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0.1 Preliminary Schedule

- April 4 **Introduction:** Content, organisation (Exercises!), start symmetries: Bravais lattices in 2D, Crystal structures
- April 8 Fourier transform, reciprocal lattice, Brillouin zones
- April 11 Adiabatic approximation, start chemical bonds
- April 15 chemical bonds, start phonons
- April 18 phonons
- April 22 Phonon dispersion, thermodynamics of phonons, density of states
- April 25 metling, anharmonicity, Bloch theorem
- April 29 nearly free electrons
- May 2 tight-binding, Bloch/Wannier states
- May 6 Many-body states for electrons, density of states
- May 9 specific heat of electrons, velocity in an electric field
- May 13 Second quant., Green's functions: Dirac picture, Linear response, one-particle GF
- May 23 ret. and adv. Green's function in frequency space, independent particles
- May 27 Causal one-particle GF; spectral density, Kramers-Kronig, Lehmann
- May 30 GF for one-particle problem with impurity, interacting self energy
- June 3 Fermi-liquid theory
- June 6 Perturbation theory until contractions
- June 10 Wick's theorem and Feynmann diagrams, up to rules
- June 13 Dyson equation, self-consistent mean field, Hartree for Hubbard model
- June 17 Mirco
- June 20 cancelled
- June 24 other Green's functions, charge susceptibility
- June 27 magnetic susceptibility
- July 1st finish magnetic susceptibility, magnetism
- July 4 Magnetism: Mean-field for Heisenberg/Ising
- July 8 Landau theory of symmetry breaking
- July 11 phonon-mediated electron-electron interaction, BCS Theory
- July 15 Superconductivity

0.2 Literature

- *For Physics:* N.W. Ashcroft and N.D. Mermin: Solid State Physics, Saunders College Publishing, 1976.
- *For Theoretical Physics:* Daniel I. Khomskii , Basic Aspects of the Quantum Theory of Solids: Order and Elementary Excitations, Cambridge University Press, 2010
- *For Theoretical Physics:* Roser Valentí, lecture notes (mostly in German), http://itp.uni-frankfurt.de/~valenti/WS14_15.php
- *For Math, Formalism and the more advanced physics:* A. Muramatsu, Solid State Theory, <http://www.itp3.uni-stuttgart.de/lehre/Archiv/ss13/solidstatetheory/solidstatetheory.en.html>
- *For Math and Formalism (and some of the more advanced physics):* C. Timm, Vielteilchentheorie (in German), http://www.physik.tu-dresden.de/~timm/personal/teaching/vtt_w10/

- *Linear-response Theory and equation of motion for Green's functions*: W. Nolting, Fundamentals of Many-body Physics, Springer, 2009
- *for Feynman diagrams*: Richard D. Mattuck, A Guide to Feynman Diagrams in the Many-Body Problem, Dover Books on Physics
- *Field-Theory focussed, mostly more advanced*., A. Altland and Ben Simons, Condensed Matter Field Theory, Cambridge University Press, 2006

0.3 Course Content

- Periodic Lattices
 - Lattice symmetries: translational and other
 - Oscillations around equilibrium: Phonons
- Electrons in periodic potentials
 - Very short review second quantization
 - Bloch's theorem
 - Nearly free electrons to tight binding
 - Many-body states for fermions and bosons: Some statistical physics
- Electron-electron interactions
- Electron-phonon interaction
- Models
 - How they are developed
 - Where they are valid
 - What we learn from them
- Properties of Solids
 - Magnetism
 - Superconductivity
 - Excitations

1 What is Solid-State Physics about?

Condensed-Matter Physics: deals with temperatures and energies "on human scales".

- *Soft Condensed Matter:* e.g. liquids, Molecules, biophysics,
- *Solid-state Physics* ("hard" condensed matter): crystals
 - glasses: locally ordered, globally disordered, usually metastable states
 - quasicrystals: local rules, symmetries (e.g. five-fold rotation) that do not work out globally
 - "normal" periodic lattices

Types of particles and interactions are in principle known: particles treated are electrons and the nuclei of the atoms, often even ionic cores that include tightly bound electrons. The relevant interaction is the electromagnetic one, in particular Coulomb interaction between charged ions and electrons. The weak and strong forces are not treated, because they act only on the "inside" of the nucleus, and gravity is neglected as well.

Typical Hamiltonian is then given by the kinetic energies of electrons and nuclei in addition to the interaction:

$$H = \underbrace{\sum_i \frac{\hat{p}^2}{2m}}_{\text{electrons}} + \underbrace{\sum_i \frac{\hat{P}^2}{2M_i}}_{\text{nuclei}} + \frac{e^2}{2} \underbrace{\sum_{i,j} \frac{1}{|\hat{r}_i - \hat{r}_j|}}_{\text{electrons}} + \frac{e^2}{2} \underbrace{\sum_{i,j} \frac{Z_i Z_j}{|\hat{R}_i - \hat{R}_j|}}_{\text{nuclei}} - e^2 \underbrace{\sum_{i,j} \frac{Z_j}{|\hat{r}_i - \hat{R}_j|}}_{\text{electron-nucleus}} \quad (1.1)$$

Capital letters denote operators for nuclei and lower-case ones those for electrons. Relativistic electrons obey the Dirac equation, but energy scales in condensed matter are far below the rest mass of the electron (the lightest particle in question), a non-relativistic treatment is thus usually sufficient. Relativistic effects can be relevant in some cases, but it is then sufficient to treat them on the level of the Pauli equation. This is still in the non-relativistic limit of the Dirac equation, but relativistic effects are included in perturbation theory in terms of $\frac{1}{mc^2}$. Such an approach yields spin-orbit coupling.

The only parameters entering this Hamiltonian are the charges Z_i and the masses M_i , with the latter being largely proportional to the former. (The differences between isotopes can be relevant for phonons, though.) However, the equation deals with an enormous number of particles that moreover interact with each other. It is this last aspect that makes a solution impossible, because non-interacting particles can in be treated using the formalism for a single particle.

Approaches to this problem are two-fold:

- Numerically solve as much as possible of this Hamiltonian. Two main approaches are used:

- Quantum chemistry: One assumes very-low-energy states of atoms to be always occupied and very-high-energy states to be empty. The middle states can be occupied or not and this forms the basis in which the Hamiltonian for interacting atoms is written, for a given position of their nuclei.
- Density-function theory: Here, the impact of all *other* electrons together with that of the ions is expressed as a potential. This potential does not depend on the actual position of the other electrons, but only uses them as a background, so that the problem looks formally like a Hamiltonian for non-interacting electrons.
- Find much simpler effective models and treat those.
 - Probably the most important and powerful concept is here *Fermi-liquid theory*: Again, one starts from states obtained for a single electron moving in a potential. The electrons are then assumed not to interact and just filled into the lowest-energy states of the potential. While this sounds crude, it works quite well, at least for low-energy properties.
 - Identify "elementary" excitations, like phonons. Energy can go into such excitations, so that their knowledge gives information on transport and finite-temperature behavior.

These two approaches are used together: e.g., quantum chemistry relies on the "model" that low-lying states are always occupied. The models in the second approach, on the other hand, have free parameters that can be fixed using the approaches of the first kind. Here, we always use the "adiabatic" approximation, where the motion of electrons and nuclei can be separated, we will discuss this a bit more later.

2 Lattices

Inspired by Ashcroft and Mernin and Prof. Muramatsu's notes.

2.1 Why we care about symmetries

In order to reduce the complexity of the problem, we want to make use of the lattice symmetries. The reason is analogous to the use of angular momentum in solving the Hydrogen atom: a continuous symmetry is connected to a conserved quantity. This in turn implies that an operator commutes with the Hamiltonian and a common eigensystem exists. It can then be easier to find the eigensystem of the conserved quantity and start diagonalizing the Hamiltonian from there. In the present case of a lattice, the available symmetries are discrete rather than continuous. This changes the situation somewhat, because the conserved quantity is then not momentum (as it would be in the case of full continuous translational invariance), but only “crystal momentum”.

We ask operators describing symmetries to have the following properties:

1. Combining two symmetry operations should give another valid symmetry operation. (If the system is really symmetric w.r.t. to the first operation, it would be weird if the second operator became forbidden.) $T(a)T(b) = T(a \cdot b)$, when repeated, this process should be associative $T(a)T(b)T(c) = T(a)T(b \cdot c) = T(a \cdot b)T(c)$.
2. It should be possible not to change the state at all, i.e., the \mathbb{I} -operator should also be a valid symmetry transformation.
3. We should be able to undo a symmetry transformation by another transformation, i.e., there should be an inverse transformation $T^{-1}(a)$ such that $T^{-1}(a)T(a) = T(a)T^{-1}(a) = \mathbb{I}$.

These properties mean that the symmetries form a group. Note that the use of \cdot in the first point is not meant to imply commutativity, i.e., $T(a)T(b)$ does not have to be the same as $T(b)T(a)$.

In describing symmetries, we use *unitary operators*: After all, the Hilbert space itself should have the symmetries, if we want to treat symmetric Hamiltonians. A unitary operator is one that keeps the scalar product (i.e. norms of states and “angles” between them) invariant, and we thus ask that $T^{-1} = T^\dagger$, because

$$\begin{aligned}\langle T\psi|T\phi\rangle &= \langle\psi|\phi\rangle & \forall\psi,\phi \\ \langle\psi|T^\dagger T\phi\rangle &= \langle\psi|\phi\rangle \\ T^\dagger T &= \mathbb{I} = T^{-1}T & \Rightarrow & T^\dagger = T^{-1}\end{aligned}\tag{2.1}$$

For an operator to be invariant with respect to a symmetry encoded in T means that the operator must not change if all vectors are transformed using T , e.g., a rotationally invariant

Hamiltonian should not change if we rotate the universe. Accordingly,

$$\langle \phi | T^\dagger H T | \psi \rangle = \langle \phi | T^{-1} H T | \psi \rangle = \langle \phi | H | \psi \rangle \quad (2.2)$$

for all ϕ and ψ and thus

$$T^{-1} H T = H, \quad \text{and} \quad H T = T H, \quad \text{resp.} \quad [H, T] = 0. \quad (2.3)$$

In general, unitary T is not Hermitian and thus not a conserved *observable* guaranteed to have real eigenvalues. But we can still hope it to be well behaved enough to have eigenvalues at all (we may need to be careful about left/right eigenvalues). It can then still be a good strategy to use eigenvectors of T to solve H .

2.2 Crystal lattices

Symmetry groups relevant in crystals are:

- *Point Group*: Operations that keep at least one lattice point constant, e.g., rotations, inversions, mirror reflections. Not commutative.
- *Group of Translations*: Operations that move each lattice points by the same vector onto another lattice point. Commutative
- *Space Group*: Combination of point group and translations. This is characteristic of the so-called *Bravais lattice*.

(Once a basis is added to the lattice, other symmetries become possible, screw axes and glide planes. We are not going to discuss them.)

A Bravais lattice is defined as the set of points \vec{R} that can be expressed as

$$\vec{R} = \sum_{i=1}^d n_i \vec{a}_i, \quad (2.4)$$

where vectors \vec{a}_i are called “basis vectors”, coefficients n_i are integer and d gives the spatial dimension, usually, $d = 1, 2$ or 3 . Expressed in words, a Bravais lattice looks exactly the same (in all directions) after it has been moved so that one of its points lies where another one used to be.

2.2.1 Crystal lattices in 2D

In two dimensions, there are three lattice systems:

- Square lattice: $|a_1| = |a_2|$ and $\vec{a}_1 \cdot \vec{a}_2 = 0$. In addition to translational invariance, symmetry operations are
 - Inversion symmetry through any lattice point
 - Mirror reflections along the lines parallel to a_1 and a_2 as well as along diagonals
 - Fourfold rotational symmetry
- Rectangular lattice: $|a_1| \neq |a_2|$ and $\vec{a}_1 \cdot \vec{a}_2 = 0$. In addition to translational invariance, symmetry operations are
 - Inversion symmetry through any lattice point

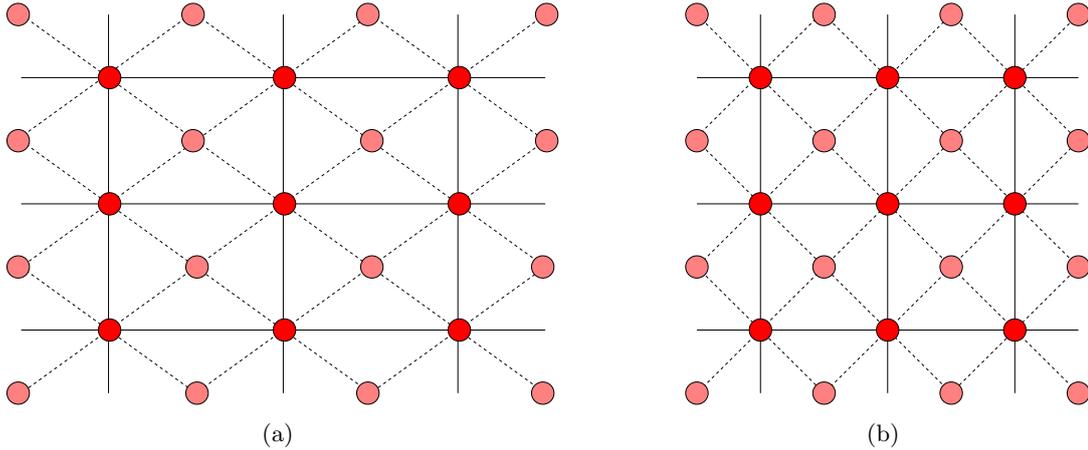


Figure 2.1: Schematic illustration concerning lattice systems and Bravais lattice / basis.

- Mirror reflections along the lines parallel to a_1 and a_2 , but not along diagonals
- Hexagonal lattice: $|a_1| = |a_2|$ and angle between \vec{a}_1 and \vec{a}_2 is 60° . In addition to translational invariance, symmetry operations are
 - Inversion symmetry through any lattice point
 - Mirror reflections along the lines parallel to a_1 , a_2 , and $a_1 - a_2$.
 - Sixfold rotational symmetry
- Oblique lattice: $|a_1| \neq |a_2|$ and $\vec{a}_1 \cdot \vec{a}_2 \neq 0$. In addition to translational invariance, only inversion symmetry remains.

A lattice that one might see as a special oblique lattice is a rectangular lattice, where additional lattice points sit in the middle of each rectangle in addition to its corners. Since this lattice has all the symmetries of the rectangular lattice, see Fig. 2.1(a), it belongs to the rectangular system rather than the oblique one. In 2D, the rectangular *lattice system* thus contains two *Bravais lattices*. In the square lattice, adding extra sites at the centers would also conserve all symmetries. However, one can here choose new basis vectors $(\vec{a}_1 \pm \vec{a}_2)/2$ and one then finds again a simple square lattice with a smaller unit cell, see Fig. 2.1(b). Consequently, the square lattice system contains only one Bravais lattice.

As a counter example, the honeycomb lattice is not a Bravais lattice: If we translate the lattice so that a lattice point \vec{R} comes to lie on the (former) position of its nearest neighbor, the lattice does not look the same as before. Mathematically, Eq. (2.4) cannot describe all lattice points. The honeycomb lattice can be obtained by putting a two-atom basis onto each lattice point of the hexagonal Bravais lattice. The atoms of a basis can also be of different kind, e.g., the differently shaded sites in Fig. 2.1 might be two different elements. In that case, we would have a simple (rectangular or square) lattice with a two-atom basis.

2.2.2 Crystal lattices in 3D

Check out standard text books, e.g. Ashcroft-Mermin.

There are 7 lattice systems:

- *Cubic*: all angles 90° , $|\vec{a}_1| = |\vec{a}_2| = |\vec{a}_3|$
Contains 3 Bravais lattices:
 - Simple/primitive cubic
 - Body-centered cubic: One site at the corner of a cube and one in its middle
 - Face-centered cubic: Additional sites at the centers of the cube's faces
 - (There is no “base centered cubic” lattice, because making one kind of cube faces special makes one of the three directions special and thus reduces the symmetry, so that this becomes a tetragonal lattice.)
- *Tetragonal*: all angles 90° , $|\vec{a}_1| = |\vec{a}_2| \neq |\vec{a}_3|$
Contains 2 Bravais lattices:
 - Simple
 - Body centered
 - (There is no “base centered tetragonal” lattice either, because this is in fact a simple tetragonal one with \vec{a}_1 and \vec{a}_2 rotated by 45° , similar to the case of Fig. 2.1(a).)
 - (By the same trick, “face centered tetragonal” is equivalent to “body centered”.)
- *Orthorhombic*: all angles 90° , $|\vec{a}_1| \neq |\vec{a}_2| \neq |\vec{a}_3|$
Contains 4 Bravais lattices:
 - Simple
 - Body centered
 - Face centered
 - Base centered: additional site in the center of the ‘floor’
- *Monoclinic*: one angle $\neq 90^\circ$, $|\vec{a}_1| \neq |\vec{a}_2| \neq |\vec{a}_3|$
Contains 2 Bravais lattices:
 - Simple
 - Base centered
- *Rhombohedral*: all angles equal, but $\neq 90^\circ$, $|\vec{a}_1| = |\vec{a}_2| = |\vec{a}_3|$
(High-symmetry axes do here not run $\parallel \vec{a}_i$.)
- *Hexagonal*: two angles 90° , one 120° , $|\vec{a}_1| = |\vec{a}_2| \neq |\vec{a}_3|$
- *Triclinic*: all angles $\neq 90^\circ$, $|\vec{a}_1| \neq |\vec{a}_2| \neq |\vec{a}_3|$

There are thus 14 Bravais lattices. Together with a basis (e.g. diamond lattice), one can have additional symmetry operations.

As an example, the point group of the cubic system contains:

- 3 axes with 4-fold rotational symmetry, $\parallel \vec{a}_1, \vec{a}_2, \vec{a}_3$
- 4 axes with 3-fold rotational symmetry, parallel diagonals through cube: $\parallel \vec{a}_1 + \vec{a}_2 + \vec{a}_3, \vec{a}_1 - \vec{a}_2 + \vec{a}_3, -\vec{a}_1 + \vec{a}_2 + \vec{a}_3, -\vec{a}_1 - \vec{a}_2 + \vec{a}_3$
- 6 axes with 2-fold rotational symmetry, parallel diagonals of faces: $\vec{a}_1 \pm \vec{a}_2, \vec{a}_1 \pm \vec{a}_3, \vec{a}_2 \pm \vec{a}_3$
- Inversion

This is called the octahedral group with inversion symmetry O_h .

2.2.3 Unit cells

If repeated along the vectors \vec{a}_i , a unit cell has to build up the complete lattice. This definition is not unique: One might always combine two unit cells into one, for example.

The face- and body-centered Bravais lattices are examples where the ‘obvious’ unit cell contains more than one lattice site. As these are Bravais lattices, it is *possible* to define them with a one-site unit cell. One way to do this would be to use new vectors \vec{a}'_i obtained by connecting the site at the corner with its nearest neighbors (in the center of the adjacent cubes/faces). This would give a so-called ‘primitive’ unit cell with just one site, but would not reveal the symmetries as well.

A special primitive unit cell is the ‘Wigner-Seitz’ cell. The Wigner-Seitz cell around a lattice point \vec{R} is given by all points that are closer to \vec{R} than they are to any other \vec{R}' . Its advantages are that it is primitive and has the proper symmetries, but its disadvantage is that its shape is often more complex.

2.3 Reciprocal Lattice

The aim of all the symmetry considerations is to make solving the Schrödinger equation easier, and the largest commutative (in order to be sure of having common eigenstates) group is the group of translations. As we know from math and from continuous translational invariance, Fourier transforms are coming in here, so we look at those. Check out a math text for Fourier transforms.

An important class of functions – and one where the topic of Fourier transforms immediately suggests itself – are lattice periodic functions. Examples might be the potential seen by electrons moving in a perfect crystal. As the function is lattice periodic, we have

$$f(\vec{x} + \vec{R}) = f(\vec{x}) \quad (2.5)$$

for any d -dimensional lattice vector $\vec{R} = \sum_{i=1}^d n_i \vec{a}_i$. Assuming that it is sufficiently well behaved (which we do assume), it can be written as

$$f(\vec{x}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} f_{\vec{G}} e^{-i\vec{G}\vec{x}}, \quad (2.6)$$

where $\Omega = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of a (not necessarily, but usually primitive) unit cell. The ‘Fourier coefficients’ are obtained by

$$f_{\vec{G}} = \frac{1}{\sqrt{\Omega}} \int_{\Omega} d^3x f(\vec{x}) e^{i\vec{G}\vec{x}}. \quad (2.7)$$

Note that various conventions exist concerning the signs in the exponential and the prefactors. For lattice periodic functions, the values of \vec{G} , for which $f_{\vec{G}} \neq 0$ are restricted:

$$f(\vec{x} + \vec{R}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} f_{\vec{G}} e^{-i\vec{G}\vec{x}} e^{i\vec{G}\vec{R}} = f(\vec{x}) \quad \Rightarrow \quad \vec{R} \cdot \vec{G} = 2\pi n \quad (2.8)$$

with integer n .

It turns out that all \vec{G} fulfilling this form themselves a (Bravais) lattice, i.e., they can be expressed as

$$\vec{G} = \sum_{i=1}^d m_i \vec{b}_i \quad (2.9)$$

with integer m_i . Furthermore, the basis vectors \vec{b}_i of this reciprocal lattice can be chosen to fulfill

$$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij} . \quad (2.10)$$

It is straightforward to see that the relation (2.10) implies that $\vec{G}\vec{R} = 2\pi n$ is fulfilled:

$$\vec{G}\vec{R} = \left(\sum_j m_j \vec{b}_j \right) \left(\sum_i n_i \vec{r}_i \right) = \sum_{i,j} \underbrace{\vec{b}_j \cdot \vec{a}_i}_{=2\pi\delta_{ij}} n_i m_j = 2\pi \underbrace{\sum_i n_i m_i}_{\text{integer}} \quad (2.11)$$

It is maybe less obvious that *all* vectors \vec{G} fulfilling $\vec{G}\vec{R} = 2\pi n$ can be expressed by (2.9). We can show this by noting that *any* reciprocal point (lattice or otherwise) can be expressed in terms of basis vectors \vec{b}_i fulfilling (2.10) as long as we allow *real* coefficients α_i . Out of all point, we now want to find all reciprocal points \vec{G} with the property

$$1 = e^{i\vec{G} \cdot \vec{R}} = \exp\left(i(\alpha_1 n_1 \underbrace{\vec{a}_1 \vec{b}_1}_{2\pi} + \alpha_2 n_2 \vec{a}_2 \vec{b}_2 + \alpha_3 n_3 \vec{a}_3 \vec{b}_3)\right) = e^{2\pi i(n_1 \alpha_1 + n_2 \alpha_2 + n_3 \alpha_3)} . \quad (2.12)$$

Due to (2.10), all terms $\vec{b}_i \vec{a}_j$ drop out for $i \neq j$. Since this relation $n_1 \alpha_1 + n_2 \alpha_2 + n_3 \alpha_3 \in \mathcal{Z}$ has to hold for arbitrary integer n_i , the alpha have themselves to be integer, i.e., any valid \vec{G} has the form (2.9) and they consequently form a Bravais lattice. This lattice is in the same system as the direct-space lattice, but can be a different Bravais lattice. The reciprocal lattice of the body-centered cubic lattice, e.g., is the face-centered cubic lattice.

A possible of choice of basis vectors is

$$\vec{b}_1 = \frac{2\pi}{\Omega} \vec{a}_2 \times \vec{a}_3 \quad (2.13)$$

$$\vec{b}_2 = \frac{2\pi}{\Omega} \vec{a}_3 \times \vec{a}_1 \quad (2.14)$$

$$\vec{b}_3 = \frac{2\pi}{\Omega} \vec{a}_1 \times \vec{a}_2 \quad (2.15)$$

or

$$b_i^\alpha = \frac{\pi}{\Omega} \epsilon_{ijk} \epsilon^{\alpha\beta\gamma} a_j^\beta a_k^\gamma \quad (2.16)$$

with the Levi-Civita tensor ϵ and α, β, γ running through components x, y and z . Clearly $\vec{a}_i \cdot \vec{b}_j = 0$ for $i \neq j$, because the cross product is orthogonal to each of its factors. For $i = j$, we get $\vec{a}_i \cdot \vec{b}_i = \frac{2\pi}{\Omega} \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ (or a cyclic permutation), yielding

$$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij} . \quad (2.17)$$

2.3.1 Fourier transforms and Periodic Boundary Conditions (PBC)

While lattice-periodic functions are important, it would be too strong a restriction to only use those. What we do want to require is translational invariance. Lattice-periodic functions obey it, with eigenvalue 1, which is not necessary: other eigenvalues would also be fine. To motivate why we stick with Fourier transforms, though, note that exponentials of the form $e^{i\vec{k}\vec{R}}$ have all the properties that (right) eigenvalues of the translation operator should have:

- As a symmetry operator, translations should be unitary, consequently, the absolute value of their eigenvalues should be 1. (Unitary operators are almost as nice as hermitian ones when it comes to eigenvalues.)
- Combining two translations by \vec{R}_1 and \vec{R}_2 into one is possible (this is a group axiom) and we further know that this operation corresponds to a translation by $\vec{R}_1 + \vec{R}_2$. This carries over to the eigenvalues of the common (as translations moreover commute) eigenvector: The product of the two eigenvalues $e^{i\vec{k}\vec{R}_1} \cdot e^{i\vec{k}\vec{R}_2}$ is indeed the eigenvalue for the combined operation $e^{i\vec{k}(\vec{R}_1 + \vec{R}_2)}$.
- Similarly, the eigenvalue of the inverse element – translation by $-\vec{R}$ – works out: $(e^{i\vec{k}\vec{R}})^{-1} = e^{i\vec{k}(-\vec{R})}$.
- A note on the possible values of \vec{k} labelling the eigenvalues: Adding a reciprocal-lattice point \vec{G} leads to the same eigenvalues for *all* translations $T_{\vec{R}_i}$, because $e^{i(\vec{k} + \vec{G})\vec{R}_i} = e^{i\vec{k}\vec{R}_i} e^{i\vec{G}\vec{R}_i} = e^{i\vec{k}\vec{R}_i}$. One can thus obtain all possible eigenvalues of the translations operators from \vec{k} of a primitive unit cell of the reciprocal lattice; the first Brillouin zone.
- In a system with *continuous* translational invariance, the translation operator can be shown to be $\hat{T}_{\vec{r}} = e^{\frac{i}{\hbar}\hat{p}\vec{r}}$ for any \vec{r} . The eigenvalues are then $e^{i\vec{k}\vec{r}}$, with $\hbar\vec{k} = \vec{p}$ the (conserved) eigenvalue of the momentum operator. Here, only translations with lattice vectors \vec{R} survive, but these should have analogous eigenvalues $e^{i\vec{k}\vec{R}}$.

The theory of Fourier transforms should consequently be helpful in understanding potential eigenfunctions.

It is customary to request *all* physical quantities to be periodic with a much larger period than the lattice, this convention is called ‘periodic boundary conditions’. It is not necessary and sometimes not used, but it is useful. All functions are expected to fulfill

$$f(\vec{x} + \sum_i N_i \vec{a}_i) = f(\vec{x}), \quad (2.18)$$

where $N_i \gg 1$ is the lattice size along lattice vector \vec{a}_i . In analogy to (2.8) and (2.9), looking at the Fourier transforms of such functions with larger periodicity gives

$$\vec{k} = \sum_{i=1}^d \frac{m_i}{N_i} \vec{b}_i. \quad (2.19)$$

The larger direct lattice thus allows much more finely spaced momentum points.

In fact, the primitive unit cell of the reciprocal lattice contains $N_1 \cdot N_2 \cdot N_3$ momenta, as many points (and degrees of freedom) as there are lattice sites in the direct lattice. The primitive unit cell usually considered (but this is in principle arbitrary) in the case of the

reciprocal lattice is its Wigner-Seitz unit cell, it is termed the first Brillouin zone (1 BZ). These momenta are ‘small’ compared to the points of the reciprocal lattice, but as there are as many as there are direct-lattice points, the degrees of freedom they can express are sufficient to express physics on ‘larger scales’, i.e., not looking into the unit cell.

We illustrate this with a few formulas: A special function that ‘cares only about the lattice sites’ is

$$f(\vec{x}) = \sum_{\vec{R}} \delta(\vec{x} + \vec{R}) \quad (2.20)$$

with the delta-distribution $\int_x dx \delta(x - x_0) f(x) = f(x_0)$. This function is clearly lattice periodic, but can just as clearly not be used to express different functions within the unit cell. \vec{x} can be anywhere in the full space, but as the sum runs over all \vec{R} , we can also take it to be within the primitive unit cell around the closest \vec{R} of the direct lattice. The Fourier transform (2.7) is

$$f_{\vec{G}} = \frac{1}{\sqrt{\Omega}} \int_{\Omega} d^3x \sum_{\vec{R}} \delta(\vec{x} + \vec{R}) e^{i\vec{G}\vec{x}} = \frac{1}{\sqrt{\Omega}} \underbrace{\int_{\Omega} d^3x}_{\int_{\text{all } \vec{x}}} \sum_{\vec{R}} \delta(\vec{x} + \vec{R}) \underbrace{e^{-i\vec{G}\vec{R}}}_{=1}, \quad (2.21)$$

where the sum over \vec{R} and the integral over Ω combine to give an integral over the full space $\vec{R} + \vec{x}$: \vec{R} gives the large distances between lattice points and $\vec{x} \in \Omega$ the small ones within the unit cell. This becomes

$$f_{\vec{G}} = \frac{1}{\sqrt{\Omega}} e^{i\vec{G}\vec{R}} = \frac{1}{\sqrt{\Omega}}. \quad (2.22)$$

Inserting this back into (2.6) gives an alternative expression of $f(\vec{x})$ that must be the same as the original (2.20), i.e.:

$$\sum_{\vec{R}} \delta(\vec{x} + \vec{R}) = f(\vec{x}) = \frac{1}{\Omega} \sum_{\vec{G}} e^{i\vec{G}\vec{x}} \quad (2.23)$$

We will use this equality to understand some aspects of Fourier transforms of functions that are *not* lattice periodic. They can be defined with respect to the large super lattice with volume $V = N_1 N_2 N_3 \Omega$:

$$f(\vec{x}) = \frac{1}{\sqrt{V}} \sum_{\text{all } \vec{k}} f_{\vec{k}} e^{-i\vec{k}\vec{x}} = \frac{1}{\sqrt{V}} \int_{\vec{q} \in 1\text{BZ}} d^3q e^{-i\vec{q}\vec{x}} \sum_{\vec{G}} e^{-i\vec{G}\vec{x}} f_{\vec{G}+\vec{q}}, \quad (2.24)$$

where general momentum \vec{k} was decomposed into a ‘large’ part \vec{G} that is a reciprocal lattice vector and a ‘small’ part \vec{q} from the first Brillouin zone. Let us now look at special functions \tilde{f} where $\tilde{f}_{\vec{G}+\vec{q}}$ is lattice periodic *in the reciprocal lattice*, i.e., $\tilde{f}_{\vec{G}+\vec{q}} = \tilde{f}_{\vec{q}}$. We then find using (2.23) that

$$\tilde{f}(\vec{x}) = \frac{1}{\sqrt{V}} \int_{\vec{q} \in 1\text{BZ}} d^3q e^{-i\vec{q}\vec{x}} \tilde{f}_{\vec{q}} \sum_{\vec{G}} e^{-i\vec{G}\vec{x}} = \frac{\Omega}{\sqrt{V}} \int_{\vec{q} \in 1\text{BZ}} d^3q e^{-i\vec{q}\vec{x}} \tilde{f}_{\vec{q}} \sum_{\vec{R}} \delta(\vec{x} + \vec{R}), \quad (2.25)$$

which is only non-zero at lattice sites \vec{R} . Such a function, which only depends on momenta \vec{q} from the first Brillouin zone can thus not ‘see’ into the unit cell. However, this type of functions, where we are not concerned with the internal structure ¹, are extremely common in condensed-matter theory. In fact, it is often said that $\vec{q} \in 1BZ$ already describes ‘everything’.

These functions \tilde{f} can also be written

$$\tilde{f}(\vec{x}) = \sqrt{\Omega} \sum_{\vec{R}} f(\vec{R}) \delta(\vec{x} + \vec{R}) \quad \text{with} \quad (2.26)$$

$$\tilde{f}(\vec{R}) = \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\vec{q}} \tilde{f}_{\vec{q}} e^{-i\vec{q}\vec{R}} \quad \text{and} \quad (2.27)$$

$$\tilde{f}_{\vec{q}} = \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\vec{R}} f(\vec{R}) e^{i\vec{q}\vec{R}}. \quad (2.28)$$

\vec{q} runs here only over the first BZ, while \vec{R} is a lattice vector of the direct lattice. Compare this to the equations (2.6) and (2.7) for lattice periodic functions, where \vec{G} is a (reciprocal) lattice vector and \vec{x} runs only over the unit cell.

We can here note that direct-space vectors \vec{R} indeed define the reciprocal lattice of the reciprocal lattice \vec{G} and a few useful formulas should be noted:

$$\int_{\Omega} d^3x e^{i(\vec{G}-\vec{G}')\vec{x}} = \Omega \delta_{\vec{G},\vec{G}'} \quad \text{and} \quad (2.29)$$

$$\int_{\Omega_B} d^3q e^{i(\vec{R}-\vec{R}')\vec{q}} = \Omega_B \delta_{\vec{R},\vec{R}'} \quad (2.30)$$

give orthonormality. $\Omega_B = (2\pi)^3/\Omega$ is the volume of the first BZ and the integral over it should be understood to refer to very finely spaced \vec{q} , i.e., a very large lattice, this limit is called the ‘thermodynamic limit’. Additionally,

$$\Omega \sum_{\vec{R}} \delta(\vec{x} + \vec{R}) = \sum_{\vec{G}} e^{i\vec{G}\vec{x}} \quad \text{and} \quad (2.31)$$

$$\Omega_B \sum_{\vec{G}} \delta(\vec{k} + \vec{G}) = \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \quad (2.32)$$

are useful.

The two special types of periodic functions that we discussed can be summarized as:

¹Resp. take it into account in other ways.

Lattice periodic functions

- Defined for all positions \vec{x} .
- Lattice periodic: $f(\vec{x})$ from primitive unit cell (=space between lattice points \vec{R}) repeated to make full lattice: $f_{\vec{x}+\vec{R}} = f_{\vec{x}}$; all unit cells equivalent.
- Only Fourier coefficients $f_{\vec{G}} \neq 0$ for reciprocal lattice vectors \vec{G} , see (2.9).
- Information on structure within unit cell.
- Identical for all \vec{R} : Can't describe variations over more than one unit cell.
- Very useful for: lattice structure (Bravais lattice and basis within unit cell).

Functions periodic in reciprocal lattice

- Defined for all momenta \vec{k} compatible with PBC, see (2.19).
- $f_{\vec{q}}$ from first BZ (=momenta between reciprocal-lattice points \vec{G}) repeated to fill complete reciprocal lattice: $f_{\vec{q}+\vec{G}} = f_{\vec{q}}$; all BZs equivalent.
- In direct space, only $f(\vec{R}) \neq 0$ at lattice sites \vec{R} .
- Information on longer length scales beyond unit cell.
- Only defined at Bravais-lattice site \vec{R} : Cannot look inside unit cell.
- Very useful for: excitations (e.g. phonons, propagating electrons).

Both types of information are of course relevant, and in general, functions do not have to be periodic in either space, combining features from both sides. In the context of condensed-matter theory as treated in this class, functions periodic in \vec{G} and defined only on lattice sites \vec{R} are, however, going to be particularly important.

3 Separation of Lattice and Electrons and Lattice Dynamics

Inspired by Prof. Muramatsu's and Prof. Valentí's notes.

In this chapter, we want to discuss on a very qualitative level how solids are formed and then discuss in more detail excitations of the ionic lattice, i.e., phonons.

3.1 Adiabatic Approximation: Separate Hamiltonians for Electrons and Ions

A way to greatly simplify the problem of coupled ionic and electronic motion in Eq. (1.1) is partly decouple the electronic and lattice degrees of freedom. Atomic units are best suited to express the Hamiltonian, the unit of energy E_0 is then the Hartree, $E_0 = \frac{me^4}{\hbar^2} = \frac{e^2}{a_0} \approx 27$ eV, where the Bohr radius $a_0 = \frac{\hbar^2}{me^2} \approx 0.5\text{\AA}$ makes a suitable unit of length. Position-space vectors \vec{r} and \vec{R} are then expressed as $\vec{r} = a_0\vec{r}'$, where \vec{r}' becomes a dimensionless number and is renamed \vec{r} . This also changes the derivatives $\partial_{r_\alpha} = \frac{1}{a_0}\partial_{r'_\alpha}$ w.r.t component $\alpha = x, y, z$, which is again renamed to ∂_{r_α} . (And analogously for coordinates \vec{R} of the nuclei.) In position space, the Hamiltonian (1.1) becomes

$$\frac{H}{E_0} = -\frac{1}{2} \sum_{k,\alpha} \frac{m}{M_k} \frac{\partial^2}{\partial R_{k,\alpha}^2} \quad (3.1)$$

$$+ \frac{1}{2} \sum_{k \neq l} \frac{Z_k Z_l}{|\hat{R}_k - \hat{R}_l|} \quad (3.2)$$

$$- \frac{1}{2} \sum_{i,\alpha} \frac{\partial^2}{\partial r_{i,\alpha}^2} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\hat{r}_i - \hat{r}_j|} \quad (3.3)$$

$$- \sum_{i,k} \frac{Z_k}{|\hat{r}_i - \hat{R}_k|} = \quad (3.4)$$

$$= T_N + T_e + V_e + V_N + V_{e-N} = T_N + H_0 \quad (3.5)$$

If the interaction V_{e-N} between electrons and nuclei, see (3.4), were small and if we could neglect it, this would decouple the two systems. If $\psi(\vec{r})$ and $\phi(\vec{R})$ are the eigenstates of the electronic and ionic Hamiltonians, any product state $\psi(\vec{r})\phi(\vec{R})$ would then be an eigenstate of the total Hamiltonian. However, the interaction term (3.4) is not smaller than the other terms and can certainly not be neglected: We know that the only the Coulomb interaction between electrons and nuclei allows the solid to form.

A term that is smaller than the others is the *kinetic* energy T_N of the nuclei (3.1), which contains a factor $\frac{m}{M_k} \approx 10^{-5}$ - 10^{-4} and a first approximation consists of leaving it out. As

electrons are much lighter than ions, they move much faster and the assumption is that at any point during the ionic motion, the electrons have time enough to be in the instantaneous ground state, i.e., the electronic state depends only on the position of the nuclei at this time, but not on their momentum. When nuclei move (comparatively slowly), the electronic state can still change, as they react to the potential energy affected by the changed ionic positions. But they remain in the ground state of the instantaneous ionic potential, such a process is called adiabatic, and the approach is therefore called *adiabatic approximation*.

The full Hamiltonian is thus divided into H_0 (3.2-3.4) and the perturbation T_N (3.1). At first sight, this does not appear to help much, because H_0 still contains terms referring to electrons *and* nuclei. However, the differential equation defined by H_0 in position space does not contain derivatives w.r.t. nuclear coordinates \vec{R} and these variables can thus be seen as parameters, much like Z_k or even a_0 . We then have a differential equation for eigenfunctions ϕ_α of the electrons, with operator H_0 acting on this function and the corresponding coordinates \vec{r} .

$$H_0(\vec{R})\phi_\alpha(\vec{r}; \vec{R}) = \epsilon_\alpha(\vec{R})\phi_\alpha(\vec{r}; \vec{R}) \quad (3.6)$$

Additionally, eigenvalues and eigenfunctions depend on parameters \vec{R} and Z_k . The ion-ion potential (3.2) is here just an additive constant (i.e. not affecting ϕ) that also depends on these parameters.

A first approximation can be to take $\epsilon_0(\vec{R})$ and $\phi_0(\vec{r}; \vec{R})$ as electronic ground-state energy and ground state for given ionic positions \vec{R} , if this is what one was interested in. One can then minimize the electronic ground-state energy $\epsilon_0(\vec{R})$ by varying positions \vec{R} of the nuclei. The resulting optimal positions should give a decent approximation to the equilibrium positions of the ions. As $\epsilon_0(\vec{R})$ defines a potential for the nuclei (it also contains the ion-ion interaction) one can also use it to classically study motion of nuclei driven by this potential, an approach used in molecular-dynamics simulation.

3.1.1 Equilibrium Positions of the Ions: How the Lattice arises

The chemical processes actually stabilizing a solid are not a main point of this class, where we mostly assume it to exist. Nevertheless, a short summary of various types of bonding is useful, even though real materials usually lie between clear scenarios.

1. *Van-der-Waals bonds*: This type of bonds exists between neutral atoms or molecules, where a dipole moment can be induced by displacing the electronic cloud to one side. Even though the atom/molecule would by itself not have any dipole moment, it may be energetically favorable to create one once two such molecules become close to each other, because the interaction between the newly-created dipoles may gain more energy than the cost of the electron displacement. Dipole-dipole interactions are not as strong as, e.g., Coulomb interaction between ions and moreover fall off quickly with distance. The van-der-Waals interaction is $\propto r^{-6}$. However, it grows with the number of involved particles, so that it can in total become quite strong. For the same reason, it prefers dense packing.

An effective potential often used to model such a scenario is the Lennard-Jones po-

tential

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (3.7)$$

The second term is the van-der-Waals interaction, while the first term takes into account the fact that the atoms/molecules are repulsive on very short distances, i.e., they cannot sit on the same spot.¹ For r/σ slightly larger than 1, it has a minimum, the equilibrium distance between two particles. This potential can be used to simulate the interplay of van-der-Waals interaction and kinetic energy.

2. *Ionic bonds:* In this case, two (or more) kinds of atoms (or molecules) are combined, the classic example is rock salt NaCl. Na has here one electron outside filled shells and Cl misses one. Since filled shells are energetically very stable, energy can be gained by transferring one electron from Na to Cl and since the atoms are then charge ions, Coulomb attraction comes into play. This Coulomb interaction between charge monopoles is strong compared to dipole-dipole interaction. It also profits from more ions being involved (suggesting dense packings), but they have to be mixed, which leads to some restrictions
3. *Covalent bonding:* Here, the electrons involved in the bondings are shared between two atoms and occupy common orbitals. Because of these orbitals, the bonds are quite directional and crystals may have quite a low packing density. The carbon-carbon bonds in diamond, which form tetrahedra, are a classic example.
4. *Metallic bonding:* When an element (e.g. Na) has electrons just outside filled shells, this electron can easily be moved away. As an s -electron of the next shell, its wave function can be quite large compared to the remaining ion and the range of its strongly repulsive short-distance interaction, and thus to the length scale of a plausible lattice constant. s orbitals of many atoms then see each other and due to their overlaps, electrons can easily move through the lattice and gain kinetic energy. This energy gain from partly filled bands stabilizes the solid.
5. *Hydrogen bonds:* Here, molecules (e.g. water) have a dipole moment (as opposed to the induced dipoles of the van-der-Waals interaction) due to the effective positive charge of the H atoms. The resulting interaction is almost close to a chemical bond.

3.1.2 Add back the kinetic energy of the ions

As a next step, we add back the kinetic energy of the ions and later decide which of the resulting terms to keep. To do so, we express the quantum mechanical state of the full system as $\psi(\vec{r}, \vec{R}) = \phi(\vec{r}; \vec{R})\chi(\vec{R})$, where we can expand the electronic part $\phi(\vec{r}; \vec{R})$ in the eigenbasis of $H_0(\vec{R})$. As an eigenbasis is complete, any function can be expressed in this way, by using

$$\phi(\vec{r}; \vec{R}) = \sum_{\alpha} c_{\alpha} \phi_{\alpha}(\vec{r}; \vec{R}). \quad (3.8)$$

¹Which can in turn be explained by the inner shells of the ions, or the nuclei, ‘seeing’ each other.

As the ϕ_α fulfill the eigenvalue equation (3.6), this gives ²

$$H_0\psi(\vec{r}, \vec{R}) = H_0 \sum_\alpha c_\alpha \phi_\alpha(\vec{r}; \vec{R}) \chi(\vec{R}) = \sum_\alpha c_\alpha \epsilon_\alpha(\vec{R}) \phi_\alpha(\vec{r}; \vec{R}) \chi(\vec{R}). \quad (3.9)$$

Applying the full Hamiltonian to this state ψ gives

$$H\psi = (H_0 + T_N)\psi = \sum_\alpha c_\alpha \epsilon_\alpha(\vec{R}) \phi_\alpha(\vec{r}; \vec{R}) \chi(\vec{R}) - \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \frac{\partial^2}{\partial R_{k,\beta}^2} \psi = \quad (3.10)$$

$$= \sum_\alpha c_\alpha \left(\epsilon_\alpha(\vec{R}) \chi(\vec{R}) - \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \frac{\partial^2 \chi(\vec{R})}{\partial R_{k,\beta}^2} \right) \phi_\alpha(\vec{r}; \vec{R}) \quad (3.11)$$

$$- \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \sum_\alpha c_\alpha \frac{\partial^2 \phi_\alpha}{\partial R_{k,\beta}^2} \chi - \sum_{k,\beta} \frac{m}{M_k} \sum_\alpha c_\alpha \frac{\partial \phi_\alpha}{\partial R_{k,\beta}} \frac{\partial \chi}{\partial R_{k,\beta}} = \quad (3.12)$$

$$\begin{aligned} & - \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \sum_\alpha \phi_\alpha \frac{\partial^2 c_\alpha}{\partial R_{k,\beta}^2} \chi - \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \sum_\alpha \frac{\partial \phi_\alpha}{\partial R_{k,\beta}} \frac{\partial c_\alpha}{\partial R_{k,\beta}} \chi - \sum_{k,\beta} \frac{m}{M_k} \sum_\alpha \phi_\alpha \frac{\partial c_\alpha}{\partial R_{k,\beta}} \frac{\partial \chi}{\partial R_{k,\beta}} = \\ & = E\psi = E \sum_\alpha c_\alpha \phi_\alpha(\vec{r}; \vec{R}) \chi(\vec{R}). \end{aligned} \quad (3.13)$$

Multiplying with the conjugate electronic ground state ϕ_0^* and integrating over all $3N_e$ electronic coordinates \vec{r} , i.e., taking a scalar product with $\langle \phi_0 |$, yields

$$E \sum_\alpha c_\alpha \chi(\vec{R}) \underbrace{\int d^{3N_e} r \phi_0^*(\vec{r}; \vec{R}) \phi_\alpha(\vec{r}; \vec{R})}_{=\delta_{\alpha,0}} = \quad (3.14)$$

$$= \sum_\alpha c_\alpha \left(\epsilon_\alpha(\vec{R}) \chi(\vec{R}) - \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \frac{\partial^2 \chi(\vec{R})}{\partial R_{k,\beta}^2} \right) \underbrace{\int d^{3N_e} r \phi_0^*(\vec{r}; \vec{R}) \phi_\alpha(\vec{r}; \vec{R})}_{=\delta_{\alpha,0}} \quad (3.15)$$

$$- \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \chi(\vec{R}) \sum_\alpha c_\alpha \int d^{3N_e} r \phi_0^* \frac{\partial^2 \phi_\alpha}{\partial R_{k,\beta}^2} \quad (3.16)$$

$$- \sum_{k,\beta} \frac{m}{M_k} \frac{\partial \chi}{\partial R_{k,\beta}} \sum_\alpha c_\alpha \int d^{3N_e} r \phi_0^* \frac{\partial \phi_\alpha}{\partial R_{k,\beta}} \quad (3.17)$$

$$- \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \frac{\partial^2 c_0}{\partial R_{k,\beta}^2} \chi - \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \sum_\alpha \frac{\partial c_\alpha}{\partial R_{k,\beta}} \chi \int d^{3N_e} r \phi_0^* \frac{\partial \phi_\alpha}{\partial R_{k,\beta}} - \sum_{k,\beta} \frac{m}{M_k} \frac{\partial c_0}{\partial R_{k,\beta}} \frac{\partial \chi}{\partial R_{k,\beta}}. \quad (3.18)$$

Assuming that $c_0 \approx 1 \neq 0$ and dividing by it, the first lines (3.14) and (3.15) give an eigenvalue equation for $\chi(\vec{R})$, with a kinetic energy $T_{N,\text{eff}}$ and some potential $\epsilon_0(\vec{R})$:

$$\left(\epsilon_0(\vec{R}) - \frac{1}{2} \sum_{k,\beta} \frac{m}{M_k} \frac{\partial^2}{\partial R_{k,\beta}^2} \right) \chi(\vec{R}) = E \chi(\vec{R}). \quad (3.19)$$

²Note that even for states $c_\alpha = \delta_{\alpha,0}$, $\psi(\vec{r}, \vec{R}) = \phi_0(\vec{r}, \vec{R}) \chi(\vec{R})$ is not strictly speaking an eigenstate of H_0 , because the 'eigenvalue' $\epsilon_0(\vec{R})$ depends on \vec{R} , which is a variable of ψ and not just some parameter, as it was for ϕ .

