Introduction to Solid State Physics

FRANK GÖHMANN

Fakultät für Mathematik und Naturwissenschaften
Bergische Universität Wuppertal
Preface

This script is based on lecture notes prepared for the regular Introduction to Theoretical Solid State Physics at the University of Wuppertal held by the author in the winter semesters of 2003/04, 2004/05, 2010/11, 2011/12, 2013/14, 2014/15 and in the summer semesters of 2006 and 2020. Due to the prevailing Covid 19 pandemic all teaching at the University of Wuppertal in the summer of 2020 went online. In order to support my students with their home training programme I decided to typeset at least the present part of my lecture notes. In regular semesters I would have delivered 28-30 lectures, 90 minutes each. Since the beginning of our semester was delayed due to the pandemic, the number of lectures was restricted to 23. For this reason I cut out two lectures on the Hartree-Fock approximation and two lectures usually devoted to recall the formalism of the second quantization. I condensed the remaining material to fit into the available 23 time slots. The missed out material as well as some of the material of the regular lectures on Advanced Theoretical Solid State Physics may follow on a later occasion, e.g., after the next pandemic. Most of the lectures are complemented with a few intermediate level homework exercises which are considered an integral part of the course. These exercises were discussed by the participants in a separate online exercise session on a weekly basis.

At the university of Wuppertal the introduction to theoretical solid state physics is part of the Master course. Students who attend this course are expected to have successfully passed the basic courses in theoretical physics (Mechanics, Electrodynamics, Quantum Mechanics, Statistical Mechanics) and a course on Advanced Quantum Mechanics.

I would like to thank all those participants of my lectures whose attention and whose questions helped to improve this manuscript. Particular thanks are due to Saskia Faulmann and Siegfried Spruck who read the entire text and pointed out a number of typos and inaccuracies to me. When I started teaching Theoretical Solid State Physics in 2003, I devised my lecture after lecture notes of my dear colleague Holger Fehske whom I would like to thank at this point. My own first lecture notes then gradually evolved over the years and most probably will continue to evolve in future. I prefer to think of the following typeset version as of a snapshot taken in the year of the pandemic 2020.

What is solid state physics?

- Application of what we have learned heretofore (QM + StatMech) to the description of `condensed matter’, no new fundamental theory.

- Arguably the most important branch of physics as far as the daily life of non-physicists is concerned, since many important technologies owe their existence our knowledge of solid state physics. Examples are the semiconductor technology, lasers, magnetic and charge based information storage devices.

- Solid state physics is intellectually most challenging with new questions arising from experiments year by year. Solids show us the universe in a nutshell. Their behaviour reaches from single-particle to highly collective. All tools of modern theoretical physics are needed for at least an approximate understanding, in particular, QFT, Feynman graphs, high-performance computing, and non-perturbative many-body techniques.
What are the goals of this lecture?

- Introduction to the basic concepts, meaning that the emphasis is, in the first instance, on the single-particle aspects.

- Service for Experimental Solid State Physics.

- Emphasis on the explanation of concepts and basic ideas, not always quantitative, justification of the use of simplified ‘model Hamiltonians’.

- Raise some understanding why many-body physics is mostly phenomenology.

- Convey the following main idea: (Collective) elementary excitations are ‘quasi-particles’ characterized by their dispersion relation $p \mapsto \varepsilon(p)$ and by certain quantum numbers like spin and charge. The most important two are ‘the phonon’ (= quantized lattice vibration) and ‘the electron’ (= quantized charge excitation of the solid, which has as much to do with the electron of elementary particle physics as water waves have to do with water).
L8 Phonons – examples and general properties
  8.1 Example 1 – the harmonic chain ............................... 39
  8.2 Example 2 – diatomic chain with alternating forces .... 40
  8.3 General properties of phonons in a 3d lattice ............. 42
  8.4 Exercise 7. Linear chain with a mass defect ................. 44
  8.5 Exercise 8. Mass defect in the thermodynamic limit ......... 45
  8.6 Exercise 9. Harmonic oscillations of a two-dimensional lattice ............................... 46

L9 Statistical mechanics of the harmonic crystal
  9.1 Partition function and free energy ............................. 46
  9.2 The Bose-Einstein distribution .................................. 46
  9.3 The density of states .............................................. 47
  9.4 Van-Hove singularities ............................................. 48
  9.5 Exercise 10. Van-Hove singularities ......................... 49
  9.6 Exercise 11. Density of states in linear chains ............... 49

L10 Specific heat of the harmonic crystal
  10.1 Low-temperature specific heat ................................ 50
  10.2 Internal energy and specific heat at high temperatures .... 51
  10.3 Debye interpolation ............................................. 52
  10.4 The anomaly of the harmonic crystal ......................... 53

L11 Neutron scattering
  11.1 Thermal neutrons .............................................. 55
  11.2 Scattering experiments and cross sections .................. 56
  11.3 Cross section and transition rate ............................. 57
  11.4 Form factor and structure factor .............................. 58
  11.5 Rewriting the structure factor ................................. 58

L12 Neutron scattering continued
  12.1 Disorder ............................................................. 59
  12.2 Summary of the theory of neutron scattering – general case .... 60
  12.3 Theory of neutron scattering – specialization to crystal structures ............................... 61
  12.4 Dynamic structure factor of the harmonic crystal ............ 61
  12.5 Expansion into multi-phonon processes .......................... 62
  12.6 Coherent elastic neutron scattering ............................ 62
  12.7 Interpretation of the Bragg condition .......................... 62
  12.8 Exercise 12. A proof of equation (12.13) ....................... 63

L13 Inelastic neutron scattering
  13.1 Debye-Waller factor .............................................. 65
  13.2 Exercise 13. Debye-Waller factor of a cubic lattice ........ 66
  13.3 Coherent inelastic scattering – the single-phonon contribution .... 66
  13.4 Measuring dispersion relations of phonons .................... 69

L14 Electronic excitations in solids
  14.1 Hamiltonian of the electrons in adiabatic approximation .... 69
  14.2 Reduction to a single-particle problem ......................... 70
  14.3 Particles in a periodic potential ................................ 72
| Section | Title                                                                 | Page |
|---------|----------------------------------------------------------------------|------|
| 14.4    | Exercise 14. Kronig-Penney model                                      | 72   |
| 14.5    | Almost free electrons                                                | 73   |
| L15     | **Particles in a periodic potential**                                |       |
| 15.1    | Degenerate levels                                                    | 76   |
| 15.2    | Example $d = 1$                                                       | 77   |
| 15.3    | The tight-binding method                                              | 78   |
| L16     | **Electrons in a periodic potential**                                 |       |
| 16.1    | Method of orthogonalized plane waves                                  | 80   |
| 16.2    | Other methods                                                        | 81   |
| 16.3    | Summary                                                              | 81   |
| 16.4    | Exercise 15. Electronic band structure in one-dimensional solids by WKB | 81   |
| 16.5    | The Fermi distribution                                                | 83   |
| 16.6    | Grand canonical potential of the electron gas                        | 84   |
| 16.7    | Fermi energy and Fermi surface                                       | 84   |
| L17     | **Low-temperature specific heat of the electron gas**                |       |
| 17.1    | Specific heat of metals                                               | 86   |
| 17.2    | Specific heat of insulators                                           | 88   |
| L18     | **Electrons in solids – the second quantized picture**               |       |
| 18.1    | An auxiliary potential                                                | 90   |
| 18.2    | Bloch basis and Wannier basis                                         | 91   |
| 18.3    | Hamiltonian in second quantization                                   | 91   |
| 18.4    | Exercise 16. Wannier functions in one dimension                      | 92   |
| 18.5    | Exercise 17. Spinless Fermions on the lattice                        | 93   |
| L19     | **The Hubbard model**                                                |       |
| 19.1    | Motivation and definition                                            | 94   |
| 19.2    | Tight-binding approximation                                           | 95   |
| 19.3    | Interpretation of the Hubbard Hamiltonian                             | 96   |
| 19.4    | Exercise 18. Peierls phases                                           | 99   |
| L20     | **The strong-coupling limit**                                        |       |
| 20.1    | Degenerate perturbation theory – a reminder                          | 100  |
| 20.2    | Application to the Hubbard model at strong coupling                  | 102  |
| 20.3    | Explicit form of the projection operators                            | 102  |
| 20.4    | Application to $H_2$                                                  | 102  |
| 20.5    | Exercise 19. Strong coupling limit of the Hubbard model              | 103  |
| L21     | **Heisenberg model and Mott transition**                             |       |
| 21.1    | Heisenberg Hamiltonian in the language of Fermi operators            | 103  |
| 21.2    | Heisenberg model in the language of spin operators                   | 104  |
| 21.3    | Interpretation of the exchange interaction                           | 105  |
| 21.4    | Mott transition                                                      | 107  |
| 21.5    | Exercise 20: A short XXX chain                                       | 107  |
### L.22 Linear response theory

- 22.1 Time evolution of the statistical operator ........................................ 108
- 22.2 Time evolution of expectation values ............................................. 109
- 22.3 Absorption of energy ....................................................................... 109
- 22.4 Application to quantum spin chains ............................................... 110

### L.23 Microwave absorption by the Heisenberg-Ising chain

- 23.1 The isotropic chain ........................................................................ 111
- 23.2 Resonance shift and line width in the anisotropic case .................... 112
- 23.3 The shifted moments of the dynamic susceptibility ......................... 113
- 23.4 Exercise 21: Shifted moments ......................................................... 115

### References

116
L1 The Hamiltonian of the solid and its eigenvalue problem

1.1 Hamiltonian of the solid

Solid state physics is quantum mechanics and statistical mechanics of many ($\sim 10^{23}$) particles at ‘low energies’ (typically $\sim 1$ meV). Relativistic effects (retardation, spin-orbit coupling, . . . ) can often be neglected in the explanation of phenomena in solids (apart from the fact the spin is a relativistic effect). The large number of particles $N_p$ is best taken care of by considering the thermodynamic limit $N_p \to \infty$ which typically brings about simplifications of the theory.

In solid state physics not only the electrons composing the solid but also the ions are regarded as elementary. The only relevant interaction is the Coulomb interaction. Thus, the Hamiltonian of the solid is the Hamiltonian of non-relativistic ions and electrons interacting via Coulomb interaction,

$$
H = \sum_{j=1}^{L} \frac{\|P_j\|^2}{2M_j} + \sum_{1 \leq j < k \leq L} \frac{Z_j Z_k e^2}{\|R_j - R_k\|} \quad \leftarrow \text{ions, charge } Z_j e, \text{ mass } M_j
$$

$$
+ \sum_{j=1}^{N} \frac{\|P_j\|^2}{2m} + \sum_{1 \leq j < k \leq N} \frac{e^2}{\|r_j - r_k\|} \quad \leftarrow \text{electrons, charge } -e, \text{ mass } m
$$

$$
- \sum_{j=1}^{L} \sum_{k=1}^{N} \frac{Z_j e^2}{\|R_j - r_k\|}. \quad \leftarrow \text{ion-electron interaction } (1.1)
$$

↑ kinetic energy ↑ Coulomb interaction

Here $L$ is the number of ions and $N$ is the number of electrons. The Hamiltonian of the solid is the same as in atomic and molecular physics. The only difference is in the number of constituents. A solid is a very large molecule. The numbers that separate the sub-disciplines are

- $L = 1$ atomic physics
- $L \sim 100$ molecular physics
- $L \sim 10^{23}$ solid state physics

There is no sharp distinction between a molecule and a solid. In between molecules and solids are macro molecules. DNA, for instance, is composed of about $2 \cdot 10^{11}$ atoms.

1.2 Natural units

A first understanding of the length and energy scales in solids comes from a dimensional analysis that allows us to introduce natural units. Asking, when the kinetic energy of an electron associated with a given wavelength is of the same order of magnitude as the Coulomb energy of two electrons one wavelength apart from each other,

$$
\frac{\hbar^2}{2m\ell^2} \sim E \sim \frac{e^2}{\ell}, \quad (1.2)
$$
we recover the typical length scale of atomic physics
\[ \ell \sim \frac{\hbar^2}{m e^2} = a_0 = 0.529 \cdot 10^{-10} \text{ m} \sim \frac{1}{20} \text{ nm}, \] (1.3)
the Bohr radius. The Coulomb energy of two electrons at this distance,
\[ E = \frac{e^2}{a_0} = \frac{m e^4}{\hbar^2} = 2 \text{ Ry} = 27.2 \text{ eV}, \] (1.4)
is twice the ionization energy of a hydrogen atom (which is one Rydberg (1 Ry)) and thus a typical atomic binding energy.

Measuring all lengths in units of the Bohr radius (i.e., replacing \( r_j/a_0 \rightarrow r_j, R_j/a_0 \rightarrow R_j \)) and the energy in units of 2 Ry (by replacing \( H/(m e^4/\hbar^2) \rightarrow H \)) we obtain the Hamiltonian of the solid in natural units,
\[ H = -\frac{1}{2} \sum_{j=1}^L m/M_j \frac{\partial^2 R_j}{\partial \alpha_j^2} + H_{\text{el}}(\textbf{R}), \] (1.5)
where
\[ H_{\text{el}}(\textbf{R}) = \sum_{1 \leq j < k \leq L} \frac{Z_j Z_k}{\|\textbf{R}_j - \textbf{R}_k\|} - \frac{1}{2} \sum_{j=1}^N \frac{\partial^2 r_j}{\partial \alpha_j^2} + \sum_{1 \leq j < k \leq N} \frac{1}{\|r_j - r_k\|} - \sum_{j=1}^L \sum_{k=1}^N \frac{Z_j}{\|\textbf{R}_j - r_k\|}. \] (1.6)
Here we have used the summation convention with respect to Greek indices and the further convention that \( \textbf{R} = (\textbf{R}_1, \ldots, \textbf{R}_L) \). Similarly, we shall write \( \textbf{r} = (r_1, \ldots, r_N) \).

Our scale analysis shows us that the ionisation numbers \( Z_j \) and the mass ratios \( m/M_j \) are the only parameters of the system. The variation of these pure numbers is responsible for the rich phenomenology of molecules and solids and, in fact, of the world around us as we perceive it with our senses.

Note that the mass ratio
\[ \frac{m}{M_j} \sim 10^{-4} \] (1.7)
in (1.5) is a small parameter. This fact turns out to be of fundamental importance for the theory of solids and determines much of the structure of the world around us.

1.3 An eigenvalue problem for the ions
If we naively send all masses \( M_j \) in (1.5) to infinity, the kinetic energy of the ions goes to zero, the ions stop moving. The corresponding ionic parts of the eigenfunctions separate multiplicatively and become products of delta functions of the form \( \delta(\textbf{R}_j - \textbf{R}_j^{(0)}) \). If the masses are large but finite, the ions will still move, but slower than the electrons. Their wavefunctions will not be delta functions, but typically more localized than those of the electrons.

Our favorite classical example system of interacting point particles of very different masses is the planetary system. The ratio of the earth mass \( m \) to the sun mass \( M \), for instance, is about \( m/M = 1/3 \times 10^{-5} \). Earth and sun exert equal but oppositely directed
forces $\pm F$ onto each other, $M \ddot{X} = F = -m \ddot{x}$, if $X$ and $x$ are the position vectors of sun and earth, respectively. This means that sun experiences a much smaller average acceleration than the earth. Consequentially, as compared to the sun, the earth moves much faster and has a much larger orbit around the center of mass of the sun-earth system. In this case, as the mass ratio is so small, the center of mass lies inside the sun. Hence, to a very good approximation, the earth moves around the sun and follows it along its way through the universe.

In a similar way we expect the electrons in a solid to follow the slower motion of the more massive ions. Translated into the language of quantum mechanics we expect that the joint motion of electrons and ions can be approximately described by a product of an ionic wave function times an electronic wave function calculated for fixed positions of the ions. The latter would be interpreted as a conditional probability amplitude for the electrons given the positions of the ions. The product structure would mimic the fact in probability theory that the joint probability $p(A \cap B)$ of two events $A$ and $B$ (corresponding to the wave function of electrons and ions) is equal to $p(A|B)p(B)$, where $p(B)$ is the probability of $B$ (corresponding to the ions) and $p(A|B)$ is the conditional probability of $A$ given $B$ (corresponding to the electronic wave function for fixed positions of the ions).

We shall try to work out this idea more formally. Let us start with the 'electronic eigenvalue problem'

$$H_{el}(R) \varphi(r|R) = \varepsilon(R) \varphi(r|R)$$  \hspace{1cm} (1.8)

which depends parametrically on the positions $R$ of all ions. For every $R$ the eigenstates $\varphi_n(r|R)_{n \in \mathbb{N}}$ of $H_{el}(R)$ corresponding to the eigenvalues $\varepsilon_n(R)$ form a basis of the electronic Hilbert space. Hence, every solution $\Psi(r, R)$ of the full eigenvalue problem $H \Psi = E \Psi$ can be expanded in terms of the $\varphi_n$,

$$\Psi(r, R) = \sum_{n \in \mathbb{N}} \varphi_n(r|R) \phi_n(R).$$  \hspace{1cm} (1.9)

Assuming the $\varphi_n$ to be known we want to derive an eigenvalue problem for the $\phi_n$ which will later be interpreted as the ionic wave functions. For this purpose we insert (1.9) into the full eigenvalue problem and write the result as

$$(H - E) \Psi(r, R) = \sum_{m \in \mathbb{N}} \left\{ \varphi_m(r|R) \left[ -\frac{1}{2} \sum_{j=1}^{L} \frac{m}{M_j} \partial^2_{R_j} + \varepsilon_m(R) - E \right] \phi_m(R) \right. $$

$$ - \left. \frac{1}{2} \sum_{j=1}^{L} \frac{m}{M_j} \left[ 2 \left( \partial_{R_j} \varphi_m \right) (r|R) \partial_{R_j} \phi_m + \left( \partial^2_{R_j} \varphi_m \right) (r|R) \right] \phi_m(R) \right\} = 0.$$  \hspace{1cm} (1.10)

From here we obtain an equation for the $\phi_n$ upon multiplication by $\varphi^*_n(r|R)$ and integration over $r$,

$$\left[ -\frac{1}{2} \sum_{j=1}^{L} \frac{m}{M_j} \partial^2_{R_j} + \varepsilon_n(R) - E \right] \phi_n(R) = \sum_{m \in \mathbb{N}} C_{nm}(R) \phi_m(R),$$  \hspace{1cm} (1.11)

where

$$C_{nm}(R) = A_{nm}(R) + B_{nm}(R),$$  \hspace{1cm} (1.12a)
\[ A_{nm}(\mathbf{R}) = \sum_{j=1}^{L} \frac{m}{M_j} \int d^{3}r \, \varphi_{n}^{*}(\mathbf{r} | \mathbf{R}) (\partial_{R_{j}} \varphi_{m})(\mathbf{r} | \mathbf{R}) \partial_{R_{j}}^{\alpha}, \quad (1.12b) \]

\[ B_{nm}(\mathbf{R}) = \frac{1}{2} \sum_{j=1}^{L} \frac{m}{M_j} \int d^{3}r \, \varphi_{n}^{*}(\mathbf{r} | \mathbf{R}) (\partial_{R_{j}}^{2} \varphi_{m})(\mathbf{r} | \mathbf{R}). \quad (1.12c) \]

If there is no external magnetic field we may assume that the \( \varphi_{n} \) are real. Then, using that

\[ \int d^{3}r \, \varphi_{n}(\mathbf{r} | \mathbf{R})(\partial_{R_{j}} \varphi_{n})(\mathbf{r} | \mathbf{R}) = \frac{1}{2} \partial_{R_{j}}^{\alpha} \int d^{3}r \, \varphi_{n}^{2}(\mathbf{r} | \mathbf{R}) = 0, \quad (1.13) \]

we see that \( A_{nn}(\mathbf{R}) = 0 \). Introducing the notation

\[ T = -\frac{1}{2} \sum_{j=1}^{L} \frac{m}{M_j} \partial_{R_{j}}^{2}, \quad (1.14) \]

we can therefore rewrite (1.11) in the form

\[ \left[ T + \varepsilon_{n}(\mathbf{R}) - B_{nm}(\mathbf{R}) - E \right] \phi_{n}(\mathbf{R}) = \sum_{m \in N, m \neq n} C_{nm}(\mathbf{R}) \phi_{m}(\mathbf{R}). \quad (1.15) \]

This equation still contains the full information about the ion system. The ions are now coupled through their Coulomb interaction (contained in \( \varepsilon_{n}(\mathbf{R}) \)) and through the electrons, whose degrees of freedom have been formally integrated out. Equation (1.15) will turn out to be an appropriate starting point for a perturbative analysis of the ion system with \( m/M_j \) taken as a small parameter.

### 1.2 Born-Oppenheimer approximation

#### 2.1 More scaling arguments

Classically we have a general idea, how the time scale, e.g. for the motion of a particle of mass \( m \) with one degree of freedom in a potential \( V \), depends on the mass. The Lagrangian of such a system is

\[ L = \frac{M(\dot{x})^{2}}{2} - V(x) = \frac{m}{2} \left( \frac{\dot{x}}{\sqrt{M/m}} \right)^{2} - V(x). \quad (2.1) \]

Denoting by \( x_{\mu}(t) \) a trajectory of a particle with mass \( \mu \), we see that

\[ x_{M}(t) = x_{m} \left( \frac{t}{\sqrt{M/m}} \right) \quad (2.2) \]

is a trajectory of a particle of mass \( M \). The motion slows down if \( M > m \). Heavier particles (of the same energy) move slower. In particular, oscillators oscillate with lower frequency if their mass is enlarged.

In quantum mechanics we have to consider the stationary Schrödinger equation, a time-independent problem. Hence, we are rather interested in how the spatial behaviour of the eigenfunctions varies with mass. For the bounded motion around an equilibrium position
described by a quadratic minimum of the potential we may recourse to the harmonic oscillator

\[ H = \frac{p^2}{2M} + \frac{Kx^2}{2}. \quad (2.3) \]

Comparing kinetic and potential energy in a similar scaling argument as in (1.2),

\[ \frac{\hbar^2}{2m\ell^2} \sim E \sim \frac{K\ell^2}{2}, \quad (2.4) \]

we find the intrinsic length scale

\[ \ell = \left( \frac{\hbar^2}{mK} \right)^{\frac{1}{3}}. \quad (2.5) \]

Comparing the extension \( L \) of an eigenfunction of a heavy particle of mass \( M \) with the extension \( \ell \) of a lighter particle of mass \( m \) we obtain a ratio of

\[ \frac{L}{\ell} = \left( \frac{m}{M} \right)^{\frac{1}{4}}. \quad (2.6) \]

This means that the larger the mass the more localized becomes the wave function. On the other hand, in a more localized wave function the particle is closer to the origin and the harmonic approximation is better justified.

### 2.2 Exercise 1. The heavy harmonic oscillator

The same conclusions as above can be drawn from the solution of the eigenvalue problem of the harmonic oscillator (2.3).

(i) Determine the full width at half height of the ground state wave function of the harmonic oscillator. How does it depend on the mass of the oscillator?

(ii) Consider the oscillator with a quartic correction term

\[ H = \frac{p^2}{2m} + \frac{Kx^2}{2} + \frac{K'x^4}{4!}, \quad (2.7) \]

where \( K' > 0 \). Show that the correction can be taken into account perturbatively if the mass is large. For this purpose use \( \ell \) as defined in (2.5) as a small parameter. Calculate the correction to the ground state energy in first order perturbation theory. How does it depend on the mass of the oscillator?

### 2.3 Application to the ionic motion and adiabatic decoupling

Let \( M \) be a typical ion mass, e.g. the arithmetic average of all ion masses \( M = \langle \{M_j\} \rangle \). Then

\[ \kappa = \left( \frac{m}{M} \right)^{\frac{1}{4}} \quad (2.8) \]

is an intrinsic length parameter for the bounded motion of the ions.

We expect that the eigenvalue problem (1.15) has solutions which, on the scale of the electronic wave functions, are strongly localized around certain equilibrium positions \( R^{(0)} \).
To take account of this expectation we introduce new coordinates $u$ on the scale of the electronic wave functions and relative to this equilibrium position, setting

$$\mathbf{R} = \mathbf{R}^{(0)} + \kappa \mathbf{u}.$$  \hfill (2.9)

For the wave functions we shall write

$$\tilde{\phi}_n(u) = \phi_n(R).$$ \hfill (2.10)

Using the new coordinates (2.9) we can make the $\kappa$ dependence of the operators in (1.15) explicit. For this purpose we define the rescaled operators

$$T_u = -\frac{1}{2} \sum_{j=1}^{L} \frac{M}{M_j} \partial^2_{\nu_j^\alpha},$$ \hfill (2.11a)

$$\tilde{A}_{nm}(R) = \frac{L}{2} \sum_{j=1}^{M} \frac{M_j}{M} \int d^3N_R \varphi^*_n(r|R)(\partial_{R_j^\alpha} \varphi_m)(r|R) \partial_{\nu_j^\alpha},$$ \hfill (2.11b)

$$\tilde{B}_{nm}(R) = \frac{1}{2} \sum_{j=1}^{L} \frac{M_j}{M} \int d^3N_R \varphi^*_n(r|R)(\partial^2_{R_j^\alpha} \varphi_m)(r|R),$$ \hfill (2.11c)

which remain finite for $\kappa \to 0$. With these definitions the eigenvalue problem (1.15) assumes the form

$$\left[ \kappa^2 T_u + \varepsilon_n(R^{(0)} + \kappa \mathbf{u}) - \kappa^4 \tilde{B}_{nn}(R^{(0)} + \kappa \mathbf{u}) - E \right] \tilde{\phi}_n(u)$$

$$= \kappa^3 \sum_{m \in \mathbb{N}, m \neq n} \left( \tilde{A}_{nm}(R^{(0)} + \kappa \mathbf{u}) + \kappa \tilde{B}_{nm}(R^{(0)} + \kappa \mathbf{u}) \right) \tilde{\phi}_m(u).$$ \hfill (2.12)

Recall that we assume that the wave functions $\phi_n$ are strongly localized around $R^{(0)}$, implying that the redefined functions $\tilde{\phi}_n$ are strongly localized around $u = 0$. For this reason it makes sense to expand the operators in (2.12) which act on the functions $\tilde{\phi}_n$ in a Taylor series in $\kappa$, and to solve the resulting eigenvalue problem perturbatively for small $\kappa$. The latter means to look for solutions in the form of formal series in $\kappa$,

$$E = E^{(0)} + \kappa E^{(1)} + \ldots,$$ \hfill (2.13a)

$$\tilde{\phi}_n(u) = \tilde{\phi}^{(0)}_n(u) + \kappa \tilde{\phi}^{(1)}_n(u) + \ldots$$ \hfill (2.13b)

Inserting these perturbation series into (2.12) and performing the Taylor expansion we obtain

$$\left( \kappa^2 T_u + \varepsilon_n(R^{(0)} + \kappa \mathbf{u}) + \kappa^2 \varepsilon^{(1)}_n(\mathbf{u}) + \kappa^4 \varepsilon^{(3)}_n(\mathbf{u}) + \kappa^4 \varepsilon^{(4)}_n(\mathbf{u}) + \ldots \right)$$

$$\times \left( \tilde{\phi}^{(0)}_n(\mathbf{u}) + \kappa \tilde{\phi}^{(1)}_n(\mathbf{u}) + \kappa^2 \tilde{\phi}^{(2)}_n(\mathbf{u}) + \kappa^3 \tilde{\phi}^{(3)}_n(\mathbf{u}) + \ldots \right)$$

$$= \kappa^3 \sum_{m \in \mathbb{N}, m \neq n} \left( \tilde{A}_{nm}(R^{(0)} + \ldots) \left( \tilde{\phi}^{(0)}_m(\mathbf{u}) + \kappa \tilde{\phi}^{(1)}_m(\mathbf{u}) + \kappa^2 \tilde{\phi}^{(2)}_m(\mathbf{u}) + \ldots \right) \right).$$ \hfill (2.14)
Here we compare the coefficients in front of the powers of $\kappa$ order by order. To the order $\kappa^0$ we obtain
\[ (\varepsilon_n(R^{(0)}) - E^{(0)})\phi_n^{(0)}(u) = 0 . \] (2.15)
Let $\phi^{(0)}_\ell(u) \neq 0$ for some $\ell \in \mathbb{N}$, $\varepsilon_\ell(R^{(0)})$ non-degenerate. Then
\[ E^{(0)} = \varepsilon_\ell(R^{(0)}), \quad \phi_n^{(0)}(u) = 0 \quad \forall n \neq \ell . \] (2.16)

For $n \neq \ell$ we conclude for the higher orders in $\kappa$ that
\begin{align*}
\mathcal{O}(\kappa) & : \quad (\varepsilon_n(R^{(0)}) - \varepsilon_\ell(R^{(0)}))\phi_n^{(1)}(u) = 0 \Rightarrow \phi_n^{(1)}(u) = 0 , \quad \text{(2.17a)} \\
\mathcal{O}(\kappa^2) & : \quad (\varepsilon_n(R^{(0)}) - \varepsilon_\ell(R^{(0)}))\phi_n^{(2)}(u) = 0 \Rightarrow \phi_n^{(2)}(u) = 0 , \quad \text{(2.17b)} \\
\mathcal{O}(\kappa^3) & : \quad (\varepsilon_n(R^{(0)}) - \varepsilon_\ell(R^{(0)}))\phi_n^{(3)}(u) = A_{n\ell}(R^{(0)})\phi_\ell^{(0)}(u) \\
& \quad \Rightarrow \phi_n^{(3)}(u) = \frac{A_{n\ell}(R^{(0)})\phi_\ell^{(0)}(u)}{\varepsilon_n(R^{(0)}) - \varepsilon_\ell(R^{(0)})} . \quad \text{(2.17c)}
\end{align*}

The latter equation means that at order $\kappa^3 \sim 1/1000$ the wave function $\Psi(r|R)$ (1.9) of the coupled electron ion system ceases to be a simple product of two factors.

For $n = \ell$ we find at order $\kappa$ that
\[ (\varepsilon^{(1)}(u) - E^{(1)})\phi_\ell^{(0)}(u) = 0 \Rightarrow E^{(1)} = \varepsilon^{(1)}_\ell(u) = \sum_{j=1}^{L} \frac{\partial \varepsilon_\ell(R^{(0)})}{\partial R_j^\alpha}u_j^\alpha . \] (2.18)

But $E^{(1)}$ must be independent of $u$ which can only hold if
\[ \frac{\partial \varepsilon_\ell(R^{(0)})}{\partial R_j^\alpha} = 0 . \] (2.19)

Then, necessarily,
\[ E^{(1)} = 0 . \] (2.20)

For higher orders of $\kappa$ we remain with the equation
\[ (T_u + \varepsilon^{(2)}_\ell(u) + \kappa \varepsilon^{(3)}_\ell(u) + \kappa^2 \varepsilon^{(4)}_\ell(u) - \kappa^2 B_{nn}(R^{(0)}) - E^{(2)} - \kappa E^{(3)} - \kappa^2 E^{(4)}) \times (\phi^{(0)}_\ell(u) + \kappa \phi^{(1)}_\ell(u) + \kappa^2 \phi^{(2)}_\ell(u)) \]
\[ = \kappa^4 \sum_{m \in \mathbb{N}, m \neq \ell} \tilde{A}_{\ell m}(R^{(0)})\phi^{(3)}_m(u) + \mathcal{O}(\kappa^5) \]
\[ = \kappa^4 \sum_{m \in \mathbb{N}, m \neq \ell} \frac{\tilde{A}_{\ell m}(R^{(0)})\tilde{A}_{m\ell}(R^{(0)})\phi^{(0)}_\ell(u)}{\varepsilon_m(R^{(0)}) - \varepsilon_\ell(R^{(0)})} + \mathcal{O}(\kappa^5) . \] (2.21)

Conceiving this as an equation up to the order $\kappa^2$, we see that the right hand side can be consistently neglected.
2.4 Summary and interpretation

(i) Within the scheme of the above perturbation theory the solutions $\phi_{n,\ell}$, $E_{n,\ell}$ of the eigenvalue problem

$$ (T + \varepsilon_n(R) - B_{nn}(R) - E)\phi(R) = 0 \quad (2.22) $$

consistently determine the eigenfunctions of the solid in product form

$$ \Psi_{n,\ell}(r, R) = \varphi_n(r|R)\phi_{n,\ell}(R) \quad (2.23) $$

up to the fourth order expansion of $\varepsilon_n(R)$ in $\kappa$ and up to the zeroth order expansion of $B_{nn}(R)$ in $\kappa$. $\varphi_n(r|R)$ is interpreted as a conditional probability amplitude and $\phi_{n,\ell}(R)$ as an ionic wave function. The product form then means that the electrons follow the motion of the ions.

(ii) The approximation (2.22), (2.23) is called the Born-Oppenheimer approximation and originated in molecular physics [2, 3]. Another common name is ‘the adiabatic approximation’.

(iii) Within the Born-Oppenheimer approximation the equilibrium positions of the ions are determined by the condition

$$ \frac{\partial \varepsilon_n(R(0))}{\partial R_\alpha^j} = 0. \quad (2.24) $$

In solids the ions arrange themselves in regular lattices.

(iv) Consistently up to the second order in $\kappa$ the eigenvalue problem (2.22) takes the form

$$ (T_\alpha + \varepsilon_n^{(2)}(u) - E)\tilde{\phi}^{(0)}(u) = 0 \quad (2.25) $$

where

$$ \varepsilon_n^{(2)}(u) = \frac{1}{2} \sum_{j,k=1}^{L} \frac{\partial^2 \varepsilon_n(R^{(0)})}{\partial R_j^\alpha \partial R_k^\beta} u_j^{\alpha} u_k^{\beta}. \quad (2.26) $$

This is called the harmonic approximation. Since only $\tilde{\phi}^{(0)}$ is taken into account in the harmonic approximation, it is consistent to consider the electronic wave function only to lowest order $\varphi(r|R^{(0)})$ as well. In this approximation the electrons move in a static lattice determined by the equilibrium positions of the ions (like the earth was approximately moving around a static sun in our entrance example).

(v) Notice that, in spite of the ratio of electron to ion mass being very small, our actual expansion parameter $\kappa \sim 1/10$ is only moderately small.

(vi) Our perturbative analysis becomes questionable, if the electronic levels are degenerate or close to degenerate (it is well justified for the electronic ground state of an insulator, but problematic for a metal).

(vii) Many properties of solids can be understood qualitatively and often also quantitatively within the harmonic approximation. Most of the treatment of solids in this lecture will be based on it. It explains e.g. the scattering of light or neutrons, the propagation of sound and the specific heat.
(viii) An example of an effect which cannot be explained within the harmonic approxima-
tion is the thermal extension of a solid. It is a higher order effect and therefore small. Still it can be understood within the adiabatic approximation if we proceed to the fourth order expansion of \( \varepsilon_n(R) \).

2.5 Exercise 2. A simple application of Born-Oppenheimer

A heavy particle \((M)\) and a light particle \((m \ll M)\) move inside an infinitely high potential well of width \(L\). The particles experience an attractive interaction described by the potential \( W(r - R) = -\lambda \cdot \delta(r - R) \), where \( \lambda > 0 \) and \( R \) and \( r \) are the positions of the heavy and light particle, respectively.

Calculate the spectrum of the corresponding Hamiltonian

\[
H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} - \lambda \cdot \delta(r - R) \tag{2.27}
\]

in Born-Oppenheimer approximation:

(i) In step one transform the Hamiltonian into a dimensionless form and neglect the kinetic energy of the heavy particle. Determine the (unnormalized) eigenfunctions and an equation for the energy eigenvalues \( \varepsilon(R) \) of the light particle. It may turn out to be useful to distinguish the cases \( \varepsilon < 0, \varepsilon = 0 \) and \( \varepsilon > 0 \). Recall the relation

\[
\frac{\partial \varphi}{\partial r}(R + 0) - \frac{\partial \varphi}{\partial r}(R - 0) = -\frac{2m\lambda}{\hbar^2} \varphi(R), \tag{2.28}
\]

for the jump of the derivative of the wave function caused by the \( \delta \)-function.

(ii) In step two sketch the energy \( \varepsilon(R) \) of the light particle for the ground state and for the first excited state as a function of the position of the heavy particle. What is the meaning of \( \varepsilon(R) \) and how should we include (qualitatively) the energy levels of the heavy particle into our picture?

L3 Crystal lattices

Within the adiabatic approximation the electrons and ions form bound states, molecules or solids, in which the ions oscillate around the minima \( R^{(0)} \) of the effective potentials \( \varepsilon_n(R) \) determined by the mutual Coulomb interaction of the ions and the energy eigenvalues of the electrons for fixed ion positions. We derived this statement in the previous lecture presupposing that such minima exist. The argument would have been more convincing if we would have been able to prove the existence of minima starting with the Hamiltonian (1.1). Such undertaking seems to be out of reach with our current methods. Still, in nature, atoms always form bound states at low enough temperatures (the only notable exception being helium which condenses into a ‘super fluid’ before solidification). If many atoms are put together in stoichiometric ratios they form periodic structures called crystals. Crystals are formed, since (i) two atoms prefer a certain binding length and (ii) no direction is preferred in the large (this is very much like packing balls into a box and carefully shaking it such that the balls find their equilibrium positions).

In this and in the following lecture we introduce the terminology and certain mathematical structures needed for the description of crystal lattices.
3.1 The Bravais lattice

The most important structural feature of a crystal is that it can be thought of as being generated by periodic repetitions of a finite elementary structure, the unit cell, in three space directions.

Let \( a_1, a_2, a_3 \in \mathbb{R}^3, \langle a_1, a_2 \times a_3 \rangle = \det(a_1, a_2, a_3) \neq 0. \) Then

\[
B = \{ x \in \mathbb{R}^3 | x = \ell_1 a_1 + \ell_2 a_2 + \ell_3 a_3, \ell_j \in \mathbb{Z} \},
\]

(3.1)

conceived as an Abelian group, is called a (3d) Bravais lattice. \( B \) is called the Bravais lattice of a crystal, if \( B \) is the group of all translations which map the (infinitely extended) crystal onto itself. Similarly we can define Bravais lattices in any number of dimensions. In the examples and exercises we will frequently work with \( d = 1 \) and \( d = 2 \).

Remark. We shall develop part of the theory of infinite crystals which is expected to give a realistic description, if the ratio of the number of ions at the surface to the number of ions in the bulk is small. For a typical macroscopic total number of \( L \sim 10^{24} \) ions, of the order of \( L^2/3 \sim 10^{16} \) of them are at the surface, and the ratio is \( \sim 10^{-8} \).

Bravais lattice vectors \( a_j, j = 1, 2, 3 \), that generate the Bravais lattice as an Abelian group with respect to vector addition are called primitive (lattice) vectors. They are not unique.

Lemma 1. Let \( a_j, j = 1, 2, 3, \) a set of primitive vectors of a Bravais lattice. Then

\[
b_i = \sum_{j=1}^{3} m_{ij} a_j, \quad i = 1, 2, 3, \text{ primitive } \iff m_{ij} \in \mathbb{Z} \text{ and } |\det m| = 1.
\]

Proof. \( \Rightarrow: \) primitive \( \Rightarrow m_{ij}^{-1} \in \mathbb{Z} \Rightarrow \det m^{-1} = 1/\det m \in \mathbb{Z} \Rightarrow (\text{since } \det m \in \mathbb{Z}): \det m = \pm 1.
\)

\( \Leftarrow: \) Cramer’s rule and \( \det m = \pm 1 \Rightarrow m_{ij}^{-1} \in \mathbb{Z} \Rightarrow \text{primitive}. \)

Since \( |\det m| = 1 \) it follows that

\[
V_u = |\det(b_1, b_2, b_3)| = |\det(a_1, a_2, a_3)|,
\]

(3.2)

the volume of the parallelepiped spanned by a set of primitive vectors, is independent of their choice.

By definition, the unit cell of a crystal with Bravais lattice \( B \) is a simply connected finite volume (of size \( V_u \)) which covers \( \mathbb{R}^3 \) through translation by \( B \). We often use a special unit cell, the Wigner-Seitz cell, which reflects the symmetries of the Bravais lattice, and is defined as

\[
W = \{ x \in \mathbb{R}^3 | \|x\| \leq \|x - g\| \forall g \in B \setminus \{0\} \}.
\]

(3.3)

Geometrically this is the set of points in \( \mathbb{R}^3 \) for which the closest Bravais lattice point is the origin. It can be constructed by drawing lines from the origin to the neighbouring sites in the Bravais lattice and erecting the perpendicular bisectors on these lines.

Exercise: Draw the Wigner-Seitz cells for 2d Bravais lattices composed of equilateral squares and triangles.
3.2 The reciprocal lattice

The reciprocal lattice which we shall define now is a lattice which, in a sense, is dual to the Bravais lattice. It is one of the most important notions in solid state physics and will accompany us throughout this lecture.

Given a Bravais lattice \( B \) and a set of primitive vectors \( \{a_j\}_{j=1}^{3} \), generating it, we would like to know how to decompose any \( x \in \mathbb{R}^3 \) with respect to the \( a_j \), i.e., we would like to know its coordinates with respect to the basis \( \{a_1, a_2, a_3\} \). Suppose that \( \{b_j\}_{j=1}^{3} \) exist such that

\[
\langle a_j, b_k \rangle = 2\pi \delta_{jk}.
\]

(3.4)

Then

\[
2\pi x_j = \langle x, b_j \rangle, \quad x = \frac{\langle x, b_j \rangle a_i}{2\pi},
\]

(3.5)

where we have employed the summation convention in the second equation. If (3.4) is satisfied, then \( \{a_j\}_{j=1}^{3} \) and \( \{b_j\}_{j=1}^{3} \) are called reciprocal (dual) to each other. The lattice

\[
\mathcal{B} = \{ x \in \mathbb{R}^3 | x = \ell_1 b_1 + \ell_2 b_2 + \ell_3 b_3, \ell_j \in \mathbb{Z} \}
\]

(3.6)

is called the reciprocal lattice (associated with the Bravais lattice \( B \)).

