

Band theory of solids

Christian Bergfjord & Selda Ekiz

June 2, 2010



The Schrödinger equation for an electron in periodic potential is, in one dimension,

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x) + U(x)\psi(x) = \epsilon\psi(x) \quad (1)$$

where

$$U(x + a) = U(x) \quad (2)$$

for all x where a is the lattice constant.

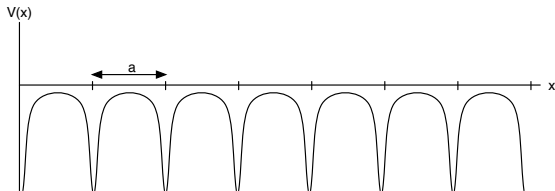


Figure: A periodical potential

Bloch's theorem

We assume that the probability density for the electrons is a periodic function, so that it is the same in every unit cell

$$|\psi(x + a)|^2 = |\psi(x)|^2 \quad \text{that is} \quad \psi(x + a) = e^{ik_a}\psi(x) \quad (3)$$

with some real k . Given equation 3, the function

$$u_k(x) = e^{-ikx}\psi(x) \quad (4)$$

fulfils

$$\begin{aligned} u_k(x + a) &= e^{-ik(x+a)}\psi(x + a) = e^{-ikx}e^{-ika}\psi(x + a) \\ &= e^{-ikx}e^{-ika}e^{ika}\psi(x) = e^{-ikx}\psi(x) = u_k(x) \end{aligned} \quad (5)$$

so that u_k has the same periodicity as the lattice.



Bloch's theorem

The result

$$\psi(x) = e^{ikx} u_k(x) \quad \text{with} \quad u_k(x + a) = u_k(x) \quad (6)$$

is a plane wave modulated with a function which has the lattice's periodicity. This is called Bloch's theorem.

Proof - Fourier expansion

We consider a one-dimensional infinite atomic lattice. The potential set up by this lattice is naturally periodic, and can be written as

$$V(x) = \sum U(x - x_i) = \sum_{n=-\infty}^{\infty} U(x - na) \quad (7)$$

where a is the lattice constant. U are the independent wells localised around each atom.



We now consider the solution on a subset of size $L = Na$

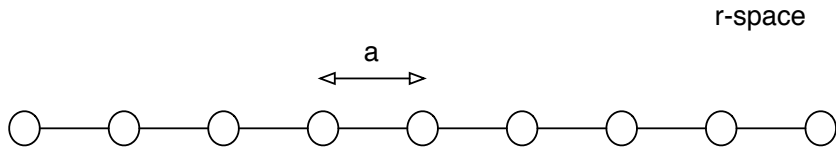


Figure: Subset of size $L = Na$, where $N = 8$



We start by expanding the wave $\psi(x)$ and the potential $U(x)$ in Fourier series,

$$\psi(x) = \sum \tilde{\psi}(k_n) e^{ik_n x} \quad (8)$$

$$U(x) = \sum \tilde{U}(K_m) e^{iK_m x} \quad (9)$$

The allowed wave numbers in the two equations are not the same since the periodicity of $\psi(x)$ requires $\psi(x) = \psi(x + Na)$ giving

$$k_n = \frac{2\pi n}{aN} = \frac{nG}{N} \quad (10)$$

whereas U has period equal to the lattice spacing, $U(x) = U(x + a)$ giving

$$K_m = \frac{2\pi m}{a} = mG \quad (11)$$



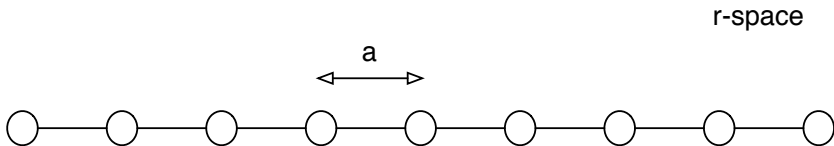


Figure: Subset of size $L = Na$, where $N = 8$

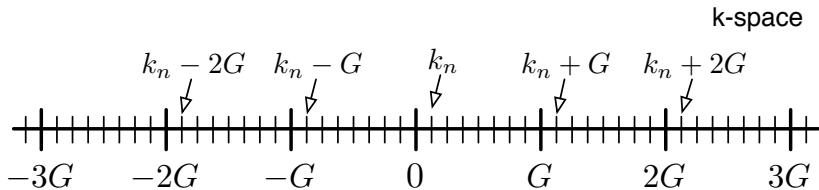


Figure: Example of k_n and K_m values



Inserting the expansions into the one-particle Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x) + U(x) \psi(x) = \epsilon \psi(x) \quad (12)$$

