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PREFACE

From the hydrogen atom to the many body problem.

So, you have learned how to solve the quantum mechanical problem of a particle in a box. Depending on your interests you may have even learned how to solve atomic problems, such as the simple hydrogen atom. If you have struggled through the math for these 'simple' problems, you are probably aware that working with (mathematical expressions of) wave functions is often not very convenient. The mathematical complexity of these simple problems and the ingenuity that goes into solving them is quite formidable.

The problem to be discussed during this course is relatively simple to define: solve the Schrödinger equation for a bunch of electrons and nuclei that obey the following Hamiltonian:

$$H = -\frac{\hbar^2}{2m_e}\sum_j \nabla_j^2 - \sum_p \frac{\hbar^2}{2M_p}\nabla_p^2 + \frac{1}{2}\sum_j\sum_{k\neq j}\frac{e^2}{r_{jk}} - \sum_j\sum_p \frac{Z_p e^2}{|r_j - R_p|} + \frac{1}{2}\sum_p\sum_{q\neq p}\frac{Z_p Z_q e^2}{R_{pq}}$$

where sums over j and k run over all the electrons in the system and the sums over p and q over all nuclei. This Hamiltonian appears quite impressive, but if you restrict the sums to one electron and one nucleus it is just the hydrogen atom Hamiltonian. For two protons and two electrons it is already getting complicated and you'll have to resort to some approximations to actually solve the problem. Nevertheless, you can show that this can be done with sufficient accuracy that we can actually predict properties of molecular Hydrogen. Now imagine doing this for a 'simple' solid[1]. For the simplest of solids the sums run over N nuclei and NZ electrons, where N is of the order 10^{21} cm^{-3} (and Z is the atomic number). For the more mathematically inclined: we are seeking the solution to a set of approximately 10^{21} coupled partial differential equations. For the less mathematically inclined: the mathematicians have shown that this problem can be classified as 'NP-hard' (non-polynomial hard), which means that it can't be solved (even numerically) in a reasonably finite amount of time. The problem of solving the Schrödinger equation with the above Hamiltonian is known as the (quantum) '**many-body problem**' and is the most actively researched subfield of physics of all time.

The first goal of this course is to show you how this problem can be approximately solved. I will show you that in 'simple' solids the approximation is in fact quite good and allows us to predict the behavior of such solids. I will explain how these approximations can be improved to achieve almost perfect agreement, even for slightly more complex solids. At the end of the course you will be able to appreciate that the Hamiltonian written down above gives rise to solids that behave as metals or insulators, but also to magnets and superconductors.

The second goal of this course is to show you how the approximate solutions[2] to the many-body problem can be used to calculate or explain the properties of solids as they are observed in simple daily experiments. For example, I expect you to be able to explain why silicon-dioxide (a.k.a glass) is transparent and copper is not.

The third and final goal of this course is to get you excited about, and interested in, the largest field of physics: condensed matter physics.

About these lecture notes

First and for all: I am greatly indebted to Tobias Bouma without whom these notes would have looked a whole lot different (most likely sloppily hand written, possibly coffee stained.). These lecture notes are however still a work in progress. If you find mistakes or have suggestions for improvement: please make an effort to bring it to my attention. Students to come will thank you! These notes are based on the great works of much more experienced teachers than I am. In setting up this course I have occasionally borrowed derivations or followed a certain approach to solve a problem based on their work. The books on which this is based are much more extensive and therefore great material for further study:

- Introduction to solid state physics, *Charles Kittel*.
- Solid state physics, *Neil Ashcroft & David Mermin*.
- Solid-state physics, *Harald Ibach & Hans Luth*.
- Solid state theory, *Walter Harrison*.
- The physics of solids, *Eleftherios Economou*.

[1] *'Simple' refers here to solids for which we can make semi-accurate theoretical predictions. An example is copper. A slightly more 'complex' solid is iron. The difficulty with iron is to predict the critical temperature below which it becomes magnetic. Then there are complex solids, such as* $YBa_2Cu_3O_{7-\delta}$ *with properties for which we have no theory yet.*

[2] *That's right, there is not a single 'right' solution. There are many known solutions and the correct physical solution depends on the question you want answered.*

THE ELECTRONIC STRUCTURE OF SOLIDS

The tight binding approximation

KEYPOINTS:

- ☞ Many problems in condensed matter physics can be reduced to a two level problem.
- ☞ Bloch's theorem states that the electron wave functions will have the same periodicity as the crystal lattice.
- ☞ Wavefunctions in solids are characterized by the quantum number $\vec{k}$ (the band momentum), and the electron spin.

1.1 Introduction

The theory of quantum mechanics tells us that the evolution of a quantum mechanical system is governed by the time dependent Schrödinger equation,

$$i\hbar\frac{d\Psi(x,t)}{dt} = \hat{H}\Psi(x,t) \tag{1.1}$$

where $\hat{H}$ is the Hamiltonian consisting of a potential and kinetic term. There are two important observations to make here. The first observation is that we can separate out the time dependence *if the potential does not depend on time*. In that case we can simplify the problem to solving the time *independent* Schrödinger equation,

$$\hat{H}\psi(x) = E\psi(x) \tag{1.2}$$

The full solution to equation 1.1 is then obtained by multiplying the time independent solution, $\psi(x)$, with

$$\phi(t) = e^{-iEt/\hbar} \tag{1.3}$$

In this course (and in most of solid state physics) we will be concerned with time independent potentials [3] and hence we need only ever worry about Eq. 1.2.

Show that..

$\Psi(x,t) \equiv \psi(x)\phi(t)$ is indeed a solution of Eq. 1.1.

The second observation is a bit more mundane: I have written the wavefunction with the argument x. For the remainder of these notes I will use this label to indicate anything ranging from the 1 dimensional variable 'x' to a set of N variables describing the positions and spins of N particles (i.e. $x \equiv \{\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2, ..., \vec{r}_N, \sigma_N\}$) where N can be a large number. Where necessary I will specify the exact meaning, but it is such an easy (and widely used) short hand that I could not resist the temptation.

Similarly, very often (but not always) I will use units in which $\hbar \equiv 1$ or $c \equiv 1$ or possibly both at the same time. I will therefore occasionally (most likely during lectures) run into problems with units. In these cases it helps to remind oneself that 1 electronVolt = 11604 Kelvin = 8065.14 cm^{-1}. These are probably the three most useful numbers any physicist should remember. You use them whenever you want to compare or convert an energy scale (typically measured in eV) to a temperature scale (typically measured in Kelvin) or a length scale (not typically measured in wavenumber $k = 2\pi/\lambda$, so you'll have to make one further mental step).

With these preliminaries in mind it is time to introduce the Hamiltonian of a solid. Just to be completely clear, for a given solid Eq. 1.2 reads,

$$\hat{H}\psi(\{r_1; r_2; ...; r_N\}; \{R_1; R_2; ...; R_M\}) = E\psi(\{r_1; r_2; ...; r_N\}; \{R_1; R_2; ...; R_M\}) \tag{1.4}$$

with $\hat{H}$ depending on the conjugate particle operators $\{r_1; ...; r_N\}$, $\{R_1; ...; R_M\}$, $\{p_1; ...; p_N\}$ and $\{P_1; ...; P_M\}$. As usual, the Hamiltonian contains two parts: a kinetic term and a potential term, $\hat{H} \equiv \hat{K} + \hat{V}$. The kinetic term is the simplest. As you should remember from previous courses the operator $\hat{p} \equiv -i\hbar\partial/\partial\hat{x}$ can be used to define the kinetic energy. The total kinetic energy is simply the expectation value of the sum over the kinetic energy of all particles. So we need the kinetic energy operator for N atoms:

$$\hat{K} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_P \frac{\hbar^2}{2M_P}\nabla_P^2 \tag{1.5}$$

For reasons that will become apparent, I have already split the sum into two parts. The first term (with lowercase indices) describes the kinetic energy of $Z_P N_P$ electrons, while the second term (uppercase indices) describes the kinetic energy of the nuclei. If we consider just the kinetic energy, it is in fact quite easy to solve Eq. 1.2. Since each of the terms in Eq. 1.5 depend on the operators of only one particle, we can separate the wavefunction into a product of wavefunctions that depend on only one set of particle coordinates:

$$\psi(\{r_1; ...; r_N\}; \{R_1; ...; R_M\}) = \phi(r_1)\phi(r_2)...\Phi(R_N); \tag{1.6}$$

The **single particle wavefunction** ϕ is the solution of the eigenvalue problem,

$$-\frac{\hbar^2}{2m}\nabla^2\phi(r) = E\phi(r) \tag{1.7}$$

which is easy to solve (see Exercises).

The potential energy term is slightly more complicated. As you might have expected the **Coulomb interaction** is the main contributor[4]. So without further ado the operator describing the potential energy is (r_{jk} is shorthand for $|r_j - r_k|$):

$$\hat{V} = \frac{1}{2}\sum_j\sum_{k\neq j}\frac{e^2}{r_{jk}} - \sum_j\sum_P\frac{Z_P e^2}{|r_j - R_P|} + \frac{1}{2}\sum_P\sum_{Q\neq P}\frac{Z_P Z_Q e^2}{R_{PQ}} \tag{1.8}$$

---

[3] *The only case where we will encounter a sort of time dependent potential is in the last chapter on superconductivity. Strangely, the time dependence we will discuss there emerges from Eq. 1.2.*

[4] *Other terms can be included (for example the spin-orbit interaction), but these are much weaker compared to the Coulomb interaction and can be taken care of in a perturbative approach.*

As before, the indices indicate whether the sum runs over electrons or nuclei. One difficulty here is that we should make sure that we don't double-count the interactions (which is why there is a factor 1/2 in front of the first and last term) and that a particle can't interact with itself (hence the restriction $k \neq j$ on the sum). A more major difficulty is the fact that the Coulomb interaction 'couples' the particle coordinates together. The upshot is that the nice factorization into single particle problems leading to Eq. 1.6 is no longer possible. We now need to find a solution for all N particles simultaneously. This problem is known as the **many-body problem**. In principle it is possible to solve such a problem numerically, but unfortunately the Hilbert space for this problem grows exponentially with the number of particles. Practically this means that it is possible to simulate problems with up to about 100 particles in a reasonable amount of time, which is a long cry from the near infinity of particles in a real solid. As we will see in the remainder of this chapter, it is possible to approximate this complicated problem with an effective single particle problem. For those readers interested in the many-body problem dedicated texts are recommended[5].

To set the stage before solving any realistic problems, we will have a look at the simplest possible multi particle problem. This simple problem will demonstrate a few principles that underly approximations made in the many-body problem.

1.2 The hydrogen molecule

As a first step towards the approximate solution, we will sketch the steps to solve a simplified version of the hydrogen molecule problem (figure 1.1). We consider two hydrogen atoms, for which we already know the solutions (i.e. the orbitals $\phi_{nlm}(\vec{r}) = R_{nl}(r)Y_l^m(\vartheta, \phi)$ with eigenenergies $E_n = -\hbar^2/2ma_0^2n^2$). We ignore all orbitals except for the 1s-orbital and denote it in bra-ket notation as $|i\rangle$. This allows us to write down the Schrödinger equation for an isolated hydrogen atom as:

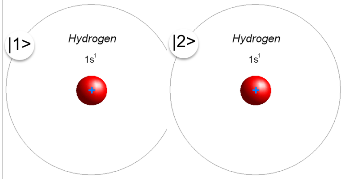

Figure 1.1: We consider the hydrogen molecule as consisting of two hydrogen atoms, each with a single 1s orbital.

$$H_i |i\rangle = \varepsilon_i |i\rangle \tag{1.9}$$

With these preliminaries in place we can now write down the hydrogen molecule problem. The Schrödinger equation will be of the form

$$H |\psi(1;2)\rangle = (H_1 + H_2 + H_{1,2}) |\psi(1;2)\rangle = E |\psi(1;2)\rangle \tag{1.10}$$

The Hamiltonian will contain three parts: an 'independent' part referring to the kinetic and potential energy of the electron on hydrogen atom 1 and one on hydrogen atom 2. Of course, if we bring the two atoms close enough together the orbitals on the individual atoms will start to overlap and we will get an additional term resulting from the interactions between the two electrons and nuclei. If we imagine this to happen as a more or less adiabatic process, the wave function of the hydrogen molecule will be a linear superposition,

$$|\psi(1;2)\rangle = c_1 |1\rangle + c_2 |2\rangle \tag{1.11}$$

of the original hydrogen 1s-orbitals. The coefficients $c_{1,2}$ are to be determined by finding the solution to Eq. 1.10, with

$$H = |1\rangle\, \varepsilon_1 \,\langle 1| + |2\rangle\, \varepsilon_2 \,\langle 2| - |2\rangle\, t \,\langle 1| - |1\rangle\, t^\star \,\langle 2| \tag{1.12}$$

The first two terms in the hydrogen molecule Hamiltonian represent the (ground-state) energy of the atomic orbitals of atom 1 and 2, while the last two terms represent the interaction energy (parametrized by t) resulting from the interaction between the two atoms. To find the coefficients $c_{1,2}$ and the new eigenenergies of the hydrogen molecule we need to solve the following **two level problem**[6]

Show that..

the combination of Eq. 1.10, 1.11 and 1.12 leads to Eq. 1.13

$$\begin{bmatrix} \varepsilon & -t \\ -t & \varepsilon \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \tag{1.13}$$

As usual we obtain the new eigen energies by diagonalizing the 2 × 2-matrix[7]. This gives,

$$E_\pm = \varepsilon \pm t \tag{1.14}$$

with the corresponding eigenfunctions

$$|-\rangle = \frac{1}{\sqrt{2}} \left(|1\rangle + |2\rangle\right) \tag{1.15}$$

and

$$|+\rangle = \frac{1}{\sqrt{2}} \left(|1\rangle - |2\rangle\right) \tag{1.16}$$

[5] The Many-body problem, *Advanced Book Classics.*

[6] *Because the hydrogen atoms are identical we take $\varepsilon_1 = \varepsilon_2$. Furthermore we assume t to be a real number.*

[7] *Remember that this is done most easily by setting the determinant of the matrix equation equal to zero and solve for the eigenenergies.*

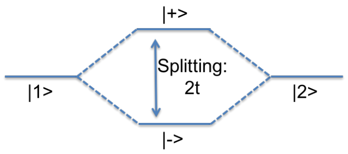

Figure 1.2: The solutions of the hydrogen molecule and their energies relative to the original atomic orbitals.

The resulting energy diagram of the hydrogen molecule is depicted in figure 1.2 together with the original atomic energy levels. Within a few steps and without too much effort we have solved a quite complicated 4 particle problem. How did we achieve this? There are a few hidden ingredients leading to a tremendous simplification. First of all, we have ignored the excited states of the hydrogen atom(s). It turns out that as long as we are interested in the ground state properties of the hydrogen molecule and not its excited states this is in fact a very reasonable approximation. This approximation means in practice that we have reduced a large **Hilbert space** to a very simple one. Another way of saying this is that we have assumed that the Hilbert space is spanned by a complete, orthonormal set of states (i.e. $|1\rangle\langle 1| + |2\rangle\langle 2| = 1$). This approximation is reasonable as long as the interaction between the two hydrogen atoms can be assumed to be a perturbation (i.e. $|t| << |\varepsilon|$). Under this approximation the new eigenfunctions are linear superpositions of the original states and the problem is relatively straight forward to solve. The energy diagram in Fig. 1.2 shows that the new groundstate ($|-\rangle$) is lower in energy than the original atomic eigenfunction. At the same time a second state ($|+\rangle$) is formed that has a higher energy and is thus an excited state. Each of these states can harbor 2 electrons (one with spin up and one with spin down). The lowest energy is obtained when the two electrons of the hydrogen atoms both occupy the $|-\rangle$ state, resulting in an energy gain of $2t$ for the formation of a hydrogen molecule. For this reason $|-\rangle$ is called a **bonding** state. The state $|+\rangle$ has a higher energy relative to the original atomic orbitals and is therefore called an **anti-bonding** state.

Part of the reason for introducing this very simplified picture of the hydrogen atom is that the 'standard model' of the electronic structure of solids proceeds much along the same lines. The eigenstates describing solids are in general linear superpositions,

$$|\psi_G(r_1;...;r_N)\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(\mathbf{r}_1) & \chi_2(\mathbf{r}_1) & \cdots & \chi_N(\mathbf{r}_1) \\ \chi_1(\mathbf{r}_2) & \chi_2(\mathbf{r}_2) & \cdots & \chi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_N) & \chi_2(\mathbf{r}_N) & \cdots & \chi_N(\mathbf{r}_N) \end{vmatrix} \tag{1.17}$$

of a suitably chosen set of basis states χ_i. As we shall see, we can very often reduce a problem involving N interacting particles to a set of independent two-level problems. It is important to keep in mind that describing solids by linear combinations of (atomic) eigenstates is an approximation.

1.3 Crystal structures

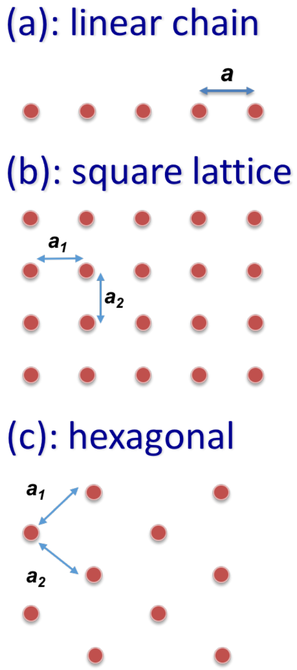

Figure 1.3: Most used lattices during the course. (a): the only one dimensional periodic arrangement of atoms, the linear chain. Also indicated is the lattice vector a. (b,c): the two dimensional square and hexagonal lattice are the most important 2D lattices.

One of the key concepts in condensed matter physics is that of a periodic lattice of atoms. Interestingly, the concept was introduced well before it was possible to experimentally demonstrate the existence of atoms let alone their periodic arrangement in crystals. It turns out that crystal structures come with a limited diversity. The number of possible **lattice systems** is determined by symmetry and dimensionality. In one space dimension there exists only one type of lattice (fig. 1.3a). There are five possible lattices in two dimensional space, two of which are depicted in fig. 1.3b and 1.3c. The remaining lattices are obtained from these two by simple deformations of these lattices. The number of possible lattices grows quickly with the number of space dimensions: in three space dimensions there are 14 possibilities, while there are 52 lattices possible in four space dimensions. Fortunately, it is not at all necessary to know these structures by heart to understand the basic concepts of condensed matter systems.

During most of the course we will only consider three particular lattices: the 1D **linear chain**, the 2D **square lattice** and the 3D **cubic lattice**. This does not mean that crystal symmetry plays no role in condensed matter physics. It is the crucial concept necessary to understand the origin of the differences between materials. For example, diamonds and soot are both made of carbon atoms. The huge difference in appearance and properties (beautifully transparant and insulating vs. pure blackness and highly conducting) finds its origin in a small difference in the periodic arrangement of the carbon atoms dictated by a different lattice symmetry (face centered cubic vs hexagonal). For what follows you need to remember two main concepts: (i) atoms are arranged according to a periodic pattern and (ii) they are separated by lattice vectors $\vec{a}$. In the simplest case the periodicity is the same in all independent spatial directions (e.g. **isotropic**). If you are completely unfamiliar with the concept of crystal structures you are advised to look up relevant literature[8]. Note that lattice site is not an equivalent word for atom. Each lattice site can in fact contain multiple atoms. One therefore more often speaks of unit cells rather than lattice sites. Each unit cell then contains a number of atoms.

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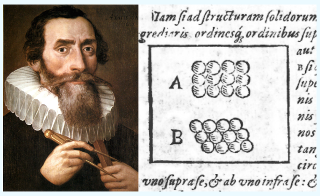
[8] , Introduction to solid state physics, *Wiley*, *Wikipedia*, Crystal structure. *[Online]. Available:* `https://en.wikipedia.org/wiki/Crystal_structure`.

Strena seu de Nive Sexangula



Johannes Kepler is probably best known for his work in astronomy, especially his laws on the motion of planets. He is however better described as a mathematician. He deserves a mention at this point for a major contribution to condensed matter physics before the field even existed (or perhaps he should be credited for starting it). In 1611 he wrote the treatise 'A New Year's Gift of Hexagonal Snow' for a friend in which he hypothesized for the first time that the hexagonal symmetry of water crystals arose from the hexagonal arrangement of water particles. He went on to conjecture that a hexagonal arrangement of spheres would result in the densest possible packing of space. The formal proof for this conjecture was delivered by a team led by Thomas Hales in 2014 (!). Image credits: `https://en.wikipedia.org/wiki/Johannes_Kepler`

1.4 From the many-body problem towards single particle solutions

To make progress in the description of the electronic properties of solids it is necessary to simplify Eq. 1.4 along the same lines as was done for the hydrogen molecule. Lets have a closer look at the Hamiltonian,

$$H=-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2-\sum_p \frac{\hbar^2}{2M_p}\nabla_p^2+U_{ee}(r_{ik})+U_{ei}(r_i,R_p)+U_{ii}(R_{pq}) \tag{1.18}$$

A first simplification can be made if we apply the Born-Oppenheimer approximation[9]. As we will see later the movement of the ions is in fact crucial to understand some of the most astonishing aspects of solids, but to zeroth order we ignore them. Under this approximation the Hamiltonian thus reads:

$$H=-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2+U_{ee}(r_{ik})+U_{ei}(r_i,R_p) \tag{1.19}$$

The first term in the sum refers to the kinetic energy of the electrons, the second term to the Coulomb repulsion between the electrons and the last term to the interaction between the electrons and the nuclei. This last term can be assumed to be a static potential in which the electrons move, since we have assumed that the movement of the nuclei can be neglected. The remaining difficulty is now in the term $U_{ee}(r_{ik})$. In this chapter we will approximate it by a kind of '**mean-field approximation**': we replace this complicated many-body interaction by an effective potential landscape through which each electron moves. The justification for this is unfortunately beyond the scope of this book. I hope you will appreciate the fact that within this approximation we will be able to solve problems and obtain solutions that can be verified in a laboratory. In essence, what we have achieved by applying successive approximations is that the complicated, dynamic potential landscape through which both the electrons and ions move is replaced by a single, static potential landscape as indicated in by the solid lines in Fig. 1.4. This potential landscape is called the (effective) **lattice potential**, U_{lat} and it allows us to reduce the Hamiltonian to,

$$H=-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2+U_{lat}(r_i) \tag{1.20}$$

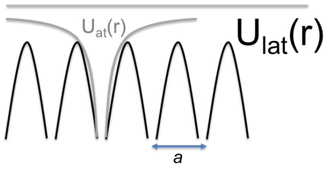


Figure 1.4: The effective lattice potential is indicated in black. It consists of overlapping atomic potentials (indicated in gray) and an effective mean-field potential generated by all other electrons.

This is a tremendous simplification: we are now left with a set of independent single particle problems to solve. Note that we haven't actually solved or changed anything yet. All we have done so far is to replace the complicated sum of potentials with a single effective one. Also note that we do not *a priori* know the shape of the lattice potential, $U_{lat}(\vec{r})$. Without a shape for this lattice potential we will never get any closer to a working theory that explains the differences between solids[10]. Fortunately, we only really need to know the symmetries of the crystal structure and the original atomic wavefunctions to get a good description of the electronic structure. The atomic wavefunctions are more easily calculated, while in many cases of interest somebody, somewhere has done the necessary x-ray diffraction experiments to determine the crystal symmetries and the crystal structure. With the crystal symmetries and structure in hand we have enough information to solve the single particle problem for a given solid. To conclude this section, we note that we now have to solve the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2+U(\vec{r})\right]\psi(\vec{r})=\varepsilon\psi(\vec{r}) \tag{1.21}$$

---

[9] *The Born-Oppenheimer approximation as applied to molecules or atoms assumes that the motion of electrons and nuclei can be treated separately. It is generally validated by arguing that the ion mass, M_p is much larger than the electron mass m_e.*

[10] *There is one exception, in the (nearly) free electron model the lattice potential is assumed to be almost completely flat and featureless. Remarkably this oversimplified model actually gives a good understanding of many properties of metals.*

where we have introduced the shorthand $U(\vec{r})$ for the lattice potential. I hope you recognize this as the Schrödinger equation of a particle in a box and that in principle you should be able to solve such problems, provided the potential $U(\vec{r})$ is simple enough. To solve this for the case where $U(\vec{r})$ is a complicated periodic function we need to make use of an important theorem.

1.5 Bloch's theorem

The essence of **Bloch's theorem** is very simple. It states:

The single particle wave function of electrons in solids can be expressed in terms of a basis of wavefunctions and has the same periodicity and symmetry as the crystal.

Despite its simplicity, it is one of the cornerstones of condensed matter physics and leads to a very powerful description of electrons in solids. To prove Bloch's theorem, we start by casting the periodicity imposed by the crystal structure and symmetry in mathematical form. This is done simply by choosing a lattice potential with the same symmetries as the crystal.

$$U(\vec{r}) = U(\vec{r}+\vec{R}) \tag{1.22}$$

where $\vec{R} = n\vec{a}$ with n some integer and $\vec{a}$ is the set of shortest vectors connecting two lattice sites (see Fig. 1.4 for examples). We now note that based on Eq. 1.21 we have

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + U(\vec{r}+\vec{R})\right]\psi(\vec{r}+\vec{R}) = \varepsilon\psi(\vec{r}+\vec{R}) \tag{1.23}$$

which can be rewritten as (using Eq. 1.22),

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + U(\vec{r})\right]\psi(\vec{r}+\vec{R}) = \varepsilon\psi(\vec{r}+\vec{R}) \tag{1.24}$$

But this is just the Schrödinger equation for the wave function $\psi(\vec{r})$, so:

$$\psi(\vec{r}+\vec{R}) = c(\vec{R})\psi(\vec{r}) \tag{1.25}$$

Show that..

$|c(\vec{R})|^2 = 1$ and $c(\vec{R}'+\vec{R}) = c(\vec{R}')c(\vec{R})$

Since we must have $|c(\vec{R})|^2 = 1$ and $c(\vec{R}'+\vec{R}) = c(\vec{R}')c(\vec{R})$ it follows that the function $c(\vec{R}) \equiv exp(i\vec{k}\cdot\vec{R})$, such that

$$\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r}) \tag{1.26}$$

Eq. 1.26 is a statement of Bloch's theorem, which allows us to cast the problem onto a 'basis' of wavefunctions. To do this, we recast Eq. 1.26 in the following form,

$$\psi_{\mathrm{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_k(\vec{r}) \tag{1.27}$$

where $\vec{k}$ is the electron wavevector (such that $\vec{p} = \hbar\vec{k}$). It is easy to see that this wavefunction has the same periodicity as the crystal if we require that,

$$u_k(\vec{r}) = u_k(\vec{r}+\vec{R}) \tag{1.28}$$

By combining Eq. 1.27 with the Schrödinger equation, we obtain the following differential equation that the $u_k(\vec{r})$ should obey:

$$\left[-\frac{\hbar^2}{2m_e}\left(\nabla + i\vec{k}\right)^2 + U(\vec{r})\right]u_{\mathrm{k}}(\vec{r}) = \varepsilon_{\mathrm{k}}u_{\mathrm{k}}(\vec{r}) \tag{1.29}$$

Since the lattice potential is assumed to be periodic, we should be able to expand it in a Fourier series,

$$U(\vec{r}) = \sum_G U_G e^{i\vec{G}\cdot\vec{r}} \tag{1.30}$$

From this Fourier series it is easy to show that the vectors $\vec{G}$ have to be chosen with care. Since,

$$U(\vec{r}+\vec{R}) = \sum_G U_G e^{i\vec{G}\cdot\left(\vec{r}+\vec{R}\right)} = e^{i\vec{G}\cdot\vec{R}}U(\vec{r}), \tag{1.31}$$

we must have,

$$\vec{G}\cdot\vec{R} = 2n\pi. \tag{1.32}$$

such that indeed $U(\vec{r}+\vec{R}) = U(\vec{r})$. For a given set of lattice vectors the above relation defines the set 'reciprocal lattice' vectors. For the specific case of a three dimensional crystal we have,

$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \tag{1.33}$$

and

$$\vec{G} = p\vec{b}_1 + q\vec{b}_2 + r\vec{b}_3 \tag{1.34}$$

A little linear algebra shows that for G to satisfy Eq. 1.32, the $\vec{b}_i$ should satisfy,

$$\vec{b}_i = \frac{2\pi\left(\vec{a}_j \times \vec{a}_k\right)}{V_{cell}} \tag{1.35}$$

Show that..

with the given choice for the reciprocal lattice vectors $\vec{G}$ indeed satisfies Eq. 1.32

Note that the vectors $\vec{b}_i$ have the dimension of inverse length, just like the electron momentum (since $k = 2\pi/\lambda$). Therefore Eq. 1.34 combined with Eq. 1.35 defines a lattice similar to Eq. 1.33, but with dimension of inverse length (or with dimension of momentum!). For this reason it is called the reciprocal (or inverse) lattice. This has a crucial implication: not only is the wave function periodic in real space, it is also periodic in momentum space. As you can see from the definition of the reciprocal lattice vectors (Eq. 1.35), they are uniquely determined by and different for each set of real space vectors. The reciprocal lattices corresponding to the simple lattices depicted in Fig. 1.3b,c are also square and hexagonal lattices respectively. For more complicated real space lattices, complicated reciprocal lattices can, of course, be constructed. The power of these statements will (hopefully) become clear in the next section.

1.6 The tight-binding problem

We can use Bloch's theorem to recast the problem defined by Eq. 1.21. For a general form of the lattice potential this is still a complicated problem, since the number of terms that we need to retain in its Fourier expansion (Eq. 1.30) can become quite large. The problem is typically solved in two opposing limits. The **weak potential** limit [11] is typically used to describe metals. We will here not spend too much time on this problem and instead leave it as an exercise. This situation is also known as the (nearly) free electron model and has been discussed extensively during the course 'GM1'. The formal derivation is not all that complicated and since it follows roughly the same steps as the derivation in the opposite limit (to be discussed here) we leave it as an exercise to the reader (see Exercise 2). The second limit is known as the 'atomic' potential limit or **tight-binding** limit. In this limit we assume that we can replace the crystal potential by regularly spaced atomic potentials. This implies that the solutions (e.g. the wavefunctions) in fact closely resemble the atomic wavefunctions. By comparing the atomic potential with the approximate crystal potential (Fig. 1.4) we expect this to work well for materials consisting of atoms where the highest occupied orbitals are s– and p–wave orbitals (for example silicon or carbon allotropes etc.).

Before continuing, let us remind ourselves of the atomic problem. The Hamiltonian is simply:

$$H_{at} = -\frac{\hbar^2}{2m}\nabla^2 + U_{at}(\vec{r}) \tag{1.36}$$

where $\vec{r}$ refers to the electron coordinates. The Schrödinger equation is,

$$H_{at}\psi_n(\vec{r}) = E_n\psi_n(\vec{r}) \tag{1.37}$$

which has solutions $\psi_{1s}, \psi_{2s}, \psi_{2p}, \ldots$ with corresponding eigenenergies. Now, referring to Fig. 1.4 and Eq. 1.21, suppose we would write our Hamiltonian in the following way:

$$\begin{aligned} H &= -\frac{\hbar^2}{2m}\nabla^2 + U_{eff}(\vec{r}) \\ &= -\frac{\hbar^2}{2m}\nabla^2 + U_{at}(\vec{r}) + \sum_{\vec{R}\neq 0} U_{at}(\vec{r}-\vec{R}) \end{aligned} \tag{1.38}$$

where $\vec{R}$ is a vector of the real space lattice. We now notice that the first two terms in the second line exactly correspond to the atomic Hamiltonian, Eq. 1.36. We can now use the solution to the atomic problem to rewrite the Schrödinger equation for an electron moving through the crystal potential. Let's act with the full Hamiltonian on an atomic orbital $\psi_n(\vec{r})$. We find,

$$\begin{aligned} H\psi_n(\vec{r}) &= H_{at}\psi_n(\vec{r}) + \Delta U(\vec{r}-\vec{R})\psi_n(\vec{r}) \\ &= E_n\psi_n(\vec{r}) + \Delta U(\vec{r}-\vec{R})\psi_n(\vec{r}) \end{aligned}$$

Where we have introduced the term $\Delta U(\vec{r}-\vec{R})$, representing the modification of the potential at position $\vec{r}$ due to the nuclei at positions $\vec{R}$. If this term equaled zero, the problem would in fact be solved (as we would trivially have the atomic problem).

---

[11] *In this limit the lattice potential is replaced by a very weakly modulated potential. This situation describes electrons moving through the lattice in energy states close to the top of the lattice potential depicted in Fig. 1.4.*

Now imagine what happens if we slowly turn on the lattice potential arising from all the other nuclei. If this is done sufficiently slowly (adiabatically), the eigenfunctions shouldn't change all that much. However, as the last term on the 2nd line shows, the $\psi_n(\vec{r})$ are no longer the correct eigenfunctions of the Hamiltonian. To proceed we make an *ansatz* about the structure of the wavefunction. If we were trying to solve an atomic problem (for example, including spin-orbit interaction), a reasonable *ansatz* would be a linear superposition of the atomic orbitals

$$\phi(\vec{r}) = \sum_n b_n \psi_n^{at}(\vec{r}) \tag{1.39}$$

However, this wavefunction does not satisfy Bloch's theorem. Since we know that $\Delta U(\vec{r}-\vec{R})$ will introduce the lattice periodicity, we take as the ansatz,

$$\psi_k(\vec{r}) = \sum_{R,n} b_n \psi_n^{at}(\vec{r}-\vec{R}) e^{i\vec{k}\cdot\vec{R}} \tag{1.40}$$

Note that this wavefunction is exactly equivalent to Eq. 1.27 if we identify the $u_k(\vec{r})$ with the linear superposition Eq. 1.39. Note that we have expressed our lattice wavefunction in a basis of wavefunctions (the atomic orbitals).

All we need to do next is find the coefficients b_n and the modified eigenvalues. These will of course depend on the shape we choose for $\Delta U(\vec{r}-\vec{R})$. Unfortunately, nobody knows what $\Delta U(\vec{r}-\vec{R})$ looks like. Moreover, it will be different for each and every crystal: the precise potential at a given lattice site will depend on the atomic species of its neighbors, the number of neighbors, the atomic species of the neighbor's neighbors and so on. The aim of the coming page(s) is to solve the problem as far as we can without making any assumption about the actual form of $\Delta U(\vec{r}-\vec{R})$. There is one important point that should be stressed: if we would know the exact shape of $\Delta U(\vec{r}-\vec{R})$, the final result would be the exact solution of the single particle problem. So far, we have made no approximations (we only actually enforce the tight binding limit if we make assumptions about $\Delta U(\vec{r}-\vec{R})$).
The first step is to define the problem. The Schrödinger equation reads

$$H\psi_k(\vec{r}) = E_k \psi_k(\vec{r}) \tag{1.41}$$

The left-hand side can be rewritten, using our *ansatz* wavefunction, as:

$$H\psi_k(\vec{r}) = \sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n \left[H_{at} + \Delta U(\vec{r}-\vec{R})\right] \psi_n(\vec{r}-\vec{R}) \tag{1.42}$$

Making use of Eq. 1.37, we can replace H_{at} by the atomic eigenvalues. The Schrödinger equation then reads:

$$\sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n E_n \psi_n(\vec{r}-\vec{R}) + \sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n \Delta U(\vec{r}-\vec{R}) \psi_n(\vec{r}-\vec{R}) = E_k \sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n \psi_n(\vec{r}-\vec{R}) \tag{1.43}$$

Now we make use of a little trick; we multiply both sides by $\psi_m^\star$ and integrate,

$$\begin{aligned} &\sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n E_n \int d\vec{r} \psi_m^\star(\vec{r}) \psi_n(\vec{r}-\vec{R}) + \sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n \int d\vec{r} \psi_m^\star(\vec{r}) \Delta U(\vec{r}-\vec{R}) \psi_n(\vec{r}-\vec{R}) \\ &\quad = E_k \sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n \int d\vec{r} \psi_m^\star(\vec{r}) \psi_n(\vec{r}-\vec{R}) \end{aligned} \tag{1.44}$$

Lets take a closer look at the first term. We can separate it into a term where $\vec{R} = 0$ and a sum for $\vec{R} \neq 0$,

$$\sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n E_n \int d\vec{r} \psi_m^\star(\vec{r}) \psi_n(\vec{r}-\vec{R}) = \sum_n b_n E_n \int d\vec{r} \psi_m^\star(\vec{r}) \psi_n(\vec{r}) + \sum_{R\neq 0,n} e^{i\vec{k}\cdot\vec{R}} b_n E_n \int d\vec{r} \psi_m^\star(\vec{r}) \psi_n(\vec{r}-\vec{R}) \tag{1.45}$$

The first term can be rewritten by making use of the **completeness relation** for the atomic orbitals,

$$\int d\vec{r} \psi_m^\star(\vec{r}) \psi_n(\vec{r}) = \delta_{m,n} \tag{1.46}$$

By summing over all atomic orbitals we pick out the orbital m. Therefore,

$$\sum_{R,n} e^{i\vec{k}\cdot\vec{R}} b_n E_n \int d\vec{r} \psi_m^\star(\vec{r}) \psi_n(\vec{r}-\vec{R}) = b_m E_m + \sum_{R\neq 0,n} e^{i\vec{k}\cdot\vec{R}} b_n E_n \int d\vec{r} \psi_m^\star(\vec{r}) \psi_n(\vec{r}-\vec{R}) \tag{1.47}$$

we can further simplify this expression by introducing the definition,

$$\alpha_{m,n}(\vec{R}) \equiv \int d\vec{r}\psi_m^\star(\vec{r})\psi_n(\vec{r}-\vec{R}) \tag{1.48}$$

The term appearing on the right-hand side of Eq. 1.44 can be treated similarly. For the second term on the left-hand side of Eq. 1.44 we introduce two terms:

$$\beta_{m,n} \equiv \int d\vec{r}\psi_m^\star(\vec{r})\Delta U(\vec{r})\psi_n(\vec{r}) \tag{1.49}$$

and

$$\gamma_{m,n}(\vec{R}) \equiv \int d\vec{r}\psi_m^\star(\vec{r})\Delta U(\vec{r}-\vec{R})\psi_n(\vec{r}-\vec{R}) \tag{1.50}$$

By reorganizing some terms we now have:

$$(E_k - E_m)\, b_m = \sum_n b_n \left[\beta_{m,n} - (E_k - E_n)\sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\alpha_{m,n}(\vec{R}) + \sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\gamma_{m,n}(\vec{R})\right] \tag{1.51}$$

Show that..

Eq. 1.51 can be obtained from Eq 1.44

This is the most important result of this chapter. With this expression you will be able to derive the electronic dispersion, a.k.a. the **band structure**, for a given crystal structure and a given set of integrals $\alpha_{m,n}$,$\beta_{m,n}$ and $\gamma_{m,n}$. Throughout this course I will refer to this expression as the **central equation**. Note that the difficulty of solving the Schrödinger equation is still not solved, but is now hidden in the set of integrals and orbitals. Lets consider the (rough) meaning of the integrals first. In fact, the only integral that we have any real feeling for is $\alpha_{m,n}(\vec{R})$. This integral is called the **overlap** integral. If the atomic problem is solved accurately this integral is easily calculated with similar accuracy. In most cases this integral is typically small compared to the other terms appearing in the central equation and is therefore often ignored[12]. The other two integrals involve the lattice potential and are strongly dependent on the crystal structure (coordination number, symmetry etc.) and the flavors of atoms involved. There are empirical formulas for these integrals that can be used in simple cases (e.g. to understand the band structure of silicon), but personally I find this rather uninteresting. As far as this course is concerned both integrals provide a number and we can obtain this number by matching calculated band structures to measured ones. Despite the difficulty of obtaining accurate values for these integrals we can understand their origin. If we look at the structure of Eq. 1.49 we see that it involves the atomic orbitals on site $\vec{r}$ as well as $\Delta U(\vec{r})$ only. The latter is the deviation of the local potential from the atomic potential. As figure 1.4 demonstrates, this deviation is pretty small, so to first order this doesn't really affect the wavefunctions. As we will see in the next section and in the exercises, this term is mainly responsible for a shift in the energy of a given orbital. The last integral (Eq. 1.50) is the most complicated to interpret. It involves wavefunctions on different sites, just like the $\alpha_{m,n}$, but it also involves the lattice potential. This integral is known as the **hopping integral**: if finite this term is responsible for coupling different lattice sites and making it energetically favorable for electrons to delocalize[13]. In the next section I will describe a simple method to use the central equation to solve a given tight-binding problem followed by the simplest possible example. To close this section I would like to stress that tight-binding theory is a phenomenological approach: its accuracy depends on the accuracy with which the three integrals are determined and we have no way to test this accuracy. The power of the method lies in the fact that it gives a clear insight in the origin of measured band structures and it allows one to easily parameterize the electronic structure for more complicated calculations (for example, in the calculation of the optical response of solids).

1.7 The central equation and a simple example

In this section we will look at a simple scheme that can be used together with the central equation to solve for the electronic structure of solids. Note that the method is completely general and in principle exact: if the three integrals would be known exactly, the resulting band structure would be the exact solution to the single particle Schrödinger equation for an electron moving through a complicated lattice potential landscape. In general, we will not be interested in the electron wavefunctions in the solid itself. We therefore do not have to solve for the coefficients b_n. We will only be interested in the eigenvalues, the 'E_k'. Note that for each electron momentum k we will have an independent solution. To solve a tight binding problem using the central equation we will always follow the following steps:

[12] *Please don't take this to mean that it is always negligible. It is typically an important factor when d-orbitals are involved.*

[13] *The overlap integral also couples different sites, but does not lead to a net gain in energy.*

- Determine how many orbitals per lattice site should be included.
- Write down the relation between coefficient b_m and all other coefficients b_n.
- This requires writing down N equations for N unknown coefficients. It is therefore possible to eliminate the coefficients all together.
- From the resulting equation solve for E_k in terms of the three integrals $\alpha_{m,n}, \beta_{m,n}$ and $\gamma_{m,n}$.
- To continue you need more information about the crystal structure and the relative importance of the integrals. The crystal structure defines the set of vectors $\vec{R}$ required to work out the sums over $\vec{R}$, while the relative importance of the integrals will be given for a given exercise discussed during the course.
- The last step is to simplify the exponentials appearing in Eq. 1.51.

To illustrate how this works in practice we will now consider the simplest possible problem: a linear chain of hydrogen atoms. This example allows me to illustrate all the necessary tricks and also gives some insight into the physics of solids and their electronic structure. Since it describes a linear chain of hydrogen atoms it is however pretty much useless from a practical point of view (since these do not exist in nature to the best of my knowledge). The difficulty of solving a tight binding problem depends strongly on how many atomic orbitals we keep in the calculation. To know how many atomic orbitals we need to keep in order to describe a realistic problem with some accuracy requires some experience. For the hydrogen chain we will keep just the 1s orbital. This is a reasonable approximation if we are interested in the low energy properties. In the atomic problem, the 1s and 2s orbitals are separated by several electronVolt (eV). This will not change drastically when we consider the chain and therefore to very good approximation we need just the 1s orbital[14].