It is easy to solve (3.4) for the \( b_j \). For this purpose we rewrite it in matrix form

\[
(a_1, a_2, a_3)^t (b_1, b_2, b_3) = 2\pi I_3,
\]

(3.7)

where \( I_3 \) is the \( 3 \times 3 \) unit matrix, and use Cramer’s rule,

\[
(b_1, b_2, b_3) = 2\pi ((a_1, a_2, a_3)^{-1})^t = \frac{2\pi}{V_u} (a_2 \times a_3, a_3 \times a_1, a_1 \times a_2).
\]

(3.8)

Without restriction of generality we have assumed here that \( \det(a_1, a_2, a_3) > 0 \).

3.3 Properties of the reciprocal lattice

(i) Involutivity. Equation (3.4) implies that \( \mathcal{B} = B \). The reciprocal of the reciprocal lattice is the original Bravais lattice.

(ii) Brillouin zone. The Wigner-Seitz cell of the reciprocal lattice is called the (first) Brillouin zone. It plays an important role in solid state physics.

(iii) Volume of the Brillouin zone. Fix a set of primitive reciprocal lattice vectors \( b_j \) and denote the volume of the parallelepiped spanned by these vectors by

\[
V_R = \det(b_1, b_2, b_3).
\]

(3.9)

Taking the determinant on the left and right hand side of the first equation (3.7) we see that

\[
V_R = \frac{(2\pi)^3}{V_u}
\]

(3.10)

is the volume of the unit cells of the reciprocal lattice, which is the same as the volume of the Brillouin zone.
(iv) Lattice planes. A lattice plane \( S \subset \mathbb{R}^3 \) associated with a Bravais lattice \( B \) is a plane for which \( \exists \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \in B \) primitive, \( \exists \ell \in \mathbb{Z} \) such that
\[
\mathbf{x}_{\ell,m,n} = \ell \mathbf{a}_1 + m \mathbf{a}_2 + n \mathbf{a}_3 \in S, \quad \forall m, n \in \mathbb{Z}.
\] (3.11)

Let \( \mathbf{b}_1 = 2\pi(\mathbf{a}_2 \times \mathbf{a}_3)/V_u \) the reciprocal to \( \mathbf{a}_1 \). Then
\[
S = \{ \mathbf{x} \in \mathbb{R}^3 | \langle \mathbf{x}, \mathbf{b}_1 \rangle = 2\pi \ell \}. \quad (3.12)
\]
Thus, for every lattice plane there is a primitive reciprocal lattice vector \( \mathbf{b}_1 \in B \) and an \( \ell \in \mathbb{Z} \) such that (3.12) holds. If we vary \( \ell \) in (3.12) we obtain a family of equidistant lattice planes. Conversely, given any primitive vector \( \mathbf{b}_1 \in B \) and any \( \ell \in \mathbb{Z} \), the plane \( S \) defined by (3.12) is a lattice plane. Thus, families of lattice planes are in one-to-one correspondence with primitive vectors of the reciprocal lattice.

(v) Miller indices. Lattice planes play an important role in the spectroscopy of solids. We shall see in the course of this lecture that waves impinging on a crystal are reflected as if they were reflected by families of lattice planes. In spectroscopy the families of lattice planes are usually labeled by the so-called Miller indices defined relative to a fixed triple \( \{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\} \) of primitive vectors of the reciprocal lattice. According to lemma 1, every primitive vector \( \mathbf{b} \in B \) can be uniquely presented as
\[
\mathbf{b} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3, \quad m_j \in \mathbb{Z}.
\] (3.13)
The triple \( (m_1, m_2, m_3) \) is then the Miller index of the family of lattice planes associated with \( \mathbf{b} \). Accordingly, one speaks of the \( (m_1, m_2, m_3) \) plane (e.g., of the \( (1,0,0) \) plane). By convention, a bar is used instead of a minus sign, such that e.g. \( (1, -1, 0) = (1, 1, 0) \). As a reference triple \( \{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\} \) one usually uses primitive vectors of minimal possible length.

3.4 Exercise 3. Real space interpretation of the Miller indices

Let \( m_j \neq 0, j = 1, 2, 3 \), the Miller indices of a family of lattice planes. Convince yourself that they indicate in which three points
\[
\mathbf{x}_j = \frac{\mathbf{a}_j}{m_j}, \quad j = 1, 2, 3,
\] (3.14)
the lines along the \( \mathbf{a}_j \) directions cut the lattice plane with \( \ell = 1 \) in (3.12). Note that in the excluded cases with one or two of the \( m_j \) being equal to zero there is no intersection in the corresponding direction. The lines are parallel to the lattice plane.

3.5 Lattice periodic functions

Many quantities that characterize the state of a crystal have the same periodicity as the crystal itself. For this reason we will often have to deal with periodic functions whose periods are the primitive vectors of a Bravais lattice. These are often conveniently described by their Fourier series.

Let us recall Fourier series in one spatial dimension. In this case the unit cell is necessarily an interval \([0, a]\), where \( a > 0 \) is called the lattice spacing or lattice constant,
and the primitive vector is equal to \( a \). A lattice periodic function \( f : \mathbb{R} \to \mathbb{C} \) is a function satisfying
\[
f(x) = f(x + a) \quad \forall x \in \mathbb{R}.
\] (3.15)

A natural basis for the expansion of such functions can be constructed as follows. Let \( \varphi \in [0, 2\pi) \) and
\[
z = e^{i\varphi} = e^{i(\varphi+2\pi)} = e^{i\frac{2\pi}{a}(\frac{\varphi}{a}+a)}.
\] (3.16)

Setting
\[
x = \frac{\varphi a}{2\pi}, \quad b = \frac{2\pi}{a}, \quad k_m = mb
\] (3.17)
we see that
\[
ab = 2\pi
\] (3.18)
implying that \( b \) generates the reciprocal lattice, and that the functions
\[
z^m = e^{ik_m x}, \quad m \in \mathbb{Z},
\] (3.19)
are linear independent and periodic with period \( a \).

If the series
\[
f(x) = \sum_{m \in \mathbb{Z}} A_{k_m} e^{i k_m x}
\] (3.20)
converges uniformly, \( f \) is periodic with period \( a \) and continuous, and
\[
\frac{1}{a} \int_0^a dx \ e^{-ik_n x} f(x) = \sum_{m \in \mathbb{Z}} A_{k_m} \frac{1}{a} \int_0^a dx \ e^{i(k_m-k_n)x} = A_{k_n}.
\] (3.21)

By means of the latter formula we can associate a sequence of Fourier coefficients \( (A_{k_n})_{n \in \mathbb{Z}} \) and a Fourier series (3.20) with every complex valued function \( f \) that is integrable on \([0, a]\). In the following we will understand Fourier series in such a formal sense. But when we will be dealing with concrete examples, we will have in mind that the convergence properties of Fourier series are a delicate matter and that, in general, neither uniform nor pointwise convergence is guaranteed.

In order to construct Fourier series that have the periodicity defined by a Bravais lattice \( B \), we fix a set of primitive vectors \( \{a_1, a_2, a_3\} \) and a set of reciprocal vectors \( \{b_1, b_2, b_3\} \) satisfying (3.4). Then
\[
z_j = e^{i(b_j\cdot x)} = e^{i(b_j\cdot x+a_k)}, \quad j, k = 1, 2, 3,
\] (3.22)
and the monomials
\[
z_1^\ell z_2^m z_3^n = e^{i((b_1+m b_2+n b_3)\cdot x)}, \quad \ell, m, n \in \mathbb{Z},
\] (3.23)
are linear independent and periodic with all \( a \in B \) being periods. In analogy with the 1d case we may define \( k_{\ell mn} = \ell b_1 + m b_2 + n b_3 \) and the Fourier series
\[
f(x) = \sum_{\ell, m, n \in \mathbb{Z}} A_{k_{\ell mn}} e^{i(k_{\ell mn}\cdot x)} = \sum_{k \in B} A_k e^{i(k\cdot x)},
\] (3.24)
where
\[
A_k = \frac{1}{V_u} \int_U d^3x \ e^{-i(k\cdot x)} f(x)
\] (3.25)
and the integral is over a unit cell \( U \) of volume \( V_u \).

With these remarks on Fourier series we have obtained an interpretation of the reciprocal lattice. The reciprocal lattice is a lattice in Fourier space dual to the real space Bravais lattice.
L4 Crystal symmetries

4.1 The crystal lattice

We define a (physical) crystal lattice as the set $M$ of the positions (measured as expectation values) of the ions of a solid in its ground state. The translational symmetry of the crystal (lattice) is described by the corresponding Bravais lattice. In general there are several ions in a unit cell of the Bravais lattice. The positions of the ions inside a unit cell determine the so-called lattice basis. If every unit cell contains only one ion, the crystal is called simple. In this case it can be identified with its Bravais lattice. A crystal that is not simple is called a crystal with basis.

4.2 The Euclidean group

The Euclidean group is the group of all maps $\mathbb{R}^3 \rightarrow \mathbb{R}^3$ which leave the distance between any two arbitrary points invariant. It consists of all pairs $(A, a)$ of orthogonal transformations $A \in O(3)$ and translations $a \in \mathbb{R}^3$,

$$(A, a)x = Ax + a.$$  

(4.1)

Then

$$(A, a)(B, b)x = (A, a)(Bx + b) = ABx + Ab + a = (AB, Ab + a)x,$$  

(4.2)

implying that two group elements are multiplied according to the rule

$$(A, a)(B, b) = (AB, Ab + a).$$  

(4.3)

4.3 The symmetry group of a crystal

The symmetry group $R$ of a crystal $M$ is defined as

$$R = \{ (A, a) \in E(3) \mid (A, a)M = M \},$$  

(4.4)

i.e., as the subgroup of $E(3)$ that leaves $M$ invariant. If we identify $b$ with $(\text{id}, b)$ for every $b \in B$, the Bravais lattice of $M$, we see that $B$ is a subgroup of $R$ (since it leaves $M$ invariant and is a group).

Remark. $(\text{id}, a) \in R$ implies that $a \in B$, but $(A, a) \in R$, $A \neq \text{id}$ does not imply that $a \in B$. In crystals with basis smaller translations may occur which are parts of so-called glide reflections or screw rotations. For an example see Figure[1]

Lemma 2. Let $R$ be the symmetry group of a crystal with Bravais lattice $B$. Then $B \subset R$ is a normal subgroup of $R$.

Proof. Let $b \in B$, $(A, a) \in R$. $\Rightarrow (A, a)(\text{id}, b) = (A, Ab + a) = (\text{id}, Ab)(A, a)$, $\Rightarrow (\text{id}, Ab)M = M \Rightarrow Ab \in B$. Thus, $(A, a)(\text{id}, b)(A, a)^{-1} \in (\text{id}, B)$ for every $b \in B$, meaning that the Bravais lattice is an invariant (= normal) subgroup of $R$.  

4.4 The point group of a crystal

For a crystal $M$ with symmetry group $R$ define

$$R_0 = \{ A \in O(3) | \exists g \in R \text{ s. th. } g = (A, a) \}$$ (4.5)

the set of all ‘$O(3)$ parts’ of $R$.

Lemma 3. $R_0$ is a subgroup of $O(3)$, the so-called point group of the crystal.

Proof. (i) $A, B \in R_0 \Rightarrow \exists a, b \in \mathbb{R}^3 \text{ s. th. } (A, a), (B, b) \in R \Rightarrow (AB, Ab + a) \in R \Rightarrow AB \in R_0$. (ii) $(A, a)^{-1} = (A^{-1}, -A^{-1}a) \in R \Rightarrow A^{-1} \in R_0$. (iii) $\text{id} \in R_0$. (i)-(iii) $R_0$ is a group.

Remark. In general, $R_0 M \neq M$, i.e. the point group of $M$ does not necessarily leave $M$ invariant.

We have seen in the proof of lemma 2 that $b \in B, (A, a) \in R \Rightarrow Ab \in B$. Since, $A \in R_0$, it follows that $R_0 B \subset B$, $B$ is invariant under $R_0$. This has two important implications:

(i) The set of all point groups must be restricted, since not all subgroups of $O(3)$ can leave a Bravais lattice invariant.

(ii) Bravais lattices can be classified according to the point groups which leave them invariant.

4.5 Remarks on point groups

(i) All point groups are subgroups of $O(3)$ by construction. Thus, $A \in R_0 \Rightarrow \det A = \pm 1$. If $\det A = 1 \forall A \in R_0$, then $R_0$ is called a point group of the first kind, otherwise a point group of the second kind. Point groups of the first kind consist of only rotations.
(ii) The inversion $i \in O(3)$ is defined by $i \mathbf{x} = -\mathbf{x} \forall \mathbf{x} \in \mathbb{R}^3$, \(\Rightarrow\) det $i = -1$. For point groups of the second kind we distinguish point groups containing $i$ from point groups not containing $i$.

(iii) Since $\mathbf{b} \in B \Rightarrow -\mathbf{b} \in B$ for every Bravais lattice vector, the symmetry groups of the Bravais lattices are point groups of the second kind which do contain $i$.

(iv) Which rotations are possible? The fact that any point group must leave a Bravais lattice invariant restricts the possible rotation angles. It means that every rotation $D \in R_0$ must map primitive vectors on vectors in $B$,

\[ Da_j = m_{jk}a_k, \quad m_{jk} \in \mathbb{Z}. \quad (4.6) \]

Define a basis transformation $M$ in $\mathbb{R}^3$ by

\[ Ma_j = e_j, \quad \Rightarrow MDM^{-1}e_j = m_{jk}e_k, \]

\[ \Rightarrow \text{tr } D = \text{tr } MDM^{-1} = m_{jk}(e_j,e_k) = m_{jj} \in \mathbb{Z}. \quad (4.7) \]

Recall how the rotation angle is related to the trace of a rotation matrix. The trace is invariant under coordinate transformation. Hence, we may calculate it in a coordinate system in which the axis of rotation is the $z$-axis. Denoting the rotation angle by $\varphi$ we obtain

\[ \text{tr } D = \text{tr } \begin{pmatrix} \cos(\varphi) & \sin(\varphi) \\ -\sin(\varphi) & \cos(\varphi) \end{pmatrix} = 1 + 2 \cos(\varphi). \quad (4.8) \]

Combining (4.7) and (4.8) we conclude that allowed angles $\varphi$ must satisfy the condition $2 \cos(\varphi) \in \mathbb{Z}$, or

\[ \cos(\varphi) = 0, \pm \frac{1}{2}, \pm 1. \quad (4.9) \]

Thus, the only admissible values of $\varphi \in [0,2\pi)$ are

\[ \varphi = 0, \frac{\pi}{3}, \frac{\pi}{2}, \frac{2\pi}{3}, \pi. \quad (4.10) \]

The corresponding rotation axes are called 6-fold, 4-fold, 3-fold, 2-fold.

(v) Point groups do not only contain only rotation axes of finite order, they are also finite groups. Comparison with the known finite subgroups of $SO(3)$ leaves 11 point groups of the first kind compatible with (4.10). From these we can construct altogether 32 point groups. Their number is, in particular, finite.

4.6 Classification of all point and space groups

The full symmetry groups $R$ of crystals $M$ are discrete subgroups of $E(3)$ which contain a Bravais lattice $B$ as a normal subgroup. Their number is finite as well. In mathematics (and crystallography) such groups are called space groups. They have been completely classified and can be described by symmetry elements like rotations, reflections, glide reflections and screw rotations. The table gives an overview over the group theoretic classification of the Bravais lattices and crystals.
Bravais lattices  crystals

point groups  7 crystal systems (4 in 2d)  32 crystal classes (13 in 2d)
space groups  14 Bravais classes (5 in 2d)  230 (17 in 2d)

It is very instructive to have a look at least at the pictorial representations of the crystal systems and Bravais classes. They are shown in Figure 2.

4.7 Exercise 4. Lattice planes in the cubic face-centered lattice

As we have seen in section 3.3 all families of lattice planes of a Bravais lattice can be characterized by normal vectors, which can be expanded in a basis $b_1, b_2, b_3$ of primitive vectors of the reciprocal lattice. For a (perpendicular) distance $d$ of the planes the reciprocal lattice vector $\mathbf{k} = \sum_{i=1}^{3} m_i b_i$ is of length $2\pi/d$. Since the $m_j$ have no common divisor, $\mathbf{k}$ is the shortest reciprocal vector perpendicular to the planes.

(i) Show that the density of lattice points per unit area in the lattice planes is $d/V_u$, where $V_u$ is the volume of the unit cell spanned by $a_1, a_2, a_3$.

(ii) Show that the reciprocal lattice of the face-centered cubic lattice with lattice constant $a$ is a body-centered cubic lattice with lattice constant $4\pi/a$. By definition the lattice constant $a$ is the edge length of the cube which envelops the unit cell of the face-centered cubic lattice with primitive vectors

$$a_1 = \frac{a}{2}(e_x + e_z), \quad a_2 = \frac{a}{2}(e_x + e_y), \quad a_3 = \frac{a}{2}(e_x + e_y).$$

$e_x, e_y, e_z$ is the canonical orthonormal basis of $\mathbb{R}^3$. The corresponding primitive vectors for the body-centered cubic lattice with lattice constant $a'$ are

$$a_1 = \frac{a'}{2}(-e_x + e_y + e_z), \quad a_2 = \frac{a'}{2}(e_x - e_y + e_z), \quad a_3 = \frac{a'}{2}(e_x + e_y - e_z).$$

(iii) Find the Miller indices $(m_1, m_2, m_3)$ of that plane of the face-centered cubic lattice which has the highest density of lattice points. Here it may be helpful to use the connection between the density and the reciprocal lattice vector $\mathbf{k}$.

4.8 Exercise 5. Face centered tetragonal structure

Why does the face centered tetragonal structure not appear in the list of the 14 Bravais classes? How does this lattice fit into one of the 14 Bravais classes?

L5 The action of the Bravais lattice on states

5.1 Shift operators, lattice momentum and Bloch’s theorem

For a set of primitive vectors $\{a_1, a_2, a_3\} \in B$ define the corresponding shift operators $U_{a_j}$, acting on a single-particle space of states, by

$$U_{a_j} \Psi(x) = \Psi(x + a_j).$$ (5.1)
### Crystal system

| Crystal System | Group | Primitive | Base-centered | Body-centered | Face-centered |
|----------------|-------|-----------|---------------|---------------|---------------|
| Triclinic      | $C_i$ | ![Triclinic Primitive](image1) | ![Triclinic Base-centered](image2) | ![Triclinic Body-centered](image3) | ![Triclinic Face-centered](image4) |
| Monoclinic     | $C_{2h}$ | ![Monoclinic Primitive](image5) | ![Monoclinic Base-centered](image6) | ![Monoclinic Body-centered](image7) | ![Monoclinic Face-centered](image8) |
| Orthorhombic   | $D_{2h}$ | ![Orthorhombic Primitive](image9) | ![Orthorhombic Base-centered](image10) | ![Orthorhombic Body-centered](image11) | ![Orthorhombic Face-centered](image12) |
| Tetragonal     | $D_{4h}$ | ![Tetragonal Primitive](image13) | ![Tetragonal Base-centered](image14) | ![Tetragonal Body-centered](image15) | ![Tetragonal Face-centered](image16) |
| Rhombohedral   | $D_{3d}$ | ![Rhombohedral Primitive](image17) | ![Rhombohedral Base-centered](image18) | ![Rhombohedral Body-centered](image19) | ![Rhombohedral Face-centered](image20) |
| Hexagonal      | $D_{6h}$ | ![Hexagonal Primitive](image21) | ![Hexagonal Base-centered](image22) | ![Hexagonal Body-centered](image23) | ![Hexagonal Face-centered](image24) |
| Cubic          | $O_h$  | ![Cubic Primitive](image25) | ![Cubic Base-centered](image26) | ![Cubic Body-centered](image27) | ![Cubic Face-centered](image28) |

---

**Figure 2:** The crystal systems and Bravais classes (from Wikipedia, the free encyclopedia). A parallelepiped representing the point-group symmetry of a Bravais lattice has six parameters, three lengths of its edges and three angles. If all edge lengths and all angles are mutually distinct, the symmetry is minimal (only the inversion). This is the triclinic crystal class in the table. Considering all possible degeneracies (two right angles, to equal edge lengths etc.) one runs through all the listed symmetry classes, the crystal systems. Some of them can be realized by several Bravais lattices, giving the different Bravais classes. The second column in the table contains the name of the point group in so-called Schönflies notation.
Then
\[ U_{a_j}^{-1} = U_{a_j}^+, \quad [U_{a_j}, U_{a_k}] = 0, \quad j, k = 1, 2, 3. \] (5.2)

For any Bravais lattice vector \( \mathbf{R} = \ell \mathbf{a}_1 + m \mathbf{a}_2 + n \mathbf{a}_3 \) the operator
\[ U_{\mathbf{R}} = U_{\mathbf{a}_1}^\ell U_{\mathbf{a}_2}^m U_{\mathbf{a}_3}^n \] (5.3)
is therefore uniquely defined and naturally acts as
\[ U_{\mathbf{R}} \Psi(x) = \Psi(x + \mathbf{R}) \] (5.4)
on single-particle wave functions.

Equation (5.2) implies that the \( U_{a_j} \) have a joint system of eigenfunctions. If \( \Psi \) is such an eigenfunction, then
\[ U_{a_j} \Psi(x) = \Psi(x + a_j) = \omega(a_j) \Psi(x). \] (5.5)

Since \( U_{a_j} \) is unitary, \( |\omega(a_j)| = 1 \) implying that \( \exists v_j \in \mathbb{R} \) such that \( \omega(a_j) = e^{i2\pi v_j} \). Let \( \mathbf{R} = \ell \mathbf{a}_1 + m \mathbf{a}_2 + n \mathbf{a}_3, \mathbf{k} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3 \). Then
\[ \Psi(x + \mathbf{R}) = U_{\mathbf{R}} \Psi(x) = e^{i2\pi(\ell v_1 + mv_2 + nv_3)} \Psi(x) = e^{i\langle \mathbf{k}, \mathbf{R} \rangle} \Psi(x). \] (5.6)

Thus, for every common eigenfunction \( \Psi \) of the three generators \( U_{a_j} \) of lattice translations \( \exists \mathbf{k} \in \mathbb{R}^3 \) such that (5.6) holds for all \( \mathbf{R} \in \mathbf{B} \). The vector \( \mathbf{k} \) is a triple of quantum numbers characterizing the eigenstates of the lattice translation operators in very much the same manner as the momentum \( \mathbf{p} \) is a triple of quantum numbers that characterize the eigenstates of the operator of infinitesimal translations, the momentum operator. For this analogy \( \mathbf{k} \) is called the lattice momentum.

Let \( \mathbf{g} \in \mathbf{B}, \mathbf{R} \in \mathbf{B} \). Then \( \langle \mathbf{g}, \mathbf{R} \rangle = m2\pi \) for some \( m \in \mathbb{Z} \) and \( e^{i\langle \mathbf{k} + \mathbf{g}, \mathbf{R} \rangle} = e^{i\langle \mathbf{k}, \mathbf{R} \rangle} \). This means that \( \mathbf{k} \) and \( \mathbf{k} + \mathbf{g} \) characterize the same eigenstate of the lattice translation operator, or that the lattice momentum is defined only modulo reciprocal lattice vectors. For this reason we may restrict the domain of definition of \( \mathbf{k} \) to any unit cell of the reciprocal lattice. This domain is conventionally taken as the first Brillouin zone, which explains the importance of the latter.

In the language of group theory the lattice momenta \( \mathbf{k} \) label the irreducible representations of the Bravais lattice. Since the Bravais lattice is an Abelian group, all of its irreducible representations must be one-dimensional. They act by multiplication with complex numbers as can be seen in equation (5.6).

The Hamiltonian of the solid (1.1) is invariant under any infinitesimal translation. For this reason the center of mass momentum of the solid is conserved. In nature the translation symmetry is affected by a mechanism called spontaneous symmetry breaking. After separating the center of mass motion the ground state of the Hamiltonian (1.1) is less symmetric than the Hamiltonian itself. Instead of the full translation symmetry it exhibits a discrete translation symmetry with an underlying Bravais lattice \( \mathbf{B} \). Effective Hamiltonians describing the dynamics above the ground state again have the reduced symmetry described by a Bravais lattice. The simplest example for a class of such effective Hamiltonians is the Hamiltonian a single electron in a lattice periodic potential. The study of this class of Hamiltonians is called band theory. We will have a closer look at it below. In any case, single-particle Hamiltonians \( H \) which are invariant under the action of a Bravais lattice,
\[ [H, U_{a_j}] = 0, \quad j = 1, 2, 3, \] (5.7)
play an important role in solid state physics. As we have seen, their wave functions can be labeled by the lattice momentum quantum numbers. This is the statement of Bloch’s theorem.

**Theorem 1.** Bloch [1]. The eigenfunctions of a single-particle Hamiltonian \( H \), periodic with respect to a Bravais lattice \( B \), can be labeled by lattice momenta \( k \in \mathbb{BZ} \), where \( \mathbb{BZ} \subset \mathbb{B} \) is the Brillouin zone associated with \( B \). An eigenfunction \( \Psi_k \) of \( H \) then has the following properties with respect to translations by Bravais lattice vectors,

\[
\Psi_k(x + R) = e^{i\langle k, R \rangle} \Psi_k(x)
\]

for all \( R \in B \).

Let \( \Psi_{k,\alpha} \) an eigenstate with lattice momentum \( k \) of a lattice periodic Hamiltonian \( H \). Here we denote all other quantum numbers needed to specify the state by \( \alpha \). According to Bloch’s theorem \( u_{k,\alpha}(x) = e^{-i\langle k, x \rangle} \Psi_{k,\alpha}(x) \) is a lattice periodic function, \( u_{k,\alpha}(x + R) = u_{k,\alpha}(x) \). This implies the following corollary to Bloch’s theorem.

**Corollary 1.** The eigenfunctions of a lattice periodic single-particle Hamiltonian \( H \) are of the form

\[
\Psi_{k,\alpha}(x) = e^{i\langle k, x \rangle} u_{k,\alpha}(x),
\]

where \( k \in \mathbb{BZ} \) is a lattice momentum vector and \( u_{k,\alpha} \) is a lattice periodic function.

Hence, we may think of the eigenfunctions of a lattice periodic Hamiltonian as of amplitude-modulated plane waves, for which the modulation has the periods of the corresponding Bravais lattice.

### 5.2 Periodic boundary conditions

For the calculation of thermodynamic quantities in the framework of statistical mechanics (in particular) it is necessary to count states. For this reason we prefer systems of finite size which have a discrete spectrum. In solid state physics this can be enforced by introducing ‘boundaries’ (by putting the system into a box). After having counted the states one considers the limit, when the systems size goes to infinity (the thermodynamic limit).

In general, boundaries are incompatible with lattice translations induced by a Bravais lattice. They break the translational symmetry and invalidate Bloch’s theorem. A way out of this dilemma is by employing periodic boundary conditions.

For a \( d \)-dimensional system periodic boundary conditions can be realized by starting with a parallelepiped and identifying opposite faces. This amounts to bending the parallelepiped to a torus in \( d + 1 \) dimensions. For this reason periodic boundary conditions are also sometimes called toroidal boundary conditions.

Imposing periodic boundary conditions on a 1d system of \( L \) sites with lattice constant \( a \) we find for a state with lattice momentum \( k \) that

\[
\Psi_k(x + aL) = \Psi_k(x) = e^{ikaL} \Psi_k(x).
\]

For this to hold, the lattice momentum must be restricted to the values

\[
k = m\frac{2\pi}{aL},
\]

for all \( m \).
where \( m \in \mathbb{Z} \) in such a way that \( k \) lies in the Brillouin zone. The reciprocal lattice is generated by \( b = \frac{2\pi}{a} \). The Brillouin zone is the interval \( BZ = [-\pi/a, \pi/a) \), and \( k \in BZ \iff -L/2 \leq m < L/2 \). Thus, for every \( L \in \mathbb{N} \) there are \( L \) inequivalent \( k \)s in the Brillouin zone.

The argument is similar in any number of dimensions. In order to obtain the lattice momentum quantization condition, e.g. in 3d, we expand \( k \) in a basis of primitive vectors of the reciprocal lattice, \( k = v_1b_1 + v_2b_2 + v_3b_3 \). Then, for a state \( \Psi_k \) of lattice momentum \( k \),

\[
\Psi_k(x + La_j) = e^{i\langle k, La_j \rangle} \Psi_k(x) = \Psi_k(x), \tag{5.12}
\]

requiring that \( \langle k, La_j \rangle = 2\pi v_jL = 2\pi m_j \) for \( m_j \in \mathbb{Z} \). Restricting \( k \) to the first Brillouin zone means

\[
v_j = \frac{m_j}{L} \mod 1 \iff -\frac{L}{2} \leq m_j < \frac{L}{2}, \tag{5.13}
\]

i.e., there are \( L^3 \) inequivalent lattice momenta in the first Brillouin zone. Let us rephrase this statement in the following form.

**Lemma 4.** There are as many lattice momenta in the Brillouin zone that are compatible with periodic boundary conditions as unit cells in the crystal.

**Remark.** In 3d periodic boundary conditions cannot be physically realized. However, the density of states of a macroscopically large system (\( \sim 10^{23} \) particles) is practically independent of the boundary conditions. As long as we are not interested in the boundaries themselves, periodic boundary conditions are justified.

**Remark.** Mathematically periodic boundary conditions imply that we are dealing with functions that are periodic with periods of the large parallelepiped spanned by \( La_1, La_2, La_3 \). Hamiltonians must be defined in a way that is compatible with this periodicity. On the corresponding space of states the generators \( U_{a_j} \) of translations by primitive vectors turn into generators of the cyclic group of order \( L \),

\[
U_{a_j}^L = \text{id}, \quad j = 1, 2, 3, \tag{5.14}
\]

which equivalently might have served as a starting point for introducing periodic boundary conditions.

### L6  Phonons – spectrum and states

#### 6.1  The Hamiltonian of the lattice vibrations in harmonic approximation

In lecture L2 we have discussed the Born-Oppenheimer approximation. We have seen that, in this approximation, the motion of the much heavier ions decouples from the motion of the electrons up to fourth order in an expansion in the deviations \( u \) of the ion positions from their equilibrium values \( R^{(0)} \). In most of this lecture we shall be dealing with ideal solids. By definition, the equilibrium positions of the ions \( R^{(0)} \) in an ideal solid are the points of a crystal lattice. Solids in nature can be very close to ideal. The idealization of a perfect crystal is a good starting point to describe real solids.

Consider a crystal with Bravais lattice \( B \) and \( N \) ions per unit cell. In such a crystal it makes sense to label the coordinates of the vector \( u \) as \( u^{(0)}(R) \), where \( R \in B \) and

\[
\alpha = (r, j) \in I = \{1, \ldots, N\} \times \{x, y, z\}, \tag{6.1}
\]
Here \( r = 1, \ldots, N \) counts the ions in a unit cell, and \( j = x, y, z \) denotes their Cartesian coordinates. For the dimensionless ion masses (cf. Section 2.3) we introduce the notation

\[
\mu_\alpha = \mu_{(r,j)} = \frac{M_r}{M}
\]

(6.2)

Then the operator \( T_u \), equation (2.11a), of the kinetic energy of the ions takes the form

\[
T_u = -\frac{1}{2} \sum_{R \in B} \sum_{\alpha \in I} \frac{1}{\mu_\alpha} \partial^2 \alpha_u(R).
\]

(6.3)

We shall treat the motion of the ions within the harmonic approximation (2.25). This will allow us to develop a rather simple and general theory which nevertheless describes many of the experimental observations quite accurately. Within the harmonic approximation the potential energy of the ions can be written as

\[
V(u) = \frac{1}{2} \sum_{R, S \in B} \sum_{\alpha, \beta \in I} u^\alpha(R) K_{\alpha\beta}(R, S) u^\beta(S),
\]

(6.4)

where

\[
K_{\alpha\beta}(R, S) = \left. \frac{\partial^2 \varepsilon_0(X)}{\partial X^\alpha(R) \partial X^\beta(S)} \right|_{X=R(0)}
\]

(6.5)

is the so-called force matrix (see (2.26)).

Thus, the Hamiltonian of the lattice vibrations in harmonic approximation is

\[
H = -\frac{1}{2} \sum_{R \in B} \sum_{\alpha \in I} \frac{1}{\mu_\alpha} \partial^2 \alpha_u(R) + \frac{1}{2} \sum_{R, S \in B} \sum_{\alpha, \beta \in I} u^\alpha(R) K_{\alpha\beta}(R, S) u^\beta(S).
\]

(6.6)

It is a quadratic form in the position operators of the ions and the corresponding derivatives. We will diagonalize this quadratic form. This will reduce the spectral problem of the Hamiltonian to the spectral problem of independent harmonic oscillators describing the quantized normal modes of the ideal harmonic solid. In order to control the number of the normal modes, we will employ periodic boundary conditions as introduced in the previous lecture.

### 6.2 Implications of the translational invariance

Fix a set of primitive vectors \( \{a_1, a_2, a_3\} \subset B \). Define the action of \( B \) on functions \( v \) on \( B \) obeying periodic boundary conditions by

\[
U_{a_j} v(R) = v(R + a_j).
\]

(6.7)

The space spanned by such functions is a finite dimensional vector space. For the action of \( U_{a_j} \) on this space there is an \( L \in \mathbb{N} \) such that \( U_{a_j}^L = \text{id}, j = 1, 2, 3 \). Thus, if \( \omega_j \) is an eigenvalue of \( U_{a_j} \) we must have \( |\omega_j| = 1 \) (because of unitarity) and \( \omega_j^L = 1 \). It follows that

\[
\omega_j = e^{i m_j 2\pi} = e^{i(k, a_j)}
\]

(6.8)

for some \( k = (m_1 b_1 + m_2 b_2 + m_3 b_3)/L \in BZ \). As we have seen in the previous lecture there are altogether \( L^3 \) such vectors.
It is easy to find the corresponding eigenfunctions of the shift operators. If \( v_k \) is an eigenfunction with lattice momentum \( k \), and \( R = \ell a_1 + ma_2 + na_3 \in B \), then

\[
v_k(R) = v_k(\ell a_1 + ma_2 + na_3) = U_{a_1}^\ell U_{a_2}^m U_{a_3}^n v_k(0) = \omega_1^\ell \omega_2^m \omega_3^n v_k(0) = e^{i(k, R)} v_k(0)
\]

for all \( R \in B \). This determines \( v_k \) up to normalization. We fix the normalization by setting

\[
v_k(0) = \frac{1}{\sqrt{L^3}}.
\]

All joint eigenfunctions of the \( U_{a_j} \) are of this form, and all these functions are joint eigenfunctions of the \( U_{a_j} \). Hence, they form a basis of on the space of complex valued functions on \( B \).

**Remark.**

(i) We have just invented the (discrete) Fourier transformation.

(ii) With the choice (6.10) the usual Hermitian scalar product of two eigenfunctions takes the values

\[
\langle v_k, v_q \rangle = \sum_{R \in B} v_k^*(R) v_q(R) = \frac{1}{L^3} \sum_{R \in B} e^{-i(k - q, R)} = \delta_{k, q}
\]

for any two \( k, q \in BZ \).

### 6.3 Block diagonalization of the force matrix

We will first of all diagonalize the force matrix \( K_{\alpha\beta}(R, S) \) defined in (6.5). For this purpose and for later use as well we list its main properties.

(i) Symmetry. From its very definition as a second derivative matrix and from the commutativity or the partial derivatives we get at once that

\[
K_{\alpha\beta}(R, S) = K_{\beta\alpha}(S, R).
\]

(ii) Translation symmetry.

\[
K_{\alpha\beta}(R + a, S + a) = K_{\alpha\beta}(R, S) \quad \forall \ a \in B.
\]

Inserting here \( a = -S \) we obtain

\[
K_{\alpha\beta}(R, S) = K_{\alpha\beta}(R - S, 0) = K_{\alpha\beta}(R - S),
\]

where the second equation is a definition. The meaning is that forces between ions depend only on the relative positions of unit cells.

(iii) In crystal lattices with inversion symmetry we have in addition that

\[
K_{\alpha\beta}(R) = K_{\alpha\beta}(-R).
\]

Combining this with (6.12) we see that the force matrix in crystal lattices with inversion symmetry is symmetric in every unit cell,

\[
K_{\alpha\beta}(R) = K_{\beta\alpha}(R).
\]
The force matrix defines an operator on the space of functions with periodic boundary conditions on $B$,

$$\hat{K}_{\alpha\beta} f(R) = \sum_{S \in B} K_{\alpha\beta}(R - S) f(S). \quad (6.17)$$

It is easy to see that $\hat{K}_{\alpha\beta}$ commutes with the shift operators $U_{a_j}, j = 1, 2, 3$,

$$U_{a_j} \hat{K}_{\alpha\beta} f(R) = \sum_{S \in B} K_{\alpha\beta}(R + a_j - S) f(S)$$

$$= \sum_{S \in B} K_{\alpha\beta}(R - S) f(S + a_j) = \hat{K}_{\alpha\beta} U_{a_j} f(R), \quad \Leftrightarrow \quad \hat{K}_{\alpha\beta}, U_{a_j} = 0. \quad (6.18)$$

Hence, $U_{a_j}$ and $\hat{K}_{\alpha\beta}$ possess a joint system of eigenfunctions. Since the $v_k$, equation (6.9), form already an orthonormal basis of non-degenerate eigenfunctions, they must be also eigenfunctions of $\hat{K}_{\alpha\beta}$,

$$\hat{K}_{\alpha\beta} v_k(R) = \kappa_{\alpha\beta}(k) v_k(R). \quad (6.19)$$

In order to block diagonalize the quadratic form (6.4) we expand the displacements $u^\alpha(R)$ into their Fourier modes,

$$u^\alpha(R) = \sum_{k \in BZ} \xi_k^\alpha v_k(R). \quad (6.20)$$

Using that $u^\alpha(R) \in \mathbb{R}$ and $v^*_k = v_{-k}$ we see that

$$\xi_k^\alpha = \xi_{-k}. \quad (6.21)$$

Inserting (6.20) into (6.4) and making use of (6.19), (6.21) we obtain

$$V(u) = \frac{1}{2} \sum_{\alpha, \beta \in I} \langle u^\alpha, \hat{K}_{\alpha\beta} u^\beta \rangle = \frac{1}{2} \sum_{\alpha, \beta \in I} \sum_{q, k \in BZ} \xi^\alpha_{-q} \xi^\beta_k \langle v_q, \hat{K}_{\alpha\beta} v_k \rangle$$

$$= \frac{1}{2} \sum_{q \in BZ} \sum_{\alpha, \beta \in I} \xi^\alpha_{-q} \kappa_{\alpha\beta}(q) \xi^\beta_q, \quad (6.22)$$

the block diagonal form of the potential energy.

### 6.4 Transformation of the kinetic energy

Let us now apply the same transformation to the kinetic energy operator. First of all

$$\langle u^\alpha, v_{-k} \rangle = \sum_{q \in BZ} \xi^\alpha_{-q} \langle v_q, v_{-k} \rangle = \xi^\alpha_k = \sum_{S \in B} u^\alpha(S) v_{-k}(S), \quad (6.23)$$

implying that

$$\frac{\partial}{\partial u^\alpha(R)} = \sum_{k \in BZ} \frac{\partial \xi^\alpha_k}{\partial \xi_k^\alpha} \frac{\partial}{\partial \xi_k^\alpha} = \sum_{k \in BZ} v_{-k}(R) \frac{\partial}{\partial \xi_k^\alpha}. \quad (6.24)$$

It follows that
\[ T_u = -\frac{1}{2} \sum_{\alpha \in I} \mu_\alpha \sum_{R \in B} \sum_{q,k \in BZ} v_{-q}(R) v_{-k}(R) \frac{\partial}{\partial \xi_{q,R}} \frac{\partial}{\partial \xi_{k,R}} \]

\[ = -\frac{1}{2} \sum_{\alpha \in I} \mu_\alpha \sum_{q,k \in BZ} \langle v_{q}, v_{-k} \rangle \frac{\partial}{\partial \xi_{q,\alpha}} \frac{\partial}{\partial \xi_{k,\alpha}} = -\frac{1}{2} \sum_{q \in BZ} \sum_{\alpha \in I} \mu_\alpha \frac{\partial}{\partial \xi_{q,\alpha}} \frac{\partial}{\partial \xi_{q,\alpha}}. \] (6.25)

Here we have used (6.11) in the second equation. We see that the lattice Fourier transformation has diagonalized \( T_u \).

In the next step we want to completely diagonalize the force matrix while keeping the diagonal form of the kinetic energy operator. To achieve the latter goal, we first rescale the complex coordinates, setting

\[ \eta^\alpha_q = \sqrt{\mu_\alpha} \xi^\alpha_q \Rightarrow \partial_{\eta^\alpha_q} = \frac{1}{\sqrt{\mu_\alpha}} \partial_{\xi^\alpha_q}. \] (6.26)

Further defining

\[ \tilde{\kappa}_{\alpha\beta}(q) = \frac{\kappa_{\alpha\beta}(q)}{\sqrt{\mu_\alpha \mu_\beta}} \] (6.27)

we obtain the following form of the Hamiltonian (6.6),

\[ H = \frac{1}{2} \sum_{q \in BZ} \left\{ -\sum_{\alpha \in I} \frac{\partial}{\partial \eta^\alpha_{-q}} \frac{\partial}{\partial \eta^\alpha_{q}} + \sum_{\alpha,\beta \in I} \eta^\alpha_{-q} \tilde{\kappa}_{\alpha\beta}(q) \eta^\beta_{q} \right\}. \] (6.28)

### 6.5 Properties of the matrix \( \tilde{\kappa}(q) \)

Before we can proceed we have to understand the properties of the matrix \( \tilde{\kappa}(q) \).

