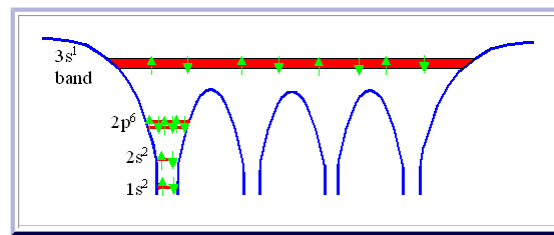


2.1.4 Periodic Potentials and Bloch's Theorem

The Bloch Theorem

✎ In the most simplified version of the free electron gas, the true three-dimensional potential was ignored and approximated with a constant potential conveniently put at 0 eV .

- The true potential, however, e.g. for a **Na** crystal including some energy states, is periodic and looks more like this:



✎ Semiconducting properties will not emerge without some consideration of the periodic potential - we therefore have to solve the Schrödinger equation for a suitable periodic potential. There are several (for real potentials always numerical) ways to do this, but as stated before, it can be shown that *all* solutions must have certain general properties. These properties can be used to make calculations easier and to obtain a general understanding of the effects of a periodic potential on the behavior of electron waves.

- The starting point is a potential $V(\mathbf{r})$ determined by the crystal lattice that has the periodicity of the lattice, i.e.

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

- With \mathbf{T} = any translation vector of the lattice under consideration.
 - We then will obtain some wavefunctions $\psi_{\mathbf{k}}(\mathbf{r})$ which are solutions of the Schrödinger equation for $V(\mathbf{r})$. [As before](#), we use a quantum number " \mathbf{k} " (three numbers, actually) as an index to distinguish the various solutions.
- ✎ The *Bloch theorem* in essence formulates a condition that *all* solutions $\psi_{\mathbf{k}}(\mathbf{r})$, for *any* periodic potential $V(\mathbf{r})$ whatsoever have to meet. In one version it ascertains

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \cdot \exp(\mathbf{i} \cdot \mathbf{k} \cdot \mathbf{r})$$

- With \mathbf{k} = any allowed wave vector for the electron that is obtained for a *constant* potential, and $u_{\mathbf{k}}(\mathbf{r})$ = arbitrary functions (distinguished by the index \mathbf{k} that marks the particular solution we are after), but *always with the periodicity of the lattice*, i.e.

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) = u_{\mathbf{k}}(\mathbf{r})$$

- ✎ Any wavefunction meeting this requirement we will henceforth call a **Bloch wave**.
- ✎ The Bloch theorem is quite remarkable, because, as said before, it imposes very special conditions on *any* solution of the Schrödinger equation, no matter what the form of the periodic potential might be.
 - We notice that exactly as in the [case of the constant potential](#), the wave vector \mathbf{k} has a *twofold role*: It is still a wave vector in the plane wave part of the solution, but also an index to $\psi_{\mathbf{k}}(\mathbf{r})$ and $u_{\mathbf{k}}(\mathbf{r})$ because it contains all the quantum numbers, which enumerate the individual solutions.
- ✎ Bloch's theorem is a *proven* theorem with perfectly general validity. We will first give some ideas about the prove of this theorem, and then discuss what it means for real crystals. As always with hindsight, Bloch's theorem can be proved in many ways; the links give some examples. Here we only look at general outlines of how to prove the theorem:
 - It follows rather directly from applying *group theory* to crystals. In this case one looks at symmetry properties that are invariant under translation.
 - It can easily be proved by working with *operator algebra* in the context of formal quantum theory mathematics.
 - It can be directly proved in *simple ways* - but then only for special cases or with not quite kosher "tricks".
 - It can be proved (and used for further calculations), by expanding $V(\mathbf{r})$ and $\psi(\mathbf{r})$ into a *Fourier series* and then rewriting the Schrödinger equation. This is a particularly useful way because it can also be used for obtaining specific results for the periodic potential. This proof is demonstrated in detail in the [link](#), or in the book of [Ibach and Lüth](#).
- ✎ Bloch's theorem can also be rewritten in a somewhat different form, giving us a second version:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) = \psi_{\mathbf{k}}(\mathbf{r}) \cdot \exp(\mathbf{i} \mathbf{k} \cdot \mathbf{T})$$

- This means that *any* function $\psi_{\mathbf{k}}(\mathbf{r})$ that is a solution to the Schrödinger equation of the problem, differs only by a phase factor $\exp(\mathbf{i} \mathbf{k} \cdot \mathbf{r})$ between *equivalent positions* in the lattice.

