

PX385: Condensed Matter Physics I

Warwick Physics Society

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0.1 Introduction, Credits and Notation

0.1.1 Credits

A big thank you to

- Chung, all chapters.
- Tenam, for magnetism and superconductivity.

0.1.2 How to use the guide

Anything in a white box with a blue title frame like

| |
|--|
| Title here |
| Content placed in these contains information or principles that must be remembered for the exams . This applies information placed in the same colour box, but without a title! |

Any equation which contains a regular, black box like $\boxed{\textit{this}}$ is important information but you shouldn't need to memorise it.

This guide is very detailed, almost like its own set of lecture notes. It aims to answer as many questions as possible regarding both the maths and the physics in this module. Any parts non-examinable will be explicitly marked non-examinable. Beware that this can change over the years if this guide isn't updated and therefore check with the lecturer.

0.1.3 Tips

- It is guaranteed that at least one thing from every chapter will be examined
- Know the 1D models for vibration (phonons) and for electrons and how to derive them
- Remember how to interpret the different figures, diagrams and graphs (there's quite a lot!) and understand their theoretical consequences/meaning. In the exams, they sometimes ask to draw something or ask you to read off the graphs!
- Know the main assumptions of the different theories: free electron, tight binding, BCS (this has been asked multiple times in past papers).
- There is a set of problems on the handouts, so do all of them! And the exams!

Chapter 1

Crystal Structures

This section is about what types of atoms and bonds make up crystals and how we classify them.

1.1 Making a solid

A many-particle quantum system obeys a many-particle time-independent Schrödinger equation (MP-TISE)

$$\hat{H}\Psi = E\Psi \quad (1.1)$$

where Ψ is the system wavefunction.

1.1.1 Bonding

We recap types of bonding and their properties, you may be familiar with these so feel free to skip to the next section.

Definition 1.1.1. Ionic bonding occurs when it is energetically favourable for an electron to be transferred from one atom to another.

Ionic solids are solids where all atoms partake in ionic bonding. The properties of ionic solids are

- Strong bonds: if you transfer electrons, one atom has a net + charge and the other has a net - charge. Therefore there is strong electrostatic attraction.
- High melting temperature. Energy is needed to break those electrostatic bonds.
- Brittle.
- Electrons generally held in place, so ionic solids are insulators.

Moreover, we will be considering different types of energies in order to analyse these solids.

Definition 1.1.2. The **ionisation energy** E_{ion} is the minimum energy needed to remove one electron.

Definition 1.1.3. The **electron affinity** E_{aff} is the energy *gain* from creating a negative ion.

Definition 1.1.4. The **cohesive energy** E_{ion} energy gain from adding positive and negative ions.

Definition 1.1.5. The **energy cost** $\Delta E = E_{\text{ion}} - E_{\text{aff}} - E_{\text{coh}}$

Moreover,

A bond is created if $\Delta E < 0$, i.e. it is energetically favourable to create one.

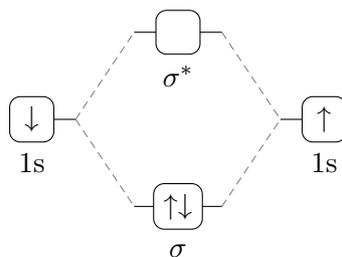


Figure 1.1: Bonding and anti-bonding splittings for a hydrogen molecule. The two 1s electrons enter a bonding orbital σ which is at lower energy (hence placed lower) compared to the individual orbitals.

Definition 1.1.6. A **covalent bond** is the sharing of valence electrons from atoms

I.e., there is some binding energy due to the shared electrons which keeps them in place. Note that a pair of atoms can have multiple covalent bonds. A single covalent bond is formed when one electron from one atom is shared with one electron from the other atom, so that each atom effectively ‘gains’ an electron. The goal of covalent bonding is to form a full valence shell which is the most stable.

- A hydrogen molecule $\text{H} - \text{H}$ has a single covalent bond since each hydrogen atom has a single $1s^1$ electron. They share them to form a covalent bond.
- A carbon double bond $\text{C} = \text{C}$, such as in alkenes or some acids. Each carbon shares 2 electrons from their $2p^2$. Note these carbons will usually also bond with something else to complete an outer shell.
- A nitrogen triple bond, in the naturally occurring N_2 denoted by $\text{N} \equiv \text{N}$ gas.

How a covalent bond works

Each electron can be thought of as in the potential well of each atom of width L .

Then if you bring the atoms, the potential well is larger and it’s now of width $2L$. Moreover, when 2 atoms covalently bond, different types of orbitals form. You don’t need to know anything about this in detail but the electrons enter a **bonding orbital** which is of *lower energy* compared to the electrons in the isolated atoms

Here are some properties of covalent materials

- non-ductile
- tends to form insulators or semiconductors

Definition 1.1.7. Metallic bonding is when the valence electrons are shared amongst all atoms.

Here,

- Electrons are **delocalised**. This results in good thermal and electrical conductivity.
- Bonds are non-directional, so are quite ductile.

Definition 1.1.8. van der Waals bonds are bonds created due to instantaneous electric dipoles on neighbouring atoms.

To see why this occurs, know that orbitals are places where electrons are allowed to go, but electrons are always moving around the nucleus, so at some points in time there will be places where there are slightly more electrons on one side of the atom than the other - this creates a net dipole moment across the atom, thus giving one side a “slight positive charge” and the other a slight negative charge. This induces dipoles in other nearby atoms.

Suppose atom one has dipole moment \mathbf{p}_1 and atom two has moment \mathbf{p}_2 . Atom two has $\mathbf{p}_2 = \chi \mathbf{E}$ where \mathbf{E} is the electric field due to atom one. where

$$\mathbf{E} = \frac{|\mathbf{p}_1|}{4\pi\epsilon_0 R^3}(-\hat{\mathbf{z}})$$

The potential energy

$$U = -\frac{|\mathbf{p}_1|^2 \chi}{(4\pi\epsilon_0 R^3)^3}$$

So the force is proportional to R^{-7} . It is tiny and attractive. On average, $\langle \mathbf{p}_1 \rangle = 0$ but $\langle |\mathbf{p}_1|^2 \rangle \neq 0$ where $\langle \cdot \rangle$ denotes the expectation value over position.

Definition 1.1.9. Hydrogen bonding is a special type of dipole-dipole attraction between molecules. It is when more electronegative atoms attract hydrogen atoms (including those atoms attached to bonds).

Definition 1.1.10. Mixed bonding is when there are covalent bonds *in* layers and van der Waal interactions *between* layers.

An example of mixed bonding is graphite. There are vdW interactions between the layers of carbon, but the individual carbons are covalently bonded to other carbons in the same layer.

1.2 Crystals

Definition 1.2.1. A **crystal** is a solid whose atoms are arranged in a regular, repeating pattern that extends over a large distance.

1.2.1 The Crystal Lattice

There will be 2 accepted definitions of a crystal lattice:

Definition 1.2.2. A **crystal lattice** is an infinite set of points defined by integer sums of a set of linearly independent **primitive lattice vectors** (PLVs).

or

Definition 1.2.3. a set of points where the environment of any given point is the same as that of any other point.

In 2D, we can move along 2 different axes. We can choose our PLVs to be those that are nearest neighbours, so that every lattice point is an integral linear combination of these PLVs. See Fig. 1.2. Note that PLVs are **not unique** (imagine scaling your axes by some factor of 2 or

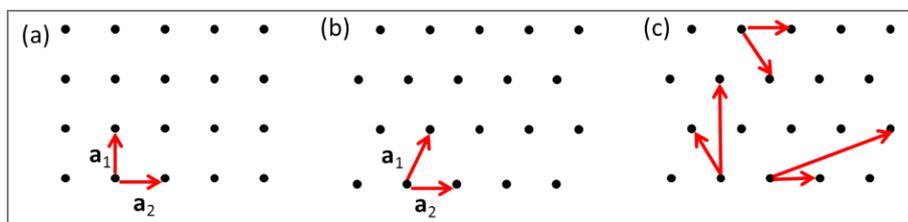


Figure 1.2: Lattice and choices of PLVs for (a) square lattice; (b), (c) triangular (or hexagonal) lattice. Reproduced from handout.

something).

1.2.2 Lattice and bases

Definition 1.2.4. A repeating pattern is called the **basis**

A periodic structure can be represented as a lattice of repeating patterns. This basis could be just an atom of a single element, or it could be more complicated things.

1.2.3 The Unit Cell

There are 3 accepted definitions

| Unit Cell |
|---|
| A region of space such that, when identical units are stacked together it completely fills all of space. OR A repeated motif which is the building block of the periodic structure. OR A primitive unit cell contains exactly one lattice point. |

Some examples are given in Fig. 1.3. If you can't see why *A* contains one lattice point, imagine

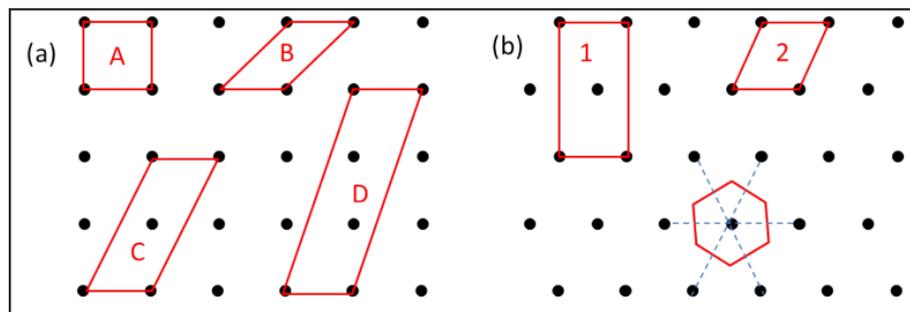


Figure 1.3: Unit cells for (a) square lattice and (b) triangular lattice.

that the edges go to the middle of each circle (point). Then a quarter of the circle faces *into* the unit cell. In general, for both 2D and 3D, try to visualise what faces *into* the cell. You should be able to deduce from definitions that *B* is also a primitive unit cell, but *C* and *D* in Fig. 1.3 are just primitive cells but not unit cells.

An important characterisation of the primitive unit cell is *how* do you get one? You get one by the **Wigner-Seitz method**

| Wigner-Seitz Method |
|--|
| This method will always construct a unit cell. <ol style="list-style-type: none"> 1. Start with a point. Draw lines to every nearest neighbour. 2. Take the perpendicular bisector of each line 3. Extend the perpendicular bisectors so that they intersect with each other. The shape formed by the intersection points is your unit cell, or Wigner-Seitz cell In 3D, instead of lines, you will use planes, and the unit cell will enclose a volume |

You won't be expected to draw any in the exam (probably), but understand that this method always produces a unit cell.

1.2.4 Lattices in 3D

There are 14 types of 3D lattices called the **Bravais lattices**. There are only 3 that you need to remember. You can see [this wikipedia page](#) for a table of all of them.

Definition 1.2.5. A **simple cubic lattice** (SC) (also called p-cubic, or primitive cubic) is a cube of side length a where each lattice point is shared between 8 lattice points. See Fig. 1.4a.

You should be able to visualise that each lattice point has $1/8$ th of it facing into the cube, therefore there is $8 \times 1/8 = 1$ lattice point. This therefore is also primitive. We can choose our

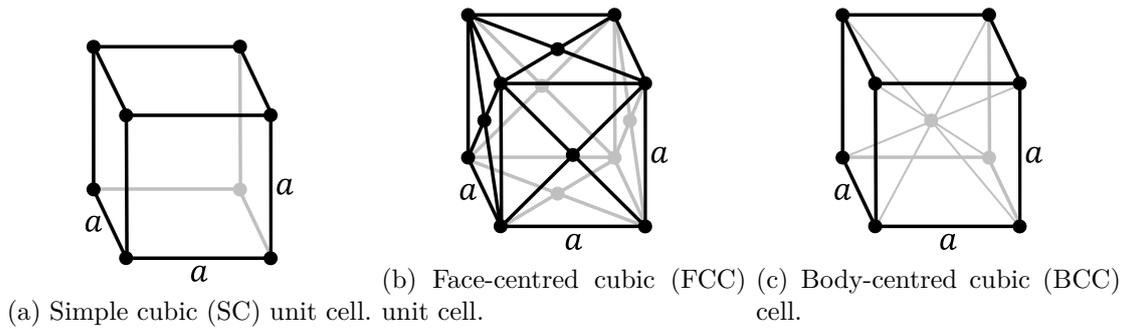


Figure 1.4: Graphical depiction of cubic unit cells. Source: [Wikipedia](#). If you are asked to draw any lattices, you only need to draw the points at their positions, the cube edge and label the distances to any points inside the cube.

PLVs are

$$\mathbf{a}_1 = (a, 0, 0) \quad \mathbf{a}_2 = (0, a, 0) \quad \mathbf{a}_3 = (0, 0, a) \quad (1.2)$$

An example of a SC is polonium.

Definition 1.2.6. A **body-centred cubic** (BCC, or cubic I) is a simple cubic with an additional point in the centre, as in Fig. 1.4c.

Since a SC had one lattice point in total, a BCC lattice has 2 lattice points. We note a few properties about BCC.

Definition 1.2.7. The **coordination number** z is the number of nearest neighbours.

Definition 1.2.8. The **atomic packing factor** is the percentage of space filled by spheres. We imagine the lattice points as hard spheres.

To find the packing factor:

Atomic Packing Factor

1. Place an atom on each lattice point
2. Assume atoms are spheres of radius R
3. Calculate percentage of space filled by atoms.

The atomic density of BCC for single **elements** is $2/a^3$.

Definition 1.2.9. A **face-centred cubic** (FCC, or cubic-F) is a simple cubic structure with points at the *centre* of each *face* as in Fig. 1.4b.

Copper and silver are examples of naturally occurring FCC elements.

- FCC is the **densest** packing for cubic lattices.
- $8 \times 1/8 + 6 \times 1/6 = 4$ lattice points in the primitive cell.
- The atomic density is $4/a^3$
- The coordination number $z = 12$.
- The PLVs are

$$\left[\frac{a}{2}, \frac{a}{2}, 0 \right], \left[\frac{a}{2}, 0, \frac{a}{2} \right], \left[0, \frac{a}{2}, \frac{a}{2} \right] \quad (1.3)$$

We've been talking about the atomic density. It's quite easy to find and has come up in previous exam papers.

Finding Atomic Density

1. Find the volume of the unit cell V_{cell} . For a cube it's a^3 for a cube with side lengths of a .
 2. Find the volume occupied by lattice points, V .
 3. Compute V/V_{cell} .
- If we have a 2D cell, of course the volumes become areas instead.

The atomic packing factor and atomic density are not exactly the same. The atomic density is the ratio of space occupied by atoms to total space available but the atomic packing fraction is the fraction of space occupied by atoms.

1.2.5 Visualising structures

So far, we've been drawing everything in a 3D projection from the side like in Fig. 1.4a, Fig. 1.4c and Fig. 1.4b. This is useful for intuition but the main issue is it doesn't tell us information about lattice points on every face (they are obscured so the pictures aren't so cluttered).

We now introduce our **plan view** where we now imagine we are above the cubes and looking directly down into it (its soul). Then what we can do is label the z coordinate of each atom (don't get confused with the coordination number) and progressively add to our plan view.

Let us consider the BCC structure. Start at $z = 0$. We just get the 4 base corners. We do not label points at $z = 0$ for convenience. This is demonstrated in Fig. 1.5. Now, the BCC has a point at $z = a/2$ in the middle of the square face. Therefore we add a point in the middle and label it as $a/2$, as in Fig. 1.5(b). Finally, we see the top layer at $z = a$ has the same 4 corner points in the plan view, so we just omit those labels as in Fig. 1.5(c).

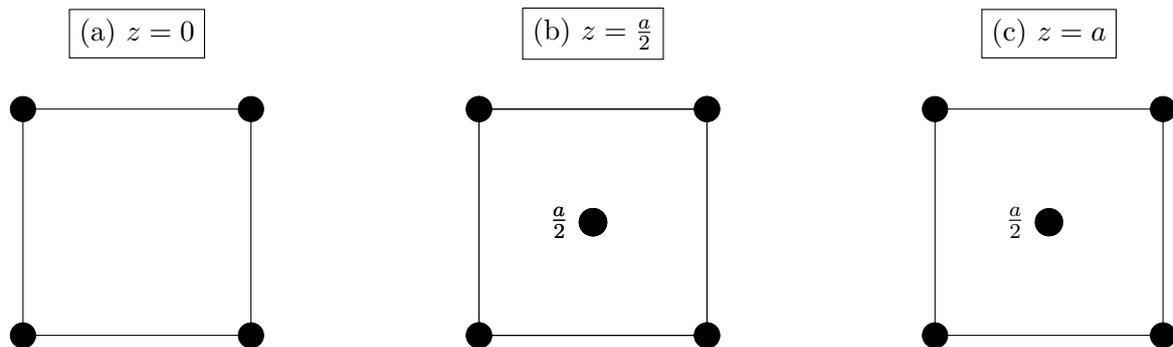


Figure 1.5: The plan view method for a BCC structure. (a) is at $z = 0$, when we just have the base 4 corners. Going up to $z = a/2$ which contains the next lattice point, we label it as in (b). (c) is the representation of the entire cube.

1.2.6 Real materials

You need to know how to identify the lattice and bases for real materials. We will consider 3 examples: sodium, CsCl and ZnS. In this subsection, we will remain in the plan view. Each of the materials in Fig. 1.6 have different bases and lattices. We will go through an algorithm to write down the bases and lattices

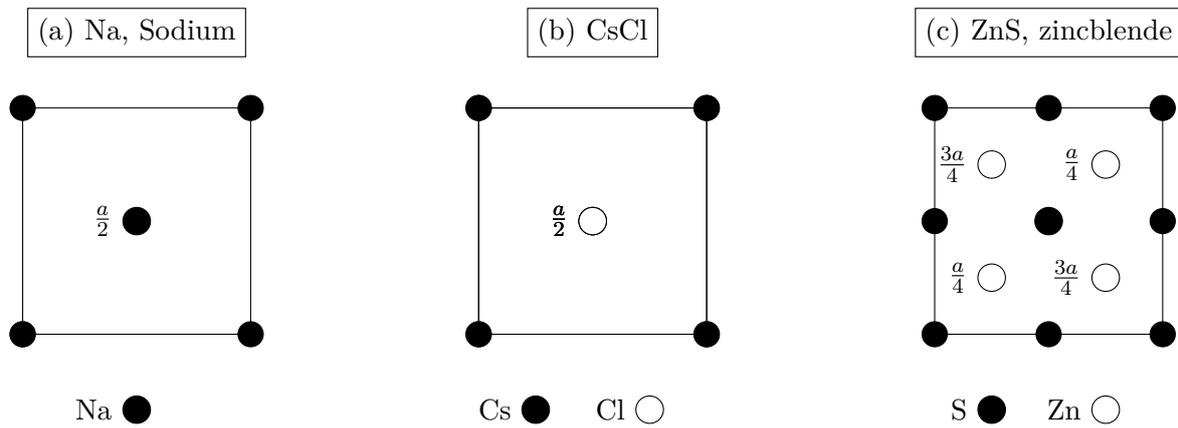


Figure 1.6: The plan view taken at $z = a$ for: (a) Sodium, BCC; (b) CsCl, simple cubic; (c) ZnS, FCC.

Determining the lattice and basis

1. Identify unique elements. Remember that different elements will correspond to different bases, even if they might have the same lattice if you were to keep drawing out cells.
2. Identify the lattice that corresponds to (one of) the atom type.
3. Identify the atom positions in the unit cell - this will be your basis. Note if every lattice point is the same atom, the basis is $[0, 0, 0]$

The basis is denoted in the form $[x, y, z]$ where, given a reference atom of the same type, it means at every integer multiples of the vector $[x, y, z]$, place an atom of that same type here (imagine continually drawing atoms).

We will now apply this algorithm to the examples in Fig. 1.6.

- For the sodium lattice, only sodium exists, therefore we can see that this is an FCC lattice. Since every lattice point is sodium, the basis is $[0, 0, 0]$ - this means repeat the sodium atom at every lattice point.
- For CsCl, we identify 2 atoms: Cs at the corners and Cl at the centre. Applying step 2, we see that Cs forms a **simple cubic** lattice. Now applying step 3, we have decided to focus on the Cs pattern, so our bases must be with respect to the Cs atoms. In the simple cubic lattice, we have a Cs atom at every lattice point, so the Cs basis is $[0, 0, 0]$. Now, we have Cl atoms at the centre of every Cs cell. We see that this is at a position $[a/2, a/2, a/2]$ from any Cs atom, therefore its basis is also $[a/2, a/2, a/2]$.
- This looks complicated but again, take it step-by-step. 1) We have 2 types: Zn and S atoms. 2) The S atoms form a FCC lattice. 3) We are now focused on the S atoms. Its basis is therefore $[0, 0, 0]$. Note the Zn atoms are always displaced by $[a/4, a/4, a/4]$ away from any S atom. Therefore its basis is also $[a/4, a/4, a/4]$.

Remark. We can also drop all factors of a from our diagrams and bases since it's just a constant. It's therefore also valid to write $[1/4, 1/4, 1/4]$ instead of $[a/4, a/4, a/4]$.

If you struggle with visualising this, draw out the cell in 3D, focus your attention on *one* atom of *one* type. Pretend atoms of other type don't exist, then find the lattice of your chosen atom type. Its basis is $[0, 0, 0]$ Now add all the other atoms back. From your chosen atom, find the displacement vector needed to reach it. Do this for at least one atom of every type. Since crystals are periodic, these displacement vectors will also be the basis for that atom type.

IMPORTANT. There is one further case. What if we replace the Zn and S atoms in Fig. 1.6(c)

with pure carbon. This is actually what diamond is! The question is now, what is the basis? Notice that none of the 3 cubic lattices we know fit with that cell. So, let's remove the carbons that replaced the Zn atoms - then we have an FCC lattice so carbon has a basis at $[0, 0, 0]$. Now add the remaining carbons back - these have a basis of $[1/4, 1/4, 1/4]$. Therefore to describe diamond, we need 2 different bases for the same atom type!

In summary, these are the different cases of lattice and basis that can happen

- Multiple types, each atom type has a basis
- Same atom type, only one basis (this will be $[0, 0, 0]$)
- Same atom type, multiple bases.

Probably the best tip that can be given is try to decompose your cell into some combination of the 3 patterns until you can find a pattern which you can easily identify with an atom type.

1.2.7 Directions, planes and Miller indices

Imagine you have your (cubic) system. Fix to a lattice point and place x, y, z axes down as in Fig. 1.7. Each direction (unit) vector can be written as $[1, 0, 0]$, $[0, 1, 0]$, $[0, 0, 1]$. Note the notation $[\bar{1}, 0, 0]$ means the direction $[1, 0, 0]$ in the **negative direction**.

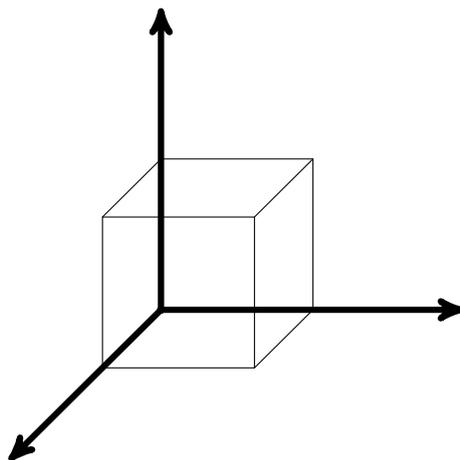


Figure 1.7: Cubic unit cell on 3D axes. We can draw vectors and planes on this.

If you are asked to draw vectors, remember to consider the bar notation and then draw them as vectors from the origin.

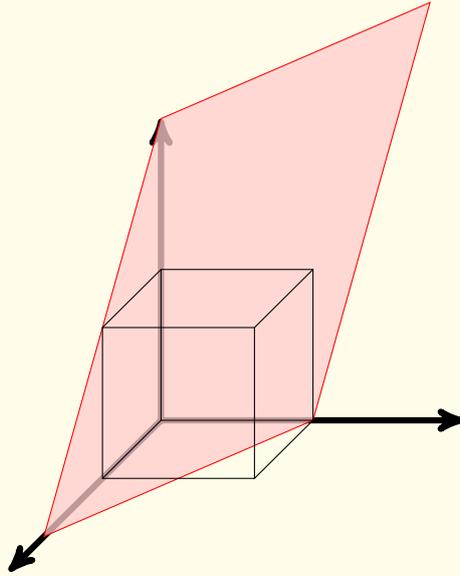
Also, vectors parallel to another vector are scalar multiples of it. Therefore when it comes to the notation $[x, y, z]$, if x, y, z have a common multiple, we can remove it. Namely,

$[x, y, z]$ should be reduced to the simplest set of integers

Now we have been talking about individual vectors, but we can also discuss planes. In particular, if we line up a plane with a face of the cube, we can note where it intersects each axis. Suppose for generality, instead of a unit cube, we have a unit cuboid with side lengths a, b, c (for the x, y, z directions respectively). Suppose the plane nearest the origin, (but not going through the origin) intersects the axes of the unit cell at $a/h, b/k, c/l$ where $h, k, l \in \mathbb{Z}$, then the family of parallel planes is referred to by its **Miller indices** which are denoted by (h, k, l) .

So what this allows us to do is to characterise different slices of our unit cell, where our slice is the plane we decide to use to cut through our unit cell. We will go through some examples

EXAMPLE 1.



Q: Find the Miller indices of the above plane where the plane intersects at $x = 2a, y = a, z = 2a$.

A: We suppose that $2a = a/h \implies h = \frac{1}{2}$. Similarly for y, z , we find $k = 1, l = 1/2$. So the Miller indices should be $(1/2, 1, 1/2)$. However, recall that Miller indices are integers, so multiply by the lowest common multiple to get $(1, 2, 1)$.

It is important to note that since Miller indices are written in the form of most reduced integers, any **parallel planes** correspond to the same Miller index. Because of this, there is a useful formula that gets the spacing between any parallel plane:

Parallel plane spacing

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}} \quad (1.4)$$

assuming you have a set of orthogonal axes and a unit cuboid with side lengths a, b, c respectively.