we find

$$\sum_n \left(\frac{\hbar^2}{2m} k_n^2 - \epsilon \right) \tilde{\psi}(k_n) e^{ik_n x} + \sum_{m,n} \tilde{U}(K_m) \tilde{\psi}(k_n) e^{(k_n + K_m)x} = 0$$

This matrix equation is easier to evaluate if we use the Dirac notation on equation 12



Dirac notation

First, we have that the states - or the Fourier expansion functions for the potential

n -th state, leading to n -th position in the matrix,

We remember that

$$k_n = n \frac{2\pi}{Na} = n \frac{G}{N} = n \frac{2\pi}{L} \quad (13)$$

i.e. n -th state is $|k_n\rangle$,

$$|k_n\rangle \rightarrow \psi_{k_n}(x) \rightarrow \frac{1}{\sqrt{L}} e^{ik_n x} \quad (14)$$

$$\langle k_n| \rightarrow \psi_{k_n}^*(x) \rightarrow \frac{1}{\sqrt{L}} e^{-ik_n x}$$



Dirac notation

We remember that

$$U(x) = \sum_m \tilde{U}(K_m) e^{iK_m x} \quad \text{with} \quad K_m = \frac{2\pi n}{a} = nG \quad (15)$$

where

$$\tilde{U}(K_m) = \frac{1}{L} \int_L U(x) e^{-iK_m x} dx \quad (16)$$



Dirac notation

The equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x) + U(x)\psi(x) = \epsilon\psi(x) \quad (17)$$

can be represented as

$$H = T + U \quad (18)$$

$$H_{kl} = T_{kl} + U_{kl} \quad (19)$$

We have that

$$\langle k_l | k_k \rangle = \int_L \psi_{k_k}^*(\tau) \psi_{k_l}(\tau) d\tau = \frac{1}{L} \int_L e^{-ik_k x} e^{ik_l x} dx = \delta_{kl} \quad (20)$$



Dirac notation

Which gives us

$$\langle k_l | T | k_k \rangle = \frac{1}{L} \int_L e^{-ik_k x} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) e^{ik_l x} dx = \frac{\hbar^2 k_l^2}{2m} \delta_{kl} \quad (21)$$

and

$$\langle k_l | U | k_k \rangle = \sum_m \tilde{U}(K_m) \langle k_l | e^{iK_m x} | k_k \rangle \quad (22)$$

where

$$\langle k_l | e^{iK_m x} | k_k \rangle = \frac{1}{L} \int_L e^{-ik_k x} e^{iK_m x} e^{ik_l x} dx = \delta_{k, l+Nm} \quad (23)$$

$$\delta_{k, l+Nm} \neq 0 \rightarrow k_k = k_l + K_m \quad (24)$$



Dirac notation

The matrix representing U is a band matrix with all elements equal to zero except of those satisfying:

If $k = l + Nm$, then $U_{kl} \neq 0$

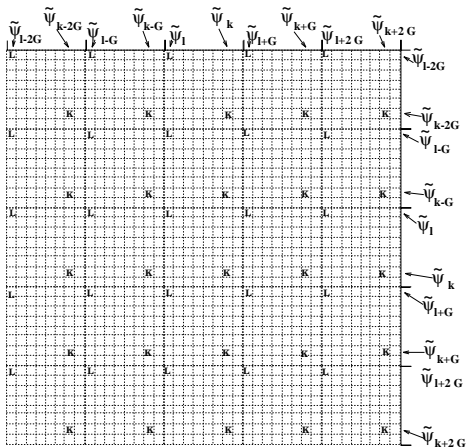
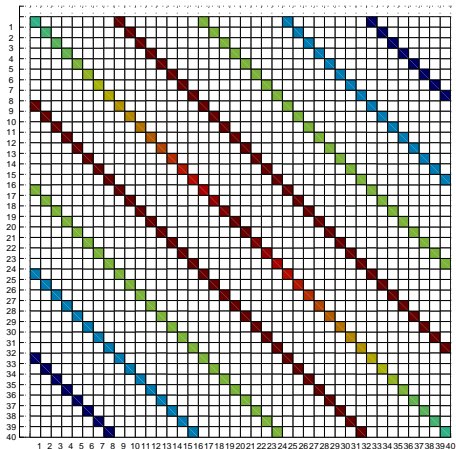
The matrix representing T is a diagonal matrix

The matrix H (the matrix representing total energy)

$$H_{kl} = T_{kl} + U_{kl} = \frac{\hbar^2 k_l^2}{2m} \delta_{kl} + \sum_m \tilde{U}_{K_m} \delta_{k,l+Nm} \quad (25)$$



Matrices



Rearranging the basis states

The basis states must be arranged into groups which have nonzero matrix elements

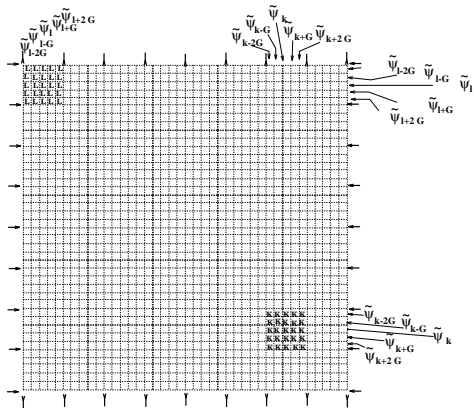
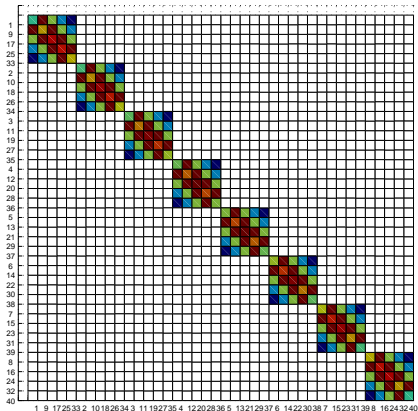
We can see that each of the values from the

$$\frac{2\pi}{a} = G \quad k_n \text{ from } \left(-\frac{\pi}{a} \leq k_n \leq \frac{\pi}{a}\right) \quad (26)$$

region (this is the length N) will define one non-zero block



Rearranging the basis states



Bloch's theorem

In one block all the k'_n are of the form ($k'_n = k_n + K_m = k_n + mG$) so that the functions can be written as

$$\psi(x) = \sum_n \tilde{\psi}(k'_n) e^{ik'_n x} \rightarrow \sum_m \tilde{\psi}(k_n + mG) e^{i(k_n + mG)x} \quad (27)$$

Taking out the common $e^{ik_n x}$ so that

$$\psi(x) = e^{i(k_n x)} \sum_m \tilde{\psi}(k_n + mG) e^{imGx} \quad (28)$$

where the sum is of exactly the same form as the sum for the potential

$$U(x) = \sum \tilde{U}(K_m) e^{iK_m x} \quad (29)$$

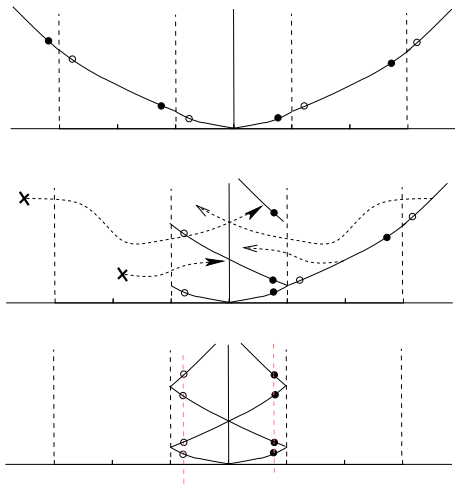
since K_m and mG run over the same values.