(i) \( \tilde{\kappa}(q) \) is Hermitian, since

\[ \kappa^\ast_{\alpha\beta}(q) = \langle v_q, \tilde{K}_{\alpha\beta} v_q \rangle^* \]

\[ = \sum_{R,S \in B} v_q(R) K_{\alpha\beta}(R - S) v_{-q}(S) \]

\[ = \sum_{R,S \in B} v_q(R) K_{\beta\alpha}(S - R) v_{-q}(S) \]

\[ = \sum_{R,S \in B} v_{-q}(R) K_{\beta\alpha}(R - S) v_q(S) = \langle v_q, \tilde{K}_{\beta\alpha} v_q \rangle = \kappa_{\beta\alpha}(q). \] (6.29)

Here we have used the symmetry of the force matrix in the third equation.

(ii) \( \tilde{\kappa}(q) \) is non-negative. This follows, since the potential energy \( V \) is assumed to have a total minimum for \( u = 0 \) with \( V = 0 \). Hence

\[ V(u) = \frac{1}{2} \sum_{\alpha,\beta \in I} \eta^\alpha_{-q} \tilde{\kappa}_{\alpha\beta}(q) \eta^\beta_{q} \geq 0. \] (6.30)

(iii) \( \tilde{\kappa}(q) \) and \( \tilde{\kappa}(-q) \) are similar matrices. First of all

\[ \kappa^\ast_{\alpha\beta}(q) = \sum_{R,S \in B} v_q(R) K_{\alpha\beta}(R - S) v_{-q}(S) = \kappa_{\alpha\beta}(-q), \] (6.31)
since the force matrix is real. Then also
\[ \tilde{\kappa}^*_{\alpha\beta}(q) = \tilde{\kappa}_{\alpha\beta}(-q). \] (6.32)

According to (i) and (ii) the matrix \( \tilde{\kappa}(q) \) can be diagonalized by a unitary transformation and has a non-negative spectrum \( \{\omega_{\alpha}^2(q)\}_{\alpha \in I} \) for every \( q \in BZ \). Let \( \{y_{\alpha}(q)\}_{\alpha \in I} \) the set of corresponding orthonormal eigenvectors. Then
\[ \tilde{\kappa}^*(q)y_{\alpha}(q) = \omega_{\alpha}^2(q)y_{\alpha}(q) = \tilde{\kappa}(-q)y_{\alpha}(q)^* \] (6.33)

implying that \( \{\omega_{\alpha}^2(q)\}_{\alpha \in I} \) is the spectrum of \( \tilde{\kappa}(-q) \). Hence, \( \tilde{\kappa}(q) \) and \( \tilde{\kappa}(-q) \) are similar matrices.

Since, on the other hand,
\[ \tilde{\kappa}(-q)y_{\alpha}(-q) = \omega_{\alpha}^2(-q)y_{\alpha}(-q) \] (6.34)

by definition of the eigenvectors and eigenvalues, the identification
\[ y_{\alpha}(-q) = y_{\alpha}(q)^* \] (6.35)

(which is one possible choice of indexing the eigenvectors of \( \tilde{\kappa}(-q) \) once the eigenvectors of \( \tilde{\kappa}(q) \) are given) implies that
\[ \omega_{\alpha}^2(q) = \omega_{\alpha}^2(-q). \] (6.36)

### 6.6 Exercise 6. Classical harmonic chain with various boundary conditions

The lectures on lattice vibrations will be accompanied by a set of exercises on the classical harmonic chain with broken translation invariance. We shall study the influence of fixed and open boundary conditions and of a mass defect. There is a good deal to learn from these exercises, namely something about the irrelevance of the boundary conditions as far as bulk thermodynamic properties are concerned, but also something about the typical effects of impurities, such as the appearance of localized states and impurity levels inside the band gap.

We start with an important technical device, the transfer matrix, and with the effect of fixed and open boundary conditions. For this purpose consider \( N \) masses \( m_1, \ldots, m_N \) coupled to a linear, harmonic chain by \( N - 1 \) springs with force constants \( k > 0 \). Periodic boundary conditions are realized by an additional identical spring connecting the masses \( m_1 \) and \( m_N \). For fixed boundary conditions, the masses \( m_1 \) and \( m_N \) are coupled with springs of spring constants \( k \) to a rigid wall, while open boundaries are realized if the masses \( m_1 \) and \( m_N \) are not at all coupled to each other.

In this exercise we shall consider the particular case of equal masses \( m_1 = \ldots = m_N = m \). We want to analyze the harmonic chain by the so-called transfer matrix method. Upon slight modifications, it is possible to treat the different boundary conditions in a similar way.

(i) Find the equations of motion for the deviations \( x_n \) from the equilibrium positions in the periodic case. Employing the ansatz \( x_n(t) = e^{i\omega t} x_n \) the equations of motion imply an eigenvalue problem of the form \( Tx = \Omega^2x \) with \( x = (x_1, \ldots, x_N)^t \). Obtain the matrix \( T \), and show how \( \Omega \) depends on \( \omega, m \) and \( k \).
(ii) Show, that, with the substitution $\psi(n) = x_n, \varphi(n) = \psi(n-1)$, the eigenvalue problem in (i) can be reformulated as

$$
\begin{pmatrix}
\psi(n+1) \\
\varphi(n+1)
\end{pmatrix} = L_n(\Omega^2) \begin{pmatrix}
\psi(n) \\
\varphi(n)
\end{pmatrix}, \quad L_n(\Omega^2) = L(\Omega^2) = \begin{pmatrix}
2 - \Omega^2 & -1 \\
1 & 0
\end{pmatrix}.
$$

In the periodic case $L_n(\Omega^2)$ is independent of the site index. Calculate the eigenvalues and the corresponding eigenvectors of $L(\Omega^2)$. Because $L(\Omega^2)$ acts like a translation operator, it is useful to write the eigenvalues in the form $e^{\pm i\kappa}$. Diagonalize the equation

$$
\begin{pmatrix}
\psi(n+1) \\
\varphi(n+1)
\end{pmatrix} = L_n(\Omega^2) \begin{pmatrix}
\psi(1) \\
\varphi(1)
\end{pmatrix}.
$$

How can $\Omega^2$ be expressed in terms of $\kappa$?

(iii) The periodic boundary conditions turn into $\psi(N+1) = \psi(1)$ and $\varphi(N+1) = \varphi(1)$. From this determine all possible eigenfrequencies $\omega$!

(iv) Which modification is required for fixed boundaries? Determine all possible eigenfrequencies $\omega$ in this case.

(v) Show that the modifications necessary for open boundaries lead to the equation

$$
(1 - \Omega^2, -1) L^{N-2}(\Omega^2) \begin{pmatrix}
1 - \Omega^2 \\
1
\end{pmatrix} = 0.
$$

With this, calculate again all possible eigenfrequencies $\omega$. What is the physical meaning of the solution $\omega = 0$? How are the eigenfrequencies of the open chain and of the chain with fixed boundaries connected with each other?

### L7 Phonons – spectrum and states continued

#### 7.1 Reduction of the Hamiltonian to a diagonal quadratic form

For every $q \in BZ$ we define a unitary $3N \times 3N$ matrix

$$
Y(q) = (y_{(1,x)}(q), \ldots, y_{(N,z)}(q)).
$$

This matrix diagonalizes $\vec{\kappa}(q)$,

$$
\vec{\kappa}(q) = Y(q) \text{diag}(\omega^2_{(1,x)}, \ldots, \omega^2_{(N,z)}) Y^+(q)
$$

and, because of (6.35), has the property that

$$
Y(q)^* = Y(-q).
$$

Letting

$$
x_q = Y^+(q) \eta_q \iff x^\alpha_q = \langle y^\alpha(q), \eta_q \rangle
$$

we see that

$$
\sum_{\alpha, \beta \in I} \eta^\alpha_q \vec{\kappa}_{\alpha\beta}(q) \eta^\beta_q = \eta^T_{-q} \vec{\kappa}(q) \eta_q = \sum_{\alpha \in I} \omega^2_{\alpha}(q) x^\alpha_q x^\alpha_q,
$$

where

$\vec{\kappa}_{\alpha\beta}(q)$ are the components of $\vec{\kappa}(q)$.
while for the kinetic term

\[
\sum_{\alpha \in I} \frac{\partial}{\partial \eta^\alpha_{-q}} \frac{\partial}{\partial \eta^\alpha_{q}} = \sum_{\alpha, \beta, \gamma \in I} \partial x^\beta_{-q} \partial x^\gamma_{-q} \frac{\partial}{\partial \eta^\alpha_{-q}} \frac{\partial}{\partial \eta^\alpha_{q}} \partial x^\gamma_{q} \nonumber \]

\[
= \sum_{\alpha, \beta, \gamma \in I} Y^+ \alpha(-q) Y^+ \alpha(q) \frac{\partial}{\partial x^\beta_{-q}} \frac{\partial}{\partial x^\gamma_{q}} = \sum_{\alpha \in I} \frac{\partial}{\partial x^\alpha_{-q}} \frac{\partial}{\partial x^\alpha_{q}} . \tag{7.6}
\]

Here we have used (7.3) in the last equation. Altogether, we have transformed \( H \) into a diagonal quadratic form,

\[
H = \frac{1}{2} \sum_{q \in BZ} \sum_{\alpha \in I} \left\{ -\frac{\partial}{\partial x^\alpha_{-q}} \frac{\partial}{\partial x^\alpha_{q}} + \omega_\alpha^2(q) x^\alpha_{-q} x^\alpha_{q} \right\} . \tag{7.7}
\]

The term in the bracket can be interpreted as the Hamiltonian of a 1d harmonic oscillator with ‘complex coordinates’.

### 7.2 Zero modes

Before going on we have to discuss the question whether the functions \( \omega_\alpha(q) \) can be zero. What we can say is that there are always at least three values of \( \alpha \) for which \( \omega_\alpha(0) = 0 \). These special ‘modes’ are connected with the center of mass motion of the solid. Their existence can be inferred from the translation invariance of the Hamiltonian (6.6) which is inherited from the full Hamiltonian (1.5) of the solid. For (6.6) translation invariance means invariance under the transformation

\[
u^{(r,j)}(R) \mapsto \nu^{(r,j)}(R) + \epsilon^j, \tag{7.8}
\]

for all \( \epsilon^j \in \mathbb{R} \) and every \( (r, j) \in I \). This transformation leaves the kinetic energy (6.3) trivially invariant. For the potential energy (6.4) we infer that

\[
\frac{\partial}{\partial \epsilon^j} V_{\mid \epsilon^j=0} = \frac{1}{2} \sum_{R, S \in B} \sum_{r, s=1}^{N} \sum_{\ell=x, y, z} \left( K_{(r,j)(s,\ell)}(R - S) u^{(s,\ell)}(S) + u^{(r,\ell)}(R) K_{(r,\ell)(s,j)}(R - S) \right)
\]

\[
= \sum_{R, S \in B} \sum_{r, s=1}^{N} \sum_{\ell=x, y, z} K_{(r,j)(s,\ell)}(R - S) u^{(s,\ell)}(S) = 0 \tag{7.9}
\]

for arbitrary \( u^{(s,\ell)}(S) \in \mathbb{R} \). Here we have used the symmetry (6.12) of the force matrix in the second equation. Setting all but one of the displacements equal to zero and this one equal to one we obtain the relation

\[
\sum_{R \in B} \sum_{r=1}^{N} K_{(r,j)(s,\ell)}(R) = 0 \tag{7.10}
\]

for the force matrix, which holds for all \( (s, \ell) \in I \) and \( j = x, y, z \). On the other hand

\[
\kappa_{\alpha\beta}(0) = \langle v_0, \tilde{K}_{\alpha\beta} v_0 \rangle = \frac{1}{L^3} \sum_{R, S \in B} K_{\alpha\beta}(R - S) = \sum_{R \in B} K_{\alpha\beta}(R) . \tag{7.11}
\]
Setting $\alpha = (r,j), \beta = (s,\ell)$ summing over $r$ and using (7.10) we conclude that

$$
\sum_{r=1}^{N} \sqrt{\mu_r \mu_s} \tilde{\kappa}(r,j)(s,\ell)(0) = 0
$$

(7.12)

for all $(s,\ell) \in I$ and $j = x, y, z$. Thus, there are three independent linear relations between the rows of the matrix $\tilde{\kappa}(0)$ which therefore has at least a threefold eigenvalue zero. We may order the spectrum of $\tilde{\kappa}_{\alpha\beta}(0)$ in such a way that the corresponding eigenvectors are $y_{(1,j)}(0), j = x, y, z$. The corresponding ‘normal coordinates’ are $x_{0}^{(1,j)} = \langle y_{(1,j)}(0), \eta_{0} \rangle$.

Using this notation, the Hamiltonian (7.7) splits into

$$
H = T_{\text{cm}} + \frac{1}{2} \sum_{(q,\alpha) \in I \setminus (0,1)} \left\{ -\frac{\partial}{\partial x_{-q}^{\alpha}} \frac{\partial}{\partial x_{q}^{\alpha}} + \omega_{\alpha}(q) x_{-q}^{\alpha} x_{q}^{\alpha} \right\}.
$$

(7.13)

where

$$
T_{\text{cm}} = -\frac{1}{2} \sum_{j=x,y,z} \frac{\partial^2}{\partial (x_{0}^{(1,j)})^2}
$$

(7.14)

can be interpreted as the kinetic energy of the center of mass motion of the crystal.

The center of mass motion of the crystal is unbounded. If there were any other ‘zero modes’, i.e., a higher than threefold degeneracy of the eigenvalue zero, then there would be another eigenvector $y_{\alpha}(q)$ corresponding to unbounded motion. This would necessarily involve an unbounded relative motion of different parts of the crystal, meaning that the crystal would disintegrate. In the following we shall exclude this possibility and concentrate on stable crystals. We shall also discard the center of mass motion. Then we remain with the Hamiltonian of the proper lattice vibrations which we denote

$$
H_{\text{ph}} = H - T_{\text{cm}} = \frac{1}{2} \sum_{(q,\alpha) \in Q} \left\{ -\frac{\partial}{\partial x_{-q}^{\alpha}} \frac{\partial}{\partial x_{q}^{\alpha}} + \omega_{\alpha}(q) x_{-q}^{\alpha} x_{q}^{\alpha} \right\}.
$$

(7.15)

Here we have introduced the notation

$$
Q = \{ (q,\alpha) = BZ \times I | \omega_{\alpha}(q) \neq 0 \}.
$$

(7.16)

The subindex ‘ph’ refers to ‘phonon’ which is the name of a quantized normal mode of the lattice.

### 7.3 Diagonalization of the phonon Hamiltonian

To accomplish a complete diagonalization of the Hamiltonian $H_{\text{ph}}$ we introduce the operators

$$
a_{q}^{\alpha} = \sqrt{\frac{\omega_{\alpha}(q)}{2} x_{q}^{\alpha}} + \frac{1}{\sqrt{2 \omega_{\alpha}(q)}} \frac{\partial}{\partial x_{-q}^{\alpha}},
$$

(7.17a)

$$
a_{+q}^{\alpha} = \sqrt{\frac{\omega_{\alpha}(q)}{2} x_{-q}^{\alpha}} - \frac{1}{\sqrt{2 \omega_{\alpha}(q)}} \frac{\partial}{\partial x_{q}^{\alpha}}.
$$

(7.17b)
for all \((q, \alpha) \in Q\). They satisfy the commutation relations (exercise: check it!)

\[
[a^\alpha_q, a^\beta_k] = 0 = [a^+\alpha_q, a^+\beta_k], \quad [a^\alpha_q, a^+\beta_k] = \delta_{q,k}\delta^\alpha_\beta.
\] (7.18)

Inverting (7.17) we obtain

\[
x^\alpha_q = \frac{a^\alpha_q + a^+\alpha_q}{\sqrt{2\omega^\alpha_q(q)}}, \quad \frac{\partial}{\partial x^\alpha_q} = \sqrt{\frac{\omega^\alpha_q(q)}{2}}(a^\alpha_q - a^+\alpha_q).
\] (7.19)

The latter equation implies that

\[
\omega^2_{\alpha}(q)x^\alpha_q x^\alpha_q - \frac{\partial}{\partial x^\alpha_q} \frac{\partial}{\partial x^\alpha_q} = \frac{\omega^\alpha_q(q)}{2}(a^\alpha_q + a^+\alpha_q)(a^\alpha_q + a^+\alpha_q) - \frac{\omega^\alpha_q(q)}{2}(a^\alpha_q - a^+\alpha_q)(a^\alpha_q - a^+\alpha_q)
\]

\[
= \omega^\alpha_q(q)(a^+\alpha_q a^\alpha_q + a^+\alpha_q a^\alpha_q + 1),
\] (7.20)

whenever \(\omega^\alpha_q(q) \neq 0\). Here we have used the evenness of the functions \(\omega^\alpha\), equation (6.36), and the commutation relations (7.18). Inserting (7.20) into (7.15) and using once more that \(\omega^\alpha\) is an even function of \(q\) we arrive at

\[
H_{ph} = \sum_{(q, \alpha) \in Q} \omega^\alpha_q(q)(a^+\alpha_q a^\alpha_q + \frac{1}{2}).
\] (7.21)

Thus, \(H_{ph}\) is decomposed into a sum of independent harmonic oscillators.

### 7.4 Creation and annihilation operators in terms of the original displacements

Going step by step backwards, we express the creation and annihilation operators of the phonons in terms of the original displacement variables and their associated momentum operators

\[
p^\alpha(R) = -i \frac{\partial}{\partial u^\alpha(R)}.
\] (7.22)

We obtain

\[
x^\alpha_q = \sum_{\beta \in I} Y^+_{\alpha\beta}(q) \eta^\beta_q = \sum_{\beta \in I} Y^+_{\alpha\beta}(q) \sqrt{\mu^\beta} \xi^\beta_q
\]

\[
= \sum_{\beta \in I} Y^+_{\alpha\beta}(q) \sqrt{\mu^\beta} \langle u^\beta, v^{-q} \rangle = \frac{1}{\sqrt{L^3}} \sum_{R \in B} \sum_{\beta \in I} e^{-i(q,R)} \sqrt{\mu^\beta} Y^+_{\alpha\beta}(q) \eta^\beta(R)
\] (7.23)

and

\[
\frac{\partial}{\partial x^\alpha_q} = \sum_{\beta \in I} \frac{\partial \eta^\beta_q}{\partial x^\alpha_q} \frac{\partial}{\partial \eta^\beta_q} = \sum_{\beta \in I} \frac{Y_{\alpha\beta}(-q)}{\sqrt{\mu^\beta}} \frac{\partial}{\partial \xi^\beta_{-q}} = \sum_{\beta \in I} \frac{Y^+_{\alpha\beta}(q)}{\sqrt{\mu^\beta}} \frac{\partial}{\partial \xi^\beta_{-q}}
\]

\[
= \frac{1}{\sqrt{L^3}} \sum_{R \in B} \sum_{\beta \in I} e^{-i(q,R)} \frac{Y^+_{\alpha\beta}(q)}{\sqrt{\mu^\beta}} \xi^\beta(R) p^\beta(R).
\] (7.24)
Inserting the latter two equations into the definitions (7.17) of the annihilation and creation operators we obtain

\[ a^\alpha_q = \frac{1}{\sqrt{L^3}} \sum_{R \in B} \sum_{\beta \in I} e^{-i(q,R)} Y^{\gamma + \alpha}_\beta(q) \left[ \sqrt{\frac{\mu \beta \omega_\alpha(q)}{2}} u^\beta(R) + \frac{ip^\beta(R)}{\sqrt{2 \mu \beta \omega_\alpha(q)}} \right] \], \hspace{1cm} (7.25a)

\[ a^{+ \alpha}_q = \frac{1}{\sqrt{L^3}} \sum_{R \in B} \sum_{\beta \in I} e^{i(q,R)} Y^{\gamma \alpha}_\beta(q) \left[ \sqrt{\frac{\mu \beta \omega_\alpha(q)}{2}} u^\beta(R) - \frac{ip^\beta(R)}{\sqrt{2 \mu \beta \omega_\alpha(q)}} \right] \]. \hspace{1cm} (7.25b)

In this form it is obvious that \( a^\alpha_q \) and \( a^{+ \alpha}_q \) are mutually adjoint operators.

### 7.5 Construction of the eigenstates

Let

\[ \Psi_0(u) = \exp \left\{ -\frac{1}{2} \sum_{(k,\beta) \in Q} \omega_\beta(k)x^\beta_k \right\} \]. \hspace{1cm} (7.26)

Then

\[ \frac{\partial \Psi_0(u)}{\partial x^-_q} = \left( -\frac{\omega_\alpha(q)x^\alpha_q}{2} - \frac{\omega_\alpha(-q)x^\alpha_q}{2} \right) \Psi_0(u) = -\omega_\alpha(q)x^\alpha_q \Psi_0(u) \]

\[ \iff a^\alpha_q \Psi_0(u) = 0 \] \hspace{1cm} (7.27)

for all \((q, \alpha) \in Q\). Hence,

\[ H_{ph} \Psi_0(u) = E_0 \Psi_0(u) \hspace{0.5cm}, \hspace{0.5cm} E_0 = \frac{1}{2} \sum_{(q,\alpha) \in Q} \omega_\alpha(q) \]. \hspace{1cm} (7.28)

\( \Psi_0 \) is the ground state, since it is the ground state for every 1d harmonic oscillator in the sum (7.21).

Comparing (7.26) and (7.15) and recalling the original definition (6.4) of the harmonic potential, we obtain the ground state wave function as a function of the displacements \( u \) of the ions,

\[ \Psi_0(u) = e^{-V(u)} = \exp \left\{ -\frac{1}{2} \sum_{R \in B} \sum_{\alpha,\beta \in I} u^\alpha(R) K_{\alpha\beta}(R,S) u^\beta(S) \right\} \]. \hspace{1cm} (7.29)

which is a natural generalization of the 1d case.

A general phonon state is generated by the multiple action of phonon creation operators \( a^{+ \alpha}_q \) on the ground state which, for this reason, is also sometimes called the phonon vacuum (exercise: repeat the construction of excited states for the 1d harmonic oscillator based on the Heisenberg algebra (7.18)). Such states are parameterized by maps \( Q \rightarrow \mathbb{N}_0 \), \((q, \alpha) \mapsto n^\alpha_q \). Accordingly we shall denote them as

\[ \Psi_n(u) = \prod_{(q,\alpha) \in Q} (a^{+ \alpha}_q)^{n^\alpha_q} \Psi_0(u) \]. \hspace{1cm} (7.30)

It follows from the commutation relations (7.18) that

\[ H_{ph} \Psi_n(u) = E_n \Psi_n(u) \hspace{0.5cm}, \hspace{0.5cm} E_n = \sum_{(q,\alpha) \in Q} \omega_\alpha(q)(n^\alpha_q + \frac{1}{2}) \]. \hspace{1cm} (7.31)
The eigenvectors $y_\alpha(q)$ of $\tilde{\kappa}(q)$, together with the corresponding eigenfrequencies $\omega_\alpha(q)$, determine the creation operators $a_\alpha^+(q)$, equation (7.25b), since $Y_\alpha^\beta(q) = (y_\alpha)_\beta$. In analogy with the expression for the quantized electro-magnetic field we shall call them polarization vectors.

Let us summarize the insight we have gained so far in the following

**Theorem 2.** In order to obtain the spectrum (7.31) and the eigenstates (7.29), (7.30) of the vibrational motion of the ions in a solid in harmonic approximation, it suffices to calculate the dispersion relations $\omega_\alpha(q)$ and the polarization vectors $y_\alpha(q)$. For this purpose one first calculates the matrix

$$\tilde{\kappa}_{\alpha\beta}(q) = \sum_{R \in B} e^{-i(q,R)} K_{\alpha\beta}(R) \sqrt{\mu_\alpha \mu_\beta}$$  (7.32)

and then its eigenvectors $y^\alpha(q)$ and eigenvalues $\omega^2_\alpha(q)$.

The input here is the force matrix. In applications it comes from quantum chemical calculations or from simple heuristic models. Note that in (7.32) every matrix element $\tilde{\kappa}_{\alpha\beta}(q)$ is represented as a (finite) Fourier series (cf. section 3.5) defining it as a periodic function in reciprocal space with periods in $\tilde{B}$. We expect the forces between ions to decay rapidly with distance and the convergence of the Fourier series (7.32) in the thermodynamic limit to be uniform, implying that the limit function is differentiable in $q$.

### L.8 Phonons – examples and general properties

#### 8.1 Example 1 – the harmonic chain

To start with we reconsider the harmonic chain within the framework of the general theory. This is a 1d problem with one ion per unit cell, thus no indices $\alpha, \beta$ are required and $\mu = 1$. Denoting the lattice spacing by $a$ we obtain

$$q = n \frac{2\pi}{L} \cdot \frac{2\pi}{a}, \quad R = \ell a$$  (8.1)

for the quantized lattice momenta $q$ and the Bravais lattice vectors $R$.

The model force matrix is

$$K(R, S) = K(\ell a, ma) = K(\ell - m) = \omega_0^2 (2\delta_{\ell,m} - \delta_{\ell,m+1} - \delta_{\ell,m-1}),$$  (8.2)

where we have to keep the periodic boundary conditions in mind. This is a $1 \times 1$ matrix. The polarization vector is $y = 1$ and

$$\tilde{\kappa}(q) = \sum_{\ell} e^{-i2\pi \ell \cdot q} \omega_0^2 (2\delta_{\ell,0} - \delta_{\ell,1} - \delta_{\ell,-1}) = \omega_0^2 2 \left(1 - \cos(2\pi n/L)\right)$$

$$= 2\omega_0^2 \left(1 - \cos(qa)\right) = 4\omega_0^2 \sin^2(qa/2) = \omega^2(q).$$  (8.3)

It follows that

$$\omega(q) = 2\omega_0 |\sin(qa/2)|$$  (8.4)

which is called the dispersion relation of the harmonic chain with nearest-neighbour interactions.
8.2 Example 2 – diatomic chain with alternating forces

The classical model for this configuration is given by the equations of motion

\[ \begin{align*}
\mu_1 \ddot{u}_1(R) &= \alpha_1 (u_2(R) - u_1(R)) - \alpha_2 (u_1(R) - u_2(R - a)), \\
\mu_2 \ddot{u}_2(R) &= \alpha_2 (u_1(R + a) - u_2(R)) - \alpha_1 (u_2(R) - u_1(R)),
\end{align*} \tag{8.5} \]

where

\[ \mu_j = \frac{2m_j}{m_1 + m_2}, \quad j = 1, 2, \tag{8.6} \]

are the dimensionless masses and \( \alpha_1, \alpha_2 \) dimensionless force constants (see Figure 3). The corresponding force matrix is \( (\mathbf{F} = - \nabla V) \)

\[ \mathbf{K}(R, S) = \begin{pmatrix}
(\alpha_1 + \alpha_2)\delta_{R,S} & -\alpha_1\delta_{R,S} - \alpha_2\delta_{R,S+a} \\
-\alpha_1\delta_{R,S} - \alpha_2\delta_{R,S-a} & (\alpha_1 + \alpha_2)\delta_{R,S}
\end{pmatrix}. \tag{8.7} \]

It follows that

\[ \kappa(q) = \begin{pmatrix}
\alpha_1 + \alpha_2 & -\alpha_1 - \alpha_2 e^{-iqa} \\
-\alpha_1 - \alpha_2 e^{iqa} & \alpha_1 + \alpha_2
\end{pmatrix}, \tag{8.8} \]

and

\[ \tilde{\kappa}(q) = \begin{pmatrix}
\frac{\alpha_1 + \alpha_2}{\mu_1} & \frac{-\alpha_1 - \alpha_2 e^{-iqa}}{\sqrt{\mu_1\mu_2}} \\
\frac{-\alpha_1 - \alpha_2 e^{iqa}}{\sqrt{\mu_1\mu_2}} & \frac{\alpha_1 + \alpha_2}{\mu_2}
\end{pmatrix}. \tag{8.9} \]

As it should be, this is a Hermitian \( 2 \times 2 \) matrix. We have to calculate its eigenvalues and eigenvectors.

For the eigenvalues \( \lambda_{\pm} \) of a \( 2 \times 2 \) matrix \( A \) we have the general formula (exercise: check it!)

\[ \lambda_{\pm} = \frac{\text{tr} A}{2} \pm \sqrt{\left( \frac{\text{tr} A}{2} \right)^2 - \det A}. \tag{8.10} \]

For the matrix \( \tilde{\kappa}(q) \) we calculate

\[ \text{tr} \tilde{\kappa}(q) = \frac{2(\alpha_1 + \alpha_2)}{\mu_1\mu_2}, \tag{8.11a} \]

\[ \det \tilde{\kappa}(q) = \frac{\alpha_1\alpha_2}{\mu_1\mu_2} 4 \sin^2 \left( \frac{qa}{2} \right). \tag{8.11b} \]

It follows that
\[
\omega^2(q) = \frac{\alpha_1 + \alpha_2}{\mu_1 \mu_2} \pm \sqrt{\left(\frac{\alpha_1 + \alpha_2}{\mu_1 \mu_2}\right)^2 - \frac{\alpha_1 \alpha_2}{\mu_1 \mu_2} 4 \sin^2 \left(\frac{qa}{2}\right)}
\]

\[
= \frac{(\alpha_1 + \alpha_2)(m_1 + m_2)^2}{4m_1 m_2} \left\{ 1 \pm \sqrt{1 - \frac{4\alpha_1 \alpha_2}{(\alpha_2 + \alpha_2)^2 (m_1 + m_2)^2} \sin^2 \left(\frac{qa}{2}\right)} \right\}. \quad (8.12)
\]

Recalling that \( 4xy \leq (x + y)^2 \Leftrightarrow 0 \leq (x - y)^2 \) for all \( x, y \in \mathbb{R} \) we may conclude that

\[
0 < \frac{4\alpha_1 \alpha_2}{(\alpha_2 + \alpha_2)^2 (m_1 + m_2)^2} \leq 1
\]

as it must be for \( \omega^2_\pm(q) \) to be real.

The two branches \( \omega_\pm \) of the dispersion relation are sketched in Figure 4. Note that the lower branch is going to zero linearly as \( q \) goes to zero,

\[
\omega_-(q) = v_s q + \mathcal{O}(q^2), \quad v_s = \sqrt{\frac{\alpha_1 \alpha_2}{2(\alpha_1 + \alpha_2)} a}. \quad (8.14)
\]

This is the limit of long wave lengths. For this reason the branch is called the acoustic branch, \( v_s \) is the sound velocity.

The branch \( \omega_+ \) is called the optical branch. The normal modes at small \( q \) in the acoustic branch correspond to motions when the two atoms in the unit cell move in phase, while small values of \( q \) in the optical branch correspond to motions when the two atoms move against each other. This can be seen by looking at the polarization vectors, which we leave as an exercise. As we see in Figure 4 the frequencies in the optical branch are higher than in the acoustic branch. In real solids typical optical branches correspond to frequencies in the infrared.
The numbers
\[ W_\pm = \max \omega_\pm(q) - \min \omega_\pm(q) \] (8.15)
are called the band width of the optical and acoustic branches. They quantify the ranges of available frequencies or bands. In real solids, like in our Figure, optical bands have typically smaller band widths than acoustic bands. The number
\[ g = \min \omega_+(q) - \max \omega_-(q) \] (8.16)
is called the band gap. It corresponds to a range of ‘forbidden frequencies’. As we shall see the existence of bands and band gaps explain many of the characteristic feature of solids observed in experiments.

It is interesting to see, how the monoatomic chain of example 1 is recovered for \( \alpha_1 = \alpha_2 = \alpha \) and \( m_1 = m_2 \). For this special choice of parameters
\[ \omega_\pm^2(q) = 2\alpha \left( 1 \pm \cos \left( \frac{qa}{2} \right) \right), \] (8.17)
since \(|q| \leq \pi/a\). This can be rewritten as
\[ \omega_-^2(q) = 4\alpha \sin^2 \left( \frac{qa}{4} \right), \] (8.18a)
\[ \omega_+^2(q) = 4\alpha \cos^2 \left( \frac{qa}{4} \right) = 4\alpha \sin^2 \left( \frac{q}{a} \pm \frac{2\pi}{a} \left( \frac{q}{2} \right) \right). \] (8.18b)
We see that \( \omega_+ \) is the same function as \( \omega_- \), shifted by \( \pm \frac{2\pi}{a} \). The band gaps have vanished, and by shifting \( \omega_+ \) on the interval \([-\pi/a,0]\) by \(2\pi/a\) to the right and the same function on the interval \([0,\pi/a]\) by \(2\pi/a\) to the left, we obtain the function \( \omega_- \) on the doubled Brillouin zone \([-2\pi/a,2\pi/a]\). Thus, we have two equivalent descriptions, two branches of the dispersion relation on the original Brillouin zone \([-\pi/a,\pi/a]\) or one branch on \([-2\pi/a,2\pi/a]\). The doubling of the Brillouin zone corresponds to a bisection of the unit cell in the Bravais lattice (exercise: draw the pictures!).

8.3 General properties of phonons in a 3d lattice

(i) There are \(3N\) branches \(\omega_\alpha(q)\) of the dispersion relation for a crystal lattice with \(N\) atoms per unit cell.

(ii) In the thermodynamic limit the lattice momenta \(q\) densely fill the Brillouin zone, and the matrix \(\tilde{\kappa}(q)\) as defined in equation (7.32) becomes a continuously differentiable function of \(q\). Then, due to the implicit function theorem, the functions \(\omega_\alpha^2(q)\) become differentiable functions of \(q\). As also follows from (7.32) they are naturally extended as periodic functions on the reciprocal lattice \(\overline{B}\).

(iii) There are precisely three acoustic branches for which \(\omega_\alpha(0) = 0\). All other branches are optical branches with \(\min \omega_\alpha > 0\). Since any continuous functions assumes its extremum on compact sets, every phonon band has finite band width.

(iv) Of the three acoustic branches one has longitudinal, the others have transversal polarization. In general the longitudinal acoustic modes are faster than the transversal acoustic modes (reversing force is larger for pressure waves than for shear waves, becomes clear when thinking about transition to fluid).
(v) The dispersion relations of the phonons are invariant under the action of the point group $R_0$ of the crystal,

$$\omega_\alpha(\mathbf{q}) = \omega_\alpha(G\mathbf{q}) \quad (8.19)$$

for all $(\mathbf{q}, \alpha) \in Q$, for all $G \in R_0$.

**Proof.** Let $G \in R_0 \subset O(3)$. Then $G$ acts naturally, as a rotation or a rotation followed by an inversion, on the Bravais lattice and on the displacements $u^{(rj)}(\mathbf{R})$, $j = x, y, z$, of the individual ions from their equilibrium positions. The latter action combines into the action of a representation $D$ of $R_0$ on the vectors of displacement $\mathbf{u}$,

$$u'^\alpha(G\mathbf{R}) = \sum_{\beta \in I} D^\beta_\alpha(G) u^\beta(\mathbf{R}). \quad (8.20)$$

This transformation leaves the kinetic energy and the potential energy of the Hamiltonian (7.15) of the harmonic crystal separately invariant, as all ions simultaneously undergo the same $O(3)$ transformation, which does not affect their relative displacements. The crystal lattice is not necessarily invariant under this transformation, but the effect on the crystal lattice is at most a translation, since any point group operation can be seen as a combination of a space group operation and a translation. This is another way of understanding the point group invariance of the Hamiltonian (7.15).

Let us work out the consequences of the invariance for the representation $D$. First of all, setting $\mathbf{R}' = G\mathbf{R}$,

$$\frac{\partial}{\partial u^\alpha(\mathbf{R})} = \sum_{\beta \in I} \frac{\partial u'^\beta(\mathbf{R}')}{\partial u^\alpha(\mathbf{R})} \frac{\partial}{\partial u'^\beta(\mathbf{R}')}, \quad (8.21)$$

and hence

$$T_u = -\frac{1}{2} \sum_{\mathbf{R} \in B} \sum_{\alpha \in I} \frac{1}{\mu_\alpha} \frac{\partial^2}{\partial u^\alpha(\mathbf{R})^2}$$

$$= -\frac{1}{2} \sum_{\mathbf{R} \in B} \sum_{\alpha \in I} \frac{1}{\mu_\alpha} \sum_{\beta,\gamma \in I} D^\beta_\alpha(G) D^\gamma_\alpha(G) \frac{\partial}{\partial u'^\beta(\mathbf{R}')} \frac{\partial}{\partial u'^\gamma(\mathbf{R}')}$$

$$= -\frac{1}{2} \sum_{\mathbf{R} \in B} \sum_{\beta,\gamma \in I} \left[ \sum_{\alpha \in I} D^\beta_\alpha(G) D^\gamma_\alpha(G) \frac{\partial}{\partial u'^\beta(\mathbf{R}')} \frac{\partial}{\partial u'^\gamma(\mathbf{R}')} \right] \quad (8.22)$$

where we have used the invariance of $B$ under $R_0$ in the third equation. Form invariance of the kinetic energy now means that

$$\sum_{\alpha \in I} D^\beta_\alpha(G) D^\gamma_\alpha(G) \frac{\partial}{\partial u'^\beta(\mathbf{R}')} \frac{\partial}{\partial u'^\gamma(\mathbf{R}')} = \frac{\delta^{\beta \gamma}}{\mu_\beta}. \quad (8.23)$$

Similarly, the potential energy transforms like

$$V(\mathbf{u}) = \frac{1}{2} \sum_{\mathbf{R}, \mathbf{S} \in B} \sum_{\alpha,\beta \in I} u^\alpha(\mathbf{R}) K_{\alpha\beta}(\mathbf{R} - \mathbf{S}) u^\beta(\mathbf{S})$$
\[ \frac{1}{2} \sum_{R,S \in B} \sum_{\alpha,\beta \in I} u^\alpha(G R) K_{\alpha\beta}(G(R - S)) u^\beta(G S) \]

\[ = \frac{1}{2} \sum_{R,S \in B} \sum_{\alpha,\beta \in I} u^\alpha(R) \left[ \sum_{\gamma,\delta \in I} D^\gamma_\alpha(G) K_{\gamma\delta}(G(R - S)) D^\delta_\beta(G) \right] u^\beta(S). \quad (8.24) \]

Then form invariance of this expression implies that

\[ K_{\alpha\beta}(R - S) = \sum_{\gamma,\delta \in I} D^\gamma_\alpha(G) K_{\gamma\delta}(G(R - S)) D^\delta_\beta(G). \quad (8.25) \]

It follows that

\[ \sum_{\gamma,\delta \in I} D^\gamma_\alpha(G) \kappa_{\gamma\delta}(G q) D^\delta_\beta(G) = \sum_{R \in B} e^{-i(G q, R)} \sum_{\gamma,\delta \in I} D^\gamma_\alpha(G) K_{\gamma\delta}(G R) D^\delta_\beta(G) \]

\[ = \sum_{R \in B} e^{-i(G q, R)} \sum_{\gamma,\delta \in I} D^\gamma_\alpha(G) K_{\gamma\delta}(G R) D^\delta_\beta(G) = \kappa_{\alpha\beta}(q). \quad (8.26) \]

Here we have used (8.25) and the fact that \( \langle G q, G R \rangle = \langle q, R \rangle \) in the last equation.

Equation (8.26) is equivalent to saying that

\[ \tilde{\kappa}_{\alpha\beta}(q) = \sum_{\gamma,\delta \in I} D^\gamma_\alpha(G) \tilde{\kappa}_{\gamma\delta}(G q) D^\delta_\beta(G), \quad (8.27) \]

where

\[ D^\alpha_\beta(G) = \sqrt{\frac{\mu_\alpha}{\mu_\beta}} D^\alpha_\beta(G). \quad (8.28) \]

and therefore

\[ \sum_{\beta \in I} D^\beta_\gamma(G) D^\delta_\gamma(G) = \sum_{\beta \in I} D^\beta_\gamma(G) D^\gamma_\beta(G) = \sqrt{\mu_\alpha \mu_\gamma} \sum_{\beta \in I} \frac{D^\beta_\gamma(G) D^\gamma_\beta(G)}{\mu_\beta} = \delta_{\alpha\gamma}. \quad (8.29) \]

This means that \( \kappa(q) \) and \( \tilde{\kappa}(G q) \) are similar matrices which implies our claim.

\[ \square \]

### 8.4 Exercise 7. Linear chain with a mass defect

For equal masses the solution of the periodic chain in Exercise 6 leads to the acoustic phonons of the simple one-dimensional lattice. If the masses are different, however, there is, in general, no simple closed solution, not even of the one-dimensional problem.

In the following we shall study the influence of a mass defect. We assume that all masses but one are equal to \( m \) and that the remaining mass is equal to \( m(1 + \mu) \). As in Exercise 6 the ansatz of an harmonic time dependence leads to an eigenvalue problem of the form

\[ \begin{pmatrix} \psi(1) \\ \varphi(1) \end{pmatrix} = \begin{pmatrix} \psi(N + 1) \\ \varphi(N + 1) \end{pmatrix} = L_N \cdots L_1 \begin{pmatrix} \psi(1) \\ \varphi(1) \end{pmatrix}, \quad L_n = \begin{pmatrix} 2 - \Omega_n^2 & -1 \\ 1 & 0 \end{pmatrix}. \quad (8.30) \]

Here \( \psi(n) \) and \( \varphi(n) \) are defined as in Exercise 6, and \( \Omega_n^2 = m_n \omega^2 / k \) with \( m_1 = m(1 + \mu) \) and \( m_j = m \) for \( j = 2, \ldots, N \).
(i) Solve the eigenvalue problem (8.30) and show that $\kappa$ in $\Omega^2 = 4 \sin^2(\kappa/2)$ satisfies the transcendental equation

$$\tan \left( \frac{N\kappa}{2} \right) + \mu \tan \left( \frac{\kappa}{2} \right) = 0$$

(8.31)
or $e^{i\kappa} = \pm 1$ or $e^{iN\kappa} = 1$.

