

In this section, we introduce some model systems which are frequently treated and with which we shall later demonstrate and test the elements of the abstract theory. In formulating the model Hamiltonians, we can practice the transformation from the first to the second quantisation. The examples chosen are all taken from the field of theoretical solid-state physics and will be preceded by some introductory remarks.

A solid is certainly a many-body system,

$$\text{Solid} = \sum_{i=1}^N (\text{particles})_i ,$$

composed of atoms or molecules which interact with one another. Each *particle* consists of one or more positively-charged atomic nuclei and a negatively-charged electron cloud. One distinguishes between **core electrons** and **valence electrons**. The core electrons are strongly bound and are localised in the immediate neighbourhood of the nuclei. They as a rule occupy closed electronic shells – exceptions are e.g. the $4f$ electrons of the rare earths – and thus have hardly any influence on the characteristic properties of the solid. This is in contrast to the valence electrons, which occupy non-closed shells and are responsible for the bonding to form a solid. Of course, this separation into core and valence electrons is not always clear cut. It already represents a certain approximation. A **lattice ion** refers in this sense to the ensemble of the atomic nucleus plus the core electrons. This leads to the following **model**:

Solid:

an interacting system of particles consisting of lattice ions and valence electrons.

How is the corresponding Hamiltonian constructed?

$$H = H_e + H_i + H_{ei} . \quad (2.1)$$

The **subsystem of the electrons** is described by the operator H_e :

$$H_e = \sum_{i=1}^{N_e} \frac{p_i^2}{2m} + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{i,j}^{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \equiv H_{e,\text{kin}} + H_{ee} . \quad (2.2)$$

N_e is the number of valence electrons. The first term represents their kinetic energy, the second term is their Coulomb interaction. \mathbf{r}_i , \mathbf{r}_j are the position vectors of the electrons.

The **subsystem of the ions** is defined by the operator H_i :

$$H_i = \sum_{\alpha=1}^{N_i} \frac{p_\alpha^2}{2M_\alpha} + \frac{1}{2} \sum_{\alpha,\beta}^{\alpha \neq \beta} V_i(\mathbf{R}_\alpha - \mathbf{R}_\beta) \equiv H_{i,\text{kin}} + H_{ii} . \quad (2.3)$$

The ion-ion interaction need not be precisely specified at this point. It is in every case a pairwise interaction. It is partially responsible for the fact that the equilibrium positions of the ions, $\mathbf{R}_\alpha^{(0)}$, define a strictly periodic crystal lattice. The ions exhibit oscillations around these equilibrium positions; the oscillation energy is quantised. The elementary quantum is called a **phonon**. It is therefore expedient to separate H_{ii} further into

$$H_{ii} = H_{ii}^{(0)} + H_p . \quad (2.4)$$

$H_{ii}^{(0)}$ determines for example the bonding in the solid, and H_p the lattice dynamics.

The **interaction of the two subsystems** is finally given by

$$H_{ei} = \sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_i} V_{ei}(\mathbf{r}_i - \mathbf{R}_\alpha) , \quad (2.5)$$

where here also, a further separation is expedient:

$$H_{ei} = H_{ei}^{(0)} + H_{e-p} . \quad (2.6)$$

$H_{ei}^{(0)}$ refers to the interaction of the electrons with the ions in their equilibrium positions. H_{e-p} is the electron-phonon interaction.

An exact solution for the overall system (2.1) would appear to be impossible. An approximation can be formulated in the following three steps:

1. Electronic motions, e.g. in a rigid ionic lattice: $H_e + H_{ei}^{(0)}$.
2. Ionic motions, e.g. in a homogeneous electron gas H_p .
3. Coupling, e.g. the perturbation-theoretical treatment of H_{e-p} .

Following this concept, in the following section, we discuss the electronic subsystem.