This proves the *Bloch theorem*.

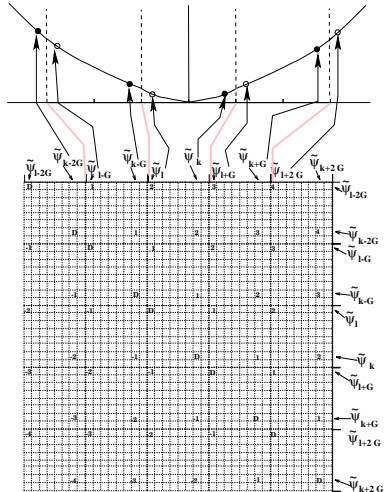


Diagonal energies

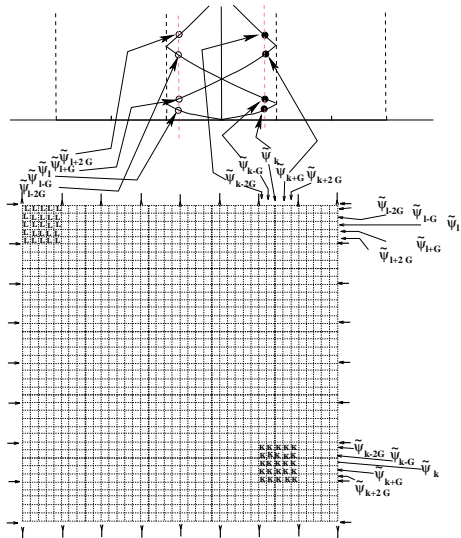
We plot the diagonal energies and in the three versions of the picture we follow the use of the periodicity condition.



This figure shows the original diagonal energies on the parabola, together with the matrix .

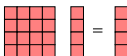
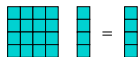
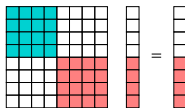
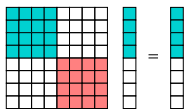


This figure shows that the periodicity-moving in the First Brillouin zone corresponds to the rearrangements of the matrix shown in the previous side.



Diagonalization

Diagonalization of block matrix - independent diagonalization of each block

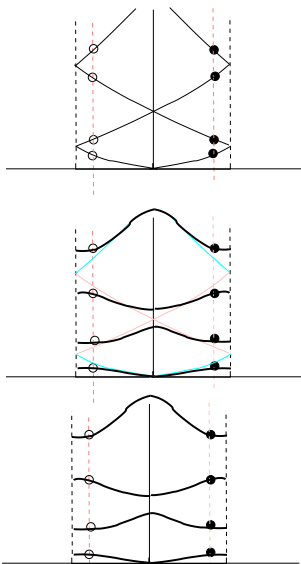


	$\tilde{\Psi}_{k-2G}$	$\tilde{\Psi}_{k-G}$	$\tilde{\Psi}_k$	$\tilde{\Psi}_{k+G}$	$\tilde{\Psi}_{k+2G}$	
$E_{k-2G} + \tilde{U}_0$	\tilde{U}_G	\tilde{U}_{2G}				$\tilde{\Psi}_{k-2G}$
\tilde{U}_{-G}	$E_{k-G} + \tilde{U}_0$	\tilde{U}_G	\tilde{U}_{2G}			$\tilde{\Psi}_{k-G}$
\tilde{U}_{2G}	\tilde{U}_{-G}	$E_k + \tilde{U}_0$	\tilde{U}_G	\tilde{U}_{2G}		$\tilde{\Psi}_k$
		\tilde{U}_{2G}	$E_{k+G} + \tilde{U}_0$	\tilde{U}_G		$\tilde{\Psi}_{k+G}$
			\tilde{U}_{2G}	$E_{k+2G} + \tilde{U}_0$		$\tilde{\Psi}_{k+2G}$



Diagonalization

- ▶ *First Brillouin zone* before and after the matrices diagonalization.
- ▶ For each value of allowed k , a matrix must be diagonalized.
- ▶ The eigenvalues (originating from closely placed diagonal values) get pushed away from each other, as indicated.



