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Applications of Quantum Mechanics

University of Cambridge Part II Mathematical Tripos

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Recommended Books and Resources

There are many good books on quantum mechanics. Here's a selection that I like:

- Griffiths, *Introduction to Quantum Mechanics*

An excellent way to ease yourself into quantum mechanics, with uniformly clear explanations. For this course, it covers both approximation methods and scattering.

- Shankar, *Principles of Quantum Mechanics*
- James Binney and David Skinner, *The Physics of Quantum Mechanics*
- Weinberg, *Lectures on Quantum Mechanics*

These are all good books, giving plenty of detail and covering more advanced topics. Shankar is expansive, Binney and Skinner clear and concise. Weinberg likes his own notation more than you will like his notation, but it's worth persevering.

This course also contains topics that cannot be found in traditional quantum textbooks. This is especially true for the condensed matter aspects of the course, covered in Sections 3, 4 and 5. Some good books include

- Ashcroft and Mermin, *Solid State Physics*
- Kittel, *Introduction to Solid State Physics*
- Steve Simon, *Solid State Physics Basics*

Ashcroft & Mermin and Kittel are the two standard introductions to condensed matter physics, both of which go substantially beyond the material covered in this course. I have a slight preference for the verbosity of Ashcroft and Mermin. The book by Steve Simon covers only the basics, but does so very well. (An earlier draft can be downloaded from his homepage; see below for a link.)

A number of lecture notes are available on the web. Links can be found on the course webpage: http://www.damtp.cam.ac.uk/user/tong/aqm.html

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0. Introduction

Without wishing to overstate the case, the discovery of quantum mechanics is the single greatest achievement in the history of human civilisation.

Quantum mechanics is an outrageous departure from our classical, comforting, common sense view of the world. It is more baffling and disturbing than anything dreamt up by science fiction writers. And yet it is undoubtably the correct description of the Universe we inhabit and has allowed us to understand Nature with unprecedented accuracy. In these lectures we will explore some of these developments.

The applications of quantum mechanics are many and various, and vast swathes of modern physics fall under this rubric. Here we tell only a few of the possible stories, laying the groundwork for future exploration. There are two major topics.

Much of these lectures is devoted to *condensed matter physics* or, more precisely, *solid state physics*. This is the study of "stuff", of how the wonderfully diverse properties of solids can emerge from the simple laws that govern electrons and atoms. We will develop the basics of the subject, learning how electrons glide through seemingly impenetrable solids, how their collective motion is described by a Fermi surface, and how the vibrations of the underlying atoms get tied into bundles of energy known as phonons. We will learn that electrons in magnetic fields can do strange things and start to explore some of the roles that geometry and topology play in quantum physics.

The second major topic is *scattering theory*. In the past century, physicists have developed a foolproof and powerful method to understand everything and anything: you take the object that you're interested in and you throw something at it. This technique was pioneered by Rutherford who used it to understand the structure of the atom. It was used by Franklin, Crick and Watson to understand the structure of DNA. And, more recently, it was used at the LHC to demonstrate the existence of the Higgs boson. In fact, throwing stuff at other stuff is the single most important experimental method known to science. It underlies much of what we know about condensed matter physics and all of what we know about high-energy physics.

In many ways, these lectures are where theoretical physics starts to fracture into separate sub-disciplines. Yet areas of physics which study systems separated by orders of magnitude — from the big bang, to stars, to materials, to information, to atoms and beyond — all rest on a common language and background. The purpose of these lectures is to build this shared base of knowledge.

1. Scattering Theory

The basic idea behind *scattering theory* is simple: there's an object that you want to understand. So you throw something at it. By analysing how that something bounces off, you can glean information about the object itself.

A very familiar example of scattering theory is called "looking at things". In this section we're going to explore what happens when you look at things by throwing a quantum particle at an object.

1.1 Scattering in One Dimension

We start by considering a quantum particle moving along a line. The maths here will be simple, but the physics is sufficiently interesting to exhibit many of the key ideas.

The object that we want to understand is some potential $V(x)$. Importantly, the potential is localised to some region of space which means that $V(x) \to 0$ as $x \to \pm\infty$. An example is shown to the right. We will need the potential to fall-off to be suitably fast in what follows although, for now, we won't be careful about what this means. A quantum particle moving along the line is governed by the Schrödinger equation,

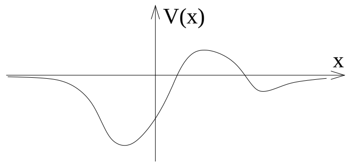


Figure 1:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \tag{1.1}$$

Solutions to this equation are energy eigenstates. They evolve in time as $\psi(x,t) = e^{-iEt/\hbar}\psi(x)$. For any potential, there are essentially two different kinds of states that we're interested in.

- *Bound States* are states that are localised in some region of space. The wavefunctions are normalisable and have profiles that drop off exponentially far from the potential

$$\psi(x) \sim e^{-\lambda|x|} \quad \text{as} \quad |x| \to \infty$$

Because the potential vanishes in the asymptotic region, the Schrödinger equation (1.1) relates the asymptotic fall-off to the energy of the state,

$$E = -\frac{\hbar^2\lambda^2}{2m} \tag{1.2}$$

In particular, bound states have $E < 0$. Indeed, it is this property which ensures that the particle is trapped within the potential and cannot escape to infinity.

Bound states are rather special. In the absence of a potential, a solution which decays exponentially to the left will grow exponentially to the far right. But, for the state to be normalisable, the potential has to turn this behaviour around, so the wavefunction decreases at both $x \to -\infty$ and $x \to +\infty$. This will only happen for specific values of λ. Ultimately, this is why the spectrum of bound states is discrete, like in the hydrogen atom. It's where the name "quantum" comes from.

- *Scattering States* are not localised in space and, relatedly, the wavefunctions are not normalisable. Instead, asymptotically, far from the potential, scattering states take the form of plane waves. In one dimension, there are two possibilities

$$\text{Right moving:} \quad \psi \sim e^{ikx}$$
$$\text{Left moving:} \quad \psi \sim e^{-ikx}$$

where $k > 0$. To see why these are left or right moving, we need to put the time dependence back in. The wavefunctions then take the form $e^{\pm ikx - iEt/\hbar}$. The peaks and troughs of the wave move to the right with the plus sign, and to the left with the minus sign. Solving the Schrödinger equation in the asymptotic region with $V = 0$ gives the energy

$$E = \frac{\hbar^2 k^2}{2m}$$

Scattering states have $E > 0$. Note that, in contrast, to bound states, nothing special has to happen to find scattering solutions. We expect to find solutions for any choice of k.

This simple classification of solutions already tells us something interesting. Suppose, for example, that the potential looks something like the one shown in the figure. You might think that we could find a localised solution that is trapped between the two peaks, with $E > 0$. But this can't happen because if the wavefunction is to be normalisable, it must have $E < 0$. The physical reason, of course, is quantum tunnelling which allows the would-be bound state to escape to infinity. We will learn more about this situation in Section 1.1.5.

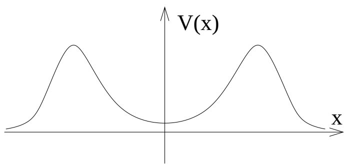


Figure 2:

1.1.1 Reflection and Transmission Amplitudes

Suppose that we stand a long way from the potential and throw particles in. What comes out? This is answered by solving the Schrödinger equation for the scattering states. Because we have a second order differential equation, we expect that there are two independent solutions for each value of k. We can think of these solutions physically as what you get if you throw the particle in from the left or in from the right. Let's deal with each in turn.

Scattering from the Left

We throw the particle in from the left. When it hits the potential, one of two things can happen: it can bounce back, or it can pass straight through. Of course, this being quantum mechanics, it can quite happily do both at the same time. Mathematically, this means that we are looking for a solution which asymptotically takes the form

$$\psi_R(x) \sim \begin{cases} e^{ikx} + re^{-ikx} & x \to -\infty \\ te^{ikx} & x \to +\infty \end{cases} \tag{1.3}$$

We've labelled this state ψ_R because the ingoing wave is *right*-moving. This can be seen in the first term e^{ikx} which represents the particle we're throwing in from $x \to -\infty$. The second term re^{-ikx} represents the particle that is reflected back to $x \to -\infty$ after hitting the potential. The coefficient $r \in \mathbf{C}$ is called the *reflection amplitude*. Finally, the term te^{ikx} at $x \to +\infty$ represents the particle passing through the potential. The coefficient $t \in \mathbf{C}$ is called the *transmission coefficient*. (Note: in this formula t is a complex number that we have to determine; it is not time!) There is no term e^{-ikx} at $x \to +\infty$ because we're not throwing in any particles from that direction. Mathematically, we have chosen the solution in which this term vanishes.

Before we proceed, it's worth flagging up a conceptual point. Scattering is clearly a dynamical process: the particle goes in, and then comes out again. Yet there's no explicit time dependence in our ansatz (1.3); instead, we have a solution formed of plane waves, spread throughout all of space. It's best to think of these plane waves as describing a beam of particles, with the ansatz (1.3) giving us the steady-state solution in the presence of the potential.

The probability for reflection R and transmission T are given by the usual quantum mechanics rule:

$$R = |r|^2 \quad \text{and} \quad T = |t|^2$$

In general, both R and T will be functions of the wavenumber k. This is what we would like to calculate for a given potential and we will see an example shortly. But, before we do this, there are some observations that we can make using general statements about quantum mechanics.

Given a solution $\psi(x)$ to the Schrödinger equation, we can construct a conserved probability current

$$J(x) = -i\frac{\hbar}{2m}\left(\psi^\star\frac{d\psi}{dx} - \psi\frac{d\psi^\star}{dx}\right)$$

which obeys $dJ/dx = 0$. This means that $J(x)$ is constant. (Mathematically, this is the statement that the Wronskian is constant for the two solutions to the Schrödinger equation). For our scattering solution ψ_R, with asymptotic form (1.3), the probability current as $x \to -\infty$ is given by

$$\begin{aligned} J(x) &= \frac{\hbar k}{2m}\Big[\left(e^{-ikx} + r^\star e^{+ikx}\right)\left(e^{ikx} - re^{-ikx}\right) + \left(e^{ikx} + re^{-ikx}\right)\left(e^{-ikx} - r^\star e^{+ikx}\right)\Big] \\ &= \frac{\hbar k}{m}\left(1 - |r|^2\right) \qquad \text{as } \ x \to -\infty \end{aligned}$$

Meanwhile, as $x \to +\infty$, we have

$$J(x) = \frac{\hbar k}{2m}|t|^2 \qquad \text{as } \ x \to +\infty$$

Equating the two gives

$$1 - |r|^2 = |t|^2 \quad \Rightarrow \quad R + T = 1 \tag{1.4}$$

This should make us happy as it means that probabilities do what probabilities are supposed to do. The particle can only get reflected or transmitted and the sum of the probabilities to do these things equals one.

Scattering from the Right

This time, we throw the particle in from the right. Once again, it can bounce back off the potential or pass straight through. Mathematically, we're now looking for solutions which take the asymptotic form

$$\psi_L(x) \sim \begin{cases} t'e^{-ikx} & x \to -\infty \\ e^{-ikx} + r'e^{+ikx} & x \to +\infty \end{cases} \tag{1.5}$$

where we've now labelled this state ψ_L because the ingoing wave, at $x \to +\infty$, is *left*-moving. We've called the reflection and transmission amplitudes r' and t'.

There is a simple relation between the two solutions ψ_R in (1.3) and ψ_L in (1.5). This follows because the potential $V(x)$ in (1.1) is a real function, so if ψ_R is a solution then so is $\psi_R^\star$. And, by linearity, so is $\psi_R^\star - r^\star \psi_R$ which is given by

$$\psi_R^\star(x) - r^\star \psi_R(x) \sim \begin{cases} (1-|r|^2)e^{-ikx} & x \to -\infty \\ t^\star e^{-ikx} - r^\star t e^{ikx} & x \to +\infty \end{cases}$$

This takes the same functional form as (1.5) except we need to divide through by $t^\star$ to make the normalisations agree. (Recall that scattering states aren't normalised anyway so we're quite at liberty to do this.) Using $1-|r|^2 = |t|^2$, this tells us that there is a solution of the form (1.5) with

$$t' = t \quad \text{and} \quad r' = -\frac{r^\star t}{t^\star} \tag{1.6}$$

Notice that the transition amplitudes are always the same, but the reflection amplitudes can differ by a phase. Nonetheless, this is enough to ensure that the reflection probabilities are the same whether we throw the particle from the left or right: $R = |r|^2 = |r'|^2$.

An Example: A Pothole in the Road

Let's compute r and t for a simple potential, given by

$$V(x) = \begin{cases} -V_0 & -a/2 < x < a/2 \\ 0 & \text{otherwise} \end{cases}$$

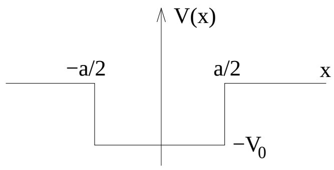


Figure 3:

with $V_0 > 0$. This looks like a pothole in the middle of an, otherwise, flat potential.

Outside the potential, we have the usual plane waves $\psi \sim e^{\pm ikx}$. In the middle of the potential, the solutions to the Schrödinger equation (1.1) take the form

$$\psi(x) = Ae^{iqx} + Be^{-iqx} \qquad x \in [-a/2, a/2] \tag{1.7}$$

where

$$q^2 = \frac{2mV_0}{\hbar^2} + k^2$$

To compute the reflection and transmission amplitudes, r, r' and t, we need to patch the solution (1.7) with either (1.3) or (1.5) at the edges of the potential.

Let's start by scattering from the left, with the solution (1.3) outside the potential. Continuity of the wavefunction at $x = \pm a/2$ tells us that

$$e^{-ika/2} + re^{ika/2} = Ae^{-iqa/2} + Be^{iqa/2} \quad \text{and} \quad te^{ika/2} = Ae^{iqa/2} + Be^{-iqa/2}$$

Meanwhile, matching the derivatives of ψ at $x = \pm a$ gives

$$\frac{k}{q}\left(e^{-ika/2} - re^{ika/2}\right) = Ae^{-iqa/2} - Be^{iqa/2} \quad \text{and} \quad \frac{kt}{q}e^{ika/2} = Ae^{iqa/2} - Be^{-iqa/2}$$

These are four equations with four unknowns: A, B, r and t. One way to proceed is to add and subtract the two equations on the right, and then do the same for the two equations on the left. This allows us to eliminate A and B

$$A = t\left(1 + \frac{k}{q}\right)e^{i(k-q)a/2} = \left(1 + \frac{k}{q}\right)e^{-i(k-q)a/2} + r\left(1 - \frac{k}{q}\right)e^{i(k+q)a/2}$$

$$B = t\left(1 - \frac{k}{q}\right)e^{i(k+q)a/2} = \left(1 - \frac{k}{q}\right)e^{-i(k+q)a/2} + r\left(1 + \frac{k}{q}\right)e^{i(k-q)a/2}$$

We've still got some algebraic work ahead of us. It's grungy but straightforward. Solving these two remaining equations gives us the reflection and transmission coefficients that we want. They are

$$\begin{aligned} r &= \frac{(k^2 - q^2)\sin(qa)e^{-ika}}{(q^2 + k^2)\sin(qa) + 2iqk\cos(qa)} \\ t &= \frac{2iqke^{-ika}}{(q^2 + k^2)\sin(qa) + 2iqk\cos(qa)} \end{aligned} \tag{1.8}$$

Even for this simple potential, the amplitudes are far from trivial. Indeed, they contain a lot of information. Perhaps the simplest lesson we can extract comes from looking at the limit $k \to 0$, where $r \to -1$ and $t \to 0$. This means that if you throw the particle very softly ($k \to 0$), then it won't make it through the potential; it's guaranteed to bounce back.

Conversely, in the limit $k \to \infty$, we have $r = 0$. (Recall that $q^2 = k^2 + 2mV_0/\hbar^2$ so we also have $q \to \infty$ in this limit.) By conservation of probability, we must then have $|t| = 1$ and the particle is guaranteed to pass through. This is what you might expect; if you throw the particle hard enough, it barely notices that the potential is there.

There are also very specific values of the incoming momenta for which $r = 0$ and the particle is assured of passage through the potential. This occurs when $qa = n\pi$ with $n \in \mathbf{Z}$ for which $r = 0$. Notice that you have to fine tune the incoming momenta so that it depends on the details of the potential which, in this example, means V_0 and a.

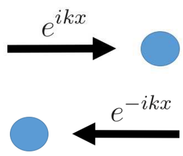
We can repeat the calculation above for scattering from the right. In fact, for our pothole potential, the result is exactly the same and we have $r = r'$. This arises because $V(x) = V(-x)$ so it's no surprise that scattering from the left and right are the same. We'll revisit this in Section 1.1.3.

1.1.2 Introducing the S-Matrix

The *S-matrix* is a convenient way of packaging the information about reflection and transmission coefficients. It is useful both because it highlights new features of the problem, and because it generalises to scattering in higher dimensions.

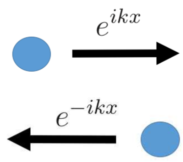
We will start by writing the above solutions in slightly different notation. We have two ingoing asymptotic wavefunctions, one from the left and one from the right

$$\text{Ingoing} \left\{ \begin{array}{lll} \text{right-moving:} & \mathcal{I}_R(x) = e^{+ikx} & x \to -\infty \\ \text{left-moving:} & \mathcal{I}_L(x) = e^{-ikx} & x \to +\infty \end{array} \right.$$



Similarly, there are two outgoing asymptotic wavefunctions,

$$\text{Outgoing} \left\{ \begin{array}{lll} \text{right-moving:} & \mathcal{O}_R(x) = e^{+ikx} & x \to +\infty \\ \text{left-moving:} & \mathcal{O}_L(x) = e^{-ikx} & x \to -\infty \end{array} \right.$$



The two asymptotic solutions (1.3) and (1.5) can then be written as

$$\begin{pmatrix} \psi_R \\ \psi_L \end{pmatrix} = \begin{pmatrix} \mathcal{I}_R \\ \mathcal{I}_L \end{pmatrix} + \mathcal{S} \begin{pmatrix} \mathcal{O}_R \\ \mathcal{O}_L \end{pmatrix} \tag{1.9}$$

where

$$\mathcal{S} = \begin{pmatrix} t & r \\ r' & t' \end{pmatrix} \tag{1.10}$$

This is the *S-matrix*. As we've seen, for any given problem the entries of the matrix are rather complicated functions of k.

The S-matrix has many nice properties, some of which we will describe in these lectures. One of the simplest and most important is that $\mathcal{S}$ is unitary. To see this note that

$$\mathcal{S}\mathcal{S}^\dagger = \begin{pmatrix} |t'|^2 + |r|^2 & t'r'^\star + rt^\star \\ t'^\star r' + tr^\star & |t|^2 + |r'|^2 \end{pmatrix}$$

Unitarity then follows from the conservation of probability. The off-diagonal elements vanish by virtue of the relations $t' = t$ and $r' = -r^\star t/t^\star$ that we found in (1.6). Meanwhile, the diagonal elements are equal to one by (1.4) and so $\mathcal{S}\mathcal{S}^\dagger = \mathbf{1}$. The equivalence between conservation of probability and unitarity of the S-matrix is important, and will generalise to higher dimensions. Indeed, in quantum mechanics the word "unitarity" is often used synonymously with "conservation of probability".

One further property follows from the fact that the wavefunctions $\psi_R(x)$ and $\psi_L(x)$ do not change under complex conjugation if we simultaneously flip $k \to -k$. In other words $\psi(x;k) = \psi^\star(x;-k)$. This means that the S-matrix obeys

$$\mathcal{S}^\star(k) = \mathcal{S}(-k)$$

There are a number of other, more hidden properties of the S-matrix that we will uncover below.

1.1.3 A Parity Basis for Scattering

As we've seen above, for symmetric potentials, with $V(x) = V(-x)$, scattering from the left and right is the same. Let's first make this statement more formal.

We introduce the *parity* operator P which acts on functions $f(x)$ as

$$P : f(x) \to f(-x)$$

For symmetric potentials, we have $[P, H] = 0$ which means that eigenstates of the Hamiltonian can be chosen so that they are also eigenstates of P. The parity operator is Hermitian, $P^\dagger = P$, so its eigenvalues λ are real. But we also have $P^2 f(x) = f(x)$, which means that the eigenvalues must obey $\lambda^2 = 1$. Clearly there are only two possibilities: $\lambda = +1$ and $\lambda = -1$, This means that eigenstates of the Hamiltonian can be chosen to be either even functions ($\lambda = +1$) or odd functions ($\lambda = -1$).

Above we worked with scattering eigenstates ψ_R and ψ_L. These are neither odd nor even. Instead, for a symmetric potential, they are related by $\psi_L(x) = \psi_R(-x)$. This is the reason that symmetric potentials have $r = r'$. If we want to work with the parity eigenstates, we take

$$\begin{aligned}\psi_+(x) &= \psi_R(x) + \psi_L(x) = \psi_R(x) + \psi_R(-x) \\ \psi_-(x) &= -\psi_R(x) + \psi_L(x) = -\psi_R(x) + \psi_R(-x)\end{aligned}$$

which obey $P\psi_\pm(x) = \pm\psi_\pm(x)$.

Often, working with parity eigenstates makes the algebra a little easier. This is particularly true if our problem has a parity-invariant potential, $V(x) = V(-x)$.

The Pothole Example Revisited

Let's see how the use of parity eigenstates can make our calculations simpler. We'll redo the scattering calculation in the pothole, but now we'll take the asymptotic states to be ψ_+ and ψ_-. Physically, you can think of this experiment as throwing in particles from both the left and right at the same time, with appropriate choices of signs.