The labels m, n appearing in the sums in Eq. 1.51 are encoding for the different orbitals. We could introduce the notation $n = 1 \rightarrow 1s$-orbital, $n = 2 \rightarrow 2s$-orbital, but personally I find it much more convenient to just let the sum run over $m, n = 1s, 2s, 2p$.... With just the $1s$-orbital as the basis we have from Eq. 1.51[15]

$$(E_k - E_{1s})b_{1s} = b_{1s}\left[\beta_{1s,1s} - (E_k - E_{1s})\sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\alpha_{1s,1s}(\vec{R}) + \sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\gamma_{1s,1s}(\vec{R})\right] \tag{1.52}$$

We have in this case ($N = 1$) a single equation depending on a single coefficient (b_{1s}) and we can trivially eliminate it and solve for E_k (for convenience we drop one $1s$ label on the integrals):

$$E_k = E_{1s} + \frac{\beta_{1s} + \sum_{R\neq 0} \gamma_{1s}(\vec{R})e^{i\vec{k}\cdot\vec{R}}}{1 + \sum_{R\neq 0} \alpha_{1s}(\vec{R})e^{i\vec{k}\cdot\vec{R}}} \tag{1.53}$$

Note that so far we have really made no assumption about the crystal structure. Our only assumption has been that we need to consider 1s orbitals only. The result in Eq. 1.53 is in fact valid for an arbitrary lattice structure with arbitrary spatial dimension. For the special case of a 1D chain of (equally spaced) hydrogen atoms the set of lattice vectors $\vec{R} = na$, where a is the distance between two neighboring atoms and $|n| = 1, 2, 3...$ (note that we need to sum over positive and negative integers, or write two exponentials in the sum to include neighbors on the left and on the right of a given site.). This allows us to replace the sum over lattice sites $\vec{R}$ with a sum over atomic sites n:

$$E_k = E_{1s} + \frac{\beta_{1s} + \sum_{|n|\neq 0} \gamma_{1s}(na)e^{ik_x na}}{1 + \sum_{|n|\neq 0} \alpha_{1s}(na)e^{ik_x na}} \tag{1.54}$$

The next step is to determine the relative importance of the overlap integrals. Lets consider the $\alpha_{1s}(\vec{R})$ integral. Looking back to Eq. 1.48, we see that this integral is given by the overlap between a $1s$-orbital on site $\vec{r}$ and a $1s$-orbital on site $\vec{r} + \vec{R}$. Given the radial probability of the $1s$-orbital (see Fig. 1.5), we expect the overlap integrals to become increasingly smaller for atoms separated by more than one lattice site. In other words, we only expect this integral to have any importance for **nearest neighbors**. As a result we stop summing after $|n| = 1$ and keep just two exponentials.

$$\sum_{|n|\neq 0} \alpha_{1s}(na)e^{ik_x na} = \alpha_{1s}(-a)e^{-ik_x a} + \alpha_{1s}(a)e^{ik_x a} \tag{1.55}$$

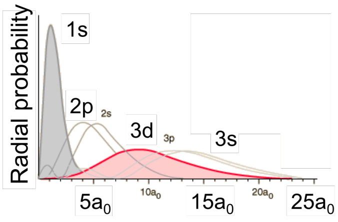


Figure 1.5: Radial distribution of the probability distribution for the atomic orbitals. $a_0 \approx 0.53$ Å is the Bohr radius. Image credit: `http://hyperphysics.phy-astr.gsu.edu`.

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[14] *This reasoning breaks down when we consider higher angular momentum orbitals. For example, the 3d orbitals consist of 5 individual orbitals (m_l=-2,...,2). In the absence of symmetry breaking terms, these orbitals are degenerate and we ought to keep all 5 of them.*

[15] *To ease writing in more complicated problems this is a good point to introduce the notation* $\tilde{\gamma} = \sum_{\vec{r}} e^{i\vec{k}\cdot\vec{r}}\gamma(\vec{R})$.

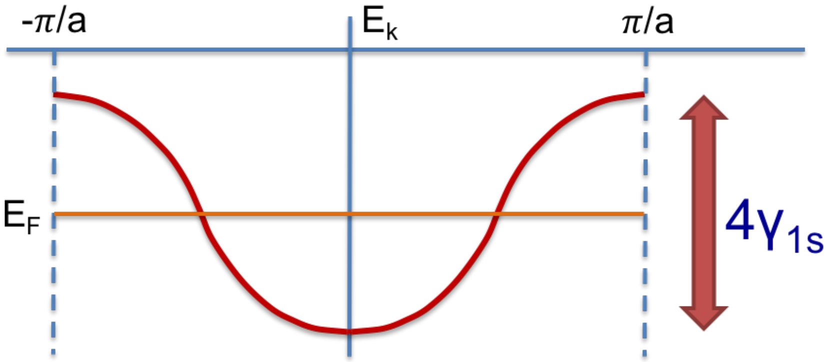

Figure 1.6: The dispersion for a linear chain in the 1st Brillouin zone. The zone boundary is indicated by the dashed lines. Note that the total width (bandwidth) in energy ranges from -2γ_{1s} to 2γ_{1s}.

Since we are considering a simple chain with 1s-orbitals, the problem is **inversion** symmetric between atoms on the left and on the right, i.e. $\alpha_{1s}(-a) = \alpha_{1s}(a)$, and we can combine the two exponentials into a cosine.

$$\sum_{|n|\neq 0} \alpha_{1s}(na)e^{ik_x na} = \alpha_{1s}\left[e^{-ik_x a} + e^{ik_x a}\right] = 2\alpha_{1s}\cos(k_x a) \tag{1.56}$$

A similar argument can be applied (in this particular case) to the sum over the hopping integrals $\gamma_{1s}(na)$. It can be shown[16] that these integrals become smaller with increasing distance between the lattice sites (falling off as $1/d$, where d is the distance) and it usually suffices to keep only nearest and **next-nearest** neighbors. For this example we will only keep the nearest neighbor hopping integral. This again reduces the sum over lattice sites to just two sites ($\pm a$) and we finally obtain:

$$E_k = E_{1s} + \frac{\beta_{1s} + 2\gamma_{1s}(a)\cos(k_x a)}{1 + 2\alpha_{1s}(a)\cos(k_x a)} \tag{1.57}$$

For simplicity we further ignore the contribution of the α_{1s} term and set it to zero:

$$E_k = E_{1s} + \beta_{1s} + 2\gamma_{1s}(a)cos(k_x a) \tag{1.58}$$

This is a reasonably simple result. We find that the energy eigenvalues for the electron wavefunctions (labelled with quantum number $\vec{k}$) are given by the energy of the atomic orbital, shifted by a small correction (β_{1s}) due to the slight modification of the atomic potential by neighboring atoms. On top of this we find that electrons with small momentum gain energy with respect to the atomic eigen energy, while high momentum states pay a bit of energy. This is quite similar to what happens in molecules (see figure 1.2, imagine that the bonding state coincides roughly with the $k = 0$ state here). In principle we could now continue to work out expressions for the coefficients b_m (which would be trivial in this case.), but most of the time the **dispersion relation** already provides a lot of insight.

The dispersion is plotted in Fig. 1.6. There are a number of important points to make about this simple result. As we have seen in Sec. 1.5, reciprocal space is periodic. For a linear chain, the reciprocal lattice vector is given by $2\pi/a$ (see Eq. 1.32). Therefore we only have to plot the dispersion in the so-called first **Brillouin zone**. This is also called the reduced zone scheme. The next Brillouin zone will be an exact copy of this Brillouin zone[17]. Another important quantity is the **Fermi energy**. The Fermi energy is defined as the energy separating occupied electronic states from unoccupied electronic states. To determine the Fermi energy we first need to know which states are occupied and to this end we first need to do some simple counting of states. For the linear chain of hydrogen atoms we have started with N 1s-orbitals, each occupied with one electron. We had better have enough empty states to harbor all those electrons. It is not difficult to show that, for a linear chain of length L with N lattice sites separated by distance a, the volume per k-point is $2\pi/Na$. Subsequently, there are N available states in our one dimensional dispersion and thus a grand total of $2N$ states if we include the spin degeneracy of each state. We started out with N hydrogen atoms, each carrying a single electron and therefore we need to distribute N electrons over 2N available states. The lowest energy configuration is thus achieved by occupying the bottom half of the band. At absolute zero temperature there will be a sharp cutoff between occupied and unoccupied states indicated in Fig. 1.6 by the Fermi energy (E_F). In this example, the Fermi energy lies in the band. This implies that there are empty states just above and occupied states just below the Fermi energy. It will therefore cost an infinitesimal

[16] *W. Harrison,* Electronic Structure and the Properties of Solids, *W.H. Freeman, San Francisco, 1980.*

[17] *For 3D crystal structures this can become quite a bit more complicated. See for examples* `https://en.wikipedia.org/wiki/Brillouin_zone`.

Show that..

the volume per k-point in a 3D volume is given by $\Delta k = \frac{V^{1stBZ}}{N_1 N_2 N_3}$. This can be done using Eq. 1.32 and Eq. 1.35

amount of energy to excite an electron from an occupied to an unoccupied state. It turns out that this is what ‘defines’ a **metal**: if we apply even the smallest perturbation (e.g. electric field) along the chain, some electrons can (asymmetrically) occupy the band and a current will flow. If on the other hand we would consider a chain of Helium atoms (with 2 electrons per atom) the band would be exactly filled and the Fermi level would lie just above the top of the band. In this case, there are no ‘empty’ states for electrons to occupy; the band simply stops and there are no allowed solutions of the Schrödinger equation at higher energy. We can apply a perturbation as large as we like, but without empty states for the electrons to occupy no transitions can take place. This is what defines a good **insulator**. Of course, in more realistic cases there will be other atomic orbitals than just the 1*s*-orbital and there will be more bands beyond the single cosine band of Fig. 1.6. Nevertheless, the energy separation between subsequent bands can be very large. If the energy gap between a fully occupied band and an empty band becomes small compared to, for example, temperature we use the term **semi-conductor** rather than insulator.

In the previous paragraph I have discussed some properties that can be gleaned directly from the electronic dispersion of a linear chain of 1*s*-orbitals. Most of the related concepts have been extensively discussed during the course GM-1 and I cannot repeat all of them here. If we move beyond the simplest example and include more orbitals, more atoms per unit cell and/or more spatial dimensions the method to solve the problem remains the same. Some important details do change however. For example, in one spatial dimension (and in the absence of interactions between the electrons[18]) we have the simple rule that chains of atoms are metallic if the atoms have an odd number of electrons, while they are insulating if there are an even number of electrons. This simple rule breaks down in higher dimension and quite often the mixing of atomic orbitals results in overlapping bands. To get an idea of what a ‘real’ band structure looks like, the band structure of silicon-carbide is shown in Fig. 1.7. Some important features of tight-binding band structures in higher dimensions will be discussed in the exercises at the end of this chapter. What the bandstructure of silicon-carbide shows is that the lowest ‘1*s*’ - band indeed looks pretty much cosine like. Note that a given band does *not* correspond to a particular atomic orbital. As soon as more than one orbital is involved these orbitals will mix together and form bands with varying amounts of orbital character. Fig. 1.7 also shows significant deviation from simple cosine like bands for higher energy bands.

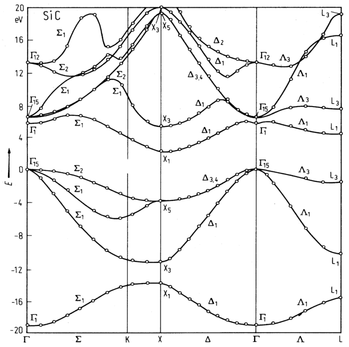

Figure 1.7: Band structure of silicon carbide along high symmetry directions of the Brillouin zone. Image credit: Hemstreet, L.A., Fong, C.Y. Silicon Carbide - 1973, Eds. Marshall, R.C., Faust, J.W., Ryan, C.E., Univ. of South Carolina Press, Columbia, S.C. 1974, 284.

There is one important aspect that we have not touched upon yet: in a more realistic problem where there is more than one orbital per unit cell there will be two bands and they will be separated at the zone boundary by a **band gap**. This can be seen clearly in Fig. 1.7 where the lowest band is separated from all others. The origin of bandgaps will be discussed in the exercises at the end of the chapter.

1.8 The electron and the quasiparticle

Personally, this section discusses one of my favorite bits of (solid state) physics. On the one hand it seems mundane, yet on the other hand it is extremely deep and a little bit magical. It also applies to many more physical situations than the case discussed here and we will encounter it a few more times during the course. Moreover, it indirectly led to many important discoveries, including the Higgs mechanism and the formulation of Quantum ElectroDynamics. It goes as follows.

Most of you will have an internal picture of an electron, perhaps a nice spherical, silvery colored object. If you don’t have such a picture before your mind’s eye, imagine that it looks like a nice spherical, silvery colored ball (you are even allowed to image reflections of the surroundings in its surface). Apart from the fact that an electron is an elementary particle and therefore a point-like object with no real diameter, such a description works well for ordinary electrons in vacuum. This little particle has a mass ($9.10938356 \cdot 10^{-31}$ kg to be precise) and a charge ($1.60217662 \cdot 10^{-19}$ Coulomb) that does not vary from one electron to the next (as they are indistinguishable particles). This particle we call ‘electron’. Now imagine an electron moving through a solid. Wrong. It is not simply a ball bouncing around in between a bunch of larger balls. Forget the whole spherical, silvery ball thing. It doesn’t exist in a solid. There are several ways to see this; I will discuss a few of them. The first hint that electrons in solids are different comes from the uncertainty principle. As discussed in the previous sections the band momentum k is a good quantum number. You have shown that each electrons occupies a well defined momentum state with a very small volume. Since Δk is small, the uncertainty principle states that Δx must be large. Indeed for a good metal the wave function can extend over almost a millimeter! There is however a more mathematical approach to express these ideas. The first is to ask the question: ‘What is

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[18] *Electrons always interact. Theoretically it has been found that metals do not exist in 1 dimension, but instead a so-called Luttinger liquid is formed. In this liquid the electron falls apart into two objects: a charged particle and a spin particle. These objects move independently. The experimental verification of these ideas is still actively pursued (also in Amsterdam!).*

the momentum of an electron in a solid?'. To answer this question we should evaluate the expectation value of the momentum operator for a 'band' electron

$$\langle \vec{p} \rangle = \left\langle \psi_k \left| \frac{\hbar}{i} \nabla \right| \psi_k \right\rangle \tag{1.59}$$

To evaluate the right-hand side, we make use of the tight-binding ansatz Eq. 1.40. This gives the following:

$$\langle \vec{p} \rangle = \frac{\hbar}{i} \sum_{R,R',n,n'} b^\star_{n'} \psi^\star_{n'}(\vec{r} - \vec{R}') e^{-i\vec{k}\cdot\vec{R}'} \nabla b_n \psi_n(\vec{r} - \vec{R}) e^{i\vec{k}\cdot\vec{R}} \tag{1.60}$$

This can be simplified a bit to,

$$\begin{aligned} \langle \vec{p} \rangle &= \frac{\hbar}{i} \sum_{R',R,n,n'} b^\star_{n'} b_n \psi^\star_{n'}(\vec{r} - \vec{R}') \nabla \psi_n(\vec{r} - \vec{R}) e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \\ &= \frac{\hbar}{i} \sum_{R,n,n'} b^\star_{n'} b_n \psi^\star_{n'}(\vec{r} - \vec{R}') \nabla \psi_n(\vec{r} - \vec{R}) \delta_{R,R'} \\ &= \sum_{n,n'} b^\star_{n'} b_n \left\langle \psi^{at}_{n'} \left| \vec{p} \right| \psi^{at}_n \right\rangle \end{aligned} \tag{1.61}$$

which shows that the physical momentum is a complicated sum of expectation values and not simply equivalent to the crystal momentum $\hbar\vec{k}$. Finally the mass of the electron has changed. For free electrons we have:

$$E = \frac{\hbar^2 k^2}{2m_e} \tag{1.62}$$

The electron mass is therefore equivalent to

$$\frac{1}{m_e} = \frac{1}{\hbar^2} \nabla^2_k E_k \tag{1.63}$$

A similar expression can be used to approximately define the mass of electrons in solids. This can be seen by writing down the Taylor expansion for the electronic dispersion,

$$\varepsilon(k) = \varepsilon(k_0) + \frac{1}{2} \sum_{i=1}^{3} \left(\frac{\partial^2 \varepsilon}{\partial k_i^2} \right)_{k=k_0} (k_i - k_{i0})^2 + \ldots \tag{1.64}$$

By comparison with Eq. 1.63 we see that the second order term can be used to define the band mass of the electron as,

$$\left(\frac{\partial^2 \varepsilon}{\partial k_i^2} \right)_{k=k_0} = \frac{\hbar^2}{m_{b,i}} \tag{1.65}$$

To summarize, electrons in solids are not the same objects as free electrons. Electrons in solids are therefore often called **quasiparticles**. These quasiparticles come in many more flavors than just simple electrons. Quasiparticles can become very light or very heavy and they can even have fractional electron charge. The development of these ideas in the early 1930's, 1940's and 1950's eventually led physicists like Hans Bethe and Richard Feynman to the formulation of an exact theory of electromagnetism (quantum electrodynamics or QED). It is this theory that allows the exact calculation, with many digits accuracy, of the (vacuum) values of the electron charge and mass quoted at the beginning of this section. Feynman's formulation of QED in turn proved to be extremely useful in the formulation of a complete theory of electron-phonon superconductivity. We will return to this topic at the end of the course. Since its inception the term quasiparticle is now applied more generally in the context of condensed matter physics. The low energy excitations of a solid can be similarly viewed as quasiparticles. Basically any low energy **excitation** (literally, an excited state of the solid) that can be quantified with a quantum number (typically momentum) and which has a long (→ ∞) lifetime can be viewed as a quasiparticle. Probably the best known quasiparticle, other than the quasi-electron, is the phonon. This is a low energy coherent vibration of the lattice. Just like the electron, phonons follow a dispersion relation and provide a unique fingerprint for each and every solid. In some sense phonons are the solid state equivalent of the rotational and vibrational levels of molecules and their dispersion forms from these levels in much the same way as the electronic dispersion from the atomic orbitals. Other quasi-particles that we will encounter during this course are the polariton, the spinon and the boguliubon.

EXERCISES I

ELECTRONIC STRUCTURE OF SOLIDS

In the following set of exercises we will discuss some problems that discuss either basic condensed matter questions, or are related to solving tight binding problems.

THE FREE ELECTRON MODEL

1

In this exercise you will work through a derivation of the free electron model. The aim of this exercise is to remind yourself of some important concepts concerning the electronic structure of solids in momentum space. The free electron model starts from the opposite limit compared to the tight-binding approximation. We consider electrons moving through the 'top' of the atomic potential (Fig. 1.4). In this situation, the atomic orbitals are not a good starting point to construct the Bloch wavefunctions. Instead, we assume that we can use plane waves as a basis for our Bloch wave function,

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} a_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \tag{E1.1}$$

As before, we expand the atomic potential in Fourier components:

$$U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \tag{E1.2}$$

$\mathcal{A}$ Show that the Schrödinger equation leads to:

$$\frac{\hbar^2}{2m} \sum_{\vec{k}} k^2 a_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \sum_{\vec{k}',\vec{G}} U_{\vec{G}} a_{\vec{k}'} e^{i(\vec{k}'+\vec{G})\cdot\vec{r}} = \epsilon_k \sum_{\vec{k}''} a_{\vec{k}''} e^{i(\vec{k}'')\cdot\vec{r}} \tag{E1.3}$$

$\mathcal{B}$ Show that this equation leads to the following relation between the Fourier components of the Bloch wave:

$$\left(\frac{\hbar^2 k^2}{2m} - \epsilon_k\right) a_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} a_{\vec{k}-\vec{G}} = 0 \quad \forall k \tag{E1.4}$$

$\mathcal{C}$ Show that for a weak potential ($U \approx 0$) you end up with,

$$\epsilon_k \approx \frac{\hbar^2 k^2}{2m} \tag{E1.5}$$

Note that in this case you have found the solution corresponding to the following Schrödinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \phi(r) = E\phi(r) \tag{E1.6}$$

with $\phi(r)$ a plane wave.

THE KRONIG-PENNEY MODEL

2

In the previous exercise you derived the 'central equation' for the nearly free electron model. In this exercise we will look at arguably the simplest model of a condensed matter system (the Kronig-Penney model), that gives a first idea of how the electronic structure of solids comes about. The Kronig Penney model consists of a chain of atoms (in 1 dimension) where the atomic nuclei are replaced by a Delta function potential (see fig. 1.8). The lattice potential is thus given by,

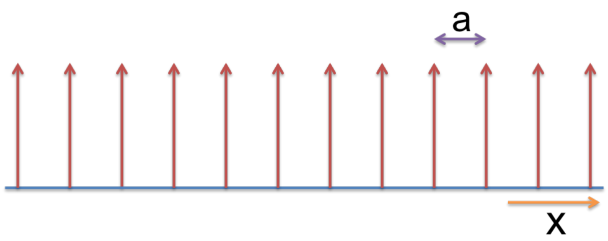


Figure 1.8: Dirac comb potential with lattice spacing a. The strength of each δ peak is A.

$$U(x) = A \sum_{n=-\infty}^{\infty} \delta(x - na) \tag{E1.7}$$

A Consider a finite chain of 2N+1 atoms (i.e. $n = -N \ldots N$) with periodic boundary conditions and show that the Fourier components U_G of $U(x)$ are given by:

$$U_G = \frac{A}{a} \tag{E1.8}$$

Hint: Use the fact that $\sum_{n=1}^{N} cos(Gna) = N$.

B Show that the $a(k)$ appearing in the central equation (Eq. E1.4) can be written as:

$$a(k) = -\frac{2mA}{\hbar^2 a}\frac{f(k)}{k^2 - \frac{2m\varepsilon}{\hbar^2}} \tag{E1.9}$$

C Show that $f(k)$ has the property,

$$f(k) = f(k - 2\pi n/a) \tag{E1.10}$$

D Show that the expression in Eq. E1.9 is equivalent to the condition,

$$-\frac{2mA}{\hbar^2 a}\sum_n \frac{1}{(k - \frac{2\pi n}{a})^2 - \frac{2m\varepsilon}{\hbar^2}} = 1 \tag{E1.11}$$

E define $\varepsilon \equiv \frac{\hbar^2 K^2}{2m}$ to show that,

$$\sum_n \frac{1}{(k - \frac{2\pi n}{a})^2 - \frac{2m\varepsilon}{\hbar^2}} = \frac{a}{2K}\frac{\sin(Ka)}{\cos(Ka) - \cos(ka)} \tag{E1.12}$$

Hint: use the following relation: $\sum_n 1/(n\pi + x) = cot(x)$

F Show that ε and k have the following implicit relation,

$$\cos(ka) = \cos(Ka) + \frac{1}{bK}\sin(Ka) \tag{E1.13}$$

Show that this relation implies energy gaps in the E vs. k relation. These energy gaps are the band gaps discussed in the lectures.

COHESION ENERGY

3

In this exercise we estimate the gain in kinetic energy that is partly responsible for the cohesion energy of a solid. One of the factors contributing to the cohesion energy of solids is the kinetic energy gain arising from the opening of band gaps. In this exercise we estimate the kinetic energy for electrons in a 2D simple, square lattice.

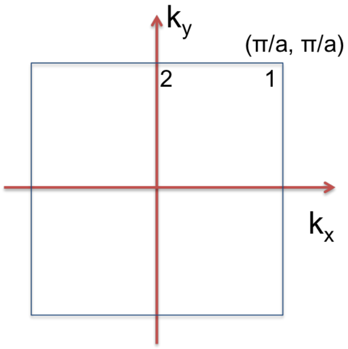


Figure 1.9: 2D Brillouin zone of the simple square lattice.

A Show for a simple square lattice in 2D that the kinetic energy at a corner of the first Brillouin zone (point 1) is larger than at the midpoint of the side-face of the Brillouin zone (point 2) by a factor of 2.

B What is this factor for a 3D simple cubic lattice?

C Give a condition that determines whether a divalent metal will be an insulator or a metal.[19]

THE DENSITY OF STATES

[19] *Hint: in the previous exercise we have seen that a band gap U opens between different bands at the zone boundary.*

4 The density of states is a fundamental quantity related to the electronic band structure. The density of states measures how many "quantum states" are available in a solid, per unit of energy. This important quantity determines many properties of solids (for example, the specific heat, resistivity etc.). In this exercise we will derive the general expression for the density of states in D dimensions.

$\mathcal{A}$ The *number* of states per unit energy, $R(E)$, is defined as:

$$R(E) = \sum_k \tag{E1.14}$$

where the sum runs over all k such that $\epsilon(k) \leq E$. Use the fact that in the limit $V \to \infty$,

$$\sum_k \to \frac{V}{(2\pi)^D} \int d^D k \tag{E1.15}$$

to show that in the free electron model,

$$R(E) = \frac{L^D m^{D/2}}{2^{D/2}(\pi\hbar)^D} c_D E^{D/2} \tag{E1.16}$$

Hint: the volume of a D dimensional sphere is $c_D k^D$.

$\mathcal{B}$ The Fermi energy, E_F, is defined as the energy separating occupied from unoccupied states (at T=0). Show that for a system with N_e electrons,

$$N_e = \frac{2L^D}{(2\pi)^D} c_D k_F^D. \tag{E1.17}$$

$\mathcal{C}$ Use the definition of the density of states ($\varrho(E) \equiv dR(E)/dE$), to show that,

$$E^D_{k,min} \equiv 2\int_0^{E_F} dE \varrho(E) E = \frac{D}{D+2} N_e E_F. \tag{E1.18}$$

5

Tight-binding bands of $YBa_2Cu_4O_{7-\delta}$

The HTSC cuprates are a family of materials consisting of many different compositions. One famous example is $YBa_2Cu_4O_{7-\delta}$. By changing the oxygen content this material can be tuned from an insulator to a HTSC superconductor with $T_c \approx 97$ K. The unit cell consists of "chain"-layers (top and bottom of the unit cell) separated by BaO layers from the CuO_2 plains (central two layers separated by Ytterbium). The BaO layers are pretty good insulators and electronically separate the other layers. The result is an electronic bandstructure consisting of nearly independent quasi 1 dimensional Cu-O chains and quasi 2 dimensional CuO_2 planes. In the following exercises we will calculate the most important features of the bandstructure using the tight binding approach. Note: the structure of this exercise is typical for an exercise you may be expected to solve during an exam.

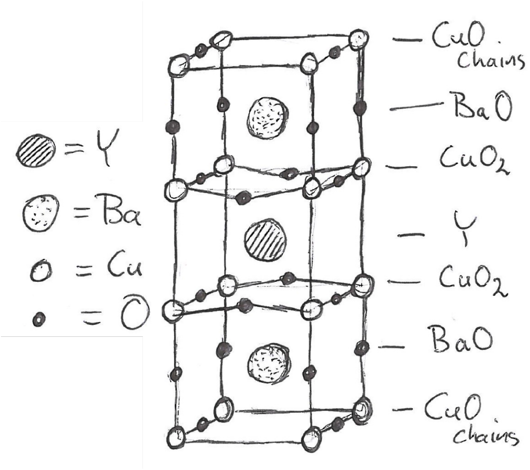


Figure 1.10: Unit cell of YBCO with different elements indicated. The unit cell consists of a stack of alternating 1D CuO chains and 2D CuO_2 planes.

$\mathcal{A}$ We will be interested in the highest occupied band only. Which orbitals do you think are relevant? Draw the unit cell of the Cu-O chain and indicate for both Cu and O the orbital that is likely most relevant[20].

---

[20] *In a solid the* 4s*-orbital has a lower energy compared to the* 3d*-orbital and is completely filled.*

B Show that from the tight binding assumption it follows that:

$$\begin{bmatrix} (E_k-\varepsilon_p-\beta_{pp}) & -\left(\beta_{pd}+\sum_{R\neq 0}e^{i\vec{k}\cdot\vec{R}}\gamma_{pd}(\vec{R})\right) \\ -\left(\beta_{dp}+\sum_{R\neq 0}e^{i\vec{k}\cdot\vec{R}}\gamma_{dp}(\vec{R})\right) & (E_k-\varepsilon_d-\beta_{dd}) \end{bmatrix}\begin{bmatrix} b_p \\ b_d \end{bmatrix}=0 \qquad \text{(E1.19)}$$

Note that some of the overlap integrals are neglected. Can you give arguments why?

C Show that the eigenvalues of the matrix above are:

$$E_k^{\pm}=\frac{\tilde{\varepsilon}_d+\tilde{\varepsilon}_p}{2}\pm\frac{1}{2}\sqrt{(\tilde{\varepsilon}_d-\tilde{\varepsilon}_p)^2+16\tilde{\gamma}_{pd}^2\sin^2\left(\frac{ka}{2}\right)} \qquad \text{(E1.20)}$$

Assume that nearest neighbor hopping is the only relevant coupling.

D Discuss how the case $\tilde{\varepsilon}_d\approx\tilde{\varepsilon}_p$ compares to the 1s-orbital case discussed during the lecture. Make a plot of the bandstructure. Will the chains be metallic or insulating?

E Discuss what happens in the opposite limit where $|\tilde{\varepsilon}_p-\tilde{\varepsilon}_d| >> \gamma_{pd}$.

F Sketch the CuO_2 plane and indicate the unit cell.

G How many bands do you expect to count in figure 1.11? Why are there exactly this many bands?

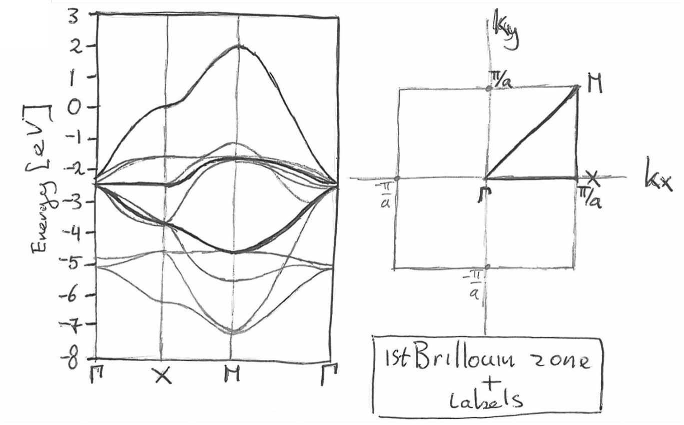


Figure 1.11: Left: tight binding bandstructure of the CuO_2-plane along high symmetry directions. Right: First Brillouin zone with high symmetry point labeling.

H It turns out that there is only one band crossing the Fermi level (see fig. 1.11). In the following we will calculate its dispersion. Based on the unit cell you sketched in *F*, which of the orbitals sketched in Fig. 1.12 do you expect to have the largest overlap? Draw the unit cell again, but now with the 3 relevant orbitals for the band crossing the Fermi level. Indicate the relevant tight-binding parameters (e.g. ε_p, ε_d, β_{pd} and γ_{pd}). What can you say about the relative sign of β_{pd} and γ_{pd} ?

I We are now ready to solve the problem. Follow the same route as in Exc. 5B to show that:

$$\begin{bmatrix} (E_k-\tilde{\varepsilon}_p) & -\beta_{p_xp_y} & A_1 \\ -\beta_{p_xp_y} & (E_k-\tilde{\varepsilon}_p) & A_2 \\ A_3 & A_4 & (E_k-\tilde{\varepsilon}_d) \end{bmatrix}\begin{bmatrix} b_{p_x} \\ b_{p_y} \\ b_d \end{bmatrix}=0 \qquad \text{(E1.21)}$$

For simplicity set $\beta_{p_xp_y}=\beta_{p_xp_y}=0$ and solve the above matrix equation. Show that there are 3 solutions (as expected):

$$E_k^{NB}=\tilde{\varepsilon}_p \qquad \text{(E1.22)}$$

and

$$E_k^{\pm}=\frac{\tilde{\varepsilon}_d+\tilde{\varepsilon}_p}{2}\pm\frac{1}{2}\sqrt{(\tilde{\varepsilon}_d-\tilde{\varepsilon}_p)^2+16\tilde{\gamma}_{pd}^2\left[\sin^2\left(\frac{k_xa}{2}\right)+\sin^2\left(\frac{k_ya}{2}\right)\right]} \qquad \text{(E1.23)}$$

HINT: $\gamma_{pd}=\gamma_{dp}$.

J Take ε_p=-2 eV, $(\varepsilon_d-\varepsilon_p)=1$ eV and $\gamma_{pd}=1.5$ eV. Plot the bandstructure along the high symmetry directions. Can you sketch how the Fermi surface changes as you shift the value of ε_p from 0 to ≈ -3 eV?

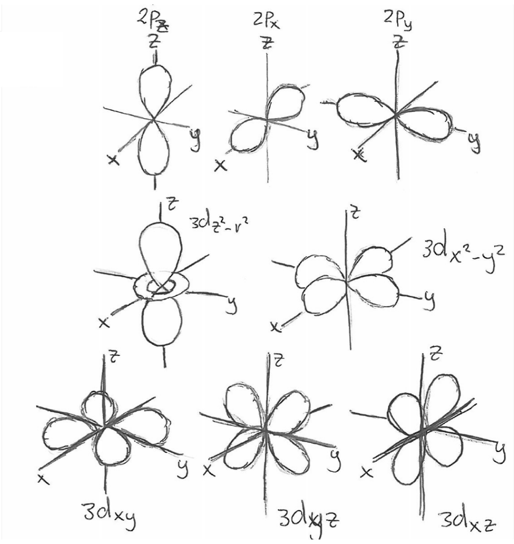


Figure 1.12: 2*p* and 3*d* orbital probability distributions.

ELECTROMAGNETISM MATTERS

Optical properties of solids.

KEYPOINTS:

- ☞ In solids photons behave as particles dressed with polarization clouds
- ☞ The optical response of a solid is a sensitive probe of the electronic structure
- ☞ The classical Drude-Lorentz model captures the interaction between light and matter.

2.1 Introduction

The study of solids is largely based on the measurement of their electronic or magnetic properties. Simple examples include the resistivity of a material, which enables us to distinguish between metals and insulators, or its magnetization. Most modern probes of condensed matter systems (angle resolved photoemission spectroscopy, optical spectroscopy) make use of the interaction between light and matter or between the electrons themselves (such as in scanning tunneling spectroscopy). The reason that these probes are most useful is simple: the interaction keeping solids together is electromagnetic as well. In other words, the Coulomb interaction keeps crystals together and the most effective probes directly couple to this interaction. In later chapters I will discuss the origin of magnetism and superconductivity and observable properties related to them. Since these properties are electromagnetic in origin, this chapter will provide you with an overview of the electrodynamics of solids. Unfortunately, a derivation of the full quantum mechanical description is quite laborious and not very insightful. Instead we will stick to a classical description. At the end of this chapter I will try to give you some feeling where the quantum mechanical description deviates. At the same time this will show that the quantum mechanical picture is mathematically almost equivalent to the classical one. Because of this reason, optical properties of solids are to this day most often described using the pre quantum mechanics Drude-Lorentz model. In the following all fields, currents, charge densities etc. are implied to be position and time dependent if not written explicitly. Parts of this chapter are based on published notes[2], which I wrote based on lectures given by Prof. Dr. Dirk van der Marel during the XIth summerschool on strongly correlated electron systems in Salerno, Italy.

2.2 Maxwell's equations in the presence of matter

It is quite easy, in principle, to write down Maxwell's equations for a solid with microscopic granularity[21]:

$$\nabla \cdot \vec{e} = 4\pi \varrho_{micro}, \tag{2.1}$$

$$\nabla \times \vec{e} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{b}, \tag{2.2}$$

$$\nabla \cdot \vec{b} = 0, \tag{2.3}$$

$$\nabla \times \vec{b} = \frac{1}{c}\frac{\partial}{\partial t}\vec{e} + \frac{4\pi}{c}\vec{j}_{micro}. \tag{2.4}$$

Here $\vec{e}$ and $\vec{b}$ are the microscopic electric and magnetic fields respectively. ϱ_{micro} is the total microscopic charge distribution and j_{micro} the total microscopic current distribution [22]. You could imagine chopping up a crystal into subunits, each with its own microscopic charge and current density. Indeed the smallest sensible unit would be a unit cell. The charge distribution for a collection of point sources with charge q_i can be written classically,

$$\varrho_{micro} = \sum_i q_i \delta(\vec{r} - \vec{r}_i), \tag{2.5}$$

or quantum mechanically as,

$$\varrho_{micro} = -e\Psi^\star(\vec{r})\Psi(\vec{r}). \tag{2.6}$$

Equations (2.1-2.4) are however not very practical to work with. As a first step we will rewrite them in a more familiar form. To this end we average the fields, charge and current distributions over a volume ΔV,

$$\varrho_{total}(\vec{r}) = \frac{1}{\Delta V}\int_{\Delta V} \varrho_{micro}(\vec{r} + \vec{r}\,')d^3\vec{r}\,', \tag{2.7}$$

$$\vec{j}_{total}(\vec{r}) = \frac{1}{\Delta V}\int_{\Delta V} \vec{j}_{micro}(\vec{r} + \vec{r}\,')d^3\vec{r}\,', \tag{2.8}$$

and similarly for $\vec{E}$ and $\vec{B}$. This is sensible under the condition that $a_0 \ll \Delta V \ll (2\pi c/\omega)^3$ where a_0 is the Bohr radius and ω the frequency of light. What this inequality is telling us is that the interaction between light and matter is such, that details of the precise charge distribution or current density on length scales comparable to the wavelength of light are important. This is an equivalent expression of the diffraction limit. At the same time it doesn't seem to make sense that the macroscopic properties are sensitively

[21] *Note that all subsequent equations are written in the C.G.S. system of units. To convert them to S.I. units, replace 4π by $1/\varepsilon_0 c$, $E_{S.I.}$ by $cE_{C.G.S.}$ and finally c by $4\pi/\mu_0$. The C.G.S. units are standard use in optical spectroscopy.*

[22] *With 'total' I mean charge or current due to sources inside and outside the solid.*

dependent on details of the atomic nucleus. Using these averaged charge and current densities we arrive at the standard **Maxwell equations**,

$$
\begin{aligned}
\nabla \cdot \vec{E}_{total}(\vec{r},t) &= 4\pi \varrho_{total}(\vec{r},t), && (2.9)\\
\nabla \times \vec{E}_{total}(\vec{r},t) &= -\frac{1}{c}\frac{\partial}{\partial t}\vec{B}_{total}(\vec{r},t), && (2.10)\\
\nabla \cdot \vec{B}_{total}(\vec{r},t) &= 0, && (2.11)\\
\nabla \times \vec{B}_{total}(\vec{r},t) &= \frac{1}{c}\frac{\partial}{\partial t}\vec{E}_{total}(\vec{r},t) + \frac{4\pi}{c}\vec{J}_{total}(\vec{r},t). && (2.12)
\end{aligned}
$$

These relations are valid both inside and outside the solid. In order to see how matter interacts with propagating electromagnetic waves we have to distinguish between **induced sources** and **external sources**. We write $\vec{J}_{total} \equiv \vec{J}_{ext} + \vec{J}_{ind}$ and $\varrho_{total} \equiv \varrho_{ext} + \varrho_{ind}$. Both the induced and external charge distributions and current densities have to obey the continuity equations separately,

$$\nabla \cdot \vec{J}_{ind/ext} + \frac{\partial}{\partial t}\varrho_{ind/ext} = 0. \qquad (2.13)$$

The continuity relation is very useful as it allows us to focus on just the current density: if known, the charge density follows. There are three different sources for macroscopic, induced currents that we can distinguish,

$$\vec{J}_{ind} = \vec{J}_{cond} + \frac{\partial \vec{P}}{\partial t} + c\nabla \times \vec{M}. \qquad (2.14)$$

The first term on the right hand side, $\vec{J}_{cond}$, corresponds to the response of free (unbound) charges to an applied field. To understand the origin of the second term we refer to Fig. 2.13. We will mostly consider time varying electric fields (e.g. photons) in this chapter. Imagine a collection of atoms in a given volume. These atoms consist of both positive (red) and negative (blue) charges that will respond to the electric field to form a dipole moment. Since the electric field is time dependent, the dipole moment will be time dependent as well and a corresponding oscillating current will develop. This current is described by the second term and is often referred to as the **bound charge** response. Physically it corresponds to a change in the total polarization, $\vec{P}$. Finally, we include a term representing a current due to (induced) magnetization. Note that this last term is purely transversal (the divergence of a rotation is always zero) and so is easy to distinguish from the other two terms. It is also most often negligible and we will not spend much attention to it. Since the induced free charge current due to photons is necessarily transversal, $\nabla \cdot \vec{J}_{cond} = 0$, we can use the continuity equations to show that the induced free charge density has to be zero and as a consequence that the total induced charge density,

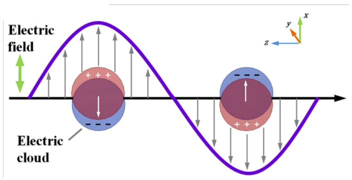


Figure 2.13: In a time varying electric field current has to flow to accommodate the changes in dipole moment.

$$\varrho_{ind} = -\nabla \cdot P. \qquad (2.15)$$

It is sometimes convenient to introduce new fields

$$
\begin{aligned}
\vec{D}(\vec{r},t) \equiv \vec{E}_{ext}(\vec{r},t) \equiv \vec{E}(\vec{r},t) + 4\pi\vec{P}(\vec{r},t), && (2.16)\\
\vec{H}(\vec{r},t) \equiv \vec{B}(\vec{r},t) - 4\pi\vec{M}(\vec{r},t), && (2.17)
\end{aligned}
$$

which are known as the displacement and magnetic fields[23] so that using equations (2.14-2.17) in equations (2.9) and (2.12) we find,

$$
\begin{aligned}
\nabla \cdot \vec{D}(\vec{r},t) = 4\pi\varrho_{ext}(\vec{r},t), && (2.18)\\
\nabla \times \vec{H}(\vec{r},t) = \frac{1}{c}\frac{\partial}{\partial t}\vec{D}(\vec{r},t) + \frac{4\pi}{c}\vec{J}_{ext}(\vec{r},t) + \frac{4\pi}{c}\vec{J}_{cond}(\vec{r},t). && (2.19)
\end{aligned}
$$

These equation can be simplified a little bit if we restrict ourselves to the interior of the solid where the external charge and current density is by definition zero. Some reshuffling allows us to cast the Maxwell equations in almost symmetric form:

$$
\begin{aligned}
\nabla \cdot \vec{D}(\vec{r},t) = 0, && (2.20)\\
\nabla \cdot \vec{B}(\vec{r},t) = 0, && (2.21)\\
\nabla \times \vec{H}(\vec{r},t) = \frac{1}{c}\frac{\partial}{\partial t}\vec{D}(\vec{r},t) + \frac{4\pi}{c}\vec{J}_{cond}(\vec{r},t), && (2.22)\\
\nabla \times \vec{E}(\vec{r},t) = -\frac{1}{c}\frac{\partial}{\partial t}\vec{B}(\vec{r},t). && (2.23)
\end{aligned}
$$

From the Maxwell equations we can derive the wave equations describing the propagation of electromagnetic waves in a medium. To make this possible we need to make an assumption about the relation between applied fields on the one hand and induced currents on the other. This is achieved by applying the ideas of linear response theory.

[23] *As a matter of historic perspective, the $\vec{B}$ field was originally known as the magnetizing field (i.e. the field that induces a change in the magnetization) and the H field as the total field. The latter is thus the actual 'magnetic' field.*

2.3 Linear Response Theory

Linear response theory is really an assumption about the nature of response functions. The theory is widely applicable also outside the current scope. It is not really a theorem (exceptions are well know), but for our purpose we will cast it in a form that makes it look like a theorem:

The response of a system to a perturbation is linearly proportional to this perturbation.