1.2.8 Defects

Not all real crystals form a perfect structure at room temperature. There may be defects, such as point defects, dislocations, or grain boundaries. Point defects include vacancies, where an atom is missing from a lattice point, and impurities, where a different atom sits at a lattice point. These will distort the structure. We will state different types of defects

Definition 1.2.10. An **ideal crystal** is the state of minimum energy of identical particles at $T = 0\text{K}$.

Point defects

- **Schottky defect** - vacancy - one atom missing from a lattice site which **distorts** the lattice.

It takes energy E_V to create a vacancy (energy must be put in to excite atom away). At temperature T , expect the number of vacancies $n = Ne^{-E_V/k_B T}$ where N is the number

of atoms in the crystal.

- **Frenkel defect** - vacancy plus interstitial atom (one that's not on a lattice point). Distorts the lattice. Needs $5 \sim 10\times$ more energy than a vacancy.
- **Impurities** - different material on the surface. Distorts the lattice.
- **Colour centre** - irradiate a crystal with photons. This causes a colour change due to lattice damage. For example, when welding some metals, you can get pretty blue and red hues.

Dislocations

- Edge dislocations - see Fig. 1.8(a)
- Screw dislocations - see Fig. 1.8(b)

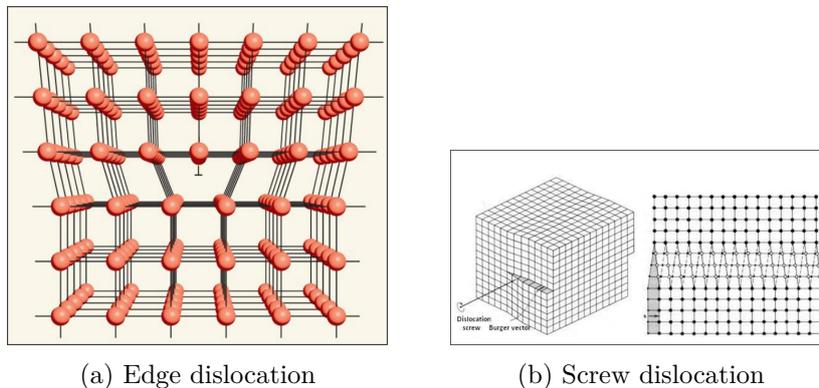


Figure 1.8: Examples of dislocations. (a) is an edge dislocation, where cell edges are distorted from their normal position. (b) is screw dislocation where we have atoms are pushed in opposite directions away from each other.

Grain boundaries

Most real materials are made up of smaller crystals joined together. However, the boundaries of these may not line up perfectly. These form grain boundaries.

1.2.9 Reciprocal lattice and Brillouin zones

Physicists generally want to work in a system that's easier to do maths with. If you think about the size of a unit cell, these will be in the order of $10^{-7} \sim 10^{-9}\text{m}$. Moreover, when doing experiments like diffraction, we usually observe interference patterns and cast them in terms of wavevectors, not the actual distance. In solid state physics, there is an equivalent notion where instead of considering a real lattice, we consider the **reciprocal lattice**.

Definition 1.2.11. The **reciprocal lattice** is itself a lattice where the spacing between points are integer multiples of $2\pi/a$, if the real lattice had a spacing of a .

In 3D, if you had multiple spacings a, b, c in x, y, z respectively, your reciprocal lattice space will have $2\pi/a, 2\pi/b, 2\pi/c$ respectively. Note that $2\pi/a$ is the **wavenumber** in the x direction which we denote k_x . The same definition goes for k_y, k_z . Now, hopefully you start to see the connection between the reciprocal lattice and diffraction!

Equivalent to the PLVs in Definition 1.2.2, we have

Definition 1.2.12. The **reciprocal lattice vectors** (RLVs) are the primitive lattice vectors in reciprocal space.

The RLVs are denoted \mathbf{b}_i and the general vector as $G\mathbf{G}_{hkl}$ so that

$$\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \quad (1.5)$$

We will return to talking about these in later sections, but hopefully this rings a bell.

Now, if we have a reciprocal lattice, can we have a ‘reciprocal unit cell’? the answer is yes, and it is called a **Brillouin zone** (BZ). Since our units are effectively wavevectors, the Brillouin zone is talked about in wavenumbers - in particular every Brillouin zone is of length $2\pi/a$ (and $2\pi/b, 2\pi/c$ in the other directions).

In particular, the **first Brillouin zone** is in the interval $[-\frac{\pi}{a}, \frac{\pi}{a}]$. The second BZ is in the interval $[-\frac{2\pi}{a}, -\frac{\pi}{a}] \cup [\frac{\pi}{a}, \frac{2\pi}{a}]$ etc. In 3D, you’d talk about these as the unions of volumes in each axis.

1.3 Crystal Dynamics

We now move onto oscillating atoms. Generally speaking, between 2 nearest neighbours, the potential follows a **Lennard-Jones potential** as seen in Fig. 1.9. In order to conduct further analysis, we will do a Taylor expansion around x_{eq} for small Δx . We note that $|x_{\text{eq}} - x_{\text{min}}| \sim |x_{\text{eq}} - x_{\text{max}}| \approx k_B T$.

$$V_{\text{eff}}(x) = V(x_{\text{eq}}) + \frac{1}{2}k(x - x_{\text{eq}})^2 + k_3(x - x_{\text{eq}})^3 + \dots \quad (1.6)$$

Going to second order, we now model our oscillating atoms like masses on a spring.

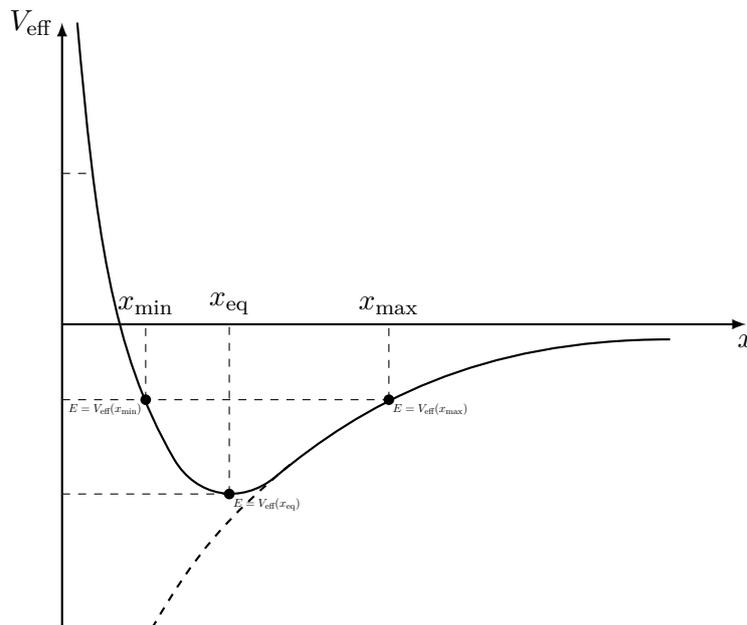


Figure 1.9: Effective potential of nearest neighbour atoms. The atoms oscillate between x_{min} and x_{max} with their equilibrium position being x_{eq} .

1.3.1 Vibration on a 1D chain

Our system looks like this We define $x_n^{\text{eq}} = na$ where a is the chain length at equilibrium. It is the equilibrium position of the n^{th} atom. The potential is then dependent on the extension:

$$V_{\text{tot}} = \sum_i V_{\text{eff}}(x_{i+1} - x_i) = \frac{1}{2}k \sum_i (\delta x_{i+1} - \delta x_i)^2 \quad (1.7)$$

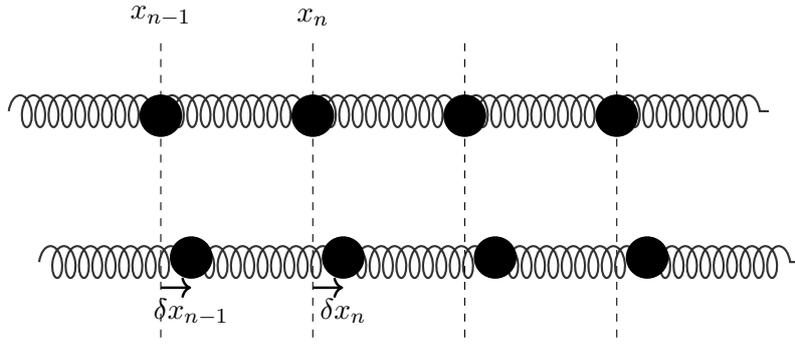


Figure 1.10: 1D chain of atoms modelled as a harmonic oscillator in series. The top set of atoms is at the equilibrium position, and the bottom set is the system at a slightly later time δt when they have been allowed to move.

We now want to find the force on the n^{th} atom. We do this not by differentiating with respect to the position x_n , but rather differentiate with respect to the *extension* δx_n . Doing this gets

$$F_n = -\frac{\partial V_{\text{tot}}}{\partial(\delta x_n)} \quad (1.8)$$

$$= -\frac{1}{2}k \frac{\partial}{\partial(\delta x_n)} [(\delta x_{n+1} - \delta x_n)^2 + (\delta x_n - \delta x_{n-1})^2] \quad (1.9)$$

$$= \frac{-1}{2}k [-2(\delta x_{n+1} - \delta x_n) + 2(\delta x_n - \delta x_{n-1})] \quad (1.10)$$

$$= k[\delta x_{n+1} - 2\delta x_n + \delta x_{n-1}] \quad (1.11)$$

$$\implies F_n = m\delta\ddot{x}_n \quad (1.12)$$

where to differentiate in the second line is a partial derivative, so all terms not including δx_n goes to 0. What we have is a second-order linear ODE in time. We propose a trial solution

$$\delta x_n = A \exp[i(kx_n^{\text{eq}} - \omega t)] = A \exp[i(kna - \omega t)] \quad (1.13)$$

i.e., we are treating our oscillations as if there was a wave propagating through the atoms, which is disturbing them. We now substitute this into our ODE:

$$\begin{aligned} m\delta\ddot{x}_n &= -m\omega^2 A e^{i(kna - \omega t)} \\ &= kA e^{-i\omega t} [e^{ik(n+1)a} - 2e^{ikna} + e^{ik(n-1)a}] \\ &= kA e^{i(kna - \omega t)} [e^{ika} - 2 + e^{-ika}] \end{aligned} \quad (1.14)$$

Therefore, we can find an expression for ω :

$$\begin{aligned} m\omega^2 &= k \left[2 - (e^{ika} + e^{-ika}) \right] \\ &= 2k[1 - \cos(ka)] \\ &= 4k \sin^2 \left(\frac{ka}{2} \right) \end{aligned} \quad (1.15)$$

From this, we deduce

$$\boxed{\omega = 2\sqrt{\frac{k}{m}} \left| \sin \left(\frac{ka}{2} \right) \right|} \quad (1.16)$$

This is the **1D chain dispersion relation**. It relates ω , k and is periodic every $2\pi/a$.

The dispersion relation in Eq. (1.16) tells us a bunch of things

- Periodic in k

- A system which is periodic in real space with period a will be periodic in reciprocal space with period $2\pi/a$.
- A periodic unit in reciprocal space is a BZ. This is as we saw in Section 1.2.9.

Moreover,

$$e^{iG_p x_n} = e^{i\frac{2\pi p}{a} n a} = e^{i2\pi p n} = 1 \quad (1.17)$$

Remark. In this expression, we removed the boldfont since we are still working in 1D. If this was a 3D lattice space, we should have $\mathbf{G}_{hkl} \cdot \mathbf{x}_n$.

At small k , i.e. large λ

$$\begin{aligned} \omega &= 2\sqrt{\frac{k}{m}} \left| \sin\left(\frac{ka}{2}\right) \right| \simeq 2\sqrt{\frac{K}{m}} \left| \frac{ka}{2} \right| \simeq \sqrt{\frac{k}{m}} a |k| \\ v &= \frac{\omega}{k} \text{ is the same as } v_g = \frac{d\omega}{dk} \Rightarrow \text{elastic wave.} \end{aligned} \quad (1.18)$$

1.3.2 Phonons

Definition 1.3.1. A **phonon** is an excitation of quantised modes of vibration

Much like how the photon is a quantum of *radiation*, the phonon is the quantum for *vibration*.

We know $p = \hbar k$ for each phonon which means these aren't localised particles. We class $\hbar k$ as the **crystal momentum** here rather than just momentum as we know by periodicity k and $k + 2\pi/a$ are equivalent. We therefore have the crystal momentum to be well-defined in the 1st BZ.

1.3.3 Vibrations in a Diatomic molecule

Suppose now we have 2 types of atoms on our 1D chain. Our system now looks like Fig 1.11. For simplicity, set $m_1 = m_2 = m$. Suppose there are distinct constants k_1, k_2 . We will skip the

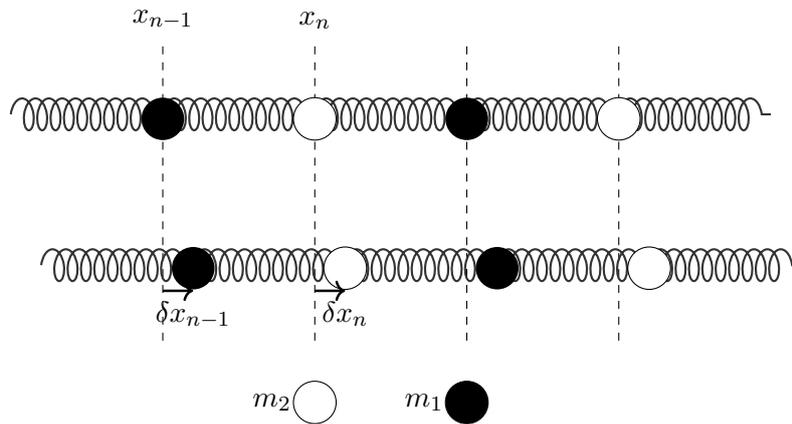
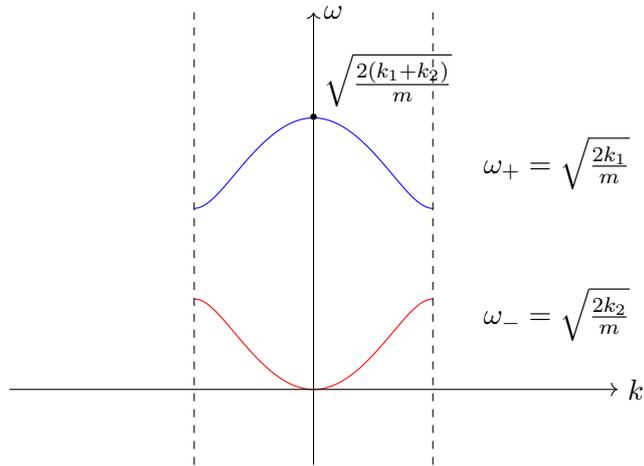


Figure 1.11: 1D chain of 2 atom types modelled as a harmonic oscillator in series. The top set of atoms is at the equilibrium position, and the bottom set is the system at a slightly later time δt when they have been allowed to move.

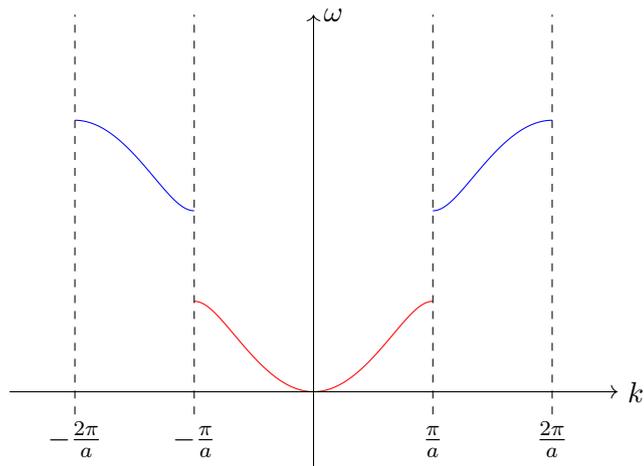
maths (see Appendix A). and we get

$$\omega^2 = \frac{k_1 + k_2}{m} \pm \frac{1}{m} \sqrt{(k_1 + k_2)^2 - 4k_1 k_2 \sin^2\left(\frac{ka}{2}\right)} \quad (1.19)$$

For each k , there are 2 solutions for ω . If we plot these in the first BZ we get Figure 1.12 displays 2 branches termed the acoustic and optical modes, for good reason.



(a) Reduced Zone Scheme.



Second BZ First BZ Second BZ

(b) Extended Zone Scheme.

Figure 1.12: Bandstructure for a diatomic molecule modelled as a harmonic oscillator. The graph in red is the negative solution of Eq. (1.19), termed the **acoustic mode** and the graph in blue is the **optical mode** and corresponds to the positive root. (a) Bandstructure in **reduced zone scheme**. (b) Bandstructure in **extended zone scheme**.

- Optical phonons are out-of-phase movements of the atoms in the lattice, one atom moving to the left, and its neighbour to the right. They are called optical because fluctuations in displacement create an electrical polarization that couples to the electromagnetic field. Hence, they can be excited by infrared radiation. Moreover there are both longitudinal and transverse optical modes, which you can visualise better with a 3D lattice like sodium chloride.
- Acoustic phonons are coherent movements of atoms of the lattice out of their equilibrium positions, so some atoms are closer together whilst others are farther apart, like a sound wave propagating through air.

$$\begin{aligned}\omega_-^2 &\simeq \frac{k_1 + k_2}{m} - \frac{1}{m} \sqrt{(k_1 + k_2)^2 - 4k_1k_2 \left(\frac{ka}{2}\right)^2} \\ &\simeq \frac{k_1 + k_2}{m} - \frac{k_1 + k_2}{m} \sqrt{1 - \frac{k_1k_2(ka)^2}{(k_1 + k_2)^2}}\end{aligned}$$

Remember, for small x , $\sqrt{1-x} \simeq 1 - x/2$ so

$$\omega_-^2 \simeq \frac{k_1 + k_2}{m} - \frac{k_1 + k_2}{m} \left(1 - \frac{k_1k_2(ka)^2}{2(k_1 + k_2)^2}\right) \quad (1.20)$$

$$\simeq \frac{k_1k_2(ka)^2}{2m(k_1 + k_2)} \quad (1.21)$$

$$\implies \omega_- \propto k \quad (1.22)$$

In general,

- In 1D, n atoms in a primitive unit cell, n modes for each value of k . We get 1 acoustic mode and $n - 1$ optical modes.
- In d -dimensions, n atoms in a primitive unit cell, nd modes for each value of k . We get d acoustic modes and $d(n - 1)$ optical modes.

Again imagine a 3D lattice of atoms, e.g sodium chloride. The acoustic mode corresponds to in phase oscillations. There are 2 optical modes. One of them is transverse: take one of the layers and oscillate it in one direction. Then take another layer, and make it oscillate perpendicular to the first layer, out of phase - this is the transverse optical mode. The second optical mode is to make the second layer oscillate directly in the opposite direction out of phase - this is the longitudinal optical mode.

We can represent Fig. 1.12a in a different way. It is currently in the **reduced zone scheme** where we draw all modes as contained within $[-\frac{\pi}{a}, \frac{\pi}{a}]$. However what we can do is ‘unfold’ the optical mode and draw it only in the second BZ, as in Fig. 1.12b.

1.4 Brillouin Zones and Scattering

We now aim to concretely make the connection between the stuff in Section 1.2.9.

- Real space lattice points are defined by $\mathbf{R} = \sum_{i=1}^3 n_i \mathbf{a}_i$ where \mathbf{a}_i are PLVs in 3D. Note you can replace the 3 in the sum by d for d -dimensions.
- $\mathbf{G} = \sum_{i=1}^3 m_i \mathbf{b}_i$ defines points on the reciprocal lattice.
- Much like how real lattices are periodic, if you shift \mathbf{k} by \mathbf{G} so that a lattice point $\mathbf{k}' = \mathbf{k} + \mathbf{G}$, then the points \mathbf{k}' and \mathbf{k} are equivalent - i.e. they have the exact same environment.

Lemma 1.4.1. Given PLVs for the real lattice $\{\mathbf{a}_i\}$ and RLVs for the reciprocal lattice $\{\mathbf{b}_i\}$ then the following holds

- $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$

where we define $V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$ and

$$\mathbf{b}_1 = \frac{2\pi(\mathbf{a}_2 \times \mathbf{a}_3)}{V} \quad \mathbf{b}_2 = \frac{2\pi(\mathbf{a}_3 \times \mathbf{a}_1)}{V} \quad \mathbf{b}_3 = \frac{2\pi(\mathbf{a}_1 \times \mathbf{a}_2)}{V} \quad (1.23)$$

Proof. This makes use of vector identities. Note that $\mathbf{x} \cdot (\mathbf{y} \times \mathbf{z}) = 0 \iff \mathbf{x} = \mathbf{y}$ or $\mathbf{x} = \mathbf{z}$ or $\mathbf{y} = \mathbf{z}$. Substituting in the PLVs directly proves this. \square

RLVs can be calculated for different lattices. A simple cubic lattice in real space has a simple cubic lattice in reciprocal space. An FCC lattice in real space has a BCC lattice in reciprocal space.

If $\mathbf{k}' = \mathbf{k} + \mathbf{G}$, $(k')^2 = k^2 + G^2 + 2\mathbf{k} \cdot \mathbf{G}$. But $(k')^2 = k^2$ as they are equivalent points.

So $2\mathbf{k} \cdot \mathbf{G} = -G^2$ or $2\mathbf{k} \cdot \mathbf{G} = G^2$ because if G is a reciprocal lattice vector, so is $-G$.

- All \mathbf{k} points closest to 0 than any other reciprocal lattice point are in the first BZ.
- Second closest points are in the second BZ.
- Each BZ has the same volume (3D) or area (2D).

1.4.1 Reciprocal lattice as a Fourier Transform

In this section we make the mathematical connection between real and reciprocal space by way of a fourier transform.

We define

$$\rho(\mathbf{r}) = \sum_n \delta^3(\mathbf{r} - \mathbf{r}_0) = \delta(x - x_0) \delta(y - y_0) \delta(z - z_0) \quad (1.24)$$

which is the density of lattice points - its output will be 1 when there is a lattice point and 0 otherwise. We now take the fourier transform (denoted FT). Recall that the FT of a delta function is an exponential!

$$\begin{aligned} \text{FT}[\rho(\mathbf{r})] &= \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \\ &= \frac{(2\pi)^3}{V} \sum_{\mathbf{G}} \delta^3(\mathbf{k} - \mathbf{G}) \end{aligned} \quad (1.25)$$

where in the last line we again note the exponential is non-zero if there is a reciprocal lattice point.

Now, suppose we have a basis so instead of just a single cell, we have a repeating set of identical unit cells. Then we know that $\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R})$ where \mathbf{R} is a PLV - i.e. the density function is periodic. Taking the FT now

$$\text{FT}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r}$$

Now, we have not specified what \mathbf{r} is a vector to, but it will be a vector somewhere in the unit cell. Therefore we can say we reach vector \mathbf{r} by first going to a lattice point, and then adding a displacement \mathbf{x} so that $\mathbf{r} = \mathbf{R} + \mathbf{x}$. Substituting this in gives us a change of variables and

$$\text{FT}[\rho(\mathbf{r})] = \sum_{\mathbf{R}} \int_{\text{unit cell}} e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{x})} \rho(\mathbf{x} + \mathbf{R}) d\mathbf{x} \quad (1.26)$$

$$= \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \int_{\text{unit cell}} e^{i\mathbf{k} \cdot \mathbf{x}} \rho(\mathbf{x}) d\mathbf{x} \quad (1.27)$$

where the integral term

$$S(\mathbf{k}) = \int_{\text{unit cell}} e^{i\mathbf{k}\cdot\mathbf{x}\rho(\mathbf{x})} d\mathbf{x} \quad (1.28)$$

is called the **structure factor**. We will see it again shortly.

1.4.2 Waves in crystals

Bragg condition

Proposition 1.4.1. *Define d as the spacing between planes, λ be the wavelength of incident light and θ the incident angle to the crystal. Let $n \in \mathbb{Z}$. Then if the Bragg condition*

$$2d \sin \theta = n\lambda, \quad (1.29)$$

is satisfied, constructive interference from lattice planes is possible and can be used to measure d .

The setup for Bragg's law is seen in Fig. 1.13.

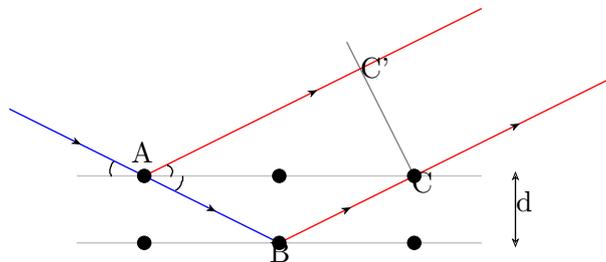


Figure 1.13: Bragg's law. The incident and reflection angles are θ . The incident wavelength (blue) is at wavevector \mathbf{k} and the scattered wave (red) is at wavelength \mathbf{k}' .

X-ray crystallography

X-rays have a typical wavelength of 1 \AA , and are scattered by atomic electrons. In traditional optical diffraction, you determine the grating spacing by diffraction extrema. The analogue with x-ray diffraction (XRD) is that your **lattice points/planes form the diffraction grating**.

- Separation of maxima in XRD gives separation of lattice planes.
- The basis is the structure of the line.

From Proposition 1.4.1, by rearranging for d , we get the minimum lattice spacing $d_{\min} = \lambda/2$. The question is now, how do we measure d ?

- Polychromatic x-rays: fire them into a sample. There will be some unscattered wavelengths and scattered wavelengths which will have maxima at specific λ
- Monochromatic x-rays: fire x-rays at the sample at different rotations around the sample. You will then observe different d and θ values which will satisfy Bragg's law when there are maxima: $2d_i \sin \theta_i = n\lambda \forall i$.
- Powder diffraction. Fire monochromatic light into a fine powder sample. You will get a cone of scattered x-rays which satisfy Bragg's law on your detector at angles 2θ from the normal, so you will effectively get a bunch of circles of maxima on your detector.