However, (3.17) mixes derivatives of ϕ and χ and couples thus the electronic and ionic kinetic energies. Additionally, (3.16) describes an operator that acts on the nuclear wave function with a weight given by derivatives of the electronic wave function, modifies thus both ϕ and χ and likewise undoes the decoupling. The adiabatic approximation neglects these terms, which is justified if they are ‘small’ compared to the terms included in H_0 as well as compared to the nuclear motion (3.19). The energy scale of H_0 is $E_0 = \frac{me^4}{\hbar^2}$. Eigenvalues of (3.19) will be discussed in detail in section 3.2, where energies $\hbar\omega = \hbar\sqrt{\frac{K}{M}}$ of lattice vibrations are related to a ‘spring constant’ K that is in turn derived from the curvature of $\epsilon_0(\vec{R})$. Using $a_0 = \frac{\hbar^2}{me^2}$ as a ‘typical’ unit of length, one estimates

$$\frac{\partial^2 \epsilon(\vec{R})}{\partial R^2} \approx \frac{E_0}{a_0^2} = \frac{me^4}{\hbar^2} \frac{m^2 e^4}{\hbar^4} = \frac{m}{\hbar^2} E_0^2 \quad \Rightarrow \quad \hbar\omega \approx \hbar\sqrt{\frac{K}{M}} \approx \sqrt{\frac{m}{M}} E_0. \quad (3.20)$$

Let us now compare the mixed terms to both electronic and ionic energy scales:

1. In estimating (3.16), it is useful to recall that the wave function $\phi(\vec{r}; \vec{R})$ knows about \vec{R} only through the interaction $V_{e-N} \propto \frac{Z_k}{|\vec{R}_k - \vec{r}|}$ between nuclei and electrons; the nuclear potential V_N only changes the eigenvalue ϵ_0 . The effect of the derivatives $\partial/\partial R_{k,\beta}$ should thus be approximately captured by $\partial/\partial r_{i,\beta}$. The integral in (3.16) thus turns out to be close to the kinetic energy of the electrons and of order E_0 . The full term is then of to order of $\frac{m}{M_k} E_0$, or $\sqrt{\frac{m}{M}} \hbar\omega$, i.e., smaller by a factor of 10^{-2} - 10^{-3} than the next smallest energy.
2. In the term (3.17), contributions for $\alpha = 0$ vanish for non-magnetic solutions ϕ . Such wave functions can be chosen real $\phi_0 = \phi_0^*$ and the derivative $\partial/\partial R$ of the total density vanishes.
3. For $\alpha \neq 0$ and/or complex ϕ , we again approximate $\partial\phi/\partial R$ by $-\partial\phi/\partial r$. The two factors $\partial\chi/\partial R$ and $\partial\phi/\partial r$ are then the nuclear and electronic momenta. In atomic units $\langle p_{\text{el.}} \rangle \approx \sqrt{E_0}$ and $\langle p_N \rangle \approx \sqrt{\frac{M}{m}} \hbar\omega$, which leads together with the prefactor $\frac{m}{M}$ and $\hbar\omega \approx \sqrt{\frac{m}{M}} E_0$ to the estimate

$$\approx \frac{m}{M} \sqrt{E_0 \frac{M}{m} \sqrt{\frac{m}{M}} E_0} = \left(\frac{m}{M}\right)^{3/4} E_0 \approx \left(\frac{m}{M}\right)^{1/4} \hbar\omega. \quad (3.21)$$

While this is still smaller than the nuclear kinetic energy, $\left(\frac{m}{M}\right)^{1/4} \approx 10^{-1}$ - 10^{-2} , i.e., the difference is not very large considering how crude the estimates are.

Finally, the terms in (3.18) contains derivatives, i.e., they are relevant if the electrons care *not* always in the instantaneous ground state, i.e., for $\partial c_0/\partial R \neq 0$. However, as perturbation theory tells us that such admixtures go with $V_{l0}/(E_l - E_0)$ [with V_{l0} the matrix element (3.21) connecting unperturbed eigenstates and $(E_l - E_0) \approx E_0$], these terms are indeed rather small.

The most important among the neglected terms, (3.17) which may not be so very small, is only non-zero when it involves different electronic eigenstates. In a perturbative treatment, energy differences $\epsilon_{\alpha \neq 0} - \epsilon_0$ between these eigenstates enter in the denominator. The term can consequently more easily be neglected if electronic eigenstates are well separated. This is a different way of expressing the prerequisite for the adiabatic approximation, namely that electrons move so fast that they can always stay in the ground state: When electronic

eigenstates remain well separated from each other during the nuclear motion, the adiabatic approximation is justified.

Even if coupling between lattice and electronic degrees of freedom cannot be neglected, the adiabatic approximation is used as a starting point and the coupling is later re-introduced as a coupling between electrons and phonons.

3.2 Lattice Dynamics and Phonons

We will now start from the effective Hamiltonian (3.19) for the lattice degrees of freedom and discuss a (quantum mechanical) description of the ionic motion. At first, however, we discuss general properties of the Hamiltonian that are also valid in a classical picture, i.e., we look at

$$H = \epsilon_0(\vec{R}) + \sum_{k,\beta} \frac{m}{M_k} \frac{p_{k,\beta}^2}{2} . \quad (3.22)$$

The effective potential $\epsilon_0(\vec{R})$ contains here both the ion-ion Coulomb interaction (3.2) and the effective interaction mediated by the electrons, and might be obtained by either solving the electronic Hamiltonian (3.6) or by some phenomenological parametrization. We are here interested in cases where the potential has a minimum for some equilibrium positions \vec{R}_k^0 , ideally an absolute minimum. In this case, the atoms form a solid or a molecule, if the minimum is deep enough.

If the atoms do not move too far from \vec{R}_k^0 (if they do, the molecule or solid dissolves), one can expand the the potential in terms of deviations \vec{u}_k , i.e., setting $\vec{R}_k = \vec{R}_k^0 + \vec{u}_k$:

$$\epsilon_0(\vec{R}) = \epsilon_0(\vec{R}^0) + \sum_{k,\alpha} \underbrace{\frac{\partial \epsilon_0}{\partial R_{k,\alpha}} \Big|_{\vec{R}=\vec{R}^0}}_{=0} u_{k,\alpha} + \frac{1}{2} \sum_{\substack{k,\alpha \\ l,\beta}} \underbrace{\frac{\partial^2 \epsilon_0}{\partial R_{k,\alpha} \partial R_{l,\beta}} \Big|_{\vec{R}=\vec{R}^0}}_{\chi_{k,\alpha;l,\beta} = \chi_{l,\beta;k,\alpha}} u_{k,\alpha} u_{l,\beta} + \dots \quad (3.23)$$

The ‘harmonic approximation’ consists of neglecting terms of orders higher than two. Since \vec{R}^0 is an equilibrium point of ϵ , first derivatives have to vanish $\frac{\partial \epsilon_0}{\partial R_{k,\alpha}} \Big|_{\vec{R}=\vec{R}^0} = 0$. The matrix χ coming from the second derivatives has a few convenient properties:

1. Since \vec{R}^0 is a minimum of ϵ and not a maximum or saddle point, χ must be positive definite.
2. As $\epsilon(\vec{R})$ is real, so is χ .
3. As partial derivatives commute, it is symmetric $\chi_{i,j} = \chi_{j,i} = \chi_{k,\alpha;l,\beta} = \chi_{l,\beta;k,\alpha}$.

As a result, one can always diagonalize χ and it has real positive eigenvalues and orthonormal eigenvectors.

It can now be convenient ³ to absorb the masses into χ so that the combined quantity is the only remaining parameter. This is achieved by rescaling distances with the mass $\tilde{u}_{k,\alpha} = \sqrt{M_k/m} u_{k,\alpha}$. The conjugate momentum is then rescaled as $\tilde{p}_{k,\alpha} = \sqrt{\frac{m}{M_k}} p_{k,\alpha}$. The

³Some treatments in the literature do this, some don't.

Hamiltonian (3.22) in harmonic approximation becomes then

$$H = \sum_{k,\beta} \frac{\tilde{p}_{k,\beta}^2}{2} + \frac{1}{2} \sum_{\substack{k,\alpha \\ l,\beta \\ D_{k,\alpha;l,\beta}=D_{i,j}}} \frac{m\chi_{k,\alpha;l,\beta}}{\sqrt{M_k M_l}} \tilde{u}_{k,\alpha} \tilde{u}_{l,\beta}, \quad (3.24)$$

where the matrix $D_{i,j}$ has the same properties as $\chi_{i,j}$. Collecting all $d \cdot N_{\text{atom}}$ ($d = \text{spatial dimension considered}$) components $\tilde{u}_{k,\alpha}$ and $\tilde{p}_{k,\alpha}$ into one long vector \tilde{u} and \tilde{p} , this becomes

$$H = \frac{1}{2} (\tilde{p}^T \tilde{p} + \tilde{u}^T D \tilde{u}), \quad (3.25)$$

where D can be diagonalized with a unitary matrix C and positive eigenvalues to

$$CDC^\dagger = \Omega = \begin{pmatrix} \omega_1^2 & 0 & \dots & \\ 0 & \omega_2^2 & 0 & \dots \\ \vdots & \vdots & & \end{pmatrix}. \quad (3.26)$$

Transforming \tilde{u} and \tilde{p} into the eigenbasis (denoted by v and p_v) then transforms the Hamiltonian into a sum over decoupled harmonic oscillators:

$$H = \frac{1}{2} (p_v^T p_v + v^T \Omega v) = \frac{1}{2} \sum_i^{dN_{\text{atom}}} (p_{v,i}^2 + \omega_i^2 v_i^2). \quad (3.27)$$

This decomposition into ‘normal modes’ characterized by frequencies ω_i is an important step in both a classical and a quantum-mechanical analysis.

We have so far not used any properties of a solid apart from the fact that we assume the effective potential to stabilize equilibrium positions of the atoms. Kinetics of the atomic nuclei in *molecules* are likewise governed by normal modes, and matrix D for a molecule might be diagonalized numerically to yield the associated frequencies. For an extended solid, this would not be possible, because the matrix is too large. In the next part, we are going to use translational invariance of solids to (at least partially) perform the diagonalization analytically.

3.2.1 Phonons in Solids

To diagonalize the matrix D , we will make use of its symmetries. Here, we discuss translational invariance. In a solid, $D_{k,\alpha;l,\beta}$ has the following properties:

1. Translational invariance, i.e., it does not change if both atoms k and l are shifted by a lattice vector \vec{R}_i . For a Bravais lattice, it must consequently only depend on the distance between the atoms $\vec{R}_i - \vec{R}_j$, i.e., $D_{i,\alpha;j,\beta} = D_{\alpha,\beta}(\vec{R}_i - \vec{R}_j)$. For a lattice with a basis, where the position \vec{R}_l of each atom can be combined from a lattice vector \vec{R}_i and vector giving the position within the unit cell \vec{r}_k as $\vec{R}_l = \vec{R}_i + \vec{r}_k$, an index indicating the atom within the basis remains, i.e., $D_{l,\alpha;l',\beta} = D_{k,\alpha;k',\beta}(\vec{R}_i - \vec{R}_j)$, with k and k' running over the atoms within the unit cell and l (l') over all atoms of the solid.
2. Inversion symmetry implies $D_{\alpha,\beta}(\vec{R}_l - \vec{R}_k) = D_{\alpha,\beta}(\vec{R}_k - \vec{R}_l)$.

3. Depending on additional lattice symmetries, more relations may exist. In a cubic system, e.g., it must be the same in x -, y - and z -direction.

Solutions of (3.24) are also expected to be translationally invariant. Using periodic boundary conditions and making use of the consideration in Sec. 2.3.1, a promising Ansatz is

$$u_{k,\alpha}(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_l = \vec{R}_i + \vec{r}_k} e^{i\vec{q}\vec{R}_l} \underbrace{\tilde{u}_{\vec{R}_l,\alpha}}_{=\tilde{u}_{l,\alpha}} = \frac{1}{\sqrt{N}} \sum_{\vec{R}_i} e^{i\vec{q}\vec{R}_i} \sum_{\vec{r}_k \in \Omega} \tilde{u}_{k,\alpha}(\vec{R}_i). \quad (3.28)$$

The sum over \vec{R}_l runs over all atoms in the solid, but to make use of translational invariance, we have to distinguish between different unit cells as opposed to different atoms within one unit cell. As for D , \vec{R}_i runs over all N unit cells of the lattice, while the second sum over smaller distances $\vec{r}_k = \vec{R}_l - \vec{R}_i$ covers all N_{basis} atoms within a unit cell Ω around \vec{R}_i . The displacement $\tilde{u}_{l,\alpha}$ of the atom at $\vec{R}_l = \vec{R}_i + \vec{r}_k$ is also denoted as $\tilde{u}_{k,\alpha}(\vec{R}_i)$. For a Bravais lattice, the simpler expression

$$u_{\alpha}(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_i} e^{i\vec{q}\vec{R}_i} \tilde{u}_{i,\alpha} = \frac{1}{\sqrt{N}} \sum_{\vec{R}_i} e^{i\vec{q}\vec{R}_i} \tilde{u}_{\alpha}(\vec{R}_i) \quad (3.29)$$

arises. Both functions are periodic in reciprocal lattice $u_{\vec{q}+\vec{G},\alpha} = u_{\vec{q},\alpha}$.

A translation operator $T_{\vec{a}_j}$ can be seen as moving the lattice so that the unit cell at \vec{R}_i becomes the one at $\vec{R}_i + \vec{a}_j$,⁴ applying such a transformation to the Ansatz gives

$$\begin{aligned} T_{\vec{a}_j} u_{\vec{q},\alpha} &= \frac{1}{\sqrt{N}} \sum_{\vec{R}_i} e^{i\vec{q}\vec{R}_i} T_{\vec{a}_j} \tilde{u}_{\vec{R}_i,\alpha} = \frac{1}{\sqrt{N}} \sum_{\vec{R}_i} e^{i\vec{q}\vec{R}_i} \tilde{u}_{\vec{R}_i+\vec{a}_j,\alpha} = e^{-i\vec{q}\vec{a}_j} \frac{1}{\sqrt{N}} \sum_{\vec{R}_i} e^{i\vec{q}(\vec{R}_i+\vec{a}_j)} \tilde{u}_{\vec{R}_i+\vec{a}_j,\alpha} = \\ &= e^{-i\vec{q}\vec{a}_j} u_{\vec{q},\alpha}, \end{aligned} \quad (3.30)$$

i.e., such a function is indeed an eigenfunction of the translation operator. For quantum-mechanical states, the approach of finding eigenstates of symmetry operators that commute with the hamiltonian is familiar; it works very similarly for classical solutions.

Since (3.28) is periodic in the reciprocal lattice, its inverse Fourier transform only uses momenta $\vec{q} \in 1^{\text{st}} BZ$ and is

$$\tilde{u}_{k,\alpha}(\vec{R}_i) = \tilde{u}_{l,\alpha} = \frac{1}{\sqrt{N}} \sum_{\vec{q} \in 1BZ} e^{-i\vec{q}\vec{R}_i} u_{k,\alpha}(\vec{q}) \quad (3.31)$$

with $\vec{R}_l = \vec{R}_i + \vec{r}_k$. For the conjugate momenta $\tilde{p}_{k,\alpha}$, an analogous transformation

$$p_{k,\alpha}(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_i} e^{i\vec{q}\vec{R}_i} \sum_{\vec{r}_k \in \Omega} \tilde{p}_{k,\alpha}(\vec{R}_i) \quad (3.32)$$

$$\tilde{p}_{k,\alpha}(\vec{R}_i) = \frac{1}{\sqrt{N}} \sum_{\vec{q} \in 1BZ} e^{-i\vec{q}\vec{R}_i} p_{k,\alpha}(\vec{q}). \quad (3.33)$$

is introduced. At this point, it may be necessary to make a comment on the two kinds of ‘momentum’ we have: $\tilde{p}_{k,\alpha}(\vec{R}_i)$ resp. $p_{k,\alpha}(\vec{q})$ that enters the kinetic energy of ion k (resp. its

⁴Alternatively, one can see it as moving the coordinate system by \vec{a}_j , so that $\vec{R}_i \rightarrow \vec{R}_i - \vec{a}_j$.

Fourier transform) on one hand and q on the other. Mathematically and formally, their role is clearly different: $\tilde{p}_{k,\alpha}(\vec{R}_i)$ is a canonical variable of the Hamiltonian, while q is here just a parameter turning up in some basis transformation. However, this basis transformation happens to be the Fourier transform, which is known to make the kinetic energy of a free particle diagonal, i.e., to be an expansion in eigenstates of \hat{p}_{free} , and we consequently expect q to have some properties of a momentum eigenvalue. This is indeed the case: Canonical variable p expresses nuclear motion near the equilibrium position within the unit cell (i.e. on length scales $\vec{r} \ll a$ without translational invariance), while q uses discrete translational invariance w.r.t. T_a to define long-range properties over many unit cells.

In \vec{q} -space, the Hamiltonian (3.24) then becomes, again using notation $\tilde{u}_{l,\alpha} = \tilde{u}_{k,\alpha}(\vec{R}_i)$,

$$\begin{aligned}
H &= \frac{1}{2N} \sum_{\vec{R}_l, \alpha} \sum_{\vec{q} \in 1BZ} e^{-i\vec{q}\vec{R}_l} p_{k,\alpha}(\vec{q}) \sum_{\vec{q}' \in 1BZ} e^{-i\vec{q}'\vec{R}_l} p_{k,\alpha}(\vec{q}') \\
&\quad + \frac{1}{2N} \sum_{\substack{l,\alpha \\ l',\beta}} \underbrace{D_{k,\alpha;k',\beta}(\vec{R}_i - \vec{R}_j)}_{=D_{l,\alpha;l',\beta}} \sum_{\vec{q} \in 1BZ} e^{-i\vec{q}\vec{R}_i} u_{k,\alpha}(\vec{q}) \sum_{\vec{q}' \in 1BZ} e^{-i\vec{q}'\vec{R}_j} u_{k',\beta}(\vec{q}') \\
&= \frac{1}{2} \sum_{\vec{q}\vec{q}'} \sum_{k,\alpha} p_{k,\alpha}(\vec{q}) p_{k,\alpha}(\vec{q}') \underbrace{\frac{1}{N} \sum_{\vec{R}_i} e^{-i(\vec{q}+\vec{q}')\vec{R}_i}}_{\delta_{\vec{q},-\vec{q}'}} \\
&\quad + \frac{1}{2} \sum_{\vec{q},\vec{q}'} \sum_{\substack{k,\alpha \\ k',\beta}} u_{k,\alpha}(\vec{q}) u_{k',\beta}(\vec{q}') \underbrace{\sum_{\Delta\vec{R}=\vec{R}_j-\vec{R}_i} D_{k,\alpha;k',\beta}(\Delta\vec{R}) e^{-i\vec{q}'\Delta\vec{R}}}_{=D_{k,\alpha;k',\beta}(\vec{q})} \underbrace{\frac{1}{N} \sum_{\vec{R}_i} e^{-i(\vec{q}+\vec{q}')\vec{R}_i}}_{\delta_{\vec{q},-\vec{q}'}} \\
&= \frac{1}{2} \sum_{\vec{q}} \left(\sum_{k,\alpha} p_{k,\alpha}(\vec{q}) p_{k,\alpha}(-\vec{q}) + \sum_{\substack{k,\alpha \\ k',\beta}} D_{k,\alpha;k',\beta}(\vec{q}) u_{k,\alpha}(\vec{q}) u_{k',\beta}(-\vec{q}) \right). \tag{3.34}
\end{aligned}$$

Even though the Hamiltonian is still not fully decoupled, finding the eigensystem of the new matrix $D_{k,\alpha;k',\beta}(\vec{q})$ should be much easier than for $D_{l,\alpha;l',\beta}(\vec{q})$, because the dimension has been reduced from $d \cdot N \cdot N_{\text{basis}} \times d \cdot N \cdot N_{\text{basis}}$ to $d \cdot N_{\text{basis}} \times d \cdot N_{\text{basis}}$. At this point, one might make use of additional symmetries to gain more insight into D .

Here, we just assume that we can somehow diagonalize $D_{k,\alpha;k',\beta}(\vec{q})$, and combine (k, α) into a single index α to simplify notation. Eigenvectors \vec{e}_μ are orthonormal

$$\vec{e}_\nu \cdot \vec{e}_\mu = \delta_{\nu,\mu} \quad \text{and} \tag{3.35}$$

$$\sum_{\nu} e_{\nu,\alpha} e_{\nu,\beta} = \delta_{\alpha,\beta} \tag{3.36}$$

and positive eigenvalues $D_\mu = \omega_\mu^2$. The eigenvalue equation then reads

$$\sum_{\beta} D_{\alpha;\beta} e_{\mu,\beta} = D_\mu e_{\mu,\alpha} = \omega_\mu^2 e_{\mu,\alpha}. \tag{3.37}$$

We then expand $u_{k,\alpha}(\vec{q}) = u_\alpha(\vec{q}) = \sum_{\nu} u_\nu(\vec{q}) \vec{e}_\nu(\vec{q})$ with $u_\nu(\vec{q}) = \vec{u}(\vec{q}) \cdot \vec{e}_\nu(\vec{q})$ and analogously for p . Inversion symmetry of the solid implies $D_{k,\alpha;k',\beta}(\vec{q}) = D_{k,\alpha;k',\beta}(-\vec{q})$ and thus also

$\bar{e}_\nu(-\vec{q}) = \bar{e}_\nu(\vec{q})$ and $\omega_\nu(-\vec{q}) = \omega_\nu(\vec{q})$. This gives

$$\begin{aligned}
H &= \frac{1}{2} \sum_{\vec{q}} \left(\sum_{\alpha} \sum_{\nu} p_{\nu,\vec{q}} \bar{e}_{\nu,\alpha}(\vec{q}) \sum_{\mu} p_{\mu,-\vec{q}} \underbrace{\bar{e}_{\mu,\alpha}(-\vec{q})}_{=\bar{e}_{\mu,\alpha}(\vec{q})} + \sum_{\alpha\beta} D_{\alpha;\beta}(\vec{q}) \sum_{\nu} u_{\nu,\vec{q}} \bar{e}_{\nu,\alpha}(\vec{q}) \sum_{\mu} u_{\mu,-\vec{q}} \bar{e}_{\mu,\beta}(-\vec{q}) \right) \\
&= \frac{1}{2} \sum_{\vec{q}} \sum_{\nu,\mu} \left(p_{\nu,\vec{q}} p_{\mu,-\vec{q}} \underbrace{\sum_{\alpha} \bar{e}_{\nu,\alpha}(\vec{q}) \bar{e}_{\mu,\alpha}(\vec{q})}_{=\delta_{\mu,\nu}} + u_{\nu,\vec{q}} u_{\mu,-\vec{q}} \sum_{\alpha} \bar{e}_{\nu,\alpha}(\vec{q}) \underbrace{\sum_{\beta} D_{\alpha;\beta}(\vec{q}) \bar{e}_{\mu,\beta}(\vec{q})}_{=\omega_{\mu}^2 \bar{e}_{\mu,\alpha}} \right) \\
&= \frac{1}{2} \sum_{\vec{q}} \sum_{\nu} \left(p_{\nu,\vec{q}} p_{\nu,-\vec{q}} + \omega_{\mu}^2(\vec{q}) u_{\nu,\vec{q}} u_{\nu,-\vec{q}} \right) \tag{3.38}
\end{aligned}$$

The Hamiltonian is now almost decoupled into independent harmonic oscillators. The decoupling of momenta \vec{q} and $-\vec{q}$ will arise automatically in our quantum-mechanical treatment, in a classical consideration, an Ansatz $u(\pm\vec{q}) = \frac{1}{2}(v_+(\vec{q}) \pm iv_-(\vec{q}))$ helps.

3.2.2 Creation and Annihilation operators for phonons

As the modes have almost been decoupled, creation and annihilation operators can now be introduced in the same manner as for the one-dimensional chain of coupled oscillators.

$$a_{\nu}(\vec{q}) = \frac{1}{2} \left(\sqrt{\frac{2\omega_{\nu}(\vec{q})}{\hbar}} u_{\nu}(\vec{q}) + i \sqrt{\frac{2}{\hbar\omega_{\nu}(\vec{q})}} p_{\nu}(\vec{q}) \right) \quad \text{and} \tag{3.39}$$

$$a_{\nu}^{\dagger}(-\vec{q}) = \frac{1}{2} \left(\sqrt{\frac{2\omega_{\nu}(\vec{q})}{\hbar}} u_{\nu}(\vec{q}) - i \sqrt{\frac{2}{\hbar\omega_{\nu}(\vec{q})}} p_{\nu}(\vec{q}) \right). \tag{3.40}$$

Note that $a_{\nu}^{\dagger}(\vec{q})$ and $a_{\nu}(\vec{q})$ are indeed adjoint operators $a_{\nu}(\vec{q}) = (a_{\nu}^{\dagger}(\vec{q}))^{\dagger}$, because $u_{\nu}^{\dagger}(\vec{q}) = u_{\nu}(-\vec{q})$ and $p_{\nu}^{\dagger}(\vec{q}) = p_{\nu}(-\vec{q})$, see (3.28) and (3.32).

In order to obtain commutation relations of the new operators, we start from position \vec{R}_k and momentum \vec{p}_k of atom k in (3.22), for which we postulate the usual quantization and commutation relations

$$[R_{k,\alpha}, R_{l,\beta}] = [p_{k,\alpha}, p_{l,\beta}] = 0, \quad [R_{k,\alpha}, p_{l,\beta}] = i\hbar\delta_{k,l}\delta_{\alpha,\beta}. \tag{3.41}$$

The rescaling to $\tilde{u}_{k,\alpha} = \sqrt{M_k/m}(\vec{R}_{k,\alpha} - \vec{R}_{k,\alpha}^0)$, with the constant number $\vec{R}_{k,\alpha}^0$, and $\tilde{p}_{k,\alpha} = \sqrt{\frac{m}{M_k}}p_{k,\alpha}$ for (3.24) keeps these relations intact. The Fourier transforms (3.28) and (3.32) lead to

$$\begin{aligned}
[u_{k,\alpha}(\vec{q}), u_{k',\beta}(\vec{q}')] &= \frac{1}{N} \sum_{\vec{R}_i, \vec{R}_j} e^{i\vec{q}\vec{R}_i} e^{i\vec{q}'\vec{R}_j} \underbrace{\sum_{\vec{r}_k, \vec{r}_{k'} \in \Omega} [\tilde{u}_{k,\alpha}(\vec{R}_i), \tilde{u}_{k',\beta}(\vec{R}_j)]}_{=0} = 0 = [p_{k,\alpha}(\vec{q}), p_{k',\beta}(\vec{q}')] \\
[u_{k,\alpha}(\vec{q}), p_{k',\beta}(\vec{q}')] &= \frac{1}{N} \sum_{\vec{R}_i, \vec{R}_j} e^{i\vec{q}\vec{R}_i} e^{i\vec{q}'\vec{R}_j} \underbrace{\sum_{\vec{r}_k, \vec{r}_{k'} \in \Omega} [\tilde{u}_{k,\alpha}(\vec{R}_i), \tilde{p}_{k',\beta}(\vec{R}_j)]}_{=i\hbar\delta_{k,k'}\delta_{\alpha,\beta}\delta_{\vec{R}_i, \vec{R}_j}} =
\end{aligned}$$

$$= i\hbar\delta_{\alpha,\beta} \underbrace{\frac{N_{\text{basis}}}{N} \sum_{\vec{R}_i} e^{i(\vec{q}+\vec{q}')\vec{R}_i}}_{=\delta_{\vec{q},-\vec{q}'}} \underbrace{\frac{1}{N_{\text{basis}}} \sum_{\vec{r}_k \in \Omega}}_{=1} = i\hbar\delta_{\alpha,\beta}\delta_{\vec{q},-\vec{q}'}, \quad (3.42)$$

where the minus sign in $-\vec{q}'$ the last relation is important. The final expansion in eigenvectors of D again leaves the situation unchanged:

$$\begin{aligned} [u_\nu(\vec{q}), p_\mu(\vec{q}')] &= \left[\sum_\alpha u_\alpha(\vec{q}) e_{\nu,\alpha}(\vec{q}), \sum_\beta p_\beta(\vec{q}') e_{\mu,\beta}(\vec{q}') \right] = \sum_{\alpha,\beta} e_{\nu,\alpha}(\vec{q}) e_{\mu,\beta}(\vec{q}') \underbrace{[u_\alpha(\vec{q}), p_\beta(\vec{q}')] }_{=i\hbar\delta_{\alpha,\beta}\delta_{\vec{q},-\vec{q}'}} = \\ &= i\hbar\delta_{\vec{q},-\vec{q}'} \underbrace{\sum_\alpha e_{\nu,\alpha}(\vec{q}) e_{\mu,\alpha}(-\vec{q})}_{=\bar{e}_\nu(\vec{q}) \cdot \bar{e}_\mu(\vec{q}') = \delta_{\nu,\mu}} = i\hbar\delta_{\vec{q},-\vec{q}'} \delta_{\nu,\mu} \end{aligned} \quad (3.43)$$

Using this result to obtain relation for the new operators gives

$$\begin{aligned} [a_\nu(\vec{q}), a_\mu(\vec{q}')] &= \frac{1}{4} \left(\frac{2\omega_\nu(\vec{q})}{\hbar} \underbrace{[u_\nu(\vec{q}), u_\mu(\vec{q}')] }_{=0} - \frac{2}{\hbar\omega_\nu(\vec{q})} \underbrace{[p_\nu(\vec{q}), p_\mu(\vec{q}')] }_{=0} \right. \\ &\quad \left. + i \frac{2}{\hbar} \left(\underbrace{[p_\nu(\vec{q}), u_\mu(\vec{q}')] }_{-i\hbar\delta_{\vec{q},-\vec{q}'}\delta_{\mu,\nu}} + \underbrace{[u_\nu(\vec{q}), p_\mu(\vec{q}')] }_{i\hbar\delta_{\vec{q},-\vec{q}'}\delta_{\mu,\nu}} \right) \right) = 0 = [a_\nu^\dagger(\vec{q}), a_\mu^\dagger(\vec{q}')] \end{aligned} \quad (3.44)$$

$$\begin{aligned} [a_\nu(\vec{q}), a_\mu^\dagger(\vec{q}')] &= \frac{1}{4} \left(\frac{2\omega_\nu(\vec{q})}{\hbar} \underbrace{[u_\nu(\vec{q}), u_\mu(-\vec{q}')] }_{=0} + \frac{2}{\hbar\omega_\nu(\vec{q})} \underbrace{[p_\nu(\vec{q}), p_\mu(-\vec{q}')] }_{=0} \right. \\ &\quad \left. + i \frac{2}{\hbar} \left(\underbrace{[p_\nu(\vec{q}), u_\mu(-\vec{q}')] }_{-i\hbar\delta_{\vec{q},\vec{q}'}\delta_{\mu,\nu}} - \underbrace{[u_\nu(\vec{q}), p_\mu(-\vec{q}')] }_{i\hbar\delta_{\vec{q},\vec{q}'}\delta_{\mu,\nu}} \right) \right) = \delta_{\vec{q},\vec{q}'} \delta_{\nu,\mu}, \end{aligned} \quad (3.45)$$

where we are back to the usual $\delta_{\vec{q},\vec{q}'}$.

The Hamiltonian is rewritten by inserting the inverted equations

$$u_\nu(\vec{q}) = \sqrt{\frac{\hbar}{2\omega_\nu(\vec{q})}} (a_\nu(\vec{q}) + a_\nu^\dagger(-\vec{q})) \quad \text{and} \quad p_\nu(\vec{q}) = -i\sqrt{\frac{\hbar m\omega_\nu(\vec{q})}{2}} (a_\nu(\vec{q}) - a_\nu^\dagger(-\vec{q})). \quad (3.46)$$

and becomes

$$\begin{aligned} H &= \frac{-1}{2} \sum_{\nu,\vec{q}} \frac{\hbar\omega_\nu(\vec{q})}{2} (a_\nu(\vec{q}) - a_\nu^\dagger(-\vec{q})) (a_\nu(-\vec{q}) - a_\nu^\dagger(\vec{q})) \\ &\quad + \sum_k \frac{\omega_k^2}{2} \frac{\hbar}{2\omega_\nu(\vec{q})} (a_\nu(\vec{q}) + a_\nu^\dagger(-\vec{q})) (a_\nu(-\vec{q}) + a_\nu^\dagger(\vec{q})) = \\ &= \sum_{\nu,\vec{q}} \frac{\hbar\omega_\nu(\vec{q})}{4} \underbrace{(a_\nu(\vec{q})a_\nu^\dagger(\vec{q}) + a_\nu^\dagger(\vec{q})a_\nu(\vec{q}) + a_\nu(\vec{q})a_\nu^\dagger(\vec{q}) + a_\nu^\dagger(\vec{q})a_\nu(\vec{q}))}_{=a_\nu^\dagger(\vec{q})a_\nu(\vec{q})+1} = \\ &= \sum_{\nu,\vec{q}} \hbar\omega_\nu(\vec{q}) \left(a_\nu^\dagger(\vec{q})a_\nu(\vec{q}) + \frac{1}{2} \right). \end{aligned} \quad (3.47)$$

It thus finally becomes the sum over many decoupled harmonic oscillators.

The eigenstates can be analyzed like those of a single harmonic oscillator, e.g., applying $a_\nu^\dagger(\vec{q})$ to an eigenstate $|\phi\rangle$ (with $H|\phi\rangle = E_\phi|\phi\rangle$) gives another eigenstate

$$\begin{aligned} H a_\nu^\dagger(\vec{q})|\phi\rangle &= a_\nu^\dagger(\vec{q})H|\phi\rangle + [H, a_\nu^\dagger(\vec{q})]|\phi\rangle = a_\nu^\dagger(\vec{q})E_\phi|\phi\rangle + \sum_{\mu, \vec{q}'} \hbar\omega_\mu(\vec{q}') [a_\mu^\dagger(\vec{q}')a_\mu(\vec{q}'), a_\nu^\dagger(\vec{q})]|\phi\rangle = \\ &= E_\phi a_\nu^\dagger(\vec{q})|\phi\rangle + \sum_{\mu, \vec{q}'} \hbar\omega_\mu(\vec{q}') a_\mu^\dagger(\vec{q}') \underbrace{[a_\mu(\vec{q}'), a_\nu^\dagger(\vec{q})]}_{=\delta_{\vec{q}, \vec{q}'}\delta_{\mu, \nu}} |\phi\rangle = (E_\phi + \hbar\omega_\nu(\vec{q})) a_\nu^\dagger(\vec{q})|\phi\rangle \end{aligned} \quad (3.48)$$

whose energy is increased by $\hbar\omega_\nu(\vec{q})$. Similarly, other observations carry over, like the existence of a lowest occupation number $n_\nu(\vec{q}) = 0$ for each mode. An eigenstate is here characterized by the number of quanta on each mode and is

$$\begin{aligned} |\phi\rangle &= |n_1(\vec{q}_1), n_2(\vec{q}_1), \dots, n_1(\vec{q}_k), \dots\rangle = \\ &= \frac{1}{\sqrt{n_1(\vec{q}_1)!}} (a_1^\dagger(\vec{q}_1))^{n_1(\vec{q}_1)} \otimes \frac{1}{\sqrt{n_2(\vec{q}_1)!}} (a_2^\dagger(\vec{q}_1))^{n_2(\vec{q}_1)} \otimes \dots \otimes \frac{1}{\sqrt{n_1(\vec{q}_k)!}} (a_1^\dagger(\vec{q}_k))^{n_1(\vec{q}_k)} \otimes \dots |0\rangle, \end{aligned} \quad (3.49)$$

with $d \cdot N$ possible modes. Its energy is

$$E_\phi = \sum_{\nu, \vec{q}} \hbar\omega_\nu(\vec{q}) n_\nu(\vec{q}) + \underbrace{\frac{\hbar}{2} \sum_{\nu, \vec{q}} \omega_\nu(\vec{q})}_{=E_0}, \quad (3.50)$$

where the second part gives the zero-point energy E_0 .

Each mode can be filled with energy quanta independently of the others, and the energy $\hbar\omega_\nu(\vec{q})$ of each quantum moreover only depends on the mode, not on its occupation. Creating such an excitation gives an eigenstate of the Hamiltonian, a very long-lived state. This leads to the concept of ‘quasi-particles’, ‘phonons’ with quantum numbers ν, \vec{q} that are created and annihilated. The energy of the phonon then $\hbar\omega_\nu(\vec{q})$, independently of other phonons, and as the total eigenenergy is given by the sum of the phonon energies, this is a case of *non-interacting* phonons.

From a physical point of view, the main conclusion to be drawn is that if the harmonic approximation is valid, then lattice dynamics can be described in terms of non-interacting phonons.

3.2.2.1 Linear phonon dispersion for some special modes

The phonon frequencies depend on the matrix $\chi_{k, \alpha; l, \beta}$ and are independent of a quantum mechanical or classical treatment of the oscillations. From classical equations of motion for coupled harmonic oscillators, we find $\ddot{u}_{i, k, \alpha} = -\omega^2 u_{i, k, \alpha}$ for a wave solution u . Here, indices i, k and α denote unit cell, atom within the unit cell and vector component. Let us now look at special solutions, where all atoms within a unit cell move by the same distance (scaled by mass). Together with the known spatial dependence on the unit cell, this gives $u_{i, k, \alpha} = u_\alpha e^{i\vec{q}\vec{R}_1}$.

The classical equation of motion is then

$$M_k \omega^2(\vec{q}) u_\alpha = - \sum_{j,l,\beta} \chi_{i,k,\alpha} u_\beta e^{i\vec{q}(\vec{R}_j - \vec{R}_i)} \quad (3.51)$$

which can be expanded in powers of \vec{q} :

$$\begin{aligned} & \left(\omega^2(\vec{q} = 0) + \frac{\partial \omega^2}{\partial \vec{q}} \vec{q} + \frac{1}{2} \sum_{\gamma, \text{gamma}\alpha'} \frac{\partial^2 \omega^2}{\partial q_\gamma \partial q_{\gamma'}} q_\gamma q_{\gamma'} \right) M_k u_\alpha = \\ & = - \sum_{j,l,\beta} \chi_{i,k,\alpha} \left(1 + i\vec{q}(\vec{R}_j - \vec{R}_i) - \frac{1}{2} (\vec{q}(\vec{R}_j - \vec{R}_i))^2 \right) u_\beta \end{aligned} \quad (3.52)$$

Let us now comparing left and right side for zeroth order in \vec{q} , where multiplication with u_α and sums over i, k , and α help:

$$\begin{aligned} \omega^2(\vec{q} = 0) M_k u_\alpha &= - \sum_{j,l,\beta} \chi_{i,k,\alpha} u_\beta \\ N M \omega^2(\vec{q} = 0) \sum_{\alpha} u_\alpha^2 &= - \sum_{\substack{i,k,\alpha \\ j,l,\beta}} \chi_{i,k,\alpha} u_\alpha u_\beta = 0 \end{aligned} \quad (3.53)$$

The right-hand side vanishes, because it is the interaction energy of a solid that has been rigidly shifted by \vec{u} , see (3.24), which must not give any contribution to the solid's internal energy. Consequently, the left-hand side also vanishes and $\omega(\vec{q} = 0) = 0$.

In first order, the right hand side vanishes due to invariance under lattice translations $\chi_{i,k,\alpha} = \chi_{k,\alpha}(\vec{R}_i - \vec{R}_j)$ and inversion symmetry $\chi_{k,\alpha}(\vec{R}_i - \vec{R}_j) = \chi_{l,\alpha}(\vec{R}_j - \vec{R}_i)$. Summing over index k gives

$$\begin{aligned} & -i \sum_k \sum_{j,l,\beta} \chi_{k,\alpha}(\vec{R}_i - \vec{R}_j) \vec{q} \cdot (\vec{R}_j - \vec{R}_i) u_\beta \\ & = \frac{-i}{2} \underbrace{\sum_{j,\beta} \sum_{k,l} \left(\chi_{k,\alpha}(\vec{R}_i - \vec{R}_j) + \chi_{l,\alpha}(\vec{R}_j - \vec{R}_i) \right)}_{\text{even}} \underbrace{\vec{q} \cdot (\vec{R}_j - \vec{R}_i)}_{\text{odd}} u_\beta \end{aligned} \quad (3.54)$$

i.e. a sum over a total function odd in $\vec{R}_j - \vec{R}_i$ that must vanish. (All odd powers vanish - luckily, as they are imaginary, while the left side is real.)

In second order, one finally has a finite contribution, so that the small- \vec{q} behavior is $\omega^2 \propto \sum_{\alpha,\beta} q_\alpha q_\beta$ or a frequency linear in q . As one can independently choose three components of a \vec{u} that is uniform within the unit cell, it is reasonable that there are 3 such linear modes. As these transport sound, they are called 'acoustic'.

In a solid with r atoms per unit cell, $3r - 3$ remaining modes have $\omega(\vec{q} = 0) > 0$. In these modes, atoms within the unit cell must move relative to each other, as this can be coupled to electro-magnetic radiation if they have different charge, these modes are called 'optical'.

3.2.3 Thermodynamics of Phonons

For a single harmonic oscillator, the partition function defining finite-temperature properties is given by the weighted sum over all available states

$$Z = \sum_{n=0}^{\infty} e^{-\frac{E_n}{k_B T}} = \sum_{n=0}^{\infty} e^{-\frac{\hbar\omega}{k_B T}(n+\frac{1}{2})} = e^{-\frac{\hbar\omega}{2k_B T}} \sum_{n=0}^{\infty} \left(e^{-\frac{\hbar\omega}{k_B T}} \right)^n = \frac{e^{-\frac{\hbar\omega}{2k_B T}}}{1 - e^{-\frac{\hbar\omega}{k_B T}}} = \frac{1}{2\sinh(\frac{\hbar\omega}{2k_B T})}, \quad (3.55)$$

where k_B is the Boltzmann constant and $\beta = \frac{1}{k_B T}$ is frequently used. Thermodynamic expectation values can then be obtained either as weighted sums or as derivatives of $\ln Z$, e.g., the average energy is

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \sum_{n=0}^{\infty} \hbar\omega \left(n + \frac{1}{2} \right) e^{-\beta\hbar\omega(n+\frac{1}{2})} = \hbar\omega \left(\frac{1}{2} + \langle n \rangle \right) \quad (3.56)$$

with the average phonon number $\langle n \rangle$.⁵ Comparing this expression to the derivative $\partial/\partial\beta$ of (3.55) gives

$$\langle E \rangle = \frac{-1}{Z} \frac{\partial}{\partial \beta} \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{Z} \left(\frac{1}{2} \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} + e^{-\frac{\beta\hbar\omega}{2}} \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \right) = \hbar\omega \left(\frac{1}{2} + \underbrace{\frac{1}{e^{\beta\hbar\omega} - 1}}_{=\langle n \rangle} \right) \quad (3.57)$$

The average occupation number is given by the so-called *Bose* function, again illustrating that the eigenstates of a harmonic oscillator can be understood in terms of non-interacting bosons. Occupation will be quite small for $T \ll \omega$, but can become large for low ω and large temperatures. There is here, however, no Bose-Einstein condensation, as the chemical potential $\mu = 0$.

The hallmark of non-interacting phonons is that

$$\langle n_\nu(\vec{q}) \rangle = \frac{1}{e^{\beta\hbar\omega_\nu(\vec{q})} - 1} \quad (3.58)$$

remains valid for the case of many available phonon modes, i.e., the occupation of each mode only depends on temperature, but not on the other modes. It is easy to verify that the joint partition function of many decoupled harmonic oscillators is the product of the individual partition functions and that the total energy of the system can be obtained as the sum over the energies in the modes:

$$\langle E \rangle = U = \sum_{\nu, \vec{q}} \hbar\omega_\nu(\vec{q}) \left(\langle n_\nu(\vec{q}) \rangle + \frac{1}{2} \right) = \sum_{\nu, \vec{q}} \hbar\omega_\nu(\vec{q}) \left(\frac{1}{e^{\beta\hbar\omega_\nu(\vec{q})} - 1} + \frac{1}{2} \right). \quad (3.59)$$

The energy of the phonon system is important, because a large part of a solid's specific heat depends on phonons. The contribution of electrons is small and only dominates at small temperatures. The easiest case to consider are very high temperatures $T \gg$, resp. $\beta \ll$. Since phonon frequencies are bounded, this assumption is applicable at high temperatures,

⁵For expectation values of other observables A , formally add a term λA to the Hamiltonian and calculate $-\frac{1}{\beta} \frac{\partial \ln Z}{\partial \lambda}$ at $\lambda = 0$.

which turn out to be still smaller than the melting point of the solid. The exponential in (3.59) can then be expanded in powers of β , yielding

$$\begin{aligned} E_{\beta \ll} &\approx \sum_{\nu, \vec{q}} \hbar \omega_{\nu}(\vec{q}) \left(\frac{1}{1 + \beta \hbar \omega_{\nu}(\vec{q}) + \dots - 1} + \frac{1}{2} \right) = \text{const.} + \sum_{\nu, \vec{q}} \hbar \omega_{\nu}(\vec{q}) \frac{1}{\beta \hbar \omega_{\nu}(\vec{q})} = \\ &= \text{const.} + k_B \cdot 3N_{\text{atoms}} T. \end{aligned} \quad (3.60)$$

The zero-point energy does not depend on T and consequently does not enter the specific heat $C = \partial E / \partial T$, which becomes in this limit $3k_B$ per atom. This is the law of Dulong-Petit and corresponds to the equipartition theorem, according to which all available degrees of freedom contribute equally to the internal energy, so that only their number is relevant.

For a slightly improved estimate, one can evaluate (3.59) for a constant phonon frequency $\omega_{\nu}(\vec{q}) = \omega$, an approach due to Einstein. This gives correctly that the heat capacity at lower temperatures is lower than $3k_B$, but is not a tremendously good approximation for intermediate to low T . The reason is that for low energies and temperatures, it becomes important that different phonon modes have different energies. Since the phonon spectrum has gapless modes with energies approaching 0 for $\vec{q} \rightarrow 0$, one can not find an analogous small- T limit with $k_B T \ll \omega_{\nu}(\vec{q})$ for all \vec{q} .

In order to get a more accurate description of the low-temperature specific heat, we focus on the acoustical phonon modes (as occupation numbers of optical modes can be assumed to be ≈ 0) and take into account their linear dispersion. In fact, we assume the dispersion to remain linear for *all* \vec{q} , not only small values, which can be justified if $\langle n_{\nu}(\vec{q}) \rangle$ drops off sufficiently before non-linear contributions become significant. As a further simplification, we assume the solid to be perfectly isotropic, i.e., $\omega_{\nu}(\vec{a}) = c|\vec{q}|$ for all $\nu = 1, 2, 3$. Again leaving out the temperature-independent zero-point energy E_0 , the sum in (3.59) is then approximated by an integral:

$$\begin{aligned} E - E_0 &= \sum_{\nu, \vec{q}} \hbar c |\vec{q}| \frac{1}{e^{\beta \hbar c |\vec{q}|} - 1} = \frac{3\hbar c V}{(2\pi)^3} \int_{1BZ} d^3 q |\vec{q}| \frac{1}{e^{\beta \hbar c |\vec{q}|} - 1} \approx \\ &\approx \frac{3\hbar c V}{2\pi^2} \int_0^? dq q^2 \cdot q \frac{1}{e^{\beta \hbar c q} - 1} = \frac{3\hbar c V}{2\pi^2} \int_0^? \frac{d\tilde{q}}{\beta \hbar c} \frac{\tilde{q}^3}{(\beta \hbar c)^3} \frac{1}{e^{\tilde{q}} - 1} = \frac{3\hbar c V}{2\pi^2 (\beta \hbar c)^4} \int_0^? d\tilde{q} \frac{\tilde{q}^3}{e^{\tilde{q}} - 1}. \end{aligned} \quad (3.61)$$

The first step - replacing the sum over the first Brillouin zone by an integral - is harmless, this is just the thermodynamic limit corresponding to very large lattices. In the second step and line, we want to exploit the assumption of isotropic space, it is then not clear how to reconcile this with the clearly lattice-dependent (and not spherically symmetric) Brillouin zone.

In the limit of low temperatures, we can evade the question, because the Bose function then drops to nearly 0 well inside the first Brillouin zone: how far the integral formally extends it then unimportant and we can take it to infinity. Moreover, the final integral only depends on temperature through its upper boundary, and if this boundary does not affect the result (and is set to ∞), all T -dependence is captured by the prefactor. Using the fact that the integral carried to ∞ is given by $\frac{\pi^4}{15}$, this leads to

$$\frac{E_{T \ll} - E_0}{N} \approx \frac{\pi^4}{15} \cdot \frac{V}{N} \frac{3k_B^4}{2\pi^2 \hbar^3 c^3} T^4 \quad \Rightarrow \quad c_{T \ll} \approx \frac{2\pi^2 k_B^4}{5\hbar^3 c^3 n} T^3 \quad (3.62)$$

For plain insulators, this is indeed the dominant contribution to the specific heat at low temperatures. Metals and magnetic systems can have a different behavior, e.g., $\propto T$ for metals. As the prefactor associated with these additional terms is very small, even their heat capacity is soon dominated by phonons and shows a $\propto T^3$ dependence.

We have now reasonable approximations for large and small T :

- At high temperature $T \gg$, heat capacity $C_{T \gg} = 3k_B N_{\text{atoms}}$ is constant. Moreover, it not depend on phonon frequencies at all, only the number of available modes enters.
- At low temperature $T \ll$, $C_{T \ll} \propto T^3$ is obtained from the linear phonon dispersion.

If one tries to combine the two approaches by simply using the low- T approximation for larger T , only would obviously overshoot the actual high- T result. The reason for the break down is that the integral boundary becomes relevant: If the Bose function becomes appreciable for higher and higher q in (3.61), ever more and more phonon mode appear to become available. In reality, however, their total number is bounded by $3N_{\text{atoms}}$.

The Debye model introduces an appropriate cut-off into the assumption of a linear dispersion, by enforcing the correct total number of states: A q -sphere with radius q_D and volume $\frac{4\pi}{3}q_D^3$ should have the same volume as the first Brillouin zone $\frac{(2\pi)^3}{\Omega} = (2\pi)^3 \frac{N}{V} = (2\pi)^3 n$, with N unit cells and density n . This sets the limit $q_D = \sqrt[3]{6\pi^2 n}$, i.e., the first Brillouin zone is replaced by a sphere. The upper boundary of the last integral in (3.61) is then $\beta \hbar c q_D$, making the integral T -dependent. (In the low- T limit discussed above, the integral boundary indeed goes to ∞ .) By introducing an energy and temperature scale given by the energy $\hbar\omega_D = \hbar c q_D$ corresponding to phonons at the momentum cut-off, we also gain a criterion for what is a ‘small’ temperature. Re-expressed in terms of the ‘Debye temperature’

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar c q_D}{k_B} = \frac{\hbar c \sqrt[3]{6\pi^2 n}}{k_B}, \quad (3.63)$$

the low- T specific heat becomes

$$c_{T \ll \Theta_D} \approx \frac{2\pi^2 k_B^4}{5\hbar^3 c^3 n} T^3 = \frac{k_B^3}{c^3 \hbar^3 q_D^3} \frac{12\pi^4 k_B}{5} T^3 = \frac{12\pi^4 k_B}{5} \left(\frac{T}{\Theta_D} \right)^3. \quad (3.64)$$

The real use of the cut-off momentum is, however, the high- T limit. By expanding the exponential in powers of β , one can check that the energy at large T is indeed determined by the available number of states and thus yields the constant specific heat. For arbitrary T , the integral can be evaluated numerically and yields a quite reasonable interpolation between the low- end high- T limits for Bravais lattices, where the neglected optical modes are not a problem.

