Solid State Physics

Summary/Overview

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based on the lecture
Solid State Physics
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from the fall term 2015
at the Chinese University of Hong Kong (CUHK)

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Content

1 Drude model

1.1 Electron Transport

Idea: metal = positive ions + sea of free electrons
Assumptions:
1. Electrons have a scattering time τ, the probability of scattering within dt ist dt/τ.
2. After a scattering event, the electron returns to $\vec{p} = 0$.
3. In between scatterings, electrons respond to external $\vec{E}$- and $\vec{B}$-fiels.

$$\Rightarrow \quad \vec{p}(t+dt) = \frac{dt}{\tau}\vec{0} + \left(1 - \frac{dt}{\tau}\right)\left(\vec{p}(t) + \vec{F}dt\right)$$

$$= \vec{p}(t) + \vec{F}dt - \frac{dt}{\tau}\vec{p}(t) + \mathcal{O}(dt^2)$$

Here, dt/τ is scattering probability, $1 - dt/\tau$ is not-scattering probability and F is the Lorentz-force of the external fields. Division by dt yields:

$$\Leftrightarrow \quad \frac{d\vec{p}}{dt} \approx \vec{F} - \frac{\vec{p}}{\tau}$$

Lorentz Force:
$\vec{F} = -e(\vec{E} + \vec{v} \times \vec{B})$

CASE A: $\vec{E} \neq 0$, $\vec{B} = 0$

$\Leftrightarrow \quad \frac{d\vec{p}}{dt} \approx -e\vec{E} - \frac{\vec{p}}{\tau} \quad \Leftrightarrow \quad m\frac{d\vec{v}}{dt} \approx -e\vec{E} - m\vec{v}/\tau$

Assuming a static state solution, one can assume $d\vec{v}/dt = 0$

$\Rightarrow \quad e\tau\vec{E} = -m\vec{v} \quad \Leftrightarrow \quad \frac{ne^2\tau}{m}\vec{E} = -ne\vec{v}$

$\Rightarrow \quad \sigma = ne^2\tau/m$

$-ne\vec{v} = \vec{j} = \sigma\vec{E}$
n: particle densitiy
σ: conductivity

CASE B: $\vec{E} \neq 0$, $\vec{B} \neq 0$

$\Leftrightarrow \quad m\frac{d\vec{v}}{dt} \approx -e(\vec{E} + \vec{v} \times \vec{B}) - m\vec{v}/\tau$

Again assuming $d\vec{v}/dt = 0$

$\Leftrightarrow \quad e\vec{E} = -e\vec{v} \times \vec{B} - m\vec{v}/\tau$

$\Leftrightarrow \quad \vec{E} = \frac{1}{ne}\vec{j} \times \vec{B} + \frac{1}{\sigma}\vec{j}$

$\vec{v} = -\vec{j}/ne$

Here, $\vec{j} \times \vec{B}/ne$ is the electrical field caused by the Hall-effect!
Assume $\vec{j} = j\vec{e}_x$ and $\vec{B} = B\vec{e}_z$, it follows

$E_y = -\frac{1}{ne}jB$

Since E_y can be measured via voltage and $\vec{j}$ as well as $\vec{B}$ are set by experiment, one can determine n this way!

1.2 Wiedemann-Franz-Law

Like $\vec{j} = \sigma\nabla\varphi$ ($\vec{E} = \nabla\varphi$), it is also true that $\vec{j}_T = \kappa\nabla T$, $\vec{j}_T$ being the thermal current and κ the thermal conductivity.

Starting with Boltzmann's kinetic theory, it is $\kappa = \frac{1}{3}nc_v\langle v\rangle\lambda$ (c_v is heat capacity per particle and $\lambda = \langle v\rangle\tau$ the scattering length). According to kinetic theory, it is:

$$c_v = \frac{3}{2}k_B, \quad \langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}} \quad \Rightarrow \quad \kappa = \frac{4}{\pi}\frac{k_B^2 n\tau T}{m}$$

Using $\sigma = ne^2\tau/m$, one can erase the unknown parameter τ and define the Lorentz number L:

$L = \frac{\kappa}{\sigma T} = \frac{4k_B^2}{\pi e^2} = $ const. (Wiedemann-Franz Law)

Problem: c_v was made for gases, but is experimentally wrong for metals. Same is true for $\langle v\rangle$.

1.3 Sommerfeld's Theory

Electrons in metals behave like a wave. To neglect surface effects, one uses periodic boundary conditions. In 1D, you take a one dimensional length L and wrap it together to a circle, so that $\psi(x) = \psi(x+L)$.

Free electrons $\Rightarrow \psi(x) \sim e^{ikx} \quad \Rightarrow \quad k = n \cdot 2\pi/L, \quad n \in \mathbb{Z}$

Density of states: $D = n/k = L/2\pi$ (states per "length-unit" in k-space)

Filling up N electrons according to the Pauli principle into the lowest states, the maximum k is $k_F = N/4D = \frac{\pi N}{2L}$

(the 4 is because of the Pauli principle and because one goes from $-k$ to k) k_F is called "Fermi Wavenumber/-vector"

Corresponding Energy: $E_F = \hbar k_F/2m = h^2 N^2/32mL^2 = k_B T_F$ (here, T_F is called "Fermi-Temperature", but it is not the actual temperature of the system!)

In three dimension, take a cube L^3 and you get $k_i = n_i \cdot 2\pi/L$. Each k-value occupies $(2\pi/L)^3$, the density is therefore $D = (L/2\pi)^3$. The k-space now is a sphere with radius k_F.

$$N = \underbrace{2}_{\text{Spin}} \cdot \underbrace{\left(\frac{4\pi}{3}k_F^3\right)}_{\substack{\text{occupied}\\\text{Volume}}} \cdot D \quad \Leftrightarrow \quad k_F = \frac{1}{L}\sqrt[3]{2\pi^2 N} = \sqrt[3]{2\pi^2 n}, \quad n = \frac{N}{L^3}$$

(attention: n is now the particle density!)

Fermi Energy: $E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$

According to Fermi-Dirac-Statistics

$$n_F\big(\beta(E-\mu)\big) = 1/\big(1 + e^{\beta(E-\mu)}\big), \quad \beta = 1/kT$$

is the probability of a state with energy E to be occupied. For $T \approx 0$, the chemical potential is $\mu \approx E_F$.

1.4 Density of States in Energy

The total energy of the system is given by

$$E_{\text{tot}} = 2\frac{V}{(2\pi)^3}\int dk^3\, E(k)n_F\big(\beta(E(k)-E_F)\big)$$

$$= 2\frac{V}{(2\pi)^3}4\pi\int_0^\infty k^2\, dk\, E(k)n_F\big(\beta(E(k)-E_F)\big)$$

Here, the factor 2 again accounts for the spins. The substitution $k = \sqrt{2mE/\hbar^2}$, $dk/dE = \sqrt{m/2\hbar^2 E}$ yields:

$$E_{\text{tot}} = V\int_0^\infty dE\, \frac{\sqrt{2E}m^{3/2}}{\pi^2\hbar^3}En_F\big(\beta(E-E_F)\big)$$

$$= \int_0^\infty dE\, E\, g(E)n_F\big(\beta(E-E_F)\big)$$

Thereby $g(E)$ is defined as

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

In 1D and 2D, g is

$$g_{1D} = \frac{L\sqrt{2m}}{\pi\hbar}\frac{1}{\sqrt{E}}, \quad g_{2D} = \frac{mL^2}{\pi\hbar^2}$$

The average energy per particle is then (in 3D at $T = 0$ K):

$$\langle E\rangle = \frac{1}{N}\int_0^{E_F} dE\, E\, g(E) = \frac{3}{5}E_F$$

1.5 Fermi-Dirac-Distribution

For $T = 0$ K, the probability for a stat with energy E goes like $p(E) = \theta(E_F - E)$. For $T > 0$ K, states with higher energies might be occupied, as described by the Fermi-Dirac-Distribution:

$$F_{FD}(E) = \frac{1}{e^{(E-\mu)/kT} + 1}$$

Here, μ is the chemical potential with $\mu(T = 0) = E_F$. Note, that $F_{FD}(\mu) = 1/2$. The chemical potential is

$$\mu(T) \approx E_F\left(1 - \frac{\pi^2}{12}\left(\frac{kT}{E_F}\right)^2\right)$$