We start with the even parity wavefunction ψ_+. We want to patch this onto a solution in the middle, but this too must have even parity. This mean that the solution in the pothole takes the form

$$\psi_+(x) = A(e^{iqx} + e^{-iqx}) \qquad x \in [-a/2, a/2]$$

which now has only one unknown coefficient, A. As previously, $q^2 = k^2 + 2mV_0/\hbar^2$. We still need to make sure that both the wavefunction and its derivative are continuous at $x = \pm a/2$. But, because we're working with even functions, we only need to look at one of these points. At $x = a/2$ we get

$$\begin{aligned}e^{-ika/2} + (r+t)e^{ika/2} &= A(e^{iqa/2} + e^{-iqa/2}) \\ \left(-e^{-ika/2} + (r+t)e^{ika/2}\right) &= \frac{q}{k}A(e^{iqa/2} - e^{-iqa/2})\end{aligned}$$

Notice that only the combination $(r+t)$ appears. We have two equations with two unknowns. If we divide the two equations and rearrange, we get

$$r + t = -e^{-ika}\ \frac{q\tan(qa/2) - ik}{q\tan(qa/2) + ik} \tag{1.11}$$

which is all a lot easier than the messy manipulations we had to do when working with ψ_L and ψ_R. Of course, we've only got an expression for $(r+t)$. But we can play the same game for the odd parity eigenstates to get a corresponding expression for $(r-t)$. Now, the solution in the pothole takes the form

$$\psi_-(x) = B(e^{iqx} - e^{-iqx}) \qquad x \in [-a/2, a/2]$$

Requiring continuity of the wavefunction and its derivative at $x = a/2$ we get

$$\begin{aligned} e^{-ika/2} + (r-t)e^{ika/2} &= B(e^{iqa/2} - e^{-iqa/2}) \\ \left(-e^{-ika/2} + (r-t)e^{ika/2}\right) &= \frac{q}{k}B(e^{iqa/2} + e^{-iqa/2}) \end{aligned}$$

Once again, dividing we find

$$r - t = e^{-ika}\frac{q + ik\tan(qa/2)}{q - ik\tan(qa/2)} \tag{1.12}$$

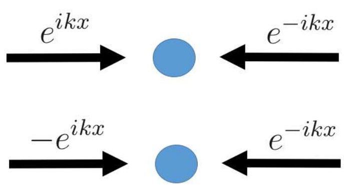
It's not immediately obvious that the expressions (1.11) and (1.12) are the same as those for r and t that we derived previously. But a little bit of algebra should convince you that they agree.

[A helping hand: this little bit of algebra is extremely fiddly if you don't go about it in the right way! Here's a reasonably a streamlined approach. First define the denominator of (1.8) as $D(k) = (q^2 + k^2)\sin(qa) + 2iqk\cos(qa)$. Using the double-angle formula from trigonometry, we can write this as $D(k) = 2\cos^2(qa/2)(q\tan(qa/2) + ik)(q - ik\tan(qa/2))$. We can then add the two expressions in (1.8), and use the double-angle formula again, to get $r + t = 2e^{-ika}\cos^2(qa/2)(q\tan(qa/2) - ik)(ik\tan(qa/2) - q)/D(k)$ This coincides with our formula (1.11). Similar games give us the formula (1.12).]

The S-Matrix in the Parity Basis

We can also think about the S-matrix using our new basis of states. The asymptotic ingoing modes are even and odd functions, given at $|x| \to \infty$ by

$$\text{Ingoing} \begin{cases} \text{parity-even:} \qquad \mathcal{I}_+(x) = e^{-ik|x|} \\ \text{parity-odd:} \qquad \mathcal{I}_-(x) = \text{sign}(x)\, e^{-ik|x|} \end{cases}$$



The two asymptotic outgoing modes are

$$\text{Outgoing} \quad \begin{cases} \text{parity-even:} \qquad \mathcal{O}_+(x) = e^{+ik|x|} \\ \\ \text{parity-odd:} \qquad \mathcal{O}_-(x) = -\text{sign}(x)\, e^{+ik|x|} \end{cases}$$

These are related to our earlier modes by a simple change of basis,

$$\begin{pmatrix} \mathcal{I}_+ \\ \mathcal{I}_- \end{pmatrix} = \mathcal{M} \begin{pmatrix} \mathcal{I}_R \\ \mathcal{I}_L \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \mathcal{O}_+ \\ \mathcal{O}_- \end{pmatrix} = \mathcal{M} \begin{pmatrix} \mathcal{O}_R \\ \mathcal{O}_L \end{pmatrix} \quad \text{with} \quad \mathcal{M} = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$

We can define an S-matrix with respect to this parity basis. In analogy with (1.9), we write asymptotic solutions as

$$\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = \begin{pmatrix} \mathcal{I}_+ \\ \mathcal{I}_- \end{pmatrix} + \mathcal{S}^P \begin{pmatrix} \mathcal{O}_+ \\ \mathcal{O}_- \end{pmatrix} \tag{1.13}$$

where we use the notation $\mathcal{S}^P$ to denote the S-matrix with respect to the parity basis. We write

$$\mathcal{S}^P = \begin{pmatrix} S_{++} & S_{+-} \\ S_{-+} & S_{--} \end{pmatrix}$$

This is related to our earlier S-matrix by a change of basis. We have

$$\mathcal{S}^P = \mathcal{M}S\mathcal{M}^{-1} = \begin{pmatrix} t + (r+r')/2 & (r-r')/2 \\ (r'-r)/2 & t-(r+r')/2 \end{pmatrix}$$

As you may expect, this basis is particularly useful if the underlying potential is symmetric, so $V(x) = V(-x)$. In this case we have $r = r'$ and the S-matrix becomes diagonal. The diagonal components are simply

$$S_{++} = t + r \quad \text{and} \quad S_{--} = t - r$$

In fact, because $\mathcal{S}^p$ is unitary, each of these components must be a phase. This follows because r and t are not independent. First, they obey $|r|^2 + |t|^2 = 1$. Moreover, when $r' = r$, the relation (1.6) becomes

$$rt^\star + r^\star t = 0 \qquad \Rightarrow \qquad \text{Re}(rt\star) = 0$$

This is enough to ensure that both S_{++} and S_{--} are indeed phases. We write them as

$$S_{++} = e^{2i\delta_+(k)} \quad \text{and} \quad S_{--} = e^{2i\delta_-(k)}$$

We learn that for scattering off a symmetric potential, all the information is encoded in two momentum-dependent *phase shifts*, $\delta_\pm(k)$ which tell us how the phases of the outgoing waves $\mathcal{O}_\pm$ are changed with respect to the ingoing waves $\mathcal{I}_\pm$.

1.1.4 Bound States

So far we've focussed only on the scattering states of the problem. We now look at the bound states, which have energy $E < 0$ and are localised near inside the potential. Here, something rather magical happens. It turns out that the information about these bound states can be extracted from the S-matrix, which we constructed purely from knowledge of the scattering states.

To find the bound states, we need to do something clever. We take our scattering solutions, which depend on momentum $k \in \mathbf{R}$, and extend them to the complex momentum plane. This means that we analytically continue out solutions so that they depend on $k \in \mathbf{C}$.

First note that the solutions with $k \in \mathbf{C}$ still obey our original Schrödinger equation (1.1) since, at no point in any of our derivation did we assume that $k \in \mathbf{R}$. The only difficulty comes when we look at how the wavefunctions behave asymptotically. In particular, any putative solution will, in general, diverge exponentially as $x \to +\infty$ or $x \to -\infty$, rendering the wavefunction non-normalisable. However, as we will now show, there are certain solutions that survive.

For simplicity, let's assume that we have a symmetric potential $V(x) = V(-x)$. As we've seen above, this means that there's no mixing between the parity-even and parity-odd wavefunctions. We start by looking at the parity-even states. The general solution takes the form

$$\psi_+(x) = \mathcal{I}_+(x) + S_{++}\mathcal{O}_+(x) = \begin{cases} e^{+ikx} \ + \ S_{++}e^{-ikx} & x \to -\infty \\ e^{-ikx} \ + \ S_{++}e^{+ikx} & x \to +\infty \end{cases}$$

Suppose that we make k pure imaginary and write

$$k = i\lambda$$

with $\lambda > 0$. Then we get

$$\psi_+(x) = \begin{cases} e^{-\lambda x} \ + \ S_{++}e^{+\lambda x} & x \to -\infty \\ e^{+\lambda x} \ + \ S_{++}e^{-\lambda x} & x \to +\infty \end{cases} \tag{1.14}$$

Both terms proportional to S_{++} decay asymptotically, but the other terms diverge. This is bad. However, there's a get-out. For any fixed k (whether real or complex), S_{++} is simply a number. That means that we're quite at liberty to divide by it. Indeed, the wavefunction above isn't normalised anyway, so dividing by a constant isn't going to change anything. We get

$$\psi_+(x) = \begin{cases} S_{++}^{-1}\, e^{-\lambda x} \; + \; e^{+\lambda x} & x \to -\infty \\ S_{++}^{-1}\, e^{+\lambda x} \; + \; e^{-\lambda x} & x \to +\infty \end{cases} \tag{1.15}$$

Now we can see the loop-hole. The wavefunction above is normalisable whenever we can find a $\lambda > 0$ such that

$$S_{++}(k) \to \infty \quad \text{ as } k \to i\lambda$$

This, then, is the magic of the S-matrix. Poles in the complex momentum plane that lie on the positive imaginary axis (i.e. $k = i\lambda$ with $\lambda > 0$) correspond to bound states. This information also tells us the energy of the bound state since, as we saw in (1.2), it is given by

$$E = -\frac{\hbar^2 \lambda^2}{2m}$$

We could also have set $k = -i\lambda$, with $\lambda > 0$. In this case, it is the terms proportional to S_{++} in (1.14) which diverge and the wavefunction is normalisable only if $S_{++}(k = -i\lambda) = 0$. However, since S_{++} is a phase, this is guaranteed to be true whenever $S_{++}(k = i\lambda)$ has a pole, and simply gives us back the solution above.

Finally, note that exactly the same arguments hold for parity-odd wavefunctions. There is a bound state whenever $S_{--}(k)$ has a pole at $k = i\lambda$ with $\lambda > 0$.

An Example: Stuck in the Pothole

We can illustrate this with our favourite example of the square well, of depth $-V_0$ and width a. We already computed the S-matrix in (1.11) and (1.12). We have,

$$S_{++}(k) = r + t = -e^{-ika}\, \frac{q\tan(qa/2) - ik}{q\tan(qa/2) + ik}$$

where $q^2 = 2mV_0/\hbar^2 + k^2$. Setting $k = i\lambda$, we see that this has a pole when

$$\lambda = q\tan\left(\frac{qa}{2}\right) \quad \text{ with } \quad \lambda^2 + q^2 = \frac{2mV_0}{\hbar^2}$$

These are the usual equations that you have to solve when finding parity-even bound states in a square well. The form of the solutions is simplest to see if we plot these equations, as shown in the left-hand of Figure 4. There is always at least one bound state, with more appearing as the well gets deeper.

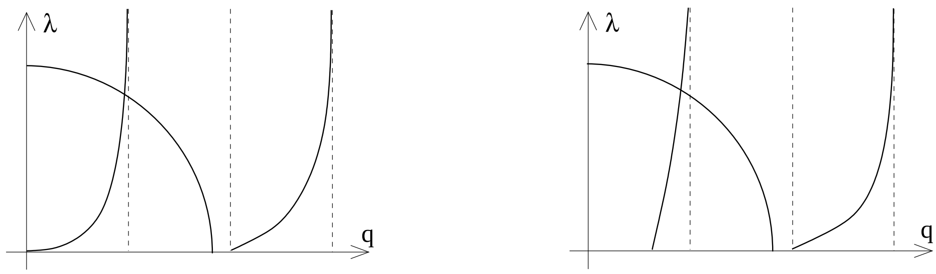


Figure 4: Bound state of even parity always exist, since the two equations shown on the left always have a solution with $\lambda, q > 0$. Bound states of odd parity, shown on the right, exist if the potential is deep enough.

Similarly, if we look at the parity-odd wavefunctions, we have

$$S_{--}(k) = t - r = e^{-ika}\frac{q + ik\tan(qa/2)}{q - ik\tan(qa/2)}$$

which has a pole at $k = i\lambda$ when

$$q = -\lambda\tan\left(\frac{qa}{2}\right) \quad \text{with} \quad \lambda^2 + q^2 = \frac{2mV_0}{\hbar^2} \tag{1.16}$$

This too reproduces the equations that we found in earlier courses in quantum mechanics when searching for bound states in a square well. Now there is no guarantee that a bound state exists; this only happens if the potential is deep enough.

1.1.5 Resonances

We might wonder if there's any other information hidden in the analytic structure of the S-matrix. In this section, we will see that there is, although its interpretation is a little more subtle.

First, the physics. Let's think back again to the example shown on the right. One the one hand, we know that there can be no bound states in such a trap because they will have $E > 0$. Any particle that we place in the trap will ultimately tunnel out. On the other hand, if the walls of the trap are very large then we might expect that the particle stays there for a long time before it eventually escapes. In this situation, we talk of a *resonance*. These are also referred to as *unstable* or *metastable* states. Our goal is to show how such resonances are encoded in the S-matrix.

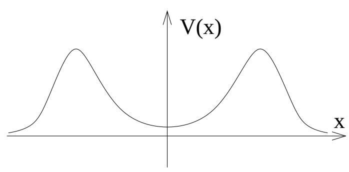


Figure 5:

Now, the maths. We'll restrict attention to parity-even functions. Suppose that the S-matrix S_{++} has a pole that lies on the complex momentum plane at position

$$k = k_0 - i\gamma$$

On general grounds, the wavefunction will have a second pole at $-k^\star = -k_0 - i\gamma$. We'd like to interpret these poles. First note that the energy is also imaginary

$$E = \frac{\hbar^2 k^2}{2m} \equiv E_0 - i\frac{\Gamma}{2} \tag{1.17}$$

with $E_0 = \hbar^2(k_0^2 - \gamma^2)/2m$ and $\Gamma = 2\hbar^2\gamma k_0/m$. An imaginary energy may sound strange, but it is has a very natural interpretation. Recall that the time dependence of the wavefunction is given by

$$e^{-iEt/\hbar} = e^{-iE_0 t/\hbar}\, e^{-\Gamma t/2\hbar} \tag{1.18}$$

This is the first clue that we need. We see that, for $\gamma > 0$, the overall form of the wavefunction decays exponentially with time. This is the characteristic behaviour of unstable states. A wavefunction that is initially supported inside the trap will be very small there at time much larger than $\tau = 1/\Gamma$. Here τ is called the *half-life* of the state, while Γ is usually referred to as the *width* of the state. (We'll see why in Section 1.2).

Where does the particle go? Including the time dependence (1.18), the same argument that led us to (1.15) now tells us that when $S_{++} \to \infty$, the solution takes the asymptotic form

$$\psi_+(x,t) = \begin{cases} e^{-iE_0 t/\hbar}\, e^{-ik_0 x}\, e^{-\gamma x - \Gamma t/2\hbar} & x \to -\infty \\ e^{-iE_0 t/\hbar}\, e^{+ik_0 x}\, e^{+\gamma x - \Gamma t/2\hbar} & x \to +\infty \end{cases} \tag{1.19}$$

The first two exponential factors oscillate. But the final factor varies as

$$e^{\pm\gamma(x \mp vt)} \quad \text{where} \quad v = \frac{\Gamma}{2\hbar\gamma} = \frac{\hbar k_0}{m}$$

This has the interpretation of a particle moving with momentum $\hbar k_0$. This, of course, is the particle which has escaped the trap.

Note that for fixed time t, these wavefunctions are not normalisable: they diverge at both $x \to \pm\infty$. This shouldn't concern us, because, although our wavefunctions are eigenstates of the Hamiltonian, they are not interpreted as stationary states. Indeed, it had to be the case. An unstable state has complex energy, but standard theorems in linear algebra tell us that a Hermitian operator like the Hamiltonian must have real eigenvalues. We have managed to evade this theorem only because these wavefunctions are non-normalisable and so do not, strictly speaking, live in the Hilbert space.

There's a lesson buried in all of this. If we were to take the standard axioms of quantum mechanics, we would simply throw away wavefunctions of the form (1.19) on the grounds that they do not lie in the Hilbert space and so are unphysical. But this would be a mistake: the wavefunctions do contain interesting physics, albeit of a slightly different variety than we are used to. Sometimes it's worth pushing our physical theories beyond our comfort zone to see what is lurking there.

The upshot of this discussion is that poles of the S-matrix in the lower-half complex plane correspond to resonances. It is often useful to write S_{++} as a function of energy rather than momentum. (They are related by (1.17)). Since S_{++} is a phase, close to a resonance it necessarily takes the form

$$S_{++} = \frac{E - E_0 - i\Gamma/2}{E - E_0 + i\Gamma/2}$$

An Example: A Pair of Delta-Functions

A pair of delta functions provide a simple and tractable example to illustrate the idea of resonances. The potential is given by

$$V(x) = V_0\Big[\delta(x-1) + \delta(x+1)\Big]$$

Recall that the effect of the delta-functions is simply to change the boundary conditions at $x = \pm 1$ when solving the Schrödinger equation. All wavefunctions should be continuous at $x = \pm 1$, but their derivatives are discontinuous. For example, at $x = +1$, solutions obey

$$\lim_{\epsilon\to 0}\Big[\psi'(1+\epsilon) - \psi'(1-\epsilon)\Big] = U_0\psi(1) \quad \text{ with } \quad U_0 = \frac{2mV_0}{\hbar^2}$$

Working in the parity basis makes life simpler, not least because you only need to consider the matching at one of the delta-functions, with the other then guaranteed. The computation of the S-matrix is a problem on the exercise sheet. You will find

$$S_{++} = e^{-2ik}\left[\frac{(2k - iU_0)e^{ik} - iU_0 e^{-ik}}{(2k + iU_0)e^{-ik} + iU_0 e^{ik}}\right]$$

Note that the denominator is the complex conjugate of the numerator, ensuring that S_{++} is a phase, as expected. The poles of this S-matrix are given by solutions to the equation

$$e^{2ik} = -\left(1 - \frac{2ik}{U_0}\right) \tag{1.20}$$

To understand the physics behind this, let's first look at the situation where $U_0 \to \infty$, so that the weight of the delta-functions gets infinitely large. Then the poles sit at

$$e^{2ik} = -1 \quad \Rightarrow \quad k = k_n = \left(n + \frac{1}{2}\right)\pi$$

These correspond to bound states trapped between the two wavefunctions. For example, the $n = 0$ state is shown in the figure. Note that they're rather unusual because the poles sit on the real k-axis, rather than the imaginary k-axis. Correspondingly, these bound states have $E > 0$. This strange behaviour is only allowed because we have an infinitely large potential which forbids particles on one side of the barrier to cross to the other.

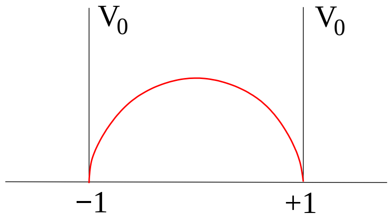


Figure 6:

As a side remark, we note that this same impenetrable behaviour is seen in scattering. When $U_0 \to \infty$, the S-matrix becomes $S_{++} \to -e^{2ik}$. This tells us that a particle coming from outside is completely reflected off the infinitely large barrier. The minus sign is the standard phase change after reflection. The factor of e^{2ik} is because the waves are forbidden from travelling through the region between the delta functions, which has width $x = 2$. As a result, the phase is shifted by e^{ikx} from what it would be if the barriers were removed.

Let's now look at what happens when U_0 is large, but finite? We'll focus on the lowest energy bound state with $n = 0$. We can expand (1.20) in $1/U_0$. (This too is left as a problem on the exercise sheet.) We find

$$k = \frac{\pi}{2} + \alpha - i\gamma$$

with

$$\alpha \approx -\frac{\pi}{2U_0} + \frac{\pi}{2U_0^2} + \mathcal{O}\left(\frac{1}{U_0^3}\right) \quad \text{and} \quad \gamma \approx \frac{\pi^2}{4U_0^2} + \mathcal{O}\left(\frac{1}{U_0^3}\right)$$

Note, in particular, that $\gamma > 0$, so the pole moves off the real axis and into the lower half-plane. This pole now has all the properties that we described at the beginning of this section. It describes a state, trapped between the two delta-functions, which decays with half-life

$$\tau = \frac{\hbar}{\Gamma} = \frac{4mU_0^2}{\hbar\pi^3}\left(1 + \mathcal{O}\left(\frac{1}{U_0}\right)\right)$$

This is the resonance.

1.2 Scattering in Three Dimensions

Our real interest in scattering is for particles moving in three spatial dimensions, with Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r})$$

Recall that there are two distinct interpretations for such a Hamiltonian

- We could think of this as the motion of a single particle, moving in a fixed background potential $V(\mathbf{r})$. This would be appropriate, for example, in Rutherford's famous experiment where we fire an alpha particle at a gold nucleus.

- Alternatively, We could think of this as the relative motion of two particles, separated by distance $\mathbf{r}$, interacting through the force $\mathbf{F} = -\nabla V(\mathbf{r})$. We could take $V(r)$ to be the Coulomb force, to describe the scattering of electrons, or the Yukawa force to describe the scattering of neutrons.

In this section, we will use language appropriate to the first interpretation, but everything we say holds equally well in the second. Throughout this section, we will work with rotationally invariant (i.e. central) potentials, so that $V(\mathbf{r}) = V(|\mathbf{r}|)$.

1.2.1 The Cross-Section

Our first goal is to decide what we want to calculate. The simple reflection and transmission coefficients of the one-dimensional problem are no longer appropriate. We need to replace them by something a little more complicated. We start by thinking of the classical situation.

Classical Scattering

Suppose that we throw in a single particle with kinetic energy E. Its initial trajectory is characterised by the *impact parameter* b, defined as the closest the particle would get to the scattering centre at $r = 0$ if there were no potential. The particle emerges with *scattering angle* θ, which is the angle between the asymptotic incoming and outgoing trajectories, as shown in the figure. By solving the classical equations of motion, we can compute $\theta(b; E)$ or, equivalently, $b(\theta; E)$.

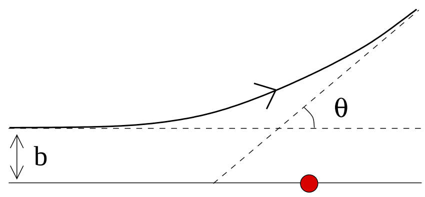


Figure 7:

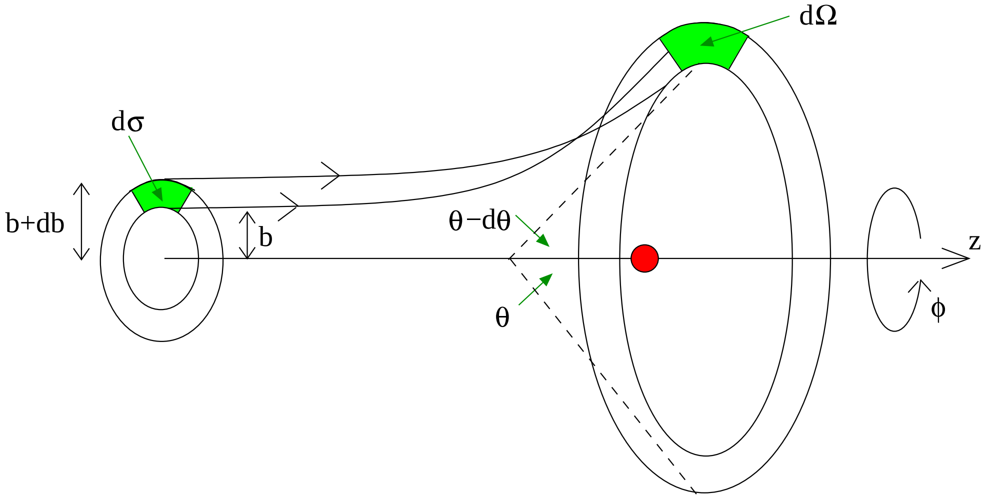


Figure 8: What becomes of an infinitesimal cross-sectional area after scattering.