Well known (and very useful) exceptions to this rule make up the field known as *non-linear optics*. Our theorem will hold if we do not make our applied perturbations too large. In the case of optics this means that it is alright to use a laser as long as we keep the power low enough. To see the power of linear response theory at work, we assume that the response of the induced polarization, magnetization and current are linear in the applied fields:

$$\vec{P} = \chi_p \vec{E}, \tag{2.24}$$

$$\vec{M} = \chi_m \vec{H}, \tag{2.25}$$

$$\vec{J} = \chi_J \vec{E}. \tag{2.26}$$

The proportionality constants are called **susceptibilities**. These are measures of how susceptible a given medium is to respond to an applied perturbation. Note that the electric field and currents can be complex quantities. The susceptibilities we have defined above are however real numbers. Unfortunately, the notation used in the description of the electromagnetic response of solids was historically developed from empirical observations. As a result, the proportionality constant χ_J is instead better known as the conductivity σ. The other two susceptibilities are also better known in a different form. These are not simply renamed symbols:

$$\varepsilon \equiv 1 + 4\pi\chi_p \tag{2.27}$$

is known as the (relative) dielectric permittivity. The second quantity,

$$\mu \equiv 1 + 4\pi\chi_m \tag{2.28}$$

is called the magnetic permeability. Using these two expressions we can rewrite the responses as:

$$\vec{P} = \frac{\varepsilon - 1}{4\pi}\vec{E} \tag{2.29}$$

$$\vec{M} = \frac{\mu^{-1} - 1}{4\pi}\vec{B} \tag{2.30}$$

$$\vec{J} = \sigma\vec{E}. \tag{2.31}$$

With these definitions the relations between the displacement field and the electric field and the magnetic and magnetizing fields become:

$$\vec{D}(\vec{r},t) = \varepsilon(\vec{r},t)\vec{E}(\vec{r},t), \tag{2.32}$$

$$\vec{H}(\vec{r},t) = \mu^{-1}(\vec{r},t)\vec{B}(\vec{r},t), \tag{2.33}$$

There are a few things to note. First of all, in vacuum $\sigma = 0$, $\varepsilon \equiv \varepsilon_0$ and $\mu \equiv \mu_0$ where the latter are the well known fundamental constants[24]. In principle, the response functions should depend on both position and time. For example, the dielectric permittivity is a response function that connects the external field $\vec{E}_{ext}$ at position $\vec{r}$ and time t with the field $\vec{E}$ at all other times and positions. So in general,

$$\vec{E}_{ext}(\vec{r},t) = \int_{-\infty}^{t}\int \varepsilon'(\vec{r},\vec{r}',t,t')\vec{E}(\vec{r}',t')d^3\vec{r}'dt'. \tag{2.34}$$

It turns out that in most solids we can assume the response function to be homogeneous[25]. With these definitions in place we are now in a position to formulate the wave equations in the presence of matter.

[24] *There is one unfortunate aspect of using C.G.S. units: in these units $\varepsilon_0 = \mu_0 = 1$. In modern electromagnetism, the light speed is not a fundamental constant, but $c \equiv 1/\sqrt{\varepsilon_0\mu_0}$.*

[25] *Spatial inhomogeneity, in particular in quasi 2D materials, can result in interesting optical properties.*

2.4 The wave equations and the polariton

To derive the wave equations, we start by taking the curl of Eq. 2.23

$$\nabla \times (\nabla \times \vec{E}) = -\frac{1}{c}\frac{\partial}{\partial t}(\nabla \times \vec{B}) \tag{2.35}$$

Show that..

$\nabla \cdot \vec{E} = 0$ by making use of the linear response equations

Using standard vector relations[26] and by noting that since $\nabla \cdot \vec{E} = 0$ in a solid we can write,

$$\nabla^2 \vec{E} = \frac{\mu}{c}\frac{\partial}{\partial t}\nabla \times \vec{H} \tag{2.36}$$

Next we make use of the third Maxwell relation, Eq. 2.22. We first rewrite it using the linear response relations as:

$$\nabla \times \vec{H} = \frac{\varepsilon}{c}\frac{\partial \vec{E}}{\partial t} + \frac{4\pi\sigma}{c}\vec{E} \tag{2.37}$$

and then we plug it back into Eq. 2.35 to obtain an equation depending on the electric field only:

$$\nabla^2 \vec{E} = \frac{\mu\varepsilon}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} + \frac{4\pi\mu\sigma}{c^2}\frac{\partial \vec{E}}{\partial t} \tag{2.38}$$

a similar exercise gives:

$$\nabla^2 \vec{H} = \frac{\mu\varepsilon}{c^2}\frac{\partial^2 \vec{H}}{\partial t^2} + \frac{4\pi\mu\sigma}{c^2}\frac{\partial \vec{H}}{\partial t} \tag{2.39}$$

These are the wave equations of electromagnetic radiation in the presence of matter. I leave it to the reader to verify that these expression reduce to the well known wave equations of EM-fields in vacuum.

The two wave equations, Eq. 2.38 and 2.39, determine the propagation of waves through a medium. The exact solutions can be very complicated, depending on the boundary conditions and other complicating factors. We will not consider such cases, but instead use the simple case of an infinite medium. In that case we can take a simple plane wave as a possible solution to the wave equations. In what follows we will only consider the propagation of electric fields. The plane wave form for the electric field is,

$$\vec{E}(\vec{r}, t) = \vec{E}_0 e^{i(\vec{q}\cdot\vec{r} - \omega t)}, \tag{2.40}$$

Inserting this into Eq. 2.38 and working out the derivatives gives:

$$-q^2 \vec{E} = -\frac{\mu\varepsilon\omega^2}{c^2}\vec{E} - \frac{i4\pi\mu\sigma\omega}{c^2}\vec{E} \tag{2.41}$$

We can eliminate the electric field and are then left with a relation between the frequency and momentum of the plane wave,

$$\omega = \frac{c}{\sqrt{\mu\left(\varepsilon + \frac{4\pi i\sigma}{\omega}\right)}}q \tag{2.42}$$

At this point it is useful to introduce complex response functions. This is really a matter of redefining some quantities. So far we have worked with the two real numbers ε and σ. We rename these to ε_1 and σ_1. We then introduce the complex **dielectric function** $\hat{\varepsilon} \equiv \varepsilon_1 + i\varepsilon_2$ and the complex **conductivity** $\hat{\sigma} \equiv \sigma_1 + i\sigma_2$. From Eq. 2.42 we see that if we take $\varepsilon_2 \equiv 4\pi\sigma_1/\omega$, we can rewrite the dispersion relation as,

$$\omega = \frac{c}{\sqrt{\mu\hat{\varepsilon}}}q \tag{2.43}$$

We could also have opted to introduce the complex conductivity instead, but this form is more compact and has a nicer physical analogy with the result obtained in vacuum. In fact, the complex conductivity and dielectric function are really equivalent in that they are related according to,

$$\hat{\sigma} = \frac{i\omega}{4\pi}(1 - \hat{\varepsilon}). \tag{2.44}$$

Equation 2.43 is one of the fundamental results of this chapter. Let me reiterate its meaning: it is the dispersion relation for electromagnetic waves (photons) in a solid. It is the equivalent of the dispersion relation for electrons in a solid. Of course, the description is purely classical and there are no hints in our description of the underlying microscopic principles that govern the behavior of electrons in solids. Instead, all material related properties are lumped into a single complex dielectric function[27]. I have glossed over several details in the derivation that will simplify Eq. 2.43:

[26] *i.e.* $\nabla \times (\nabla \times \vec{f}) = \nabla(\nabla \cdot \vec{f}) - \nabla^2 \vec{f}$.

[27] *It is in fact not such a bad approach: the dielectric function can be calculated in a quantum mechanical approach. The results of this chapter can then be used without further modification. This is a consequence of the fact that the wavelength of light is large compared to the microscopic length scales.*

Kramers-Kronig relations

A fundamental principle in physics is the principle of causality: an effect cannot precede its cause. This principle provides us with very useful relations between the real and imaginary parts of response functions. The derivation is not too complicated and can be found on e.g. wikipedia (`https://en.wikipedia.org/wiki/Kramers?Kronig_relations`). The principle of causality when applied to the electromagnetic response functions can be formulated as,

$$j(t) = \int_{-\infty}^{t} M(t-t')E(t')dt'.$$

Where $M(t-t' < 0) = 0$. This is simply a restatement of the causality principle: we switch on a driving force ($\vec{E}(t')$) at time $t - t' = 0$. So, before this moment there can be no current. This statement can be used to derive the Kramers-Kronig relations for the complex optical conductivity:

$$\sigma_1(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\sigma_2(\omega')}{\omega'-\omega}d\omega'$$

and

$$\sigma_2(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\sigma_1(\omega')}{\omega'-\omega}d\omega'.$$

where $\mathcal{P}$ denotes the Cauchy principal value. From these considerations one can also show that $\sigma(-\omega) = \sigma^\star(\omega)$, which implies that $\sigma_1(-\omega) = \sigma_1(\omega)$ and $\sigma_2(-\omega) = -\sigma_2(\omega)$. These relations between the real and imaginary parts of the optical conductivity are examples of the general relations between real and imaginary parts of causal response functions and they are referred to as Kramers-Kronig (KK) relations. They can be extremely useful both experimentally and theoretically. For example, it may be straightforward to calculate the real part of the optical conductivity. The imaginary part can then be obtained by making use of the Kramers-Kronig relations. These relations in their general form were independently derived by Hendrik Kramers (Dutch) and Ralph Kronig (German) in 1926/27. Later in life they both held appointments at the TU Delft. Image credits: wikipedia.

- As pointed out previously (Eq. 2.34) the dielectric function in principle depends on position and time.
- An equivalent formulation can be obtained by using the Fourier representation of the EM fields. In this formulation $\hat{\epsilon} \equiv \hat{\epsilon}(\vec{q},\omega)$
- Since $q \propto 1/\lambda$ and since $\lambda >> a$ with a the lattice constant, the momentum of a photon is really small compared to typical electron momenta.
- We will concern ourselves in the remainder of this chapter with optical properties of solids. Therefore we can safely assume $q \approx 0$.
- Hence, Eq. 2.43 is an implicit solution: ω appears on both sides of the relation.
- In most solids μ is really small (10^{-4}) compared to $\hat{\epsilon}$.
- We have no idea what $\hat{\epsilon}(\omega)$ looks like and so we haven't really solved anything yet.

To end this section I want to draw your attention to the following. Equation 2.43 is equally applicable outside solids. In other words, the dispersion relation of photons in vacuum is[28],

$$\omega = cq = \frac{2\pi c}{\lambda} \tag{2.45}$$

In other words, photons travel through vacuum at the speed of light and their frequency is inversely proportional to their wavelength. Hopefully, you are familiar with this result. We can use Eq. 2.45 to define the mass of a photon using the same relation as we used in chapter 1.8 (see Eq. 1.63). Fortunately, taking the 2nd derivative of Eq. 2.45 with respect to momentum equals zero and we find that the photon has no mass. Here comes the punchline: inside a solid we should really use Eq. 2.43 and the 2nd derivative is not necessarily equal to zero anymore. Put differently, photons propagating through a solid can acquire an effective mass; inside a solid photons transform into quasiparticles! The source of this transformation is found in the dielectric function. Since the real part of the dielectric function is related to the charge susceptibility (Eq. 2.27), which relates the electric field to the induced polarization (Eq. 2.24), the effective mass can be seen to find its origin in the **dressing** of the photon with a polarization cloud. The resulting quasiparticle is therefore called **polariton**.

[28] *Remember that we are using C.G.S. units and therefore $\epsilon_0 = \mu_0 = 1$.*

2.5 Polaritons

In this section we discuss some properties of electromagnetic waves propagating through solids. As mentioned above, a polariton is a photon dressed up with the excitations that exist inside solids. There are different 'types' of polaritons. For example, one can have phonon-polaritons which are photons dressed up with lattice vibration related polarization clouds. One way of understanding the changes in the photon fields is by making use of the modified dispersion relation. Since our dielectric function depends on ω, we write,

$$|q| = \frac{\sqrt{\mu\hat{\epsilon}(\omega)}\omega}{c}. \tag{2.46}$$

You are probably more familiar with the (real part of the) refractive index,

$$\hat{n}(\omega) = n + ik \equiv \sqrt{\mu\epsilon}. \tag{2.47}$$

In all cases considered here $n > 0$ and $k > 0$[29]. We also note that $Im(\epsilon) \geq 0$ but it is possible to have $Re(\epsilon) < 0$. If $k > 0$ the wave traveling through the solid gets attenuated according to,

$$\vec{E}(\vec{r}, t) = \vec{E}_0 e^{i\omega(nr/c - t) - r/\delta}. \tag{2.48}$$

The extinction of the wave occurs over a characteristic length scale δ called the skin depth,

$$\delta = \frac{c}{\omega k} = \frac{c}{\omega \, \mathrm{Im}\sqrt{\mu\epsilon_1 + i4\pi\mu\sigma_1/\omega}}. \tag{2.49}$$

Note that we can have $k > 0$ if $Im(\epsilon) = 0$ and $Re(\epsilon) < 0$ so that the wave gets attenuated even though there is no absorption. In table 2.1 we indicate some limits of the skin depth. To get a better feeling of the properties and relevance of polaritons, we need a model description of the dielectric function. The model we will use during the course is known as the **Drude-Lorentz model**. It actually consists of two ideas. The first is known as the **Drude model**, while the second is known as the **Lorentz model**. They are however nearly equivalent (the Drude model follows from a particular limit of the Lorentz model). In the next section we will discuss some of the properties of the Drude-Lorentz model.

Insulator	$\frac{4\pi\sigma_1}{\omega} \ll \epsilon_1$	$\delta \approx \frac{c}{2\pi\sigma_1}\sqrt{\frac{\epsilon_1}{\mu}}$
Metal	$\frac{4\pi\sigma_1}{\omega} \gg \epsilon_1$	$\delta \approx \frac{c}{\sqrt{2\pi\mu\sigma_1\omega}}$
Superconductor	$\frac{4\pi\sigma_1}{\omega} \ll \epsilon_1 = -\frac{c^2}{\lambda^2\omega^2}$	$\delta \approx \frac{\lambda}{\sqrt{\mu}}$

Table 2.1: Some limiting cases of the general expression Eq. (2.49). λ in the last line is the London penetration depth.

2.6 The Drude-Lorentz model

The Drude model is one of the earliest attempts to describe the electromagnetic response of a metal based on a microscopic picture. In 1900 Paul Drude published an attempt to describe the optical properties of solids based on the application of the kinetic (Boltzmann) theory to electrons (which had been discovered only a few years before in 1896 by J.J. Thomson) in the presence of electromagnetic fields.

He considered a very simple model of a solid: it consisted of negatively charged particles (electrons) that were moving on a positively charged, featureless background. Note that the nucleus (and thus the precise structure of the atom) was not discovered until 1911. He assumed that under the influence of an electric field some electrons would be displaced relative to the positive background (see Fig. 2.14) resulting in a current. Drude's major breakthrough was to apply the kinetic theory of gases to the ensemble of electrons. He imagined that electrons would move around and bounce of each other, much like atoms in a gas would. This led him to realize that there would be a characteristic (temperature dependent) time between two collisions. This collision time, τ, can be described in a newtonian picture as a damping force acting on the electrons. This damping force depends on the average velocity of the electron and a proportionality constant, Γ, known as the scattering rate:

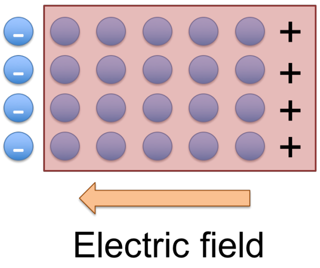


Figure 2.14: Negatively charged electrons (blue) are displaced relative to a featureless positive background (red) under the influence of an electric field.

$$\vec{F} = -m\Gamma\vec{v} \tag{2.50}$$

From these considerations it follows that the conductivity should be of the form,

$$\hat{\sigma} = \frac{ne^2}{m}\frac{1}{\Gamma - i\omega}. \tag{2.51}$$

[29] *Classically these are the only physical solutions. A current, 'hot' field of research concerns so-called meta-materials (with n or $k < 0$) that are used to make invisibility cloaks.*

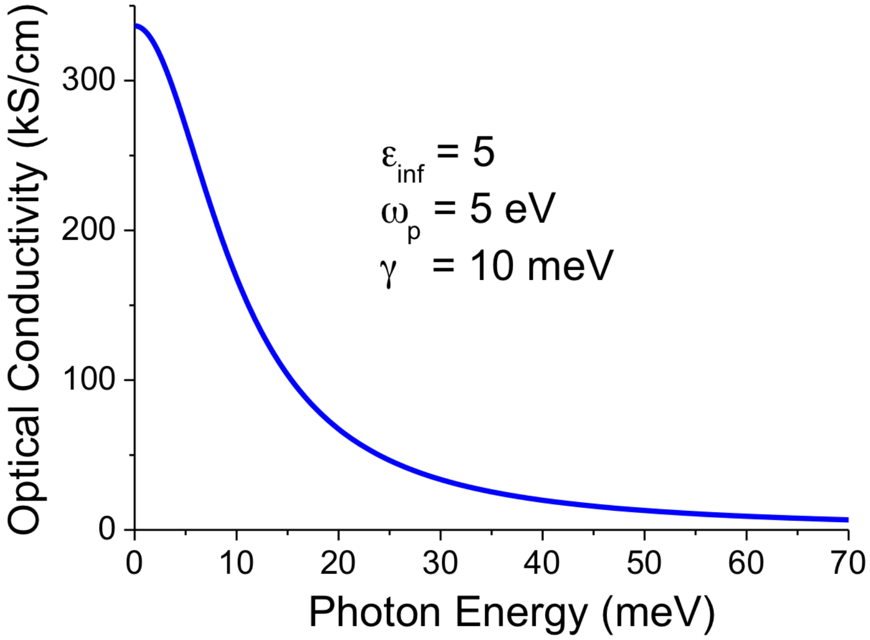


Figure 2.15: Real part of the optical conductivity as function of photon energy. The plasma frequency, ω_p, and scattering rate, γ, are indicated.

The pre-factor is often redefined as the plasma frequency $\omega_p^2 \equiv 4\pi ne^2/m$. The derivation of this expression is left as an exercise (see Exercise 1). The resulting (frequency dependent) real part of the optical conductivity is plotted in Fig. 2.15[30]. Note that the zero frequency limit of the optical conductivity is the inverse of the resistivity. In 1905, in between deriving the co-variant formulation of Maxwell's equations and working out a 'Theory of the electron', Hendrik A. Lorentz extended Drude's model to include the response of bound electrons. In addition to the damping force introduced by Drude, Lorentz included a restoring force that led him to the following expression for the optical conductivity,

$$\hat{\sigma}(\omega) = \frac{i\omega f^2}{i\omega\Gamma - (\Omega_0^2 - \omega^2)} \tag{2.52}$$

where f is the strength of the optical transition and Ω_0 is known as the resonance frequency. This expression reduces to the Drude result in the limit $\Omega_0 \to 0$.

Remarkably, these results remain approximately correct even in the quantum mechanical derivation. Unfortunately, deriving a proper quantum theory of the optical response of solids is cumbersome. We will not attempt such a derivation, but instead we take a quick look at the result. The quantum mechanical formulation of the optical conductivity is known as the **Kubo-Greenwood formula**:

$$\hat{\sigma}_{\alpha,\beta}(q,\omega) = \frac{ie^2}{V} \sum_{n,m\neq n} \frac{e^{\beta(\Omega - E_n)}}{\omega_{mn}} \left[\frac{v_{\alpha,q}^{nm} v_{\beta,-q}^{nm}}{\omega - \omega_{mn} + i\delta} + \frac{v_{\alpha,-q}^{nm} v_{\beta,q}^{nm}}{\omega + \omega_{mn} + i\delta} \right] \tag{2.53}$$

Here the subscripts α, β indicate the principal axes of the crystal, $\beta = (k_B T)^{-1}$ in the exponent and $\delta \to 0$. Furthermore,

$$v_{\alpha,q}^{nm} \equiv \langle \Psi_m | \hat{v}_{\alpha,q} | \Psi_n \rangle \tag{2.54}$$

is known as the **dipole-moment** corresponding to the optical transition of an electron from state $|\Psi_n\rangle$ with momentum $\vec{k}$ to a state $|\Psi_m\rangle$ with momentum $\vec{k} + \vec{q}$. Finally,

$$\omega_{mn} \equiv E_m - E_n \tag{2.55}$$

is the energy separation between the two states $|\Psi_{m,n}\rangle$ [31]. The Kubo-Greenwood formula describes optical excitations of the ground state of a solid, while properly taking transition probabilities and quantum statistics into account. The wavefunctions and corresponding eigenenergies can, for example, be taken from a tight binding calculation, but they can also be obtained from more complicated theoretical constructs. It can be shown (with some redefinitions that are at this point unimportant) that an equivalent formulation is given by,

$$\hat{\sigma}_{\alpha,\alpha}(q,\omega) = \frac{i\omega}{4\pi} \sum_{n,m\neq n} \frac{\Omega_{nm}^2}{i\delta\omega - (\omega_{mn}^2 - \omega^2)} \tag{2.56}$$

---

[30] *A useful set of conversions between different units that is worth remembering is: 1 eV = 8065 cm^{-1} = 11604 K.*

[31] *For those of you familiar with it: the Kubo-Greenwood formula is closely related to Fermi's golden rule.*

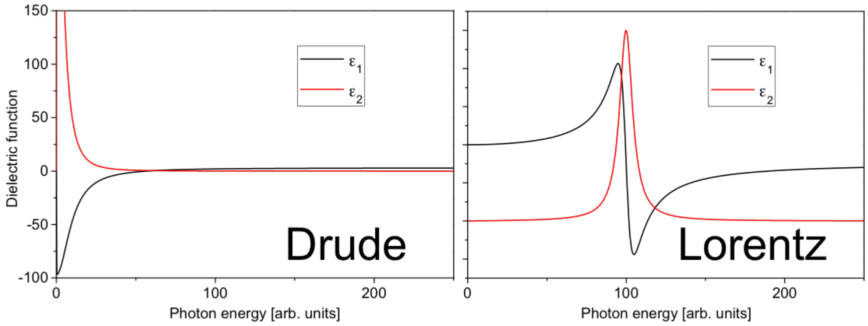


Figure 2.17: Real (black line) and imaginary (red line) components for the dielectric function. The real part of the dielectric function of the Drude model is negative at zero frequency.

This expression is very similar to Eq. 2.52 apart from the sum. This sum runs over the different electronic states and therefore corresponds to a sum over all possible **interband** transitions between occupied and unoccupied bands (see Fig. 2.16). The Lorentz model is therefore a useful and good description of any solid if we take several terms (**Lorentz oscillators**) corresponding to Eq. 2.52. Note that the Kubo-Greenwood formula only describes transitions between different bands ($m \neq n$). It is also possible to derive an expression for **intraband** transitions, which in some limit provides a justification for the Drude result. The functional form, Eq. 2.51 is however only a good description of real solids in the limit of low frequency, high temperature and in the absence of significant electron-electron or electron-phonon interactions.

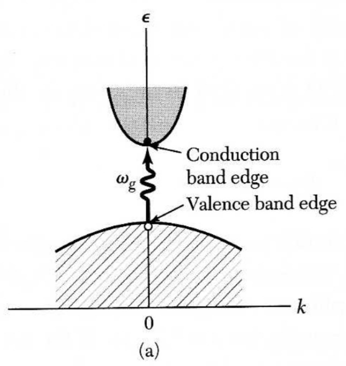


Figure 2.16: Direct interband transition between the occupied valence band and the unoccupied conduction band. The onset of the transition is indicated by ω_g.

Combining the Drude and Lorentz model we finally obtain,

$$\hat{\sigma}(\omega) = \frac{\omega_p^2}{4\pi}\frac{1}{\Gamma_f - i\omega} + \sum_i \frac{i\omega f_i^2}{i\omega\Gamma_i - (\Omega_{0,i}^2 - \omega^2)} \tag{2.57}$$

From this we can immediately determine an expression for the dielectric function,

$$\hat{\varepsilon}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)} - \sum_i \frac{4\pi f_i^2}{i\omega\Gamma_i - (\Omega_{0,i}^2 - \omega^2)} \tag{2.58}$$

We conclude this section by plotting the Drude and Lorentz oscillators for the dielectric function in Fig. 2.17.

2.7 The optical properties of solids

With a model for the dielectric function in place, we can return to our discussion of the polariton and its relevance to the optical properties of a solid. Keep in mind that the allowed solutions for electromagnetic waves in a solid are given by Eq. 2.43. In combination with the Drude-Lorentz model, Eq. 2.58, we can now solve for the proper relation between frequency and momentum of the EM waves. Note that if the dielectric function is negative, the polaritons become exponentially damped (the refractive index in Eq. 2.48 will be imaginary). This implies that if the dielectric function is negative, polariton solutions are not allowed to propagate inside the solid. We see from Fig. 2.17 that the real part of the dielectric function is negative for a finite range of frequencies on the high frequency side of the peak in the imaginary part. The actual range of frequencies where the dielectric function is negative of course depends on the chosen parameters. In Fig. 2.18 we show the polariton dispersion calculated for a Lorentz oscillator for a few parameter values. The real part of the dielectric function is shown on the left, while the polariton dispersions calculated with Eq. 2.43 are shown on the right. As you should have expected, the polariton dispersion is linear in momentum for $f = 0$, corresponding to the dispersion relation of photons in vacuum. For finite oscillator strength, the dispersion is modified and acquires a momentum dependence. Notably the modification of the dispersion is strongest close to the maximum in σ_1. If the coupling between the EM wave and the electron system (quantified by f, or in a quantum version by the expectation value of the dipole moment) is strong enough the electrons will respond to the EM wave and will oscillate in phase. If the electron system is driven too fast (i.e. for frequencies larger than the resonance frequency), it can no longer follow the oscillation and will start to lag behind in phase. For photon frequencies much larger than the resonance frequency, the electron system reacts too slow and the photon propagates unhindered.

The polariton dispersion is intimately tied to the reflection or transmission of waves at the interface between a solid and its surroundings. Imagine a photon impinging on the surface of a material: depending on its energy there may or may not be a

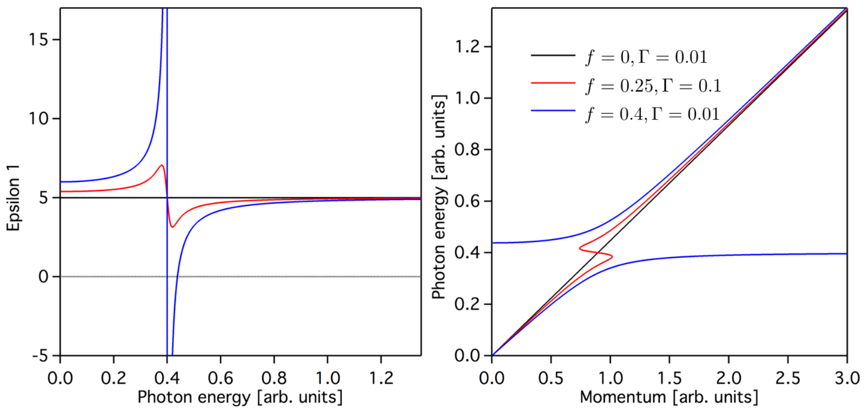


Figure 2.18: (Left): Real part of the (Lorentz) dielectric function for a few parameter values (corresponding to the values indicated in the right hand graph). Note that as the strength increases, $\varepsilon_1(\omega)$ becomes negative. The frequency range over which $\varepsilon_1(\omega)$ is negative depends on both f and Γ. (Right): Polariton solution calculated using the full complex $\hat{\varepsilon}(\omega)$ for the parameter values indicated. Note that as the width and strength increase a band of energies appears where no solutions are allowed (blue curve).

solution inside the solid. If there is a solution, the wave will enter the material and propagate for a certain distance before being attenuated. If this distance is longer than the thickness of the solid, the wave will subsequently leave the solid and continue its journey through vacuum. On the other hand, if there is no solution the energy stored in the wave needs to go somewhere. If the energy of the incoming wave is close to a resonance, the energy will be dissipated [32] inside the solid. If on the other hand the energy of the incoming wave cannot be absorbed in the material, the wave will be reflected back into the vacuum. In this situation the reflectivity of the material will be finite and the transmission zero. The reflectivity of a (semi-infinite) solid is related to the dielectric function according to,

$$R(\omega) = \left| \frac{1 - \sqrt{\hat{\varepsilon}}}{1 + \sqrt{\hat{\varepsilon}}} \right|^2 \tag{2.59}$$

At the same time, the transmission in the absence of absorption is defined simply as $1 - R(\omega)$. For a slab of finite thickness the transmission is a somewhat more complicated function of the dielectric function due to the fact that we need to consider multiple internal reflections.

We can qualitatively understand many of the optical properties of solids. First of all, we expect a fundamental difference between metals and insulators: metals are characterized by 'free' electrons and therefore the dielectric function will have a Drude peak. Figure 2.17 shows that in this case the dielectric function is negative over a range of frequencies, starting at zero frequency; at low frequency polaritons cannot propagate in a metal. This is equivalent to the well known result obtained from static electromagnetism, namely that there can be no electric field inside a perfect conductor. At higher frequencies the dielectric function turns positive and the specific frequency where this happens (in the absence of interband transitions) is known as the (screened) plasma frequency. Note that the plasma frequency is proportional to the density of free charge carriers (Eq. 2.51). For a typical metal the charge density is on the order of 10^{21} cm^{-3}, which works out to plasma frequencies on the order of a few to ten's of electronVolts. As a result metals are not transparent. Insulators on the other hand have no Drude peak and are typically transparent in the visible range of the spectrum. The amount of absorption and the frequencies where a material absorbs are crucial to determine the color of a material. For example, the difference in color between copper, gold and silver arises mainly from a difference in the onset of interband transitions (in the UV range for silver, in the blue for gold and in the green for copper).

2.8 Screening

I would like to point out a final important aspect of the dielectric function before ending this chapter. You may have wondered how it is possible that solids don't collapse or explode under the strong Coulomb repulsion or attraction between positive and negative charges. One aspect related to this is **screening**[33]. To see how screening works, consider the Maxwell equation (in SI),

$$\nabla \cdot \vec{E} = \frac{\varrho}{\varepsilon_0} \tag{2.60}$$

If we take for ϱ for the moment just two electric charges q_1 and q_2, we know that the potential becomes:

$$V(\vec{r}) = \frac{q_1 q_2}{4\pi\varepsilon_0 \left|\vec{r}_1 - \vec{r}_2\right|} \tag{2.61}$$

[32] *This requires finite ε_2!*

[33] *Another aspect is related to Fermi-Dirac statistics: electrons are fermions and as a result cannot occupy the same space. If you try to squeeze electrons into a small volume an outward pressure will develop.*

where $\vec{r} = \vec{r}_1 - \vec{r}_2$. This potential is simply the static Coulomb potential and at first glance seems to make it impossible to form a solid. Somehow the strong repulsion between the electrons is overcome. In this chapter we have seen that inside the solid we should take instead:

$$\nabla \cdot \vec{D} = \frac{\varrho}{\varepsilon_0} \tag{2.62}$$

which is equivalent to

$$\nabla \cdot \vec{E} = \frac{\varrho}{\varepsilon_0 \varepsilon(\vec{k}, \omega)} \tag{2.63}$$

From this we see that it is the dielectric function that may be responsible for a significant reduction of the Coulomb potential. This is known as 'screening' of the Coulomb potential. We can assume a very simple form of the screened Coulomb potential, namely:

$$V_{TF}(\vec{r}) = \frac{q_1 q_2}{4\pi\varepsilon_0 \vec{r}} e^{-\vec{k}_{TF}\cdot\vec{r}} \tag{2.64}$$

This potential is known as a Yukawa potential. The upshot of it is that the static Coulomb is significantly reduced in range. As a result this means that the potential energy cost of confining a bunch of electrons to a small volume is significantly reduced. In exercise 2 you are asked to show that from Eq. 2.64 follows that the dielectric function has a k-dependent piece given by,

$$\varepsilon(k) = 1 + \frac{k_{TF}^2}{k^2} \tag{2.65}$$

k_{TF} is known as the inverse screening length[34] and can be shown to be approximately given by,

$$k_{TF} \approx \sqrt{\frac{4k_F}{\pi a_B}} \tag{2.66}$$

where k_F is the Fermi wavevector and a_B the Bohr radius. This result is known as **Thomas-Fermi screening** and provides an important explanation for the screening of charged impurities in solids. More generally we observe that by comparison it follows from Eq. 2.63 that inside a solid the bare, static Coulomb interaction changes to,

$$V_{scr}(\vec{k}, \omega) = \frac{V_C(\vec{k}, \omega)}{\varepsilon(\vec{k}, \omega)} \tag{2.67}$$

This important result shows that the excitations of the solid (captured by the response function ε) combine to reduce (screen) the original Coulomb potential. This result will play an important role in Chapters 4 & 5

[34] *i.e. it corresponds to a typical length scale* $\lambda_{TF} \propto k_{TF}^{-1}$.

EXERCISES II

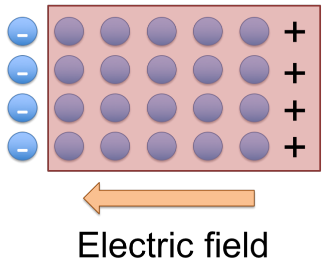
OPTICAL PROPERTIES OF SOLIDS

In these exercises you will derive some of the most used optical properties of solids. In the first exercise you will derive the Drude-Lorentz model. The dielectric function derived here forms the basis for the remaining exercises where you will derive the reflectivity of materials and some of its limits.

1

THE LORENTZ-MODEL

Consider a static background of positive ions and **bound** electrons in the presence of a time varying electron field.



A Which forces act on the electrons?

B Show that the equation of motion can be written as:

$$m(\Omega^2 - \omega^2 - i\omega\Gamma)x(\omega) = qE(\omega) \tag{E2.1}$$

Hint: start from Newton's equation F=ma and use the Fourier transforms of

$$x(t) = \int d\omega x(\omega)e^{-i\omega t} \tag{E2.2}$$

and

$$E(t) = \int d\omega E(\omega)e^{-i\omega t} \tag{E2.3}$$

C We can use the result of the previous exercise to find an expression for the complex conductivity. We are looking for an expression of the form: $j(\omega) = \hat{\sigma}(\omega)E(\omega)$. Starting from the definition of current density, $j(t) = -nev(t)$, show that:

$$\hat{\sigma}(\omega) = \frac{\omega_p^2}{4\pi} \frac{i\omega}{i\omega\Gamma - (\Omega^2 - \omega^2)} \tag{E2.4}$$

D How does the Drude expression follow from this? Give a physical explanation.

E Find the band edges of the forbidden band in which no polariton solution exists. Discuss your solution for the case $\Gamma = 0$. Use this result to explain why metals are never transparent.

2

SCREENED COULOMB POTENTIAL

In this exercise you will derive the momentum dependence of the dielectric function assuming a screened Coulomb potential.

A The Fourier transform $g(\vec{k})$ of a function $f(\vec{r})$ is given by,

$$g(\vec{k}) = \int_V e^{i\vec{k}\cdot\vec{r}} f(\vec{r}) d^3\vec{r} \tag{E2.5}$$

Use spherical coordinates to show that this can be rewritten as[35],

$$g(k) = \frac{4\pi}{k} \int_0^\infty r f(r) \sin(kr) dr \tag{E2.6}$$

B Show that the Fourier transform of the Coulomb potential $V(r) = e^2/4\pi\varepsilon_0 r$ is[36] ,

$$V(k) = \frac{e^2}{\varepsilon_0 k^2} \tag{E2.7}$$

C Show that for a dielectric function of the form

$$\varepsilon(k) = 1 + \frac{k_{TF}^2}{k^2} \tag{E2.8}$$

the potential becomes a screened Coulomb potential of the form

$$V_{TF}(\vec{r}) = \frac{q_1 q_2}{4\pi\varepsilon_0 \vec{r}} e^{-\vec{k}_{TF}\cdot\vec{r}} \tag{E2.9}$$

THE FRESNEL EQUATIONS

---

[35] *Hint: introduce a variable* $\chi = \cos(\vartheta)$ *and use* $\vec{k}\cdot\vec{r} = kr\cos(\vartheta)$.

[36] *Hint: use*

$$\frac{1}{r} = \lim_{\varepsilon\to 0} \frac{e^{-\varepsilon r}}{r}$$

3 In this exercise you will derive the Fresnel equations that describe the reflection and transmission at an interface between two media. For simplicity we will assume normal incidence.

$\mathcal{A}$ Use a plane wave expansion for the electric field $\vec{E}$ and magnetic field $\vec{B}$ in combination with the Maxwell relation Eq. 2.23 to derive the following relation between the two fields:

$$\frac{B_0}{E_0} = \sqrt{\varepsilon(q,\omega)} \tag{E2.10}$$

where we have assumed that $\mu = 1$.

$\mathcal{B}$ Now consider figure 2.19. We have an incoming wave $\vec{E}_i$ in a medium labelled 1, a transmitted wave propagating though medium 2 labelled $\vec{E}_t$ and a reflected wave $\vec{E}_r$. At the interface we must have $\vec{E}_i + \vec{E}_r = \vec{E}_t$. Show that from this it follows that,

$$\vec{B}_i - \vec{B}_r = \vec{B}_t \tag{E2.11}$$

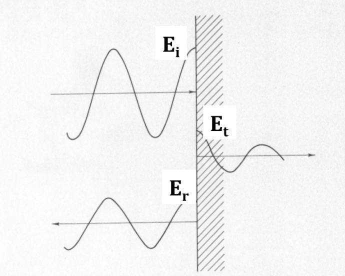


Figure 2.19: Sketch of the situation considered in the derivation of the Fresnel equations.

$\mathcal{C}$ Combine the previous results to show that,

$$\vec{E}_i - \vec{E}_r = \frac{\hat{n}_2}{\hat{n}_1}\vec{E}_t \tag{E2.12}$$

$\mathcal{D}$ Use this to define the complex reflection,

$$\hat{r} = \frac{\hat{n}_1 - \hat{n}_2}{\hat{n}_1 + \hat{n}_2} \tag{E2.13}$$

and transmission

$$\hat{t} = \frac{2\hat{n}_1}{\hat{n}_1 + \hat{n}_2} \tag{E2.14}$$

coefficients.

$\mathcal{E}$ Show that Eq. 2.59 follows from E2.13 assuming an incoming wave traveling through vacuum.

THE HAGEN-RUBENS RELATION

4 The Hagen-Rubens relation is a simple relation between the DC conductivity (or in other words, the inverse of the resistivity) and the low energy (far infrared) reflectivity of a metal. We approximate the Drude expression for the dielectric function in the limit that $\omega\tau \ll 1$ as,

$$\hat{\varepsilon}(\omega) = 1 + i\frac{4\pi\sigma_0}{\omega} \tag{E2.15}$$

Use the result of Exc. 3 to show that,

$$R(\omega) \approx 1 - \sqrt{\frac{2\omega}{\pi\sigma_0}} \tag{E2.16}$$

REFLECTIVITY OF SEMICONDUCTORS

5 In this exercise we will consider a simplified relation between the energy gap of a semi conductor and the reflectivity. A rough approximation for the dielectric function of a semi conductor can be obtained as follows. Only photons with an energy larger than the energy gap ω_g can be absorbed. Therefore the imaginary part of the dielectric function (or the real part of the optical conductivity) can be very roughly approximated by a delta function,

$$\varepsilon_2(\omega) = \frac{\omega_p^2}{2\omega}\delta(\omega - \omega_g) \tag{E2.17}$$

The Kramers-Kronig relation can now be used to derive the real part of the dielectric function,

$$\varepsilon_1(\omega) = 1 + \frac{\omega_p^2}{\omega_g^2 - \omega^2} \tag{E2.18}$$

Derive an expression for the reflectivity in the limit $\omega \ll \omega_g$

NON-MAGNETS IN A MAGNETIC FIELD

Putting the magnetism back into electromagnetism

KEYPOINTS:

- ☞ A particle in a magnetic field exhibits a large degeneracy of states.
- ☞ Bands in solids become **Landau levels**.
- ☞ The **Hall conductivity** allows measuring the electron density in a solid.

3.1 Introduction

In most materials there is only a very weak response of the electron system to the magnetic component of the photon field. There are however many interesting features that emerge when a large static magnetic field is applied. In subsequent chapters we will discuss spontaneously magnetized states of matter. As an introduction we will discuss the properties of non-magnetic materials in an applied magnetic field in this chapter.

3.2 One particle in a magnetic field

We will consider the effect of a static, applied magnetic field on a solid or crystal that is not magnetic by itself. As will become clear, some properties of materials show drastic changes in the presence of a static magnetic field. First, we will consider a simplified single particle Hamiltonian for an electron moving through a magnetic field. As a reminder, the Hamiltonian for a single particle reads,

$$\left[\frac{\hat{p}^2}{2m} + V(r)\right]\psi(r) = E\psi(r). \tag{3.1}$$

To include electromagnetism at the single particle level, we can make use of the so-called **minimal substitution**,

$$\hat{p} \to \hat{p} - \frac{q}{c}\hat{A}. \tag{3.2}$$

The minimal substitution is sufficient to take the effects of electrons moving through a static magnetic field into account[37]. The full single particle Hamiltonian is thus,

$$\left[\frac{(\hat{p} - \frac{q}{c}\hat{A})^2}{2m} + V(r)\right]\psi(r) = E\psi(r). \tag{3.3}$$

We will ignore the complication of the lattice potential and consider just the problem of an electron moving through a magnetic field. Expanding the quadratic term we have:

$$\frac{(\hat{p} - \frac{q}{c}\hat{A})^2}{2m} = \frac{1}{2m}\left(\hat{p}^2 - \frac{2q}{c}\hat{p}\cdot\hat{A} + \frac{q^2}{c^2}\hat{A}^2\right) \tag{3.4}$$

To make progress we need to have an expression for the vector potential. We will be interested in a magnetic field applied along the $\hat{\mathbf{z}}$- direction. From the relation of the magnetic field to the vector potential[38], it then follows that

$$B = B_z = (\partial_x A_y - \partial_y A_x)\hat{\mathbf{z}}. \tag{3.5}$$

It is important to remember that the electromagnetic fields are gauge invariant: we can change the vector potential according to

$$\vec{A} \to \vec{A}' = \vec{A} + \nabla\psi \tag{3.6}$$

provided that we also change the scalar potential according to,

$$\phi \to \phi' = \phi - \frac{1}{c}\frac{\partial\psi}{\partial t}. \tag{3.7}$$

This freedom allows us to cast the problem in a convenient form. Typically one works in the Coulomb gauge, $\nabla\cdot\vec{A} = 0$, but for this problem there is a much more useful gauge, known as the Landau gauge. In the Landau gauge, the vector potential is chosen to be[39]

$$\hat{A} = B\hat{x}\,\hat{\mathbf{y}}, \tag{3.8}$$

with $\hat{\mathbf{y}}$ a unit vector and $\hat{x}$ an operator. Note that this form of the vector potential is consistent with Eq. 3.5.

We can now rewrite Eq. 3.4 as:

$$\begin{aligned}&\frac{1}{2m}\left(\hat{p}^2 - \frac{2q}{c}\hat{p}\cdot\hat{A} + \frac{q^2}{c^2}\hat{A}^2\right)\\ &= \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} - \frac{q}{mc}B\hat{x}\hat{p}_y + \frac{q^2B^2}{2mc^2}\hat{x}^2 + \frac{\hat{p}_z^2}{2m}.\end{aligned} \tag{3.9}$$

Now we note that the Hamiltonian depends on $\hat{p}_y$ and $\hat{p}_z$, but not on the conjugate operators $\hat{y}$ and $\hat{z}$. As a result

$$\left[\hat{H}, \hat{p}_{y,z}\right] = 0 \tag{3.10}$$

---

[37] *The minimal substitution ignores multi-pole coupling contributions of the charge distributions.*

[38] *The magnetic field is the rotation of the vector potential, $\vec{B} = \nabla\times\vec{A}$, where explicitly,*

$$\nabla\times\vec{A} = \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{vmatrix}.$$

[39] *The general result for a particle moving in the (x,y)-plane can be obtained by using the* **symmetric gauge**, *which chooses a vector potential of the form $\vec{A} = \frac{1}{2}\left(-B\hat{y}\hat{\mathbf{x}} + B\hat{x}\hat{\mathbf{y}}\right)$. It makes the math more complicated and doesn't add anything to the discussion however.*

A particle in a magnetic field

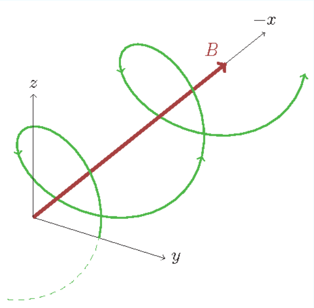
A particle moving through a magnetic field is subject to a Lorentz force. The particle (classically) follows a circular path if the Lorentz force is balanced by the centripetal force. A stable orbit is found by balancing these two forces, which yields the following relation:

$$F_c = F_L \rightarrow \frac{v_\perp}{R} = \frac{qB}{m_e c}.$$

The time required to complete a full circular orbit is of course given by $T = \frac{2\pi R}{v_\perp}$. The inverse of this period is known as the **cyclotron frequency**, ω_c. Given the above, the cyclotron frequency is

$$\omega_c = \frac{2\pi}{T} = \frac{qB}{m_e c}.$$

What this is telling you is that as the field increases, the orbits become tighter and since the speed remains constant this results in a larger number of orbits per second.



and therefore the wavefunctions must simultaneously be eigenfunctions of $\hat{p}_y$ and $\hat{p}_z$. The eigenfunctions of $\hat{p}_y$ are the plane waves,

$$\phi(y) = \frac{1}{\sqrt{V}} e^{ik_y y} \tag{3.11}$$

obeying the dispersion relation

$$\varepsilon_{k_y} = \frac{\hbar^2 k_y^2}{2m} \tag{3.12}$$

and similarly for $\hat{p}_z$.