Furthermore, note that for $E - \mu \gg kT$ F_{FD} becomes the Maxwell-Boltzmann statistics $e^{-(E-\mu)/kT}$.
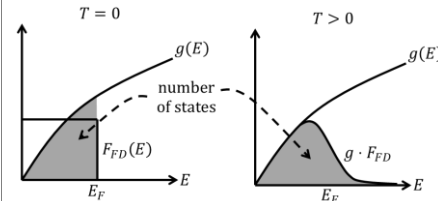
The energy of the system is

$$\Delta E = E(T) - E(0) = \int_0^\infty dE\, Eg(E)F_{FD}(E) - \int_0^{E_F} dE\, Eg(E)$$

One finds, that the heat capacity is

$$c = \frac{dE}{dT} = \frac{\pi^2}{3}g(E_F)k^2 T$$

2 Chemical Bonds

2.1 Ionic Bonds

Ionisation Energy IE:
    Energy required to remove an electron from an atom to create a positive ion

Electron Affinity EA:
    Energy gained from adding an electron to a neutral atom to create a negative ion

Cohesive Energy CE:
    Energy gained from fusing two ions together (Coulomb).

Total energy change:
$$\Delta E_{A+B \to A^+ + B^-} = \text{IE}_A - \text{EA}_B, \quad \Delta E_{A^+ + B^- \to AB} = -\text{CE}$$
$$\implies \quad \Delta E_{A+B \to AB} = \Delta E_{A+B \to A^+ + B^-} + \Delta E_{A^+ + B^- \to AB} = \text{IE}_A - \text{EA}_B - \text{CE}$$
If $\Delta E_{A+B \to AB} < 0$, the bond might be formed.
$$\text{Mulliken electronegativity} = (\text{EA} + \text{IE})/2$$

2.2 Covalent Bonds

The wider the potential box, the lower is the ground state energy. Therefore, to hydrogen atoms together form a bigger box with lower electron states: they bond.

Since two helium atoms have four bonding electrons, due to the Pauli principle not only the common ground state (which would be lower) has to be occupied, but also the first excited state, which has a higher energy than the original ground state of the isolated atoms: they don't bond.

3 Crystal Structure, Reciprocal Lattice

3.1 Describing a Lattice

A lattice is an infinite array of discrete points described by the lattice vector

$$\vec{R} = \sum_{i=1}^{3} u_i \vec{a}_i, \quad u_i \in \mathbb{N}_0$$

where $\vec{a}_i$ are linear independent. A primitive unit cell is defined by the volume $\vec{a}_1(\vec{a}_2 \times \vec{a}_3)$. Each unit cell contains one lattice point. A primitive unit cell can be constructed by the Wigner-Seitz-Method.

3.2 Lattice Types in 2D

φ is the angle between $\vec{a}_1$ and $\vec{a}_2$.

Oblique lattice:	$|\vec{a}_1|, |\vec{a}_2|$ arbitrary, $\varphi \neq 90°$
Rectangular lattice:	$|\vec{a}_1| \neq |\vec{a}_2|$ arbitrary, $\varphi = 90°$
Centered rectangular lattice:	$|\vec{a}_1| \neq |\vec{a}_2|$ arbitrary, $\varphi \neq 90°$
Hexagonal lattice:	$|\vec{a}_1| = |\vec{a}_2|$ arbitrary, $\varphi = 120°$
Square lattice:	$|\vec{a}_1| = |\vec{a}_2|$ arbitrary, $\varphi = 90°$

3.3 Lattice Types in 3D

Simple Cubic Lattice (SC):
$$\vec{a}_1 = a\vec{e}_x, \quad \vec{a}_2 = a\vec{e}_y, \quad \vec{a}_3 = a\vec{e}_z$$

Body-Centred Cubic Lattice (BCC):
$$\vec{a}_1 = a\vec{e}_x, \quad \vec{a}_2 = a\vec{e}_y, \quad \vec{a}_3 = \frac{a}{2}(\vec{e}_x + \vec{e}_y + \vec{e}_z)$$

Face-Centred Cubic Lattice (FCC):
$$\vec{a}_1 = \frac{a}{2}(\vec{e}_x + \vec{e}_y), \quad \vec{a}_1 = \frac{a}{2}(\vec{e}_y + \vec{e}_z), \quad \vec{a}_3 = \frac{a}{2}(\vec{e}_x + \vec{e}_z)$$

3.4 Notation of Directions

The direction of $\vec{R}$ can be noted down using square brackets $[abc]$ like:

$\vec{R} = 3\vec{a}_1 - 2\vec{a}_2 + \vec{a}_3 \quad \rightarrow \quad [3\bar{2}1]$ minus $\rightarrow$ bar

$\vec{R} = -6\vec{a}_1 + 12\vec{a}_2 - 3\vec{a}_3 \quad \rightarrow \quad [\bar{2}4\bar{1}]$ common divisors ign.

3.5 Lattice Planes and Miller Indices

Notation of lattice plane:
If x, y, z are the intercepts of the plane with the $\vec{a}_1$-, $\vec{a}_2$-, $\vec{a}_3$-axes, then find the smallest integers h, k, l such that

$$\frac{1}{x} : \frac{1}{y} : \frac{1}{z} = h : k : l$$

Then, (hkl) are the Miller indices of the plane. Again, use a bar for negative indices.
The vector

$$\vec{g} := h(\vec{a}_2 \times \vec{a}_3) + k(\vec{a}_3 \times \vec{a}_1) + l(\vec{a}_1 \times \vec{a}_2)$$

is normal to the plane.

3.6 Basis

Crystal can be described by a lattice plus a basis, which itself is described by basis vectors

$$\vec{r}_i = x_i \vec{a}_1 + y_i \vec{a}_2 + z_i \vec{a}_3, \quad x_i, y_i, z_i \in [0,1)$$

3.7 Reciprocal Lattice

Construction: The primitive lattice vectors of the reciprocal lattice $\vec{b}_i$ can be derived using the primitive lattice vectors of the direct lattice $\vec{a}_i$:

$$\vec{b}_1 = \frac{2\pi}{\Omega}(\vec{a}_2 \times \vec{a}_3), \quad \vec{b}_2 = \frac{2\pi}{\Omega}(\vec{a}_3 \times \vec{a}_1), \quad \vec{b}_3 = \frac{2\pi}{\Omega}(\vec{a}_1 \times \vec{a}_2)$$

$$\vec{G} = \sum_{i=1}^{3} n_i \vec{b}_i$$

Here, Omega is the volume of the primitive lattice cell:
$$\Omega := \vec{a}_1(\vec{a}_2 \times \vec{a}_3)$$

Properties:
1. $\vec{a}_i \vec{b}_j = 2\pi \delta_{ij}$
2. $|\vec{a}_1(\vec{a}_2 \times \vec{a}_3)| = (2\pi)^3 / |\vec{b}_1(\vec{b}_2 \times \vec{b}_3)|$
3. The reciprocal lattice of the reciprocal lattice is the direct lattice.
4. $e^{i\vec{G}\vec{R}} = 1$
5. $\vec{G}(hkl) = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is normal to the lattice plain (hkl).
6. The separation between two lattice plains is $d(hkl) = 2\pi / |\vec{G}(hkl)|$.

3.8 The Brillouin Zones

The first Brillouin Zone is the Wigner-Seitz-Cell, centered at the origin of the reciprocal space and contains all the points which are closer to the origin than to any reciprocal lattice point.
The construction can be done using so-called Bragg-Planes.