(ii) In order to solve (8.31) graphically we transform it into a more convenient form. For this purpose set $z = e^{i\kappa}$. First prove that

$$\frac{1}{z^N - 1} = \prod_{j=1}^{N} (z - z_j) = \frac{1}{N} \sum_{j=1}^{N} \frac{z_j}{z - z_j}$$

(8.32)
and obtain an analogous relation for $z_j^{-1}$. Here the $z_j, j = 1, \ldots, N$, are the $N$th roots of unity. Then show that (8.31) is equivalent to

$$\frac{N}{\mu} + \sum_{j=1}^{N} \frac{\Omega^2}{\Omega^2 - \Omega_j^2} = 0,$$

(8.33)
where the $\Omega_j$ are the eigenfrequencies of the problem with equal masses. Now discuss (8.33) graphically. Which equations for the frequencies do you obtain for the particular cases when $\mu = -1$ or $\mu = \infty$?

(iii) How many solution do you obtain from (8.33)? Where are the missing solutions and what is their interpretation?

8.5 Exercise 8. Mass defect in the thermodynamic limit

In exercise 7 the consequence of a mass defect on the spectrum of the harmonic chain with periodic boundaries was analyzed. All eigenfrequencies except the translation mode are either determined by

$$\sum_{j=1}^{N} \frac{\Omega^2}{\Omega^2 - \Omega_j^2} = \frac{N}{\mu},$$

(8.34)
wherein $N$ is the number of masses and $\Omega_j^2$ are the eigenvalues of the periodic chain without mass defect, or they agree with one of the $\Omega_j^2$. For a negative mass defect $-1 < \mu < 0$ there is one mode, i.e. one solution of (8.34), outside of the domain $[0,4]$ of the $\Omega_j^2$.

(i) Calculate the eigenfrequency of this mode in the thermodynamic limit $N \to \infty$ directly from (8.34).

(ii) Consider the infinite harmonic chain with $m_j = m, j \neq 0$ and $m_0 = m(1 + \mu)$. The deviations from the equilibrium positions of the masses are denoted $x_n$. Use the ansatz

$$x_n(t) = \exp(-q |n| - i\omega t)$$

(8.35)
and determine how $q$ and $\omega$ have to be chosen, to get a solution of the equation of motion of the chain. Why does this solution only make sense for negative mass defects?
8.6 Exercise 9. Harmonic oscillations of a two-dimensional lattice

Consider a two-dimensional square lattice composed of identical ions of mass \( m \) under periodic boundary condition. Every ion interacts with nearest and next-nearest neighbours. The spring constants of the harmonic potential are given by \( \beta_1 \) for nearest neighbours and by \( \beta_2 \) for next-nearest neighbours. All other interactions are assumed to be negligible. Furthermore all motions of the ions are confined to the lattice plane. Set up the force-matrix \( K_{\alpha\beta}(R, S) \) and compute \( \kappa(q) \). Diagonalize \( \kappa(q) \). How does the frequency depend on the wave vector \( q \)? Plot the dispersion relation in \((q,0)\) - and in \((q,q)\)-direction.

L9 Statistical mechanics of the harmonic crystal

9.1 Partition function and free energy

The thermodynamic properties of the harmonic crystal are completely determined by the canonical partition function

\[
Z_{ph} = \text{tr} \left\{ e^{-\frac{H_{ph}}{T}} \right\} = e^{-\frac{F_{ph}}{T}}. \tag{9.1}
\]

Here \( F_{ph} \) is the free energy of the harmonic crystal, and we are using units such that the Boltzmann constant \( k_B = 1 \). Inserting (7.21) into (9.1) we obtain

\[
Z_{ph} = \prod_{(q,\alpha) \in Q} \text{tr} \left\{ \exp \left\{ -\frac{\omega_{\alpha}(q)}{T} \left( a^{+\alpha}_q a^\alpha_q + \frac{1}{2} \right) \right\} \right\} = \prod_{(q,\alpha) \in Q} \frac{1}{2 \sinh \left( \frac{\omega_{\alpha}(q)}{2T} \right)}. \tag{9.2}
\]

It follows that

\[
F_{ph} = E_0 + T \sum_{(q,\alpha) \in Q} \ln \left( 1 - e^{-\frac{\omega_{\alpha}(q)}{T}} \right). \tag{9.3}
\]

Here we have used (9.1) and (7.28).

9.2 The Bose-Einstein distribution

From (9.2) and (9.3) we also conclude that

\[
\frac{\partial F_{ph}}{\partial \omega_{\alpha}(q)} = -\frac{T}{Z_{ph}} \frac{\partial Z_{ph}}{\partial \omega_{\alpha}(q)} = \frac{\text{tr} \left\{ \left( a^{+\alpha}_q a^\alpha_q + \frac{1}{2} \right) e^{-\frac{H_{ph}}{T}} \right\}}{\text{tr} \left\{ e^{-\frac{H_{ph}}{T}} \right\}} = \langle a^{+\alpha}_q a^\alpha_q + \frac{1}{2} \rangle = \frac{1}{2} + \frac{1}{e^{\frac{\omega_{\alpha}(q)}{T}} - 1}. \tag{9.4}
\]

Recalling that

\[
\hat{n}_q^\alpha = a^{+\alpha}_q a^\alpha_q \tag{9.5}
\]

is the occupation number operator that measures the occupancy of the mode \((q,\alpha)\), we may interpret

\[
\langle \hat{n}_q^\alpha \rangle = \frac{1}{e^{\frac{\omega_{\alpha}(q)}{T}} - 1}. \tag{9.6}
\]
as a function of \( T \) as the average occupancy of the mode \((q, \alpha)\) in a canonical ensemble of temperature \( T \). Seen as a function of \( q \) and \( \alpha \) this function measures the distribution at temperature \( T \) of the quanta of vibration energy over the modes. Equation (9.6) defines the famous Bose-Einstein distribution.

In physics we call excitations of a ‘quantum field’, that carry energy and momentum, particles. The particles associated with the quantized lattice vibrations are called phonons. Within the approximation of the harmonic crystal the phonons do not interact. According to (9.6) they form an ideal gas of non-conserved Bosons, very much like the photons which are the quanta of the electro-magnetic field. If the number of phonons would be conserved, a chemical potential that would control their number would appear in (9.6).

### 9.3 The density of states

In the theory of ideal quantum gases the free energy and all derived thermodynamic quantities in the thermodynamic limit are usually written as functionals of the density of states. We would like to briefly recall its definition and its use in approximating sums like in (9.3) by integrals. Usually the latter is done in a two-step procedure. In step one sums over lattice momenta are converted into integrals. In step two integrals over momenta are transformed into integrals over energies by means of the density of states.

Recall that the volume of the Brillouin zone is (cf. equation (3.10)) \( V_R = (2\pi)^3/V_u \), where \( V_u \) is the volume of the unit cell, and that there are \( L^3 \) lattice momenta in the Brillouin zone, if we introduce periodic boundary conditions as described in section 5.2. Then the volume of the crystal is \( V = L^3 V_u \). The volume per lattice momentum in the Brillouin zone or volume element is

\[
d^3q = \frac{V_R}{L^3} = \frac{(2\pi)^3}{V_u L^3} = \frac{(2\pi)^3}{V}.
\]  

(9.7)

Thus, the free energy (9.3) can be approximated as

\[
F_{ph} = E_0 + \frac{VT}{(2\pi)^3} \sum_{\alpha \in I} \int_{BZ} d^3q \ln \left( 1 - e^{-\frac{\omega_\alpha(q)}{T}} \right).
\]  

(9.8)

We would like to rewrite the integral on the right hand side of (9.8) as an integral over energies. For this purpose we define the counting function

\[
f_{\alpha}(\omega) = \frac{1}{V} \sum_{q \in BZ} \Theta(\omega - \omega_\alpha(q)) \xrightarrow{V \to \infty} \frac{1}{(2\pi)^3} \int_{BZ} d^3q \Theta(\omega - \omega_\alpha(q)),
\]  

(9.9)

where \( \alpha \in I \) and \( \Theta \) is the Heaviside step function. The density of states of the \( \alpha \)th phonon branch is equal to the number of states in \([\omega, \omega + \Delta\omega]\) divided by \( V \Delta\omega \) or, for \( \Delta\omega \to 0 \),

\[
g_\alpha(\omega) = f_{\alpha}'(\omega) = \frac{1}{(2\pi)^3} \int_{BZ} d^3q \delta(\omega - \omega_\alpha(q)).
\]  

(9.10)

Introducing the total density of states as

\[
g(\omega) = \sum_{\alpha \in I} g_\alpha(\omega)
\]  

(9.11)

we can rewrite the expression (9.8) for the free energy in the form

\[
F_{ph} = E_0 + VT \int_0^\infty d\omega \ g(\omega) \ln \left( 1 - e^{-\frac{\omega}{T}} \right).
\]  

(9.12)
This form will be the starting point for the discussion of the specific heat of the harmonic crystal below.

Before entering this discussion we will have a closer look at the density of states \( g(\omega) \). The integral on the right hand side of (9.10) can be interpreted as representing the ‘area’ of a surface \( S(\omega) \) in reciprocal space, where \( \omega \) is implicitly defined by

\[
\sigma(q_0) = \omega - \omega_\alpha(q_0) = 0. \tag{9.13}
\]

In the vicinity of this surface we introduce local coordinates

\[
\Delta q = n\Delta q_\perp + t_1\Delta q_1|| + t_2\Delta q_2||, \tag{9.14}
\]

where \( n \) is a unit vector normal to the surface and \( t_j\Delta q_1||, j = 1, 2 \), are parallel unit vectors. Then

\[
\sigma(q_0 + \Delta q) = -\langle \text{grad} \omega_\alpha(q_0), \Delta q \rangle + \cdots = -\| \text{grad} \omega_\alpha(q_0) \| \Delta q_\perp + \cdots \tag{9.15}
\]

and thus

\[
g_\alpha(\omega) = \frac{1}{(2\pi)^3} \int_{S(\omega)} dS \int d\Delta q_\perp \delta(-\| \text{grad} \omega_\alpha(q_0) \| \Delta q_\perp + \cdots) = \frac{1}{(2\pi)^3} \int_{S(\omega)} \frac{dS}{\| \text{grad} \omega_\alpha(q_0) \|}. \tag{9.16}
\]

This formula can be used to actually calculate the density of states, given the dispersion relations of the phonons.

### 9.4 Van-Hove singularities

The density of states \( g(\omega) \) exhibits singularities where \( \text{grad} \omega = 0 \). These are called van-Hove singularities. Their character depends on the space dimension and is different for 3d, 2d and 1d lattices. We can understand them by expanding \( \omega \) in the vicinity of a critical point \( k_0 \), \( \text{grad} \omega(k_0) = 0 \), where

\[
\omega = \omega_0 + \frac{1}{2} \langle (k - k_0), \Gamma(k - k_0) \rangle \tag{9.17}
\]

and \( \Gamma \) is the matrix of the second derivatives of \( \omega \) at \( k_0 \). Setting \( x = k - k_0 \) we have \( \text{grad} \omega = \Gamma(k - k_0) = \Gamma x \). Hence, for values of \( \omega \) close to a critical point,

\[
g_\alpha(\omega) = \frac{1}{(2\pi)^3} \int_{\langle x, \Gamma x \rangle = 2(\omega - \omega_0)} \frac{dS}{\| \Gamma x \|}. \tag{9.18}
\]

The matrix \( \Gamma \) can be diagonalized by an orthogonal transformation. Such a transformation leaves the surface element \( dS \) invariant. Hence, we may assume that \( \Gamma = \text{diag}(\gamma_1, \gamma_2, \gamma_3) \). Thus,

\[
g_\alpha(\omega) = \frac{1}{(2\pi)^3} \int_{\gamma_1x_1^2 + \gamma_2x_2^2 + \gamma_3x_3^2 = 2(\omega - \omega_0)} \frac{dS}{\sqrt{\gamma_1^2x_1^2 + \gamma_2^2x_2^2 + \gamma_3^2x_3^2}}. \tag{9.19}
\]

When discussing this integral, we have distinguish several cases. The critical point may be a minimum, a maximum or a saddle point depending on the signature of \( \Gamma \) which is defined as

\[
\text{sign} \Gamma = \text{diag}(\text{sign} \gamma_1, \text{sign} \gamma_2, \text{sign} \gamma_3). \tag{9.20}
\]
We denote the four different cases by \( m = (+, +, +) \), \( M = (-, -, -) \), \( S_1 = (+, +, -) \) and \( S_2 = (+, -, -) \). Clearly \( m \) corresponds to a minimum, \( M \) to a maximum, and \( S_1, S_2 \) to two kinds of saddle points. In 3d the singularities are of square root type in all four cases. The details will be worked out in exercise 10.

**Theorem 3.** Van Hove [14], In 3d the density of states \( g \) has at least one singularity of type \( S_1 \), and one of type \( S_2 \). The derivative at the upper edge of the spectrum is \(-\infty\).

### 9.5 Exercise 10. Van-Hove singularities

The density of states per unit volume of the \( \alpha \)th phonon branch in a crystal lattice in \( d \) dimensions is given by

\[
g_{\alpha}(\omega) = \frac{1}{(2\pi)^d} \int_{S_{\alpha}(\omega)} \frac{dS}{\| \text{grad} \, \omega_{\alpha}(\mathbf{k}) \|}, \tag{9.21}
\]

where \( S_{\alpha}(\omega) \) is the surface \( \omega_{\alpha} = \text{const.} \) in the reciprocal space. The total density of states per unit volume is the sum over all branches. Determine the four distinct types of singularities of the density of states for space dimension \( d = 3 \). For this purpose expand \( \omega_{\alpha} \) close to a critical point \( \omega_0 \),

\[
\omega_{\alpha} - \omega_0 = \gamma_1 x_1^2 + \gamma_2 x_2^2 + \gamma_3 x_3^2, \tag{9.22}
\]

and discuss the four different cases associated with different choices of the relative sign of the coefficients \( \gamma_1, \gamma_2 \) and \( \gamma_3 \). Hint: the saddle point cases require the introduction of a cut-off.

### 9.6 Exercise 11. Density of states in linear chains

The dimensionless dispersion relations of the monoatomic linear chain and of the linear chain with alternating masses with \( 0 \leq \kappa < 2\pi \) and ratio of masses \( \mu = m/M \) are given by

\[
\Omega^2(\kappa) = 4 \sin^2 \left( \frac{\kappa}{2} \right) \quad \text{and} \quad \Omega^2(\kappa) = 1 + \mu \pm \sqrt{(1 + \mu)^2 - 4 \mu \sin^2 \left( \frac{\kappa}{2} \right)}. \tag{9.23, 9.24}
\]

Calculate and sketch the densities of states. Which types of singularities do appear?

### L10 Specific heat of the harmonic crystal

Given the free energy of the phonons as a functional of the density of states \( F_{\text{ph}} \) we can calculate their internal energy,

\[
E_{\text{ph}} = F_{\text{ph}} + TS_{\text{ph}} = F_{\text{ph}} - T \frac{\partial F_{\text{ph}}}{\partial T} = E_0 - VT^2 \frac{\partial}{\partial T} \int_0^\infty d\omega \ g(\omega) \ln \left( 1 - e^{-\frac{\omega}{T}} \right) = E_0 + V \int_0^\infty d\omega \ \frac{g(\omega)\omega}{e^{\frac{\omega}{T}} - 1}. \tag{10.1}
\]

Here \( S_{\text{ph}} \) in the first equation is the entropy of the harmonic lattice vibrations. The integrand on the right hand side of the last equation has a clear interpretation as the “density of states \( g(\omega) \times \text{energy} \ \omega \times \text{thermal occupation}.”
The quantity that is measured in experiments is the specific heat

\[ C_V = \frac{\partial E_{\text{ph}}}{\partial T} = V \int_0^\infty d\omega \, g(\omega) \left( \frac{\omega / 2T}{\text{sh}(\omega / 2T)} \right)^2. \]  (10.2)

It is a linear functional of the density of states. Due to (9.11) the specific heat of the phonons is the sum of the contributions from all branches of the dispersion relation. From any model for the force matrix we can calculate the dispersion \( \omega_\alpha \), then the density of states \( g_\alpha \), and finally the specific heat by means of the above equation.

### 10.1 Low-temperature specific heat

Many bulk characteristic properties of solids at low and high temperatures are rather universal. A prime example, which we shall consider now, is provided by the contribution of the phonons to the specific heat. In order to understand its low-\( T \) behaviour we use (10.1) to present it as

\[ C_V = -V \frac{\partial}{\partial T} T^2 \frac{\partial}{\partial T} \int_0^\infty d\omega \, g(\omega) \ln(1 - e^{-\omega / 2T}) \].  (10.3)

The density of states has a Taylor series expansion around \( \omega = 0 \). Let \( \omega_0 > 0 \) be its radius of convergence and fix \( \delta \) such that \( 0 < \delta < \omega_0 \).

\[
\int_0^\infty d\omega \, g(\omega) \ln(1 - e^{-\omega / 2T}) = \int_0^\delta d\omega \, g(\omega) \ln(1 - e^{-\omega / 2T}) + O(T^\infty)
\]

\[
= \sum_{n=0}^{\infty} \frac{g^{(n)}(0)}{n!} \int_0^{\delta/T} dx \, x^n \ln(1 - e^{-x}) + O(T^\infty) . \]  (10.4)

Using the Taylor expansion of the logarithm we can estimate the integral on the right hand side as

\[
\int_0^{\delta/T} dx \, x^n \ln(1 - e^{-x}) = \int_0^\infty dx \, x^n \ln(1 - e^{-x}) + O(T^\infty)
\]

\[
= -\sum_{k=1}^{\infty} \frac{1}{k^{n+1}} \int_0^\infty dx \, x^k + O(T^\infty) = -\sum_{k=1}^{\infty} \frac{1}{k^{n+2}} \int_0^\infty dx \, x^{k} e^{-x} + O(T^\infty)
\]

\[
= -\zeta(n + 2) \Gamma(n + 1) + O(T^\infty) , \]  (10.5)

where \( \Gamma \) is the gamma function and \( \zeta \) Riemann’s zeta function. Inserting (10.5) and (10.4) into (10.3) we obtain the low-\( T \) expansion of the specific heat,

\[ C_V = V \sum_{n=0}^{\infty} g^{(n)}(0)(n + 1)(n + 2)\zeta(n + 2)T^{n+1} , \]  (10.6)

which holds up to exponentially small corrections in the temperature.

Equation (10.6) holds separately for every phonon branch. If we replace \( g \) by \( g_\alpha \), we obtain the contribution \( C_{V,\alpha} \) of the phonon branch number \( \alpha \) to the specific heat. For every optical branch the density of states at \( \omega = 0 \) is identically zero and so are all the coefficients in its Taylor expansion around this point. Thus,

\[ C_{V,\alpha} = O(T^\infty) \]  (10.7)
for every optical branch. In other words, the low-\(T\) specific heat of the phonons is entirely determined by the three acoustic branches.

Consider an acoustic phonon branch with (isotropic) sound velocity \(v\). Then

\[ \omega(q) = v||q|| \]  \hspace{1cm} (10.8)

for small \(q\). The corresponding counting function (9.9) for small \(\omega\) is

\[ f(\omega) = \frac{1}{(2\pi)^3} \int_{BZ} d^3q \Theta(\omega - v||q||) = \frac{1}{2\pi^2} \int_0^{\omega/v} dq \ q^2. \]  \hspace{1cm} (10.9)

Hence, for each acoustic branch with sound velocity \(v_\alpha\), the density of states at small \(\omega\) is

\[ g(\omega) = \frac{\omega^2}{2\pi^2v^3}. \]  \hspace{1cm} (10.10)

According to (10.6) the contribution to the specific heat is

\[ C_{V,\alpha} = \frac{2\pi^2VT^3}{15v_\alpha^3} + \mathcal{O}(T^4). \]  \hspace{1cm} (10.11)

Here we have used that \(\zeta(4) = \pi^4/90\). Summing over the three acoustic branches we obtain the total low-\(T\) specific heat of the ions in harmonic approximation,

\[ C_V = \frac{2\pi^2VT^3}{5\langle v^3 \rangle_h} + \mathcal{O}(T^4), \]  \hspace{1cm} (10.12)

where \(\langle \cdot \rangle_h\) stands for the harmonic mean of the sound velocities.

Equation (10.12) is the \(T^3\) law for the specific heat of insulators (in conductors the electrons contribute significantly to \(C_V\)). In simple solids it holds up to temperatures of about 10K. Notice that (10.12) implies that the low-\(T\) specific heat can be determined by measuring the sound velocities, or, taking it the other way round, that the average sound velocity can be obtained from a specific heat measurement.

### 10.2 Internal energy and specify heat at high temperatures

Recall that, for \(|x| < 2\pi\),

\[ \frac{x}{e^x - 1} = 1 - \frac{x}{2} + \sum_{n=1}^{\infty} \frac{B_{2n}}{(2n)!} x^{2n}, \]  \hspace{1cm} (10.13)

where the \(B_{2n}\) are the Bernoulli numbers. This allows us to derive a convergent high-\(T\) expansion of the internal energy of the phonon gas. Inserting (10.13) into (10.1) we obtain

\[ E_{ph} = E_0 + VT \int_0^\infty d\omega g(\omega) \left\{ 1 - \frac{\omega}{2T} + \sum_{n=1}^{\infty} \frac{B_{2n}}{(2n)!} \left( \frac{\omega}{T} \right)^{2n} \right\} \]

\[ = E_0 + 3N_{at} \left\{ T - \frac{\langle \omega \rangle_g}{2} + \sum_{n=1}^{\infty} \frac{B_{2n}}{(2n)!} \left( \frac{\langle \omega^2 \rangle_g}{T} \right)^{2n-1} \right\}. \]  \hspace{1cm} (10.14)
Here $N_{at} = NL^3$ is the total number of ions and $\langle \cdot \rangle_g$ denotes the average with respect to the probability density

$$p_g(\omega) = \frac{g(\omega)}{\int_0^\infty d\omega \, g(\omega)}. \quad (10.15)$$

Thus, $\langle \omega^m \rangle_g$ is the $m$th moment of the probability density. In the derivation of (10.14) we have used that

$$\int_0^\infty d\omega \, g(\omega) = \lim_{\omega \to +\infty} \sum_{\alpha \in I} f_\alpha(\omega) = 3NL^3 \quad (10.16)$$

which follows from (9.9).

Equation (10.14) implies the high-$T$ series representation

$$C_V = -3N_{at} \sum_{n=0}^\infty \frac{(2n-1)B_{2n}}{(2n)!} \langle \omega^{2n} \rangle_g T^{-2n} = 3N_{at} - \frac{N_{at} \langle \omega^2 \rangle_g}{4T^2} + O(T^{-4}) \quad (10.17)$$

for the specific heat. Here we have used that $B_0 = 1$ and $B_2 = 1/6$. The leading order contribution corresponds to the Dulong-Petit law

$$C_V = 3N_{at} \quad (10.18)$$

indicating a constant heat capacity at high temperature, whence the name ‘heat capacity’. Note that this high-temperature limit is approached monotonously from below.

### 10.3 Debye interpolation

We have seen that the specific heat of the phonon gas shows universal behaviour at low and high temperatures. Let us seek for a simple model interpolating between these two universal regimes. For this purpose we take the low-frequency form of the density of states and cut it off at a frequency $\omega_D$ in such a way that the normalization condition (10.16) is satisfied. Let us further introduce an effective sound velocity

$$\overline{v} = \langle v^3 \rangle_\hbar^{\frac{1}{3}}. \quad (10.19)$$

Then our model density of states is

$$g_D(\omega) = \frac{3\omega^2}{2\pi^2 \overline{v}^3} \Theta(\omega_D - \omega), \quad (10.20)$$

where the cut-off frequency $\omega_D$ is fixed by the condition

$$\int_0^\infty d\omega \, g_D(\omega) = \frac{\omega_D^2}{2\pi^2 \overline{v}^3} = \frac{3N_{at}}{V} \quad (10.21)$$

implying that

$$\omega_D = \overline{v} \left( \frac{6\pi^2 N_{at}}{V} \right)^{\frac{1}{3}} = N^{\frac{1}{3}} \overline{v} r_R, \quad (10.22)$$

where

$$r_R = \left( \frac{V_R}{4\pi/3} \right)^{\frac{1}{3}} \quad (10.23)$$
Figure 5: Debye model of the specific heat of the phonon gas in solids.

is a reciprocal length parameter sometimes called the ‘radius of the Brillouin zone’. \( g_D \) is called Debye density of states and the frequency \( \omega_D \) the Debye frequency. These notions go back to the Dutch-American noble laureate Peter Debye [5].

The internal energy for the Debye density of states is

\[
E_{\text{ph}} = E_0 + \frac{9N_{\text{at}}T^4}{\omega_D^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\omega/T} - 1}.
\]  

Defining the Debye function

\[
D(x) = \frac{3}{x^3} \int_0^x dt \frac{t^3}{e^t - 1}
\]

we may recast the internal energy as

\[
E_{\text{ph}} = E_0 + 3N_{\text{at}}T D(\omega_D/T),
\]

while the corresponding specific heat takes the form

\[
C_V = 3N_{\text{at}} \left\{ D\left(\frac{\omega_D}{T}\right) - \frac{\omega_D}{T} D'\left(\frac{\omega_D}{T}\right) \right\}.
\]

This is called the Debye formula or the Debye interpolation formula. According to this formula the specific heat of the phonon gas is a universal function of \( \omega_D/T \) (see Figure[5]). With respect to the phonon gas contribution to the specific heat different solids are distinguished by a single parameter, the Debye frequency. Because it is simple and at the same time covers the basic features of the temperature dependence of the specific heat, the Debye model is prevailing in experimental solid state physics.

10.4 The anomaly of the harmonic crystal

Usually the basic tasks in statistical physics are to derive the specific heat and the equation of state, expressing the pressure \( p = -\partial F/\partial V \) as a function of \( T \) and \( V \). For the harmonic crystal one can find the statement that the pressure is temperature independent,

\[
\left( \frac{\partial p}{\partial T} \right)_V = 0,
\]  

(10.28)
in several places in the textbook literature. This should be related to the scale invariance of
the equations of motion in harmonic potentials, but at the moment I do not know of any
really convincing derivation in the general case.

Equation (10.28) implies several thermodynamic anomalies. Since
\[
\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V, \quad (10.29)
\]
it follows, for instance, that the thermal expansion coefficient
\[
\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = 0. \quad (10.30)
\]
This contradicts our experience that solids usually expand when they are heated. We
conclude that the thermal expansion of solids is a feature that must be attributed the higher
order corrections to the harmonic crystal. Another anomaly implied by (10.28) is, for
instance, \( C_V = C_p \), the coincidence of the specific heats at constant pressure and constant
volume.

The simplest model system for which we can verify (10.28) is a classical chain of
particles of equal masses \( m \) that interact with their nearest neighbours through a pair
potential \( V(r) \), where \( r \) is the distance between the particles. Let us consider \( N + 1 \)
such particles with coordinates \( x_n, n = 0, \ldots, N \), and nearest-neighbour distances \( r_n =
x_n - x_{n-1}, n = 1, \ldots, N \). Then the Hamiltonian of the system is
\[
H = \sum_{n=0}^{N} \frac{p_n^2}{2m} + \sum_{n=1}^{N} V(r_n), \quad (10.31)
\]
where the \( p_n \) are the momenta canonically conjugate to the \( x_n \). Note that this system
has no periodic boundary conditions. Instead of applying periodic boundary conditions
for the interaction we apply an external mechanic pressure to control the length of the
system. This can be achieved by adding a term \( (x_N - x_0)p \) to the Hamiltonian (10.31). As
a configuration space \( K \) for the particles we consider a ring of finite length \( L \) on which the
‘springs’ connecting neighbouring particles can be arbitrarily expanded by moving them
several times relative to each other around the ring, but the center of mass of all particles is
confined to the ring. This construction is necessary in order to regularize the integral
\[
Z = \frac{1}{(N+1)!} \int_{\mathbb{R}^{N+1}} \frac{d^{N+1}p}{(2\pi \hbar)^{N+1}} \int_K d^{N+1}x \exp\left\{ -\frac{1}{T} (H + (x_N - x_0)p) \right\} \quad (10.32)
\]
representing the classical partition function. It would be otherwise divergent. By construction
\[
-T \partial_p \ln Z = \langle x_N - x_0 \rangle = \ell \quad (10.33)
\]
is the average length of the system at given \( T \) and \( p \) which justifies the interpretation of \( p \)
as the pressure.

It is not difficult to calculate the integral on the right hand side of (10.32). The
momentum integration reduces to Gaussian integrals, whereas the remaining integrals over
the configuration space can be dealt with after introducing Jacobi coordinates
\[
s = \frac{1}{N+1} \sum_{n=0}^{N} x_n, \quad r_n = x_n - x_{n-1}, \quad n = 1, \ldots, N. \quad (10.34)
\]
This transformation is linear, and it is easy to see that its Jacobi matrix equals one. Taking this into account we obtain

\[
Z = \frac{L}{(N+1)!} \left( \frac{mT}{2\pi \hbar^2} \right)^{N+1/2} \left( \int_{-\infty}^{\infty} dr \ e^{-(V(r)+pr)/T} \right)^N. \tag{10.35}
\]

It follows that

\[
\ell = -NT\partial_p \ln \left( \int_{-\infty}^{\infty} dr \ e^{-(V(r)+pr)/T} \right). \tag{10.36}
\]

In general the latter expression does depend on \( T \), but if we insert the harmonic potential

\[
V(r) = \frac{m\omega_0^2}{2} (r - a)^2, \tag{10.37}
\]

where \( a \) is the ‘rest length’ of the potential, then

\[
\ell = N \left( a - \frac{p}{m\omega_0^2} \right) \tag{10.38}
\]

which we interpret as the thermodynamic length of the system. If we now solve for the pressure \( p \), we end up with

\[
p = m\omega_0^2 \left( a - \frac{\ell}{N} \right) \tag{10.39}
\]

which, indeed, does not depend on \( T \). Note that, unlike the pressure of gases, the pressure here can have either sign, a negative pressure contracting the chain, if it is expanded over its equilibrium length.

### L11 Neutron scattering

#### 11.1 Thermal neutrons

Neutron scattering experiments in solids are performed with so-called thermal neutrons. These are neutrons with energies between \( 5 - 10 \text{ meV} \) (\( T \simeq 60 - 1000 \text{K}, \ \lambda \simeq 0.4 - 0.1 \text{ nm} \)). Thermal neutrons are one of the most important probes for studying the properties of solids and fluids. This has several reasons.

(i) The neutron is electrically neutral. It penetrates deeply into the solid, can come close to the atomic nuclei and is scattered by nuclear forces.

(ii) Because of their relatively large mass the de Broglie wave length of thermal neutrons is of the order of magnitude of atomic distances in solids and fluids.

(iii) Their energy is of the order of magnitude of the energy of elementary excitations in solids. If a neutron is scattered inelastically its relative change of energy is generally large enough to be resolved experimentally. Hence, neutrons do not only resolve the structure of solids, but can be also used to measure their excitation spectra, e.g. the dispersion relations of phonons.

(iv) Neutrons carry a magnetic moment which is sensitive against intra-atomic magnetic fields. Therefore they can be used to measure short-wavelength magnetic structures (antiferromagnetism!) and magnetic excitations.
The typical geometry of a scattering experiment is sketched in Figure 6. A stationary current of incident particles impinges on a target and is scattered. Detectors in equal distance from the target measure the current scattered in direction $(\vartheta, \varphi)$, where $\vartheta$, $\varphi$ are spherical coordinates. We denote the counting rate at $(\vartheta, \varphi)$ for particles with energies in an infinitesimal interval around $E$ by $\Delta n(\vartheta, \varphi, E)$. In a stationary situation the counting rate is expected to be proportional to the current density $\|j\|$ of the incident current $j$. Hence, the counting rate normalized by the current density of the incident current,

$$\Delta \sigma = \frac{\Delta n}{\|j\|},$$

is expected to be independent of the current and to characterize the target. If we further divide by the solid angle $\Delta \Omega = \sin(\vartheta) \Delta \vartheta \Delta \varphi$ and by the width $\Delta E$ of the energy interval, we obtain a quantity called the differential cross section,

$$\frac{\Delta \sigma}{\Delta \Omega \Delta E} = \frac{\Delta n}{\Delta \Omega \Delta E \|j\|}.$$  

In the limit of infinite energy and angle resolution this function is denoted

$$\frac{d^2 \sigma}{d\Omega dE}(\vartheta, \varphi, E).$$
11.3 Cross section and transition rate

We shall assume that the incident neutron beam is monochromatic and coherent. Quantum mechanically it is then represented by a plane wave

$$\Psi(x) = \frac{e^{i(k \cdot x)}}{\sqrt{V}} \tag{11.5}$$

with wave vector $k$ and ‘normalization volume $V$’ (we shall use units such that $\hbar = 1$). The corresponding current is

$$j(x) = -\frac{i}{2m}(\Psi^*(x)\partial_x \Psi(x) - \Psi(x)\partial_x \Psi^*(x)) = \frac{k}{mV}. \tag{11.6}$$

The interaction of the neutrons with the target determines the transition rate $P(k, k')$ for a transition from an incoming wave with wave vector $k$ to a scattered wave with wave vector $k'$ under the influence of the perturbation caused by the target (recall the time-dependent perturbation theory from the quantum mechanics lecture). Since $\frac{d^3 k'}{(2\pi)^3/V}$ is the number of states in the volume $d^3 k'$ around $k'$ we can express the counting rate as

$$dn = P(k, k') \frac{d^3 k'}{(2\pi)^3/V} = P(k, k') \frac{V k'^2 \, d\Omega}{(2\pi)^3} = \frac{mV}{(2\pi)^3} P(k, k') k' \, dE \, d\Omega \tag{11.7}$$

Using (11.6) and (11.7) in (11.3) we have expressed the differential cross section in terms of the transition rate,

$$\frac{d^2 \sigma}{d\Omega \, dE}(\theta, \varphi, E) = \frac{k'}{k} \frac{(mV)^2}{(2\pi)^3} P(k, k'). \tag{11.8}$$

This formula connects the basic measurable quantity on the left hand side with a quantity depending on the microscopic properties of the target on the right hand side.

Let us recall how the transition rate appears in quantum mechanics. It is usually first encountered in the context of time-dependent perturbation theory and Fermi’s ‘golden rule’ which states in our case that

$$P(k, k') = 2\pi \sum_f \delta(\varepsilon_i - \varepsilon_f) |\langle \Psi_f, U \Psi_i \rangle|^2 \tag{11.9}$$

is the rate for transitions $\Psi_i \rightarrow \Psi_f$, where $\Psi_i = \Psi_k(x)\phi_i$ is a fixed initial state and $\Psi_f = \Psi_k'(x)\phi_f$ runs through all possible final states with fixed $k'$. Here $\phi_i$ and $\phi_f$ denote eigenstates of the ions (recall that the neutrons interact with the ions!). Hence, the energies of initial and final states $\varepsilon_i$ and $\varepsilon_f$ are

$$\varepsilon_i = E_i + \frac{k^2}{2m}, \quad \varepsilon_f = E_f + \frac{k'^2}{2m}, \tag{11.10}$$

where $E_i$ and $E_f$ are the energies of the ionic states. Introducing the notation $\omega = (k^2 - k'^2)/2m$ the energy difference in (11.9) takes the form

$$\varepsilon_i - \varepsilon_f = E_i - E_f + \omega. \tag{11.11}$$

The potential $U$ that describes the interaction of the neutrons with the ions is of the form

$$U(x) = \sum_{R \in B} \sum_{r=1}^N u(x - x_r(R)) \tag{11.12}$$

where the $x_r(R)$ are the position vectors of the ions. In order to simplify the notation we suppress from now on the sum over the ion positions in the unit cell. It will always come with the sum over the Bravais lattice an can be restored at any later stage if necessary.
11.4 Form factor and structure factor

Substituting the explicit form of the potential and of the factorized wave functions we can calculate the matrix elements in (11.9),

\[
\langle \Psi_i, U \Psi_f \rangle = \frac{1}{V} \sum_{R \in B} \int d^3x \ e^{-i\langle q, x \rangle} \int \left[ \prod_{S \in B} d^3x(S) \right] \phi_i^* u(x - x(R)) \phi_f,
\]

where \( q = k - k' \). We see that the integrals factorize into a factor that depends on the interaction potential between the neutrons and the ions and a factors that depends on the crystal structure. Denoting

\[
b(q) = \int d^3x \ e^{-i\langle q, x \rangle} u(x),
\]

\[
\langle \phi_i, e^{-i\langle q, x(R) \rangle} \phi_f \rangle = \int \left[ \prod_{S \in B} d^3x(S) \right] \phi_i^* e^{-i\langle q, x(R) \rangle} \phi_f
\]

we obtain the following factorized form of the transition rate,

\[
P(k, k') = \frac{2\pi}{V^2} |b(q)|^2 \delta(\varepsilon_i - \varepsilon_f) \left| \sum_{R \in B} \langle \phi_i, e^{-i\langle q, x(R) \rangle} \phi_f \rangle \right|^2.
\]

Here \( |b(q)|^2 \) is called the atomic form factor, since it depends only on the interaction of the individual ions with the neutrons. The sum over \( f \) divided by \( N_{\text{at}} \) is called the dynamic structure factor \( S(q, \omega) \). It contains the information about the structure and the dynamics of the ions. Inserting the expression (11.15) for the transition rate into (11.8) we obtain a formula for the differential cross section,

\[
\frac{d^2\sigma}{d\Omega dE}(\vartheta, \varphi, E) = \frac{k'}{k} \frac{m^2}{(2\pi)^2} |b(q)|^2 \delta(\varepsilon_i - \varepsilon_f) \left| \sum_{R \in B} \langle \phi_i, e^{-i\langle q, x(R) \rangle} \phi_f \rangle \right|^2.
\]

Note that this formula is very general.

(i) With slight modifications it holds for fluids as well.

(ii) It solely relies on Fermi’s golden rule (= time dependent perturbation theory + Born approximation).

11.5 Rewriting the structure factor

Using the ‘Fourier inversion formula’

\[
\delta(\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t}
\]

we obtain the following expression for the dynamic structure factor.

\[
S(q, \omega) = \frac{1}{N_{\text{at}}} \int_{-\infty}^{\infty} \frac{dt}{2\pi} \sum_f \sum_{R,S \in B} e^{-i(E_i - E_f + \omega)t} \langle \phi_i, e^{-i\langle q, x(S) \rangle} \phi_f \rangle \langle \phi_f, e^{i\langle q, x(R) \rangle} \phi_i \rangle
\]
Here we have used that
\[
e^{-i(E_f - E_i)t} \langle \phi_f, e^{i(q \cdot x(R))} \phi_i \rangle = \langle \phi_f, e^{i(q \cdot x(R))} e^{-iHt} \phi_i \rangle = \langle \phi_f, e^{i(q \cdot x(R))} \phi_i \rangle = \langle \phi_f, e^{i(q \cdot x(R))} \phi_i \rangle,
\]
where \(H\) is an effective Hamiltonian for the ion-ion interaction. The expectation value under the sum on the right hand side of (11.18) is called a dynamical two-point correlation function. The appearance of such a correlation function is generic. As we shall see with further examples below, most spectroscopic experiments and transport experiments in solids measure two- or four-point correlation functions.

L12 Neutron scattering continued

12.1 Disorder

So far we have assumed that the scattering potentials of all nuclei are equal. This is only true if the solid (the fluid) consists of a single isotope and if all nuclear spins are aligned (nuclear spin ferromagnet) or zero. In reality the latter conditions are almost never satisfied. We typically rather have to deal with mixtures of different isotopes and with nuclear spin paramagnets. This means that we have to modify our above derivation, replacing
\[
u(R)(x - x(R)) \rightarrow v(R)(x - x(R)), \quad b(q) \rightarrow b(R)(q).
\]
(12.1)
In particular \(b(R)(q)\) remains under the sum over the Bravais lattice in the expression for the differential cross section, which now reads
\[
\frac{d^2 \sigma}{d\Omega dE(\theta, \phi, E)} = \frac{k'}{k} \frac{m^2}{(2\pi)^2} \int \frac{dt}{2\pi} e^{-i\omega t} \sum_{R,S \in B} b(R)(q) b^*_S(q) \langle \phi_i, e^{-i(q \cdot x(S))} e^{i(q \cdot x(R,t))} \phi_i \rangle.
\]
(12.2)
In order to simplify this expression again, we assume that the potentials \(u(R)\) are randomly distributed. We shall indicate the disorder average by brackets \(\langle \cdot \rangle_d\). We assume that the distribution underlying the average is such that the mean value of \(b(R)(q)\) is translation invariant and, for this reason, use the notation
\[
\langle b(q) \rangle_d = \langle b(R)(q) \rangle_d.
\]
(12.3)
It further reasonable to assume that potentials at different lattice sites are uncorrelated, implying that
\[
\langle b(R)(q)b^*_S(q) \rangle_d = \langle b(R)(q) \rangle_d \langle b^*_S(q) \rangle_d = |\langle b(q) \rangle_d|^2
\]
(12.4)
for \(R \neq S\). Let us further introduce the averaged coherent and incoherent atomic form factors
\[
\sigma_{coh} = \frac{m^2}{\pi} |\langle b(q) \rangle_d|^2, \quad \sigma_{inc} = \frac{m^2}{\pi} (|\langle b(q) \rangle_d|^2 - |\langle b(q) \rangle_d|^2).
\]
(12.5)
Averaging the differential cross section over the disorder then results in

\[
\frac{d^2 \sigma}{d\Omega dE}(q, \varphi, E) = \frac{k'}{k} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \left\{ \sum_{R, S \in B} \frac{\sigma_{\text{coh}}}{4\pi} \langle \phi_i, e^{-i(q, x(S))} e^{i(q, x(R, t))} \phi_i \rangle \right. \\
+ \left. \sum_{R \in B} \frac{\sigma_{\text{inc}}}{4\pi} \langle \phi_i, e^{-i(q, x(R))} e^{i(q, x(R, t))} \phi_i \rangle \right\}. \tag{12.6}
\]

So far we have assumed that the ions are in a pure initial state \( \phi_i \). This is not realistic in experiments on a macroscopic sample. In a macroscopic sample the ions have to be described by a density matrix. If the crystal can exchange energy with its environment it will be the density matrix of the canonical ensemble in which each state \( \phi_i \) is occupied with probability \( e^{-E_i/T}/Z \), where \( Z \) is the canonical partition function. Performing the canonical ensemble average and denoting the canonical expectation values by \( \langle \cdot \rangle_T \) we obtain the final formula for the theory of neutron scattering.