Show that..

Eq. 3.10 implies that the eigenfunctions of the Hamiltonian are also eigenfunctions of $\hat{p}_{y,z}$.

To solve the full Schrödinger equation with the Hamiltonian, Eq. 3.9, we can now make use of the separability of the wavefunctions[40]. There is only a single term containing $\hat{p}_z$ and we can evaluate it immediately: it contributes a term $\varepsilon_{k_z} = \hbar^2 k_z^2/2m$ to the energy. This leaves us with:

$$\begin{aligned} H\psi(x,y) &= \left[\frac{\hat{p}_x^2}{2m} + \frac{q^2B^2}{2mc^2}\hat{x}^2 + \frac{\hat{p}_y^2}{2m} - \frac{q}{mc}B\hat{x}\hat{p}_y\right]\psi(x,y) \\ &= \left[\frac{\hat{p}_x^2}{2m} + \frac{q^2B^2}{2mc^2}\hat{x}^2 + \frac{\hbar^2 k_y^2}{2m} - \frac{q}{mc}B\hat{x}\hbar k_y\right] e^{ik_y y}\psi(x), \end{aligned} \tag{3.13}$$

Now we note that Eq. 3.13 only depends on the operators $\hat{x}$ and $\hat{p}_x$, so that it represents a 1D problem[41]. The remaining problem is in fact a well known one, but it appears unfamiliar due to the form in which it is written. If we introduce the cyclotron frequency $\omega_c \equiv qB/m_e c$ and complete a square,

$$H\psi(x,y) = \left[\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega_c^2\hat{x}^2 - \omega_c\hbar k_y\hat{x} + \frac{\hbar^2k_y^2}{2m}\right]\psi(x,y) \tag{3.14}$$

$$= \left[\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega_c^2\left(\hat{x} - \frac{\hbar k_y}{m\omega_c}\right)^2\right]\psi(x,y) \tag{3.15}$$

Finally, we define $x_0 = \hbar k_y/m\omega_c$ to find:

$$H\psi(x,y) = \left[\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega_c^2(\hat{x} - x_0)^2\right]\psi(x,y) \tag{3.16}$$

Hopefully, you'll recognize this as a quantum harmonic oscillator (QHO) problem. This is a standard problem in quantum physics, and the eigenvalues and eigenfunctions are well known. The eigenvalues are,

$$E_n = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{\hbar^2 k_\parallel^2}{2m}. \tag{3.17}$$

The first term (with $n = 0, 1, 2, \ldots$) represent the energies of subsequent levels of the harmonic oscillator, while the second term originates in the velocity perpendicular to the x-direction[42].

[40] *That is, the wave function can be written as $\psi(x,y,z) = \phi(x)\phi(y)\phi(z)$.*

[41] *In the symmetric gauge this works out slightly differently. As the name suggests the wavefunction will not be separable in (x,y) and the Hamiltonian will contain symmetric contributions for both x and y.*

[42] *Eq. 3.17 is equally valid if we had chosen the symmetric gauge with initial velocity in arbitrary direction. The second term then represents the contribution to the energy arising from the motion parallel (or tangential) to the classical orbit, hence the $\parallel$ sign.*

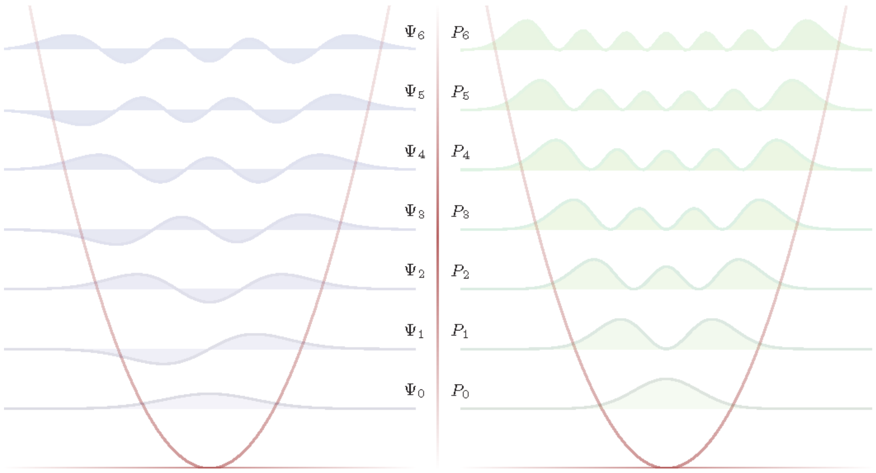


Figure 3.20: (Left) The first few wavefunctions corresponding to Eq. 3.18. Ψ_n denotes the n-th excited state of the oscillator. Note that the center of the well corresponds to the radius of the classical orbit. (Right) Probability functions, $P_n = |\Psi_n|^2$. Note that for the lowest energy, the probability peaks exactly at the classical orbit, while for higher energy levels the probability to find the particle away from the classical orbit increases.

The eigenfunctions for arbitrary n are Hankel functions (the derivation of which is beyond the scope of this course) of the form,

$$\psi(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega_c}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega_c (x-x_0)^2}{2\hbar}} H_n\left(\sqrt{\frac{m\omega_c}{\hbar}}(x-x_0)\right), \tag{3.18}$$

with the Hermite polynomials, H_n, given by

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}\left(e^{-x^2}\right). \tag{3.19}$$

These expressions probably don't provide you with a lot of insight, the graphical representation is however more telling. For $n = 0$ the eigenfunction is Gaussian distribution around the average position x_0. The eigenfunctions for larger n are n-modal bell-shaped curves, as shown in figure 3.20.

Translating the QHO problem to our context, we have thus found that in a magnetic field, a particle doesn't just describe a circular orbit as in the classical case. Instead the probability to find the particle exactly at the classical orbital (with radius x_0) is maximal only for the lowest energy level. At higher energies the wave functions become more complex and the analogy with the circular orbit is lost[43].

So what happens when we adjust the magnetic field? Looking back to our definition of x_0 to see what happens as function of magnetic field,

$$x_0 = \frac{\hbar k_y}{m\omega_c} = \frac{\hbar k_y c}{qB}, \tag{3.20}$$

we find that with increasing magnetic field, x_0 becomes smaller and thus the orbit becomes more localized. Another thing to note is that the standard deviation of our normal distribution decreases for larger B, and thus the orbits in some sense become more classical.

3.3 From single particle physics to Landau levels

In the previous section we discussed the quantum problem of a single particle in a magnetic field. We now wish to make the link to solid state physics. This is, at some level, actually not all that complicated if we make some assumptions. First of all, we will assume that we are dealing with a metal. In that case, we can refer back to some of the assumptions underlying the (nearly) free electron model. In other words, we can assume that the main contribution of the lattice potential is to change the electronic dispersion to that of 'free' quasi-particles, i.e. $\epsilon_k = \hbar^2 k^2/2m$ with m not necessarily the free electron mass. We imagine that we have solved this problem first and then add the complication of a static magnetic field. After the first step we have ended up with a complete set of N orthonormal solutions to the Schrödinger equation. The energy of these solutions becomes modified according an expression similar to Eq. 3.17. There is however a crucial modification for electrons moving through a periodic potential: the momentum becomes quantized! In other words, in the presence of the periodic lattice potential we should have taken the quantized momentum parallel to the orbit,

$$k_y = \frac{2\pi N}{L_y}. \tag{3.21}$$

[43] *If we had used the symmetric gauge, we would have found that the particles describe circular orbits with radius* $r_0^2 = x_0^2 + y_0^2$.

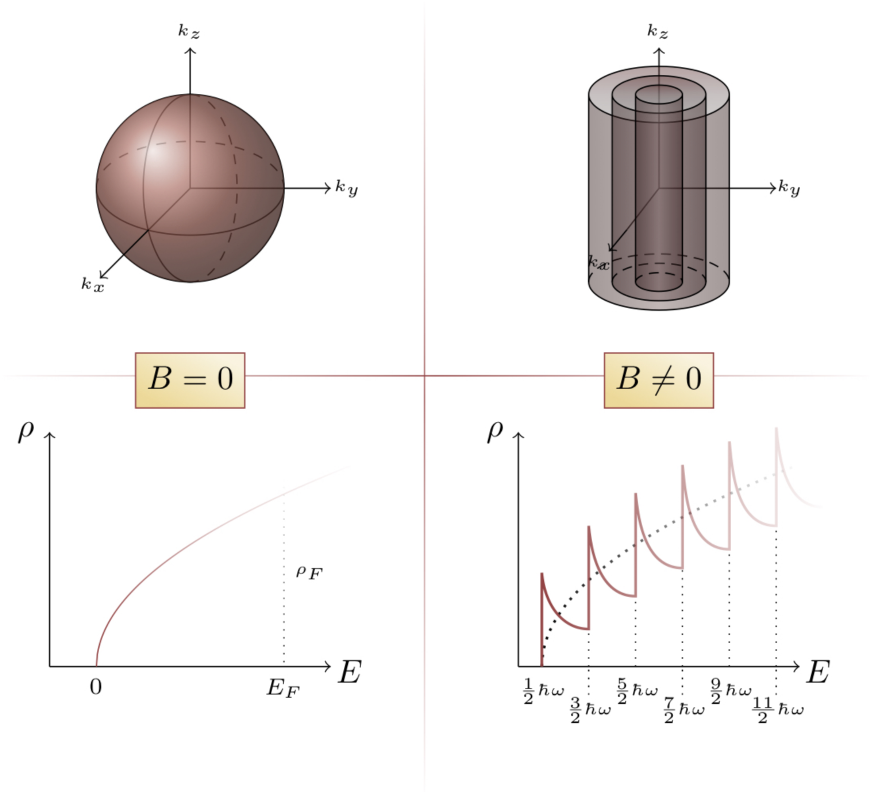


Figure 3.21: (Top left) Fermi surface for three dimensions for a zero *B*-field (the Fermi sphere). (Bottom left) Corresponding density of states fin the absence of a magnetic field. The density of states ϱ has a square root dependence on energy *E*. (Top right) Density of states for a finite *B*-field, resulting in Fermi cylinders (or Landau levels). (Bottom right) Corresponding density of states. The peaks appearing in the density of states correspond to a multiple times the cyclotron frequency. Also note that the energy position of these peaks depends on the applied magnetic field.

where L_y is the dimension of the crystal in the y-direction and N the number of lattice sites along the same direction. Let's also assume that the electron is confined to the solid,

$$0 < x_0 < L_x. \tag{3.22}$$

The combination of these two boundary conditions leads to:

$$0 < N < \frac{m\omega_c L_x L_y}{2\pi\hbar}. \tag{3.23}$$

This provides a maximum on the number, or degeneracy, of a given harmonic oscillator level n. Since the area of the crystal is $A = L_x L_y$, we can substitute our cyclotron frequency to find

$$N = \frac{BA}{\left(\frac{hc}{e}\right)} = \frac{\Phi}{2\Phi_0}. \tag{3.24}$$

Here Φ is the total flux and $\Phi_0 = \frac{2e}{hc}$ is the **flux quantum**, a constant per electron[44].

The interpretation is a bit different. We are now working in a periodic momentum space and the electrons form bands that are clustered around specific energies. These bands are much more confined in energy and are thus known as **Landau levels**. We find that each level consists of a large number of states[45]. Just like a 'normal' electronic band structure problem, we now start adding electrons to the state with $n = 0$ until we have filled up all the available states. We then continue to fill levels with larger n until we run out of electrons.

To see how the discussion above impacts on observable properties of materials depends on the effective dimensionality of the material. In the nearly free electron model in three dimensions the density of states has a square root energy dependence (see Exc. 4). This situation is sketched on the left in Fig. 3.21. In the top left panel the Fermi sphere is shown in the absence of magnetic field. The density of states is shown in the bottom left panel. As soon as we apply a finite magnetic field this picture changes to what is shown on the right hand side. The Fermi sphere breaks up into cylinders[46] and the density of states acquires additional features. The additional peaks in the density of states correspond in energy to the energy level of the harmonic oscillators and have great significance for the behavior of solids in applied fields. As an example consider the resistivity of a material. The Drude model tells you that (see Eq. 2.51) the resistivity of a metal is approximately given by,

$$\varrho = \frac{m}{ne^2}\frac{1}{\tau} \tag{3.25}$$

[44] *The factor two in the numerator of the fraction is a reminder of the fact that we can put two electrons in each electron state, one with spin up, and one with spin down.*

[45] *Note that the flux quantum* $\Phi_0 = 2.067 \cdot 10^{-15}$ *Wb. Since 1 Wb = 1 T·m*^{2}*, we have a total of* $2 \cdot 10^{14}$ *states available per m*^{2} *in a 1 Tesla field. Typical electron densities for a metal are of the same order of magnitude.*

[46] *This is not entirely correct. The cylinders will be deformed along the* k_z *direction in a real crystal. The sketch in Fig 3.21 would apply to a quasi two dimensional crystal where the dispersion along the* k_z *direction is negligible.*

The n appearing in the denominator is the density of free electrons and this is mainly determined by the density of states at the Fermi level. If the density of states at the Fermi level is zero (for example because there is a gap in the dispersion at the Fermi level), it will cost a lot of energy to excite electrons and the resistivity will be high. If on the other hand the density of states is high both above and below the Fermi level, it will hardly cost any energy to excite a lot of electrons and the resistivity will be low. For a metal we will have a density of states as in the lower left panel of Fig. 3.21 and the resistivity will be a certain value. Now we switch on our magnetic field and slowly crank up the field. As the field increases the peaks in the density of states depicted in the lower right hand panel of Fig. 3.21 will shift along the horizontal axis. As a result the density of states will oscillate and consequently also the resistivity will oscillate. These oscillations are known as **Shubnikov - de Haas oscillations**. The resistivity is however not the only quantity that will oscillate; many other transport properties such as specific heat and the magnetic susceptibility[47] will display similar **quantum oscillations** in magnetic field.

3.4 Conductivity revisited

In the previous chapter we have derived an expression for the optical properties of a solid in a magnetic field. In Exc. 1 we found that the optical conductivity in a magnetic field is a tensor and the relation between the current and the applied electric field is given by,

$$\vec{j} = \overleftrightarrow{\sigma}\vec{E} \tag{3.26}$$

with the components of the conductivity tensor,

$$\sigma_{xx} = \sigma_{yy} = \frac{\omega_p^2(\Gamma - i\omega)}{4\pi[(\Gamma - i\omega)^2 + \omega_c^2]}, \quad \sigma_{xy} = -\sigma_{yx} = \frac{\omega_p^2\omega_c}{4\pi[(\Gamma - i\omega)^2 + \omega_c^2]}. \tag{3.27}$$

This is an interesting result. In zero field, the cyclotron frequency ω_c is zero and the off-diagonal components vanish. The diagonal components of the conductivity tensor reduce to the standard Drude result. For a more arbitrary direction of the field we end up with a rank 3 tensor for the conductivity,

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}. \tag{3.28}$$

In most cases the off-diagonal elements are zero,

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}, \tag{3.29}$$

If the system is time reversal invariant, the off-diagonal components have to be zero. Since a magnetic field breaks time reversal invariance, the off-diagonal components become finite[48].

In compact notation the current is related to the field as,

$$\begin{bmatrix} j_x \\ j_y \end{bmatrix} = \hat{\sigma}_H \begin{bmatrix} (\Gamma - i\omega) & \omega_c \\ -\omega_c & (\Gamma - i\omega) \end{bmatrix} \begin{bmatrix} E_x \\ E_y \end{bmatrix}. \tag{3.30}$$

where,

$$\hat{\sigma}_H = \frac{\omega_p^2}{4\pi[(\Gamma - i\omega)^2 + \omega_c^2]} \tag{3.31}$$

We will use these expressions for a discussion of the Hall effect in the next section.

3.5 The Hall effect

The above result turns out to be very useful in the characterization of materials as we will now show. There is one difficulty however. Resistivity is defined as the inverse of the conductivity, σ^{-1}, so we have to invert a 3×3 matrix to calculate the resistance in a B-field. The matrix equation we would have to invert has the form[49]

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}^{-1} \begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix}. \tag{3.32}$$

---

[47] *The latter effect is known as the de Haas - van Alphen effect.*

[48] *Note that some materials don't require a magnetic field to have finite off-diagonal elements. An example thereof would be a ferromagnet.*

[49] *Recasting our linear response expression to Ohm's law, $V = I \cdot R$.*

Inverting a general 3 × 3 matrix is not very funny, but if we choose the $\vec{B}$-field along a principal axis, we can reduce the problem to inverting a 2 × 2-matrix. Inverting a general 2 × 2 conductivity tensor gives,

$$\begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{bmatrix}^{-1} = \frac{1}{\sigma_{xx}\sigma_{yy} - \sigma_{yx}\sigma_{xy}} \begin{bmatrix} \sigma_{yy} & -\sigma_{xy} \\ -\sigma_{yx} & \sigma_{xx} \end{bmatrix}. \tag{3.33}$$

For an isotropic material[50] we can simplify this expression to,

$$\begin{bmatrix} \varrho_{xx} & \varrho_{xy} \\ \varrho_{yx} & \varrho_{yy} \end{bmatrix} = \frac{1}{\sigma_{xx}^2 + \sigma_{xy}^2} \begin{bmatrix} \sigma_{xx} & -\sigma_{xy} \\ \sigma_{xy} & \sigma_{xx} \end{bmatrix} \tag{3.34}$$

to obtain

$$\varrho_{xx} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2} \qquad \varrho_{xy} = \frac{-\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2}. \tag{3.35}$$

We can now make use of Eq. 3.30 to determine the resistivity[51] of a material in a magnetic field,

$$\overleftrightarrow{\varrho} = \left(\sigma_H \begin{bmatrix} \Gamma & \omega_c \\ -\omega_c & \Gamma \end{bmatrix} \right)^{-1}, \tag{3.36}$$

which gives,

$$\overleftrightarrow{\varrho} = \frac{4\pi}{\omega_p^2} \begin{bmatrix} \Gamma & -\omega_c \\ \omega_c & \Gamma \end{bmatrix}. \tag{3.37}$$

Now we can use the definition of the plasma and cyclotron frequencies to simplify the off-diagonal elements and find:

$$\varrho_{xy} = \frac{4\pi\omega_c}{\omega_p^2} = \frac{4\pi\left(\frac{eB}{mc}\right)}{\left(\frac{4\pi n e^2}{m}\right)} = \frac{B}{nec}. \tag{3.38}$$

This turns out to be a very useful result. Imagine that we have a material in a $\vec{B}$-field and we apply some voltage. The electrons moving through the material are deflected by the magnetic field and heap up near the sides of the material. At the same time, positively charged 'holes' heap up on the opposite side of the material. This imbalance in charge density causes a voltage to appear. Note that no net current flows between the two edges[52].

Using our expression

$$E_y = \frac{B}{nec} j_x, \tag{3.39}$$

we can then derive a **Hall voltage**, which reads[53]

$$V_{H,y} = R_H B \frac{I_x}{d}. \tag{3.40}$$

From which the Hall coefficient $R_H \equiv -\frac{1}{nec}$ follows. The Hall coefficient depends on a single material specific quantity: the electron density n. Therefore, we can measure directly the electron density if we measure the Hall voltage in an applied magnetic field. It turns out that band structure plays an important role in determining the Hall resistance. For example, it is possible that the Hall voltage changes sign (i.e. is opposite to what you would expect based on geometry of the experiment). In this case the density is interpreted as a 'hole density'[54].

3.6 Magnetism in the tight-binding model I: bound charge response

So far we have considered two descriptions of solids: the free electron model and the tight binding model. The former is useful when we consider metals, while the latter is useful for the description of semi-conductors. It is important to remember that the tight-binding model is in principle complete as it encompasses also the description of metals[55]. There is however one problem with both of these descriptions: it is not at all clear how to explain certain other properties of solids. What about ferromagnetism? Superconductivity? In the next two chapters we'll discuss the origin of such **emergent** properties. Before we turn our attention to emergent properties of solids however, we will discuss magnetic properties that are captured within the tight-binding model. Let's go back to the magnetic susceptibility. In chapter 2.3, we've defined it as

$$\vec{M} = \chi_m \vec{H}, \tag{3.41}$$

---

[50] *i.e. when $\sigma_{xx} = \sigma_{yy}$. This is almost always the case for real systems.*

[51] *Note that the resistivity has $\omega = 0$.*

[52] *This would require energy input!*

[53] *One way to obtain this result is by taking a voltage delta between two potentials,*

$$\Delta V = \phi_2 - \phi_1.$$

By definition, the electrostatic potential is

$$\phi = -\int_C \vec{E} \cdot d\vec{s}.$$

Since both vectors point in the same direction, the previous expression for the voltage delta becomes

$$\Delta V = -\int_0^2 E ds + \int_0^1 E ds$$

and therefore

$$\Delta V = ED.$$

Filling in the previously derived electric field yields the desired expression V_H.

[54] *Remember our discussion of quasiparticles and effective mass in the first chapter. If the dispersion is such that the effective mass is negative, the convention is to change the sign of the charge and speak about holes rather than electrons.*

[55] *The main reason for using the Jellium model at all is that it is conceptually simple and mathematically more tractable.*

The role of Fermi-Dirac statistics

So far temperature hasn't played any role in our description of solids; our discussion has effectively focussed on absolute zero. Since we are mostly concerned with electrons, which are fermions, the thermal statistics is governed by the Fermi-Dirac distribution,

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\varepsilon_F)}+1},$$

where $\beta = 1/k_B T$. When we are dealing with simple metals at finite temperature, the main difference is that thermal fluctuations allow the electrons to occupy excited states with some probability. Taking kinetic energy as an example, we find that at finite temperature it is given by,

$$E_K = 2\int_0^\infty d\varepsilon\varrho(\varepsilon)f(\varepsilon)\varepsilon,$$

rather than the regular expression for kinetic energy:

$$E_K = 2\int_0^{E_F} d\varepsilon\varrho(\varepsilon)\varepsilon.$$

A more general statement, applicable beyond linear response would be,

$$\chi_m = \frac{\partial\vec{M}}{\partial\vec{H}}. \tag{3.42}$$

In the tight-binding approach the material is *not* magnetically ordered in the absence of a magnetic field. Depending on the details there are now two possible responses of the solid to an applied magnetic field. The first option is that the magnetic susceptibility is positive, $\chi_m > 0$. This is called **paramagnetism**[56]. In the second case, the susceptibility is negative and $\chi_m < 0$, which is referred to as **diamagnetism**.

To determine the response of a given solid we need to distinguish between the response of bound and free electrons, just as in the case of the Drude-Lorentz model. We first discuss bound electrons. This will provide a complicated response already consisting of both a paramagnetic and diamagnetic response. The reason for separating between bound and free responses is the following. As you are probably aware, an isolated free atom has a specific magnetic moment associated with it. This is a result of the combination of the nuclear moment, the total electron moment and the way the lowest energy is obtained (e.g. through Hund's rules). This 'permanent' moment is not changed very much in solids[57]. For the discussion of the 'local' (or bound) charge response to an applied magnetic field we can again make use of the 'minimally substituted' Hamiltonian,

$$H = \frac{1}{2m}\left(\hat{p}^2 - \frac{2q}{c}\hat{p}\cdot\hat{A} + \frac{q^2}{c^2}\hat{A}^2\right) + V(r). \tag{3.43}$$

In the case at hand it helps to split the Hamiltonian into two parts: H_0 (the original Hamiltonian) and an interaction term H_{int}[58],

$$H = H_0 + H_{\text{int}}, \tag{3.44}$$

where the two parts are defined as

$$\begin{cases} H_0 &= \frac{\hat{p}^2}{2m} + V(\vec{R}) \\ H_{\text{int}} &= -\frac{q}{mc}\hat{p}\cdot\hat{A} + \frac{q^2}{2mc^2}\hat{A}^2. \end{cases} \tag{3.45}$$

As before we assume we have solved the tight-binding problem defined by H_0. We now make use of the symmetric gauge[59] and make the appropriate substitution for the vector potential corresponding to a magnetic field applied along the $\hat{z}$-axis, to obtain

$$\begin{aligned} H_{\text{int}} &= -\frac{q}{mc}\hat{p}\cdot\hat{A} + \frac{q^2}{2mc^2}\hat{A}^2 && (3.46)\\ &= -\frac{ie\hbar B}{2mc}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) + \frac{e^2B^2}{8mc^2}(x^2+y^2) && (3.47)\\ &= -\mu_B B l_z + \frac{e^2B^2}{8mc^2}(x^2+y^2). && (3.48) \end{aligned}$$

---

[56] *As in: parallel to the applied magnetic field.*

[57] *It is not exactly equal to the moment of a free atom. It depends weakly on the local environment or symmetry. We will ignore these details.*

[58] *As you might have guessed we will use this separation to essentially apply perturbation theory.*

[59] *Where the vector potential is given by*

$$\vec{A} = \frac{1}{2}(-B\hat{y}\hat{\mathbf{x}} + B\hat{x}\hat{\mathbf{y}})$$

.

Derivation of the Curie-Weiss relation

One derivation is by taking the eigenvalues for the energy of an atom $E_i = g\mu_B B J_z$ with $J_z = -J, \ldots, J$, and

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

The partition function in this case is $Z = \sum_i e^{-\beta E_i}$, while the Helmholtz free energy F is given by $F = -k_B T \ln Z$. For small B-fields, the partition function Z can be expanded as

$$Z = \sum_i \left(1 - \beta E_i + \frac{1}{2}\beta E_i^2 - \ldots\right).$$

Since, in the ground state, the sum runs of $2J+1$ levels and $\sum E_i = \sum J_z = 0$ since $J_z = -J, \ldots, J$, the resulting expression for the partition sum is then

$$Z = 2J + 1 + \frac{1}{2}(g\mu_B \beta B)^2 \sum_i J_z^2.$$

This last sum can once again be evaluated as $\sum_i J_z^2 = 1/3 \sum_i |J|^2 = 1/3(2J+1)J(J+1)$. Here, $2J+1$ is the number of states and $J(J+1)$ is the expectation value. Putting things together, we find an expression for the Helmholtz free energy of

$$F = -k_B T \ln\left[(2J+1)\left(1 + \frac{1}{6}(g\mu_B \beta B)^2 J(J+1)\right)\right].$$

where we have introduced the orbital angular momentum, l_z in the last line. The first term in the last line thus represents a dipole moment like interaction between the electron and the magnetic field, whereby the electron orbital moment wants to align itself along the field. The second term is associated with an induced moment that opposes the field. At this point it is important to observe that the minimal substitution applies to charged particles, while here we are in fact dealing with electrons. Apart from a charge electrons have spin. The electron spin itself is a magnetic moment of the same order of magnitude as the orbital moment and should thus be included as well. We therefore add a component, $H_s = -\vec{\mu} \cdot \vec{B}$, to the Hamiltonian, where the spin moment is given by, $\vec{\mu} = -g_0 \mu_B \vec{s}$. Combining this with the orbital moment, we find,

$$H_{\text{int}} = \mu_B B(l_z + g_0 s_z) + \frac{e^2 B^2}{8mc^2}(x^2 + y^2). \tag{3.49}$$

This result holds for a single electron. For an atom we find,

$$H_{\text{int}} = -\mu_B B(\vec{L} + 2\vec{S}) + \frac{e^2 B^2}{8mc^2} \sum_{i=1}^{Z^\star} (x^2 + y^2). \tag{3.50}$$

The first term corresponds to the paramagnetic term, the second to the diamagnetic term. In general the first term is larger, however some atoms have $\vec{L} = \vec{S} = 0$, in which case the diamagnetic term dominates.

It goes too far to work through the full statistical derivation of the relation between the magnetic moment and the perturbation arising from the application of the magnetic field. Instead, we quote the following relation[60],

$$\chi_m = -\frac{1}{V}\frac{\partial}{\partial B}\left\langle \frac{\partial H_{int}}{\partial B} \right\rangle. \tag{3.51}$$

We now apply this expression to the diamagnetic contribution of the interaction Hamiltonian. This gives:

$$\left\langle \frac{\partial H_{int}}{\partial B} \right\rangle = \frac{e^2 B}{4mc^2} Z^\star \frac{2}{3} \left\langle r^2 \right\rangle. \tag{3.52}$$

Since we are considering the response of electrons bound to an atom under an applied magnetic field, the result is completely independent of details of the crystal. Under this approximation the response of a crystal is simply N times the response of a single atom. Therefore,

$$\chi_m = -\frac{Ne^2}{6Vmc^2} Z^\star \left\langle r^2 \right\rangle. \tag{3.53}$$

For simple monatomic solids where the constituent atoms have filled shells ($L = S = J = 0$) this is the final result. This type of magnetic response is known as **Larmor diamagnetism**.

---

[60] *Classically, the change in the total internal energy of the system under applied field is* $\delta U_{int} = \int \vec{M} \cdot \delta\vec{B} dV$. *From this it follows that* $\vec{M} = 1/V(\partial U/\partial B)$.

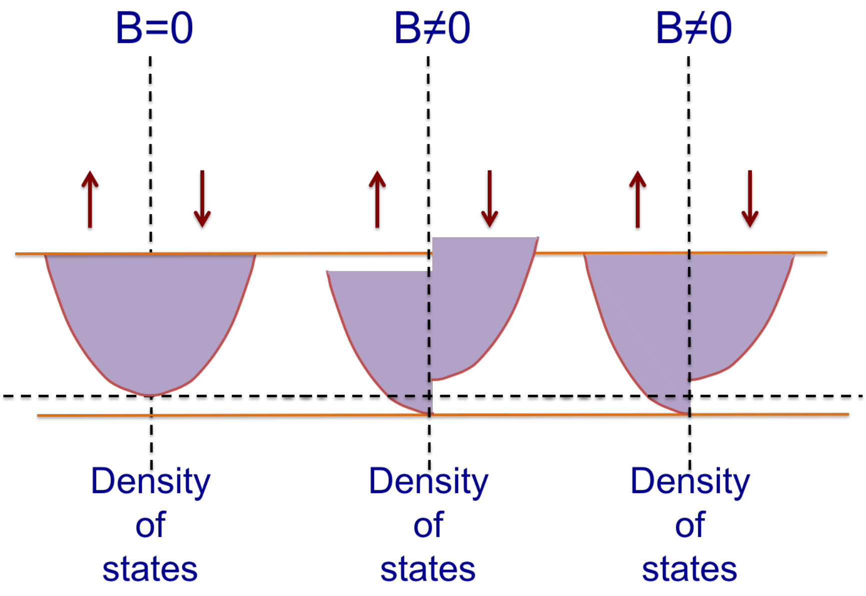


Figure 3.22: (Left): Density-of-states separated for spin-up and spin-down states in the absence of magnetic field. As we have discussed, the electronic dispersion (and thus the DOS) is degenerate in spin. (Middle): If we apply a magnetic field, the Zeeman interaction will raise the energy for spins opposite to the field, while lowering the energy for spins parallel to the field. (Right): The electrons will redistribute over spin-up and spin-down states. As a result the total energy is lowered and a small magnetization emerges.

The paramagnetic response is more complicated and the full derivation (see infobox) is a bit tedious and essentially a statistical physics problem. Nevertheless, the result is quite famous and known as the Curie-Weiss susceptibility:

$$\chi_m = \frac{n_i p^2 \mu_B^2}{3k_B T} = \frac{C}{T}. \tag{3.54}$$

where n_i is the density of ions contributing to the paramagnetic response and $p = g\sqrt{J(J+1)}$[61]. The key feature that distinguishes the Curie-Weiss susceptibility from other contributions is its $1/T$ temperature dependence.

3.7 Magnetism in the tight-binding model II: free charge response

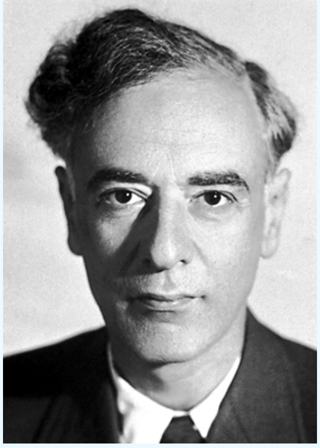
Let us now turn to the magnetic susceptibility arising from (nearly) free electrons. One might expect that this follows exactly the same approach as for the Curie-Weiss law, replacing the density of ions, n_i, with the density of electrons. This turns out to be wrong and the reason for this can be gleaned from Fig. 3.22. Let's take for simplicity the density of states of the free electron gas in three dimensions, it depends on energy as $\varrho(E) \propto \sqrt{E}$ for both spin-up and spin-down states[62]. Due to the degeneracy the spin-up density exactly cancels the spin-down density and the associated magnetic moment equals zero. Following the derivation of the Curie-Weiss law, we first considered a single ion and then used statistical methods to arrive at the susceptibility. We cannot use the same method here since electrons are fermions and therefore not free to arbitrarily flip their spin. In fact, looking at the left panel of Fig. 3.22, only a fraction of the total number of electrons (i.e. those close to the Fermi level) are allowed to flip their spin.

So what happens in response to an applied field? First of all, similar to the Zeeman effect the degeneracy between spin-up and spin-down states is broken (middle panel Fig. 3.22). As a result the total energy of the system is increased if the density of spin-up and spin-down electrons remains equal. The total energy can be lowered however: if the electrons above E_F flip their spin, they can occupy a lower energy state. This results in a larger occupation of a particular spin-orientation (right panel Fig. 3.22) and consequently a finite magnetic moment. It is not so complicated to estimate the magnetic moment. In particular, we have for the number of up-electrons (assuming spin-up to be parallel to the field for the moment):

[61] *As mentioned in the beginning of this section the end result depends slightly on the atom and crystal structure involved. For crystals containing 3d elements (e.g. copper) the expression for p is more accurately given by* $p = 2\sqrt{S(S+1)}$.

[62] *The spin states in the tight-binding model are degenerate in energy!*

Landau once said…



The derivation for the diamagnetic contribution of free electrons in the magnetic field is absolutely terrifying. This was even more so the case when it was just derived and presented by the physicist Lev Landau, somebody who contributed significantly to the area of magnetism in the first part of the 20th century. The resulting expression,

$$\chi_{m,\text{dia}} = -\frac{1}{3}\chi_{m,\text{Pauli}},$$

was initially invoked as a triviality in one of Landau's papers, but had no additional information reinforcing it as the correct answer. Nobody seemed to understand why this was the case initially, but no one dared asking Landau why this expression had to be true. After all, one does not question information presented in this manner, especially coming from a superior during in the 'Russian school', where hierarchy was very strict.
After Landau's death, several physicists took on the task to either confirm or deny the result. It took them **ten years** to confirm it.

$$\begin{aligned}
N_+ &= \frac{1}{2}\int_{-\mu B}^{E_F} d\varepsilon \varrho(\varepsilon + \mu B) && (3.55)\\
&= \frac{1}{2}\int_{0}^{E_F+\mu B} d\varepsilon \varrho(\varepsilon) && (3.56)\\
&\approx \frac{1}{2}\int_{0}^{E_F} d\varepsilon \varrho(\varepsilon) + \frac{1}{2}\int_{E_F}^{E_F+\mu B} \varrho(E_F) && (3.57)\\
&\approx \frac{1}{2}\int_{0}^{E_F} d\varepsilon \varrho(\varepsilon) + \frac{1}{2}\mu B \varrho(E_F). && (3.58)
\end{aligned}$$

Similarly, we find $N_- \approx \frac{1}{2}\int_0^{E_F} d\varepsilon\varrho(\varepsilon) - \frac{1}{2}\mu B\varrho(E_F)$. This allows us to calculate the magnetic moment as the difference between spin-up and spin-down electrons,

$$M = \mu_B(N_+ - N_-) = \mu_B^2\varrho(E_F)B = \frac{3N\mu_B^2}{2E_F}B. \tag{3.59}$$

From this expression we can derive the properly volume averaged susceptibility as[63],

$$\chi_m = \frac{3N\mu_B^2}{2VE_F} = \frac{3n\mu_B^2}{2k_BT_F}. \tag{3.60}$$

In the second step we have introduced the Fermi temperature, which is related to the Fermi energy simply as $E_F = k_BT_F$. Note that the final result is indeed very similar to the ionic contribution. We see that instead of the full electron density only a shell of volume T/T_F contributes to the free charge paramagnetic response. The end result is that the Curie-Weiss temperature dependence is replaced by the Fermi temperature, T_F.

The derivation of the diamagnetic contribution for free electrons is beyond the scope of this course. We will only denote here the result as quoted in the famous Landau & Lifschitz,

$$\chi_{m,\text{dia}} = -\frac{1}{3}\chi_{m,\text{Pauli}}, \tag{3.61}$$

with $\chi_{m,\text{Pauli}}$ the paramagnetic contribution of free electrons. This last term is known as **Landau diamagnetism** and holds as long as temperature is larger than the corresponding cyclotron frequency scale (i.e. $k_BT >> \hbar\omega_c$). There are two points to make. First, the paramagnetic and diamagnetic term come hand in hand: the response of the free electron gas is therefore paramagnetic. Second, in section 3.3 we found that the density of states in a magnetic field changes drastically. In particular we showed that the density of states oscillates in a magnetic field. This has an impact on the magnetic susceptibility of the free electron gas as well (but not on the ionic contribution!), which will oscillate with field. The result derived here holds in the limit of low fields.

To conclude, the total magnetic susceptibility of a non-magnetically ordered material has several contributions. These are paramagnetic and diamagnetic depending on whether they are parallel or opposite to the applied magnetic field. There is a contribution from bound and free electrons. The free electron terms can be combined

[63] *i.e.* $\chi_m = 1/V(\partial M/\partial B)$.

and result in a single paramagnetic contribution. The total magnetization of a material under an applied magnetic field is thus,

$$\vec{M} = \left(\underbrace{\frac{n_{\text{free}}\mu_B^2}{k_B T_F}}_{\text{Free electrons}} + \underbrace{\frac{n_i p^2 \mu_B^2}{3k_B T}}_{\text{Paramagnetism}} - \underbrace{\frac{n_i e^2}{6mc^2} Z^\star \left\langle r^2 \right\rangle}_{\text{Diamagnetism}} \right) \vec{B}. \tag{3.62}$$

Depending on the details the magnetization can be positive or negative. In case it is **p**ositive we will find **p**aramagnetism, $\chi_m > 0$. In case it is negative, diamagnetism dominates:

$$\begin{aligned} \chi_m > 0 &\;\; \text{paramagnetism} \\ \chi_m < 0 &\;\; \text{diamagnetism} \end{aligned}$$

EXERCISES III

MAGNETIC PHENOMENA.

In these exercises we will discuss the properties of particles and non-magnetically ordered materials in magnetic fields.

THE DRUDE MODEL IN MAGNETIC FIELD.

1

In the previous chapter we have derived the Drude-Lorentz model. In this exercise we will derive a similar result, but now in the presence of a magnetic field. This result will form the basis for our discussion of the Hall conductivity in the next chapter. Using the Lorentz force and extending our previously obtained result, we can derive similar results for materials in a magnetic field. We start by considering the forces acting on the electrons

$\mathcal{A}$ Write down the equation of motion for a charged particle moving through a magnetic field in the presence of an oscillating electric field. For simplicity assume $\Omega_0 = 0$ (i.e. we'll consider the Drude model in magnetic field).

$\mathcal{B}$ Assuming a magnetic field applied along the z-direction (i.e. $\vec{B} = B_0\hat{z}$), show that this can be written as[64].

$$(\Gamma - i\omega)\vec{v} = -\frac{e}{m}\vec{E} - \frac{eB}{mc}\left(v_y\hat{\mathbf{x}} - v_x\hat{\mathbf{y}}\right) \tag{E3.1}$$

$\mathcal{C}$ Using the definition of the current [65] and the cyclotron frequency, rewrite this as

$$(\Gamma - i\omega)\vec{j} = \frac{\omega_p^2}{4\pi}\vec{E} - \omega_c\left(j_y\hat{\mathbf{x}} - j_x\hat{\mathbf{y}}\right). \tag{E3.2}$$

$\mathcal{D}$ Note that on the left hand side we have a three component current $\vec{j}$, while on the right hand side we have only the three component field $\vec{E}$. The $\hat{\mathbf{z}}$-component of the current is thus,

$$\vec{j}_z = \frac{\omega_p^2}{4\pi(\Gamma - i\omega)}E_z \tag{E3.3}$$

This is exactly the Drude conductivity! Derive two relations between the x– and y–components of the current and electric field and show that these can be solved to give,

$$j_x = \frac{\omega_p^2}{4\pi[(\Gamma - i\omega)^2 + \omega_c^2]}\left[(\Gamma - i\omega)E_x - \omega_c E_y\right] \tag{E3.4}$$

$$j_y = \frac{\omega_p^2}{4\pi[(\Gamma - i\omega)^2 + \omega_c^2]}\left[\omega_c E_x + (\Gamma - i\omega)E_y\right]. \tag{E3.5}$$

$\mathcal{E}$ Show that this can be cast in the form quoted in the main text:

$$\begin{bmatrix} j_x \\ j_y \end{bmatrix} = \hat{\sigma}_H \begin{bmatrix} (\Gamma - i\omega) & -\omega_c \\ \omega_c & (\Gamma - i\omega) \end{bmatrix} \begin{bmatrix} E_x \\ E_y \end{bmatrix}. \tag{E3.6}$$

with,

$$\hat{\sigma}_H = \frac{\omega_p^2}{4\pi[(\Gamma - i\omega)^2 + \omega_c^2]} \tag{E3.7}$$

QUANTUM OSCILLATIONS

2

This exercise is adapted from the book by E. Economou (see literature list in Chapter 1)

$\mathcal{A}$ The density of states displayed in Fig. 3.21 suggests that there would be a peak at the Fermi level in the density of states if,

$$E_F = \hbar\omega_c\left(n + \frac{1}{2}\right) \tag{E3.8}$$

Show that this implies that there would be a peak in the density of states whenever,

$$\frac{1}{B} = \frac{2\pi e}{c\hbar A_F}\left(n + \frac{1}{2}\right) \tag{E3.9}$$

where $A_F \equiv \pi k_F^2$ is the maximal cross-section of the Fermi sphere. This implies that any quantity related to the density of states (resistivity, susceptibility, specific heat) will oscillate with a period $\Delta(1/B) = 2\pi e/c\hbar A_F$

---

[64] *Remember:*

$$v(t) = \int d\omega v(\omega)e^{-i\omega t}$$

$$E(t) = \int d\omega E(\omega)e^{-i\omega t}.$$

[65] *i.e. using* $\vec{j} = -ne\vec{v}$.