Another way to transform the sum in (3.59) into a more convenient integral is available, because the total energy only depends on \vec{q} via the phonon *energy*. One can consequently formulate an equivalent energy integral

$$\frac{1}{N} \sum_{\vec{q} \in 1BZ} f(\omega_{\vec{q}}) \rightarrow \frac{V}{(2\pi)^3 N} \int_{1BZ} d^3 q f(\omega_{\vec{q}}) \rightarrow \int_{\omega} d\omega g(\omega) f(\omega), \quad (3.65)$$

where all the information on the phonon spectrum is contained in $g(\omega)$, the *density of states*. It can be obtained as

$$g(\omega) = \frac{1}{N} \sum_{\vec{q} \in 1BZ} \sum_{\nu} \delta(\omega - \omega_{\nu}(\vec{q})) = \frac{1}{(2\pi)^3 n} \int_{1BZ} d^3 q \sum_{\nu} \delta(\omega - \omega_{\nu}(\vec{q})) \quad (3.66)$$

and $g(\omega)d\omega$ is the number of states with energies in the interval $[\omega, \omega + d\omega]$.

The Debye model approximates it by

$$g(\omega) = \frac{3}{2\pi^2 c^3 n} \omega^2 \quad \text{for } \omega \leq \omega_D = c q_D = c \sqrt[3]{6\pi^2 n} \quad \text{and} \\ g(\omega) = 0 \quad \text{for } \omega > \omega_D. \quad (3.67)$$

Here, it does not add much convenience, because the steps in evaluating it are like the ones used in the integrals above. However, once obtained, the density of states can be used to obtain further quantities. Most importantly, more complex situations can make it easier to find (e.g. experimentally) just $g(\omega)$ rather than the full phonon dispersion.

3.2.4 Lattice Stability and Melting

Based on Khomskii's book.

The expectation value of u vanishes for all eigenstates of the harmonic oscillator, because the potential is symmetric and negative u are exactly balanced by positive ones. We can instead use $\langle u^2 \rangle$ as a measure for the average deviation from equilibrium, one might expect the lattice to become unstable if it becomes comparable to the lattice constant, i.e. for $\langle u^2 \rangle \approx a^2$.

Let us first look at just a single phonon mode, where u is expressed in creation and annihilation operators according to Eq. (3.46) and where we set all atom masses to M and undo the scaling by \sqrt{M} that led to \tilde{u} in Eq. (3.24):

$$\langle u^2 \rangle = \frac{1}{M} \frac{\hbar}{2\omega} \left(\underbrace{\langle a a \rangle}_{=(n-2|n)=0} + \underbrace{\langle a^\dagger a^\dagger \rangle}_{=0} + \underbrace{\langle a a^\dagger \rangle}_{=n+1} + \underbrace{\langle a^\dagger a \rangle}_{=n} \right) = \frac{\hbar}{\omega M} \left(n + \frac{1}{2} \right). \quad (3.68)$$

Expectation values of operators that change the phonon number vanish. Clearly, $\langle u^2 \rangle$ most easily becomes large for small ω and small masses M , i.e., when oscillations cost only little energy and small kinetic energy allows big swings. We also see that even without phonons and at $T = 0$, $\langle u^2 \rangle > 0$, these are the zero-point fluctuations.

ω^2 denotes an eigenvalue of the matrix D , which combines the mass M of the atom and the curvature of its potential, see Eq. (3.24). For a rough estimate, and $\chi \approx \frac{\mathcal{V}}{a^2}$, where \mathcal{V} is the atom-atom interaction at distance a . Then, setting $\hbar = 1$,

$$\omega^2 \approx \frac{\mathcal{V}}{M a^2} \quad \text{and} \quad \frac{\langle u^2 \rangle}{a^2} \approx \frac{1}{a} \sqrt{\frac{1}{M \mathcal{V}}} \left(n + \frac{1}{2} \right). \quad (3.69)$$

Light masses and weak atomic interactions thus make the crystal most susceptible to being destabilized by phonons, plausibly enough. It turns out that for $T = 0$, where $n = 0$ and only zero-point fluctuations contribute, only He is light enough and has weak enough interactions not to form a solid.

However, we do not have just a single phonon mode and $\omega(\vec{q})$ becomes small in acoustic modes of all solids as $\vec{q} \rightarrow 0$. In order to estimate how strong the impact of these small- \vec{q} modes is compared to all the other high-energy modes, a more careful thermodynamical treatment is necessary. Averaging over all modes gives for a d -dimensional crystal

$$\langle u^2 \rangle = \frac{\hbar}{M} \frac{V}{(2\pi)^d} \int_{1BZ} d^d q \langle u_\nu^2(\vec{q}) \rangle = \frac{\hbar}{M} \frac{V}{(2\pi)^d} \int_{1BZ} d^d q \frac{1}{\omega_\nu(\vec{q})} \left(\langle n_\nu(\vec{q}) \rangle + \frac{1}{2} \right)$$

$$= \frac{\hbar}{M} \frac{V}{(2\pi)^d} \int_{1BZ} d^d q \frac{1}{\omega_\nu(\vec{q})} \left(\frac{1}{e^{\beta\hbar\omega_\nu(\vec{q})} - 1} + \frac{1}{2} \right). \quad (3.70)$$

Both $\frac{1}{\omega_\nu(\vec{q})}$ and $\langle n_\nu(\vec{q}) \rangle$ become largest for the acoustic modes at small \vec{q} , so we focus on these as in the Debye model, setting $\omega_\nu(\vec{q}) = c|q|$.

In this isotropic approximation, the integral becomes

$$\langle u^2 \rangle = \frac{\hbar}{M} \frac{V}{(2\pi)^d} \int_0^{q_D} \underbrace{dq 2^{d-1} \pi q^{d-1}}_{d^d q} \frac{1}{cq} \left(\frac{1}{e^{\beta\hbar cq} - 1} + \frac{1}{2} \right) \propto \int_0^{q_D} dq q^{d-2} \left(\frac{1}{e^{\beta\hbar cq} - 1} + \frac{1}{2} \right), \quad (3.71)$$

whose convergence decisively depends on the dimension.

- For a one-dimensional crystal, i.e. a chain, even the more harmless zero-point fluctuations (coming from the $\frac{1}{2}$) diverges, because

$$\int_0^{q_D} \frac{dq}{q} \quad (3.72)$$

diverges logarithmically. A strictly one-dimensional solid is thus expected to melt even at $T = 0$.

- For two (or three) dimensions, the zero-point fluctuations are not as disastrous, because $\int_0^{q_D} dq$ (as well as $\int_0^{q_D} dq q$) are finite.
- Let us now look at finite T and $\langle n_\nu(\vec{q}) \rangle$, where we focus on phonons with very small energies $cq \ll k_B T$. The exponent in the Bose function is then small and the series expressing the exponential can be truncated, leading to

$$\int_0^{q_D} dq q^{d-2} \frac{1}{e^{\beta\hbar cq} - 1} \approx \int_0^{q_D} dq q^{d-2} \frac{1}{1 + \beta\hbar cq - 1} = \frac{1}{\beta\hbar c} \int_0^{q_D} dq q^{d-3}. \quad (3.73)$$

This integral diverges for $d = 2$ (and even more so for $d = 1$, so that two-dimensional crystals are not expected to be stable at (any) $T > 0$

As we will discuss later in Sec. 6.1.2.2, these statements can be extended beyond phonons and lead to the “Mermin-Wagner theorem” that forbids long-range order in many low-dimensional models.

3.2.5 Anharmonic Effects

Motivated by Khomskii’s book.

Even classically, the harmonic potential gives the same frequency ω regardless of the oscillation’s amplitude while this is not true in anharmonic potentials, even if they are symmetric. In an actual solid or molecule, the ion-ion potential, e.g. (3.7), is necessarily anharmonic and asymmetric, because the repulsion on very short distances is very strong, while the binding potential towards longer distances will be shallower. In the classical problem, ω then depends on the amplitude. In the quantum-mechanical treatment, this means that the energy for adding a phonon depends on how many phonons are already there – the problem becomes one of *interacting* phonons.

One aspect of an asymmetric potential is that the average position $\langle u \rangle$ increases slightly when there are strong phonon amplitudes, because the positive u are larger than (the absolute values of) the negative ones. Adding a small asymmetric u^3 term to the potential can be treated in perturbation theory and we can find from Eq. (3.46) that it can be expressed using operators like $a^\dagger a^\dagger a$ or $a a^\dagger a$. As such terms change the number of phonons, the first-order eigenvector corrections in perturbation theory will mix in states with more or fewer phonons, with weights that again depend on the number of phonons present. The anharmonic potential creates and annihilates phonons, whose lifetime is then finite - they are “quasi” particles rather than particles.

Both the quantum-mechanical eigenstates and – possibly even more so – the thermodynamic treatment are based on the assumption of *non-interacting* phonons. As we will see in later chapters, obtaining eigenstates and partition functions for interacting particles is orders of magnitude harder and usually impossible even for simplified models. On the other hand, some properties due to anharmonicity resp. phonon-phonon interaction (e.g. thermal expansion) are relevant, and any trick that allows us to discuss them in terms of *effectively non-interacting* phonons would be highly welcome.

Such a way out is the *quasi-harmonic approximation*, where the phonon frequency can be chosen to depend on volume and/or temperature, but where phonons are otherwise still assumed not to interact. The volume-dependence is often expressed by the phenomenological Grüneisen relation

$$\frac{d \ln \omega}{d \ln V} = -\gamma \quad (3.74)$$

with the Grüneisen constant γ . (For a perfectly harmonic potential, γ of course vanishes.) The volume-dependent partition function (and hence the free energy at a given volume) is then obtained by inserting the volume-dependent ω into the partition function Eq. (3.55). This is an approximation, because that formula is derived for independent phonons, but a non-constant ω has been found to make up for this to some extent. Instead of a volume-dependent frequency, one can also have ω depending on temperature T (via the equilibrium volume $V(T)$) or on pressure.

A related concept is that of *phonon softening*: One might find that $\omega_\nu(\vec{q})$ approaches 0 for some $\vec{q} \neq 0$ (or ν from the optical branches) and as volume/temperature/pressure/*dots* approaches some “critical” value. In fact, one may even find $\omega_\nu^2(\vec{q}) \rightarrow 0$ and in a calculation might find that it becomes negative beyond this point. This must of course not be: The existence of a stable crystal requires eigenvalues ω^2 of the dynamical matrix to be non-negative. The whole treatment used here would then not be applicable from the outset. Physically, the system will go into a new state (e.g. melt or form a different lattice structure) when reaching the critical point. Very similar concept apply to magnons and magnetic ordering transitions.

4 Electrons in a Periodic Potential

Inspired by Prof. Muramatsu's and Prof. Valentí's notes.

In this chapter, we focus on the electronic subsystem, i.e., on Eq. (3.6). The ion-ion potential (3.2) is here no longer considered, because its contribution to the electronic problem is only a constant energy shift, leaving

$$H_{\text{el.}} = \sum_i \frac{p_i^2}{2m} + \sum_{i,k} \frac{Z_k e}{|\hat{r}_i - \hat{R}_k|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\hat{r}_i - \hat{r}_j|} = \sum_i \frac{p_i^2}{2m} + \sum_i V(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\hat{r}_i - \hat{r}_j|}. \quad (4.1)$$

The potential $V(\vec{r}_i)$ comes from the nuclear charges, which are here seen as fixed, is the same for all electrons and is moreover lattice periodic $V(\vec{r} + \vec{R}_i) = V(\vec{r})$ for all Bravais-lattice sites \vec{R}_i .

4.1 Bloch's theorem

As discussed in Sec. 2.1, symmetries of the Hamiltonian H , i.e., operators that commute with it, are helpful, because they share an eigensystem with H and their eigenstates may be easier to find. As discussed in Sec. 2.3.1, the most important symmetry on the lattice is discrete translational invariance w.r.t. translation by a lattice vector \vec{R}_i . We had also discussed in Sec. 2.3.1 that the eigenvalues of the translation operators $T_{\vec{R}}$ are given by $e^{i\vec{k}\vec{R}}$ with \vec{k} from the first Brillouin zone.

These symmetry considerations apply to interacting as well as non-interacting electrons. When it comes to obtaining actual eigenstates, however, the electron-electron interaction, i.e., the last term in (4.1), makes the problem much harder. As we have seen with phonons in the Sec. 3.2.3, many-particle states can be obtained from single-particle states easily, if there are no interactions. Moreover, electron-electron interaction in solids often turns out to be relatively weak, so that we will here focus on non-interacting electrons and only consider the first two terms of (4.1). The Hamiltonian is then

$$H_{\text{non.-int.}} = \sum_i \left(\frac{p_i^2}{2m} + V(\vec{r}_i) \right) \quad (4.2)$$

and as the first step, we will discuss possible eigenstates of one single electron.

The eigenstate $\psi_{\vec{k}}(\vec{r})$ of $T_{\vec{R}}$ corresponding to \vec{k} should fulfill

$$T_{\vec{R}}\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{R}}\psi_{\vec{k}}(\vec{r}). \quad (4.3)$$

From the consideration of Sec. 2.3.1, we know that \vec{k} is from the first Brillouin zone. Let us now look at the impact of translations on the function $u_{\vec{k}} = e^{-i\vec{k}\vec{r}}\psi_{\vec{k}}$:

$$u_{\vec{k}}(\vec{r} + \vec{R}) = T_{\vec{R}}u_{\vec{k}}(\vec{r}) = e^{-i\vec{k}(\vec{r} + \vec{R})}\psi_{\vec{k}}(\vec{r} + \vec{R}) = e^{-i\vec{k}\vec{r}} e^{-i\vec{k}\vec{R}} e^{i\vec{k}\vec{R}}\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}), \quad (4.4)$$

i.e. $u_{\vec{k}}$ is lattice periodic. Inversely, the one-electron eigenstate $\psi_{\vec{k}}$ can be expressed as

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} u_{\vec{k}}(\vec{r}) \quad \text{with} \quad u_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r}). \quad (4.5)$$

This is Bloch's theorem.¹

The Schrödinger equation for a single electron moving in a periodic potential can then be rewritten to give an equation for $u_{\vec{k}}(\vec{r})$:

$$H_{\text{el.}} \psi_{\vec{k}}(\vec{r}) = \left(\frac{p^2}{2m} + V(\vec{r}) \right) \psi_{\vec{k}}(\vec{r}) = \left(-\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right) e^{i\vec{k}\vec{r}} u_{\vec{k}}(\vec{r}) = \quad (4.6)$$

$$= e^{i\vec{k}\vec{r}} \left(-\frac{\hbar^2}{2m} (\nabla^2 - 2i\vec{k}\nabla - |k|^2) + V(\vec{r}) \right) u_{\vec{k}}(\vec{r}) =$$

$$= e^{i\vec{k}\vec{r}} \left(\frac{\hbar^2}{2m} (-i\nabla + k)^2 + V(\vec{r}) \right) u_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}} \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} \epsilon_{\vec{k}} u_{\vec{k}}(\vec{r})$$

$$\Rightarrow h_{\vec{k}} u_{\vec{k}}(\vec{r}) = \left(\frac{\hbar^2 (-i\nabla + k)^2}{2m} + V(\vec{r}) \right) u_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}} u_{\vec{k}}(\vec{r}) \quad (4.7)$$

For any k , this is an effective Schrödinger equation for function $u_{\vec{k}}(\vec{r})$ square integrable over the primitive unit cell of the lattice.

As the effective $h_{\vec{k}}$ is Hermitian, its eigensystem is a basis and there must in fact be infinitely many eigenstates. This gives a new index n , so that the eigenvalue equation for $u_{n\vec{k}}(\vec{r})$ reads

$$\left(\frac{\hbar^2}{2m} (-i\nabla + k)^2 + V(\vec{r}) \right) u_{n,\vec{k}}(\vec{r}) = h_{\vec{k}} u_{n,\vec{k}}(\vec{r}) = \epsilon_{n,\vec{k}} u_{n,\vec{k}}(\vec{r}). \quad (4.8)$$

The corresponding eigenvalues $\epsilon_{n,\vec{k}}$ with \vec{k} from the first Brillouin zone define the 'band structure' of the solid and we are going to discuss band structures in depth later.

W.r.t to the band index n , the $u_{n,\vec{k}}$ are orthonormal:

$$\frac{1}{\Omega} \int_{\Omega} d^3r u_{n,\vec{k}}^*(\vec{r}) u_{m,\vec{k}}(\vec{r}) = \delta_{n,m} \quad (4.9)$$

(No statement can yet be made concerning different k , k' .) The Bloch wave functions ψ then also acquire index n , as they are not lattice periodic, one should here integrate over the whole lattice with volume $V = N\Omega$. However, it makes sense to decompose positions $\vec{r} = \vec{R} + \vec{r}'$ so that \vec{R} is the closest primitive lattice vector and \vec{r}' runs over the unit cell:

$$\frac{1}{V} \int_V d^3r u_{n,\vec{k}}^*(\vec{r}) e^{-i\vec{k}\vec{r}} e^{i\vec{k}'\vec{r}} u_{m,\vec{k}'}(\vec{r}) = \frac{1}{V} \sum_{\vec{R}} \int_{\Omega} d^3r' \underbrace{u_{n,\vec{k}}^*(\vec{R} + \vec{r}')}_{=u_{n,\vec{k}}^*(\vec{r}')} u_{m,\vec{k}'}(\vec{R} + \vec{r}') e^{-i\vec{k}(\vec{r}'+\vec{R})} e^{i\vec{k}'(\vec{r}'+\vec{R})} =$$

¹In essence, something like Bloch's theorem remains valid for interacting electrons as well, because the symmetries are still applicable. But it is not that helpful for the many-body wave function: even if one can keep using total crystal momentum as a conserved quantity, the exponentially large number of ways to distribute it over the involved electrons keeps the problem almost as hard as before.

$$= \frac{1}{\Omega} \int_{\Omega} d^3r' u_{n,\vec{k}}^*(\vec{r}') u_{m,\vec{k}'}(\vec{r}') e^{-i\vec{r}'(\vec{k}-\vec{k}')} \underbrace{\frac{1}{N} \sum_{\vec{R}} e^{i(\vec{k}+\vec{k}')\vec{R}}}_{=\delta_{\vec{k},\vec{k}'}} = \delta_{\vec{k},\vec{k}'} \delta_{n,m} \quad (4.10)$$

As long as the $u_{n,\vec{k}}$ are a basis for functions defined on Ω , the Bloch states $\psi_{n,\vec{k}}$ are one for function on V .

4.2 Nearly Free Electrons

In general the Schrödinger equation (4.8) for $u_{n,\vec{k}}$ cannot be solved exactly. We are now going to discuss an approximation valid for weak potentials $V(\vec{r})$, which is appropriate for solids that easily donate shallowly bound electrons, e.g., alkali metals. Since the situation is dominated by the kinetic energy and since the kinetic energy is most easily treated in momentum space, we Fourier transform the Schrödinger equation, however, using the Bloch wave function $\psi_{n,\vec{k}}$.

4.2.1 Schrödinger equation for Bloch waves in Momentum space

As a preparation for treating nearly free electrons, we transform the Schrödinger equation for Bloch states into momentum space. Equation (4.8) contains parameter \vec{k} , which we know from its relation to the translation operator to have some connection to ‘momentum’, but is otherwise written in position space. Here, we are fully going to momentum space.

The potential $V(\vec{r})$ is lattice periodic and its Fourier decomposition thus only involves reciprocal-lattice points \vec{G} :

$$V(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\vec{r}} \quad \text{with} \quad V_{\vec{G}} = \frac{1}{\sqrt{\Omega}} \int_{\Omega} d^3r V(\vec{r}) e^{-i\vec{G}\vec{r}} \quad (4.11)$$

The Bloch wave function ψ is not lattice periodic, but only obeys periodic boundary conditions. Its Fourier transform then contains all \vec{q} that are compatible with the larger lattice. These can be decomposed into a ‘large’ component \vec{G} taken from the reciprocal lattice and a ‘small’ one \vec{k} running over the first Brillouin zone $\vec{q} = \vec{G} + \vec{k}$, i.e.,

$$\psi(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\text{all } \vec{q}} c_{\vec{q}} e^{i\vec{q}\vec{r}} = \frac{1}{\sqrt{V}} \sum_{\vec{G}} e^{i\vec{G}\vec{r}} \int_{1BZ} d^3k c_{\vec{G}+\vec{k}} e^{i\vec{k}\vec{r}}. \quad (4.12)$$

The lattice has here again be taken to be so big that the sum over the allowed momenta of the first BZ can be approximated by an integral. One then finds from (4.7)

$$\frac{1}{\sqrt{V}} \left(-\frac{\hbar^2 \nabla^2}{2m} + \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\vec{r}} \right) \sum_{\text{all } \vec{q}} e^{i\vec{q}\vec{r}} c_{\vec{q}} = \epsilon \frac{1}{\sqrt{V}} \sum_{\text{all } \vec{q}} e^{i\vec{q}\vec{r}} c_{\vec{q}}. \quad (4.13)$$

In the kinetic energy, ∇^2 only acts on the exponential and thus gives $-\vec{q}^2$; in the potential energy, it makes sense to rename the variable \vec{q} :

$$\sum_{\text{all } \vec{q}} \frac{\hbar^2 \vec{q}^2}{2m} e^{i\vec{q}\vec{r}} c_{\vec{q}} + \sum_{\vec{G}} \frac{V_{\vec{G}}}{\sqrt{\Omega}} \sum_{\text{all } \vec{q}} e^{i(\vec{G}+\vec{q})\vec{r}} c_{\vec{q}} = \sum_{\text{all } \vec{q}} \frac{\hbar^2 \vec{q}^2}{2m} e^{i\vec{q}\vec{r}} c_{\vec{q}} + \sum_{\vec{G}} \frac{V_{\vec{G}}}{\sqrt{\Omega}} \sum_{\text{all } \vec{q}'=\vec{G}+\vec{q}} e^{i\vec{q}'\vec{r}} c_{\vec{q}'-\vec{G}} =$$

$$= \sum_{\text{all } \vec{q}} \left(\frac{\hbar^2 \vec{q}^2}{2m} c_{\vec{q}} + \sum_{\vec{G}} \frac{V_{\vec{G}}}{\sqrt{\Omega}} c_{\vec{q}-\vec{G}} \right) e^{i\vec{q}\vec{r}} = \epsilon \sum_{\text{all } \vec{q}} e^{i\vec{q}\vec{r}} c_{\vec{q}}. \quad (4.14)$$

Functions $e^{i\vec{q}\vec{r}}$ are orthonormal, the sum can consequently only vanish if each term vanishes separately, giving

$$\left(\epsilon - \frac{\hbar^2 \vec{q}^2}{2m} \right) c_{\vec{q}} = \sum_{\vec{G}} \frac{V_{\vec{G}}}{\sqrt{\Omega}} c_{\vec{q}-\vec{G}}. \quad (4.15)$$

The coefficient at momentum \vec{q} is thus mixed with coefficients for other $\vec{q} + \vec{G}$, but only with momenta differing by a reciprocal lattice vector. This becomes clearer if one uses again a decomposition of \vec{q} into a reciprocal-lattice vector \vec{G}_0 and a vector \vec{k} from the first Brillouin zone

$$\left(\epsilon - \frac{\hbar^2 (\vec{k} + \vec{G}_0)^2}{2m} \right) c_{\vec{k}+\vec{G}_0} = \sum_{\vec{G}} \frac{V_{\vec{G}}}{\sqrt{\Omega}} c_{\vec{k}+\vec{G}_0-\vec{G}} = \sum_{\vec{G}} \frac{V_{\vec{G}+\vec{G}_0}}{\sqrt{\Omega}} c_{\vec{k}-\vec{G}} = \sum_{\vec{G}} \frac{V_{\vec{G}_0-\vec{G}}}{\sqrt{\Omega}} c_{\vec{k}+\vec{G}}. \quad (4.16)$$

The equation is diagonal in \vec{k} from the first Brillouin zone, just like (4.8). In fact, any solution will be a linear combination of $c_{\vec{k}+\vec{G}}$ with fixed \vec{k} , so that the solution has the form of a Bloch wave with lattice-periodic $u_{\vec{k}}$:

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{q}=\vec{G}+\vec{k}} c_{\vec{q}} e^{i\vec{q}\vec{r}} = \frac{1}{\sqrt{V}} \sum_{\vec{G}} c_{\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G})\vec{r}} = \frac{e^{i\vec{k}\vec{r}}}{\sqrt{V}} \sum_{\vec{G}} c_{\vec{k}+\vec{G}} e^{i\vec{G}\vec{r}} = e^{i\vec{k}\vec{r}} u_{\vec{k}}(\vec{r}) \quad (4.17)$$

As a corollary, we can note that the Fourier coefficients of $u_{\vec{k}}(\vec{r})$ are given by $c_{\vec{k}+\vec{G}}$ and thus depend only on $\vec{k}+\vec{G}$, but not on \vec{k} and \vec{G} separately. Equation (4.14) also illustrates that the conserved quantity related to lattice translational invariance is not momentum (which is not fully conserved, because space is not fully homogeneous), but only the reduced momentum \vec{k} , i.e., the part that is left after subtracting the closest reciprocal-lattice vector.

4.2.2 Free electrons and the Periodic Lattice

As a first approximation, we now consider a vanishing potential $V(\vec{r}) = 0$. Since the electrons do then not feel the lattice, the solutions must be the plane waves

$$\psi_{\vec{q}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{q}\vec{r}} \quad \text{with eigenenergies} \quad \epsilon_{\vec{q}} = \frac{\hbar^2 \vec{q}^2}{2m} \quad (4.18)$$

of a free electron. The point of this subsection is to translate this solution into the language of an existing lattice, so that we can then switch the potential on and investigate its effect onto plane-wave-based solutions.

The eigenenergies of course form a parabola centered around $\vec{q} = 0$, where the values of \vec{q} are the same as the ‘all’ \vec{q} of the solid if the free electron is restricted to a box with periodic boundary conditions. In the ‘solid’ language of Eq. (4.16), we would instead restrict \vec{k} to the first BZ and make up for this by allowing many values of \vec{G}_0 : There are many parabolas centered at all \vec{G}_0 , but only of each, the section running through the first BZ is allowed, see Fig. 4.1. This can be seen like ‘folding back’ the parabola at the zone boundaries. Both must be equivalent, allowing only one branch but all \vec{q} is called ‘extended zone’ scheme while folding back is called ‘reduced zone’ scheme.

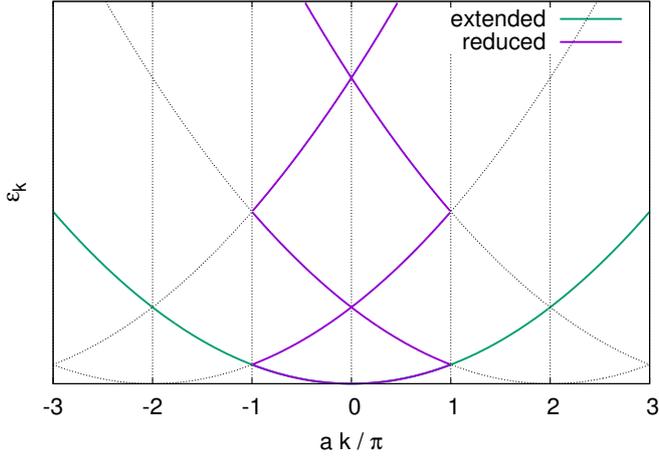


Figure 4.1: Extended and reduced zone schemes for free electrons. All states are found by either (i) taking one parabola centered at $k = 0$ and taking it to $k = \pm\infty$ or (ii) restricting k to $|k| \leq \pi/a$, but taking into account all parabolas centered at $2\pi n$ for integer n .

4.2.3 Weak potential: Perturbation Theory

In order to re-introduce the potential, we use perturbation theory. From the reduced-zone scheme, one sees that for most \vec{k} , the eigenenergies are well separated, as long as the potential's matrix elements are much smaller than this spacing, one can use non-degenerate perturbation theory. As a basis to express ψ_k , we use the eigenbasis of the free electron in the reduced-zone scheme, i.e., each state is uniquely determined by the combination \vec{k} (from the first BZ) and \vec{G}_0 (reciprocal-lattice vector):

$$\psi_{\vec{k}, \vec{G}_0}^0(\vec{r}) = \frac{1}{\sqrt{V}} e^{i(\vec{k} + \vec{G}_0)\vec{r}} \quad \text{with} \quad \epsilon_{\vec{k}, \vec{G}_0}^0 = \frac{\hbar^2(\vec{k} + \vec{G}_0)^2}{2m}. \quad (4.19)$$

The first-order correction to the energy is then given by expectation values of the operator \hat{V} , which has matrix elements $\frac{V_{\vec{G} + \vec{G}_0}}{\sqrt{\Omega}} = \langle \vec{k}, \vec{G}_0 | \hat{V} | \vec{k}, -\vec{G} \rangle = \{V\}_{\vec{G}_0, -\vec{G}}$, see (4.16):

$$\epsilon_{\vec{k}, \vec{G}_0}^1 = \langle \vec{k}, \vec{G}_0 | \hat{V} | \vec{k}, \vec{G}_0 \rangle = \frac{1}{\sqrt{\Omega}} \langle \vec{k}, \vec{G}_0 | \sum_{\vec{G}} | \vec{k}, \vec{G}_0 \rangle V_{\vec{G} + \vec{G}_0} \underbrace{\langle \vec{k}, -\vec{G} | \vec{k}, \vec{G}_0 \rangle}_{=\delta_{\vec{G}, -\vec{G}_0}} = \frac{1}{\sqrt{\Omega}} V_0. \quad (4.20)$$

According to (4.11), this is just the average potential, which can be chosen to be 0 and does not affect energy differences.

First-order eigenstate correction in perturbation theory mixes in small contributions from other \vec{G} :

$$|\vec{k}, \vec{G}\rangle^1 = \sum_{\vec{G} \neq \vec{G}_0} |\vec{k}, \vec{G}\rangle \frac{\langle \vec{k}, \vec{G} | \hat{V} | \vec{k}, \vec{G}_0 \rangle}{\epsilon_{\vec{k}, \vec{G}_0} - \epsilon_{\vec{k}, \vec{G}}} = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G} \neq \vec{G}_0} \frac{V_{\vec{G} + \vec{G}_0}}{\epsilon_{\vec{k}, \vec{G}_0} - \epsilon_{\vec{k}, -\vec{G}}} |\vec{k}, -\vec{G}\rangle \quad (4.21)$$

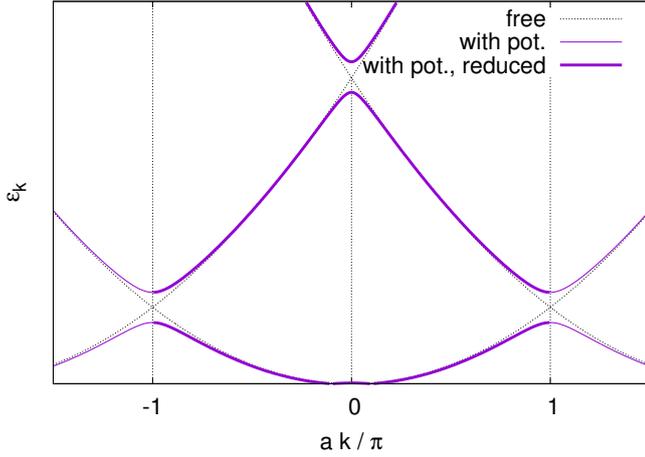


Figure 4.2: Lifting of the band degeneracy at the zone boundary due to the potential V .

and second-order energy correction follows as

$$\epsilon_{\vec{k}, \vec{G}_0}^2 = \sum_{\vec{G} \neq \vec{G}_0} \frac{|\langle \vec{k}, \vec{G} | \hat{V} | \vec{k}, \vec{G}_0 \rangle|^2}{\epsilon_{\vec{k}, \vec{G}_0} - \epsilon_{\vec{k}, \vec{G}}} = \frac{-1}{\Omega} \sum_{\vec{G} \neq \vec{G}_0} \frac{V_{\vec{G} + \vec{G}_0}^2}{\epsilon_{\vec{k}, -\vec{G}} - \epsilon_{\vec{k}, \vec{G}_0}} = \frac{-1}{\Omega} \sum_{\vec{G} \neq \vec{G}_0} \frac{V_{\vec{G}_0 - \vec{G}}^2}{\epsilon_{\vec{k}, \vec{G}} - \epsilon_{\vec{k}, \vec{G}_0}} \quad (4.22)$$

These corrections should be small as long as V is weak and perturbation theory is justified, especially since first-order terms vanish.

The potentially more interesting case arises when two energies are degenerate $\epsilon_{\vec{k}, \vec{G}_1} = \epsilon_{\vec{k}, \vec{G}_2} = \epsilon$. From the reduced-zone scheme, it follows that this is the case at both the zone boundaries and the zone center. It does then not make sense to do perturbation theory for each eigenstate separately, but one instead considers the two-dimensional subspace $\{|\vec{k}, \vec{G}_1\rangle, |\vec{k}, \vec{G}_2\rangle\}$. Matrix elements of \hat{V} acting in this subspace are

$$\langle \vec{k}, \vec{G}_1 | \hat{V} | \vec{k}, \vec{G}_1 \rangle = \langle \vec{k}, \vec{G}_2 | \hat{V} | \vec{k}, \vec{G}_2 \rangle = \frac{1}{\sqrt{\Omega}} V_0 \quad (4.23)$$

$$\langle \vec{k}, \vec{G}_2 | \hat{V} | \vec{k}, \vec{G}_1 \rangle = \langle \vec{k}, \vec{G}_1 | \hat{V} | \vec{k}, \vec{G}_2 \rangle^* = \frac{V_{\vec{G}_2 - \vec{G}_1}}{\sqrt{\Omega}} \quad (4.24)$$

and the effective first-order 2×2 Hamiltonian is

$$\begin{pmatrix} \epsilon_{\vec{k}, \vec{G}_1} + \frac{V_0}{\sqrt{\Omega}} & \frac{V_{\vec{G}_2 - \vec{G}_1}}{\sqrt{\Omega}} \\ \frac{V_{\vec{G}_2 - \vec{G}_1}}{\sqrt{\Omega}} & \epsilon_{\vec{k}, \vec{G}_2} + \frac{V_0}{\sqrt{\Omega}} \end{pmatrix} \quad (4.25)$$

and the eigenvalues at the degenerate point are $\pm | \frac{V_{\vec{G}_2 - \vec{G}_1}}{\sqrt{\Omega}} |$. The two degenerate levels also feel additional second-order corrections from all other levels as well, but at and close to the degeneracy, the first-order splitting captured by this 2×2 Hamiltonian dominates. Once $|\epsilon_{\vec{k}, \vec{G}_1} - \epsilon_{\vec{k}, \vec{G}_2}| > | \frac{V_{\vec{G}_2 - \vec{G}_1}}{\sqrt{\Omega}} |$, the potential-driven splitting becomes less crucial and goes over into the purely second-order corrections discussed above. We thus find that corrections to

the free-electron spectrum are second order (i.e. small) wherever levels are well separated. Near band crossings, however, the periodic potential can lift the degeneracies by connecting states coming from parabolas centered at \vec{G}_1 and \vec{G}_2 , see Fig. 4.2.

4.3 Tight-Binding Bands

The approximation of nearly free electrons may be good for s -states in alkali metals, but we will now consider the ‘opposite’ case, where electrons are not free at all, but are tightly bound to ‘their’ atom. This approximation holds for inner states of the ions, for whom the potential of other ions is well screened by conduction electrons, and to a lesser extent for d and f electrons close to the Fermi level.

The starting point of the tight-binding approximation are atomic orbitals $\psi_n(\vec{r} - \vec{R}_m)$, i.e., eigenstates of the one-atom Schrödinger equation centered at \vec{R}_m , neglecting the electron-electron interaction. If we have many atoms, the atomic orbitals remain eigenstates if they are so well separated that an electron at site \vec{R}_m does not feel the potential from sites $\vec{R}_{m' \neq m}$, i.e., $\psi_n(\vec{r} - \vec{R}_m)V(\vec{r} - \vec{R}'_m) \propto \delta_{m,m'}$. One-atom wave functions $\psi_n(\vec{r} - \vec{R}_m)$ are of course not translationally invariant, but we can write a Bloch state as a superposition of atomic wave functions from atoms on all lattice positions \vec{R} :

$$\psi_{n,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \psi_n(\vec{r} - \vec{R}) \quad (4.26)$$

To check that this is indeed a Bloch function, we have to verify the behavior w.r.t. to lattice translations:

$$\psi_{n,\vec{k}}(\vec{r} + \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}'} e^{i\vec{k}\vec{R}'} \psi_n(\vec{r} + \vec{R}' - \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}'' = \vec{R}' - \vec{R}} e^{i\vec{k}\vec{R}'' + \vec{R}} \psi_n(\vec{r} - \vec{R}'') = e^{i\vec{k}\vec{R}} \psi_{n,\vec{k}}(\vec{r}). \quad (4.27)$$

When applying the one-electron Hamiltonian to this wave function, we split off the ‘large’ part arising when wave function and potential are centered at the same lattice site from the rest. Concerning the kinetic energy, we make use of the fact that $e^{i\vec{k}\vec{R}}$ is a constant.

$$\begin{aligned} \hat{H}\psi_{n,\vec{k}}(\vec{r}) &= \left(\frac{\vec{p}^2}{2m} + \sum_{\vec{R}} V(\vec{r} - \vec{R}) \right) \frac{1}{\sqrt{N}} \sum_{\vec{R}'} e^{i\vec{k}\vec{R}'} \psi_n(\vec{r} - \vec{R}') = \\ &= \frac{1}{\sqrt{N}} \sum_{\vec{R}'} e^{i\vec{k}\vec{R}'} \frac{\vec{p}^2}{2m} \psi_n(\vec{r} - \vec{R}') + \frac{1}{\sqrt{N}} \sum_{\vec{R}} V(\vec{r} - \vec{R}) \left(e^{i\vec{k}\vec{R}} \psi_n(\vec{r} - \vec{R}) + \sum_{\vec{R}' \neq \vec{R}} e^{i\vec{k}\vec{R}'} \psi_n(\vec{r} - \vec{R}') \right) = \\ &= \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \underbrace{\left(\frac{\vec{p}^2}{2m} + V(\vec{r} - \vec{R}) \right)}_{= \epsilon_n^0 \psi_n(\vec{r} - \vec{R})} \psi_n(\vec{r} - \vec{R}) + \frac{1}{\sqrt{N}} \sum_{\vec{R}, \vec{R}' \neq \vec{R}} e^{i\vec{k}\vec{R}'} V(\vec{r} - \vec{R}) \psi_n(\vec{r} - \vec{R}') \end{aligned} \quad (4.28)$$

At this point, we make use of the eigenvalue equation of the one-atom problem, which we assume to be solved. The corresponding atomic eigenenergy is our zeroth-order approximation

ϵ_n^0 for eigenstate n ; it does not depend on crystal momentum \vec{k} :

$$\hat{H}\psi_{n,\vec{k}}(\vec{r}) = (\hat{H}_0 + \hat{V}')\psi_{n,\vec{k}}(\vec{r}) = \epsilon_n^0 \psi_{n,\vec{k}}(\vec{r}) + \underbrace{\frac{1}{\sqrt{N}} \sum_{\vec{R}, \vec{R}' \neq \vec{R}} e^{i\vec{k}\vec{R}'} V(\vec{r} - \vec{R}) \psi_n(\vec{r} - \vec{R}')}_{=\hat{V}'\psi_{n,\vec{k}}(\vec{r})} \quad (4.29)$$

The ‘perturbation’ given by the potential of all *other* atoms will now be considered in perturbation theory. As \vec{k} is a good quantum number due to Bloch’s theorem and further assuming the atomic levels to be nondegenerate,² we are then interested in expectation values

$$\begin{aligned} \langle \psi_{n,\vec{k}}(\vec{r}) | \hat{V}' | \psi_{n,\vec{k}}(\vec{r}) \rangle &= \frac{1}{N} \int d^3r \sum_{\vec{R}_1} e^{-i\vec{k}\vec{R}_1} \psi_n^*(\vec{r} - \vec{R}_1) \sum_{\vec{R}_2} V(\vec{r} - \vec{R}_2) \sum_{\vec{R}_3 \neq \vec{R}_2} e^{-i\vec{k}\vec{R}_3} \psi_n(\vec{r} - \vec{R}_3) = \\ &= \frac{1}{N} \sum_{\substack{\vec{R}_1, \vec{R}_2 \\ \vec{R}_3 \neq \vec{R}_2}} e^{i\vec{k}(\vec{R}_3 - \vec{R}_1)} \int d^3r V(\vec{r} - \vec{R}_2) \psi_n^*(\vec{r} - \vec{R}_1) \psi_n(\vec{r} - \vec{R}_3). \end{aligned} \quad (4.30)$$

Integral with three different centers $\vec{R}_1 \neq \vec{R}_2 \neq \vec{R}_3 \neq \vec{R}_1$ will be neglected, because they are expected to be extremely small, as at least two of the three factors (ψ^* , ψ and V) have to be small.

There are two types of integrals with two different centers, where only one factor is small, either $\vec{R}_1 = \vec{R}_2 \neq \vec{R}_3$ or $\vec{R}_1 = \vec{R}_3 \neq \vec{R}_2$. The second type with $\vec{R}_1 = \vec{R}_3$ leads to

$$\begin{aligned} &\frac{1}{N} \sum_{\vec{R}_1, \vec{R}_2 \neq \vec{R}_1} e^{i\vec{k}\cdot 0} \int d^3r V(\vec{r} - \vec{R}_2) \psi_n^*(\vec{r} - \vec{R}_1) \underbrace{\psi_n(\vec{r} - \vec{R}_1)}_{=\vec{r}'} = \\ &= \frac{1}{N} \sum_{\vec{R}_1, \vec{R}_2 \neq \vec{R}_1} \int d^3r' V(\vec{r}' + \underbrace{\vec{R}_1 - \vec{R}_2}_{=\Delta\vec{R}}) |\psi_n(\vec{r}')|^2 = \frac{1}{N} \sum_{\substack{\vec{R}_1 \\ \Delta\vec{R} \neq 0 \\ =N}} \sum_{\Delta\vec{R} \neq 0} \int d^3r V(\vec{r} + \Delta\vec{R}) |\psi_n(\vec{r})|^2 = \beta_n, \end{aligned} \quad (4.31)$$

which is the average potential energy due to all other atoms. This term does not depend on \vec{k} and thus gives only a constant energy shift. The other ‘small, but not that small’ integral with $\vec{R}_1 = \vec{R}_2$ becomes

$$\begin{aligned} &\frac{1}{N} \sum_{\vec{R}_1, \vec{R}_3 \neq \vec{R}_1} e^{i\vec{k}(\vec{R}_3 - \vec{R}_1)} \int d^3r V(\vec{r} - \vec{R}_1) \psi_n^*(\vec{r} - \vec{R}_1) \underbrace{\psi_n(\vec{r} - \vec{R}_3)}_{=\vec{r}'} = \\ &= \frac{1}{N} \sum_{\vec{R}_1, \vec{R}_3 \neq \vec{R}_1} e^{i\vec{k}(\vec{R}_3 - \vec{R}_1)} \int d^3r' V(\vec{r}' + \underbrace{\vec{R}_3 - \vec{R}_1}_{=\Delta\vec{R}}) \psi_n^*(\vec{r}' + \vec{R}_3 - \vec{R}_1) \psi_n(\vec{r}') = \\ &= \frac{N}{N} \sum_{\Delta\vec{R} \neq 0} e^{i\vec{k}\Delta\vec{R}} \int d^3r V(\vec{r}' + \Delta\vec{R}) \psi_n^*(\vec{r} + \Delta\vec{R}) \psi_n(\vec{r}) = \sum_{\Delta\vec{R} \neq 0} e^{i\vec{k}\Delta\vec{R}} \gamma_n(\Delta\vec{R}) \end{aligned} \quad (4.32)$$

and finally lifts the degeneracy between different \vec{k} .

²This is in fact often not a valid assumption, as the d and f orbitals relevant for a tight-binding description can be degenerate. In that case, one has to allow \vec{k} -dependent mixing of ‘pure’ atomic orbitals.

A slight technical complication arises through the fact that (4.26) fulfills the definition of a Bloch function, but is not normalized, because *atomic* orbital centered at different \vec{R}_n are not perfectly orthogonal. Their overlap $\alpha_n(\Delta\vec{R})$ is small, but of the order of the $\gamma_n(\Delta\vec{R})$, so that we should be careful:

$$\begin{aligned} \langle \psi_{n,\vec{k}}(\vec{r}) | \psi_{n,\vec{k}}(\vec{r}) \rangle &= \frac{1}{N} \sum_{\vec{R}_1, \vec{R}_2} e^{i\vec{k}(\vec{R}_2 - \vec{R}_1)} \int d^3r \psi_n^*(\vec{r} - \vec{R}_1) \psi_n(\vec{r} - \vec{R}_2) = \\ &= \sum_{\Delta\vec{R}} e^{i\vec{k}\Delta\vec{R}} \int d^3r \psi_n^*(\vec{r} + \Delta\vec{R}) \psi_n(\vec{r}) = 1 + \sum_{\Delta\vec{R} \neq 0} e^{i\vec{k}\Delta\vec{R}} \alpha_n(\Delta\vec{R}) \end{aligned} \quad (4.33)$$

Collecting all contributions, the first-order approximation to the energy of the atomic state n is

$$\epsilon_n \approx \frac{\langle \psi_{n,\vec{k}}(\vec{r}) | (\hat{H}_0 + \hat{V}') | \psi_{n,\vec{k}}(\vec{r}) \rangle}{\langle \psi_{n,\vec{k}}(\vec{r}) | \psi_{n,\vec{k}}(\vec{r}) \rangle} = \epsilon_n^0 + \frac{\beta_n + \sum_{\Delta\vec{R} \neq 0} e^{i\vec{k}\Delta\vec{R}} \gamma_n(\Delta\vec{R})}{1 + \sum_{\Delta\vec{R} \neq 0} e^{i\vec{k}\Delta\vec{R}} \alpha_n(\Delta\vec{R})}. \quad (4.34)$$

Taking into account that all α , β , γ are small and consequently only keeping them in linear order yields

$$\epsilon_n \approx \epsilon_n^0 + \beta_n + \sum_{\Delta\vec{R} \neq 0} e^{i\vec{k}\Delta\vec{R}} \gamma_n(\Delta\vec{R}), \quad (4.35)$$

which can be further approximated assuming that $\gamma(\Delta\vec{R})$ will fall off fast beyond the first few neighbors $\Delta\vec{R} \geq \vec{a}_i$.

As an example, let's consider a one-dimensional chain with only nearest-neighbor integrals appreciably different from 0. As expectation values resp. norms the final results must be real. Inversion symmetry also has to be fulfilled. The tight-binding band structure becomes here

$$\epsilon_n(\vec{k}) = \epsilon_n^0 + \beta_n + e^{ika} \gamma_n(a) + e^{-ika} \gamma_n(a) = \epsilon_n^0 + \beta_n + 2\gamma_n(a) \cos(ka), \quad (4.36)$$

which is the typical tight-binding dispersion of particles that can tunnel to neighboring sites. If second-neighbor tunneling is also significant, another term $\propto \cos 2ka$ arises.

In the tight-binding approximation, the potential of all other atoms is consequently responsible for generating a dispersion. The existence of several bands separated by energy gaps is here due to the spacing of the atomic orbitals, without the potential coming from the other atoms, these bands would be dispersionless.

4.3.1 Wannier functions

As discussed above, the Bloch function (4.26) from atomic orbitals is not normalized, because the atomic wave functions are not orthogonal to each other. Using (4.33), we can normalize it ³ and find a normalized Bloch function

$$\phi_{n,\vec{k}}(\vec{r}) = \frac{\psi_{n,\vec{k}}(\vec{r})}{|\psi_{n,\vec{k}}|} = \frac{1}{\sqrt{N}} \frac{\sum_{\vec{R}} e^{i\vec{k}\vec{R}} \psi_n(\vec{r} - \vec{R})}{\sqrt{1 + \sum_{\Delta\vec{R} \neq 0} e^{i\vec{k}\Delta\vec{R}} \alpha_n(\Delta\vec{R})}} \quad \text{with } \langle \phi_{n,\vec{k}} | \phi_{m,\vec{k}'} \rangle = \delta_{n,m} \delta_{\vec{k},\vec{k}'}. \quad (4.37)$$

³If several (nearly) degenerate atomic orbitals are involved, this becomes more complicated, but in principle still doable.