Now consider a uniform beam of particles, each with kinetic energy E. We want to understand what becomes of this beam. Consider the cross-sectional area, denoted $d\sigma$ in Figure 8. We write this as

$$d\sigma = b\, d\phi\, db$$

The particles within $d\sigma$ will evolve to the lie in a cone of solid angle $d\Omega$, given by

$$d\Omega = \sin\theta\, d\phi\, d\theta$$

where, for central potentials, the infinitesimal angles $d\phi$ are the same in both these formulae. The *differential cross-section* is defined to be

$$\frac{d\sigma}{d\Omega} = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right|$$

The left-hand side should really be $|d\sigma/d\Omega|$, but we'll usually drop the modulus. The differential cross-section is a function of incoming momentum k, together with the outgoing angle θ.

More colloquially, the differential cross-section can be thought of as

$$\frac{d\sigma}{d\Omega}\, d\Omega = \frac{\text{Number of particles scattered into } d\Omega \text{ per unit time}}{\text{Number of incident particles per area } d\sigma \text{ per unit time}}$$

We write this in terms of *flux*, defined to be the number of particles per unit area per unit time. In this language, the differential cross-section is

$$\frac{d\sigma}{d\Omega} = \frac{\text{Scattered flux}}{\text{Incident flux}}$$

3. Band Structure

In this chapter, we start our journey into the world of condensed matter physics. This is the study of the properties of "stuff". Here, our interest lies in a particular and familiar kind of stuff: solids.

Solids are collections of tightly bound atoms. For most solids, these atoms arrange themselves in regular patterns on an underlying crystalline lattice. Some of the electrons of the atom then disassociate themselves from their parent atom and wander through the lattice environment. The properties of these electrons determine many of the properties of the solid, not least its ability to conduct electricity.

One might imagine that the electrons in a solid move in a fairly random fashion, as they bounce from one lattice site to another, like a ball in a pinball machine. However, as we will see, this is not at all the case: the more fluid nature of quantum particles allows them to glide through a regular lattice, almost unimpeded, with a distorted energy spectrum the only memory of the underlying lattice.

In this chapter, we will focus on understanding how the energy of an electron depends on its momentum when it moves in a lattice environment. The usual formula for kinetic energy, $E = \frac{1}{2}mv^2 = p^2/2m$, is one of the first things we learn in theoretical physics as children. As we will see, a lattice changes this in interesting ways, the consequences of which we will explore in chapter 4.

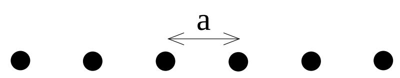
3.1 Electrons Moving in One Dimension

We begin with some particularly simple toy models which capture much of the relevant physics. These toy models describe an electron moving in a one-dimensional lattice. We'll take what lessons we can from this before moving onto more realistic descriptions of electrons moving in higher dimensions.

3.1.1 The Tight-Binding Model

The tight-binding model is a caricature of electron motion in solid in which space is made discrete. The electron can sit only on the locations of atoms in the solid and has some small probability to hop to a neighbouring site due to quantum tunnelling.

To start with our "solid" consists of a one-dimensional lattice of atoms. This is described by N points arranged along a line, each separated by distance a.



Consider a single electron moving on this lattice. We will assume that the electron can only sit on a given lattice point; it's not allowed to roam between lattice points. This is supposed to mimic the idea that electrons are bound to the atoms in a lattice and goes by the name of the *tight-binding approximation*. (We'll see exactly what we're neglecting in this approximation later.)

When the electron sits on the n^{th} atom, we denote the quantum state as $|n\rangle$. These states are considered orthogonal to each other, so

$$\langle n|m\rangle = \delta_{nm}$$

Clearly the total Hilbert space has dimension N, and is spanned by $|n\rangle$ with $n = 1, \ldots, N$.

What kind of Hamiltonian will govern the dynamics of this electron? If the electron just remains on a given atom, an appropriate Hamiltonian would be

$$H_0 = E_0 \sum_n |n\rangle\langle n|$$

Each of the position states $|n\rangle$ is an energy eigenstate of H_0 with energy E_0. The electrons governed by this Hamiltonian don't move. This Hamiltonian is boring.

To make things more interesting, we need to include the possibility that the electron can tunnel from one site to another. How to do this? Well, the Hamiltonian governs time evolution. In some small time increment of time Δt, a state evolves as

$$|\psi\rangle \mapsto |\psi\rangle - \frac{i\Delta t}{\hbar} H|\psi\rangle + \mathcal{O}(\Delta t^2)$$

This means that if we want the possibility for the electron to hop from one site to another, we should include in the Hamiltonian a term of the form $|m\rangle\langle n|$ which takes an electron at site n and moves it to an electron at site m.

There is one last ingredient that we want to feed into our model: locality. We don't want electrons to disappear and reappear many thousands of lattice spacings down the line. We want our model to describe electrons hopping from one atom to neighbouring atoms. This motivates our final form of the Hamiltonian,

$$H = E_0 \sum_n |n\rangle\langle n| - t \sum_n \Big(|n\rangle\langle n+1| + |n+1\rangle\langle n| \Big) \tag{3.1}$$

First a comment on notation: the parameter t is called the *hopping parameter*. It is not time; it is simply a number which determines the probability that a particle will hop to a neighbouring site. (More precisely, the ratio t^2/E_0^2 will determine the probability. of hopping.) It's annoying notation, but unfortunately t is the canonical name for this hopping parameter so it's best we get used to it now.

Now back to the physics encoded in H. We've chosen a Hamiltonian that only includes hopping terms between neighbouring sites. This is the simplest choice; we will describe more general choices later. Moreover, the probability of hopping to the left is the same as the probability of hopping to the right. This is required because H must be a Hermitian operator.

There's one final issue that we have to address before solving for the spectrum of H: what happens at the edges? Again, there are a number of different possibilities but none of the choices affect the physics that we're interested in here. The simplest option is simply to declare that the lattice is periodic. This is best achieved by introducing a new state $|N+1\rangle$, which sits to the right of $|N\rangle$, and is identified with $|N+1\rangle \equiv |1\rangle$.

Solving the Tight-Binding Model

Let's now solve for the energy eigenstates of the Hamiltonian (3.1). A general state can be expanded as

$$|\psi\rangle = \sum_m \psi_m |m\rangle$$

with $\psi_n \in \mathbf{C}$. Substituting this into the Schrödinger equation gives

$$H|\psi\rangle = E|\psi\rangle \quad \Rightarrow \quad E_0 \sum_m \psi_m |m\rangle - t\Big(\sum_m \psi_{m+1}|m\rangle + \psi_m |m+1\rangle\Big) = E\sum_n \psi_m |m\rangle$$

If we now take the overlap with a given state $\langle n|$, we get the set of linear equations for the coefficients ψ_n

$$\langle n|H|\psi\rangle = E\langle n|\psi\rangle \quad \Rightarrow \quad E_0\psi_n - t(\psi_{n+1} + \psi_{n-1}) = E\psi_n \tag{3.2}$$

These kind of equations arise fairly often in physics. (Indeed, they will arise again in Section 5 when we come to discuss the vibrations of a lattice.) They are solved by the ansatz

$$\psi_n = e^{ikna} \tag{3.3}$$

Or, if we want to ensure that the wavefunction is normalised, $\psi_n = e^{ikna}/\sqrt{N}$. The exponent k is called the *wavenumber*. The quantity $p = \hbar k$ plays a role similar to momentum in our discrete model; we will discuss the ways in which it is like momentum in Section 3.1.4. We'll also often be lazy and refer to k as *momentum*.

The wavenumber has a number of properties. First, the set of solutions remain the same if we shift $k \to k + 2\pi/a$ so the wavenumber takes values in

$$k \in \left[-\frac{\pi}{a}, +\frac{\pi}{a}\right) \tag{3.4}$$

This range of k is given the fancy name *Brillouin zone*. We'll see why this is a useful concept that deserves its own name in Section 3.2.

There is also a condition on the allowed values of k coming from the requirement of periodicity. We want $\psi_{N+1} = \psi_1$, which means that $e^{ikNa} = 1$. This requires that k is quantised in units of $2\pi/aN$. In other words, within the Brillouin zone (3.4) there are exactly N quantum states of the form (3.3). But that's what we expect as it's the dimension of our Hilbert space; the states (3.3) form a different basis.

States of the form (3.3) have the property that

$$\psi_{n\pm1} = e^{\pm ika}\psi_n$$

This immediately ensures that equation (3.2) is solved for any value of k, with the energy eigenvalue

$$E = E_0 - 2t\cos(ka) \tag{3.5}$$

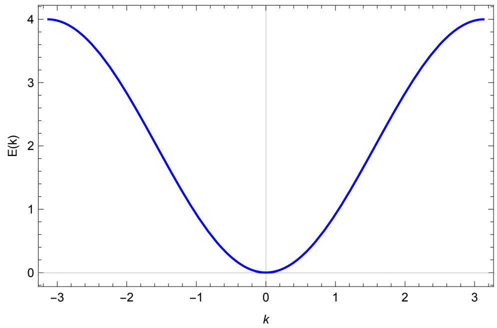


Figure 23:

The spectrum is shown in the figure for $t > 0$. (The plot was made with $a = t = 1$ and $E_0 = 2$.) The states with $k > 0$ describe electrons which move to the right; those with $k < 0$ describe electrons moving to the left.

There is a wealth of physics hiding in this simple result, and much of the following sections will be fleshing out these ideas. Here we highlight a few pertinent points

- The electrons do not like to sit still. The eigenstates $|n\rangle$ of the original Hamiltonian H_0 were localised in space. One might naively think that adding a tiny hopping parameter t would result in eigenstates that were spread over a few sites. But this is wrong. Instead, all energy eigenstates are spread throughout the whole lattice. Arbitrarily small local interactions result in completely delocalised energy eigenstates.

- The energy eigenstates of H_0 were completely degenerate. Adding the hopping term lifts this degeneracy. Instead, the eigenstates are labelled by the wavevector

k and have energies (3.5) that lie in a range $E(k) \in [E_0 - 2t, E_0 + 2t]$. This range of energies is referred to a *band* and the difference between the maximum and minimum energy (which is $4t$ in this case) is called the *band width.* In our simple model, we have just a single energy band. In subsequent models, we will see multiple bands emerging.

- For suitably small momentum, $k \ll \pi/a$, we can Taylor expand the energy (3.5) as

$$E(k) \approx (E_0 - 2t) + ta^2k^2$$

Up to a constant, this takes the same form as a free particle moving in the continuum,

$$E_{\text{free}} = \frac{\hbar^2 k^2}{2m} \tag{3.6}$$

This is telling us that low energy, low momentum particles are unaware that they are moving on an underlying lattice. Instead, they act as if they are moving along a continuous line with *effective mass* $m^\star = \hbar^2/2ta^2$. Notice that in this model the effective mass has nothing to do with the physical mass of the electron; it is inherited from properties of the lattice.

- There is a cute reciprocity between the properties of momentum and position. We know from our first course on quantum mechanics that if space is made finite — for example, a particle in a box, or a particle moving on a circle — then momentum becomes discrete. We also saw this above as the periodic boundary conditions enforced the wavenumber to be quantised in units of $2\pi/Na$.

  However, our tight-binding model also exhibits the converse phenomenon: when we make space discrete, momentum becomes periodic: it has to lie in the Brillouin zone (3.4). More generally, discreteness is the Fourier transform of compactness.

A First Look at Metals and Insulators

There's further physics to uncover if we consider more than one electron moving in the lattice. This section is just to give a flavour of these ideas; we will discuss them in more detail in Section 4.1. For simplicity, we will assume that the electrons do not interact with each other. Now the state of the system is governed by the Pauli exclusion principle: two electrons are not allowed to occupy the same state.

As we have seen, our tight-binding model contains N states. However, each electron has two internal states, spin $|\uparrow\rangle$ and spin $|\downarrow\rangle$. This means that, in total, each electron can be in one of $2N$ different states. Invoking the Pauli exclusion principle, we see that our tight-binding model makes sense as long as the number of electrons is less than or equal to $2N$.

The Pauli exclusion principle means that the ground state of a multi-electron system has interesting properties. The first two electrons that we put in the system can both sit in the lowest energy state with $k = 0$ as long as they have opposite spins. The next electron that we put in finds these states occupied; it must sit in the next available energy state which has $k = \pm 2\pi/Na$. And so this continues, with subsequent electrons sitting in the lowest energy states which have not previously been occupied. The net result is that the electrons fill all states up to some final k_F which is known as the *Fermi momentum*. The boundary between the occupied and unoccupied states in known as the *Fermi surface*. Note that it is a surface in momentum space, rather than in real space. We will describe this in more detail in Section 4.1. (See also the lectures on Statistical Physics.)

How many electrons exist in a real material? Here something nice happens, because the electrons which are hopping around the lattice come from the atoms themselves. One sometimes talks about each atom "donating" an electron. Following our chemist friends, these are called *valence electrons*. Given that our lattice contains N atoms, it's most natural to talk about the situation where the system contains ZN electrons, with Z an integer. The atom is said to have valency Z.

Suppose $Z = 1$, so we have N electrons. Then only half of the states are filled and $k_F = \pi/2a$. This is shown in the figure. Note that there are as many electrons moving to the left (with $k < 0$) as there are electrons moving to the right ($k > 0$). This is the statement that there is no current in the ground state of the system.

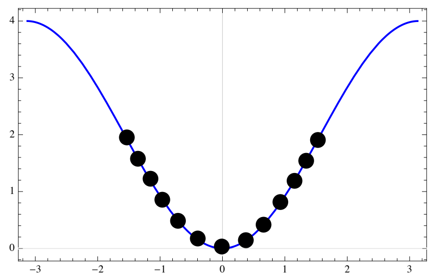


Figure 24:

We can now ask: what are the low-energy excitations of the system? We see that there are many: we can take any electron just below the Fermi surface and promote it to an electron just above the Fermi surface at a relatively small cost in energy. This becomes particularly relevant if we perturb the system slightly. For example, we could ask: what happens if we apply an electric field? As we will describe in more detail in 4.1.1, the ground state of the system re-arranges itself at just a small cost of energy: some left-moving states below the Fermi surface become unoccupied, while right-moving states above the Fermi surface become occupied. Now, however, there are more electrons with $k > 0$ than with $k < 0$. This results in an electrical current. What we have just described is a *conductor*.

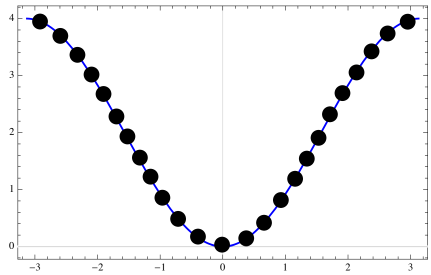


Figure 25:

Let's contrast this with what happens when we have $2N$ electrons in the system. Now we don't get any choice about how to occupy states since all are occupied. Said another way, the *multi-particle* Hilbert space contains just a single state: the fully filled band. This time, if we perturb with an electric field then the electrons can't move anywhere, simply because there's no where for them to go: they are locked in place by the Pauli principle. This means that, despite the presence of the electric field, there is no electric current. This is what we call an *insulator*. (It is sometimes said to be a *band* insulator to distinguish it from other mechanisms that also lead to insulating behaviour.)

The difference between a conductor and an insulator is one of the most striking characterisations of materials, one that we all learn in high school. The rough sketch above is telling us that this distinction arises due to quantum phenomena: the formation of energy bands and the Pauli exclusion principle. We'll explore this more in Section 4.1.

3.1.2 Nearly Free Electrons

The tight-binding model is an extreme cartoon of the real physics in which space is discrete; electrons are stuck on atomic sites with a non-vanishing probability to hop to a neighbouring site. In this section we present another cartoon that is designed to capture the opposite extreme.

We will assume that our electron is free to move anywhere along the line, parameterised by the position x. To mimic the underlying lattice, we add a weak, periodic potential $V(x)$. This means that we consider the Hamiltonian

$$H = \frac{p^2}{2m} + V(x)$$

where $p = -i\hbar d/dx$ is the usual momentum operator. The periodicity of the potential means that it satisfies

$$V(x + a) = V(x) \tag{3.7}$$

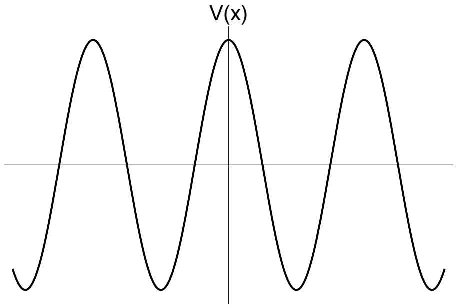


Figure 26: A periodic sine wave.

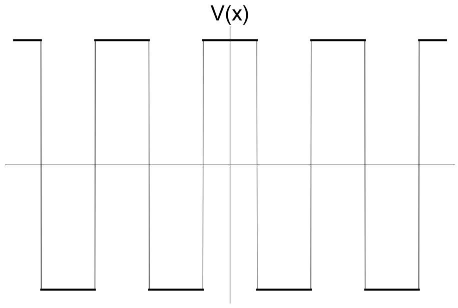


Figure 27: A periodic square wave.

For example, the potential could take the form of a sine wave, or a square wave as shown in the figure, or it could be a an infinite series of delta functions. For much of our discussion we won't need the exact form of the potential.

To avoid discussing edge effects, it's again useful to consider the particle moving on a circle $\mathbf{S}^1$ of length (circumference) L. This is compatible with the periodicity requirement (3.7) only if $L/a = N \in \mathbf{Z}$. The integer N plays the role of the number of atoms in the lattice.

In the absence of the potential, the eigenstates are the familiar plane waves $|k\rangle$, labelled by the momentum $p = \hbar k$. Because we are on a circle, the wavenumber of k is quantised in units of $2\pi/L$. The associated wavefunctions are

$$\psi_k(x) = \langle x|k\rangle = \frac{1}{\sqrt{L}} e^{ikx} \tag{3.8}$$

These states are are orthonormal, with

$$\langle k|k'\rangle = \frac{1}{L}\int dx\ e^{i(k'-k)x} = \delta_{k,k'} \tag{3.9}$$

(Recall that we are living on a circle, so the momenta k are discrete and the Kronecker delta is the appropriate thing to put on the right-hand side.) Meanwhile, the energy of a free particle is given by

$$E_0(k) = \frac{\hbar^2 k^2}{2m} \tag{3.10}$$

Our goal is to understand how the presence of the potential $V(x)$ affects this energy spectrum. To do this, we work perturbatively. However, perturbation theory in the present situation is a little more subtle than usual. Let's see why.

Perturbation Theory

Recall that the first thing we usually do in perturbation theory is decide whether we have non-degenerate or degenerate energy eigenstates. Which do we have in the present case? Well, all states are trivially degenerate because the energy of a free particle moving to the right is the same as the energy of a free particle moving to the left: $E_0(k) = E_0(-k)$. But the fact that the two states $|k\rangle$ and $|-k\rangle$ have the same energy does not necessarily mean that we have to use degenerate perturbation theory. This is only true if the perturbation causes the two states to mix.

To see what happens we will need to compute matrix elements $\langle k|V|k'\rangle$. The key bit of physics is the statement that the potential is periodic (3.7). This ensures that it can be Fourier expanded

$$V(x) = \sum_{n\in\mathbf{Z}} V_n\, e^{2\pi i n x/a} \qquad \text{with} \quad V_n = V_{-n}^\star$$

where the Fourier coefficients follow from the inverse transformation

$$V_n = \frac{1}{a}\int_0^a dx\; V(x)\, e^{-2\pi i n x/a}$$

The matrix elements are then given by

$$\langle k|V|k'\rangle = \frac{1}{L}\int dx\; \sum_{n\in\mathbf{Z}} V_n\, e^{i(k'-k+2\pi n/a)x} = \sum_{n\in\mathbf{Z}} V_n\, \delta_{k-k',2\pi n/a} \tag{3.11}$$

We see that we get mixing only when

$$k = k' + \frac{2\pi n}{a}$$

for some integer n. In particular, we get mixing between degenerate states $|k\rangle$ and $|-k\rangle$ only when

$$k = \frac{\pi n}{a}$$

for some n. The first time that this happens is when $k = \pi/a$. But we've seen this value of momentum before: it is the edge of the Brillouin zone (3.4). This is the first hint that the tight-binding model and nearly free electron model share some common features.

With this background, let's now try to sketch the basic features of the energy spectrum as a function of k.

Low Momentum: With low momentum $|k| \ll \pi/a$, there is no mixing between states at leading order in perturbation theory (and very little mixing at higher order). In this regime we can use our standard results from non-degenerate perturbation theory. Expanding the energy to second order, we have

$$E(k) = \frac{\hbar^2 k^2}{2m} + \langle k|V|k\rangle + \sum_{k' \neq k} \frac{|\langle k|V|k'\rangle|^2}{E_0(k) - E_0(k')} + \ldots \tag{3.12}$$

From (3.11), we know that the first order correction is $\langle k|V|k\rangle = V_0$, and so just gives a constant shift to the energy, independent of k. Meanwhile, the second order term only gets contributions from $|k'\rangle = |k + 2\pi n/a\rangle$ for some n. When $|k| \ll \pi/a$, these corrections are small. We learn that, for small momenta, the particle moves as if unaffected by the potential. Intuitively, the de Broglie wavelength $2\pi/k$ of the particle much greater than the wavelength a of the potential, and the particle just glides over it unimpeded.

The formula (3.12) holds for low momenta. It also holds for momenta $\pi n/a \ll k \ll \pi(n+1)/a$ which are far from the special points where mixing occurs. However, the formula knows about its own failings because if we attempt to use it when $k = n\pi/a$ for some n, the the numerator $\langle k|V|-k\rangle$ is finite while the denominator becomes zero. Whenever perturbation theory diverges in this manner it's because we're doing something wrong. In this case it's because we should be working with degenerate perturbation theory.

At the Edge of the Brillouin Zone: Let's consider the momentum eigenstates which sit right at the edge of the Brillouin zone, $k = \pi/a$, or at integer multiples

$$k = \frac{n\pi}{a}$$

As we've seen, these are the values which mix due to the potential perturbation and we must work with degenerate perturbation theory.