2.1 Crystal Electrons

2.1.1 Non-interacting Bloch Electrons

We first consider electrons in a rigid ionic lattice, which do not interact with each other, but rather only with the periodic lattice potential, i.e. we are looking for the solutions corresponding to the eigenstates of the following Hamiltonian:

$$H_0 = H_{e,\text{kin}} + H_{\text{ei}}^{(0)} . \quad (2.7)$$

The so-called **lattice potential** is defined by the ions which are fixed in their equilibrium positions

$$\widehat{V}(\mathbf{r}_i) = \sum_{\alpha=1}^{N_i} V_{\text{ei}}(\mathbf{r}_i - \mathbf{R}_{\alpha}^{(0)}) . \quad (2.8)$$

More precisely, we have for the positions of the ions $\mathbf{R}_{\alpha}^{(0)}$:

$$\begin{aligned} \mathbf{R}_{\alpha}^{(0)} &\Rightarrow \mathbf{R}_s^n = \mathbf{R}^n + \mathbf{R}_s, \\ \mathbf{n} &= (n_1, n_2, n_3); \quad n_i \in \mathbf{Z} . \end{aligned} \quad (2.9)$$

Here, \mathbf{R}^n defines the Bravais lattice:

$$\mathbf{R}^n = \sum_{i=1}^3 n_i \mathbf{a}_i . \quad (2.10)$$

$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the primitive translations, and \mathbf{R}_s are the position vectors of the basis atoms. The periodicity mentioned above refers to the Bravais lattice:

$$\widehat{V}(\mathbf{r}_i + \mathbf{R}^n) \stackrel{!}{=} \widehat{V}(\mathbf{r}_i) . \quad (2.11)$$

$\widehat{V}(\mathbf{r}_i) = \widehat{V}(\hat{\mathbf{r}}_i)$ is a single-particle operator, and this can be inserted into:

$$H_{\text{ei}}^{(0)} = \sum_{i=1}^{N_e} \widehat{V}(\hat{\mathbf{r}}_i) . \quad (2.12)$$

We thus have to solve the following eigenvalue equation:

$$h_0 \psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon(\mathbf{k}) \psi_{\mathbf{k}}(\mathbf{r}) . \quad (2.13)$$

We refer to $\psi_{\mathbf{k}}(\mathbf{r})$ as a **Bloch function** and $\varepsilon(\mathbf{k})$ as the corresponding **Bloch energy**. \mathbf{k} is a wave vector within the first Brillouin zone. h_0 refers to the operator

$$h_0 = \frac{\mathbf{p}^2}{2m} + \widehat{V}(\hat{\mathbf{r}}) . \quad (2.14)$$

The solution of (2.13) for realistic lattices is a non-trivial problem. Using the periodicity (2.11) of the lattice potential, one can derive the fundamental **Bloch's Theorem**:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}^n) = e^{i\mathbf{k} \cdot \mathbf{R}^n} \psi_{\mathbf{k}}(\mathbf{r}) . \quad (2.15)$$

Employing the usual *ansatz*

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} , \quad (2.16)$$

the amplitude function must have the periodicity of the lattice:

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}^n) = u_{\mathbf{k}}(\mathbf{r}) . \quad (2.17)$$

The Bloch functions $\psi_{\mathbf{k}}(\mathbf{r})$ form a complete, orthonormalised system:

$$\int d^3r \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}'}(\mathbf{r}) = \delta_{\mathbf{k}, \mathbf{k}'} , \quad (2.18)$$

$$\sum_{\mathbf{k}}^{\text{1. BZ}} \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') . \quad (2.19)$$

The sum runs over all the wave vectors \mathbf{k} in the first Brillouin zone. Owing to the periodic boundary conditions, these are discrete. Since h_0 contains no spin parts, its eigenfunctions can be factored into a spin and a configuration-space function:

$$\begin{aligned} |\mathbf{k}\sigma\rangle &\iff \text{Bloch state} , \\ \langle \mathbf{r} | \mathbf{k}\sigma \rangle &= \psi_{\mathbf{k}\sigma}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r}) \chi_{\sigma} , \\ \chi_{\uparrow} &= \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \chi_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} . \end{aligned} \quad (2.20)$$

If we consider electrons from different energy bands, the Bloch function is also characterised by a band index n . We limit ourselves here, however, to electrons within a single band.