Scattering

In order to understand how the scattering works, we need to invoke some quantum mechanics. We treat the incident wave as a particle. The sample provides a potential $V(\mathbf{r})$. The transition

rate from $\mathbf{k} \rightarrow \mathbf{k}'$, some scattered wavelength is given by Fermi's golden rule

$$\Gamma(\mathbf{k}, \mathbf{k}') = \frac{2\pi}{\hbar} \underbrace{|\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2}_{\text{interaction matrix}} \underbrace{\delta(E_{k'} - E_k)}_{\text{assumes elastic scattering.}} \quad (1.30)$$

Now we can directly evaluate the matrix element in brackets.

$$\begin{aligned} \langle \mathbf{k}' | V | \mathbf{k} \rangle &= \int \psi_{\mathbf{k}'}^* V(\mathbf{r}) \psi_{\mathbf{k}} d\mathbf{r} \\ &= \int \left(\frac{e^{-i\mathbf{k}' \cdot \mathbf{r}}}{\sqrt{L^3}} \right) V(\mathbf{r}) \left(\frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{\sqrt{L^3}} \right) d\mathbf{r} \\ &= \frac{1}{L^3} \int e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} V(\mathbf{r}) d\mathbf{r} \\ &= \tilde{V}(\mathbf{k}' - \mathbf{k}) \end{aligned} \quad (1.31)$$

However we know the potential is periodic, so write $\mathbf{r} = \mathbf{R} + \mathbf{x}$ and perform our change of variables

$$\begin{aligned} \langle \mathbf{k}' | V | \mathbf{k} \rangle &= \frac{1}{L^3} \sum_{\mathbf{R}} \int_{\text{unit cell}} e^{-i(\mathbf{k}' - \mathbf{k}) \cdot (\mathbf{R} + \mathbf{x})} V(\mathbf{R} + \mathbf{x}) d\mathbf{x} \\ &= \frac{1}{L^3} \sum_{\mathbf{R}} e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} \int_{\text{unit cell}} e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{x}} V(\mathbf{x}) d\mathbf{x} \end{aligned} \quad (1.32)$$

Now notice that the sum will vanish unless

Laue condition

$$\mathbf{k}' - \mathbf{k} = \mathbf{G} \quad (1.33)$$

This is an alternative condition to scattering. The question is how does it compare to Bragg's law?

Theorem 1.4.1. *Bragg's law and Laue condition are equivalent.*

Proof. We suppose $\mathbf{G} = n\mathbf{G}_{\min}$, $n = \min\{h, \min k, \min l\} := \mathbf{G}_{\min}$, i.e. an integer multiple of the smallest RLW. The plane spacing is therefore $d = 2\pi/|\mathbf{G}_{\min}|$. Moreover $\mathbf{k} \cdot \mathbf{G} = \sin \theta = -\mathbf{k}' \cdot \mathbf{G}$. To see this, go back to Fig. 1.13.

Evaluating Laue's condition, then $\mathbf{k} - \mathbf{k}' = \mathbf{G}$, if $|\mathbf{k}| = |\mathbf{k}'| = \frac{2\pi}{\lambda}$, then we get scattering.

$$\begin{aligned} \mathbf{k} - \mathbf{k}' &= \mathbf{G} = \frac{2\pi}{\lambda} (\hat{\mathbf{k}} - \hat{\mathbf{k}}') \\ \mathbf{G} \cdot \mathbf{G} &= \hat{\mathbf{G}} \cdot \left[\frac{2\pi}{\lambda} (\hat{\mathbf{k}} - \hat{\mathbf{k}}') \right] \\ |\mathbf{G}| &= \frac{2\pi}{\lambda} [\sin \theta - (-\sin \theta)] = \frac{2\pi}{\lambda} 2 \sin \theta \\ \lambda &= \frac{2\pi}{|\mathbf{G}|} \cdot 2 \sin \theta = \frac{2\pi}{n |\mathbf{G}_{\min}|} 2 \sin \theta = \frac{2d}{n} \sin \theta \end{aligned}$$

We have recovered Bragg's law, so they are in fact the same thing. \square

Scattering amplitudes

Evaluating the interaction matrix

$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \frac{1}{L^3} \sum_{\mathbf{R}} e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} \int_{\text{unit cell}} e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{x}} V(\mathbf{x}) d\mathbf{x} \quad (1.34)$$

this is the product of 2 terms. The sum term again says whether there is scattering (Laue condition). The integral term is again the **structure factor**, which describes what the crystal looks like. We define it as

$$S(\mathbf{G}) = \int_{\text{unit cell}} e^{-i\mathbf{G}\cdot\mathbf{x}} V(\mathbf{x}) d\mathbf{x} \quad (1.35)$$

Additionally, the intensity $I_{hkl} \propto |S_{hkl}|$ (because remember we can identify any \mathbf{G} with the coefficients hkl). Finally, in the unit cell, the total potential is given by the superposition of the potentials from individual atoms at positions \mathbf{x}_j so

$$V(\mathbf{x}) = \sum_j V_j(\mathbf{x} - \mathbf{x}_j) \quad (1.36)$$

Neutron Scattering

Neutrons are neutral, so the scattering can be modelled as collisions with nuclei. We therefore assume the interaction is very short and localised around nuclei and say

$$V(\mathbf{x}) \simeq \sum_j f_j \delta(\mathbf{x} - \mathbf{x}_j) \quad (1.37)$$

where f_j is the **atomic form factor** which gives the magnitude of the interaction with a given nucleus.

X-ray scattering

This is mainly from electrons, so the potential V should be related to the electron density. We write the total potential as

$$V(\mathbf{x}) \simeq \sum_j z_j g_j(\mathbf{x} - \mathbf{x}_j) \quad (1.38)$$

We write the structure factor as

$$S(\mathbf{G}) \simeq \sum_j f_j(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{x}_j} \quad (1.39)$$

where again f_j is the form factor, defined here as

$$f_j(\mathbf{G}) = \int e^{i\mathbf{G}\cdot\mathbf{x}} V_j(\mathbf{x}) d\mathbf{x} \quad (1.40)$$

for this module, we assume the form factor to just be a number.

These 2 scattering methods have advantages and disadvantages

- X-rays scatter strongly from heavier atoms, as $f_j \propto Z_j$
- Neutron scattering – f_j varies erratically with z_j .

1.4.3 Examples using the structure factor

EXAMPLE 2.

We start with the simple cubic lattice. Here, there is an atom at every single lattice point, so the basis gives the positions $\mathbf{x}_j = [0, 0, 0]$. Therefore $S_{hkl} = f e^{i\mathbf{G}\cdot\mathbf{0}} = f$. This means

For simple cubic lattices, the intensity is constant for every combination of h, k, l .

EXAMPLE 3.

We consider CsCl, which is simple cubic but has chlorine atoms in the middle. We just again apply the definition of the structure factor to the bases of each element.

$$\begin{aligned} S_{hkl} &= f_{\text{Cs}} e^{i\mathbf{E}\cdot\mathbf{0}} + f_{\text{Cl}} e^{i\mathbf{G}\cdot\mathbf{x}_{\text{Cl}}} \\ &= f_{\text{Cs}} + f_{\text{Cl}} e^{i(h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3)\cdot(\frac{1}{2}\mathbf{a}_1+\frac{1}{2}\mathbf{a}_2+\frac{1}{2}\mathbf{a}_3)} \end{aligned}$$

Recall $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$

$$\begin{aligned} S_{hkl} &= f_{\text{Cs}} + f_{\text{Cl}} e^{i2\pi(\frac{h}{2}+\frac{k}{2}+\frac{l}{2})} \\ \text{effectively, } &e^{i2\pi(hx_j+ky_j+lz_j)} \\ &= f_{\text{Cs}} + f_{\text{Cl}} e^{i\pi(n+k+l)} \\ &= f_{\text{Cs}} + f_{\text{Cl}} (-1)^{h+k+l} \end{aligned} \tag{1.41}$$

We see here the scattering depends on the form factors of both the atoms, as well as particular combinations of h, k, l .

EXAMPLE 4.

We consider pure Cs, which has a BCC structure. Following our algorithm, we can decompose it into a simple cubic with a basis at $[0, 0, 0]$ with an extra basis at $[1/2, 1/2, 1/2]$. We can copy our CsCl example replacing the Cl with Cs and we get

$$S_{hkl} = f_{\text{Cs}} \left(1 + (-1)^{h+k+l} \right) \tag{1.42}$$

EXAMPLE 5.

We consider copper, Cu, which is FCC. However we can again treat it as a simple cubic with extra bases. Therefore our total basis is

$$[0, 0, 0], [1/2, 1/2, 0], [1/2, 0, 1/2], \left[0, \frac{1}{2}, \frac{1}{2} \right]$$

Substituting this into S_{hkl} gives

$$\begin{aligned} S_{hkl} &= \sum_j f_j e^{i2\pi(hx_j+ky_j+lz_j)} \\ &= f_{\text{Cu}} \left[e^{i2\pi(0)} + \underbrace{e^{i2\pi(h/2+k/2)}}_{+e^{i2\pi(h/2+l/2)} + e^{i2\pi(k/2+l/2)}} \right] \\ S_{hkl} &= f_{\text{Cu}} \left[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l} \right] \end{aligned} \tag{1.43}$$

We see that we have different cases

- If h, k, l are all even or all odd, $S_{hkl} = 4f_{\text{Cu}}$
- If h, k are even, l odd, then $S_{hkl} = 0$

We can generalise our examples to any non-simple-cubic lattice with a basis:

$$S_{hkl} = S_{hkl}^{\text{lattice}} \times S_{hkl}^{\text{basis}} \tag{1.44}$$

This says that if we have a lattice (e.g FCC, BCC) we evaluate the structure factor for that first and set $f_j = 1$. Then if we have extra bases, we evaluate those together, all at once in one structure factor using the right f_j for each atom. You should hopefully see that this is what we are also doing in all of our examples.

Chapter 2

Free electrons

2.1 Heat Capacity

The classical approach is that $C = 3k_B$ per atom. This worked well for most materials at room temperature.

2.1.1 Einstein Model

This isn't the best model. You can just skim read it and move onto the next subsection. We again model atoms as harmonic oscillators, with energy $E_n = (n + \frac{1}{2}) \hbar\omega$ for 1D. The expected energy $\langle E \rangle = \sum_n p_n E_n$. From statistical mechanics, we find that the atoms follow a Boltzmann distribution with

$$p_n = \frac{e^{-E_n/k_B T}}{Z} \qquad Z = \sum_n e^{-E_n/k_B T} \qquad (2.1)$$

Consider phonons, the number in a given mode n_B satisfies

$$n_B = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

This is the **Bose occupation factor**. Then $\langle E \rangle = \hbar\omega (n_B + 1/2)$. In the high T limit;

$$\begin{aligned} \langle E \rangle &= \frac{1}{2} \hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \\ &\simeq \frac{1}{2} \hbar\omega + \hbar\omega \left[\frac{\hbar\omega}{k_B T} + \frac{1}{2} \left(\frac{\hbar\omega}{k_B T} \right)^2 + \dots \right]^{-1} \\ &\simeq \frac{1}{2} \hbar\omega + k_B T \left[1 - \frac{1}{2} \left(\frac{\hbar\omega}{k_B T} \right) + \dots \right] \end{aligned}$$

So if $\hbar\omega \ll k_B T$, $\langle E \rangle \simeq k_B T$ in one dimension. This allows us to find the heat capacity

$$\begin{aligned} C &= \frac{\partial \langle E \rangle}{\partial T} \simeq k_B \\ \langle E_{3D} \rangle &= 3 \langle E_{1D} \rangle. \end{aligned}$$

2.1.2 Debye model

Now this is getting a bit better. It has been observed at that low temperatures, $C \propto T^3$. We should obtain this in theory if our physics is correct. To do this, we make some assumptions

Assumptions of the Debye model

- Assume speed of sound v_s is independent of polarisation 2 direction of propagation. (it isn't)
- Assume $v_s = \omega/k$ (???)
- Assume sample is a box of volume $V = L^3$. (checks out)

From PX285 Statistical Mechanics you should recall

Definition 2.1.1. The **density of states** $g(k)dk$ is defined as

$$g(k)dk = \text{number of allowed } k\text{-states with } k \rightarrow k + dk \quad (2.2)$$

We need to evaluate it for our case

$$\begin{aligned} g(k)dk &= 3 \times \frac{\text{Vol. of spherical shell, thickness } dk}{\text{vol. of one } k\text{-state}} \\ &= 3 \times \frac{4\pi k^2 dk}{(2\pi/L)^3} = \frac{3V k^2 dk}{2\pi^2} \end{aligned}$$

where the factor of 3 comes from the number of polarisations of light in 3D. You can polarise along x, y, z . We make a change of variables from wavenumber to frequency using our assumptions to get

$$g(\omega)d\omega = \frac{3V\omega^2}{2\pi^2 v_s^2} d\omega \quad (2.3)$$

To find our heat capacity, we need our expected energy. This is the integral of our energy function times the density of states over every state.

$$\begin{aligned} \langle E \rangle &= \int_0^\infty g(\omega) d\omega \hbar\omega (n_B + 1/2) \\ &= \frac{3V\hbar}{2\pi^2 v_s^3} \int_0^\infty \left[\omega^3 \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} \right) + T\text{-independent terms} \right] d\omega \\ &\text{let } x = \hbar\omega/k_B T \\ \langle E \rangle &= \frac{3v\hbar}{2\pi^2 v_s^3} \left(\frac{k_B T}{\hbar} \right)^4 \underbrace{\int_0^\infty \frac{x^3}{e^x - 1} dx}_{\pi^4/15} + T\text{-independent terms} \end{aligned} \quad (2.4)$$

The integral is a standard integral and you do not have to know it for the exam. Our result is that $\langle E \rangle \propto T^4$ but we have observed $C \propto T^3$ (which isn't entirely true btw). So why do we have a discrepancy? It's because we integrated to infinity. Instead, let's cut off the integral at some frequency ω_D (since realistically we only have so many accessible states). We suppose the number of modes is given by

$$3N = \int_0^{\omega_D} g(\omega) d\omega = \frac{\omega_D^3 V}{2\pi^2 v_s^3} \quad (2.5)$$

where 3 is a factor from polarisation and N is the number of atoms. We can evaluate $\langle E \rangle$ again and we find the following:

- At high T , $C = 3k_B N$ in 3D.
- At low T , get T^3 dependence (yay)
- In metals, $C = \gamma T + \alpha T^3 + \dots$

So now we have another discrepancy, in that with metals, we have a linear term! Why is this?

2.2 Sommerfield/Free electron theory

Our discrepancy arises because metals are real atoms, and have electrons. We again make some assumptions

Assumptions of Free electron theory

- Crystal structure doesn't matter (it does)
- Ion cores are uniformly spaced (not in reality)
- Electrons move in a constant electrostatic potential (they don't). We assume the internal electric field is also zero.
- Electrostatic repulsion between electrons doesn't exist (it does).

Electrons obey the Fermi-Dirac distribution

$$n_F = \frac{1}{e^{\hbar\omega/k_B T} + 1} \quad (2.6)$$

where μ is the chemical potential. Now, electrons are quantum particles so we need to invoke more quantum mechanics. Recall

$$E = \frac{\hbar^2 |\mathbf{k}|^2}{2m} \quad \mathbf{p} = \hbar\mathbf{k} \quad g(k)dk = \frac{V k^2}{2\pi^2} dk \quad (2.7)$$

We can recast the density of states in energy as

$$g(E)dE = 2g(k)dk \quad (2.8)$$

where the factor of 2 comes from 2 electron spin states per wavevector state - remember they obey the Pauli exclusion principle! Rearranging for energy E :

$$k = \frac{(2m)^{1/2} E^{1/2}}{\hbar}, \quad \frac{dk}{dE} = \frac{(2m)^{1/2}}{2\hbar E^{1/2}} \quad (2.9)$$

$$g(E) = 2g(k) \frac{dk}{dE} = 2 \frac{V}{2\pi^2} \left(\frac{2mE}{\hbar^2} \right) \frac{(2m)^{1/2}}{2\hbar E^{1/2}} \quad (2.10)$$

$$= \frac{V(2m)^{3/2}}{2\pi^2 \hbar^3} E^{1/2} \quad (2.11)$$

There are N electrons. We can find the Fermi energy and Fermi wavevector by assuming $T = 0$. At this temperature, the chemical potential is the Fermi energy.

$$N = \int_0^{E_F} g(E)dE = \frac{V(2m)^{3/2}}{2\pi^2 \hbar^3} \frac{2}{3} E_F^{3/2} \quad (2.12)$$

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} = \mu(T = 0)$$

Moreover,

$$E_F = \frac{\hbar^2 k_F^2}{2m}, \text{ so } k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3} \quad (2.13)$$

So all the free electrons occupy a sphere of radius k_F called the **Fermi surface**. Note that it is an abstract surface where each point *inside* represents filled states and points outside are empty. Other 'Fermi' quantities are

- $T_F E_F / k_B$, the **Fermi temperature**.
- $\mathbf{p}_F = \hbar\mathbf{k}_F$, the **Fermi momentum**
- $v_F = \frac{\hbar k_F}{m}$ the **Fermi speed**

The physics we are interested in is dependent on valence electrons, because they are the ones which participate in interactions since they can move.

2.2.1 Electronic heat capacity

To determine this, we make one approximation: that only electrons within energy $k_B T$ of μ are excited. This allows us to Taylor expand around $T = 0$

$$E(T) \simeq E(T = 0) + \frac{\tilde{\gamma}}{2} [g(E_F) k_B T] k_B T \quad (2.14)$$

where $\tilde{\gamma}/2$ is a fudge factor, the term $g(E_F)k_B T$ is the density of states near the edge of the Fermi surface and the extra $k_B T$ the average excitation per electron. Differentiating with respect to T , the electronic heat capacity is

$$C_{\text{el}} \simeq \tilde{\gamma} g(E_F) k_B^2 T$$

We need to find $g(E_F)$ which we recall from Eq. (2.7)

$$\begin{aligned} g(E) &= \frac{V}{2\pi^2} \frac{(2m)^{3/2} \hbar^3}{E} \\ g(E) &= \frac{V}{2\pi^2} \left(\frac{3\pi^2 N}{V} \right) \frac{E^{1/2}}{E_F^{3/2}} = \frac{3}{2} \frac{N}{E_F} \left(\frac{E}{E_F} \right)^{1/2} \\ g(E_F) &= \frac{3}{2} \frac{N}{E_F}. \\ C_{\text{el}} &= \tilde{\gamma} \frac{3}{2} \frac{N}{E_F} k_B^2 T \simeq \boxed{\frac{3}{2} \tilde{\gamma} N k_B \left(\frac{T}{T_F} \right)} \end{aligned} \quad (2.15)$$

So we have recovered our linear term we needed earlier!

2.2.2 Transport Properties

With the theory of free electrons in mind, we can now apply it to understand the consequences of electrons in motion - i.e. transport properties.

Electrical Conductivity

Suppose we apply electric and magnetic fields \mathbf{E}, \mathbf{B} across our metal. This means a force is exerted since electrons are charged, and this force is given by the Lorentz force law.

$$\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (2.16)$$

Due to this, the distribution of states will change, and we can understand this through the Fermi surface, which is an abstract depiction of the space of states. In particular, for our scenario here,

Assuming there are no collisions, an applied electric and magnetic field will displace and distort the Fermi surface in k -space.

The effect of the magnetic field on the Fermi sphere will be seen later in the course. For now, let us assume $\mathbf{B} = \mathbf{0}$ and $\mathbf{E} \neq \mathbf{0}$. By equating forces, we know the net force on electrons is due to the electric force, so

$$\mathbf{F} = \hbar \frac{d\mathbf{k}}{dt} = -e\mathbf{E} \implies \mathbf{k}(t) - \mathbf{k}(0) = \delta\mathbf{k} = -\frac{e\mathbf{E}}{\hbar} t \quad (2.17)$$

Namely, an electric field only displaces the Fermi sphere by some vector $\delta\mathbf{k}$. Note that we had a linear first order ODE in time so the integration should be trivial.

Now let us allow the electrons to collide. This could be due to

- Collisions from other electrons
- Collision from impurities
- Defects
- Phonon interactions

Now if electrons get scattered, this means they get knocked out of one state \mathbf{k} and into a different state, say \mathbf{k}' . In the Fermi sphere picture, this means the electrons closest to the edge on one side of the sphere get scattered across to the other side of the sphere, where outside of the side are empty states.

The applied electric field can be held uniform and constant, so the displaced Fermi sphere is in a steady state. Then after some collision time τ elapses, the change in wavevector is $\delta\mathbf{k} = -eE\tau/\hbar$. Within a constant field \mathbf{E} , suppose there are n electrons per unit volume. The electric current density $\mathbf{j} = -nev$ which means the mean drift velocity \mathbf{v} is

$$\mathbf{v} = \frac{-e\mathbf{E}\tau}{m} \quad (2.18)$$

and the electric current density is

$$\mathbf{j} = \frac{ne^2\tau}{m}\mathbf{E} = \sigma\mathbf{E} \quad (2.19)$$

where the last equality is Ohm's Law which you should recall from PX285 Electromagnetic Theory & Optics and σ is the conductivity (tensor). This result will be used again throughout the course and is worth remembering.

- Suppose we have a perfect crystal - i.e. no defects. Then the scattering time $\tau \rightarrow \infty$ as $T \rightarrow 0$. This is because only phonons cause scattering since at really low temperatures, thermal excitations and drift velocities are almost negligible.
- For real materials: there is a finite scattering time τ_0 even at $T = 0$ because of defects, as well as phonon scattering. Therefore

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{\text{phonon}}} \quad (2.20)$$

- The **mean free path** is $\ell = v_F\tau$

Moreover, since we have the conductivity in Eq. (2.19), we can get the **resistivity**

$$\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau} = \frac{m}{ne^2} \left(\frac{1}{\tau_0} + \frac{1}{\tau_{\text{phonon}}} \right) = \rho(0) + \rho_{\text{phonon}}(T) \quad (2.21)$$

This equation is called **Matthiessen's rule** and its graph is shown in Fig. 2.1¹

¹(NON-EXAMINABLE) You do not need to know the functional form of Matthiessen's rule. However, there are many factors including impurities, phonon-phonon scattering, as well as electron-phonon scattering which is the only one considered in this module. In this case, Matthiessen's rule becomes

$$\frac{1}{\tau_{\text{phonon}}} = \frac{n_c \epsilon^2 \omega}{\rho v_g^2 k_B T} \sqrt{\frac{\pi m^* v_g^2}{2k_B T}} \exp\left(-\frac{m^* v_g^2}{2k_B T}\right)$$

The parameter n_c is the concentration of conduction electrons, ϵ is the deformation potential, ρ is mass density and m^* is the effective electron mass.

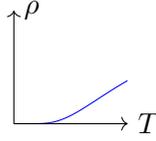


Figure 2.1: Matthiessen's rule

Thermal conductivity, κ

We will use the following result from statistical mechanics as truth

$$\kappa = \frac{1}{3} C_V v_F \ell \quad (2.22)$$

where C_V is the heat capacity at constant volume, v_F is the Fermi speed and ℓ is the mean free path. However, from E. (2.15) we calculated the electronic heat capacity - this was at constant volume so we substitute it into Eq. (2.22), as well as $\ell = v_F \tau$:

$$\begin{aligned} \kappa &= \frac{1}{3} \frac{\pi^2}{2} n k_B \left(\frac{T}{T_F} \right) v_F^2 \tau \\ &= \boxed{\frac{\pi^2 n k_B^2 \tau T}{3m}} \end{aligned} \quad (2.23)$$

Wiedemann-Franz Law

This law describes how the isochoric heat capacity C_V varies with conductivity σ and temperature T .

$$\begin{aligned} \frac{\kappa}{\sigma T} &= \frac{\pi^2 n k_B^2 \tau T}{3m} \cdot \frac{m}{ne^2 \tau} \cdot \frac{1}{T} \\ &= \frac{\pi^2 k_B^2}{3e^2} = 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-2} \\ &= L \end{aligned} \quad (2.24)$$

where L is a constant called the **Lorenz number**. However the issue with this result is that experiments show a temperature-dependent result. This suggests that τ is different for the two scattering processes.

Classical Hall effect

Now let's turn on our magnetic field to be uniform, oriented in the z -direction so $\mathbf{B} = B\hat{\mathbf{z}}$ and non zero. Moreover we allow collisions and scattering. The net force is then

$$\hbar \left(\frac{d}{dt} + \frac{1}{\tau} \right) \mathbf{k} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) = m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \mathbf{v} \quad (2.25)$$

$$m \frac{d\mathbf{v}}{dt} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \frac{m\mathbf{v}}{\tau} \quad (2.26)$$

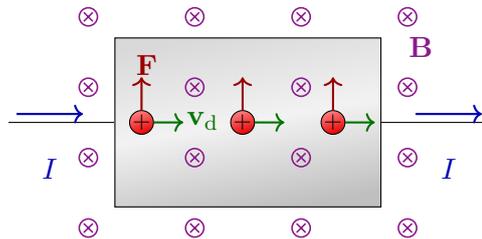
At steady state, the net force is zero and $\mathbf{j} = -nev$. Therefore we evaluate and

$$\begin{aligned} 0 &= -e\mathbf{E} + \frac{\mathbf{j} \times \mathbf{B}}{n} + \frac{m}{ne\tau} \mathbf{j} \\ \mathbf{E} &= \frac{1}{ne} \mathbf{j} \times \mathbf{B} + \frac{m}{ne^2\tau} \mathbf{j} \end{aligned} \quad (2.27)$$

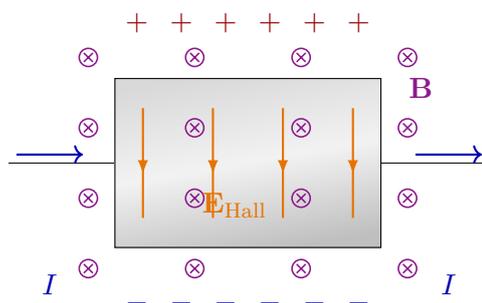
We define

$$\mathbf{E}_{\text{Hall}} = \frac{1}{ne} \mathbf{j} \times \mathbf{B} \quad \mathbf{E}_{\parallel} = \frac{m}{ne^2\tau} \mathbf{j} \quad (2.28)$$

to be the **Hall electric field** and parallel electric field respectively. So what we see is we have the generation of an internal electric field which separates positive and negative charges in the conductor, as seen in Fig. 2.2. This creates \mathbf{E}_{Hall} which means we can measure a voltage if we were to connect the perpendicular edges of the conductor. This voltage is the **Hall voltage**.