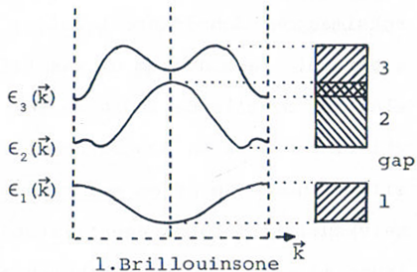
Energy bands

It is possible to assign indices n to the levels in such a way that for given n , the eigenstates and eigenvalues are periodic functions of k in the reciprocal lattice

$$\psi_{n,k+K}(r) = \psi_{nk}(r) \quad (30)$$

$$\epsilon_{n,k+K} = \epsilon_{nk} \quad (31)$$

For each n , the set of electron levels specified by $\epsilon_n(k)$ is called an *energy band*. $\epsilon_n(k)$ varies continuously as k vary, because k appears as a parameter in H_k



Energy bands

Number of states in a band

The number of orbitals in a band within the first Brillouin zone is equal to the number of unit cells N in the the crystal. Since each band has N states inside the first zone, and each state can accommodate two electrons, of opposite spin, it follows that the maximum number of electrons that may occupy a single band is $2N$.

This result is significant, as it is used to predict whether a solid is going to behave as a metal or an insulator.



Metal and non metal

Metal or non metal?

A metal is a solid in which an electric current flows under application of electric field

An non metal is a solid where the electric field does not produce an electric current



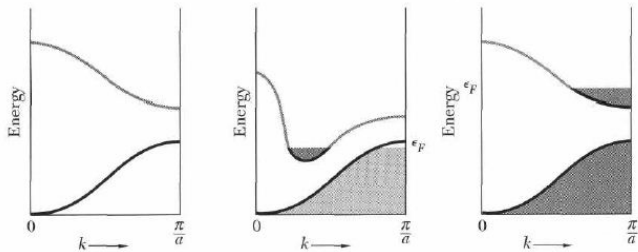
Metal and non metal

The ground state of N Bloch electrons is constructed by occupying all one-electron levels that are less than the Fermi energy ϵ_F .

$$\epsilon_n(\mathbf{k}) < \epsilon_F \quad (32)$$

Whether a solid is a metal or a non metal depends on where the Fermi level is in relation to the energy bands:

a) non metal b) Semi metal because of band overlap c) metal

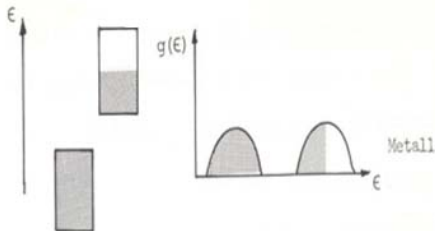


Metal

The number of electrons in each unit cell has to be an integer, which means that when there is no band overlap each band will either be full, half-full or empty

If there are odd numbers of electrons in each primitive unit cell, then the solid is a metal.

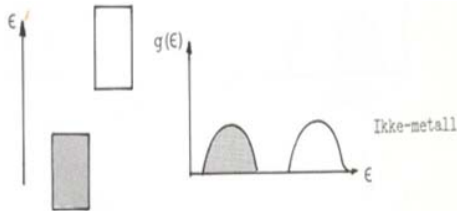
This is the result of the fact that the valence band is not completely filled.



Non metal

An even number of electrons results in a non-metal, but only if the energy bands do not overlap.

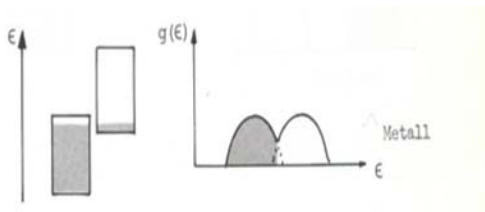
If the valence electrons exactly fill one or more bands, leaving the others empty, the solid will be an non metal.