We define:

$$a_{\mathbf{k}\sigma}^+ \quad (a_{\mathbf{k}\sigma}) : \quad \text{creation (annihilation) operator for a Bloch electron.}$$

Since H_0 is a single-particle operator, it follows from (1.100) that:

$$H_0 = \sum_{\substack{k\sigma \\ k'\sigma'}} \langle k\sigma | h_0 | k'\sigma' \rangle a_{k\sigma}^+ a_{k'\sigma'} .$$

The matrix elements can be computed in a straightforward manner:

$$\langle k\sigma | h_0 | k'\sigma' \rangle = \varepsilon(k') \langle k\sigma | k'\sigma' \rangle = \varepsilon(k) \delta_{kk'} \delta_{\sigma\sigma'} , \quad (2.21)$$

since $|k\sigma\rangle$ is an eigenstate of h_0 . It then follows that:

$$H_0 = \sum_{k\sigma} \varepsilon(k) a_{k\sigma}^+ a_{k\sigma} = \sum_{k\sigma} \varepsilon(k) n_{k\sigma} . \quad (2.22)$$

The Bloch operators $a_{k\sigma}, a_{k\sigma}^+$ of course fulfil the fundamental commutation relations:

$$[a_{k\sigma}, a_{k'\sigma'}]_+ = [a_{k\sigma}^+, a_{k'\sigma'}^+]_+ = 0 , \quad (2.23)$$

$$[a_{k\sigma}, a_{k'\sigma'}^+]_+ = \delta_{kk'} \delta_{\sigma\sigma'} . \quad (2.24)$$

If we neglect the crystalline structure of the solid and consider the ionic lattice merely as a positively-charged background for the electronic system, ($\widehat{V}(\mathbf{r}) = \text{const}$), then the Bloch functions become plane waves,

$$\psi_k(\mathbf{r}) \xrightarrow{[\widehat{V}=\text{const}]} \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} , \quad (2.25)$$

and the Bloch energies, due to $p^2/2m = -(\hbar^2/2m)\Delta$, are:

$$\varepsilon(\mathbf{k}) \xrightarrow{[\widehat{V}=\text{const}]} \frac{\hbar^2 k^2}{2m} . \quad (2.26)$$

(V is the volume of the solid. It is important to distinguish between V and the lattice potential \widehat{V} !) We will discuss two other representations of H_0 which are important for applications, e.g. the

field operators

$$\widehat{\psi}_\sigma^+(\mathbf{r}), \quad \widehat{\psi}_\sigma(\mathbf{r}) ,$$

which are to be understood as in (1.63) through (1.69), with the addition that we now also take the spin of the electron into account. The generalisation of the formulas given in Chap. 1 is evident. Thus, for example:

$$[\hat{\psi}_\sigma(\mathbf{r}), \hat{\psi}_{\sigma'}^+(\mathbf{r}')]_+ = \delta(\mathbf{r} - \mathbf{r}') \delta_{\sigma\sigma'} . \quad (2.27)$$

From this it follows for H_0 :

$$\begin{aligned} H_0 &= \sum_{\sigma, \sigma'} \iint d^3r d^3r' \langle \mathbf{r}\sigma | h_0 | \mathbf{r}'\sigma' \rangle \hat{\psi}_\sigma^+(\mathbf{r}) \hat{\psi}_{\sigma'}(\mathbf{r}') = \\ &= \sum_{\sigma, \sigma'} \iint d^3r d^3r' \delta_{\sigma\sigma'} \left(-\frac{\hbar^2}{2m} \Delta_{r'} + \hat{V}(\mathbf{r}') \right) \delta(\mathbf{r} - \mathbf{r}') \hat{\psi}_\sigma^+(\mathbf{r}) \hat{\psi}_{\sigma'}(\mathbf{r}') = \\ &= \sum_{\sigma} \int d^3r \hat{\psi}_\sigma^+(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \Delta_r + \hat{V}(\mathbf{r}) \right) \hat{\psi}_\sigma(\mathbf{r}) . \end{aligned} \quad (2.28)$$