Let's recall the basics of degenerate perturbation theory. We focus on the subsector of the Hilbert space formed by the two degenerate states, in our case $|k\rangle$ and $|k'\rangle = |-k\rangle$. To leading order in perturbation theory, the new energy eigenstates will be some linear combination of these original states $\alpha|k\rangle + \beta|k'\rangle$. We would like to figure out what choice of α and β will diagonalise the new Hamiltonian. There will be two such choices since there must, at the end of the day, remain two energy eigenstates. To determine the correct choice of these coefficients, we write the Schrödinger equation, restricted to this subsector, in matrix form

$$\begin{pmatrix} \langle k|H|k\rangle & \langle k|H|k'\rangle \\ \langle k'|H|k\rangle & \langle k'|H|k'\rangle \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \tag{3.13}$$

We've computed the individual matrix elements above: using the fact that the states $|k\rangle$ are orthonormal (3.9), the unperturbed energy (3.10) and the potential matrix elements (3.11), our eigenvalue equation becomes

$$\begin{pmatrix} E_0(k) + V_0 & V_n \\ V_n^\star & E_0(k') + V_0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \tag{3.14}$$

where, for the value $k = -k' = n\pi/a$ of interest, $E_0(k) = E_0(k') = n^2\hbar^2\pi^2/2ma^2$. It's simple to determine the eigenvalues E of this matrix: they are given by the roots of the quadratic equation

$$(E_0(k) + V_0 - E)^2 - |V_n|^2 = 0 \quad \Rightarrow \quad E = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2} + V_0 \pm |V_n| \tag{3.15}$$

This is important. We see that a gap opens up in the spectrum at the values $k = \pm n\pi/a$. The size of the gap is proportional to $2|V_n|$.

It's simple to understand what's going on here. Consider the simple potential

$$V = 2V_1 \cos\left(\frac{2\pi x}{a}\right)$$

which gives rise to a gap only at $k = \pm\pi/a$. The eigenvectors of the matrix are $(\alpha, \beta) = (1, -1)$ and $(\alpha, \beta) = (1, 1)$, corresponding to the wavefunctions

$$\begin{aligned} \psi_+(x) &= \langle x|\Big(|k\rangle + |-k\rangle\Big) \sim \cos\left(\frac{\pi x}{a}\right) \\ \psi_-(x) &= \langle x|\Big(|k\rangle - |-k\rangle\Big) \sim \sin\left(\frac{\pi x}{a}\right) \end{aligned}$$

The density of electrons is proportional to $|\psi_\pm|^2$. Plotting these densities on top of the potential, we see that ψ_+ describes electrons that are gathered around the peaks of the potential, while ψ_- describes electrons gathered around the minima. It is no surprise that the energy of ψ_+ is higher than that of ψ_-.

Close to the Edge of the Brillouin Zone: Now consider an electron with

$$k = \frac{n\pi}{a} + \delta$$

for some small δ. As we've seen, the potential causes plane wave states to mix only if their wavenumbers differ by some multiple of $2\pi/a$. This means that $|k\rangle = |n\pi/a + \delta\rangle$ will mix with $|k'\rangle = |-n\pi/a + \delta\rangle$. These states don't quite have the same kinetic energy, but they have very *nearly* the same kinetic energy. And, as we will see, the perturbation due to the potential V will mean that these states still mix strongly.

To see this mixing, we need once again to solve the eigenvalue equation (3.13) or, equivalently, (3.14). The eigenvalues are given by solutions to the quadratic equation

$$\Big(E_0(k) + V_0 - E\Big)\Big(E_0(k') + V_0 - E\Big) - |V_n|^2 = 0 \tag{3.16}$$

The only difference from our previous discussion is that $E(k)$ and $E(k')$ are now given by

$$E(k) = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a} + \delta\right)^2 \quad \text{and} \quad E(k') = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a} - \delta\right)^2$$

and the quadratic equation (3.16) becomes

$$\left(\frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{a^2} + \delta^2\right) + V_0 - E\right)^2 - \left(\frac{\hbar^2}{2m}\frac{2n\pi\delta}{a}\right)^2 - |V_n|^2 = 0$$

This equation has two solutions, $E = E_\pm$, given by

$$E_\pm = \frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{a^2} + \delta^2\right) + V_0 \pm \sqrt{|V_n|^2 + \left(\frac{\hbar^2}{2m}\frac{2n\pi\delta}{a}\right)^2}$$

We're ultimately interested in this expression when δ is small, where we anticipate that the effect of mixing will be important. But, as a sanity check, let's first expand it in the opposite regime, when we're far from the edge of the Brillouin zone and δ is large compared to the gap V_n. In this case, a little bit of algebra shows that the eigenvalues can be written as

$$E_\pm = E_0(n\pi/a \pm \delta) + V_0 \pm \frac{|V_n|^2}{E_0(n\pi/a + \delta) - E_0(n\pi/a - \delta)}$$

But this coincides with the the expression that we got from second-order, non-degenerate perturbation theory (3.12). (Or, more precisely, because we have kept just a single mixing term in our discussion above we get just a single term in the sum in (3.12); for some choice of potentials, keeping further terms may be important.)

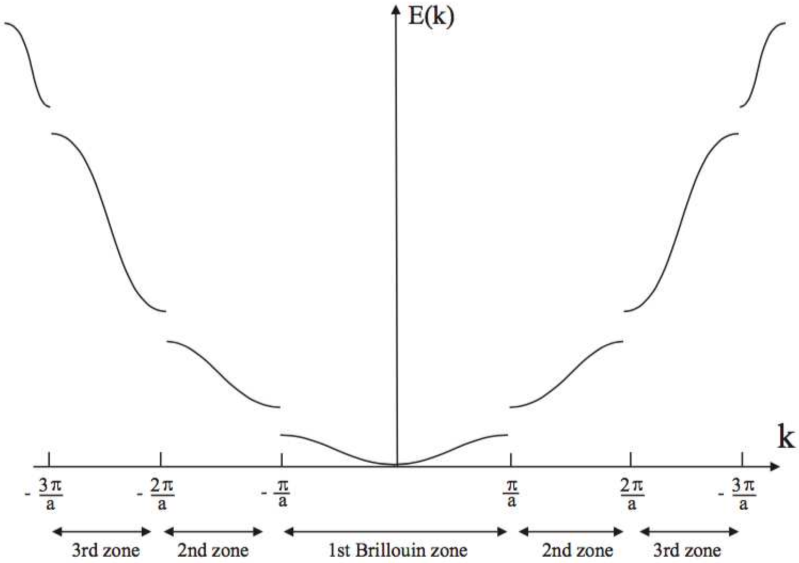


Figure 28: Energy dispersion for the free electron model.

Our real interest is what happens close to the edge of the Brillouin zone when δ is small compared to the gap V_n. In this case we can expand the square-root to give

$$E_\pm \approx \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2} + V_0 \pm |V_n| + \frac{\hbar^2}{2m}\left(1 \pm \frac{1}{|V_n|}\frac{n^2\hbar^2\pi^2}{ma^2}\right)\delta^2$$

The first collection of terms coincide with the energy at the edge of the Brillouin zone (3.15), as indeed it must. For us, the important new point is in the second term which tells us that as we approach the gaps, the energy is quadratic in the momentum δ.

Band Structure

We now have all we need to sketch the rough form of the energy spectrum $E(k)$. The original quadratic spectrum is deformed with a number of striking features:

- For small momenta, $k \ll \pi/a$, the spectrum remains roughly unchanged.
- The energy spectrum splits into distinct bands, with gaps arising at $k = n\pi/a$ with $n \in \mathbf{Z}$. The size of these gaps is given by $2|V_n|$, where V_n is the appropriate Fourier mode of the potential.

  The region of momentum space corresponding to the n^{th} energy band is called the n^{th} *Brillouin zone*. However, we usually call the 1^{st} Brillouin zone simply *the* Brillouin zone.

- As we approach the edge of a band, the spectrum is quadratic. In particular, $dE/dk \to 0$ at the end of a band.

The relationship $E(k)$ between energy and momentum is usually called the *dispersion relation.* In the present case, it is best summarised in a figure.

Note that the spectrum within the first Brillouin zone $|k| \leq \pi/a$, looks very similar to what we saw in the tight-binding model . In particular, both models have a gap at the edge of the Brillouin zone $k = \pm\pi/a$ which is a feature that will persist as we explore more complicated situations. The qualitative differences in the two models show arises because the tight-binding model has a finite number of states, all contained in the first Brillouin zone, while the nearly-free electron model has an infinite number of states which continue for $|k| > \pi/a$.

3.1.3 The Floquet Matrix

One of the main lessons that we learned above is that there are gaps in the energy spectrum. It's hard to overstate the importance of these gaps. Indeed, as we saw briefly above, and will describe in more detail in 4.1.1, the gaps are responsible for some of the most prominent properties of materials, such as the distinction between conductors and insulators.

Because of the important role they play, we will here describe another way to see the emergence of gaps in the spectrum that does not rely on perturbation theory. Consider a general, periodic potential $V(x) = V(x+a)$. We are interested in solutions to the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{3.17}$$

Since this is a second order differential equation, we know that there must be two solutions $\psi_1(x)$ and $\psi_2(x)$. However, because the potential is periodic, it must be the case that $\psi_1(x+a)$ and $\psi_2(x+a)$ are also solutions. These two sets of solutions are therefore related by some linear transformation

$$\begin{pmatrix} \psi_1(x+a) \\ \psi_2(x+a) \end{pmatrix} = F(E) \begin{pmatrix} \psi_1(x) \\ \psi_2(x) \end{pmatrix} \tag{3.18}$$

where $F(E)$ is a 2×2 matrix which, as the notation suggests, depends on the energy of the solution E. It is known as the *Floquet matrix* and has a number of nice properties.

Claim: $\det(F) = 1$.

Proof: First some gymnastics. We differentiate (3.18) to get

$$\begin{pmatrix} \psi_1'(x+a) \\ \psi_2'(x+a) \end{pmatrix} = F(E) \begin{pmatrix} \psi_1'(x) \\ \psi_2'(x) \end{pmatrix}$$

We can combine this with our previous equation by introducing the 2×2 matrix

$$W(x) = \begin{pmatrix} \psi_1(x) & \psi_1'(x) \\ \psi_2(x) & \psi_2'(x) \end{pmatrix}$$

which obeys the matrix equation

$$W(x+a) = F(E)W(x) \tag{3.19}$$

Consider $\det W = \psi_1\psi_2' - \psi_1'\psi_2$. You might recognise this from the earlier course on *Differential Equations* as the *Wronskian*. It's simple to show, using the Schrödinger equation (3.17), that $(\det W)' = 0$. This means that $\det W$ is independent of x so, in particular, $\det W(x+a) = \det W(x)$. Taking the determinant of (3.19) then tells us that $\det F = 1$ as claimed. $\square$

Claim: $\mathrm{Tr}\, F$ is real.

Proof: We always have the choice pick the original wavefunctions $\psi_1(x)$ and $\psi_2(x)$ to be entirely real for all x. (If they're not, simply take the real part and this is also a solution to the Schrodinger equation). With this choice, the Floquet matrix itself has real elements, and so its trace is obviously real. But the trace is independent of our choice of basis of wavefunctions. Any other choice is related by a transformation $F \to AFA^{-1}$, for some invertible matrix A and this leaves the trace invariant. Hence, even if the components of $F(E)$ are complex, its trace remains real. $\square$

To understand the structure of solutions to (3.18), we look at the eigenvalues, λ_+ and λ_- of $F(E)$. Of course, these too depend on the energy E of the solutions. Because $\det F = 1$, they obey $\lambda_+\lambda_- = 1$. They obey the characteristic equation

$$\lambda^2 - (\mathrm{Tr}\, F(E))\lambda + 1 = 0$$

The kind of solution that we get depends on whether $(\mathrm{Tr}\, F(E))^2 < 4$ or $(\mathrm{Tr}\, F(E))^2 > 4$.

$\underline{(\operatorname{Tr} F(E))^2 < 4}$: In this case, the roots are complex and of equal magnitude. We can write

$$\lambda_+ = e^{ika} \quad \text{and} \quad \lambda_- = e^{-ika}$$

for some k which, assuming that the roots are distinct, lies in the range $|k| < \pi/a$. To see what this means for solutions to (3.18), we introduce the left-eigenvector of $(\alpha_\pm, \beta_\pm)F = \lambda_\pm(\alpha_\pm, \beta_\pm)$. Then the linear combinations $\psi_\pm = \alpha_\pm \psi_1 + \beta_\pm \psi_2$ obey

$$\psi_\pm(x + a) = e^{\pm ika} \psi_\pm(x)$$

These are extended states, spread (on average) equally throughout the lattice. They corresponds to the bands in the spectrum.

$\underline{(\operatorname{Tr} F(E))^2 > 4}$: Now the eigenvalues take the form

$$\lambda_1 = e^{\mu a} \quad \text{and} \quad \lambda_2 = e^{-\mu a}$$

for some μ. The corresponding eigenstates now obey

$$\psi_\pm(x + a) = e^{\pm \mu a} \psi_\pm(x)$$

States of this form are not allowed: they are unbounded either as $x \to +\infty$ or as $x \to -\infty$. These values of energy E are where the gaps occur in the spectrum.

We have to work a little harder when $F(E) = 4$ and the two eigenvalues are degenerate, either both $+1$ or both -1. This situations corresponds to the edge of the band. Consider the case when both eigenvalues are $+1$. Recall from your first course on *Vectors and Matrices* that attempting to diagonalise such a 2×2 matrix can result in two different canonical forms

$$PF(E)P^{-1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{or} \quad PF(E)P^{-1} = \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix}$$

In the former case, there are two allowed solutions. In the latter case, you can check that one solution is allowed, while the other grows linearly in x.

3.1.4 Bloch's Theorem in One Dimension

In both models described above, we ended up labelling states by momentum $\hbar k$. It's worth pausing to ask: why did we do this? And how should we think of k?

Before we get to this, let's back up and ask an even more basic question: why do we label the states of a free particle by momentum? Here, the answer is because momentum is conserved. In the quantum theory, this means that the momentum operator commutes with the Hamiltonian: $[p, H] = 0$, so that we can simultaneously label states by both energy and momentum. Ultimately, Noether's theorem tells us that this conservation law arises because of translational invariance of the system.

Now let's look at our system with a lattice. We no longer have translational invariance. Correspondingly, in the nearly-free electron model, $[p, H] \neq 0$. Hopefully this now makes our original question sharper: why do we get to label states by k?!

While we don't have full, continuous translational invariance, both the models that we discussed do have a discrete version of translational invariance

$$x \to x + a$$

As we now show, this is sufficient to ensure that we can label states by something very similar to "momentum". However, the values of this momentum are restricted. This result is known as *Bloch's Theorem.* Here we prove the theorem for our one-dimensional system; we will revisit it in Section 3.3.1 in higher dimensions.

The Translation Operator

For concreteness, let's work with continuous space where states are described by a wavefunction $\psi(x)$. (There is a simple generalisation to discrete situations such as the tight-binding model that we describe below.) We introduce the translation operator T_l as

$$T_l\,\psi(x) = \psi(x + l)$$

First note that T_l is a unitary operator. To see this, we just need to look at the overlap

$$\begin{aligned}\langle\phi|T_l|\psi\rangle = \int dx\ \phi(x)^\star\, T_l\psi(x) &= \int dx\ \phi(x)^\star\psi(x + l) \\ &= \int dx\ \phi(x - l)^\star\psi(x) = \int dx\ [T_{-l}\,\phi(x)]^\star\psi(x)\end{aligned}$$

where, in the step to the second line, we've simply shifted the origin. This tells us that $T_l^\dagger = T_{-l}$. But clearly $T_l^{-1} = T_{-l}$ as well, so $T_l^\dagger = T_l^{-1}$ and the translation operator is unitary as claimed.

Next note that the set of translation operators form an Abelian group,

$$T_{l_1} T_{l_2} = T_{l_1 + l_2} \tag{3.20}$$

with $[T_{l_1}, T_{l_2}] = 0$.

The translation operator is a close cousin of the familiar momentum operator

$$p = -i\hbar \frac{d}{dx}$$

The relationship between the two is as follows: the unitary translation operator is the exponentiation of the Hermitian momentum operator

$$T_l = e^{ilp/\hbar}$$

To see this, we expand the exponent and observe that $T_l \psi(x) = \psi(x + l)$ is just a compact way of expressing the Taylor expansion of a function

$$\begin{aligned} T_l \psi(x) &= \left(1 + \frac{ilp}{\hbar} + \frac{1}{2}\left(\frac{ilp}{\hbar}\right)^2 + \dots\right)\psi(x) \\ &= \left(1 + l\frac{d}{dx} + \frac{l^2}{2}\frac{d^2}{dx^2} + \dots\right)\psi(x) = \psi(x + l) \end{aligned}$$

We say that the momentum operator is the "generator" of infinitesimal translations.

A quantum system is said to be invariant under translations by l if

$$[H, T_l] = 0 \tag{3.21}$$

Phrased in this way, we can describe both continuous translational symmetry and discrete translational symmetry. A system has continuous translational invariance if (3.21) holds for all l. In this case, we may equivalently say that $[p, H] = 0$. Alternatively, a system may have discrete translational invariance if (3.21) holds only when l is an integer multiple of the lattice spacing a. Now p does not commute with H.

Let's look at the case of discrete symmetry. Now we can't simultaneously diagonalise p and H, but we can simultaneously diagonalise T_a and H. In other words, energy eigenstates can be labelled by the eigenvalues of T_a. But T_a is a unitary operator and its eigenvalues are simply a phase, $e^{i\theta}$ for some θ. Moreover, we want the eigenvalues to respect the group structure (3.20). This is achieved if we write the eigenvalue of T_l

as $e^{i\theta} = e^{ikl}$ for some k, so that the eigenvalue of T_{na} coincides with the eigenvalue of T_a^n. The upshot is that eigenstates are labelled by some k, such that

$$T_a \psi_k(x) = \psi_k(x+a) = e^{ika}\psi_k(x)$$

Now comes the rub. Because the eigenvalue is a phase, there is an arbitrariness in this labelling: states labelled by k have the same eigenvalue under T_a as states labelled by $k + 2\pi/a$. To remedy this, we will simply require that k lies in the range

$$k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right) \tag{3.22}$$

We recognise this as the first Brillouin zone.

This, then, is the essence of physics on a lattice. We can still label states by k, but it now lies in a finite range. Note that we can approximate a system with continuous translational symmetry by taking a arbitrarily small; in this limit we get the usual result $k \in \mathbf{R}$.

This discussion leads us directly to:

Bloch's Theorem in One Dimension: In a periodic potential, $V(x) = V(x+a)$, there exists a basis of energy eigenstates that can be written as

$$\psi_k(x) = e^{ikx}u_k(x)$$

where $u_k(x) = u_k(x+a)$ is a periodic function and k lies in the Brillouin zone (3.22).

Proof: We take ψ_k to be an eigenstate of the translation operator T_a, so that $\psi_k(x+a) = e^{ika}\psi_k(x)$. Then $u_k(x+a) = e^{-ik(x+a)}\psi_k(x+a) = e^{-ikx}\psi_k(x) = u_k(x)$. $\square$

Bloch's theorem is rather surprising. One might think that the presence of a periodic potential would dramatically alter the energy eigenstates, perhaps localising them in some region of space. Bloch's theorem is telling us that this doesn't happen: instead the plane wave states e^{ikx} are altered only by a periodic function $u(x)$, sometimes referred to as a *Bloch function*, and the fact that the wavenumber is restricted to the first Brillouin zone.

Finally, note that we've couched the above discussion in terms of wavefunctions $\psi(x)$, but everything works equally well for the tight-binding model with the translation operator defined by $T_a|n\rangle = |n+1\rangle$.

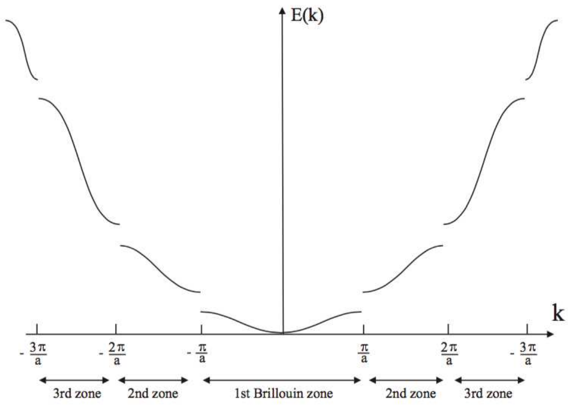


Figure 29: The extended zone scheme.

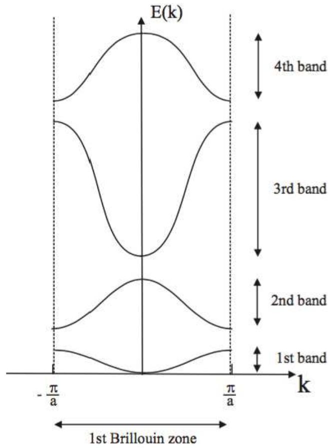


Figure 30: The reduced zone scheme.

Crystal Momentum

The quantity $p = \hbar k$ is the quantity that replaces momentum in the presence of a lattice. It is called the *crystal momentum*. Note, however, that it doesn't have the simple interpretation of "mass $\times$ velocity". (We will describe how to compute the velocity of a particle in terms of the crystal momentum in Section 4.2.1.)

Crystal momentum is conserved. This becomes particularly important when we consider multiple particles moving in a lattice and their interactions. This, of course, sounds the same as the usual story of momentum. Except there's a twist: crystal momentum is conserved only mod $2\pi/a$. It is perfectly possible for two particles to collide in a lattice environment and their final crystal momentum to differ from their initial crystal momentum by some multiple of $2\pi/a$. Roughly speaking, the lattice absorbs the excess momentum.

This motivates us to re-think how we draw the energy spectrum. Those parts of the spectrum that lie outside the first Brillouin zone should really be viewed as having the same crystal momentum. To show this, we draw the energy spectrum as a multi-valued function of $k \in [-\pi/a, \pi/a)$. The spectrum that we previously saw in Figure 28 then looks like

The original way of drawing the spectrum is known as the *extended zone scheme*. The new way is known as the *reduced zone scheme*. Both have their uses. Note that edges of the Brillouin zone are identified: $k = \pi/a$ is the same as $k = -\pi/a$. In other words, the Brillouin zone is topologically a circle.

In the reduced zone scheme, states are labelled by both $k \in [-\pi/a, \pi/a)$ and an integer $n = 1, 2, \ldots$ which tells us which band we are talking about.

3.2 Lattices

The ideas that we described above all go over to higher dimensions. The key difference is that lattices in higher dimensions are somewhat more complicated than a row of points. In this section, we introduce the terminology needed to describe different kinds of lattices. In Section 3.3, we'll return to look at what happens to electrons moving in these lattice environments.