(a) Charge carriers passing through a metal immersed in a uniform magnetic field \mathbf{B} going into the page. The electric field is in the direction of the (conventional) current I .



(b) Movement of current under the field produces an internal Hall electric field.

Figure 2.2: Depiction of the classical Hall effect.

We define the **resistivity tensor** $\underline{\rho}$ such that $\mathbf{E} = \underline{\rho}\mathbf{j}$. This has 9 components for three dimensions: $\rho_{xx}, \rho_{yy}, \rho_{zz}, \rho_{xy}, \rho_{yx}, \rho_{yz}, \rho_{zy}, \rho_{xz}, \rho_{zx}$. Since there is no current in the direction of z , $\rho_{xz} = \rho_{zx} = \rho_{yz} = \rho_{zy} = 0$. Moreover from Eq. (2.28) we have $\rho_{xx} = \rho_{yy} = \rho_{zz} = \frac{m}{ne^2\tau}$ and $\rho_{xy} = -\rho_{yx} = B/(ne)$.

Remark. Why suddenly define the tensor? It's a direct way to get the total electric field in terms of the resistivities, since by Ohm's law $\mathbf{E} = \sigma\mathbf{j}$. If you're unsure how to prove it, write everything out in components by setting $\mathbf{j} = (j_x, j_y, j_z)$ and $\mathbf{B} = (B_x, B_y, B_z)$. Then the RHS becomes

$$\frac{1}{ne}\mathbf{j} \times \mathbf{B} + \frac{m}{ne^2\tau}\mathbf{j} = \frac{1}{ne} \begin{bmatrix} j_y B_z - j_z B_y \\ -j_x B_z + j_z B_x \\ j_x B_y - j_y B_x \end{bmatrix} + \frac{m}{ne^2\tau} \begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix}$$

Now we want to be able to recast it so

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \begin{bmatrix} \rho_{xx} & \rho_{xy} & \rho_{xz} \\ \rho_{yx} & \rho_{yy} & \rho_{yz} \\ \rho_{zx} & \rho_{zy} & \rho_{zz} \end{bmatrix} \begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} \quad (2.29)$$

From expanding everything out, we see that the only terms that are purely in j_i are the diagonal terms which have a coefficient of $m/(ne^2\tau)$. From there you can show the off-diagonal terms must correspond to the vector containing the current times field terms. In our case, the magnetic field was aligned along $\hat{\mathbf{z}}$ so our tensor becomes

$$\begin{bmatrix} \frac{m}{ne^2\tau} & \frac{1}{ne} & 0 \\ -\frac{1}{ne} & \frac{m}{ne^2\tau} & 0 \\ 0 & 0 & \frac{m}{ne^2\tau} \end{bmatrix} \quad (2.30)$$

Finally, we can define the **Hall coefficient**

$$R_H = \frac{\rho_{yx}}{|\mathbf{B}|} = -\frac{1}{ne} \quad (2.31)$$

The importance of the Hall coefficient for our purposes is it allows us to predict the **number density of conduction electrons** so that

$$0 \leq n_c = -\frac{1}{R_H e n_{\text{atomic}}} \quad (2.32)$$

where n_{atomic} is the atomic density of the conductor. The issue is that the free electron model predicts **negative number densities** which is impossible, and is usually interpreted as charge carriers of the opposite sign.

Chapter 3

Bandstructures

3.1 Nearly free electron theory

Our free electron theory from the previous chapter was not ideal. For starters, we ignored the crystal structure which lead to incorrect predictions in the Hall effect. We are now going to consider crystals and come up with a hopefully improved model.

Let the wavefunction describing the electron in the \mathbf{k} th state be

$$\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \quad (3.1)$$

i.e., treat electrons kind of like waves.

In a crystal, atoms are repeated. Therefore, if each atom has a potential (e.g., electrostatic), then this potential is periodic. By Eq. (1.33), we require $|\mathbf{k}| = |\mathbf{k} + \mathbf{G}|$ for diffraction by Theorem 1.4.1. Therefore $\mathbf{k} \cdot \mathbf{k} = (\mathbf{k} + \mathbf{G}) \cdot (\mathbf{k} + \mathbf{G})$.

In 1D, from Section 1.4, we have

$$2kG = -G^2 \implies k = \pm \frac{G}{2} = \pm \frac{n\pi}{a} \quad (3.2)$$

This is a **reflection at the BZ boundary** by the Bragg condition in Proposition 1.4.1. This means that a right travelling wave will be Bragg reflected at the BZ boundary and become left-travelling (in a 1D crystal), while any left-travelling wave will be Bragg reflected and become a right-travelling wave.

There are two possible electron wavefunctions from superposition of these waves at the 1st BZ boundary,

$$\begin{aligned} \psi_+ &= e^{ikx} + e^{-ikx} = e^{i\left(\frac{\pi x}{a}\right)} + e^{-i\left(\frac{\pi x}{a}\right)} = 2 \cos\left(\frac{\pi x}{a}\right) \\ \psi_- &= e^{ikx} - e^{-ikx} = e^{i\frac{\pi x}{a}} - e^{-i\frac{\pi x}{a}} = 2i \sin\left(\frac{\pi x}{a}\right) \end{aligned} \quad (3.3)$$

Since the charge density is proportional to $\Psi^*\Psi$ then this has the effect of piling up electrons in different regions; Ψ_+ on the lattice sites, and Ψ_- between the lattice sites. Since these regions have different potentials the electrons must have different energies, and **energy gaps open up at the BZ boundary**.

3.1.1 Energy gaps using QM

Using time-independent perturbation theory from PX3A2, we will derive the closed form of the energy gaps. We can consider the periodic potential $V(\mathbf{r})$ as the perturbation and the

unperturbed Hamiltonian as $H_0 = |\mathbf{k}\rangle = E_0 |\mathbf{k}\rangle$ where $|\mathbf{k}\rangle$ is the free electron in state \mathbf{k} . The new Hamiltonian is therefore $H = H_0 + V$. Then

$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \frac{1}{L^3} \int e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} V(\mathbf{r}) d\mathbf{r} = \tilde{V}(\mathbf{k}' - \mathbf{k}) = V_{\mathbf{G}} \quad (3.4)$$

where \tilde{V} is the Fourier transform of the periodic potential. To first order, perturbation theory gives the first order energy as

$$E(\mathbf{k}) = E_0(\mathbf{k}) + \langle \mathbf{k}' | V | \mathbf{k} \rangle = E_0(\mathbf{k}) + V_0 \quad (3.5)$$

however V_0 is a constant, so we can arbitrarily set it to 0 since potentials are defined on your choice of reference. We therefore proceed to a second-order perturbation

$$E(\mathbf{k}) = E_0(\mathbf{k}) + V_0 + \sum_{\mathbf{k}'=\mathbf{k}+\mathbf{G}} \frac{|\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2}{E_0(\mathbf{k}) - E_0(\mathbf{k}')} = E_0(\mathbf{k}) + V_0 + \sum_{\mathbf{k}'=\mathbf{k}+\mathbf{G}} \frac{|V_{\mathbf{G}}|^2}{E_0(\mathbf{k}) - E_0(\mathbf{k}')}. \quad (3.6)$$

At the BZ boundary we know that $E_0(\mathbf{k}) = E_0(\mathbf{k}')$ as due to the Laue condition and so we need to use degenerate perturbation theory. We won't recap the algorithm, please see our [PX3A2 Notes](#) for that - we will proceed directly onto the method.

We let our wavefunction $|\Psi\rangle = \alpha |\mathbf{k}\rangle + \beta |\mathbf{k}'\rangle$ where $|\mathbf{k}\rangle$ is the incident electron state and $|\mathbf{k}'\rangle$ is the scattered electron state. Recall that the Hamiltonian in a matrix representation is computed from the inner products $\langle i | H | j \rangle$ where i, j will be different combinations of \mathbf{k}, \mathbf{k}' . Computing the inner products gives the Schrödinger equation as

$$\begin{pmatrix} E_0(\mathbf{k}) & V_{\mathbf{G}}^* \\ V_{\mathbf{G}} & E_0(\mathbf{k} + \mathbf{G}) \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (3.7)$$

This is just an matrix equation and we only need to find the eigenvectors and eigenvalues of H - this is so we know what our energies are. Solving the secular determinant is

$$(E_0(\mathbf{k}) - E)(E_0(\mathbf{k} + \mathbf{G}) - E) - |V_{\mathbf{G}}|^2 = 0 \quad (3.8)$$

$$\implies \boxed{E_{\pm} = E_0(\mathbf{k}) \pm |V_{\mathbf{G}}|} \quad (3.9)$$

in 1D, which are the new energies of the electron at the boundary. This gives the coefficients $\alpha = \pm \beta$ That's cool, but we want a general result for near the boundary. Indeed, let $\delta > 0$ be small and we consider the wavenumbers $k = (n\pi/a) + \delta$ and $k' = -(n\pi/a) + \delta$. We know that $E_0(k) = \hbar^2 k^2 / 2m$ so substitute these new k values directly and do a lot of algebra. If you just want the result, skip to Eq. (3.11). Substituting E_0 into the secular determinant gives

$$\left[\frac{\hbar^2}{2m} \left(\frac{n\pi}{a} + \delta \right)^2 - E \right] \left[\frac{\hbar^2}{2m} \left(-\frac{n\pi}{a} + \delta \right)^2 - E \right] - |V_{\mathbf{G}}|^2 = 0 \quad (3.10)$$

Notice that after getting rid of the minus sign in the brackets of the second product, we have a polynomial in the form $(f + g)(f - g) - |V_{\mathbf{G}}|^2 = 0$. Therefore $f^2 = g^2 + |V_{\mathbf{G}}|^2$. We set f to be the term involving E and g to be the term independent of E and we get

$$\begin{aligned} \left[\frac{\hbar^2}{2m} \left(\left(\frac{n\pi}{a} \right)^2 + \delta^2 \right) - E \right]^2 &= \left(\frac{\hbar^2}{2m} \cdot \frac{2n\pi\delta}{a} \right)^2 + |V_{\mathbf{G}}|^2 \\ \frac{\hbar^2}{2m} \left(\left(\frac{n\pi}{a} \right)^2 + \delta^2 \right) - E &= \pm \sqrt{\left(\frac{\hbar^2}{2m} \cdot \frac{2n\pi\delta}{a} \right)^2 + |V_{\mathbf{G}}|^2} \\ E_{\pm} &= \frac{\hbar^2}{2m} \left(\frac{n\pi}{a} \right)^2 + \frac{\hbar^2 \delta^2}{2m} \pm |V_{\mathbf{G}}| \sqrt{1 + \left(\frac{\hbar^2}{2m} \cdot \frac{2n\pi\delta}{a/V_{\mathbf{G}}} \right)^2} \end{aligned}$$

We use a Taylor expansion on the root term by writing $\sqrt{1+x} \simeq 1 + \frac{1}{2}x$ since we have assumed δ to be small, so substituting that in

$$\begin{aligned} E_{\pm} &= \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2 + \frac{\hbar^2\delta^2}{2m} \pm |V_G| \pm \frac{1}{2} \left(\frac{\hbar^2}{2m} \cdot \frac{2n\pi\delta}{a}\right)^2 \frac{1}{|V_G|} \\ &= \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2 \pm |V_G| + \frac{\hbar^2\delta^2}{2m} \left[1 \pm \frac{\hbar^2}{m} \left(\frac{n\pi}{a}\right)^2 \frac{1}{|V_G|}\right] \end{aligned}$$

and we are done. Now, let's look at this result in more detail

$$E_{\pm} \approx \underbrace{\frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2}_{E_0(k)\text{at boundary}} \pm \underbrace{|V_G|}_{\text{bandgap}} + \underbrace{\frac{\hbar^2\delta^2}{2m} \left(1 \pm \frac{\hbar^2}{m} \left(\frac{n\pi}{a}\right)^2 \frac{1}{|V_G|}\right)}_{\text{Quadratic dispersion}} \quad (3.11)$$

From perturbation theory, the energies tell us that near the boundaries of the BZ, the energy is quadratic, hence plotting the bandstructure with energy on the vertical axis produces Fig. 3.1.

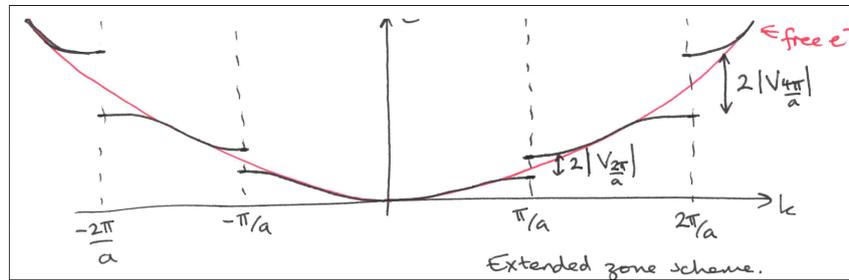


Figure 3.1: Bandstructure of Nearly free-electron theory with energy gaps (black). The free electron prediction is shown in red.

So the unperturbed states have now been split to two energies E_+ and E_- with the difference $E_+ - E_- \simeq 2|V_G|$ by the periodic perturbation. In fact, these 2 eigenvalues and the existence of a bandgap allow us to determine how semiconductors work, as well as metals and insulators.

3.1.2 Metals and Insulators

In 1D, the number of k -states in a BZ is the number of unit cells in the entire system. If a primitive unit cell has 1 electron, then the band is **half-full** since there are 2 spin states per k -state. We can illustrate this with a Fermi surface - the surface in this case *is* the bandstructure itself. If you're unsure about this, remember Fermi surfaces are surfaces of *states*, not actual position. Anything which correctly describes a state could be a Fermi surface of some sorts.

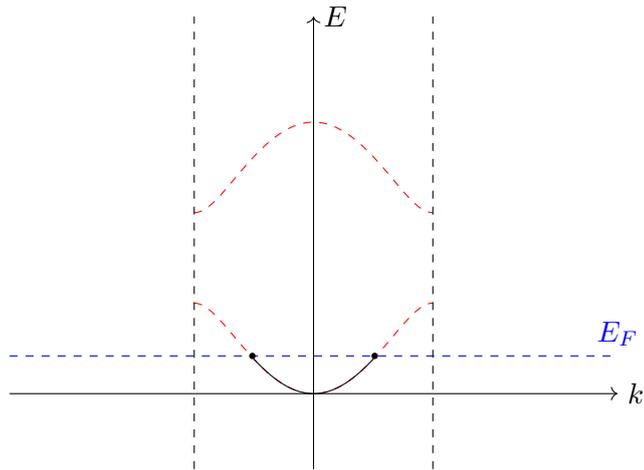
For the 1D chain and nearly free electron model, the Fermi surface is shown on the bandstructure in Fig. 3.2. The most important thing to note is that when an electric field is applied, the Fermi surface is not distorted, but is shifted towards the right. This means there are now free states on the left as can be seen on Fig. 3.2b which allows electrons to move to fill in those states. Movement of electrons creates a current. This defines a **metal**.

Definition 3.1.1. A **metal** is a crystal whose primitive unit cell has 1 electron per \mathbf{k} -state, so a current is allowed to flow.

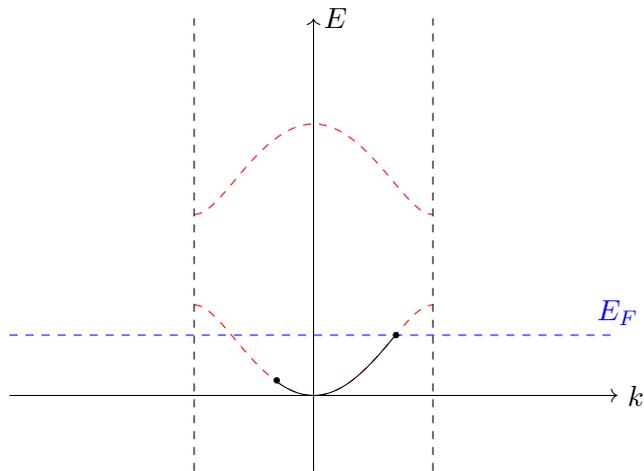
Now let's suppose we have a **divalent** material, i.e. 2 electrons in a primitive unit cell at state \mathbf{k} . By the Pauli exclusion principle, they must have opposite spin and so no more electrons can occupy the state \mathbf{k} . Therefore the first level is **completely filled** and our bandstructure looks like Fig. 3.3. We define

Definition 3.1.2. The **valence band** is the outermost completely full energy level

and



(a) Half-filled Fermi surface (black) for electrons in a 1D nearly free electron model, with no applied field.



(b) Half-filled Fermi surface (black) for electrons in a 1D nearly free electron model, with an applied electric field, but no magnetic field.

Figure 3.2: Fermi surfaces for the nearly free electron model. Note that when an electric field is applied, the surface shifts and E_F increases, leaving unfilled states to the left.

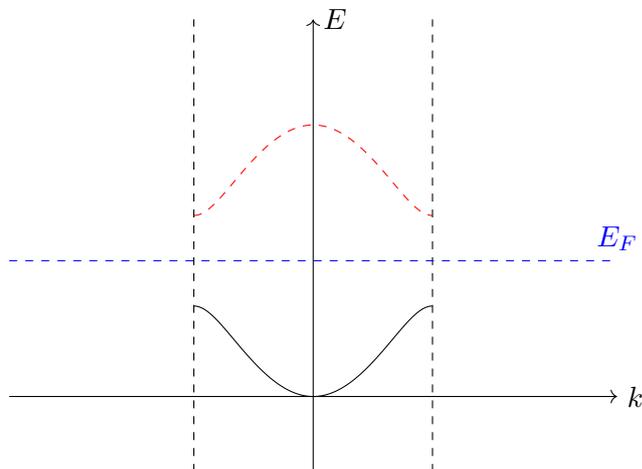


Figure 3.3: Fermi surface for a divalent material. We see the first level is completely full and the Fermi energy is halfway between the bandgap.

Definition 3.1.3. The **conduction band** is the first band above a bandgap that electrons can move into to allow movement (conduction).

In the divalent case, the dashed red band level in Fig. 3.3 is the conduction band whereas the solid black line - a completely occupied Fermi surface - is the valence band. At $T = 0$, an electric field will not be able to displace the electrons.

Definition 3.1.4. An **insulator** is a material whose electrons cannot be excited into conduction by an electric field (at $T = 0$).

Now let's raise the temperature a bit, this means electrons get thermal energy. At room T , if the bandgap is around 4 eV or less, then it's **possible for electrons to be thermally excited into the conduction band**. This is called a **semiconductor**.

3.1.3 Real materials

Alkali materials

These materials have 1 conduction electron - the 1 electron in their valence shell can be excited into movement. Suppose the applied potential V is weak.

- The Fermi surface volume is half the BZ volume
- Alkalis have BCC lattices
- the free electron Fermi surface is a sphere

What happens is as you increase V , the Fermi surface distorts and states just inside the BZ are pushed down in energy and electrons start to preferentially fill these. This process is shown in Fig. 3.4.

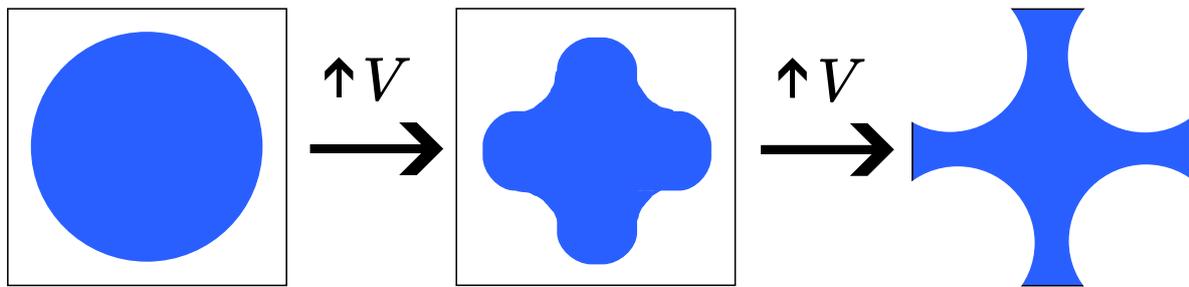


Figure 3.4: Distortion of a 2D Fermi surface under a stronger periodic potential.

- States just inside the BZ boundary (near the edge of the FS) get pushed down in energy.
- States just outside get pushed up
- Electrons fill lowest energy levels first

For a divalent material the Fermi surface will have the same volume as the first BZ, see left of Fig. 3.5. If the electrons are assumed to fill only the first BZ completely (i.e. under a strong potential) we will have an insulator with bandgaps at the BZ boundaries, see right of Fig. 3.5. However, normally we see a distortion of the free electron Fermi surface where the filled states start going past the boundary with empty states at the corners as seen in the middle of Fig. 3.5.

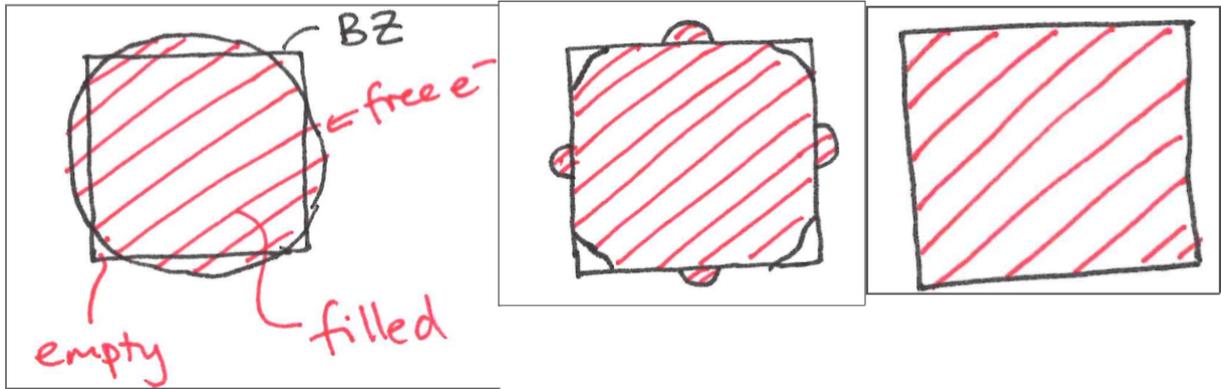


Figure 3.5: (Left) 2D Fermi surface for the free electron model. (Middle): Distortion of the FS for a metal. Note the filled states exit the boundary, but there are still empty states at the corners. (Right) Fermi surface for a very strong potential.

3.1.4 Bloch's theorem

Bloch's theorem is central to constructing wavefunctions for periodic systems. This asks how come we can use a plane wave to describe the wavefunction of an electron, even if we have a large periodic potential. The solution is we use a modified periodic function

Bloch's theorem

Theorem 3.1.1. *Bloch's theorem. The wavefunction of an electron in a periodic potential is given by*

$$\psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}^{\alpha}(\mathbf{r}) \quad (3.12)$$

where the exponential term on the right hand side is a plane wave and the second part is the Bloch function. Moreover, you can represent any wavefunction as a product of a wave function and some other function, and here the Bloch function has the periodicity of the structure in consideration, i.e. if the crystal has periodicity \mathbf{R} then $u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r})$. The index α labels each state at \mathbf{k} in the reduced zone scheme.

In a crystal,

$$u_{\mathbf{k}}^{\alpha}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{G},\mathbf{k}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (3.13)$$

therefore

$$\Psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{G},\mathbf{k}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (3.14)$$

which is 0 unless the Laue condition Eq. (1.33) is satisfied.

Remark. We've actually been using Bloch's theorem implicitly. Refer back to Eq. (3.3) which had no periodic potential and so $u = 1$.

3.2 Tight binding model

Once $V(\mathbf{r})$ gets large we can't treat it as a perturbation. Instead we can take the opposite limit to the nearly free electron model - that **the electrons spend most of their time bound to the ionic cores, and can occasionally hop from atom to atom** - this is the *tight-binding model*. We will only look at this in 1 dimension, but it's the basis to all advanced band structure calculations. The derivation has historically not appeared in the past 5 years so you can skip to Eq. (3.22).

In the 1D chain model the electrons are well localised (on the ionic cores) so we can start by thinking about their atomic orbitals. Each atom is labelled with a number n , and we write the

atomic orbital for the isolated atom as $|n\rangle$. Moreover,

- Assume N atoms and site N is identical to site zero, i.e. periodic boundary conditions.
- Assume atomic orbitals are orthogonal $\langle n|m\rangle = \delta_{nm}$
- The trial wavefunctions for electrons are $|\psi\rangle = \sum_n \phi_n |n\rangle$ where ϕ_n are some functions.