3.9 Fourier-Analysis of a Periodic Function

Since the lattice is periodic, so are quantities such as electron concentration, potential energy usw. Consider a general function with periodicity

$$f(\vec{r}) = f(\vec{r} + \vec{R}),$$

$\vec{R}$ being the lattice vector. Apply Fourier-Transformation:

$$f(\vec{r} + \vec{R}) = \sum_k f(\vec{k}) e^{i\vec{k}(\vec{r}+\vec{R})} = \sum_k f(\vec{k}) e^{i\vec{k}\vec{r}} e^{i\vec{k}\vec{R}} \overset{!}{=} f(\vec{r})$$

$$\Rightarrow \quad e^{i\vec{k}\vec{R}} \overset{!}{=} 1 \quad \Leftrightarrow \quad \vec{k} = \vec{G}$$

For Fourier-Tranformation, only the $\vec{k}$-values are important which equal $\vec{G}$:

$$f(\vec{r}) = \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G}\vec{r}}$$

4 Elastic Scattering of Waves

4.1 Scattering Particles

Photons: Scattered by atomic electrons, gives crystal structure

Neutrons: Scattered by all particles with spin (electrons, nuclei), gives crystal structure as well as magnetic structure

Electrons: Charged, can't penetrated deep into the solid, useful for surfaces

4.2 Scattering at one Particle

Consider scattering at one particle.
Incoming wave:

$$A = A_0 e^{i(\vec{k}\vec{r} - \omega t)}$$

Elastic scattering: $\omega = \omega', k = k', \vec{k} \neq \vec{k}'$
Total wave:

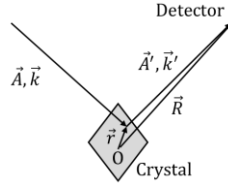$$A' = A_0 e^{i(\vec{k}\vec{r} - \omega t)} f \frac{e^{ik'|\vec{R} - \vec{r}|}}{|\vec{R} - \vec{r}|}$$

f: atomic factor (element, scattering angle ...)
last term: scattered, spherical wave
Approximation: $|\vec{R} - \vec{r}| \approx R$ in the denominator. In the exponent, however, this is to rough:

$$k'|\vec{R} - \vec{r}| = \vec{k}'(\vec{R} - \vec{r}) = \vec{k}'\vec{R} - \vec{k}'\vec{r} \approx kR - \vec{k}'\vec{r}$$

$$\Rightarrow \quad A' = \frac{A_0}{R} e^{i(kR - \omega t)} f e^{-i\vec{r}\Delta\vec{k}}, \quad \Delta\vec{k} := \vec{k}' - \vec{k} \text{ (scattering vec.)}$$

4.3 Scattering at many Particles

Sum over all particles i equals sum over all lattice points $\vec{R}$ and basis atoms $\vec{r}_j$:

$$A' = \frac{A_0}{R} e^{i(kR - \omega t)} \sum_i f_i e^{-i\vec{r}_i \Delta\vec{k}} = \frac{A_0}{R} e^{i(kR - \omega t)} \sum_{\vec{R}} \sum_j f_j e^{-i(\vec{R} + \vec{r}_j)\Delta\vec{k}}$$

$$= \frac{A_0}{R} e^{i(kR - \omega t)} \underbrace{\sum_{\vec{R}} e^{-i\vec{R}\Delta\vec{k}}}_{=a(\Delta\vec{k})} \underbrace{\sum_j f_j e^{-i\vec{r}_j \Delta\vec{k}}}_{=S(\Delta\vec{k})}$$

Intensity:

$$I = |A'|^2 = \frac{|A_0|^2}{R^2} |a(\Delta\vec{k})|^2 |S(\Delta\vec{k})|^2$$

Consider $a(\Delta\vec{k})$:
For $\Delta\vec{k} \neq \vec{G} \Rightarrow a = 0$ (the phase factors cancel each other out)
But for $\Delta\vec{k} = \vec{G} \Rightarrow a = \sum_{\vec{R}} 1$, which is huge.
Hence, one gets a very intense scattered wave for $\Delta\vec{k} = \vec{G}$, which is called Laue condition (Max von Laue).

4.4 Connection to Bragg-Condition

For X-ray scattering at crystals, there is also the Bragg-Condition
$$2d \sin\theta = n\lambda$$
It is equivalent to the Laue-Condition:
$$\Delta\vec{k} = \vec{k}' - \vec{k} = \vec{G} \iff k'^2 = k^2 + G^2 + 2\vec{k}\vec{G} \iff -2\vec{k}\vec{G} = G^2$$
In the last step was used, that $\vec{k}$ and $\vec{k}'$ differ only in direction, not in length (elastic scattering).
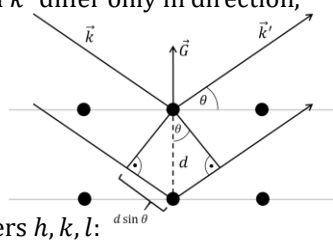Left-hand-side:
$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ might not be the shortest possible vector.
Therefore, it can be written as
$\vec{G} = n\vec{G}_s, n \in \mathbb{N}$ with $\vec{G}_s$ being the shortest possible vector with integers h, k, l:

$$-2\vec{k}\vec{G} = -2\vec{k}n\vec{G}_s = 2knG_s \sin\theta = 2\left(\frac{2\pi}{\lambda}\right) n \left(\frac{2\pi}{d}\right) \sin\theta \overset{!}{=} G^2$$

$$= \left(n\frac{2\pi}{d}\right)^2 \iff 2d\sin\theta = n\lambda$$

4.5 Ewald Sphere

In reciprocal space, draw the vector $\vec{k}$ (direction of incoming beam), such that it ends in a reciprocal lattice point. Since $k' = k$, the possible $\vec{G} = \vec{k}' - \vec{k}$-vectors lay on a sphere with radius k. But $\vec{G}$ can by its definition only lay between to reciprocal lattice points. Therefore, only in the $\vec{k}'$-direction, where a lattice point lays on the sphere, constructive interference is possible.

4.6 Brillouin-Zone and Laue Condition

As in seen in 4.4, the Laue condition could be rewritten as
$$-2\vec{k}\vec{G} = G^2$$
The minus sign doesn't matter here, so shift $\vec{G} \to -\vec{G}$ and get

$$2\vec{k}\vec{G} = G^2 \iff \vec{k}\left(\frac{1}{2}\vec{G}\right) = \left(\frac{1}{2}G\right)^2$$
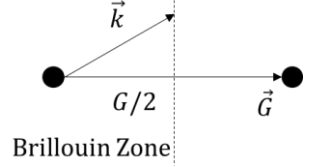
Since a dot product yields $\vec{a}\vec{b} = ab_a$, where b_a is the projection length on $\vec{a}$, the above equation is true, if $\vec{k}$ lays on the Brillouin zone edge.

4.7 Example I: Simple Cubic (SC)

For simple cubic, it is $\vec{a}_i = a\vec{e}_i$ and $\vec{b}_i = 2\pi/a \, \vec{e}_i$ and therefore
$$d = \frac{2\pi}{G(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
The Bragg condition gives
$$\frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin\theta = n\lambda$$
Hence, for each tuple h, k, l, n, there is one angle θ with a maximum (but e.g. $(hkl) = (110)$ and (101) give the same θ).

4.8 Example II: Face Centred Cubic (FCC)

A FCC can be defined as a SC with a basis $\vec{r}_j$
$$\begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad \frac{a}{2}\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}, \quad \frac{a}{2}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \quad \frac{a}{2}\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$$
Remember $A' \sim a(\Delta\vec{k})S(\Delta\vec{k})$, where maxima are only for $\Delta\vec{k} = \vec{G}$ and therefore $A' \sim a(\vec{G})S(\vec{G})$. What is $S(\vec{G})$ (for $f_j = f$)?

$$S(\vec{G}) = \sum_j f_j e^{-i\vec{r}_j\vec{G}} = f\left(1 + e^{-i\frac{2\pi a}{a} \frac{1}{2}(h+k+0)} + e^{\cdots} + e^{\cdots}\right)$$

$$= f\left(1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)}\right)$$

$$= \begin{cases} 4f, & hkl \text{ are all even or odd} \\ 0, & \text{otherwise} \end{cases}$$

If hkl als all even or odd, the sums $h + k$ etc. are all even and the exponent becomes a multiple of 2π. If only one or two of hkl is even, two e-functions are -1 and one is 1 which gives 0 in total. Therefore, the solution is the same as for simple cubic, but even/odd-combinations of hkl are not allowed.