An additional, frequently-used particular configuration representation makes use of

Wannier functions

$$\omega_\sigma(\mathbf{r} - \mathbf{R}_i) = \frac{1}{\sqrt{N_i}} \sum_k^{1.BZ} e^{-ik \cdot \mathbf{R}_i} \psi_{k\sigma}(\mathbf{r}) . \quad (2.29)$$

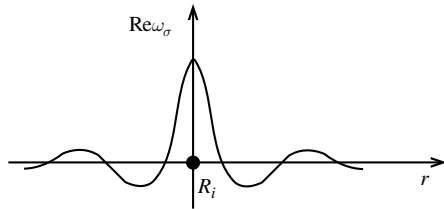
A typical feature of these functions is their relatively strong concentration around each lattice position \mathbf{R}_i (Fig. 2.1). With (2.18) as well as

$$\frac{1}{N_i} \sum_k^{1.BZ} e^{ik \cdot (\mathbf{R}_i - \mathbf{R}_j)} = \delta_{ij} , \quad (2.30)$$

one can readily prove the orthogonality relation:

$$\int d^3r \omega_\sigma^*(\mathbf{r} - \mathbf{R}_i) \omega_{\sigma'}(\mathbf{r} - \mathbf{R}_j) = \delta_{\sigma\sigma'} \delta_{ij} . \quad (2.31)$$

Fig. 2.1 The qualitative position dependence of the real part of a Wannier function



Using the notations

$$\begin{aligned}
 |i\sigma\rangle &\iff \text{Wannier state,} \\
 \langle \mathbf{r} | i\sigma \rangle &= \omega_\sigma(\mathbf{r} - \mathbf{R}_i), \\
 a_{i\sigma}^\dagger \quad (a_{i\sigma}) &: \text{creation (annihilation) operator for an electron} \\
 &\quad \text{in a Wannier state at the lattice site } \mathbf{R}_i,
 \end{aligned} \tag{2.32}$$

in second quantisation, H_0 is given by

$$H_0 = \sum_{ij\sigma} T_{ij} a_{i\sigma}^\dagger a_{j\sigma}, \tag{2.33}$$

and describes in an intuitively clear manner the *hopping* of an electron with spin σ from the lattice site \mathbf{R}_j – where it is annihilated – to the lattice site \mathbf{R}_i , where it is created. T_{ij} is therefore also called the

“hopping” integral.

We start with:

$$\begin{aligned}
 \langle i\sigma | h_0 | j\sigma' \rangle &= \delta_{\sigma\sigma'} \langle i\sigma | h_0 | j\sigma \rangle = \\
 &= \delta_{\sigma\sigma'} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \sigma_1, \sigma_2}} \langle i\sigma | \mathbf{k}\sigma_1 \rangle \langle \mathbf{k}\sigma_1 | h_0 | \mathbf{k}'\sigma_2 \rangle \langle \mathbf{k}'\sigma_2 | j\sigma \rangle = \\
 &= \delta_{\sigma\sigma'} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \sigma_1, \sigma_2}} \varepsilon(\mathbf{k}') \langle i\sigma | \mathbf{k}\sigma_1 \rangle \langle \mathbf{k}\sigma_1 | \mathbf{k}'\sigma_2 \rangle \langle \mathbf{k}'\sigma_2 | j\sigma \rangle = \\
 &= \delta_{\sigma\sigma'} \sum_{\mathbf{k}, \sigma_1} \varepsilon(\mathbf{k}) \langle i\sigma | \mathbf{k}\sigma_1 \rangle \langle \mathbf{k}\sigma_1 | j\sigma \rangle.
 \end{aligned} \tag{2.34}$$

