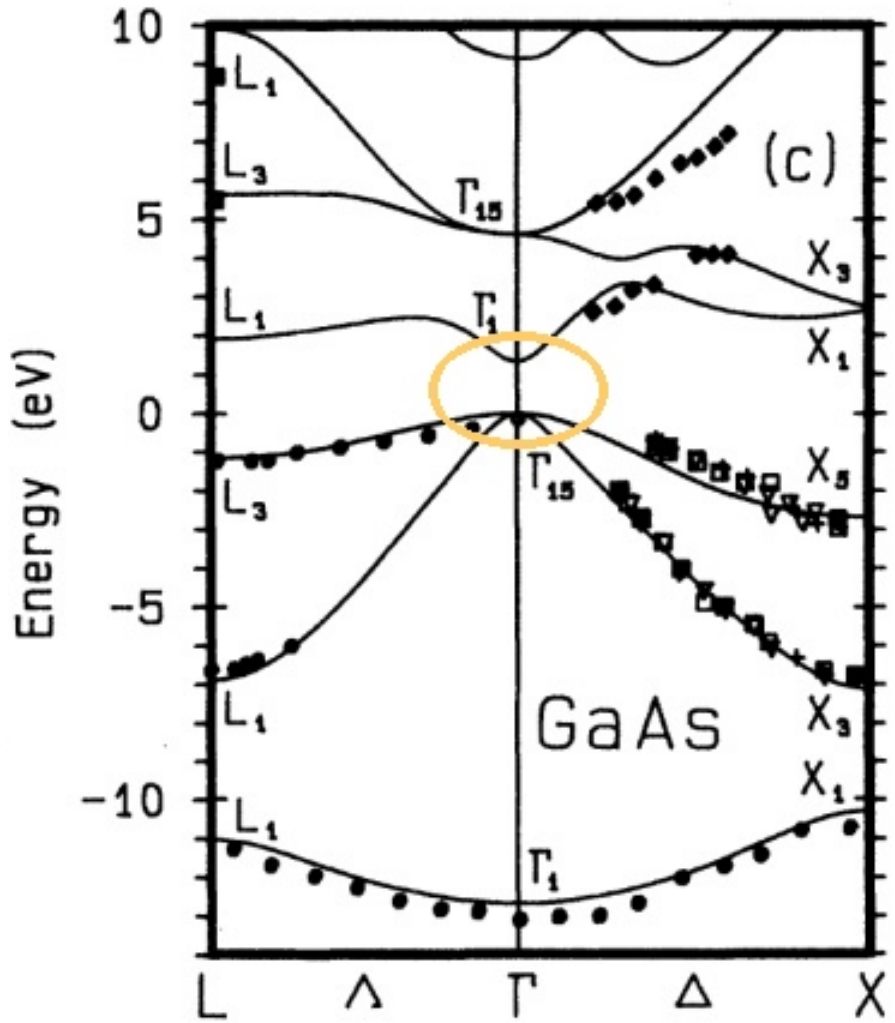


Transitions

Because the lowest N_e states are occupied by electrons, at 0K there is an energy below which all states are occupied, and above which all states are empty; this is the Fermi energy. Many band-structures are shifted so that the Fermi energy is at zero, but if not the Fermi energy will usually be marked clearly.

In semi-conductors and insulators there is a region of energy just above the Fermi energy which has no bands in it – this is called the band gap.