This normalized Bloch function can be Fourier transformed back into position space. As (4.26) is periodic in reciprocal space $\psi_{n,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r})$ and consequently $\phi_{n,\vec{k}+\vec{G}}(\vec{r}) = \phi_{n,\vec{k}}(\vec{r})$, the Bloch function is of the type of functions that Fourier transform like (2.27) and (2.28).

$$\phi_{n,\vec{R}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k} \in 1\text{BZ}} \phi_{n,\vec{k}}(\vec{r}) e^{-i\vec{k}\vec{R}} \quad \text{and} \quad (4.38)$$

$$\phi_{n,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} \phi_{n,\vec{R}}(\vec{r}) e^{i\vec{k}\vec{R}}. \quad (4.39)$$

This Fourier-transformed normalized Bloch function is then properly orthonormal:

$$\begin{aligned} \langle \phi_{n,\vec{R}} | \phi_{m,\vec{R}'} \rangle &= \frac{1}{N} \sum_{\vec{k}, \vec{k}' \in 1\text{BZ}} e^{-i\vec{k}\vec{R}} e^{+i\vec{k}'\vec{R}'} \underbrace{\int d^3r \phi_{n,\vec{k}'}^*(\vec{r}) \phi_{m,\vec{k}}(\vec{r})}_{=\delta_{\vec{k},\vec{k}'} \delta_{n,m}} \\ &= \delta_{n,m} \frac{1}{N} \sum_{\vec{k} \in 1\text{BZ}} e^{-i\vec{k}(\vec{R}-\vec{R}')} = \delta_{n,m} \delta_{\vec{R},\vec{R}'}. \end{aligned} \quad (4.40)$$

This orthonormalized variant of the atomic wave functions is called ‘Wannier function’. From (4.3) and (4.38), we can define a function $\phi_n(\vec{r}-\vec{R})$ that is similar to an atomic orbital centered at \vec{R} :

$$\phi_{n,\vec{R}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k} \in 1\text{BZ}} \phi_{n,\vec{k}}(\vec{r}) e^{-i\vec{k}\vec{R}} = \frac{1}{\sqrt{N}} \sum_{\vec{k} \in 1\text{BZ}} \phi_{n,\vec{k}}(\vec{r}-\vec{R}) = \phi_n(\vec{r}-\vec{R}) \quad (4.41)$$

$$\phi_{n,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} \phi_n(\vec{r}-\vec{R}) e^{i\vec{k}\vec{R}}. \quad (4.42)$$

4.4 Thermodynamics of Non-interacting Electrons

As long as electron-electron interaction is neglected, the energy of a many-electron state is given by the sum of the energies of the filled states $E = \sum_{n,\vec{k},\sigma} \epsilon_n(\vec{k}) n_{n,\vec{k},\sigma}$. (The energy does here not depend in spin σ , but might in general.) Compared to the bosonic phonon modes discussed in Sec. 3.2.3, there are two differences:

- The full partition function for a single fermion mode is given by far fewer states, because there can be at most one fermion in each state:

$$Z = e^{-\beta\epsilon_0} + e^{-\beta\epsilon_1} = 1 + e^{-\beta\epsilon}. \quad (4.43)$$

Nevertheless, the result is similarly simple.

- The solid should have a fixed total number of electrons to be charge neutral.

The fixed particle number would suggest the canonical ensemble. Only states with the correct total number of particles should then be counted in the partition function, i.e.

$$Z = \sum_{\{n_{n,\vec{k},\sigma}\}} e^{-\beta \sum_{n,\vec{k},\sigma} \epsilon_n(\vec{k}) n_{n,\vec{k},\sigma}} \cdot \delta(N - \sum_{n,\vec{k},\sigma} n_{n,\vec{k},\sigma}). \quad (4.44)$$

However, this restriction undoes to a large extent the advantage gained from the independent-electron approximation, because the canonical partition function cannot be factorized into partition functions for single-electron states.

We consequently use the grand-canonical ensemble and introduce a chemical potential. The many-electron partition function given by all bands n , momenta \vec{k} and spin σ is given by

$$Z = \sum_{\{n_{n,\vec{k},\sigma}\}} e^{-\beta(\sum_{n,\vec{k},\sigma} \epsilon_n(\vec{k}) n_{n,\vec{k},\sigma} - \mu \sum_{n,\vec{k},\sigma} n_{n,\vec{k},\sigma})} = \prod_{n,\vec{k},\sigma} \left(e^{\beta(\epsilon_n(\vec{k}) - \mu)} + 1 \right). \quad (4.45)$$

As above, the spin does here not affect the energy $\epsilon_n(\vec{k})$, but may do so in a magnetic solid. The average occupation number is obtained analogously to the boson case and can be seen as a ‘Fermi function’ $f(\epsilon)$:

$$\langle n_{n,\vec{k},\sigma} \rangle = \frac{1}{e^{\beta(\epsilon_n(\vec{k}) - \mu)} + 1} = f(\epsilon_n(\vec{k})) \quad (4.46)$$

At low temperatures, i.e. large $\beta \rightarrow \infty$, the sign of $\epsilon - \mu$ is crucial: For positive $\epsilon - \mu$, the exponential becomes very large, $f(\epsilon > \mu)$ goes to 0 exponentially and the Fermi function thus resembles the Bose function as well as the classical Boltzmann distribution in this limit.⁴ For a negative sign, the exponential becomes very small and $f(\epsilon < \mu)$ approaches 1 exponentially from below. (This is very different from bosons or classical particles!) For $\epsilon = \mu$, it is exactly $f(0) = \frac{1}{2}$. The lower T is the closer $f(\epsilon)$ becomes to a step function.

The ‘canonical’ ground state with a fixed particle number is obtained by filling the N_e electrons into the N_e states with lowest energy. One can then define the Fermi energy E_F as the energy up to which the states have to be filled in order to give the appropriate number of electrons, i.e.

$$N_e = \sum_{n,\vec{k},\sigma} \theta(E_F - \epsilon_n(\vec{k})). \quad (4.47)$$

The lowest state is here assumed to be at energy 0⁵, so that E_F measures the energy difference from the highest occupied state to the bottom of the band. For free electrons, one could analogously sum over the available momentum states up to a ‘Fermi momentum’.

Definitions of Fermi energy and momentum make use of the ground state and a fixed particle number. In the grand canonical ground state, all states with energies below μ are filled, all states above are empty. For a metal at $T = 0$, $E_F = \mu$ follows. (For an insulator at $T = 0$, μ is not well defined.) At finite T , the particle number is determined by the chemical potential μ and the Fermi function, i.e.

$$N_e = \sum_{n,\vec{k},\sigma} \langle n_{n,\vec{k},\sigma} \rangle = \sum_{n,\vec{k},\sigma} \frac{1}{e^{\beta(\epsilon_n(\vec{k}) - \mu)} + 1} \quad (4.48)$$

Even though the particle number can fluctuate in the grand canonical ensemble, its probability density is actually quite sharply peaked in most cases. We are later going to discuss that μ in general depends on T .

⁴When there are very few particles, the question of their exchange statistics does not play a large role.

⁵The lowest state that counts for the number of electrons considered, i.e., the bottom of the conduction band. Tightly bound ionic core levels are at negative energies. For free electrons, the lowest possible energy is 0.

4.4.1 Density of States and Sommerfeld approach

The grand canonical partition function can be obtained from the energy bands $\epsilon_n(\vec{k})$ and once one knows Z , thermodynamic expectation values can be obtained as its derivative. However, Z actually only includes the *energy* of a state and does not otherwise reference the dispersion. As long as the observable of interest can also be expressed in terms of the energy, it is then enough to know the density of states

$$\rho(\omega) = \frac{1}{N} \sum_{n, \vec{k}, \sigma} \delta(\omega - \epsilon_n(\vec{k})) = \frac{2}{N} \sum_{n, \vec{k}} \delta(\omega - \epsilon_n(\vec{k})), \quad (4.49)$$

which gives the number of states available in $[\omega, \omega + d\omega]$ as $\rho(\omega)d\omega$. The number of electrons is then given by

$$\frac{N_e}{N} = \int_{-\infty}^{\infty} d\omega \rho(\omega) f(\omega) \quad (4.50)$$

and total energy is, for example, given by

$$U = \langle E \rangle = N \int_{-\infty}^{\infty} d\omega \rho(\omega) f(\omega) \omega. \quad (4.51)$$

Other quantities of interest $h(\omega)$ may also be expressed using the density of states and an approach due to Sommerfeld can be used to evaluate the integrals:

$$\int_{-\infty}^{\infty} d\omega f(\omega) \underbrace{\rho(\omega) h(\omega)}_{\tilde{h}(\omega)} = f(\omega) \tilde{H}(\omega) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} d\omega \frac{df(\omega)}{d\omega} \tilde{H}(\omega) \quad (4.52)$$

with $\tilde{h} = \frac{d\tilde{H}}{d\omega}$. $\tilde{H}(\omega)$ can be assumed to vanish fast enough for $\omega \rightarrow -\infty$, because it contains ρ , which is certainly 0 for very small energies, and $f(\omega)$ goes to 0 exponentially for $\omega \rightarrow \infty$. The boundary term is thus 0. The derivative of the Fermi function

$$-\frac{df(\omega)}{d\omega} = \frac{\beta e^{\beta(\omega-\mu)}}{(e^{\beta(\omega-\mu)} + 1)^2} = \frac{\beta}{(e^{\beta(\omega-\mu)} + 1)(e^{-\beta(\omega-\mu)} + 1)} \quad (4.53)$$

has the properties:

- It is symmetric around $\omega = \mu$,
- It goes to 0 exponentially with $\beta|\omega - \mu| \gg 1$, i.e., for $|\omega - \mu| \gg k_B T$ and is only appreciable for $|\omega - \mu|$ of the order of $k_B T$.
- Its limit for $\beta \rightarrow \infty$ resp. $T \rightarrow 0$ is a δ -function.

At least for low temperatures – and for many metals, 'low' can be quite large – only a small region around μ will contribute to the integral and it makes sense to expand \tilde{H} in powers of $(\omega - \mu)$. The series

$$\tilde{H}(\omega) = \tilde{H}(\mu) + \sum_{n=1}^{\infty} \frac{(\omega - \mu)^n}{n!} \left. \frac{d^n \tilde{H}}{d\omega^n} \right|_{\omega=\mu} = \tilde{H}(\mu) + \sum_{n=1}^{\infty} \frac{(\omega - \mu)^n}{n!} \left. \frac{d^{n-1} \tilde{h}}{d\omega^{n-1}} \right|_{\omega=\mu} \quad (4.54)$$

is then inserted into the integral

$$\begin{aligned} \int_{-\infty}^{\infty} d\omega f(\omega) \tilde{h}(\omega) &= \tilde{H}(\mu) \int_{-\infty}^{\infty} d\omega \frac{-df}{d\omega} + \sum_{n=1}^{\infty} \left. \frac{d^{n-1} \tilde{h}}{d\omega^{n-1}} \right|_{\omega=\mu-\infty} \int_{\omega=\mu-\infty}^{\infty} d\omega \frac{-df}{d\omega} \frac{(\omega-\mu)^n}{n!} = \\ &= \tilde{H}(\mu) \underbrace{(-f(\omega))}_{=1} \Big|_{-\infty}^{\infty} + \sum_{n=1}^{\infty} \left. \frac{d^{n-1} \tilde{h}}{d\omega^{n-1}} \right|_{\omega=\mu-\infty} \int_{\omega=\mu-\infty}^{\infty} d\chi \frac{-df}{d\chi} \frac{(\chi/\beta)^n}{n!} \end{aligned} \quad (4.55)$$

The function $\tilde{H}(\mu)$ can then be expressed as an integral over \tilde{h} again. In the sum over n , a variable substitution $\chi = \beta(\omega - \mu)$ makes the integral independent of β (it already is independent of \tilde{h}). Moreover, the fact that $\frac{df}{d\omega}$ is symmetric around $\omega - \mu$, see (4.53) means that odd powers of $\omega - \mu$ drop out of the sum. The integral can then be expressed in terms of the Riemann zeta function and one gets

$$\int_{-\infty}^{\infty} d\omega f(\omega) \tilde{h}(\omega) = \int_{-\infty}^{\mu} d\omega \tilde{h}(\omega) + \sum_{n=1}^{\infty} (k_B T)^{2n} \left. \frac{d^{2n-1} \tilde{h}}{d\omega^{2n-1}} \right|_{\omega=\mu} \underbrace{\int_{-\infty}^{\infty} d\chi \frac{-df}{d\chi} \frac{\chi^n}{n!}}_{=a_m=(2-2^{-2(n-1)}) \zeta(2n)} . \quad (4.56)$$

The first two values of the integral are $a(1) = \frac{\pi^2}{6}$ and $a(2) = \frac{7\pi^4}{360}$, the large- n limit of $\zeta(n)$ is 1, so that $a(n)$ goes to 2. For small $k_B T$, we can then expect the first (few) term(s) of the series to yield a good description.

We can then calculate the electron number N_e depending on temperature, up to second order in T :

$$\frac{N_e}{N} = \int_{-\infty}^{\infty} d\omega f(\omega) \rho(\omega) = \int_{-\infty}^{\mu} d\omega \rho(\omega) + (k_B T)^2 \left. \frac{d\rho}{d\omega} \right|_{\omega=\mu} \frac{\pi^2}{6} + \mathcal{O}(T^4) \quad (4.57)$$

The right-hand side depends on T , but on the other hand, we know that the particle number should remain constant. The solution is that μ has to adjust and becomes T -dependent as well. In lowest orders and assuming that $\rho(\omega \approx E_F)$ does not vary too wildly, one can approximate

$$\begin{aligned} \frac{N_e}{N} &= \underbrace{\int_{-\infty}^{E_F} d\omega \rho(\omega)}_{=N_e/N} + \underbrace{\int_{E_F}^{\mu(T)} d\omega \rho(\omega)}_{\approx \rho(E_F)(\mu(T)-E_F)} + \frac{\pi^2}{6} \rho'(E_F) (k_B T)^2 + \mathcal{O}(T^4) \\ \Rightarrow \rho(E_F)(\mu(T) - E_F) + \frac{\pi^2}{6} \rho'(E_F) (k_B T)^2 &= 0 \end{aligned} \quad (4.58)$$

$$\Rightarrow \mu(T) = E_F - \frac{\pi^2}{6} \frac{\rho'(E_F)}{\rho(E_F)} (k_B T)^2 \quad (4.59)$$

If ρ grows with ω ($\rho' > 0$), widening the region $k_B T$ contributing to the integrals means that more states are gained to the right than are lost to the left – μ has to become a bit lower to balance this.

In order to find the specific heat, we calculate the electronic energy (4.51) in lowest orders of T :

$$\begin{aligned}
u &= \frac{U}{N} = \int_{-\infty}^{\infty} d\omega f(\omega) \underbrace{\rho(\omega)\omega}_{\tilde{h}(\omega)} = \int_{-\infty}^{\mu(T)} d\omega \rho(\omega)\omega + (k_B T)^2 \frac{\pi^2}{6} \frac{d}{d\omega}(\omega\rho(\omega)) \Big|_{\omega=\mu} + \mathcal{O}(T^4) = \\
&= \underbrace{\int_{-\infty}^{E_F} d\omega \rho(\omega)\omega}_{=u_0} + \int_{E_F}^{\mu(T)} d\omega \rho(\omega)\omega + (k_B T)^2 \frac{\pi^2}{6} \rho(\mu) + (k_B T)^2 \frac{\pi^2}{6} \mu\rho'(\mu) + \mathcal{O}(T^4) = \\
&= u_0 + E_F \rho(E_F)(\mu - E_F) + (k_B T)^2 \frac{\pi^2}{6} \rho(\mu) + (k_B T)^2 \frac{\pi^2}{6} \mu\rho'(\mu) + \mathcal{O}(T^4) \quad (4.60)
\end{aligned}$$

As $\mu - E_F$ is of order T^2 , replacing μ by E_F in $\mu\rho'(\mu)$ gives corrections of higher order T^4 , as does the approximation of the integral $\int_{E_F}^{\mu}$. One can then use (4.58) to note that the second and fourth term cancel, leaving

$$u = u_0 + \frac{\pi^2}{6} \rho(E_F) (k_B T)^2 + \mathcal{O}(T^4). \quad (4.61)$$

The energy of the electrons in a metal thus grows with T^2 and the electronic contribution to the specific heat is

$$c_V = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} \rho(E_F) k_B^2 T + \mathcal{O}(T^3). \quad (4.62)$$

At very low T , this should definitely dominate over the phonon contribution $\propto T^3$. The prefactors have to be evaluated to reveal at what temperature the phonons start to play a role, we will do this for the free electron gas in the next section. As $c_V \propto \rho(E_F)$, we can also note that the electronic specific heat vanishes if there are not states around the Fermi energy – the case for insulators.

4.4.2 The Free Electron Gas

As an example, we can discuss free electrons, because the integrals can be evaluated for this case. It is here simpler *not* to go the the ‘lattice language’ of decomposing total momentum into a part \vec{q} from the first BZ and a reciprocal lattice vector, as was done in Fig. 4.1. Instead, we keep the free electron energy $\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$ with \vec{k} going over all momenta and just one single band. Assuming a charge neutral solid gives us the total number N_e of electrons, which in turn determines the Fermi momentum k_F :

$$N_e = 2 \sum_{|\vec{k}| \leq k_F} = \frac{2V}{(2\pi)^3} \int_{|\vec{k}| \leq k_F} d^3 k = \frac{V}{\pi^2} \int_0^{k_F} dk k^2 = \frac{V}{3\pi^2} k_F^3 \quad \Rightarrow \quad k_F = \sqrt[3]{3\pi^2 \frac{N_e}{V}} \quad (4.63)$$

The corresponding Fermi energy is then

$$E_F = \epsilon(k_F) = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2 \sqrt[3]{(3\pi^2 \frac{N_e}{V})^2}}{2m}. \quad (4.64)$$

The density of states of free electrons is given by

$$\begin{aligned}\rho(\omega) &= \frac{2}{N} \sum_{\vec{k}} \delta(\omega - \epsilon(\vec{k})) = \frac{V}{N\pi^2} \int_0^\infty dk k^2 \delta\left(\omega - \frac{\hbar^2 k^2}{2m}\right) = \\ &= \frac{V}{N\pi^2} \int_0^\infty dk k^2 \frac{1}{|\frac{\hbar^2 k}{m}|} \delta\left(k - \frac{\sqrt{2m\omega}}{\hbar}\right) = \frac{V}{N} \frac{\sqrt{2m^3}}{\pi^2 \hbar^3} \sqrt{\omega} \theta(\omega).\end{aligned}\quad (4.65)$$

(The step function $\theta(\omega)$ ensures that no free-electron states are found at negative energies.) Such a square-root density of states starting at the bottom of a conduction band is indeed often (approximately) found in ‘simple’ metals like alkali metals, whose conduction electrons are nearly free. The density of states will typically have some additional features, where the lattice potential leads to gaps at parts of the Brillouin zone. Clearly, the opening of a gap over all momenta at the same energy, i.e., a full gap leads to a drastically different density of states, because it vanishes for energies in the gap.

The density of states can also be expressed in terms of the Fermi energy as

$$\rho(\omega) = \frac{V}{N} \frac{\sqrt{2m^3}}{\pi^2 \hbar^3} \sqrt{E_F} \sqrt{\frac{\omega}{E_F}} \theta(\omega) = \frac{N_e}{N} \frac{3}{2} \frac{1}{\sqrt{E_F}} \sqrt{E_F} \sqrt{\frac{\omega}{E_F}} \theta(\omega) = \frac{3Z_e}{2E_F} \sqrt{\frac{\omega}{E_F}} \theta(\omega), \quad (4.66)$$

with $Z_e = \frac{N_e}{N}$ the number of valence electrons per unit cell. Inserting this free-electron density of states into (4.62) gives the specific heat of the free-electron gas at low temperatures as

$$c_V = \frac{\pi^2}{3} \frac{3Z_e}{2E_F} \sqrt{\frac{E_F}{E_F}} k_B^2 T = \frac{Z_e \pi^2}{2} k_B \frac{k_B T}{E_F}. \quad (4.67)$$

For the purpose of the electronic specific heat, a ‘small’ temperature is consequently one that is smaller than the temperature associated with the Fermi energy. Since we are in principle free to shift the one-particle energies, it is important to specify that E_F here refers to the energy difference between the highest occupied electron state (at $T = 0$) and the bottom of the conduction band: The origin of the energy comparison of $k_B T$ and E_F is that it relates electrons found ‘close to’ μ (and hence with a filling different from 0 or 1) and the total number of electrons.

Typical Fermi energies $E_F \approx 2$ to 10 eV of simple metals are quite large compared to room temperature $k_B T_{\text{room}} \approx \frac{1}{40}$ eV. The Debye temperature, which defines the scale of ‘small’ T for the phonon specific heat, is in many cases comparable to room temperature. Moreover, the prefactors of the phononic contribution $\frac{12\pi^4}{5} \approx 234$ is much larger than the coefficient $\frac{\pi^2}{2} \approx 5$ of the electronic part. Consequently, one can expect that the specific heat of metals shows at least three distinct regimes:

- Very low T (small for both electrons and phonons), where the linear term coming from the electrons dominates, because the larger phononic prefactor is suppressed by $(T/\Theta_D)^3$ compared to the only linear $k_B T/E_F$.
- Intermediate T , where the low- T expansion still holds for both electrons and phonons, but where (larger) $(T/\Theta_D)^3$ is no longer small enough to suppress the larger prefactor of the phononic part. The T^3 behavior driven by phonons dominates in this regime.
- Large T , where the equipartition theorem wins and the specific heat saturates.

This is indeed experimentally found for many metals.

4.4.3 Metals – Insulators – Semiconductors

As (4.56) suggests that many properties depend mostly on the electronic states near the Fermi energy, it becomes clear that the density of states there is crucial. We discussed in detail the case of metals, where it is large. The opposite scenario is found when it is zero, i.e., when a band is completely filled and the next one completely empty. The electronic specific heat then vanishes and the material is an insulator. As we had seen in the discussion of both nearly free electrons, see Fig. 4.2, and tightly bound ones, fillings where this can happen are not very exotic special cases, but correspond to a total number of electrons given by the number of states in the first Brillouin zone times an integer. As spin degeneracy allows to fill two electrons into one state, an even number of valence electrons per unit cell is a candidate for an insulator.

A somewhat intermediate case arises when the chemical potential is in a gap, but this gap is not too large compared to $k_B T$. In this case, some empty states (=holes) will be found in the highest filled (=‘valence’) band and some electron in the lowest empty (=‘conduction’) band. The Fermi function for large $\beta(\epsilon(\vec{k}) - \mu)$ can be approximated as a Boltzmann distribution $e^{-\beta(\epsilon(\vec{k}) - \mu)}$. This gives many properties a temperature dependence $e^{-\beta\Delta E/2}$, with ΔE being the gap, because about this number of electron/holes are created at T and can participate, this is called ‘activated’ behavior.

4.5 Electrons in an electric field – and a periodic potential

Talking about “metals” and “insulators”, the question of electron motion in an electric field naturally comes up. Let us here first discuss the behaviour of a single Bloch state, without considering thermodynamics. The velocity of the electron or wave packet is the time-derivative of its position, i.e.

$$\langle \vec{v} \rangle = \langle \dot{\vec{r}} \rangle = \frac{i}{\hbar} [H, \vec{r}] = \frac{\partial H}{\partial \vec{p}} = \frac{\vec{p}}{m} \quad (4.68)$$

$$\text{with } [H, r_\alpha] = \sum_\beta \frac{\partial H}{\partial p_\beta} \underbrace{[p_\beta, r_\alpha]}_{=i\hbar\delta_{\alpha,\beta}} = -i\hbar \frac{\partial H}{\partial p_\alpha} = -i\hbar \frac{p_\alpha}{m} \quad (4.69)$$

in the Heisenberg picture. We would like to know this quantity in the presence of a uniform electric field.

4.5.1 Weak field, simplest approximation

A constant electric field driving the electrons can be straightforwardly modelled as an electronic onsite potential $\phi(\vec{r})$ that varies linearly with position, e.g. $\phi(\vec{r}) = E \cdot x$. Strictly speaking, this spoils translational invariance, even with respect to lattice distortions, but if the external potential is much weaker than the periodic lattice potential, we can at first neglect this effect and continue to use Bloch states. We thus calculate

$$\langle \vec{v} \rangle = \langle \psi_{n,\vec{k}} | \frac{\vec{p}}{m} | \psi_{n,\vec{k}} \rangle = \langle n, \vec{k} | e^{-i\vec{k}\vec{r}} \frac{\vec{p}}{m} e^{i\vec{k}\vec{r}} | n, \vec{k} \rangle \quad (4.70)$$

with a lattice periodic $|u_{n,\vec{k}}\rangle = |n, \vec{k}\rangle$, i.e., $u_{n,\vec{k}}(\vec{r}) = \langle \vec{r} | n, \vec{k} \rangle = u_{n,\vec{k}}(\vec{r} + \vec{R}) = \langle \vec{r} + \vec{R} | n, \vec{k} \rangle$. This gives

$$\begin{aligned} \langle n, \vec{k} | e^{-i\vec{k}\vec{r}} \frac{\vec{p}}{m} e^{i\vec{k}\vec{r}} | n, \vec{k} \rangle &= \langle n, \vec{k} | e^{-i\vec{k}\vec{r}} \frac{-i\hbar}{m} \nabla e^{i\vec{k}\vec{r}} | n, \vec{k} \rangle = \langle n, \vec{k} | \frac{-i\hbar}{m} \nabla | n, \vec{k} \rangle + \langle n, \vec{k} | \frac{-i\hbar}{m} \cdot i\hbar\vec{k} | n, \vec{k} \rangle \\ &= \langle n, \vec{k} | \frac{\vec{p} + \hbar\vec{k}}{m} | n, \vec{k} \rangle. \end{aligned} \quad (4.71)$$

One notes that we would have obtained the same directly from Eq. (4.68) when applied to the \vec{k} -space Bloch Hamiltonian $h_{\vec{k}}$ from Eq. (4.8):

$$\vec{v} = \dot{\vec{r}} = \frac{i}{\hbar} [h_{\vec{k}}, \vec{r}] = \frac{\partial h_{\vec{k}}}{\partial \vec{p}} = \frac{\vec{p} + \hbar\vec{k}}{m}. \quad (4.72)$$

This works, because Eq. (4.8) is a perfectly valid Hamiltonian in its own right that just happens to be parametrized by some \vec{k} ; it can thus also be used to define time dependence, at least as long as \vec{k} is a conserved quantity.

Taking the derivative w.r.t. \vec{k} of Eq. (4.8) gives

$$\begin{aligned} \frac{\partial \epsilon_{n,\vec{k}}}{\partial \vec{k}} &= \frac{\partial}{\partial \vec{k}} \langle n, \vec{k} | h_{\vec{k}} | n, \vec{k} \rangle = \left(\frac{\partial}{\partial \vec{k}} \langle n, \vec{k} | \right) h_{\vec{k}} | n, \vec{k} \rangle + \langle n, \vec{k} | \left(\frac{\partial}{\partial \vec{k}} h_{\vec{k}} \right) | n, \vec{k} \rangle + \langle n, \vec{k} | h_{\vec{k}} \left(\frac{\partial}{\partial \vec{k}} | n, \vec{k} \rangle \right) = \\ &= \langle n, \vec{k} | \left(\frac{\partial}{\partial \vec{k}} h_{\vec{k}} \right) | n, \vec{k} \rangle = \langle n, \vec{k} | \frac{\vec{p} + \hbar\vec{k}}{m} | n, \vec{k} \rangle = \hbar \langle \vec{v} \rangle. \end{aligned} \quad (4.73)$$

We have here used

$$\begin{aligned} \langle n, \vec{k} | n, \vec{k} \rangle = 1 &\Rightarrow \frac{\partial}{\partial \vec{k}} \langle n, \vec{k} | n, \vec{k} \rangle = \left(\frac{\partial}{\partial \vec{k}} \langle n, \vec{k} | \right) | n, \vec{k} \rangle + \langle n, \vec{k} | \frac{\partial}{\partial \vec{k}} | n, \vec{k} \rangle = 0 \\ &\Rightarrow \left(\frac{\partial}{\partial \vec{k}} \langle n, \vec{k} | \right) h_{\vec{k}} | n, \vec{k} \rangle + \langle n, \vec{k} | h_{\vec{k}} \frac{\partial}{\partial \vec{k}} | n, \vec{k} \rangle = \epsilon_{n,\vec{k}} \frac{\partial}{\partial \vec{k}} \langle n, \vec{k} | n, \vec{k} \rangle = 0 \end{aligned} \quad (4.74)$$

One can thus obtain the group velocity in a Bloch state from just the energy dispersion, without any reference to the eigenstate $|n, \vec{k}\rangle$. Specifically, the electrons are faster if the band dispersion is steeper.

4.5.1.1 Effective mass and $\vec{k} \cdot \vec{p}$ perturbation theory

As one can describe the velocity just using the band dispersion, comparison to free-electron bands is tempting. Their characteristic is of course that they are quadratic in \vec{k} , i.e., their curvature is constant and given by the electron mass. Analogously, one can define an effective mass for general bands as a tensor-valued function of \vec{k} :

$$\left(\frac{1}{m^*} \right)_{i,j}(\vec{k}) = \frac{1}{\hbar^2} \frac{\partial}{\partial k_i} \frac{\partial}{\partial k_j} \epsilon_{n,\vec{k}} \quad (4.75)$$

Interestingly, one can obtain an approximation for this quantity at $\vec{k} \approx \vec{k}_0$ *without* taking the derivative w.r.t. \vec{k} , by using just $|n, \vec{k}_0\rangle$. However, one then has to refer to the wave function and to include more than one band.

This approach is based on perturbation theory, which we will here discuss for $\vec{k}_0 = 0$ (the Γ point), with \vec{k} as the small parameter. Equation (4.8) is rearranged to

$$\left(\frac{\vec{p}^2}{2m} + V(\vec{r}) + \frac{\vec{k}\vec{p}}{m} \right) |n, \vec{k}\rangle = \left(\epsilon_{n, \vec{k}} - \frac{\hbar^2 \vec{k}^2}{2m} \right) |n, \vec{k}\rangle, \quad (4.76)$$

where perturbation theory up to second order in $\vec{k} \cdot \vec{p}$ gives

$$\begin{aligned} \epsilon_{n, \vec{k}} &\approx \epsilon_{n, 0} + \frac{\hbar^2 \vec{k}^2}{2m} + \frac{\hbar \vec{k}}{m} \langle n, \vec{k} = 0 | \vec{p} | n, 0 \rangle + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle n, 0 | \vec{k} \vec{p} | n', 0 \rangle|^2}{\epsilon_n(0) - \epsilon_{n'}(0)} = \\ &\epsilon_{n, 0} + \frac{\hbar^2 \vec{k}^2}{2m} + \frac{\hbar \vec{k}}{m} \langle n, 0 | \vec{p} | n, 0 \rangle + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\vec{k} \langle n, 0 | \vec{p} | n', 0 \rangle|^2}{\epsilon_n(0) - \epsilon_{n'}(0)}. \end{aligned} \quad (4.77)$$

The dispersion is thus determined by the expectation values of \vec{p} and if the bands are well separated, only few n' have to be taken into account to obtain a solid approximation. These are relatively few numbers, which makes this approximation scheme appealing. One can here also note that since inversion symmetry enforces $\langle n, \vec{k} = 0 | \vec{p} | n, 0 \rangle = 0$, (non-degenerate) bands at the Γ -points are quadratic in \vec{k} .

4.5.2 Replacing spatial dependence by time dependence: anomalous velocity

Based on D. Xiao, M.-C. Chang, and Q. Niu, *Rev. Mod. Phys.* **82**, 1959 (2010).

As mentioned above, an electric scalar potential $\phi(\vec{r})$ varying in space – as needed for a constant electric field – destroys translational invariance. However, the definition of the electric field $\vec{E} = \nabla\phi - \frac{\partial}{\partial t}\vec{A}$ permits an alternative way to describe the electric field, namely with a *time*-dependent, but spatially uniform, vector potential $\vec{A}(t)$. The Hamiltonian is then

$$H(t) = \frac{(p + \frac{e}{\hbar}\vec{A}(t))^2}{2m} + V(\vec{r}) \quad \text{with} \quad V(\vec{r} + \vec{R}) = V(\vec{r}) \quad \text{and} \quad A(\vec{r} + \vec{R}) = A(\vec{r}). \quad (4.78)$$

As $\vec{A}(t)$ is constant in space, it's lattice periodicity is trivial.

Since $H(t)$ is lattice periodic, its eigenstates have the form of Bloch states and one can cast the Hamiltonian in the form of Eq. (4.8):

$$h_{\vec{k}}(t) |n, \vec{k}, t\rangle = \left(\frac{(\vec{p} + \frac{e}{\hbar}\vec{A}(t) + \hbar\vec{k})^2}{2m} + V \right) |n, \vec{k}, t\rangle = \epsilon_{n, \vec{k}}(t) |n, \vec{k}, t\rangle. \quad (4.79)$$

Since $H(t)$ is lattice periodic with the same periodicity at all times, it continues to commute with translations by lattice vectors, implying that \vec{k} remains a good quantum number $\frac{\partial}{\partial t}\vec{k} = 0$. One can also check that an expression like (4.72) still holds, i.e.,

$$\hbar\vec{v} = \frac{\partial H(t)}{\partial \vec{p}} = \frac{\partial h_{\vec{k}}(t)}{\partial \vec{k}}. \quad (4.80)$$

Finally, the eigenstates to the time-dependent Hamiltonian will themselves depend on time in a non-trivial manner.

Apart from an overall phase, their time dependence can be approximated in perturbation theory as ⁶

$$|n, \vec{k}, t\rangle \approx |n, \vec{k}\rangle - i\hbar \sum_{n' \neq n} \frac{|n', \vec{k}\rangle \langle n', \vec{k} | \frac{\partial n}{\partial t} \rangle}{\epsilon_n - \epsilon_{n'}} \quad (4.81)$$

where $|n, \vec{k}\rangle$ denotes the eigenstate of the initial Hamiltonian $h_{\vec{k}}(t=0)$ without a vector potential. This approximation is then used to evaluate the first order of the time-dependent expectation value of velocity from Eq. (4.80), where index \vec{k} of the eigen vectors will be suppressed for clarity (it is a conserved quantity and hence the same everywhere):

$$\hbar \langle \vec{v} \rangle = \langle n, t | \frac{\partial}{\partial \vec{k}} h_{\vec{k}}(t) | n, t \rangle \approx \frac{\partial \epsilon_{n, \vec{k}}}{\partial \vec{k}} \langle n | n, \rangle - i\hbar \sum_{n' \neq n} \frac{\langle n | \frac{\partial h_{\vec{k}}(t)}{\partial \vec{k}} | n' \rangle \langle n' | \frac{\partial n}{\partial t} \rangle}{\epsilon_n - \epsilon_{n'}} + i\hbar \sum_{n' \neq n} \frac{\langle \frac{\partial n}{\partial t} | n' \rangle \langle n' | \frac{\partial h_{\vec{k}}(t)}{\partial \vec{k}} | n \rangle}{\epsilon_n - \epsilon_{n'}} \quad (4.82)$$

To reformulate this, we use a trick similar to that of Eq. (4.74), but based on the orthogonality of the instantaneous eigenstates $|n, t\rangle$:

$$\begin{aligned} \langle n, t | n', t \rangle = 0 &\Rightarrow \frac{\partial}{\partial \vec{k}} \langle n, t | n', t \rangle = \left(\frac{\partial}{\partial \vec{k}} \langle n, t | \right) | n', t \rangle + \langle n, t | \frac{\partial}{\partial \vec{k}} | n', t \rangle = 0 \\ \text{and } \langle n, t | h_{\vec{k}}(t) | n', t \rangle = \epsilon_n(t) \cdot 0 = 0 &\Rightarrow \frac{\partial}{\partial \vec{k}} \langle n, t | h_{\vec{k}}(t) | n', t \rangle = \\ &= \left(\frac{\partial}{\partial \vec{k}} \langle n, t | \right) h_{\vec{k}}(t) | n', t \rangle + \langle n, t | h_{\vec{k}}(t) | \frac{\partial}{\partial \vec{k}} | n', t \rangle + \langle n, t | \frac{\partial h_{\vec{k}}(t)}{\partial \vec{k}} | n', t \rangle \\ &= \epsilon_{n'} \left(\frac{\partial}{\partial \vec{k}} \langle n, t | \right) | n', t \rangle - \epsilon_n \left(\frac{\partial}{\partial \vec{k}} \langle n, t | \right) | n', t \rangle + \langle n, t | \frac{\partial h_{\vec{k}}(t)}{\partial \vec{k}} | n', t \rangle = 0 \\ \Rightarrow \langle n, t | \frac{\partial h_{\vec{k}}(t)}{\partial \vec{k}} | n', t \rangle &= (\epsilon_n - \epsilon_{n'}) \left(\frac{\partial}{\partial \vec{k}} \langle n, t | \right) | n', t \rangle. \end{aligned} \quad (4.83)$$

We then get

$$\hbar \langle \vec{v} \rangle \approx \frac{\partial \epsilon_{n, \vec{k}}}{\partial \vec{k}} - i\hbar \sum_{n' \neq n} \left(\left\langle \frac{\partial n}{\partial \vec{k}} | n' \right\rangle \langle n' | \frac{\partial n}{\partial t} \right) - \left\langle \frac{\partial n}{\partial t} | n' \right\rangle \langle n' | \frac{\partial n}{\partial \vec{k}} \right) \quad (4.84)$$

where we can formally extend the sum over all n' including $n = n'$, because this added term is in any case 0. The sum $\sum_{n'} |n'\rangle \langle n'| = \mathbb{I}$ is then just the identity and can be left out:

$$\langle \vec{v} \rangle \approx \frac{\partial \epsilon_{n, \vec{k}}}{\hbar \partial \vec{k}} - i \left(\left\langle \frac{\partial n}{\partial \vec{k}} \left| \frac{\partial n}{\partial t} \right. \right\rangle - \left\langle \frac{\partial n}{\partial t} \left| \frac{\partial n}{\partial \vec{k}} \right. \right\rangle \right). \quad (4.85)$$

The first part is just the velocity we had before in Eq. (4.73), the additional part that depends on the eigenfunctions $|n\rangle$ is called ‘‘anomalous velocity’’. The anomalous velocity is the so-called ‘‘Berry-curvature’’ of the band and if one integrates over a filled band – so that the contributions to the ‘‘normal’’ velocity exactly cancel – it determines transport.

In the problem at hand, we would like to formulate $\langle \vec{v} \rangle$ in terms of \vec{k} only, i.e., without referring to time that we have after all only introduced as a ‘‘gauge trick’’. This can be

⁶See appendix to D. Xiao, M.-C. Chang, and Q. Niu, Rev. Mod. Phys. **82**, 1959 (2010).

done by noting that only the combination $\hbar\vec{q} = \hbar\vec{k} + \frac{e}{\hbar}\vec{A}(t)$ enters the Hamiltonian. Time-derivatives can then be obtained by applying the chain rule

$$\frac{\partial}{\partial t} = \sum_{\alpha} \frac{\partial}{\partial q_{\alpha}} \frac{\partial q_{\alpha}}{\partial t} = -\frac{e}{\hbar} \sum_{\alpha} E_{\alpha} \frac{\partial}{\partial q_{\alpha}} \quad \text{with} \quad \frac{\partial}{\partial q_{\alpha}} = \frac{\partial}{\partial k_{\alpha}} \quad (4.86)$$

Focussing on the x -component, the anomalous velocity becomes

$$i\frac{e}{\hbar} \sum_{\alpha} E_{\alpha} \left(\left\langle \frac{\partial n}{\partial k_x} \middle| \frac{\partial n}{\partial k_{\alpha}} \right\rangle - \left\langle \frac{\partial n}{\partial k_{\alpha}} \middle| \frac{\partial n}{\partial k_x} \right\rangle \right) = i\frac{e}{\hbar} E_y \left(\left\langle \frac{\partial n}{\partial k_x} \middle| \frac{\partial n}{\partial k_y} \right\rangle - \left\langle \frac{\partial n}{\partial k_y} \middle| \frac{\partial n}{\partial k_x} \right\rangle \right) + i\frac{e}{\hbar} E_z \left(\left\langle \frac{\partial n}{\partial k_x} \middle| \frac{\partial n}{\partial k_z} \right\rangle - \left\langle \frac{\partial n}{\partial k_z} \middle| \frac{\partial n}{\partial k_x} \right\rangle \right). \quad (4.87)$$

Comparison of components reveals that this can be summarized to

$$\langle \vec{v} \rangle \approx \frac{\partial \epsilon_{n,\vec{k}}}{\hbar \partial \vec{k}} - i\frac{e}{\hbar} \vec{E} \times \langle \nabla n | \times | \nabla n \rangle, \quad (4.88)$$

where $i\langle \nabla n | \times | \nabla n \rangle$ is the Berry curvature of the band n .

Very strong magnetic fields that are comparable to lattice potentials imply that one goes beyond perturbation theory, one then has to deal with “magnetic Bloch bands”, where the trick is to restore formally the translational invariance that a system in a constant magnetic is physically expected to have.⁷ The theory developed here is then also relevant “topological insulators”, as the connection to the Berry curvature introduces topological concepts.

⁷Again see D. Xiao, M.-C. Chang, and Q. Niu, Rev. Mod. Phys. **82**, 1959 (2010).

5 Green's functions for Many-Body Systems

In this chapter, we are going to introduce techniques for many-body systems. Sections 4.4 and 3.2.3 already treated many-electron and many-phonon scenarios using statistical physics. However, this approach is only valid as long as occupation $\langle n \rangle_{\vec{k}}$ in a state \vec{k} does not depend on that of the others. While this is often a decent approximation, see the successful description of the specific heat of metals, it neglects *interactions* between the particles, which are sometimes important.

The first important ingredient is the formalism of *second quantization*, which is here assumed as known from advanced quantum mechanics. The second aspect are Green's functions, which will be discussed in more detail. Green's functions are in general mathematical objects that get us from a solution to a partial differential equation at some time t' and position \vec{r}' to other times t and \vec{r} . Here, we are going to make this concept useful to many-body systems via two routes. One is to extend the 'propagator' of the one-particle Schrödinger equation (which is a partial differential equation) to a many-body setting and the other route is to note that very similar objects also describe the reaction of a system to some external perturbation (linear response theory).

5.1 Some aspects of Second Quantization

One aspect that was only shortly mentioned and hardly used in Quantum Mechanics are 'field operators'. We had introduced them based on momentum eigenstates, but in general, for any basis $\psi_\nu(\vec{r})$ of a one-particle Hilbert space with corresponding creation and annihilation operators a_ν and a_ν^\dagger , one can obtain field operators as

$$\hat{\psi}^\dagger(\vec{r}) = \sum_\nu \psi_\nu^*(\vec{r}) a_\nu^\dagger \quad \text{and} \quad \hat{\psi}(\vec{r}) = \sum_\nu \psi_\nu(\vec{r}) a_\nu. \quad (5.1)$$

A relation that we will often need is the commutator of an annihilation operator a_ν and a non-interacting Hamiltonian $H_0 = \sum_\nu \epsilon_\nu a_\nu^\dagger a_\nu$.

$$[a_\nu, H_0] = \sum_\mu \epsilon_\mu [a_\nu, a_\mu^\dagger a_\mu] = \sum_\mu \epsilon_\mu \left(\underbrace{[a_\nu, a_\mu^\dagger]}_{=\delta_{\nu,\mu}} a_\mu \mp a_\mu^\dagger \underbrace{[a_\nu, a_\mu]}_{=0} \right) = \epsilon_\nu a_\nu. \quad (5.2)$$

This holds both for bosons (commutator is used) and fermions (anticommutator).

5.2 Linear Response Theory

Based on Nolting's textbook.

In order to learn about a system, one might probe it with some time-dependent external field. The time dependence allows us to switch it on or off, so that we can start from the

‘clean’ system and – as we will see – also gives access to excitation energies. We would then expect the change in some observable $A(t)$ to depend on the applied field $f(t')$ at earlier times $t' < t$. The system’s susceptibility is captured by its ‘response function’ $g(t-t')$ depending on the time elapsed between the application of the field and the measurement. The expected result would then be a convolution

$$\langle \Delta A \rangle(t) = \int_{t'=0}^t dt' f(t') \tilde{g}(t-t') = \int_{t'=0}^{\infty} dt' f(t') \theta(t-t') \tilde{g}(t-t') = \int_{t'=0}^{\infty} dt' f(t') g(t-t'), \quad (5.3)$$

where $g(t')$ should ideally be independent of $f(t)$, so that the information is characteristic of the system under consideration rather than reflecting just the probe. It might alternatively also be of interest to go beyond this limit and study a strongly perturbed system, this then goes into the realm of ‘non-equilibrium physics’, but we will here focus on the regime of ‘small’ perturbations. A suitable approach for this case is time-dependent perturbation theory.

As was discussed in Advanced Quantum Mechanics, time-dependent perturbation theory starts from a decomposition of the Hamiltonian in Schrödinger picture into a time-independent H_0 and a part containing the time dependence:

$$H(t) = H_0 + V(t). \quad (5.4)$$

One then makes use of the ‘Dirac’-picture, where operators carry the ‘trivial’ time dependence

$$A_D(t, t_0) = e^{\frac{i}{\hbar} H_0(t-t_0)} A_S e^{-\frac{i}{\hbar} H_0(t-t_0)} \quad (5.5)$$

and states $|\phi(t, t_0)\rangle_D = e^{\frac{i}{\hbar} H_0(t-t_0)} |\phi(t, t_0)\rangle_S$ obey

$$\begin{aligned} i\hbar \frac{d}{dt} |\phi(t, t_0)\rangle_D &= i\hbar \frac{d}{dt} \left(e^{\frac{i}{\hbar} H_0(t-t_0)} |\phi(t, t_0)\rangle_S \right) = \\ &= i\hbar \frac{i}{\hbar} H_0 e^{\frac{i}{\hbar} H_0(t-t_0)} |\phi(t, t_0)\rangle_S + e^{\frac{i}{\hbar} H_0(t-t_0)} \underbrace{i\hbar \frac{d}{dt} |\phi(t, t_0)\rangle_S}_{=H(t)|\phi(t, t_0)\rangle_S} \\ &= e^{\frac{i}{\hbar} H_0(t-t_0)} (-H_0 + H(t)) |\phi(t, t_0)\rangle_S = e^{\frac{i}{\hbar} H_0(t-t_0)} V(t) |\phi(t, t_0)\rangle_S = \\ &= \underbrace{e^{\frac{i}{\hbar} H_0(t-t_0)} V(t)}_{=V_D(t)} \underbrace{e^{-\frac{i}{\hbar} H_0(t-t_0)} e^{\frac{i}{\hbar} H_0(t-t_0)} |\phi(t, t_0)\rangle_S}_{=|\phi(t, t_0)\rangle_D} = V_D(t) |\phi(t, t_0)\rangle_D. \end{aligned} \quad (5.6)$$

At time $t = 0$, the states in Dirac-, Heisenberg- and Schrödinger-picture all coincide.

The differential equation for the state cannot be integrated easily, because H_0 and V do not have to commute, so that $V(t)$ at different times definitely does not have to commute. However, one can write a series expansion in powers of V for the time-evolution operator and the gist of *linear* response theory is to keep only terms linear in V , i.e.,

$$U_D(t, t_0) = 1 + \frac{1}{i\hbar} \int_{t'=t_0}^t dt' V_D(t') U_D(t', t_0) = 1 + \frac{1}{i\hbar} \int_{t'=t_0}^t dt' V_D(t') \left(1 + \frac{1}{i\hbar} \int_{t''=t_0}^{t'} dt'' V_D(t'') U_D(t'', t_0) \right)$$

$$\approx 1 - \frac{i}{\hbar} \int_{t'=t_0}^t dt' V_D(t'). \quad (5.7)$$

The advantage of the Dirac picture is that it provides one time-evolution operator (that for the state) in powers of ‘small’ V , so that we see where to make an approximation. (At this point, the discussion of time-dependent perturbation theory in Adv. Qu. Mech. started to go in a different direction.)

We can now calculate the approximate ground-state expectation value of some observable A in the Dirac picture:

$$\begin{aligned} \langle A \rangle(t) &= {}_D \langle \psi_0(t) | A_D(t) | \psi_0(t) \rangle_D = \langle \psi_0(t=0) | U_D(t, t_0)^{-1} A_D(t) U_D(t, t_0) | \psi_0(t=0) \rangle \\ &\approx \langle \psi_0(0) | \left(1 + \frac{i}{\hbar} \int_{t'=0}^t dt' V_D(t') \right) A_D(t) \left(1 - \frac{i}{\hbar} \int_{t''=0}^t dt'' V_D(t'') \right) | \psi_0(0) \rangle \\ &= \langle \psi_0(0) | A_D(t) | \psi_0(0) \rangle + \frac{i}{\hbar} \int_{t'=0}^t dt' \langle \psi_0(0) | (V_D(t') A_D(t) - A_D(t) V_D(t')) | \psi_0(0) \rangle \end{aligned} \quad (5.8)$$

Operators A_D and V_D both have a ‘trivial’ time dependence (5.5) in addition to the ‘explicit’ time dependence of V_D . The quantities on the right-hand side can be seen as obtained in the Heisenberg picture for $H = H_0$, i.e., the first term is the expectation value of A without any perturbation $V(t)$. We now make the further assumption that we can express $\hat{V}_S(t) = f(t)\hat{B}$, i.e., that the explicit time dependence is carried by some ‘number’ that only multiplies a constant operator. This may seem a strict restriction, but applies to many situation, e.g., a magnetic field (number) coupling to spin (constant operator) or an electric field (number) coupling to polarization (constant operator). Expressing the *change* of $\langle A \rangle$ due to $V(t)$ and changing the notation from the Dirac to the Heisenberg picture, we find

$$\begin{aligned} \langle \Delta A \rangle(t) &= \langle A \rangle_{H_0+V(t)} - \langle A \rangle_{H_0} = -\frac{i}{\hbar} \int_{t'=0}^t dt' \langle [A_H(t), V_H(t')] \rangle \\ &= -\frac{i}{\hbar} \int_{t'=0}^t dt' f(t') \langle [A_H(t), B_H(t')] \rangle, \end{aligned} \quad (5.9)$$

where operators A_H and B_H only have ‘trivial’ time dependence.

Comparison to (5.3) allows us now to identify the response function, a so-called ‘retarded Green’s function’,

$$G_{AB}^R(t, t') = -\frac{i}{\hbar} \theta(t - t') \langle [A_H(t), B_H(t')] \rangle, \quad (5.10)$$

where the expectation value can be obtained in the ground state or at finite temperature; we are here going to focus on $T = 0$ for simplicity. Before discussing specific response functions, we now show that Green’s functions can also reasonably be extended to other cases, e.g. where A is not a Hermitian observable, and discuss useful properties common to all Green’s functions.

5.3 Schrödinger Time-evolution Operator and One-particle Green's function

Inspired by Prof. Timm's lecture notes.