Semi metal

Even if the number of electrons per unit cell is even, does not automatically make it an insulator. Because if the bands overlap in energy, one can have two partly filled bands and not one filled band.

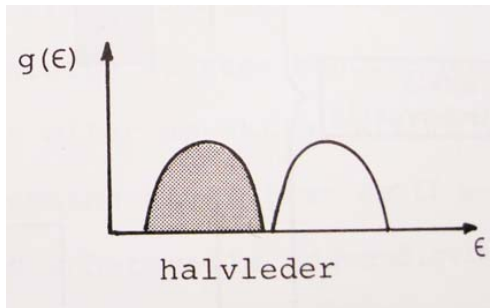
This is called a semi metal.



Semiconductor

If the gap between the valence band and the band immediately above it is small enough (< 2 eV), then electrons are readily excitable thermally from the former to the latter band causing both bands to be partially filled and both contribute to the electric conduction.

This is called a semiconductor



Dynamics of electrons in a lattice

Group velocity

The transmission velocity of a wave packet is the **group velocity**, given as

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{d\epsilon}{dk} \quad (33)$$

where ω is the wave's angular frequency and k is the wave number. This is the velocity of the energy propagation in the medium.

Velocity of Bloch electrons - like group velocity

The velocity of a Bloch electron in an energy level specified by the band index n and the wave vector \vec{k} can be found by deriving the expectation of momentum in a Bloch state. As we shall see, it gives the same value as mv_g , that is a (mass x group velocity)-like expression.



Velocity of Bloch electrons

We start from the equation for the periodic function $u_{\epsilon, \vec{k}}(\vec{x})$

$$\left[-\frac{\hbar^2}{2m} (\nabla + i\vec{k})^2 + U(r) \right] u_{\epsilon, \vec{k}} = \epsilon(k) u_{\epsilon, \vec{k}} \quad (34)$$

Taking $\frac{\partial}{\partial k_x}$ and multiplying by $u_{\epsilon, \vec{k}}^*$ and integrating over the whole space, we get

$$\begin{aligned} \frac{\hbar}{m} \int u_{\epsilon, \vec{k}}^* \left(-i\hbar \frac{\partial}{\partial x} + \hbar k_x \right) u_{\epsilon, \vec{k}} + \int u_{\epsilon, \vec{k}}^* H \left(\frac{\partial u_{\epsilon, \vec{k}}}{\partial k_x} \right) \\ = \int u_{\epsilon, \vec{k}}^* \left(\frac{\partial \epsilon(k)}{\partial k_x} \right) u_{\epsilon, \vec{k}} + \int \epsilon(k) u_{\epsilon, \vec{k}}^* \left(\frac{\partial u_{\epsilon, \vec{k}}}{\partial k_x} \right) \end{aligned} \quad (35)$$



Velocity of Bloch electrons

We combine the second terms on each side which give

$$\int \left\{ u_{\epsilon, \vec{k}}^* (H - \epsilon(k)) \right\} \left(\frac{\partial u_{\epsilon, \vec{k}}}{\partial k_x} \right) \quad (36)$$

The term in the $\{ \dots \}$ is zero (Complex Conjugation) and we are then left with

$$\frac{\hbar}{m} \int u_{\epsilon, \vec{k}}^* \left(-i\hbar \frac{\partial}{\partial x} + \hbar k_x \right) u_{\epsilon, \vec{k}} = \int u_{\epsilon, \vec{k}}^* \left(\frac{\partial \epsilon(k)}{\partial k_x} \right) u_{\epsilon, \vec{k}} \quad (37)$$

or simply

$$\frac{\hbar}{m} \int u_{\epsilon, \vec{k}}^* \left(-i\hbar \frac{\partial}{\partial x} + \hbar k_x \right) u_{\epsilon, \vec{k}} = \left(\frac{\partial \epsilon(k)}{\partial k_x} \right) \quad (38)$$