3.2.1 Bravais Lattices

The simplest kind of lattice is called a *Bravais lattice*. This is a periodic array of points defined by integer sums of linearly independent basis vectors $\mathbf{a}_i$. In two-dimensions, a Bravais lattice Λ is defined by

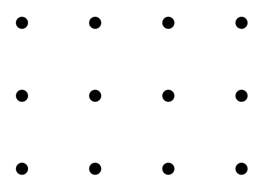


Figure 31:

$$\Lambda = \{\mathbf{r} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 \quad , \quad n_i \in \mathbf{Z}\}$$

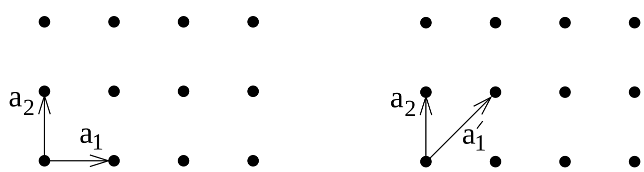
An obvious example is the square lattice shown to the right. We will see further examples shortly.

In three dimensions, a Bravais lattice is defined by

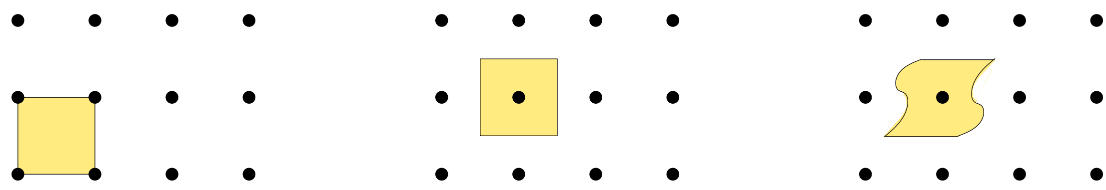
$$\Lambda = \{\mathbf{r} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad , \quad n_i \in \mathbf{Z}\}$$

These lattices have the property that any point looks just the same as any other point. In mathematics, such an object would simply be called a lattice. Here we add the word *Bravais* to distinguish these from more general kinds of lattices that we will meet shortly.

The basis vectors $\mathbf{a}_i$ are called *primitive lattice vectors*. They are not unique. As an example, look at the 2-dimensional square lattice below. We could choose basis vectors ($\mathbf{a}_1$,$\mathbf{a}_2$) or ($\mathbf{a}'_1$,$\mathbf{a}_2$). Both will do the job.



A *primitive unit cell* is a region of space which, when translated by the primitive lattice vectors $\mathbf{a}_i$, tessellates the space. This means that the cells fit together, without overlapping and without leaving any gaps. These primitive unit cells are not unique. As an example, let's look again at the 2-dimensional square lattice. Each of the three possibilities shown below is a good unit cell.



Each primitive unit cell contains a single lattice point. This is obvious in the second and third examples above. In the first example, there are four lattice points associated to the corners of the primitive unit cell, but each is shared by four other cells. Counting these as a 1/4 each, we see that there is again just a single lattice point in the primitive unit cell.

Although the primitive unit cells are not unique, each has the same volume. It is given by

$$V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)| \tag{3.23}$$

Because each primitive unit cell is associated to a single lattice point, $V = 1/n$ where n is the density of lattice points.

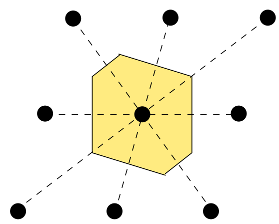
Note finally that the primitive unit cell need not have the full symmetry of the lattice. For example, the third possible unit cell shown above for the square lattice is not invariant under 90° rotations.

For any lattice, there is a canonical choice of primitive unit cell that does inherit the symmetry of the underlying lattice. This is called the *Wigner-Seitz* cell, Γ. (It sometimes goes by the name of the *Voronoi cell.*) Pick a lattice point which we choose to be at the origin. The Wigner-Seitz cell is defined is defined to be the region of space around such that the origin is the closest lattice point. In equations,

$$\Gamma = \{\mathbf{x} : |\mathbf{x}| < |\mathbf{x} - \mathbf{r}| \ \ \forall\, \mathbf{r} \in \Lambda \text{ s.t. } \mathbf{r} \neq 0\ \}$$

The Wigner-Seitz cells for square and triangular lattices are given by

There is a simple way to construct the Wigner-Seitz cell. Draw lines from the origin to all other lattice points. For each of these lines, construct the perpendicular bi-sectors; these are lines in 2d and planes in 3d. The Wigner-Seitz cell is the inner area bounded by these bi-sectors. Here's another example.



Examples of Bravais Lattices in 2d

Let's look at some examples. In two dimensions, a Bravais lattice is defined by two non-parallel vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, with angle $\theta \neq 0$ between them. However, some of these lattices are more special than others. For example, when $|\mathbf{a}_1| = |\mathbf{a}_2|$ and $\theta = \pi/2$, the lattice is square and enjoys an extra rotational symmetry.

We will consider two Bravais lattices to be equivalent if they share the same symmetry group. With this definition, there are five possible Bravais lattices in two dimensions. They are

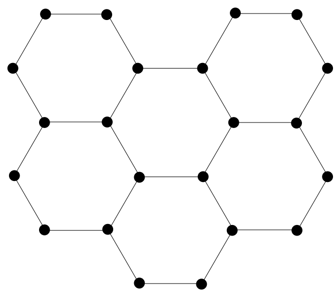
- **Square:** $|\mathbf{a}_1| = |\mathbf{a}_2|$ and $\theta = \pi/2$. It has four-fold rotation symmetry and reflection symmetry.
- **Triangular:** $|\mathbf{a}_1| = |\mathbf{a}_2|$ and $\theta = \pi/3$ or $\theta = 2\pi/3$. This is also sometimes called a hexagonal lattice. It has six-fold rotation symmetry.
- **Rectangular:** $|\mathbf{a}_1| \neq |\mathbf{a}_2|$ and $\theta = \pi/2$. This has reflection symmetry.
- **Centred Rectangular:** $|\mathbf{a}_1| \neq |\mathbf{a}_2|$ and $\theta \neq \pi/2$, but the primitive basis vectors should obey $(2\mathbf{a}_2 - \mathbf{a}_1) \cdot \mathbf{a}_1 = 0$. This means that the lattice looks like a rectangle with an extra point in the middle.

- **Oblique:** $|\mathbf{a}_1| \neq |\mathbf{a}_2|$ and nothing special. This contains all other cases.

The square, triangular and oblique lattices were shown on the previous page where we also drew their Wigner-Seitz cells.

Not all Lattices are Bravais

Not all lattices of interest are Bravais lattices. One particularly important lattice in two dimensions has the shape of a honeycomb and is shown below.



This lattice describes a material called *graphene* that we will describe in more detail in Section 4.1.3. The lattice is not Bravais because not all points are the same. To see this, consider a single hexagon from the lattice as drawn below.

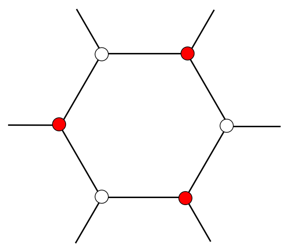
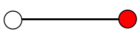


Figure 32:

Each of the red points is the same: each has a neighbour directly to the left of them, and two neighbours diagonally to the right. But the white points are different. Each of them has a neighbour directly to the right, and two neighbours diagonally to the left.

Lattices like this are best thought by decomposing them into groups of atoms, where some element of each group sits on the vertices of a Bravais lattice. For the honeycomb lattice, we can consider the group of atoms . The red vertices form a triangular lattice, with primitive lattice vectors

$$\mathbf{a}_1 = \frac{\sqrt{3}a}{2}(\sqrt{3}, 1) \quad , \quad \mathbf{a}_2 = \frac{\sqrt{3}a}{2}(\sqrt{3}, -1)$$

Meanwhile, each red vertex is accompanied by a white vertex which is displaced by

$$\mathbf{d} = (-a, 0)$$

This way we build our honeycomb lattice.

This kind of construction generalises. We can describe any lattice as a repeating group of atoms, where each group sits on an underlying Bravais lattice Λ. Each atom in the group is displaced from the vertex of the Bravais lattice by a vector $\mathbf{d}_i$. Each group of atoms, labelled by their positions $\mathbf{d}_i$ is called the *basis*. For example, for the honeycomb lattice we chose the basis $\mathbf{d}_1 = 0$ for red atoms and $\mathbf{d}_2 = \mathbf{d}$ for white atoms, since the red atoms sat at the positions of the underlying triangular lattice. In general there's no requirement that any atom sits on the vertex of the underlying Bravais lattice. The whole lattice is then described by the union of the Bravais lattice and the basis, $\cup_i\{\Lambda + \mathbf{d}_i\}$.

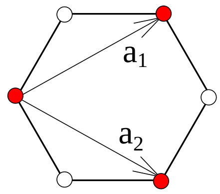


Figure 33:

Examples of Bravais Lattices in 3d

It turns out that there are 14 different Bravais lattices in three dimensions. Fortunately we won't need all of them. In fact, we will describe only the three that arise most frequently in Nature. These are:

- **Cubic:** This is the simplest lattice. The primitive lattice vectors are aligned with the Euclidean axes

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \quad , \quad \mathbf{a}_2 = a\hat{\mathbf{y}} \quad , \quad \mathbf{a}_3 = a\hat{\mathbf{z}}$$

  And the primitive cell looks has volume $V = a^3$. The Wigner-Seitz cell is also a cube, centered around one of the lattice points.

- **Body Centered Cubic (BCC):** This is a cubic lattice, with an extra point placed at the centre of each cube. We could take the primitive lattice vectors to be

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \quad , \quad \mathbf{a}_2 = a\hat{\mathbf{y}} \quad , \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$$

  However, a more symmetric choice is

$$\mathbf{a}_1 = \frac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \quad , \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \quad , \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

  The primitive unit cell has volume $V = a^3/2$.

  The BCC lattice can also be thought of as a cubic lattice, with a basis of two atoms with $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. However, this doesn't affect the fact that the BCC lattice is itself Bravais.

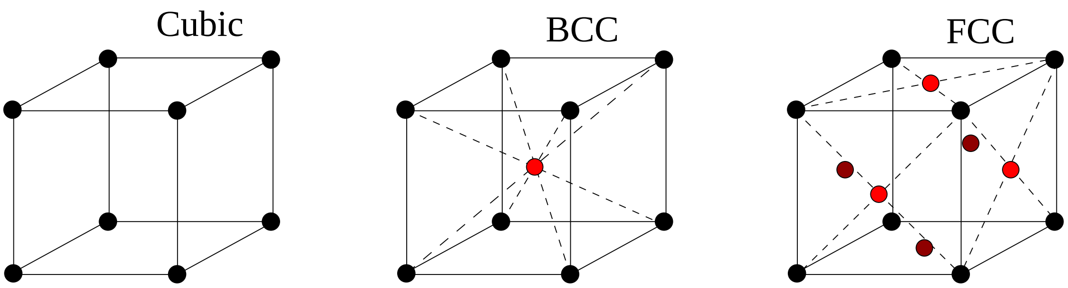


Figure 34: Three Bravais lattices. The different coloured atoms are there in an attempt to make the diagrams less confusing; they do not denote different types of atoms.

The Alkali metals (Li, Na, K, Rb, Cs) all have a BCC structure, as do the Vanadium group (V, Nb, Ta) and Chromium group (Cr, Mo, W) and Iron (Fe). In each case, the lattice constant is roughly $a \approx 3$ to 6×10^{-10} m.

- **Face Centered Cubic (FCC):** This is again built from the cubic lattice, now with an extra point added to the centre of each face. The primitive lattice vectors are

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \quad , \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}) \quad , \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

The primitive unit cell has volume $V = a^3/4$.

The FCC lattice can also be thought of as a cubic lattice, now with a basis of four atoms sitting at $\mathbf{d}_1 = 0$, $\mathbf{d}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$, $\mathbf{d}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$ and $\mathbf{d}_4 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$. Nonetheless, it is also a Bravais lattice in its own right.

Examples of FCC structures include several of the Alkaline earth metals (Be, Ca, Sr), many of the transition metals (Sc, Ni, Pd, Pt, Rh, Ir, Cu, Ag, Au) and the Noble gases (Ne, Ar, Kr, Xe) when in solid form, again with $a \approx 3$ to 6×10^{-10} m in each case.

The Wigner-Seitz cells for the BCC and FCC lattices are polyhedra, sitting inside the cube. For example, the Wigner-Seitz cell for the BCC lattice is shown in the right-hand figure.

Examples of non-Bravais Lattices in 3d

As in the 2d examples above, we can describe non-Bravais crystals in terms of a basis of atoms sitting on an underlying Bravais lattice. Here are two particularly simple examples.

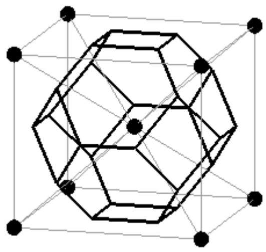


Figure 35: Wigner-Seitz cell for BCC

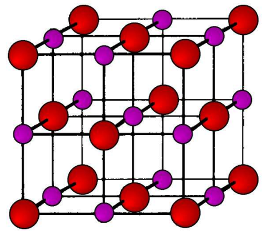


Figure 36: Salt.

Diamond is made up of two, interlaced FCC lattices, with carbon atoms sitting at the basis points $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = \frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. Silicon and germanium also adopt this structure.

Another example is salt ($NaCl$). Here, the basic structure is a cubic lattice, but with Na and Cl atoms sitting at alternate sites. It's best to think of this as two, interlaced FCC lattices, but shifted differently from diamond. The basis consists of a Na atom at $\mathbf{d} = 0$ and a Cl atom at $\mathbf{d}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. This basis then sits on top of an FCC lattice.

3.2.2 The Reciprical Lattice

Given a Bravais lattice Λ, defined by primitive vectors $\mathbf{a}_i$, the *reciprocal lattice* $\Lambda^\star$ is defined by the set of points

$$\Lambda^\star = \{\mathbf{k} = \sum_i n_i \mathbf{b}_i \ , \ n_i \in \mathbf{Z}\}$$

where the new primitive vectors $\mathbf{b}_i$ obey

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\, \delta_{ij} \tag{3.24}$$

$\Lambda^\star$ is sometimes referred to as the *dual lattice*. In three dimensions, we can simply construct the lattice vectors $\mathbf{b}_i$ by

$$\mathbf{b}_i = \frac{2\pi}{V}\frac{1}{2}\epsilon_{ijk}\, \mathbf{a}_j \times \mathbf{a}_k$$

where V is the volume of unit cell of Λ (3.23). We can also invert this relation to get

$$\mathbf{a}_i = \frac{2\pi}{V^\star}\frac{1}{2}\epsilon_{ijk}\, \mathbf{b}_j \times \mathbf{b}_k$$

where $V^\star = |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)| = (2\pi)^3/V$ is the volume of $\Gamma^\star$, the unit cell of $\Lambda^\star$. Note that this shows that the reciprocal of the reciprocal lattice gives you back the original.

The condition (3.24) can also be stated as the requirement that

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 \quad \forall \ \ \mathbf{r} \in \Lambda \ , \ \ \mathbf{k} \in \Lambda^\star \tag{3.25}$$

which provides an alternative definition of the reciprocal lattice.

Here are some examples:

- The cubic lattice has $\mathbf{a}_1 = a\hat{\mathbf{x}}$, $\mathbf{a}_2 = a\hat{\mathbf{y}}$ and $\mathbf{a}_3 = a\hat{\mathbf{z}}$. The reciprocal lattice is also cubic, with primitive vectors $\mathbf{b}_1 = (2\pi/a)\hat{\mathbf{x}}$, $\mathbf{b}_2 = (2\pi/a)\hat{\mathbf{y}}$ and $\mathbf{b}_3 = (2\pi/a)\hat{\mathbf{z}}$
- The BCC lattice has $\mathbf{a}_1 = \frac{a}{2}(-\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})$, $\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}}-\hat{\mathbf{y}}+\hat{\mathbf{z}})$ and $\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}}+\hat{\mathbf{y}}-\hat{\mathbf{z}})$. The reciprocal lattice vectors are $\mathbf{b}_1 = (2\pi/a)(\hat{\mathbf{y}}+\hat{\mathbf{z}})$, $\mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{x}}+\hat{\mathbf{z}})$ and $\mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}}+\hat{\mathbf{y}})$. But we've seen these before: they are the lattice vectors for a FCC lattice with the sides of the cubic cell of length $4\pi/a$.

  We see that the reciprocal of a BCC lattice is an FCC lattice and vice versa.

The Reciprocal Lattice and Fourier Transforms

The reciprocal lattice should not be thought of as sitting in the same space as the original. This follows on dimensional grounds. The original lattice vectors $\mathbf{a}_i$ have the dimension of length, $[\mathbf{a}_i] = L$. The definition (3.24) then requires the dual lattice vectors $\mathbf{b}_i$ to have dimension $[\mathbf{b}_i] = 1/L$. The reciprocal lattice should be thought of as living in Fourier space which, in physics language, is the same thing as momentum space. As we'll now see, the reciprocal lattice plays an important role in the Fourier transform.

Consider a function $f(\mathbf{x})$ where, for definiteness, we'll take $\mathbf{x} \in \mathbf{R}^3$. Suppose that this function has the periodicity of the lattice Λ, which means that $f(\mathbf{x}) = f(\mathbf{x}+\mathbf{r})$ for all $\mathbf{r} \in \Lambda$. The Fourier transform is

$$\begin{aligned} \tilde{f}(\mathbf{k}) = \int d^3x \ e^{-i\mathbf{k}\cdot\mathbf{x}} f(\mathbf{x}) &= \sum_{\mathbf{r}\in\Lambda} \int_\Gamma d^3x \ e^{-i\mathbf{k}\cdot(\mathbf{x}+\mathbf{r})} f(\mathbf{x}+\mathbf{r}) \\ &= \sum_{\mathbf{r}\in\Lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} \int_\Gamma d^3x \ e^{-i\mathbf{k}\cdot\mathbf{x}} f(\mathbf{x}) \end{aligned} \tag{3.26}$$

In the second equality, we have replaced the integral over $\mathbf{R}^3$ with a sum over lattice points, together with an integral over the Wigner-Seitz cell Γ. In going to the second line, we have used the periodicity of $f(\mathbf{x})$. We see that the Fourier transform comes with the overall factor

$$\Delta(\mathbf{k}) = \sum_{\mathbf{r}\in\Lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{3.27}$$

This is an interesting quantity. It has the following property:

Claim: $\Delta(\mathbf{k}) = \mathbf{0}$ unless $\mathbf{k} \in \Lambda^\star$.

Proof: Since we're summing over all lattice sites, we could equally well write $\Delta(\mathbf{k}) = \sum_{\mathbf{r}\in\mathbf{\Lambda}} \mathbf{e}^{-\mathbf{ik}\cdot(\mathbf{r}-\mathbf{r_0})}$ for any $\mathbf{r}_0 \in \Lambda$. This tells us that $\Delta(\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}_0}\,\Delta(\mathbf{k})$ for any $\mathbf{r}_0 \in \Lambda$. This means that $\Delta(\mathbf{k}) = 0$ unless $e^{i\mathbf{k}\cdot\mathbf{r}_0} = 1$ for all $\mathbf{r}_0 \in \Lambda$. But this is equivalent to saying that $\Delta(\mathbf{k}) = 0$ unless $\mathbf{k} \in \Lambda^\star$. $\square$

In fact, we can get a better handle on the function (strictly, a distribution) $\Delta(\mathbf{k})$. We have

Claim: $\Delta(\mathbf{k}) = V^\star \sum_{\mathbf{q}\in\Lambda^\star} \delta(\mathbf{k}-\mathbf{q})$.

Proof: We can expand $\mathbf{k} = \sum_i k_i \mathbf{b}_i$, with $k_i \in \mathbf{R}$, and $\mathbf{r} = \sum_i n_i \mathbf{a}_i$ with $n_i \in \mathbf{Z}$. Then, using (3.24), we have

$$\Delta(\mathbf{k}) = \sigma(k_1)\sigma(k_2)\sigma(k_3) \quad \text{where} \quad \sigma(k) = \sum_{n=-\infty}^{\infty} e^{-2\pi i k n}$$

The range of the sum in $\sigma(k)$ is appropriate for an infinite lattice. If, instead, we had a finite lattice with, say, $N+1$ points in each direction, (assume, for convenience, that N is even), we would replace $\sigma(k)$ with

$$\sigma_N(k) = \sum_{n=-N/2}^{N/2} e^{-2\pi i k n} = \frac{e^{-2\pi i k(N/2+1)} - e^{2\pi i k N/2}}{e^{-2\pi i k} - 1} = \frac{\sin(N+1)\pi k}{\sin \pi k}$$

This function is plotted on the right for $-1/2 < k < 1/2$. We have chosen a measly $N = 10$ in this plot, but already we see that the function is heavily peaked near the origin: when $k \sim \mathcal{O}(1/N)$, then $\sigma_N(k) \sim \mathcal{O}(N)$. As $N \to \infty$, this peak becomes narrower and taller and the area under it tends towards 1. To see this last point, replace $\sin(\pi k) \approx \pi k$ and use the fact that $\int_{-\infty}^{+\infty} \sin(x)/x = \pi$. This shows that the peak near the origin tends towards a delta function.