- This implies immediately that the probability of finding an electron *is the same at any equivalent position in the lattice since*, exactly [as we expected](#), because

$$[\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{T})]^2 = [\psi_{\mathbf{k}}(\mathbf{r})]^2 \cdot [\exp(i\mathbf{k}\mathbf{T})]^2 = [\psi_{\mathbf{k}}(\mathbf{r})]^2$$

- Since $[\exp(i\mathbf{k}\mathbf{T})]^2 = 1$ for all \mathbf{k} and \mathbf{T} .

That this *second version* of Bloch's theorem is equivalent to the first one may be seen as follows.

- If we write the wave function in the first form $\psi_{\mathbf{k}}(\mathbf{r}) = \mathbf{u}_{\mathbf{k}}(\mathbf{r}) \cdot \exp(i\mathbf{k}\mathbf{r})$ and consider its value at an equivalent lattice position $\mathbf{r} + \mathbf{T}$ we obtain

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) &= \mathbf{u}_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) \cdot \exp[i\mathbf{k} \cdot (\mathbf{r} + \mathbf{T})] = \mathbf{u}_{\mathbf{k}}(\mathbf{r}) \cdot \exp(i\mathbf{k}\mathbf{r}) \cdot \exp(i\mathbf{k}\mathbf{T}) = \psi_{\mathbf{k}}(\mathbf{r}) \cdot \exp(i\mathbf{k}\mathbf{T}) \\ &= \mathbf{u}_{\mathbf{k}}(\mathbf{r}) &= \psi_{\mathbf{k}}(\mathbf{r}) &\quad \text{q.e.d.} \end{aligned}$$

Bloch's theorem has many more forms and does not only apply for electrons in periodic potentials, but for all kinds of waves, e.g. phonons. However, we will now consider the theorem to be proven and only discuss some of its implications.

Implications of the Bloch Theorem

One way of looking at the Bloch theorem is to interpret the periodic function $\mathbf{u}_{\mathbf{k}}(\mathbf{r})$ as a kind of *correction factor* that is used to generate solutions for periodic potentials from the simple solutions for constant potentials.

- We then have [good reasons](#) to assume that $\mathbf{u}_{\mathbf{k}}(\mathbf{r})$ for \mathbf{k} vectors *not close to a Brillouin zone* will only be a minor correction, i.e. $\mathbf{u}_{\mathbf{k}}(\mathbf{r})$ should be close to 1.

But in any case, the quantity \mathbf{k} , while still being the wave vector of the plane wave that is part of the wave function (and which may be seen as the "backbone" of the Bloch functions), has lost its simple meaning: It can no longer be taken as a *direct* representation of the momentum \mathbf{p} of the wave via $\mathbf{p} = \hbar\mathbf{k}$, or of its wavelength $\lambda = h/k$, since:

- The momentum of the electron moving in a periodic potential is no longer constant (as we will see shortly); for the standing waves resulting from (multiple) reflections at the Brillouin zones it is actually *zero* (because the velocity is zero), while \mathbf{k} is not.
- There is no unique wavelength to a plane wave modulated with some arbitrary (if periodic) function. Its Fourier decomposition can have any spectra of wavelengths, so which one is the one to associate with \mathbf{k} ?

To make this clear, sometimes the vector \mathbf{k} for Bloch waves is called the "**quasi** wave vector".

Instead of associating \mathbf{k} with the *momentum of the electron*, we may identify the quantity $\hbar\mathbf{k}$, *which is obviously still a constant*, with the so-called **crystal momentum** \mathbf{P} , something like the *combined* momentum of crystal and electron.

- Whatever its name, $\hbar\mathbf{k}$ is a constant of motion related to the particular wave $\psi_{\mathbf{k}}(\mathbf{r})$ with the index \mathbf{k} . Only if $V = 0$, i.e. there is no periodic potential, is the electron momentum equal to the crystal momentum; i.e. the part of the crystal is zero.
- The crystal momentum \mathbf{P} , while not a "true" momentum which should be expressible as the product of a distinct mass and a velocity, still has many properties of momentums, in particular **it is conserved** during all kinds of processes.
- This is a major feature for the understanding of semiconductors, as we will see soon enough!

One more difference to the constant potential case is crucial: If we know the wavefunction for *one* particular \mathbf{k} -value, we also know the wavefunctions for infinitely many other \mathbf{k} -values, too.