The remaining matrix elements can then be computed as follows:

$$\begin{aligned}
 \langle i\sigma | \mathbf{k}\sigma_1 \rangle &= \int d^3r \langle i\sigma | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{k}\sigma_1 \rangle = \\
 &= \int d^3r \omega_\sigma^*(\mathbf{r} - \mathbf{R}_i) \psi_{\mathbf{k}\sigma_1}(\mathbf{r}) = \\
 &= \frac{1}{\sqrt{N_i}} \sum_{\mathbf{k}'} e^{i\mathbf{k}' \cdot \mathbf{R}_i} \int d^3r \psi_{\mathbf{k}'\sigma}^*(\mathbf{r}) \psi_{\mathbf{k}\sigma_1}(\mathbf{r}) = \\
 &= \frac{1}{\sqrt{N_i}} \sum_{\mathbf{k}'} e^{i\mathbf{k}' \cdot \mathbf{R}_i} \delta_{\mathbf{k}\mathbf{k}'} \delta_{\sigma\sigma_1} = \delta_{\sigma\sigma_1} \frac{e^{i\mathbf{k} \cdot \mathbf{R}_i}}{\sqrt{N_i}}.
 \end{aligned}$$

This yields in (2.34):

$$\langle i\sigma \mid h_0 \mid j\sigma' \rangle = \delta_{\sigma\sigma'} T_{ij} \quad (2.35)$$

with

$$T_{ij} = \frac{1}{N_i} \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} . \quad (2.36)$$

The inverse relation is given by:

$$\varepsilon(\mathbf{k}) = \frac{1}{N_i} \sum_{i,j} T_{ij} e^{-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} , \quad (2.37)$$

as can be verified by substituting in (2.36) and employing (2.30).

The relation between the Bloch and the Wannier operators can be found in the same way as shown in (1.66) for the example of the field operators:

$$a_{i\sigma} = \frac{1}{\sqrt{N_i}} \sum_{\mathbf{k}}^{1.\text{BZ}} e^{i\mathbf{k} \cdot \mathbf{R}_i} a_{\mathbf{k}\sigma} , \quad (2.38)$$

$$a_{\mathbf{k}\sigma} = \frac{1}{\sqrt{N_i}} \sum_{i=1}^{N_i} e^{-i\mathbf{k} \cdot \mathbf{R}_i} a_{i\sigma} . \quad (2.39)$$

From the commutation relations for the Bloch operators (2.23) and (2.24), the commutation relations for the Wannier operators then follow immediately:

$$[a_{i\sigma}, a_{j\sigma'}]_+ = [a_{i\sigma}^+, a_{j\sigma'}^+]_+ = 0, \quad (2.40)$$

$$[a_{i\sigma}, a_{j\sigma'}^+]_+ = \delta_{ij} \delta_{\sigma\sigma'} . \quad (2.41)$$

2.1.2

The Jellium Model

This model is adequate for the description of simple metals and is based on the following assumptions:

1. N_e electrons within the volume $V = L^3$ interact with each other via the Coulomb interaction

$$H_{ee} = \frac{e^2}{8\pi\epsilon_0} \sum_{i,j}^{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} . \quad (2.42)$$

2. The ions are singly positively charged:

$$N_e = N_i = N . \quad (2.43)$$

3. The ions form a *homogeneously distributed* background and thus guarantee
(a) charge neutrality, (b) a constant lattice potential.

The Bloch functions then become plane waves:

$$\psi_{k\sigma}(\mathbf{r}) \Rightarrow \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \chi_{\sigma} . \quad (2.44)$$

4. Periodic boundary conditions for V give rise to discrete wave numbers:

$$\mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z), \quad n_{x,y,z} \in \mathbf{Z} . \quad (2.45)$$

How is the Hamiltonian for the model corresponding to these assumptions formulated in first quantisation? It should contain three terms:

$$H = H_e + H_+ + H_{e+} . \quad (2.46)$$

H_e is to be interpreted as in (2.2) and is the pivotal term. H_+ describes the homogeneously distributed ionic charges, where *homogeneously distributed* is taken to imply that the ion density $n(\mathbf{r})$ is position-independent:

$$n(\mathbf{r}) \Rightarrow \frac{N}{V} . \quad (2.47)$$

Then we have for H_+ :

$$H_+ = \frac{e^2}{8\pi\epsilon_0} \iint d^3r d^3r' \frac{n(\mathbf{r}) \cdot n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} e^{-\alpha|\mathbf{r} - \mathbf{r}'|} . \quad (2.48)$$