Now, we want to find the ϕ_n . To do this we write the Schrödinger equation in matrix form so that

$$\sum_m H_{nm} \phi_m = \sum_m \langle n|H|m\rangle \phi_m = E \phi_n \quad (3.15)$$

Now, the Hamiltonian is the sum of kinetic and potential terms, where the kinetic energy is that of the electron and the potential term is the sum of potentials from the nucleus at site j . Then

$$H = K + \sum_j V_j \quad (3.16)$$

$$H |m\rangle = (K + V_m) |m\rangle + \sum_{j \neq m} V_j |m\rangle \quad (3.17)$$

$$= E_{\text{atomic}} |m\rangle + \sum_{j \neq m} \langle n|V_j|m\rangle |m\rangle \quad (3.18)$$

Since we allow electrons to transfer between electrons, we require n, m to be close. We approximate the potential element $\langle n|V_j|m\rangle$ as

$$\sum_{j \neq m} \langle n|V_j|m\rangle = \begin{cases} V_0 & n = m \\ -b & n = m \pm 1 \\ 0 & \text{otherwise} \end{cases} \quad (3.19)$$

where V_0 is a shift of the energy at the m th nucleus due to the other nuclei (a potential barrier) and b determines the strength of the hopping. Then we can write the Hamiltonian as

$$H_{nm} = E_0 \delta_{nm} - b(\delta_{n+1,m} + \delta_{n-1,m}) \quad (3.20)$$

where $E_0 = E_{\text{atomic}} + V_0$. We see b depends on the atomic spacing a , and is large when a is small. In 1D, we propose our solution to be a normalised plane wave

$$\phi_n = \frac{e^{-ikna}}{\sqrt{N}} \quad (3.21)$$

Lemma 3.2.1. *The above choice of ϕ_n solves the Schrödinger equation.*

Proof. By direct substitution:

$$\begin{aligned} \sum_m H_{nm} \phi_m &= E_0 \phi_n - b(\phi_{n+1} + \phi_{n-1}) \\ &= E_0 \frac{e^{-ikna}}{\sqrt{N}} - b \left[\frac{e^{-ik(n+1)a}}{\sqrt{N}} + \frac{e^{-ik(n-1)a}}{\sqrt{N}} \right] \\ &= \frac{e^{-ikna}}{\sqrt{N}} [E_0 - b \underbrace{(e^{-ika} + e^{ika})}_{2 \cos(ka)}] \\ &= E \phi_n \end{aligned}$$

□

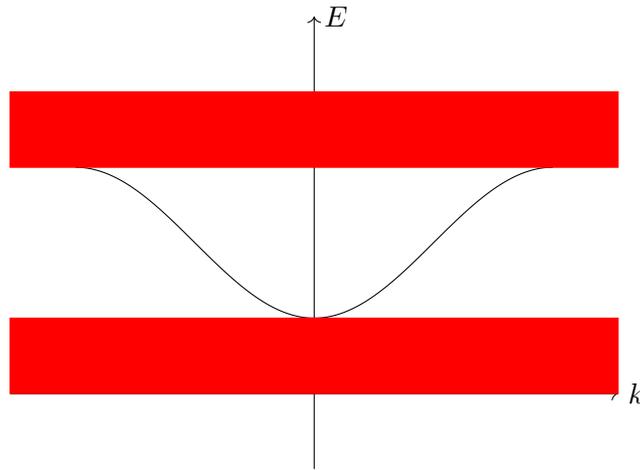


Figure 3.6: The energies of electrons in the tight binding model. The red rectangles indicate the bandgaps, where states cannot lie.

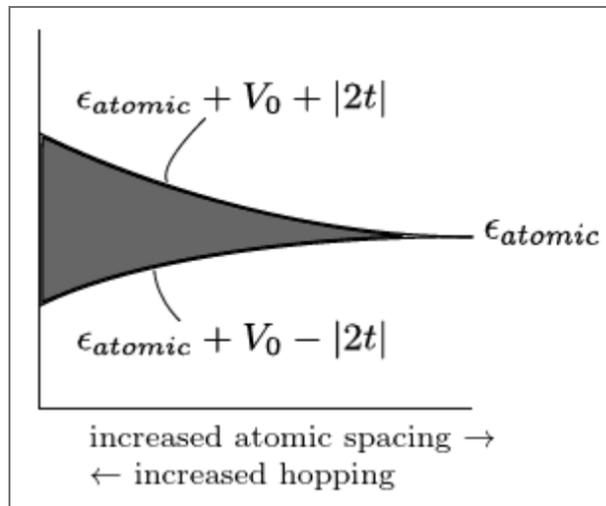


Figure 3.7: Dependence of bandwidth on interatomic spacing, reproduced from Steve Simon’s *The Oxford Solid State Basics*. Note that $\epsilon_{\text{atomic}} = E_{\text{atomic}}$ and $t = b$ to reconcile our notation.

Therefore

$$E = E_0 - 2b \cos(ka) \quad (3.22)$$

This means we have a **band of allowed states** surrounded by bandgaps as seen in Fig. 3.6. Now, the cosine curve has peaks at ± 1 , so if we plot everything in the **reduced zone scheme**, our electron dispersion in terms of the atomic spacing looks something like

Unlike free electrons, the electron dispersion in Fig. 3.6 has a maximum energy ($E_0 + |V_0| + |2b|$) as well as a minimum energy ($E_0 + |V_0| - |2b|$). Electrons only have eigenstates within a certain energy **band**. The word “band” is used both to describe the energy range for which eigenstates exist, as well as to describe one connected branch of the dispersion curve. (In this picture there is only a single mode at each k , hence one branch, hence a single band.)

Definition 3.2.1. The energy gap between the bottom of the band and the top of the band is called the **bandwidth** or **bandgap**.

Within the bandgap, there is at least one k -state having that energy, but outside the bandgap, no such k -states exists. In our case, the bandwidth is $|4b|$ and is determined by the magnitude of the hopping, which depends on nuclei spacing since hopping depends on orbital overlap from nuclei. This behaviour is shown in Fig. 3.7.

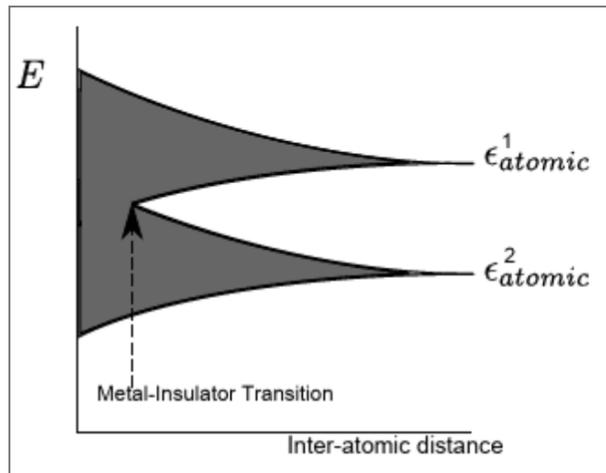


Figure 3.8: Dependence of energy on interatomic spacing for an atom with multiple orbitals, reproduced from Steve Simon's *The Oxford Solid State Basics*. Note that $\epsilon_{\text{atomic}} = E_{\text{atomic}}$ and the labels 1,2 denote each orbital.

Interpreting the electron dispersion

This is a small aside to if you don't understand how to interpret Fig. 3.7. The vertical axis is usually energy (or frequency if you happen to read *phonon* dispersions) whilst the x axis is the atomic spacing. As a increases, we see that the energies start to converge to E_{atomic} which makes sense since as the atoms get far away, their effect on electrons is much weaker.

However we see as interatomic spacing decreases, the energy bandwidth gets larger, because more orbitals overlap to a greater extent on average, which increases hopping potential and the ability for electrons to seriously gain or decrease in energy.

Now, on that note, refer back to Fig. 1.1. We saw that ionic bonding occurs when electrons transfer between atoms - this is exactly what we are modelling here by way of electron 'hops'. Moreover we created bonding and antibonding orbitals of lower and higher energies respectively. We see that we create effectively the same thing, we have a range of energies that increase and a range that decrease.

3.2.1 Multiple orbitals in the unit cell

Now what if we have a more complicated atom where multiple orbitals can partake in bonding? Then we will have multiple *branches* of the electron dispersion as seen in Fig. 3.8.

To interpret this, continue the black lines all the way to the E axis - then we will have 3 regions - the top branch occupied by E_{atomic}^1 , the bottom branch E_{atomic}^2 and the middle region.

We see that the middle region is an *intersection* of the two orbitals - this means electrons can continuously transfer between the 2 orbitals - i.e. we can get a current of electrons - i.e. a **metal**. This is why their first point of intersection is called the **metal-insulator transition**. The well-separated orbitals on the right is where the atomic spacing is large enough so that the material is considered an insulator.

Note that as the bands overlap, we will fill all the *lowest energy states first*, i.e. partially fill the lower and upper bands, and we have a metal.

3.3 Consequences of the periodic potential

3.3.1 Effective mass

By Taylor expanding the cosine term in Eq. (3.22) to quadratic order, we have

$$E \simeq \text{const} + bk^2a^2 \quad (3.23)$$

giving a parabolic dispersion around $k = 0$. For the free electron model, we had $E = \hbar^2k^2/2m$. We suppose that there is some m^* such that

$$\frac{\hbar^2k^2}{2m^*} = bk^2a^2 \implies m^* = \frac{\hbar^2}{2ba^2} \quad (3.24)$$

and we call m^* the **effective mass**. An alternative way to derive the effective mass is to consider the group velocity

Group velocity

$$v_g = \frac{1}{\hbar} \frac{\partial E}{\partial \mathbf{k}} \quad (3.25)$$

where we have boldfaced the k to show this applies to any dimension.

Then the ‘group acceleration’ (in 1D)

$$\frac{\partial v}{\partial t} = \frac{1}{\hbar} \frac{\partial^2 E}{\partial t \partial k} = \frac{1}{\hbar} \frac{\partial^2 E}{\partial k^2} \frac{\partial k}{\partial t} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} F \quad (3.26)$$

Then by Newton’s laws

$$F = m^* \frac{\partial v}{\partial t} \implies m^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}} \quad (3.27)$$

If $E = \text{const} + bk^2a^2$ we recover our original result.

3.3.2 Holes

We can describe a system by considering a few empty states close to the top of a band - **holes** - rather than doing the maths for a large number of electrons which have poorly characterised states. For a full band of electrons, each with $\mathbf{k}_j, \mathbf{v}_j, E(\mathbf{k}_j)$, and with $E = 0$ defined as the top of the band,

$$\sum_j \mathbf{k}_k = 0 \quad (3.28)$$

If you remove an electron (e.g., exciting it to another band) then a hole is created in the original band with wavevector \mathbf{k}_h so that

$$\mathbf{k}_h = \sum_{j \neq l} \mathbf{k}_j = -\mathbf{k}_l \quad (3.29)$$

where \mathbf{k}_l is the wavevector for the removed electron. Moreover, $E(\mathbf{k}_h) = -E(\mathbf{k}_l)$

$$\mathbf{v}_h = \frac{1}{\hbar} \nabla_{\mathbf{k}_h} (E_h) = \frac{1}{\hbar} \nabla_{\mathbf{k}_l} (-E(\mathbf{k}_l)) = \mathbf{v}_l \quad (3.30)$$

and therefore

$$m_h^* = -m_e^* \quad (3.31)$$

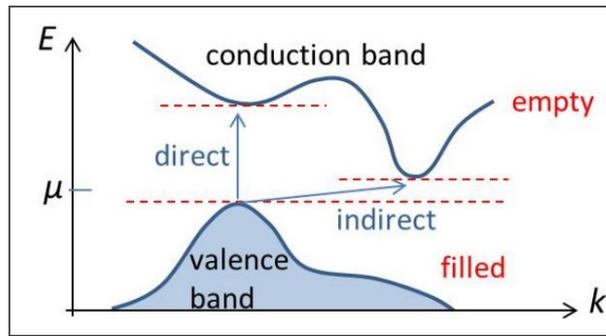


Figure 3.9: Direct and indirect bandgaps

3.3.3 Optical Properties

For insulators and semiconductors (see Fig. 3.9), a photon can only be absorbed if it has an energy larger than the band gap between filled states and empty states. This gives the distinctive colour of many crystals. Adding impurities can change the colour, even for a very small fraction of impurities, as it changes the band structure. The direct band gap transitions will dominate, although there may be a small effect from the indirect gap. In metals the photons are all absorbed, excite the electrons, and are then re-emitted, leading to a ‘shiny’ surface (when it’s not corroded).

Chapter 4

Semiconductors and Real bandstructures

From now on, we will refer to the term ‘conduction band’ as CB and ‘valence band’ as VC.

4.1 Introduction to Semiconductors

4.1.1 Semiconductor Basics

As in Fig. 3.9 we have direct and indirect bandgaps between the valence and conduction bands - see Section 3.1.2 for a brief recap of the Fermi surfaces of metals and insulators. We define

Definition 4.1.1. The minimum energy needed to reach the conduction band is the **conduction energy** E_c

Definition 4.1.2. The minimum energy needed to *leave* the valence band is the **valence energy** E_v

The direct bandgap is therefore $E_g = E_c - E_v$. We ignore the existence of any indirect bandgaps by assuming our Fermi surfaces are parabolic as in Eq. (3.23). Assume we have a full valence band and empty conduction band and excite an electron to get a hole.

The hole then relatively attracts electrons, so itself moves down the valence band to a lower energy. It therefore costs energy to excite the hole as

$$E_{\text{hole}} = \text{const} + \frac{\hbar^2 |\mathbf{k} - \mathbf{k}_{\text{max}}|}{2m_h^*} \quad (4.1)$$

Moreover, there are 2 types of holes. We first want to talk about the *curvature* of the bands, characterised by the second derivative $\frac{\partial^2 E}{\partial k^2}$. A sad-looking (*n*-shape) parabola has a negative curvature (second derivative is negative) - this is given by the valence band. The conduction band has a positive curvature. In particular,

Definition 4.1.3. A **heavy hole** has a less negative curvature than a **light hole**.

This means a heavy hole moves more gradually down the conduction band than a light hole. The ratio of the energies is on the order of 10, in units of the electron mass.

Doping

Doping is the idea of introducing impurities (other substances, called **dopants**) to modify the bandstructure of semiconductors. You should know what these terms are for the exam.

Definition 4.1.4. An **intrinsic** semiconductor is a pure material. The number density of electrons in the CB $n = p$, the the number density of holes in the VB.

Definition 4.1.5. An **extrinsic** semiconductor contains impurities, or **dopants**. Here, $n \neq p$.

Moreover, there are different types of dopants

Definition 4.1.6. A **donor** or **n-type** dopant has one extra electron.

- The electron is usually weakly bound to the donor atom
- Therefore it is easily excited to the CB

Definition 4.1.7. An **acceptor** or **p-type** dopant has one fewer electron.

- The electron in VB is easily captured by the acceptor atom
- Therefore it leaves a mobile hole in VB

4.1.2 Statistical Mechanics of Semiconductors

The density of states in 3D of free electrons is

$$g(E) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} \quad (4.2)$$

We can write the correspond density of states for electrons in CB and holes in VB:

$$g_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} \quad g_v(E) = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} (E_v - E)^{1/2} \quad (4.3)$$

For a fixed chemical potential μ (at low T) the number density of electrons in the CB is

$$n(T) = \int_{E_c}^{\infty} \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} e^{-\beta(E-\mu)} dE \quad (4.4)$$

where we have used the fact that the number density $n(T) = \int_{E_c}^{\infty} g_c(E) n_F dE$ where n_F is the Fermi-Dirac distribution as in Eq. (2.6) approximated as $\exp\{\beta(E - \mu)\}$ for $\beta(E - \mu) \gg 1$.

To solve this integral, we can temporarily replace the prefactors before the integral with the symbol C and make the substitution $y^2 = E - E_c$ and $2ydy = dE$

$$n(T) = C \int_0^{\infty} y e^{-\beta y^2} dy, = -2C \frac{\partial}{\partial \beta} \left(\int_0^{\infty} e^{-\beta y^2} dy \right) = -2C \frac{\partial}{\partial \beta} \left(\frac{1}{2} \sqrt{\frac{\pi}{\beta}} \right) = \frac{C\sqrt{\pi}}{2\beta^{3/2}}, \quad (4.5)$$

where we have used the standard result for the integral in parentheses (which you don't need to memorise). We can follow the exact same procedure for $p(T)$, the number density of holes since the form is almost exact the same except $E_c - E$ gets replaced with $E - E_v$ and we use the effective mass of holes instead. Therefore

$$n(T) = \frac{1}{4} \left(\frac{2m_e^* k_B T}{\pi \hbar^2} \right)^{3/2} e^{-(E_c - \mu)/k_B T} \quad p(T) = \frac{1}{4} \left(\frac{2m_h^* k_B T}{\pi \hbar^2} \right)^{3/2} e^{-(\mu - E_v)/k_B T} \quad (4.6)$$

If we product these things together we get the **Law of Mass Action**.

$$n(T)p(T) = \frac{1}{2} \left(\frac{k_B T}{\pi \hbar^2} \right)^{3/2} (m_e^* m_h^*)^{3/2} e^{-(E_c - E_v)/k_B T} \quad (4.7)$$

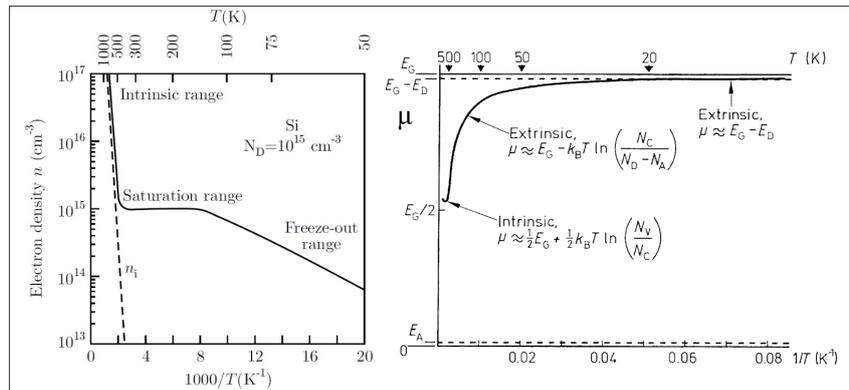


Figure 4.1: Left: Temperature dependence of electron density in n-doped Si. From *Singleton*. Gradient of n_i depends E_g . Right: Temperature dependence of chemical potential in n-doped Ge. From Hook and Hall. The chemical potential moves in the opposite direction for p-type material. Note **you only need to know the shapes of the graphs, each section of the graphs and what quantities each axis represents**

The only things you need to know for this are

Law of Mass Action

The quantity $n(T)p(T)$ is independent of μ (chemical potential), and therefore works for both extrinsic and intrinsic semiconductors.

Intrinsic

This is when $n = p$. Taking the ratio $n/p = 1$ and

$$\frac{n}{p} = \left(\frac{m_e^*}{m_n^*} \right)^{3/2} e^{-(E_c + E_v - 2M)/k_B T} = 1 \quad (4.8)$$

We want to rearrange for μ . This gets us

$$\mu = \frac{1}{2} (E_c + E_v) + \frac{3}{4} k_B T \ln \left(\frac{m_h^*}{m_e^*} \right) \quad (4.9)$$

If $T = 0$, μ is in the middle of the bandgap.

Extrinsic

$n \neq p$ but by Law of mass action we have $np = n_i^2$ where n_i is the **intrinsic carrier density** and by electrical neutrality $n - p = N_D^+ - N_A^-$ where N_D^+, N_A^- are the **concentrations of ionised donors and acceptors respectively**.

- A semiconductor will behave like an intrinsic semiconductor at high temperature, where carriers are easily thermally activated across the energy gap.
- As temperature is reduced a region is reached where thermal activation is small, but any donor or acceptor atoms are ionised and charge carriers are available
- At much lower temperatures these start to ‘freeze out’ and e.g. the electrons are stuck near the donor atoms

The information is summarised in Fig. 4.1. Note you only need to know what the general shape of each graph is and what the axes variables are.

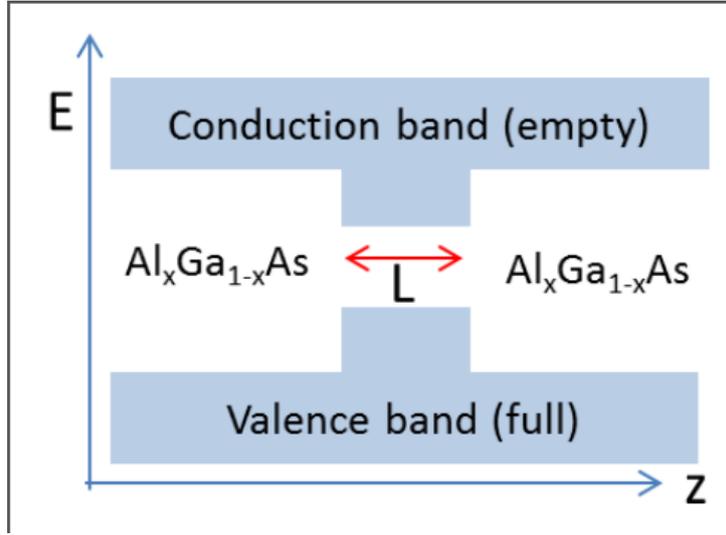


Figure 4.2: 2 layers of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ with GaAs sandwiched in-between them (the steps in the bands). These steps act as potential wells.

4.1.3 Transport in semiconductors

Under an electric field, electrons and holes obey the Lorentz force law

$$\begin{aligned} m_e^* \left(\frac{d\mathbf{v}_e}{dt} + \frac{\mathbf{v}_e}{\tau_e} \right) &= -e\mathbf{E} \\ m_h^* \left(\frac{d\mathbf{v}_h}{dt} + \frac{\mathbf{v}_h}{\tau_h} \right) &= e\mathbf{E} \end{aligned} \quad (4.10)$$

By considering the steady state you can show that $\mathbf{v}_e = \mu_e \mathbf{E}$ and $\mathbf{v}_h = \mu_h \mathbf{E}$, where μ_e and μ_h are the electron and hole **mobilities**. The current is given by

$$\mathbf{j} = -ne\mathbf{v}_e + pe\mathbf{v}_h = (ne\mu_e + pe\mu_h) \mathbf{E} = \sigma \mathbf{E}, \quad (4.11)$$

where $\sigma = ne\mu_e + pe\mu_h$. in summary

- intrinsic: electrons and holes both contribute to conductivity
- extrinsic: majority carriers dominate (typically)
- Can use Hall effect to determine which are majority carriers.

4.2 Bandstructure engineering and devices

4.2.1 Designer bandgaps

We can tailor bandgaps for specific applications with dopants. For alloys, suppose we dope AlAs with Ga, then the alloy formed is denoted $\text{Ga}_{1-x}\text{Al}_x\text{As}$ then the bandgap is approximately $[(1-x) \times 1.4 + x \times 2.7] \text{eV}$. The energy gap for GaAs at $k = 0$ is 1.4 eV, while for AlAs it is 1.4 eV.

4.2.2 Quantum wells

We can sandwich a thin layer of size L of GaAs between 2 layers of $\text{Ga}_{1-x}\text{Al}_x\text{As}$. This creates a quantum well which can trap electrons as in Fig. 4.2.

Suppose we orient the material face on in the $x - z$ plane where the material increases with height on the z -axis.

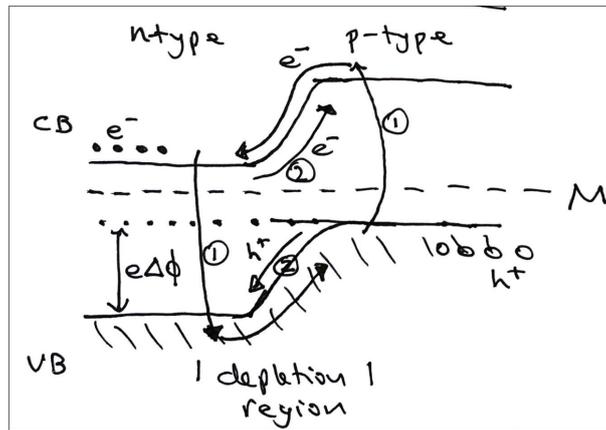


Figure 4.3: Figure of p-n junction. Reproduced from written lecture notes.

Modulation doping

Electrons and holes fall into the lower energy well where there are no impurities to scatter from.

Carriers in the well

The carriers are trapped in bound states in the z -direction, but are free to move in the $x - y$ plane, like a 2D electron gas.

4.2.3 p-n junction

A p-n junction is made by sticking an n-doped material to a p-doped material. At the interface, electrons from the conduction band in the n-doped region can drop down to annihilate the holes in the valence band of the p-doped material, with an energy gain of E_g , forming a **depletion region** in the middle where there are no carriers. However, because of the net charge left behind by the charged ions, moving the electrons across the depletion region costs an energy $-e\nabla\phi$, where $\Delta\phi$ is the electrostatic potential difference between the n-doped and p-doped regions. This is summarised in

Moreover, you need to know how currents evolve

Currents in a p-n junction

1. Electrons and holes are excited across the gap and swept through by the potential difference $\Delta\phi$.
2. The **saturation current** is an exponential-decay law

$$I_0 = Ae^{-E_g/k_B T} \quad (4.12)$$

where A is a constant which depends on the physical properties of the system.

3. Electrons and holes are excited over the potential barrier
4. In equilibrium at zero bias, there is no net current.

Diodes

They have a forward bias, i.e. allow current in one direction only. The potential barrier is smaller, around 1 eV but the bandgap is the same.

The total current is

$$I_{\text{TOT}} = I_0 \left(\exp \left[\frac{eV}{\beta_0 T} \right] - 1 \right) \quad (4.13)$$

Plotting the diode characteristic (I-V graph) we get 3 distinct regions as seen in Fig. 4.4. Sum-

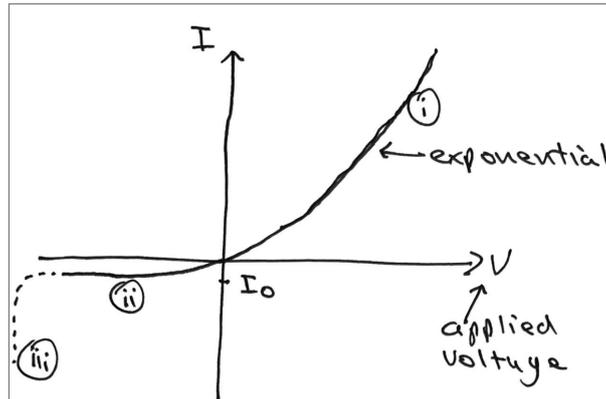


Figure 4.4: IV characteristic for a real diode.

marising:

- i Forward bias (current moves in forwards direction)
- ii Reverse bias (current moves backwards, which it shouldn't for a diode).
- iii Zener breakdown: reverse bias so strong quantum tunnelling of electrons occurs from VB to CB (from p-side to n-side) which breaks the diode.