One way of treating partial differential equations like the one-particle Schrödinger equation is to find the corresponding Green's function that fulfills

$$\left(i\hbar \frac{d}{dt} - \hat{H}\right) G(\vec{r}, t; \vec{r}', t') = \delta(\vec{r} - \vec{r}') \delta(t - t'), \quad (5.11)$$

because this Green's function then allows us to obtain solutions $\psi(t)$ for arbitrary initial conditions $\psi(t' = 0)$ as

$$\begin{aligned} |\psi(t)\rangle &= G(t, t') |\psi(t')\rangle, \quad \text{resp.} \\ \psi(\vec{r}, t) &= \langle \vec{r} | \psi(t) \rangle = \langle \vec{r} | G(t, t') \int d^3 r' |\vec{r}'\rangle \langle \vec{r}' | \psi(t') \rangle = \int d^3 r' G(\vec{r}, t; \vec{r}', t') \psi(\vec{r}', t'). \end{aligned} \quad (5.12)$$

On the other hand, we know that the time evolution of a Schrödinger state is given by the Schrödinger time-evolution operator $|\psi(t)\rangle = U(t, t') |\psi(t')\rangle$, so that

$$G(\vec{r}, t; \vec{r}', t') = \langle \vec{r} | U(t, t') | \vec{r}' \rangle \quad \text{for } t > t'. \quad (5.13)$$

Since we also know that $i\hbar \frac{d}{dt} U(t, 0) = H U(t, 0)$ and $U(0, 0) = \mathbb{I}$, we can conclude from the right-hand side of (5.11) that a solution is

$$G^R(\vec{r}, t; \vec{r}', t') = -\frac{i}{\hbar} \theta(t - t') \langle \vec{r} | U(t, t') | \vec{r}' \rangle = -\frac{i}{\hbar} \theta(t - t') \langle \vec{r} | e^{-\frac{i}{\hbar} H(t-t')} | \vec{r}' \rangle. \quad (5.14)$$

As this is not the only solution of (5.11), it has here obtained a superscript R in order to denote that this retarded Green's function applies to later times $t > t'$. A different solution is given by the 'advanced' Green's function

$$G^A(\vec{r}, t; \vec{r}', t') = \frac{i}{\hbar} \theta(t' - t) \langle \vec{r} | U(t, t') | \vec{r}' \rangle = \frac{i}{\hbar} \theta(t' - t) \langle \vec{r} | e^{-\frac{i}{\hbar} H(t-t')} | \vec{r}' \rangle, \quad (5.15)$$

which applies to earlier times $t' < t$.

One can reformulate these Green's functions by inserting a sum over eigenstates $|\psi_\nu\rangle$ of H at equal time, where they form a basis (e.g. $|\psi_\nu(t = 0)\rangle$ at time $t = 0$) and finds

$$\begin{aligned} G^{R/A}(\vec{r}, t; \vec{r}', t') &= \pm \frac{i}{\hbar} \theta(\pm(t - t')) \sum_\nu \langle \vec{r} | \psi_\nu(0) \rangle e^{-\frac{i}{\hbar} E_\nu(t-t')} \langle \psi_\nu(0) | \vec{r}' \rangle = \\ &= \pm \frac{i}{\hbar} \theta(\pm(t - t')) \sum_\nu \underbrace{e^{-\frac{i}{\hbar} E_\nu t} \langle \vec{r} | \psi_\nu(0) \rangle}_{=\psi_\nu(\vec{r}, t)} \underbrace{e^{\frac{i}{\hbar} E_\nu t'} \langle \psi_\nu(0) | \vec{r}' \rangle}_{=\psi_\nu^*(\vec{r}', t')} = \\ &= \pm \frac{i}{\hbar} \theta(\pm(t - t')) \sum_\nu \psi_\nu^*(\vec{r}', t') \psi_\nu(\vec{r}, t). \end{aligned} \quad (5.16)$$

The Green's function for the one-particle Schrödinger equation gives the wave function at time t and position \vec{r} from that at t' and \vec{r}' , it 'propagates' the electronic wave function and is consequently also called 'propagator'. The aim is to generalize this concept to the

many-body case. As we have seen in Sec. 4.4 that non-interacting electrons can be treated almost like a single particle, consistency requires the many-body version of this Green's function to become equivalent to the single-particle result (5.16).

It turns out that the following gives the desired result:

$$G^R(\vec{r}, t; \vec{r}', t') = -\frac{i}{\hbar}\theta(t-t')\langle GS | [\hat{\psi}(\vec{r}, t), \hat{\psi}^\dagger(\vec{r}', t')]_{\pm} | GS \rangle. \quad (5.17)$$

The expectation value is here again obtained in the (many-body) ground state $|GS\rangle$, $\hat{\psi}(\vec{r}, t)$ and $\hat{\psi}^\dagger(\vec{r}', t')$ are field operators and the choice of the *anticommutator* yields the correct single-particle behavior in the case of fermions.

We use (5.1) to express field operators in terms of creators/annihilators of particles in states ν . The time-dependent Heisenberg field operators contain time-dependent creation/annihilation operators, whose time dependence is in turn particularly simple for *non-interacting* particles, where (5.2) holds and

$$i\hbar \frac{d}{dt} a_\nu(t) = [a_\nu, H_0](t) = \epsilon_\nu a_\nu \quad \Rightarrow \quad a_\nu(t) = e^{-\frac{i}{\hbar}\epsilon_\nu t} a_\nu(t=0) \quad (5.18)$$

$$\text{resp. } a_\nu^\dagger(t) = e^{\frac{i}{\hbar}\epsilon_\nu t} a_\nu^\dagger(t=0). \quad (5.19)$$

Note that this equation of motion breaks down for Hamiltonians including interactions and the integration can then not be carried out analytically! However, as long as (5.2) holds, the Green's function becomes

$$\begin{aligned} G^R(\vec{r}, t; \vec{r}', t') &= -\frac{i}{\hbar}\theta(t-t') \sum_{\mu, \nu} \psi_\mu(\vec{r}, 0) \psi_\nu^*(\vec{r}', 0) \langle GS | [a_\mu(t), a_\nu^\dagger(t')]_{\pm} | GS \rangle = \\ &= -\frac{i}{\hbar}\theta(t-t') \sum_{\mu, \nu} \psi_\mu(\vec{r}, 0) \psi_\nu^*(\vec{r}', 0) e^{-\frac{i}{\hbar}\epsilon_\mu t} e^{\frac{i}{\hbar}\epsilon_\nu t'} \underbrace{\langle GS | [a_\mu(t=0), a_\nu^\dagger(t'=0)]_{\pm} | GS \rangle}_{=\delta_{\nu\mu}} = \\ &= -\frac{i}{\hbar}\theta(t-t') \sum_{\nu} \psi_\nu(\vec{r}, t) \psi_\nu^*(\vec{r}', t'). \end{aligned} \quad (5.20)$$

We find here for non-interacting particles indeed the first-quantization single-particle result (5.14), as long as the many-body Green's function for fermions contains the anti-commutator.

The Green's function (5.17) with field operators is related to the Green's function for the Schrödinger equation in position space. It is equally possible to define second-quantization Green's functions based on other bases than $|\vec{r}\rangle$, starting from the Schrödinger equation written in such an alternative basis, e.g. (crystal-)momentum rather than position. The corresponding Green's function is then given by matrix elements of the time-evolution operator that are analogous to (5.13), but use the basis of choice, e.g., for a basis ν :

$$G^{R/A}(\nu, t; \nu', t') = \mp \frac{i}{\hbar}\theta(t-t') \langle \nu | U(t, t') | \nu' \rangle. \quad (5.21)$$

The “many-body” version involves creation/annihilation operators a_ν^\dagger and a_ν with this basis ν . As an example, the natural path to proceed from the Schrödinger equation (4.8) for Bloch states leads to Bloch particles with indices for band, momentum and spin and a Green's function

$$G^R(n, \vec{k}, \sigma, t; n', \vec{k}', \sigma', t') = -\frac{i}{\hbar}\theta(t-t') \langle GS | \left[a_{n, \vec{k}, \sigma}(t), a_{n', \vec{k}', \sigma'}^\dagger(t') \right]_{\pm} | GS \rangle. \quad (5.22)$$

5.3.1 Green's "functions" as operators

Finally, a certain dichotomy arises in the use of - in particular "one-particle" - Green's functions. On one hand, Eqs. (5.14) and (5.21) give them as matrix elements, which makes them functions of some parameters (\vec{r} and \vec{r}' or ν and ν' in addition to t and t'). Green's functions are indeed often discussed as functions, e.g., a later section will discuss their analytic properties. On the other hand, their strong relation to the time-evolution *operator* leads to a second way of using them: The whole operator, whose matrix elements we discussed, can also be referred to as a Green's "function". With hats for emphasis this gives in "first quantization"

$$\hat{G}^{R/A}(t; t') = \mp \frac{i}{\hbar} \theta(t - t') \hat{U}(t, t') \quad (5.23)$$

resp. a matrix with elements

$$\{\hat{G}^{R/A}(t; t')\}_{\nu, \mu} = \mp \frac{i}{\hbar} \theta(t - t') \langle GS | [a_\nu(t), a_\mu^\dagger(t')]_{\pm} | GS \rangle \quad (5.24)$$

in second quantization.

5.4 Tools, Rules, and Technical Details concerning Green's functions

5.4.1 Advanced and Causal Green's functions

The retarded Green's (5.14) function describing solutions of the first-quantization Schrödinger equation at later times $t > t'$ has a counter part (5.15) for earlier times $t < t'$. The counter part also quite analogously generalizes to Green's function in a many-body settings, i.e., the 'advanced' counter part to (5.17) becomes

$$G^A(\vec{r}, t; \vec{r}', t') = + \frac{i}{\hbar} \theta(t' - t) \langle GS | [\hat{\psi}(\vec{r}, t), \hat{\psi}^\dagger(\vec{r}', t')]_{\pm} | GS \rangle \quad (5.25)$$

and that to (5.10) is of course

$$G_{AB}^A(t, t') = \frac{i}{\hbar} \theta(t' - t) \langle [A_H(t), B_H(t')] \rangle. \quad (5.26)$$

A third variant is the 'causal' Green's function defined using a variant of the time-order operator T_ϵ that puts the earlier operator to the right and additionally gives a minus sign for $t' > t$ and those Green's functions that use the anti-commutator. Combining one-particle and response quantities into a formula for general operators A and B , it is:

$$\begin{aligned} G_{AB}^C(t, t') &= -\frac{i}{\hbar} \langle T_\epsilon(A_H(t), B_H(t')) \rangle = \begin{cases} -\frac{i}{\hbar} \langle A_H(t) B_H(t') \rangle & \text{for } t > t' \\ \pm \frac{i}{\hbar} \langle B_H(t') A_H(t) \rangle & \text{for } t' > t \end{cases} = \\ &= -\frac{i}{\hbar} \theta(t - t') \langle A_H(t) B_H(t') \rangle \pm \frac{i}{\hbar} \theta(t' - t) \langle B_H(t') A_H(t) \rangle. \end{aligned} \quad (5.27)$$

The plus sign (which implies a sign change due to T_ϵ) is here chosen for anti-commutator Green's functions and the minus sign for commutator Green's functions.

5.4.2 Equation of Motion, Frequency Domain

Based on Nolting's textbook.

One way to calculate Green's functions is based on their equation of motion. For any retarded Green's function, response functions (5.10) or one-particle propagators (5.17), the time derivative is given by the equation of motion in the Heisenberg picture

$$\begin{aligned}
 i\hbar \frac{d}{dt} G_{AB}^R(t, t') &= \delta(t-t') \langle [A(t), B(t)]_{\pm} \rangle + \theta(t-t') \langle \left[\frac{d}{dt} A(t), B(t') \right]_{\pm} \rangle = \\
 &= \delta(t-t') \langle [A(t), B(t)]_{\pm} \rangle - \frac{i}{\hbar} \theta(t-t') \langle [[A, H](t), B(t')]_{\pm} \rangle = \\
 &= \delta(t-t') \langle [A(t), B(t)]_{\pm} \rangle + G_{[A, H]B}^R(t, t') \quad (5.28)
 \end{aligned}$$

Note that the time derivative of an operator always yields the commutator, even for fermion operators. The time derivative of the Green's function is here expressed in terms of some other Green's function. In general, $G_{[A, H]B}^R$ is rather more complicated than G_{AB}^R itself, but it may offer a starting point for some approximation.

It is easy to verify that the advanced Green's function G^A obeys the same equation of motion, as does the causal Green's function of Eq. (5.27). The different Green's functions, see Sec. 5.4.1, obey however different boundary conditions, namely

$$\begin{aligned}
 G^R(t < t') &= 0 \quad (5.29) \\
 G^A(t > t') &= 0 \quad \text{and} \\
 G^C &= \begin{cases} -\frac{i}{\hbar} \langle A_H(t) B_H(t') \rangle & \text{for } t > t' \\ \pm \frac{i}{\hbar} \langle B_H(t') A_H(t) \rangle & \text{for } t' > t \end{cases} .
 \end{aligned}$$

It is now convenient to note that unless the system's Hamiltonian H (which becomes the H_0 of the linear-response scenario) itself carries some time dependence (in addition to that covered by $V(t)$), both response functions and one-particle Green's functions only depend on the time *difference* $t - t'$, but not on t and t' separately. The equal-time commutator in (5.28) then no longer depends on time at all. It is then often convenient to replace the single time variable $t - t'$ by a frequency, i.e., to Fourier transform Green's functions. The exact definitions used vary in the literature when it comes to where 2π or \hbar go, but one possibility is

$$f(\omega) = \int_{-\infty}^{\infty} dt f(t) e^{i\omega t} \quad \text{and} \quad (5.30)$$

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega f(\omega) e^{-i\omega t} \quad \text{resp.} \quad (5.31)$$

$$f(t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dE f(E) e^{-i\frac{E}{\hbar}t} \quad \text{with} \quad f(E) = f(\hbar\omega) . \quad (5.32)$$

$$(5.33)$$

With the usual replacement $i\hbar \frac{d}{dt} \rightarrow \hbar\omega$, the equation of motion in frequency space becomes the algebraic equation

$$\hbar\omega G_{AB}^R(\omega) = \langle [A, B]_{\pm} \rangle + G_{[A, H]B}^R(\omega) . \quad (5.34)$$

A notation used on the Nolting book for Green's functions, $G_{A,B}^{R/A/C}(\omega) = \langle\langle A; B \rangle\rangle^{R/A/C}(\omega)$ can be useful.

5.4.2.1 Example: Green's function for non-interacting particles

As an example, let us discuss non-interacting particles whose one-particle Hamiltonian has known eigenvalues ϵ_ν , i.e., $H = \sum_\nu \epsilon_\nu a_\nu^\dagger a_\nu$. The index ν might also stand for a combination of crystal momentum \vec{k} , band n and spin σ . The equation of motion for the Green's function is then

$$\begin{aligned} \hbar\omega G_{a_\nu; a_\mu^\dagger}^{R/A}(\omega) &= \hbar\omega G^{R/A}(\nu, \mu, \omega) = \langle [a_\nu, a_\mu^\dagger]_\pm \rangle + G_{[a_\nu, H]; a_\mu^\dagger}^{R/A}(\omega) = \\ &= \delta_{\nu, \mu} + G_{\epsilon_\nu a_\nu; a_\mu^\dagger}^{R/A}(\omega) = \delta_{\nu, \mu} + \epsilon_\nu G^{R/A}(\nu, \mu, \omega), \end{aligned} \quad (5.35)$$

where we use the fact that a Green's function is composed of expectation values of (anti-)commutators, both linear operations, so that for a number ϵ_ν , $G_{\epsilon_\nu a_\nu; a_\mu^\dagger}^{R/A}(\omega) = \epsilon_\nu G_{a_\nu; a_\mu^\dagger}^{R/A}(\omega) = \epsilon_\nu G^{R/A}(\nu, \mu, \omega)$. The Green's function then becomes

$$G^{R/A}(\nu, \mu, \omega) = \frac{\delta_{\nu, \mu}}{\hbar\omega - \epsilon_\nu} \quad \text{resp.} \quad G^{R/A}(\omega) = (\hbar\omega - H)^{-1}. \quad (5.36)$$

Since $G^R(t)$ and $G^A(t)$ both obey (5.28), they both fulfill the same algebraic equation, which implies (formally) the same result. The impact of the different boundary conditions (5.29) on $G^R(\omega)$ and $G^A(\omega)$ is discussed in the following subsection Sec. 5.4.2.2.

As Eq. (5.36) is a matrix equation, it should hold in any basis, not just in its eigenbasis. This is indeed true, as can be shown in analogy to (5.35), but starting from the more general one-particle Hamiltonian $H = \sum_{\nu, \mu} h_{\nu, \mu} a_\nu^\dagger a_\mu$:

$$\begin{aligned} \hbar\omega G^{R/A}(\nu, \mu, \omega) &= \langle [a_\nu, a_\mu^\dagger]_\pm \rangle + G_{[a_\nu, H]; a_\mu^\dagger}^{R/A}(\omega) = \delta_{\nu, \mu} + \sum_{\nu', \mu'} h_{\nu', \mu'} G_{[a_\nu, a_{\nu'}^\dagger, a_{\mu'}]; a_\mu^\dagger}^{R/A}(\omega) = \\ &= \delta_{\nu, \mu} + \sum_{\nu', \mu'} h_{\nu', \mu'} \delta_{\nu, \nu'} G^{R/A}(\mu', \mu, \omega) = \delta_{\nu, \mu} + \left\{ H G^{R/A}(\omega) \right\}_{\nu, \mu}, \end{aligned} \quad (5.37)$$

where $\{H G^{R/A}(\omega)\}_{\nu, \mu}$ denotes a matrix element of the product $H G^{R/A}$ given by the application of the one-particle Hamiltonian (just the matrix elements, not including the creation/annihilation operators) to the matrix of Green's functions. This uses the ‘‘Green's functions as operator’’ picture mentioned in Sec. 5.3.1.

5.4.2.2 Slight shift of ω off the real axis to ensure convergence

The result above is in principle fine, but omits a detail that merits discussion: For strictly real ω , the integrals defining the Fourier transform of $G^{R/A}(t - t')$ might not converge. Since $|\langle [A(t - t'), B(0)] \rangle|$ can remain constant for large $|t - t'|$, see e.g. (5.20), the boundaries $t - t' \rightarrow \pm\infty$ arising in the integrals for G^R and G^A give ill-defined results. A solution is to introduce a factor ensuring convergence, implying Fourier transforms

$$G^R(\omega) = \lim_{\eta \rightarrow 0} \int_{-\infty}^{\infty} dt G^R(t) e^{i\omega t} e^{-\eta t} = \lim_{\eta \rightarrow 0} \int_0^{\infty} dt G^R(t) e^{i(\omega + i\eta)t} = \lim_{\eta \rightarrow 0} G^R(\omega + i\eta) \quad (5.38)$$

$$G^A(\omega) = \lim_{\eta \rightarrow 0} \int_{-\infty}^0 dt G^R(t) e^{i(\omega - i\eta)t} = \lim_{\eta \rightarrow 0} G^A(\omega - i\eta). \quad (5.39)$$

As $G^{R/A}$ starts/ends at $t = 0$, the small η needs to ensure convergence only for positive (G^R) or negative (G^A) t and has opposite sign for the two Green's functions. On physical grounds, we justify the presence of η by arguing that it only affects infinite time while relevant times are possibly very large, but finite. Mathematically, the limit $\lim_{\eta \rightarrow 0}$ usually makes sense.

Functions G^R and G^A can be defined for complex ω as well, and in fact, a convenient way to see them is to note that G^R is well defined (and analytic) for any ω with positive imaginary part while G^A is well defined for $\mathcal{I}(\omega) < 0$. G^C has poles both for negative and for positive imaginary parts: a similar analysis as the one presented here reveals that the real and imaginary parts of the poles have opposite sign. The different boundary conditions in time-domain, see Eq. (5.29) thus imply different analyticity in frequency space.

Emphasizing again real frequencies, the non-interacting Green's function (5.36) becomes

$$G^R(\nu, \mu, \omega) = \lim_{\eta \rightarrow 0} \frac{\delta_{\nu, \mu}}{\hbar\omega - \epsilon_\nu + i\eta} \quad \text{and} \quad G^A(\nu, \mu, \omega) = \lim_{\eta \rightarrow 0} \frac{\delta_{\nu, \mu}}{\hbar\omega - \epsilon_\nu - i\eta}. \quad (5.40)$$

The limit $\lim_{\eta \rightarrow 0}$ is very often not explicitly written, a notation $\pm i\eta$, $\pm i\delta$ or $\pm 0^+$ in this context usually means an arbitrarily small shift off the real axis.

5.4.3 Lehmann representation and Spectral Density

Based on Nolting's textbook.

The Lehmann (or 'spectral') representation uses excitation energies and matrix elements of operators A and B to express Green's functions. It is useful for some applications, especially in numerics, and also helps in understanding a few features of Green's functions, especially their relation to excitations.

All types of Green's functions build on expectation values of correlation functions $\langle A(t - t')B(0) \rangle$, which can be expressed using eigenstates $|m\rangle$ and eigenenergies E_m . With ground state $|GS\rangle$ and ground-state energy E_0 , one finds in the Heisenberg picture

$$\begin{aligned} \langle A(t - t')B(0) \rangle &= \sum_m \langle GS | e^{\frac{i}{\hbar}H(t-t')} A(0) e^{-\frac{i}{\hbar}H(t-t')} |m\rangle \langle m|B(0)|GS\rangle = \\ &= \sum_m e^{-\frac{i}{\hbar}(E_m - E_0)(t-t')} \langle GS|A|m\rangle \langle m|B|GS\rangle \quad \text{and} \end{aligned} \quad (5.41)$$

$$\langle B(0)A(t - t') \rangle = \sum_m e^{+\frac{i}{\hbar}(E_m - E_0)(t-t')} \langle GS|B|m\rangle \langle m|A|GS\rangle. \quad (5.42)$$

Another natural quantity is the 'spectral density' given by the (anti-)commutator. The Fourier transform simply replaces the exponentials by δ distributions, yielding

$$S_{AB}(t) = \frac{1}{2\pi} \langle [A(t), B(0)]_{\pm} \rangle \quad (5.43)$$

$$S_{AB}(\omega) = \sum_m \left(\delta\left(\omega - \frac{E_m - E_0}{\hbar}\right) \langle GS|A|m\rangle \langle m|B|GS\rangle \right) \quad (5.44)$$

$$\pm \delta\left(\omega + \frac{E_m - E_0}{\hbar}\right) \langle GS|B|m\rangle \langle m|A|GS\rangle \Big).$$

The 2π in the time-dependent function is related to the Fourier transform (5.31). This quantity gives a signal at energy $E_m - E_0$ if the corresponding matrix element is non-zero, which is in turn the case if operators A and B connect the ground state to an excited state $|m\rangle$. They can then be seen to create/remove an excitation with energy $E_m - E_0$. Very often $B = A^\dagger$, examples are the one-particle Green's function $G(\vec{k}, n, \sigma; \omega)$ for Bloch electrons (5.22), but also the response of magnetization to a magnetic field, because the latter adds a term proportional to the magnetization to the Hamiltonian. In these cases, $S_{AB}(\omega)$ is real and $S_{AB}(\omega) \geq 0$.

To obtain retarded and advanced Green's functions from the spectral density, we simply have to multiply with $\theta(\pm t)$, resp. to convolute with the Fourier transform of the step function. The latter is given by

$$f_\pm(t) = \mp i\theta(\pm t) \quad \Rightarrow \quad f_\pm(\omega) = \lim_{\eta \rightarrow 0} \frac{1}{\omega \pm i\eta}, \quad (5.45)$$

so that one finds

$$G^{R/A}(\omega) = \int d\omega' S_{AB}(\omega') f_\pm(\omega - \omega') = \lim_{\eta \rightarrow 0} \int d\omega' \frac{S_{AB}(\omega')}{\omega - \omega' \pm i\eta} = \quad (5.46)$$

$$= \lim_{\eta \rightarrow 0} \sum_m \left(\frac{\langle GS|A|m\rangle \langle m|B|GS\rangle}{\omega - \frac{E_m - E_0}{\hbar} \pm i\eta} \pm \frac{\langle GS|B|m\rangle \langle m|A|GS\rangle}{\omega + \frac{E_m - E_0}{\hbar} \pm i\eta} \right). \quad (5.47)$$

The plus (minus) signs refer to the retarded (advanced) Green's function. One here clearly sees that $G^R(\omega)$ ($G^A(\omega)$) is analytic for $\mathcal{I}(\omega) > 0$ ($\mathcal{I}(\omega) < 0$).

In the case of the causal Green's function, it is easier to start from the correlation functions and one obtains

$$G^c(\omega) = \lim_{\eta \rightarrow 0} \sum_m \left(\frac{\langle GS|A|m\rangle \langle m|B|GS\rangle}{\omega - \frac{E_m - E_0}{\hbar} + i\eta} \pm \frac{\langle GS|B|m\rangle \langle m|A|GS\rangle}{\omega + \frac{E_m - E_0}{\hbar} - i\eta} \right), \quad (5.48)$$

i.e., its poles $\tilde{\omega}$ have $\mathcal{I}(\tilde{\omega}) < 0$ when $\mathcal{R}(\tilde{\omega}) > 0$ and at $\mathcal{I}(\tilde{\omega}) > 0$ when $\mathcal{R}(\tilde{\omega}) < 0$.

5.4.3.1 Example: Spectral density for non-interacting particles

With $A = a_\nu$ and $B = a_\mu^\dagger$ and ν, μ denoting eigenstates of the one-particle Hamiltonian $H = \sum_\nu \epsilon_\nu a_\nu^\dagger a_\nu$, the spectral density (5.44) is

$$S(\nu, \mu; \omega) = \sum_m \left(\delta\left(\omega - \frac{E_m - E_0}{\hbar}\right) \langle GS|a_\nu|m\rangle \langle m|a_\mu^\dagger|GS\rangle \right. \\ \left. + \delta\left(\omega + \frac{E_m - E_0}{\hbar}\right) \langle GS|a_\mu^\dagger|m\rangle \langle m|a_\nu|GS\rangle \right), \quad (5.49)$$

where the ground state $|GS\rangle$ is the Fermi sea. In the first term, a_μ^\dagger can only create a particle if that state is empty in the ground state, i.e., if $\epsilon_\mu > E_F$. In that case, the only difference between the ground state and excited state $|m\rangle$ is that μ is occupied in $|m\rangle$, which gives the

energy $E_m = E_0 + \epsilon_\mu - \mu$. There is only one relevant excited state $|m\rangle = a_\mu^\dagger|GS\rangle$, i.e., the sum over m gives only one non-zero contribution, for which $|\langle m|a_\mu^\dagger|GS\rangle| = 1$. a_ν has to annihilate this extra particle in order to give non-zero overlap with the ground state bra, which implies $\nu = \mu$. In the second term, a_ν can analogously only act if $\epsilon_\nu < E_F$, $E_m = E_0 - (\epsilon_\nu - \mu)$ and again $\nu = \mu$.

These considerations yield

$$\begin{aligned} S(\nu, \mu; \omega) &= \left(\delta\left(\omega - \frac{\epsilon_\mu - \mu}{\hbar}\right) \delta_{\nu, \mu} \theta(\epsilon_\mu - E_F) + \delta\left(\omega + \frac{-(\epsilon_\mu - \mu)}{\hbar}\right) \delta_{\nu, \mu} \theta(E_F - \epsilon_\mu) \right), \\ &= \delta_{\nu, \mu} \delta\left(\omega - \frac{\epsilon_\mu - \mu}{\hbar}\right) \underbrace{(\theta(\epsilon_\mu - E_F) + \theta(E_F - \epsilon_\mu))}_{=1}. \end{aligned} \quad (5.50)$$

The ‘‘one-particle spectral density’’ of a non-interacting electron gas thus has delta peaks at the one-particle eigenenergies, both for occupied and empty states. It does consequently not depend on temperature either.

Specifying the quantum state ν by momentum \vec{k} , band index n and spin σ , one can also write the spectral density as a function of momentum:

$$S_{n, \sigma}(\vec{k}, \omega) = \delta\left(\omega - \frac{\epsilon_n(\vec{k}) - \mu}{\hbar}\right). \quad (5.51)$$

The delta-peaks follow here the band structure. A spectral density $S_{n, \sigma}(\vec{r}, \vec{r}'; \omega)$ as a function of position can be obtained either by Fourier transforming $S_{n, \sigma}(\vec{k}, \omega)$ or by inserting position-dependent operators (a_i and a_j^\dagger for Wannier states or $\hat{\psi}(\vec{r})$ and $\hat{\psi}^\dagger(\vec{r}')$ for field operators) into (5.44). Note that a spectral density obtained from operators that do not create/annihilate particles in eigenstates is usually not diagonal, i.e. $S(i, j; \omega) \neq 0$ for $i \neq j$, so that $A^\dagger = B$ does not have to hold and $S(i, j; \omega)$ can become complex.

5.4.4 Some exact Relations, Kramers-Kronig

Based on Nolting’s textbook.

For $\omega \rightarrow \infty$, $G^{R/A} \propto \frac{1}{\omega}$. An intuitive reason is that we might only consider states up to a certain excitation energy, to that only such a tail survives for large ω . (The Hamiltonian for a solid allows in principle empty free-electron states at arbitrarily high energies, but we are not interested in those.)

We will use the Dirac identity

$$\frac{1}{x - x_0 \pm i\delta} = \mathcal{P} \frac{1}{x - x_0} \mp i\pi \delta(x - x_0) \quad \text{resp.} \quad \int dx \frac{f(x)}{x - x_0 \pm i\delta} = \mathcal{P} \int dx \frac{f(x)}{x - x_0} \mp i\pi f(x_0), \quad (5.52)$$

where the ‘principal value’ can then be obtained by a simultaneous limit on the left- and right-hand sides. (As a consequence, positive and negative divergencies tend to cancel as long as $f(x \approx x_0)$ is smooth, and the principal-value integral converges more easily.)

We define the function

$$f^{R/A}(\omega', \omega) = \frac{G^{R/A}(\omega')}{\omega' - \omega \pm i\delta}, \quad (5.53)$$

with the the + sign for G^R and f^R and the minus sign for G^A and f^A . For a fixed real ω , f^R (f^A) as a function of ω' has poles with negative (positive) imaginary part.

Keeping real ω fixed, we then integrate this function $f^{R/A}(\omega')$ over a closed path that goes over the real axis from $\omega' = -\infty$ to $\omega' = +\infty$ and then back in a semi circle at positive (negative) imaginary numbers. Since the retarded (advanced) Green's function is analytic for $\mathcal{I}(\omega') \geq 0$ ($\mathcal{I}(\omega') \leq 0$), this integral has to vanish. Since $G^{R/A} \propto \frac{1}{\omega'}$ and $f^{R/A} \propto \frac{1}{(\omega')^2}$ for large ω' , the integral over the semi circle vanishes by itself. Consequently, the integral over the real axis has to vanish likewise, giving

$$0 = \int_{-\infty}^{\infty} d\omega' \frac{G^{R/A}(\omega')}{\omega' - \omega \pm i\delta} = \mathcal{P} \int_{-\infty}^{\infty} d\omega' \frac{G^{R/A}(\omega')}{\omega' - \omega} \mp i\pi G^{R/A}(\omega)$$

$$G^{R/A}(\omega) = \pm \frac{i}{\pi} \mathcal{P} \int_{-\infty}^{\infty} d\omega' \frac{G^{R/A}(\omega')}{\omega - \omega'}. \quad (5.54)$$

Of course, real and imaginary part each have to be 0, which allows us to write relations between imaginary and real part of $G^{R/A}(\omega)$ for real ω :

$$\mathcal{R}(G^{R/A}(\omega)) = \mp \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} d\omega' \frac{\mathcal{I}(G^{R/A}(\omega'))}{\omega - \omega'} \quad (5.55)$$

$$\mathcal{I}(G^{R/A}(\omega)) = \pm \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} d\omega' \frac{\mathcal{R}(G^{R/A}(\omega'))}{\omega - \omega'}. \quad (5.56)$$

These so-called *Kramers-Kronig relations* hold for Green's functions defined from arbitrary operators A and B and allow us to know the full Green's function from just the real or just the imaginary part. For $B = A^\dagger$, $S_{AB}(\omega)$ is real and $S_{AB}(\omega) \geq 0$. In this case, expressions for the imaginary and real parts can be obtained directly from (5.46) by use of (5.52):

$$\mathcal{R}(G^{R/A}(\omega)) = \mathcal{P} \int_{-\infty}^{\infty} d\omega' \frac{S(\omega')}{\omega - \omega'} \quad (5.57)$$

$$\mathcal{I}(G^{R/A}(\omega)) = \mp \pi S(\omega) \quad (5.58)$$

For real S_{AB} , similar relations can moreover be obtained from (5.48) for the causal Green's function:

$$\mathcal{R}(G^C(\omega)) = \mathcal{R}(G^R(\omega)) = \mathcal{R}(G^A(\omega)) = \mathcal{P} \int_{-\infty}^{\infty} d\omega' \frac{S(\omega')}{\omega - \omega'} \quad (5.59)$$

$$\mathcal{I}(G^C(\omega)) = -\text{sgn}(\omega)\pi S(\omega) \quad (5.60)$$

5.4.5 “The” Green's function: Causal one particle Green's function

Even though much of the formalism can be applied to Green's functions involving general operators and to retarded/advanced Green's functions, a special place is held by the causal “one-particle” Green's function, i.e., by (5.27) or its spectral representation (5.48).

Let us for illustration obtain the causal free-electron Green's function from Eq. (5.48), in analogy to the spectral density of Sec. 5.4.3.1:

$$\begin{aligned}
G_{\nu,\mu}^c(\omega) &= \lim_{\eta \rightarrow 0} \sum_m \left(\frac{\langle GS|a_\nu|m\rangle\langle m|a_\mu^\dagger|GS\rangle}{\omega - \frac{E_m - E_0}{\hbar} + i\eta} + \frac{\langle GS|a_\mu^\dagger|m\rangle\langle m|a_\nu|GS\rangle}{\omega + \frac{E_m - E_0}{\hbar} - i\eta} \right) = \\
&= \lim_{\eta \rightarrow 0} \left(\frac{\theta(\epsilon_\mu - \mu)\delta_{\nu,\mu}}{\omega - \frac{\epsilon_\mu - \mu}{\hbar} + i\eta} + \frac{\theta(\mu - \epsilon_\mu)\delta_{\nu,\mu}}{\omega + \frac{-(\epsilon_\mu - \mu)}{\hbar} - i\eta} \right) = \delta_{\nu,\mu} \lim_{\eta \rightarrow 0} \left(\underbrace{\frac{\theta(\epsilon_\mu - \mu)}{\omega - \frac{\epsilon_\mu - \mu}{\hbar} + i\eta}}_{>0} + \underbrace{\frac{\theta(\mu - \epsilon_\mu)}{\omega - \frac{\epsilon_\mu - \mu}{\hbar} - i\eta}}_{<0} \right),
\end{aligned} \tag{5.61}$$

where we again see that poles occur for both positive and negative imaginary parts of ω . To be specific, (empty) states with $\epsilon_\nu > \mu$ have poles with $\mathcal{I}(\omega) < 0$ and (occupied) states with $\epsilon_\nu < \mu$ have poles with $\mathcal{I}(\omega) > 0$.

While it is most natural to express the Green's function in terms of eigenstates of the corresponding one-particle Hamiltonian (e.g. Bloch states), one may occasionally want to write them for a general basis (e.g. position space). Let us discuss the example of field operators, i.e., the independent-electron Green's function in position space. Expanding the field operators according to Eq. (5.1), we find

$$\begin{aligned}
G^c(\omega, \vec{r}, \vec{r}') &= \lim_{\eta \rightarrow 0} \sum_m \left(\frac{\langle GS|\hat{\psi}(\vec{r})|m\rangle\langle m|\hat{\psi}^\dagger(\vec{r}')|GS\rangle}{\omega - \frac{E_m - E_0}{\hbar} + i\eta} + \frac{\langle GS|\hat{\psi}^\dagger(\vec{r}')|m\rangle\langle m|\hat{\psi}(\vec{r})|GS\rangle}{\omega + \frac{E_m - E_0}{\hbar} - i\eta} \right) = \\
&= \lim_{\eta \rightarrow 0} \sum_m \sum_{\nu,\mu} \psi_\nu(\vec{r})\psi_\mu^*(\vec{r}') \left(\frac{\langle GS|a_\nu|m\rangle\langle m|a_\mu^\dagger|GS\rangle}{\omega - \frac{E_m - E_0}{\hbar} + i\eta} + \frac{\langle GS|a_\mu^\dagger|m\rangle\langle m|a_\nu|GS\rangle}{\omega + \frac{E_m - E_0}{\hbar} - i\eta} \right) = \\
&= \sum_{\nu,\mu} \psi_\nu(\vec{r})\psi_\mu^*(\vec{r}')G_{\nu,\mu}^c = \sum_\nu \psi_\nu(\vec{r})\psi_\nu^*(\vec{r}')G_{\nu,\nu}^c.
\end{aligned} \tag{5.62}$$

The result amounts thus to the applying the same basis transformation that we used in Eq. (5.1) to the Green's function. (E.g. a Fourier transform from momentum to position spaces with $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}$.)

5.5 From particle to quasi particle, self energy, Fermi liquid

5.5.1 Dyson equation and self-energy for one-particle problems

Inspired by Prof. Timm's lecture notes.

As a first illustration, we first discuss a non-interacting impurity problem. Loss of translational invariance is enough of an issue to make methods used for interacting particles (perturbation theory, the concept of a self energy) useful. On the other hand, a noninteracting problem is still much simpler than an interacting one, helping us to understand the solution.

We assume that the Hamiltonian has two parts $H = H_0 + V$, of which the first is already diagonal:

$$H_0 = \sum_{\nu \neq 0} \epsilon_\nu a_\nu^\dagger a_\nu + \epsilon_0 a_0^\dagger a_0 \tag{5.63}$$

Presumably, we were able to diagonalize the ν levels by use of translational invariance, state 0 describes an impurity. The second part V couples the impurity to the other levels:

$$V = \sum_{\nu \neq 0} \left(t_{\nu}^* a_{\nu}^{\dagger} a_0 + t_{\nu} a_0^{\dagger} a_{\nu} \right). \quad (5.64)$$

Clearly, the eigenstates of H_0 are no longer eigenstates of H . We would like to diagonalize the full system H , but if it is too large, the loss of translational invariance may keep us from doing this. As a way out, we look at the Green's functions.

Fourier transforming Eq. (5.11) into frequency space yields

$$(\hbar\omega - \hat{H}) G(\omega) = (\hbar\omega - H_0 - V) G(\omega) = 1 \quad (5.65)$$

$$\text{and } (\hbar\omega - H_0) G_0(\omega) = 1, \quad (5.66)$$

where G and G_0 are the Greens functions corresponding to H and H_0 . These can be rewritten to

$$G_0^{-1} = \hbar\omega - H_0 \quad \text{and} \quad G^{-1} = \hbar\omega - H_0 - V \quad (5.67)$$

$$\text{resp. } G^{-1} = G_0^{-1} - V, \quad (5.68)$$

i.e., we obtain the ‘‘full’’ Green’s function G in terms of the ‘‘unperturbed’’ one G_0 and the perturbation V . One can then go on to express G as a series in powers of V :

$$G_0 G_0^{-1} G = G = G_0 (G^{-1} + V) G = G_0 + G_0 V G = G_0 + G_0 V (G_0 + G_0 V G) = \dots \quad (5.69)$$

This is again a variant of the Dyson series that arises similarly in many instances.

The second approach that we introduce here is the ‘self energy’. To do so, we focus on the impurity state 0 itself, i.e., we try to obtain Green’s function $G_{0,0}^R(\omega)$. As we still have non-interacting electrons, its equation of motion (5.34) is of the same form as (5.37):

$$(\hbar\omega + i\eta) G_{0,0}^R(\omega) = 1 + \epsilon_0 G_{0,0}^R(\omega) + \sum_{\nu} t_{\nu}^* G_{\nu,0}^R(\omega), \quad (5.70)$$

where we also need

$$(\hbar\omega + i\eta) G_{\nu,0}^R(\omega) = 0 + \epsilon_{\nu} G_{\nu,0}^R(\omega) + t_{\nu} G_{0,0}^R(\omega) \quad \Rightarrow \quad G_{\nu,0}^R(\omega) = \frac{t_{\nu} G_{0,0}^R(\omega)}{\hbar\omega - \epsilon_{\nu} + i\eta} \quad (5.71)$$

which we plug into (5.70). One then finds the full impurity Green’s function

$$\begin{aligned} (\hbar\omega + i\eta) G_{0,0}^R(\omega) &= 1 + \epsilon_0 G_{0,0}^R(\omega) + \sum_{\nu} \frac{|t_{\nu}|^2}{\hbar\omega - \epsilon_{\nu} + i\eta} G_{0,0}^R(\omega) \\ G_{0,0}^R(\omega) &= \frac{1}{\hbar\omega - \epsilon_0 - \sum_{\nu} \frac{|t_{\nu}|^2}{\hbar\omega - \epsilon_{\nu} + i\eta} + i\eta} = \frac{1}{\hbar\omega - \epsilon_0 - \Sigma^R(\omega) + i\eta}. \end{aligned} \quad (5.72)$$

The retarded self energy

$$\Sigma^R(\omega) = \sum_{\nu} \frac{|t_{\nu}|^2}{\hbar\omega - \epsilon_{\nu} + i\eta} = \sum_{\nu} \mathcal{P} \frac{|t_{\nu}|^2}{\hbar\omega - \epsilon_{\nu}} - i\pi \sum_{\nu} |t_{\nu}|^2 \delta(\hbar\omega - \epsilon_{\nu}) \quad (5.73)$$

captures the impact of the hybridization between impurity and remaining system, i.e., the effects due to the perturbation (5.64).

To see the effect of Σ^R , we can evaluate Σ^R analytically for a simple case: We assume that the ϵ_ν are evenly spaced, i.e., a constant density of states $\rho(E) = D$ and that $|t_\nu| = t$ is constant. As in Sec. 4.4.1, we then replace the sum over ν by an integral involving ρ . The real part of the self energy vanishes here, because ρ is symmetric around any value of ω and positive and negative contributions to the integral then cancel. The imaginary part becomes

$$-\pi \sum_{\nu} \delta(\hbar\omega - \epsilon_\nu) = -\pi \int_{-\infty}^{\infty} dE \rho(E) |t|^2 \delta(\hbar\omega - E) = -\pi |t|^2 D, \quad (5.74)$$

i.e. a constant. In general less symmetric scenarios, positive and negative integrals would only *almost* cancel in the real part, so that finite $\mathcal{R}(\Sigma^R)$ implies a shift of the original impurity potential ϵ_0 . Both real and imaginary part will in general depend on ω , this can also lead to extra poles.

The main effect of the imaginary part is a broadening. This can most easily be seen by looking at the spectral density, which corresponds to a measurable quantity:

$$S_{0,0}(\omega) = -\pi \mathcal{I}(G^R(\omega)) = -\pi \frac{\mathcal{I}(\Sigma^R(\omega))}{(\hbar\omega - \epsilon_0 - \mathcal{R}(\Sigma^R(\omega)))^2 + (\mathcal{I}(\Sigma^R(\omega)))^2}, \quad (5.75)$$

which becomes a Lorentzian if the ω dependence of Σ^R is weak. For $t \rightarrow 0$, the Lorentzian becomes a δ -peak at ϵ_0 . A finite width can be seen as a finite life time and we thus see that the particle described by the δ -peak becomes a ‘quasi’-particle once the state is coupled to the remaining system.

5.5.2 Self-energy for interacting systems, Fermi-liquid theory

For an interacting system, i.e., a Hamiltonian including two-particle terms, the equation of motion includes so-called ‘higher’ Green’s functions involving operators of the form $A = a a^\dagger$ and $B = a^\dagger$.

The necessary steps are:

$$H = H_0 + V = \sum_{\nu} \epsilon_{\nu} a_{\nu}^{\dagger} a_{\nu} + \sum_{\mu, \mu', \lambda, \lambda'} V_{\mu, \mu', \lambda, \lambda'} a_{\mu}^{\dagger} a_{\mu'}^{\dagger} a_{\lambda'} a_{\lambda} \Rightarrow \quad (5.76)$$

$$\begin{aligned} [a_{\nu}, H] &= \epsilon_{\nu} a_{\nu} + \sum_{\mu, \mu', \lambda, \lambda'} V_{\mu, \mu', \lambda, \lambda'} [a_{\nu}, a_{\mu}^{\dagger} a_{\mu'}^{\dagger} a_{\lambda'} a_{\lambda}] = \\ &= \epsilon_{\nu} a_{\nu} + \sum_{\mu, \mu', \lambda, \lambda'} V_{\mu, \mu', \lambda, \lambda'} ([a_{\nu}, a_{\mu}^{\dagger} a_{\mu'}^{\dagger}] a_{\lambda'} a_{\lambda} + a_{\mu}^{\dagger} a_{\mu'}^{\dagger} \underbrace{[a_{\nu}, a_{\lambda'} a_{\lambda}]}_{=0}) = \\ &= \epsilon_{\nu} a_{\nu} + \sum_{\mu, \mu', \lambda, \lambda'} V_{\mu, \mu', \lambda, \lambda'} ([a_{\nu}, a_{\mu}^{\dagger}]_+ a_{\mu'}^{\dagger} a_{\lambda'} a_{\lambda} - a_{\mu}^{\dagger} [a_{\nu}, a_{\mu'}^{\dagger}]_+ a_{\lambda'} a_{\lambda}) = \\ &= \epsilon_{\nu} a_{\nu} + \sum_{\mu', \lambda, \lambda'} (V_{\nu, \mu', \lambda, \lambda'} - V_{\mu', \nu, \lambda, \lambda'}) a_{\mu'}^{\dagger} a_{\lambda'} a_{\lambda} \Rightarrow \end{aligned} \quad (5.77)$$

$$(\hbar\omega - \epsilon_{\nu}) G_{\nu, \mu}(\omega) = \delta_{\nu, \mu} + \sum_{\mu', \lambda, \lambda'} (V_{\nu, \mu', \lambda, \lambda'} - V_{\mu', \nu, \lambda, \lambda'}) \langle\langle a_{\mu'}^{\dagger} a_{\lambda'} a_{\lambda}; a_{\mu}^{\dagger} \rangle\rangle(\omega) \quad (5.78)$$

The higher Green's functions $\langle\langle \dots \rangle\rangle$ are not known and are formally replaced by

$$\sum_{\mu', \lambda, \lambda'} (V_{\nu, \mu', \lambda, \lambda'} - V_{\mu', \nu, \lambda, \lambda'}) \langle\langle a_{\mu'}^\dagger a_{\lambda'} a_{\lambda}; a_{\mu}^\dagger \rangle\rangle(\omega) = \sum_{\lambda} \Sigma_{\nu, \lambda}(\omega) G_{\lambda, \mu}, \quad (5.79)$$

i.e. a matrix product of some equally unknown quantity Σ and the desired one-particle Green's function. While this seems a bit *ad hoc*, one can motivate it by noting that Green's functions are just functions and with enough flexibility in Σ , one should be able to express (almost) any left-hand side in such a manner. The equation of motion is then in matrix notation

$$\hbar\omega G = \mathbb{I} + H_0 G + \Sigma G \quad (5.80)$$

The one-particle Green's function G can then formally be obtained as

$$G(\omega) = \frac{\mathbb{I}}{\hbar\omega - H_0 - \Sigma(\omega)} = \frac{\mathbb{I}}{G_0^{-1} - \Sigma(\omega)}. \quad (5.81)$$

Again, $\mathcal{R}(\Sigma)$ shifts the one-particle peaks in the spectral density while $\mathcal{I}(\Sigma)$ broadens them and these effects dominate for weak ω dependence. Assuming that the interactions preserve translational invariance (which they do for any finite quantum system, but might not in the case of symmetry breaking), $G(\omega)$ remains diagonal in \vec{k} , and accordingly $\Sigma_{\vec{k}, \vec{k}'} = \delta(\vec{k} - \vec{k}') \Sigma_{\vec{k}}(\omega)$.

The above equation of motion Eq. (5.78) is valid for retarded, advanced and causal Green's functions. The difference between the three cases is in the requirements on their analyticity, see Sec. 5.4.2.2. These requirements are based only on the step functions in time, i.e., they apply to any Green's function, not only one-particle functions and do not imply non-interacting particles. Retarded (advanced) interacting Green's functions are thus still analytic in the upper (lower) half plane, e.g., the imaginary part of Σ^R (Σ^A) is negative (positive). This can also be seen by noting that the higher Green's function arising in Eq. (5.78) is of the same kind as the original one and obeys the same rule concerning the location of poles.

For the causal Green's function, $\mathcal{I}(\Sigma^C(\omega)) > 0$ (< 0) for $\epsilon + \mathcal{R}(\Sigma^C) < 0$ (> 0), i.e., the imaginary part of $\Sigma_{\vec{k}}^C$ changes sign when the (renormalized) band crosses the Fermi energy. At the Fermi energy, $\mathcal{I}(\Sigma_{\vec{k}_F}^C)$ consequently either has to vanish or to diverge. Divergence would suppress the Green's function and thus imply an insulator, so that one can conclude that the presence of a Fermi surface implies that quasi particles close to it have nearly infinite life time, i.e., behave like non-interacting electrons.¹

This idea is due to Landau and known as the ‘‘Fermi liquid’’, i.e., the electrons are more correlated than in the independent-electron ‘‘Fermi gas’’, but are still recognizable as individual fermions. As discussed in Sec. 4.4, the states near the Fermi energy determine thermodynamic properties (as well as transport, for similar reasons). Since these states are well described by effectively independent electrons, many results from the Fermi gas can be expected to carry over to Fermi liquids and thus to realistic metals.

A more quantitative estimate arrives at $\Gamma \propto (\omega - E_F)^2$, see the notes by Prof. Muramatsu.

¹There is a way out of this rule and that is that the weight of the pole, the ‘quasi-particle weight’, can vanish. This can happen in one-dimensional systems, but is otherwise rare!

5.6 Perturbation Theory: Adiabatic switching on of the interaction

Mostly based on Nolting's text book, see also lecture notes by Prof. Muramatsu.

One use of the Green's-function formalism is a perturbation-theory scheme, where the interaction is slowly switched on starting from the non-interacting Hamiltonian. The hope is that – if one does this slowly enough – the system then time-evolves into the ground state of the interacting Hamiltonian. We will first study how and how far such a scheme works, i.e., discuss the Gell-Mann and Low theorem, and then present two tricks (Wick's theorem and Feynman diagrams) that help greatly in evaluating the terms arising in the perturbation theory.