BCC: Easily can be shown that for BCC $h + k + l$ must be even.

4.9 Example III: Sodium-Chloride (NaCl)

Use simple cubic lattice with eight atom basis:
$$\text{Na}^+: \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}; \frac{a}{2}\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}; \frac{a}{2}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}; \frac{a}{2}\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}; \quad \text{Cl}^-: \frac{a}{2}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}; \frac{a}{2}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; \frac{a}{2}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}; \frac{a}{2}\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$
Now, $S(\vec{G})$ becomes:
$$S(\vec{G}) = f_{\text{Na}^+}\left(1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)}\right)$$
$$+ f_{\text{Cl}^-} e^{-i\pi(h+k+l)}\left(1 + e^{i\pi(k+l)} + e^{i\pi(h+l)} + e^{i\pi(h+k)}\right)$$
$$= \begin{cases} 4(f_{\text{Na}^+} + f_{\text{Cl}^-}), & hkl \text{ are all even} \\ 4(f_{\text{Na}^+} - f_{\text{Cl}^-}), & hkl \text{ are all odd} \\ 0 & \text{otherwise} \end{cases}$$

5 Lattice Waves

5.1 Bloch's Theorem

A lattice with lattice vector $\vec{R}$ has a discrete translational symmetry. Hence, for the displacement $u_{\vec{R}}$ at lattice point $\vec{R}$ is true:

$$u_{\vec{R}} = e^{i\vec{q}\vec{R}} u_{\vec{0}}$$

This becomes clear, if one looks at the harmonic wave solution:

$$e^{i\vec{q}\vec{R}} u_{\vec{0}} = e^{i\vec{q}\vec{R}} A e^{i(\vec{q}\vec{0}-\omega t)} = A e^{i(\vec{q}\vec{R}-\omega t)} = u_{\vec{R}}$$

Obviously, it is enough, to consider the $\vec{q}$'s of the first Brillouin zone, since $\vec{q}' = \vec{q} + \vec{G}$ yields:

$$u_{\vec{R}} = A e^{i(\vec{q}'\vec{R}-\omega t)} = A e^{i\left((\vec{q}+\vec{G})\vec{R}-\omega t\right)} = A e^{i(\vec{q}\vec{R}-\omega t)}$$

Remember, that $e^{i\vec{R}\vec{G}} = 1$.

5.2 Monoatomic Chain

Let there be a 1D chain with N atoms at positions $x_n = na, n \in \mathbb{N}$ with mass m, connected by springs with spring constant κ. Using periodic boundary conditions, the last and the first atom are also connected by spring. The force on the n-th particle is:

$$F_n = -\kappa(u_n - u_{n-1}) - \kappa(u_n - u_{n+1}) = -\kappa(2u_n - u_{n-1} - u_{n+1})$$
$$= m\ddot{u}_n$$

with displacements u_n. To get the normal modes, one uses $u_n \sim e^{-i\omega t}$ where all atoms have the same time dependence:

$$-\kappa(2u_n - u_{n-1} - u_{n+1}) = -m\omega^2 u_n \qquad (*)$$

As a matrix, this looks like this:

$$\frac{\kappa}{m}\begin{pmatrix} 2 & -1 & & & -1 \\ -1 & 2 & -1 & & \\ & -1 & 2 & -1 & \\ & & -1 & 2 & \\ -1 & & & -1 & 2 \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ \\ u_N \end{pmatrix} = \omega^2 \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ \\ u_N \end{pmatrix}$$

One solution is like a wave travelling through the chain:

$$u_n(t) = A e^{-i(qna-\omega t)}$$

Plugging in into $(*)$ yields:

$$-\kappa(2e^{-iqna} - e^{-iqna}e^{iqa} - e^{-iqna}e^{-iqa}) = -m\omega^2 e^{-iqna}$$

$$\Leftrightarrow \quad \frac{2\kappa}{m}\left(1 - \frac{1}{2}(e^{iqa} + e^{-iqa})\right) = \omega^2$$

$$\Leftrightarrow \quad \omega^2 = \frac{2\kappa}{m}(1 - \cos qa) = \frac{4\kappa}{m}\sin^2\left(\frac{qa}{2}\right)$$

And hence, the "phonon dispersion relation" follows as:

$$\omega(q) = 2\sqrt{\frac{\kappa}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

If the lattice constant is a, the reciprocal lattice constant is $2\pi/a$ and hence, the first Brillouin zone is $q \in [-\pi/a, \pi/a]$. At $q = -\pi/a, \pi/a$, $\omega(q)$ has maxima and repeats itself afterwards periodically: Therefore, higher Brillouin zones can be translated back into the first one.

Since the lattice point are discrete, there are always many ways for many q's to find waves fitting through all the point, but there is always one with the largest wavelength and the smallest $q_1 \in [-\pi/a, \pi/a]$.

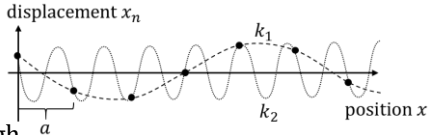For $q \to 0$ ($\lambda \gg a$): $\omega \approx \sqrt{\kappa/m}\, aq$

$$\Rightarrow \quad v = \frac{\partial\omega}{\partial q} = \sqrt{\frac{\kappa}{m}}a = \sqrt{\frac{\kappa a}{m/a}} = \sqrt{\frac{C}{\rho}}$$

Here, C is the elastic modulus, ρ the densitiy and hence, v the speed of sound.

$$\max\omega(q) = 2\sqrt{\kappa/m}$$

The periodic boundary condition yields $u_{n+N} = A e^{iq(n+N)a - i\omega t} = A e^{iqna - i\omega t} = u_n$. Hence, $qNa \in 2\pi\mathbb{Z} \quad \Leftrightarrow \quad q \in 2\pi\mathbb{Z}/Na$.

$$\Rightarrow \quad \Delta q = 2\pi/Na \quad \Rightarrow \quad \text{Number of modes:} \quad (2\pi/a)/\Delta q = N$$

5.3 Diatomic Chain

A diatomic chain consists of two different atoms (upper and lower case letters):

$$M\ddot{U}_n = -\kappa(U_n - u_{n-1}) - \kappa(U_n - u_n)$$
$$m\ddot{u}_n = -\kappa(u_n - U_n) - \kappa(u_n - U_n)$$

Note, that n does not number atoms but bases. Using the Ansatz

$$U_n = A e^{iqna}e^{-i\omega t} \qquad u_n = B e^{iqna}e^{-i\omega t}$$

yields

$$-\omega^2 MA = -\kappa(2A - Be^{-iqa} - B)$$
$$-\omega^2 mB = -\kappa(2B - Ae^{iqa} - A)$$

which is in matrix form

$$\begin{pmatrix} \dfrac{2\kappa}{M} & -\dfrac{\kappa}{M}(1 + e^{-iqa}) \\ -\dfrac{\kappa}{m}(1 + e^{iqa}) & \dfrac{2\kappa}{m} \end{pmatrix}\begin{pmatrix} A \\ B \end{pmatrix} = \omega^2 \begin{pmatrix} A \\ B \end{pmatrix}$$

This matrix has the eigenvalues

$$\omega^2(q) = \frac{\kappa(M+m)}{Mm} \pm \kappa\sqrt{\left(\frac{M+m}{Mm}\right)^2 - \frac{4}{Mm}\sin^2\frac{qa}{2}}$$