### 12.2 Summary of the theory of neutron scattering – general case

First of all the dynamic structure factor at finite temperature becomes

\[
S(q, \omega) = \frac{1}{N_{\text{at}}} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \sum_{R, S \in B} \langle e^{-i(q, x(S))} e^{i(q, x(R, t))} \rangle_T. \tag{12.7}
\]

The differential cross section splits into a coherent part and an incoherent part,

\[
\frac{d^2 \sigma}{d\Omega dE} = \frac{d^2 \sigma}{d\Omega dE}_{\text{coh}} + \frac{d^2 \sigma}{d\Omega dE}_{\text{inc}}, \tag{12.8}
\]

where

\[
\frac{d^2 \sigma}{d\Omega dE}_{\text{coh}} = \frac{\sigma_{\text{coh}} k'}{k} N_{\text{at}} S(q, \omega), \tag{12.9a}
\]

\[
\frac{d^2 \sigma}{d\Omega dE}_{\text{inc}} = \frac{\sigma_{\text{inc}} k'}{k} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \sum_{R \in B} \langle e^{-i(q, x(R))} e^{i(q, x(R, t))} \rangle_T. \tag{12.9b}
\]

These formulae are widely used in order to analyze the data of neutron scattering experiments. Before specializing them to crystal structures we would like make a few general comments.

(i) In our derivation of \( (12.7) \) we have used the letters \( R \) and \( S \) in \( x(R), x(S) \) as mere particle labels, which is the reason why equation \( (12.7) \), if properly read, also defines the dynamic structure factor of a fluid or a glass. When we used the notation \( R \in B \) we had in mind to apply the formula to a mono-atomic (simple) lattice, but so far \( B \) was rather an index set which may refer to any labeling of the ions. Similar formulae hold, in particular, for a lattice with basis.

(ii) The factors \( \sigma_{\text{coh}} \) and \( \sigma_{\text{inc}} \) depend, in the experimentally relevant range of neutron wave lengths of the order of inter-atomic distances only weakly on \( q \), since the potentials \( u_R \) vary on a scale of the size of the nuclei. For this reason \( \sigma_{\text{coh}} \) and \( \sigma_{\text{inc}} \) can often be treated as constants.
(iii) The most interesting contribution to the differential cross section is the dynamic structure factor \( S(q, \omega) \). It is completely determined by the properties of the sample and independent of the properties of the neutrons.

(iv) The incoherent cross section sums contributions from the same nuclei at different times. It carries no information about the structure of the sample. If all \( b_R(q) \) are identical, the incoherent part vanishes. Its occurrence is a direct consequence of the disorder in the system.

### 12.3 Theory of neutron scattering – specialization to crystal structures

What happens if we specialize (12.7) to a mono-atomic crystal is, that the Hamiltonian is invariant under the action of the Bravais lattice \( B \), implying that

\[
\langle e^{-i(q \cdot x(S))} e^{i(q \cdot x(R,t))} \rangle_T = \langle e^{-i(q \cdot x(0))} e^{i(q \cdot x(R-S,t))} \rangle_T. \tag{12.10}
\]

Inserting this into (12.7) and also using that, \( x(R) = R + u(R) \), where \( u(R) \) is the deviation from the equilibrium position at \( R \), we obtain

\[
S(q, \omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \sum_{R \in B} e^{i(q \cdot R)} \langle e^{-i(q \cdot u(0))} e^{i(q \cdot u(R,t))} \rangle_T. \tag{12.11}
\]

The dynamic structure factor of the ions in a crystal lattice is the spatio-temporal Fourier transform of the dynamical two-point function \( \langle e^{-i(q \cdot u(0))} e^{i(q \cdot u(R,t))} \rangle_T \).

Similarly, the incoherent part of the differential cross section simplifies to

\[
\frac{d^2\sigma}{d\Omega dE} \bigg|_{\text{inc}} = \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} N a t \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \langle e^{-i(q \cdot u(0))} e^{i(q \cdot u(0,t))} \rangle_T, \tag{12.12}
\]

the Fourier transformation in time of the auto correlation function \( \langle e^{-i(q \cdot u(0))} e^{i(q \cdot u(0,t))} \rangle_T \).

### 12.4 Dynamic structure factor of the harmonic crystal

The harmonic approximation brings more simplifications about. If \( A \) and \( B \) are any two operators that depend linearly on the deviations \( u(R) \) of the ions from their equilibrium position and linearly on the conjugate momentum \( p(R) \), then

\[
\langle e^A e^B \rangle_T = e^{\frac{1}{2}(A^2+2AB+B^2)}_T, \tag{12.13}
\]

where the canonical averages are calculated with the Hamiltonian of the harmonic crystal (see exercise 12.8). Applying this formula to \( A = -i(q \cdot u(0)) \) and \( B = i(q \cdot u(R, t)) \) and denoting

\[
2W(q) = \langle (q \cdot u(0))^2 \rangle_T = \langle (q \cdot u(R, t))^2 \rangle_T, \tag{12.14}
\]

we obtain the following formula for the dynamic structure factor of the harmonic crystal,

\[
S(q, \omega) = \frac{e^{-2W(q)}}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \sum_{R \in B} e^{i(q \cdot R)} e^{i(q \cdot u(0))} e^{i(q \cdot u(R,t))} T. \tag{12.15}
\]

The function \( W(q) \) is called the Debye-Waller factor.
12.5 Expansion into multi-phonon processes

A harmonic crystal has \(3N_{\text{nat}}\) eigenstates which can be excited independently. Denote the corresponding occupation numbers \(n_1, \ldots, n_{3N_{\text{nat}}}\). Transition matrix elements can be classified according to the differences in occupation numbers between the initial state \(\{n_i\}\) and final state \(\{n'_i\}\).

**Elastic processes.** \(n_i = n'_i\), all occupation numbers remain unaltered, no exchange of energy between crystal and neutron.

**Single-phonon processes.** \(\exists \alpha \in \{1, \ldots, 3N_{\text{nat}}\}\) such that \(n_i = n'_i\) \(\forall i \neq \alpha, n'_\alpha = n_\alpha \pm 1\), the occupation number of a single mode is changed due to the scattering process.

**Multi-phonon processes.** The occupation numbers of several modes are changed.

We shall see below that the \(n\)th term in the expansion

\[
\langle(q,u(0))|q,u(R,t)\rangle_T = 1 + \langle \cdots \rangle_T + \frac{1}{2} \langle \cdots \rangle_T^2 + \cdots \tag{12.16}
\]

can be identified with the \(n\)-phonon processes.

12.6 Coherent elastic neutron scattering

The contribution of the first term in (12.16) to the dynamic structure factor is

\[
S_0(q,\omega) = N_{\text{nat}} e^{-2W(q)} \delta(\omega) \sum_{K \in \overline{B}} \delta_{K,q} . \tag{12.17}
\]

Recall that the argument of the delta function is \(\omega = (k^2 - k'^2)/2m\). Hence, the condition \(\omega = 0\) imposed by the delta function in (12.17) is the condition of energy conservation for the scattered neutrons which justifies the interpretation of the zeroth order term as the elastic scattering term. Since \(k, k' > 0\), the zeroth order structure factor (12.17) can only be non-vanishing if \(k = k'\). Consequentially, we obtain the expression

\[
\frac{d^2\sigma}{d\Omega dE} \bigg|_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} N_{\text{nat}}^2 e^{-2W(k-k')} \delta(\omega) \sum_{K \in \overline{B}} \delta_{K,k-k'} \tag{12.18}
\]

for the elastic contribution to the coherent differential cross section of the harmonic crystal. The sum over Kronecker deltas on the right hand side means that elastic scattering takes place, if the wave vectors \(k\) of the incident neutron beam and \(k'\) of the scattered beam differ by a reciprocal lattice vector \(K\),

\[
k - k' = K \in \overline{B}. \tag{12.19}
\]

This is the famous Bragg condition which also holds in X-ray diffraction experiments.

12.7 Interpretation of the Bragg condition

The interpretation of the Bragg condition in reciprocal space is depicted in Figure 7. The Bragg condition is often formulated as a relation between the distance \(d\) of lattice planes in the original Bravais lattice, the angle \(\vartheta\) between incident and scattered neutron and
the wave length \( \lambda = 2\pi/k \) of the incident neutron. Recalling from section 3.3 that the reciprocal lattice vector \( K \) corresponds to a family of lattice planes perpendicular to \( K \) in such a way that \( K = ||K|| = n \cdot 2\pi/d \) for some \( n \in \mathbb{N} \) and taking into account that elastic scattering implies \( k = k' \), we conclude that

\[
K^2 = k^2 + k'^2 - 2kk' \cos(\vartheta) = k^24\sin^2(\vartheta/2) = (n2\pi/d)^2
\]

\[
\Rightarrow n\lambda = 2d\sin(\vartheta/2). \quad (12.20)
\]

Relative to the Bravais lattice we can interpret the Bragg condition in the following way.

(i) The scattering occurs as if it would happen at the lattice planes according to the reflection law of geometric optics.

(ii) Waves which are reflected by parallel planes interfere constructively, meaning the difference in optical distance between two ‘rays’ reflected from consecutive lattice planes must be an integer multiple of the wave length,

\[
2\ell - b = 2\ell - 2a \cos(\vartheta/2) = 2\ell - 2\ell \cos^2(\vartheta/2) = 2\ell \sin^2(\vartheta/2) = 2d\sin(\vartheta/2) = n\lambda. \quad (12.21)
\]

12.8 Exercise 12. A proof of equation (12.13)

In the derivation of the formula (12.15) for the dynamic structure factor of the harmonic crystal we have used equation (12.13). Here we would like to provide a step-by-step derivation (cf. [11]).

Consider a system of harmonic oscillators with Hamiltonian

\[
H = \sum_i \omega_i (a_i^+ a_i + \frac{1}{2}), \quad (12.22)
\]
where the $a_i$ and $a_j^+$ are annihilation and creation operators with commutation relations
$[a_i, a_j] = 0 = [a_i^+, a_j^+]$, $[a_i, a_j^+] = \delta_{ij}$. Let

$$A = \sum_i (\alpha_i a_i + \beta_i a_i^+), \quad B = \sum_i (\gamma_i a_i + \delta_i a_i^+), \quad (12.23)$$

where $\alpha_i, \beta_j, \gamma_k, \delta_l \in \mathbb{C}$. Denote the canonical ensemble average with Hamiltonian (12.22) by $\langle \cdot \rangle$. Our goal is to prove that

$$\langle e^A e^B \rangle = e^{\frac{1}{2}(A^2 + 2AB + B^2)} \quad . (12.24)$$

The proof will be based on the formula

$$e^A e^B = e^{\frac{1}{2}[A,B]} e^{A+B} \quad (12.25)$$

which should be familiar from the introductory lecture on quantum mechanics and follows from the Baker-Campbell-Hausdorff formula (exercise: recall the derivation of both formulae). It holds whenever $\text{ad}_A[A, B] = \text{ad}_B[A, B] = 0$ (where the adjoint action of an operator $X$ on any operator $Y$ is defined by $\text{ad}_X Y = [X, Y]$).

(i) Define

$$C = \sum_i c_i a_i, \quad D = \sum_i d_i a_i^+ \quad . (12.26)$$

Use (12.25) to show that

$$\langle e^C e^D \rangle = e^{[C,D]} \langle e^D e^C \rangle = e^{[C,D]} \langle e^{\text{ad}_{\text{H}/T} C} e^D \rangle \quad . (12.27)$$

(ii) Let

$$C_n = e^{n \text{ad}_{\text{H}/T} C}, \quad n \in \mathbb{N}_0 \quad . (12.28)$$

Show that

$$\langle e^C e^D \rangle = e^{\sum_{k=0}^n C_k D} \langle e^{C_{n+1}} e^D \rangle \quad . (12.29)$$

(iii) Show that (formally) $\lim_{n \to \infty} C_n = 0$ and that the series $\sum_{k=0}^\infty C_n$ has a formal limit. Denoting this limit by $S$ and using that $\langle e^D \rangle = 1$, equation (12.29) then implies that

$$\langle e^C e^D \rangle = e^{[S,D]} \quad . (12.30)$$

(iv) Show in a similar way as above that

$$\langle CD \rangle = [S, D] \quad . (12.31)$$

Thus,

$$\langle e^C e^D \rangle = e^{(CD)} \quad . (12.32)$$

(v) Use (12.25) and (12.32) to prove (12.24).
L13 Inelastic neutron scattering

13.1 Debye-Waller factor

If we solve equations (7.25) for \(u^\alpha(R)\) we obtain

\[
u^\alpha(R) = \frac{1}{\sqrt{L^3}} \sum_{(\alpha,\beta) \in Q} e^{i(q,R)} Y^\beta_\beta(q) \frac{a^\alpha_\beta + a^{+\beta}_- - q}{\sqrt{2\mu_\alpha\omega_\beta(q)}}, \tag{13.1}
\]

the deviations of the ions from their equilibrium positions in a center of mass frame of reference (the zero modes are excluded in the summation, see section 7.2).

Let us assume for simplicity that we are dealing with a mono-atomic lattice. Then the \(L^3 = N_{at}\). The scalar products defining the Debye-Waller factor (12.14) become

\[
\langle q, u(0) \rangle = \frac{1}{N_{at}} \sum_{k \in BZ} \sum_{k \neq 0} \frac{\langle q, y_\alpha(k) \rangle \langle q, y_\beta(k') \rangle}{\sqrt{2\omega_\alpha(k)} \sqrt{2\omega_\beta(k')}} \langle (a^\alpha_\alpha k + a^{+\alpha}_- k) (a^\beta_\beta k + a^{+\beta}_- k') \rangle_T
\]

where the \(y_\alpha(k)\) are the polarization vectors defined below (7.31). It follows that

\[
2W(q) = \langle \langle q, u(0) \rangle^2 \rangle_T
\]

\[
= \frac{1}{N_{at}} \sum_{k, k' \in BZ} \sum_{k, k' \neq 0} \frac{\langle q, y_\alpha(k) \rangle \langle q, y_\beta(k') \rangle}{\sqrt{2\omega_\alpha(k)} \sqrt{2\omega_\beta(k')}} \langle (a^\alpha_\alpha k + a^{+\alpha}_- k) (a^\beta_\beta k + a^{+\beta}_- k') \rangle_T
\]

\[
= \frac{1}{N_{at}} \sum_{k \in BZ} \sum_{k \neq 0} \frac{\langle q, y_\alpha(k) \rangle \langle q, y_\alpha(-k) \rangle}{2\omega_\alpha(k)} \text{cth} \left( \frac{\omega_\alpha(k)}{2T} \right)
\]

\[
= \frac{1}{N_{at}} \sum_{k \in BZ} \sum_{k \neq 0} \frac{|\langle q, y_\alpha(k) \rangle|^2}{2\omega_\alpha(k)} \text{cth} \left( \frac{\omega_\alpha(k)}{2T} \right). \tag{13.3}
\]

Here we have used (cf. 9.6)

\[
\langle (a^\alpha_\alpha k + a^{+\alpha}_- k) (a^\alpha_\beta k + a^{+\beta}_- k') \rangle_T = \delta^{\alpha\beta} \delta_{k,-k'} \langle a^\alpha_\alpha k a^{+\alpha}_- k + a^{+\alpha}_- k a^\alpha_\beta k' \rangle_T
\]

\[
= \delta^{\alpha\beta} \delta_{k,-k'} (2\hat{n}_\alpha k + 1) \text{th} \left( \frac{\omega_\alpha(k)}{2T} \right) \tag{13.4}
\]

in the second equation and (6.35) in the third equation. Taking the thermodynamic limit in (13.3) we end up with

\[
2W(q) = \frac{V_u}{(2\pi)^3} \sum_{\alpha=x,y,z} \int_{BZ} d^3 k \frac{|\langle q, y_\alpha(k) \rangle|^2}{2\omega_\alpha(k)} \text{cth} \left( \frac{\omega_\alpha(k)}{2T} \right). \tag{13.5}
\]

Here two remarks are in order.

(i) In general (13.5) cannot be rewritten by means of the density of states, since the polarization vectors \(y_\alpha(k)\) depend on \(k\) not necessarily through \(\omega_\alpha(k)\).
(ii) The Debye-Waller factor describes the weakening of the coherent scattering due to thermal fluctuation and as a function of the change of momentum $q$, i.e. as a function of the scattering angle. It appears as a prefactor $e^{-2W(q)}$ in the dynamic structure factor. Since $W(q)$ is quadratic in $q$, the weakening is larger for larger $q$.

In elastic scattering, where $q$ must equal a reciprocal lattice vector $K$, the scattering is strong in the direction corresponding to minimal $K$ or maximal distance between the associated family of lattice planes. Recall (cf. exercise 4.7) that this family has maximal density of lattice points within a plane.

As a function of the temperature the scattered intensity weakens with growing $T$, since

$$\cosh\left(\frac{\omega_\alpha(k)}{2T}\right) \sim \frac{2T}{\omega_\alpha(k)}$$

as $T \to \infty$, leading to a linear temperature dependence of $W(q)$ and to a suppression of the scattered intensity exponentially in $T$.

### 13.2 Exercise 13. Debye-Waller factor of a cubic lattice

For a cubic lattice consisting of $N$ atoms the Debye-Waller factor can be written as

$$2W(q) = \frac{Vq^2}{N} \int_0^\infty \frac{d\omega}{\omega^2} E(\omega) g(\omega),$$

wherein $g(\omega)$ is the density of states (per branch), $q$ is the difference of momenta and $E(\omega)$ is the average of the energy of the phonons with frequency $\omega$,

$$E(\omega) = \omega \left[ n(\omega, T) + \frac{1}{2} \right], \quad n(\omega, T) = \left[ \exp(\omega/T) - 1 \right]^{-1}.$$

(i) Calculate the Debye-Waller factor for a cubic Bravais lattice by using the Einstein model for the phonons. This is a model for an optical phonon branch, where all ions oscillate with the same frequency $\omega_0$; thus all $N$ states are located at $\omega_0$, and the density of states is given by $g(\omega) = (N/V)\delta(\omega - \omega_0)$. Determine $2W(q)$ for $T \ll \omega_0$ or $T \gg \omega_0$, respectively.

(ii) What is the Debye-Waller factor for the Debye model? What follows for $2W(q)$ in the limits $T \ll \omega_D$ and $T \gg \omega_D$?

### 13.3 Coherent inelastic scattering – the single-phonon contribution

Let us now consider the contribution of the second term in (12.16) to the dynamic structure factor,

$$S_1(q, \omega) = \frac{e^{-2W(q)}}{2\pi} \int_{-\infty}^\infty dt \ e^{-i\omega t} \sum_{R \in B} e^{i\langle q, R \rangle} \langle \langle q, u(0) \rangle \langle q, u(R, t) \rangle \rangle_T.$$  

As we shall see, this term corresponds to the single-phonon contributions. This can be understood from a closer inspection of the two-point function on the right hand side. We infer from (13.1) that

$$\langle q, u(R) \rangle = \frac{1}{\sqrt{N_{zt} \sum_{k \in BZ} \sum_{\alpha = x,y,z} e^{i(k, R)} \frac{q \cdot y_\alpha(k)}{\sqrt{2\omega_\alpha(k)}} (a_k^\alpha + a_k^\alpha)}.$$  

(13.10)
This evolves in time into

{\begin{align*}
\langle \mathbf{q}, \mathbf{u}(\mathbf{R}, t) \rangle &= e^{iHT} \langle \mathbf{q}, \mathbf{u}(\mathbf{R}) \rangle e^{-iHT} \\
&= \frac{1}{\sqrt{N_{at}}} \sum_{\mathbf{k} \in BZ} \sum_{\alpha=x,y,z} \sum_{\mathbf{k} \neq 0} e^{i\langle \mathbf{k}, \mathbf{R} \rangle} \frac{\langle \mathbf{q}, \mathbf{y}_\alpha(\mathbf{k}) \rangle}{\sqrt{2\omega_\alpha(\mathbf{k})}} (a_\mathbf{k}^\dagger e^{-i\omega_\alpha(\mathbf{k})t} + a_\mathbf{k} e^{i\omega_\alpha(\mathbf{k})t}) .
\end{align*}}

(13.11)

Hence, performing a similar calculation as in (13.3),

{\begin{align*}
\langle \langle \mathbf{q}, \mathbf{u}(0) \rangle \langle \mathbf{q}, \mathbf{u}(\mathbf{R}, t) \rangle \rangle_T &= \\
&= \frac{1}{N_{at}} \sum_{\mathbf{k}, \mathbf{k}' \in BZ} \sum_{\alpha, \beta = x, y, z} \sum_{\mathbf{k} \neq 0} e^{i\langle \mathbf{k}, \mathbf{R} \rangle} \frac{\langle \mathbf{q}, \mathbf{y}_\alpha(\mathbf{k}) \rangle \langle \mathbf{q}, \mathbf{y}_\beta(\mathbf{k}') \rangle}{\sqrt{2\omega_\alpha(\mathbf{k})} \sqrt{2\omega_\beta(\mathbf{k}')}} \\
&\quad \times \delta^{\alpha\beta} \delta_{\mathbf{k}, -\mathbf{k}'} \langle \langle \mathbf{n}_\mathbf{k} \rangle \rangle_T e^{-i\omega_\alpha(\mathbf{k})t} + \langle \mathbf{n}_\mathbf{k} \rangle_T e^{i\omega_\alpha(\mathbf{k})t} \\
&= \frac{1}{N_{at}} \sum_{\mathbf{k} \in BZ} \sum_{\alpha = x, y, z} \sum_{\mathbf{k} \neq 0} e^{i\langle \mathbf{k}, \mathbf{R} \rangle} \frac{|\langle \mathbf{q}, \mathbf{y}_\alpha(\mathbf{k}) \rangle|^2}{2\omega_\alpha(\mathbf{k})} \left\{ \frac{e^{-i\omega_\alpha(\mathbf{k})t}}{e^{\omega_\alpha(\mathbf{k})/T} - 1} + \frac{e^{i\omega_\alpha(\mathbf{k})t}}{1 - e^{-\omega_\alpha(\mathbf{k})/T}} \right\} \\
&= \frac{1}{N_{at}} \sum_{\mathbf{k} \in BZ} \sum_{\alpha = x, y, z} \sum_{\mathbf{k} \neq 0} \frac{|\langle \mathbf{q}, \mathbf{y}_\alpha(\mathbf{k}) \rangle|^2}{2\omega_\alpha(\mathbf{k})} \left\{ \frac{e^{i(\langle \mathbf{k}, \mathbf{R} \rangle - \omega_\alpha(\mathbf{k})t)}}{e^{\omega_\alpha(\mathbf{k})/T} - 1} + \frac{e^{-i(\langle \mathbf{k}, \mathbf{R} \rangle - \omega_\alpha(\mathbf{k})t)}}{1 - e^{-\omega_\alpha(\mathbf{k})/T}} \right\} .
\end{align*}}

(13.12)

(13.13)

Here we have substituted $-\mathbf{k}$ for $\mathbf{k}$ in the second sum in the last equation and have used that $\omega_\alpha(\mathbf{k})$ and $\langle \langle \mathbf{q}, \mathbf{y}_\alpha(\mathbf{k}) \rangle \rangle^{2}$ are even functions of $\mathbf{k}$.

Inserting the latter equation into (13.9) we obtain the single-phonon contribution to the dynamic structure factor in the form

{\begin{align*}
S_1(\mathbf{q}, \omega) = S_{1,+}(\mathbf{q}, \omega) + S_{1,-}(\mathbf{q}, \omega) ,
\end{align*}}

(13.14)

where

{\begin{align*}
S_{1,+}(\mathbf{q}, \omega) &= \frac{e^{-2W(\mathbf{q})}}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \sum_{\mathbf{R} \in B} e^{i\langle \mathbf{q}, \mathbf{R} \rangle} \\
&\quad \times \frac{1}{N_{at}} \sum_{\mathbf{q}' \in BZ} \sum_{\alpha = x, y, z} \sum_{\mathbf{q}' \neq 0} \frac{|\langle \mathbf{q}, \mathbf{y}_\alpha(\mathbf{q}') \rangle|^2}{2\omega_\alpha(\mathbf{q}')} \frac{\delta(\omega - \omega_\alpha(\mathbf{q}'))}{1 - e^{-\omega_\alpha(\mathbf{q}')/T}} \\
&= e^{-2W(\mathbf{q})} \sum_{\mathbf{q}' \in BZ} \sum_{\alpha = x, y, z} \sum_{\mathbf{q}' \neq 0} \frac{|\langle \mathbf{q}, \mathbf{y}_\alpha(\mathbf{q}') \rangle|^2}{2\omega_\alpha(\mathbf{q}')} \frac{\delta(\omega - \omega_\alpha(\mathbf{q}'))}{e^{\omega_\alpha(\mathbf{q}')/T} - 1} \sum_{\mathbf{K} \in B} \delta_{\mathbf{K}, \mathbf{q}+\mathbf{q}'} .
\end{align*}}

(13.15)

and

{\begin{align*}
S_{1,-}(\mathbf{q}, \omega) &= e^{-2W(\mathbf{q})} \sum_{\mathbf{q}' \in BZ} \sum_{\alpha = x, y, z} \sum_{\mathbf{q}' \neq 0} \frac{|\langle \mathbf{q}, \mathbf{y}_\alpha(\mathbf{q}') \rangle|^2}{2\omega_\alpha(\mathbf{q}')} \frac{\delta(\omega + \omega_\alpha(\mathbf{q}'))}{e^{\omega_\alpha(\mathbf{q}')/T} - 1} \sum_{\mathbf{K} \in B} \delta_{\mathbf{K}, \mathbf{q}+\mathbf{q}'} .
\end{align*}}

(13.16)
These are those contributions to the dynamic structure factor, where precisely one phonon is excited (emitted) or absorbed. We shall denote the corresponding contributions to the differential cross section

\[
\frac{d^2\sigma}{d\Omega dE}\bigg|_{\text{coh},1\pm} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} S_{1,\pm}(q, \omega).
\]

(13.17)

Like the elastic cross section these cross sections are ‘discontinuous’ and describe a pattern of bright spots at certain energy and momentum transfers. The delta functions and Kronecker deltas in (13.15) and (13.16) force the dispersion relations of the scattered neutron and the phonons to match in the following sense.

**Emission of a phonon.** In $S_{1,+}$ the momenta of the neutron and the phonon involved in the scattering process must satisfy

\[
q = k - k' = q' + K,
\]

(13.18)

where $k - k'$ is the momentum transfer to the lattice and $q'$ is the momentum taken by the phonon, i.e. the phonon takes the momentum transferred to the lattice and reduced to the Brillouin zone. For the energies we have the matching condition

\[
\omega = \frac{k'^2 - k^2}{2m} = \omega_\alpha(q') = \omega_\alpha(q - K) = \omega_\alpha(k - k'),
\]

(13.19)

where we have used the periodicity of $\omega_\alpha$ with respect to the reciprocal lattice in the last equation. Since $\omega_\alpha \geq 0$ we see that $k \geq k'$ in this process. The lattice absorbs energy, ‘a phonon is emitted.’

The temperature dependence of the emission is encoded in the factor $1/(1 - e^{-\omega_\alpha(q')/T})$ in $S_{1,+}$. This factor decreases as $T$ decreases but stays finite for $T \to 0+$.

**Absorption of a phonon.** For $S_{1,-}$ the momentum balance is

\[
q = k - k' = -q' + K
\]

(13.20)

which we interpret such that the neutron takes momentum $q' - K$. The relation for the exchange of energy between the scattered neutron and the phonon involved in the process is

\[
-\omega = \frac{k'^2 - k^2}{2m} = \omega_\alpha(q') = \omega_\alpha(K - q) = \omega_\alpha(k' - k).
\]

(13.21)

Here $k' \geq k$, and energy is absorbed by the neutron, which is interpreted as a phonon being absorbed in the process.

In this case the temperature dependence comes in through a factor $1/(e^{\omega_\alpha(q')/T} - 1)$ which vanishes as $T \to 0+$. At zero temperature no phonon remains in the system and there is nothing left to be absorbed.
13.4 Measuring dispersion relations of phonons

Dispersion relations of phonons can be inferred from the differential cross section. Assume that a beam of mono-energetic neutrons impinges on a crystal and the velocity distribution of the neutrons scattered in a fixed direction \( \mathbf{n} \) is measured. Strong scattering in direction \( \mathbf{n} \) takes place whenever \( k' = k'n \) satisfies one of the resonance conditions (13.19) or (13.21) for emission or absorption. The situation is then as sketched in Figure 8. In the example we have assumed a simple lattice with a longitudinal acoustic phonon with dispersion \( \omega_\ell \) (gray line) and two degenerate transversal acoustic phonons with dispersion \( \omega_t \) (dashed gray line). The blue line represents the energy loss of the scattered neutron if it has momentum \( k' \). The scattering is likely only if there is a phonon of momentum \( k - k'\mathbf{n} \) modulo reciprocal lattice vectors, which can be emitted at this energy. Similarly, the dashed blue line shows the energy gain of the neutron if a phonon is absorbed in the scattering process. One of the resonance conditions is satisfied if one of the dispersion curves intersects with the blue or dashed blue line. The red line represents schematically the corresponding cross-section. If the energy of the incident neutrons is varied the blue and dashed blue lines sweep over the dispersion curves of the phonons and the full dispersion relation in \( \mathbf{n} \) direction is mapped out.

L14 Electronic excitations in solids

14.1 Hamiltonian of the electrons in adiabatic approximation

We saw in section L2 that the adiabatic principle implies a decoupling of the lattice and electronic degrees of freedom. To leading order, the dynamics of the electrons is governed by the Hamiltonian

\[
H_{el}(\mathbf{R}) = -\frac{1}{2} \sum_{j=1}^{N} \nabla^2_{\mathbf{r}_j} + \sum_{j=1}^{N} \sum_{k=1}^{L} \frac{-Z_k}{\|\mathbf{r}_j - \mathbf{R}_k\|} + \sum_{1 \leq j < k \leq N} \frac{1}{\|\mathbf{r}_j - \mathbf{r}_k\|} + M, \tag{14.1}
\]

Figure 8: Schematic picture explaining how phonon dispersion relations can be inferred from the differential cross section.
where the ions are fixed to their equilibrium positions $\mathbf{R}_k$ and

$$M = \sum_{1 \leq j < k \leq L} \frac{Z_j Z_k}{\|\mathbf{R}_j - \mathbf{R}_k\|}$$
(14.2)

is the electro-static energy of the ions, the so-called Madelung energy. The latter plays no role for the dynamics of the electrons. Thus, to leading order in the adiabatic approximation, the electrons in a crystal are described by a repulsive Coulomb gas with interaction $V_{\text{elel}}$ that is filled into the periodic potential $V_1$ generated by the ions sitting on their equilibrium positions.

Because of the mutual Coulomb interaction of the electrons, this is still an interacting many-body quantum system, and imperturbable optimism is required to believe that it can ever be solved exactly or numerically with sufficient accuracy. At least at the current stage of our knowledge drastic further approximations are necessary in order to be able to make any quantitative prediction.

### 14.2 Reduction to a single-particle problem

(i) Only the valence electrons (electrons outside closed shells) contribute significantly to the typical properties of solids, because they are responsible for the chemical bonding and are distributed over the solid. For this reason we shall interpret $V_1$ as the potential of ions with completely filled shells (Coulomb with reduced charge number $Z_j$; example sodium, alkali metal, one valence electron, $Z = 1$).

(ii) If the electron-electron interaction $V_{\text{elel}}$ could be neglected, the ‘electronic problem’ would be reduced to the problem of a single particle in the periodic potential $V_1$.

(iii) Instead of simply neglecting the electron-electron interaction, we shall try to split it into an ‘effective single-particle contribution’ which modifies the periodic potential $V_1$ and a residual ‘many-body contribution’ which for the understanding of certain quantities can be neglected in many cases, at least in the first instance. Some ideas about the systematic derivation of an effective single-particle description will be explained below.

(iv) An intuitive explanation of how the reduction to a single-particle problem is possible is through the notions of ‘screening’ and ‘mean fields’. The full many-body Hamiltonian $H_{\text{el}}$ is invariant under the action of the Bravais lattice associated with the equilibrium positions of the ions, $[H_{\text{el}}, U_R] = 0 \forall \mathbf{R} \in B$. Hence, following the same reasoning as for the derivation of Bloch’s theorem in section 5.1, we see that the lattice momentum $\mathbf{k} \in BZ$ is a good quantum number for the many-body eigenfunctions and that those transform like

$$\Psi_k(\mathbf{r}_1 + \mathbf{R}, \ldots, \mathbf{r}_N + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \Psi_k(\mathbf{r}_1, \ldots, \mathbf{r}_N),$$
(14.3)

$\mathbf{R} \in B$, under the action of the Bravais lattice. It follows that

$$|\Psi_k(\mathbf{r}_1 + \mathbf{R}, \ldots, \mathbf{r}_N + \mathbf{R})|^2 = |\Psi_k(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2$$
(14.4)

for all $\mathbf{R} \in B$. The electronic charge density associated with this state,
\[ D(x) = -e \int d^3N r |\Psi_k(r_1, \ldots, r_N)|^2 \sum_{j=1}^{N} \delta(x - r_j) \]
\[ = -eN \int d^3(N-1) r |\Psi_k(x, r_2, \ldots, r_N)|^2, \] (14.5)

clearly inherits the invariance under translations by Bravais lattice vectors, since

\[ D(x + R) = -e \int d^3N r |\Psi_k(r_1 + R, \ldots, r_N + R)|^2 \sum_{j=1}^{N} \delta(x - r_j + R) \]
\[ = -e \int d^3N r |\Psi_k(r_1 + R, \ldots, r_N + R)|^2 \sum_{j=1}^{N} \delta(x - r_j) = D(x), \] (14.6)

where we have used (14.4) in the third equation. We imagine this as the charge density ‘screening’ the ionic potential \( V_I \) and combining together with it to an effective periodic potential which would be felt by an additional electron inserted as a probe into the solid. This ‘screened periodic potential’ provides an intuitive single-particle description for the electron gas in a crystal: a particle moving in the mean field of all other particles.

(v) Another way of thinking about the existence of an effective single-particle description of the solid is the following. Consider the excitations of the full many-particle system (14.1). If there are excitations with charge quantum numbers \( \pm e \) which do have a dispersion, i.e. excitations for which a definite change of (lattice) momentum of the many-body system always comes with one and the same definite change of energy, then we call them quasi-particle excitations or simply particles. It is always possible to define a single-particle Hamiltonian (in momentum representation) that has exactly the same dispersion relation (the same spectrum) as the full many-particle Hamiltonian (14.1). This Hamiltonian may be seen as an effective single-particle Hamiltonian of the full system. How well it describes the full system depends on the details. Unlike e.g. in the harmonic crystal which realizes an ideal gas of phonons, the two- and multi-particle excitations of the full electronic system are not just superpositions of single-particle excitations. Still, the effective interactions between the quasi-particles may be weak, in which case the effective single-particle description will give a good description of at least the thermodynamic properties of the system.

It is beyond the current capabilities of theoretical physics to prove the existence of quasi particles for the Hamiltonian (14.1). But many experiments show that solids generically admit quasi-particle electronic excitations with charge quantum numbers \( \pm e \). These are called ‘electrons’ and ‘holes’ (the holes are the solid-state analogues of the positrons). Experiments show in addition that the interaction between several electrons or holes or between the electrons and the holes can often be neglected in the first instance.
14.3 Particles in a periodic potential

The above discussion should provide enough motivation to study the general problem of a particle moving in a periodic potential. The corresponding Hamiltonian is

\[ H = -\frac{1}{2} \partial_x^2 + V(x) \]  

with \( x \in \mathbb{R}^3 \) and \( V(x) = V(x + R) \) for all \( R \in B \). The study of this Hamiltonian will lead us to the extraordinarily successful band model of solids.

Let us start with some general remarks.

(i) The one dimensional Kronig-Penney model with potential

\[ V(x) = V_0 \sum_{\ell \in \mathbb{Z}} a \delta(x - \ell a), \]  

where \( a \) is the lattice constant and \( V_0 \) the strength of the interaction, is the only simple but non-trivial model of particles in a periodic potential which admits a closed analytic solution. The next simple case \( V(x) = -V_0 \cos(2\pi x/a) \) involves Mathieu functions. Its understanding requires already some mathematical effort.

(ii) There is no other choice than trying to understand the general properties of particles in a periodic potential by the common means of mathematics or theoretical physics. As far as the mathematical part is concerned it would be instructive to study Floquet theory as part of the theory of ordinary differential equations. For time limitations we refrain from touching this interesting subject and rather go ahead with typical methods of theoretical physics which are based on perturbation theory.

14.4 Exercise 14. Kronig-Penney model

The Kronig-Penney model is a simple one-dimensional model for the understanding of the band structure in solids. Consider an electron of mass \( m \) moving in a periodic potential

\[ V(x) = V_0 \sum_{n=-\infty}^{\infty} a \delta(x - na). \]  

Here \( V_0 \) is the strength of the potential and \( a \) the lattice constant. Note that either sign of \( V_0 \) makes sense. For \( V_0 > 0 \) the potential is repulsive, for \( V_0 < 0 \) it is attractive.

(i) Introduce dimensionless units such that the time-independent Schrödinger equation takes the form

\[ H \varphi(y) = \left[ -\frac{\partial^2}{\partial y^2} + 2c \sum_{n=-\infty}^{\infty} \delta(y - n) \right] \varphi(y) = q^2 \varphi(y). \]  

Which connections exist between \( x \) and \( y \), \( c \) and \( V_0 \), and between \( q^2 \) and the energy \( E \)?

(ii) Because of the periodicity of the potential, the Hamiltonian \([14.10]\) commutes with the shift operator defined by \( T \varphi(y) = \varphi(y + 1) \). Thus, \( H \) and \( T \) have a common system of eigenfunctions, i.e., the eigenvalue equations

\[ H \varphi(y) = q^2 \varphi(y), \]  

\[ (14.11a) \]
\[ T \varphi(y) = e^{ik} \varphi(y) \quad (14.11b) \]

can be solved simultaneously. Determine the solutions of (14.11) as a function of \( k \) and \( q \). Which equation connects \( k \) with \( q \)? For the calculation it is sufficient to consider the Schrödinger equation with the general solution \( \varphi(y) = Ae^{iqy} + Be^{-iqy} \) in the interval \([0,1]\). Note that \( q \) can take real as well as imaginary values.

(iii) Discuss the dispersion relation \( \cos(k) = \cos(q) + (c/q) \sin(q) \) following from (ii) graphically. Observe that \( k \) has to be real in order for \( \varphi(y) \) to be bounded and normalizable. Therefore the eigenstates of \( H \) and \( T \) are restricted on certain energy bands.

### 14.5 Almost free electrons

The qualitative features of the motion of particles can be understood from time-independent perturbation theory. Since \( V(x) \) is periodic, it has the Fourier series representation (cf. section 3.5)

\[ V(x) = \sum_{g \in B} V_g e^{i⟨g,x⟩}, \quad V_g = \frac{1}{V_u} \int_U d^3x \ e^{-i⟨g,x⟩} V(x). \quad (14.12) \]

Here we took the liberty to set \( V_0 = 0 \) which just fixes the zero point of the energy. In order to be able to apply perturbation theory we assume that \( V(x) \) is a weak periodic potential in the sense that \( V_g = \lambda v_g \), where \( |v_g| \) is uniformly bounded in \( \lambda \) and \( |\lambda| \ll 1 \).

Since \([H, U_R] = 0\) for all \( R \in B \) the assumptions of the Bloch theorem (cf. section 5.1) are fulfilled. Hence, the eigenfunctions \( \Psi_k \) of \( H \) have definite lattice momentum \( k \in BZ \) and are of the form

\[ \Psi_k(x) = e^{i⟨k,x⟩} u_k(x), \quad (14.13) \]

where \( u_k(x) = u_k(x + R) \) for all \( R \in B \) and thus has a Fourier series representation

\[ u_k(x) = \sum_{g \in B} u_{k,g} e^{-i⟨g,x⟩}, \quad u_{k,g} = \frac{1}{V_u} \int_U d^3x \ e^{i⟨g,x⟩} u_k(x). \quad (14.14) \]

Inserting this back into (14.13) we see that

\[ \Psi_k(x) = \sum_{g \in B} u_{k,g} e^{i⟨k-g,x⟩}. \quad (14.15) \]

If we substitute this representation into the Schrödinger equation for \( H \) and use (14.12), we obtain

\[ \sum_{g'' \in B} \left( \frac{1}{2} ||k-g''||^2 - \varepsilon(k) \right) u_{k,g''} e^{-i⟨g'',x⟩} + \sum_{g',g'' \in B, g'' \neq 0} \lambda v_{g'} u_{k,g''} e^{i⟨g'-g'',x⟩} = 0. \quad (14.16) \]

Here we multiply by \( e^{i⟨g,x⟩} / V_u \) and integrate over \( x \) over the unit cell. Then

\[ \left( \frac{1}{2} ||k-g||^2 - \varepsilon(k) \right) u_{k,g} + \lambda \sum_{g' \in B, g' \neq g} v_{g'-g} u_{k,g'} = 0. \quad (14.17) \]
This is an eigenvalue problem for the vector $u_k$ of the Fourier components $u_{k,g}$, $g \in \mathcal{B}$. We will study it perturbatively in $\lambda$.