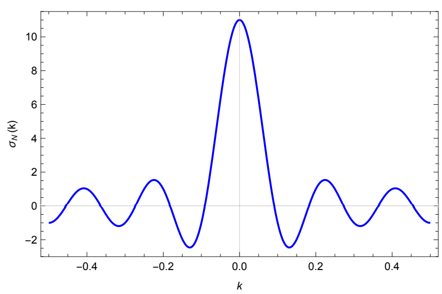


Figure 37:

The function $\sigma_N(k)$ is periodic. We learn that, for large N, $\sigma_N(k)$ just becomes a series of delta functions, restricting k to be integer valued

$$\lim_{N\to\infty} \sigma_N(k) = \sum_{n=-\infty}^{\infty} \delta(k-n)$$

Looking back at (3.27), we see that these delta functions mean that the Fourier transform is only non-vanishing when $\mathbf{k} = \sum_i k_i \mathbf{b}_i$ with $k_i \in \mathbf{Z}$. But this is precisely the condition that $\mathbf{k}$ lies in the reciprocal lattice. We have

$$\Delta(\mathbf{k}) = \sum_{\mathbf{r}\in\Lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} = V^\star \sum_{\mathbf{q}\in\Lambda^\star} \delta(\mathbf{k}-\mathbf{q}) \tag{3.28}$$

We can understand this formula as follows: if $\mathbf{k} \in \Lambda^\star$, then $e^{-i\mathbf{k}\cdot\mathbf{r}} = 1$ for all $\mathbf{r} \in \Lambda$ and summing over all lattice points gives us infinity. In contrast, if $\mathbf{k} \notin \Lambda^\star$, then the phases $e^{-i\mathbf{k}\cdot\mathbf{r}}$ oscillate wildly for different $\mathbf{r}$ and cancel each other out. □

The upshot is that if we start with a continuous function $f(\mathbf{x})$ with periodicity Λ, then the Fourier transform (3.26) has support only at discrete points $\Lambda^\star$,

$$\tilde{f}(\mathbf{k}) = \Delta(\mathbf{k})S(\mathbf{k}) \quad \text{with} \quad S(\mathbf{k}) = \int_\Gamma d^3x \; e^{-i\mathbf{k}\cdot\mathbf{x}} f(\mathbf{x})$$

Here $S(\mathbf{k})$ is known as the *structure factor*. Alternatively, inverting the Fourier transform, we have

$$f(\mathbf{x}) = \frac{1}{(2\pi)^3}\int d^3k \; e^{i\mathbf{k}\cdot\mathbf{x}}\,\tilde{f}(\mathbf{k}) = \frac{V^\star}{(2\pi)^3}\sum_{\mathbf{q}\in\Lambda^\star} e^{i\mathbf{q}\cdot\mathbf{x}}\,S(\mathbf{q}) \tag{3.29}$$

This tells us that any periodic function is a sum of plane waves whose wavevectors lie on the reciprocal lattice, We'll revisit these ideas in Section 3.4 when we discuss x-ray scattering from a lattice.

3.2.3 The Brillouin Zone

The Wigner-Seitz cell of the reciprocal lattice is called the *Brillouin zone*.

We already saw the concept of the Brillouin zone in our one-dimensional lattice. Let's check that this coincides with the definition given above. The one-dimensional lattice is defined by a single number, a, which determines the lattice spacing. The Wigner-Seitz cell is defined as those points which lie closer to the origin than any other lattice point, namely $r \in [-a/2, a/2)$. The reciprocal lattice is defined by (3.24) which, in this context, gives the lattice spacing $b = 2\pi/a$. The Wigner-Seitz cell of this reciprocal lattice consists of those points which lie between $[-b/2, b/2) = [-\pi/a, \pi/a)$. This coincides with what we called the Brillouin zone in Section 3.1.

The Brillouin zone is also called the *first Brillouin zone*. As it is the Wigner-Seitz cell, it is defined as all points in reciprocal space that are closest to a given lattice point, say the origin. The n^{th} *Brillouin zone* is defined as all points in reciprocal space that are n^{th} closest to the origin. All these higher Brillouin zones have the same volume as the first.

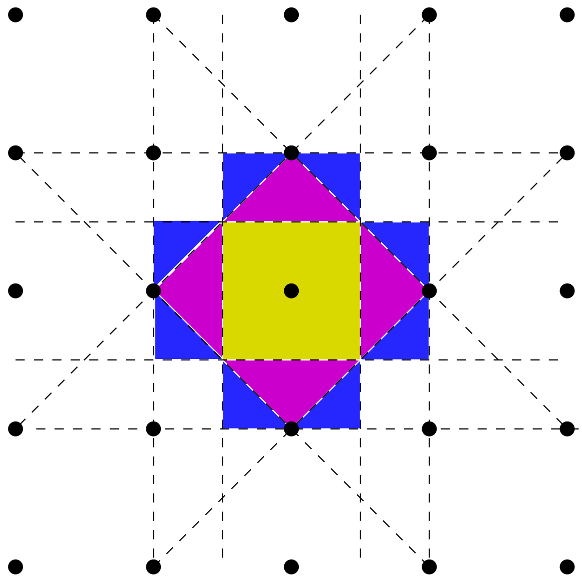


Figure 38: The Brillouin zones for a 2d square lattice. The first is shown in yellow, the second in pink, the third in blue.

We can construct the Brillouin zone boundaries by drawing the perpendicular bisectors between the origin and each other point in $\Lambda^\star$. The region enclosing the origin is the first Brillouin zone. The region you can reach by crossing just a single bisector is the second Brillouin zone, and so on. In fact, this definition generalises the Brillouin zone beyond the simple Bravais lattices.

As an example, consider the square lattice in 2d. The reciprocal lattice is also square. The first few Brillouin zones on this square lattice are shown in Figure 38.

For the one-dimensional lattice that we looked at in Section 3.1, we saw that the conserved momentum lies within the first Brillouin zone. This will also be true in higher dimensions. This motivates us to work in the *reduced zone scheme*, in which these higher Brillouin zones are mapped back into the first. This is achieved by translating them by some lattice vector. The higher Brillouin zones of the square lattice in the reduced zone scheme are shown in Figure 39.

Finally, note that the edges of the Brillouin zone should be identified; they label the same momentum state $\mathbf{k}$. For one-dimensional lattices, this results in the Brillouin zone having the topology of a circle. For d-dimensional lattices, the Brillouin zone is topologically a torus $\mathbf{T}^d$.

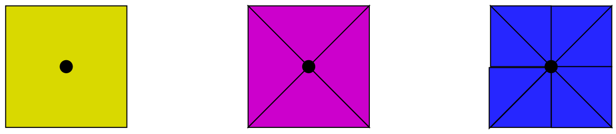


Figure 39: The first three Brillouin zones for a square lattice in the reduced zone scheme.

Crystallographic Notation

The Brillouin zone of real materials is a three-dimensional space. We often want to describe how certain quantities – such as the energy of the electrons – vary as we move around the Brillouin zone. To display this information graphically, we need to find a way to depict the underlying Brillouin zone as a two-dimensional, or even one-dimensional space. Crystallographers have developed a notation for this. Certain, highly symmetric points in the Brillouin zone are labelled by letters. From the letter, you're also supposed to remember what underlying lattice we're talking about.

For example, all Brillouin zones have an origin. The concept of an "origin" occurs in many different parts of maths and physics and almost everyone has agreed to label it as "0". Almost everyone. But not our crystallographer friends. Instead, they call the origin Γ.

From hereon, it gets more bewildering although if you stare at enough of these you get used to it. For example, for a cubic lattice, the centre of each face is called X, the centre of each edge is M while each corner is R. Various labels for BCC and FCC lattices are shown in Figure 40

3.3 Band Structure

> "When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal.... I found to my delight that the wave differed from a plane wave of free electron only by a periodic modulation.This was so simple that I didn't think it could be much of a discovery, but when I showed it to Heisenberg he said right away, 'That's it.'."
> *Felix Bloch*

Now that we've developed the language to describe lattices in higher dimensions, it's time to understand how electrons behave when they move in the background of a fixed lattice. We already saw many of the main ideas in the context of a one-dimensional lattice in Section 3.1. Here we will describe the generalisation to higher dimensions.

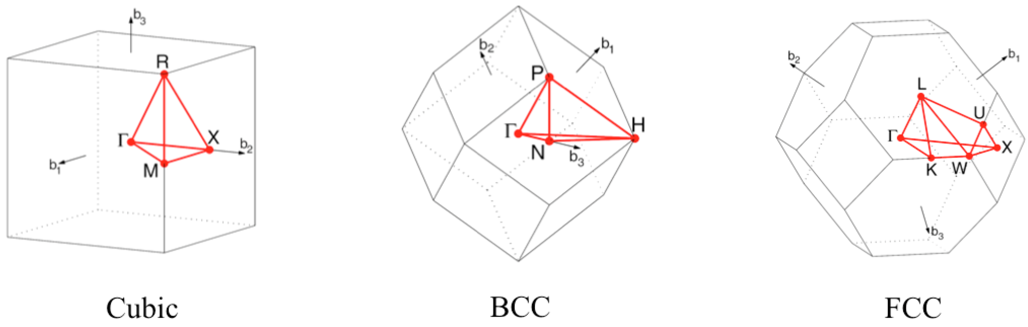


Figure 40: The labels for various special points on the Brillouin zone.

3.3.1 Bloch's Theorem

Consider an electron moving in a potential $V(\mathbf{x})$ which has the periodicity of a Bravais lattice Λ,

$$V(\mathbf{x}+\mathbf{r}) = V(\mathbf{x}) \quad \text{for all } \mathbf{r} \in \Lambda$$

Bloch's theorem states that the energy eigenstates take the form

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}\, u_{\mathbf{k}}(\mathbf{x})$$

where $u_{\mathbf{k}}(\mathbf{x})$ has the same periodicity as the lattice, $u_{\mathbf{k}}(\mathbf{x}+\mathbf{r}) = u_{\mathbf{k}}(\mathbf{x})$ for all $\mathbf{r} \in \Lambda$.

There are different ways to prove Bloch's theorem. Here we will give a simple proof using the ideas of translation operators, analogous to the one-dimensional proof that we saw in Section 3.1.4. Later, in Section 3.3.2, we will provide a more direct proof by decomposing the Schrödinger equation into Fourier modes.

Our starting point is that the Hamiltonian is invariant under discrete translations by the lattice vectors $\mathbf{r} \in \Lambda$. As we explained in Section 3.1.4, these translations are implemented by unitary operators $T_{\mathbf{r}}$. These operators form an Abelian group,

$$T_{\mathbf{r}} T_{\mathbf{r}'} = T_{\mathbf{r}+\mathbf{r}'} \tag{3.30}$$

and commute with the Hamiltonian: $[H, T_{\mathbf{r}}] = 0$. This means that we can simultaneously diagonalise H and $T_{\mathbf{r}}$, so that energy eigenstates are labelled also labelled by the eigenvalue of each $T_{\mathbf{r}}$. Because $T_{\mathbf{r}}$ is unitary, this is simply a phase. But we also have the group structure (3.30) that must be respected. Suppose that translation of a given eigenstate by a basis element $\mathbf{a}_i$ gives eigenvalue

$$T_{\mathbf{a}_i}\psi(\mathbf{x}) = \psi(\mathbf{x}+\mathbf{a}_i) = e^{i\theta_i}\psi(\mathbf{x})$$

Then translation by a general lattice vector $\mathbf{r} = \sum_i n_i \mathbf{a}_i$ must give

$$T_{\mathbf{r}}\psi(\mathbf{x}) = \psi(\mathbf{x}+\mathbf{r}) = e^{i\sum_i n_i\theta_i}\psi(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{r}}\psi(\mathbf{x})$$

where the vector $\mathbf{k}$ is defined by $\mathbf{k}\cdot\mathbf{a}_i = \theta_i$. In other words, we can label eigenstates of $T_{\mathbf{r}}$ by a vector $\mathbf{k}$. They obey

$$T_{\mathbf{r}}\psi_{\mathbf{k}}(\mathbf{x}) = \psi_{\mathbf{k}}(\mathbf{x}+\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\psi_{\mathbf{k}}(\mathbf{x})$$

Now we simply need to look at the function $u_{\mathbf{k}}(\mathbf{x}) = e^{-i\mathbf{k}\cdot\mathbf{x}}\psi_{\mathbf{k}}(\mathbf{x})$. The statement of Bloch's theorem is that $u_{\mathbf{k}}(\mathbf{x})$ has the periodicity of Λ which is indeed true, since $u_{\mathbf{k}}(\mathbf{x}+\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{x}}e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{\mathbf{k}}(\mathbf{x}+\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{x}}\psi_{\mathbf{k}}(\mathbf{x}) = u_{\mathbf{k}}(\mathbf{x})$.

Crystal Momentum

The energy eigenstates are labelled by the wavevector $\mathbf{k}$, called the *crystal momentum.* There is an ambiguity in the definition of this crystal momentum. This is not the same as the true momentum. The energy eigenstates do not have a well defined momentum because they are not eigenstates of the momentum operator $\mathbf{p} = -i\hbar\nabla$ unless $u_{\mathbf{k}}(\mathbf{x})$ is constant. Nonetheless, we will see as we go along that the crystal momentum plays a role similar to the true momentum. For this reason, we will often refer to $\mathbf{k}$ simply as "momentum".

There is an ambiguity in the definition of the crystal momentum. Consider a state with a crystal momentum $\mathbf{k}' = \mathbf{k}+\mathbf{q}$, with $\mathbf{q}\in\Lambda^\star$ a reciprocal lattice vector. Then

$$\psi_{\mathbf{k}'}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}e^{i\mathbf{q}\cdot\mathbf{x}}u_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}\tilde{u}_{\mathbf{k}}(\mathbf{x})$$

where $\tilde{u}_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{q}\cdot\mathbf{x}}u_{\mathbf{k}}(\mathbf{x})$ also has the periodicity of Λ by virtue of the definition of the reciprocal lattice (3.25).

As in the one-dimensional example, we have different options. We could choose to label states by $\mathbf{k}$ which lie in the first Brillouin zone. In this case, there will typically be many states with the same $\mathbf{k}$ and different energies. This is the *reduced zone scheme.* In this case, the energy eigenstates are labelled by two indices, $\psi_{\mathbf{k},n}$, where $\mathbf{k}$ is the crystal momentum and n is referred to as the *band index.* (We will see examples shortly.)

Alternatively, we can label states by taking any $\mathbf{k}\in\mathbf{R}^d$ where d is the dimension of the problem. This is the *extended zone scheme.* In this case that states labelled by $\mathbf{k}$ which differ by $\Lambda^\star$ have the same crystal momenta.

3.3.2 Nearly Free Electrons in Three Dimensions

Consider an electron moving in $\mathbf{R}^3$ in the presence of a weak potential $V(\mathbf{x})$. We'll assume that this potential has the periodicity of a Bravais lattice Λ, so

$$V(\mathbf{x}) = V(\mathbf{x}+\mathbf{r}) \quad \text{for all } \mathbf{r} \in \Lambda$$

We treat this potential as a perturbation on the free electron. This means that we start with plane wave states $|\mathbf{k}\rangle$ with wavefunctions

$$\langle \mathbf{x}|\mathbf{k}\rangle \sim e^{i\mathbf{k}\cdot\mathbf{x}}$$

with energy $E_0(\mathbf{k}) = \hbar k^2/2m$. We want to see how these states and their energy levels are affected by the presence of the potential. The discussion will follow closely the one-dimensional case that we saw in Section 3.1.2 and we only highlight the differences.

When performing perturbation theory, we're going to have to consider the potential $V(\mathbf{x})$ sandwiched between plane-wave states,

$$\langle \mathbf{k}|V(\mathbf{x})|\mathbf{k}'\rangle = \frac{1}{\text{Volume}} \int d^3x \; e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}}\, V(\mathbf{x})$$

However, we've already seen in (3.29) that the Fourier transform of a periodic function can be written as a sum over wavevectors that lie in the reciprocal lattice $\Lambda^\star$,

$$V(\mathbf{x}) = \sum_{\mathbf{q}\in\Lambda^\star} e^{i\mathbf{q}\cdot\mathbf{x}}\, V_{\mathbf{q}}$$

(Note: here $V_{\mathbf{q}}$ is the Fourier component of the potential and should not be confused with the volumes of unit cells which were denoted as V and $V^\star$ in Section 3.2.) This means that $\langle \mathbf{k}|V(\mathbf{x})|\mathbf{k}'\rangle$ is non-vanishing only when the two momenta differ by

$$\mathbf{k} - \mathbf{k}' = \mathbf{q} \quad \mathbf{q} \in \Lambda^\star$$

This has a simple physical interpretation: a plane wave state $|\mathbf{k}\rangle$ can scatter into another plane wave state $|\mathbf{k}'\rangle$ only if they differ by a reciprocal lattice vector. In other words, only momenta $\mathbf{q}$, with $\mathbf{q} \in \Lambda^\star$, can be absorbed by the lattice.

Another Perspective on Bloch's Theorem

The fact that that a plane wave state $|\mathbf{k}\rangle$ can only scatter into states $|\mathbf{k}+\mathbf{q}\rangle$, with $\mathbf{q} \in \Lambda^\star$, provides a simple viewpoint on Bloch's theorem, one that reconciles the quantum state with the naive picture of the particle bouncing off lattice sites like a ball in a pinball machine. Suppose that the particle starts in some state $|\mathbf{k}\rangle$. After scattering, we might expect it to be some superposition of all the possible scattering states $|\mathbf{k}+\mathbf{q}\rangle$. In other words,

$$\psi_{\mathbf{k}}(\mathbf{x}) = \sum_{\mathbf{q}\in\Lambda^\star} e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{x}}\, c_{\mathbf{k}-\mathbf{q}}$$

for some coefficients $c_{\mathbf{k}-\mathbf{q}}$. We can write this as

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}} \sum_{\mathbf{q}\in\Lambda^\star} e^{i\mathbf{q}\cdot\mathbf{x}}\, c_{\mathbf{k}-\mathbf{q}} = e^{i\mathbf{k}\cdot\mathbf{x}}\, u_{\mathbf{k}}(\mathbf{x})$$

where, by construction, $u_{\mathbf{k}}(\mathbf{x}+\mathbf{r}) = u_{\mathbf{k}}(\mathbf{x})$ for all $\mathbf{r}\in\Lambda$. But this is precisely the form guaranteed by Bloch's theorem.

Although the discussion here holds at first order in perturbation theory, it is not hard to extend this argument to give an alternative proof of Bloch's theorem, which essentially comes down to analysing the different Fourier modes of the Schrödinger equation.

Band Structure

Let's now look at what becomes of the energy levels after we include the perturbation. We will see that, as in the 1d example, they form bands. The resulting eigenstates $\psi_{\mathbf{k},n}(\mathbf{x})$ and their associated energy levels $E_n(\mathbf{k})$ are referred to as the *band structure* of the system.

Low Momentum: Far from the edge of the Brillouin zone, the states $|\mathbf{k}\rangle$ can only scatter into states $|\mathbf{k}+\mathbf{q}\rangle$ with greatly different energy. In this case, we can work with non-degenerate perturbation theory to compute the corrections to the energy levels.

On the Boundary of the Brillouin zone: Things get more interesting when we have to use degenerate perturbation theory. This occurs whenever the state $|\mathbf{k}\rangle$ has the same energy as another state $|\mathbf{k}+\mathbf{q}\rangle$ with $\mathbf{q}\in\Lambda^\star$,

$$E_0(\mathbf{k}) = E_0(\mathbf{k}+\mathbf{q}) \quad\Rightarrow\quad k^2 = (\mathbf{k}+\mathbf{q})^2 \quad\Rightarrow\quad 2\mathbf{k}\cdot\mathbf{q} + q^2 = 0$$

This condition is satisfied whenever we can write

$$\mathbf{k} = -\frac{1}{2}\mathbf{q} + \mathbf{k}_\perp$$

where $\mathbf{q}\cdot\mathbf{k}_\perp = 0$. This is the condition that we sit on the perpendicular bisector of the origin and the lattice point $-\mathbf{q}\in\Lambda^\star$. But, as we explained in Section 3.2.3, these bisectors form the boundaries of the Brillouin zones. We learn something important: momentum states are degenerate only when they lie on the boundary of a Brillouin zone. This agrees with what we found in our one-dimensional example in Section 3.1.2.

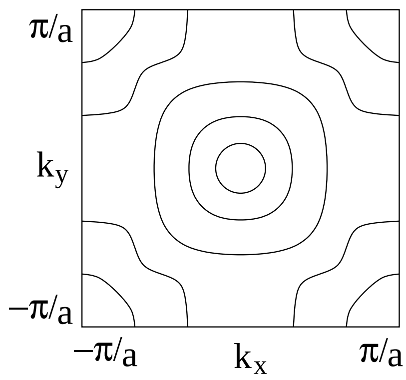


Figure 41: Energy contours for nearly-free electrons in the first Brillouin zone.

We know from experience what the effect of the perturbation $V(\mathbf{x})$ will be: it will lift the degeneracy. This means that a gap opens at the boundary of the Brillouin zone. For example, the energy of states just inside the first Brillouin zone will be pushed down, while the energy of those states just outside the first Brillouin zone will be pushed up. Note that the size of this gap will vary as we move around the boundary..

There is one further subtlety that we should mention. At a generic point on the boundary of the Brillouin zone, the degeneracy will usually be two-fold. However, at special points — such as edges, or corners — it often higher. In this case, we must work with all degenerate states when computing the gap.

All of this is well illustrated with an example. However, it's illustrated even better if you do the example yourself! The problem of nearly free electrons in a two-dimensional square lattice is on the problem sheet. The resulting energy contours are shown in Figure 41.

Plotting Band Structures in Three Dimensions

For three-dimensional lattice, we run into the problem of depicting the bands. For this, we need the crystallographer's notation we described previously. The spectrum of free particles (i.e. with no lattice) is plotted in the Brillouin zone of BCC and FCC lattices in Figure 42[5].

We can then compare this to the band structure of real materials. The dispersion relation for silicon is also shown in Figure 42. This has a diamond lattice structure, which is plotted as FCC. Note that you can clearly see the energy gap of around 1.1 eV between the bands.

[5]Images plotted by Jan-Rens Reitsma, from Wikimedia commons.

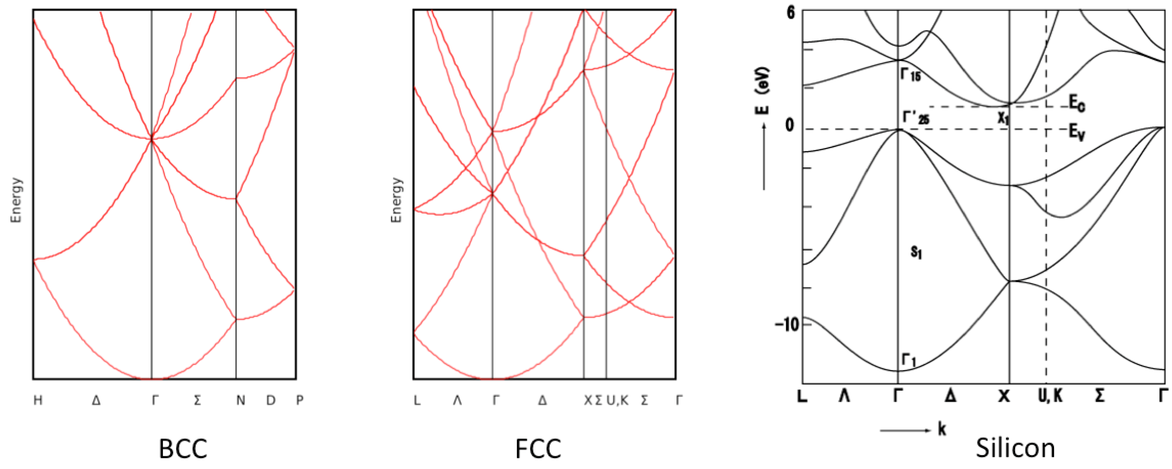


Figure 42: Free band structure (in red) for BCC and FCC, together with the band structure for silicon, exhibiting a gap.