Velocity of Bloch electrons

This gives, going back to the whole wavefunctions $\psi_{\epsilon, \vec{k}}$

$$\frac{\hbar}{m} \int \psi_{\epsilon, \vec{k}}^* \left(-i\hbar \frac{\partial}{\partial \mathbf{x}} \right) \psi_{\epsilon, \vec{k}} = \frac{\partial \epsilon(k)}{\partial k_x} \quad (39)$$

i.e. we can write that

$$\frac{1}{\hbar} \frac{\partial \epsilon(k)}{\partial k_x} = \frac{1}{m} \langle p_x \rangle \rightarrow \langle v_x \rangle \quad (40)$$

i.e. meaning the expectation value of momentum divided by mass, which classically is velocity, and this expression has the same form as the group velocity. Note that we have derived this by manipulations with symbols, instead of referring directly to group velocity argument. Remember,

$$(v_g)_x = \frac{\partial \omega}{\partial k_x} = \frac{1}{\hbar} \frac{d\epsilon}{dk_x} \quad (41)$$



Bloch electrons and constant force potential

If the electron is affected by an additional external field given by

$$V(\vec{x}) = -\vec{F} \cdot \vec{x} \quad (42)$$

the wave vector \vec{k} will change.

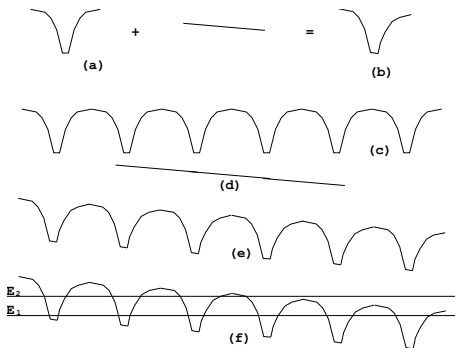


Figure: Potentials: Periodic plus constant field



Bloch electrons and constant force potential

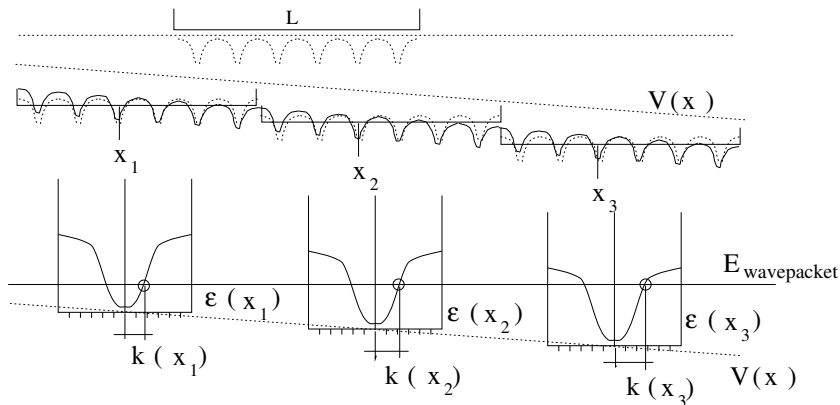


Figure: This figure shows a construction of position dependent bands, including how the other quantities are changing. In particular, it shows why the wave number k is function of position, by showing the bands displaced according to the changing potential energy $V(x)$.

Bloch electrons and constant force potential

If E is the energy of a state, or central energy of a wave packet, it will correspond to a different ϵ at the varying positions.

We see that

$$\Delta\epsilon = -\Delta V \quad (43)$$

Since the relation between ϵ and k is identical in each of the segments, we can e.g. write for each position x

$$\epsilon_k(x) = \epsilon(k(x)) \quad (44)$$

where the function $\epsilon(k)$ is the relation between energy and wavenumber for force-free case.

For a given wavepacket, we can write $\Delta x = v_g(x)\Delta t$, where we already indicate that even the group velocity can - and will - depend on the position.