The reference point are free electrons, $\lambda = 0$. Then

\[
\left( \frac{1}{2} \| k - g \|^2 - \varepsilon(k) \right) u_{k,g} = 0 \quad \forall \ g \in \mathcal{B}.
\]

Clearly, the solutions of this eigenvalue problem are

\[
\varepsilon_h(k) = \frac{1}{2} \| k - h \|^2, \quad u_{k,g} = \delta_{g,h}
\]

for all $h \in \mathcal{B}$. They are parameterized by reciprocal lattice vectors.

Example: free electrons in 1d. If $a > 0$ is the lattice constant, then

\[
\mathcal{B} = \left\{ g \in \mathbb{R} \big| g = n \frac{2\pi}{a}, \ n \in \mathbb{Z} \right\}, \quad BZ = \left[ -\frac{\pi}{a}, \frac{\pi}{a} \right].
\]

It follows that

\[
\varepsilon_0(k) = \frac{k^2}{2}, \quad \varepsilon_{\pm \frac{2\pi}{a}}(k) = \frac{1}{2} \left( k \mp \frac{2\pi}{a} \right)^2, \ldots,
\]

where $k \in BZ$, are the different branches of the dispersion relation. The situation is sketched in Figure 9.

For non-zero potential we assume that the eigenvalues and the Fourier coefficients of the wave functions can be expanded in an asymptotic series in $\lambda$,

\[
\varepsilon_h(k) = \frac{1}{2} \| k - h \|^2 + \lambda \varepsilon_h^{(1)}(k) + \lambda^2 \varepsilon_h^{(2)}(k) + \mathcal{O}(\lambda^3),\]

where $k \in BZ$.
We choose the normalization of $u_k$ such that $u_k^{(1)} = 0$. Then (14.22) in (14.17) for $g = h$ implies

$$-\lambda \epsilon_h^{(1)}(k) - \lambda^2 \epsilon_h^{(2)}(k) + \lambda \sum_{g' \in \mathcal{B} \atop g' \neq h} v_{g' - h} u_{k,g'}^{(1)} = O(\lambda^3). \tag{14.23}$$

Thus,

$$\epsilon_h^{(1)}(k) = 0, \quad \epsilon_h^{(2)}(k) = \sum_{g \in \mathcal{B} \atop g \neq h} v_{g - h} u_{k,g}^{(1)}, \tag{14.24}$$

whence, for $g \neq h$,

$$\left(\frac{1}{2} \|k - g\|^2 - \frac{1}{2} \|k - h\|^2 - \lambda^2 \epsilon_h^{(2)}(k) - \ldots\right) (\lambda u_{k,g}^{(1)} + \ldots) + \lambda \sum_{g' \in \mathcal{B} \atop g' \neq g} v_{g' - g} (\delta_{g',h} + \lambda u_{k,g'}^{(1)} + \ldots) = 0, \tag{14.25}$$

implying that

$$u_{k,g}^{(1)} = \frac{2v_{h-g}}{\|k - h\|^2 - \|k - g\|^2} \tag{14.26}$$

if $\|k - g\| \neq \|k - h\|$. If we insert this back into (14.23) and use that $v_{-g} = v_g^*$ we obtain the second order corrections to the energies,

$$\epsilon_h(k) = \frac{1}{2} \|k - h\|^2 + \lambda^2 \sum_{g \in \mathcal{B} \atop g \neq 0} \frac{2|v_g|^2}{\|k - h\|^2 - \|k - h - g\|^2} + O(\lambda^3). \tag{14.27}$$

As we see, for a weak periodic potential, the energy in second order perturbation theory can be expressed in terms of the Fourier coefficients of the potential.

If

$$\|k - h\| = \|k - h - g\| \tag{14.28}$$

for some $g \in \mathcal{B}$, $g \neq 0$ and some $k \in BZ$, then the expression (14.27) is singular at that specific value of $k$. In order to interpret this problem set $h = 0$. Then (14.28) reduces to

$$\|k\| = \|k - g\|. \tag{14.29}$$

If $g$ runs through the nearest-neighbour sites of the origin in $\mathcal{B}$, this equation describes the boundaries of the Brillouin zone. Hence, we expect that the exact solution of the problem exhibits a strong deviation of the dispersion relation from the dispersion relation of free electrons at the boundary of the Brillouin zone. For $h \neq 0$ additional singular manifolds appear due to back-folding into the Brillouin zone.

For the interpretation of the perturbative result we further recall that the perturbation theory is applied to each individual energy level, in our case for fixed $h$ and $k$. Equation (14.27) is valid for all $h, k$ which do not satisfy (14.28). If (14.28) is satisfied for a pair $h, k$, we have to modify our calculation, applying the scheme of degenerate perturbation theory instead.
L15 Particles in a periodic potential

15.1 Degenerate levels

Fix \(k\) and assume that there are precisely two vectors \(h, h' \in B\), \(h \neq h'\), such that

\[ \|k - h\| = \|k - h'\|. \tag{15.1} \]

Then (14.17) has two degenerate zeroth order solutions with energies

\[ \epsilon_h(k) = \frac{1}{2} \|k - h\|^2 = \frac{1}{2} \|k - h'\|^2 = \epsilon_{h'}(k). \tag{15.2} \]

and Fourier coefficients

\[ u_{k,g} = a \delta_{g,h} + b \delta_{g,h'} \tag{15.3} \]

where \(a, b \in \mathbb{C}\) are to be determined. The space of solutions is two-dimensional. We assume again an asymptotic dependence of the dispersion relations on the interaction parameter \(\lambda\) as in (14.22a). The corresponding ansatz for the Fourier coefficients (14.22b) has to be modified due to the degeneracy,

\[ u_{k,g} = a \delta_{g,h} + b \delta_{g,h'} + \mathcal{O}(\lambda). \tag{15.4} \]

Substituting this into (14.17) for \(g = h, h'\) and comparing coefficients at order \(\lambda\) we obtain

\[ -\epsilon^{(1)}(k)a + v_{h'-h}b = \mathcal{O}(\lambda), \]
\[ -\epsilon^{(1)}(k)b + v_{h-h'}a = \mathcal{O}(\lambda). \tag{15.5} \]

The solvability condition for this homogeneous system implies that \(\epsilon^{(1)}(k) = \pm |v_{h-h'}|\).

Thus, the two degenerate energy levels split into

\[ \epsilon^\pm(k) = \frac{1}{2} \|k - h\|^2 \pm \lambda |v_{h-h'}| + \mathcal{O}(\lambda^2). \tag{15.6} \]

By way of contrast to the non-degenerate case, the corrections to the eigenstates are now of first order in \(\lambda\). This means that close to the Brillouin zone boundaries the analytic structure of the corrections change. As mentioned above, this makes only sense if we consider a finite system under periodic boundary conditions. Still, we take it as another indication that the strongest effect on the dispersion relation of a free particle by a weak periodic perturbation is at the boundaries of the Brillouin zone.

The possible values of the coefficients \(a, b\) follow from

\[ a_\pm |v_{h-h'}| + b_\pm v_{h'-h} = 0 \iff \frac{a_\pm}{b_\pm} = \pm \frac{v_{h'-h}}{|v_{h-h'}|} = \pm e^{2i\delta} \]

\[ \iff \left( \begin{array}{c} a_+ \\ b_+ \end{array} \right) = \frac{1}{\sqrt{2}} \left( \begin{array}{c} e^{i\delta} \\ e^{-i\delta} \end{array} \right), \quad \left( \begin{array}{c} a_- \\ b_- \end{array} \right) = \frac{1}{\sqrt{2}} \left( \begin{array}{c} e^{i\delta} \\ -e^{-i\delta} \end{array} \right). \tag{15.7} \]

**Remark.** We have considered a two-fold degeneracy. At special symmetric points at the boundaries of the Brillouin zone in more than one dimension higher degeneracies (like four or six) may occur.
Figure 10: The opening of band gaps at degenerate points of the dispersion relation schematically for almost free, periodically perturbed electrons in 1d. The dashed lines represent the dispersion of free particles parameterized by the lattice momentum and are the same as in Figure 9. The blue line represent the deformation of the free-particle dispersion under the influence of a periodic perturbation.

15.2 Example \( d = 1 \)

(i) Let \( h = 0 \) and \( h' = 2\pi/a \). Then a degeneracy occurs at \( k = \pi/a \), and

\[
\varepsilon^\pm\left(\frac{\pi}{a}\right) = \frac{1}{2} \left( \frac{\pi}{a} \right)^2 \pm \lambda |v_{2\pi/a}|. \tag{15.8}
\]

(ii) Let \( h = 2\pi/a \) and \( h' = -2\pi/a \). Then the spectrum is degenerate at \( k = 0 \),

\[
\varepsilon^\pm(0) = \frac{1}{2} \left( \frac{2\pi}{a} \right)^2 \pm \lambda |v_{4\pi/a}|. \tag{15.9}
\]

The two cases are sketched in Figure 10. We observe the ‘opening of band gaps’ at the degenerate points in the dispersion relation. Band gaps are most characteristic for the phenomenology of crystalline solids.

In order to develop more intuition we discuss the wave functions connected with the first case above. These are

\[
\Psi^\pm(x) = a_\pm e^{i\pi x/a} + b_\pm e^{-i\pi x/a} + O(\lambda) = \frac{1}{\sqrt{2}} \left( e^{i(\pi x/a + \delta)} \pm e^{-i(\pi x/a + \delta)} \right) + O(\lambda)
\]

\[
= \sqrt{2} \left\{ \begin{array}{c}
\cos(\pi x/a + \delta) \\
\sin(\pi x/a + \delta)
\end{array} \right\} + O(\lambda). \tag{15.10}
\]

It follows that

\[
|\Psi^\pm(x)|^2 = 1 \pm \cos(2(\pi x/a + \delta)). \tag{15.11}
\]
The periodic potential $V$, on the other hand, has the Fourier series representation

$$V(x) = \lambda (v_{-2\pi/a} e^{-i2\pi x/a} + v_{2\pi/a} e^{i2\pi x/a}) + \text{higher Fourier modes}$$

$$= 2\lambda |v_{2\pi/a}| \cos \left(2(\pi x/a + \delta)\right) + \text{higher Fourier modes}. \quad (15.12)$$

Drawing (15.11) and (15.12) in the same picture and choosing $\lambda < 0$ (attractive effective potential near origin) we see that for $\Psi^+$ the particle is in the average in the valleys of the potential, whereas it is more on the hills for $\Psi^-$. Accordingly, $\varepsilon^+ (\pi/a) < \varepsilon^- (\pi/a)$ in this case.

### 15.3 The tight-binding method

So far we have studied the formation of energy bands starting from free electrons (plane waves) subject to a periodic perturbation. Now we would like to turn to the opposite extreme. We shall start with atomic wave functions and ask what happens, when the atoms are brought close to each other. For simplicity we assume a mono-atomic lattice with $N_{\text{at}}$ atoms.

(i) Let $\phi_a(x)$ an atomic wave function of an electron. In order to satisfy Bloch’s theorem we consider the linear combination

$$\psi_{ak}(x) = \frac{1}{\sqrt{N_{\text{at}}}} \sum_{\mathbf{R} \in B} e^{i\langle \mathbf{k}, \mathbf{R} \rangle} \phi_a(x - \mathbf{R}), \quad (15.13)$$

$k \in BZ$.

(ii) Further define

$$j(\mathbf{R} - \mathbf{R}') = \int_V d^3 x \, \phi_a^*(x - \mathbf{R}') \phi_a(x - \mathbf{R}), \quad (15.14a)$$

$$h(\mathbf{R} - \mathbf{R}') = \int_V d^3 x \, \phi_a^*(x - \mathbf{R}') (H \phi_a)(x - \mathbf{R}), \quad (15.14b)$$

where $H$ is the one-particle Hamiltonian (14.7). Since the atomic wave functions decay exponentially fast with the distance from the nucleus, we expect these functions to behave as

$$j(\mathbf{R} - \mathbf{R}') \sim \delta_{\mathbf{R}, \mathbf{R}'} h(0), \quad (15.15a)$$

$$h(\mathbf{R} - \mathbf{R}') \sim \delta_{\mathbf{R}, \mathbf{R}'} h(0), \quad (15.15b)$$

if the interatomic distance becomes large. It follows that, asymptotically for large interatomic distances,

$$\langle \phi_{ak}, \phi_{ak'} \rangle = \delta_{\mathbf{k}, \mathbf{k}'}, \quad (15.16a)$$

$$\langle \phi_{ak}, H \phi_{ak'} \rangle = h(0) \delta_{\mathbf{k}, \mathbf{k}'}. \quad (15.16b)$$

Thus, for large interatomic distances, the functions $\phi_{ak}$ are a set of approximate eigenfunctions of $H$ corresponding to an $N_{\text{at}}$-fold degenerate atomic level.
(iii) This highly degenerate level splits under the influence of the mutual perturbations of the atoms, if they come closer to each other. In order to take into account the perturbation we determine the norms and energy expectation value in these states,

\[
\|\varphi_{ak}\|^2 = \int_V d^3x \, |\varphi_{ak}(x)|^2 = \frac{1}{N_{at}} \sum_{\mathbf{R}, \mathbf{R}' \in B} e^{i(k \cdot (\mathbf{R} - \mathbf{R}')}} j(\mathbf{R} - \mathbf{R}') = 1 + \sum_{\mathbf{R} \in B, \mathbf{R} \neq 0} e^{i(k \cdot \mathbf{R})} j(\mathbf{R}).
\]

(15.17)

Note that the sum on the right hand side vanishes for large lattice spacing. For the expectation value of the energy we obtain in a similar way

\[
E(k) = \int_V d^3x \, \frac{\varphi_{ak}^*(x) H \varphi_{ak}(x)}{\|\varphi_{ak}\|^2} = \frac{1}{\|\varphi_{ak}\|^2 N_{at}} \sum_{\mathbf{R}, \mathbf{R}' \in B} e^{i(k \cdot (\mathbf{R} - \mathbf{R}'))} h(\mathbf{R} - \mathbf{R}') = \frac{1}{\|\varphi_{ak}\|^2} \sum_{\mathbf{R} \in B} e^{i(k \cdot \mathbf{R})} h(\mathbf{R}) = \frac{1}{\|\varphi_{ak}\|^2} \left( h(0) + \sum_{\mathbf{R} \in B, \mathbf{R} \neq 0} e^{i(k \cdot \mathbf{R})} h(\mathbf{R}) \right),
\]

(15.18)

where again the sum in the brackets on the right hand side vanishes for large lattice spacing.

(iv) Let us now assume that the functions \(j(\mathbf{R})\) and \(h(\mathbf{R})\) decrease rapidly with increasing distance from the origin in \(B\). Then

\[
1 \gg j(\mathbf{R}_{nn}) \gg j(\mathbf{R}_{nnn}) \gg \ldots,
\]

(15.19a)

\[
|h(0)| \gg h(\mathbf{R}_{nn}) \gg h(\mathbf{R}_{nnn}) \gg \ldots,
\]

(15.19b)

where ‘nn’ refers to nearest neighbours to the origin, ‘nnn’ to next-to-nearest neighbours etc. It follows that

\[
E(k) = h(0) + \sum_{\mathbf{R} \in \{\mathbf{R}_{nn}\} \subset B} e^{i(k \cdot \mathbf{R})} \left( h(\mathbf{R}) - h(0) j(\mathbf{R}) \right) + \text{nnn terms}.
\]

(15.20)

This formula describes the so-called ‘tight-binding bands’ which give a realistic description of bands with ‘pronounced atomic character’ for which the electrons are close to the atoms. We shall denote

\[
t(\mathbf{R}) = h(\mathbf{R}) - h(0) j(\mathbf{R}).
\]

(15.21)

We conclude from the inversion symmetry of the Bravais lattice that \(t(\mathbf{R}) = t(-\mathbf{R})\). For this reason tight-binding bands are sums over cosines.

(v) Example fcc lattice: The fcc lattice has 12 nearest neighbours to the origin located at

\[
\mathbf{R} = \frac{a}{2} \begin{cases} (\pm 1, \pm 1, 0) \\ (0, \pm 1, \pm 1) \\ (\pm 1, 0, \pm 1) \end{cases},
\]

(15.22)
and \( t(R) = t \) by symmetry. Hence,

\[
E(k) = h(0) + t \sum_{\sigma, \sigma'} \left( e^{i\alpha(\sigma k_x + \sigma' k_y)/2} + e^{i\alpha(\sigma k_y + \sigma' k_z)/2} + e^{i\alpha(\sigma k_x + \sigma' k_z)/2} \right)
\]

\[
= h(0) + 4t \left\{ \cos\left(\frac{ak_x}{2}\right) \cos\left(\frac{ak_y}{2}\right) + \cos\left(\frac{ak_y}{2}\right) \cos\left(\frac{ak_z}{2}\right) + \cos\left(\frac{ak_z}{2}\right) \cos\left(\frac{ak_x}{2}\right) \right\}.
\]

(15.23)

Note that the band width is proportional to \( t \). This means that small overlaps of the wave function induces narrow bands. The tight-binding model is thus expected to provide a good description of narrow energy bands in solids.

(vi) We close this section with two remarks. First, the tight binding bands can be better justified by introducing so-called Wannier orbitals instead of atomic orbitals (see below).

Second, perhaps the most important insight we can gain from the above reasoning is the intuitive physical picture. Under the influence of the mutual interaction an \( N_{\text{at}} \)-fold degenerate energy level splits into a band with \( N_{\text{at}} \) states. This means that bands can be classified according to the character of the underlying atomic orbitals as \( s, p, d, f \) bands. Our calculation above makes sense for an isolated \( s \)-orbital. For \( p, d, f \) orbitals we cannot start with a single atomic state \( \phi_a \), but have to take into account a set \( \{ \phi_a(x) \}_{a=1}^{a_{\text{max}}} \) of atomic states. This corresponds to a combination of the LCAO (linear combination of atomic orbitals) method of molecular physics with the tight-binding method. Like in molecular physics hybrid orbitals (like \( s-d \) orbitals) may appear in the general case.

**L16  Electrons in a periodic potential**

**16.1  Method of orthogonalized plane waves**

The tight-binding method works for low-energy narrow bands formed by atomic states in which, in the average, the electrons are close to the ions. A method for the calculation of more realistic band structure is obtained by combining the tight binding method with the method of almost free electrons. This is called the OPW (orthogonalized plane waves) method.

We assume that the low-lying states are known. They may be, for instance, sufficiently well described by the tight-binding wave function (15.13),

\[
H \varphi_{ak} \simeq E_{tb}(k) \varphi_{ak}, \quad E_{tb}(k) = \sum_{\mathbf{R}_{\text{min}} \in B} e^{i(k, \mathbf{R})} t(\mathbf{R}).
\]

(16.1)

Let

\[
P = \sum_{\mathbf{k} \in BZ} P_k,
\]

(16.2)

the projector onto the subspace of the full Hilbert space that is spanned by the \( \varphi_{ak} \). In order to determine the remaining part of the spectrum it suffices to consider
\[ H(1 - P)\Psi(x) = E(1 - P)\Psi(x) \]

\[ \Leftrightarrow H\Psi(x) + (E - H)P\Psi(x) = H\Psi(x) + \sum_{k \in BZ} (E - E_{tb}(k))P_k\Psi(x) \]

\[ = \left[ \frac{p^2}{2} + V(x) + \sum_{k \in BZ} (E - E_{tb}(k))P_k \right] \Psi(x) = E\Psi(x). \quad (16.3) \]

Here

\[ W(E, x) = V(x) + \sum_{k \in BZ} (E - E_{tb}(k))P_k \quad (16.4) \]

is called a ‘pseudo potential’. The pseudo potential is not a potential, since in position representation it is represented by an integral operator. Note that

\[ W(E, x) - V(x) > 0, \quad (16.5) \]

since \( E > E_{tb} \). We interpret this in such a way that \( W(E, x) \) includes the effects of screening as discussed above. It is therefore a more appropriate starting point for a perturbation theory for almost free electrons.

### 16.2 Other methods

Within the ‘augmented plane wave method’ the Schrödinger equation is solved in spheres around the ions and plane waves are fitted into the space between the spheres (were the potential is assumed to be negligible).

The KKR (Korringa, Kohn, Rostocker) method is a variant of the augmented plane wave method, where, in a first step, the Green function of the Laplace operator is used in order to transform the Schrödinger equation into an integral equation.

### 16.3 Summary

(i) For the understanding of many of the electronic properties of solids it suffices to take into account the interaction of the electrons only in so far as they screen the attractive potential of the core ions. The remaining problem is the problem of independent electrons in a periodic potential.

(ii) Electrons in a periodic potential are characterized by the branches \( \varepsilon_n(k), n \in \mathbb{N} \), of their dispersion relation. As opposed to the spectral problem of phonons the number of branches for the electrons is infinite. The branches are called energy bands, their entirety is called the ‘band structure’ of the solid.

(iii) Like for the phonons the \( \varepsilon_n(k) \) become differentiable functions of \( k \) in the thermodynamic limit which exhibit the full translation symmetry of the reciprocal lattice and the full point group symmetry of the solid.

### 16.4 Exercise 15. Electronic band structure in one-dimensional solids by WKB

The Schrödinger equation for a non-relativistic electron of mass \( M \) in a 1d periodic potential of period \( L \) reads

\[ \frac{d^2\psi}{dx^2} + [E - V(x)]\psi(x) = 0. \quad (16.6) \]
Here the energy and the length are measured in units of $\frac{h^2}{2ML^2}$ and $L$, respectively.

We would like to solve equation (16.6) by means of the WKB-approximation and find a condition which determines the band structure, i.e. all allowed energy values $E$.

Setting $p(x) = \sqrt{E - V(x)}$ we can express the general WKB-solution of the Schrödinger equation for a single potential barrier $V(x)$ (see figure) in the classically accessible regions left and right of the barrier as

$$E < V_{\text{max}} : \frac{1}{\sqrt{p(x)}} \exp[\pm i \int_{a_0}^{x} dy p(y)], \ x < a_0,$$

$$E > V_{\text{max}} : \frac{1}{\sqrt{p(x)}} \exp[\pm i \int_{b_0}^{x} dy p(y)], \ x > b_0.$$

(i) The general solution is in each case a linear combination with coefficients $A_0, B_0$ or $F_1, G_1$ for the left and right classically accessible region, respectively. The coefficients are related by a $2 \times 2$ matrix $M$. Conclude from the time-inversion invariance that $M_1^* = M_2^*$, $M_1^2 = M_2^1$. For this purpose consider

$$M \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} F_1 \\ G_1 \end{pmatrix}, \quad M \begin{pmatrix} B_0 \\ A_0 \end{pmatrix} = \begin{pmatrix} G_1 \\ F_1 \end{pmatrix}. \quad (16.7)$$

(ii) The current conservation $|A_0|^2 - |B_0|^2 = |F_1|^2 - |G_1|^2$ implies $\det M = 1$. Let $T$ be the transmission coefficient and $R = 1 - T$ the reflection coefficient with the corresponding phase shifts $e^{i\mu}$ and $e^{-i\nu}$. Verify the representation

$$M = \begin{pmatrix} \frac{1}{\sqrt{T}} \sqrt{R} e^{i\mu} & -\frac{1}{\sqrt{T}} e^{-i(\mu+\nu)} \\ -\frac{1}{\sqrt{R}} e^{-i(\mu+\nu)} & \frac{1}{\sqrt{T}} e^{-i\mu} \end{pmatrix}. \quad (16.8)$$

(iii) A periodic continuation of the potential barrier leads to another representation of the solution in the classically accessible domain $b_0 < x < a_1$,

$$E < V_{\text{max}} : \frac{A_1}{\sqrt{p(x)}} \exp[i \int_{a_1}^{x} dy p(y)] + \frac{B_1}{\sqrt{p(x)}} \exp[-i \int_{a_1}^{x} dy p(y)], \quad (16.9)$$

$$E > V_{\text{max}} : \frac{A_1}{\sqrt{p(x)}} \exp[i \int_{b_1}^{x} dy p(y)] + \frac{B_1}{\sqrt{p(x)}} \exp[-i \int_{b_1}^{x} dy p(y)]. \quad (16.10)$$

Which matrix connects $A_1, B_1$ with $F_1, G_1$, if we set $\phi(E) = \int_{b_0}^{a_1} dy p(y), \ E < V_{\text{max}}$ rwp. $\phi(E) = \int_{0}^{1} dy p(y), \ E \geq V_{\text{max}}$? Calculate the transfer matrix $P$ which links the coefficients $A_0, B_0$ and $A_1, B_1$ of two neighbouring cells.
(iv) The full solution for the periodic potential stays bounded as long as $P$ has eigenvalues of absolute value 1. Show that this fact implies a condition that determines the band structure,

$$\left| \frac{\cos[\phi(E) + \mu]}{\sqrt{T(E)}} \right| \leq 1.$$  \hspace{1cm} (16.11)

(v) For a potential of the form $V(x) = V_0 \cos(2\pi x)$, $V_0 > 0$, the Schrödinger equation \(16.6\) of the non-relativistic particle is equal to the Mathieu equations. The transition coefficient $T(E)$ of a single potential barrier in WKB-approximation follows as

$$T(E) = \frac{1}{1 + e^{2W}}, \quad W(E) = \int_a^b |p(y)| \, dy, \quad E < V_0,$$

$$T(E) = \frac{1}{1 + e^{-2W}}, \quad W(E) = \left| \int_y^{y_2} |p(y)| \, dy \right|, \quad E > V_0,$$

where for $E > V_0$ the integral has to be calculated on the direct line between both imaginary reversal points. Represent $\phi(E)$ and $W(E)$ by complete elliptical integrals of the first and second kind $K(m)$ and $E(m)$, with the dimensionless parameter $m = \frac{E+V_0}{2V_0}, \quad E < V_0$ and $m = \frac{2V_0}{E+V_0}, \quad E > V_0$, respectively!

(vi) Choosing different parameters $m$ (and thus fixing $E/V_0$) it is possible to sketch the regions in the $V_0,E$-diagram for $\mu \approx 0$, where the solutions are bounded. Find such type of diagram in the literature.

16.5 The Fermi distribution

Electrons are Fermions. According to the Pauli principle many-electron wave functions must be totally anti-symmetric under the permutations of any two electrons. Consequentially, in a system of many non-interacting electrons (or holes) no two of them can be in the same single-particle state. When we calculate the grand canonical partition function we therefore have to count every single-particle state as either unoccupied or occupied by just one electron (or hole),

$$Z_e = \prod_{n=0}^{\infty} \prod_{\mathbf{k} \in BZ} \left(1 + e^{-\frac{\varepsilon_n(k)-\mu}{T}} \right).$$  \hspace{1cm} (16.12)

Here $1 = e^0$ stands for an unoccupied state, while $e^{-\frac{\varepsilon_n(k)-\mu}{T}}$ stands for an occupied state. Every factor on the right hand side of \(16.12\) represents the partition function corresponding to a single-electron state. Hence, the grand-canonical probability for having this state occupied is

$$f(\varepsilon_n(k) - \mu) = \frac{e^{-\frac{\varepsilon_n(k)-\mu}{T}}}{1 + e^{-\frac{\varepsilon_n(k)-\mu}{T}}} = \frac{1}{e^{-\frac{\varepsilon_n(k)-\mu}{T}} + 1}.$$  \hspace{1cm} (16.13)

As we recall from our lecture on statistical mechanics, this is the Fermi distribution function.
16.6 Grand canonical potential of the electron gas

As for every ideal gas of spin-$\frac{1}{2}$ Fermions we can immediately write down the total particle number \(N\), internal energy \(E\) and entropy \(S\) of the system as sums involving the Fermi function,

\[
N(T, \mu) = 2 \sum_{n=0}^{\infty} \sum_{k \in BZ} f(\varepsilon_n(k) - \mu),
\]

\[
E(T, \mu) = 2 \sum_{n=0}^{\infty} \sum_{k \in BZ} f(\varepsilon_n(k) - \mu) \varepsilon_n(k),
\]

\[
S(T, \mu) = -2 \sum_{n=0}^{\infty} \sum_{k \in BZ} \left\{ f(\varepsilon_n(k) - \mu) \ln(f(\varepsilon_n(k) - \mu)) 
+ (1 - f(\varepsilon_n(k) - \mu)) \ln(1 - f(\varepsilon_n(k) - \mu)) \right\}.
\]

Here the factor of 2 accounts for the spin degree of freedom. The grand canonical potential is obtained as

\[
\Omega(T, \mu) = E(T, \mu) - TS(T, \mu) - \mu N(T, \mu)
\]

\[
= 2T \sum_{n=0}^{\infty} \sum_{k \in BZ} \left\{ f \ln(1/f - 1) + f \ln f + (1 - f) \ln(1 - f) \right\}
\]

\[
= -2T \sum_{n=0}^{\infty} \sum_{k \in BZ} \ln(1 + e^{-\frac{\varepsilon_n(k) - \mu}{T}}).
\]

In a similar way as for the phonon gas we can rewrite the sums over all lattice momenta asymptotically for large volume \(V\) first as an integral over the Brillouin zone and then as an integral over all energies. For the second step we need to define an electronic density of states. We proceed as for the phonon gas and first of all introduce the density of states for a single branch of the dispersion relation,

\[
g_n(\varepsilon) = \frac{1}{(2\pi)^3} \int_{BZ} d^3k \, \delta(\varepsilon - \varepsilon_n(k)) = \frac{1}{(2\pi)^3} \int_{S(\varepsilon)} \frac{dS}{\| \text{grad}_k \varepsilon_n(k) \|},
\]

where \(S(\varepsilon)\) is the surface implicitly determined by the equation \(\varepsilon = \varepsilon_n(k)\). With this the (total) density of states is defined as

\[
g(\varepsilon) = 2 \sum_{n=0}^{\infty} g_n(\varepsilon).
\]

Again a factor of 2 is included to take the spin degrees of freedom into account.

**Remark.** Our statements about van-Hove singularities in section 9.4 remain valid for electrons.

16.7 Fermi energy and Fermi surface

Two important notions in solid state physics are the ‘Fermi energy’ and the ‘Fermi surface’. Using the density of states introduced above we may write the particle number as a function of temperature and chemical potential as

\[
N(T, \mu) = V \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) f(\varepsilon - \mu).
\]


Since
\[ \partial_{\mu}N(T, \mu) = \frac{V}{4T} \int_{-\infty}^{\infty} d\varepsilon \frac{g(\varepsilon)}{\cosh^{2}((\varepsilon - \mu)/2T)} > 0, \tag{16.19} \]
equation (16.18) can be inverted at any \( T > 0 \) to give \( \mu = \mu(T, N) \) (the latter fact follows, of course, also from general arguments on the equivalence of thermodynamic ensembles in the thermodynamic limit).

The Fermi energy \( E_F \) is defined as the chemical potential at \( T = 0 \),
\[ E_F = \lim_{T \to 0^+} \mu(T, N). \tag{16.20} \]
It is clear from (16.18) and (16.19) that the Fermi energy depends only on the particle density \( N/V \) and is a monotonically increasing function of the particle density. In a canonical ensemble description, i.e. if we fix the particle number and consider \( \mu \) as a function of \( N \) and \( T \), we obtain the pointwise limit,
\[ \lim_{T \to 0^+} f(\varepsilon - \mu(T, N)) = \Theta(E_F - \varepsilon), \tag{16.21} \]
where \( \Theta \) is the Heaviside function. This reflects the fact that in the ground state all single-particle states with energies up to \( E_F \) are occupied, while those with energies larger than \( E_F \) are unoccupied.

For the electronic ground state of solids (within the band model) exist two alternatives,
\( (i) \) \( g(E_F) > 0 \), \( (ii) \) \( g(E_F) = 0 \),
\( (16.22) \)
which come with drastically different phenomenologies. In case (i) the Fermi energy lies within a band. In case (ii) it is situated in a band gap (cf. Figure [11]). In case (i) excitations of arbitrarily small energy are possible. In case (ii), due to the Pauli principle, the smallest possible excitation energy is equal to the band gap. In case (i) an arbitrarily small electric field causes a current, in case (ii) this does not happen. This is our first explanation, within a single-particle picture, of the difference between conductors and insulators.

In conductors the Fermi energy is in at least one band, and the equations
\[ \varepsilon_n(\mathbf{k}) = E_F \text{ for } n \in \mathbb{N} \tag{16.23} \]
determine a surface in reciprocal space which is called the Fermi surface \( S_F \). The volume enclosed by the Fermi surface
\[ \text{Int } S_F = \{ \mathbf{k} \in \mathbb{R}^3 \mid \varepsilon_n(\mathbf{k}) \leq E_F, n \in \mathbb{N} \} \tag{16.24} \]
is called the Fermi sphere. In general the Fermi surface has a complicated shape and topology (not necessarily simply connected). It is of crucial importance for the understanding of the transport properties of solids, in particular in the presence of a magnetic field.

L17 Low-temperature specific heat of the electron gas

A first quantitative example, showing that it makes a big difference whether or not the Fermi energy lies within a band, is the thermodynamics of band electrons at low temperature.
Expressing the grand canonical potential (16.15) by means of the electronic density of states (16.16), (16.17) we obtain

\[
\Omega(T, \mu) = -TV \int_{-\infty}^{\mu} \! d\varepsilon \, g(\varepsilon) \ln\left(1 + e^{-\frac{\varepsilon - \mu}{T}}\right). \tag{17.1}
\]

In order to prepare for the low-\(T\) analysis we rewrite this as

\[
\Omega(T, \mu) = V \int_{-\infty}^{\mu} \! d\varepsilon \, g(\varepsilon)(\varepsilon - \mu) - TV \int_{-\infty}^{\infty} \! d\varepsilon \, g(\varepsilon) \ln\left(1 + e^{-\frac{|\varepsilon - \mu|}{T}}\right). \tag{17.2}
\]

Since \(g(x)\) is the density of states of an electronic band structure, there are two interlaced sequences \((a_n, b_n)_{n \in \mathbb{N}}\) with \(a_n < b_n < a_{n+1} < b_{n+1}\) and \(g(x) \neq 0 \quad \forall \ x \in (a_n, b_n)\), \(g(x) = 0 \quad \forall \ x \in [b_n, a_{n+1}]\). If \(\mu\) is in one of the band gaps \((b_n, a_{n+1})\), then the second integral on the right hand side of (17.2) vanishes exponentially fast for \(T \to 0\), which is not the case, if \(\mu\) is situated inside a band.

### 17.1 Specific heat of metals

Both cases require a separate asymptotic analysis. Let us start with the metallic case \(\mu \in (a_n, b_n)\) for some \(n \in \mathbb{N}\). We assume that \(g\) is analytic in \((a_n, b_n)\). Then it has a Taylor series expansion around \(\varepsilon = \mu\) with some finite radius of convergence \(\delta > 0\),

\[
g(\varepsilon) = \sum_{k=0}^{\infty} \frac{g^{(k)}(\mu)}{k!} (\varepsilon - \mu)^k, \quad \text{if } |\varepsilon - \mu| < \delta. \tag{17.3}
\]

It follows that

\[
\Omega(T, \mu) - V \int_{-\infty}^{\mu} \! d\varepsilon \, g(\varepsilon)(\varepsilon - \mu)
\]
\[ -TV \sum_{k=0}^{\infty} \frac{g^{(k)}(\mu)}{k!} \int_{\mu - \epsilon}^{\mu + \delta} d\epsilon \, (\epsilon - \mu)^k \ln \left( 1 + e^{-|\epsilon|/T} \right) + O(T^\infty) \]
\[ = -V \sum_{k=0}^{\infty} \frac{g^{(k)}(\mu)}{k!} T^{k+2} \int_{-\delta/T}^{\delta/T} dx \, x^k \ln \left( 1 + e^{-|x|} \right) + O(T^\infty) \quad (17.4) \]

Here we have substituted \( x = (\epsilon - \mu)/T \) in the second equation. The remaining integral vanishes for symmetry reasons if \( k \) is odd. If \( k = 2m \) we obtain
\[ \int_{-\delta/T}^{\delta/T} dx \, x^{2m} \ln \left( 1 + e^{-|x|} \right) = 2 \int_0^{\infty} dx \, x^{2m} \ln \left( 1 + e^{-x} \right) + O(T^\infty) \]
\[ = 2 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \int_0^{\infty} dx \, x^{2m} e^{-nx} + O(T^\infty) = 2(2m)! \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n^{2m+2}} + O(T^\infty) \]
\[ = (2m)! (2 - 2^{-2m}) \zeta(2m + 2) + O(T^\infty) \quad (17.5) \]

where \( \zeta \) is Riemann’s zeta function. Inserting this back into (17.4) we obtain the low-\( T \) asymptotic series
\[ \Omega(T, \mu) = V \int_{-\infty}^{\mu} d\epsilon \, g(\epsilon)(\epsilon - \mu) \]
\[ - V \sum_{k=0}^{\infty} (2 - 2^{-2k}) \zeta(2k + 2) g^{(2k)}(\mu) T^{2k+2} + O(T^\infty) \quad (17.6) \]

for the grand canonical potential.

The corresponding series for the particle number and entropy in a grand canonical description are
\[ N(T, \mu) = -\frac{\partial \Omega(T, \mu)}{\partial \mu} = V \int_{-\infty}^{\mu} d\epsilon \, g(\epsilon) \]
\[ + V \sum_{k=0}^{\infty} (2 - 2^{-2k}) \zeta(2k + 2) g^{(2k+1)}(\mu) T^{2k+2} + O(T^\infty) \quad (17.7a) \]
\[ S(T, \mu) = -\frac{\partial \Omega(T, \mu)}{\partial T} \]
\[ = V \sum_{k=0}^{\infty} (2 - 2^{-2k})(2k + 2) \zeta(2k + 2) g^{(2k)}(\mu) T^{2k+1} + O(T^\infty) \quad (17.7b) \]

The asymptotic series allow us to calculate the low-temperature expansion of the specific heat order by order, using
\[ C_V = T \frac{\partial S}{\partial T} \bigg|_N = T \left( \frac{\partial S}{\partial T} \bigg|_\mu + \frac{\partial S}{\partial \mu} \bigg|_T \frac{\partial \mu}{\partial T} \right) \bigg|_N \quad (17.8) \]

Equation (17.7a) can be used iteratively to obtain \( \mu \) as a function of \( N \) and \( T \). The equation
\[ \frac{N}{V} = \int_{-\infty}^{E_f} d\epsilon \, g(\epsilon) \quad (17.9) \]
following from (17.7a) at $T = 0$, determines $E_F = \mu(0,N)$ as a function of the density of particles $N/V$. Since only $T^2$ enters (17.7a), $\mu$ must be even in $T$,

$$ \mu = E_F + \alpha T^2 + \mathcal{O}(T^4). $$

(17.10)

Inserting this into (17.7a) and using (17.9) we can calculate $\alpha$,

$$ \int_{E_F}^{\mu} d\varepsilon g(\varepsilon) + \zeta(2) g'(\mu) T^2 = (\mu - E_F) g(\mu) - g'(\mu) \frac{(\mu - E_F)^2}{2} + \zeta(2) g'(\mu) T^2 + \mathcal{O}(T^6) $$

$$ = (\alpha g(E_F) + \zeta(2) g'(E_F)) T^2 + \mathcal{O}(T^4) = \mathcal{O}(T^4) $$

$$ \Rightarrow \alpha = -\zeta(2) \frac{g'(E_F)}{g(E_F)} \Rightarrow \mu = E_F - \zeta(2) \frac{g'(E_F)}{g(E_F)} T^2 + \mathcal{O}(T^4). $$

(17.11)

Furthermore, using (17.11) we get at once that

$$ T \frac{\partial S}{\partial T} \bigg|_{\mu} = 2\zeta(2) T V g(E_F) + \mathcal{O}(T^3), $$

(17.12a)

$$ T \frac{\partial S}{\partial \mu} \bigg|_{T} = 2\zeta(2) T^2 V g'(E_F) + \mathcal{O}(T^4). $$

(17.12b)

Using (17.11) and (17.12a) in (17.8) and recalling that $\zeta(2) = \pi^2/6$ we finally arrive at the sought for low-temperature asymptotics of the specific heat of a metal,

$$ C_V = \frac{\pi^2}{3} TV g(E_F) + \mathcal{O}(T^3). $$

(17.13)

Let us add a few comments in conclusion.

(i) The above low-$T$ asymptotic expansion of the thermodynamic quantities of a Fermi gas goes back to Sommerfeld [13] and is called the Sommerfeld expansion.

(ii) Equation (17.13) is an important result stating that the electronic contribution to the specific heat of metals is linear in $T$ and proportional to the density of states at the Fermi energy.

(iii) Taking it the other way round, we see that we can experimentally determine the density of states of a metal close to its Fermi energy by measuring its specific heat.

(iv) Since typical electronic energies in solids, like band gaps or band widths, are of the order of 1 eV, low-temperature expansions for the electrons in solids are usually valid even above room temperature.