Band structure



Densities of States

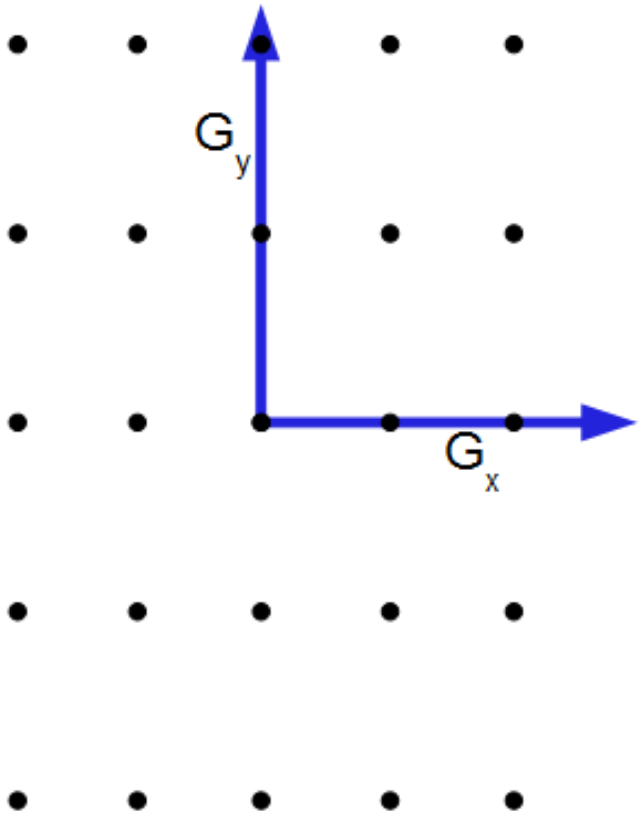
The band structure is a good way to visualise the wavevector-dependence of the energy states, the band-gap, and the possible electronic transitions.

The actual transition probability depends on how many states are available in both the initial and final energies. The band structure is not a reliable guide here, since it only tells you about the bands along high symmetry directions.

Densities of States

What we need is the full density of states across the whole Brillouin zone, not just the special directions. We have to sample the Brillouin zone evenly, just as we do for the calculation of the ground state.

Densities of States



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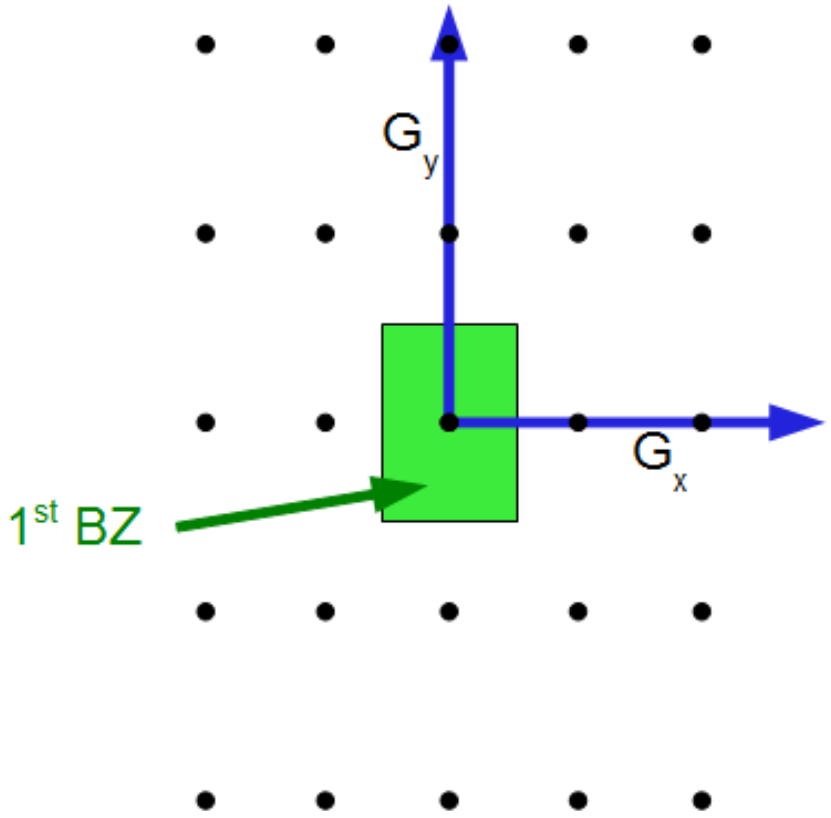