Bloch electrons and constant force potential

We can thus write

$$\frac{\Delta k}{\Delta x} \rightarrow \frac{\Delta k}{v_g(x)\Delta t} \quad (45)$$

Once we have established this, we can go to a limiting chain

$$\frac{dk}{dt} = v_g(x) \frac{dk}{dx} = \frac{1}{\hbar} \frac{d\epsilon}{dk} \frac{dk}{dx} \quad (46)$$

This can be continued by realizing that $\Delta\epsilon = -\Delta V$,

$$\frac{dk_x}{dt} = \frac{1}{\hbar} \frac{\partial\epsilon}{\partial x} = -\frac{1}{\hbar} \frac{\partial V}{\partial x} \quad (47)$$

i.e.

$$\frac{dk_x}{dt} = \frac{F_x}{\hbar} \quad (48)$$



Effective mass

We continue by considering the time development of the group velocity. As far as the wavepacket is changing the middle energy $\epsilon(x)$ and wavenumber $\vec{k}(x)$, also the group velocity \vec{v}_g will be changing along \vec{x} .

In the following we mean \vec{v}_g when using \vec{v} .

In the same way as before, we can talk about a time derivative of a quantity, in the sense that the time specifies the position of the wave packet $\vec{x}(t)$.

We thus write

$$\frac{dv_i}{dt} = \frac{d}{dt} \frac{1}{\hbar} \frac{d\epsilon}{dk_i} = \frac{1}{\hbar} \frac{d}{dk_i} \left(\frac{d\epsilon}{dt} \right) \quad (49)$$

To evaluate the Time derivative of ϵ is the same type of operation as to evaluate the time derivative of the group velocity, our starting point here.



Effective mass

To perform this operation, we consider the variation of \vec{k} with time, i.e.

$$\left(\frac{d\epsilon}{dt}\right) = \left(\sum_{j=1}^3 \frac{\partial \epsilon}{\partial k_j} \frac{dk_j}{dt}\right) \quad (50)$$

Inserting this paranthesis in the previous equation, we obtain

$$\frac{dv_i}{dt} = \frac{1}{\hbar} \frac{\partial}{\partial k_i} \left(\sum_{j=1}^3 \frac{\partial \epsilon}{\partial k_j} \frac{dk_j}{dt}\right) \quad (51)$$

Replacing the dk_j/dt by F_j/\hbar , we obtain

$$\frac{dv_i}{dt} = \frac{1}{\hbar^2} \sum_{j=1}^3 \frac{\partial^2 \epsilon}{\partial k_i \partial k_j} F_j \quad (52)$$

Inverted mass tensor

$$\vec{a} = \left(\frac{1}{\vec{m}^*}\right) \vec{F} \quad (53)$$



Effective mass

Inverted mass components

$$a_i = \sum_j \left(\frac{1}{m^*} \right)_{i,j} F_j \quad (54)$$

As partial derivative

$$\left(\frac{1}{m^*} \right)_{i,j} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon(\vec{k})}{\partial k_i \partial k_j} \quad (55)$$

The following figure illustrates how we can understand the behaviour of the effective mass at the various positions in the band.



Dynamics of electrons in a lattice

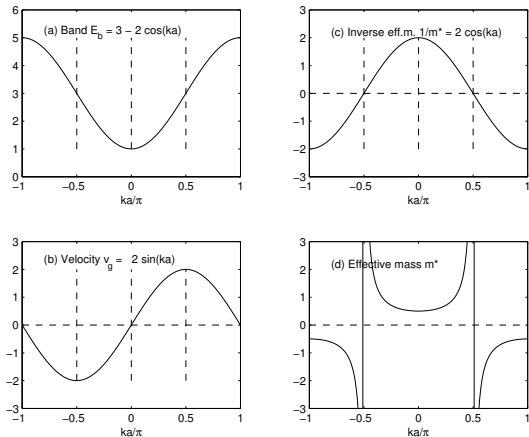


Figure: An analytic model for a band - and the concepts of group velocity and effective mass.

Density of states

The effective mass can be used to describe the density of states in the band. One can use a formula analogous to that one used for the Fermi gas

$$g(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{\frac{3}{2}} |\epsilon - \epsilon_b|^{\frac{1}{2}} \quad (56)$$

where ϵ_b is the minimal or maximal energy in the band. The effective mass is infinite in the region where the dispersion relation means locally no dispersion (locally linear proportionality). Thus, effectively local phase velocity = group velocity.
non-dispersive waves \Leftrightarrow infinite effective mass