LEDs

This is how they work

1. p-n junction is again in a forwards bias.
2. Electrons move from n-type to p-type CB and then fall into VB, recombining with hole and emitting a photon
3. Colour of LED tuned by bandgap size (since it will determine energy and thus wavelength of emitted photon)
4. Uses **direct bandgap semiconductors only**, i.e. not Si!

Solar cells

- p-n junction exposed to light
- Electron+hole pair created near depletion zone
- This pair accelerated by electrostatic potential - forms a **photocurrent** of carriers
- Crystalline Si cells currently dominate most solar cells.

Transistors

A MOSFET is a **Metal-Oxide-Semiconductor-Field-Effect-Transistor**. It is a semiconductor with a layer of oxide (an insulator) on top, which is then layered by a metal.

Consider the surface of a p-type material. Then with no voltage applied, we have a few conduction electrons in the CB and a bunch of holes in the VB as in Fig. 4.5a. Then if we apply a voltage, we get Fig. 4.5b. Specifically, we get an **inversion layer** at the surface where the carrier type is charged. We use this effect to make our transistor. The metal layer is connected to a gate where applied voltage will pass through. The semiconducting part is formed of 2 n-type lobes (one connected to a source, the other to a drain) surrounded by the depletion layer. The

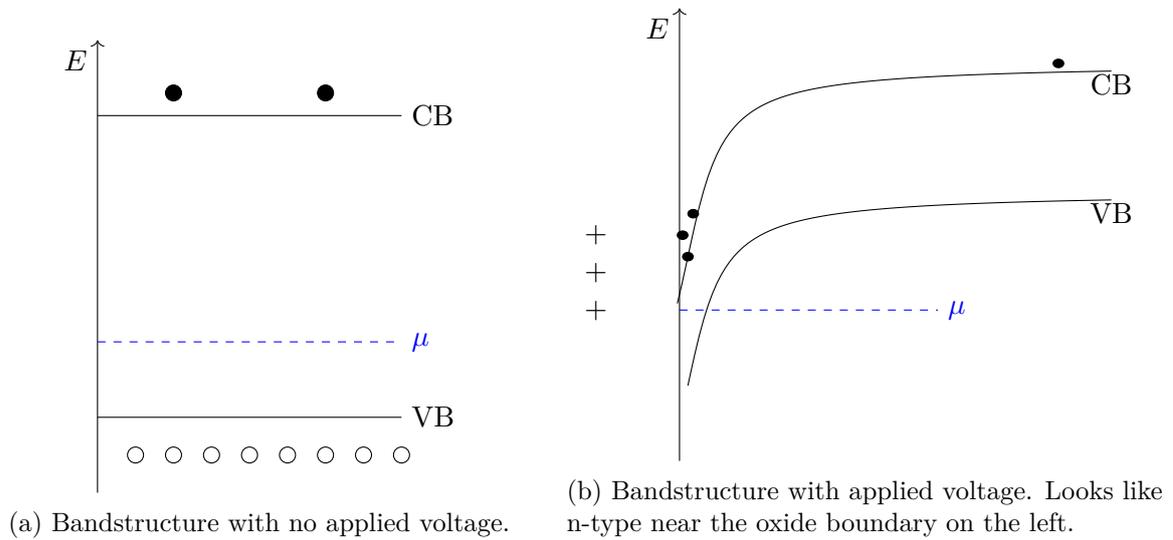


Figure 4.5: Transistor (p-type) bandstructure at the semiconductor-oxide boundary.

rest of the space is filled with p-type material. This can be seen in Fig. 4.6a. Little current passes through the source and drain.

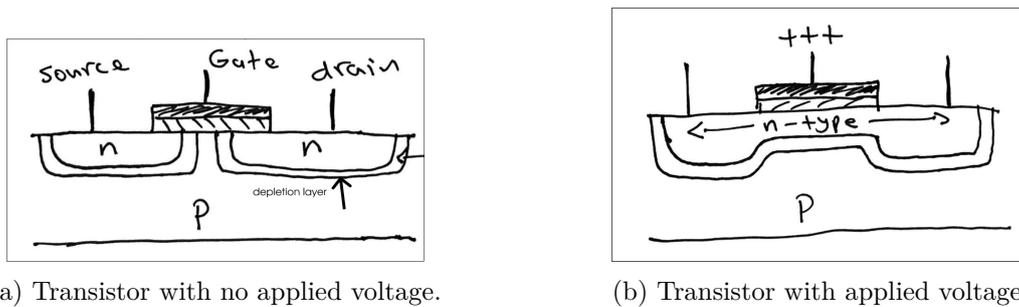


Figure 4.6: Transistor with and without voltage. Screenshots taken from Dr Paul Goddard's lectures.

Upon applying a voltage through the gate we get Fig. 4.6b. The n-type lobes merge and a high current passes from the source to the drain.

4.3 Measuring Bandstructures

4.3.1 Effect of magnetic field

Electrons obey the Lorentz force law

$$\hbar \frac{d\mathbf{k}}{dt} = -e\mathbf{v} \times \mathbf{B} \quad (4.14)$$

This force is perpendicular to \mathbf{B} and \mathbf{v} so doesn't change the energy. Therefore, an electron in a k -state stays at exactly the same energy on application of a magnetic field, but moves through other k -states with the same energy, hence an electron will **traverse an orbit on a surface of constant energy in a plane perpendicular to the magnetic field.**

In a metal, the surface of constant energy that interests us the most is the Fermi surface, because it is the electrons at this energy (the Fermi energy E_F) that define many of the physical properties of the material.

Equation (3.25) tells us

Real-space velocity of an electron at a point on the Fermi surface is always perpendicular to the Fermi surface at that point.

Knowing this, we can try to find the orbital period T . We can do this by performing a path integral over time (we must use a path integral since the path can change)

$$T = \oint dt = \oint \frac{dt}{dk} dk = \oint \frac{\hbar}{e|\mathbf{v} \times \mathbf{B}|} = \oint \frac{\hbar}{ev_{\perp}B} \quad (4.15)$$

where v_{\perp} is the component perpendicular to \mathbf{B} which we just established is Eq. (3.25) but differentiating w.r.t k_{\perp} instead. Substituting this in we get

$$T = \frac{\hbar^2}{eB} \oint \left(\frac{dE}{dk_{\perp}} \right)^{-1} dk \quad (4.16)$$

Now, we can invert the derivative (we assume we can since the energy is only a function of wavenumber and vice-versa, alternatively use chain rule). Doing this we get

$$T = \frac{\hbar^2}{eB} \frac{dA_k}{dE} \quad (4.17)$$

such that we define

Cyclotron mass

$$\omega_C = \frac{eB}{m_{\text{CR}}^*} \qquad m_{\text{CR}}^* = \frac{\hbar^2}{2\pi} \frac{dA_k}{dE} \quad (4.18)$$

where dA_k is the infinitesimal area (1-form) of the Fermi surface between 2 infinitesimally close contours on the Fermi surface. Note that the cyclotron mass is not necessarily the same as the effective mass

For a nearly free electron, we have a spherical Fermi surface so the orbit area is $A_k = \pi k_F^2$. The orbit energy is $E_k = \hbar^2 k^2 / 2m^* = \hbar^2 A_k^2 / 2\pi m^*$. We then get that $m^* = m_{\text{CR}}^*$, so here the 2 quantities coincide.

Landau Levels

The magnetic field quantises angular momentum - we should take this into account.

At $\mathbf{B} = \mathbf{0}$ we have effectively free electrons, so the Fermi surface is spherical and the energy is given by

$$E = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2 + k_z^2) \quad (4.19)$$

Now give a magnetic field aligned along $\hat{\mathbf{z}}$, so $\mathbf{B} = B\hat{\mathbf{z}}$. Then we have **free orbits in a plane perpendicular to \mathbf{B}** . Therefore the energy has both perpendicular and parallel components, so

$$E = \underbrace{\left(l + \frac{1}{2} \right) \hbar \omega_C}_{\text{Parallel to } \mathbf{B}} + \underbrace{\frac{\hbar^2 k_z^2}{2m^*}}_{\text{Parallel motion unaffected}} \quad (4.20)$$

These allowed energy levels are called **Landau levels**. Moreover, this turns the Fermi surface in k -space to be a collection of concentric **Landau tubes** as seen in Fig. 4.7. The k -space area of the l^{th} orbit is

$$A_l = \pi(k_x^2 + k_y^2) = \left(l + \frac{1}{2} \right) \frac{2\pi eB}{\hbar} \quad (4.21)$$

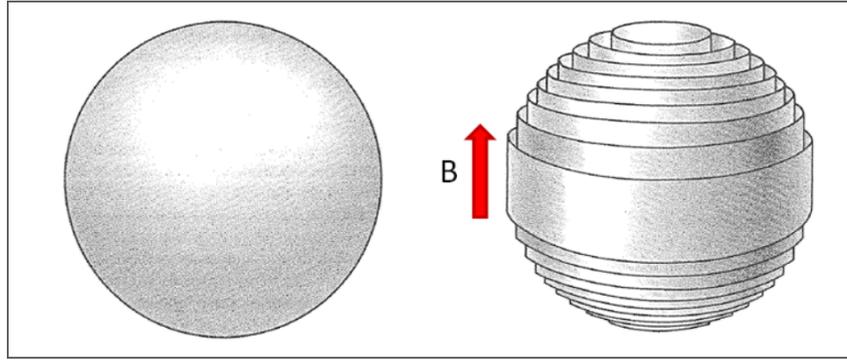


Figure 4.7: Left: Free-electron Fermi surface. Right: Formation of Landau tubes on application of a magnetic field. Adapted from Hook & Hall.

from equating the k_x, k_y components of the quantised and semiclassical energies. Moreover, much like how in the free electron model, filled states lie inside the Fermi sphere, here the filled electron states lie inside the *Landau tubes*. If you were to place the tubes on top of the sphere in Fig. 4.7 then we see empty states are created where the gaps are between the tubes and the sphere. The density of states then for Landau levels is shown in Fig. 4.8.

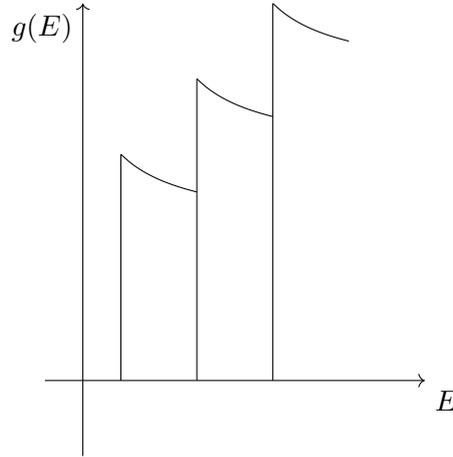


Figure 4.8: Density of states of the Fermi surface when a magnetic field is applied. The sharp jumps are due to accessing a new Landau tube, with falloff due to motion along k_z .

- A_l (the tube cross section in Eq. (4.21)) increases as B increases in strength.
- Density of allowed states at E_F oscillates with increasing B as more tubes appear in the Fermi surface
- As a result, properties of metals will oscillate with B

4.3.2 Quantum Oscillators

These are oscillations of physical properties as a function of B , and are **periodic in $1/B$** , which has units of teslas, despite being a frequency. These are observed in magnetisation (de Haas-van Alphen effect), resistivity (Shubnikov-de Hass effect), sound velocity etc.

Recall each frequency of oscillation is caused by Landau levels traversing an **extremal cross-section** of the Fermi surface in the plane perpendicular to \mathbf{B} . By Eq. (4.21), we can consider 2 adjacent extremal Fermi surfaces with area A_{ext} :

$$\left(l + \frac{1}{2}\right) \frac{2\pi e B_l}{\hbar} \qquad \left((l+1) + \frac{1}{2}\right) \frac{2\pi e B_{l+1}}{\hbar} \qquad (4.22)$$

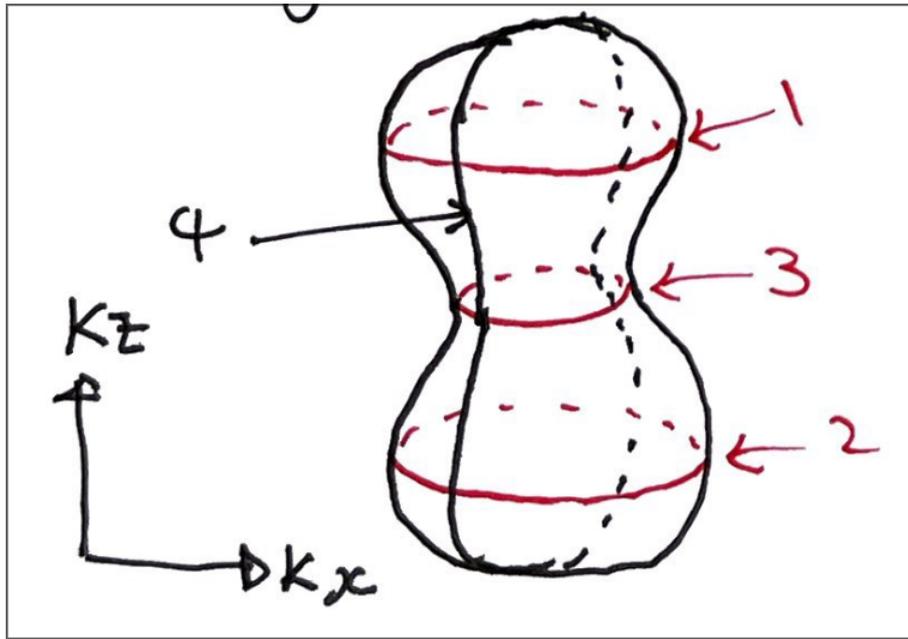


Figure 4.9: Peanut FS with 4 extremal closed orbits displayed. The magnetic field is oriented in the \hat{z} direction. Drawn by Dr. Paul Goddard.

Then the period of oscillation (measured in inverse teslas) is

$$\Delta\left(\frac{1}{B}\right) = \frac{1}{B_{l+1}} - \frac{1}{B_l} = \frac{2\pi}{\hbar A_{\text{ext}}} \quad (4.23)$$

Therefore

Frequency of quantum oscillations

$$F = \frac{1}{\Delta(1/B)} = \frac{\hbar A_{\text{ext}}}{2\pi e} \quad (4.24)$$

where F is the frequency measured in teslas. Additionally

Quantum oscillations require **closed** extremal Fermi surface orbits.

As an example, we can consider a peanut-looking Fermi surface (you can actually measure this) in Fig. 4.9 We see that for B parallel to z , we have 3 extremal orbits marked in red, 1,2,3, in Fig. 4.9 (remember magnetic fields cause *perpendicular motion*) whereas if it was parallel to x , then we get only 1 extremal orbit marked in black.

In order to map out the Fermi surface,

1. Measure quantum oscillations in different directions of applied B
2. Apply a Fourier transform to your data to get frequencies
3. Use these to map out your Fermi surface.

Finally, a note about quantum oscillations to close off this subsection

Quantum oscillations

Quantum oscillations increase with

- decreasing T (period) - leads to sharper Fermi surfaces.
- increasing B - better-resolved Landau levels.
- An electron will do many orbits before scattering if $\omega_c \tau \gg 1$ where τ is a scattering time

4.3.3 Cyclotron resonance (CR)

We use electromagnetic radiation to excite electrons between Landau levels and find ω_c

CR in metals

The **skin depth** δ (from PX285 Electromagnetic Theory) for metals is approximately

$$\delta = \sqrt{\frac{2\rho}{\omega\mu}} \quad (4.25)$$

where ω is the angular frequency of applied current, μ is the permeability of the metal and $\rho = 1/\sigma$ is the resistivity of the metal. This skin depth is the depth below the surface of the conductor at which the current density has fallen to $1/e$ (e here being the exponential constant).

Now, the skin depth means that radiation cannot access the bulk of the metal. Therefore, if you apply a range of magnetic fields B to the metal, we can find the maxima in absorption by

$$\omega = j\omega_c = j \frac{eB}{m_{\text{CR}}^*} \quad (4.26)$$

where $j \in \mathbb{Z}$ and m_{CR}^* is the cyclotron mass of an extremal FS orbit. An alternative condition holds when $\omega_c\tau \gg 1$ and then

$$\Delta \left(\frac{1}{B} \right) = \frac{e}{\omega m_{\text{CR}}^*} \quad (4.27)$$

CR in semiconductors

The conductivity of semiconductors is generally small (much smaller than a metal), the skin depth is large and the microwave field fully penetrates the sample. The selection rule for angular momentum and LL states that $\Delta l = \pm 1$ so Eq. (4.27) holds under the correct conditions and m_{CR}^* is that of a general **extremal orbit** instead.

- Low temperatures needed to reduce scattering
- Additional radiation $\hbar\omega_0 \gg E_g$ can be used to create additional charge carriers
- Light and heavy holes seen
- More than 1 electron resonance observed if CB is anisotropic - note that m_{CR}^* can change across BZs!

4.4 2D electron gas (2DEG)

You can trap an electron in a semiconductor device (e.g. a MOSFET or a quantum well) such that it is free to move in the x and y directions, but trapped in the z -direction. Your boundary conditions on the electron wavefunction is

$$\psi(x, y, z) = \begin{cases} 0 & z = 0, a \\ \psi(x + L, y + L, z + L) & \end{cases} \quad (4.28)$$

where L is the length of the sample along x, y . You've seen this already when solving for potential wells and

$$\psi = e^{ik_x x} e^{ik_y y} \sin(k_z z) \quad (4.29)$$

where $k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{\pi n_z}{L}$, i.e. plane waves in the $x - y$ plane and a standing wave along z . The energy eigenvalue is therefore

$$E = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2) + \frac{n_z^2 \pi^2 \hbar^2}{2m^* a^2} \quad (4.30)$$

i.e. the energy is the sum of free electron motion in the $x - y$ plane and the energy of the potential well in z that the electron is trapped in - makes sense.

4.4.1 Density of states

In 2D, the Fermi surface is a circle embedded in k -space along k_x, k_y . Therefore

$$g(k)dk = 2 \times \frac{2\pi k dk}{(2\pi/L)^2} = 2 \times \frac{\text{area of ring radius } k \text{ and thickness } dk}{\text{area of one state}} = \boxed{\frac{Ak}{\pi} dk} \quad (4.31)$$

where the prefactor of 2 comes from **spin degeneracy** of the electron and A is the area in the xy plane. We can cast this in terms of energy by using the chain rule using Eq. (4.30), setting $k = \sqrt{k_x^2 + k_y^2}$ and differentiating with respect to k to get

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m^*} \implies g(E)dE = g(k)dk \frac{dE}{dk} = \frac{Am^*}{\pi \hbar^2} dE \quad (4.32)$$

i.e. the density of states in 2D does not depend on E !

4.4.2 Quantum Hall effect

We can use the 2DEG to discover a very unusual observation - a quantisation of the classical Hall effect seen in Section 2.2.2. Measurements show

$$\rho_{xx} \rightarrow 0 \quad \rho_{xy} = \frac{1}{\nu} \frac{h}{e^2}, \nu \in \mathbb{Z} \quad (4.33)$$

i.e. we saw **plateaus** in ρ_{xy} .

To recap, the general conductivity tensor in 2D is

$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{bmatrix} \quad (4.34)$$

but here $-\sigma_{xy} = \sigma_{yx}$ and $\sigma_{xx} = \sigma_{yy}$ assuming symmetry. We can find the resistivity tensor by taking the **inverse** of the conductivity so

$$\rho_{xx} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2} \quad \rho_{xy} = \frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2} \quad (4.35)$$

Now what we didn't discuss in Section 2.2.2 is the energy. We know from quantum modules that applying a magnetic field causes Zeeman splitting so that the energies get their degeneracy lifted. In particular, it is similar to Eq. (4.20) but instead of energy due to motion in z , since we don't have z motion, we replace it with the Zeeman energy

$$E = \left(l + \frac{1}{2} \right) \hbar \omega_c \pm \frac{1}{2} g \mu_B B \quad (4.36)$$

These are the following consequences

- LLs broadened due to scattering
- LL's split due to Zeeman lifting
- Each split contains N_{LL} electrons per unit area

This is seen in Fig. 4.10 The DOS in Eq. (4.32) after substituting N_{LL} produces

$$g(E) = \frac{2N_{LL}}{\hbar \omega_c} = \frac{m^*}{\pi \hbar^2} \quad (4.37)$$

and so

$$N_{\text{LL}} = \frac{eB}{h} \quad (4.38)$$

i.e. **the Landau Levels increase in E and B increases in strength** and whenever

$$\frac{n}{N_{\text{LL}}} = \nu \in \mathbb{Z} \quad (4.39)$$

then a whole number of LLs are *completely full* and μ lies in a gap in the DOS as seen in Fig. 4.10.

Therefore

$$\sigma_{xx} \rightarrow 0 \implies \rho_{xx} \rightarrow 0$$

and $\rho_{xy} \rightarrow 1/\sigma_{xy}$ such that

$$\rho_{xy} = \frac{B}{ne} = \frac{1}{\nu} \frac{h}{e^2} \quad (4.40)$$

this is independent of B and accounts for observations in the quantum Hall plateaus.

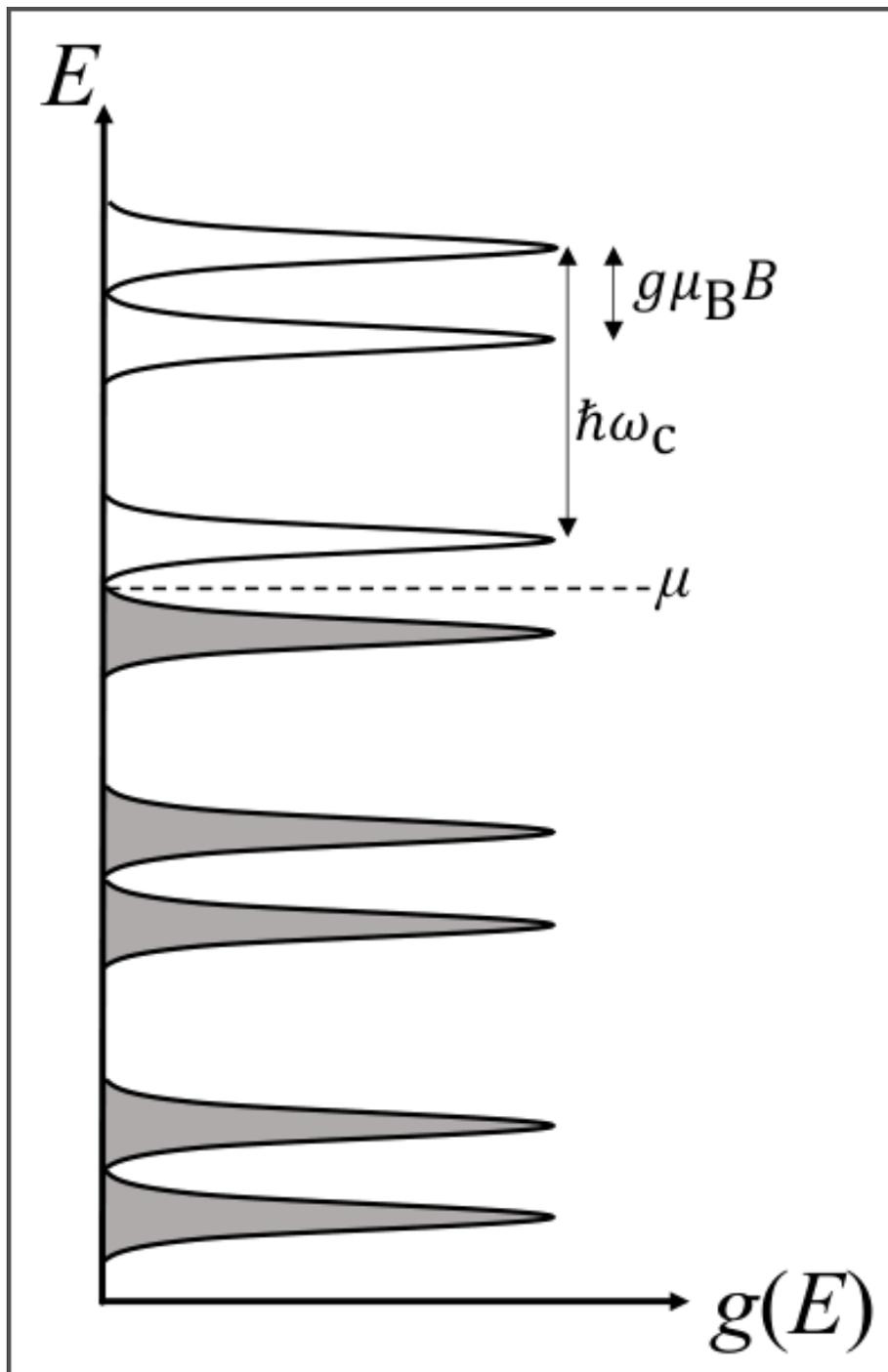


Figure 4.10: Allowed electron energy levels against density of states showing split Landau levels

Chapter 5

Magnetism

Band theory does not explain magnetism, magnetism arises from the quantum mechanical behaviour of electrons. Magnetic materials are hence testbeds of quantum and statistical theories in physics.

Disclaimer: Images in this section have been taken from Paul Goddard's lecture notes, by June they will be replaced with original images.

5.1 The basics

Classically, magnetic moments caused by current loops gives rise to magnetism. The magnetic moment is perpendicular to the loop, and is most generally given by a volume integral over some volume current loop:

$$\boldsymbol{\mu} = \frac{1}{2} \iiint \hat{\mathbf{r}} \times \mathbf{J} dV \quad (5.1)$$

where \mathbf{r} is position and \mathbf{J} is some current density. For a simple current loop in the plane that is independent of position, this reduces to the more familiar

$$\boldsymbol{\mu} = \frac{1}{2} \int I \mathbf{r} \times d\mathbf{r} \quad (5.2)$$

5.1.1 Magnetic Fields

A magnetic solid consists of a large number of atoms each with magnetic moment μ .