3

The Pauli susceptibillity

This exercise is adapted from the book by C. Kittel (see literature list in Chapter 1) The Pauli susceptibility (at absolute zero) can be derived by another method. Let

$$N^{+} = \frac{1}{2}N(1+\delta), \quad N^{-} = \frac{1}{2}N(1-\delta) \tag{E3.10}$$

be the number of spin-up and spin-down electrons.

A Show that in a magnetic field B, the total energy of a spin up band is given by[66],

$$E^{+} = E_0(1+\delta)^{5/3} - \frac{1}{2}N(1+\delta)\mu B \tag{E3.11}$$

Derive a similar expression for E^{-}.

B Find the groundstate by minimizing the total energy and solve for δ (in the limit $\delta << 1$). Show that,

$$\delta = \frac{9N\mu B}{20E_0} \tag{E3.12}$$

C Show that the magnetization, defined as,

$$M = \mu\left(N^{+} - N^{-}\right) \tag{E3.13}$$

agrees with Eq. 3.60.

---

[66] *Hint: remember that the kinetic energy of a band of free electrons is given by,*

$$E_K = \frac{3}{5}NE_F$$

THE HUBBARD MODEL

or the emergence of magnetism from interacting electrons

4.1 Introduction

In the previous chapter we have dealt with the movement of electrons in 'simple' solids under applied magnetic fields. With simple I mean that the electrons are moving independently from each other through an effective lattice potential. One of the key equations that we have used,

$$\vec{M} = \chi_m \vec{H}, \tag{4.1}$$

tells us that in the absence of an applied magnetic field the magnetization in a solid is zero. This is a bit problematic if you realize that such a thing as iron exists, which of course is magnetic all by itself. In fact, I tried to be meticulous in stressing a couple of times that we were considering non-magnetically ordered states. Understanding the origin of **spontaneous magnetism** in solids turns out to have its surprises and it has taken quite a bit of time before people figured out the theoretical framework[67]. Lets look back to the first chapter. We started with the Schrödinger equation for a solid and concluded that it was too complicated. After making what appeared to be sensible approximations we obtained a differential equation describing the motion of a particle in some 'mean-field' potential. The solution to this differential equation turned out to be a linear superposition of essentially atomic orbitals with a quantized energy spectrum. These energy states are spin degenerate[68] and therefore the ground state of the system will never be magnetic. To make this absolutely clear: imagine that you have a lattice of hydrogen atoms (i.e. one electron per unit cell, only the 1*s*-orbitals will be occupied). As we have shown in the first chapter these orbitals will form a single energy band of momentum states. Now we start adding electrons to the momentum eigenstates in such a way that the energy is minimal. This means that the first two electrons will occupy the lowest in energy momentum state (i.e. k=0); one of the electrons with spin-up, one with spin-down. The net magnetization of the solid after the first two electrons is zero. After we have added the remaining 10^{23} electrons, the magnetization will be exactly zero (for a solid with an even number of atoms) or the magnetization will be exactly one Bohr magneton[69] (for an odd number of atoms), which is a pretty small number on the scale of things (it is in fact about 10^{21} times too small).

To conclude, despite all the things that can be calculated within the tight-binding approach, it does not contain spontaneous magnetism. This chapter explains how you can get spontaneous magnetism.

4.2 Ferromagnetism & ground states

Let us stay with a concrete example for a moment. At temperatures well above 1040 K, iron is a metal that is well described with the free electron gas. In the absence of a magnetic field its magnetization would be zero. When we apply a magnetic field it will display a paramagnetic response with a Curie-Weiss type of behavior[70]. It becomes more interesting when we apply a magnetic field and then lower the temperature below 1040 K. At first nothing seems to change: it is still a metal and it still has a magnetization. The interesting bit is that when we now slowly decrease the magnetic field to zero, a finite magnetization will remain. A new state has emerged: the ferromagnet! It turns out that iron undergoes a **phase transition** from a metallic paramagnet to a metallic (or **itinerant**) ferromagnet. The transition temperature is known as the **Curie temperature**. If we further lower the temperature all the way to absolute zero, iron will remain a ferromagnet. This implies that the real ground state of iron is in fact ferromagnetic and this goes beyond the standard (tight-binding) model we have constructed. The only way we can obtain a different groundstate is by taking a step back and look at the original Hamiltonian,

$$H = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + U_{ee}(r_{ik}) + U_{ei}(r_i, R_p) \tag{4.2}$$

Remember that the first term is the kinetic energy of the electrons, the second term the electron-electron interaction (Coulomb repulsion) and the last term is the electron-lattice interaction. The transition temperature of iron is around 1000 K, or equivalently about 100 meV. The energy scale associated with the electron-phonon interaction is too small (on the order of 20 meV). The energy associated with the Coulomb interaction is much larger (typically a few eV), but it is also screened due to the presence of all the other electrons (see Chapter 2.8). It is therefore the most likely candidate to explain ferromagnetism. To proceed we will have to make some changes to the approximations we made. As pointed out in Chapter 1, it is not possible to take the full Coulomb interaction into account: the problem is simply to hard to solve, even numerically. We

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[67] *And to be honest, we still don't have a good theory to understand at which temperature something like iron becomes magnetic.*

[68] *Meaning that it costs the same energy to occupy a given eigenstate with a spin-up or spin-down electron.*

[69] $\mu_B = 9.27400968(20) \cdot 10^{-24}$ *J/T.*

[70] *As long as temperature remains larger than 1040 K.*

will therefore focus on the simplest possible approximation, which is to add a repulsive term that acts between two electrons if they are on the same atom. This repulsion together with the fact that electrons are fermions and therefore obey Fermi-Dirac statistics turns out to be enough to understand magnetic materials. The resulting model is known as the Hubbard model. Before discussing this model, lets first look at the simplest possible realization of this model to get some intuition of the role played by statistics and interactions. This is a toy model for the hydrogen molecule.

4.3 The hydrogen molecule

In the first chapter we have already looked at the model for two interacting hydrogen atoms. Each hydrogen atom has an individual Hamiltonian H_i corresponding to atom $i = 1, 2$,

$$H_i = -\frac{\hbar^2}{2m_i}\nabla_i^2 + V(r_i). \tag{4.3}$$

To let the hydrogen atoms interact, we added an interaction, t, that coupled the two atoms. We then solved the Schrödinger equation by solving the matrix equation,

$$\begin{bmatrix} \varepsilon & -t \\ -t & \varepsilon \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \tag{4.4}$$

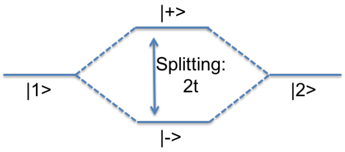

Figure 4.23: Energy diagram of the solutions to matrix equation 4.4.

Previously, we labeled the original states $|1\rangle$ and $|2\rangle$, but here it will be more convenient to label the states $|A\rangle$ and $|B\rangle$ and to use numbers to count the electrons. So, the eigenvalues corresponding to 4.4 are,

$$E_\pm = \varepsilon \pm t \tag{4.5}$$

and the corresponding eigenvectors can be denoted as

$$|-\rangle = \frac{1}{\sqrt{2}}\big(|A\rangle + |B\rangle\big) \quad \text{and} \quad |+\rangle = \frac{1}{\sqrt{2}}\big(|A\rangle - |B\rangle\big), \tag{4.6}$$

where $|-\rangle$ en $|+\rangle$ are called respectively the bonding and anti-bonding states. The total energy of the molecule is of course lower than the energy of the individual atoms[71], since the total energy of the bonding state $|-\rangle$ is lower than the energy of the individual $|A\rangle$ and $|B\rangle$ states. However, in this consideration we have ignored the electrons themselves. The question remains what happens when we add electrons to the orbitals. Now, each hydrogen atom comes with one electron and we can add these to the $|\pm\rangle$ states, denoting them with numbers. The lowest energy will be obtained if we add both electrons to the $|-\rangle$ state[72]. The total wavefunction will then be given by,

$$|\psi\rangle = |1,-\rangle|2,-\rangle = \frac{1}{2}\big(|1,A\rangle + |1,B\rangle\big)\big(|2,A\rangle + |2,B\rangle\big). \tag{4.7}$$

This wavefunction implies that the electrons will delocalize between the two nuclei: there is an equal chance of finding electron '2' on atom A (indicated by state $|2,A\rangle$) as there is of finding it on atom B (since state $|2,B\rangle$ has an equal coefficient in the total wavefunction). If we expand the product we can regroup the orbitals as follows,

$$= \frac{1}{2}\big(|1,A\rangle|2,A\rangle + |1,B\rangle|2,A\rangle + |1,A\rangle|2,B\rangle + |1,B\rangle|2,B\rangle\big) \tag{4.8}$$

$$= \frac{1}{2}\big(|\Psi_I(1,2)\rangle + |\Psi_{HL}(1,2)\rangle\big). \tag{4.9}$$

The first term is called the ionic wave function, Ψ_I, while the second is the **Heitler-London wave function** Ψ_{HL}. They are defined as,

$$|\Psi_I(1,2)\rangle \equiv \big(|1,A\rangle|2,A\rangle + |1,B\rangle|2,B\rangle\big) \tag{4.10}$$

$$|\Psi_{HL}(1,2)\rangle \equiv \big(|1,A\rangle|2,B\rangle + |1,B\rangle|2,A\rangle\big) \tag{4.11}$$

From this we see that the Heitler-London wave function describes the situation where two electrons have the highest probability of being on different atoms, while the ionic wave function describes the situation where the two electrons are both found at the same atom. Each of the four possibilities occurs with equal likelihood[73] and this cannot be right. We would expect that the situation would be different if we include the Coulomb repulsion between the two electrons. This repulsion should somehow lower the energy of the states where the two electrons spend most of their time on different atoms, or raise the energy of the states where they remain on the same atom. At the same time, we have also left spin out of the problem and this is expected to

[71] *This is the reason why natural hydrogen comes in the form of* H_2 *molecules rather than in H atoms!*

[72] *This state is fully occupied after this. Note that one electron should have spin-up and the other spin-down.*

[73] *Each of the states appearing in 4.8 has the same coefficient, so the probability for each state is the same.*

play an important role as well. Most importantly, the ionic wavefunction *cannot* be occupied if the two electrons are in the same spin state. Or similarly, the fact that electrons are fermions is inconsistent with the above definition of the Heitler-London wavefunction. We therefore reevaluate the problem from the very beginning.

We will start by constructing the Hilbert space for this problem. To keep things insightful we will only consider the $1s$-orbitals, which means that we will not have to worry about angular momentum states in our problem. We would like to take the role played by spin into account. However, we will explicitly only consider the H_2 molecule and so there really are just 6 states in the entire Hilbert space:

$$|\uparrow,\uparrow\rangle,\ |\downarrow,\downarrow\rangle,\ |\downarrow,\uparrow\rangle,\ |\uparrow,\downarrow\rangle,\ |\downarrow\uparrow,0\rangle,\ |0,\uparrow\downarrow\rangle. \tag{4.12}$$

Next we need to construct the Hamiltonian. We will do this by considering the expectation values of different states. First of all, there are states that are equivalent to the states of the separated Hydrogen atoms.

$$\langle\uparrow,\downarrow|H|\uparrow,\downarrow\rangle = 2\varepsilon \tag{4.13}$$

and its counterpart with the spins reversed. In other words, the expectation value that a state with exactly one electron occupying each atom ($|\uparrow,\downarrow\rangle$) remains the same state ($\langle\uparrow,\downarrow|$) after acting on it with the Hamiltonian is 2ε. Similar to the previous problem we need an interaction that couples the two atoms. We use the same hopping integral, quantified by a single parameter t. This means

$$\langle\uparrow,\downarrow|H|0,\uparrow\downarrow\rangle = -2t \tag{4.14}$$

Note the minus sign: the electron is now able to delocalize from its original atom and this *reduces* the total kinetic energy. So far we have not changed anything (apart from considering spin more explicitly). Now comes the crucial part: counterbalancing the gain in energy due to the delocalization exemplified by the previous expression, it will cost an energy U for two electrons to occupy the same atom. This can be expressed as,

$$\langle 0,\uparrow\downarrow|H|0,\uparrow\downarrow\rangle = 2\varepsilon + U. \tag{4.15}$$

To see this, imagine two hydrogen atoms flying through the universe on a collision course. The energy associated with each electron is ε, hence for the two atoms the total energy will be 2ε. At the moment of collision one electron is captured by an atom and a proton flies of, leaving behind a proton with two electrons. The 'orbital' energy is still energy 2ε, but now the two electrons need to spend a lot of time in each other vicinity at a cost of the Coulomb potential U. The total energy of this state is thus $2\varepsilon + U$. Although it is possible to add further interaction, it turns out that this is the 'bare bones' model that we need. We therefore set all remaining expectation values between states equal to zero[74].

The expectation values for the Hamiltonian together with a complete set of states spanning the Hilbert space is sufficient to now write down the problem. The solution will in general be expressed in terms of the basis states. We therefore expect the solution to be of the form,

$$|\psi\rangle = c_1|\downarrow,\uparrow\rangle + c_2|\uparrow,\downarrow\rangle + c_3|\uparrow,\uparrow\rangle + c_4|\downarrow,\downarrow\rangle + c_5|\uparrow\downarrow,0\rangle + c_6|0,\uparrow\downarrow\rangle. \tag{4.16}$$

It now becomes important to specify a certain order for the basis. If we use the order specified by Eq. 4.16, we can write down the Schrödinger equation in the following form,

$$\begin{bmatrix} 2\varepsilon & 0 & 0 & 0 & -2t & -2t \\ 0 & 2\varepsilon & 0 & 0 & -2t & -2t \\ 0 & 0 & 2\varepsilon & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\varepsilon & 0 & 0 \\ -2t & -2t & 0 & 0 & 2\varepsilon + U & 0 \\ -2t & -2t & 0 & 0 & 0 & 2\varepsilon + U \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} \tag{4.17}$$

From here on it is a trivial task to find the solutions: we only need to diagonalize this 6×6 matrix. This is a tedious task and I will not bother you with the calculation[75]. Instead figure 4.24 summarizes the result. Of course, we find 6 eigenenergies in total. We can label these energies simply by looking at their values. There are 3 degenerate eigenenergies with a value 2ε. Since this is exactly the same energy as the total energy of two non-interacting H atoms, we will call these solutions **non-bonding**. Then there are two states that depend on both t and U. The one with lowest energy is also the groundstate and it has a lower energy than the individual atoms[76]. This state is called, for obvious reasons, the bonding state while the highest energy state is known as the

Show that..

all the expectation values defined by Eq. 4.13-4.15 are satisfied by the Hamiltonian appearing in Eq. 4.17.

---

[74] *An obvious extension of this model would involve a spin dependent interaction.*

[75] *Note that the matrix in Eq. 4.17 is quite sparse. It is actually not so difficult to solve for the Eigenvalues if you use the rule that you need to find the solutions by setting* $det[H] = 0$.

[76] *Note that this is true for any finite* t*. As soon as there is a finite overlap between the orbitals of the individual atoms, it will be energetically more favorable to form a molecule!*

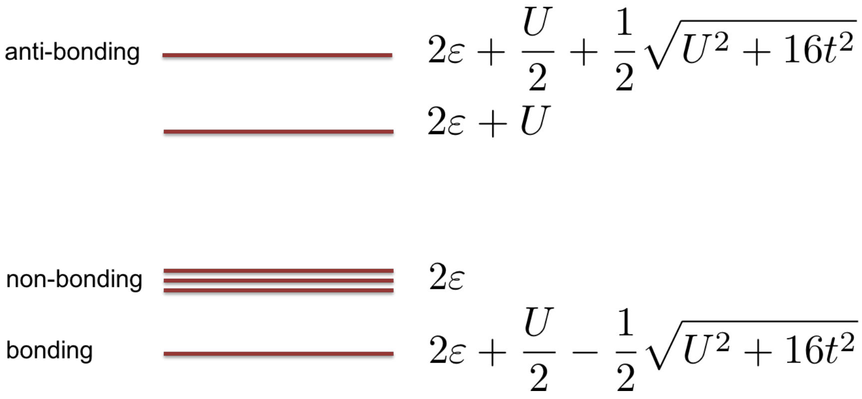

Figure 4.24: Eigenenergies of the H_2 molecule. We find a bonding solution, 3 degenerate non-bonding solutions and an anti-bonding solution.

anti-bonding state. The 6th intermediate energy state is less relevant to our discussion and we will further ignore it.

Now that we have the eigenenergies, we can also calculate the corresponding eigenfunctions. This is yet another tedious exercise that leads to the following result:

$$\text{Anti-bonding state}\ \frac{1}{\sqrt{2\left(1+\frac{4t^2}{U^2}\right)}}\left[\left(|\downarrow,\uparrow\rangle + |\uparrow,\downarrow\rangle\right) + \frac{2t}{U}\left(|\uparrow\downarrow,0\rangle + |0,\uparrow\downarrow\rangle\right)\right] \tag{4.18}$$

$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow,0\rangle - |0,\uparrow\downarrow\rangle\right) \tag{4.19}$$

$$\text{‘Triplet’ state}\ |\uparrow,\uparrow\rangle, |\downarrow,\downarrow\rangle, \frac{1}{\sqrt{2}}\left(|\downarrow,\uparrow\rangle + |\uparrow,\downarrow\rangle\right) \tag{4.20}$$

$$\text{‘Singlet’ state}\ \frac{1}{\sqrt{2\left(1+\frac{4t^2}{U^2}\right)}}\left[\left(|\downarrow,\uparrow\rangle - |\uparrow,\downarrow\rangle\right) + \frac{2t}{U}\left(|\uparrow\downarrow,0\rangle + |0,\uparrow\downarrow\rangle\right)\right] \tag{4.21}$$

The **singlet state** has the lowest energy in all of this and should thus be considered the groundstate. The term ‘singlet’ here refers to the spin part of the wave function. We can get a bit more insight if we consider for the moment $U >> t$, in which case the wavefunction simplifies to,

$$\frac{1}{\sqrt{2}}\left[|\downarrow,\uparrow\rangle - |\uparrow,\downarrow\rangle\right], \tag{4.22}$$

This is exactly the Heiter-London wavefunction if we split the wavefunction into the spin and orbital components,

$$|\Psi_{HL}\rangle = \frac{1}{\sqrt{2}}\left(|\downarrow,\uparrow\rangle - |\uparrow,\downarrow\rangle\right) \tag{4.23}$$

$$= \frac{1}{\sqrt{2}}(\phi_A(r_1), \phi_B(r_2) + \phi_A(r_2)\phi_B(r_1))\left(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\right). \tag{4.24}$$

we see that the orbital part is exactly Eq. 4.11, while the spin state ensures that the total wavefunction is anti-symmetric as required for fermionic wavefunctions. From the last line it is now also clear why this state is called the singlet: the spin part of the wavefunction corresponds to the $S = 0$, $m_s = 0$ state.

Independent of U and t there are three solutions with energy 2ε that are called **triplet states**. Note that for very large U (or very small t) the singlet and triplet states are almost degenerate in energy. This is nothing else than saying that a molecule will not form if the repulsion between the electrons is larger than the gain in kinetic energy. It is possible, depending on the atomic number of the atoms involved, that the effective, repulsive interaction is sufficiently large that any additional interaction will reduce the energy of the triplet relative to the energy of the singlet. Which of the two states (singlet or triplet) has the lowest energy can be quantified by what is known as the **exchange** energy:

$$2\mathcal{J} = \langle\Psi_s|H|\Psi_s\rangle - \langle\Psi_t|H|\Psi_t\rangle. \tag{4.25}$$

The exchange energy is a useful quantity in the sense that it allows us to determine the *magnetic* structure of the molecule. If $\mathcal{J} > 0$, the triplet state (with a total spin, $S = 1$) will have a lower total energy and thus be the groundstate, while the singlet wins if $\mathcal{J} < 0$[77] (with a total spin, $S = 0$).

---

[77] *In nature it turns out that* $\mathcal{J} < 0$ *for almost any binary molecule. In fact,* O_2 *is the only example I know where the triplet state has a lower energy.*

To recapitulate: we added the Coulomb interaction and spin[78] to the problem and ended up with the insight that the groundstate wavefunctions (although nominally the same from the orbital point of view) can become spin polarized (i.e. have a finite magnetic moment). I hope it is also clear that this very simplified problem (2 electrons, 1 orbital per lattice site and a total of 2 lattice sites) already provides quite a rich detail. We will now see how the same principle, at work in condensed matter systems with 10^{23} electrons, results in several differently ordered magnetic states.

4.4 Magnetically ordered states

In this chapter we will consider two distinct magnetically ordered states: the **ferromagnet** and the **anti-ferromagnet**. Conceptually, these states are very similar to the singlet and triplet states considered above. But what do we mean by magnetic order? In the previous chapter we have considered the response of a solid to a magnetic field. We have seen that the magnetization of the solid is proportional to the magnetic field[79]

$$\vec{M} = \chi \vec{B} \tag{4.26}$$

where the susceptibility χ was positive (paramagnetism) or negative (diamagnetism). A magnetically ordered state is a state in which the average magnetic moment per unit cell is finite in the *absence* of a magnetic field. This does not necessarily mean that the total magnetization, $\vec{M} \neq 0$. This is exemplified in figure 4.25, where the ferromagnetic groundstate is shown on the left. In this case, the magnetization on each site i is on average $\langle m_i \rangle = n/2$, where n counts the total number of electrons per lattice site[80]. Since the magnetization is the same on each lattice site this particular configuration will have a finite total magnetization,

$$\vec{M}_{FM} = \sum_i \langle m_i \rangle \neq 0 \tag{4.27}$$

In real ferromagnets one typically finds **domains** where the magnetization takes on a finite value, but where this value can vary from domain to domain. The right-hand side of figure 4.25 shows the second case we will consider: the anti-ferromagnet. As you can guess from the configuration shown, the total magnetization $\vec{M} = 0$. Nevertheless, the state can be characterized as magnetically ordered[81]. The way to do this is to divide the lattice into two sub-lattices. As you can see I gave different colors to the lattice sites. The collection of dark red sites make up one lattice, the collection of light red sites the other. The lattice of the anti-ferromagnet is called **bi-partite**. We can now define the magnetic **order parameter** as follows:

$$\vec{M}_{AFM} = \sum_{i \in A} \langle m_i \rangle - \sum_{i \in B} \langle m_i \rangle \neq 0 \tag{4.28}$$

Let me reiterate: the expressions for the magnetization defined above do *not* depend on any applied magnetic field. Both $\vec{M}_{FM}$ and $\vec{M}_{AFM}$ are called 'order parameter' because

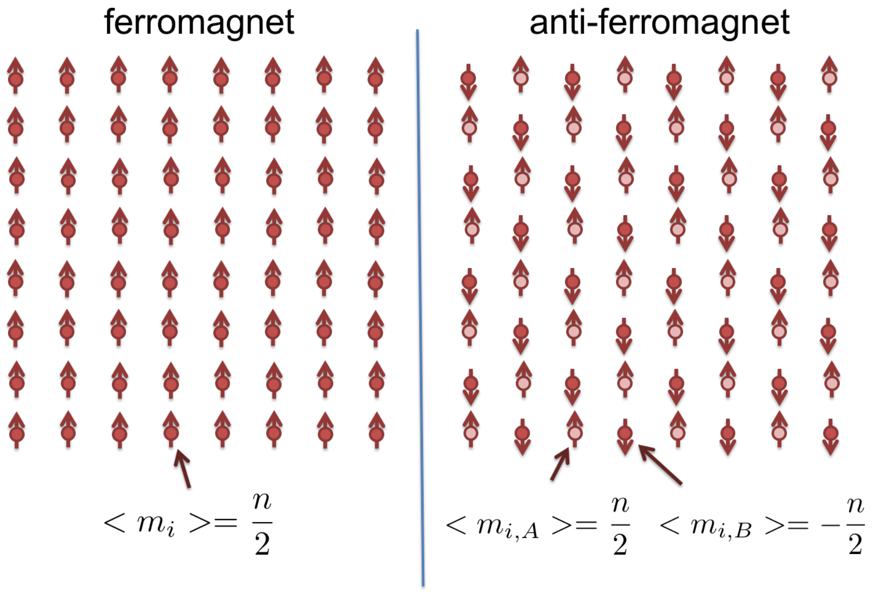

Figure 4.25: The two magnetically ordered states that we will consider in this course. Ferromagnets are characterized by equal magnetization on all lattice sites, while anti-ferromagnetic order is characterized by two sub-lattices (A and B) where the magnetization on a given has the opposite sign compared to the other sub-lattice.

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[78] *In fact, it is more appropriate to say that we have taken fermionic statistics into account.*

[79] *From here on we use the symbol χ for the magnetic susceptibility without subscripts.*

[80] *We can therefore have a total spin per lattice site of $S = 0, 1/2, 1, 3/2, 2, \ldots$.*

[81] *It is easy to 'see' from the figure that there is order in this state. It took quite a long time to prove that it was so.*

their value can be used as a measure of the presence of **long range order**. In other words, if the order parameter is non-zero the state is said to be ordered.

In the next section we will explore how magnetically ordered states come about. To keep things simple we will work from one single model: the Hubbard model. This has the advantage that there is only one model to understand. The disadvantage is that nobody knows how to solve this model, except in some limits and mostly only numerically. In the next section I will sketch a qualitative picture to explain the rationale behind the Hubbard model and its solutions. Then in the next section I will sketch a more quantitative picture based on a mean-field approach.

4.5 The Hubbard model I: a qualitative picture

Given all the good things coming out of the tight-binding theory it cannot be all that bad as a starting point. So, what I would like to do in this section is to start by using the intuition we have gained about tight-binding theory and do a 'gedanken experiment' to get a feeling for how electron-electron interactions might change the picture. As with the original model of the H_2 molecule from the first chapter, we only consider the crystal structure and the orbitals when we formulate the tight-binding problem. This is most evident in the 'central equation': the sums run over all lattice vectors and orbitals. The electrons are only put in as an afterthought. In our gedanken experiment we will start with an empty lattice of orbitals and fill it up with electrons, but we will assume that these electrons interact in the same way as in the H_2-molecule discussed in the previous section.

So we start with a situation as shown in Fig. 4.26. We have an empty lattice with sites labeled with an index i and where we have added an electron to a particular site. This electron can move about freely and the probability for hopping from site to site is indicated as γ. The Hamiltonian for this problem can be written as,

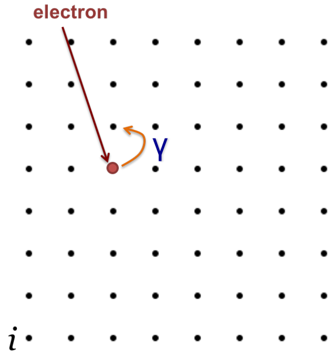

Figure 4.26: A square lattice with all empty sites. A single electron is shown that can move about in this lattice. The probability for moving is determined by γ.

$$H = \varepsilon \sum_{\vec{i}} |\vec{i}\rangle\langle\vec{i}| + \gamma \sum_{\vec{i},\delta} |\vec{i}\rangle\langle\vec{i}+\delta|. \tag{4.29}$$

where the sum over δ indicates that we should consider tunneling probabilities to neighboring lattice sites. We discussed a similar tight-binding problem in Chapter 1, which we can easily generalize to the two dimensional situation sketched here. Since we only have a single electron in the problem, we still don't have to worry about inter-electron interactions and the dispersion relation is simply given by,

$$E = E_0 + 2V_2(\cos(k_x a) + \cos(k_y a)). \tag{4.30}$$

As in the previous section I would now like to add electron-electron interactions to see how the solution changes. However, adding a long-range interaction like the Coulomb potential makes the problem mathematically intractable on a lattice[82]. Fortunately, having many electrons will partly solve this problem. As pointed out in section 2.8 the bare Coulomb potential in a solid is screened by the presence of the other electrons. This means that the potential falls off much faster than the usual $1/r$. With this idea in mind John Hubbard proposed a 'simple' approximation that allowed him to partially solve the problem of an infinity of interacting particles. His proposal was to add an interaction to the Hamiltonian of the form,

$$H_{int} = \begin{cases} U & \text{If } e_1 \text{ and } e_2 \text{ are in the same orbital} \\ 0 & \text{If } e_1 \text{ and } e_2 \text{ are in different orbitals} \end{cases} \tag{4.31}$$

Note that for two electrons to occupy the same orbital requires them to have opposite spin. This restriction will immediately enforce the Pauli principle (i.e. no two fermions can occupy the same state). Although this interaction seems a tremendous simplification already, it is still a very difficult problem that can only be solved (numerically) in a few particular instances. To understand how magnetism comes about we will focus on the simplest incarnation of the Hubbard model, namely the single orbital case on a 2D lattice[83]. We can express the Hubbard interaction in terms of operators as follows:

$$H_{int} = U \sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}. \tag{4.32}$$

The operators $\hat{n}_{i\sigma}$ are known as density operators. They can take on two values, e.g. $\hat{n}_{i\sigma}$ = 0,1. It is an easy exercise to verify that this indeed corresponds to the Hamiltonian proposed by Hubbard. H_{int} measures the total number of doubly occupied sites and the energy cost associated with it. The full Hubbard model hamiltonian is thus,

$$H = \varepsilon \sum_{\vec{i}} |\vec{i}\rangle\langle\vec{i}| + \gamma \sum_{\vec{i},\delta} |\vec{i}\rangle\langle\vec{i}+\delta| + U \sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}. \tag{4.33}$$

[82] *There is an interesting link here to quantum information science. To perform large scale quantum computations one would like to work with highly entangled states (states where many particles are simultaneously interacting with each other). The wavefunction of a solid is exactly such a state because of the long range interactions. It is not possible (yet) to prepare solids for quantum computing. One of the interesting problems that could be tackled with a quantum computer is the simulation of the N-particle wavefunction that we are right now trying to approximate.*

[83] *The 1D case would be 'simpler', but already requires a level of mathematics that I do not want to touch upon. The 2D case discussed here applies qualitatively to the high temperature superconductors, which is why I chose this version.*

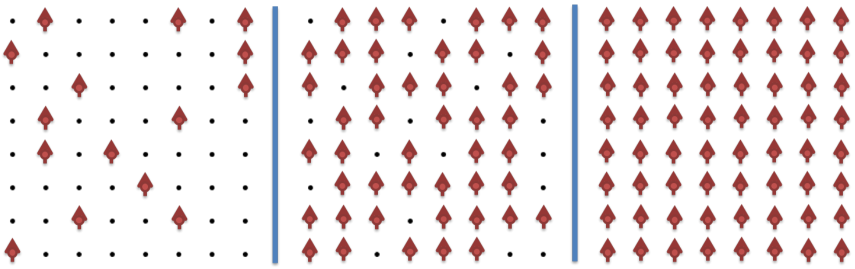

Figure 4.27: Three different filling levels of the Hubbard model. Left: Approximately 1/8th filling where it is still relatively easy for electrons to move around without occupying the same site. Middle: Close to half filling, only a few electrons can still move. Right: Half filling, where it is now impossible to move an electron without flipping a spin.

How does adding this term change the solution? One important difference with previous exercises is that we now explicitly need to take spin into account (as the interaction is dependent on spin). You can qualitatively see how the solution changes as follows: start by imagining an empty lattice and add one electron to it. The situation is exactly that of Fig. 4.26 and the solution will be the tight binding solution. Now imagine adding an additional electron. In a large (infinite) 2 dimensional lattice this will hardly make a difference. There are a few configurations (N^2 to be precise) that will each add an energy U to the groundstate energy. I can prevent this by putting both electrons on the lattice with spin pointing up. To flip the spin of an electron will cost energy (and requires an additional term in the Hamiltonian or finite temperature). Therefore it seems that this is the lowest energy configuration[84]. Lets keep adding electrons. from here on I will use the word filling to denote the number of electrons in our hypothetical crystal. Since we have assumed one orbital per lattice site, there will only be a single tight binding band. This band, as usual, will have 2N available states associated with it. Therefore having exactly one electron per lattice site is called **half-filling**, which corresponds to a density, n=1. Figure 4.27 shows a series of snapshots with varying number of electrons. As the filling increases the number of configurations with doubly occupied sites grows quickly. This results in a reduced mobility for the electrons. However, if we look to the left panel of Fig. 4.27 there is still plenty of space for the electrons to move and due to them all having parallel spin they can never occupy the same site. The real groundstate of the Hubbard model at low filling with large enough interaction U turns out to indeed be a linear superposition of all realizations of the configuration shown on the left. Since all spins are pointing in the same direction...this is a ferromagnetic groundstate! This is the key result of this section: starting from a tight-binding picture we obtain a ferromagnet if we (non-perturbatively) include a repulsive interaction and the Pauli exclusion principle.

There is more. Let's add even more electrons. As we approach half filling (middle and right snapshots) the phase space for electrons to move becomes smaller and smaller until exactly at half-filling the electrons can no longer move at all. The only way to move an electron to a different site is to flip its spin (which costs energy) and then doubly occupy a site (which costs even more energy). It seems to follow that the image shown on the right is an exact graphical representation of the groundstate at half filling[85]. Not only is this state a ferromagnet, it is also an insulator.

It turns out that there is in fact a little caveat to our gedanken experiment: calculations will show that our reasoning is correct at low filling. However, at half-filling the argument is in fact wrong. I have argued so far that by keeping spins parallel, the potential energy associated with the Coulomb repulsion, U is minimized. This is correct, however to find the groundstate we should also consider kinetic energy. At half filling the electrons are localized on lattice sites. This means, according to the uncertainty principle, that the kinetic energy term $\propto \hat{p}^2$ is in fact very large. It turns out that the anti-ferromagnetic groundstate (shown on the right in Fig. 4.25) has a lower energy. In the antiferromagnetic state there will be 'virtual' fluctuations where an electron moves to a neighboring site and back again. These fluctuations reduce the kinetic energy as the electrons are allowed to somewhat delocalize. This groundstate is known as the Mott-Hubbard insulator. To summarize: if we have exactly one electron per lattice site in a model with on-site repulsive interactions, the Pauli exclusion principle enforces the groundstate to be an anti-ferromagnetic insulator. This state is in fact much more interesting than the 'standard' tight binding state. It is a highly correlated or **entangled** state. In the tight binding picture all that mattered was the fact that there were bands in energy in which the electrons resided. The quasiparticles in this system were non-interacting particles and that was it. In the anti-ferromagnetic groundstate, moving a single electron immediately influences the motion of all its neighbors. There will be a doubly occupied site and, in the 2D square lattice case,

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[84] *There are some subtleties here that I will not be able to explain during this course. If you work through the real calculations, you will find that the solutions (wavefunctions) are linear superpositions of configurations. If U is finite, the coefficient for a configuration with doubly occupied sites will be smaller than one without doubly occupied sites.*

[85] *Note that there is exactly one configuration at half-filling without any doubly occupied sites. The configuration shown is thus unique.*

three sites that now feel an empty neighboring site. This will however impact also on the next nearest neighbors as they cannot fluctuate to the doubly occupied site anymore. This **strongly correlated electron** state has different quasiparticles as well. Not only are there charged excitations (i.e. quasi-electrons similar to the tight binding quasi-electrons) there are now a completely new set of quasi-particle excitations known as **spin waves**. Before discussing all of this in more detail we first sketch the new energy landscape at half filling. The configurations can be indicated schematically as spin states, where the lowest energy state is the anti-ferromagnet and is separated from the first doubly occupied site by an energy U,

$$\text{Second excited state } 2U \qquad |\uparrow, 0, \downarrow\uparrow, \downarrow, \ldots 0, \uparrow\downarrow\rangle \tag{4.34}$$

$$\text{First excited state } U \qquad |\uparrow, 0, \downarrow\uparrow, \downarrow, \ldots \uparrow, \downarrow\rangle \tag{4.35}$$

$$\text{Ground state } 0 \qquad |\uparrow, \downarrow, \uparrow, \downarrow, \ldots \uparrow, \downarrow\rangle \tag{4.36}$$

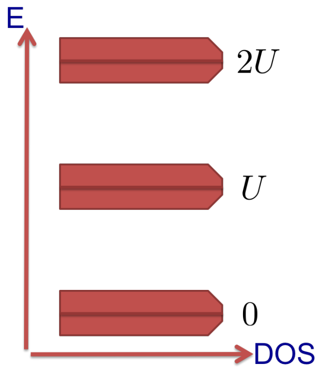


Figure 4.28: Schematic representation of the density of states of the Hubbard model at half-filling. The groundstate (no doubly occupied sites) is separated from the first excited state (one doubly occupied site) by an energy U.

What is not entirely clear from the preceding discussion is that a band of states will form around the groundstate (just like a tight binding band). This is indicated in Fig. 4.28 by the red hatched area. Different bands are now separated by energy gaps of the order $U \propto 2$ eV. The origin of the bandwidth of a **Hubbard sector** lies in the fact that electrons are still allowed to virtually fluctuate between different sites. Remember the reason behind the anti-ferromagnetic state being lowest in energy: the electrons are allowed to virtually fluctuate from site to site. The energy associated with such a process can be represented graphically as,

$$|\uparrow, \downarrow, \uparrow, \ldots \uparrow, \downarrow\rangle \tag{4.37}$$

$$\gamma\downarrow$$

$$|\uparrow, 0, \downarrow\uparrow, \ldots \uparrow, \downarrow\rangle \tag{4.38}$$

$$\gamma\downarrow$$

$$|\uparrow, \downarrow, \uparrow, \ldots \uparrow, \downarrow\rangle \tag{4.39}$$

where the intermediate state has an energy U associated with it. Although such a fluctuation would cost energy, from a perturbation theory analysis one finds that a *second* order process like this, would result in a bandwidth of the order,

$$J \propto \left| \frac{\gamma^2}{U} \right| . \tag{4.40}$$

where J is called the exchange interaction. It can be shown (but we will not do this) that in the limit of large U the Hamiltonian Eq. 4.33, has a different interpretation in perturbation theory. Note that in the limit of large U, the exchange interaction becomes a small number, thereby enabling a perturbative approach. The resulting model (up to second order in the perturbation) can be cast in the following form:

$$H = cst - J \sum_{i,\delta} \hat{S}_i \cdot \hat{S}_{i+\delta} \tag{4.41}$$

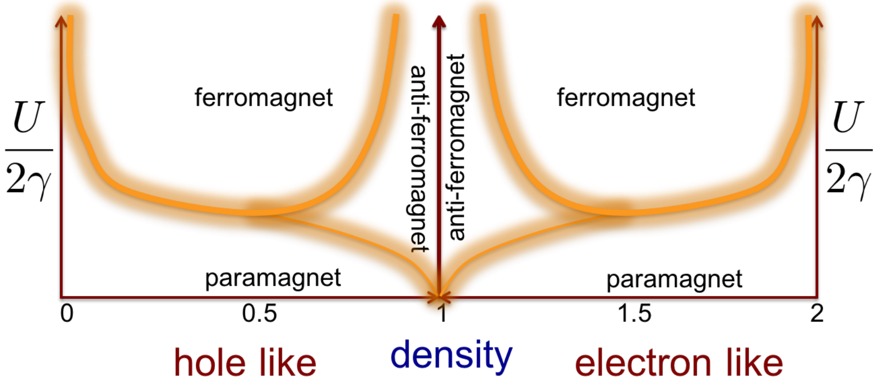
is known as the **Heisenberg model**. The groundstate of this model depends on the sign of J: if $J > 0$ the groundstate is a ferromagnet, while if $J < 0$ the groundstate is anti-ferromagnetic. We leave the discussion of the groundstate and excited states for the exercises.

To conclude this section we will construct a qualitative phase diagram of the Hubbard model. We have already worked out two limits. For $U = 0$, we have the tight binding model. In Chapter 3 we concluded that this described a paramagnetic metal. At half filling and large U we have an anti-ferromagnetic insulator. To construct qualitatively the rest of the phase diagram, we do our gedanken experiment in reverse. We start with the perfect anti-ferromagnet (Fig. 4.25) and remove one electron. As you might imagine, this won't change all too much. Now keep randomly removing electrons (some with up- and some with down-spin). The result will be a randomly distributed collection of up and down spins that are free to move about. This sounds very much like a paramagnetic metal. On the other hand we argued above that this should be a ferromagnetic metal. As simple as this model seems to be, there is no real resolution to this difference. The current version of the Hubbard model looks something like what is sketched in Fig. 4.29. Starting on the left (n=0) we have a paramagnetic metal. This is just the tight-binding result that survives even infinite U[86]. With increasing filling the Hubbard model remains a paramagnetic metal for small enough U, until the singular limit of $n = 1$ is reached where the system turns into an anti-ferromagnetic insulator for even infinitesimally small U. Adding an additional electron beyond half filling (a case we haven't yet discussed) turns out to have the same

---

[86] *For the nearly trivial reason that a single electron cannot doubly occupy a lattice site.*

Figure 4.29: The approximate phase diagram of the Hubbard model as function of carrier concentration (or filling). The density is defined as nr. of electrons per lattice sites.



effect as removing one electron[87]. Close to half filling for large enough U it is well established that the Hubbard model remains anti-ferromagnetic.

The debate about the presence of ferromagnetism is still an active field of research, but it appears that it strongly depends on the details of parameter choices and the lattice structure. Another actively researched question is whether the Hubbard model can 'spontaneously' lead to superconductivity. This is an interesting question, because it is widely believed that the single band, square lattice Hubbard model (or a close cousin with superexchange interactions) is the basic model describing the cuprate high temperature superconductors. For those of you wondering why these questions haven't been resolved yet: away from integer filling it requires intensive numerical computations to find the groundstate energies.

There is one last remark about the phase diagram of the Hubbard model: it is probably the first **'zero-temperature' phase diagram** you have encountered. This is actually quite different from 'conventional' phase transitions in which the system moves from one phase to another phase as temperature increases (e.g. ice to water). In these phase transitions, temperature fluctuations drive the transition. This is not the case in zero-temperature phase transitions where it is really the quantum fluctuations that drive the transition. The strength of the quantum fluctuations is controlled by the parameter(s) driving the transition (density and Coulomb U in our case). There are many neat effects related to these **quantum phase transitions**.

4.6 The Hubbard model II: a more quantitative picture

It is possible to establish the qualitative picture presented in the previous section more rigorously. However, the math involved is too advanced to present here. It requires so-called 'second-quantization' techniques that will be introduced in a later course.

However....

You do have some of the relevant mathematical tools to do a somewhat less sophisticated approach. The description we will introduce here is not wrong, it is just not very accurate[88]. Before continuing, lets summarize a few points:

- As soon as we add Coulomb repulsion, correlations between electrons become important.
- Due to the Pauli principle the electron spins will align (anti-)parallel.
- We end up with either paramagnetism, ferromagnetism or anti-ferromagnetism.