How Many States in the Brillouin Zone?

The Brillouin zone consists of all wavevectors $\mathbf{k}$ that lie within the Wigner-Seitz cell of the reciprocal lattice $\Lambda^\star$. How many quantum states does it hold? Well, if the spatial lattice Λ is infinite in extent then $\mathbf{k}$ can take any continuous value and there are an infinite number of states in the Brillouin zone. But what if the spatial lattice is finite in size?

In this section we will count the number of quantum states in the Brillouin zone of a finite spatial lattice Λ. We will find a lovely answer: the number of states is equal to N, the number of lattice sites.

Recall that the lattice Λ consists of all vectors $\mathbf{r} = \sum_i n_i \mathbf{a}_i$ where $\mathbf{a}_i$ are the primitive lattice vectors and $n_i \in \mathbf{Z}$. For a finite lattice, we simply restrict the value of these integers to be

$$0 \leq n_i \leq N_i$$

for some N_i. The total number of lattice sites is then $N = N_1 N_2 N_3$ (assuming a three-dimensional lattice). The total volume of the lattice is VN where $V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$ is the volume of the unit cell.

The basic physics is something that we've met before: if we put a particle in a box, then the momentum $\hbar\mathbf{k}$ becomes quantised. This arises because of the boundary conditions that we place on the wavefunction. It's simplest to think about a finite, periodic lattice where we require that the wavefunction inherits this periodicity, so that

$$\psi(\mathbf{x} + N_i\mathbf{a}_i) = \psi(\mathbf{x}) \quad \text{for each } i = 1, 2, 3 \tag{3.31}$$

But we know from Bloch's theorem that energy eigenstates take the form $\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}u_{\mathbf{k}}(\mathbf{x})$ where $u_{\mathbf{k}}(\mathbf{x} + \mathbf{a}_i) = u_{\mathbf{k}}(\mathbf{x})$. This means that the periodicity condition (3.31) becomes

$$e^{iN_i\mathbf{k}\cdot\mathbf{a}_i} = 1 \quad \Rightarrow \quad \mathbf{k} = \sum_i \frac{m_i}{N_i}\mathbf{b}_i$$

where $m_i \in \mathbf{Z}$ and $\mathbf{b}_i$ are the primitive vectors of the reciprocal lattice defined in (3.24). This is sometimes called the *Born-von Karmen* boundary condition.

This is the quantisation of momentum that we would expect in a finite system. The states are now labelled by integers $m_i\mathbf{Z}$. Each state can be thought of as occupying a volume in **k**-space, given by

$$\frac{|\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|}{N_1 N_2 N_3} = \frac{V^\star}{N}$$

where $V^\star$ is the volume of the Brillouin zone. We see that the number of states that live inside the Brillouin zone is precisely N, the number of sites in the spatial lattice.

3.3.3 Wannier Functions

Bloch's theorem tells that the energy eigenstates can be written in the form

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}u_{\mathbf{k}}(\mathbf{x})$$

with **k** lying in the first Brillouin zone and $u_{\mathbf{k}}(\mathbf{x})$ a periodic function. Clearly these are delocalised throughout the crystal. For some purposes, it's useful to think about these Bloch waves as arising from the sum of states, each of which is localised at a given lattice site. These states are called *Wannier functions*; they are defined as

$$w_{\mathbf{r}}(\mathbf{x}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}}\,\psi_{\mathbf{k}}(\mathbf{x}) \tag{3.32}$$

where the sum is over all **k** in the first Brillouin zone.

The basic idea is that the Wannier wavefunction $w_{\mathbf{r}}(\mathbf{x})$ is localised around the lattice site $\mathbf{r} \in \Lambda$. Indeed, using the periodicity properties of the Bloch wavefunction, it's simple to show that $w_{\mathbf{r}+\mathbf{r}'}(\mathbf{x} + \mathbf{r}') = w_{\mathbf{r}}(x)$, which means that we can write $w_{\mathbf{r}}(\mathbf{x}) = w(\mathbf{x} - \mathbf{r})$.

The Wannier functions aren't unique. We can always do a phase rotation $\psi_{\mathbf{k}}(\mathbf{x}) \rightarrow e^{i\chi(\mathbf{k})}\psi_{\mathbf{k}}(\mathbf{k})$ in the definition (3.32). Different choices of $\chi(\mathbf{k})$ result in differing amounts of localisation of the state $w_{\mathbf{r}}(\mathbf{x})$ around the lattice site $\mathbf{r}$.

We can invert the definition of the Wannier function to write the original Bloch wavefunction as

$$\psi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{r}\in\Lambda} e^{i\mathbf{k}\cdot\mathbf{r}}\, w(\mathbf{x}-\mathbf{r}) \tag{3.33}$$

which follows from (3.28).

The Wannier functions have one final, nice property: they are orthonormal in the sense that

$$\begin{aligned} \int d^3x\; w^\star(\mathbf{x}-\mathbf{r}')w(\mathbf{x}-\mathbf{r}) &= \frac{1}{N}\int d^3x \sum_{\mathbf{k},\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}'-i\mathbf{k}\cdot\mathbf{r}}\psi^\star_{\mathbf{k}'}(\mathbf{x})\psi_{\mathbf{k}}(\mathbf{x}) \\ &= \frac{1}{N}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})} = \delta(\mathbf{r}-\mathbf{r}') \end{aligned}$$

where, in going to the second line, we have used the orthogonality of Bloch wavefunctions for different $\mathbf{k}$ (which, in turn, follows because they are eigenstates of the Hamiltonian with different energies).

3.3.4 Tight-Binding in Three Dimensions

We started our discussion of band structure in Section 3.1.1 with the one-dimensional tight binding model. This is a toy Hamiltonian describing electrons hopping from one lattice site to another. Here we'll look at this same class of models in higher dimensional lattices.

We assume that the electron can only sit on a site of the lattice $\mathbf{r}\in\Lambda$. The Hilbert space is then spanned by the states $|\mathbf{r}\rangle$ with $\mathbf{r}\in\Lambda$. We want to write down a Hamiltonian which describes a particle hopping between these sites. There are many different ways to do this; the simplest is

$$H = \sum_{\mathbf{r}\in\Lambda} E_0|\mathbf{r}\rangle\langle\mathbf{r}| - \sum_{<\mathbf{r}\mathbf{r}'>} t_{\mathbf{r}'-\mathbf{r}}\Big(|\mathbf{r}\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}|\Big)$$

where the label $<\mathbf{r}\mathbf{r}'>$ means that we only sum over pairs of sites $\mathbf{r}$ and $\mathbf{r}'$ which are nearest neighbours in the lattice. Alternatively, if these nearest neighbours are connected by a set of lattice vectors $\mathbf{a}$, then we can write this as

$$H = \sum_{\mathbf{r}\in\Lambda}\left[E_0|\mathbf{r}\rangle\langle\mathbf{r}| - \sum_{\mathbf{a}} t_{\mathbf{a}}\,|\mathbf{r}\rangle\langle\mathbf{r}+\mathbf{a}|\right] \tag{3.34}$$

Note that we've just got one term here, since if $|\mathbf{r}+\mathbf{a}\rangle$ is a nearest neighbour, then so is $|\mathbf{r}-\mathbf{a}\rangle$. The Hamiltonian is Hermitian provided $t_{\mathbf{a}} = t_{-\mathbf{a}}$ This Hamiltonian is easily solved. The eigenstates take the form

$$|\psi(\mathbf{k})\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{r}\in\Lambda} e^{i\mathbf{k}\cdot\mathbf{r}} |\mathbf{r}\rangle \tag{3.35}$$

where N is the total number of lattice sites. It's simple to check that these states satisfy $H|\psi(\mathbf{k})\rangle = E(\mathbf{k})|\psi(\mathbf{k})\rangle$ with

$$E(\mathbf{k}) = E_0 - \frac{1}{2}\sum_{\mathbf{a}} 2t_{\mathbf{a}} \cos(\mathbf{k}\cdot\mathbf{a}) \tag{3.36}$$

where the factor of $1/2$ is there because we are still summing over all nearest neighbours, including $\pm\mathbf{a}$. This exhibits all the properties of that we saw in the tight-binding model. The energy eigenstates (3.35) are no longer localised, but are instead spread throughout the lattice. The states form just a single band labelled, as usual, but by crystal momentum $\mathbf{k}$ lying in the first Brillouin zone. This is to be expected in the tight-binding model as we start with N states, one per lattice site, and we know that each Brillouin zone accommodates precisely N states.

As a specific example, consider a cubic lattice. The nearest neighbour lattice sites are $\mathbf{a} \in \Big\{(\pm a,0,0),(0,\pm a,0),(0,0,\pm a)\Big\}$ and the hopping parameters are the same in all directions: $t_{\mathbf{a}} = t$. The dispersion relation is then given by

$$E(\mathbf{k}) = E_0 - 2t\Big(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\Big) \tag{3.37}$$

The width of this band is $\Delta E = E_{\rm max} - E_{\rm min} = 12t$.

Note that for small k, the dispersion relation takes the form of a free particle

$$E(\mathbf{k}) = \text{constant} + \frac{\hbar^2\mathbf{k}^2}{2m^\star} + \ldots$$

where the effective mass $m^\star$ is determined by various parameters of the underlying lattice, $m^\star = \hbar^2/2ta^2$. However, at higher k the energy is distorted away from the that of a free particle. For example, you can check that $k_x \pm k_y = \mp\pi/a$ (with $k_z = 0$) is a line of constant energy.

3.3.5 Deriving the Tight-Binding Model

Above, we have simply written down the tight-binding model. But it's interesting to ask how we can derive it from first principles. In particular, this will tell us what physics it captures and what physics it misses.

To do this, we start by considering a single atom which we place at the origin. The Hamiltonian for a single electron orbiting this atom takes the familiar form

$$H_{\rm atom} = \frac{\mathbf{p}^2}{2m} + V_{\rm atom}(\mathbf{x})$$

The electrons will bind to the atom with eigenstates $\phi_n(\mathbf{x})$ and discrete energies $\epsilon_n < 0$, which obey

$$H_{\rm atom}\phi_n(\mathbf{x}) = \epsilon_n\phi_n(\mathbf{x})$$

A sketch of a typical potential $V_{\rm atom}(\mathbf{x})$ and the binding energies ϵ_n is shown on the right. There will also be scattering states, with energies $\epsilon > 0$, which are not bound to the atom.

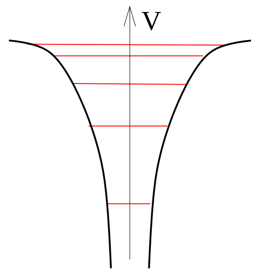


Figure 43:

Our real interest lies in a lattice of these atoms. The resulting potential is

$$V_{\rm lattice}(\mathbf{x}) = \sum_{\mathbf{r}\in\Lambda} V_{\rm atom}(\mathbf{x}-\mathbf{r})$$

This is shown in Figure 44 for a one-dimensional lattice. What happens to the energy levels? Roughly speaking, we expect those electrons with large binding energies — those shown at the bottom of the spectrum — to remain close to their host atoms. But those that are bound more weakly become free to move. This happens because the tails of their wavefunctions have substantial overlap with electrons on neighbouring atoms, causing these states to mix. This is the physics captured by the tight-binding model.

The weakly bound electrons which become dislodged from their host atoms are called *valence electrons*. (These are the same electrons which typically sit in outer shells and give rise to bonding in chemistry.) As we've seen previously, these electrons will form a band of extended states.

Let's see how to translate this intuition into equations. We want to solve the Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + V_{\rm lattice}(\mathbf{x}) \tag{3.38}$$

Our goal is to write the energy eigenstates in terms of the localised atomic states $\phi_n(\mathbf{x})$. Getting an exact solution is hard; instead, we're going to guess an approximate solution.

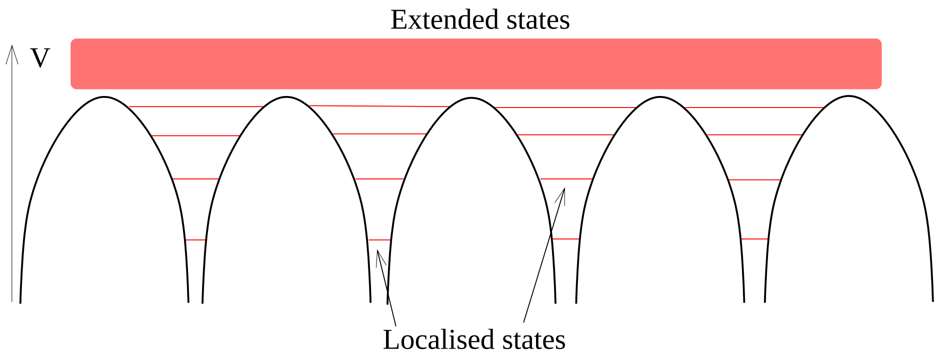


Figure 44: Extended and localised states in a lattice potential.

First, let's assume that there is just a single valence electron with localised wavefunction $\phi(\mathbf{x})$ with energy ϵ . We know that the eigenstates of (3.38) must have Bloch form. We can build such a Bloch state from the localised state $\phi(\mathbf{x})$ by writing

$$\psi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{r}\in\Lambda} e^{i\mathbf{k}\cdot\mathbf{r}}\, \phi(\mathbf{x}-\mathbf{r}) \tag{3.39}$$

where N is the number of lattice sites. This is a Bloch state because for any $\mathbf{a} \in \Lambda$, we have $\psi_{\mathbf{k}}(\mathbf{x}+\mathbf{a}) = e^{i\mathbf{k}\cdot\mathbf{a}}\,\psi_{\mathbf{k}}(\mathbf{x})$. Note that this is the same kind of state (3.35) that solved our original tight-binding model. Note also that this ansatz takes the same form as the expansion in terms of Wannier functions (3.33). However, in contrast to Wannier functions, the wavefunctions $\phi(\mathbf{x})$ localised around different lattice sites are not orthogonal. This difference will be important below.

The expected energy for the state (3.39) is

$$E(\mathbf{k}) = \frac{\langle\psi_{\mathbf{k}}|H|\psi_{\mathbf{k}}\rangle}{\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle}$$

First, the denominator.

$$\begin{aligned}\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle &= \frac{1}{N}\sum_{\mathbf{r},\mathbf{r}'\in\Lambda} e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}\int d^3x\ \phi^\star(\mathbf{x}-\mathbf{r})\phi(\mathbf{x}-\mathbf{r}') \\ &= \sum_{\mathbf{r}\in\Lambda} e^{-i\mathbf{k}\cdot\mathbf{r}}\int d^3x\ \phi^\star(\mathbf{x}-\mathbf{r})\phi(\mathbf{x}) \\ &\equiv 1 + \sum_{\mathbf{r}\neq 0} e^{-i\mathbf{k}\cdot\mathbf{r}}\alpha(\mathbf{r})\end{aligned}$$

where, in going to the second line, we've used the translational invariance of the lattice. The function $\alpha(\mathbf{r})$ measures the overlap of the wavefuntions localised at lattice sites separated by $\mathbf{r}$.

Next the numerator. To compute this, we write $H = H_{\text{atom}} + \Delta V(\mathbf{x})$ where

$$\Delta V(\mathbf{x}) = V_{\text{lattice}}(\mathbf{x}) - V_{\text{atom}}(\mathbf{x}) = \sum_{\mathbf{r}\in\Lambda,\mathbf{r}\neq 0} V_{\text{atom}}(\mathbf{x}-\mathbf{r})$$

We then have

$$\begin{aligned}
\langle\psi_{\mathbf{k}}|H|\psi_{\mathbf{k}}\rangle &= \frac{1}{N}\sum_{\mathbf{r},\mathbf{r}'\in\Lambda} e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}\int d^3x\ \phi^\star(\mathbf{x}-\mathbf{r})(H_{\text{atom}}+\Delta V)\phi(\mathbf{x}-\mathbf{r}') \\
&= \sum_{\mathbf{r}\in\Lambda} e^{-i\mathbf{k}\cdot\mathbf{r}}\int d^3x\ \phi^\star(\mathbf{x}-\mathbf{r})(H_{\text{atom}}+\Delta V)\phi(\mathbf{x}) \\
&\equiv \epsilon\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle + \Delta\epsilon + \sum_{\mathbf{r}\neq 0} e^{-i\mathbf{k}\cdot\mathbf{r}}\gamma(\mathbf{r})
\end{aligned}$$

Here $\Delta\epsilon$ is the shift in the energy of the bound state $\phi(\mathbf{x})$ due to the potential ΔV,

$$\Delta\epsilon = \int d^3x\ \phi^\star(\mathbf{x})\Delta V(\mathbf{x})\phi(\mathbf{x})$$

Meanwhile, the last term arises from the overlap of localised atoms on different sites

$$\gamma(\mathbf{r}) = \int d^3x\ \phi^\star(\mathbf{x}-\mathbf{r})\,\Delta V(\mathbf{x})\,\phi(\mathbf{x})$$

The upshot of this is an expression for the expected energy of the Bloch wave (3.39)

$$E(\mathbf{k}) = \epsilon + \frac{\Delta\epsilon + \sum_{\mathbf{r}\neq 0} e^{-i\mathbf{k}\cdot\mathbf{r}}\,\gamma(\mathbf{r})}{1+\sum_{\mathbf{r}\neq 0} e^{-i\mathbf{k}\cdot\mathbf{r}}\,\alpha(\mathbf{r})}$$

Under the assumption that $\alpha(\mathbf{r}) \ll 1$, we can expand out the denominator $(1+x)^{-1} \approx 1-x$, and write

$$E(\mathbf{k}) = \epsilon + \Delta\epsilon + \sum_{\mathbf{r}\neq 0} e^{-i\mathbf{k}\cdot\mathbf{r}}\Big(\gamma(\mathbf{r}) - \alpha(\mathbf{r})\,\Delta\epsilon\Big) \tag{3.40}$$

This still looks rather complicated. However, the expression simplifies because the overlap functions $\alpha(\mathbf{r})$ and $\gamma(\mathbf{r})$ both drop off quickly with separation. Very often, it's sufficient to take these to be non-zero only when $\mathbf{r}$ are the nearest neighbour lattice sites. Sometimes we need to go to next-to-nearest neighbours.

An Example: s-Orbitals

Let's assume that $\alpha(\mathbf{r})$ and $\gamma(\mathbf{r})$ are important only for $\mathbf{r}$ connecting nearest neighbour lattice sites; all others will be taken to vanish. We'll further take the valence electron to sit in the s-orbital. This has two consequences: first, the localised wavefunction is rotationally invariant, so that $\phi(\mathbf{r}) = \phi(r)$. Second, the wavefunction can be taken to be real, so $\phi^\star(\mathbf{x}) = \phi(\mathbf{x})$. With these restrictions, we have

$$\alpha(\mathbf{r}) = \int d^3x \phi(\mathbf{x} - \mathbf{r})\phi(\mathbf{x}) = \alpha(-\mathbf{r})$$

We want a similar expression for $\gamma(\mathbf{r})$. For this, we need to make one further assumption: we want the crystal to have *inversion symmetry*. This means that $V(\mathbf{x}) = V(-\mathbf{x})$ or, more pertinently for us, $\Delta V(\mathbf{x}) = \Delta V(-\mathbf{x})$. We can then write

$$\begin{aligned}\gamma(\mathbf{r}) &= \int d^3x\ \phi(\mathbf{x} - \mathbf{r})\Delta V(\mathbf{x})\phi(\mathbf{x}) \\ &= \int d^3x'\ \phi(-\mathbf{x}' - \mathbf{r})\Delta V(-\mathbf{x}')\phi(-\mathbf{x}') \\ &= \int d^3x' \phi(|\mathbf{x}' + r|)\Delta V(\mathbf{x}')\phi(|\mathbf{x}'|) \\ &= \gamma(-\mathbf{r})\end{aligned}$$

where we have defined $\mathbf{x}' = -\mathbf{x}$ in the second line and used both the inversion symmetry and rotational invariance of the s-orbital in the third. Now we can write the energy (3.40) in a slightly nicer form. We need to remember that the vectors $\mathbf{r}$ span a lattice which ensures that if $\mathbf{r}$ is a nearest neighbour site then $-\mathbf{r}$ is too. We then have

$$E(\mathbf{k}) = \epsilon + \Delta\epsilon + \sum_{\mathbf{a}} \cos(\mathbf{k}\cdot\mathbf{a}) \Big(\gamma(\mathbf{a}) - \Delta\epsilon\, \alpha(\mathbf{a})\Big) \tag{3.41}$$

where $\mathbf{a}$ are the nearest neighbour lattice sites. We recognise this as the dispersion relation that we found in our original tight-binding model (3.36), with $E_0 = \epsilon + \Delta\epsilon$ and $t_{\mathbf{a}} = \gamma(\mathbf{a}) - \Delta\epsilon\, \alpha(\mathbf{a})$.

So far we've shown that the state (3.39) has the same energy as eigenstates of the tight-binding Hamiltonian. But we haven't yet understood when the state (3.39) is a good approximation to the true eigenstate of the Hamiltonian (3.38).

We can intuit the answer to this question by looking in more detail at (3.41). We see that the localised eigenstates $\phi(\mathbf{x})$, each of which had energy ϵ, have spread into a band with energies $E(\mathbf{k})$. For this calculation to be valid, it's important that this band doesn't mix with other states. This means that the energies $E(\mathbf{k})$ shouldn't be too low, so that it has overlap with the energies of more deeply bound states. Nor should $E(\mathbf{k})$ be too high, so that it overlaps with the energies of the scattering states which will give rise to higher bands. If the various lattice parameters are chosen so that it sits between these two values, our ansatz (3.39) will be a good approximation to the true wavefunction. Another way of saying this is that if we focus on states in the first band, we can approximate the Hamiltonian (3.38) describing a lattice of atoms by the tight-binding Hamiltonian (3.34).

A Linear Combination of Atomic Orbitals

What should we do if the band of interest does overlap with bands from more deeply bound states? The answer is that we should go back to our original ansatz (3.39) and replace it with something more general, namely

$$\psi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{r}\in\Lambda} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{n} c_n \phi_n(\mathbf{x}-\mathbf{r}) \tag{3.42}$$

where this time we sum over all localised states of interest, $\phi_n(\mathbf{x})$ with energies ϵ_n. These are now weighted with coefficients c_n which we will determine shortly. This kind of ansatz is known as a *linear combination of atomic orbitals*. Among people who play these kind of games, it is common enough to have its own acronym (*LCAO* obviously).