Magnetisation of the material, \mathbf{M} = total magnetic moment per unit volume, measured over a large scale so local variations are not seen. Magnetisation is equivalent to the induced field.

Recall in free space the magnetic field is given by $\mathbf{B} = \mu_0 \mathbf{H}$. In a magnetic material this becomes:

Magnetic field in a magnetic material

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) \quad (5.3)$$

Magnetisation in a linear material

$$\mathbf{M} = \chi \mathbf{H} \quad (5.4)$$

where we call χ 'magnetic susceptibility', it's a dimensionless quantity equal to the magnetic susceptibility induced by a field \mathbf{H} per unit volume.

Therefore, $\mathbf{B} = \mu_0 (1 + \chi) \mathbf{H} = \mu_0 \mu_r \mathbf{H}$ Remember that χ is often very small.

5.1.2 Types of magnets we will encounter

Definitions

- Paramagnet - A material with $\chi > 0$, \mathbf{M} is in **same** direction and PARAllel to \mathbf{H} .
- Diamagnet - A material with $\chi < 0$, \mathbf{M} is in the opposite direction to \mathbf{H} .
- Ferromagnet - a form of ordered magnetic state, \mathbf{M} can be non-zero in the absence of an applied field \mathbf{H} .

The number of electrons in the outer shell will usually determine whether χ is positive or negative. If the shell is full, the paramagnetic term equals zero and the atom will be diamagnetic. Whenever we have both paramagnetism and diamagnetism, paramagnetism dominates.

5.1.3 Hund's rules

Recall Hund's rules from PX3A2. The behaviour of a material depends on the filling of electron levels, and Hund's rules can be used to determine if an atom has a net magnetic moment.

5.1.4 Atom in a magnetic field

Each electron in an atom is at a position \mathbf{r}_i with momentum \mathbf{p}_i . The Hamiltonian of the electrons in zero field can be written as:

$$H_0 = \sum_i^{Z_A} \left(\frac{\mathbf{p}_i^2}{2m} + V(\mathbf{r}_i) \right) \quad (5.5)$$

for an atom with atomic number Z_A and in a potential $V(\mathbf{r}_i)$. This Hamiltonian will change when a magnetic field is applied. If the field is uniform, the vector potential is $\mathbf{A} = \frac{(\mathbf{B} \times \mathbf{r})}{2}$. We must also consider the canonical momentum $\mathbf{p} - q\mathbf{A}$ which tells us how the charged particle will behave in the \mathbf{B} field. The Hamiltonian in a field for a whole atom becomes:

$$H = H_0 + \sum_i^Z \frac{e^2}{8m} |\mathbf{B} \times \mathbf{r}_i|^2 + \mu_B \mathbf{B} \cdot (\mathbf{L} + g\mathbf{S}) \quad (5.6)$$

where H_0 is the Hamiltonian in zero field, and the subsequent terms are the diamagnetic and paramagnetic term respectively. \mathbf{L} and \mathbf{S} can be determined from Hund's rules

In equilibrium our system wants to minimise energy, therefore terms want to be a minimum value. The paramagnetic term will have its largest negative value if \mathbf{B} is **antiparallel** to \mathbf{L} and \mathbf{S} .

5.1.5 Statistical mechanics

We recap some brief equations from statistical mechanics. For our purposes, the probability distribution we will use for energy is a Boltzmann distribution, where the state with energy E_i has a probability

$$p_i \propto e^{-\beta E_i}, \quad (5.7)$$

of occurring, where $\beta = 1/k_B T$ and the exponential is called the Boltzmann weight.

The full Boltzmann distribution is

$$p(E_i) = \frac{e^{-\beta E_i}}{Z} \quad Z = \sum_i e^{-\beta E_i} \quad (5.8)$$

where Z is the sum of all Boltzmann weights. It is from Z that the rest of the properties of a statistical mechanical system can be derived, as we will see shortly. For the exam, you can be expected to know how to derive a quantity for a given system.

Definition 5.1.1. The **free energy** F is the amount of energy in the system that is available to perform thermodynamic work at **constant temperature**. Moreover,

$$F = -k_B T \ln(Z) = U - TS \quad (5.9)$$

where U is the internal energy, T is temperature (in Kelvin) and S is the entropy.

The change in the free energy is the maximum amount of work that the system can perform in a process at constant temperature.

5.2 Paramagnetism

A semiclassical picture of paramagnetism is of \mathbf{H} competing with T (as T causes thermal agitation of the magnetic moments). The figure below shows how the moments try to align with \mathbf{H} .

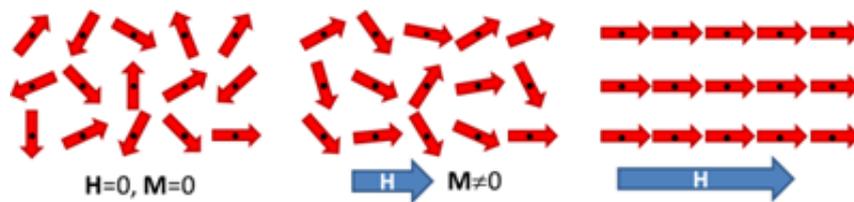


Figure 5.1: Paramagnetic magnetic in magnetic field.

5.2.1 Curie Paramagnetism

Spin-1/2 paramagnet

Curie paramagnetism for localised moments on atoms in a crystal lattice: First, let's consider a $\mathbf{S} = \frac{1}{2}$ paramagnet, $\mathbf{L} = 0$ and:

$$H_{\text{para}} = g\mu_B \mathbf{B} \cdot \mathbf{S} \quad (5.10)$$

For the spin-half state, the eigenstates are $\pm\mu_B B$ and so we can write our partition function Z as

$$Z = e^{-\mu_B B/k_B T} + e^{\mu_B B/k_B T} = 2 \cosh\left(\frac{\mu_B B}{k_B T}\right) \quad (5.11)$$

The free energy $F = -k_B T \ln(Z)$ and the magnetic moment is then given by

$$\mu = \left(-\frac{\partial F}{\partial B}\right)_T \quad (5.12)$$

where the derivative is held at fixed temperature T and F is the free energy.

Therefore for the spin-1/2 case,

$$\mu = \mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right) \quad (5.13)$$

The magnetisation is then the total magnetic moment

Magnetisation from magnetic moment

$$M = n\mu \quad (5.14)$$

where n is the number density of magnetic moments (spins).

So for the spin- $\frac{1}{2}$ paramagnet this becomes

$$M = n\mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right) \quad (5.15)$$

Taking the bit inside tanh to be small, i.e. $\tanh(x) \approx x$, and using the following equation for susceptibility:

Magnetic susceptibility

$$\chi = \left. \frac{dM}{dH} \right|_{H \rightarrow 0} = \mu_0 \left. \frac{dM}{dB} \right|_{B \rightarrow 0} \quad (5.16)$$

we can show that $\chi = \frac{n\mu_0\mu_B^2}{k_B T}$. We have assumed χ and $\frac{B}{T}$ to be small in these calculations.

We have shown that for **Curie paramagnetism**, $\chi \sim \frac{1}{T}$.

Spin- J paramagnet

This is a generalisation of the spin-1/2 case, where we imagine our material is made up of localised moments. Our Hamiltonian is now

$$H_{\text{para}} = \mu_B \mathbf{B} \cdot (\mathbf{L} + g\mathbf{S}) := \mu_B \tilde{g} \mathbf{B} \cdot \mathbf{J} \quad (5.17)$$

where $\mathbf{J} = \mathbf{L} + g\mathbf{S}$ is the total angular momentum, and \tilde{g} is the **Landé g-factor** defined as

$$\tilde{g} = \frac{1}{2}(g+1) + \frac{1}{2}(g-1) \left[\frac{S(S+1) - L(L+1)}{J(J+1)} \right] \quad (5.18)$$

The methodology is exactly the same, just more complicated. We skip it and the full solution (which does NOT need to be known for the exam) is

$$M = n\tilde{g}\mu_B J B_J(x) \quad (5.19)$$

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right) \quad (5.20)$$

is called the **Brillouin function** which we will meet again a few times and the variable x is

$$x = \frac{\tilde{g}\mu_B B J}{k_B T} \quad (5.21)$$

The susceptibility is

$$\chi = \frac{n\mu_0 (\tilde{g}\mu_B)^2 J(J+1)}{3K_B T} \quad (5.22)$$

All you need to know is the term $(\tilde{g}\mu_B)^2 J(J+1) = \mu_{\text{eff}}^2$ and μ_{eff} is called the **effective magnetic moment**.

5.2.2 Paramagnetism in metals

Suppose you apply a magnetic field \mathbf{H} . The energy E is lower if the spin of conduction electrons \mathbf{S} points in the opposite direction to \mathbf{H} locally. Therefore the net magnetic moment aligns with \mathbf{H} . Therefore Eq. (5.14) extends to

$$M = -(n_{\uparrow} - n_{\downarrow})\mu_B \quad (5.23)$$

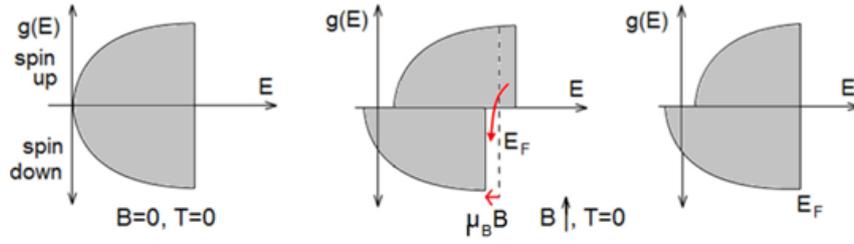


Figure 5.2: Left: density of states in an undisturbed electrons. Middle+right: Pauli paramagnetism in an applied field.

where n_{\uparrow} is the number density of *spin-up* electrons and n_{\downarrow} is the number density of *spin-down* electrons. This is why most metals with empty/unfilled orbitals are paramagnetic since they have a net magnetic moment, although there are exceptions.

The density of states for these electrons under no field is shown on the left of Fig. 5.2.

Applying a magnetic field will cause spin flips. This causes the density of states of each spin to shift by energy $\mu_B B$ as in the middle of Fig. 5.2, so M increases by $2\mu_B$ and,

$$M \simeq \frac{1}{2}g(E_F)\mu_B B 2\mu_B \simeq \mu_B^2 g(E_F)B \quad (5.24)$$

Therefore the **Pauli susceptibility** is

Pauli susceptibility

$$\chi_{\text{Pauli}} \simeq \mu_0 \mu_B^2 g(E_F) \quad (5.25)$$

This is constant in T and $\chi_{\text{Pauli}} \ll \chi_{\text{Curie}}$ usually. χ_{Pauli} is positive and therefore paramagnetic!

5.3 Diamagnetism

All materials have a diamagnetic response, however it can only be observed when $J = 0$. When $J \neq 0$, paramagnetism dominates.

5.3.1 Langevin/Larmor Diamagnetism

Langevin magnetism arises from electrons whizzing around atoms. From the diamagnetic term in the Hamiltonian seen earlier, can write an expectation value for the energy of the diamagnetic term for a single electron:

$$\epsilon_{\text{dia}} = \frac{e^2}{8m} \langle |\mathbf{B} \times \mathbf{r}|^2 \rangle \quad (5.26)$$

If $\mathbf{B} = B\hat{z}$, then $\mathbf{B} \times \mathbf{r} = (-B \cdot y, B \cdot x, 0)$ and $|\mathbf{B} \times \mathbf{r}|^2 = B^2(x^2 + y^2)$

Therefore,

$$\epsilon_{\text{dia}} = \frac{e^2 B^2}{8m} \langle x^2 + y^2 \rangle \quad (5.27)$$

where $\langle x^2 + y^2 \rangle$ is the measure of the excursion the electron makes in the x-y plane as it orbits the atom.

If the atom is **rotationally symmetric**, then $\langle x^2 + y^2 \rangle = \frac{2}{3} \langle x^2 + y^2 + z^2 \rangle = \frac{2}{3} \langle r^2 \rangle$

thus $\epsilon_{\text{dia}} = \frac{e^2 B^2}{8m} \frac{2}{3} \langle r^2 \rangle$ where $\langle r^2 \rangle$ is approximately the area of orbit.

Using the magnetic moment per electron $\mu = -\frac{dE}{dB} = -\frac{e^2 B}{6m} \langle r^2 \rangle$

$$\mathbf{M} = -\frac{ne^2 B}{6m} \langle r^2 \rangle \quad (5.28)$$

Larmor Susceptibility

$$\chi = \mu_0 \left. \frac{d\mathbf{M}}{dB} \right|_{B \rightarrow 0} = -\frac{ne^2 \mu_0}{6m} \langle r^2 \rangle \quad (5.29)$$

- value is small in general less than any Curie paramagnetism and usually less than Pauli paramagnetism.
- value can be large if the electron excursion $\langle r^2 \rangle$ is large.

5.3.2 Landau Diamagnetism (in metals)

We previously saw that the spin of conduction electrons gives rise to Pauli paramagnetism. The orbital motion of conduction electrons in an applied magnetic field (due to the Lorentz force) leads to Landau diamagnetism, which is caused by the formation of Landau levels (long proof in Blundell's textbook).

$$\chi_{\text{Landau}} = -\frac{1}{3} \mu_0 \mu_B^2 g(\epsilon_F) \left(\frac{m_e}{m^*} \right)^2 = -\frac{1}{3} \chi_{\text{Pauli}} \left(\frac{m_e}{m^*} \right)^2 \quad (5.30)$$

This suggests that paramagnetism dominates in metals. However, we have ignored the effect of band structure in calculating these, and the fact that Pauli paramagnetism is concerned with conduction electrons only. In fact,

Susceptibility for a metal

$$\chi_{\text{metal}} = \chi_{\text{Pauli}} \left[1 - \frac{1}{3} \left(\frac{m_e}{m^*} \right)^2 \right] \quad (5.31)$$

For most metals, $m^* = m_e \rightarrow$ paramagnetism. But if $m^* \ll m_e$ (e.g. semiconductors), can observe diamagnetism

5.3.3 Diamagnetic levitation

It is possible to levitate solid objects in which diamagnetism dominates. For this, we need strong \mathbf{B} and strong field gradient $\frac{d\mathbf{B}}{dz}$.

For levitation, $\mathbf{F} = \mu \frac{d\mathbf{B}}{dz} = \rho V g$ as we need to balance force due to gravity.

Diamagnetic levitation

$$\mathbf{B} \frac{d\mathbf{B}}{dz} = \frac{\mu_0 \rho g}{x} \quad (5.32)$$

Can create microgravity conditions for experiments using diamagnetic levitation

5.4 Magnetic Order

When magnetic moments on neighbouring atoms are allowed to interact, spontaneous magnetisation arises in some materials even when $\mathbf{H} = 0$. This is due to the **exchange interaction**

between spins as the dipole-dipole interaction is typically too weak. The spins order in patterns as shown in Fig. 5.3 (when the material is below a certain temperature and the exchange interaction dominates over thermal fluctuations). There are other possible ordering patterns, such as the helical magnetism shown in rare earths, but we'll concentrate on these three types.

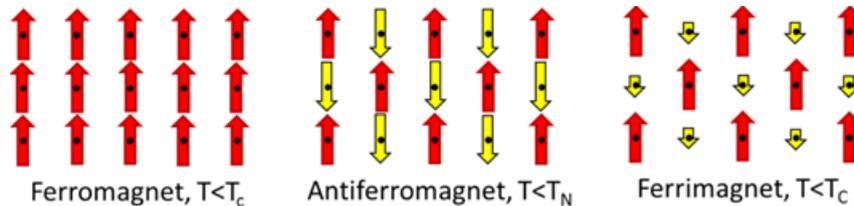


Figure 5.3: Three of the possible magnetic ordering structures.

For a ferromagnet and ferrimagnet, $\mathbf{M} \neq 0$ but for an antiferromagnet, $\mathbf{M} = 0$

5.4.1 Simple models of magnetic order

An effective spin model starts with a Hamiltonian:

$$H = - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_i g\mu_B \mathbf{B} \cdot \mathbf{S}_i \quad (5.33)$$

J_{ij} is an **exchange constant** determining the relative strength of the interactions between spins i and j , so the entire first term is the **exchange energy**. The second sum is the Zeeman energy as spins are coupled to the magnetic field.

If $J_{ij} > 0$ energy is lower if spins align - this is ferromagnetism (it becomes energetically *favourable*). If $J_{ij} < 0$ the spins find it energetically favourable to *anti-align* - this is anti-ferromagnetism.

Nearest-neighbour model

This model is appropriate for **short-range interactions**. The exchange term in Eq. (5.33) becomes

$$H_{\text{ex}} = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \quad (5.34)$$

where $J_{ij} \rightarrow J$ is a constant and $\langle i, j \rangle$ means sum over **nearest neighbours**.

Easy and hard axes

This model is appropriate for spins that are affected easily by their local environment.

Definition 5.4.1. The **easy axis** is the crystallographic direction along which moments like to point.

Combining this with the nearest-neighbour Hamiltonian gives

$$H = - \sum_{\langle i,j \rangle} JS_i \cdot \mathbf{S}_j - \kappa \sum_i (S_i^z)^2 \quad (5.35)$$

where the second term is the **anisotropy energy** arising due to coupling between the spin and the crystal lattice (its environment). Here, we've set the easy axis to be along z .

- If $\kappa > 0$ spins want to align with the easy axis (z in this case)
- If $\kappa < 0$ spins want to be perpendicular to the easy axis, either in the **hard axis** or **easy plane**.

- **Weak anisotropy** is when $\kappa \ll J$ - exchange energy dominates
- **Strong anisotropy** is when $\kappa \gg J$ - anisotropy energy dominates

We therefore get different behaviours as $k_B T$ is reduced.

Ising model

Probably every physicist's favourite simulation model. Here, we assume spin is **always** aligned along $\hat{\mathbf{z}}$. Equation (5.33) reduces to

$$H = - \sum_{\langle i,j \rangle} J S_i^z S_j^z + J \mu_B B \sum_i S_i^z \quad (5.36)$$

5.4.2 Weiss Model of Ferromagnetism

This is a type of **mean-field theory** (see PX3A7 Statistical Physics) where we try to encode the system information in terms of statistical weights rather than the quantities themselves. The question we want to answer is

What temperature does magnetic order set in?

Weiss assumed a spin will align due to a mean field proportional to \mathbf{M} arising from all the other spins, thus creating an **effective magnetic field** \mathbf{B}_{eff} experienced by the spin:

$$\mathbf{B}_{\text{eff}} = \mathbf{B} + \lambda \mathbf{M} \quad (5.37)$$

where \mathbf{B} is the applied field and $\lambda \mathbf{M}$ is the mean field.

Recalling the Hamiltonian in Eq. (5.33), the Hamiltonian for site i denoted by H_i will be

$$H_i = -2\mathbf{S}_i \cdot \sum_j J_{ij} \mathbf{S}_j + g\mu_B \mathbf{B} \cdot \mathbf{S}_i := g\mu_B \mathbf{B}_{\text{mf}} \cdot \mathbf{S}_i + g\mu_B \mathbf{B} \cdot \mathbf{S}_i \quad (5.38)$$

where (confusingly) the mean field on site i is

$$\mathbf{B}_{\text{mf}} = \lambda \mathbf{M} = \frac{-2}{g\mu_B} \sum_j J_{ij} \mathbf{S}_j \quad (5.39)$$

Therefore we can rewrite the site Hamiltonian as

$$H_i = g\mu_B \mathbf{S}_i \cdot (\mathbf{B} + \mathbf{B}_{\text{mf}}) \quad (5.40)$$

Spin- $\frac{1}{2}$ model

What we derived in Eq. (5.40) is insanely similar to Eq. (5.10). We therefore can use the same method to solve and we get for a **Weiss ferromagnet**:

$$M = nM_B \tanh \left(\frac{\mu_B}{k_B T} [B + \lambda M] \right) \quad (5.41)$$

Notice both sides have M inside. We have to solve numerically the system

$$\begin{aligned} M &= nM_B \tanh x \\ M &= \frac{k_B T}{\mu_B \lambda} x \end{aligned} \quad (5.42)$$

where x is the stuff inside tanh for the magnetisation. This yields 3 regimes: high T , $T = T_c$ (the critical temperature) and low T as seen in Fig. 5.4.

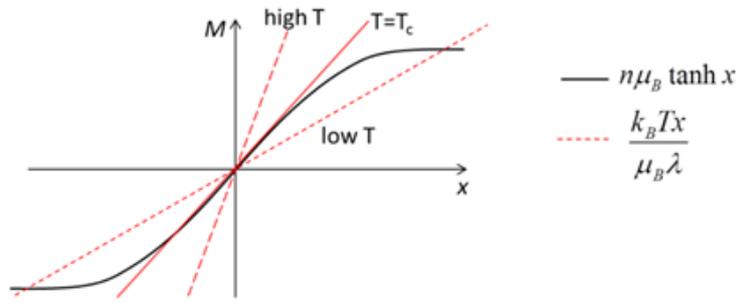


Figure 5.4: Magnetisation from Weiss model of ferromagnetism

- High T : no ordering ($x = 0, M = 0$)
- Low T : $M = 0$ (unstable) and 2 non-zero intersections which produce magnetic order
- $T = T_c$, the **critical temperature** or **Curie temperature** which is the boundary between ordered and unordered.

To get T_c , we equate the gradients from our system of equations and get

Curie temperature

$$T_c = \frac{n\mu_B^2 \lambda}{k_B} \quad (5.43)$$

Now we have the magnetisation, we can find the susceptibility in our different regimes.

At high temperatures, x is small so $\tanh x \simeq x$ and so

$$\begin{aligned} M &\simeq \frac{n\mu_B^2}{k_B T} (B + \lambda M) \\ M \left(1 - \frac{n\mu_B^2 \lambda}{k_B T} \right) &= \frac{n\mu_B^2}{k_B} \frac{B}{T} \\ M &= \frac{n\mu_B^2}{k_B} \frac{B}{(T - T_c)} \end{aligned} \quad (5.44)$$

However, we know by Eq. (5.16):

$$\chi = \mu_0 \left. \frac{dM}{dB} \right|_{B \rightarrow 0} = \frac{n\mu_0 \mu_B^2}{K_B} \frac{1}{(T - T_c)} \quad (5.45)$$

Therefore we obtain the all-important

Curie-Weiss Law

$$\chi \sim \frac{1}{T - T_c} \quad (5.46)$$

at high T (i.e. above T_c)

which we can use to find T_c experimentally.

Spin- J model

Since we showed that our Hamiltonian was similar to that of the spin- $\frac{1}{2}$ paramagnet, we can generalise this easily to spin- J . Again, because the maths is complicated (more of an algebra

problem than a physics problem). We get

$$M = n\tilde{g}\mu_B J B_J(x) \quad (5.47)$$

$$x = \frac{\tilde{g}\mu_B B_{\text{eff}} J}{k_B T} \quad (5.48)$$

$$(5.49)$$

Solving these equations simultaneously at $B = 0$ is again similar to the paramagnetic case and we get

$$T_c = \frac{n\tilde{g}^2\mu_B^2 J(J+1)\lambda}{3k_B} = \frac{n\mu_{\text{eff}}^2\lambda}{3k_B} \quad (5.50)$$

Applying a field at high temperatures

$$X = \frac{n\mu_0\mu_{\text{eff}}^2}{3k_B} \frac{1}{(T - T_c)} \quad (5.51)$$

which is another demonstration of the Curie-Weiss law!

Some things to note about these results

- J is again, the *total angular momentum*
- the coefficients $n\tilde{g}\mu_B J = M_S$ is called the **saturation magnetisation**
- $B_J(x)$ is the Brillouin function Eq. (5.20).

5.4.3 Néel model of antiferromagnetism

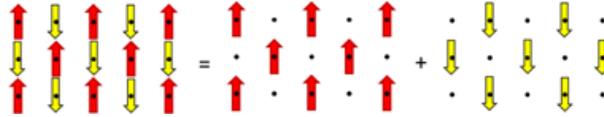


Figure 5.5: Representation of antiferromagnetism.

We imagine a crystal is a sum of **sublattices** as in Fig. 5.5. We label the sublattices as (a) and (b). Using a mean field approach as before, we assume each sublattice experiences a mean field $\propto \mathbf{M}$ from the other sublattice. We encapsulate this behaviour in the following set of equations

$$\mathbf{B}_{\text{eff}}^{\text{a,b}} = \mathbf{B} - |\lambda| \mathbf{M}_{\text{b,a}} \quad \mathbf{M}_{\text{TOT}} = \mathbf{M}_{\text{a}} + \mathbf{M}_{\text{b}} \quad (5.52)$$

We skip straight to the solution of the spin- J model (derivation non-examinable)

$$M_{\text{a,b}} = M_S B_J \left(-\frac{\tilde{g} M_B J |\lambda| M_{\text{b,a}}}{k_B T} \right) \quad (5.53)$$

where M_S is the saturation magnetisation equal to

$$M_S = n^1 \tilde{g} \mu_B J \quad (5.54)$$

where the superscript 1 on the number density n^1 is the number density of **one sublattice**. However, we say on average, the magnetic field exerted is equal and opposite, i.e. $\mathbf{M}_{\text{a}} = \mathbf{M}$ and $\mathbf{M}_{\text{b}} = -\mathbf{M}$ so the magnetisation on one sublattice is

$$M = M_S B_J \left(\tilde{g} \frac{\mu_B J |\lambda| M}{k_B T} \right) \quad (5.55)$$

We set the argument to B_J as x so we have the system of simultaneous equations

$$M = M_S B_J(x) \quad x = \tilde{g} \frac{\mu_B J |\lambda| M}{k_B T} \quad (5.56)$$

We can solve this and compare with the Weiss model

- At high T , each sublattice has $\mathbf{M} = 0$
- At low T , each sublattice has $\mathbf{M} \neq 0$
- At the **ordering/Néel temperature** T_N , the gradients of the simultaneous equations are the same as $x \rightarrow 0$

We therefore Taylor expand $B_J(x)$ to first order

$$B_J(x) \simeq \frac{J+1}{3J}x \quad (5.57)$$

so

$$\frac{dM}{dx} = M_S \frac{J+1}{3J} = \frac{k_B T_N}{\tilde{g}\mu_B J |\lambda|} \leftarrow \text{from argument of M} \quad (5.58)$$

and the Néel temperature is

Néel temperature

$$T_N = \frac{\tilde{g}\mu_B(J+1)|\lambda|\mu_S}{3k_B} = \frac{n^1\mu_{\text{eff}}^2|\lambda|}{3k_B} \quad (5.59)$$

5.4.4 How to identify your magnet

Experimentalists can identify whether a material is ferromagnetic or antiferromagnetic by measuring χ at high T in the paramagnetic state (i.e. $T > T_C$ or $T > T_N$). The results can be fitted to:

$$\chi \sim \frac{1}{T - \theta_{CW}} \quad (5.60)$$

Curie-Weiss Temperature

- $\theta_{CW} < 0 \rightarrow$ antiferromagnet, $T_N = -\theta_{CW}$
- $\theta_{CW} = 0 \rightarrow$ paramagnet
- $\theta_{CW} > 0 \rightarrow$ ferromagnet, $T_c = \theta_{CW}$

Using θ_{CW} to determine ordering temperature is a good minimal model however a better model will also consider the effect of spins from the same sublattice. We were essentially only considering nearest neighbour interactions. As the size of interactions increase, it becomes more crucial to consider the next nearest neighbour.