At this point it is good to note that there are essentially two types of ferromagnetism: **local ferromagnetism** and **itinerant ferromagnetism**. The former arises when there are atoms in the unit cell in a high spin state (remember Hund's rules!). We will be more interested in the latter however. Itinerant ferromagnets are metals like Fe, Co and Ni. Clearly, because they are metals there is a large number of nearly free electrons that are completely delocalized. It is therefore somewhat difficult to understand how one should relate this to the definition of an average magnetic moment per unit cell (fig. 4.25). In this section we will make an approximation to the Hubbard model that will set the stage for working out the origin of ferromagnetism in the next section. The approach is known as the **mean-field approximation** and it is in fact similar in spirit to the single-particle approximation explained in the first chapter. Let's begin by

[87] *There is a larger cost associated with adding an electron though!*

[88] *I am not sure how to state the problem. What we are about to discuss is not wrong, it just lacks the quantitativeness of the tight-binding model.*

recalling the definition of the Hubbard model.

$$H = \varepsilon \sum_{\vec{i}} |\vec{i}\rangle\langle\vec{i}| + \gamma \sum_{\vec{i},\vec{\delta}} |\vec{i}\rangle\langle\vec{i}+\vec{\delta}| + U\sum_{i} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}. \tag{4.42}$$

The difference with tight-binding is as explained above in the last term. The reason it is a complicated term is that it couples two electrons together (one with spin up and one with spin down). Wouldn't life be easier if these electrons were 'decoupled'? Remember that this was in fact how we achieved the tight binding solution in the first place. We assumed that the electron were moving in an effective potential field resulting from the presence of all other atoms and electrons. The mean field approximation is made in similar spirit; it decouples products of operators. A general formulation of the mean field approximation is as follows. We redefine an arbitrary operator as,

$$\hat{O} = \langle\hat{O}\rangle + \delta\hat{O}. \tag{4.43}$$

The first term is the average expectation value of the operator, while the latter term are the fluctuations around this expectation value. The first term is a *number*, while the last term is still an operator. We can always write an operator like this, but we lack a mathematical form for the fluctuation term. Nevertheless, the idea is that the mean-field approximation 'works' if the fluctuations around the average (mean) value (field) of the operator $\langle\hat{O}\rangle$ are small. To see how this helps, we calculate the product of two operators. We find,

$$\hat{O}\hat{O} = \langle\hat{O}\rangle\langle\hat{O}\rangle + \langle\hat{O}\rangle\delta\hat{O} + \langle\hat{O}\rangle\delta\hat{O} + \delta\hat{O}\delta\hat{O}. \tag{4.44}$$

This where the approximation is made. Since the fluctuations are small, terms that are second order in the fluctuations (i.e. the last term) can be neglected and we are left with,

$$\hat{O}\hat{O} \approx \langle\hat{O}\rangle\langle\hat{O}\rangle + \langle\hat{O}\rangle\delta\hat{O} + \langle\hat{O}\rangle\delta\hat{O} \tag{4.45}$$

This appears not to help too much, since we are now left with a number (first term) and then two terms containing an unknown, undefined operator. The trick is to eliminate this operator. This can be achieved making use of Eq. 4.43, while noting that:

$$\delta\hat{O} = \hat{O} - \langle\hat{O}\rangle \tag{4.46}$$

If we replace the fluctuation terms we obtain,

$$\hat{O}\hat{O} = \langle\hat{O}\rangle\hat{O} + \hat{O}\langle\hat{O}\rangle - \langle\hat{O}\rangle\langle\hat{O}\rangle \tag{4.47}$$

And that is the magic of the mean-field approximation. By throwing away a term containing the square of the fluctuations, we have decoupled a product of operators into an expression that contains only a single operators (multiplied by its expectation value).

We can follow the same steps for the last term of Eq. 4.42 and find,

$$\hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} \approx \langle\hat{n}_{i,\downarrow}\rangle\hat{n}_{i,\uparrow} + \hat{n}_{i,\downarrow}\langle\hat{n}_{i,\uparrow}\rangle - \langle\hat{n}_{i,\downarrow}\rangle\langle\hat{n}_{i,\uparrow}\rangle. \tag{4.48}$$

Show that..

Eq. 4.48 follows from a mean-field approximation of the Hubbard Hamiltonian.

To gain some more physical insight in this result we now introduce two new quantities:

$$\langle n\rangle = \langle\hat{n}_{i,\downarrow}\rangle + \langle\hat{n}_{i,\uparrow}\rangle \tag{4.49}$$

$$\langle m\rangle = \langle\hat{n}_{i,\downarrow}\rangle - \langle\hat{n}_{i,\uparrow}\rangle \tag{4.50}$$

The first line is the average electron density per lattice site, while the second line is the average magnetization. We can express the spin-up and spin-down densities in terms of these average values,

$$\langle\hat{n}_{i,\downarrow}\rangle = \frac{\langle n\rangle + \langle m\rangle}{2}, \quad \langle\hat{n}_{i,\uparrow}\rangle = \frac{\langle n\rangle - \langle m\rangle}{2}. \tag{4.51}$$

Putting it all together we have,

$$U\sum_i \hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} = \sum_i \varepsilon_\uparrow\hat{n}_{i,\uparrow} + \hat{n}_{i,\downarrow}\varepsilon_\downarrow - \frac{U}{4}(\langle n\rangle^2 - \langle m\rangle^2) \tag{4.52}$$

Show that..

Eq. 4.52 follows from the mean field expression for the operators (Eq. 4.48) together with the definitions of the average density and magnetization.

where I have introduced two new quantities,

$$\varepsilon_{\uparrow,\downarrow} = \frac{U}{2}(\langle n\rangle \mp \langle m\rangle) \tag{4.53}$$

The last step is to express the remaining density operators in terms of the basis states $|i,\sigma\rangle$[89],

$$\hat{n}_{i,\sigma} = |i,\sigma\rangle\,\langle i,\sigma| \tag{4.54}$$

---

[89] *The density operator just counts the number of electrons per site.*

This allows us to finally write the mean-field Hubbard Hamiltonian as,

$$H = \sum_{\vec{i},\sigma} \tilde{\varepsilon}_\sigma |\vec{i}\rangle\langle\vec{i}| + \gamma \sum_{\vec{i},\vec{\delta},\sigma} |\vec{i},\sigma\rangle\langle\vec{i}+\vec{\delta},\sigma| - \frac{U}{4}(\langle n\rangle^2 - \langle m\rangle^2) \tag{4.55}$$

with $\tilde{\varepsilon}_\sigma = \varepsilon + \varepsilon_\sigma$. This looks exactly like our original tight-binding Hamiltonian! The only difference is in the fact that we now have an added spin label. There is however no term coupling the two spins (as in the original Hubbard Hamiltonian) and therefore we can solve the problem for spin-up and spin-down electrons separately. This will result in energy bands and all the rest of it. We can in principle again define different limits (weak-binding vs. tight-binding) and use all the terminology we developed when discussing single-electron problems (e.g. Fermi level, density of states etc). There is a 'but': the energies for spin-up and spin-down, Eq. 4.53, depend on the average density and magnetization and we do not know these values yet. We still need to solve this problem self-consistently. Finding a self-consistent solution is typically done as follows. One starts by assuming a value for the average density and magnetization. These values are used to calculate the groundstate energy and corresponding wave functions. The latter are then used to calculate new values for the average density and magnetization. These are then used to calculate a new groundstate energy and corresponding wave functions. This loop is repeated until the densities and energy don't change upon repeating the loop.

To determine the phase diagram and the boundaries between the different magnetically ordered phases is now a matter of calculation. You pick a value of U and a certain filling (this is done by imposing a constraint on the total density and magnetization) and work through the self-consistency loop. This is a rather complicated scheme that we will not pursue. Instead, we will use our mean-field Hamiltonian to derive a condition for the emergence of ferromagnetism.

4.7 The Stoner criterion

In this section we will derive a condition that explains when (and hopefully also why) ferromagnetism appears. For what follows it will help to read the discussion on paramagnetism in section 3.7 again. In that case we considered nearly free electrons in a magnetic field. We found that the Zeeman interaction was responsible for creating an energy difference between spin-up and spin-down electrons, resulting in a higher density of states at the Fermi level for one of the two spin species. In the presence of Coulomb repulsion something similar happens and we can use our mean-field Hamiltonian to make this insightful.

The idea is simple: we need to find a condition such that our mean-field Hamiltonian,

$$H = H_\uparrow + H_\downarrow - \frac{U}{4}(\langle n\rangle^2 - \langle m\rangle^2), \tag{4.56}$$

produces a finite average magnetization. This condition can be derived by realizing that for finite magnetization to appear, such a state must have a *lower* energy than the state with zero average magnetization. The average magnetization can be expressed in terms of the density of states as follows. When we integrate the density of states up to the Fermi level, we obtain the total charge density. By splitting the density of states in a spin-up and a spin-down component, we can thus measure the density of electrons with spin-up and with spin-down. To have a finite magnetization thus means that $\langle m\rangle = n_\uparrow - n_\downarrow$ should be non-zero. Referring to Fig. 4.30, this can happen only if more electrons occupy a particular spin state, which results in a slightly shifted Fermi level for this spin state. We define the difference between the two Fermi levels as $2\delta \equiv E_{F,\uparrow} - E_{F,\downarrow}$. This means that we can express the magnetization as,

$$\langle m\rangle = n_\uparrow - n_\downarrow = \frac{1}{V}\left[\int_0^{\varepsilon_F+\delta} \varrho_\uparrow(\varepsilon)d\varepsilon - \int_0^{\varepsilon_F-\delta} \varrho_\downarrow(\varepsilon)d\varepsilon\right] \tag{4.57}$$

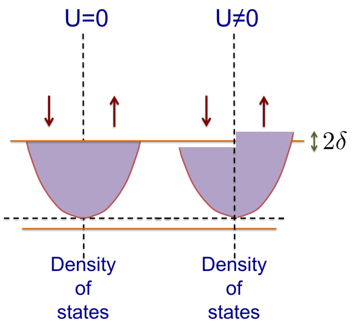


Figure 4.30: Density of states for spin-up and spin-down electrons in the absence (left) and presence (right) of a Coulomb repulsion U. We want to derive a condition such that some electrons spontaneously flip their spin, resulting in an increase of spin-density. δ indicates the energy cost associated with this.

Of course, this will never happen in the nearly free electron model. The electrons with spin-up state in Fig. 4.30 have a higher energy than what they would have if they would occupy spin-down states; the magnetization will always be zero. Let's see how this works out in the mean-field Hubbard model.

Since the density of states is approximately constant about the Fermi level, we assume for simplicity that $\varrho_\sigma(\varepsilon) \approx \varrho_\sigma(\varepsilon_F)$. The two integrals can then be combined into one since $\varrho_\uparrow(\varepsilon_F) = \varrho_\downarrow(\varepsilon_F)$. The magnetization is thus,

$$\langle m\rangle = \frac{1}{V}\int_{\varepsilon_F-\delta}^{\varepsilon_F+\delta} \varrho(\varepsilon)d\varepsilon \approx \frac{1}{V}\cdot\varrho(\varepsilon_F)\int_{\varepsilon_F-\delta}^{\varepsilon_F+\delta} d\varepsilon = \frac{1}{V}\cdot 2\varrho(\varepsilon_F)\delta. \tag{4.58}$$

The total magnetization, $\langle m\rangle = 2\varrho(\varepsilon_F)\delta$, will thus be finite if a minimization of the total energy leads to a finite δ. To see when this happens requires us to calculate the total energy, which can be done making use of the density of states as well (see also exercise 4 in Ch. 1)

The *total* energy is defined as

$$E = -\frac{U}{4}(\langle n\rangle^2 - \langle m\rangle^2) + 2\int_0^{\varepsilon_F} \tilde{\varepsilon}\varrho(\varepsilon)d\varepsilon. \tag{4.59}$$

We will first evaluate the integral, which can be done in the same fashion as the previous integral[90]. We split the integral in a spin-up and spin-down component and then assume there is an imbalance between the two populations. The energy per state is given by the energy eigenvalues, $\tilde{\varepsilon}_\sigma$ of the mean field Hamiltonian[91]. This gives,

$$E = \int_0^{\varepsilon_F+\delta} (\varepsilon+\varepsilon_\uparrow)\varrho_\uparrow(\varepsilon)d\varepsilon + \int_0^{\varepsilon_F-\delta} (\varepsilon+\varepsilon_\downarrow)\varrho_\downarrow(\varepsilon)d\varepsilon \tag{4.60}$$

$$= \int_0^{\varepsilon_F} \left[(\varepsilon+\varepsilon_\uparrow)\varrho_\uparrow(\varepsilon) + (\varepsilon+\varepsilon_\downarrow)\varrho_\downarrow(\varepsilon)\right] d\varepsilon$$

$$+ \int_{\varepsilon_F}^{\varepsilon_F+\delta} (\varepsilon+\varepsilon_\uparrow)\varrho_\uparrow(\varepsilon)d\varepsilon - \int_{\varepsilon_F-\delta}^{\varepsilon_F} (\varepsilon+\varepsilon_\downarrow)\varrho_\downarrow(\varepsilon)d\varepsilon. \tag{4.61}$$

The first integral can be easily evaluated and gives,

$$= E_0 + \frac{U}{4}\langle n\rangle^2 \tag{4.62}$$

$$+ \int_{\varepsilon_F}^{\varepsilon_F+\delta} (\varepsilon+\varepsilon_\uparrow)\varrho_\uparrow(\varepsilon)d\varepsilon - \int_{\varepsilon_F-\delta}^{\varepsilon_F} (\varepsilon+\varepsilon_\downarrow)\varrho_\downarrow(\varepsilon)d\varepsilon. \tag{4.63}$$

where E_0 is the total energy of the system *without* interactions. To calculate the remaining two integrals we again make the approximation that the density of states about the Fermi level is constant. We find for the integral with spin-up,

$$\int_{\varepsilon_F}^{\varepsilon_F+\delta} (\varepsilon+\varepsilon_\uparrow)\varrho_\uparrow(\varepsilon)d\varepsilon \approx \varrho(\varepsilon_F)\int_{\varepsilon_F}^{\varepsilon_F+\delta} (\varepsilon+\varepsilon_\uparrow)d\varepsilon$$

$$= \varrho(\varepsilon_F)\left[\varepsilon_F\delta + \frac{\delta^2}{2} + \varepsilon_\uparrow\delta\right] \tag{4.64}$$

and similarly

$$\int_{\varepsilon_F-\delta}^{\varepsilon_F} (\varepsilon+\varepsilon_\downarrow)\varrho_\downarrow(\varepsilon)d\varepsilon \approx \varrho(\varepsilon_F)\left[\varepsilon_F\delta - \frac{\delta^2}{2} + \varepsilon_\downarrow\delta\right]. \tag{4.65}$$

If we now add everything together, using the definition of $\varepsilon_\uparrow$ and $\varepsilon_\downarrow$ and reintroducing the constant energy term, we find that the total energy is given by,

$$E = E_0 + \frac{U}{4}\langle n\rangle^2 - \frac{U}{4}(\langle n\rangle^2 - \langle m\rangle^2) + \varrho(\varepsilon_F)\left[\delta^2 + \delta(\varepsilon_\uparrow - \varepsilon_\downarrow)\right] \tag{4.66}$$

$$= E_0 + \frac{U}{4}\langle m\rangle^2 + \varrho(\varepsilon_F)\left[\delta^2 - \delta U\langle m\rangle\right]. \tag{4.67}$$

The last step is to realize that we still need to fulfill the self-consistency condition. That is, we can make use of our expression for the magnetization, Eq. 4.58, to eliminate δ from the total energy. This gives,

$$E = E_0 + \frac{U}{4}\langle m\rangle^2 + \varrho(\varepsilon_F)\left[\frac{\langle m\rangle^2}{4\varrho^2(\varepsilon_F)} - \frac{\langle m\rangle}{2\varrho(\varepsilon_F)}U\langle m\rangle\right], \tag{4.68}$$

which can be simplified to,

$$E = E_0 + \frac{\langle m\rangle^2}{4}\left[\frac{1}{\varrho(\varepsilon_F)} - U\right], \tag{4.69}$$

And that is our final result. The first term in Eq. 4.69 is the groundstate energy of the nearly free electron model. In chapter 3 we have seen that this groundstate is a paramagnetic metal. The second term is derived from the mean-field approximation of the Hubbard interaction (i.e. a remaining Coulomb interaction between electrons). Note that the *total energy* will be lowered if,

$$\frac{\langle m\rangle^2}{4}\left[\frac{1}{\varrho(\varepsilon_F)} - U\right] < 0 \tag{4.70}$$

[90] *We will 'forget' the constant for a moment to ease writing. We don't neglect it though! It will be reinserted at the end.*

[91] *The result presented here is general, but assume $\gamma = 0$ for the moment.*

which is fulfilled if,

$$\rho(\epsilon_F)U > 1. \tag{4.71}$$

Stoner was the first to derive this result and he realized that this provided a criterion for ferromagnetism to emerge in a metal, hence the name 'Stoner criterion'. If Eq. 4.71 is satisfied the system can gain some potential energy by spontaneously rearranging some spins, resulting in a spontaneous magnetization (i.e. in the absence of a magnetic field). So what determines whether a material is magnetic or not? It turns out that in most metals the screened Coulomb repulsion (our Hubbard interaction) is approximately equally large. For example Cu and Fe are neighbors in the periodic table, both have approximately equal numbers of electrons, both are metallic etc. So U is approximately the same in both cases (and also quite small). The reason that Fe is magnetic and Cu not is therefore not related to the strength of the interaction U. Figure 4.31 shows calculated spectra for the density of states of three simple metallic ferromagnets (Fe, Co and Ni). We see in each case a large peak in the DOS right at the Fermi level. The idea that a large density of states at the Fermi energy results in ferromagnetism is in hindsight understandable. Imagine that there is a small, but non-negligible potential energy cost for two electrons being close together. If the density of states is large *at the Fermi energy*, it will cost very little energy for many electrons to occupy a state with opposite spin. As a result of having on average parallel spin (finite magnetization) these electrons can no longer come close to each other (occupy the same quantum state) and this eventually lowers the total energy. The key is therefore in having a large phase space at low energy cost.

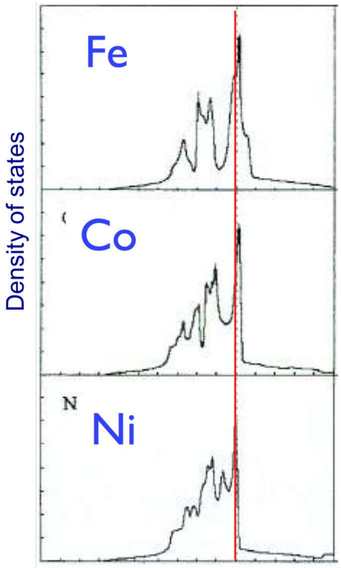


Figure 4.31: Density of states of Fe, Co and Ni. In each case we find a large density of states at the Fermi level. This is the driving force behind ferromagnetism.

4.8 The Heisenberg model

At the end of section 4.5 I explained how the Hubbard model in the limit of strong interactions can be mapped to the Heisenberg model. The mathematical framework behind this is a bit more advanced and we will not derive it[92]. Instead we will focus our attention on the Heisenberg model itself. Keep in mind that this is a good model for materials where the Coulomb repulsion is strong (which means high free carrier density together with small dielectric function). The Hamiltonian is simple to write down in full generality,

$$H = -\sum_{i,j} J_{ij}\hat{S}_i \cdot \hat{S}_j. \tag{4.72}$$

where J_{ij} is an **exchange interaction** and the $\hat{S}$ are spin operators[93]. The lattice can be chosen to have D dimensions and the sum over δ, which couples different lattice sites as in the tight binding model, can run over as many neighbors as one wishes. The Heisenberg model is again one of those models that does not have a solution in generality. Nevertheless, several solutions are known for particular versions of the model. Let's consider two simple examples to focus the discussion a bit. The first model is the Heisenberg model on a 1D chain with nearest neighbor spin interactions only. This simplifies the Heisenberg Hamiltonian to,

$$H_{1D} = -J\sum_i \hat{S}_i \cdot \hat{S}_{i+1}. \tag{4.73}$$

The second model we will consider is the **Ising model** in 1D on a chain. This model is a simplification of Eq. 4.73 where the x, y- components of the spin operator are ignored,

$$H = -J\sum_i \hat{S}_{z,i}\hat{S}_{z,i+1} \tag{4.74}$$

It is relatively straightforward to understand the solution of these two models when $J > 0$. The groundstate energy (or the expectation value of H_{1D}) will be minimized when all spins are pointing in the same direction (since the inner-product will be largest in that case). Since we are free to choose the spin direction for H_{1D}, we can have them all pointing along the z-direction. This shows you then that the groundstate energy of both the 1D Heisenberg and Ising models are the same ($E_g = -JNS^2$ to be precise). Since the energy is minimal when all spins are pointing in the same direction, both models have a ferromagnetic groundstate at zero temperature. It is also relatively straightforward to determine the **first excited state** in this case (see exercise 2). In the Ising case, the first excited state is exactly $2JS$ higher in energy[94]. Note that this is the energy cost associated with changing the spin on a given site by $S = 1$. The excited states of the 1D Heisenberg model are more interesting however. The difference between the groundstate and an excited state are indicated in Fig. 4.32. In the Ising model the spins cannot tilt in the x, y-direction and therefore it is necessary to flip the spin by one quantum on a given site. This means that it will always cost $2JS$, no matter where

---

[92] *For those interested: it requires a so-called Hubbard-Stratanovich transformation in which you define the spin-operators as exponentials of the basis states. By applying this transformation and solving for a set of coefficients, you can work out a transformed Hamiltonian such that it is diagonal. The diagonal elements then tell you the spectrum of this Hamiltonian.*

[93] *In the exercises you will refresh your memory of their properties.*

[94] *This is the energy cost of flipping a single spin. Since the interactions are identical along the chain it doesn't matter where you flip the spin (except if the chain is finite! Then it will cost less energy to flip a spin at the very end.). See exercise 2 for details.*

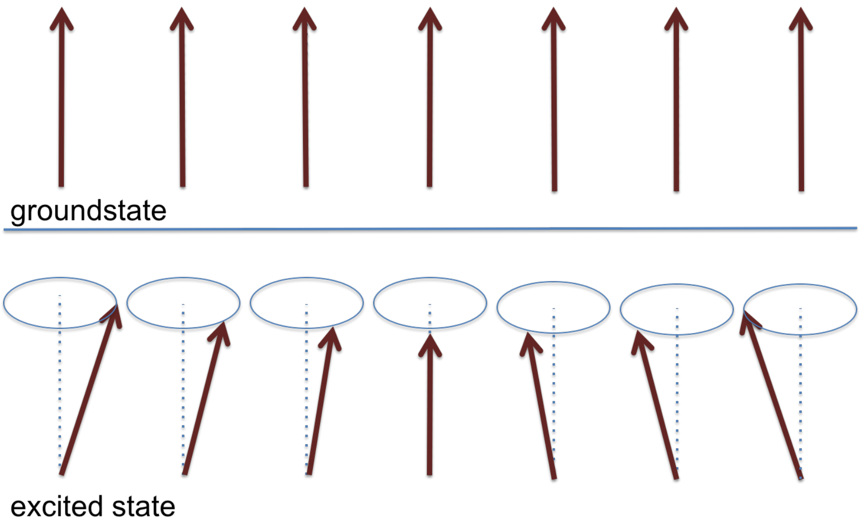


Figure 4.32: Top: snapshot of the groundstate for the case $J > 0$. Note that all spins are pointing up. Bottom: Snapshot (exaggerated) of an excited state. The spin on every site is slightly tilted away from the z-axis in a coherent fashion, such that the energy cost of flipping a spin is minimized.

you put the spin. In the Heisenberg model on the other hand, flipping a spin on a given site still costs the same, but we can now also choose to flip the spin 'halfway' towards the x-axis on one site and halfway on a neighboring site. The change in spin is still $S = 1$, but it will only be a fraction of the energy compared to the Ising model because the two spins that are half flipped can still have their spins parallel. Taking this idea a step further (again, see exercise 2) we can make a total spin-flip $S = 1$ also by tilting the spin on all sites ever so little away from the z-axis. This will then hardly cost any energy and one says that the spin-flip 'delocalizes': it is spread out over the entire chain. It turns out that a whole energy band of excitations is possible that can be characterized as having different frequencies (or better wavelengths). These solutions are called **spinwaves** or **magnons**. Their dispersion (Fig. 4.33) is given by,

$$E = -JNS^2 + 2JS\,[1 - \cos(ka)] \tag{4.75}$$

where a is the lattice spacing. There are some interesting analogies to make with how band electrons behave in solids. In the case of electrons (Chapter 1) we had particles in free space that turned into quasi-particles as a result of a periodic potential. We ended up with band electrons characterized by a momentum k. In the current case we start with spins that, as soon as a periodic interaction is switched on (lattice + exchange interaction), turn into spin waves. They can also be characterized by a similar quantum number k. In fact, even the dispersion of these quasi-particles is the same (a cosine band). There are also differences. First of all, the spin waves have $S = 1$ and are therefore *bosonic* quasi-particles. Moreover, there is not really a particle that we call 'spin' that carries a spin moment of $S = 1$. The spin waves are therefore more like the phonons: they are an emergent property of the solid. Since the spin waves are bosonic, they all condense into the $k = 0$ state at T=0. This has to be of course: the groundstate is the perfect ferromagnet and so at T=0 there can be no excited spin wave. In the next section we will see that the thermal occupation of spin waves results in fluctuations of the ferromagnetic order parameter (the magnetization M). These fluctuations increase with temperature until, at a critical temperature, the ferromagnetic state is completely destroyed and we are left with a paramagnet. In the subsequent sections we will derive the temperature dependence of the magnetization and see how the spin waves play their role in the ferromagnetic phase transition.

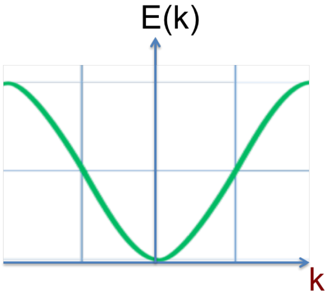


Figure 4.33: Dispersion relation obtained for the 1D Heisenberg model.

4.9 Magnetization as a function of temperature

In the previous section we have seen that the excited states of the Heisenberg model can be described by spin waves that follow Bose-Einstein statistics. This means that with increasing temperature more and more excited states will get occupied. Thermal fluctuations of the magnetic order translate to 'vibrations' of the spin moments, just like thermal fluctuations of the crystalline order translate to vibrations of the atomic positions. Let me stress this once more: spin waves and lattice vibrations are an emergent property that appears in a solid as a result of periodicity; the origin of spin waves and lattice vibrations is the same.

In a real solid at zero temperature there will be a certain magnetization per unit cell, corresponding to a number of times a spin-1/2 moment. These moments will all be aligned along a certain direction. Since the total magnetization of the solid is given by the sum over all unit cells, the total magnetization will be as large as possible at zero temperature. If we now turn on and slowly increase temperature, more and more spin waves will be excited according to the Bose-Einstein distribution. The number of spin waves with momentum k that is excited at a given temperature is given by,

$$\langle n_k \rangle = \frac{1}{e^{\epsilon/k_B T} - 1}. \tag{4.76}$$

where $\epsilon = \hbar\omega$ and k_B is Boltzmann's constant. Since each spin wave corresponds with an excited state that carries a certain moment, the total or average magnetization decreases with temperature. We can calculate the low temperature magnetization as follows.

At low temperature we can approximate the spin wave dispersion by expanding the cosine up to second order,

$$\hbar\omega = JSa^2k^2. \tag{4.77}$$

Now, we need to estimate the magnetization per unit cell. This is of course given by the expectation value of the local spin moment,

$$\langle m_i \rangle = -g\mu_B \langle \hat{S}_{i,z} \rangle \tag{4.78}$$

We can express this in terms of the occupation number of spin waves by realizing that the total spin S will be reduced by the average number of excited states per unit cell,

$$\langle m_i \rangle = -g\mu_B \big(S - \langle \hat{n}_i \rangle\big) \tag{4.79}$$

Note that the correct quantum number for a spin wave is its momentum k (and thus not its position). We therefore do not have an easy expression for $\langle \hat{n}_i \rangle$[95]. However, we do know the occupation number of spin waves with a given momentum k for a given temperature. Therefore, if we sum over all k-states and then divide by the number of unit cells N, we get the average density per unit cell[96],

$$\langle \hat{n}_i \rangle = \frac{1}{N} \sum_k \langle \hat{n}_k \rangle. \tag{4.80}$$

This sum can be converted to an integral as follows,

$$\sum_k \ldots \to \frac{V}{(2\pi)^3} \int_0^\infty 4\pi k^2 \ldots dk. \tag{4.81}$$

The integral is most easily performed by changing variables to energy, ϵ. To do this we make use of the approximate dispersion relation, Eq. 4.77, and its derivative[97],

$$\frac{d\omega}{dk} = 2JSa^2k \quad \text{and therefore} \quad dk = \frac{d\omega}{2JSa^2k}. \tag{4.82}$$

Substituting variables thus gives,

$$\begin{aligned}
\langle \hat{n}_i \rangle &= \frac{1}{N} \sum_k \langle \hat{n}_k \rangle \\
&= \frac{1}{N} \frac{V}{(2\pi)^3} \int_0^\infty 4\pi \frac{\omega}{JSa^2} \frac{d\omega}{2JSa^2k} \langle n_k \rangle \\
&= \frac{1}{N} \frac{V}{(2\pi)^3} \int_0^\infty 4\pi \frac{\omega}{JSa^2} \frac{d\omega}{2JSa^2} \sqrt{\frac{JSa^2}{\omega}} \langle n_k \rangle \\
&= \frac{V}{4\pi^2 N} \int_0^\infty \frac{\sqrt{\omega}}{JSa^2\sqrt{JSa^2}} \langle n_k \rangle d\omega,
\end{aligned} \tag{4.83}$$

Next we substitute the Bose-Einstein distribution and collect all factors. This gives,

$$= \frac{V}{4\pi^2 a^3 N} \frac{1}{(JS)^{3/2}} \int_0^\infty \frac{\sqrt{\omega}}{e^{\omega/k_B T} - 1} d\omega. \tag{4.84}$$

Now note that the volume V in the numerator of the pre-factor cancels with N times the volume of the unit cell (a^3). By making the substitution, $x = \omega/k_B T$[98] we find

$$\langle \hat{n}_i \rangle = \frac{1}{4\pi^2} \left(\frac{k_B T}{JS} \right)^{3/2} \int_0^\infty \frac{\sqrt{x}}{e^x - 1} dx \tag{4.85}$$

---

[95] *Indeed, the low momentum states are completely delocalized over the entire chain since* $\lambda \to \infty$ *for* $k \to 0$.

[96] *Note that we assume here a finite chain, while we started with the excited states of an infinite one. In general this will work out correctly if we take the limit of* $N \to \infty$ *at the end of the calculation. In this particular case, the final result will turn out not to depend on* N.

[97] *In what follows I will set* $\hbar = 1$. *The final result turns out not to depend on* $\hbar$, *so this is just a means to simplify the expressions along the way.*

[98] *Since* $x = \omega/k_B T$ *and therefore* $\omega = xk_B T$, *the relation between the infinitesimals* $d\omega$ *and* dx *is* $d\omega = k_B T dx$.

The last integral is a standard integral that evaluates to

$$\int_0^\infty \frac{\sqrt{x}}{e^x - 1} dx = \frac{1}{2}\sqrt{\pi}\left(\frac{3}{2}\right) \tag{4.86}$$

The zeta function can be looked up in a table and so we find,

$$\langle \hat{n}_i \rangle \approx 0.0586 \left(\frac{k_B T}{JS}\right)^{3/2}. \tag{4.87}$$

The total magnetization at low temperature is thus given by

$$M = \frac{N\langle m_i \rangle}{V} = -\frac{Ng\mu_B S}{V}\left(1 - \frac{\langle n_i \rangle}{S}\right), \tag{4.88}$$

The pre-factor is of course the magnetization at zero temperature and so we have,

$$M(T) = M(0)\left[1 - \frac{0.0586}{S}\left(\frac{k_B T}{JS}\right)^{3/2}\right]. \tag{4.89}$$

which is known as **Bloch's law**. In principle this expression already tells you that at sufficiently high temperature the magnetization will disappear. The critical temperature obtained from this expression is however incorrect: the approximation of the cosine dispersion is not valid at higher temperatures. It is hard to indicate exactly when this approximation breaks down. At intermediate temperatures there all kinds of detailed processes that we have ignored in our treatment. We can however make a more exact prediction of what happens near the phase transition. This will be the topic of the next section.

4.10 The ferromagnetic phase transition in the mean-field approximation

Close to the phase transition there will be strong fluctuations of the local magnetic moments due to thermal energy. Since at high temperature states with many different k's will be excited there will be fluctuations of the magnetization on all lengths scales. It is this regime that it makes some sense to apply the mean-field approximation. After all, viewed from a single unit cell there will be an effective magnetic field B that will be more or less static in time, which will average out to zero right at the phase transition itself.

We will follow the recipe of section 4.6. Our Heisenberg Hamiltonian is a product of two operators and so we find,

$$\hat{H} = -J \sum_{i,j} \hat{S}_i \cdot \hat{S}_j \tag{4.90}$$

$$\approx -J \sum_{i,j} \left[\hat{S}_i \cdot \langle \hat{S}_j \rangle + \langle \hat{S}_i \rangle \cdot \hat{S}_j + \langle \hat{S}_i \rangle \cdot \langle \hat{S}_j \rangle\right]. \tag{4.91}$$

Show that..

the Heisenberg Hamiltonian can be approximated in mean-field by Eq. 4.91

We ignore the last term as it gives only an offset to the final energy. Also note that the average value of the spin operator on site i is of course equivalent to the value of the spin operator on site j (at least for ferromagnetic interactions). We can therefore write,

$$\hat{H} \approx -2J \sum_{i,j} \hat{S}_i \cdot \langle \hat{S}_j \rangle. \tag{4.92}$$

It is at this point not difficult to also include a real applied magnetic field B. This adds a term $g\mu_B B$ to the Hamiltonian. Now note that the sum over j can be interpreted as an effective magnetic field acting on the spin at site i. In other words,

$$\hat{H} = -\sum_i \hat{S}_i \left[\sum_j 2J\langle \hat{S}_j \rangle - g\mu_B B\right]. \tag{4.93}$$

We can now interpret the term in brackets as a total effective field acting on the spin at site i by recasting the Hamiltonian in the following form[99],

$$\hat{H} = g\mu_B \sum_i \hat{S}_i \cdot B_{eff}. \tag{4.94}$$

where,

$$B_{\text{eff}} = -\left[\frac{2J}{g\mu_B}\sum_j \left\langle \hat{S}_j \right\rangle - B\right]. \tag{4.95}$$

[99] *Compare this with the Hamiltonian in paragraph 3.6.*

We can also express the average spin moment in terms of the magnetization per unit cell,

$$B_{\text{eff}} = B + J\sum_j \frac{2\langle \hat{m}_j \rangle}{(g\mu_B)^2}. \tag{4.96}$$

so that the Hamiltonian is a function of the magnetization. At the same time, the magnetization is determined by the free energy (see chapter 3),

$$\langle m_i \rangle = -\frac{\partial F}{\partial B_{\text{eff}}}. \tag{4.97}$$

We'll first need to calculate the free energy,

$$F = -k_B T \ln\left(\sum_m e^{-\frac{E_m}{k_B T}}\right) \tag{4.98}$$

where the energy eigenvalues are the standard Zeeman energy levels,

$$E_m = g\mu_B B_{eff} m_s \tag{4.99}$$

where $m_s = -S...S$ is the magnetic quantum number[100]. If we consider small fields or high temperature, the exponential in Eq. 4.98 can be expanded as[101],

$$e^{-\beta E_m} = 1 - \beta E_m + \frac{1}{2}\beta^2 E_m^2 - \ldots, \tag{4.100}$$

To calculate the free energy we need to sum over all $2S+1$ energy eigenvalues. Note that since the quantum number m_s runs from $-S$ to $+S$ all odd powers of the energy eigenvalues sum to zero. We therefore have up to second order,

$$\sum_m 1 + \frac{1}{2}\beta^2 E_m^2 = (2S+1) + (2S+1)\frac{1}{2}\left(\beta g\mu_B B_{eff}\right)^2 \frac{1}{3}S(S+1) \tag{4.101}$$

where I have used the fact that $S_z^2 = \vec{S}^2/3$. The free energy is thus,

$$\begin{aligned} F &\approx -k_B T \ln\left((2S+1)(1 + \frac{1}{6}\left(\beta g\mu_B B_{eff}\right)^2 S(S+1)\right) \\ &= -k_B T \ln(2S+1) - k_B T \ln\left(1 + \frac{1}{6}\left(\beta g\mu_B B_{eff}\right)^2 S(S+1)\right) \end{aligned} \tag{4.102}$$

From which the magnetization follows using Eq. 4.97,

$$\langle m_i \rangle = k_B T \frac{\frac{1}{3}(g\mu_B\beta)^2 B_{\text{eff}} S(S+1)}{1 + \frac{1}{6}(g\mu_B\beta B_{\text{eff}})^2 S(S+1)}. \tag{4.103}$$

We can ignore the term in the denominator proportional to B_{eff}^2 (since we are working in the small field limit). Therefore,

$$\langle m_i \rangle = k_B T \frac{1}{3}(g\mu_B\beta)^2 B_{\text{eff}} S(S+1). \tag{4.104}$$

If we now define $p' \equiv g\sqrt{S(S+1)}$ we have,

$$\langle m_i \rangle = \frac{(p'\mu_B)^2 B_{\text{eff}}}{3k_B T}. \tag{4.105}$$

This apparently simple result is exactly the inverse temperature Curie-Weiss law that we obtained in section 3.6. Apparently, because in the current case we have an *effective* magnetic field, rather than an applied magnetic field and the effective field still depends on the magnetization. Remember: the last step in any mean-field approximation is to solve for the 'mean-field' (in this case the magnetization) self-consistently. In the case at hand it brings us to the ferromagnetic phase transition. Let's combine Eq. 4.96 with Eq. 4.105:

$$\langle m_i \rangle = \frac{(p'\mu_B)^2}{3k_B T}\left[B + \frac{2}{(g\mu_B)^2}\sum_j \langle m_j \rangle J\right] \tag{4.106}$$

Now we note that in a ferromagnet, translational invariance requires that $\langle m_j \rangle = \langle m_i \rangle$,

$$\langle m_i \rangle = \frac{(p'\mu_B)^2 B}{3k_B T} + \frac{2(p'\mu_B)^2\langle \hat{m}_i \rangle}{3k_B T(g\mu_B)^2}\sum_j J. \tag{4.107}$$

[100] *This follows exactly the derivation of the Zeeman energy, except that in this case we are working with an effective field that includes neighboring spins.*

[101] $\beta \equiv (k_B T)^{-1}$.

This is the general result. The question now arises if we can find a solution where $\langle m_i \rangle \neq 0$. This is most easily seen by setting $B = 0$ in which case our expression simplifies to,

$$\begin{aligned}\langle \hat{m}_i \rangle &= \frac{2(p'\mu_B)^2 \langle \hat{m}_i \rangle}{3k_B T (g\mu_B)^2} \sum_j J \\ &= \frac{2S(S+1)\langle \hat{m}_i \rangle}{3k_B T} \sum_j J \qquad (4.108)\end{aligned}$$

We thus have to satisfy the following condition,

$$\langle \hat{m}_i \rangle \left(1 - \frac{2S(S+1)}{3k_B T} \sum_j J \right) = 0. \qquad (4.109)$$

There are now two options (i) $\langle m_i \rangle = 0$ in which case only the paramagnetic term survives (i.e. no ferromagnetism) and (ii),

$$\frac{2S(S+1)}{3k_B T} \sum_j J = 1 \qquad (4.110)$$

In which case it will be possible to have a finite magnetization in the absence of a magnetic field and still satisfy the self-consistency condition. The critical temperature where this condition is satisfied is called the **Curie temperature** and it is defined as,

$$T_C = \frac{2S(S+1)}{3k_B} \sum_j J, \qquad (4.111)$$

This self-consistency still holds in the presence of a finite magnetic field. Looking back to Eq. 4.107 we have,

$$\langle \hat{m}_i \rangle \left(1 - \frac{2S(S+1)}{3k_B T} \sum_j J \right) = \frac{(p'\mu_B)^2 \vec{B}}{3k_B T}. \qquad (4.112)$$

where we now recognize our expression for the Curie temperature on the lefthand-side. We can thus simplify this to,

$$\langle m_i \rangle \left(1 - \frac{T_C}{T} \right) = \frac{(p'\mu_B)^2 \vec{B}}{3k_B T} \qquad (4.113)$$

which after rearranging finally gives us the following expression for the total magnetization,

$$\vec{M} = \frac{N\langle m_i \rangle}{V} = \frac{np'^2 \mu_B^2 \vec{B}}{3k_B (T - T_C)}, \qquad (4.114)$$

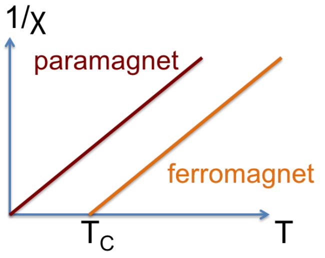


Figure 4.34: Comparison of the inverse magnetic susceptibility for a material with and without ferromagnetic transition. In the former case the susceptibility has a finite temperature intercept where $\chi^{-1} = 0$ (i.e. where the susceptibility diverges.)

The susceptibility that follows from this is sketched in Fig. 4.34. Also shown for comparison is the result that we obtained in Chapter 3 for the paramagnet. Since the susceptibility diverges for both the paramagnet and the ferromagnet, it is customary to plot χ^{-1} instead[102]. The result we obtained is valid for $T \geq T_C$. To obtain the result just below T_C, we need to calculate the sum in Eq. 4.98 exactly. This can be done by realizing that the exponential is essentially a geometrical series. Writing out the expansion we find,

$$\begin{aligned}\sum_m e^{-\beta E_m} = \sum_m e^{-\beta g \mu_B B_{\text{eff}} m_s} &= \sum_m e^{-c m_s} \qquad (4.115) \\ &= e^{-c(-S)} + \cdots + e^{-c(S)}. \qquad (4.116)\end{aligned}$$

where we have defined $c \equiv g\mu_B \beta B_{\text{eff}}$. We can perform the sum by rewriting the last line as,

$$\sum_m e^{-\beta E_m} = e^{-cS} \left[1 + \cdots + e^{c2S} \right], \qquad (4.117)$$

The terms in brackets form a geometrical series[103] that can be summed,

$$\sum_i e^{-\beta E_i} = e^{-cS} \frac{1 - e^{c(2S+1)}}{1 - e^c} = \frac{e^{-c(S+\frac{1}{2})} - e^{c(S+\frac{1}{2})}}{e^{-c/2} - e^{c/2}}, \qquad (4.118)$$

where in the last expression we've multiplied both the numerator as well as the denominator with $e^{-c/2}$. We can now calculate the free energy as

$$F = -\frac{1}{\beta} \ln \left(\frac{\sinh \left[c \left(S + 1/2 \right) \right]}{\sinh \left(c/2 \right)} \right) \qquad (4.119)$$

[102] *It is not possible to measure the divergence in an experimental setting. By plotting chi*$^{-1}$ *one can extrapolate the measured data set. If it extrapolates to zero at finite temperature the material is a ferromagnet.*

[103] $$\sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}.$$

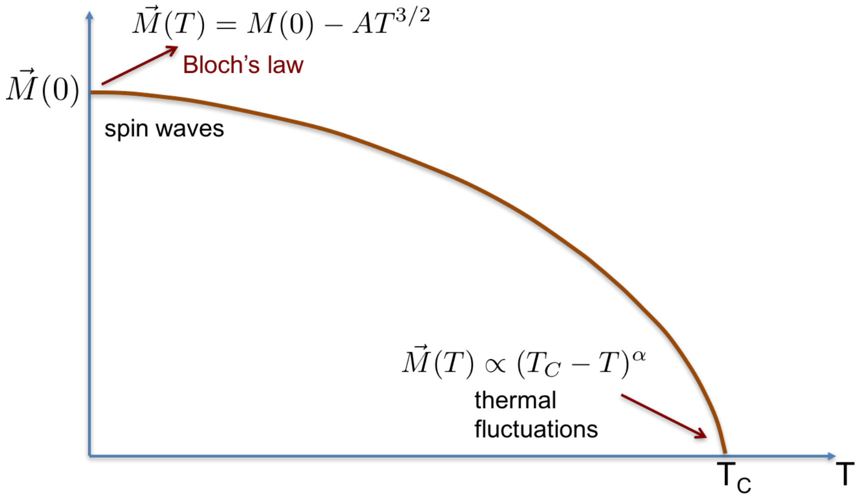


Figure 4.35: Phase diagram of the Heisenberg ferromagnet. Indicated are the low and high temperature regime of the temperature dependent magnetization.