This is the phonon dispersion relation for 1D diatomic chain. The lower branch is called the *acustic mode*, the upper one the *optical mode*. Hence, the speed of sound is $\partial\omega/\partial q$. Since for audible sound $q \ll \pi/a$, those effects take place near zero, where the speed of sound is constant for variation of q.
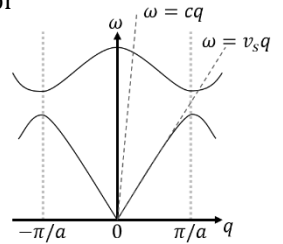
Amplitude of the two atoms (using equation of motion):

$$\frac{B}{A} = \frac{2\kappa - \omega^2 M}{\kappa(1 + e^{-iqa})}$$

For $qa \ll 1$ (hence, center of Brillouin zone):

$$\omega^2(q) \approx \frac{\kappa(M+m)}{Mm} \pm \kappa\sqrt{\left(\frac{M+m}{Mm}\right)^2 - \frac{4}{Mm}\left(\frac{qa}{2}\right)^2}$$

$$= \frac{\kappa(M+m)}{Mm}\left(1 \pm \sqrt{1 - \frac{Mm}{(M+m)^2}q^2a^2}\right)$$

$$\approx \frac{\kappa(M+m)}{Mm}\left(1 \pm \left(1 - \frac{Mm}{2(M+m)^2}q^2a^2\right)\right)$$

$$= \frac{\kappa(M+m)}{Mm}\left(1 \pm 1 \mp \frac{Mm}{2(M+m)^2}q^2a^2\right) \approx \begin{cases} \dfrac{\kappa q^2 a^2}{2(M+m)} & \text{LA} \\ \dfrac{2\kappa(M+m)}{Mm} & \text{LO} \end{cases}$$

(LA = longitudinal acoustic, LO = longitudinal optical)

LA: $\quad \dfrac{B}{A} \approx \dfrac{2\kappa - \dfrac{\kappa q^2 a^2}{2(M+m)}M}{\kappa(1+1)} \approx 1 \qquad$ same amplitude, phase

LA: $\quad \dfrac{B}{A} \approx \dfrac{2\kappa - \dfrac{2\kappa(M+m)}{Mm}M}{\kappa(1+1)} = -\dfrac{M}{m} \qquad$ antiphase

For $q \to \pm\pi/a$:

$$\omega^2 \approx \frac{\kappa(M+m)}{Mm} \pm \kappa\sqrt{\left(\frac{M+m}{Mm}\right)^2 - \frac{4}{Mm}}$$

$$= \frac{\kappa(M+m)}{Mm} \pm \kappa\sqrt{\frac{M^2 + 2Mm + m^2 - 4Mm}{(Mm)^2}}$$

$$= \frac{\kappa(M+m)}{Mm} \pm \frac{\kappa(M-m)}{Mm} = \begin{cases} \dfrac{2\kappa}{M} & \text{LA} \\ \dfrac{2\kappa}{m} & \text{LO} \end{cases}$$

LA: $\quad \dfrac{B}{A} \approx \dfrac{2\kappa - 2\kappa}{\kappa(1 + e^{-iqa})} = 0 \qquad M$ oscillates, m at rest

LA: $\quad \dfrac{B}{A} \approx \dfrac{2\kappa - \dfrac{2\kappa}{m}M}{\kappa(1-1)} = \infty \qquad M$ at rest, m oscillates

6 Thermal Properties due to Phonons

6.1 Excited States of the Modes

For a system with a p-atom basis, N lattice points and motion in d dimension, there are pd branches and Npd normal modes. Let's label the branches with an index s and the modes using the wave vector $\vec{q}$. Then, the normal modes are characterized by $\omega_s(\vec{q})$. For one particular harmonic oscillator, the energy is:
$$\epsilon_{s\vec{q}} = \hbar\omega_s(\vec{q})\left(n_{s\vec{q}} + 1/2\right)$$
$n_{s\vec{q}}$ is given by the Bose-Einstein-distribution with $\mu = 0$:
$$n_{s\vec{q}} = \frac{1}{e^{\beta\hbar\omega_s(\vec{q})} - 1}$$
Therefore, the total energy can be given as ($E_0 \equiv E(T = 0)$):
$$E = \sum_{s,\vec{q}} \epsilon_{s\vec{q}} = \sum_{s,\vec{q}} \hbar\omega_s(\vec{q})\left(n_{s\vec{q}} + 1/2\right) = E_0 + \sum_{s,\vec{q}} \frac{\hbar\omega_s(\vec{q})}{e^{\beta\hbar\omega_s(\vec{q})} - 1}$$

6.2 Einstein Model

Einstein's assumption: $\omega_s(\vec{q}) = \omega_E = \text{const.}$
$$\Rightarrow E = E_0 + \sum_{s,\vec{q}} \frac{\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1} = E_0 + Npd\frac{\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1}$$
$$\Rightarrow C = \frac{\partial E}{\partial T} = kNpd\left(\frac{\hbar\omega_E}{kT}\right)^2 \frac{e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E} - 1)^2}$$
For $kT \gg \hbar\omega_E$:
$$\Rightarrow C \approx kNpd\left(\frac{\hbar\omega_E}{kT^2}\right)^2 \frac{1}{(\beta\hbar\omega_E)^2} = nRpd$$
For $d = 3$, $n = p = 1$, this is just $3R \approx 25\,\text{J/K mol}$. For $kT \ll \hbar\omega_E$
$$\Rightarrow C \approx kNpd\left(\frac{\hbar\omega_E}{kT^2}\right)^2 e^{-\beta\hbar\omega_E} \sim e^{-\beta\hbar\omega_E} = e^{-\Theta_E/T}$$
with the Einstein temperature $\Theta_E = \hbar\omega_E/k$.

6.3 Debye Model

To calculate a sum $\sum_{s,\vec{q}} F_s(\vec{q})$, it's convenient to turn it into an integral $\int d^d q / D_d(q)$, which needs the density of q-states. In section 1.3, these density is given by $D_d(q) = (L/2\pi)^d$:

One dimension:
$$\int_{-\pi/a}^{\pi/a} dq\,\frac{L}{2\pi} = \int_0^{\pi/a} dq\,\frac{L}{\pi} = \int_0^{\omega_{\max}} d\omega\,\frac{1}{\frac{d\omega}{dq}}\frac{L}{\pi} \Rightarrow D_1(\omega) = \frac{L}{\pi\frac{d\omega}{dq}}$$
Now, Debye's approximation is $\omega(q) \approx v_s q$ (linear). Hence:
$$D_1(\omega) = \frac{L}{\pi v_s} \Rightarrow \int_0^{\omega_D} d\omega\,D_1(\omega) \overset{!}{=} N \Leftrightarrow \omega_D = \frac{\pi v_s N}{L} = \frac{\pi v_s}{a} = v_s q_d$$
Three dimensions:
$$\int d^3 q\left(\frac{L}{2\pi}\right)^3 = \int dq\,4\pi q^2\left(\frac{L}{2\pi}\right)^3 = \int d\omega\,\frac{4\pi\omega^2}{v_s^3}\left(\frac{L}{2\pi}\right)^3$$
In the last step, using $\omega(q) \approx v_s q$ led to $dq = d\omega/v_s$. Hence:
$$D_3(\omega) = \frac{4\pi\omega^2}{v_s^3}\left(\frac{L}{2\pi}\right)^3 = \frac{V}{2\pi^2}\frac{\omega^2}{v_s^3}$$
In 3D, there are three different acoustic branches with sound velocities $v_{s,i}$, $i = 1,2,3$. The densities of states of each branches can naturally be added up to the total density of states:
$$D_3(\omega) = \frac{V}{2\pi^2}\left(\frac{1}{v_{s,1}^3} + \frac{1}{v_{s,2}^3} + \frac{1}{v_{s,3}^3}\right)\omega^2 = \frac{V}{2\pi^2}\frac{3}{v_0^3}\omega^2$$
For simplicity, they are put together into an effective velocity v_0.
$$\int_0^{\omega_D} d\omega\,D_3(\omega) = \frac{V}{2\pi^2 v_0^3}\omega_D^3 \overset{!}{=} 3N \Leftrightarrow \frac{3V}{2\pi^2 v_0^3} = \frac{9N}{\omega_D^3}$$
Hence, it's possible to calculate the energy:
$$E = E_0 + \sum_{s,\vec{q}} \frac{\hbar\omega_s(\vec{q})}{e^{\beta\hbar\omega_s(\vec{q})} - 1} = E_0 + \int_0^{\omega_D} d\omega\,D_3(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$
$$= E_0 + \frac{9N}{\omega_D^3}\int_0^{\omega_D} d\omega\,\omega^2\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$
$$\Rightarrow \quad C = \frac{\partial E}{\partial T} = \frac{9Nk}{\omega_D^3}\int_0^{\omega_D} d\omega\,\omega^2\left(\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)^2 e^{\beta\hbar\omega}$$
$$= 9Nk\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\theta_D}{T}} dx\,\frac{x^4 e^x}{(e^x - 1)^2}$$
Here, $\Theta_D = \hbar\omega_D/k$ and $x = \beta\hbar\omega$.
For $T \gg \Theta_D$:
$$C \approx 9Nk\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\theta_D}{T}} dx\,\frac{x^4(1 + x)}{x^2} \approx 9Nk\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\theta_D}{T}} dx\,x^2 = 3Nk$$
For $T \ll \Theta_D$:
$$\frac{\Theta_D}{T} \to \infty \quad \Rightarrow \quad C \sim T^3$$