- This follows from yet another formulation of Bloch's theorem:
- If $\psi_{\mathbf{k}}(\mathbf{r}) = \mathbf{u}_{\mathbf{k}}(\mathbf{r}) \cdot \exp(i\mathbf{k}\mathbf{r})$ is a particular Bloch wave solving the Schrödinger equation of the problem, then the following function is also a solution.

$$\psi_{\mathbf{k} + \mathbf{g}}(\mathbf{r}) = \mathbf{u}_{\mathbf{k} + \mathbf{g}}(\mathbf{r}) \cdot \exp i[\mathbf{k} + \mathbf{g}]\mathbf{r}$$

- With \mathbf{g} = arbitrary reciprocal lattice vector as always.

This is rather easy to show and you should attempt it yourself. It has a far reaching consequence:

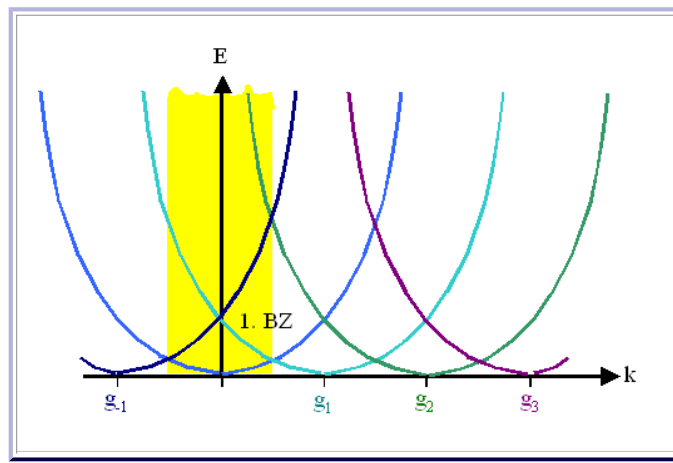
- If $\psi_{\mathbf{k}}(\mathbf{r})$ is a solution of the Schrödinger equation for the system, it will always be associated with a specific energy $E(\mathbf{k})$ which is a constant of the system for the particular sets of quantum numbers embodied by \mathbf{k} . Since $\psi_{\mathbf{k}}(\mathbf{r})$ is identical to $\psi_{\mathbf{k} + \mathbf{g}}(\mathbf{r})$, its specific energy $E(\mathbf{k} + \mathbf{g})$ must be identical to $E(\mathbf{k})$, or

$$E(\mathbf{k} + \mathbf{g}) = E(\mathbf{k})$$

This is a major insight. However, there is also a difficulty:

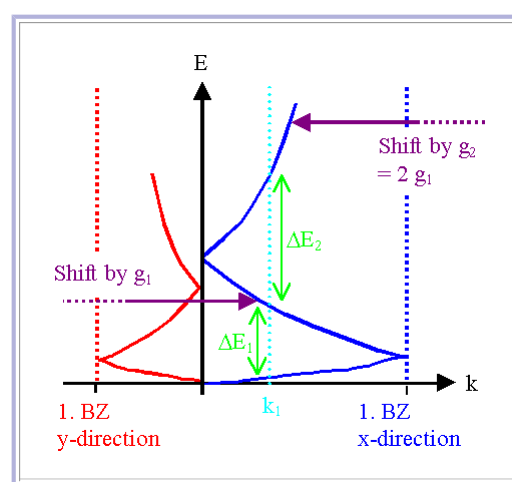
- The equation does *not* mean that two electrons with wave vectors \mathbf{k} and $\mathbf{k} + \mathbf{g}$ have the same energy ([see below](#)), but that *any* reciprocal lattice point can serve as the origin of the $E(\mathbf{k})$ function.

- Lets visualize this for the case of an infinitesimally small periodic potential - we have the periodicity, but not a real potential. The $E(k)$ function than is practically the same as in the case of free electrons, but starting at *every* point in reciprocal space:



- Indeed, we do have $E(k + g) = E(k)$, *but for dispersion curves that have a different origin.*
- We have even more, we now have also *many* energy values for *one* given k , and in particular *all possible energy values are contained within the first Brillouin zone* (between $-1/2g_1$ and $+1/2g_1$ in the picture).