From the free energy, we can calculate a magnetization by taking the derivative,

$$\langle m_i \rangle = -g\mu_B \left\{ \left(S+\frac{1}{2}\right) \coth\left[c\left(S+\frac{1}{2}\right)\right] - \frac{1}{2}\coth\left(\frac{c}{2}\right) \right\} \tag{4.120}$$

This is the exact result so far, but again we have the magnetization appearing both on the left- and right-hand side. We can numerically solve for the magnetization from this. Close to (but still below) the Curie temperature we can expand $\coth(x) = x^{-1} + x/3 - x^3/45 + \ldots$ and solve for the magnetization. The resulting expression (for $B = 0$) for the average magnetization can be written in the form,

$$\langle m_i \rangle = \frac{1}{A}\left(\frac{T_C}{T} - 1\right)^{1/2}, \tag{4.121}$$

where,

$$A^{-1} = \sqrt{\frac{5}{3}} \frac{S(S+1)}{\sqrt{S^2+S+1/2}} g\mu_B \left(\frac{T}{T_C}\right)^{3/2} \tag{4.122}$$

We now define a reduced temperature as,

$$t \equiv \frac{T - T_C}{T_C} \tag{4.123}$$

which gives,

$$\frac{T}{T_C} = 1 + t \tag{4.124}$$

or equivalently,

$$\frac{T_C}{T} = \frac{1}{1+t} \tag{4.125}$$

With some algebra it is now easy to show that the magnetization can be written as (with B some pre-factor),

$$\langle m_i \rangle^2 = B\,(t+1)^2 - (t+1)^3 \tag{4.126}$$

Show that..

Eq. 4.126 follows from Eq. 4.121. Use this to find the leading order behavior of the magnetization.

From this we find that the **leading order** behavior of the magnetization for t close to zero (i.e. for $T \leq T_C$) is,

$$\langle m_i \rangle \simeq B|t|^{1/2} \tag{4.127}$$

It is equally possible to derive the susceptibility from Eq. 4.120 along similar lines. In this case you have to take the derivative with respect to the magnetic field before expanding the coth functions. The result is (also for $T \leq T_C$),

$$\chi \simeq C|t|^{-1} \tag{4.128}$$

The crucial result is of course that the magnetization is finite below the critical temperature, indicating that we have indeed found ferromagnetism. The next section summarizes these results.

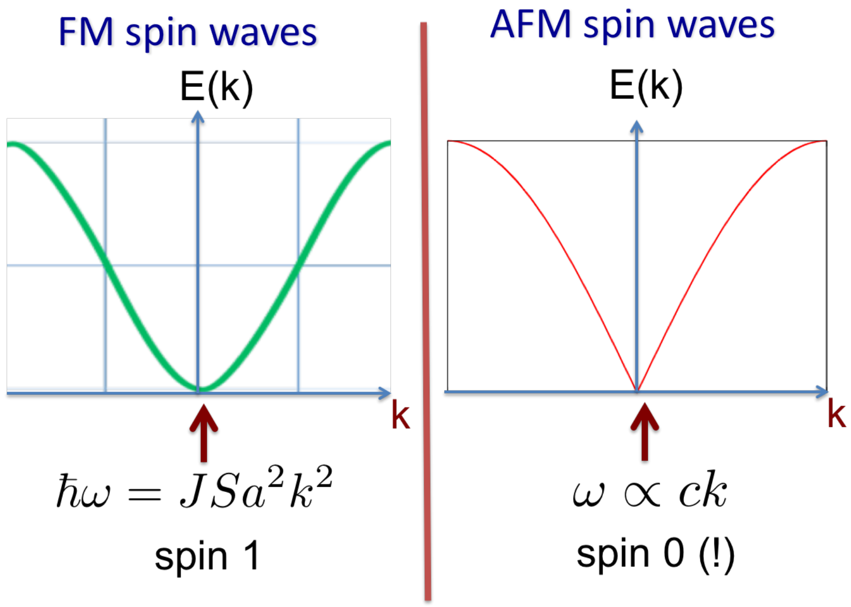


Figure 4.36: Comparison of the spin wave dispersion of a ferromagnet and an anti-ferromagnet. Note the different behavior of the spin-waves for $k \to 0$.

4.11 Summary of the ferromagnetic groundstate

We can now combine the results obtained in the preceding sections into a temperature phase diagram for the ferromagnet. In the exercises you have shown that the Heisenberg model allows a ferromagnetic groundstate at zero temperature for $J > 0$. You also showed that the Heisenberg model had excited states that can be characterized as bosonic quasi-particles called spin-waves. At zero temperature the spin-waves condense into the $k = 0$ state and the system is fully polarized. In real materials[104] there will be a zero temperature magnetization $\vec{M}(0)$. If we now turn on thermal fluctuations (e.g. at finite temperature) spin waves will be excited and these will start to reduce the magnetization. This gives rise at very low temperature to a Bloch law behavior of the magnetization (i.e. $M(T) \simeq -AT^{3/2}$). As temperature increases more and more spin waves are excited and the average magnetization per unit cell will start to strongly fluctuate. At some temperature the fluctuations are so strong that the magnetization averages to zero. The magnetization just below this critical temperature follows a power law behavior and right above this critical temperature the magnetization (in the absence of an applied magnetic field) will be zero. The susceptibility at the critical temperature diverges right at the critical temperature. This is the 'classical' behavior of a phase transition: right at the transition a response function diverges, indicating that the system is in a meta-stable state.

We summarize this in Fig. 4.35. Note that for temperatures in between the low temperature limit and the critical temperature we have no simple expression. As a final note to conclude our discussion of the ferromagnetic state I would like to point out that the **critical exponents**[105] that we obtained in mean field theory are actually not correct. An analysis of the Heisenberg model (using the exact 'Bethe ansatz' approach) shows that the actual critical exponents are,

$$\langle m_i \rangle \simeq B|t|^{1/3} \tag{4.129}$$

and,

$$\chi \simeq C|t|^{-4/3} \tag{4.130}$$

These exponents can indeed be confirmed by experiment. This concludes what we will discuss in this course. There are several interesting facts/features of the ferromagnetic state that you can read about in textbooks. An interesting example is the occurrence of domain walls in real ferromagnets. The idea behind their appearance is simple (i.e. it reduces the total energy), but their theoretical description and effect on observables is surprisingly rich (featuring links to the mathematics of topology, solitons etc.).

4.12 Anti-ferromagnetism

So what about anti-ferromagnetism? Unfortunately, a more quantitative picture of the anti-ferromagnetic state is a bit more complex. You have discovered some

[104] *e.g. where the Heisenberg model really is just an approximation that focusses on the behavior of the magnetization. Real materials are a bit more complicated.*

[105] *The critical exponent α of a phase transition is defined as $X \simeq t^{\alpha}$ where X is an observable or a response function and t is the reduced temperature.*

of the difficulty in the last exercise. The anti-ferromagnet is however a lot more interesting from a theoretical physics point of view. The anti-ferromagnetic state in fact corresponds to a highly entangled, correlated state. There is an important difference between the ferromagnet and the anti-ferromagnet. This difference becomes visible by plotting the spectrum of excited states (see Fig. 4.36). The leading order term of the spin-wave dispersion in the case of an anti-ferromagnet is *not* quadratic, but linear!. That doesn't sound spectacular at first, but it makes a crucial difference. For example, the spin waves of the ferromagnet are *massive* while the anti-ferromagnetic variant is *massless*. The anti-ferromagnetic spin waves also carry a different spin (s=0, rather than spin 1). The origin of these differences lies in the fact that the anti-ferromagnetic state is a **spontaneously broken symmetry** state. The details of this go too far to discuss here. For now you'll have to take it for granted that the Hubbard Hamiltonian can be shown to be invariant under global rotational symmetry. It is not hard to visualize that the ferromagnet still obeys global rotational symmetry (i.e. when you rotate the total magnetization nothing really changes). For the anti-ferromagnet on the other hand you cannot rotate all spins in the same direction simultaneously without increasing the total energy. Because I would like to discuss the superconducting state in some detail as well and because this also represents a spontaneously broken symmetry state I will leave the discussion of the anti-ferromagnet for another time.

Exercises IV

Spin problems

The content of this set of exercises has again not been discussed during class. Due to a missed lecture hour, we are a bit behind on the planned schedule. The exercise is a bit different from what I had in mind, but the details will be discussed in class.

Spin operators

1

We recall the basic spin operator relations[106]. The spin operators commute:

$$\begin{aligned}\left[\hat{S}_x, \hat{S}_y\right] &= i\hat{S}_z \\ \left[\hat{S}^2, \hat{S}_a\right] &= 0\end{aligned} \tag{E4.1}$$

where $a = x, y, z$. Remember that you can cyclically permute the x, y and z labels. We will be looking at lattices where spins are bound to a single site i. The commutation relation between spin components on different sites i, j is:

$$\left[\hat{S}_{x,i}, \hat{S}_{y,j}\right] = i\delta_{ij}\hat{S}_{z,i}. \tag{E4.2}$$

In other words: operators on different lattice sites commute with each other. Recall also that:

$$\begin{aligned}\hat{S}_z|s, m_s\rangle &= m_s|S, m_s\rangle \\ \hat{S}^2|s, m_s\rangle &= S(S+1)|S, m_s\rangle.\end{aligned} \tag{E4.3}$$

where $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$. We will use the shorthand notation $|s, m_s\rangle = |S_z\rangle$, with $\hat{S}_z|S_z\rangle = S_z|S_z\rangle$. We will also need the **spin-ladder operators**:

$$\hat{S}_{\pm,i} \equiv \hat{S}_{x,i} \pm i\hat{S}_{y,i}, \tag{E4.4}$$

which obey the commutation relations

$$\begin{aligned}\left[\hat{S}_{+,i}, \hat{S}_{-,j}\right] &= 2\delta_{ij}\hat{S}_{z,i} \\ \left[\hat{S}_{z,i}, \hat{S}_{\pm,j}\right] &= \pm\delta_{ij}\hat{S}_{\pm,j}.\end{aligned} \tag{E4.5}$$

The spin ladder operators act on a spinstate $|s_z, i\rangle$ in the following way:

$$\begin{aligned}\hat{S}_{+,i}|s_z\rangle &= \alpha|S_{z,i}+1\rangle \\ \hat{S}_{-,i}|s_z\rangle &= \beta|S_{z,i}-1\rangle.\end{aligned} \tag{E4.6}$$

The coefficients can be determined (by you) as follows.

A First find expressions for the products $\hat{S}_+\hat{S}_-$ and $\hat{S}_-\hat{S}_+$ in terms of $\hat{S}^2$ and $\hat{S}_z$. Hint: First use equation E4.4 and then use the definition of $\hat{S}^2$.

B Show that $\langle S_z|\hat{S}_-\hat{S}_+|S_z\rangle = |\alpha|^2$ and $\langle S_z|\hat{S}_+\hat{S}_-|S_z\rangle = |\beta|^2$. Hint: Remember that the hermitian conjugate $\left(A|\psi\rangle\right)^\dagger = \langle\psi|A^\dagger$ and carefully look at equation E4.4.

C Combine the results of exercise 1a and 1b with the equations from E4.3 to find the coefficients of $\hat{S}_-$ and $\hat{S}_+$:

$$\hat{S}_{i,\pm}|S_z\rangle = \sqrt{S(S+1) - S_z(S_z \pm 1)}|S_{z,i} \pm 1\rangle. \tag{E4.7}$$

Note that this expression can be recast as

$$\hat{S}_{i,\pm}|S_z\rangle = \sqrt{(S \mp S_z)(S + 1 \pm S_z)}|S_{z,i} \pm 1\rangle. \tag{E4.8}$$

D Finally show that the product $\hat{S}_i \cdot \hat{S}_j$ can be written as:

$$\hat{S}_i \cdot \hat{S}_j = \hat{S}_{z,i}\hat{S}_{z,j} + \frac{1}{2}\left(\hat{S}_{+,i}\hat{S}_{-,j} + \hat{S}_{-,i}\hat{S}_{+,j}\right). \tag{E4.9}$$

The Heisenberg spin model: the quantum case

---

[106] *In the following, we set $\hbar = 1$.*

2

The ‘simplest’ model describing interactions between electron spins is the Heisenberg model:

$$H = -\sum_{i=1}^{N}\sum_{j=1}^{N} J_{ij}\hat{S}_i \cdot \hat{S}_j. \tag{E4.10}$$

This turns out to be quite complicated. For periodic systems, the above expression can be rewritten as:

$$H = -\sum_{i \neq j} J_{ij}\hat{S}_i \cdot \hat{S}_j. \tag{E4.11}$$

There is no general solution: it all depends on what we choose for J_{ij} and the dimensionality of the lattice. This should at this point remind you of the tight binding model: there we had a number of orbitals per lattice site (atom) which ‘coupled’ together through overlap integrals. As you have seen in previous exercises, the solution depends on the number of orbitals per unit cell you include (here J_{ij}) and the dimensionality of the lattice. In this problem we will consider a linear, one-dimensional chain of spins with nearest neighbor couplings only where $J_{ij} = \delta_{i,j+1}J$[107]. This reduces the problem to[108]:

$$H = -J\sum_{i=1}^{N} \hat{S}_i \cdot \hat{S}_{i+1}. \tag{E4.12}$$

An even simpler spin model (in fact the simplest) is the nearest neighbor Ising model:

$$H = -J\sum_{i=1}^{N} \hat{S}_{z,i}\hat{S}_{z,i+1}. \tag{E4.13}$$

For our choice $J > 0$ it is ‘obvious’ that the groundstate[109] of the system will be ferromagnetically ordered (all spins pointing in the same direction). We will ‘prove’ this statement for the Ising model first.

A Find the energy E_G of the ferromagnetically ordered state. Hint: You can get the energy by acting with the Hamiltonian E4.13 on this state.

$$|G\rangle = |S_{1,z} = S, S_{2,z} = S, \ldots, S_{N,z} = S\rangle. \tag{E4.14}$$

B We choose the values of S to be positive. Show that the energy of the state:

$$|m\rangle = \frac{\hat{S}_{m,-}|G\rangle}{\sqrt{2S}} \tag{E4.15}$$

is $E_m = E_G + 2JS$. You can also show (but you don’t have to) that $\hat{S}_{m,+}|G\rangle = 0$. Hint: first prove the relation

$$\hat{S}_{z,i}\hat{S}_{z,j}|m\rangle = \left(S - \delta_{i,m}\right)\left(S - \delta_{j,m}\right)|m\rangle. \tag{E4.16}$$

We started out with all spins pointing up (total $S_{z,i} = S$) and have now found that the first excited state ($|m\rangle$ has all spins pointing up, except at site m, where $S_{z,m} = S - 1$) has a higher energy than that state. Hence, $|G\rangle$ is the groundstate. In general $S = n/2$ with n an integer. For the special case of spin 1/2 systems, the $S_\pm$ operators are called spin flip operators. We now turn to the Heisenberg chain, equation E4.12.

C First prove the relations:

$$\begin{aligned} \hat{S}_{-,i}\hat{S}_{+,j}|m\rangle &= 2S\delta_{j,m}|i\rangle \\ \hat{S}_{+,i}\hat{S}_{-,j}|m\rangle &= 2S\delta_{i,m}|j\rangle + 2\delta_{i,j}\left(S - \delta_{m,i}\right)|m\rangle. \end{aligned} \tag{E4.17}$$

D The next step is to show that equation E4.12 is equal to:

$$H = -J\sum_{i=1}^{N} \hat{S}_i \cdot \hat{S}_{i+1} = -J\sum_{i=1}^{N}\left[\hat{S}_{z,i}\hat{S}_{z,i+1} + \frac{1}{2}\left(\hat{S}_{+,i}\hat{S}_{-,i+1} + \hat{S}_{-,i}\hat{S}_{+,i+1}\right)\right]. \tag{E4.18}$$

Hint: This is trivial given exercise 1d.

E We now calculate the groundstate energy E_G of the Heisenberg model. This is done in exactly the same way as problem 2a. Assume again that $|G\rangle = |S_{1,z} = S, S_{2,z} = S, \ldots, S_{N,z} = S\rangle$.

---

[107] *With $J > 0$.*

[108] *This is assuming periodic boundary conditions, or in other words: the chain is closed on itself.*

[109] *At zero temperature.*

$\mathcal{F}$ We can start putting things together. Just like in the Ising case we now consider the first excited state, Eq. (19). Show that:

$$H|m>= E_G|m> +2JS|m> -JS(|m+1> +|m-1>) \tag{E4.19}$$

Hint: First write down an expression for each individual term of the Hamiltonian acting on $|m>$ using Eq. 20, 21 and 22.

We have a small problem. If you compare the result of Exc. 2b and Exc. 2f you see that in the former case we had:

$$H|m>= E_m|m> \tag{E4.20}$$

while now we have:

$$H|m>= E_m|m> -JS(|m+1> +|m-1>) \tag{E4.21}$$

The state $|m>$ is no longer an eigenstate of the Hamiltonian! The problem is however not hard to solve using the tools developed in the first part of the course. If you forget for a moment that we are dealing with spins, Eq. E4.21 has the form of a nearest neighbor tight binding model. The energy (E_m) of the 'orbital' at site m is modified by the 'overlap' with orbitals on sites $m \pm 1$ where the overlap integral is replaced by JS. To find the correct excited states of the Heisenberg chain we should take the periodicity of the lattice into account: Bloch's theorem.

$\mathcal{G}$ Use Bloch's theorem to find the eigenenergies of the excited states of the Heisenberg chain. Hint: Bloch's theorem states that

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_m e^{i\vec{k}\cdot\vec{R}_m} |m\rangle \tag{E4.22}$$

Use this to compute $\langle k|H|k\rangle$.

$\mathcal{H}$ Bonus: can you explain where the difference between the Ising chain and the Heisenberg chain comes from and what it means physically? Hint: it might make it easier to understand the difference by plotting the band structure for both cases in one graph.

3 The Heisenberg spin model: classical case.

Last time we looked at the simplest spin model: the Heisenberg model. If we change the index from i to p[110], the Hamiltonian reads

$$H = -J \sum_{p=1}^{N} \hat{S}_p \cdot \hat{S}_{p+1} \tag{E4.23}$$

or equivalently

$$H = -J \sum_{p=1}^{N} \left[\hat{S}_{z,p}\hat{S}_{z,p+1} + \frac{1}{2}\left(\hat{S}_{+,p}\hat{S}_{-,p+1} + \hat{S}_{-,p}\hat{S}_{+,p+1} \right) \right]. \tag{E4.24}$$

We found the groundstate energy for $J > 0$ and the excitation spectrum. Today we investigate the case where $J < 0$.

$\mathcal{A}$ For $J < 0$, we expect the anti-ferromagnetic state to be the groundstate. This state can be written as

$$|G\rangle = |\uparrow, \downarrow, \uparrow, \ldots, \downarrow\rangle = |S_{1,z} = S, S_{2,z} = -S, \ldots, S_{N,z} = -S\rangle \tag{E4.25}$$

or

$$|G\rangle = |S_z = S, p \in A\rangle |S_z = -S, p \in B\rangle. \tag{E4.26}$$

Show that this state is *not* an eigenstate of the Heisenberg Hamiltonian.

This is in fact a problem. What happens here is that the groundstate 'spontaneously' breaks the spin-rotational symmetry of the original Hamiltonian. It is also quite spectacular: we have a model with one tuning knob, J, which is easy to solve on one hand ($J > 0$) and completely unsolvable on the other hand ($J < 0$). In one dimension, there actually is a solution, known as the Bethe ansatz solution, but that is beyond the scope of this course. For higher dimensions no solution is known. There must be one: anti-ferromagnets are frequently observed in nature. The fact that this state breaks a continuous symmetry has an interesting consequence for the excitation spectrum. This is the subject of this exercise.

---

[110] *At one point I got stuck with the index i, which lead to expressions of* $\sqrt{-1}$.

Approximate solutions are possible, but they are hard to obtain (and definitely not without the use of second quantized operators). Interestingly, it is possible to calculate the spin dispersions using a classical model for the spin system. As discussed in the lecture, magnetism is a purely quantum phenomenon so you might wonder why this would work. To convince you that it *could* work, we will first calculate the spin waves of the ferromagnet again. This is a warming up for the anti-ferromagnetic case, which is exactly twice as complicated, but follows the same path.

B We start with the Hamiltonian from equation E4.23 with $J > 0$ (the ferromagnet). We will treat the operators as classical vectors $\vec{S}$ of length S. In this case, $\vec{S}_p \cdot \vec{S}_{p+1} = S^2$. Show that then, you can write the term with index p:

$$-\vec{\mu}_p \cdot \vec{B}_{\text{eff},p} \tag{E4.27}$$

where $\mu_p = -g\mu_B \vec{S}_p$. Hint: Since we are dealing with classical objects, you don't have to worry about commutation relations.

C In classical mechanics, Newton's equations state that the angular momentum will change if a torque acts on it:

$$\frac{\partial \vec{L}}{\partial t} = \vec{\tau}. \tag{E4.28}$$

For a magnetic moment, the torque is equal to $\vec{\tau} = \vec{\mu} \times \vec{B}$. Use this to derive the equations of motion for the individual spin components (S^x, S^y and S^z). Hint: The angular momentum associated with a classical spin is $\hbar\vec{S}$. Consider the motion of the spin at site p in the effective B-field only.

D If everything went right, you should now have equations that link the rate of change of $\vec{S}_p$ to products of the type $S^x_p S^z_{p+1}$. The resulting set is nonlinear and not easy to solve. We make the following approximation: we assume that the amplitude of the excitation is small, compared to the total spin. Linearize the equations of motion by setting $S^z_p = S$ and neglecting terms that are the product of S^x and S^y. You should now have:

$$\begin{aligned} \frac{\partial S^x_p}{\partial t} &= \frac{JS}{\hbar}\left(2S^y_p - S^y_{p-1} - S^y_{p+1}\right) \\ \frac{\partial S^y_p}{\partial t} &= -\frac{JS}{\hbar}\left(2S^x_p - S^x_{p-1} - S^x_{p+1}\right) \\ \frac{\partial S^z_p}{\partial t} &= 0. \end{aligned} \tag{E4.29}$$

E As usual, we look for traveling wave solutions:

$$\begin{aligned} S^x_p &= Ae^{i(pka-\omega t)} \\ S^y_p &= Be^{i(pka-\omega t)}. \end{aligned} \tag{E4.30}$$

Using this ansatz, solve the equations of motion and find the spin wave dispersion.

MAGNONS OF THE ANTI-FERROMAGNET

Now that we have warmed up to the classical equations of motion, we can consider the anti-ferromagnetic case. The calculation is identical, except for the fact that we now have a bipartite lattice.

A We will need to include more terms from the Hamiltonian of exercise 3. The calculation is easiest if we assign spin up to spins on positions $2p$ (the even sites) and spin down to positions $2p+1$. This means that you will now have to write down the equations of motion for both S_{2p} and S_{2p+1}. Show that doing this leads to four equations similar to those obtained in exercise 1d. You can make the same approximation as was used before.

B Solving this set of four equations requires an extra step. Show that the four equations can be reduced to two equations by forming the equations of motion for $S^+ = S^x + iS^y$.

C Find the dispersion relation for the anti-ferromagnetic magnons using a similar ansatz as in exercise 3e.

D Can you comment on the difference between the ferromagnetic and anti-ferromagnetic dispersions? Discuss the qualitative difference between the two for small momentum and compare the small momentum dispersions to other dispersions we have encountered during the course (for example nearly free electrons or photons).

SUPERCONDUCTIVITY

A tale of a love triangle: two electrons and one phonon.

5.1 A new state of matter: a brief history

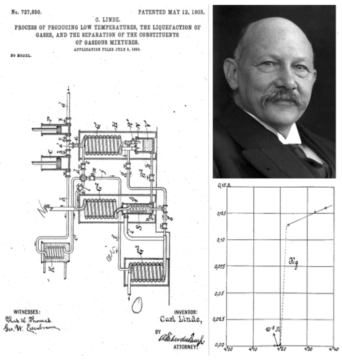


Figure 5.37: Left: Original schematic submitted by Carl Linde to the US patent office (source: https://commons.wikimedia.org). Top right: H.K. Onnes in 1913. Picture taken after receiving the Nobel prize in physics. Bottom right: original sketch with data points indicating the disappearance of resistivity.

The last chapter ends very appropriately with a Dutch discovery. Around the turn of the 20th century (July 10th, 1908 to be precise) Heike Kamerlingh Onnes was able to turn a small amount of Helium into liquid. This was a phenomenal result that many had strived to achieve (James Dewar was his fiercest competitor). Helium was in fact the last gas to be turned into liquid. To achieve this Onnes used an ingenious series of cooling stages (Fig. 5.37) comprising expansion and compression vessels. This technique, called liquefaction, allowed him to routinely create a cryogenic liquid and for a while he had the coldest place (4.2 K to be precise) on earth in his laboratory. With the machinery to refrigerate stuff in place he turned to fundamental studies of the resistivity of metals at extreme low temperatures. Earlier experiments had led him to the idea that as one approached absolute zero temperature, metals would turn into perfect conductors. Lord Kelvin, James Dewar and others however predicted (correctly) that impurities would always lead to a finite resistivity even at zero temperature. Having access to the lowest possible temperatures, Onnes started by measuring the resistivity of silver and gold. He soon realized that to study the resistivity he needed to purify these metals: there were too many impurities (thus proving Dewar right). From his work on liquefaction, Onnes had obtained the recipe to purify mercury. And so it was that on April 8, 1911 Gilles Holst (Onnes' assistant) and Kamerlingh Onnes cooled mercury to the lowest possible temperature they could achieve. Have a look at the original data plot in fig. 5.37. Onnes owes his Nobel prize to the fortuitous fact that (i) he could purify mercury and (ii) that for Helium to be kept in its liquid state a bit longer, he had found out that it helped to slightly reduce the pressure above it. The latter fact meant that he was able to reach 4.18 K (instead of the boiling point of helium which is 4.25 K), while the former meant that he had pure enough mercury such that the critical temperature was maximal (T_c=4.2 K). As happens so often the stars lined up on the evening of April 8th and superconductivity was (barely) discovered[111].

Superconductivity became the 'enigma' of solid state physics in the 20th century. Many famous physicists (Einstein included) tried to construct a theoretical model to describe the superconducting state and failed. As we will discuss in this chapter, superconductivity is a purely quantum phenomenon. It is impossible to understand from a classical point of view. In the end several crucial experiments led to the first working theory. First, Kamerlingh-Onnes discovered in 1912 that a current flowing through a superconductor did not diminish with time. In 1933, Meissner and Ochsenfeld discovered that the magnetic field inside a superconductor was exactly zero. Another 'smoking gun' experiment was the discovery of the isotope effect (1950-1953)[112]. In an isotope effect experiment one takes a naturally occurring elemental superconductor (e.g. Hg, Pb, Nb etc) and determines its critical temperature. Then the element is replaced by its isotope as much as possible ($Hg^{200} \rightarrow Hg^{198}$) and the critical temperature is determined again. For elemental superconductors it was found that the critical temperature depends on the mass of the element involved as,

$$T_c \propto \frac{1}{M^{1/2}}. \qquad (5.1)$$

A little later Bardeen, Cooper and Schrieffer published their seminal work (1957). We will discuss their achievements in more detail below, but it pays to summarize their results up front. They 'predicted'[113] that the nearly free electron gas was unstable to attractive interactions between the electrons. In other words, they could show that if you include a finite attractive interaction between pairs of electrons, they would form new 'quasiparticle' states (called Cooper pairs[114]) that would have charge $2e$ and total spin moment $S = 0$. These new quasiparticles would therefore obey Bose-Einstein statistics and undergo a kind of Bose-Einstein condensation into a zero momentum state. Although they suggested that the electron-phonon interaction might be the origin of these attractive interactions, they constructed their theory in a interaction independent fashion. Among the experimental predictions the most famous one is probably the opening of a gap in the density of states at the Fermi level. At the time of writing it was not possible to directly measure the density of states, but this effect would be clearly visible in several experimental probes, such as the specific heat or the optical spectrum. The BCS theory was (and still is) a great success and it delivered Bardeen his second Nobel prize in physics[115].

After BCS it took a few years to verify and explore the implications of their theory that, in the end, led to a 'complete' theory of electron-phonon superconductivity in 1962 due to Eliashberg. In the next section I'll explain how you can turn the repulsive Coulomb interaction into an attractive potential between two electrons as well as the role played by the phonons.

[111] *The next metal he chose to investigate was Tin. He reported that it didn't show the hallmark 'supraconductive' properties of mercury. T_c of tin is 3.7 K. Less than half a degree difference.*

[112] *Emanuel Maxwell from the National Bureau of Standards, Washington D.C., submitted a paper to Physical review in 1950 where the isotope effect was first reported. The paper starts as follows: 'The existence of a small quantity of Hg^{198} at the NBS prompted us to investigate its properties as a superconductor.'*

He reported a change of T_c = 4.156 K for natural Hg to T_c = 4.177 K. This seemingly insignificant difference holds the key to the mechanism!

[113] *The theoretical framework makes experimental predictions as well. Most of them were of course 'after the fact'.*

[114] *The story goes that Cooper had this insight on his train ride home after a long day of discussion with the other two gentleman.*

[115] *To date he remains the only person to have ever won two Nobel prizes in physics. His first prize was awarded in 1956 for the discovery of the transistor, a year before the BCS paper. In 1972 he received the prize again for the theory of SC.*

5.2 Repulsion becomes attraction

The question that remained unanswered after BCS theory was how an attractive interaction between electrons would come about. There is only one interaction that couples two electrons together in a solid and this is the repulsive Coulomb interaction. However, as we have seen in Chapter 2, the Coulomb interaction in a solid is screened by the other charges in a solid by the dielectric function. As exercise E2.2 shows the Fourier transform of the Coulomb potential can be written as,

$$V_s(k,\omega) = \frac{q_1 q_2}{\varepsilon(k,\omega)k^2} \tag{5.2}$$

where the momentum dependence of the dielectric function in its simplest form is,

$$\varepsilon(k) = 1 + \frac{k_{TF}^2}{k^2}. \tag{5.3}$$

Here k_{TF} is the Thomas-Fermi screening length, the distance over which electrons can screen the disturbance caused by an accumulation of charge. However, since the k-dependent piece of the dielectric function is positive, the Coulomb repulsion between two electrons ($q_1 = q_2 = -e$) will always remain repulsive. So what about the frequency dependent piece of the dielectric function? Within the Drude-Lorentz model we ended up with the following expression,

$$\begin{aligned}\hat{\varepsilon}(\omega) = 1 &- \frac{\omega_p^2}{\omega(\omega + i\Gamma)} - \sum_{ph} \frac{4\pi f_{ph}^2}{i\omega\Gamma_{ph} - (\Omega_{0,ph}^2 - \omega^2)} \\ &- \sum_i \frac{4\pi f_i^2}{i\omega\Gamma_i - (\Omega_{0,i}^2 - \omega^2)}.\end{aligned} \tag{5.4}$$

Here the first term was the intraband (Drude) response, the second term a contribution due to optical phonons and the last term derives from interband transitions. For the sake of briefness, let us assume that the only important part is the phonon contribution[116]. Taking just a single phonon mode into account we can drop the sum over different optical branches and find,

$$\hat{\varepsilon}(k,\omega) = 1 + \frac{k_{TF}^2}{k^2} - \frac{4\pi f_{ph}^2}{i\omega\Gamma_{ph} - (\Omega_{0,ph}^2 - \omega^2)} \tag{5.5}$$

which we should now insert into Eq. 5.2. This gives,

$$V(k,\omega) = \frac{e^2}{k^2 + k_{TF}^2 - k^2 \frac{4\pi f_{ph}^2}{i\omega\Gamma_{ph} - (\Omega_{0,ph}^2 - \omega^2)}} \tag{5.6}$$

which needs some rewriting to see if this is attractive. For simplicity we assume an infinite lifetime of the phonon mode ($\Gamma = 0$) and divide out a term $(k^2 + k_{TF}^2)$:

$$V(k,\omega) = \frac{e^2}{(k^2 + k_{TF}^2)\left(1 - k^2 \frac{4\pi f_{ph}^2}{(k^2 + k_{TF}^2)(\omega^2 - \Omega_{0,ph}^2)}\right)} \tag{5.7}$$

Next we multiply by '1',

$$V(k,\omega) = \frac{e^2(\omega^2 - \Omega_{0,ph}^2)}{(k^2 + k_{TF}^2)\left((\omega^2 - \Omega_{0,ph}^2 - k^2 \frac{4\pi f_{ph}^2}{(k^2 + k_{TF}^2)}\right)} \tag{5.8}$$

Now note that in the denominator the second term in brackets defines a momentum dependent divergence. In other words, at a frequency,

$$\omega_k^2 = \left[\Omega_{0,ph}^2 + k^2 \frac{4\pi f_{ph}^2}{k^2 + k_{TF}^2}\right] \tag{5.9}$$

the interaction diverges. Note that this frequency is (almost) completely determined by the properties of the phonon mode (the resonance frequency and the oscillator strength f_{ph}). Inserting this back into the expression for the potential energy we have,

$$V(k,\omega) = \frac{e^2(\omega^2 - \Omega_{0,ph}^2)}{(k^2 + k_{TF}^2)(\omega^2 - \omega_k^2)} \tag{5.10}$$

[116] *We are considering electron-phonon superconductors after all.*

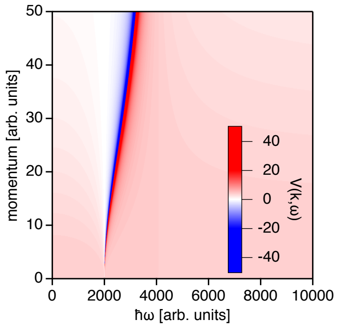


Figure 5.38: Color plot of the potential in Eq. 5.10 for suitably chosen parameters. The color scale is chosen such that white corresponds to (close to) zero, while blue is attractive and red is repulsive.

Now note that the numerator will be negative if $\omega < \Omega_{o,ph}$, while the denominator will be negative for $\omega < \omega_k$. Looking back to equation 5.9, we see that $\omega_k > \Omega_{o,ph}$ for a small range of frequencies. In other words, the potential will be negative for $\Omega_{o,ph} < \omega < \omega_k$. Figure 5.38 shows the potential as a function of momentum and frequency for a suitably chosen set of parameters. Note that I have restricted the color range to highlight what happens at low energy and momentum. The most important point is of course the fact that you can see a reasonable 'blue' area, which is where the potential is attractive.

This is the crucial ingredient behind superconductivity: the interaction between electrons and phonons gives rise to a **dynamic interaction** that can become attractive. The reason for calling the interaction 'dynamic' arises from the frequency dependent piece of the interaction. In our current model we have assumed a simplified nearly free electron gas where the Coulomb potential depends on the magnitude of momentum, but not on the direction. This is really a result of the fact that we started by assuming a spherically symmetric dispersion. In real materials the momentum dependence can be much more complicated as a result of bandstructure and crystal symmetry. This in principle can give rise to different types of superconductivity. We will return to this point later.

5.3 The Cooper problem

In the previous section we have seen how the electron-phonon interaction can result in an attractive potential between two electrons. But what is the wavefunction for two electrons under the influence of an attractive interaction? Cooper realized that such an attractive interaction would result in a bound state of the two particles (very much like an H_2 molecule)[117]. In this section we will follow his derivation of both the wave function and its properties. It is possible to use the form of the potential derived in the previous section, but we will very quickly have to resort to numerical evaluation of integrals. Instead we will follow Cooper on his train ride home and assume that the potential is spherically symmetric and has the form,

$$V(r) = \begin{cases} -V & \omega < \omega_D \\ 0 & \omega \geq \omega_D \end{cases} \tag{5.11}$$

This is just a constant spherical potential well which is attractive over some range of energies. What this actually means in the Cooper problem will be discussed in more detail at the end[118]. In what follows we will consider the quantum mechanical problem of two electrons interacting with an attractive potential and solve it by (i) guessing a trial wavefunction, (ii) transform coordinates to center of mass coordinates, (iii) use a variational approach to determine the binding energy for the formation of a bound state. As usual, we first define the Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V(r_1 - r_2)\right]\Psi_k(r_1, r_2) = E\Psi_k(r_1, r_2) \tag{5.12}$$

Let's start with a first guess of the wave function for two particles with momenta k_1 and k_2. What would be your guess for the wavefunction? I hope that based on reading the previous chapters, your answer is,

$$\Psi(r_1, r_2) = Ae^{ik_1\cdot r_1} + Be^{ik_2\cdot r_2} \tag{5.13}$$

Unfortunately, this is also wrong. The key insight contributed by Cooper, was that this is not the correct wavefunction. The linear combination principle breaks down for this particular problem. Note that this is a crucial departure from the basic mathematical structure of early quantum mechanics. The idea had always been that for a given physical system it must be possible to write down a complete set of basis states and that the wavefunction had to be a linear combination of these states. In terms of linear algebra, any vector (groundstate) in the (Hilbert) space defined by a set of basis vectors can be expressed as a vector sum (linear combination) of these basis vectors. If you imagine a universe with two non-interacting electrons, your Hilbert space is spanned by two plane wave states. Adiabatically turning on a small interaction, you would expect that the new groundstate is a linear combination of these two plane wave states. Cooper made a radical departure from this and postulated a new guess[119]:

$$\Psi(r_1, r_2) = Ae^{i(k_1\cdot r_1 + k_2\cdot r_2)} \tag{5.14}$$

Note that the energy associated with this state (without interactions) is still,

$$E_0 = \frac{\hbar^2}{2m}\left(k_1^2 + k_2^2\right) \tag{5.15}$$

[117] *If you wonder why the two electrons do not simply 'collapse' under an attractive interaction: apart from the potential energy there is also kinetic energy. The Heisenberg principle will tell you that as you confine the two electrons in a smaller and smaller energy, their kinetic energy ($\propto \Delta k$) will increase. The 'size' of the bound state can in fact be estimated from the balance of kinetic and potential energy.*

[118] *The notation is a bit strange: the potential does not depend on r, but on ω and so it is attractive independent of r if the energy of the pair is smaller than ω_D.*

[119] *The A appearing here is just a normalization factor.*

as you would find for two independent electrons. The reason Cooper chose this particular form is that it allowed him to rewrite the problem in centre of mass coordinates. In this case we will have,

$$\begin{aligned} K &= k_1 + k_2, \quad & k &= \frac{k_1 - k_2}{2} && (5.16)\\ R &= \tfrac{r_1+r_2}{2}, \quad & r &= r_1 - r_2 && (5.17) \end{aligned}$$

where K, R refers to the centre of mass, while k, r refers to the motion relative to the centre of mass. With these definitions we can rewrite the wavefunction as,

$$\Psi(R, r) = Ae^{i(K\cdot R + k\cdot r)} \tag{5.18}$$

And the energy in the absence of interactions will be,

$$E_0 = \frac{\hbar^2}{m}\left(\frac{K^2}{4} + k^2\right) \tag{5.19}$$

or in the case $K = 0$[120],

$$E_0 = \frac{\hbar^2 k^2}{m} \tag{5.20}$$

The lowest energy for a Cooper pair is thus obtained if $K = 0$, which means $k_1 = -k_2$ with a corresponding wave function,

$$\Psi(r_1, r_2) = Ae^{i(k\cdot r_1 - k\cdot r_2)} = Ae^{ikr} = \Psi_k(r) \tag{5.21}$$

We now have a single plane wave, trial solution that is fundamentally different from the ones we have used so far. The Schrödinger equation for such a pair reads

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V(r_1 - r_2)\right]\Psi_k(r) = E_k\Psi_k(r) \tag{5.22}$$

which can now be rewritten as,

$$\left[(E_0 - E_k) + V(r)\right]\Psi_k(r) = 0 \tag{5.23}$$

Assuming now that the wave function has the form of a superposition of our newfound trial states,

$$\Psi_k(r) = A\sum_k a_k e^{ikr} \tag{5.24}$$

the Schrödinger equation transforms to,

$$A\sum_k (E_0 - E_k)a_k e^{ikr} + A\sum_k V(r)a_k e^{ikr} = 0 \tag{5.25}$$

Just like we did for the tight binding problem, we now multiply by $e^{-ik'r}$ and integrate[121],

$$\begin{aligned} \sum_k \int d^3r(E_0 - E_k)a_k e^{i(k-k')r} + \sum_k \int d^3r V(r)a_k e^{i(k-k')r} &= 0 && (5.26)\\ \sum_k (E_0 - E_k)a_k\delta_{k,k'} + \sum_k \int d^3r V(r)a_k e^{i(k-k')r} &= 0 && (5.27)\\ (E_0 - E_{k'})a_{k'} + \sum_k \int d^3r V(r)a_k e^{i(k-k')r} &= 0. && (5.28) \end{aligned}$$

And this brings us to a new 'central equation', but this time for two electrons bound in a cooper pair. The solutions of course depend on our choice for the potential. As mentioned above, the simplest choice is to assume a constant spherically symmetric potential. The neat result obtained by BCS is that, no matter what the potential looks like, as soon as there is a non-zero attractive potential, Cooper pairs will form. Note that the second term in 5.28 contains just the Fourier coefficients of the potential,

$$\begin{aligned} (E_0 - E_{k'})a_{k'} + \sum_k a_k \int d^3r V(r)e^{i(k-k')r} &= 0 && (5.29)\\ (E_0 - E_{k'})a_{k'} + \sum_k a_k V_{k,k'} &= 0 && (5.30) \end{aligned}$$

Hopefully, the pattern looks familiar. We started by assuming a trial wave function consisting of a linear combination of basis states. From the Schrödinger equation we then obtain a relation between all coefficients of the trial wavefunction. The next step

[120] *For a single particle we would find* $E_0 = \frac{\hbar^2 k^2}{2m}$.

[121] *Note that on the second line we can transform one integral to a δ-function, but not for the second term since there is an additional r dependence in the potential. We have also dropped the A.*

will be to eliminate the dependence on the coefficients (e.g. by solving a set of coupled equations using linear algebra) and find the energy spectrum of the solutions. To solve the last set of expressions we take a slightly different approach and follow the original derivation of Cooper.