5.4.5 Other magnetic ordering

Very brief look into magnetic ordering in rare earths, where magnetic moments lie in layers with strong ferromagnetism within layers. Allow spins in adjacent layers to deviate by angle θ . Steps taken in lecture to find possible angle θ between magnetic moments of adjacent layers, namely we take into account

- J_1 , the **nearest-neighbour interaction**
- J_2 , the **next-to-nearest-neighbour interaction** (sometimes referred to as a $J_1 - J_2$ spin chain)

Therefore the energy of spin in i^{th} layer will have the form of

$$E_i = -2 \sum_i (J_1 \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J_2 \mathbf{S}_i \cdot \mathbf{S}_{i+2}) = -2S^2 N (J_1 \cos(\theta) + J_2 \cos(2\theta)) \quad (5.61)$$

Minimise

$$\frac{dE_i}{d\theta} = 0 = 2S^2N \sin(\theta)(J_1 + 4J_2 \cos(\theta)) \quad (5.62)$$

If $\sin(\theta) = 0$:

- $\theta = 0 \rightarrow$ Ferromagnetic ordering between layers
- $\theta = \pi \rightarrow$ Antiferromagnetic ordering

If $J_1 \cos(\theta) + J_2 \cos(2\theta) = 0$: then $\cos(\theta) = -\frac{J_1}{4J_2}$ and the angle of the spins would rotate from layer to layer, creating helical ordering!

The actual ground state thus depends on the relative size of J_1 and J_2 .

5.5 Domains and Hysteresis

5.5.1 Ferromagnetic Domains

Previously we assumed all spins within a ferromagnet point in the same direction. This is valid on a microscopic scale, but for a larger sample it is possible to have $\mathbf{M} = 0$. Macroscopic ferromagnets can save long-range dipolar energy by forming small regions in the sample called domains. (i.e. the material can minimise energy by reducing the magnetic dipole fields that extend out into free space.

In a single domain, $\mathbf{M} \neq 0$. Over the entire sample however, \mathbf{M}_{tot} can be zero for $\mathbf{H} = 0$.

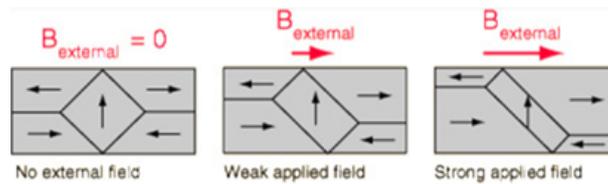


Figure 5.6: Domains in a material, on application of a magnetic field (from hyperphysics).

As \mathbf{H} increases, domains with \mathbf{M} parallel to \mathbf{H} grow, as shown in Fig. 5.6.

5.5.2 Domain Walls

The geometry of the domains depends on the geometry of the sample, relative energies of the dipole fields, exchange interactions, and disorder in the sample. In an Ising model the spins are constrained to point either up or down, resulting in a sharp wall with strong easy axis anisotropy. However, in real materials the wall is larger, as it is energetically unfavourable to have such a sudden change.

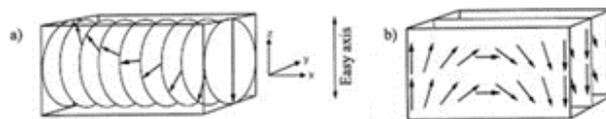


Figure 5.7: (a) Bloch and (b) Néel domain walls

Fig. 5.7 shows Bloch and Néel type domain walls, where the spins are allowed to orient slightly different to the preferred direction of their neighbour, causing a small increase in energy each time (weak anisotropy). In the Bloch wall, \mathbf{M} rotates parallel to the wall.

The energy cost to rotate spins is found by considering

$$\epsilon_1 = -2JS_1 \cdot S_2 = -2JS^2 \cos(\theta) \quad (5.63)$$

By comparing energy for $\theta = 0, \epsilon_1 = -2JS^2$ and small θ , $\epsilon_1 = -2JS^2(1 - \frac{\theta^2}{2}) + \dots$. Thus the energy cost $\delta\epsilon_1 = JS^2\theta^2$ per pair. If the wall is N lattice spacings long and length $L = Na$, then $\theta = \frac{\pi}{N}$ and the spins are rotated by π across the entire length of the wall.

The total energy cost of the wall is

$$N\delta\epsilon_1 = NJ\delta^2 \left(\frac{\pi}{N}\right)^2 = \frac{JS^2\pi^2}{N} \quad (5.64)$$

This suggests that an infinite wall minimises energy. However, we need to also consider the easy-axis anisotropy term κ which, in the Ising model, costs us $\approx \kappa S^2$ for each spin not pointing along the easy axis (up or down).

The wall energy:

$$E_{\text{TOT}} = \frac{JS^2\pi^2}{N} + N\kappa S^2 \quad (5.65)$$

$$\frac{dE_{\text{TOT}}}{dN} = 0 = -\frac{JS^2\pi^2}{N^2} + \kappa S^2 \quad (5.66)$$

Therefore the optimal number of spins in a wall is

$$N = \pi\sqrt{\frac{J}{\kappa}} \quad (5.67)$$

The domain wall is very narrow if $\kappa \gg J$. N is typically greater than 100.

5.5.3 Hysteresis

Magnetisation occurs by incremental changes in domain walls as \mathbf{B} is applied.

However domain walls can get pinned on disorder in the material, meaning we require activation energy to move the walls, hence leading to hysteresis.

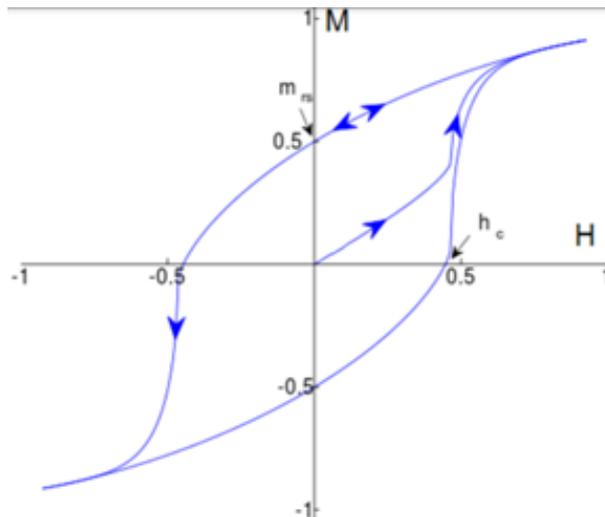


Figure 5.8: M-H loop showing initial magnetisation and then hysteresis.

The remnant magnetisation \mathbf{M}_r is the y -axis intercept and the coercive field \mathbf{H}_c is the x -axis intercept.

Area under hysteresis loop

Small Area:

- soft ferromagnet
- easy to magnetise and switch \mathbf{M}
- useful in motors and transformers

Large Area:

- hard ferromagnet
- hard to magnetise, large \mathbf{M}_r
- permanent magnets

Chapter 6

Superconductivity

Superconductivity describes the emergent quantum phenomenon where certain materials exhibit zero resistivity and expels all magnetic flux below a **superconducting critical temperature** T_c . The vanishing of resistivity is seen in Fig. 6.1.

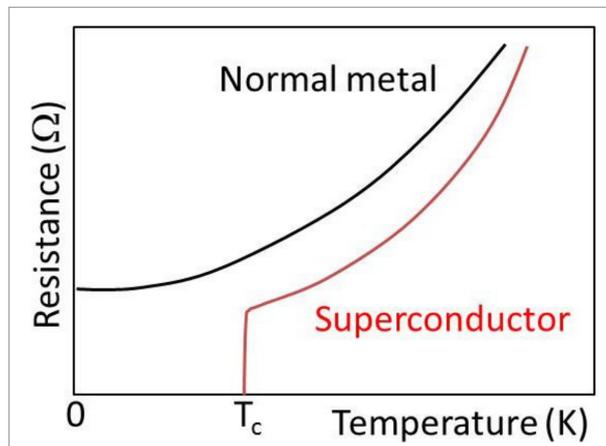


Figure 6.1: Resistance against temperature graph for a normal material and a superconductor.

Note that $\rho = 0$ inside a superconductor but the electric field $\mathbf{E} = \rho\mathbf{J}$ where \mathbf{J} is the electric current density. Therefore:

Superconductors have zero electric field

This has one main consequence

Current decay

Superconductors have persistent currents - ones which essentially don't decay. Moreover currents obey an exponential decay law

$$I = I_0 e^{-t/\tau} \quad (6.1)$$

where τ is the time constant, which is about 10^5 years (don't need to know this), so yes they basically don't decay on the timescales we use them on.

Note that this chapter is *brief* and you only need to know the stuff in boxes.

6.1 Meissner effect

If a material in the superconducting state is subjected to a magnetic field (say, using an electromagnet to raise the external field from 0 T to a field $B_{\text{ext}} < B_c$, a critical field), a supercurrent is induced at the very surface of the superconductor which exclude and expel B_{ext} , such that

Meissner effect

$\mathbf{B} = 0$ in the bulk of a superconductor

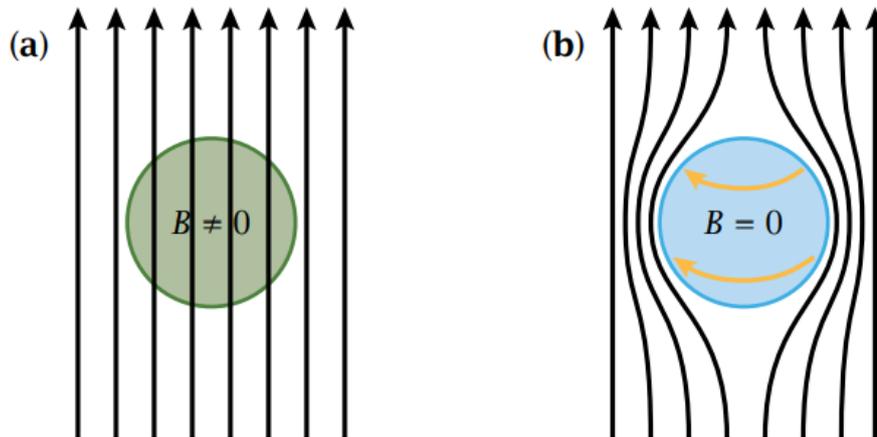


Figure 6.2: (a) Above T_c , external fields are able to penetrate the material. (b) shows the same material now in the superconducting state (below T_c). Non-examinable: Supercurrents flow horizontally around the material (shown in yellow) and cause the external fields to be repulsed from the surface.

Inside the superconductor

$$\mathbf{B} = \mu_0(1 + \chi_{\text{SC}})\mathbf{H} = 0 \quad (6.2)$$

$$\implies \chi_{\text{SC}} = -1 \quad (6.3)$$

Superconductors are perfect diamagnets.

It is important to note that the diamagnetism is due to **surface currents** and not atomic orbits.

However, the expelled flux density close to the surface of the superconductor **can depend on sample shape**. For example, take a sphere and place it in a uniform field. Then the magnetic field lines are more dense closer to the equator than they are at the poles.

This can lead to complicated intermediate states, where part of the sample remains superconducting, but other parts remain normal (i.e., regions of no superconductivity). For the sphere example, this results in planes of non-superconducting regions parallel to the field lines.

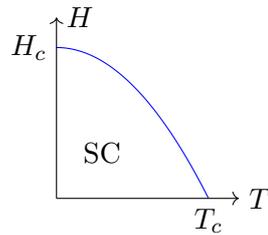
6.2 Type I Superconductors

Type I Superconductors

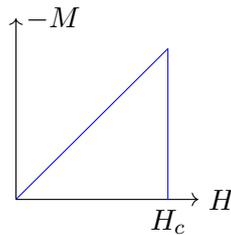
Type I superconductors have one critical magnetic field H_c above which superconductivity is destroyed.

This applies to all elements except Nb, V, Tc. We will ignore compounds since that is very complicated and non-examinable.

The classification of these superconductors imply there is a *phase transition* at some critical field (see PX3A7 Statistical Physics). We can construct the phase diagram for this as seen in Fig. 6.3(a).



(a) Phase diagram for Type I superconductors. The boundary is a parabola.



(b) Magnetisation of Type I superconductor against applied field. The gradient is 1.

Figure 6.3: Graphs displaying the important properties of Type 1 superconductors.

In particular, the critical magnetic field at temperature T is

Critical magnetic field

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c} \right)^2 \right] \quad (6.4)$$

6.3 Type II Superconductors

Type II Superconductors

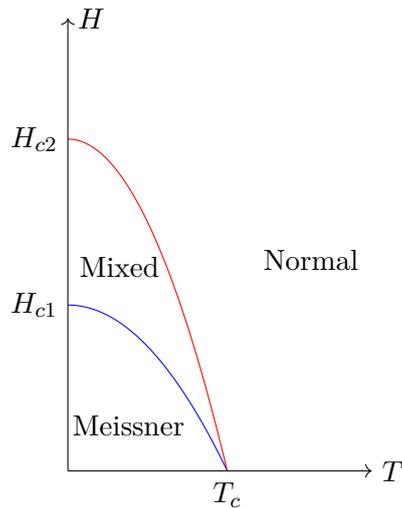
Type II Superconductors have 2 critical phases.

- At $H < H_{c1}$, we have the **Meissner state** which is the same as in Type 1: $\rho = 0, \chi = -1$.
- At $H_{c1} < H < H_{c2}$, we have the **Mixed state** where $\rho = 0, \chi \neq -1$.
- At $H > H_{c2}$, superconductivity is destroyed.

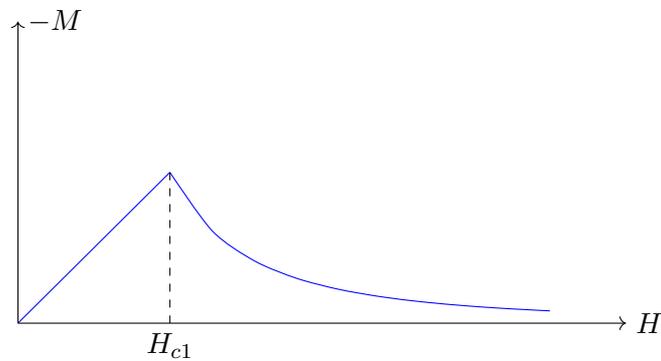
The phase diagram is shown in Fig. 6.4(a) and the magnetisation in Fig. 6.4(b).

The most important things to note are

- In a mixed state, fine filaments (regions) of the material become normal. This means that the external magnetic flux can penetrate the material.
- The magnetisation graph in Fig. 6.4(b) is linear from the origin to H_{c1} with gradient 1. After that, it tapers down towards 0 as $H \rightarrow H_{c2}$ in a hyperbolic fashion - i.e. draw a reciprocal graph like $1/x$.
- $\mu_0 H_{c1} \sim 10^{-2} \text{T}$ but $\mu_0 H_{c2}$ can be large.



(a) Phase diagram for Type II superconductors. The boundaries are parabolas.



(b) Magnetisation of Type II superconductor against applied field.

Figure 6.4: Graphs displaying the important properties of Type 2 superconductors.

6.4 BCS Theory

This is the most prominent theory that explains superconductors in the low temperature limit. More to come in PX446 Condensed Matter Physics II.

Definition 6.4.1. The charge carriers in superconductors are called **Cooper pairs**, which are bound states of **two** electrons.

Now you may question how electrons can pair up - after all, they must obey the Pauli exclusion principle. However, it was shown by Cooper (one of the pioneers of this theory) that arbitrarily small attraction between electrons in a metal can cause a paired state of electrons to have a lower energy than the Fermi energy.

Now, the only thing that could do this is if something happened in the *lattice itself* to do so - a magnetic field cannot force electrons to magically be attracted to each other. The way this happens is through **electron-phonon interactions** as in Fig. 6.5.

Non examinable: Classical visualisation of how an attractive force can arise between two negatively charged electrons in a Cooper pair:

- An electron moves through a lattice of positive ions, causing a distortion where the positive ions move slightly towards the electron.
- The ion is slower to move back to its original position compared to the lightweight speedy

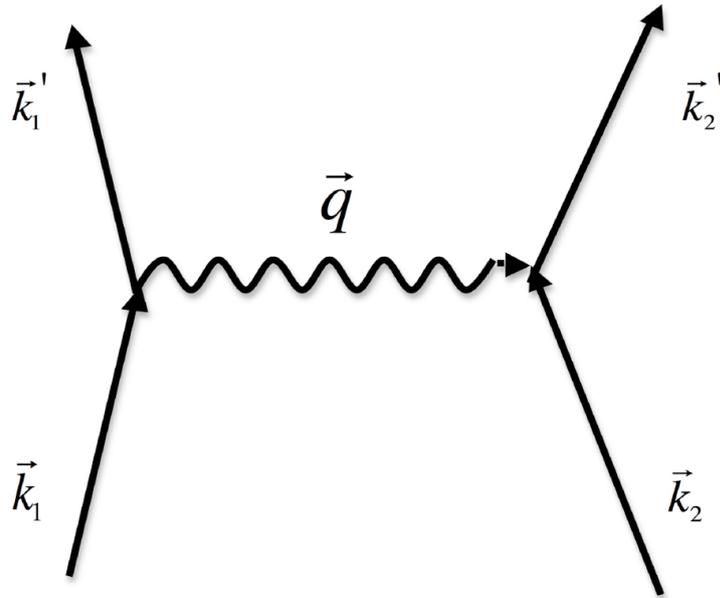


Figure 6.5: Electron-phonon scattering of 2 electrons with momenta $\mathbf{k}_1, \mathbf{k}_2$ to final state $\mathbf{k}'_1, \mathbf{k}'_2$ via a phonon (wavy line) with momentum \mathbf{q} .

electron, resulting in a region of net positive charge, attracting a second electron.

Extra info: Cooper pairs can be quite far apart; imagine the two electrons in a Cooper pair dancing in synchrony, but at opposite ends of a packed dance floor of other Cooper pairs. Q: Why do Cooper pairs only dance in winter? A: As thermal energy can easily break the pairing interaction energy of around 10^{-3} eV Q: What music were the Cooper pair dancing to? A: EDM

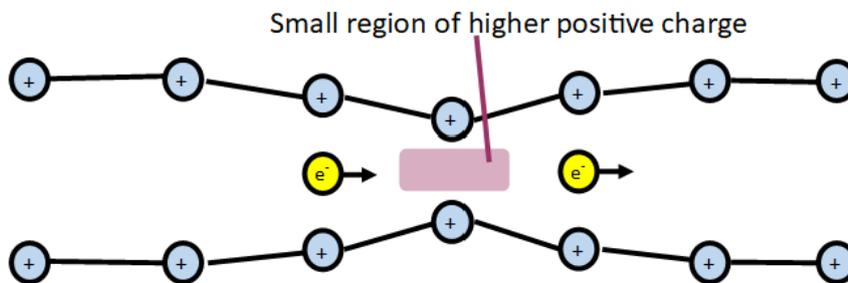


Figure 6.6: Schematic of the formation of Cooper pairs within a lattice. As the right electron distorts the lattice, the left electron is influenced to pursue it due to the region of higher positive charge. This will occur across the entire lattice. Drawn by Connor Jacques

Cooper pairs carry current without any dissipation, so the resistivity $\rho = 0$. Moreover since the electrons are weakly attracted, energy $E > 2\Delta$ is needed to break a Cooper pair. Here, Δ is a positive energy scale for one electron. This is confirmed by electromagnetic absorption where a photon of energy $\hbar\omega > 2\Delta$ produced 2 electrons. This means the superconducting state is protected by an **energy gap** of size Δ :

| BCS Energy Gap | |
|---|-------|
| $3.52k_B T_c = 2\Delta_0 \tag{6.5}$ | (6.5) |
| where Δ_0 is the maximal energy gap . | |

6.5 High T_c superconductors

The most common high T_c superconductors are cuprate superconductors, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where tuning δ tunes properties. These are **quasi-2D** materials where the electrons are mostly confined to CuO_2 planes and $\rho_{\parallel} \ll \rho_{\perp}$ where ρ_{\parallel} is parallel to the CuO_2 plane.

Modifying δ introduces carriers into the plane - this is **doping**. There are 3 regimes of doping to know about, summarised in the following list and in Fig. 6.7, whose numbers correspond to the list.

1. Low doping: insulating antiferromagnet at low T
2. Optimal doping: get superconductor below T_c
3. High doping: normal metal/alloy.

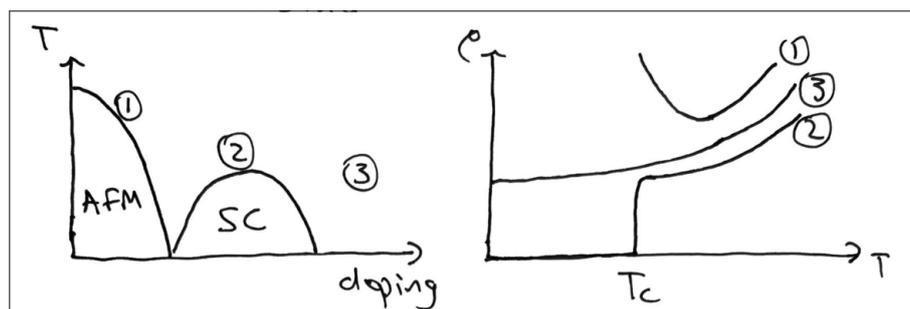


Figure 6.7: Regimes of doping, drawn by Dr. Paul Goddard.

Current Understanding of High T_c Superconductors

Type II Superconductors have 2 critical phases.

- There exists an energy gap.
- The electrons do pair up.
- However there is no consensus as to the mechanism that causes the electrons to pair up.

6.5.1 Extra (non-examinable)

Cuprates are just one type of high temperature superconductor. Other families of high temperature superconductors are shown in Fig. 6.8. The name 'high temperature/ T_c superconductors' can be misleading as high temperatures refer to above 77 K, the boiling point of nitrogen.

A detailed explanation of the path to discovering superconductivity, including discussion of the BCS theory can be found in Stephen Blundell's 'Very Short Introduction to Superconductivity' book, available online through the Warwick library.

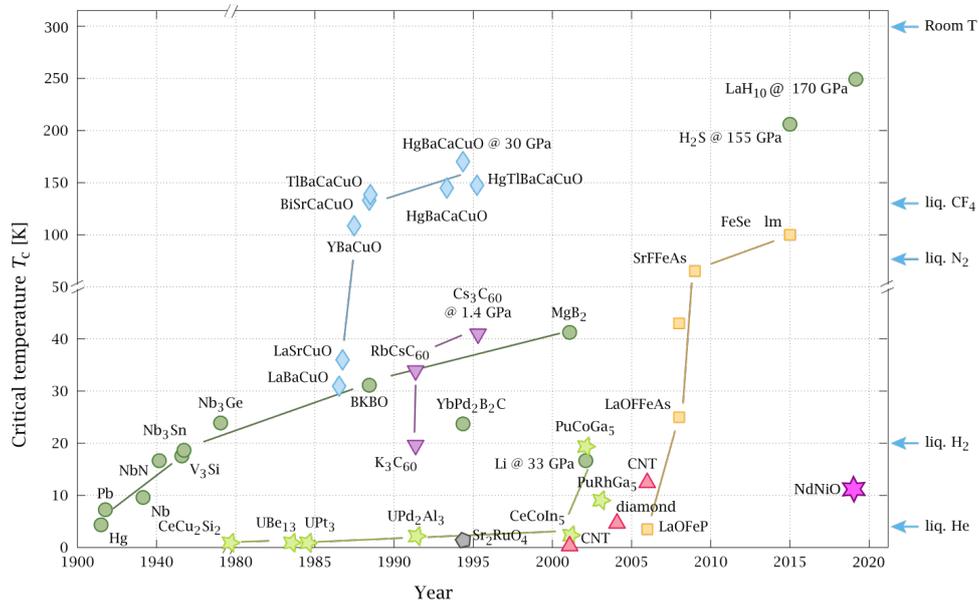


Figure 6.8: Timeline of superconducting materials showing evolution of T_c s from 1900 to 2020. Temperatures at which popular coolants liquefy shown on right, including liquid nitrogen which divides high temperature superconductors from low temperature superconductors. Notable families include conventional 'BCS' superconductors (green circles); cuprates (blue diamonds); iron-based (yellow squares); organic (purple triangles). Note a change in increment value from 50 K on the T_c axis and from 1980 in the Year axis.

Appendix A

(Non-examinable) Vibration on a 1D chain

TBD and NON-EXAMINABLE.