5.6.1 Gell-Mann and Low theorem

The aim is to obtain observables for an interacting system with Hamiltonian $H = H_0 + V$, where H_0 is a one-particle Hamiltonian (i.e., describes non-interacting electrons and is “easy” to solve) and V is here given by two-particle operators (e.g. Coulomb repulsion between electrons).

The plan is to introduce an adiabatically slow time dependence, i.e., the time-dependent Hamiltonian

$$H(t) = H_0 + \tilde{V}(t) = H_0 + e^{-\alpha|t|}V, \quad (5.82)$$

with small $\alpha > 0$ that we will (try to) let go to 0 later. At $t = \pm\infty$, $H = H_0$ and the ground state $|\phi_0\rangle$ is the known ground state of H_0 , here the Fermi sea. At $t = 0$, $H = H_0 + V$ whose ground state $|\psi_0\rangle$ we are actually interested in. Ideally,

$$|\psi_0\rangle = U(0, -\infty)|\phi_0\rangle, \quad (5.83)$$

where $U(0, -\infty)$ describes time evolution from $-\infty$ to 0, at least for small enough α .

As is usually discussed in the context of time-dependent perturbation theory, the Dirac picture is here most convenient, because it splits time evolution into (a) an “easy” part due to H_0 and (b) a “difficult” part, for which it provides an expansion in powers of $\tilde{V}(t)$. We thus go back to the Dirac time-evolution operator of Sec. 5.2, but go beyond first order. The time-evolution operator is then

$$\begin{aligned} U^D(t, t_0) &= 1 + \frac{1}{i\hbar} \int_{t_1=t_0}^t dt_1 \tilde{V}^D(t_1) U^D(t_1, t_0) = 1 + \frac{1}{i\hbar} \int_{t_1=t_0}^t dt_1 \tilde{V}^D(t'_1) \left(1 + \frac{1}{i\hbar} \int_{t_2=t_0}^{t_1} dt_2 \tilde{V}^D(t_2) U^D(t_2, t_0) \right) \\ &= \sum_{n=0}^{\infty} \left(\frac{-i}{\hbar} \right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \tilde{V}^D(t_1) \tilde{V}^D(t_2) \cdots \tilde{V}^D(t_n), \end{aligned} \quad (5.84)$$

where the time dependence of the operators $\tilde{V}(t)$ contains both the exponential of Eq (5.82) and the trivial one of Eq. (5.5). For technical reasons that will emerge later, it would be more convenient if all integrals went from t_0 to t . One effect that extending the range would clearly have is that the (hyper-)volume we integrate over becomes too large, by a factor $n!$. A second effect is that we would then have earlier operators to the left of later ones,

in contrast to the desired formula. This is, at this point somewhat symbolically, taken into account by introducing a time-ordering operators T , so that we rewrite the terms in the series as

$$U^D(t, t_0) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar} \right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n T(\tilde{V}^D(t_1) \tilde{V}^D(t_2) \dots \tilde{V}^D(t_n)) . \quad (5.85)$$

For some more detail, see the Nolting book.

After seeing that $U^D(t, t_0)$ can be written as a perturbative expansion in \tilde{V} , so that its approximate evaluation seems at least in principle possible, we can check whether and how the scheme of Eq. (5.83) might work. We commit to the Dirac picture, i.e., we are looking for $|\psi_0(t=0)\rangle^D$ starting from $|\phi_0(-\infty)\rangle^D = |\phi_0(-\infty)\rangle_H = |\phi_0(-\infty)\rangle_S = |\phi_0(-\infty)\rangle$. However, the limit

$$\lim_{\alpha \rightarrow 0} |\psi^\alpha(0)\rangle^D = \lim_{\alpha \rightarrow 0} U_\alpha^D(0, -\infty)|\phi_0\rangle \quad (5.86)$$

does unfortunately not exist. As is discussed, e.g., in Nolting's book, a divergent phase is the problem. Accordingly, the following limit can (depending on the problem at hand) exist:

$$\lim_{\alpha \rightarrow 0} |\psi_0^\alpha\rangle = \lim_{\alpha \rightarrow 0} \frac{|\psi^\alpha(0)\rangle^D}{\langle \phi_0 | \psi^\alpha(0) \rangle^D} = \lim_{\alpha \rightarrow 0} \frac{U_\alpha^D(0, -\infty)|\phi_0\rangle}{\langle \phi_0 | U_\alpha^D(0, -\infty)|\phi_0\rangle} . \quad (5.87)$$

*The Gell-Mann and Low theorem states that if the limit (5.87) exists in all orders n of the perturbation (5.85), it is an eigenstate of $H = H_0 + \tilde{V}$.*²

That said, the eigenstate reached does not have to be the ground state. Another state can have lower energy, which implies that there must have been a level crossing during the time evolution. This can lead to a break down of convergence (which may or may not be detected), but if the two states have different symmetries, it can also go unnoticed. This can happen in the case of symmetry breaking, e.g., to a superconducting state.

5.6.2 Expectation values of the interacting system

We can now use the adiabatically time-evolved ground state 5.87 to calculate expectation values at $t = 0$, i.e., for the interacting system. As the interaction is switched on *very slowly*, $H(t \neq 0)$ remains $H = H_0 + \tilde{V}$ for small times $|t| \ll \infty$ and expectation values of operators at other times

$$A_\alpha^H(t) = U_\alpha^S(0, t) A^S U_\alpha^S(t, 0) = U_\alpha^D(0, t) A^D(t) U_\alpha^D(t, 0) \quad (5.88)$$

still refer to the fully interacting Hamiltonian. ($\alpha \rightarrow 0$ parametrizes the switching on, see above.) Such expectation values are

$$\lim_{\alpha \rightarrow 0} \frac{\langle \psi_0^\alpha | U_\alpha^D(0, t) A^D(t) U_\alpha^D(t, 0) | \psi_0^\alpha \rangle}{\langle \psi_0^\alpha | \psi_0^\alpha \rangle} , \quad (5.89)$$

where the explicit normalization becomes necessary due to the denominator of Eq. 5.87.

²For a sketch of the proof, see Nolting's book. For more, see the book by Fetter and Valecka.

If the interacting ground state 5.87. is unique, i.e., non-degenerate, then the state

$$\lim_{\alpha \rightarrow 0} |\psi_0^\alpha\rangle = \lim_{\alpha \rightarrow 0} \frac{U_\alpha^D(0, \infty)|\phi_0\rangle}{\langle \phi_0|U_\alpha^D(0, \infty)|\phi_0\rangle}. \quad (5.90)$$

reached by evolution from $+\infty$ has to be the same state. We now replace the bra in the expectation value above by this alternative expression for the interacting ground state. The expectation value becomes then

$$\begin{aligned} \langle A \rangle(t) &= \lim_{\alpha \rightarrow 0} \frac{\langle \psi_0^\alpha|U_\alpha^D(0, t)A^D(t)U_\alpha^D(t, 0)|\psi_0^\alpha\rangle}{\langle \psi_0^\alpha|\psi_0^\alpha\rangle} = \\ &= \lim_{\alpha \rightarrow 0} \frac{\langle \phi_0|U_\alpha^D(\infty, 0)U_\alpha^D(0, t)A^D(t)U_\alpha^D(t, 0)U_\alpha(0, -\infty)|\phi_0\rangle}{\langle \phi_0|U_\alpha(\infty, 0)U_\alpha(0, -\infty)|\phi_0\rangle} = \\ &= \lim_{\alpha \rightarrow 0} \frac{\langle \phi_0|U_\alpha^D(\infty, t)A^D(t)U_\alpha^D(t, -\infty)|\phi_0\rangle}{\langle \phi_0|U_\alpha(\infty, -\infty)|\phi_0\rangle} \end{aligned} \quad (5.91)$$

with $A^D(t) = e^{iH_0t/\hbar} A e^{-iH_0t/\hbar}$. The denominators of Eqs. (5.87) and (5.90) still cancel with the norm, even though their relative phase would merit some discussion.³

The denominator of Eq. (5.91) is given by the time-evolution operator going all the way from $-\infty$ to $+\infty$, which follows from Eq. (5.85) as

$$\begin{aligned} \langle \phi_0|U_\alpha^D(\infty, -\infty)|\phi_0\rangle &= \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar}\right)^n \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \cdots \int_{-\infty}^{\infty} dt_n \times \\ &\quad \times \langle \phi_0|T(\tilde{V}^D(t_1)\tilde{V}^D(t_2)\dots\tilde{V}^D(t_n))|\phi_0\rangle = \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar}\right)^n \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \cdots \int_{-\infty}^{\infty} dt_n e^{-\alpha(|t_1|+|t_2|+\dots+|t_n|)} \langle \phi_0|T(V^D(t_1)V^D(t_2)\dots V^D(t_n))|\phi_0\rangle, \end{aligned} \quad (5.92)$$

where $V^D(t) = e^{\frac{i}{\hbar}H_0t} V e^{-\frac{i}{\hbar}H_0t}$ carries only the trivial time dependence.

Looking closely⁴ at the power series of the time-evolution operators shows that the operators $A^D(t)$ is basically just inserted at the appropriate time into the time-ordered products making up $U(\infty, -\infty)$. The expectation value can thus be expanded as

$$\begin{aligned} \langle A \rangle(t) &= \frac{1}{\langle \phi_0|U_\alpha^D(\infty, -\infty)|\phi_0\rangle} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar}\right)^n \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \cdots \int_{-\infty}^{\infty} dt_n e^{-\alpha(|t_1|+|t_2|+\dots+|t_n|)} \times \\ &\quad \times \langle \phi_0|T(V^D(t_1)V^D(t_2)\dots V^D(t_n)A^D(t))|\phi_0\rangle. \end{aligned} \quad (5.93)$$

For a time-ordered product $T(A(t), B(t'))$, the expectation value generalizes naturally to

$$\begin{aligned} \langle T(A^H(t), B^H(t')) \rangle &= \frac{1}{\langle \phi_0|U_\alpha^D(\infty, -\infty)|\phi_0\rangle} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar}\right)^n \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \cdots \int_{-\infty}^{\infty} dt_n e^{-\alpha(|t_1|+|t_2|+\dots+|t_n|)} \times \\ &\quad \times \langle \phi_0|T(V^D(t_1)V^D(t_2)\dots V^D(t_n)A^D(t)B^D(t'))|\phi_0\rangle, \end{aligned} \quad (5.94)$$

³It is plausible enough, so let's not go there.

⁴E.g. Nolting's text book.

which suggests that causal Green's functions can be most readily expressed in such a fashion.

The next two subsections will discuss two 'tricks' that greatly simplify the evaluation of the terms on the perturbation series (5.93) and (5.94), where *Wick's theorem* tells us that we only need to keep combinations of Green's functions and *Feynman diagrams* help us in systematically finding all relevant combinations.

5.6.3 Wick's Theorem

Based on notes by Prof. Muramatsu and textbook by Nolting

As a first step, we note that we could replace the "pure" time-order operator of Eqs. (5.93) and (5.94), which comes from the time-evolution operators and does not include a sign change, with the time-order operator T_ϵ that was used in the definition (5.27) of the causal Green's function, which changes sign when two fermionic one-particle operators are exchanged: Since the interactions considered contain an even number of fermion-operators, any T_ϵ -exchange would give $(-1)^2 = 1$, i.e., not in fact do anything different from T .

As a second step, we introduce a completely different way of ordering operators, the "normal-ordered" product. It is defined as having all annihilation operators shifted to the right and all creation operators to the left; the order within each category is arbitrary. To analyze its properties, it is helpful to go from operators $a_{\vec{k}}$ and $a_{\vec{k}}^\dagger$ annihilation and creating fermions to $\gamma_{\vec{k}}$ and $\gamma_{\vec{k}}^\dagger$ that annihilate/create *excitations* of the Fermi sea. They are

$$\gamma_{\vec{k}}^\dagger = \begin{cases} a_{\vec{k}}^\dagger & \text{for } \epsilon_{\vec{k}} > E_F \\ a_{\vec{k}} & \text{for } \epsilon_{\vec{k}} \leq E_F \end{cases} \quad \text{and} \quad \gamma_{\vec{k}} = (\gamma_{\vec{k}}^\dagger)^\dagger. \quad (5.95)$$

As the Fermi sea contains no excitations, it can also be called the "Fermi vacuum". If a normal-ordered product of γ^\dagger/γ operators is applied to the Fermi sea, it vanishes, because annihilating an excitation that is not there gives a factor 0. Non-interacting expectation values of normal-ordered products are thus *very* easy to calculate, as they all vanish.

Next, we define a quantity called "contraction" as the difference between the time-ordered (using T_ϵ) and the normal-ordered products:

$$\underline{A(t)B(t')} = T_\epsilon(A(t), B(t')) - N(A(t), b(t')). \quad (5.96)$$

Using these definitions 5.95 and 5.96, we can tabulate contractions for γ -operators and translate them back into the original fermion operators a^\dagger and a . This leads to ⁵

$$\begin{aligned} \underline{a_{\vec{k}}(t)a_{\vec{k}'}^\dagger(t')} &= \delta_{\vec{k},\vec{k}'} \begin{cases} e^{-\frac{i}{\hbar}(\epsilon_{\vec{k}}-E_F)(t-t')} & \text{for } t > t', \epsilon_{\vec{k}} > E_F \\ 0 & \text{for } t < t', \epsilon_{\vec{k}} > E_F \\ 0 & \text{for } t > t', \epsilon_{\vec{k}} \leq E_F \\ -e^{-\frac{i}{\hbar}(\epsilon_{\vec{k}}-E_F)(t-t')} & \text{for } t < t', \epsilon_{\vec{k}} \leq E_F \end{cases} = \\ &= (\theta(t-t')(1 - \langle n_{\vec{k}} \rangle) - \theta(t'-t)\langle n_{\vec{k}} \rangle) e^{-\frac{i}{\hbar}(\epsilon_{\vec{k}}-E_F)(t-t')}. \end{aligned} \quad (5.97)$$

Comparison to the causal non-interacting one-particle Green's function (in time domain), see Sec. 5.4.5, then reveals

$$\underline{a_{\vec{k}}(t)a_{\vec{k}'}^\dagger(t')} = iG_{\vec{k}}^c(t-t'), \quad \underline{a_{\vec{k}}^\dagger(t')a_{\vec{k}}(t)} = -iG_{\vec{k}}^c(t-t'). \quad (5.98)$$

⁵See, e.g., Nolting.

Non-interacting expectation values of a time-ordered product can then be expressed in terms of expectation values of normal-ordered products (which vanish) and causal Green's functions.

Wick's theorem extends this concept to more than two operators, and for us, the important result is that the only remaining terms are products of contractions, where *all* operators are paired into contractions, i.e., Green's functions. This brings us a decisive step closer to evaluating the power series, but finding all possible pairings and their Fermi signs is still a considerable task. Feynman diagrams help with the associated book keeping.

5.6.4 Feynman diagrams

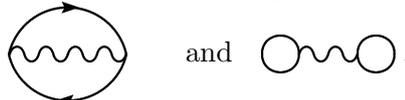
See notes by Prof. Muramatsu.

Feynman diagrams use pictures to find all relevant (we are going to see what this means) ways to pair operators into contractions. The picture for a non-interacting Green's function is a straight line with an arrow indicating time or momentum direction. The picture for a two-particle interaction is a wavy line with four straight legs indicating the four fermion operators:

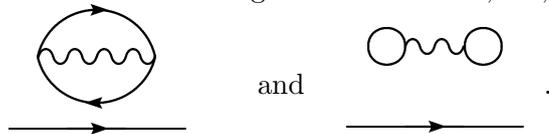

(5.99)

The time-ordered product making up a causal one-particle Green's function, see Eq. (5.94), contains just the 'original' creation and annihilation operators. These are indicated by two "external" legs going into and coming out of the "total picture".

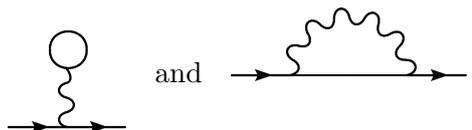
- In 0th order, the denominator (5.92) is just one and the numerator consists of just the two external legs. The only way to combine them is to connect them to each other. This gives one non-interacting Green's function, as expected.
- In 1st order, the denominator (5.92) is given by one interaction, i.e., one picture like (5.99). Its four legs can be combined in two ways:⁶


(5.100)

The numerator has the two external legs in addition to one interaction. There are now two basic possibilities: We can connect the two legs to each other, so that the remaining interaction gives the same two diagrams as the denominator (5.100). The connected legs then add a non-interacting Green's function, i.e., we find


(5.101)

The other possibility is to connect the external legs to the interaction, which yields


(5.102)

⁶The little fermion loops should also have arrows, but they are more difficult to typeset.

- Combining 0th and 1st order, the numerator can be written as a product, with the understanding that we keep (for the moment) only diagrams up to first order:

$$= \left(\text{fermion line with wavy line} + \text{fermion line with tadpole} \right) \left(1 + \text{fermion line with wavy loop} + \text{fermion line with bubble} \right) \quad (5.103)$$

The second of these parentheses contains precisely the same terms as the denominator (up to first order), so that it exactly cancels.

- As the numerators always contains two external legs in addition to the the same interactions as the denominator, one can convince oneself that this factorization and cancellation remains effective in higher orders. *We thus only have to consider ‘connected’ diagrams!*

Working in momentum and frequency space, the procedure in order n becomes then:

1. Draw all topologically distinct ⁷ connected diagrams with n interactions (5.99) and two external legs. (Together with the four legs of each interaction, there are $2n + 1$ non-interacting Green’s functions somewhere in the picture.)
2. Assign directed momentum and frequency (energy) to each line; also to the interaction lines, even if the interaction should be momentum and/or frequency independent. Fermion lines are furthermore assigned a spin.
3. At each vertex

$$\begin{array}{c} \vec{q}, \omega' \\ \swarrow \\ \vec{k}_1, \omega_1, \sigma_1 \quad \vec{k}_2, \omega_2, \sigma_2 \end{array} \quad (5.104)$$

momentum, energy and spin must be conserved, i.e., the outgoing ones must equal the incoming ones $\omega_1 = \omega_2 + \omega'$, $\vec{k}_1 = \vec{k}_2 + \vec{q}$, and $\sigma_1 = \sigma_2$.

4. Each solid line is a non-interacting causal Green’s function $G_\sigma^c(\vec{k}, \omega)$.
5. Each wavy line is the (Fourier transformed) matrix element $V(\vec{q})$ [or $V(\vec{q}, \omega)$] of the interaction, i.e., without creation/annihilation operators. Examples will be given in Eqs. (5.124) and (5.134).
6. Integrate/sum over all internal momenta, frequencies and spins.
7. Diagrams with L fermion loops get a factor $(-1)^L$.
8. Overall factor of $(\frac{i}{\hbar})^n$.

To complete the first-order analysis, we need to evaluate the diagrams drawn in (5.102). In the “Hartree” term with its fermion bubble, momentum and energy conservation at the

⁷I.e.leave out images that are just flipped upside down, and similar.

upper vertex implies $\vec{q} = 0$ and $\omega = 0$ for the interaction line. Integrations over \vec{k}' , σ' and ω' remain to be carried out:

$$\begin{aligned}
 \begin{array}{c} \vec{k}', \sigma' \\ \circ \\ \vec{q}=0 \\ \text{---} \\ \vec{k}, \sigma \end{array} &= -i\hbar \sum_{\sigma'} V^{\sigma, \sigma'}(\vec{q}=0, \omega=0) \int \frac{d^3 k'}{\tilde{k}'} \int d\omega' G_{\vec{k}', \sigma'}^0(\omega') e^{i\omega' 0^+} = \\
 &= \sum_{\sigma'} V^{\sigma, \sigma'}(0, 0) \int \frac{d^3 k'}{\tilde{k}'} \langle n_{\vec{k}', \sigma'} \rangle = \sum_{\sigma'} V^{\sigma, \sigma'}(0, 0) N \langle n_{\sigma'} \rangle_0 \quad (5.105)
 \end{aligned}$$

In the case of Coulomb interaction, the Hartree term thus contributes the potential coming from a charged background given by the other electrons. (The total number of lattice sites N typically cancels with a $\frac{1}{N}$ contained in $V(\vec{q}, \omega)$.) In the Fock diagram, spins are constrained to be the same everywhere:

$$\begin{array}{c} \vec{k}' - \vec{k} \\ \text{---} \\ \vec{k}, \sigma \quad \vec{k}', \sigma \quad \vec{k}, \sigma \end{array} = i\hbar \int \frac{d^3 k'}{\tilde{k}'} \int d\omega' G(\vec{k}', \omega') V^{\sigma, \sigma}(\vec{k}' - \vec{k}, \omega' - \omega). \quad (5.106)$$

This term does not have an obvious classical interpretation.

5.6.5 Dyson equation and Self energy: Summing some kinds of diagrams to infinite order:

We had seen in Sec. 5.5.2 that the impact of the interaction can be expressed via the self energy, so that the Green's function can formally be obtained via a Dyson equation, see Sec. 5.5.1. We are here going to see how these concepts work in the context of Feynman diagrams and are going to see that a Dyson equation with an approximated self-energy automatically includes some higher-order diagrams.

Let us start by identifying what diagrams take the role of the self energy. The interacting equation of motion written using the self energy (5.80) together with the analogous equation $\hbar\omega G_0 = \mathbb{1} + H_0 G_0$ for the non-interacting Green's function G_0 gives the Dyson series analogous to (5.69):

$$\begin{aligned}
 (\hbar\omega - H_0)G = \mathbb{1} + \Sigma G = G_0^{-1}G \quad \Rightarrow \quad G = G_0 + G_0 \Sigma G = G_0 + G_0 \Sigma (G_0 + G_0 \Sigma G) = \\
 = G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \dots \quad (5.107)
 \end{aligned}$$

In Feynman diagrams, the same Dyson series is "written" as

$$\Rightarrow = \rightarrow + \rightarrow \text{---} \text{---} \Rightarrow + \rightarrow \text{---} \text{---} \text{---} \Rightarrow + \rightarrow \text{---} \text{---} \text{---} \text{---} \Rightarrow + \dots, \quad (5.108)$$

where $\text{---} \text{---} \text{---} = \Sigma$ illustrates the self energy.

Comparing the first-order part of (5.108) the first-order interacting Green's function obtained in the previous section yields

$$\Rightarrow = \rightarrow + \rightarrow \text{---} \text{---} \Rightarrow + \rightarrow \text{---} \text{---} \text{---} \Rightarrow + \rightarrow \text{---} \text{---} \text{---} \text{---} \text{---} \Rightarrow, \quad (5.109)$$

so that the first-order self energy Σ^1 can be read off as

$$\Sigma^1 = \text{[diagram: wavy line loop]} + \text{[diagram: wavy line with circle]}. \quad (5.110)$$

Inserting it into the Dyson equation/series leads to another version of the “first-order” interacting Green’s function

$$G = \frac{1}{G_0^{-1} - \Sigma^1} = \text{[diagram: arrow]} + \text{[diagram: arrow with wavy line loop]} + \text{[diagram: arrow with wavy line and circle]} + \text{[diagram: arrow with two wavy lines]} + \text{[diagram: arrow with wavy line and circle]} + \text{[diagram: arrow with wavy line and circle]} + \dots \quad (5.111)$$

i.e., it contains a number of higher-order diagrams.

Let us now compare the second-order diagrams from the Dyson series to all Feynman diagrams arising in second order:

$$\text{[diagram: two circles on a line]} + \text{[diagram: two wavy lines on a line]} + \text{[diagram: circle and wavy line on a line]} + \text{[diagram: wavy line and circle on a line]} \quad (5.112)$$

$$\text{[diagram: wavy line loop on a line]} + \text{[diagram: two circles on a line]} + \text{[diagram: circle and wavy line on a line]} + \text{[diagram: wavy line loop with circle on a line]} \quad (5.113)$$

$$\text{[diagram: wavy line loop on a line]} + \text{[diagram: circle on a line]} \quad (5.114)$$

The first four diagrams (5.112), which are the ones that the Dyson series contributes based on Σ^1 , can be decomposed into first-order diagrams by cutting one single non-interacting-fermion line. The remaining diagrams cannot be cut in such manner and these are called “irreducible”.

As the Dyson series “glues” one self energy after another with a non-interacting Green’s function in the middle, one can easily convince oneself that this remains true in higher orders. Modified rules for Feynman diagrams are then:

1. Draw all topologically distinct, connected, and *irreducible* diagram of order n .
2. Insert the obtained self energy (up to order n) into the Dyson equation.

In this manner, some kinds of diagrams are automatically included up to infinite order.

5.6.6 (Self-Consistent) Hartree Approximation to the Hubbard model

Based on Nolting's textbook.

We will here compare approaches based on equations of motion and based on digrams - the former does not need the apparatus of the last few sections, but the latter is faster once one knows the technique. Both methods can be extended to be "self consistent", which allows symmetry-broken solutions.

5.6.6.1 Via equations of motion

One try to obtain the one-particle spectral density of the Hubbard Hamiltonian

$$H = H_0 + H_1 = \sum_{i,j,\sigma} t_{i,j} c_{i,\sigma}^\dagger c_{j,\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (5.115)$$

by using the equation of motion. H_0 contains here hopping between sites, but also the chemical potential μ for $i = j$. For the retarded Green's function, $\omega \rightarrow \omega + i\eta$ and

$$\hbar(\omega + i\eta) G_{ij,\sigma}^R(\omega) = \langle [c_{i\sigma}, c_{j\sigma'}^\dagger]_+ \rangle + G_{[c_{i\sigma}, H]c_{j\sigma'}^\dagger}^R(\omega), \quad (5.116)$$

where $G_{[c_{i\sigma}, H]c_{j\sigma'}^\dagger}^R(\omega)$ denotes a 'higher' Green's function involving operator $[c_{i\sigma}, H]$ instead of $c_{i\sigma}$:

$$G_{[c_{i\sigma}, H]c_{j\sigma'}^\dagger}^R(t) = \langle\langle [c_{i\sigma}, H]; c_{j\sigma'}^\dagger \rangle\rangle^R(t) = -\frac{i}{\hbar} \theta(t) \langle [[c_{i\sigma}, H]_-, c_{j\sigma'}^\dagger]_+ \rangle. \quad (5.117)$$

One thus needs the commutator

$$\begin{aligned} [c_{i\sigma}, H_0 + H_1]_- &= \sum_{i',j',\sigma'} t_{i',j'} [c_{i\sigma}, c_{i',\sigma'}^\dagger c_{j',\sigma'}]_- + \frac{U}{2} \sum_{i',\sigma'} [c_{i\sigma}, n_{i'\sigma'} n_{i'-\sigma'}]_- = \\ &= \sum_{i',j',\sigma'} t_{i',j'} \underbrace{[c_{i\sigma}, c_{i',\sigma'}^\dagger]_+}_{=\delta_{ii'}\delta_{\sigma\sigma'}} c_{j',\sigma'} + \frac{U}{2} \sum_{i',\sigma'} ([c_{i\sigma}, n_{i'\sigma'}]_- n_{i'-\sigma'} + n_{i'\sigma'} [c_{i\sigma}, n_{i'-\sigma'}]_-) = \\ &= \sum_{j'} t_{i,j'} c_{j',\sigma} + \frac{U}{2} \sum_{i',\sigma'} (\delta_{ii'} \delta_{\sigma\sigma'} c_{i',\sigma'} n_{i'-\sigma'} + n_{i'\sigma'} \delta_{ii'} \delta_{\sigma,-\sigma'} c_{i',-\sigma'}) = \\ &= \sum_{j'} t_{i,j'} c_{j',\sigma} + U c_{i\sigma} n_{i,-\sigma}, \end{aligned} \quad (5.118)$$

which yields for the equation of motion

$$\hbar(\omega + i\eta) G_{ij,\sigma}^R(\omega) = \hbar \delta_{ij} + \sum_{j'} t_{i,j'} G_{j'j,\sigma}^R(\omega) + U \langle\langle c_{i\sigma} n_{i,-\sigma}; c_{j\sigma'}^\dagger \rangle\rangle^R(\omega), \quad (5.119)$$

where $\langle\langle A; B \rangle\rangle^R(\omega)$ is again a notation for a Green's function with operators A and B .

One could now set up another equation of motion for the higher Green's function, however, this will lead to an even higher one with more operators.⁸ Instead, one can use an

⁸Except for the special case of the infinitely narrow band $t = 0$, where the equation decouples.

approximation: Replace two of the operators by the expectation value of their product, i.e., by a number. Calculated with a Fermi-gas ground state, the expectation value of one single creation or annihilation operator certainly vanishes. Similarly, any expectation value of the form $\langle c_{\sigma}^{\dagger} c_{-\sigma} \rangle = 0$, because the Hamiltonian conserves the z -component of the spin. The only remaining possibility is then

$$c_{i\sigma} n_{i,-\sigma} \rightarrow c_{i\sigma} \langle n_{i,-\sigma} \rangle. \quad (5.120)$$

As a further approximation, we assume that translational invariance is preserved and set $\langle n_{i,-\sigma} \rangle = \langle n_{-\sigma} \rangle$. This leads us to

$$\begin{aligned} \hbar(\omega + i\eta) G_{ij,\sigma}^R(\omega) &= \hbar \delta_{ij} + \sum_{j'} t_{i,j'} G_{j'j,\sigma}^R(\omega) + U \langle n_{-\sigma} \rangle G_{ij,\sigma}^R(\omega) \quad \text{resp.} \\ (\omega - U \langle n_{-\sigma} \rangle + i\eta) G_{ij,\sigma}^R(\omega) &= \delta_{ij} + \sum_{j'} \frac{t_{i,j'}}{\hbar} G_{j'j,\sigma}^R(\omega). \end{aligned} \quad (5.121)$$

For each ω and $\sigma = \uparrow, \downarrow$, this is a matrix equation for the matrix $G_{ij,\sigma}^R$ that contains the hopping matrix \hat{T} , so that

$$\begin{aligned} (\omega - U \langle n_{-\sigma} \rangle - \hat{T} + i\eta) \hat{G}_{\sigma}^R(\omega) &= \mathbb{I} \quad \text{resp} \\ \hat{G}_{\sigma}^R(\omega) &= (\omega - U \langle n_{-\sigma} \rangle - \hat{T} + i\eta)^{-1}. \end{aligned} \quad (5.122)$$

Except for the constant shift $U \langle n_{-\sigma} \rangle$, which gets added to μ , this is the same equation as for non-interacting electrons, which is solved by Fourier transform, yielding

$$G_{\vec{k},\sigma}^R = \frac{1}{\omega - (\epsilon_{\vec{k}} - \mu + U \langle n_{-\sigma} \rangle) / \hbar + i\eta}. \quad (5.123)$$

The Hartree approximation thus changes the energy by a term containing the interaction U as well as the density of opposite spins. It becomes correct in the band limit $U \rightarrow 0$, but not in the ‘atomic’ limit $t \rightarrow 0$. The quasi particles keep infinite life time in this approximation.

5.6.6.2 Via diagrams

For comparison, let us look how to treat this problem using diagrams. To do so, it is better to transform the Hamiltonian into momentum space from the beginning

$$\begin{aligned} H &= H_0 + H_1 = \sum_{\vec{k},\sigma} (\epsilon(\vec{k}) - \mu) n_{\vec{k},\sigma} + \frac{U}{2N^2} \sum_{i,\sigma} \sum_{\vec{p},\vec{p}',\vec{k},\vec{k}'} e^{i(\vec{p}-\vec{p}'+\vec{k}-\vec{k}')\vec{r}_i} a_{\vec{p},\sigma}^{\dagger} a_{\vec{p}',\sigma} a_{\vec{k},-\sigma}^{\dagger} a_{\vec{k}',-\sigma} = \\ &= \sum_{\vec{k},\sigma} (\epsilon(\vec{k}) - \mu) n_{\vec{k},\sigma} + \frac{U}{2N} \sum_{\sigma} \sum_{\vec{p},\vec{p}',\vec{k},\vec{k}'} a_{\vec{p},\sigma}^{\dagger} a_{\vec{p}',\sigma} a_{\vec{k},-\sigma}^{\dagger} a_{\vec{k}',-\sigma} \underbrace{\frac{1}{N} \sum_{i,\sigma} e^{i(\vec{p}-\vec{p}'+\vec{k}-\vec{k}')\vec{r}_i}}_{=\delta_{\vec{p}+\vec{k},\vec{p}'+\vec{k}'}} = \\ &= \sum_{\vec{k},\sigma} (\epsilon(\vec{k}) - \mu) n_{\vec{k},\sigma} + \frac{U}{N} \sum_{\vec{q}} \left(\sum_{\vec{p}} a_{\vec{p}+\vec{q},\uparrow}^{\dagger} a_{\vec{p},\uparrow} \right) \left(\sum_{\vec{p}'} a_{\vec{p}'-\vec{q},\downarrow}^{\dagger} a_{\vec{p}',\downarrow} \right). \end{aligned} \quad (5.124)$$

$$\Sigma^{(1)}(\mathbf{k}, \omega) = \text{---} \bullet \text{---} \circlearrowleft \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \text{---} \bullet \text{---}$$

Figure 5.1: First-order diagrams

H_1 is the interaction potential that defines the vertices in the diagrams, special features about this one are (i) $U(\vec{q}) = \frac{U}{N}$ does not depend on \vec{q} and (ii) the two interacting electrons have to have opposite spin. The corresponding diagram is

$$\begin{array}{c} \vec{k}-\vec{q}, \sigma \\ \swarrow \\ \vec{q} \\ \searrow \\ \vec{k}', -\sigma \\ \swarrow \\ \vec{k}, \sigma \\ \searrow \\ \vec{k}', -\sigma \end{array} \quad . \quad (5.125)$$

In first order, possible diagrams are shown in Fig. 5.1. Any full line is a non-interacting Green's function and thus preserves momentum and spin. Any wiggly line represents an interaction and thus needs to have two legs with spin 'up' and two with 'down'. For the first diagram,

$$\begin{array}{c} \vec{k}', -\sigma \\ \circlearrowleft \\ \vec{q}=0 \\ \text{---} \bullet \text{---} \\ \vec{k}, \sigma \end{array} \quad , \quad (5.126)$$

this implies that the spin of the Green's function in the 'fermion loop' is opposite to that of the 'base line'. As the incoming the Green's functions to the left and the outgoing one to the right should moreover have the same momentum $\vec{k} = \vec{k} + \vec{q}$, $\vec{q} = 0$ for the wiggly line. Only \vec{k}' remains to be integrated over in the self energy

$$\begin{array}{c} \vec{k}', -\sigma \\ \circlearrowleft \\ \vec{q}=0 \\ \text{---} \bullet \text{---} \\ \vec{k}, \sigma \end{array} = -U(\vec{q}=0) \int_{\vec{k}'} d^3 k' \int d\omega' iG_{\vec{k}', -\sigma}^0(\omega') e^{i\omega'0^+} = \frac{U}{N} \int_{\vec{k}'} d^3 k' \langle n_{\vec{k}', -\sigma} \rangle = \frac{U}{N} N \langle n_{-\sigma} \rangle . \quad (5.127)$$

In the second diagram of Fig. 5.1, one cannot correctly assign the spins at all and it consequently vanishes:

$$\begin{array}{c} \vec{q}=0 \\ \text{---} \bullet \text{---} \\ \vec{k}, \sigma \quad \vec{k}, ? \quad \vec{k}, -\sigma \end{array} = 0 , \quad (5.128)$$

because U does not couple electrons with the same spin.

This then yields as an equation relating the 'dressed' Green's function G to the 'bare' one G^0 :

$$\Sigma_{\vec{k}, \sigma}^1(\omega) = \Sigma_{\sigma}^1 = U \langle n_{-\sigma} \rangle \quad (5.129)$$

$$G_{\vec{k}, \omega}^{-1} = (G_{\vec{k}, \omega}^0)^{-1} - \frac{1}{\hbar} \Sigma_{\vec{k}, \omega} = \omega \pm i\eta - (\epsilon(\vec{k}) - \mu)/\hbar - \frac{U}{\hbar} \langle n_{-\sigma} \rangle \quad (5.130)$$

$$G_{\vec{k},\omega} = \frac{1}{\omega - (\epsilon(\vec{k}) + U\langle n_{-\sigma} \rangle - \mu)/\hbar} . \quad (5.131)$$

As the self energy is here purely real, we might also insert it into retarded and advanced Green's functions; in general, we would have to use the formulas based on the Kramers-Kronig relation, see Sec. 5.4.4, to obtain these other Green's functions from the causal one.

The advantage of the diagrammatic approach is that it is faster once one has learned the technique and that the approximation is known to take into account all terms of the same order in U , while the decoupling of the higher Green's function may seem more arbitrary.

5.6.6.3 Self Consistency

In the above, the expectation value is calculated with the free Green's function, i.e., for the non-interacting system. The approximation can be improved if it is instead obtained *self consistently*. To do so, one might

- start with $\langle n_{\downarrow} \rangle$ and $\langle n_{\uparrow} \rangle$ of the free system,
- use it to obtain Green's functions $G_{\vec{k},\uparrow}$ and $G_{\vec{k},\downarrow}$,
- get $\langle n_{\downarrow} \rangle$ and $\langle n_{\uparrow} \rangle$ from these Green's functions
- ...
- until the results no longer change.

In the diagrams, this implies that the Green's function forming the circle in (5.105) is the dressed one. In second order and if both Hartree and Fock terms contribute, the diagrams included via self consistency are the ones in (5.113), i.e., diagrams like (5.114) are not taken into account.

However, it might be an even better strategy to start with initial $\langle n_{\uparrow} \rangle \neq \langle n_{\downarrow} \rangle$, even though they are equal in the non-interacting system. If the iteration converges to a solution with different densities, and if that solution has lower energy, then the interactions support magnetism. A symmetry is then spontaneously broken. This self-consistent mean-field approximation with potentially finite magnetization $n_{\uparrow} - n_{\downarrow}$ is also referred to as 'Stoner' approach to ferromagnetism. Perturbation theory without self consistency will, in contrast, always remain symmetric for up and down spins in all orders.

To carry the idea of self-consistent symmetry breaking further, $G_{\sigma,\sigma'} \propto \delta_{\sigma,\sigma'}$ would also no longer have to be enforced, the interactions might also self consistently allow it to converge to a finite value; the Fock diagram in (5.106) does then not necessarily vanish. Closer inspection shows that this does not add new physics: $\langle n_{\uparrow} \rangle - \langle n_{\downarrow} \rangle \neq 0$ allows magnetization along the z axis of the spin, $\langle c_{\uparrow}^{\dagger} c_{\downarrow}^{\dagger} \rangle \neq 0$ permits it within the x - y plane. As all spin directions are here equivalent, this is equivalent.

Finally, one might also think of allowing $\langle c_{\uparrow}^{\dagger} c_{\downarrow}^{\dagger} \rangle \neq 0$. Incorporating this into the present diagrammatic approach is tricky, because it relies on Green's functions with one creation and one annihilation operator. (In the equation-of-motion approach, this is more straightforward.) We are going to discuss later how to treat this situation, which corresponds to superconducting solutions.

5.6.7 Note on finite Temperatures

Green's functions can be extended to finite temperatures in a straightforward manner: the ground-state expectation value in definitions like (5.10), (5.17) or (5.44) simply has to be replaced by expectation values for finite temperatures. The formalism of Feynman diagrams mostly carries over as well, the few necessary adjustments go by the name of "Matsubara formalism".

5.7 Response functions

Based on Nolting's textbook.

Going back to Sec. 5.2, where Green's functions were introduced as quantities characterizing a system's reaction to some external probe, we are now going to investigate such quantities. Here, the commutator Green's function is relevant rather than the anti-commutator needed for fermion single-particle Green' functions. The functions here will turn out to be 'two-particle' quantities that involve two creation and annihilation operators and thus describe charge-neutral excitations.

5.7.1 Charge-charge correlation

The charge susceptibility expresses how strongly the electronic charge at site i and time t reacts to a charge difference at site j and time t' , i.e.,

$$\chi_{i,j}(t, t') = \frac{i}{\hbar} \langle [n_i(t), n_j(t')]_- \rangle. \quad (5.132)$$

This quantity is relevant to, for example, screening of charges. But another importance comes from the fact that similar charge correlations arise in Coulomb-interaction terms: as system whose kinetic energy makes it "susceptible", i.e., where $\langle n_i n_j \rangle$ is "important", can then be pushed into an ordered state by an interaction $V_{i,j} n_i n_j$.

In translationally invariant systems, the correlation should of course only depend on distance $\vec{r}_i - \vec{r}_j$ and one would of average over all sites i . Additionally Fourier transforming from distance $\vec{r}_i - \vec{r}_j$ into momentum space gives

$$\chi_{\vec{q}}(t, t') = \frac{i}{\hbar N} \sum_i \sum_{\vec{r}_i - \vec{r}_j} e^{i\vec{q}(\vec{r}_i - \vec{r}_j)} \langle [n_i(t), n_j(t')]_- \rangle = \frac{i}{\hbar N} \langle [(\sum_i e^{i\vec{q}\vec{r}_i} n_i(t)), (\sum_j e^{-i\vec{q}\vec{r}_j} n_j(t'))]_- \rangle \quad (5.133)$$

becomes a Green's function for Fourier transforms of the density. A typical translationally invariant Coulomb-interaction in momentum space becomes: ⁹

$$\begin{aligned} H_1 &= \frac{1}{2} \sum_{i,j} V(\vec{r}_i - \vec{r}_j) n_i n_j = \sum_{\substack{i,i \\ \sigma, \sigma'}} V(\vec{r}_i - \vec{r}_j) n_{i,\sigma} n_{j,\sigma'} = \\ &= \frac{1}{2N^2} \sum_{\substack{i,i \\ \sigma, \sigma'}} V(\vec{r}_i - \vec{r}_j) \sum_{\substack{\vec{k}, \vec{k}' \\ \vec{p}, \vec{p}'}} e^{i(\vec{k} - \vec{k}')\vec{r}_i} e^{i(\vec{p} - \vec{p}')\vec{r}_j} c_{\vec{k},\sigma}^\dagger c_{\vec{k}',\sigma} c_{\vec{p},\sigma'}^\dagger c_{\vec{p}',\sigma'} = \end{aligned}$$

⁹The factor $\frac{1}{2}$ takes the double counting of all pairs i, j into account.

$$\begin{aligned}
&= \sum_{\sigma, \sigma'} \sum_{\substack{\vec{k}, \vec{k}' \\ \vec{p}, \vec{p}'}} c_{\vec{k}, \sigma}^\dagger c_{\vec{k}', \sigma} c_{\vec{p}, \sigma'}^\dagger c_{\vec{p}', \sigma'} \underbrace{\sum_{\vec{r}_i - \vec{r}_j} \frac{V(\vec{r}_i - \vec{r}_j)}{2N} e^{i(\vec{k} - \vec{k}')(\vec{r}_i - \vec{r}_j)}}_{V(\vec{k} - \vec{k}')} \underbrace{\frac{1}{N} \sum_j e^{i(\vec{k} - \vec{k}' + \vec{p} - \vec{p}')\vec{r}_j}}_{=\delta_{\vec{k} - \vec{k}', \vec{p} - \vec{p}'}} = \\
&= \sum_{\sigma, \sigma'} \sum_{\substack{\vec{q} \\ \vec{k}, \vec{k}'}} \frac{V(\vec{q})}{2} c_{\vec{k} + \vec{q}, \sigma}^\dagger c_{\vec{k}, \sigma} c_{\vec{k}' - \vec{q}, \sigma'}^\dagger c_{\vec{k}', \sigma'} = \\
&= \sum_{\vec{q}} \frac{V(\vec{q})}{2} \left(\sum_{\vec{k}, \sigma} c_{\vec{k} + \vec{q}, \sigma}^\dagger c_{\vec{k}, \sigma} \right) \left(\sum_{\vec{k}', \sigma'} c_{\vec{k}' - \vec{q}, \sigma'}^\dagger c_{\vec{k}', \sigma'} \right) = \sum_{\vec{q}} V(\vec{q}) \rho_{\vec{q}} \rho_{-\vec{q}} \quad (5.134)
\end{aligned}$$

with usually $V(\vec{q}) = V(-\vec{q})$. Moreover, it often turns out that the $\vec{q} = 0$ term is precisely canceled by potential from the ionic background. This contribution is consequently often excluded, i.e., $V(\vec{q} = 0) = 0$.

The quantity

$$\rho_{\vec{q}} = \sum_{\vec{k}, \sigma} c_{\vec{k} - \vec{q}, \sigma}^\dagger c_{\vec{k}, \sigma} = \quad (5.135)$$

$$= \frac{1}{N} \sum_{\vec{k}, \sigma} \sum_{i, j} e^{-i(\vec{k} - \vec{q})\vec{r}_i} e^{i\vec{k}\vec{r}_j} c_{i, \sigma}^\dagger c_{j, \sigma} = \sum_{i, j, \sigma} e^{i\vec{q}\vec{r}_i} c_{i, \sigma}^\dagger c_{j, \sigma} \underbrace{\frac{1}{N} \sum_{\vec{k}, \sigma} e^{-i\vec{k}(\vec{r}_i - \vec{r}_j)}}_{=\delta_{i, j}} \quad (5.136)$$

is on the other hand the Fourier transform of the density and

$$\rho_{\vec{q}} = \sum_{\sigma} \rho_{\vec{q}, \sigma} = \rho_{-\vec{q}}^\dagger. \quad (5.137)$$

On the other hand, (5.135) shows us that $\rho_{\vec{q}}$ moves electrons into states with different momentum.

5.7.1.1 Equation of motion for the charge susceptibility – non-interacting case

To obtain the charge susceptibility, we use here the equations of motion, first just with a non-interacting Hamiltonian $H_0 = \sum_{\vec{k}, \sigma} \epsilon_{\vec{k}} n_{\vec{k}, \sigma}$. Written fully in momentum space, going to frequency space and employing the notation $\langle\langle \dots \rangle\rangle^R(\omega)$ for a Green's function, (5.133) becomes

$$\chi_{\vec{q}}(\omega) = \langle\langle \rho_{\vec{q}}; \rho_{-\vec{q}} \rangle\rangle^R(\omega) = \langle\langle \sum_{\vec{k}, \sigma} c_{\vec{k}, \sigma}^\dagger c_{\vec{k} + \vec{q}, \sigma}; \sum_{\vec{k}', \sigma'} c_{\vec{k}' + \vec{q}, \sigma'}^\dagger c_{\vec{k}', \sigma'} \rangle\rangle^R(\omega) \quad (5.138)$$

To reduce writing for the intermediate steps, we focus on 'components' of (5.133) and look for

$$f_{\vec{k}, \sigma}(\vec{q}, \omega) = \langle\langle c_{\vec{k}, \sigma}^\dagger c_{\vec{k} + \vec{q}, \sigma}; \rho_{-\vec{q}} \rangle\rangle^R(\omega). \quad (5.139)$$

To evaluate the equation of motion (5.34), we need the commutator

$$[c_{\vec{k}, \sigma}^\dagger c_{\vec{k} + \vec{q}, \sigma}, \rho_{-\vec{q}}]_- = \sum_{\vec{k}', \sigma'} [c_{\vec{k}, \sigma}^\dagger c_{\vec{k} + \vec{q}, \sigma}, c_{\vec{k}' + \vec{q}, \sigma'}^\dagger c_{\vec{k}', \sigma'}] = \sum_{\vec{k}', \sigma'} (\delta_{\vec{k} + \vec{q}, \vec{k}' + \vec{q}} \delta_{\sigma, \sigma'} c_{\vec{k}, \sigma}^\dagger c_{\vec{k}', \sigma'} - \delta_{\vec{k}, \vec{k}'} \delta_{\sigma, \sigma'} c_{\vec{k}' + \vec{q}, \sigma'}^\dagger c_{\vec{k} + \vec{q}, \sigma})$$

$$= n_{\vec{k},\sigma} - n_{\vec{k}+\vec{q},\sigma} \quad (5.140)$$

as well as the commutator with the non-interacting Hamiltonian H_0 :

$$\begin{aligned} [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, H_0]_- &= \sum_{\vec{k}',\sigma'} (\epsilon_{\vec{k}'} - \mu) [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, c_{\vec{k}',\sigma'}^\dagger c_{\vec{k}',\sigma'}] = \\ &= \sum_{\vec{k}',\sigma'} (\epsilon_{\vec{k}'} - \mu) (\delta_{\vec{k}+\vec{q},\vec{k}'} \delta_{\sigma,\sigma'} c_{\vec{k},\sigma}^\dagger c_{\vec{k}',\sigma'} - \delta_{\vec{k},\vec{k}'} \delta_{\sigma,\sigma'} c_{\vec{k}',\sigma'}^\dagger c_{\vec{k}+\vec{q},\sigma}) = (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}) c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma} \end{aligned} \quad (5.141)$$

Collecting (5.140) and (5.141), the equation of motion (5.34) becomes

$$\begin{aligned} \hbar(\omega + i\eta) f_{\vec{k},\sigma}(\vec{q}, \omega) &= \hbar \langle [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, \rho_{-\vec{q}}]_- \rangle + \langle \langle [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, H_0]_-; \rho_{-\vec{q}} \rangle \rangle^R(\omega) = \\ &= \hbar (\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle) + (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}) \langle \langle c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}; \rho_{-\vec{q}} \rangle \rangle^R(\omega) \\ &= \hbar (\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle) + (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}) f_{\vec{k},\sigma}(\vec{q}, \omega) \\ \Rightarrow f_{\vec{k},\sigma}(\vec{q}, \omega) &= \frac{\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle}{\omega - (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})/\hbar + i\eta} \end{aligned} \quad (5.142)$$

$$\Rightarrow f_{\vec{k},\sigma}(\vec{q}, \omega) = \frac{\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle}{\omega - (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})/\hbar + i\eta} \quad (5.143)$$

and

$$\chi_{\vec{q}}^0(\omega) = \sum_{\vec{k},\sigma} f_{\vec{k},\sigma}(\vec{q}, \omega) = \sum_{\vec{k},\sigma} \frac{\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle}{\omega - (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})/\hbar + i\eta}. \quad (5.144)$$

The result is given by the excitation energies arising from moving an electron from \vec{k} to $\vec{k}+\vec{q}$ and the weights determining which excitations can be created:¹⁰ we can move the electron, if one state is empty and the other occupied. Such processes, which move an electron from an occupied to an empty state, are called ‘particle-hole’ excitations.