The sum over momenta cannot be evaluated without making an explicit choice for the Fourier coefficients of the potential. Cooper noted that there would likely be restrictions on the allowed momenta in the sum. After all, the Pauli principle combined with energy and momentum conservation will prevent most scattering processes. In the case of phonon assisted scattering (as discussed above), the allowed energy range is determined by the average phonon energy. This is exemplified in Eq. 5.11 that depends on a frequency ω_D, the Debye frequency, which is a measure of this average phonon energy[122]. It is important to note that this average energy is typically a small number compared to the energies of the electrons involved. For example, for Pb the Debye frequency is about 5 meV, while the Fermi energy is on the order of 5 eV. They differ by a factor 1000! The interaction potential enables two electrons with momenta k_1, k_2 to scatter to a new state with k_1', k_2' by 'borrowing' some energy from a phonon. Since this energy is small compared to the Fermi energy, only a small fraction of all electrons is sensitive to this interaction. This is depicted in Fig. 5.39 where the narrow range of momenta states around the Fermi level is indicated within which scattering can take place conserving both energy and momentum. From Fig. 5.39 we see that the two particle momentum has to fulfill the condition,

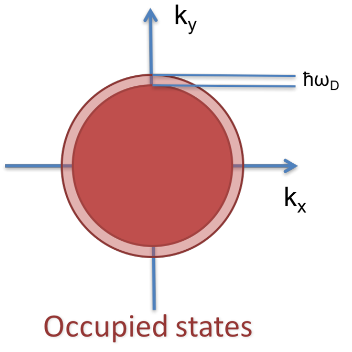


Figure 5.39: Fermi surface (dark red) with a narrow shell of energies with $\epsilon_F < \epsilon_k < \epsilon_F + \hbar\omega_D$ indicated in light red.

$$2\epsilon_F < \frac{\hbar^2 k^2}{2m} < 2\epsilon_F + 2\hbar\omega_D \tag{5.31}$$

We therefore take,

$$V_{k,k'} = \begin{cases} -V_0 & \epsilon_F < \epsilon_k < \epsilon_F + \hbar\omega_D \\ 0 & otherwise. \end{cases} \tag{5.32}$$

Starting from Eq. 5.30, we thus have,

$$(E_0 - E_{k'})a_{k'} = \sum_k a_k V_0 = C \tag{5.33}$$

where C is a constant. This implies that,

$$a_{k'} = \frac{C}{E_0 - E_{k'}} \tag{5.34}$$

This observation allows us to eliminate the coefficients. Summing Eq. 5.34 over momenta we obtain,

$$\sum_k a_k = C \sum_k \frac{1}{E_0 - E_k} \tag{5.35}$$

Since from 5.33 we have,

$$V_0 \sum_k a_k = C \rightarrow \sum_k a_k = \frac{C}{V_0} \tag{5.36}$$

we can eliminate the sum over a_k to find a relation between the eigenvalues and the interaction,

$$\frac{1}{V_0} = \sum_k \frac{1}{E_0 - E_k}. \tag{5.37}$$

Keeping the restrictions arising from our choice of the potential in mind, we can transform the sum over momenta into an integral over energies[123],

$$\frac{1}{V_0} = \int_{\epsilon_F}^{\epsilon_f + \hbar\omega_D} \frac{f(E_0)dE_0}{E_0 - E}. \tag{5.38}$$

where $f(E_0)$ is the density of states for pairs with energy E_0. Since we allow only pairs to form within a narrow energy shell around the Fermi level, the density of pairs is approximately equal to the density of states for electrons at the Fermi level,

$$\frac{1}{V_0} = \varrho(\epsilon_F) \int_{\epsilon_F}^{\epsilon_f + \hbar\omega_D} \frac{dE_0}{E_0 - E}. \tag{5.39}$$

The integral is now easy and gives,

$$\frac{1}{V_0} = \varrho(\epsilon_F) \ln\left(\frac{\epsilon_F + \hbar\omega_D - E}{\epsilon_F - E}\right) \tag{5.40}$$

$$= \varrho(\epsilon_F) \ln\left(1 + \frac{\hbar\omega_D}{\epsilon_F - E}\right) \tag{5.41}$$

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[122] *In the full electron-phonon interaction theory the precise frequency dependence of the phonon branches is taken into account.*

[123] *We make use here of Eq. 5.20.*

from which we can estimate the gain in energy for electrons to form a bound state as follows. To form a bound state the energy needs to be lower than the energy of the free electrons. In other words, $E = \varepsilon_F - \Delta$ where Δ is the energy gain per particle. From this is it follows that $\varepsilon_F - E = \Delta$ and so,

$$\frac{1}{\varrho(\varepsilon_F)V_0} = \ln\left(1 + \frac{\hbar\omega_D}{\Delta}\right). \tag{5.42}$$

Solving for the binding energy we find,

$$\Delta = \frac{\hbar\omega_D}{e^{1/\varrho(\varepsilon_F)V_0} - 1} \tag{5.43}$$

For small interactions, $\varrho(\varepsilon_F)V_0 \ll 1$, this further simplifies to,

$$\Delta = \hbar\omega_D e^{-1/V_0\varrho(\varepsilon_F)}. \tag{5.44}$$

This is an interesting result: it shows that no matter how small the interaction V_0 is, if it is non-zero electrons will always gain some energy by forming a bound state. It also shows that you cannot turn an insulator into a superconductor. The early recognition that BCS got for their theory derives from another feature of this expression. Very roughly one expects the critical temperature to be proportional to the bound state energy[124] i.e.,

$$\Delta \propto k_B T_C \tag{5.45}$$

Comparing this with Eq. 5.44 we find,

$$k_B T_C \approx \omega_D \approx \sqrt{\frac{k}{M}}, \tag{5.46}$$

which provided a very simple explanation for the isotope effect. The Cooper solution also gives a simple explanation for the 'zero resistance' state. As in a normal metal, the conductivity (or resistivity) is determined by states close to the Fermi level, which deep in the superconducting state will consist of Cooper pairs. Looking back to our wave function and Schrödinger equation we see that the wave function for a pair can be written as[125],

$$\Psi(k + K/2, -k + K/2) = e^{iKR}\Psi(k, -k) \tag{5.47}$$

This means that the velocity of a pair is simply,

$$v = \frac{\hbar K}{2m}. \tag{5.48}$$

and hence current will be proportional to,

$$j_s = -\frac{n_s e\hbar}{2m}K. \tag{5.49}$$

where n_s is the supercurrent density. So, let's imagine that we set a current in motion. In a normal metal we will reach an equilibrium between the acceleration provided by the electric field and the (random) scattering of electrons on impurities. In these collisions an electron changes its momentum from a state k to a state $k' = k + q$ with an associated loss in energy. Remember that these scattering processes take place close to the Fermi level. In the superconducting state there is now an additional restriction: for the momentum to change we first need to remove the electron from the Cooper pair state and there is an energy cost of 2Δ associated with that. In other words, when

$$\frac{\hbar^2(k + K/2)^2}{m} - \frac{\hbar^2k^2}{m} < 2\Delta \tag{5.50}$$

there is not enough energy to break up the Cooper pair. Since the typical momentum of each electron in the pair is of the order of the Fermi momentum, k_F, we have ($K << k_F$),

$$\frac{\hbar^2 k_F K}{m} < 2\Delta \tag{5.51}$$

Combining this with our expression for the current, we find that as long as we satisfy the condition,

$$j_s < -\frac{n_s e\Delta}{\hbar k_F} \tag{5.52}$$

there is no mechanism by which the electrons can lose energy. This is the origin of the zero-resistance state: it costs almost no energy to set Cooper pairs in motion (just as in the free electron model, $\varepsilon \propto K^2$) and as soon as you set a Cooper pair flow in motion there is no way to dissipate the energy.

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[124] *This is 'easy' to see: if the energy associated with thermal fluctuations, k_BT, is larger than the energy of the bound state, Δ, Cooper pairs will be destroyed.*

[125] *Since the potential does not depend on K or R, the wavefunction is separable and the K dependent piece has to be an eigenfunction of the total momentum. Hence it can be written as a 'plane wave'.*

5.4 The Bardeen-Cooper-Schrieffer groundstate energy

In the previous section we cheated a little: we started out by calculating the gain in energy of a Cooper pair (involving only 2 electrons) and then made some statements that concerned all electrons at the same time. In this section we will fix this and take Cooper's idea about bound electron states and try to do the same exercise for all electrons at once. This turns out to be a bit more complicated, but the physical idea is exactly the same[126].

We start again with the Cooper wavefunction (written in bra-ket notation now),

$$\Psi_k(r) = |k\rangle|-k\rangle. \tag{5.53}$$

Since this is the proper solution to the two particle problem for a given k, we might expect that the wavefunction for all pairs is a linear superposition of pair wavefunctions, i.e.:

$$\Psi = \sum_k c_k|k\rangle|-k\rangle. \tag{5.54}$$

Alas, just like linear superpositions didn't work for two particles, it doesn't work for many particles either. BCS had another ingenious ingredient to their theory. The Cooper pair is essentially a 'particle in a box' model and as such does not directly apply to a solid. After all, all the electrons are indistinguishable and it is not obvious why two particular electrons are likely to form a pair. Even when many electrons do form pairs, it will cost no energy for electrons to exchange *between* different pairs. This doesn't feel very comfortable. It also doesn't fit well with the identification of 'particles' with excitations of a solid. Just like band-electrons are the excitations of the metallic state and spin-waves are the excitations of the ferromagnet, Cooper pairs are excitations of the superconductor. In both other cases we had a description of the 'vacuum' state (a.k.a. the groundstate). For the metal it is a linear superposition of the single particle wave functions (atomic orbitals) while in the ferromagnet it is a linear superposition of spin states. We also remarked (without further specification) that the anti-ferromagnetic groundstate was special. The superconducting groundstate also turns out to be special. In the case of a superconductor a symmetry of the Hamiltonian is also broken[127] and as a result a linear superposition of basis states is no longer appropriate. So what should we choose? Unfortunately, it is not so easy to justify the choice we are about to make without resorting to 'second quantization'. It boils down to the observation that in interactions between Cooper pairs, 2 pairs are involved: scattering two particles from a state $(k, -k)$ to a state $(k', -k')'$ implies that an 'empty' Cooper state $(k', -k')$ becomes occupied and a new empty Cooper state $(k, -k)$ is created. This led BCS to suggest that the correct wavefunction should take as basis states,

$$\phi_2(k) \equiv u_k\,|O_k\rangle + v_k\,|k, -k\rangle \tag{5.55}$$

The function ϕ_2 exemplifies precisely this mixing of empty and full Cooper states. $|O_k\rangle$ represents an empty Cooper pair, while $|k, -k\rangle$ represents an occupied state. The coefficients u_k and u_k measure the relative mixture of empty and occupied for a given state. Note that they depend on the internal momentum of the pair, anticipating on the outcome of the calculation to follow[128]. For reasons beyond the scope of these notes the trial wavefunction becomes,

$$|G\rangle \equiv \prod_k \phi_2(k) = \prod_k \left(u_k\,|O_k\rangle + v_k\,|k, -k\rangle\right) \tag{5.56}$$

and not a linear superpositions of the ϕ_2. $|G\rangle$ has an uncomfortable property: the total number of particles is not conserved. To see this, we start writing out the product,

$$|G\rangle = (u_{k_1}u_{k_2}...u_{k_N}\,|O_{k_1}\rangle\,|O_{k_2}\rangle\,...\,|O_{k_N}\rangle) + (v_{k_1}\,|k_1, -k_1\rangle\,u_{k_2}...u_{k_N}\,|O_{k_2}\rangle\,...\,|O_{k_N}\rangle) + ... \tag{5.57}$$

and note that the first term contains no electrons, the second 2 electrons, the third term will contain 4 electrons and so on. This is a real problem, but we will fix it in a moment. To continue, we now need to define the problem we are trying to solve. Similar to what we did for the Hubbard model, we start from a known Hamiltonian (written in 'first quantized' form),

$$H_q = \sum_q \varepsilon(q)\,|q\rangle\,\langle q| = \sum_q \varepsilon(q)\hat{n}_q \tag{5.58}$$

where we identified $\hat{n}_q \equiv |q\rangle\,\langle q|$ as the Fourier components of the single particle density operator and the $\varepsilon(q)$ describes a band crossing the Fermi level. We add to this Hamiltonian a potential energy term $\hat{H}_{e-e}$. We do not necessarily need to provide an explicit form this interaction. Instead, we make use of the ideas we developed in

[126] *This section and the next follow largely the derivation presented in the book by Economou (see reading list).*

[127] *The symmetry that is broken is known as a U(1) gauge symmetry. It is because of this symmetry that you are free to choose the electromagnetic gauge potential.*

[128] *At this point it is not obvious why momentum should be involved. u and v are just complex numbers. As we will see, the precise value does depend on momentum.*

solving the Cooper problem by stating that the potential has Fourier components $V_{k,k'}$. This can perhaps be made more insightful by showing you the Feynman diagram describing the scattering process (Fig. 5.40). This figure shows that two electrons (one Cooper pair) with momenta $(k, -k)$ are scattered by the interaction to new states with momenta $(k', -k')$. In this process momentum needs to be conserved, and so the interaction will necessarily depend on both k and k'. This brings us to the point where we can start to calculate the groundstate energy from,

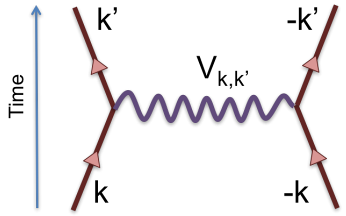

Figure 5.40: Feynman diagram for the scattering of a Cooper pair to a new state. The interaction is indicated as the wiggly line.

$$\langle G|\, H\, |G\rangle = \langle G|\, H_q\, |G\rangle + \langle G|\, H_{e-e}\, |G\rangle \tag{5.59}$$

Let's look at the first term on the r.h.s. of this. The energy is just a number so,

$$\langle G|\, H_q\, |G\rangle = \sum_q \varepsilon(q) \langle G|\, \hat{n}_q\, |G\rangle \tag{5.60}$$

and this just counts the number of particles with momentum q in the state $|G\rangle$. Making use of the definition of $|G\rangle$ (Eq. 5.56) we have[129],

$$\langle G|\, \hat{n}_q\, |G\rangle = \prod_{k,k'} \langle \phi_2(k)|\, \hat{n}_q\, |\phi_2(k')\rangle \tag{5.61}$$

We can evaluate the action of the density operator on the state $|\phi_2(k')\rangle$ as,

$$\hat{n}_q\, |\phi_2(k')\rangle = \hat{n}_q u_{k'}\, |O_{k'}\rangle + \hat{n}_q v_{k'}\, |k', -k'\rangle \tag{5.62}$$

If you have never seen these kind of operations before, i'll first give you an explanation of how to evaluate this in words. The operator $\hat{n}$ 'measures' the number of particles. In our case we have a momentum number operator that counts particles with momentum q. If this operator acts on a random quantum state with momentum k it will always be zero. Unless...$k = q$. A simple mathematical way to formulate exactly this is,

$$\hat{n}_q\, |k\rangle = \delta_{q,k}\, |k\rangle \tag{5.63}$$

The delta function is zero except when $q = k$ and we see that $|k\rangle$ is an eigenvector of the operator $\hat{n}_k$ with eigenvalue 1. Now to evaluate Eq. 5.62, we observe that the number of particles with momentum q in the unoccupied Cooper state $|O_{k'}\rangle$ is (quite obviously) exactly zero. It is an empty state after all. There are however two particles in the occupied state and so,

$$\hat{n}_q\, |\phi_2(k')\rangle = v_{k'}\delta_{q,k'}\, |k', -k'\rangle + v_{k'}\delta_{q,-k'}\, |k', -k'\rangle \tag{5.64}$$

We can now evaluate the expectation value of the momentum density operator as,

$$\langle \phi_2(k)|\, \hat{n}_q\, |\phi_2(k')\rangle = (u_k^\star \langle O_k| + v_k^\star \langle k, -k|)(v_{k'}\delta_{q,k'}\, |k', -k'\rangle + v_{k'}\delta_{q,-k'}\, |k', -k'\rangle) \tag{5.65}$$

Writing out this product we get 4 terms, but the two terms in which $|O_k\rangle$ appears evaluate to zero[130]. This leaves,

$$\langle \phi_2(k)|\, \hat{n}_q\, |\phi_2(k')\rangle = v_k^\star v_{k'}\delta_{q,k'}\, \langle k, -k|k', -k'\rangle + v_k^\star v_{k'}\delta_{q,-k'}\, \langle k, -k|k', -k'\rangle \tag{5.66}$$

now we note that the bra-kets appearing here are orthogonal if they do not have the same momentum. Therefore we can replace these with a δ-function (i.e. $\langle k, -k|k', -k'\rangle = \delta_{k,k'}$)

$$\langle \phi_2(k)|\, \hat{n}_q\, |\phi_2(k')\rangle = v_k^\star v_{k'}\delta_{q,k'}\delta_{k,k'} + v_k^\star v_{k'}\delta_{q,-k'}\delta_{k,k'} \tag{5.67}$$

This now allows us to evaluate Eq. 5.60

$$\langle G|\, H_k\, |G\rangle = \prod_{k,k'} \sum_q \varepsilon(q) \langle \phi_2(k)|\, \hat{n}_q\, |\phi_2(k')\rangle \tag{5.68}$$

It is not quite obvious how to deal with both the sum and the product simultaneously. However when you expand the product, there is only one term corresponding to the diagram in Fig. 5.40 for every k and k' and these appear in all combinations. In other words for every k and k' there will be a term of the form,

$$\varepsilon(q) \langle \phi_2(k_1)|\phi_2(k_1')\rangle \langle \phi_2(k_2)|\phi_2(k_2')\rangle \ldots \langle \phi_2(k)|\, \hat{n}_{q_1}\, |\phi_2(k')\rangle \ldots \langle \phi_2(k_N)|\phi_2(k_N')\rangle \tag{5.69}$$

Because the states $|\phi_2(k')\rangle$ are supposed to be normalized, all these terms evaluate to 1 except the one containing the expectation value of $\hat{n}_q$. Inserting Eq. 5.67 in this term and summing over all possible q gives a single term,

$$\varepsilon(k') v_k^\star v_{k'} \delta_{k,k'} + \varepsilon(-k') v_k^\star v_{k'} \delta_{k,k'} \tag{5.70}$$

---

[129] *Notice that we get two products, one over k and one over k'.*

[130] *This is because the overlap $\langle O_k|k', -k'\rangle$ is zero.*

and since we will obtain such a term for all possible k, k' we need to sum over these variables. Therefore,

$$\langle G| H_k |G\rangle = \sum_{k,k'} \varepsilon(k')v_k^\star v_{k'}\delta_{k,k'} + \varepsilon(-k')v_k^\star v_{k'}\delta_{k,k'} = 2\sum_k \varepsilon(k)v_k^\star v_k \tag{5.71}$$

where in the second step we have used the fact that $\varepsilon(-k) = \varepsilon(k)$.

The next step in our calculation of the groundstate energy requires us to evaluate the potential term,

$$\langle G| H_{e-e} |G\rangle = \prod_{k,k'} \langle \phi_2(k)| \hat{H}_{e-e} |\phi_2(k')\rangle \tag{5.72}$$

This is really a bit more tricky. To understand how to evaluate this we refer back to Fig. 5.40. As indicated, time progresses in the vertical direction in this Feynman diagram. That means that in the bottom part of the figure the state,

$$|\phi_2(k)\rangle = (u_k |O_k\rangle + v_k |k, -k\rangle) \tag{5.73}$$

has a large v_k and small u_k, while simultaneously the state $|\phi_2(k')\rangle$ has a large $u_{k'}$ and small $v_{k'}$. At the end of the interaction the roles are reversed. This implies that (i) the interaction only links states k and k' and (ii) only 1 term gives a finite contribution. In other words, we can replace the product by a sum (similar to what was done in Eq. 5.71)

$$\langle G| H_{e-e} |G\rangle = \sum_{k,k'} \langle \phi_2(k')| \langle \phi_2(k)| H_{e-e} |\phi_2(k)\rangle |\phi_2(k')\rangle \tag{5.74}$$

and we need to evaluate the product appearing here. It is not hard to see that out of the 16 terms arising from this product only 1 corresponds to the diagram in Fig. 5.40. Therefore we are left with,

$$\langle G| H_{e-e} |G\rangle = \sum_{k,k'} u_k^\star v_{k'}^\star \langle k', -k'| H_{e-e} |k, -k\rangle u_{k'} v_k \tag{5.75}$$

The term in brackets is just a number quantifying the interaction strength for electron states scattering from a state with momentum k to a state with momentum k',

$$\langle G| H_{e-e} |G\rangle = \frac{1}{V}\sum_{k,k'} u_k^\star v_{k'}^\star u_{k'} v_k \mathcal{V}_{k,k'} \tag{5.76}$$

The energy for the BCS groundstate is thus given by,

$$\langle G| H |G\rangle = 2\sum_k \varepsilon(k)v_k^\star v_k + \frac{1}{V}\sum_{k,k'} u_k^\star v_{k'}^\star u_{k'} v_k \mathcal{V}_{k,k'} \tag{5.77}$$

The next step we need to take is to find expressions for u_k and v_k, such that the total energy is lower than the energy of the original metallic state[131]. It turns out that this is not so simple: the BCS groundstate $|G\rangle$ is not an eigenstate of the Hamiltonian; as pointed out before the number of particles is not conserved. The problem can be fixed by working with the grand canonical ensemble, which is the topic of the next section.

5.5 Optimizing the BCS grand thermodynamic potential

In the grand canonical ensemble we minimize the **grand thermodynamic potential**,

$$\Omega = U - TS - \mu N_e \tag{5.78}$$

rather than the energy U itself. Since we are going to be interested in the groundstate for the moment, we can work at zero temperature ignoring the term $-TS$. The chemical potential in a solid is fixed and chosen to be equal to the Fermi level in the normal, non-superconducting state: $\mu \equiv E_F$. This is not unreasonable since at elevated temperatures, above the critical temperature, the system needs to return to a normal metal where the chemical potential and Fermi level are the same. The total energy U is given by Eq. 5.77, while the total number of particles is given by[132],

$$N_e = \sum_q \langle G| n_q |G\rangle = 2\sum_k v_k^\star v_k \tag{5.79}$$

Note that this expression actually makes sense: $|v_k|^2$ is the probability of occupying the state $|k, -k>$. Each of these states has 2 particles in it and therefore summing over all the occupied states should give the total number of particles. By including this as a condition in the optimization of the energy functional we ensure that the total

[131] *Note that if we set $\mathcal{V}_{k,k'}$ to zero, we end up with $v_k = 1$ and we have a tight-binding metal.*

[132] *Following the same arguments as the one leading to Eq. 5.71.*

number of particles remains fixed at N_e. Putting it all together we find that we need to optimize the following potential:

$$\Omega = 2\sum_k \varepsilon(k) v_k^\star v_k + \frac{1}{V}\sum_{k,k'} u_k^\star v_{k'}^\star u_{k'} v_k \mathcal{V}_{k,k'} - 2E_F \sum_k v_k^\star v_k \tag{5.80}$$

which can be simplified to,

$$\Omega = 2\sum_k \delta\varepsilon(k) v_k^\star v_k + \frac{1}{V}\sum_{k,k'} u_k^\star v_{k'}^\star u_{k'} v_k \mathcal{V}_{k,k'} \tag{5.81}$$

by defining $\delta\varepsilon(k) \equiv \varepsilon(k) - E_F$. Next we note that the grand thermodynamic potential, corresponding to an energy, is a real number. It is however expressed in terms of complex numbers u_k and v_k and their complex conjugates. It is therefore sufficient to minimize Ω with respect to one of these components[133]. In other words, taking:

$$\frac{\partial\Omega}{\partial v_k^\star} = 0 \tag{5.82}$$

will minimize the grand thermodynamic potential. We can make use of the normalization of the wave function to find a relation between the derivative of $u_k^\star$ and $v_k^\star$. By taking the derivative of

$$u_k u_k^\star + v_k v_k^\star = 1 \tag{5.83}$$

with respect to $v_k^\star$ we find,

$$\frac{\partial u_k^\star}{\partial v_k^\star} = -\frac{v_k}{u_k} \tag{5.84}$$

This should be used as a chain rule when minimizing the grand thermodynamic potential Eq. 5.81 using Eq. 5.82. From this we find that the grand thermodynamic potential is minimized when,

$$2\delta\varepsilon(k) v_k + \frac{1}{V}\sum_{k'} u_k^\star u_{k'} v_{k'} \mathcal{V}_{k',k} - \frac{1}{V}\frac{v_k^2}{u_k}\sum_{k'} u_{k'} v_{k'}^\star \mathcal{V}_{k,k'} = 0 \tag{5.85}$$

At this point we are going to make the assumption that we are dealing with a homogeneous system, so that we can take u_k and v_k as real numbers[134]. Rearranging then gives,

$$2\delta\varepsilon(k) v_k u_k = \frac{v_k^2}{V}\sum_{k'} u_{k'} v_{k'} \mathcal{V}_{k,k'} - \frac{u_k^2}{V}\sum_{k'} u_{k'} v_{k'} \mathcal{V}_{k',k}, \tag{5.86}$$

which can be rewritten as,

$$2\delta\varepsilon(k) v_k u_k = (v_k^2 - u_k^2)\Delta_k \tag{5.87}$$

by defining the gap function,

$$\Delta_k \equiv \frac{1}{V}\sum_{k'} u_{k'} v_{k'} \mathcal{V}_{k,k'} \tag{5.88}$$

Equation 5.87 can be turned into a self-consistent solution by making use of the normalization of the wavefunction, $u_k^2 + v_k^2 = 1$. In order to do this we square Eq. 5.87 and write,

$$\begin{aligned}(2\delta\varepsilon(k))^2 v_k^2 u_k^2 &= (v_k^2 - u_k^2)^2 \Delta_k^2 \\ &= (v_k^4 + u_k^4 - 2v_k^2 u_k^2)\Delta_k^2 \\ &= ((v_k^2 + u_k^2)^2 - 4v_k^2 u_k^2)\Delta_k^2 \\ &= (1 - 4v_k^2 u_k^2)\Delta_k^2 \end{aligned} \tag{5.89}$$

Where we made use of the normalization condition in the last step. Rearranging gives,

$$4\left[\delta\varepsilon(k)^2 + \Delta_k^2\right] v_k^2 u_k^2 - \Delta_k^2 = 0 \tag{5.90}$$

This is a fourth order equation for the u_k and v_k that can be solved (using the normalization condition once more) to give,

$$u_k^2 = \frac{1}{2}\left(1 \pm \frac{\delta\varepsilon(k)}{\sqrt{\delta\varepsilon(k)^2 + \Delta_k^2}}\right) \tag{5.91}$$

and

$$v_k^2 = \frac{1}{2}\left(1 \mp \frac{\delta\varepsilon(k)}{\sqrt{\delta\varepsilon(k)^2 + \Delta_k^2}}\right) \tag{5.92}$$

Show that..

...Eq.'s 5.91 and 5.92 satisfy the self-consistency and normalization condition.

---

[133] *See for example, D.G. Messerschmitt @ http://www.eecs.berkeley.edu/Pubs/TechRpts/2006/EECS-2006-93.pdf*

[134] *If the u_k and v_k are complex, this results in an overall complex phase of the wavefunction. In a uniform material this phase is meaningless and we can ignore it. In Ginzburg-Landau theory non-uniformity is taken into account and the phase does matter.*

and that is the final result. We have obtained expressions for the coefficients appearing in the BCS wavefunction that minimize the grand thermodynamic potential. It remains to show that this potential has a lower energy than the normal state grand thermodynamic potential. That is, we need to determine:

$$\Omega_N - \Omega_{SC} = 2\sum_{k<k_F}\delta\varepsilon_k - 2\sum_{k<k_F}\delta\varepsilon_k v_k^2 - 2\sum_{k>k_F}\delta\varepsilon_k v_k^2 - \langle G|\, H_{e-e}\,|G\rangle \tag{5.93}$$

This is not completely trivial. It can be shown that this is equivalent to,

$$\Omega_N - \Omega_{SC} = \sum_k \left[\frac{\Delta_k^2}{2E_k} + \frac{|\delta\varepsilon_k|^2}{E_k} - |\delta\varepsilon_k|\right] \tag{5.94}$$

which after changing from sum to integral over energy and making the standard approximation of the density of states at the fermi level gives,

$$\Omega_N - \Omega_{SC} = \frac{1}{2}\varrho(\varepsilon_F)\Delta^2 \tag{5.95}$$

A more elegant result is obtained when we combine Eq. 5.88 with the expressions for the wave function coefficients. This gives,

$$\Delta_k = -\frac{1}{V}\sum_{k'}\frac{\mathcal{V}_{k,k'}\Delta_{k'}}{2\sqrt{\delta\varepsilon(k')^2 + \Delta_{k'}^2}} \tag{5.96}$$

which is known as the **BCS gap equation**. This equation is really equivalent to a self-consistency condition. For a given set of Fourier coefficients $\mathcal{V}_{k,k'}$, we solve for the gap Δ_k. If Eq. 5.96 has a non-trivial (e.g. non-zero) solution, the normal state is unstable and a superconductor will form. Although this is the real result we set out to obtain, we have achieved much more along the way. If you got lost in the purely mathematical treatment so far: the next section aims to explain you the physics underlying it all.

5.6 Bogoliubov quasiparticles and the energy spectrum of a superconductor

The physics behind superconductivity is really quite strange. The origin behind the strangeness is quantum mechanics: a superconductor is a material in which the electronic properties are described by a single, macroscopic coherent quantum state. What does that mean? It means that the concept of electrons should really be forgotten when you think about the low energy properties of the superconducting state. Instead, the system is described by a coherent state that can be called a 'vacuum state'. There are no particles in this state (hence the name). If we somehow implant a minimal bit of energy in this vacuum state (and the minimal quantum turns out to be 2Δ) we will create a particle pair called a Cooper pair. This is not a coupled pair of electrons. It is a particle with a certain mass and charge equal to two electron charges. It has spin zero (at least in the elementary superconductors that fall within the BCS universality class). This particle is sometimes also called Bogoliubon after the mathematician that invented a neat trick to diagonalize the BCS hamiltonian in second quantization in three lines.

Before explaining the energy spectrum in a bit more detail, I would like to reiterate this point. A superconductor is not simply a collection of bound states of electron pairs! The wave function describing electrons involved in the superconducting dance is really a completely different object from the 'simple' plane wave or tight binding states from which we derive our intuition. In the superconducting wavefunction the coordinates and momenta of all the electrons are coupled together into one single wavefunction!

To elucidate the results obtained in the previous section I will now first discuss the energy spectrum in the normal state in terms of our new wave function. To discuss normal state properties turns out to be relatively straightforward. We will refer to Fig. 5.41 in what follows. Interestingly, the normal state tight-binding metal can be equally well described by the BCS wave function. To see this we set Δ_k to zero in Eq. 5.91 and 5.92. We also note that the real solution has to describe the band dispersion in the normal state and so the only appropriate choice for the signs is determined by the condition that $v_k = 1$ and $u_k = 0$ for $\varepsilon(k) < E_F$. We therefore obtain,

$$v_k^2 = \frac{1}{2}\left(1 - \frac{\varepsilon(k) - E_f}{|\varepsilon(k) - E_F|}\right) \tag{5.97}$$

$$u_k^2 = \frac{1}{2}\left(1 + \frac{\varepsilon(k) - E_f}{|\varepsilon(k) - E_F|}\right) \tag{5.98}$$

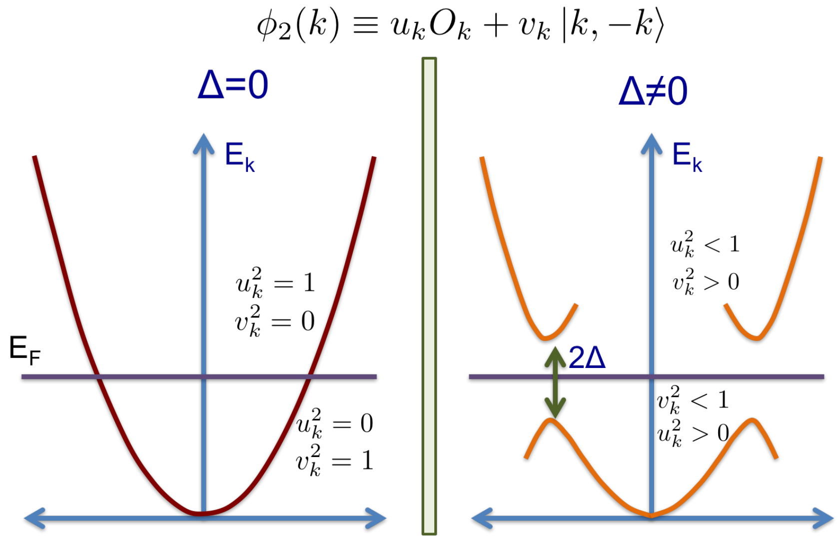

Figure 5.41: The energy spectrum for the normal (left) and superconducting (right) states. The SC state is characterized by a gap at the Fermi level, which is considered to be the order parameter of the SC state. Also indicated in both cases are the approximate values for the v_k and u_k.

In the context of the BCS wave function this describes exactly the energy spectrum of the normal metal. For momenta $k < k_F$ we have $v_k = 1$ and the state $|k, -k\rangle$ is completely occupied. At the same time, for $k > k_F$ we have that $u_k = 1$ and the state $|O_k\rangle$ is completely occupied. This is equivalent to saying that (at T=0 if $\Delta = 0$) all electron states below the Fermi level are occupied and all states above the Fermi level are empty.

Now comes the magic of the superconducting state. We assume for the moment that there is a momentum independent, finite attractive interaction (i.e. $\mathcal{V}_{k,k'} = -V_0$ for a range of energies, see Eq. 5.11). This allows us to rewrite Eq. 5.96 as,

$$\frac{V}{V_0} \sum_{k'} = \frac{1}{2\sqrt{\delta\varepsilon(k')^2 + \Delta^2}} \tag{5.99}$$

This can be solved following a similar approach as was used for the Cooper problem (Eq. 5.38). The end result is in fact equivalent to the result obtained there (Eq. 5.44). We have found that in the presence of a finite attractive interaction a finite gap develops. In fact, the new energy spectrum will be given by:

$$E_k \equiv \sqrt{\delta\varepsilon(k)^2 + \Delta_k^2} = \sqrt{(\varepsilon(k) - \mu)^2 + \Delta_k^2} \tag{5.100}$$

which shows that Δ really corresponds to a gap in the excitation spectrum. This is exemplified in the right-hand panel of figure 5.41. As is clear from a comparison with the spectrum on the left, a gap develops around the Fermi level of order 2Δ. At the same time, the values of the u_k and v_k are no longer strictly equal to one or zero. Instead, their value close to the original Fermi level indicates that the wavefunction attains a strong mixed particle-hole character. The variation of the wave function coefficients can be calculated quite easily and they are shown in Fig. 5.42.

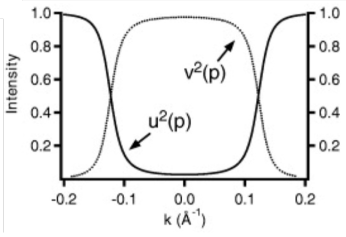

Figure 5.42: Variation of the coefficients u_k and v_k along a high symmetry momentum direction.

To conclude this section we note that the BCS gap equation in fact allows many more solutions. We repeat it here once more,

$$\Delta_k = -\frac{1}{V} \sum_{k'} \frac{\mathcal{V}_{k,k'} \Delta_{k'}}{2\sqrt{\delta\varepsilon(k')^2 + \Delta_{k'}^2}} \tag{5.101}$$

So far we have assumed that the interaction responsible for superconductivity is the electron-phonon interaction. We have shown in section 5.2 that the simplest form of the electron-phonon interaction results in a momentum independent interaction that is attractive over a small range of energies. As the gap equation Eq. 5.99 shows, this is enough to provide a finite, momentum independent gap. Superconductors that follow this paradigm are called **s-wave superconductors**. Note that the characterization 's-wave' has *nothing* to do with the orbital character of the wave function! A band containing any mixture of s-, p- and d- orbitals crossing the Fermi level can support s-wave superconductivity. The nomenclature actually arises from the spherical symmetry that is implied by the momentum independence of the gap: everywhere on the Fermi surface of an s-wave superconductor a gap of size Δ opens. It is however completely *reasonable* to assume that the interaction has a momentum dependence. In this case the nature of the gap can be completely different (and momentum dependent!). An interesting example is realized in the high-T_c cuprate superconductors. It is well established that the superconducting gap in that case follows a so-called **d-wave symmetry** (see Fig. 5.43). Interestingly, a possible interaction leading to such a symmetry was proposed around the same time as the announcement of the discovery of the cuprate superconductors. Scalapino, Loh and Hirsch proposed a model that involved anti-ferromagnetic spin-waves (see Chapter 4) as possible mediators of an interaction between the electrons on 23 June, 1986. The interesting part is that the interaction in this case is purely repulsive. The resulting order parameter is,

$$\Delta_k = \Delta_0 \left(\cos(k_x a) - \cos(k_y a)\right) \tag{5.102}$$

which has the interesting property that it is negative in two quadrants of the Brillouin zone and positive in the other two quadrants[135]. Note that only Δ_k^2 enters in the expression for the energy spectrum so that the gap in the spectrum is always positive. However, the negative values (corresponding to an oscillating phase) have experimental consequences and can be observed in experiments where a junction is formed between a conventional s-wave and a d-wave superconductor. In a similar spirit it turns out to be possible to form **p-wave superconductors**. These come in different flavors because now the orbital part of the SC wavefunction is anti-symmetric. The p-wave superconductors can therefore come with three different spin-configurations (e.g. $|\uparrow,\uparrow\rangle$, $|\downarrow,\downarrow\rangle$ and $(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle)/2$). Not many p-wave superconductors are known. One of them, UCoGe, was discovered in 2007 in Amsterdam by Y. Huang, A. de Visser and collaborators.

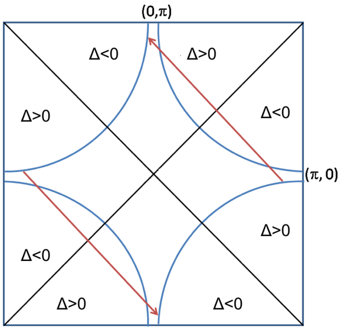

Figure 5.43: Fermi surface of a high T_c superconductor (blue lines) and interactions coupling different momentum states. Since the interactions are repulsive, the gap has to change sign between these quadrants.

5.7 Epilogue

That is it. For now this is the last section of this set of lecture notes. I will discuss experimental properties of superconductors during the lectures and let you derive some in the following set of exercises. Perhaps next year this section will be replaced with something more substantive. To be honest, I feel a bit ashamed as experimental physicist not to have described some of the marvelous experiments that can be done to really bring the topic to life.

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[135] *This implies that the gap is zero at 4 special locations in momentum space!*

EXERCISES V

ELECTRODYNAMICS OF SUPERCONDUCTORS

In this set of exercises, you will investigate the properties of superconductors in a magnetic field (e.g. the Meissner effect) and the interaction between light and superconductors.

MAXWELL RELATIONS

In lecture 5, we discussed the interaction of light and matter. In this first section, we summarize the Maxwell relations as well as a few useful relations. The four Maxwell relations are:

$$\begin{aligned} \nabla \cdot \vec{D} &= 0 \\ \nabla \cdot \vec{B} &= 0 \\ \nabla \times \vec{E} &= -\frac{1}{c}\frac{\partial \vec{B}}{\partial t} \\ \nabla \times \vec{H} &= \frac{1}{c}\frac{\partial \vec{D}}{\partial t} + \frac{4\pi}{c}\vec{j}. \end{aligned} \tag{E5.1}$$

You will also need the relation between the magnetic field and the vector potential:

$$B = \nabla \times \vec{A}. \tag{E5.2}$$

We will work in the Coulomb gauge, for which $\nabla \cdot \vec{A} = 0$. Finally, keep the following useful identity in mind:

$$\nabla \times \left(\nabla \times \vec{F}\right) = \nabla\left(\nabla \cdot \vec{F}\right) - \nabla^2 \vec{F}. \tag{E5.3}$$

In the exercises that follow, I will work in CGS notation, so that

$$\begin{aligned} \vec{H} &= \vec{B} \\ \vec{D} &= \vec{E}, \end{aligned} \tag{E5.4}$$

i.e., we will not consider induced polarization or magnetization.

THE LONDON EQUATIONS

1

Well before the BCS theory was around, the brothers Fritz and Heinz London gave a description of several known electromagnetic properties of superconductors, based on the Maxwell equations. Starting from the Maxwell equations, they derived several relations that together have become known as the **London equations**.

Historically, superconductors were considered to consist of two ‘fluids’: the first was the normal state electron fluid and the second the superconducting fluid. As a result, the response of a superconductor in applied magnetic or electric fields consists of two terms. For example, the total current density $\vec{j}$ is defined as:

$$\vec{j} = \vec{j}_n + \vec{j}_{sc}, \tag{E5.5}$$

where the labels n and sc correspond to respectively normal and superconducting. Close to the zero temperature, the response will be dominated by the superconducting response[136]. In the first exercise, we are going to derive several equivalent forms of the London equations and will use them in the ensuing exercises.

A Starting from Newton’s equations, find an expression for

$$\frac{\partial j_{sc}}{\partial t}. \tag{E5.6}$$

Hint: First figure out which forces are working on the superconducting electrons. You can assume for now that the normal electrons do not contribute to the current. Also keep the *two* defining aspects of a superconductor in mind.

B Prove that:

$$\nabla \times \vec{j}_{sc} + \frac{e^2 n_s}{mc}\vec{B} = 0. \tag{E5.7}$$

C Using the result of exercise 1b, show that the following relation is satisfied:

$$\vec{j}_{sc} = -\frac{e^2 n_s}{mc}\vec{A}. \tag{E5.8}$$

---

[136] *This happens at* $k_B T < \hbar\omega_D/2$.

$\mathcal{D}$ Again using the result of exercise 1b, show that:

$$\nabla^2 \vec{j}_{sc} = \frac{1}{\lambda_L^2} \vec{j}_{sc} \quad \text{and} \quad \nabla^2 \vec{B} = \frac{1}{\lambda_L^2} \vec{B}, \tag{E5.9}$$

where λ_L is defined as:

$$\lambda_L = \sqrt{\frac{mc^2}{4\pi n_s e^2}}. \tag{E5.10}$$

Hint: For this exercise, you can assume that $\partial E / \partial t = 0$.

2

THE MEISSNER EFFECT

Meissner and Ochsenfeld observed experimentally that the magnetic field inside a superconductor is zero. When a superconductor is placed in a magnetic field, surface supercurrents will start to flow, completely cancelling the field inside the superconductor. In other words: a superconductor behaves like a perfect diamagnet. In this exercise, you will calculate the magnetic field and current inside a superconductor. Consider a semi infinite superconductor, occupying the half space, $z0$ (see fig. 5.44). Using the result of exercise 1d, calculate the magnetic field inside the superconductor, assuming a constant magnetic field outside the superconductor, oriented along the x-direction. Also calculate the current density inside the superconductor. Hint: If necessary, the boundary conditions are $B(z=0) = B_{z=0}$ and $B(z=\infty) = 0$. For the current density, keep line 4 of equations E5.1 in mind.

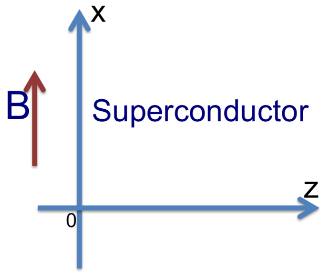

Figure 5.44: The geometry for calculating the magnetic field inside a superconductor.

3

OPTICAL PROPERTIES OF SUPERCONDUCTORS

In seminar 3, you derived the Drude-Lorentz model for bound and free electrons. Having seen how superconductivity changes the dispersions near the Fermi level, you might anticipate that the optical properties change as well. Unfortunately, the classical approach can't take the truly quantum mechanical effects behind superconductivity properly into account. A calculation of the optical conductivity in the superconducting state is surprisingly difficult and can only be done analytically using severe approximations. In fact, the correct description requires numerical calculation of a bunch of complicated integrals.

In this last exercise, we will calculate some optical properties of superconductors based on the London equations.

$\mathcal{A}$ Start with the result of exercise 1a and calculate the corresponding optical conductivity. Discuss the result in comparison to the Drude model. What form do $\sigma_1(\omega)$ and $\sigma_2(\omega)$ take?

$\mathcal{B}$ In this exercise, we will derive the photon wave equation inside a superconductor. Show that from line 3 of equations E5.1, it follows that:

$$\nabla^2 \vec{E} = \frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} + \frac{4\pi\sigma}{c^2}\frac{\partial \vec{E}}{\partial t} + \frac{1}{\lambda_L^2}\vec{E}. \tag{E5.11}$$

Hint: Use equation E5.5 and the result of 1a at some point. Remember that for normal metals, $j = \sigma \vec{E}$, but not for superconductors.

$\mathcal{C}$ Now that we have the wave equation, we can calculate the photon dispersion relation. Use equation E5.11 to find the photon dispersion relation. Hint: You can use a plane wave as ansatz for the solution to the wave equation.

$\mathcal{D}$ Plot the resulting dispersion for the case that $1/\lambda_L^2 \gg \sigma_0$ (this is the same as saying $n_s \gg n_n$) and contrast it with the case of photons in vacuum. What is the 'mass' of the photon? Hint: in this regime, you can just put $\sigma = 0$.

PS: The London penetration depth is about 10 nanometers. This results in a photon mass $m_{ph} \approx 10^{-36}$ kg. . .

FURTHER READING

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