7 Electron States in Crystals

7.1 Bloch's Theorem

In the ideal Fermi-gas idea, electrons are treated as free particles ($V = 0$, $\psi \sim e^{ikx}$). In a lattice: $V(\vec{r}) = V(\vec{r} + \vec{R})$ and hence
$$|\psi(\vec{r})|^2 = |\psi(\vec{r} + \vec{R})|^2 \quad \text{but in general} \quad \psi(\vec{r}) \neq \psi(\vec{r} + \vec{R}).$$
$$\implies \quad \psi(\vec{r} + \vec{R}) = e^{i\Theta(\vec{R})}\psi(\vec{r})$$
What is the function $\Theta(\vec{R})$?
$$\psi(\vec{r} + \vec{R}_1 + \vec{R}_2) = \begin{cases} e^{i\Theta(\vec{R}_1 + \vec{R}_2)}\psi(\vec{r}) \\ e^{i\Theta(\vec{R}_2)}e^{i\Theta(\vec{R}_1)}\psi(\vec{r}) \end{cases}$$
Hence, Θ is linear in $\vec{R}$ and dimensionless, which yields $\Theta(\vec{R}) = \vec{k}\vec{R}$. This yields Bloch's Theorem in two equivalent versions:
$$\psi(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{R}}\psi(\vec{r}); \quad \psi(\vec{r}) = e^{i\vec{k}\vec{r}}u_{\vec{k}}(\vec{r}), \quad u_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r})$$
Plug $\psi(\vec{r}) = e^{i\vec{k}\vec{r}}u_{\vec{k}}(\vec{r})$ into the Schrödinger equation and get:
$$-\frac{\hbar^2}{2m}(\nabla + i\vec{k})^2 u_{\vec{k}}(\vec{r}) + V(\vec{r})u_{\vec{k}}(\vec{r}) = E_{\vec{k}}u_{\vec{k}}(\vec{r})$$
Properties: $E_{n,\vec{k}} = E_{n,-\vec{k}}$ and $E_{n,\vec{k}} = E_{n,\vec{k}+\vec{G}}$.

7.2 Energy Bands

Schrödinger Equation (actually $E_{\vec{k}} \equiv E_{\vec{k},n}$):
$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) + V(\vec{r})\psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\psi_{\vec{k}}(\vec{r})$$
Since $u_{\vec{k}}$ and V are periodic, recall section 3.9:
$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}}(\vec{G})e^{i\vec{G}\vec{r}}, \qquad V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}}e^{i\vec{G}\vec{r}}$$
Hence, calculate first
$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2\sum_{\vec{G}} C_{\vec{k}}(\vec{G})e^{i(\vec{k}+\vec{G})\vec{r}}$$
$$= \sum_{\vec{G}} C_{\vec{k}}(\vec{G})\frac{\hbar^2(\vec{k}+\vec{G})^2}{2m}e^{i\vec{k}\vec{r}}e^{i\vec{G}\vec{r}} = \sum_{\vec{G}} C_{\vec{k}}(\vec{G})E^0_{\vec{k}+\vec{G}}e^{i\vec{k}\vec{r}}e^{i\vec{G}\vec{r}}$$
(with $E^0_{\vec{k}+\vec{G}} := \hbar^2(\vec{k}+\vec{G})^2/2m$) and the SG is:
$$\sum_{\vec{G}} C_{\vec{k}}(\vec{G})(E^0_{\vec{k}+\vec{G}} - E_{\vec{k}})e^{i\vec{G}\vec{r}} + \sum_{\vec{G},\vec{G}'} V_{\vec{G}'}C_{\vec{k}}(\vec{G})e^{i(\vec{G}+\vec{G}')\vec{r}} = 0$$
Now, multiply both sides by $e^{-i\vec{G}''\vec{r}}$, integrate and use $\int d^3r\, e^{i(\vec{G}-\vec{G}'')\vec{r}} = \delta_{\vec{G},\vec{G}''}$:
$$C_{\vec{k}}(\vec{G}'')(E^0_{\vec{k}+\vec{G}''} - E_{\vec{k}}) + \sum_{\vec{G}'} V_{\vec{G}'}C_{\vec{k}}(\vec{G}'' - \vec{G}') = 0$$
Now get a matrix for the 1D case, where $\vec{G}'' = G_n$ with $G_n = n\,2\pi/a$. For example for $\vec{G}'' = G_2 = 2G_1$ is the equation above:
$$C_k(2G_1)(E^0_{k+2G_2} - E_k) + V_0 C_k(2G_1) + V_{G_1}C_k(G_1) + V_{2G_1}C_k(0)$$
$$+ \cdots = 0$$
Hence, the matrix is:
$$\begin{pmatrix} (E^0_k - E_k + V_0) & V_{-G_1} & V_{-G_2} & V_{-G_3} & \cdots \\ V_{G_1} & (E^0_{k+G_2} - E_k + V_0) & V_{-G_1} & V_{-G_2} & \cdots \\ V_{2G_1} & V_{G_1} & (E^0_{k+2G_2} - E_k + V_0) & V_{-G_1} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix} \vdots \\ C_k(0) \\ C_k(G_1) \\ C_k(2G_1) \\ \vdots \end{pmatrix} = 0$$
or equivalently:
$$\begin{pmatrix} (E^0_k + V_0) & V_{-G_1} & V_{-G_2} & V_{-G_3} & \cdots \\ V_{G_1} & (E^0_{k+G_2} + V_0) & V_{-G_1} & V_{-G_2} & \cdots \\ V_{2G_1} & V_{G_1} & (E^0_{k+2G_2} + V_0) & V_{-G_1} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix} \vdots \\ C_k(0) \\ C_k(G_1) \\ C_k(2G_1) \\ \vdots \end{pmatrix} = E_k\begin{pmatrix} \vdots \\ C_k(0) \\ C_k(G_1) \\ C_k(2G_1) \\ \vdots \end{pmatrix}$$
Again, actually $E_k \equiv E_{k,n}$. For each n, E_k defines an energy band in k-space.

7.3 Empty Lattice Approximation

Assume, $V(\vec{r}) = 0$, but keep lattice concepts (periodicity etc.). Using the equation from 7.2
$$C_{\vec{k}}(\vec{G}'')(E^0_{\vec{k}+\vec{G}''} - E_{\vec{k}}) + \sum_{\vec{G}'} V_{\vec{G}'}C_{\vec{k}}(\vec{G}'' - \vec{G}') = 0$$
with $V_{\vec{G}'} = 0$ yields
$$E_{\vec{k}} = E^0_{\vec{k}+\vec{G}} = \frac{\hbar^2(\vec{k}+\vec{G})^2}{2m}$$
Hence, for each $\vec{k}$, which is restricted to the 1st Brillouin zone, there a multiple possible energy values (for multiple $\vec{G}$'s).