5.7.1.2 Equation of motion for the charge susceptibility – with interaction

To include interactions, we need $\langle \langle [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, H_1]; \rho_{-\vec{q}} \rangle \rangle^R(\omega)$ to complete (5.142), i.e.

$$[c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, H_1] = \sum_{\vec{q}'} \frac{V(\vec{q}')}{2} [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, \rho_{\vec{q}'} \rho_{-\vec{q}'}] = \sum_{\vec{q}'} \frac{V(\vec{q}')}{2} ([c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, \rho_{\vec{q}'}] \rho_{-\vec{q}'} + \rho_{\vec{q}'} [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, \rho_{-\vec{q}'}]). \quad (5.145)$$

The remaining commutators give

$$\begin{aligned} [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, \rho_{\vec{q}'}] &= \sum_{\vec{k}',\sigma'} [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, c_{\vec{k}',\sigma'}^\dagger c_{\vec{k}'+\vec{q}',\sigma'}] = \sum_{\vec{k}',\sigma'} (c_{\vec{k},\sigma}^\dagger c_{\vec{k}'+\vec{q}',\sigma'} \delta_{\vec{k}+\vec{q},\vec{k}'} - c_{\vec{k}',\sigma'}^\dagger c_{\vec{k}+\vec{q},\sigma} \delta_{\vec{k},\vec{k}'+\vec{q}'}) \delta_{\sigma,\sigma'} = \\ &= c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\sigma} - c_{\vec{k}-\vec{q}',\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma} \quad \text{and} \end{aligned} \quad (5.146)$$

$$[c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, \rho_{-\vec{q}'}] = c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q}-\vec{q}',\sigma} - c_{\vec{k}+\vec{q}',\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma} \quad (5.147)$$

¹⁰ We could consequently have obtained this result more easily from the Lehman representation (5.47), but the equation of motion will be more useful for the interacting case discussed next.

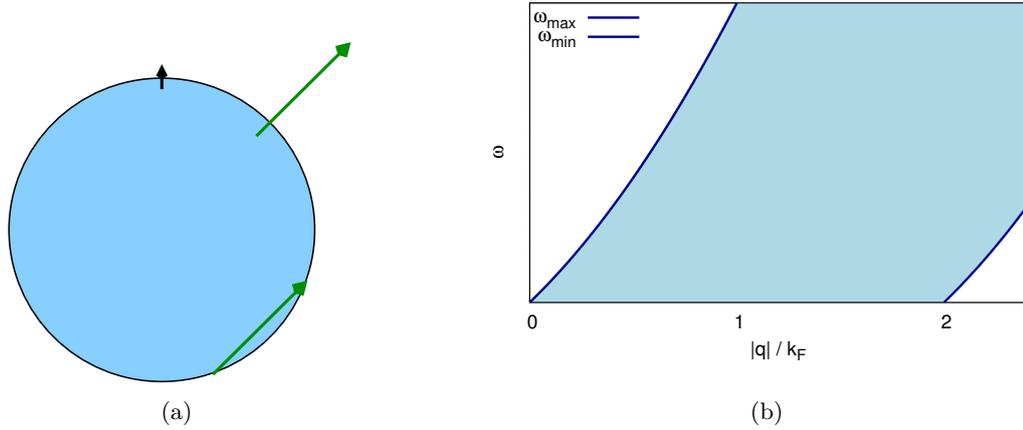


Figure 5.2: Possible particle-hole excitations building χ^0 . In (a), the circle illustrates a 2D Fermi surface, the short black arrow indicates a very small \vec{q} that will confer small excitation energy of at most $\propto |\vec{q}|$. The longer green arrow illustrates that for larger momenta, their orientation determines whether they lead to a small or large energy transfer. For $|\vec{q}| \leq k_F$, zero-energy particle-hole excitations are possible. Shading in (b) shows the energy-momentum range of the particle-hole excitations, between minimal and maximal energy transfer. In a large systems, poles lie here dense.

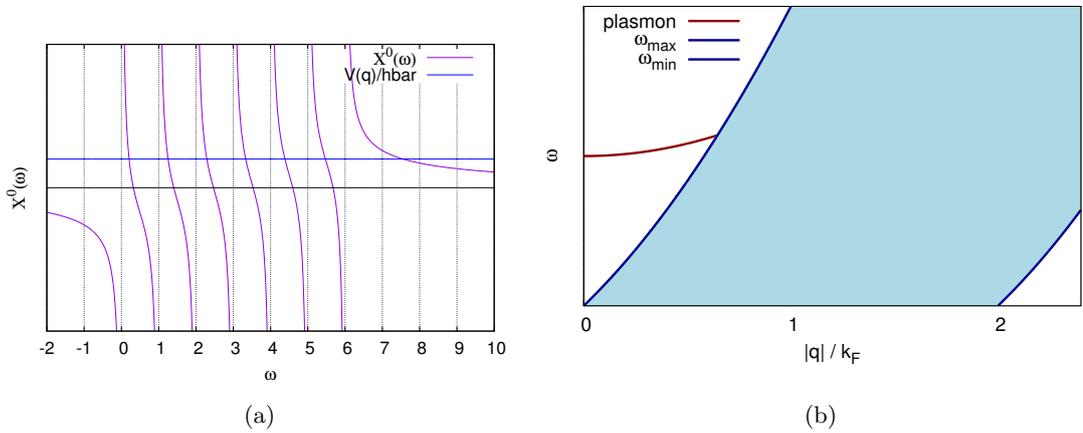


Figure 5.3: (a) Non-interacting charge susceptibility $\chi^0(\omega)$ for a fixed \vec{q} . Poles are the particle-hole excitations, $\chi^{\text{RPA}}(\omega)$ has additional poles wherever $\chi^0(\omega)$ meets the blue horizontal line. Most of these lie within the dense spectrum if Fig. 5.2(b), but the one with highest energy is outside, see (b), where the plasmon frequency is drawn in addition to the particle-hole continuum

The full equation of motions is then

$$\begin{aligned}
\hbar(\omega + i\eta)f_{\vec{k},\sigma}(\vec{q}, \omega) &= \hbar\langle [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, \rho_{-\vec{q}}] \rangle + \langle\langle [c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}, H_0 + H_1]; \rho_{-\vec{q}} \rangle\rangle^R(\omega) = \\
&= \hbar(\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle) + (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})f_{\vec{k},\sigma}(\vec{q}, \omega) \\
&\quad + \sum_{\vec{q}'} \frac{V(\vec{q}')}{2} \left(\langle\langle (c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\sigma} - c_{\vec{k}-\vec{q}',\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}) \rho_{-\vec{q}'}; \rho_{-\vec{q}} \rangle\rangle^R(\omega) + \right. \\
&\quad \left. \langle\langle \rho_{\vec{q}'} (c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q}-\vec{q}',\sigma} - c_{\vec{k}+\vec{q}',\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma}) ; \rho_{-\vec{q}} \rangle\rangle^R(\omega) \right) \quad (5.148)
\end{aligned}$$

This equation of motion is exact, but cannot be solved, because the higher Green's functions are not known. If we write another equation of motion for them, even more Green's functions come into play. A full solution is here not possible.

In order to find at least an approximate solution, we decouple the equation of motion by replacing some operators by their expectation values. In the so-called 'random-phase approximation', this is done in a Hartree way, where taking the non-interacting expectation values moreover implies that momentum and spin have to be conserved for each. The pattern is then $c_A^\dagger c_B \rho \rightarrow \langle c_A^\dagger c_B \rangle \rho$, because $\langle \rho \rangle$ would only conserve momentum for $\vec{q} = 0$, where $V(\vec{q} = 0) = 0$. 'Fock' terms, where ρ would be split, are not included in this approximation.

For the first term, one then finds

$$c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\sigma} \rho_{-\vec{q}'} \rightarrow \langle c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\sigma} \rangle \rho_{-\vec{q}'} = \langle n_{\vec{k},\sigma} \rangle \delta_{-\vec{q},\vec{q}'} \rho_{\vec{q}} \quad (5.150)$$

which becomes

$$\sum_{\vec{q}'} \frac{V(\vec{q}')}{2} \langle\langle c_{\vec{k},\sigma}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\sigma} \rho_{-\vec{q}'}; \rho_{-\vec{q}} \rangle\rangle^R(\omega) \rightarrow \langle n_{\vec{k},\sigma} \rangle \frac{V(\vec{q})}{2} \langle\langle \rho_{\vec{q}}; \rho_{-\vec{q}} \rangle\rangle^R(\omega) \quad (5.151)$$

The second term gives

$$-c_{\vec{k}-\vec{q}',\sigma}^\dagger c_{\vec{k}+\vec{q},\sigma} \rho_{-\vec{q}'} \rightarrow -\langle n_{\vec{k}+\vec{q},\sigma} \rangle \delta_{-\vec{q},\vec{q}'} \rho(\vec{q}) \quad (5.152)$$

One sees easily that the terms in the last line in (5.149) give the same apart from $\vec{q} \rightarrow -\vec{q}$, with $V(-\vec{q}) = V(\vec{q})$ this then becomes just a factor of 2, yielding the total equation of motion in RPA

$$\begin{aligned}
(\hbar\omega - (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}) + i\eta)f_{\vec{k},\sigma}(\vec{q}, \omega) &= \hbar(\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle) + (\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle)V(\vec{q})\langle\langle \rho_{\vec{q}}; \rho_{-\vec{q}} \rangle\rangle^R(\omega) \\
\text{resp. } f_{\vec{k},\sigma}(\vec{q}, \omega) &= \hbar \frac{\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle}{\hbar\omega - (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}) + i\eta} + V(\vec{q})\chi^{\text{RPA}}(\vec{q}, \omega) \frac{\langle n_{\vec{k},\sigma} \rangle - \langle n_{\vec{k}+\vec{q},\sigma} \rangle}{\hbar\omega - (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}) + i\eta} \quad (5.153)
\end{aligned}$$

After summation over \vec{k} and σ and by using χ^0 from (5.144), one gets

$$\begin{aligned}
\chi^{\text{RPA}}(\vec{q}, \omega) &= \sum_{\vec{k},\sigma} f_{\vec{k},\sigma}(\vec{q}, \omega) = \chi^0(\vec{q}, \omega) + \chi^{\text{RPA}}(\vec{q}, \omega) \frac{V(\vec{q})}{\hbar} \chi^0(\vec{q}, \omega) \quad \text{resp.} \\
\chi^{\text{RPA}}(\vec{q}, \omega) &= \frac{\chi^0(\vec{q}, \omega)}{1 - \frac{V(\vec{q})}{\hbar} \chi^0(\vec{q}, \omega)} \quad (5.154)
\end{aligned}$$

This function has poles wherever χ^0 has them, i.e. for all particle-hole excitations. But it also has additional poles wherever $\chi^0(\vec{q}, \omega) = \frac{\hbar}{V(\vec{q})}$. Most of these extra poles are squeezed within the dense spectrum of the particle-hole excitations, see Fig. 5.3, but one lies at higher energies above the highest pole of χ^0 . This is the "plasmon" a collective excitation.

5.7.2 Magnetic susceptibility

Two kinds of spin-correlation functions are relevant

- Longitudinal $\langle\langle S_i^z; S_j^z \rangle\rangle$
- Transverse $\langle\langle S_i^x; S_j^y \rangle\rangle$, resp. $\langle\langle S_i^+; S_j^- \rangle\rangle$ with $S_i^\pm = S_i^x \pm iS_i^y$

In both cases, the Fourier transforms are more useful in translationally invariant systems, as for the charge correlations in (5.133); they are given by, e.g.,

$$S_{\bar{q}}^+ = \sum_i e^{i\bar{q}\bar{r}_i} S_i^+ = \sum_i e^{i\bar{q}\bar{r}_i} c_{i,\uparrow}^\dagger c_{i,\downarrow} = \frac{1}{N} \sum_{\bar{k}, \bar{k}'} c_{\bar{k},\uparrow}^\dagger c_{\bar{k}',\downarrow} e^{i(\bar{q}+\bar{k}-\bar{k}')\bar{r}_i} = \sum_{\bar{k}} c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow} \quad \text{with} \quad (5.155)$$

$$(S_{\bar{q}}^+)^{\dagger} = S_{-\bar{q}}^- = \sum_{\bar{k}} c_{\bar{k},\downarrow}^\dagger c_{\bar{k}-\bar{q},\uparrow}. \quad (5.156)$$

Analogously to the charge case, we are now going to find the transverse magnetic susceptibility first for non-interacting electrons and then for a mean-field treatment of an interacting Hamiltonian. We are looking for Green's functions

$$\langle\langle S_{\bar{q}}^+; S_{-\bar{q}}^- \rangle\rangle(\omega) = \sum_{\bar{k}} \langle\langle c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow}; S_{-\bar{q}}^- \rangle\rangle(\omega). \quad (5.157)$$

For convenience, we write the equation of motion for each term of the sum individually, where we need first the commutator

$$\begin{aligned} \langle\langle c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow}; S_{-\bar{q}}^- \rangle\rangle &= \sum_{\bar{p}} \langle\langle [c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow}, c_{\bar{p},\downarrow}^\dagger c_{\bar{p}-\bar{q},\uparrow}] \rangle\rangle = \sum_{\bar{p}} \langle\langle c_{\bar{k},\uparrow}^\dagger \underbrace{[c_{\bar{k}+\bar{q},\downarrow}, c_{\bar{p},\downarrow}^\dagger]}_{=\delta_{\bar{k}+\bar{q},\bar{p}}} + c_{\bar{p}-\bar{q},\uparrow} + c_{\bar{p},\downarrow}^\dagger \underbrace{[c_{\bar{k},\uparrow}^\dagger, c_{\bar{p}-\bar{q},\uparrow}]}_{=-\delta_{\bar{k}+\bar{q},\bar{p}}} + c_{\bar{k}+\bar{q},\downarrow} \rangle\rangle = \\ &= \langle\langle c_{\bar{k},\uparrow}^\dagger c_{\bar{k},\uparrow} \rangle\rangle - \langle\langle c_{\bar{k}+\bar{q},\downarrow}^\dagger c_{\bar{k}+\bar{q},\downarrow} \rangle\rangle = \langle\langle n_{\bar{k},\uparrow} \rangle\rangle - \langle\langle n_{\bar{k}+\bar{q},\downarrow} \rangle\rangle \end{aligned} \quad (5.158)$$

This step is almost as that involved in the charge susceptibility, (5.140) but involves opposite spins. As the next step, we obtain the commutator with the non-interacting Hamiltonian, the analogue of (5.141), where we allow here explicitly spin-dependent bands

$$[c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow}, H_0] = \sum_{\bar{k}', \sigma'} (\epsilon_{\sigma', \bar{k}'} - \mu) [c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow}, c_{\bar{k}', \sigma'}^\dagger c_{\bar{k}', \sigma'}] = \quad (5.159)$$

$$\begin{aligned} &= \sum_{\bar{k}', \sigma'} (\epsilon_{\sigma', \bar{k}'} - \mu) \left(\delta_{\downarrow, \sigma'} \delta_{\bar{k}+\bar{q}, \bar{k}'} c_{\bar{k},\uparrow}^\dagger c_{\bar{k}', \sigma'} - \delta_{\uparrow, \sigma'} \delta_{\bar{k}, \bar{k}'} c_{\bar{k}', \sigma'}^\dagger c_{\bar{k}+\bar{q},\downarrow} \right) \\ &= (\epsilon_{\downarrow, \bar{k}+\bar{q}} - \epsilon_{\uparrow, \bar{k}}) c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow} \end{aligned} \quad (5.160)$$

The equation of motion for non-interacting electrons is found and solved, see also (5.142),

$$\begin{aligned} \hbar(\omega + i\eta) \langle\langle c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow}; S_{-\bar{q}}^- \rangle\rangle^0(\omega) &= \hbar(\langle\langle n_{\bar{k},\uparrow} \rangle\rangle - \langle\langle n_{\bar{k}+\bar{q},\downarrow} \rangle\rangle) + (\epsilon_{\downarrow, \bar{k}+\bar{q}} - \epsilon_{\uparrow, \bar{k}}) \langle\langle c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow}; S_{-\bar{q}}^- \rangle\rangle^0(\omega) \\ \langle\langle c_{\bar{k},\uparrow}^\dagger c_{\bar{k}+\bar{q},\downarrow}; S_{-\bar{q}}^- \rangle\rangle(\omega) &= \hbar \frac{\langle\langle n_{\bar{k},\uparrow} \rangle\rangle - \langle\langle n_{\bar{k}+\bar{q},\downarrow} \rangle\rangle}{\omega - (\epsilon_{\downarrow, \bar{k}+\bar{q}} - \epsilon_{\uparrow, \bar{k}}) + i\eta} \end{aligned} \quad (5.161)$$

Summed over \vec{k} , the susceptibility is then

$$\langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^0(\omega) = \hbar \sum_{\vec{k}} \frac{\langle n_{\vec{k},\uparrow} \rangle - \langle n_{\vec{k}+\vec{q},\downarrow} \rangle}{\omega - (\epsilon_{\downarrow,\vec{k}+\vec{q}} - \epsilon_{\uparrow,\vec{k}}) + i\eta}, \quad (5.162)$$

which has a clear interpretation in terms of particle-hole excitations with a spin flip: A particle can be moved from \vec{k}, \uparrow into $\vec{k} + \vec{q}, \downarrow$ if the first state is occupied and the second empty; the process entails an energy change $\epsilon_{\downarrow,\vec{k}+\vec{q}} - \epsilon_{\uparrow,\vec{k}}$.

5.7.2.1 Magnetic susceptibility with interaction

Concerning electron-electron interactions, we use here the Hubbard interaction, because it only acts between electrons with different spin, see (5.125), and thus most clearly addresses the spin degree of freedom. The missing commutator is then best obtained in momentum space, i.e., using the interaction from (5.124):

$$\begin{aligned} [c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}, H_1] &= \frac{U}{N} \sum_{\vec{q}'} [c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}, \rho_{-\vec{q}'}^\uparrow \rho_{\vec{q}'}^\downarrow] = \frac{U}{N} \sum_{\vec{q}'} \left([c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}, \rho_{-\vec{q}'}^\uparrow] \rho_{\vec{q}'}^\downarrow + \rho_{-\vec{q}'}^\uparrow [c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}, \rho_{\vec{q}'}^\downarrow] \right) = \\ &= \frac{U}{N} \sum_{\vec{q}', \vec{p}} \left(\underbrace{[c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}, c_{\vec{p},\uparrow}^\dagger c_{\vec{p}-\vec{q}',\uparrow}]}_{=-\delta_{\vec{k},\vec{p}-\vec{q}'} c_{\vec{p},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}} \rho_{\vec{q}'}^\downarrow + \rho_{-\vec{q}'}^\uparrow \underbrace{[c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}, c_{\vec{p},\downarrow}^\dagger c_{\vec{p}+\vec{q}',\downarrow}]}_{=-\delta_{\vec{k}+\vec{q},\vec{p}} c_{\vec{k},\uparrow}^\dagger c_{\vec{p}+\vec{q}',\downarrow}} \right) = \\ &= \frac{U}{N} \sum_{\vec{q}'} \left(\rho_{-\vec{q}'}^\uparrow c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\downarrow} - c_{\vec{k}+\vec{q},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow} \rho_{\vec{q}'}^\downarrow \right). \end{aligned} \quad (5.163)$$

This term would generate an even higher Green's function.

In the RPA, we instead decouple it in a Hartree-Fock-like manner. Expectation values will again be based on the non-interacting model and thus have to conserve momentum and spin. The spin conservation substantially restricts the possible decouplings that can survive. Leaving out constants, one finds

$$\begin{aligned} &\frac{U}{N} \sum_{\vec{q}', \vec{k}'} \left(c_{\vec{k}',\uparrow}^\dagger c_{\vec{k}'-\vec{q}',\uparrow} c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\downarrow} - c_{\vec{k}+\vec{q},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow} c_{\vec{k}',\downarrow}^\dagger c_{\vec{k}'+\vec{q}',\downarrow} \right) \approx \\ &\frac{U}{N} \sum_{\vec{q}', \vec{k}'} \left(\underbrace{\langle c_{\vec{k}',\uparrow}^\dagger c_{\vec{k}'-\vec{q}',\uparrow} \rangle}_{\delta_{\vec{q}',0} \langle n_{\vec{k}',\uparrow} \rangle} c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\downarrow} - c_{\vec{k}',\uparrow}^\dagger \underbrace{\langle c_{\vec{k},\uparrow}^\dagger c_{\vec{k}'-\vec{q}',\uparrow} \rangle}_{\delta_{\vec{k}',\vec{k}+\vec{q}'} \langle n_{\vec{k},\uparrow} \rangle} c_{\vec{k}+\vec{q}+\vec{q}',\downarrow} - c_{\vec{k}+\vec{q},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow} \underbrace{\langle c_{\vec{k}',\downarrow}^\dagger c_{\vec{k}'+\vec{q}',\downarrow} \rangle}_{\delta_{\vec{q}',0} \langle n_{\vec{k}',\downarrow} \rangle} + c_{\vec{k}+\vec{q},\uparrow}^\dagger \underbrace{\langle c_{\vec{k}',\downarrow}^\dagger c_{\vec{k}+\vec{q},\downarrow} \rangle}_{\delta_{\vec{k}',\vec{k}+\vec{q}} \langle n_{\vec{k}+\vec{q},\downarrow} \rangle} c_{\vec{k}'+\vec{q}',\downarrow} \right) = \\ &= \frac{U}{N} c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow} \underbrace{\sum_{\vec{k}'} (\langle n_{\vec{k}',\uparrow} \rangle - \langle n_{\vec{k}',\downarrow} \rangle)}_{=N_\uparrow - N_\downarrow} - \frac{U}{N} \underbrace{(\langle n_{\vec{k},\uparrow} \rangle - \langle n_{\vec{k}+\vec{q},\downarrow} \rangle)}_{=S_{\vec{q}}^+} \sum_{\vec{q}'} c_{\vec{k}+\vec{q},\uparrow}^\dagger c_{\vec{k}+\vec{q}+\vec{q}',\downarrow} \end{aligned} \quad (5.164)$$

Note here that the surviving terms are *not* the same ones as in the previously discussed charge susceptibility, those drop here out as they would not conserve spin. Instead, we have terms coming from $\vec{q}' = 0$ as well as ‘Fock’ terms. Since the latter involve switching two operators, they involve a sign change, which will prove to be crucial.

Introducing the magnetization $m = \frac{1}{N}(N_\uparrow - N_\downarrow)$ with $N_\sigma = \sum_{\vec{k}} n_{\vec{k},\sigma}$, the equation of motion becomes

$$\hbar(\omega + i\eta) \langle\langle c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega) = \hbar(n_{\vec{k},\uparrow} - n_{\vec{k}+\vec{q},\downarrow}) + (\epsilon_{\downarrow,\vec{k}+\vec{q}} - \epsilon_{\uparrow,\vec{k}}) \langle\langle c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega)$$

$$\begin{aligned}
& + Um \langle\langle c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega) - \frac{U}{N\hbar} (\langle n_{\vec{k},\uparrow} \rangle - \langle n_{\vec{k}+\vec{q},\downarrow} \rangle) \langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega) \quad \text{resp.} \\
\langle\langle c_{\vec{k},\uparrow}^\dagger c_{\vec{k}+\vec{q},\downarrow}; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega) & = \frac{(\langle n_{\vec{k},\uparrow} \rangle - \langle n_{\vec{k}+\vec{q},\downarrow} \rangle)}{\omega - (\epsilon_{\downarrow,\vec{k}+\vec{q}} - \epsilon_{\uparrow,\vec{k}}) - Um + i\eta} \left(1 - \frac{U}{N\hbar} \langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega) \right) \quad (5.165)
\end{aligned}$$

The term Um with the magnetization can now be incorporated into $\epsilon_\sigma \rightarrow \tilde{\epsilon}_\sigma = \epsilon_\sigma \pm \frac{Um}{2}$ and $-(\epsilon_{\downarrow,\vec{k}+\vec{q}} - \epsilon_{\uparrow,\vec{k}}) - Um = -(\tilde{\epsilon}_{\downarrow,\vec{k}+\vec{q}} - \tilde{\epsilon}_{\uparrow,\vec{k}})$. Comparing to the Hartree(-Fock) treatment of the Hubbard model in Sec. 5.6.6, we see that the corresponding self energy $\Sigma^\sigma = U\langle n_{-\sigma} \rangle$ is precisely this change included here. Accordingly, even if the one-particle energy was not spin dependent to start with, it might become so in a self-consistent (mean-field) treatment.

The ‘non-interacting’ susceptibility, see Eq. (5.162), is then

$$\langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^0(\omega) = \hbar \sum_{\vec{k}} \frac{\langle n_{\vec{k},\uparrow} \rangle - \langle n_{\vec{k}+\vec{q},\downarrow} \rangle}{\omega - (\tilde{\epsilon}_{\downarrow,\vec{k}+\vec{q}} - \tilde{\epsilon}_{\uparrow,\vec{k}}) + i\eta}. \quad (5.166)$$

With a finite self-consistent $m \neq 0$ included in the one-particle energies, it already takes interactions into account at some level, but would by itself still only contain particle-hole excitations.

Summation of (5.165) over \vec{k} and inserting (5.166) gives the RPA susceptibility

$$\begin{aligned}
\langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega) & = \langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^0 \left(1 - \frac{U}{N\hbar} \langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega) \right) \\
\langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^{\text{RPA}}(\omega) & = \frac{\langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^0(\omega)}{1 + \frac{U}{N\hbar} \langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^0(\omega)}, \quad (5.167)
\end{aligned}$$

which has additional poles wherever $\langle\langle S_{\vec{q}}^+; S_{-\vec{q}}^- \rangle\rangle^0(\omega) = -\frac{N\hbar}{U}$.

In contrast to the charge susceptibility discussed in Fig. 5.3(a), the additional pole outside the particle-hole spectrum is here at energies *below* the continuous spectrum. The associated collective excitation – the magnon – is a low-energy excitation. Mathematically, this difference to the plasmon arises, because the terms surviving the mean-field decoupling have two operators switched and thus lead to opposite sign. For finite m , the particle-hole continuum has here a gap Um for $|\vec{q}| \rightarrow 0$ and it is relatively easy to show that the magnon frequency $\omega_m = 0$ for $\vec{q} = 0$. A slightly more involved estimate then gives a quadratic dependence $\omega_m \propto |\vec{q}|^2$. The magnon is visible in neutron scattering until it merges with the continuum.

5.7.3 Nesting as an indicator for potential order

Both for the charge and for the spin sector, the non-interacting susceptibility is given by particle-hole excitations, i.e., it can be understood by considering the ways we can move an electron from the occupied to the unoccupied states. The susceptibility will thus be large for a given energy and momentum, if there many processes with this momentum and energy transfer are allowed. If the non-interacting susceptibility happens to be large for $\omega \rightarrow 0$ and some momentum \vec{q}^* , then (i) many electrons can be shifted by \vec{q}^* and (ii) this costs hardly any energy. As we can only shift electrons between states if one is occupied and the other empty, $\omega \rightarrow 0$ implies that the involved states have to be very close to the Fermi surface.

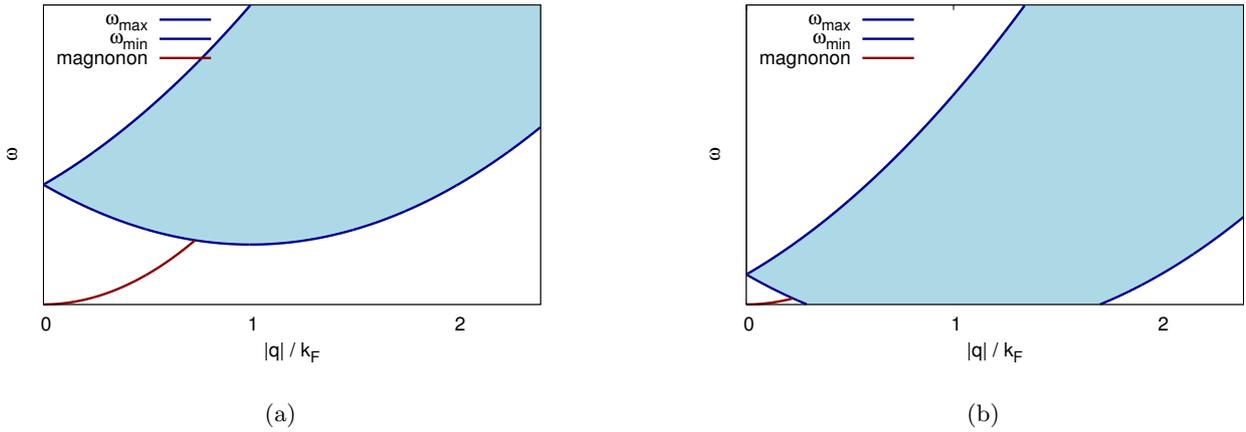


Figure 5.4: Spin susceptibility in random-phase approximation for ‘Stoner’ bands with an energy splitting Um . Shading shows the particle-hole excitations for a system, where spin-down energies and spin-up energies have a constant splitting, i.e. $\epsilon_{\vec{k},\downarrow} = \epsilon_{\vec{k},\uparrow} + c$. In a Hartree approximation, $c = Um$. (a) and (b) illustrate the situation for large and small splitting, in (a), only spin-up states are occupied. The collective magnon is shown in addition.

Such a situation thus arises if some parts of the Fermi surface can be parallel shifted into others, so-called ‘nesting’.

We have moreover seen that the electron-electron interaction in momentum representation involves the same type of operators $a_{\vec{k}+\vec{q}}^\dagger a_{\vec{k}}$, i.e., again transfer of an electron from \vec{k} to $\vec{k} + \vec{q}$, see Eqs. (5.134) and (5.124). If $\chi(\omega \rightarrow 0, \vec{q}^*)$ is large, even a weak interaction might win over the small kinetic-energy penalty and actually move the electrons giving finite expectation values of $\langle \rho_{\vec{q}^*} \rangle$ operators. In position space, this correspond to a charge- or spin-density wave with modulation vector \vec{q}^* , see (5.135). In energy-momentum space, this will open a gap at the nested portions of the Fermi surface.

Whether a charge- or a spin-modulated pattern is preferable, depends on the relative importance of ‘Hubbard-like’ and long-range interaction: The first acts only onsite and between opposite spins, while the second also couples identical spins on different sites. As an example, the square-lattice nearest-neighbor tight-binding model at half filling is perfectly nested with a nesting vector $\vec{q}^* = (\pi, \pi)$. If we consider spinless fermions¹¹, half filling is one fermion per two sites, Hubbard U is inactive and long-range interaction may support a charge-density wave. If, on the other hand, we consider spinful electrons, half-filling is one electron per site. Doubly occupied sites are suppressed by U , so that a charge-density wave would be energetically costly. Spin can still be modulated and the two-dimensional Hubbard model is indeed an antiferromagnet. Translated to position space, $\vec{q}^* = (\pi, \pi)$ corresponds to a checkerboard pattern.

¹¹Such a picture may be appropriate if only one spin state is relevant, e.g., in a magnetic metal.

6 Symmetry breaking: Magnetism and Superconductivity

6.1 Magnetism

Inspired by Khomskii's book.

When describing the interaction of electrons with electro-magnetic field, ‘minimal coupling’ is usually employed. Momentum operator \hat{p} is here replaced by $\hat{p} + c\vec{A}(\hat{x})$, where vector potential \vec{A} is an operator via its dependence on \hat{x} and the prefactor c depends on gauge choice. In Coulomb gauge $\vec{\nabla}\vec{A} = 0$ so that \hat{p} only acts on the wave function and commutes with \vec{A} . The kinetic energy in the Hamiltonian then contains terms

- $\propto \hat{p}^2$: Usual kinetic energy, together with the potential from the ions, which is still there, it gives the usual band energies $\epsilon_{\vec{k}}$.
- $\propto \hat{p}\vec{A}$: Closer analysis (see Pauli equation) shows that this term can be written as $\vec{B}\cdot(\vec{L}+2\vec{S})$. Such an interaction between magnetic field and existing magnetic moments is *paramagnetism*.
- $\propto \vec{A}^2$: These terms $\propto \vec{B}^2$ do not involve existing magnetic moments, but can be interpreted as the interaction between \vec{B} and induced moments $\propto B$. The induced moments are opposite to the magnetic field, this is *diamagnetism*.

We will here not discuss diamagnetism further and will also not have time to devote to the quantum Hall effect, but will instead focus on paramagnetism and magnetic order.

6.1.1 Paramagnetism: Existing moments without interactions

First, we will discuss how the electron spin reacts to a magnetic field, in two limits: a metal with itinerant and non-interacting electrons and an insulator with localized moments. Orbital angular momentum is here left out, because for itinerant electrons, it is often ‘quenched’, i.e., forced to be 0, which is certainly the case in s bands. The localized-moment discussion carries over to general angular momenta without much change.

6.1.1.1 Magnetic susceptibility of non-interacting electrons

Non-interacting electrons were discussed in Sec. 4.4: quantities can be obtained from the density of states by filling it using the Fermi function. The magnetic susceptibility expresses how strong a magnetization can be induced by a given magnetic field, i.e., by the difference in particle numbers for up and down electrons. For non-interacting electrons, it is determined by the balance between the magnetic energy that can be gained by turning some ‘down’ electrons into ‘up’ and the energy that is lost by then having to occupy higher-energy states due to the Pauli principle.

A magnetic field \vec{B} along z shifts the one-particle energies $\epsilon(\vec{k}) \rightarrow \epsilon(\vec{k}) \pm \frac{g\mu_B}{2}|B|$. Both the up and the down states are then filled up to some chemical potential that is the same for both spins in equilibrium μ . (Otherwise, electrons would flip spin until it evens out.) However, when filling electrons into states, it is technically equivalent to not shift the bands and instead make the chemical potential spin dependent $\mu \rightarrow \mu \mp \frac{g\mu_B}{2}|B|$.

Using the Sommerfeld approach, we had seen in Eq. (4.58) that the number of electrons can be obtained by (i) filling the states up to the chemical potential $\mu(T)$ and (ii) setting $\mu(T) = E_F$. This approximate approach instead of a more accurate calculation neglects corrections quadratic in temperature T . Making the particle number spin dependent and noting that the density of states per spin is half the total $\rho_\sigma(\omega) = \frac{1}{2}\rho(\omega)$, we find

$$\frac{N_\sigma}{N} = \int_0^{E_F \pm \frac{g\mu_B}{2}\sigma|B|} d\omega \rho_\sigma(\omega) + \mathcal{O}(T^2) = \frac{1}{2} \int_0^{E_F \pm \frac{g\mu_B}{2}\sigma|B|} d\omega \rho(\omega) + \mathcal{O}(T^2), \quad (6.1)$$

with $\sigma = \pm 1$ for up and down. In the magnetization, most of the integrals cancel and only the density of states around E_F actually contributes, giving the approximation

$$M = \frac{N_\uparrow - N_\downarrow}{N} = \frac{1}{2} \int_{E_F - \frac{g\mu_B}{2}|B|}^{E_F + \frac{g\mu_B}{2}|B|} d\omega \rho(\omega) + \mathcal{O}(T^2) = \frac{g\mu_B}{2}|B|\rho(E_F) + \mathcal{O}(T^2) \quad \text{and}$$

$$\chi = \frac{\partial M}{\partial B} = \frac{g}{2} \underbrace{\mu_B \rho(E_F)}_{\approx 1} + \mathcal{O}(T^2). \quad (6.2)$$

Temperature thus only enters in second order.

Up to second order in temperature, the susceptibility is a constant determined by the density of states at the Fermi level. A large susceptibility can be obtained in systems with many states near the Fermi level: small ‘distortions’ of the bands can then have a large impact, a mechanism similar to that discussed in Sec. 5.7.3 as favoring ordering. The scenario discussed here applies to noninteracting bands, more specifically to metals, because the $\rho(E_F) = 0$ in insulators and their susceptibility would thus vanish. Due to the approximation made, it can only be considered valid if the magnetic energy scale $\mu_B B$ is much smaller than the Fermi energy, which is usually fulfilled.

6.1.1.2 Magnetic susceptibility of non-interacting spins

The susceptibility of localized spin – as opposed to the previously discussed itinerant electrons – turns out to be quite different. Even if insulating, such a localized-spin material has a paramagnetic susceptibility with a clear temperature dependence.

The Hamiltonian of a single spin in a magnetic field is of course $H = -\mu\vec{S}\vec{B}$. Selecting the spin-quantization axis z to be parallel to \vec{B} , this becomes for a system of non-interacting localized electrons

$$H = -\frac{g\mu_B}{2}\vec{B} \sum_i \vec{\sigma}_i = -\frac{g\mu_B}{2}B \sum_i \sigma_i^z \quad (6.3)$$

where σ are the Pauli matrices and index i runs over lattice sites. The magnetization and consequently the susceptibility are likewise simply sums over the lattice sites

$$M = \frac{\sum_i \langle M_i \rangle}{N} = \frac{g\mu_B}{2N} B \sum_i \langle \sigma_i^z \rangle \quad \text{and} \quad (6.4)$$

$$\chi = \frac{g\mu_B}{2N} \sum_i \langle \sigma_i^z \rangle. \quad (6.5)$$

The susceptibility has thus only to be obtained for one single spin in a magnetic field. As it can only have two states, the involved sums over all states j are easily evaluated:

$$\langle \sigma_i^z \rangle = \frac{\sum_j \langle \sigma_i^z \rangle_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta(-\frac{g\mu_B}{2}B)} - e^{-\beta(\frac{g\mu_B}{2}B)}}{e^{-\beta(-\frac{g\mu_B}{2}B)} + e^{-\beta(\frac{g\mu_B}{2}B)}} = \tanh \frac{g\mu_B B}{2k_b T} \quad (6.6)$$

and

$$M = \frac{g\mu_B}{2N} \sum_i \tanh \frac{g\mu_B B}{2k_b T} = \frac{g\mu_B}{2} \tanh \frac{g\mu_B B}{2k_b T} \approx \mu_B \tanh \frac{g\mu_B B}{2k_b T}. \quad (6.7)$$

This result has a qualitatively different temperature and magnetic-field dependence than that for itinerant electrons.

The previously discussed itinerant-electron susceptibility was obtained for $\mu_B B \ll E_F$. Here, the energies to compare are $\mu_B B$ vs. $k_B T$. For weak magnetic fields resp. high temperature, (6.7) becomes

$$\chi \approx \frac{\partial}{\partial B} g^2 \mu_B^2 \frac{B}{4k_b T} = \frac{g^2 \mu_B^2}{4k_b T} = \frac{C}{T}. \quad (6.8)$$

This is the so-called Curie-law applied to non-interacting spins. Experimentally, $\chi \propto 1/T$ at high T is a sign for the presence of localized moments. At low T , interactions between spins tend to become important.

6.1.2 Interacting moments and ordered states

After noninteracting electrons/spins, we now consider interacting systems, which can order magnetically. For itinerant electrons at weak interactions, where a perturbation theory is valid, we had discussed ferromagnetism in the ‘Stoner’ picture in Sec. 5.6.6 and more general types¹ of magnetic/charge order in Sec. 5.7.3.

We had there used a mean-field decoupling $n_i n_j \rightarrow \langle n_i \rangle n_j + n_i \langle n_j \rangle - \langle n_i \rangle \langle n_j \rangle$ and we will use an analogous approximation for localized spins. Let us, however, recall, what approximation is made in a typical mean-field treatment:

$$\begin{aligned} n_i n_j &= (\langle n_i \rangle + (n_i - \langle n_i \rangle)) (\langle n_j \rangle + (n_j - \langle n_j \rangle)) = \\ &= \langle n_i \rangle \langle n_j \rangle + (n_i - \langle n_i \rangle) \langle n_j \rangle + \langle n_i \rangle (n_j - \langle n_j \rangle) + \underbrace{(n_i - \langle n_i \rangle)(n_j - \langle n_j \rangle)}_{\approx 0} \approx \\ &\approx n_i \langle n_j \rangle + n_j \langle n_i \rangle - \langle n_i \rangle \langle n_j \rangle \end{aligned} \quad (6.9)$$

¹These are more realistic than Stoner ferromagnetism in the case of the single-band Hubbard model.

The neglected term is thus the correlation between deviations from the average: A mean-field approach considers these fluctuations to be either very small (so that their square is negligible) or independent of each other.

At strong electron-electron interactions, doubly occupied sites cost high energy so that electrons can hardly hop at half filling. If interactions are strong enough to make such a half-filled system insulating, this so-called ‘Mott’-insulator has localized spins.

For localized spins, plausible interactions are of the form

$$H = \sum_{i,j} J_{i,j} \vec{S}_i \vec{S}_j . \quad (6.10)$$

These ‘Heisenberg’ interaction are ‘simple’ in the sense that they preserve the full rotational symmetry in spin space and do thus not assume further specifics of the system. In practice, some anisotropies are often present due to spin-orbit/lattice coupling. In reading papers and books, one has to take into account that different conventions exists concerning the notation of Heisenberg Hamiltonians:

- Sign of $J_{i,j}$: Sometimes, the Hamiltonian is written with an overall minus sign, so that ferromagnetic couplings become positive.
- Counting of pairs (i, j) : Either each bond is only counted once or the sums over i and j go both over *all* sites, so that each bond is counted twice with $J_{i,j} = J_{j,i}$. Gives a factor of two in $J_{i,j}$.

Here, we count each bond twice and $J_{i,j} > 0$ denotes antiferromagnetic coupling favoring opposite spins.

6.1.2.1 Mean-field treatment

In a mean-field decoupling, we use $\vec{S}_i \vec{S}_j \rightarrow \langle \vec{S}_i \rangle \vec{S}_j + \vec{S}_i \langle \vec{S}_j \rangle - \langle \vec{S}_i \rangle \langle \vec{S}_j \rangle$ and the Hamiltonian on one specific bond becomes

$$H_{a,b} = -\mu \vec{B} (\vec{S}_a + \vec{S}_b) + J_{a,b} \langle \vec{S}_b \rangle \vec{S}_a + J_{a,b} \vec{S}_b \langle \vec{S}_a \rangle - J_{a,b} \langle \vec{S}_b \rangle \langle \vec{S}_a \rangle = \sum_{i=a,b} \left(-\mu \vec{B} + J_{i,\bar{i}} \langle \vec{S}_{\bar{i}} \rangle \right) \vec{S}_i - \text{const.}$$

where $\bar{i} = a$ (b) for $i = b$ (a). \vec{S}_i is here still an operator, while $\langle \vec{S}_{\bar{i}} \rangle$ is a number and the term containing only these numbers will not be discussed any more at present. (It is important if one wants to calculate the overall energy, though.) The effect of “the other” spin $\vec{S}_{\bar{i}}$ onto \vec{S}_i has here been rewritten into an additional magnetic field.

Extending this treatment to all bonds and discarding the constant, the spin \vec{S}_i sees a total effective field containing both the external field \vec{B} and an internal field coming from all spins it is connected to via non-zero $J_{i,j}$:

$$H_i = -\mu \vec{B}_{i,\text{eff}} \vec{S}_i = \left(-\mu \vec{B} + \sum_j J_{i,j} \langle \vec{S}_j \rangle \right) \vec{S}_i . \quad (6.11)$$

Of course, \vec{S}_i itself also has an effect on the other spins, and this “back-feeding” is severely affected by the mean-field approach. Assuming we want to discuss ferromagnetic order, we

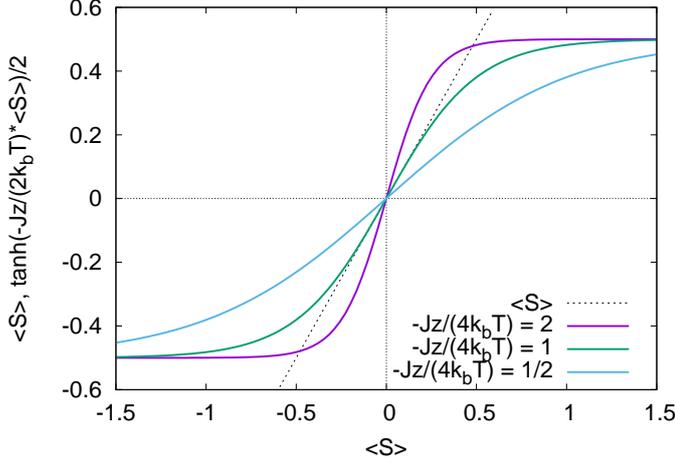


Figure 6.1: Graphical solution of Eq. (6.15) for $z = 4$ (two-dimensional square lattice), ferromagnetic $J = -1$ (setting the relevant unit of energy/temperature) and three temperatures $k_B T = \frac{z(-J)}{4} \cdot x = T_c \cdot x = 2, 1, \frac{1}{2}$ with the critical temperature T_c .

further assume $\langle \vec{S}_i \rangle \rightarrow \langle \vec{S} \rangle = \langle S \rangle \vec{e}^z$, i.e. uniform order with spins along z , the direction of \vec{B} . The total effective field acting on each spin is then

$$-\mu B_{i,\text{eff}} = -\mu B + \langle S \rangle \sum_j J_{i,j} \quad (6.12)$$

and for uniform nearest-neighbor coupling

$$\mu B_{\text{eff}} = \mu B - zJ \langle S \rangle, \quad (6.13)$$

where z is the coordination number, the number of neighbors.

The effective magnetic field acts on each spin separately (in the mean-field approximation!) and one can use (6.6). For spin 1/2, one then gets

$$g\mu_B B_{\text{eff}} = g\mu_B B - zJ \langle S \rangle \quad \text{resp.} \quad (6.14)$$

$$\langle S \rangle = \frac{1}{2} \langle \sigma^z \rangle = \frac{1}{2} \tanh \frac{g\mu_B B_{\text{eff}}}{2k_b T} = \frac{1}{2} \tanh \frac{g\mu_B B - zJ \langle S \rangle}{2k_b T}. \quad (6.15)$$

The average spin $\langle S \rangle$ is here the important variable (all other letters denote constants) that expresses the system's reaction.

The difference to non-interacting spins becomes clearest for $B \rightarrow 0$ ²: In this case, Eq. (6.7) for noninteracting spins clearly implies $\langle S \rangle = \tanh 0 = 0$. For interacting spins, $\langle S \rangle = 0$ is also always a solution of Eq. (6.15), but possibly not the only one. To see whether there are other solutions, it is helpful to plot both the left side of (6.15), i.e. $\langle S \rangle$ and the right side $\frac{1}{2} \tanh \frac{-zJ \langle S \rangle}{2k_b T}$ as a function of $\langle S \rangle$ each and to check whether they cross at any points except $\langle S \rangle = 0$. The slope of $\langle S \rangle$ is one and as the hyperbolic tangent has its maximal slope

²The role of \vec{B} has here only been to select a spin-quantization axis. This is not necessary, but a helpful trick.

at $\langle S \rangle = 0$, the curves can only have more than one crossing, if that maximal slope is larger than one, see Fig. 6.1. This criterion yields $\frac{-zJ}{4k_bT} = 1$ as the point separating the parameter space with one solution ($\langle S \rangle = 0$) from that with three. For temperatures above the ‘critical’ one, we have one solution, for temperatures below, three.

It turns out that the free energy of the additional solutions with $\langle S \rangle \neq 0$ is lower than that of $\langle S \rangle = 0$ for $T < T_C$, i.e., it is energetically favorable to have a finite magnetization. This breaks the original symmetry of the Hamiltonian, where positive and negative S^z are equivalent – in fact, for $\vec{B} = 0$, all directions of \vec{S} are equivalent. This mechanism is called ‘spontaneous symmetry breaking’.

Let us now investigate the magnetic susceptibility of interacting spins in a magnetic field. It is determined by the derivative of the magnetization per site $M = g\mu_B \langle S \rangle$ with respect to the magnetic field B , i.e.,

$$\chi = \frac{\partial M}{\partial B} = g\mu_B \frac{\partial \langle S \rangle}{\partial B} = \frac{g\mu_B}{2} \frac{\partial}{\partial B} \tanh \frac{g\mu_B B - zJ \langle S \rangle}{2k_b T}. \quad (6.16)$$

As in Eq. (6.7) for non-interacting spins, we approximate the hyperbolic tangent by a straight line, an approximation valid for small arguments, i.e., small external and internal magnetic fields compared to temperature. One then finds

$$\begin{aligned} \chi &\approx \frac{g\mu_B}{2} \frac{\partial}{\partial B} \frac{g\mu_B B - zJ \langle S \rangle}{2k_b T} = \frac{g^2 \mu_B^2}{4k_b T} + \underbrace{\frac{z(-J)}{4k_b}}_{=T_C} \frac{1}{T} \underbrace{g\mu_B \frac{\partial \langle S \rangle}{\partial B}}_{=\chi} \\ &\chi \left(1 - \frac{T_C}{T}\right) = \frac{C}{T} \end{aligned} \quad (6.17)$$

where the constant $C = \frac{g^2 \mu_B^2}{4k_b}$ is the same as in Eq. (6.7). This expression can be rewritten to give

$$\chi = \frac{C}{T - T_C}, \quad (6.18)$$

Curie’s law for ferromagnets. It starts to diverge at higher temperatures $T \rightarrow T_C > 0$, because even a small magnetic field can result in a large magnetization once the system is close to ordering spontaneously. (Nevertheless, the approximation of the tanh implies that the treatment is no longer valid at T_C .)

This consideration can even be extended to antiferromagnetic coupling. In that case, one finds the opposite sign in the denominator of (6.18), i.e., a “negative ordering temperature” indicates antiferromagnetic order: At low T , a magnetic field finds it harder to magnetize the sample than would be expected for independent spins, because they want to align in an alternating pattern.

6.1.2.2 Excitations and Validity of the Mean-field Treatment

The mean-field approximation gives a finite critical temperature T_C regardless of rotation symmetry of the spin, as an Ising Hamiltonian, where spins can only be $\pm 1/2$ would give the same result. The critical temperature is also $T_C > 0$ in all dimensions, even if the presence

of z makes it smaller in lower dimensions. After a look at low-energy excitations, we will however see that the picture is somewhat more complicated than mean-field theory suggests.