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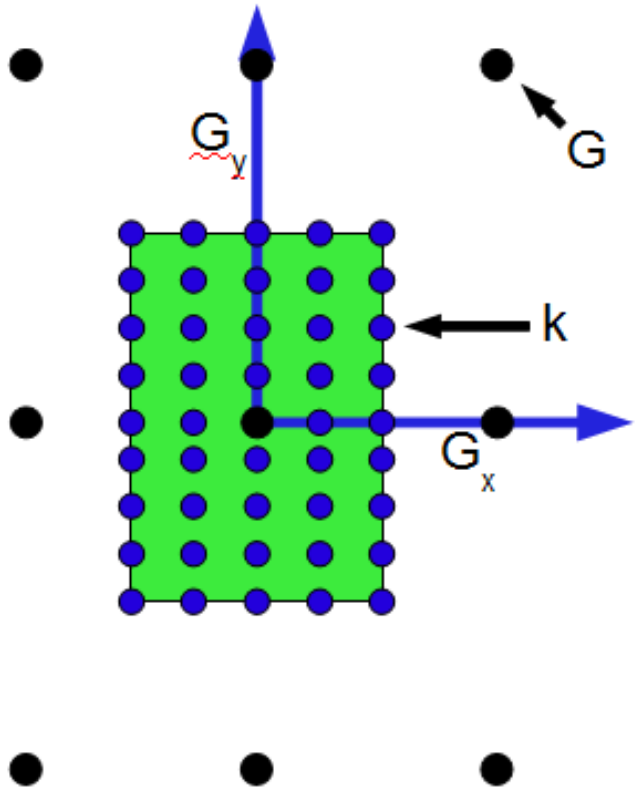
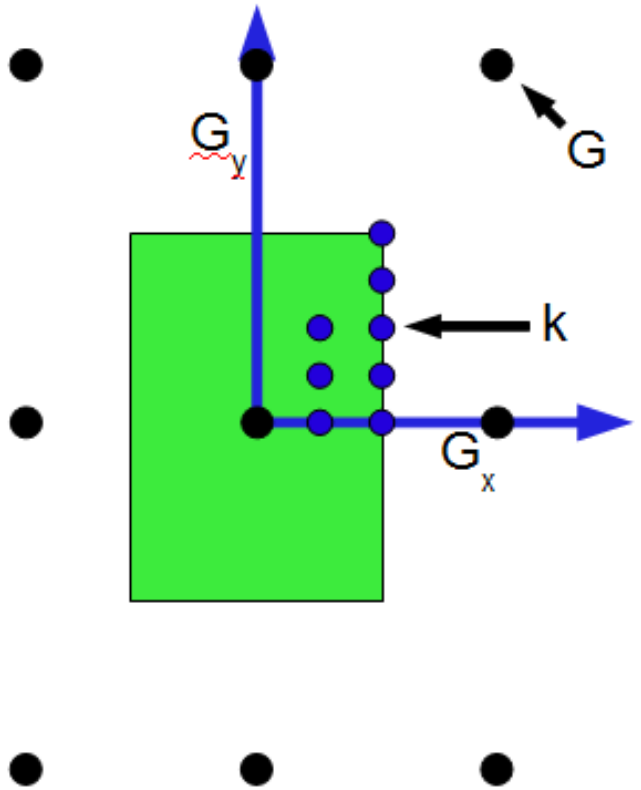


Densities of States

Often the crystal will have extra symmetries which reduce the number of **k**-point we have to sample at.

Once we've applied all of the relevant symmetries to reduce the **k**-points required, we are left with the *irreducible wedge*.

Densities of States



Computing band structures and DOS

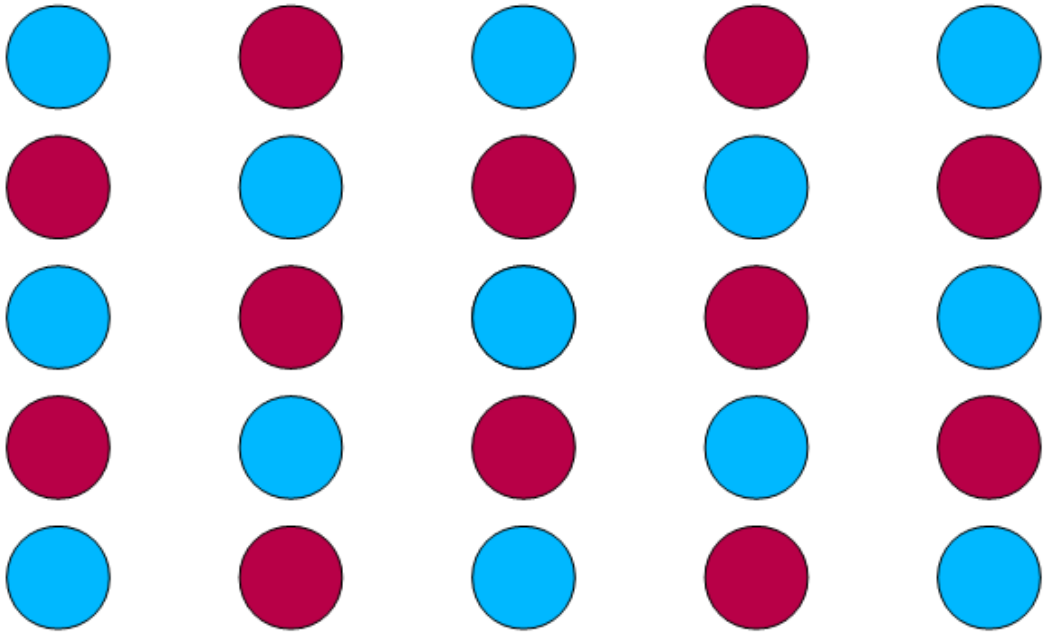
Computing a band structure or a DOS is straightforward:

- Compute the ground state density with a good **k**-point sampling
- Fix the density, and find the states at the band structure/DOS **k**-points

Because the density is fixed for the band structure/DOS calculation itself, it can be quite a lot quicker than the ground state calculation even though it may have more **k**-points.

Phonons

When a sound wave travels through a crystal, it creates a periodic distortion to the atoms.



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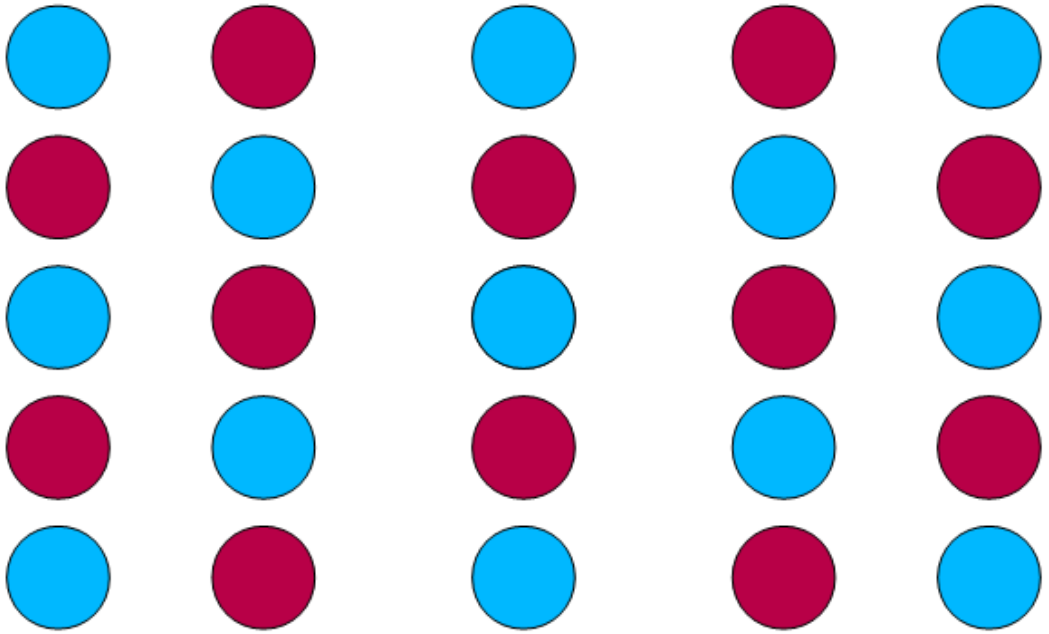

Phonons

The periodic distortion also has an associated wavevector, which we usually call **q**. This distortion is of the atomic positions so is real, rather than complex, and we can write it as:

$$d_q(\mathbf{r}) = a_q \cos(\mathbf{q}.\mathbf{r})$$

We can plot a *phonon* band structure, though we usually plot the frequency ω against **q** rather than E. This shows the frequency of different lattice vibrations, from the long-wavelength acoustic modes to the shorter optical ones.

Phonons

When a sound wave travels through a crystal, it creates a periodic distortion to the atoms.