7.4 Nearly Free Electron Model

Assume in 1D a weak V and use perturbation theory with the free electron as the known Hamiltonian and the zeroth energy order:
$$H = \frac{\vec{p}^2}{2m} + V(\vec{r}), \qquad E^0_{\vec{k}+\vec{G}} = \frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2$$
Here, the energy spectrum in continuous, the energy is defined by $|\vec{k}|$. Take now a fixed but arbitrary $\vec{k}$ and define $\epsilon^0_{\vec{k}'} := E^0_{\vec{k}+\vec{G}}$ with $\vec{k}' = \vec{k} + \vec{G}$.

NON DEGENERATE CASE:
For this $\vec{k}'$, the unperturbed eigenfunction is $\psi = |\vec{k}'\rangle = e^{i\vec{k}'\vec{r}}/\sqrt{V}$ and hence, the first order correction is an unimportant energy shift:
$$\epsilon^1_{\vec{k}'} = \langle\vec{k}'|V|\vec{k}'\rangle = \frac{1}{V}\int d^3r\, e^{-i\vec{k}'\vec{r}}V(\vec{r})e^{i\vec{k}'\vec{r}} = \frac{1}{V}\int d^3r\, V(\vec{r}) = \bar{V}$$
The second order term for this $\vec{k}'$ is:
$$\epsilon^2_{\vec{k}'} = \sum_{\substack{\vec{k}'=\vec{k}+\vec{G} \\ \vec{G}\neq 0}} \frac{|\langle\vec{k}'|V|\vec{k}\rangle|^2}{\epsilon^0_{\vec{k}} - \epsilon^0_{\vec{k}'}}$$
$$\langle\vec{k}'|V|\vec{k}\rangle = \frac{1}{V}\int d^3r\, e^{i(\vec{k}-\vec{k}')\vec{r}}V(\vec{r}) = \frac{1}{V}\int d^3r\, e^{-i\vec{G}\vec{r}}V(\vec{r}) = V_{\vec{G}}$$
Hence, the total energy is
$$E_{\vec{k}} = \frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 + \bar{V} + \sum_{\substack{\vec{k}'=\vec{k}+\vec{G} \\ \vec{G}\neq 0}} \frac{|V_{\vec{G}}|^2}{\epsilon^0_{\vec{k}} - \epsilon^0_{\vec{k}'}}$$
with $V_{\vec{G}} = V_{\vec{k}'-\vec{k}}$. Here, $\epsilon^0_{\vec{k}'}$ represents the energy of another band at $\vec{k}'$. If those bands are far from each other, $\epsilon^0_{\vec{k}} - \epsilon^0_{\vec{k}'}$ is big and the correction negligible. But for some $\vec{k}$, there a bands close to each other. If $\epsilon^0_{\vec{k}} > \epsilon^0_{\vec{k}'}$, the correction is positive and the other way around. Hence, the (formerly) small distance increases.

DEGENERATE CASE:
For some $\vec{k}$-vectors, there is a degeneracy, meaning two branches are overlapping (at the Brillouin zone boundary), in 1D e.g. $E^0_{\pi/a} = E^0_{\pi/a-2\pi/a}$ (the bands for $G = 0$ and $G = -2\pi/a$). Now, take a look at the matrix elements of a degenerate subspace of $|\vec{k}\rangle$ and $|\vec{k}+\vec{G}\rangle = |\vec{k}'\rangle$ with $E^0_{\vec{k}} = E^0_{\vec{k}'-\vec{G}}$:
$$\begin{pmatrix} \langle\vec{k}|V|\vec{k}\rangle & \langle\vec{k}|V|\vec{k}'\rangle \\ \langle\vec{k}'|V|\vec{k}\rangle & \langle\vec{k}'|V|\vec{k}'\rangle \end{pmatrix} = \begin{pmatrix} \bar{V} & V_{\vec{k}'-\vec{k}} \\ V_{\vec{k}-\vec{k}'} & \bar{V} \end{pmatrix} = \begin{pmatrix} \bar{V} & V_{\vec{k}'-\vec{k}} \\ V^*_{\vec{k}'-\vec{k}} & \bar{V} \end{pmatrix}$$
The eigenvalues are:
$$\begin{vmatrix} \bar{V} - \epsilon^1_{\vec{k}} & V_{\vec{k}'-\vec{k}} \\ V^*_{\vec{k}'-\vec{k}} & \bar{V} - \epsilon^1_{\vec{k}} \end{vmatrix} = (\bar{V} - \epsilon^1_{\vec{k}})^2 - |V_{\vec{k}'-\vec{k}}|^2 \overset{!}{=} 0$$
$$\Leftrightarrow \quad \epsilon_{1,2} = \bar{V} \pm |V_{\vec{k}'-\vec{k}}|$$
Hence, the total energy is:
$$E_{\vec{k}} = E^0_{\vec{k}} + \bar{V} \pm |V_{\vec{k}'-\vec{k}}|$$
Therefore, the gap between the bands is due to the perturbation $2|V_{\vec{k}'-\vec{k}}|$.

7.5 Tight Binding Model

Different approach: Look at the atomic states $\phi(\vec{r} - \vec{R})$ of an atom at $\vec{R}$ first:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r} - \vec{R})\right)\phi(\vec{r} - \vec{R}) = E_a\phi(\vec{r} - \vec{R})$$

Here, U is the atomic potential and E_a the atomic energy. Since $\phi(\vec{r} - \vec{R})$ is a full basis, an electronic state ψ can be written as:

$$\psi(\vec{r}) = \sum_{\vec{R}} C_{\vec{R}}\phi(\vec{r} - \vec{R})$$

where the coefficient should be $C_{\vec{R}} = 1/\sqrt{N}\, e^{i\vec{k}\vec{R}}$, to obey Bloch's theorem. Hence, the so called Boch-sum is:

$$\psi(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\vec{R}}\phi(\vec{r} - \vec{R})$$

Schrödinger equation:

$$E\psi \overset{!}{=} \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi(\vec{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U + V - U\right)\psi$$

$$= H_{\text{atom}}\psi + (V - U)\psi = E_a\psi + (V - U)\psi$$

Now apply $\int dV\,\psi^*$ on both sides and later, define $\vec{R}'' = \vec{R} - \vec{R}'$:

$$E = E_a - \int dV\,\psi^*(U - V)\psi$$

$$= E_a - \frac{1}{N}\sum_{\vec{R},\vec{R}'} e^{i\vec{k}(\vec{R}-\vec{R}')}\int dV\,\phi^*(\vec{r} - \vec{R}')(U - V)\phi(\vec{r} - \vec{R})$$

$$= E_a - \frac{1}{N}\sum_{\vec{R},\vec{R}''} e^{i\vec{k}\vec{R}''}\int dV\,\phi^*(\vec{r})(U - V)\phi(\vec{r} - \vec{R}'')$$

$$= E_a - \sum_{\vec{R}} e^{i\vec{k}\vec{R}}\int dV\,\phi^*(\vec{r})(U - V)\phi(\vec{r} - \vec{R})$$

$$= E_a - \sum_{\vec{R}} e^{i\vec{k}\vec{R}} A(\vec{R})$$

Here, $\sum_{\vec{R}} 1 = N$ was used, and the label was changed like $\vec{R}'' \to \vec{R}$. $A(\vec{R})$ is the hopping integral.