It thus is sufficient to consider only the first Brillouin zone in graphical representations - it contains all the information available about the system. This is called a **reduced representation** of the band diagram, which may look like this:

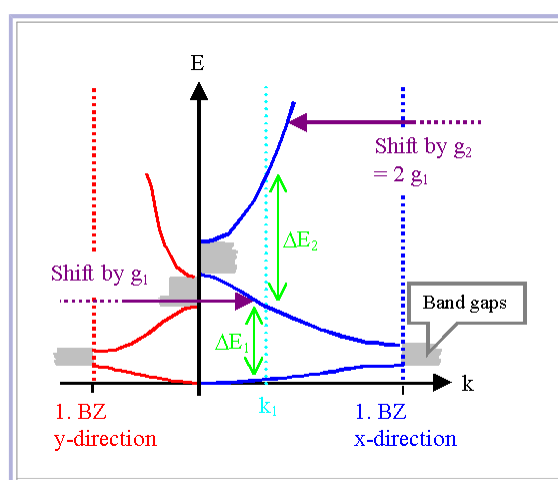


- The branches outside the **1. BZ** have been "folded back" into the **1. BZ**, i.e. translated by the appropriate reciprocal lattice vector g . To make band diagrams like this one as comprehensive as possible, the symmetric branch on the left side is omitted; instead the band diagram in a different direction in reciprocal space is shown.

Again, this looks like a specific electron could now have many energies all at once - this is, of course, *not the case*.

- Different energies, formerly distinguished by different k - vectors, are still different energies, but now the branches in the **1st** Brillouin zone coming from larger k - vectors belong to *different* bands. *Every energy branch in principle should carry an index denoting the band; this is, however, often omitted.*

The identical construction, but now for the energy functions of a *periodic potential* as [given before](#), now looks like this



- We now have **band gaps** - regions with unattainable energies - in all directions of the reciprocal lattice.

- A numerical example for the Kroning Penney Model is shown in this [link](#).











What does this mean for a particular electron, say one on the lowest branch of the blue diagram with the wave vector k_1 ? It has a definite energy E associated with it.

- But it also could have larger energies: all the values obtained for the same k but in higher branches of the band diagram.
- For a transition to the next higher branch the energy ΔE_1 is needed. *It has to be supplied from the outside world.*
- After the transition the electron has now a higher energy, but the wave vector is the same. *But wait*, in the reduced band diagram, we simply omitted a reciprocal wave vector, so its wave vector is actually $k_1 + g$. If we index the situation after the transition with "2", before with "1", we have the following equations.

$$E_2 = E_1 + \Delta E$$

$$k_2 = k_1 + g$$

$$|k_1| \neq |k_2|$$

-  This is simply [Braggs law](#), but now for *inelastic scattering*, where the magnitude of k may change - but only by a specified amount tied to a reciprocal lattice vector.
-  Since we interpreted $\hbar k$ as **crystal momentum**, we may consider *Braggs law to be the expression for the conservation of momentum in crystals*.
 -  The reduced band diagram representations thus allow a very simple graphical representation of allowed transitions of electrons from one state represented by to another state (E_2, k_2): the states must be on a vertical line through the diagram, i.e. straight up or down.
 -  An alternative way of describing the states in the spirit of the reduced diagram is to use the same wave vector k_1 for all states and a band index for the energy. The transition then goes from (E_n, k) to (E_m, k) with n, m = number of the energy band involved.
-  The possibility of working in a reduced band diagram, however, does not mean that wave vectors larger than all possible vectors contained in the **1. BZ** are not meaningful or *do not exist*:
 -  Consider an electron "shot" into the crystal with a high energy and thus a large k - e.g. in an electron microscope. If you reduce its wave vector by subtracting a suitable large g vector without regard to its energy and band number, you may also reduce its energy - you move it. e.g., from a band with a high band number to a lower one. While this may happen physically, it will only happen via many transitions from one band to the next lower one - and this takes time!
 -  Most of the time in normal applications the electron will contain its energy and its original wave vector. And it is this wave vector you must take for considering diffraction effects! An Ewald (or Brillouin) construction for diffraction will give totally wrong results for reduced wave vectors - think about it!
-  If you feel slightly (or muchly) confused at this point, that is as it should be. Blochs theorem, while relatively straightforward mathematically, is not easy to grasp in its implications to real electrons. The representation of the energy - wave vector relationship (the dispersion curves) in extended or reduced schemata, the somewhat unclear role of the wave vector itself, the relation to diffraction via Braggs law, the connection to electrons introduced from the outside, e.g. by an electron microscope (think about it for minute!), and so on, are difficult concepts not easily understood at the "gut level".
 -  While it never hurts to think about these questions, it is sufficient for our purpose to just accept the reduced band structure scheme and its implications as something useful in dealing with semiconductors - never mind the small print associated with it.
 -  However, if you want to dig deeper: These problem are to some extent rooted in the formal quantum mechanics behind Blochs theorem. It has to do with Eigenvectors and Eigenvalues of Operators; a [glimpse of these issues](#) can be found in an advanced module.