### 17.2 Specific heat of insulators

Starting once more from equation (17.2) we consider the specific heat of an insulator. By definition a band insulator has $g(E_F) = 0$. The Fermi energy is located inside a band gap, $b_n < E_F < a_{n+1}$ for some $n \in \mathbb{N}$. In this situation the closest band below the Fermi energy, the one with index $n$ here, is called ‘valence band’, the closest band above the Fermi energy, the one with index $n + 1$, ‘conduction band’. It follows from (17.2) that, for $b_n < \mu < a_{n+1}$,
\[ \Omega(T, \mu) - V \int_{-\infty}^{\mu} d\varepsilon \ g(\varepsilon)(\varepsilon - \mu) \]

\[ \sim -TV \int_{-\infty}^{\infty} d\varepsilon \ g(\varepsilon) e^{-\frac{|\varepsilon - \mu|}{T}} \sim -TV \left\{ \int_{-a_n}^{b_n} d\varepsilon \ g(\varepsilon) e^{-\frac{\varepsilon - \mu}{T}} + \int_{a_n+1}^{b_{n+1}} d\varepsilon \ g(\varepsilon) e^{-\frac{\varepsilon - \mu}{T}} \right\} \]

\[ = -TV \left\{ e^{\frac{bn - \varepsilon}{T}} \int_{-a_n}^{b_n} d\varepsilon \ g(\varepsilon) e^{\varepsilon - \frac{\varepsilon - \mu}{T}} + e^{-\frac{an+1 - \mu}{T}} \int_{a_n+1}^{b_{n+1}} d\varepsilon \ g(\varepsilon) e^{-\frac{\varepsilon - an+1}{T}} \right\} \]

\[ = -T^2V \left\{ \frac{e^{\frac{bn - \varepsilon}{T}}}{T} \int_{-a_n}^{b_n} d\varepsilon \ g(b_n + Tx)e^x + e^{-\frac{an+1 - \mu}{T}} \int_{0}^{\infty} d\varepsilon \ g(a_{n+1} + Tx)e^{-x} \right\}. \] (17.14)

Here we have neglected contributions that are exponentially smaller than the displayed terms. In order to further simplify the remaining integrals we have to recall that for 3d systems there are square-root type van-Hove singularities at the band edges. This means that there are \( \alpha_v, \alpha_c > 0 \) such that within the respective bands

\[ g(b_n + Tx) \sim \alpha_v \sqrt{-Tx}(1 + O(Tx)), \quad g(a_{n+1} + Tx) \sim \alpha_c \sqrt{Tx}(1 + O(Tx)). \] (17.15)

Substituting this into the integrals on the right hand side of (17.14) we obtain, for instance,

\[ \int_{-\infty}^{\infty} dx \ g(b_n + Tx) e^x \sim \sqrt{T} \alpha_v \int_{0}^{\infty} dx \sqrt{x} e^{-x} = \sqrt{T} \alpha_v \Gamma(3/2) = \frac{1}{2} \sqrt{T} \alpha_v \] (17.16)

and a similar expression for the other integral. Altogether we end up with

\[ \Omega(T, \mu) \sim V \int_{-\infty}^{\mu} d\varepsilon \ g(\varepsilon)(\varepsilon - \mu) - \frac{\sqrt{\pi}}{2} T^2 V \left\{ \alpha_v e^{-\frac{\mu - b_n}{T}} + \alpha_c e^{-\frac{a_n+1 - \mu}{T}} \right\}, \] (17.17)

which is the low-temperature asymptotics of the grand canonical potential for an insulator, when \( \mu \in (b_n, a_{n+1}) \).

Again the formulae for particle number and entropy in the grand canonical ensemble are obtained by taking derivatives (cf. (17.17)),

\[ N(T, \mu) \sim V \int_{-\infty}^{\mu} d\varepsilon \ g(\varepsilon) - \frac{\sqrt{\pi}}{2} T^2 V \left\{ \alpha_v e^{-\frac{\mu - b_n}{T}} - \alpha_c e^{-\frac{a_n+1 - \mu}{T}} \right\}, \] (17.18a)

\[ S(T, \mu) \sim \frac{\sqrt{\pi}}{2} T^2 V \left\{ (\mu - b_n) \alpha_v e^{-\frac{\mu - b_n}{T}} + (a_{n+1} - \mu) \alpha_c e^{-\frac{a_n+1 - \mu}{T}} \right\}. \] (17.18b)

For \( T \to 0+ \) in (17.18a) we still get that the integral on the right hand side with upper limit \( E_F \) is equal to the total particle number, but now this equality does not fix \( E_F \), since the integral as a function of \( \mu \) is constant for \( \mu \in [b_n, a_{n+1}] \), thus non-invertible. Since \( \mu \) is continuous in a vicinity of \( T = 0 \), we see that the integral exactly equals \( N \) even for small finite temperatures. Hence, the second term on the right hand side must vanish asymptotically,

\[ \frac{\sqrt{\pi}}{2} T^2 V \left\{ \alpha_v e^{-\frac{\mu - b_n}{T}} - \alpha_c e^{-\frac{a_n+1 - \mu}{T}} \right\} \sim 0, \] (17.19)
which determines \( \mu \) at small \( T \) to be
\[
\mu = \frac{b_n + a_{n+1}}{2} + \frac{T}{2} \ln \left( \frac{\alpha_v}{\alpha_c} \right) + O(T^\infty).
\]
(17.20)

In particular,
\[
E_F = \frac{b_n + a_{n+1}}{2}.
\]
(17.21)

The Fermi energy of an insulator is in the middle of the band gap.

By definition
\[
\Delta = a_{n+1} - b_n
\]
(17.22)
is the ‘width of the band gap’ or simply ‘the band gap’. Using (17.8), (17.18b) and (17.20)-(17.22) one straightforwardly obtains the expression
\[
C_V = \frac{\alpha_v + \alpha_c}{2} \sqrt{\frac{\pi}{T}} V \left( \frac{\Delta}{2} \right)^2 e^{-\frac{\Delta^2}{2T}} (1 + O(T))
\]
(17.23)
for the low-temperature asymptotic behaviour of the specific heat of a band insulator.

Here again a few concluding remarks are in order.

(i) The functional form of the low-\( T \) specific heat in (17.23) is called ‘thermally activated behaviour’. One says that the activation barrier equals half of the band gap.

(ii) The size of the electronic contribution to the specific heat of an insulator depends in an extremal way on the band gap. Example:
\[
\Delta = 0.5 \text{ eV} \Rightarrow e^{-\frac{\Delta^2}{2T}} \approx 10^{-4},
\]
(17.24a)
\[
\Delta = 3.0 \text{ eV} \Rightarrow e^{-\frac{\Delta^2}{2T}} \approx 10^{-24}
\]
(17.24b)
at \( T \approx 300 \text{K} \). This makes the difference, as far as the electronic specific heat is concerned, between insulators and ‘semi-conductors’.

(iii) For an insulator in the low-temperature regime the electrons contribute almost nothing to the specific heat. The specific heat of insulators is mostly determined by the phonons. In conductors, on the other hand, the electrons do contribute to the specific heat and even dominate it at low enough temperatures. For this reason metals have, in general, a larger heat capacity than insulators.

L18 Electrons in solids – the second quantized picture

We recall that the Hamiltonian (14.1) of the electrons in solids in adiabatic approximation is
\[
H_{el} = \sum_{j=1}^{N} \left\{ \frac{1}{2} \| p_j \|^2 + V_l(x_j) \right\} + \sum_{1 \leq j < k \leq N} V_c(x_j - x_k),
\]
(18.1)
where \( V_l(x) \) is the periodic potential of the ions in the crystal, \( V_c(x) = 1/\|x\| \) is the Coulomb potential, and \( N \) is the number of electrons we are taking into account.
18.1 An auxiliary potential

Our aim in the following lectures is to proceed beyond the single-particle approximation. To begin with, we remark that we can introduce an auxiliary potential $V_A(x)$ without changing too much the structure of the Hamiltonian. Let

$$V(x) = V_I(x) + V_A(x). \quad (18.2)$$

Then

$$H_{el} - \sum_{j=1}^{N} \left\{ \frac{1}{2} \| p_j \|^2 + V(x_j) \right\} = \sum_{1 \leq j < k \leq N} V_C(x_j - x_k) - \sum_{j=1}^{N} V_A(x_j)$$

$$= \sum_{1 \leq j < k \leq N} \left\{ V_C(x_j - x_k) - \frac{V_A(x_j) + V_A(x_k)}{N-1} \right\}_{=U(x_j,x_k)}$$

$$\Leftrightarrow H_{el} = \sum_{j=1}^{N} \left\{ \frac{1}{2} \| p_j \|^2 + V(x_j) \right\} + \sum_{1 \leq j < k \leq N} U(x_j,x_k). \quad (18.3)$$

Note that the choice of the auxiliary potential is entirely at our disposal. We may, for instance, choose the mean field potential defined in section 14.2. If we neglect $U$ we are applying a single-particle approximation. Good single-particle approximations are obtained for appropriate choices of $V_A$. A single-particle approximation is good, if the two-particle matrix elements of $U(x,y)$ calculated with eigenstates of the single-particle Hamiltonian

$$h(x,p) = \frac{\| p \|^2}{2} + V(x) \quad (18.4)$$

are small for single-particle energies close to the Fermi surface.

18.2 Bloch basis and Wannier basis

In the following calculation we will not fix the auxiliary potential $V_A$. Our only explicit assumption is that it is periodic. Implicitly we shall also assume that it allows us to take screening into account. Due to the periodicity the eigenfunctions of $h$ are ‘Bloch functions’ $\varphi_{\alpha k}$ labeled by a band index $\alpha \in \mathbb{N}$ and a lattice momentum $k \in BZ$,

$$h\varphi_{\alpha k}(x) = \varepsilon_{\alpha}(k)\varphi_{\alpha k}(x). \quad (18.5)$$

We shall call the $\varepsilon_{\alpha}(k)$ the single-particle energies. The Bloch theorem implies

$$\varphi_{\alpha k}(x) = e^{i(k,x)} u_{\alpha k}(x) \quad (18.6)$$

with a lattice periodic function $u_{\alpha k}$. The set $\{ \varphi_{\alpha k} \}_{\alpha \in \mathbb{N}, k \in BZ}$ is a single-particle orthonormal basis of the electronic Hilbert space called the ‘Bloch basis’.

Define

$$\phi_{\alpha}(x) = \frac{1}{\sqrt{L}} \sum_{k \in BZ} \varphi_{\alpha k}(x), \quad (18.7)$$
where $L$ is the number of unit cells. Then $\{\phi_\alpha(x - R_j) | \alpha \in \mathbb{N}, R_j \in B\}$ is another orthonormal basis (prove it!) called the Wannier basis. $\phi_\alpha(x)$ is called a Wannier function. The Wannier functions generalize the atomic orbitals in section 15.3.

Bloch basis and Wannier basis are connected via Fourier transformation,

$$
\frac{1}{\sqrt{L}} \sum_{j=1}^{L} e^{i(k \cdot R_j)} \phi_\alpha(x - R_j) = \frac{1}{\sqrt{L}} \sum_{j=1}^{L} \sum_{p \in \text{BZ}} e^{i(k \cdot R_j)} e^{i(p \cdot x - R_j)} u_{\alpha p}(x - R_j)
$$

$$
= \sum_{p \in \text{BZ}} e^{i(p \cdot x)} u_{\alpha p}(x) \frac{1}{\sqrt{L}} \sum_{j=1}^{L} e^{i(k \cdot p \cdot R_j)} = \varphi_{\alpha k}(x). \quad (18.8)
$$

Here we have used that the second sum on the right hand side of the second equation equals $L \delta_{k,p}$.

### 18.3 Hamiltonian in second quantization

Let $c_{\alpha k,a}^+$ the creation operator of a Bloch electron of spin $\alpha \in \{\uparrow, \downarrow\}$. The operators

$$c_{\alpha j,a}^+ = \frac{1}{\sqrt{L}} \sum_{k \in \text{BZ}} e^{-i(k \cdot R_j)} c_{\alpha k,a}^+ \quad (18.9)$$

are then an alternative set of creation operators, creating electrons in Wannier orbitals. This can be seen by writing down the corresponding field operators,

$$
\Psi_\alpha^+(x) = \sum_{\alpha k} \varphi_{\alpha k}^*(x) c_{\alpha k,a}^+ = \sum_{\alpha k} \varphi_{\alpha k}^*(x) \frac{1}{\sqrt{L}} \sum_{j=1}^{L} e^{i(k \cdot R_j)} c_{\alpha j,a}^+
$$

$$
= \sum_{j=1}^{L} \left( \frac{1}{\sqrt{L}} \sum_{\alpha k} \varphi_{\alpha k}^*(x) e^{i(k \cdot R_j)} \right) c_{\alpha j,a}^+ = \sum_{\alpha} \sum_{j=1}^{L} \varphi_{\alpha}^*(x - R_j) c_{\alpha j,a}^+ \quad (18.10)
$$

According to the general prescription (see lecture on QM) the Hamiltonian in ‘occupation number representation’ (‘second quantization’) can be written as

$$
H_{el} = \int d^3x \, \Psi_\alpha^+ (x) h \Psi_\alpha (x) + \frac{1}{2} \int d^3x \int d^3y \, \Psi_\alpha^+ (x) U(x,y) \Psi_\beta (y) \Psi_\beta (y) \Psi_\alpha (x)
$$

$$
= \sum_{\alpha, \beta, i, j} \int d^3x \, \phi_{\alpha}^*(x - R_i) h \phi_{\beta} (x - R_j) c_{\alpha i,a}^+ c_{\beta j,a}^+
$$

$$
+ \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta, i, j, k, \ell} \int d^3x \int d^3y \, \phi_{\alpha}^*(x - R_i) \phi_{\beta}^* (y - R_j) U(x,y) \phi_{\gamma} (y - R_k) \phi_{\delta} (x - R_\ell) \times
$$

$$
= \sum_{\alpha, \beta, \gamma, \delta, i, j, k, \ell} U^{\alpha \beta \gamma \delta}_{ijk \ell} c_{\alpha i,a}^+ c_{\beta j,a}^+ c_{\gamma k,b} c_{\delta \ell,a}^+ \quad (18.11)
$$

*Note the change of notation!
Here implicit summation over the spin indices $a, b$ is implied. The $t_{ij}^{\alpha}$ are called ‘transition matrix elements’ or ‘hopping matrix elements’, the $U_{ijk\ell}^{\alpha\beta\gamma\delta}$ are called ‘interaction parameters’.

Note that:

(i) So far the Hamiltonian is only rewritten in ‘second quantization’. No other approximation than the adiabatic approximation has been applied.

(ii) In this form it is the starting point of the ‘theory of strongly correlated electron systems’.

(iii) An optimal choice of the Wannier functions (through an optimal choice of $V_A$) minimizes the strength and the range of the interaction parameters.

(iv) Suppose the auxiliary potential $V_A$ can be chosen in such a way that the interaction parameters are always small. Then they can be neglected and we are in the realm of band theory.

(v) If the Wannier functions can be constructed in such a way that they resemble atomic wave function in the sense that they are localized around the origin and decay sufficiently fast away from it, then the interaction parameters become short-range, and it may be justified to consider only on-site or near-neighbour contributions.

18.4 Exercise 16. Wannier functions in one dimension

The dispersion relation of a free non-relativistic particle of mass $m$ is $\varepsilon(k) = \hbar^2 k^2 / 2m$. Consider a lattice of $N$ sites and physical length $L$ under periodic boundary conditions. Then only $N$ discrete wave vectors of the form $k = 2\pi n / L$, $n \in \mathbb{Z}$, are possible inside the Brillouin zone. All wave vectors outside will be folded back to the Brillouin zone, i.e. new bands with dispersion $\varepsilon(k + 2\pi m / a)$ develop, where $a = L / N$ is the lattice constant and $m \in \mathbb{Z}$ is the band index. The corresponding Bloch functions are labeled in the following way,

$$\varphi_{m,k}(x) = \frac{1}{\sqrt{L}} \exp \left[ i(k + m \frac{2\pi}{a}) x \right]. \quad (18.12)$$

Construct the complementary Wannier basis $\{ \phi_m(x - R_i) \}, i = 1, \ldots, N$, in the thermodynamic limit ($N, L \to \infty, L/N = a = \text{const.}$). This requires to calculate

$$\phi_m(x) = \frac{1}{\sqrt{N}} \sum_{k \in \text{BZ}} \varphi_{m,k}(x), \quad (18.13)$$

where, in the thermodynamic limit, the summation over the first Brillouin zone can be replaced by an integration between the zone boundaries $\pm \pi / a$.

18.5 Exercise 17. Spinless Fermions on the lattice

Consider creation and annihilation operators $c_m^+, c_n$, $m, n = 1, \ldots, L$, of spinless Fermions. They satisfy canonical anti-commutation relations

$$\{ c_m, c_n \} = \{ c_m^+, c_n^+ \} = 0, \quad \{ c_m, c_n^+ \} = \delta_{m,n}. \quad (18.14)$$
Let $|0\rangle$ denote the Fock vacuum defined by $c_m|0\rangle = 0$, $m = 1, \ldots, L$. Non-interacting Fermions are described by the Hamiltonian

$$H = \sum_{m,n=1}^{L} t_{mn}^{m} c_{m}^{+} c_{n}^{\cdot}.$$  \hspace{1cm} (18.15)

Here the matrix $t$ with matrix elements $t_{mn}^{m}$ is called the transition matrix. It is Hermitian, $t_{mn}^{*} = t_{nm}^{m}$, by definition.

(i) Show that the canonical anti-commutation relations (18.14) are invariant under transformations of the form

$$\tilde{c}_{k} = \sum_{m=1}^{L} U_{km}^{k} c_{m},$$ \hspace{1cm} (18.16)

if the matrix $U$ with matrix elements $U_{km}^{k}$ is unitary.

(ii) Show that a unitary transformation $U$ exists which transforms the Hamiltonian (18.15) to the form

$$H = \sum_{m=1}^{L} \varepsilon c_{m}^{+} c_{m}.$$ \hspace{1cm} (18.17)

Explain why this transformation solves the eigenvalue problem $H|\psi\rangle = E|\psi\rangle$.

(iii) We say that the transformation in (ii) diagonalizes $H$. Diagonalize the Hamiltonian with transition matrix elements

$$t_{mn}^{m} = -t_{0}(\delta_{m,n+1} + \delta_{m,n-1})$$ \hspace{1cm} (18.18)

explicitly. Here the indices of the right hand side should be understood modulo $L$.

(iv) Also diagonalize the Hamiltonian with transition matrix elements

$$t_{mn}^{m} = \begin{cases} 0 & \text{if } m = n \\ \pi i \sin^{-1} \left( \frac{(m-n)\pi}{L} \right) & \text{else.} \end{cases}$$ \hspace{1cm} (18.19)

Hint: Use the canonical gauge transformation $c_{m} \mapsto e^{i\pi n/2L}c_{n}$ as well as the relation $1/(e^{-i\pi(m-n)/L} - 1) = \frac{1}{L} \sum_{k=0}^{L-1} k e^{-i\pi(m-n)k/L}$. The latter can be proved by differentiating a geometric sum with respect to an appropriate parameter.

L19 The Hubbard model

19.1 Motivation and definition

The formalism of second quantization, in which the Hamiltonian of the electrons takes the form (18.11), gives us a more intuitive access to the problem. If the Fermi surface is located within a single conduction band with band index $\alpha$, say, then the interaction between different bands can be neglected for small excitation energies, and we can suppress the band indices (Greek indices) in (18.11). If, moreover, the ‘intra-atomic Coulomb interaction’
$U_{iii}$ is dominant, then a single effective interaction parameter $U$, say, remains, and $H_{el}$ can be approximated by

$$H = \sum_{i,j} t_{ij} c_{ia}^+ c_{ja} + \frac{U}{2} \sum_i c_{ia}^+ c_{ib} c_{ia}$$

(19.1)

which defines the so-called (one-band) Hubbard model [7, 8].

(i) The Hubbard model is a ‘minimal extension’ of the band model in the sense that as few as possible of the interaction parameters of the full Hamiltonian (18.11) are taken into account.

(ii) In spite of its apparent simplicity the Hubbard model is a true many-body model. In general it is very hard to deal with by any of the means of modern theoretical physics as e.g. perturbation theory, renormalization group analysis, quantum Monte-Carlo methods.

(iii) As simple it is intuitively, the Hubbard model is the starting point for extensions. Basically all models of ‘strongly correlated electrons’ (everything beyond the band model) are extended Hubbard models which are either obtained by taking interaction parameters of wider range into account (e.g. nearest neighbours, next-to-nearest neighbours) or by taking into account a larger number of bands (e.g. two-band Hubbard model, three-band Hubbard model).

(iv) As it stands the Hubbard model is believed to give a realistic description of

- the electronic properties of solids with tight bands
- band magnetism (iron, copper, nickel)
- the interaction-induced metal-insulator transition (Mott transition)

(v) If the Hubbard Hamiltonian is supplied with periodic boundary conditions, the number of lattice sites (which is equal to the number of Wannier orbitals) is finite. As we are also dealing with a finite number of states per site, the model has a finite-dimensional space of states, and can be thought of as a ‘fully regularized’ quantum field theory. Its Hamiltonian can be represented by a finite Hermitian matrix. This makes the Hubbard model attractive for computer based approaches.

(vi) The 1d Hubbard model has the amazing feature of being integrable [10, 12]. Rather much is known about its elementary excitations and its thermodynamics [6].

19.2 Tight-binding approximation

The assumption that the Wannier functions are strongly localized in the vicinity of the ‘lattice sites’ $\mathbf{R}_j$ is compatible with the restriction of the hopping amplitudes $t_{ij}$ to nearest neighbours $\langle ij \rangle$ on the lattice, which is called the ‘tight-binding approximation’. If we introduce the ‘density operators’ (local particle-number operators)

$$n_{i\uparrow} = c_{i\uparrow}^+ c_{i\uparrow}, \quad n_{i\downarrow} = c_{i\downarrow}^+ c_{i\downarrow}$$

(19.2)

and apply the tight-binding approximation to (19.1) we obtain

$$H = -t \sum_{\langle ij \rangle} c_{ia}^+ c_{ja} + U \sum_i n_{i\uparrow} n_{i\downarrow}.$$  (19.3)
Here we have assumed isotropic nearest-neighbour hopping of strength $-t$ and the vanishing of the on-site energies $t_{ii}$, which for a homogeneous model can always be assumed, since in this case it is equivalent to a redefinition of the chemical potential. For the interaction part we have calculated

$$c_{ia}^+ c_{ib}^+ c_{i\uparrow} c_{i\downarrow} + c_{ia}^+ c_{i\uparrow} c_{ib}^+ c_{i\downarrow} = 2n_{i\uparrow} n_{i\downarrow}. \quad (19.4)$$

With the Hamiltonians (19.1) and (19.3) the terminology is not so sharp. The Hamiltonian (19.3) is also called ‘the Hubbard Hamiltonian’. And, in fact, the term Hubbard model most commonly refers to the model described by (19.3).

### 19.3 Interpretation of the Hubbard Hamiltonian

Let us have a closer look at the Hubbard Hamiltonian. For simplicity we consider the one-dimensional model,

$$H = -t \sum_{j=1}^{L} (c_{ja}^+ c_{j+1a} + c_{j+1a}^+ c_{ja}) + U \sum_{j=1}^{L} n_{j\uparrow} n_{j\downarrow}, \quad (19.5)$$

subject to periodic boundary conditions, $c_{L+1a} = c_{1a}$. Its space of states will be denoted $\mathcal{H}^{(L)}$. It is generated by filling electrons into Wannier states. According to the Pauli principle, every Wannier state may be unoccupied, occupied with one electron of spin $\uparrow$ or $\downarrow$, or with two electrons with opposite spins, giving altogether $\dim \mathcal{H}^{(L)} = 4^L$ states.

Let us construct the basis of Wannier states explicitly. For this purpose define the row vectors $x = (x_1, \ldots, x_N)$, $a = (a_1, \ldots, a_N)$, where $x_j \in \{1, \ldots, L\}$, $a_k \in \{\uparrow, \downarrow\}$ for $j, k = 1, \ldots, N$; $N \in \{1, \ldots, 2L\}$. The state

$$|x; a\rangle = c_{x_N,a_N}^+ \cdots c_{x_1,a_1}^+ |0\rangle \quad (19.6)$$

is a Wannier state representing $N$ electrons at sites $x_j$ with spins $a_j$. The set of all different states of this form,

$$B_W = \left\{|x; a\rangle \in \mathcal{H}^{(L)} \mid N = 0, \ldots, 2L, \ x_{j+1} \geq x_j, a_{j+1} > a_j \text{ if } x_{j+1} = x_j \right\}, \quad (19.7)$$

is a basis of Wannier states, since all such states are linear independent and since their number is

$$\sum_{N=0}^{2L} \binom{2L}{N} = 4^L. \quad (19.8)$$

The operators $n_{j,\uparrow}, n_{j,\downarrow}$ are the local particle number operators for electrons of spin $\uparrow$ and $\downarrow$ at site $j$. Let us recall why this name is justified. Using the canonical anti-commutation relations of the Fermi operators and the fact that the $c_{j,a}$ annihilate the Fock vacuum $|0\rangle$ we conclude that

$$[n_{j,\uparrow}, c_{k,b}^+] = \delta_{jk} \delta_{\uparrow b} c_{k,b}^+, \quad n_{j,\uparrow} |0\rangle = 0, \quad (19.9)$$

and therefore

$$n_{j,\uparrow} |x; a\rangle = \sum_{k=1}^{N} \delta_{j,x_k} \delta_{\uparrow, a_k} |x; a\rangle \quad (19.10)$$
and similarly for \( n_{j,\downarrow} \). Thus, \( n_{j,a}|x, a\rangle = |x, a\rangle \), if site \( j \) is occupied by an electron of spin \( a \), and zero elsewise.

A first interpretation of the Hubbard model can be obtained by considering separately the two contributions that make up the Hamiltonian (19.5). For \( t = 0 \) or \( U = 0 \) it can be diagonalized and understood by elementary means. For \( t = 0 \) the Hamiltonian reduces to \( H = UD \), where

\[
D = \sum_{j=1}^{L} n_{j,\uparrow} n_{j,\downarrow} .
\]  

(19.11)

Using (19.10) we can calculate the action of \( D \) on a state \( |x, a\rangle \),

\[
D|x, a\rangle = \sum_{k,l=1}^{N} \delta_{x_k,x_l} \delta_{\uparrow,a_k} \delta_{\downarrow,a_l}|x, a\rangle = \sum_{1 \leq k < l \leq N} \sum_{1 \leq k < l \leq N} \delta_{x_k,x_l} (\delta_{\uparrow,a_k} + \delta_{\downarrow,a_k})|x, a\rangle
\]

(19.12)

Here we used \( \delta_{\uparrow,a_k} \delta_{\downarrow,a_k} = 0 \) in the second equation and the Pauli principle in the third equation. As we learn from (19.12) every state \( |x, a\rangle \) is an eigenstate of the operator \( D \). Thus, \( D \) is diagonal in the Wannier basis. The limit \( t \to 0 \) of the Hubbard Hamiltonian (19.5) is called the atomic limit, because the eigenstate \( |x, a\rangle \) describes electrons localized at the sites \( x_1, \ldots, x_N \), which are identified with the loci of the atomic orbitals the electrons may occupy.

The meaning of the operator \( D \) is evident from equation (19.12). \( D \) counts the number of double-occupied sites in the state \( |x, a\rangle \). The contribution of the term \( U D \) to the energy is non-negative for positive \( U \) and increases with the number of double-occupied sites. This can be viewed as on-site repulsion among the electrons. Negative \( U \) on the other hand, means on-site attraction. Hence, it is natural to refer to \( D \) as to the operator of the on-site interaction.

In the other extreme, when \( U = 0 \), the Hamiltonian (19.5) turns into

\[
H_0 = -t \sum_{j=1}^{L} (c_{j,a}^{+}c_{j+1,a} + c_{j+1,a}^{+}c_{j,a}) .
\]  

(19.13)

This is called the tight-binding Hamiltonian. Like every translation invariant one-body Hamiltonian it can be diagonalized by discrete Fourier transformation. Let us define

\[
c_{k,a}^{+} = \frac{1}{\sqrt{L}} \sum_{j=1}^{L} e^{i\phi kj} c_{j,a}^{+}, \quad k = 0, \ldots, L - 1,
\]

(19.14)

where \( \phi = 2\pi/L \). Then, by Fourier inversion

\[
c_{j,a}^{+} = \frac{1}{\sqrt{L}} \sum_{k=0}^{L-1} e^{-i\phi jk} c_{k,a}^{+}, \quad j = 1, \ldots, L.
\]

(19.15)
Equation (19.15) is readily verified by inserting (19.14) into the right hand side and using the geometric sum formula. Clearly, \( \tilde{c}_{k+L,a} = \tilde{c}_{k,a} \). Insertion of (19.15) into (19.13) leads to

\[
H_0 = -2t \sum_{k=0}^{L-1} \sum_{a=\uparrow,\downarrow} \cos(\phi k) \tilde{n}_{k,a},
\]

(19.16)

where \( \tilde{n}_{k,a} = \tilde{c}^+_k a \tilde{c}_{k,a} \).

The Fourier transformation leaves the canonical anti-commutation relations invariant,

\[
\{ \tilde{c}_{j,a}, \tilde{c}_{k,b} \} = \{ \tilde{c}^+_j a, \tilde{c}^+_k b \} = 0, \quad (19.17a)
\]

\[
\{ \tilde{c}_{j,a}, \tilde{c}^+_k b \} = \delta_{jk} \delta_{ab}. \quad (19.17b)
\]

A transformation with this property is called canonical. Applying (19.14) to the empty lattice state \( |0\rangle \) (the Fock vacuum), we obtain

\[
\tilde{c}_{k,a} |0\rangle = 0, \quad k = 0, \ldots, L - 1, \quad a = \uparrow, \downarrow. \quad (19.18)
\]

Thus, acting with the creation operators \( \tilde{c}^+_k a \) on the empty lattice state \( |0\rangle \) we obtain an alternative basis \( B_B \). Let us introduce the row vectors \( \mathbf{q} = (q_1, \ldots, q_N) = (k_1, \ldots, k_N) \phi \) and the states

\[
|\mathbf{q}, a\rangle = \tilde{c}^+_{k_N,a_N} \cdots \tilde{c}^+_{k_1,a_1} |0\rangle. \quad (19.19)
\]

It can be shown that these states are eigenstates of a lattice momentum operator with eigenvalue \( \sum_{j=1}^{N} q_j \) mod \( 2\pi \). The set

\[
B_B = \left\{ |\mathbf{q}, a\rangle \in \mathfrak{T}^2(L) \left| N = 0, \ldots, 2L, q_{j+1} \geq q_j, a_{j+1} > a_j \text{ if } q_{j+1} = q_j \right. \right\} \quad (19.20)
\]

is a basis of \( \mathfrak{T}^2(L) \). This basis is sometimes called the Bloch basis. Electrons in Bloch states \( |\mathbf{q}, a\rangle \) are delocalized, but have definite momenta \( q_1, \ldots, q_N \).

By virtue of (19.17), the analogues of (19.9) and (19.10) are satisfied by \( \tilde{n}_{j,a} \) and \( \tilde{c}^+_k b \).

It follows that

\[
H_0|\mathbf{q}, a\rangle = -2t \sum_{j=1}^{N} \cos(q_j) |\mathbf{q}, a\rangle. \quad (19.21)
\]

Thus, the tight-binding Hamiltonian \( H_0 \) is diagonal in the Bloch basis. It describes non-interacting band electrons in a cosine-shaped band of width \( 4t \).

The tight-binding Hamiltonian \( H_0 \) and the operator \( D \) which counts the number of double-occupied sites do not commute. Therefore the Hubbard Hamiltonian can neither be diagonal in the Bloch basis nor in the Wannier basis. The physics of the Hubbard model may be understood as arising from the competition between the two contributions, \( H_0 \) and \( D \), to the Hamiltonian (19.5). The tight-binding contribution \( H_0 \) prefers to delocalize the electrons, while the on-site interaction \( D \) favours localization. The ratio

\[
u = \frac{U}{4t} \quad (19.22)
\]

is a measure for the relative contribution of both terms and is the intrinsic, dimensionless coupling constant of the Hubbard model.
19.4 Exercise 18. Peierls phases

If interacting electrons (charge $-e$, mass $m$) in a periodic potential $V(x)$ are exposed to an external electro-magnetic field, their one-particle Hamiltonian becomes

$$h = \frac{1}{2m} \left\| \mathbf{p} + \frac{e}{c} \mathbf{A}(x, t) \right\|^2 + V(x) - e\phi(x, t),$$

(19.23)

where $\mathbf{A}(x, t)$ and $\phi(x, t)$ are the vector and scalar potentials of the external field. In the lecture we considered the many-body Hamiltonian generated by $h$ relative to the Wannier basis. It was parameterized by hopping matrix elements $t_{jk}$. Here we would like to find out how the external field modifies the $t_{jk}$.

We start by fixing the gauge such that $\phi(x, t) = 0$.

(i) Let $\lambda(x, t)$ an arbitrary differentiable function. Using that $p^k = -i\partial^k$ verify the commutator relation

$$[p^k, e^{-ie\lambda(x,t)/c}] = -\frac{e}{c} \frac{\partial \lambda(x, t)}{\partial x_k} e^{-ie\lambda(x,t)/c}.$$  

(19.24)

(ii) Denote by $\phi(x - \mathbf{R}_j)$ the Wannier orbital at site $\mathbf{R}_j$ and recall that the hopping matrix elements for vanishing external fields were

$$t_{ij} = \int d^3x \phi^*(x - \mathbf{R}_i) \left[ \frac{\|p\|^2}{2m} + V(x) \right] \phi(x - \mathbf{R}_j).$$

(19.25)

Show that in the presence of the external field this has to be modified to become

$$t_{ij} = \int d^3x \phi^*(x - \mathbf{R}_i) e^{-ie\lambda/c} \left[ \frac{1}{2m} \left\{ p^k + \frac{e}{c} \left( A^k - \frac{\partial \lambda}{\partial x_k} \right) \right\} \right]^2 + V(x) \phi(x - \mathbf{R}_j),$$

(19.26)

where $\lambda$ is still arbitrary.

(iii) Choosing now

$$\lambda(x, t) = \int x_0 d\mathbf{y} A^k(y, t)$$

(19.27)

for an arbitrary fixed point $x_0$ and redefining $\bar{\phi}(x - \mathbf{R}_j) = e^{ie\lambda(x,t)/c} \phi(x - \mathbf{R}_j)$ we obtain

$$t_{ij} = \int d^3x \bar{\phi}^*(x - \mathbf{R}_i) \left[ \frac{\|p\|^2}{2m} + V(x) \right] \bar{\phi}(x - \mathbf{R}_j).$$

(19.28)

Discuss under which conditions the approximation $\bar{\phi}(x - \mathbf{R}_j) \approx e^{ie\lambda(x_0,t)/c} \phi(x - \mathbf{R}_j)$, the so-called Peierls substitution, should be valid.

(iv) Show that the Peierls substitution leads to a modification of the hopping part of the many body Hamiltonian according to the rule $t_{ij} \rightarrow t_{ij} e^{i\lambda_{ij}}$, where

$$\lambda_{ij} = \frac{e}{c} \int_{\mathbf{R}_i}^{\mathbf{R}_j} d\mathbf{y} A^k(y, t).$$

(19.29)
L20 The strong-coupling limit

In this lecture we shall consider the limiting case, when the intra-atomic Coulomb interaction $U$ of the Hubbard model is large compared to the band width $t$. We define

$$T = \sum_{j,k=1}^{L} t_{jk} c_{j,a}^{+} c_{k,a}.$$  \hspace{1cm} (20.1)

Here we only assume that $t_{jk} = t_{kj}^{*}$, guaranteeing Hermiticity of $T$, and that $t_{jj} = 0$. For fixed particle number the latter setting merely shifts the energy scale and, for this reason, does not imply any restriction to generality. As we shall see, however, this assumption will have several technical advantages in the calculations below.

Using an appropriate definition of the $t_{jk}$ and an appropriate enumeration of the lattice sites in (20.1), we may write the general Hubbard Hamiltonian (19.1) on any finite lattice, under any kind of boundary conditions and in any dimension in the form

$$H = T + UD.$$  \hspace{1cm} (20.2)

We shall assume that $U > 0$. This is natural, since positive $U$ corresponds to the repulsion of electrons in the same Wannier orbital which is expected as a consequence of their mutual Coulomb repulsion. If $|t_{jk}| \ll U$ we can consider $T$ as a small perturbation of $UD$. As we have seen in (19.12), $D$ counts the number of double-occupied sites. Thus, the eigenvalues of $UD$ are 0, $U$, $2U$, ..., $LU$. Their number grows linearly with $L$, while the number of states in $\mathcal{H}(L)$ grows exponentially like $4^L$. The eigenvalues of $UD$ are therefore highly degenerate. Let us denote the projection operators onto the corresponding eigenspaces $\mathcal{H}_n$ by $P_n$, $n = 0, 1, \ldots, L$. Then

$$\mathcal{H}(L) = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \cdots \oplus \mathcal{H}_L,$$  \hspace{1cm} (20.3)

and $D$ has the spectral decomposition

$$D = \sum_{n=0}^{L} n P_n.$$  \hspace{1cm} (20.4)

If the particle number $N \leq L$, then the ground states of $UD$ are in $\mathcal{H}_0$ which has $\dim \mathcal{H}_0 = 3^L$.

20.1 Degenerate perturbation theory – a reminder

Consider a Hamiltonian $H + \lambda V$ on a Hilbert space $\mathcal{H}$. Assume that $H$ has the spectral decomposition

$$H = \sum_{n} E_n P_n$$  \hspace{1cm} (20.5)

with mutually distinct eigenvalues $E_n$ and orthogonal projectors $P_n$ (i.e. $P_n P_m = \delta_{nm} P_n$), such that $\dim P_n \mathcal{H}$ is not necessarily equal to one. We consider $\lambda V$, $\lambda \in \mathbb{R}$, as a small perturbation of ‘strength $\lambda$’.

Define

$$R_n = \sum_{m,m \neq n} \frac{P_m}{E_n - E_m}.$$  \hspace{1cm} (20.6)
We assume that the eigenvalues and eigenvectors of the perturbed Hamiltonian $H + \lambda V$ are characterized by the quantum numbers $n$ of the unperturbed problem and sets of additional quantum numbers $\nu_n \in \{1, \ldots, \dim P_n H\}$. In other words

$$\left( H + \lambda V \right) |\Psi_{n, \nu_n}\rangle = \epsilon_{n, \nu_n} |\Psi_{n, \nu_n}\rangle$$

(20.7)

in such a way that

$$\lim_{\lambda \to 0} |\Psi_{n, \nu_n}\rangle = |\Psi^{(0)}_{n, \nu_n}\rangle \in P_n H, \quad \lim_{\lambda \to 0} \epsilon_{n, \nu_n} = E_n.$$  

(20.8)

We rewrite (20.7) in the form

$$\left( E_n - H \right) |\Psi_{n, \nu_n}\rangle = \left( \lambda V - \left( \epsilon_{n, \nu_n} - E_n \right) \right) |\Psi_{n, \nu_n}\rangle.$$  

(20.9)

Then

$$R_n \left( E_n - H \right) |\Psi_{n, \nu_n}\rangle = \left( 1 - P_n \right) |\Psi_{n, \nu_n}\rangle = R_n \left( \lambda V - \Delta_{n, \nu_n} \right) |\Psi_{n, \nu_n}\rangle,$$

$$\Leftrightarrow \quad |\Psi_{n, \nu_n}\rangle = P_n |\Psi_{n, \nu_n}\rangle + R_n \left( \lambda V - \Delta_{n, \nu_n} \right) |\Psi_{n, \nu_n}\rangle,$$

$$\Leftrightarrow \quad |\Psi_{n, \nu_n}\rangle = \sum_{k=0}^{\infty} \left[ R_n \left( \lambda V - \Delta_{n, \nu_n} \right) \right]^k |\varphi_{n, \nu_n}\rangle.$$  

(20.10)

Here the series converges if $\mathcal{H}$ is finite dimensional and $|\lambda|$ is small enough. Otherwise we may have to interpret it as an asymptotic series. Applying, on the other hand, $P_n$ to (20.9) we obtain

$$P_n V |\Psi_{n, \nu_n}\rangle = \frac{\Delta_{n, \nu_n}}{\lambda} |\varphi_{n, \nu_n}\rangle.$$  

(20.11)

Thus,

$$\sum_{k=0}^{\infty} P_n V \left[ R_n \left( \lambda V - \Delta_{n, \nu_n} \right) \right]^k |\varphi_{n, \nu_n}\rangle = \frac{\Delta_{n, \nu_n}}{\lambda} |\varphi_{n, \nu_n}\rangle.$$  

(20.12)

This is a non-linear spectral problem on $P_n \mathcal{H}$ describing the splitting of the energy level $E_n$ under the influence of the perturbation $\lambda V$. The operator on the left hand side is an effective Hamiltonian on $P_n \mathcal{H}$. Up to second order ($\Delta_{n, \nu_n} = \lambda \Delta^{(1)}_{n, \nu_n} + \lambda^2 \Delta^{(2)}_{n, \nu_n} + \ldots$) it is given by

$$H_2 = P_n V P_n + P_n V R_n \left( \lambda V - \Delta_{n, \nu_n} \right) P_n = P_n V P_n + \lambda P_n V R_n V P_n$$

$$= P_n V P_n + \lambda \sum_{m, m \neq n} \frac{P_n V P_m V P_n}{E_n - E_m}.$$  

(20.13)

Thus, up to second order in $\lambda$ equation (20.12) reduces to a linear spectral problem with an effective Hamiltonian $H_2$.