For a monoatomic simple cubic crystal with lattice constant a, the nearest neighbour atoms are at

$$\vec{R}_{1,4} = (\pm a, 0, 0), \quad \vec{R}_{2,5} = (0, \pm a, 0) \quad \text{and} \quad \vec{R}_{3,6} = (0, 0, \pm a).$$

Define $\alpha := A(\vec{R}_0) = A(\vec{0})$ and $t := A(\vec{R}_i), 1 \leq i \leq 6$. Hence, the energy up to nearest neighbour interaction is:

$$E \approx E_a - \sum_{i=0}^{6} e^{i\vec{k}\vec{R}_i} A(\vec{R}_i) = E_a - \alpha - t\sum_{i=1}^{6} e^{i\vec{k}\vec{R}_i}$$

$$= E_a - \alpha - 2t\sum_{i=1}^{3} \cos(\vec{k}\vec{R}_i) = E_a - \alpha - 2t\sum_{i=1}^{3} \cos(ak_i).$$

($k_i = k_{x,y,z}$) Here was used, that $\vec{R}_1 = -\vec{R}_4$ etc. Consider $\vec{k} \to 0$ and use $\cos(ak_i) \approx 1 - (ak_i)^2/2$:

$$E \approx E_a - \alpha - 6t + a^2tk^2$$

For this $\vec{k} \to 0$ region, an effective mass m^* can be defined by:

$$\frac{\hbar^2 k^2}{2m^*} = a^2tk^2 \quad \Leftrightarrow \quad m^* = \frac{\hbar^2}{2a^2t}$$

For an arbitrary $\vec{k}$, the reciprocal effective mass tensor is defined as:

$$\left(\frac{1}{m^3}\right)_{ij} = \frac{1}{\hbar^2}\frac{\partial}{\partial k_i}\frac{\partial}{\partial k_j}E$$

7.6 Insulators, Semiconductors, Metals

For N primitive cells, in the 1st Brillouion zone, there are N $\vec{k}$-points, each of which can hold two electrons (spin). Hence, each energy band can host at most $2N$ electrons.

The number of electrons of a material is determined by the number of atoms per primitive cell and by the valence electrons per atom. If there are only full and empty bands (no "half-full" bands), the material is either an isolator or a semiconductor, depending on the gap width between the valence and conduction band. Metalls have half-full bands.

Often band can overlap, so that there can exist several half-full bands.

7.7 Quantum Oscillations

Quantum oscillations occur if there is a magnetic field. Then:

$$\frac{d\vec{p}}{dt} = \hbar\frac{d\vec{k}}{dt} = -e\,\vec{v} \times \vec{B}$$

Using $\vec{v} = 1/\hbar\nabla_{\vec{k}}E(\vec{k})$, it follows, that

$\to \frac{d\vec{k}}{dt} \perp \vec{B}$, hence the $\vec{k}$-component parallel to $\vec{B}$ is constant.

$\to \frac{d\vec{k}}{dt} \perp \vec{v} = \frac{1}{\hbar}\nabla_{\vec{k}}E$, hence the following dot product is $0 = \frac{d\vec{k}}{dt}\nabla_{\vec{k}}E = \sum_i \frac{dk_i}{dt}\frac{dE}{dki}$, and hence $\frac{dE}{dt} = 0$.

Therefore, in $\vec{k}$-space, the possible electron orbits are the intersections of surfaces of constant energies with planes perpendicular to $\vec{B}$.

Integration over time of the first equation yields:

$$\hbar\int dt\,\frac{d\vec{k}}{dt} = -e\int dt\,\frac{d\vec{r}}{dt} \times \vec{B} \quad \Rightarrow \quad \vec{k} - \vec{k}_0 = \frac{e}{\hbar}\vec{B} \times (\vec{r} - \vec{r}_0)$$

That is to say, the projection of the orbit on a plane normal to $\vec{B}$ has the same shape as the orbit in $\vec{k}$-space.

Semi classical, there is a constriction for closed orbits:

$$\oint d\vec{r}\,\vec{p} = nh = n\,2\pi\hbar$$

Including a phase γ and mind the Hamiltonian momentum yields:

$$(n + \gamma)\,2\pi\hbar = \oint d\vec{r}\,\vec{p} = \oint d\vec{r}\,(\hbar\vec{k} - e\vec{A})$$

$$= e\oint d\vec{r}\,\vec{B} \times \vec{r} - e\oint d\vec{r}\,\vec{A} = e\vec{B}\oint \vec{r} \times d\vec{r} - e\int d\vec{S}\,\nabla \times \vec{A}$$

$$= 2e\vec{B}\vec{S} - e\int d\vec{S}\,\vec{B} = 2e\Phi - e\Phi = e\Phi$$

Here, $\vec{S}$ is the surface enclosed by the orbit and Φ is the flux. Since $\vec{B} \parallel \vec{S}$, this yields:

$$S = \frac{\Phi}{B} = (n + \gamma)\frac{2\pi\hbar}{eB}$$

The area of the orbit in reciprocal space is given by

$$S_{\text{rec}} = \left(\frac{e}{\hbar}|\vec{B}|\right)^2 S \qquad \text{Onsager's Equation}$$

The difference of two consecutive orbits is

$$\Delta S_{\text{rec}} = S_{\text{rec}}(n + 1) - S_{\text{rec}}(n) = \frac{2\pi eB}{\hbar}$$

If the B-field is enhanced, the reciprocal orbits become bigger and some of them might break through the fermi surface. For a change $\Delta(1/B)$ in the B-field, the "distance" between two orbits is

$$\Delta\left(\frac{1}{B}\right) = \frac{1}{B_{n+1}} - \frac{1}{B_n} = \frac{2\pi e(n + 1 + \gamma)}{\hbar S_{rec}} - \frac{2\pi e(n + \gamma)}{\hbar S_{rec}} = \frac{2\pi e}{\hbar S_{rec}} = \frac{1}{F}$$

This is the de Haas-van Alphen effect, F is the Haas-van Alphen frequency.

8 Semi-Conductors

8.1 Concepts of Holes

In semi-conductors, the valence but is nearly full, except some few "holes", when electrons were excited to the conduction band. It is convenient to focus on the holes.

The properties of the follow from the electron, which has been at the spot, where the hole is now:

$$\vec{k}_h = -\vec{k}_e \qquad E_h(\vec{k}_h) = -E_e(\vec{k}_e) \qquad \vec{v}_h = \vec{v}_e \qquad m_h^* = -m_e^*$$

For $T = 0$, the conduction band is full of holes and the band structure can approximately be described with

$$E_v(k) = E_v + \frac{\hbar^2 k^2}{2m_e^*} \qquad E_c(k) = E_c + \frac{\hbar^2 k^2}{2m_h^*}$$

The Fermi energy is exactly the middle of the two bands, hence

$$E_F = \mu(T = 0) = \frac{E_v + E_c}{2}$$

8.2 The Chemical Potential

To discuss $T > 0$, the Fermi-Dirac distribution is needed; for semi-conductors, $E - \mu \gg kT$ is typical:

$$f_{FD}(E) = \frac{1}{e^{(E-\mu)/kT} + 1} \approx e^{-(E-\mu)/kT}$$

The band structure for the electrons in the conduction band is

$$E_c(k) = E_c + \frac{\hbar^2 k^2}{2m_e^*}$$

with the density of states

$$g_e(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (E - E_c)^{1/2}$$

Then, the concentration of electrons in the conduction band is

$$n_c = \frac{N}{V} = \frac{1}{V} \int_{E_c}^{\infty} dE \; g_e(E) f_{FD}(E) = 2 \left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(\mu - E_c)/kT}$$

The same can be calculate for the hole concentration in the valence band p_v:

$$p_v = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_v - \mu)/kT}$$

Obviously, the product $n_c p_v$ is independent from μ, it is constant, and the constant is n_i^2:

$$n_c p_v = 4 \left(\frac{kT}{2\pi\hbar^2}\right)^3 (m_e^* m_h^*)^{3/2} e^{-(E_c - E_v)/kT} = n_i^2$$

n_i is the electron density for an intrinsic (not-doped) semi-conductor, hence:

$$n_i = 2 \left(\frac{kT}{2\pi\hbar^2}\right)^{3/2} (m_e^* m_h^*)^{3/4} e^{-(E_c - E_v)/2kT}$$

For an intrinsic semi-conductor is $n_i = n_c = p_v$.
Evaluating $n_c = p_v$ gives a formula for the chemical potential:

$$\mu = \frac{E_c + E_v}{2} + \frac{3}{4} kT \ln \frac{m_h^*}{m_e^*}$$