In the exercise, one problem showed that the elementary excitations in the 1D Heisenberg ferromagnet have vanishing energy for $\vec{k} \rightarrow 0$. With some hand waving, this can be generalized for Hamiltonians with continuous symmetry (e.g., Heisenberg spins, but also “ x - y models”, where spins live within a plane). Low-temperature states with their spontaneous magnetization aligned along equivalent directions must have the same energy, i.e., one has a continuous order parameter. If continuous path through equivalent directions can be chosen, then one can introduce one single long-wavelength twist through the system. Locally, this twists each spin a little bit from the purely ferromagnetic direction and thus costs a little bit of energy. However, for an infinitely large system, one can make the twist arbitrarily small, so that the state is practically ferromagnetic everywhere and the energy cost becomes arbitrarily small as well.³ One can thus argue that ordered states of systems with continuous symmetry should have excitations with energies going to 0, so-called ‘Goldstone’ modes.

Exercise 3 on sheet 4 dealt with the impact of low-energy acoustic phonons on the average ion positions. The conclusion had been that the quantum fluctuations caused by the phonons actually cause the average deviation from the equilibrium position to diverge in one dimension (even at $T = 0$) and two dimensions (at $T > 0$). This argument can now be generalized: The low-energy excitations present due to a continuous order parameter make deviations from that order parameter diverge and melt the order. This happens in 1D regardless of the temperature and in 2D at finite temperature. These no-go statements about long-range order in low dimensions are referred to as “Mermin-Wagner theorem”.

If the order parameter is discrete rather than continuous, e.g., in the case of the Ising model, one can not make use of the infinitely slow distortion to argue in favor of zero-energy excitations. In fact, the excitation spectrum is in these cases gapped. Long-range order can then exist at finite T in two dimensions and at $T = 0$ in one dimension. Any finite (even small) T in one dimension nevertheless destroys truly long-range order: Even if a “mistake” in the spin pattern costs energy Δ and is suppressed by a probability $e^{-\beta\Delta}$, this unlikely event will still arise *somewhere* in an infinitely long chain. While order can “go around” such isolated defects in higher dimensions, defects are fatal to order in one dimension.

6.2 (Ginzburg-)Landau Theory

Also inspired by Khomskii’s book.

After having studied magnetic ordering, we are now going to discuss very generally approach to ordering transitions. It is also a mean-field approach, but in contrast to the mean-field treatment of the Heisenberg model discussed above, it does not start from a microscopic model, but rather from global symmetry considerations. It can thus not be used to derive macroscopic properties from microscopic ingredients, but rather to find the a theoretical description consistent with observed macroscopic facts. Its strength is that it needs very few ingredients.

The goal is to describe a system that potentially has some ordering transition.

³As long as interactions are either finite in range or at least decay sufficiently fast with distance.

- The order parameter η can be a scalar (e.g. magnetization of the Ising model), a vector (e.g. magnetization of ferromagnetic and many antiferromagnetic Heisenberg models) a tensor (e.g. order parameters of some antiferromagnetic patters), it can be real or complex. We start with a real scalar for simplicity.
- The order parameter can also depend on space, the corresponding approach is then called “Ginzburg-Landau” theory, while “Landau theory” might often refers to the homogeneous case. We sart with a uniform order parameter.
- At high temperature, the order parameter is assumed to be $\eta = 0$, i.e., the system is disordered.
- At temperatures just below the ordering temperature, the order parameter is assumed to be rather small (ideally, but not necessarily, going to $\eta \rightarrow 0$ at $T \rightarrow T_C$), so that expansions in its powers make sense. (Note that this is fulfilled in the case discussed above, because a slope infinitesimally below 1 yields finite- $\langle S \rangle$ solutions infinitesimally away from 0.)

The approach is then to write the free energy as an expansion in powers of the order parameter η :

$$\begin{aligned} \Phi(\eta, T, p, \dots) = & \Phi_0(T, p, \dots) + \alpha(T, p, \dots)\eta + A(T, p, \dots)\eta^2 + C(T, p, \dots)\eta^3 + \\ & + B(T, p, \dots)\eta^4 + F(T, p, \dots)\eta^5 + D(T, p, \dots)\eta^6 + \dots \end{aligned} \quad (6.19)$$

The parameters depend continuously on temperature T and can additionally depend on other quantities, e.g., pressure. We focus here on temperature dependence and furthermore assume that the parameters depend ‘nicely’ on T , i.e., are continuously differentiable. Any jumps in thermodynamic quantities are supposed to come from phase transitions captured by η . Physically, this means that we exclude here the presence of other order parameters that might spontaneously break symmetry.

Equilibrium values for η are saddle points of Φ , i.e.,

$$\begin{aligned} \left. \frac{\partial \Phi(\eta, T, p, \dots)}{\partial \eta} \right|_{T, p, \dots = \text{const.}} = & \alpha(T, p, \dots) + 2A(T, p, \dots)\eta + \\ & + 3C(T, p, \dots)\eta^2 + 4B(T, p, \dots)\eta^3 + \dots = 0 \end{aligned} \quad (6.20)$$

In order for $\eta = 0$ to be the only solution for all $T > T_C$, the linear coefficient has to vanish $\alpha(T, p, \dots) = 0$. In many cases, a system’s (expected) inversion symmetry will moreover require positive and negative η to be equivalent, so that all odd powers drop out. The simplest case is then found for $B(T \approx T_C, p, \dots) > 0$, where we only have to keep two terms, the quadratic and the fourth power:

$$\Phi(\eta, T) = \Phi_0 + A(T)\eta^2 + B(T)\eta^4 \quad \text{resp.} \quad (6.21)$$

$$\eta \cdot (A(T) + 2B(T)\eta^2) = 0. \quad (6.22)$$

Clearly, $\eta = 0$ is always a solution. However, two more solutions

$$\eta = \pm \sqrt{-\frac{A(T)}{2B(T)}} = \pm \sqrt{\frac{|A(T)|}{2B(T)}} \quad (6.23)$$

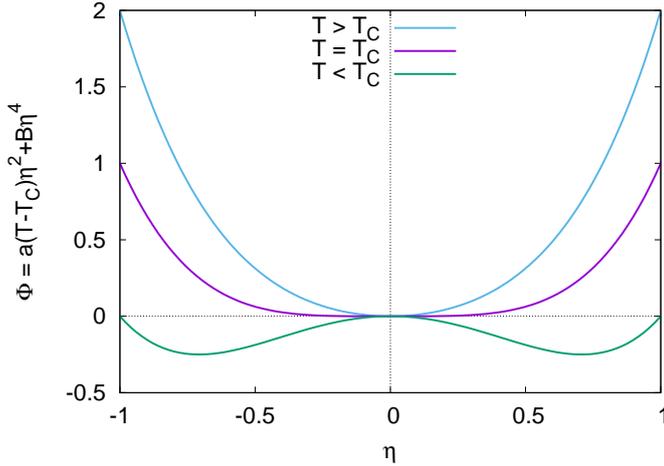


Figure 6.2: Simplest free energy (6.21) describing a second-order phase transition for three temperatures $T > T_C$, $T = T_C$ and $T < T_C$. At $T > T_C$, both the quadratic and the fourth-order term are positive, so that the only minimum is at $\eta = 0$. At $T = T_C$, the coefficient of η^2 goes through 0, so that it is negative at $T < T_C$. For large η , the fourth-order term dominates, but at small η , the quadratic term induces free-energy minima a finite η .

are found if and only if $A(T) < 0$. (Note that we required $B(T \approx T_C) > 0$.) At T_C , coefficient A must consequently change sign. One can easily check that for $A < 0$, these additional solutions give minima, while $\eta = 0$ becomes a local maximum. Focussing on the leading order in temperature, we can set $A(T \approx T_C) = a \cdot (T - T_C) + \mathcal{O}((T - T_C)^2)$ with $a > 0$.⁴ For an illustration, see Fig. 6.2. The order parameter just below T_C is then given by

$$\eta = \pm \sqrt{\frac{a \cdot (T_C - T)}{2B}}, \quad (6.24)$$

i.e., a square-root dependence. When more exact approaches are used, the ‘critical exponent’ turns out not to be $1/2$, but pure symmetry breaking transitions in fact have an order parameter growing continuously from 0, i.e., they are second order as mean-field theory suggests and as we are going to discuss next.

6.2.1 Second-order transition

An order parameter continuous at the transition is a strong hint in favor of a higher-order phase transition, but let us now in detail discuss the analytic behavior of the optimal $\Phi_{\min}(T \approx T_C)$ and its derivatives. The equilibrium order parameter η_{\min} around T_C is close to zero and lowest order gives:

$$\Phi_{\min} = \Phi_0 + A\eta_{\min}^2 + \dots = \Phi_0 \begin{cases} + 0 & \text{for } \eta_{\min}^2 = 0 \text{ at } T > T_C, \\ -\frac{a^2}{2B}(T - T_C)^2 + \dots & \text{for } \eta_{\min}^2 = \frac{a(T - T_C)}{2B} \text{ at } T \leq T_C, \end{cases} \quad (6.25)$$

⁴ $a = 0$ and $A \propto (T - T_C)^3$ is theoretically possible, but extremely unlikely, as no symmetry enforces this and it would thus need fine tuning.

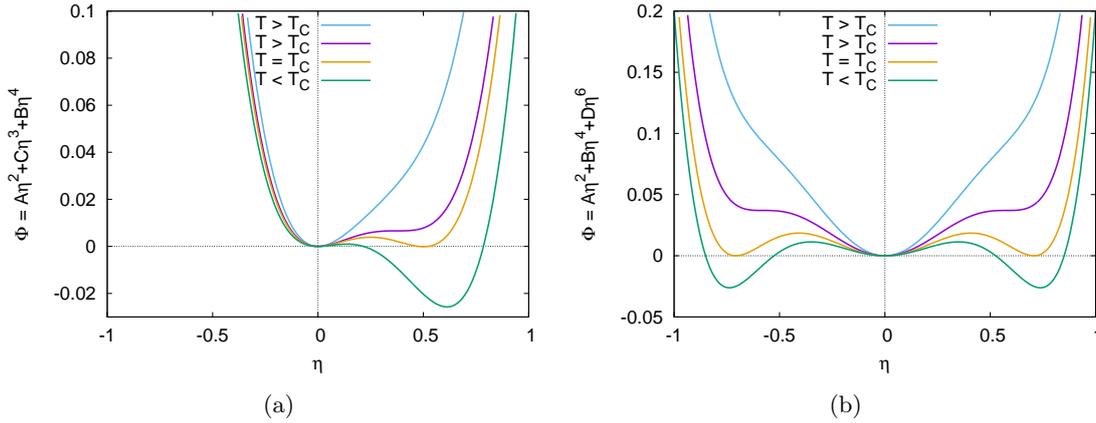


Figure 6.3: Two cases of free energies (6.19) describing a first-order phase transition. In (a), the system lacks inversion symmetry, so that a third-order term in η exists. In (b), the system is inversion symmetric, i.e., no odd powers in η are present. The fourth-order coefficient $B(T \approx T_C)$ is here negative. The sixth order becomes then important and the transitions becomes first order.

This functions is continuous at T_C .

The first derivative with respect to T , keeping all other parameters like p or V constant, is the entropy

$$S = -\frac{\partial \Phi}{\partial T} = \underbrace{-\frac{\partial \Phi_0}{\partial T}}_{=S_0} + \begin{cases} 0 & \text{for } T > T_C, \\ \frac{a^2}{B}(T - T_C) + \dots & \text{for at } T \leq T_C \end{cases}, \quad (6.26)$$

which is also continuous at T_C , i.e., there is no *first-order* phase transition.

The next derivative gives the specific heat, i.e.,

$$c_p = T \frac{\partial S}{\partial T} = T \frac{\partial S_0}{\partial T} + \begin{cases} 0 & \text{for } T > T_C, \\ T \cdot \frac{a^2}{B} + \dots & \text{for at } T \leq T_C \end{cases}, \quad (6.27)$$

which finally has a jump at T_C , i.e., there is a *second-order* phase transition.

6.2.2 Weakly first-order transitions

If the order parameter jumps to a large value at T_C , an expansion like Eq. (6.19) is not valid. But if the jump is small, the “weakly first-order” transition may still tractable.

For a first-order transition, the order parameter η should jump from 0 to a finite value at T_C . There are two basic ways to achieve this. One arises in systems without inversion symmetry. In that case, odd powers of η are allowed in the free energy, only the linear term has to vanish to allow a disordered high- T phase. For small η , adding the third power to the scenario of Fig. 6.2 leads to an asymmetry at high T that develops into a local minimum, which in turn finally dives below 0 – it is then separated from the $\eta = 0$ minimum by a maximum, see Fig. 6.3(a), and the optimal η jumps.

A second possibility can also arise in systems with inversion symmetry, i.e., with only even powers of η . If the coefficient B of the fourth-order term is negative around T_C , higher-orders become important. As $B < 0$ implies that $\Phi(\eta)$ becomes more and more negative with growing $|\eta|$, the equilibrium $|\eta|$ is large enough for the sixth order to matter. If its coefficient D positive, it will eventually penalize large η and it is enough to consider the quadratic, fourth- and sixth-order terms. For $B < 0$ and $D > 0$, varying A then leads to the scenario depicted in Fig. 6.3(b): local minima at finite *eta* arise and finally sink below the $\eta = 0$ minimum. Again, the order parameter jumps at T_C .

6.2.3 Inhomogeneous States and gradients in the order parameter

The Landau approach can be extended to include variations in the order parameter, this is called Ginzburg-Landau theory. An example might be a magnetic spiral state that is almost ferromagnetic, but with a slowly varying preferred direction. Another example is a superconductor with a boundary or with magnetic flux quanta going through it: Superconductivity has to vanish at the boundary or in the magnetic flux, and then continuously reaches its bulk value. The order parameter then becomes a function of position $\eta = \eta(\vec{r})$ and the free energy an integral over the free-energy density.

As in the uniform case, symmetry considerations suggest the terms that should be included in the free-energy integral. If variable order parameters are to be allowed, the free energy might in lowest order depend on their gradients. The free energy of inversion symmetric systems must not distinguish a direction \vec{r} from $-\vec{r}$, so that terms linear in the gradient are forbidden. Squares of the gradient are then the lowest order in which variability can enter. A plausible form of the first few orders in the free energy is then

$$\Phi = \int d^2r \left(A\eta^2(\vec{r}) + B\eta^4(\vec{r}) + G(\nabla\eta(\vec{r}))^2 + E(\nabla^2\eta(\vec{r}))^2 \right). \quad (6.28)$$

A positive $G > 0$ suppresses gradients in η , a homogeneous solution is then preferable and one would go back to using the simpler approach discussed above. At negative G , gradients can become favorable, but positive E would prevent them from becoming too large.

One application of the Ginzburg-Landau approach are magnetic spirals, in that case, one assumes that the local magnetization \vec{M} slowly rotates with constant absolute value, e.g., $M_x = \cos \vec{q}\vec{r}$ and $M_y = \sin \vec{q}\vec{r}$. It is the favorable to go into momentum space, where the gradients become multiplications with \vec{q} . One then finds $-|G|\vec{q}^2|M|^2 + E\vec{q}^4|N|^2 = 0$, which yields the optimal \vec{q} characterizing the spiral. (A and B determine the optimal $|M|^2 = \eta^2$.)

Before we discuss Ginzburg-Landau theory for superconductors, we are going to look at the microscopic ingredients of superconductivity. Historically, the phenomenological Ginzburg-Landau approach came actually came first.

6.3 Superconductivity

Inspired by Prof. Muramatsu's and Prof. Timm's lecture notes.

Presumably the most interesting feature of superconductivity is the vanishing resistance. (Even though magnetic levitation is not too bad either.) One thus needs some electronic state that is prevented from scattering. An important experimental clue was the isotope effect, where the superconducting T_C depends on the number of neutrons in the ions. The

only way for ionic mass to influence electron dynamic would be via its impact on phonon frequency. This dependence of electronic properties on phonons indicates that this is a case where the adiabatic approximation breaks down and coupling of electrons to lattice *dynamics*, i.e. phonons, has to be taken into account.

In Sec. 3.1, we had discussed the adiabatic approximation that decouples electron and lattice dynamics. On p. 23, we had found that the energy scale of the neglected electron-phonon interaction is smaller than the other scales, but not very much smaller. We had also found that the most 'dangerous' interaction terms involved different electronic eigenstates, so that the adiabatic approximation is best justified if the electronic states are well separated. This is clearly not fulfilled in a metal, where the existence of a Fermi surface implies excited states at arbitrarily low energies. Nevertheless, it is a (perhaps surprisingly) good starting point, to which we now add again as a perturbation the interaction between electrons and lattice degrees of freedom, i.e., phonons.

6.3.1 Phonon-mediated Electron-Electron Interaction

We first need a second-quantization description of electron-phonon interaction. The coupling between ions and electrons is via Coulomb attraction, i.e., a density-density interaction. The ionic density is given by a sum over ions j that can be displaced by \vec{u}_j from their equilibrium positions \vec{R}_j . For simplicity, we assume all ions to be equivalent and a one-site unit cell, i.e., a purely elemental solid with a Bravais lattice. The potential V between an electron at \vec{r} and an ion at $\vec{R}_j + \vec{u}_j$ depends on the distance $\vec{r} - \vec{R}_j - \vec{u}_j$, leading to

$$H_{\text{el.-ion}} = \int d^3r n_{\text{el.}}(\vec{r}) \cdot \sum_j V(\vec{r} - \vec{R}_j - \vec{u}_j) \quad (6.29)$$

where $n_{\text{el.}}(\vec{r})$ is the electron density. Expressing it in terms of Bloch electrons via field operators (5.1) gives

$$n_{\text{el.}}(\vec{r}) = \frac{1}{V} \sum_{\vec{k}, \vec{k}', \sigma} e^{i(\vec{k} - \vec{k}')\vec{r}} c_{\vec{k}', \sigma}^\dagger c_{\vec{k}, \sigma}. \quad (6.30)$$

As \vec{u}_j will be small compared to \vec{R}_j , a Taylor-series expansion of V is justified:

$$V(\vec{r} - \vec{R}_j - \vec{u}_j) \approx V(\vec{r} - \vec{R}_j) - \vec{\nabla}V(\vec{r} - \vec{R}_j) \cdot \vec{u}_j. \quad (6.31)$$

From the first term (zeroth order in \vec{u}), we get the ionic potential determining the electronic bands. The second term gives a coupling between electrons and ion displacement \vec{u}_j , whose Fourier transform is in turn given by phonon operators, see Eq. (3.46). The vector character of \vec{u} is taken into account by the three phonon branches ν . Combining all the Fourier components gives

$$H_{\text{el.-phonon}} = \sum_{\vec{G}} \sum_{\vec{k}, \sigma} \sum_{\vec{q}, \nu} g_{\vec{G}, \vec{q}, \nu} c_{\vec{k} + \vec{q} + \vec{G}, \sigma}^\dagger c_{\vec{k}, \sigma} \left(b_{\vec{q}, \nu} + b_{-\vec{q}, \nu}^\dagger \right). \quad (6.32)$$

The sum over reciprocal-lattice vectors \vec{G} is usually restricted to $\vec{G} = 0$, i.e., "Umklapp" processes are neglected. Moreover, the solid will now be assumed to be isotropic, so that all three branches give the same. This finally yields

$$H_{\text{el.-phonon}} = \sum_{\vec{k}, \sigma} \sum_{\vec{q}, \nu} g_{\vec{q}} c_{\vec{k} + \vec{q}, \sigma}^\dagger c_{\vec{k}, \sigma} \left(b_{\vec{q}, \nu} + b_{-\vec{q}, \nu}^\dagger \right), \quad (6.33)$$

where momentum is exchanged between the electron and phonon sectors, i.e., their dynamics are coupled.

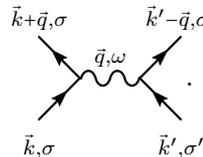
Even though the phonons are important in superconductivity, we are not really interested in them, but only in their effect on the electrons. The next step is consequently to “integrate the phonons out” and obtain the effective phonon-mediated electron-electron interaction. In this approach, we assume that mostly phonons with some finite frequency $\omega \approx \omega_D$ are important. This sounds perhaps weird, as the phonons in elemental Bravais lattices have $\omega \propto |\vec{q}| \rightarrow 0$ in the zone center, but the density of states is much larger at the zone boundary, where their dispersion is flat.

Without electron-phonon interaction, the ground state is given by a tensor product of the electronic ground state, the filled Fermi sea, and the vacuum for phonons, i.e., no phonons exist. We now perform perturbation theory with the electron-phonon interaction, where we are only interested in terms that remain in the low-energy Hilbert space of no phonons. The electrons, in contrast, are not required to remain in their ground state. In fact, we derive the effective interaction at first without any reference to the Fermi sea and consider its result as an additional term in the electronic Hamiltonian. A cleaner and more complete derivation can be carried out using diagrammatic techniques, but here, only a simplified version will be presented.

In a simple approach, we assume that the changes in electron energy caused by (6.33) are small compared to ω_D , i.e., $\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}} \ll \omega_D$. Applying the electron-phonon coupling then leads to a “high-energy” state and perturbation theory can be used. In first order, a phonon is annihilated (not possible, because none exist) or created (possible, but goes out of the interesting Hilbert space), so that it does not contribute. In second order, a contribution can arise if the second application of (6.33) annihilates the phonon created by the first; spins have to be conserved. Neglecting $\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}$ w.r.t ω_D and using $g_{-\vec{q}} = g_{\vec{q}}^*$, one finds

$$\begin{aligned}
H_{\text{el.-el.}}^{(2)} &= - \sum_{\vec{k},\sigma} \sum_{\vec{q},\nu} \sum_{\vec{k}',\sigma'} \sum_{\vec{q}',\nu'} \frac{g_{\vec{q}} g_{\vec{q}'}}{\hbar \omega_{\vec{q}'}} c_{\vec{k}+\vec{q},\sigma}^\dagger c_{\vec{k},\sigma} b_{\vec{q},\nu} c_{\vec{k}'+\vec{q}',\sigma'}^\dagger c_{\vec{k}',\sigma'} b_{-\vec{q}',\nu'}^\dagger \delta_{\nu,\nu'} \delta_{\vec{q},-\vec{q}'} \\
&= \sum_{\vec{k},\sigma} \sum_{\vec{q},\nu} \sum_{\vec{k}',\sigma'} \frac{-|g_{\vec{q}}|^2}{\hbar \omega_{\vec{q}}} c_{\vec{k}+\vec{q},\sigma}^\dagger c_{\vec{k},\sigma} c_{\vec{k}'-\vec{q},\sigma'}^\dagger c_{\vec{k}',\sigma'} \underbrace{b_{\vec{q},\nu} b_{\vec{q},\nu}^\dagger}_{=1+n_{\vec{q},\nu}=1}
\end{aligned} \tag{6.34}$$

The system can thus gain energy if two electrons are moved from \vec{k} and \vec{k}' to $\vec{k}+\vec{q}$ and $\vec{k}'-\vec{q}$, but this result is only valid if the electronic excitation energies are smaller than ω_D , implying that all involved electronic states have to be close to the Fermi level. The phonons thus mediate an effective attraction between low-energy electrons. In a diagrammatic approach, the corresponding picture is



$$\tag{6.35}$$

i.e., extremely similar to that (5.125) obtained for Coulomb interaction.

A more careful analysis can moreover give:

- The dependence of the interaction on the energy transfer between the electrons. In contrast to Coulomb repulsion, the phonon-mediated interaction is frequency depen-

dent [see the ω over the wiggly line in (6.35)] with

$$\propto \frac{\omega_D}{\omega^2 - \omega_D^2}, \quad (6.36)$$

if we replace the momentum dependence of $\omega_{\vec{q}}$ by a constant.

This can be motivated if we use (without showing it) that the total diagram (6.35) should conserve energy. One electron should in the end have gained the energy ω lost by the other, i.e., $\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}} = -(\epsilon_{\vec{k}'-\vec{q}} - \epsilon_{\vec{k}'}) = \omega$. We can then include the electronic energy in (6.34) combining terms with momentum transfers \vec{q} and $-\vec{q}$ turns out to yield $\frac{\omega_{\vec{q}}}{\omega^2 - \omega_{\vec{q}}^2}$. It has to be admitted, though, that this argument is (while popular) not fully watertight: the difference between $\frac{1}{\omega_D}$ and $\frac{\omega_D}{\omega^2 - \omega_D^2}$ is of third order, i.e., we would have to include the next order in perturbation theory to be consistent. That said, a more advanced treatment based on Green's functions supports the result.

The dependence on the electronic energy transfer ω in addition to phonon energy $\omega_{\vec{q}}$ indicates that the phonon-mediated interaction is ‘dynamic’. This in turn means that the interaction is “retarded”, i.e., the second electron feels the effect of the first only a little time later. This can be understood by noting the physical mechanism: The first electron slightly distorts the lattice (i.e., creates phonons), flies away as it is much faster than the ions, and the second electron still meets the phonons when it comes by. Due to this retardation, the electrons are not actually close to each other and do not feel too strong a Coulomb repulsion.

- The competition with Coulomb repulsion, at least for jellium. This is important, because the two effects are of similar size and obviously compete. It turns out that some attraction survives for small energy transfer.
- Renormalization due to the fact that the electron system is an interacting soup with Coulomb repulsion and phonons, e.g., this also renormalizes the “one-particle” energies. This effect smoothes the energy dependence of the interaction, so that it is no longer singular at $\omega = \omega_D$ (where the use of second-order perturbation theory is after all not justified), but again leaves low-energy attraction intact.

We thus end up with an effective electron-electron attraction that can act on electrons that are very close to the Fermi level.

6.3.2 BCS Theory of Superconductivity

Nicely discussed in Altland and Simons

BCS theory presents a variational ansatz for a somewhat further simplified Hamiltonian that can also be extended to electron-electron interactions mediated by processes different from isotropic phonons. The Hamiltonian is supposed to treat the balance between the non-interacting band energy (“kinetic energy”), whose ground state would be the Fermi sea and which consequently suppresses deviation from this state, and an effective electron-electron attraction between electrons that are close to each other in energy. As the final state cannot be expected to be “very far” from the Fermi sea, one can in fact formally extend the attraction onto all single-electron states, because the kinetic energy easily dominates for states far from the Fermi level. The dynamics of the phonon-mediated electron-electron

interaction is thus neglected here, even though it is very important in helping the attraction survive (for low-energy electrons) competition with Coulomb repulsion.

Second, we simplify the momentum dependence of Eq. (6.34), resp. diagram (6.35) by focussing on precesses where the two annihilators (creators) have opposite momentum. The rationale being this step is that the number of such pairs with total momentum 0 is largest, so that these processes tend to dominate anyway. We are going to see that this gives us Cooper pairs with vanishing total momentum. They can have finite momentum in so-called Fulde-Ferrell-Larkin-Ovchinnikov states, which arise in magnetic fields.

With these simplifications, we arrive at

$$H = \sum_{\vec{k},\sigma} (\epsilon_{\vec{k}} - \mu) c_{\vec{k},\sigma}^\dagger c_{\vec{k},\sigma} + \frac{1}{2} \sum_{\substack{\vec{k},\vec{k}' \\ \sigma,\sigma'}} V_{\vec{k},\vec{k}'} c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma}. \quad (6.37)$$

If the interaction is not mediated by phonons but via some other mechanism, $V_{\vec{k},\vec{k}'}$ can also depend on σ and σ' . Even though phonons have been integrated out, this is still an interacting Hamiltonian and thus hard to solve. Treating this in perturbation theory, e.g. via Feynman diagrams, leads to one of the instances where the series do not converge to the ground state. The ground state has symmetries fundamentally different from a Fermi liquid.

Instead of perturbation theory, we try a mean-field approach, which can incorporate symmetry breaking. Decouplings of the type we have used before would be, e.g., $\langle c_{\vec{k},\sigma}^\dagger c_{\vec{k}',\sigma} \rangle c_{-\vec{k},\sigma'}^\dagger c_{-\vec{k}',\sigma'}$. This would lead to a (spin-)density wave and in a realistic application with a more general Hamiltonian, one should certainly check whether this type of order is stable. Here, however, a spin-density wave is not the ground state, Instead, we focus on a different mean-field decoupling, namely

$$c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \rightarrow \langle c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \rangle c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} + c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \langle c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \rangle - \langle c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \rangle \langle c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \rangle. \quad (6.38)$$

Again, we neglect terms quadratic in fluctuations, as in Eq. (6.9).

The mean-field Hamiltonian then becomes

$$\begin{aligned} H_{\text{MF}} = & \sum_{\vec{k},\sigma} (\epsilon_{\vec{k}} - \mu) c_{\vec{k},\sigma}^\dagger c_{\vec{k},\sigma} + \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\vec{k}'} \sum_{\vec{k}} \underbrace{V_{\vec{k},\vec{k}'} \langle c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \rangle}_{=\Delta_{\sigma,\sigma'}^*(\vec{k}')} c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \\ & + \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\vec{k}} c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \underbrace{\sum_{\vec{k}'} V_{\vec{k},\vec{k}'} \langle c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \rangle}_{=\Delta_{\sigma,\sigma'}(\vec{k})} - \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\vec{k},\vec{k}'} V_{\vec{k},\vec{k}'} \langle c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \rangle \langle c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \rangle, \end{aligned} \quad (6.39)$$

where the last term is a constant. The spin symmetry of $\Delta_{\sigma,\sigma'}$ encodes whether the two electrons forming a pair are in a singlet or triplet state. For phonon-mediated interaction, the singlet channel is relevant.

Looking at the simplest case of $V(\vec{k},\vec{k}') = V_0$ and *singlet* pairing Eq. (6.39) leads to

$$H_{\text{MF}} = \sum_{\vec{k},\sigma} (\epsilon_{\vec{k}} - \mu) c_{\vec{k},\sigma}^\dagger c_{\vec{k},\sigma} + \frac{1}{2} \sum_{\vec{k}} \Delta^* c_{-\vec{k},\uparrow} c_{\vec{k},\downarrow} - \frac{1}{2} \sum_{\vec{k}} \Delta^* c_{-\vec{k},\downarrow} c_{\vec{k},\uparrow} \quad (6.40)$$

$$-\frac{1}{2} \sum_{\vec{k}} \Delta c_{\vec{k},\uparrow}^\dagger c_{-\vec{k},\downarrow}^\dagger + \frac{1}{2} \sum_{\vec{k}} \Delta c_{\vec{k},\downarrow}^\dagger c_{-\vec{k},\uparrow}^\dagger - \frac{1}{2V_0} \sum_{\sigma \neq \sigma'} |\Delta|^2 = \quad (6.41)$$

$$= \sum_{\vec{k},\sigma} (\epsilon_{\vec{k}} - \mu) c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma} - \Delta^* \sum_{\vec{k}} c_{-\vec{k},\downarrow} c_{\vec{k},\uparrow} - \Delta \sum_{\vec{k}} c_{\vec{k},\uparrow}^\dagger c_{-\vec{k},\downarrow}^\dagger - \frac{|\Delta|^2}{V_0}. \quad (6.42)$$

This mean-field Hamiltonian is biquadratic, i.e. each term contains exactly two fermion operators, but the terms with two creators or two annihilators mean that we need an extra step before solving it.

A useful trick is a particle-hole transformation applied to the down-electron operators,⁵ i.e.

$$h_{\vec{k},\downarrow}^\dagger = c_{-\vec{k},\downarrow}, \quad h_{\vec{k},\downarrow} = c_{-\vec{k},\downarrow}^\dagger. \quad (6.43)$$

The mean-field Hamiltonian can then be written as

$$H_{\text{MF}} = \sum_{\vec{k}} (c_{\vec{k},\uparrow}^\dagger, h_{\vec{k},\downarrow}^\dagger) \begin{pmatrix} \epsilon_{\vec{k}} - \mu & -\Delta^* \\ -\Delta & -(\epsilon_{-\vec{k}} - \mu) \end{pmatrix} \begin{pmatrix} c_{\vec{k},\uparrow} \\ h_{\vec{k},\downarrow} \end{pmatrix} - \frac{|\Delta|^2}{V_0} \quad (6.44)$$

with the so-called Nambu spinor

$$\begin{pmatrix} c_{\vec{k},\uparrow} \\ h_{\vec{k},\downarrow} \end{pmatrix} = \begin{pmatrix} c_{\vec{k},\uparrow} \\ c_{-\vec{k},\downarrow}^\dagger \end{pmatrix}. \quad (6.45)$$

This is then solved by diagonalizing the \vec{k} -dependent 2×2 matrices. Eigenenergies are clearly

$$E_{\vec{k}} = \pm \sqrt{(\epsilon_{\vec{k}} - \mu)(\epsilon_{-\vec{k}} - \mu) + |\Delta|^2} = E_{-\vec{k}} = \pm \sqrt{(\epsilon_{\vec{k}} - \mu)^2 + |\Delta|^2}, \quad (6.46)$$

where the last equation applies to the very common inversion-symmetric case with $\epsilon_{-\vec{k}} = \epsilon_{\vec{k}}$.

Eigenstates are linear superpositions of up-electron creator and down-electron annihilator. It is then a matter of convention whether one sees this combined object as a creation or as an annihilation operator, a convenient way is the following designation:

$$\begin{pmatrix} \gamma_{\vec{k},\uparrow} \\ \gamma_{-\vec{k},\downarrow}^\dagger \end{pmatrix} = U \begin{pmatrix} c_{\vec{k},\uparrow} \\ c_{-\vec{k},\downarrow}^\dagger \end{pmatrix} = \begin{pmatrix} u_{\vec{k}}^* & v_{\vec{k}} \\ -v_{\vec{k}}^* & u_{\vec{k}} \end{pmatrix} \begin{pmatrix} c_{\vec{k},\uparrow} \\ c_{-\vec{k},\downarrow}^\dagger \end{pmatrix} \quad \text{with} \quad \begin{pmatrix} E_{\vec{k}} & 0 \\ 0 & -E_{\vec{k}} \end{pmatrix} = U^\dagger H_{\vec{k}} U \quad (6.47)$$

For real Δ , $u_{\vec{k}} = \cos \theta_{\vec{k}}$ and $v_{\vec{k}} = \sin \theta_{\vec{k}}$ is a good parameterization, with $\tan 2\theta_{\vec{k}} = \frac{-\Delta}{\epsilon_{\vec{k}} - \mu}$.

For complex $\Delta_{\vec{k}} = |\Delta_{\vec{k}}| e^{i\phi_{\vec{k}}}$, the phase can be gauged away when doing the particle-hole transformation (6.43). Expressed in γ operators,⁶ the Hamiltonian is then

$$H = \sum_{\vec{k}} \left(E_{\vec{k}} \gamma_{\vec{k},\uparrow}^\dagger \gamma_{\vec{k},\uparrow} - E_{\vec{k}} \gamma_{-\vec{k},\downarrow}^\dagger \gamma_{-\vec{k},\downarrow} \right) - \frac{|\Delta|^2}{V_0} = \sum_{\vec{k}} E_{\vec{k}} \left(\gamma_{\vec{k},\uparrow}^\dagger \gamma_{\vec{k},\uparrow} + \gamma_{\vec{k},\downarrow}^\dagger \gamma_{\vec{k},\downarrow} \right) - \sum_{\vec{k}} E_{\vec{k}} + \frac{|\Delta|^2}{|V_0|}$$

⁵One can check that the full collection of operators building the Hamiltonian continue to fulfil fermion anti-commutation rules.

⁶One should check that the number of γ operators is correct, i.e., that there is no double counting of degrees of freedom, and that they fulfill fermionic anti-commutation relations. It is and they do.

$$= \sum_{\vec{k}, \sigma} E_{\vec{k}} n_{\vec{k}, \sigma} + E_0, \quad (6.48)$$

where the constant E_0 gives the ground-state energy. Since $E_{\vec{k}} \geq 0$, any γ^\dagger operator creates an excitation, which is called a Bogoliubov quasi-particle, and raises the energy. The BCS ground state is accordingly the vacuum state of the Bogoliubov operators, i.e. $\gamma_{\vec{k}, \sigma} |\psi_{\text{BCS}}\rangle = 0$ for all $\gamma_{\vec{k}, \sigma}$.

Using

$$\begin{aligned} \gamma_{-\vec{k}, \downarrow} \gamma_{\vec{k}, \uparrow} |0\rangle &= (u_{\vec{k}}^* c_{-\vec{k}, \downarrow} - v_{\vec{k}} c_{\vec{k}, \uparrow}^\dagger) (u_{\vec{k}}^* c_{\vec{k}, \uparrow} + v_{\vec{k}} c_{-\vec{k}, \downarrow}^\dagger) |0\rangle \\ &= (u_{\vec{k}}^* c_{-\vec{k}, \downarrow} - v_{\vec{k}} c_{\vec{k}, \uparrow}^\dagger) \underbrace{u_{\vec{k}}^* c_{\vec{k}, \uparrow} |0\rangle}_{=0} + v_{\vec{k}} \underbrace{u_{\vec{k}}^* c_{-\vec{k}, \downarrow} c_{-\vec{k}, \downarrow}^\dagger |0\rangle}_{=1 \cdot |0\rangle} - v_{\vec{k}}^2 c_{\vec{k}, \uparrow}^\dagger c_{-\vec{k}, \downarrow}^\dagger |0\rangle = v_{\vec{k}} \left(u_{\vec{k}}^* + v_{\vec{k}} c_{-\vec{k}, \downarrow}^\dagger c_{\vec{k}, \uparrow}^\dagger \right) |0\rangle \end{aligned}$$

such a state is given by

$$|\psi_{\text{BCS}}\rangle \propto \prod_{\vec{k}, \sigma} \gamma_{\vec{k}, \sigma} |0\rangle \propto \prod_{\vec{k}} \left(u_{\vec{k}}^* + v_{\vec{k}} c_{-\vec{k}, \downarrow}^\dagger c_{\vec{k}, \uparrow}^\dagger \right) |0\rangle. \quad (6.49)$$

The last expression is also normalized. This is a superposition of states with different numbers of Cooper pairs, even having a component with no Cooper pair.

This is rather similar to the coherent states of harmonic oscillators and the BCS ground state can indeed be seen as a fermionic counterpart. Except for the normalization, a coherent state for a single boson mode is given by

$$|z\rangle = e^{za^\dagger} |0\rangle = \left(1 + za^\dagger + \frac{1}{2} z^2 (a^\dagger)^2 + \frac{1}{6} z^3 (a^\dagger)^3 + \dots \right) |0\rangle \quad (6.50)$$

which can be generalized to several modes via a product. The same kind of state with a creation operator of a Cooper pair instead of a boson gives a much shorter sum, because the product of two or more fermion creators vanishes:

$$\begin{aligned} u_{\vec{k}}^* e^{\frac{v_{\vec{k}}}{u_{\vec{k}}^*} c_{-\vec{k}, \downarrow}^\dagger c_{\vec{k}, \uparrow}^\dagger} |0\rangle &= u_{\vec{k}}^* \left(1 + \frac{v_{\vec{k}}}{u_{\vec{k}}^*} c_{-\vec{k}, \downarrow}^\dagger c_{\vec{k}, \uparrow}^\dagger + \frac{1}{2} \left(\frac{v_{\vec{k}}}{u_{\vec{k}}^*} \right)^2 \underbrace{c_{-\vec{k}, \downarrow}^\dagger c_{\vec{k}, \uparrow}^\dagger c_{-\vec{k}, \downarrow}^\dagger c_{\vec{k}, \uparrow}^\dagger}_{=0} + 0 \right) |0\rangle = \\ &= \left(u_{\vec{k}}^* + v_{\vec{k}} c_{-\vec{k}, \downarrow}^\dagger c_{\vec{k}, \uparrow}^\dagger \right) |0\rangle. \end{aligned} \quad (6.51)$$

For bosonic fields like light, coherent states do not have a definite particle number (even though the relative variance becomes very small for large average numbers), but they do have a well-defined phase, which is the conjugate variable to photon number. The eigenstates of the Hamiltonian, in contrast, have a precise particle number, but no well-defined phase. It turns out that such an observation carries over to the BCS ground state: It has a well defined phase and ‘‘macroscopic phase coherence’’.

6.3.2.1 BCS Gap equation

From Eq. (6.46), we can conclude that creating a Bogoliubov quasiparticle costs at least energy Δ , i.e., there is a gap in the excitation spectrum. This gap stabilizes on one hand the

symmetry-broken state, but is on the other determined by $\Delta = V_0 \langle c_{\vec{k},\uparrow}^\dagger c_{-\vec{k},\downarrow}^\dagger \rangle$, i.e., depends on the ground state. One thus finds (here shown for real Δ) a self-consistency requirement

$$\begin{aligned}
\Delta &= V_0 \sum_{\vec{k}} \langle \psi_{\text{BCS}} | c_{\vec{k},\downarrow}^\dagger c_{-\vec{k},\uparrow}^\dagger | \psi_{\text{BCS}} \rangle = V_0 \sum_{\vec{k}} \langle \psi_{\text{BCS}} | (v_{\vec{k}} \gamma_{-\vec{k},\uparrow} + u_{\vec{k}} \gamma_{\vec{k},\downarrow}^\dagger) (u_{\vec{k}} \gamma_{-\vec{k},\uparrow}^\dagger - v_{\vec{k}} \gamma_{\vec{k},\downarrow}) | \psi_{\text{BCS}} \rangle = \\
&= V_0 \sum_{\vec{k}} \underbrace{(v_{\vec{k}} u_{\vec{k}} \langle \psi_{\text{BCS}} | \gamma_{-\vec{k},\uparrow} \gamma_{-\vec{k},\uparrow}^\dagger | \psi_{\text{BCS}} \rangle - u_{\vec{k}} v_{\vec{k}} \langle \psi_{\text{BCS}} | \gamma_{\vec{k},\downarrow}^\dagger \gamma_{\vec{k},\downarrow} | \psi_{\text{BCS}} \rangle)}_{=1} = \\
&= V_0 \sum_{\vec{k}} v_{\vec{k}} u_{\vec{k}} = V_0 \sum_{\vec{k}} \sin \theta_{\vec{k}} \cos \theta_{\vec{k}} = \frac{V_0}{2} \sum_{\vec{k}} \sin 2\theta_{\vec{k}} = \frac{V_0}{2} \sum_{\vec{k}} \frac{-\Delta}{E_{\vec{k}}}, \tag{6.52}
\end{aligned}$$

where the last steps require some trig identities. Obviously, $\Delta = 0$ is always a solution. For *negative* $V_0 < 0$ *only*, other solutions $\frac{2}{|V_0|} = \sum_{\vec{k}} \frac{1}{E_{\vec{k}}}$ are possible that have a finite gap.

We have here of course lost the isotope effect, because we extended the attractive interaction from states near the Fermi energy to arbitrary states. If a cut-off at $|\epsilon_{\vec{k}} - \mu| = \hbar\omega_D$ is included, one finds

$$\Delta \propto 2\omega_D e^{-\frac{1}{V_0 \rho(E_F)}} \tag{6.53}$$

for an approximately constant density of states $\rho(E_F)$ around the Fermi energy.

6.3.2.2 ‘Unconventional superconductivity’ with momentum-dependent gap

One can get superconducting solutions from positive interactions $V_{\vec{k},\vec{k}'} > 0$ as well, but only if the interaction is momentum dependent. Eq. (6.39) is replaced by its variant

$$\begin{aligned}
H_{\text{MF}} &= \sum_{\vec{k},\sigma} (\epsilon_{\vec{k}} - \mu) c_{\vec{k},\sigma}^\dagger c_{\vec{k},\sigma} + \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\vec{k}'} \sum_{\vec{k}} \underbrace{V_{\vec{k},\vec{k}'} \langle c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \rangle}_{=\Delta_{\sigma,\sigma'}^*(\vec{k}')} c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \\
&+ \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\vec{k}} c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \underbrace{\sum_{\vec{k}'} V_{\vec{k},\vec{k}'} \langle c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \rangle}_{=\Delta_{\sigma,\sigma'}(\vec{k})} - \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\vec{k}} \underbrace{V_{\vec{k},\vec{k}'} \langle c_{\vec{k},\sigma}^\dagger c_{-\vec{k},\sigma'}^\dagger \rangle \sum_{\vec{k}'} \langle c_{-\vec{k}',\sigma'} c_{\vec{k}',\sigma} \rangle}_{=\text{const.}}. \tag{6.54}
\end{aligned}$$

The off-diagonal element of the resulting equivalent to Eq. (6.40) is now \vec{k} -dependent. All formulas carry over, with a \vec{k} -dependent gap $\Delta_{\vec{k}} = f(\vec{k})|\tilde{\Delta}|$. The gap equation becomes

$$\Delta_{\vec{k}'} = \sum_{\vec{k}} V_{\vec{k},\vec{k}'} \langle \psi_{\text{BCS}} | c_{\vec{k},\downarrow}^\dagger c_{-\vec{k},\uparrow}^\dagger | \psi_{\text{BCS}} \rangle = \sum_{\vec{k}} V_{\vec{k},\vec{k}'} v_{\vec{k}} u_{\vec{k}} = -\frac{1}{2} \sum_{\vec{k}} \frac{V_{\vec{k},\vec{k}'} \Delta_{\vec{k}}}{E_{\vec{k}}}, \tag{6.55}$$

If the momentum dependence of $\Delta(\vec{k})$ includes a sign change between different \vec{k} points, it can ‘heal’ the wrong sign of a positive interaction $V_{\vec{k},\vec{k}'} > 0$: If the above sum is dominated by a region with positive $\Delta_{\vec{k}^*} > 0$, i.e. $V_{\vec{k} \approx \vec{k}^*, \vec{k}'} \gg$, finite *negative* $\Delta_{\vec{k}'} < 0$ is allowed and can solve the equation.

Moreover, the formalism can be extended to triplet states. There is then one technical aspect that turns out to be related to new physics: When we did the particle-hole transformation Eq. (6.43), we did not introduce any new operators, but just used the \downarrow -operators in

a different way. If both creation/annihilation operators in each pairing term have the same spin (e.g. \uparrow), this does not help. For most momenta \vec{k} , a way out would be to particle-hole transform $c_{\vec{k},\uparrow}$ -operators for half the of the Brillouin zone and leave the other half, which contains $c_{-\vec{k},\uparrow}$, untransformed. This scheme breaks down for special momentum points like $\vec{k} = 0, (\pi, 0), \dots$ where \vec{k} and $-\vec{k}$ are equivalent: Here, the Nambu spinor definitely double counts the physically available fermionic states. If we then undo this in the end, we may in special cases end up with ‘half’ a fermionic state, which can with some luck be seen as a Majorana fermion.

6.3.3 Ginzburg-Landau Theory of Superconductivity

Even though this was not how it historically arose, the observation of a coherent state with defined phase may somewhat motivate the choice of a complex order parameter in a superconducting Ginzburg-Landau theory. The free energy has to be real and if inhomogeneous states are in principle permitted, a plausible free energy is

$$\begin{aligned}\Phi &= \int d^2r \left(A|\psi(\vec{r})|^2 + B|\psi(\vec{r})|^4 + G|\nabla\psi(\vec{r})|^2 + \dots \right) = \\ &= \int d^2r \left(a\frac{T-T_C}{T_C}|\psi(\vec{r})|^2 + \frac{b}{2}|\psi(\vec{r})|^4 + \frac{1}{2m}|\nabla\psi(\vec{r})|^2 + \dots \right),\end{aligned}\quad (6.56)$$

where $\psi(\vec{r})$ is the complex and scalar order parameter. In a simple homogeneous system, we expect a homogeneous solution, which is corroborated by experiment, in that case $G > 0$, $\frac{1}{2m}$ is at first just a different way to write this coefficient. For $G > 0$, gradients will be 0 and the analysis can continue like for the magnetic case discussed above and $|\psi| \propto \sqrt{T_C - T}$ turns out to correspond to the superconducting gap Δ of the BCS theory.

The next step is the presence of a magnetic field and we have to find away to include it that is consistent with the known symmetries. In electromagnetism, gauge invariance is the important principle and a gauge invariant way to combine a magnetic field with a complex position-dependent function has already been used when introducing magnetic fields into quantum mechanics: $-i\hbar\nabla \rightarrow -i\hbar\nabla - \frac{e^*}{c}\vec{A}$, where charge e^* is some constant and not (yet) known. The gauge invariance means that changing $\vec{A} \rightarrow \vec{A} + \vec{\nabla}\Lambda$ does not affect the free energy, because it can be removed by a change in the phase of ψ by $\psi \rightarrow e^{ie^*\Lambda/(\hbar c)}\psi$ and the phase by itself is not observable.

To analyze Eq. (6.56), we need functional derivatives w.r.t $\vec{A}(\vec{r})$ (the charged order parameter can change the magnetic field), to $\psi(\vec{r})$ and to $\psi^*(\vec{r})$. Some of the steps are worked out in Prof. Muramatsu’s lecture notes, let us here just summarize the results:

- The derivative with respect to \vec{A} gives an equation defining a current:

$$\frac{1}{4\pi}\vec{\nabla} \times \vec{B} = \frac{\hbar e^*}{2mc} \left(\psi^* \left(-i\vec{\nabla} - \frac{e^*}{\hbar c}\vec{A} \right) \psi - \psi \left(i\vec{\nabla} - \frac{e^*}{\hbar c}\vec{A} \right) \psi^* \right) \quad (6.57)$$

As in general $\vec{\nabla} \times \vec{B} = \frac{4\pi}{c}\vec{j}$, we can read off a superconducting current as

$$\vec{j} = \frac{\hbar e^*}{2m} \left(\psi^* \left(-i\vec{\nabla} - \frac{e^*}{\hbar c}\vec{A} \right) \psi - \psi \left(i\vec{\nabla} - \frac{e^*}{\hbar c}\vec{A} \right) \psi^* \right), \quad (6.58)$$

where comparison to experiment fixes $e^* = 2e$, i.e., the charge of a Cooper pair.

- Derivatives with respect to ψ and ψ^* give equations for the order parameter:

$$\frac{1}{2m} \left(-i\hbar \vec{\nabla} - \frac{e^*}{c} \vec{A} \right)^2 \psi(\vec{r}) + a \frac{T - T_C}{T_C} \psi(\vec{r}) + b |\psi(\vec{r})|^2 \psi(\vec{r}) = 0 \quad (6.59)$$

These equations can be used to find the mean-field magnetic field and order parameter.