**Remark.** The corresponding eigenstates of the perturbed problem are obtained from (20.10), once the $|\varphi_{n, \nu_n}\rangle$ are known.
20.2 Application to the Hubbard model at strong coupling

We now apply (20.13) to (20.2). For this purpose we divide by $U$. Then $H/U = D + T/U$. Recall that $D$ has eigenvalues $0, 1, \ldots, L$. Inserting this for $n = 0$ with $V = T, \lambda = 1/U$ into (20.13) we obtain

$$H_2 = P_0 T P_0 - \frac{1}{U} \sum_{m=1}^{L} \frac{P_0 T P_m T P_0}{m}. \tag{20.14}$$

20.3 Explicit form of the projection operators

In order to express the projection operators $P_m$ in terms of Fermi operators, we introduce the function

$$G(\alpha) = \prod_{j=1}^{L} (1 - \alpha n_{j\uparrow} n_{j\downarrow}). \tag{20.15}$$

Its action on the Wannier basis is (see (19.10))

$$G(\alpha) |x; a\rangle = (1 - \alpha^n) |x; a\rangle, \tag{20.16}$$

where $n$ is the number of double-occupied sites in $|x; a\rangle$. In particular,

$$G(1) = \prod_{j=1}^{L} (1 - n_{j\uparrow} n_{j\downarrow}) = P_0. \tag{20.17}$$

Moreover,

$$\frac{(-1)^k}{k!} \partial_\alpha^k G(\alpha) \bigg|_{\alpha=1} |x; a\rangle = |x; a\rangle \begin{cases} \binom{n}{k} (1 - \alpha)^{n-k} |x; a\rangle & k \leq n \\ 0 & k > n \end{cases} = \delta_{n,k} |x; a\rangle. \tag{20.18}$$

It follows that

$$P_n = \frac{(-1)^n}{n!} \partial_\alpha^n G(\alpha) \bigg|_{\alpha=1}, \tag{20.19}$$

meaning that $G(\alpha)$ is a generating function for the projection operators $P_n, n = 0, 1, \ldots, L$.

20.4 Application to $H_2$

We will now use the explicit construction of the projection operators to express $H_2$ in terms of Fermions. First of all

$$P_0 n_{j\uparrow} n_{j\downarrow} = \prod_{k=1}^{L} (1 - n_{k\uparrow} n_{k\downarrow}) n_{j\uparrow} n_{j\downarrow} = 0 = n_{j\uparrow} n_{j\downarrow} P_0, \tag{20.20}$$

entailing that

$$G(\alpha) T P_0 = \sum_{j,k=1}^{L} t_{jk} \left[ \prod_{\ell=1}^{L} (1 - \alpha n_{\ell\uparrow} n_{\ell\downarrow}) \right] c_{j,a}^{\dagger} c_{k,a} P_0$$

$$= \sum_{j,k=1}^{L} t_{jk} (1 - \alpha n_{j\uparrow} n_{j\downarrow}) c_{j,a}^{\dagger} c_{k,a} P_0, \tag{20.21}$$
and further, using (20.18),

$$\sum_{m=1}^{L} \frac{P_m T P_0}{m} = \sum_{j,k=1}^{L} t_{j,k} n_{j\uparrow} n_{j\downarrow} c_{\uparrow, j,a}^+ c_{\downarrow, k,a} P_0 .$$  \hfill (20.22)

Using the latter equation in (20.14) we arrive at

$$H_2 = P_0 \left\{ \sum_{j,k=1}^{L} t_{j,k} c_{\uparrow, j,a}^+ c_{\downarrow, k,a} - \frac{1}{U} \sum_{j,k',\ell=1}^{L} t_{j,k'} t_{k\ell} c_{\uparrow, j,a}^+ c_{\downarrow, k,a} n_{k\uparrow} n_{k\downarrow} c_{\uparrow, k',\ell}^+ c_{\downarrow, \ell,b} \right\} P_0$$

$$= P_0 \left\{ \sum_{j,k=1}^{L} t_{j,k} c_{\uparrow, j,a}^+ c_{\downarrow, k,a} - \frac{1}{U} \sum_{j,k',\ell=1}^{L} t_{j,k'} t_{k\ell} c_{\uparrow, j,a}^+ c_{\downarrow, k,a} n_{k\uparrow} n_{k\downarrow} c_{\uparrow, k',\ell}^+ c_{\downarrow, \ell,b} \right\} P_0 .$$  \hfill (20.23)

Here we have used (20.20) and the fact that $t_{jj} = 0$ in the second equation.

$H_2$ is an effective Hamiltonian describing the splitting of the lowest level ($n = 0$) of $D$ under the influence of the perturbation by $T$. Sometimes $H_2$ is called ‘the $t$-$J$ Hamiltonian’.

Using the canonical anti-commutation relations of the Fermi operators equation (20.23) can be further simplified. After a straightforward but slightly cumbersome calculation we obtain

$$H_2 = \sum_{j,k=1}^{L} \left\{ t_{j,k} c_{\uparrow, j,a}^+ c_{\downarrow, k,a} (1 - n_j) + \frac{2|t_{j,k}|^2}{U} \left( S_{\uparrow, j}^\alpha S_{\downarrow, k}^\alpha - \frac{n_{j\uparrow} n_{j\downarrow}}{4} \right) \right\}$$

$$- \frac{1}{U} \sum_{j,k,\ell=1}^{L} t_{j,k} t_{k\ell} n_{k\uparrow} n_{k\downarrow} c_{\uparrow, j,a}^+ c_{\downarrow, k,a} c_{\uparrow, k',\ell}^+ c_{\downarrow, \ell,b} (1 - n_j) .$$  \hfill (20.24)

Note that the Hamiltonian leaves the space $\mathcal{H}_0$ invariant by construction. In (20.24) we have introduced the notation

$$n_j = n_{j\uparrow} + n_{j\downarrow} ,$$  \hfill (20.25a)

$$S_{\uparrow, j}^\alpha = \frac{1}{2} \sum_{a, b=\uparrow, \downarrow} (\sigma^\alpha)^a_b c_{\uparrow, j,a}^+ c_{\downarrow, j,b} , \quad \alpha = x, y, z ,$$  \hfill (20.25b)

for the particle density and spin density operators. The matrices $\sigma^\alpha$ are the well-known Pauli matrices.

**20.5 Exercise 19. Strong coupling limit of the Hubbard model**

Obtain (20.24) from (20.23)!

**L21 Heisenberg model and Mott transition**

**21.1 Heisenberg Hamiltonian in the language of Fermi operators**

In the previous lecture we have derived the strong coupling Hamiltonian $H_2$ by considering the ‘hopping’ $T$ as small perturbation to the atomic limit $UD$ of the Hubbard Hamiltonian.
on the subspace \( \mathcal{H}_0 \subset \mathcal{H}^{(L)} \) with no double-occupied sites. The particle number operator on \( \mathcal{H}^{(L)} \) is
\[
\hat{N} = \sum_{j=1}^{L} n_j.
\] (21.1)
Since \([\hat{N}, P_n] = [\hat{N}, T] = 0\) we see from (20.14) that \( H_2 \) preserves the particle number, 
\([\hat{N}, H_2] = 0\). This implies that \( H_2 \) leaves the subspaces \( \mathcal{H}_{0,N} \subset \mathcal{H}_0, N = 0, \ldots, L, \) of
fixed particle numbers \( N \) invariant. The case \( N = L \) is called the case of ‘half-filling’. The corresponding subspace \( \mathcal{H}_{0,L} \) is spanned by all states of the form
\[
|a\rangle_s = c_{L,a_L}^+ c_{L-1,a_{L-1}}^+ \cdots c_{1,a_1}^+ |0\rangle.
\] (21.2)
These are states for which every site is occupied by exactly one electron. Thus,
\[
(1 - n_j)|a\rangle_s = 0
\] (21.3)
for \( j = 1, \ldots, L \) and for all \( |a\rangle_s \in \mathcal{H}_{0,L} \).

Hence, we can conclude with (20.24) and (21.3) that the action of \( H_2 \) on the space \( \mathcal{H}_{0,L} \) reduces to the action of the Hamiltonian
\[
H_{\text{spin}} = \sum_{j,k=1}^{L} \frac{2|t_{jk}|^2}{U} \left( S_j^\alpha S_k^\alpha - \frac{1}{4} \right)
\] (21.4)
which is called the (isotropic) Heisenberg Hamiltonian with exchange integrals
\[
J_{jk} = \frac{2|t_{jk}|^2}{U}.
\] (21.5)
If we start from the Hubbard model with nearest-neighbour hopping
\[
t_{jk} = \begin{cases} -t & \text{for nearest-neighbour sites} \\ 0 & \text{else} \end{cases},
\] (21.6)
the resulting ‘spin Hamiltonian’ at half-filling is
\[
H_{\text{spin}} = J \sum_{(j,k)} \left( S_j^\alpha S_k^\alpha - \frac{1}{4} \right), \quad \text{where } J = \frac{2t^2}{U}.
\] (21.7)
This is called the Heisenberg-Hamiltonian with nearest-neighbour exchange interaction. The Heisenberg model is the model for the antiferromagnetism of insulators (which is ubiquitous in nature).

### 21.2 Heisenberg model in the language of spin operators

The space \( \mathcal{H}_{0,L} \), spanned by the states \( |a\rangle_s \) with \( a_j \in \{\uparrow, \downarrow\}, j = 1, \ldots, L, \) is \( 2^L \) dimensional, hence isomorphic to \((\mathbb{C}^2)^{\otimes L}\). This makes it possible to describe the action of \( H_{\text{spin}} \) directly by certain matrices acting on \((\mathbb{C}^2)^{\otimes L}\).

The vectors space \((\mathbb{C}^2)^{\otimes L}\) has the canonical basis vectors
\[
|a\rangle = e_{a_1} \otimes \cdots \otimes e_{a_L}, \quad e_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad e_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.
\] (21.8)
We would like to identify these vectors with the vectors $|\mathbf{a}\rangle$. Then, on the one hand,

$$S^a_j|\mathbf{a}\rangle_s = \frac{1}{2}(\sigma^a)_b c_{L,a}^+ \cdots c_{j+1,a}^+ c_{j,a}^+ c_{j,b}^+ \cdots c_{1,a}^+ |0\rangle = c_{j,a}^+ c_{j,a} + \delta_{j,a} c_{j,a}^+$$

$$= \frac{1}{2}(\sigma^a)_{a_j}((a_1, \ldots, a_{j-1}, a, a_{j+1}, \ldots, a_L))_s, \quad (21.9)$$

while, on the other hand,

$$\frac{1}{2}(\sigma^a)_{a_j}|(a_1, \ldots, a_{j-1}, a, a_{j+1}, \ldots, a_L)\rangle = \frac{1}{2} e_{a_1} \otimes \cdots \otimes e_{a_{j-1}} \otimes (\sigma^a)_{a_j} e_a \otimes e_{a_{j+1}} \otimes \cdots e_{a_L}$$

$$= \frac{1}{2}(I_2^{\otimes (j-1)} \otimes \sigma^a \otimes I_2^{\otimes (L-j)}) |\mathbf{a}\rangle. \quad (21.10)$$

Thus, the isomorphism $\mathcal{H}_{0,L} \cong (\mathbb{C}^2)^{\otimes L}$ induces the identification of operators

$$\frac{1}{2} I_2^{\otimes (j-1)} \otimes \sigma^a \otimes I_2^{\otimes (L-j)} \mapsto \frac{1}{2}(\sigma^a)_b c_{j,b}^+. \quad (21.11)$$

Since the operators $\sigma^a$, $a = x, y, z$, and $I_2$ form a basis of $\text{End}(\mathbb{C}^2)$, the operators $S^a_j, j = 1, \ldots, L$, as defined in (21.10), together with the identity, generate a basis of $\text{End}(\mathbb{C}^2)^{\otimes L}$. With the identification (21.11) we can interpret the Heisenberg model on ‘spin space’ $(\mathbb{C}^2)^{\otimes L}$ with Hamiltonian (21.7), where now the $S^a_j$ are the spin matrices defined in (21.10).

**Remark.** Such an identification is not possible for the $t$-$J$ model. The operator $H_2$ acts on $\mathcal{H}_0$ which contains $\mathcal{H}_{0,L}$ as a proper subspace. We have e.g. $S^a_j |0\rangle = 0$ (where $|0\rangle$ is the vacuum for Fermions).

### 21.3 Interpretation of the exchange interaction

Define

$$P = \frac{1}{2}(1 + \sigma^a \otimes \sigma^a) = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \quad (21.12)$$

Then

$$Px \otimes y = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} x_1 y_1 \\ x_1 y_2 \\ x_2 y_1 \\ x_2 y_2 \end{pmatrix} = y \otimes x. \quad (21.13)$$

This means that $P$ is a permutation (transposition) matrix. In particular,

$$P|\uparrow\downarrow\rangle = |\downarrow\uparrow\rangle. \quad (21.14)$$
Define ‘symmetrizer’ and ‘antisymmetrizer’

\[ P^\pm = \frac{1}{2} (P \pm 1). \]  

(21.15)

They satisfy

\[ (P^\pm)^2 = \frac{1}{4} (P \pm 1)^2 = \frac{1}{2} (1 \pm P) = \pm P^\pm, \]  

(21.16a)

\[ P^+ P^- = P^- P^+ = 0. \]  

(21.16b)

This means that \( \pm P^\pm \) are orthogonal projectors onto the symmetric and antisymmetric subspaces of \( \mathbb{C}^2 \otimes \mathbb{C}^2 \). The subspace \( P^+ \mathbb{C}^2 \otimes \mathbb{C}^2 \) has a basis

\[ B_t = \{ |1,1\rangle = |↑↑\rangle, \ |1,0\rangle = \frac{1}{\sqrt{2}} (|↑↓\rangle + |↓↑\rangle), \ |1,-1\rangle = |↓↓\rangle \}, \]  

(21.17)

while the 1d subspace \( P^- \mathbb{C}^2 \otimes \mathbb{C}^2 \) is generated by

\[ B_s = \{ |0,0\rangle = \frac{1}{\sqrt{2}} (|↑↓\rangle - |↓↑\rangle) \}. \]  

(21.18)

These bases are called ‘spin triplet’ and ‘spin singlet’.

Comparing (21.12), (21.15) and (21.7) we see that for \( L = 2 \)

\[ H_{\text{spin}} = JP^- . \]  

(21.19)

It follows that \( H_{\text{spin}} \) has eigenvalue 0, \(-J\). The corresponding eigenvectors are \( |1, s\rangle \), \( s = 0, \pm 1 \), and \( |0,0\rangle \). If \( J > 0 \), then the singlet \( |0,0\rangle \) is the ground state. This is called antiferromagnetism, since

\[ \sigma^z \otimes \sigma^z |0,0\rangle = -|0,0\rangle, \Rightarrow \langle 0,0|\sigma^z \otimes \sigma^z |0,0\rangle = -1. \]  

(21.20)

One says that the ground state has antiferromagnetic correlations.

In the general case

\[ H_{\text{spin}} = J \sum_{\langle jk \rangle} P^-_{jk} \]  

(21.21)

is a sum of projectors onto ‘local singlets’. An antiferromagnet \((J > 0)\) may therefore be characterized as a system which prefers local singlets. By contrast, a ferromagnet \((J < 0)\) prefers triplets. Local singlets are incompatible with the global \( SU(2) \) invariance of the Hamiltonian. For this reason the ground state of a macroscopic Heisenberg antiferromagnet is a complicated ‘many-body state’. On the other hand, the state

\[ |↑ \ldots ↑\rangle = e_{↑}^{\otimes L} \]  

(21.22)

may be seen as a tensor product of states from local triplets. It is annihilated by \( H_{\text{spin}} \) and is one of its ground states in the ferromagnetic case. The full ground state subspace can be constructed using the global \( SU(2) \) symmetry.
21.4 Mott transition

In an external electromagnetic field the hopping term in the Hubbard Hamiltonian is modified by so-called Peierls phases

\[ t_{jk} \rightarrow t_{jk} e^{i\lambda_{jk}}, \quad \lambda_{jk} \in \mathbb{R}. \] (21.23)

(cf. section 19.4). The Hubbard interaction \( U \), on the other hand remains, unchanged. It follows that the corresponding Heisenberg model (strong-coupling limit at half-filling) is not modified, since it depends only on \( |t_{jk}|^2 \). In other words, to leading order perturbation theory the Hubbard model at half-filling does not couple to an external field. The system is an insulator, although it has an odd number of electrons per unit cell, and therefore is a conductor at \( U = 0 \). This suggests that there might be an interaction induced metal-insulator transition (‘Mott transition’) somewhere in between, at a finite value \( U_c \) of the interaction. It is believed that such a transition occurs indeed in any spatial dimension. A proof only exists in \( d = 1 \), where \( U_c = 0 \).

21.5 Exercise 20: A short XXX chain

Consider the periodic Heisenberg Hamiltonian (XXX model) on a four-site 1d lattice

\[ H = P_{12} + P_{23} + P_{34} + P_{41}. \] (21.24)

Here \( P_{jk} \) is the transposition, interchanging spin states on sites \( j \) and \( k \) of the chain. Recall that the space of states of the model is the tensor product \( \mathcal{H} = \mathbb{C}^2 \otimes \mathbb{C}^2 \otimes \mathbb{C}^2 \otimes \mathbb{C}^2 \). The vectors \( e_\uparrow = (1, 0) \) and \( e_\downarrow = (0, 1) \) form a basis of \( \mathbb{C}^2 \). Hence,

\[ \mathcal{B} = \left\{ (a_1 a_2 a_3 a_4) = e_{a_1} \otimes e_{a_2} \otimes e_{a_3} \otimes e_{a_4} \in \mathcal{H} \mid a_1, a_2, a_3, a_4 = \uparrow, \downarrow \right\} \] (21.25)

is a basis of \( \mathcal{H} \).

Denote the embeddings of the Pauli matrices into \( \text{End}(\mathcal{H}) \) by \( \sigma_j^\alpha \), \( j = 1,2,3,4 \), \( \alpha = x,y,z \). Then the transpositions can be expressed as

\[ P_{jk} = \frac{1}{2}(\text{id} + \sigma_j^\alpha \sigma_k^\alpha). \] (21.26)

The operator of the total spin has components \( S^\alpha = \frac{1}{2}(\sigma_1^\alpha + \sigma_2^\alpha + \sigma_3^\alpha + \sigma_4^\alpha) \) which can be used to define the ladder operators \( S^\pm = S^x \pm iS^y \). The shift operator for the chain of length four is defined as

\[ \hat{U} = P_{12} P_{23} P_{34}. \] (21.27)

(i) Show that the operators \( H, S^2, S^z \) and \( \hat{U} \) can be simultaneously diagonalized. For this purpose verify the commutation relations

\[ [H, S^\alpha] = [\hat{U}, S^\alpha] = [H, \hat{U}] = 0, \quad [S^\alpha, S^\beta] = i\varepsilon^{\alpha\beta\gamma} S^\gamma \] (21.28)

for \( \alpha, \beta = x,y,z \).

(ii) Construct a basis of common eigenvectors and obtain the corresponding eigenvalues of the above operators. Sketch the spectrum of \( H \). Hint: Use, for instance, that \( \hat{U}^4 = \text{id} \), and use the angular momentum algebra.
L22 Linear response theory

In this lecture we study the response of a quantum many-body system, in thermal equilibrium with a heat bath of temperature $T$, to a small external perturbation. A solid is responding, for instance, with a current to an external voltage, with a thermal current to a temperature gradient, or with a deformation to external mechanic stress. An example which will be considered in some detail is the absorption of microwaves by a spin system in a homogeneous magnetic field (ESR experiment). This will allow us to take a glimpse at our own work [4, 15].

22.1 Time evolution of the statistical operator

Consider a quantum system with Hamiltonian $H$ possessing a discrete spectrum $(E_n)_{n=0}^{\infty}$ with corresponding eigenstates $\{|n\ran\}_{n=0}^{\infty}$. At time $t_0$ a time-dependent perturbation $V(t)$ is adiabatically switched on. We are interested in the time evolution of the system, assuming it initially, at times $t<t_0$, in an equilibrium state described by the statistical operator

$$\rho_0 = \frac{1}{Z} \sum_{n=0}^{\infty} e^{-\frac{E_n}{T}} |n\ran \lan n|$$

(22.1)

of the canonical ensemble. Here $T$ denotes the temperature and $Z$ the canonical partition function.

Let $U(t)$ the time evolution operator of the perturbed system. It satisfies the Schrödinger equation

$$i\partial_t U(t) = (H + V(t)) U(t)$$

(22.2)

with initial condition $U(t_0) = \text{id}$ (note that we have set $\hbar = 1$ as before). Under the influence of the perturbation the eigenstate state $|n\ran$ evolves into $|n,t\ran = U(t) |n\ran$, and the statistical operator at time $t$ becomes

$$\rho(t) = \frac{1}{Z} \sum_{n=0}^{\infty} e^{-\frac{E_n}{T}} |n,t\ran \lan n,t| = U(t) \rho_0 U^{-1}(t).$$

(22.3)

We are interested in an approximation to $\rho(t)$ linear in the strength of the perturbation $V(t)$. In order to derive this approximation we define

$$R(t) = e^{iHt} (\rho(t) - \rho_0) e^{-iHt},$$

(22.4a)

$$W(t) = e^{iHt} V(t) e^{-iHt}.$$  

(22.4b)

Then

$$i\partial_t R(t) = i\partial_t e^{iHt} U(t) \rho_0 (e^{iHt} U(t))^{-1}$$

$$= [W(t), e^{iHt} \rho(t) e^{-iHt}] = [W(t), R(t) + \rho_0].$$

(22.5)

Since $R(t_0) = 0$ by construction, we obtain

$$R(t) = -i \int_{t_0}^{t} dt' [W(t'), R(t') + \rho_0].$$

(22.6)
This Volterra equation is an appropriate starting point for a perturbation theory. Assuming \(|W(t)|\) to be small we conclude that

\[
R(t) = -i \int_{t_0}^{t} dt' [W(t'), \rho_0] + O(|W|^2),
\]

and therefore, to lowest order in \(W\),

\[
\rho(t) = \rho_0 - \frac{i e^{-iHt}}{\hbar} \int_{t_0}^{t} dt' [W(t'), \rho(t_0)] e^{iHt}.
\]

This is the statistical operator in so-called Born approximation. In the following \(t_0\) will be sent to \(-\infty\).

22.2 Time evolution of expectation values

Using (22.8) we can calculate the time evolution of the expectation value of an operator \(A\) under the influence of the perturbation. We shall denote the canonical ensemble average by \(\langle \cdot \rangle_T = \text{tr} \{ \rho_0 \cdot \}\) and write \(A(t) = e^{iHt} A e^{-iHt}\) for the Heisenberg time evolution of \(A\). Then

\[
\delta \langle A \rangle_T = \text{tr} \{ (\rho(t) - \rho_0) A \} = -i \int_{-\infty}^{t} dt' \text{tr} \{ [W(t'), \rho_0] e^{iHt} A e^{-iHt} \}
\]

\[
= -i \int_{-\infty}^{t} dt' \langle [A(t), W(t')] \rangle_T = -i \int_{-\infty}^{t} dt' \langle [A(t - t'), V(t')] \rangle_T.
\]

Here we have used the cyclic invariance of the trace in the third equation and the fact that \(H\) commutes with \(\rho_0\) in the fourth equation.

A typical example of a perturbation, which will be relevant for our discussion below, is a classical time-dependent field \(h^\alpha(t)\) coupling linearly to operators \(X^\alpha\),

\[
V(t) = h^\alpha(t) X^\alpha.
\]

In this case

\[
\delta \langle A \rangle_T = -i \int_{-\infty}^{t} dt' h^\alpha(t') \langle [A(t - t'), X^\alpha] \rangle_T.
\]

22.3 Absorption of energy

The absorbed energy per unit time is

\[
\frac{dE}{dt} = \frac{d}{dt} \text{tr} \{ \rho(t)(H + V(t)) \}
\]

\[
= -i \text{tr} \{ [H + V(t), \rho(t)](H + V(t)) \} + \text{tr} \{ \rho(t) \dot{V}(t) \}
\]

\[
= \langle \dot{V}(t) \rangle_T + \delta \langle \dot{V}(t) \rangle_T.
\]

Here we used (22.2), (22.3) in the second equation and the cyclic invariance of the trace in the third equation. Assuming that \(V(t)\) is of the form (22.10) and using (22.11) we obtain

\[
\frac{dE}{dt} = \hbar h^\alpha(t) \langle X^\alpha \rangle_T - i \int_{-\infty}^{t} dt' \hbar^\alpha(t) \hbar^\beta(t') \langle [X^\alpha(t - t'), X^\beta] \rangle_T.
\]
22.4 Application to quantum spin chains

Let us now apply the above formalism to the Heisenberg-Ising (alias XXZ) spin chain in a longitudinal static magnetic field of strength \( h \). The Hamiltonian of this model is defined as

\[
H_0 = J \sum_{j=1}^{L} \left( s_j^x s_{j+1}^x + s_j^y s_{j+1}^y + \Delta s_j^z s_{j+1}^z \right). 
\]

(22.14)

Here we have switched from Pauli matrices \( \sigma^\alpha \) to spin operators \( s^\alpha = \sigma^\alpha / 2 \). We shall assume periodic boundary conditions \( s^\alpha_0 = s^\alpha_L, \alpha = x, y, z \). The real parameter \( \Delta \) is called the anisotropy parameter. For \( \Delta = 1 \) the Hamiltonian \( H_0 \) turns into the Heisenberg Hamiltonian considered in lecture L21. Values of \( \Delta \) different from one may be needed for a more accurate modeling of real magnetic materials and are due to a combination of crystal symmetry, spin-orbit interactions and dipole-dipole interactions.

We define the operator of the total spin as

\[
S = \begin{pmatrix} S^x \\ S^y \\ S^z \end{pmatrix}, \quad S^\alpha = \frac{1}{2} \sum_{j=1}^{L} \sigma^\alpha 
\text{ for } \alpha = x, y, z. 
\]

(22.15)

If a spin system is exposed to a homogeneous magnetic field \( h \) a so-called ‘Zeeman term’ \( -\langle h, S \rangle \) must be added to the Hamiltonian. Assuming a field in \( z \)-direction our Hamiltonian takes the form

\[
H = H_0 - h S^z, 
\]

(22.16)

Note that the \( z \)-direction is special in that \([H_0, S^z] = 0\).

We perturb the spin chain by a circular polarized electro-magnetic wave propagating in \( z \)-direction. We assume that the wave length is large compared to the length of the spin chain\(^\dagger\) and idealize this assumption by setting the wave number \( k = 0 \). Then the magnetic field component of the wave is

\[
h(t) = A \begin{pmatrix} \cos(\omega t) \\ -\sin(\omega t) \\ 0 \end{pmatrix}, \quad A > 0. 
\]

(22.17)

It couples to the system by another Zeeman term

\[
V(t) = h^\alpha(t) S^\alpha. 
\]

(22.18)

Using (22.13) we obtain

\[
\frac{dE}{dt} = \langle S^\alpha \rangle_T \dot{\hat{h}}^\alpha(t) - i \int_{-\infty}^{t} dt' \langle [S^\alpha(t-t'), S^\beta] \rangle_T \dot{\hat{h}}^\beta(t') 
\]

\[
= \frac{A^2 \omega}{4} \int_{0}^{\infty} dt' \left\{ e^{i\omega(2t-t')} \langle [S^+(t'), S^+] \rangle_T - e^{-i\omega(2t-t')} \langle [S^-(t'), S^-] \rangle_T + e^{i\omega t'} \langle [S^+(t'), S^-] \rangle_T - e^{-i\omega t'} \langle [S^-(t'), S^+] \rangle_T \right\}. 
\]

(22.19)

Here we have used that

\[
\langle S^\alpha \rangle_T \dot{\hat{h}}^\alpha(t) = \langle S^\zeta \rangle_T \dot{\hat{h}}^\zeta(t) = 0, 
\]

(22.20)

\(\dagger\)The wavelength of microwaves is of the order of 10 cm.
The function \( \chi \) of the normalized absorbed intensity can be written as
\[
\chi = \frac{I(\omega, h)}{L^2 \omega A^2} \int_{-\infty}^{\infty} dt \frac{dE}{dt}
\]
\[
= \frac{\omega}{4L} \int_{0}^{\infty} dt \{ e^{i\omega t} \langle [S^+(t), S^-] \rangle_T + e^{-i\omega t} \langle [S^+, S^-(t)] \rangle_T \}
\]
\[
= \frac{\omega}{4L} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [S^+(t), S^-] \rangle_T .
\]

Introducing the function
\[
\chi''_{+ -}(\omega, h) = \frac{1}{2L} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [S^+(t), S^-] \rangle_T ,
\]
the normalized absorbed intensity can be written as
\[
I(\omega, h) = \frac{\omega}{2} \chi''_{+ -}(\omega, h) .
\]

The function \( \chi''_{+ -}(\omega, h) \) is called the (imaginary part of) the dynamic susceptibility. This function is a typical ‘response function’. Note that it is calculated as Fourier transform of the dynamical correlation function \( \langle [S^+(t), S^-] \rangle_T \).

### L.23 Microwave absorption by the Heisenberg-Ising chain

#### 23.1 The isotropic chain

In the general case \( \chi''_{+ -} \) cannot be calculated. For \( \Delta = 1 \), however, the situation simplifies drastically.
\[
[H, S] = -h[S^z, S],
\]
\[
(23.1)
\]
and the Heisenberg equation of motion for $S$ can be solved,
\[ \dot{S}^\pm = i[H, S^\pm] = -i\hbar [S^z, S^\pm] = \mp i\hbar S^\pm, \quad \Rightarrow S^\pm(t) = e^{\mp i\hbar t} S^\pm. \quad (23.2) \]

Also $S^z(t) = S^z$. Hence, the total spin behaves as
\[ S(t) = \begin{pmatrix} \cos(\hbar t) & \sin(\hbar t) \\ -\sin(\hbar t) & \cos(\hbar t) \end{pmatrix} S. \quad (23.3) \]

It is precessing clockwise about the $z$ axis.

On the other hand, inserting (23.2) into (22.23) we obtain
\[ \chi''_{+-}(\omega) = \frac{1}{2L} \int_{-\infty}^{\infty} dt \ e^{i(\omega - \hbar)t} \langle [S^+, S^-] \rangle_T = 2\pi \delta(\omega - \hbar)m(T, h). \quad (23.4) \]

where $m(T, h) = (S^z)_T/L$ is the magnetization per lattice site. The corresponding normalized absorbed intensity is
\[ I(\omega) = \pi \delta(\omega - \hbar) h m(T, h) \quad (23.5) \]
and is proportional to the magnetic energy $\hbar m(T, h)$ per lattice site. This case includes the familiar paramagnetic resonance (Zeeman effect) for which the magnetization is known more explicitly, namely, $m(T, h) = \frac{1}{2} \text{th} \left( \frac{J}{2\hbar} \right)$ for $J = 0$. In general, an exact calculation of the magnetization of the isotropic Heisenberg chain at any finite temperature is not elementary and requires the machinery of Bethe Ansatz and quantum transfer matrix [9].

Comparing (22.17), (23.3) and (23.5) we interpret the absorption of energy as a resonance between the rotating field of the incident wave and the precessing total spin of the chain. Both are rotating clockwise with angular velocity $\omega = \hbar$. If we deviate from the isotropic point $\Delta = 1$ of the Hamiltonian (18.15) we expect that energy is transferred from the 'coherent motion of the total spin' to 'other modes', causing a damping of the spin precession and hence a shift and a broadening of the $\delta$-function shaped spectral line (23.5).

### 23.2 Resonance shift and line width in the anisotropic case

At the present state of the art dynamical correlation functions, such as $\chi''_{+-}$, cannot be calculated exactly, not even for models as simple as the XXZ chain. The interaction induced shift of the resonance frequency and the width of the spectral line, on the other hand, are more simple quantities which need less information to be calculated.

For every finite $L$ and for every $n \in \mathbb{N}$ the integrals
\[ I_n = \int_{-\infty}^{\infty} d\omega \ \omega^n I(\omega) \quad (23.6) \]
exist. Since $I(\omega)$ is everywhere non-negative and since $I_0 > 0$ (see below), we may interpret $I(\omega)/I_0$ as a probability distribution with moments $I_n/I_0$. $I_1/I_0$ is the mean value of the distribution and $(I_2/I_0 - (I_1/I_0)^2)^{\frac{1}{2}}$ its variance. The quantities may be used to define the 'resonance frequency' and the line width.

Instead of the moments of the normalized absorption intensity we shall use the 'shifted moments' of the dynamical susceptibility,
\[ m_n = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi J_n} (\omega - \hbar)^n \chi''_{+-}(\omega). \quad (23.7) \]
As we shall see these quantities are more natural from a theoretical point of view as they can be more easily calculated. Using the binomial formula we can relate them to the moments of the normalized intensity,

\[
\frac{I_n}{I_0} = \frac{\int_{-\infty}^{\infty} d\omega \omega^{n+1} \chi''_{+-}(\omega)}{\int_{-\infty}^{\infty} d\omega \omega \chi''_{+-}(\omega)} = \sum_{k=0}^{n+1} h^k J^{n+1-k} m_{n+1-k}. \tag{23.8}
\]

Let us now define

\[
\delta\omega = \langle \omega \rangle - h = \frac{I_1}{I_0} - h = \frac{J m_2 + h m_1}{J m_1 + h m_0}.
\tag{23.9}
\]

\(\delta\omega\) is the ‘resonance shift’, i.e., the deviation of the resonance frequency from the resonance frequency in the isotropic case. Similarly,

\[
\Delta\omega^2 = \langle \omega^2 \rangle - \langle \omega \rangle^2 = \frac{I_2}{I_0} - \frac{I_1^2}{I_0^2} = \frac{J^2 m_3 + h m_2}{J m_1 + h m_0} - \delta\omega^2 \tag{23.10}
\]

is a measure of the line width. Hence, in order to calculate the resonance shift and the line width, we need to know the first four shifted moments \(m_0, m_1, m_2, m_3\) of the dynamic susceptibility \(\chi''_{+-}\).

### 23.3 The shifted moments of the dynamic susceptibility

In the following we shall employ the notation \(\text{ad}_X \cdot = [X, \cdot]\) for the adjoint action of an operator \(X\). Then, using that \(\text{ad}_H = \text{ad}_{H_0} - h \text{ad}_{S_z}\), that \([H_0, S^z] = 0\) and that \([S^z, S^+] = S^+\), we see that

\[
S^+(t) = e^{i t \text{ad}_H} S^+ = e^{i t \text{ad}_{H_0}} e^{-i t \text{ad}_{S_z}} S^+ = e^{-i t h} e^{i t \text{ad}_{H_0}} S^+. \tag{23.11}
\]

Thus,

\[
\chi''_{+-}(\omega) = \frac{1}{2L} \int_{-\infty}^{\infty} dt \ e^{i(\omega-h)t} \left[ e^{i t \text{ad}_{H_0}} S^+, S^- \right]_T = \frac{1}{2L} \int_{-\infty}^{\infty} dt \ e^{i(\omega-h)t} \left[ S^+, e^{-i t \text{ad}_{H_0}} S^- \right]_T. \tag{23.12}
\]

It follows that

\[
(\omega - h)^n \chi''_{+-}(\omega) = \left( \frac{-i}{2L} \right)^n \int_{-\infty}^{\infty} dt \ \left[ \partial_t^n e^{i(\omega-h)t} \right] \left[ S^+, e^{-i t \text{ad}_{H_0}} S^- \right]_T = \frac{1}{2L} \int_{-\infty}^{\infty} dt \ e^{i(\omega-h)t} \left[ S^+, \text{ad}_{H_0}^n e^{-i t \text{ad}_{H_0}} S^- \right]_T, \tag{23.13}
\]

entailing that

\[
m_n = \frac{1}{2L} \left[ [S^+, \text{ad}_{H_0}^n S^-] \right]_T. \tag{23.14}
\]

The latter formula shows that the moments \(m_n\) are static correlation functions whose range and complexity grows with growing \(n\). The first few of them can be easily calculated by hand. The most basic one is

\[
m_0 = \frac{1}{2L} \left[ [S^+, S^-] \right]_T = \frac{1}{L} \left[ S^z \right]_T = m(T, h), \tag{23.15}
\]
which is the magnetization per lattice site. The subsequent moments vanish in the isotropic point $\Delta = 1$. It turns out that they are polynomials in

$$\delta = \Delta - 1.$$  \hfill (23.16)

Unlike the magnetization they do not have an immediate interpretation. Using (23.14) they can be calculated one by one. We obtain, for instance,

$$m_1 = \delta \langle s_1^+ s_2^- - 2 s_1^z s_2^z \rangle_T,$$  \hfill (23.17a)

$$m_2 = \frac{1}{2} \delta^2 \langle s_1^z + 4 s_1^z s_2^z s_3^z - 4 s_1^z s_2^z s_3^z \rangle_T,$$  \hfill (23.17b)

$$m_3 = \frac{1}{4} \delta^2 \langle 2 s_1^+ s_2^+ s_3^- s_4^- + 4 s_1^+ s_2^- s_3^+ s_4^- - 2 s_1^+ s_2^- s_3^- s_4^+ - 8 s_1^z s_2^z s_3 s_4^- - 4 s_1^z s_2^z s_3^z s_4^- + 8 s_1^z s_2^z s_3^z s_4^- + 8 s_1^z s_2^z s_3^z s_4^- + 2 s_1^z s_2^z - 8 s_1^z s_2^z \rangle_T.$$  \hfill (23.17c)

The moments are certain combinations of static short-range correlation functions. This implies, in particular, that they all exist in the thermodynamic limit. Substituting (23.17) into (23.9) and (23.10) we have expressed our measures for the resonance shift and line width in terms of short-range static (rather than dynamical) correlation functions.

We close this subject with a number of comments.

(i) Short range static correlation functions of the XXZ chain can be calculated exactly at all values of temperatures and magnetic fields.

(ii) Our formulae show that special combinations of short-range static correlation functions can be measured, at least in principle, by macroscopic experiments.

(iii) In practice such measurements are difficult due to limitations of the experimental accuracies and limitations to experimental techniques, or due to the fact, that $\delta$ in typical spin chain materials is too small.

(iv) It follows from the existence of the moments that the shape of the ESR absorption lines cannot be Lorentzian, as is assumed by many experimentalists and in most of the more conventional theoretical approaches.

(v) Based on the expressions (23.15), (23.17) for the moments in terms of correlation functions we can prove and specify our claim that $I(\omega)$ is generally positive, even for vanishing magnetic field $h$. Using (23.15) and (23.17a) in $I_0 = \pi(J m_1 + h m_0)$ and noting that $\langle s_1^z s_2^z \rangle_T = 2 \langle s_1^z s_2^z \rangle_T$ we obtain

$$I_0 = \pi \langle h s_1^z + 2 \delta J s_2^z - s_1^z s_2^z \rangle_T.$$  \hfill (23.18)

Here the first term in the brackets is positive if $h \neq 0$ as the magnetization is positive for positive $h$ and negative for negative $h$. Note, however, that it becomes extremely small for small temperatures in the massive phase $\delta > 0$. As for the second term, for small enough $h$ and $\delta > -1$ the neighbour correlators are negative, and the $zz$-correlations are weaker than the $xx$-correlations for negative $\delta$ and stronger than the $xx$-correlations for positive $\delta$. Hence, the second term is positive even for vanishing $h$ as long as $\delta$ is non-zero.
(vi) The resonance shift and line width as determined by (23.9) and (23.10) show a simple scaling behaviour as functions of the exchange interaction $J$. Namely $\delta\omega/J$ and $\Delta\omega/J$ depend on $J$ only through the ratios $T/J$ and $h/J$. This is true for the statistical operator $\rho$, hence also for all spin correlation functions, and then by our formulae (23.15), (23.17) for $\delta\omega/J$ and $\Delta\omega/J$ as well. Note also that $\delta\omega/J$ and $\Delta\omega/J$ both vanish proportional to $\delta$ as we approach the isotropic point $\delta = 0$.

23.4 Exercise 21: Shifted moments

Obtain $m_1$ and $m_2$ from (23.14).
References

[1] F. Bloch, Über die Quantenmechanik der Elektronen in Kristallgittern, Z. Phys. 52 (1929), 555–600.

[2] M. Born and R. Oppenheimer, Zur Quantentheorie der Molekeln, Ann. d. Phys. 389 (1927), 457–484.

[3] Max Born and Kun Huang, Dynamical theory of crystal lattices, The Clarendon Press, Oxford, 1954.

[4] M. Brockmann, F. Göhmann, M. Karbach, A. Klümper, and A. Weiße, Theory of microwave absorption by the spin-1/2 Heisenberg-Ising magnet, Phys. Rev. Lett. 107 (2011), 017202.

[5] P. Debye, Zur Theorie der spezifischen Wärmen, Ann. d. Phys. 344 (1912), 789–839.

[6] F. H. L. Essler, H. Frahm, F. Göhmann, A. Klümper, and V. E. Korepin, The One-Dimensional Hubbard Model, Cambridge University Press, 2005.

[7] M. C. Gutzwiller, Effect of correlation on ferromagnetism of transition metals, Phys. Rev. Lett. 10 (1963), 159.

[8] J. Hubbard, Electron correlations in narrow energy bands, Proc. R. Soc. (London) A 276 (1963), 238.

[9] A. Klümper, Thermodynamics of the anisotropic spin-1/2 Heisenberg chain and related quantum chains, Z. Phys. B 91 (1993), 507.

[10] E. H. Lieb and F. Y. Wu, Absence of Mott transition in an exact solution of the short-range, one-band model in one dimension, Phys. Rev. Lett. 20 (1968), 1445, Erratum: ibid. 21 (1968) 192.

[11] N. D. Mermin, A short simple evaluation of expressions of the Debye-Waller form, J. Math. Phys. 7 (1966), 1038.

[12] B. S. Shastry, Exact integrability of the one-dimensional Hubbard-model, Phys. Rev. Lett. 56 (1986), 2453.

[13] A. Sommerfeld, Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik, Z. Phys. 47 (1928), 1.

[14] L. van Hove, The occurrence of singularities in the elastic frequency distribution of a crystal, Phys. Rev. 89 (1953), 1189.

[15] J. Zeisner, M. Brockmann, S. Zimmermann, A. Weiße, M. Thede, E. Ressouche, K. Yu. Povarov, A. Zheludev, A. Klümper, B. Büchner, V. Kataev, and F. Göhmann, Anisotropic magnetic interactions and spin dynamics in the spin-chain compound Cu(py)$_2$Br$_2$: An experimental and theoretical study, Phys. Rev. B 96 (2017), 024429.