The wavefunction (3.42) should be viewed as a variational ansatz for the eigenstates, where we get to vary the parameters c_n. The expected energy is again

$$E(\mathbf{k}) = \frac{\langle\psi_{\mathbf{k}}|H|\psi_{\mathbf{k}}\rangle}{\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle}$$

where, repeating the calculations that we just saw, we have

$$\begin{aligned}\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle &= \sum_{\mathbf{r}\in\Lambda}\sum_{n,n'} c^\star_{n'} c_n\, e^{-i\mathbf{k}\cdot\mathbf{r}} \int d^3x\ \phi^\star_{n'}(\mathbf{x}-\mathbf{r})\phi_n(\mathbf{x}) \\ &\equiv \sum_{\mathbf{r}\in\Lambda}\sum_{n,n'} c^\star_{n'} c_n\, e^{-i\mathbf{k}\cdot\mathbf{r}} \alpha_{n,n'}(\mathbf{r}) \end{aligned} \tag{3.43}$$

and

$$\begin{aligned}\langle\psi_{\mathbf{k}}|H|\psi_{\mathbf{k}}\rangle &= \sum_{\mathbf{r}\in\Lambda}\sum_{n,n'} c^\star_{n'} c_n\, e^{-i\mathbf{k}\cdot\mathbf{r}} \int d^3x\ \phi^\star_{n'}(\mathbf{x}-\mathbf{r})(H_{\text{atom}}+\Delta V)\phi_n(\mathbf{x}) \\ &\equiv \sum_{\mathbf{r}\in\Lambda}\sum_{n,n'} c^\star_{n'} c_n\, e^{-i\mathbf{k}\cdot\mathbf{r}} \Big(\epsilon_n \alpha_{n,n'}(\mathbf{r}) + \gamma_{n,n'}(\mathbf{r})\Big) \end{aligned} \tag{3.44}$$

Note that we've used slightly different notation from before. We haven't isolated the piece $\alpha_{n,n'}(\mathbf{r}=0) = \delta_{n,n'}$, nor the analogous $\Delta\epsilon$ piece corresponding to $\gamma_{n,n'}(\mathbf{r}=0)$. Instead, we continue to sum over all lattice points $\mathbf{r}\in\Lambda$, including the origin.

The variational principle says that we should minimise the expected energy over all c_n. This means we should solve

$$\frac{\partial E(\mathbf{k})}{\partial c^\star_{n'}} = \frac{1}{\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle}\frac{\partial}{\partial c^\star_{n'}}\langle\psi_{\mathbf{k}}|H|\psi_{\mathbf{k}}\rangle - \frac{\langle\psi_{\mathbf{k}}|H|\psi_{\mathbf{k}}\rangle}{\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle^2}\frac{\partial}{\partial c^\star_{n'}}\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle = 0$$
$$\Rightarrow \qquad \frac{\partial}{\partial c^\star_{n'}}\langle\psi_{\mathbf{k}}|H|\psi_{\mathbf{k}}\rangle - E(\mathbf{k})\frac{\partial}{\partial c^\star_{n'}}\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle = 0$$

Using our expressions (3.43) and (3.44), we can write the resulting expression as the matrix equation

$$\sum_n M_{n,n'}(\mathbf{k})c_n = 0 \tag{3.45}$$

where $M_{n,n'}(\mathbf{k})$ is the Hermitian matrix

$$M_{n,n'}(\mathbf{k}) = \sum_{\mathbf{r}\in\Lambda} e^{-i\mathbf{k}\cdot\mathbf{r}}\Big(\tilde{\gamma}_{n,n'}(\mathbf{r}) - (E(\mathbf{k}) - \epsilon_n)\alpha_{n,n'}(\mathbf{r})\Big)$$

The requirement (3.45) that $M_{n,n'}(\mathbf{k})$ has a zero eigenvalue can be equivalently written as

$$\det\, M_{n,n'}(\mathbf{k}) = 0$$

Let's think about how to view this equation. The matrix $M_{n,n'}(\mathbf{k})$ is a function of the various parameters which encode the underlying lattice dynamics as well as $E(\mathbf{k})$. But what we want to figure out is the dispersion relation $E(\mathbf{k})$. We should view the condition $\det\, M_{n,n'}(\mathbf{k}) = 0$ as an equation for $E(\mathbf{k})$.

Suppose that we include p localised states at each site, so $M_{n,n'}(\mathbf{k})$ is a $p\times p$ matrix. Then $\det\, M_{n,n'}(\mathbf{k}) = 0$ is a polynomial in $E(\mathbf{k})$ of degree p. This polynomial will have p roots; these are the energies $E_n(\mathbf{k})$ of p bands. In each case, the corresponding null eigenvector is c_n which tells us how the atomic orbitals mix in the Bloch state (3.42).

3.4 Scattering Off a Lattice

Finally, we come to an important question: how do we know that solids are made of lattices? The answer, of course, is scattering. Firing a beam of particles — whether neutrons, electrons or photons in the X-ray spectrum — at the solid reveals a characteristic diffraction pattern. Our goal here is to understand this within the general context of scattering theory that we met in Section 1.

Our starting point is the standard asymptotic expression describing a wave scattering off a central potential, localised around the origin,

$$\psi(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}} + f(\mathbf{k};\mathbf{k}')\frac{e^{ikr}}{r} \tag{3.46}$$

Here we're using the notation, introduced in earlier sections, of the scattered momentum

$$\mathbf{k}' = k\hat{\mathbf{r}}$$

The idea here is that if you sit far away in the direction $\hat{\mathbf{r}}$, you will effectively see a wave with momentum $\mathbf{k}'$. We therefore write $f(\mathbf{k},\mathbf{k}')$ to mean the same thing as $f(k;\theta,\phi)$.

Suppose now that the wave scatters off a potential which is localised at some other position, $\mathbf{r} = R$. Then the equation (3.46) becomes

$$\psi(\mathbf{r}) \sim e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} + f(\mathbf{k},\mathbf{k}')\frac{e^{ik|\mathbf{r}-\mathbf{R}|}}{|\mathbf{r}-\mathbf{R}|}$$

For $r \to \infty$, we can expand

$$|\mathbf{r}-\mathbf{R}| = \sqrt{r^2 + R^2 - 2\mathbf{r}\cdot\mathbf{R}} \approx r\sqrt{1 - 2\mathbf{r}\cdot\mathbf{R}/r^2} \approx r - \hat{\mathbf{r}}\cdot\mathbf{R}$$

We then have

$$\psi(\mathbf{r}) \sim e^{-i\mathbf{k}\cdot\mathbf{R}}\left[e^{i\mathbf{k}\cdot\mathbf{r}} + f(\mathbf{k},\mathbf{k}')e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}}\,\frac{e^{ikr}}{\mathbf{r}}\right] \tag{3.47}$$

The overall factor is unimportant, since our interest lies in the phase shift between the incident wave and the scattered wave. We see that we get an effective scattering amplitude

$$f_{\mathbf{R}}(\mathbf{k};\hat{\mathbf{r}}) = f(\mathbf{k},\mathbf{k}')\,e^{i\mathbf{q}\cdot\mathbf{R}}$$

where we have defined the transferred momentum

$$\mathbf{q} = \mathbf{k} - \mathbf{k}'$$

Now let's turn to a lattice of points Λ. Ignoring multiple scatterings, the amplitude is simply the sum of the amplitudes from each lattice point

$$f_\Lambda(\mathbf{k},\mathbf{k}') = f(\mathbf{k},\mathbf{k}')\sum_{\mathbf{R}\in\Lambda} e^{i\mathbf{q}\cdot\mathbf{R}} \tag{3.48}$$

However, we already discussed the sum $\Delta(\mathbf{q}) = \sum_{\mathbf{R}\in\Lambda} e^{i\mathbf{q}\cdot\mathbf{R}}$ in Section 3.2.2. The sum has the nice property that it vanishes unless $\mathbf{q}$ lies in the reciprocal lattice $\Lambda^\star$. This is simple to see: since we have an infinite lattice it must be true that, for any vector $\mathbf{R}_0 \in \Lambda$,

$$\Delta(\mathbf{q}) \equiv \sum_{\mathbf{R}\in\Lambda} e^{i\mathbf{q}\cdot\mathbf{R}} = \sum_{\mathbf{R}\in\Lambda} e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}_0)} = e^{-i\mathbf{q}\cdot\mathbf{R}_0}\Delta(\mathbf{q})$$

This means that either $e^{-i\mathbf{q}\cdot\mathbf{R}_0} = 1$ or $\Delta(\mathbf{q}) = 0$. The former result is equivalent to the statement that $\mathbf{q} \in \Lambda^\star$. More generally,

$$\sum_{\mathbf{R}\in\Lambda} e^{i\mathbf{q}\cdot\mathbf{R}} \equiv \Delta(\mathbf{q}) = V^\star \sum_{\mathbf{Q}\in\Lambda^\star} \delta(\mathbf{q}-\mathbf{Q}) \tag{3.49}$$

where $V^\star$ is the volume of the unit cell of $\Lambda^\star$. We see that $\Delta(\mathbf{q})$ is very strongly (formally, infinitely) peaked on the reciprocal lattice.

The upshot of this discussion is a lovely result: there is scattering from a lattice if and only if

$$\mathbf{k} - \mathbf{k}' \in \Lambda^\star \tag{3.50}$$

This is known as the *Laue condition*. If the scattered momentum does not satisfy this condition, then the interference between all the different scattering sites results in a vanishing wave. Only when the Laue condition is obeyed is this interference constructive.

Alternatively, the Laue condition can be viewed as momentum conservation, with the intuition — garnered from Section 3 — that the lattice can only absorb momentum in $\Lambda^\star$.

Solutions to the Laue condition are not generic. If you take a lattice with a fixed orientation and fire a beam with fixed $\mathbf{k}$, chances are that there are no solutions to (3.50). To see this, consider the reciprocal lattice as shown in the left-hand panel of the figure. From the tip of $\mathbf{k}$ draw a sphere of radius k. This is sometimes known as the *Ewald sphere* and its surface gives the possible transferred momenta $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. There is scattering only if this surface passes through a point on the reciprocal lattice.

To get scattering, we must therefore either find a wave to vary the incoming momentum $\mathbf{k}$, or find a way to vary the orientation of the lattice. But when this is achieved, the outgoing photons $\mathbf{k}' = k\hat{\mathbf{r}}$ sit only at very specific positions. In this way, we get to literally take a photograph of the reciprocal lattice! The resulting diffraction pattern for salt ($NaCl$) which has a cubic lattice structure is shown in the right-hand panel. The four-fold symmetry of the reciprocal lattice is clearly visible.

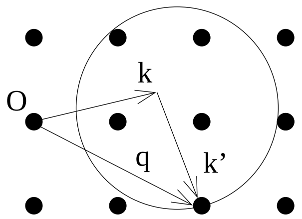


Figure 45: The Ewald sphere.

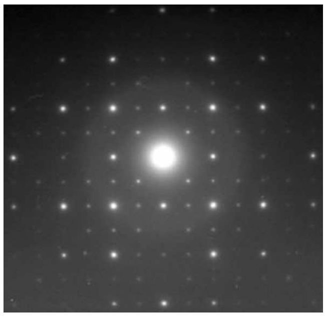


Figure 46: Salt.

3.4.1 The Bragg Condition

There is an equivalent phrasing of the Laue condition in real space. Suppose that the momentum vectors obey

$$\mathbf{k} - \mathbf{k}' = \mathbf{Q} \in \Lambda^\star$$

Since $\mathbf{Q}$ is a lattice vector, so too is $n\mathbf{Q}$ for all $n \in \mathbf{Z}$. Suppose that $\mathbf{Q}$ is minimal, so that $n\mathbf{Q}$ is not a lattice a vector for any $n < 1$. Defining the angle θ by $\mathbf{k}\cdot\mathbf{k}' = k^2\cos\theta$, we can take the square of the equation above to get

$$2k^2(1-\cos\theta) = 4k^2\sin^2(\theta/2) = Q^2 \quad \Rightarrow \quad 2k\sin(\theta/2) = Q$$

We can massage this further. The vector $\mathbf{Q} \in \Lambda^\star$ defines a set of parallel planes in Λ. Known as *Bragg planes*, these are labelled by an integer n and defined by those $\mathbf{a} \in \Lambda$ which obey $\mathbf{a}\cdot\mathbf{Q} = 2\pi n$. The distance between successive planes is

$$d = \frac{2\pi}{Q}$$

Furthermore, the wavevector k corresponds to a wavelength $\lambda = 2\pi/k$. We learn that the Laue condition written as the requirement that

$$\lambda = 2d\sin(\theta/2)$$

Repeating this argument for vectors $n\mathbf{Q}$ with $n \in \mathbf{Z}$, we get

$$n\lambda = 2d\sin(\theta/2)$$

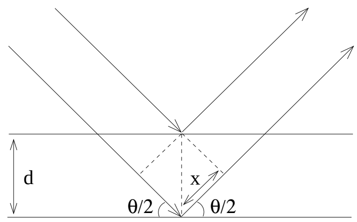


Figure 47:

Figure 48: A quasi-crystal.

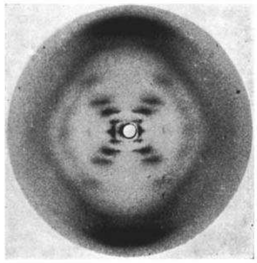


Figure 49: DNA, Photograph 51.

This is the Bragg condition. It has a simple interpretation. For $n = 1$, we assume that the wave scatters off two consecutive planes of the lattice, as shown figure. The wave which hits the lower plane travels an extra distance of $2x = 2d\sin(\theta/2)$. The Bragg condition requires this extra distance to coincide with the wavelength of light. In other words, it is the statement that waves reflecting off consecutive planes interfere constructively.

The Bragg condition gives us licence to think about scattering of light off planes in the lattice, rather than individual lattice sites. Moreover, it tells us that the wavelength of light should be comparable to the atomic separation in the crystal. This means x-rays. The technique of x-ray crystallography was pioneered by Max von Laue, who won the 1914 Nobel prize. The Bragg law was developed by William Bragg, a fellow of Trinity and director of the Cavendish. He shared the 1915 Nobel prize in physics with his father, also William Bragg, for their development of crystallographic techniques.

X-ray crystallography remains the most important technique to determine the structure of materials. Two examples of historical interest are shown in the figures. The picture on the left is something of an enigma since it has five-fold symmetry. Yet there are no Bravais lattices with this symmetry! The diffraction pictures is revealing a *quasi-crystal*, an ordered but non-periodic crystal. The image on the right was taken by Rosalind Franklin and is known as "photograph 51". It provided a major, and somewhat controversial, hint to Crick and Watson in their discovery of the structure of DNA.

3.4.2 The Structure Factor

Many crystals are described by a repeating ground of atoms, which each group sits on an underlying Bravais lattice Λ. The atoms in the group are displaced from the vertex of the Bravais lattice by a vector $\mathbf{d}_i$. We saw several examples of this in Section 3. In such a situation, the scattering amplitude (3.48) is replaced by

$$f_{\rm lattice}(\mathbf{k},\mathbf{k}') = \Delta(\mathbf{q})\, S(\mathbf{q})$$

where

$$S(\mathbf{q}) = \sum_i f_i(\mathbf{k},\mathbf{k}') e^{i\mathbf{q}\cdot\mathbf{d}_i}$$

We have allowed for the possibility that each atom in the basis has a different scattering amplitude $f_i(\mathbf{k},\mathbf{k}')$. The function $S(\mathbf{q})$ is called the *geometric structure factor*.

An Example: BCC Lattice

As an example, consider the BCC lattice viewed as a simple cubic lattice of size a, with two basis vectors sitting at $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = \frac{a}{2}(1,1,1)$. If we take the atoms on the points $\mathbf{d}_1$ and $\mathbf{d}_2$ to be identical, then the associated scattering amplitudes are also equal: $f_1 = f_2 = f$.

We know that the scattering amplitude is non-vanishing only if the transferred momentum $\mathbf{q}$ lies on the reciprocal lattice, meaning

$$\mathbf{q} = \frac{2\pi}{a}(n_1,n_2,n_3) \qquad n_i \in \mathbf{Z}$$

This then gives the structure factor

$$\begin{aligned} S(\mathbf{q}) &= f\left(e^{i\mathbf{q}\cdot\mathbf{d}_1} + e^{i\mathbf{q}\cdot\mathbf{d}_2}\right) \\ &= f\left(1 + e^{i\pi\sum_i n_i}\right) = \begin{cases} 2 & \sum n_i \text{ even} \\ 0 & \sum n_i \text{ odd} \end{cases} \end{aligned}$$

We see that not all points in the reciprocal lattice $\Lambda^\star$ contribute. If we draw the

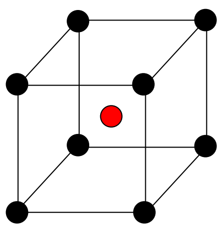


Figure 50: A BCC lattice as cubic lattice + basis.

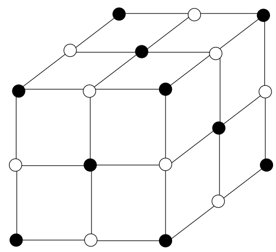


Figure 51: The reciprocal as a cubic lattice minus a basis.

reciprocal, simple cubic lattice and delete the odd points, as shown in the right-hand figure, we find ourselves left with a FCC lattice. (Admittedly, the perspective in the figure isn't great.) But this is exactly what we expect since it is the reciprocal of the BCC lattice.

Another Example: Diamond

A diamond lattice consists of two, interlaced FCC lattices with basis vectors $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = \frac{a}{4}(1,1,1)$. An FCC lattice has reciprocal lattice vectors $\mathbf{b}_1 = \frac{2\pi}{a}(-1,1,1)$, $\mathbf{b}_2 = \frac{2\pi}{a}(1,-1,1)$ and $\mathbf{b}_3 = \frac{2\pi}{a}(1,1,-1)$. For $\mathbf{q} = \sum_i n_i \mathbf{b}_i$, the structure factor is

$$S(\mathbf{q}) = f\left(1 + e^{i(\pi/2)\sum_i n_i}\right) = \begin{cases} 2 & \sum n_i = 0 \text{ mod } 4 \\ 1+i & \sum n_i = 1 \text{ mod } 4 \\ 0 & \sum n_i = 2 \text{ mod } 4 \\ 1-i & \sum n_i = 3 \text{ mod } 4 \end{cases}$$

3.4.3 The Debye-Waller Factor

So far, we've treated the lattice as a fixed, unmoving object. But we know from our discussion in Section 5 that this is not realistic. The underlying atoms can move. We would like to know what effect this has on the scattering off a lattice.

Let's return to our result (3.48) for the scattering amplitude off a Bravais lattice Λ,

$$f_\Lambda(\mathbf{k}, \mathbf{k}') = f(\mathbf{k}, \mathbf{k}') \sum_n e^{i\mathbf{q}\cdot\mathbf{R}_n}$$

where $f(\mathbf{k}, \mathbf{k}')$ is the amplitude for scattering from each site, $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, and $\mathbf{R}_n \in \Lambda$. Since the atoms can move, the position R_n are no longer fixed. We should replace

$$R_n \to R_n + \mathbf{u}_n(t)$$

where, as in Section 5, $\mathbf{u}_n$ describes the deviation of the lattice from equilibrium. In general, this deviation could arise from either thermal effects or quantum effects. In keeping with the theme of these lectures, we will restrict to the latter. But this is conceptually interesting: it means that the scattering amplitude includes the factor

$$\tilde{\Delta}(\mathbf{q}) = \sum_n e^{i\mathbf{q}\cdot\mathbf{R}_n} e^{i\mathbf{q}\cdot\mathbf{u}_n}$$

which is now a quantum operator. This is telling us something important. When a particle – whether photon or neutron – scatters off the lattice, it can now excite a phonon mode. The scattering amplitude is a quantum operator because it includes all possible end-states of the lattice.

This opens up a whole slew of new physics. We could, for example, now start to compute *inelastic scattering*, in which the particle deposits some energy in the lattice. Here, however, we will content ourselves with *elastic scattering*, which means that the the lattice sits in its ground state $|0\rangle$ both before and after the scattering. For this, we need to compute

$$\tilde{\Delta}(\mathbf{q}) = \sum_n e^{i\mathbf{q}\cdot\mathbf{R}_n} \langle 0|e^{i\mathbf{q}\cdot\mathbf{u}_n(t)}|0\rangle$$

To proceed, we need the results of Section 5.1.4 in which we treated lattice vibrations quantum mechanically. For simplicity, let's consider a simple cubic lattice so that the the matrix element above factorises into terms in the x, y and z direction. For each of these, we can use the formalism that we developed for the one-dimensional lattice.

The matrix element $\langle 0|e^{i\mathbf{q}\cdot\mathbf{u}_n}|0\rangle$ is independent of time and is also translationally invariant. This means that we can evaluate it at $t = 0$ and at the lattice site $n = 0$. For a one-dimensional lattice with N sites, the expansion (5.11) gives

$$u_0 = \sum_{k\neq 0} \sqrt{\frac{\hbar}{2mN\omega(k)}}\Big(a(k) + a^\dagger(k)\Big) \equiv A + A^\dagger$$

Here we've used the rescaling (5.14) so that the creation and annihilation operators obey the usual commutation relations $[a(k), a^\dagger(k')] = \delta_{k,k'}$. The operators $a^\dagger(k)$ create a phonon with momentum k and energy $\omega(k)$. The operators A and $A^\dagger$ then obey

$$[A, A^\dagger] = \sum_{k\neq 0} \frac{\hbar}{2mN\omega(k)}$$

Our goal now is to compute $\langle 0|e^{iq(A+A^\dagger)}|0\rangle$. For this we use the BCH formula,

$$e^{iq(A+A^\dagger)} = e^{iqA^\dagger}\, e^{iqA}\, e^{\frac{1}{2}q^2[A^\dagger,A]}$$

But the ground state of the lattice is defined to obey $a_l|0\rangle = 0$ for all l. This means that $e^{iqA}|0\rangle = |0\rangle$. We end up with the result

$$\langle 0|e^{i\mathbf{q}\cdot\mathbf{u}_0}|0\rangle = e^{-W(\mathbf{q})} \quad \text{where} \quad W(\mathbf{q}) = \sum_{\mathbf{k}} \frac{\hbar\mathbf{q}^2}{4mN\omega(\mathbf{k})}$$

This is called the *Debye-Waller factor*. We see that the scattering amplitude becomes

$$f_\Lambda(\mathbf{k}, \mathbf{k}') = e^{-W(\mathbf{q})}\, f(\mathbf{k}, \mathbf{k}')\Delta(\mathbf{q})$$

Note that, perhaps surprisingly, the atomic vibrations do not broaden the Bragg peaks away from $\mathbf{q} \in \Lambda^\star$. Instead, they only diminish their intensity.