Due to the 4th assumption, we must discuss our results in the thermodynamic limit, i.e. for $N \rightarrow \infty$, $V \rightarrow \infty$, $N/V \rightarrow \text{const}$. Owing to the long range of the Coulomb forces, the integrals then diverge. For this reason, a convergence factor $\exp(-\alpha|\mathbf{r} - \mathbf{r}'|)$ with $\alpha > 0$ is introduced. After evaluating the integrals, the limit $\alpha \rightarrow 0$ is taken.

Because of (2.47), we require the following integral in (2.48):

$$\iint d^3r d^3r' \frac{e^{-\alpha|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} = V \int_V d^3r \frac{e^{-\alpha r}}{r} \xrightarrow{V \rightarrow \infty} \frac{4\pi V}{\alpha^2} .$$

We then obtain:

$$H_+ = \frac{e^2}{8\pi\epsilon_0} \frac{\widehat{N}^2}{V} \frac{4\pi}{\alpha^2} . \quad (2.49)$$

H_+ indeed diverges for $\alpha \rightarrow 0$, but it is compensated by other terms which are yet to be discussed. H_{e+} in (2.46) describes the interactions of the electrons with the homogeneous background of ions:

$$H_{e+} = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \int d^3r \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_i|} e^{-\alpha|\mathbf{r} - \mathbf{r}_i|}. \quad (2.50)$$

With the same considerations as used for H_+ , we find:

$$\begin{aligned} H_{e+} &= -\frac{e^2}{4\pi\epsilon_0} \frac{N}{V} \sum_{i=1}^N \int d^3r \frac{e^{-\alpha|\mathbf{r} - \mathbf{r}_i|}}{|\mathbf{r} - \mathbf{r}_i|} = \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{N}{V} \sum_{i=1}^N \frac{4\pi}{\alpha^2}. \end{aligned}$$

We now replace the classical particle number N by the particle-number operator \hat{N} ; this yields:

$$H_{e+} = -\frac{e^2}{4\pi\epsilon_0} \frac{\hat{N}^2}{V} \frac{4\pi}{\alpha^2}. \quad (2.51)$$

All together, this gives for our model:

$$H = H_e - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{\hat{N}^2}{V} \frac{4\pi}{\alpha^2}. \quad (2.52)$$

This still looks critical for $\alpha \rightarrow 0$, but as we shall see, H_e contains an exactly corresponding term, which just cancels with the second term in (2.52). H_e is in fact the decisive operator, and according to (2.2), it is composed of the kinetic energy H_0 (2.7) and the Coulomb interaction H_{ee} (2.42). H_0 was already transformed to second quantisation in the previous section. H_{ee} is a typical two-particle operator, for which, according to (1.100), we find in the Bloch representation:

$$H_{ee} = \frac{1}{2} \sum_{\substack{k_1 \dots k_4 \\ \sigma_1 \dots \sigma_4}} v(k_1\sigma_1, \dots, k_4\sigma_4) a_{k_1\sigma_1}^+ a_{k_2\sigma_2}^+ a_{k_4\sigma_4} a_{k_3\sigma_3}. \quad (2.53)$$

The matrix element

$$\begin{aligned} v(k_1\sigma_1, \dots, k_4\sigma_4) &= \\ &= \frac{e^2}{4\pi\epsilon_0} \left\langle (k_1\sigma_1)^{(1)} (k_2\sigma_2)^{(2)} \left| \frac{1}{|\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}|} \right| (k_3\sigma_3)^{(1)} (k_4\sigma_4)^{(2)} \right\rangle \end{aligned}$$

is with certainty nonzero only for

$$\sigma_1 = \sigma_3 \quad \text{and} \quad \sigma_2 = \sigma_4 ,$$

since the operator itself is spin-independent:

$$\begin{aligned} v(\mathbf{k}_1\sigma_1, \dots, \mathbf{k}_4\sigma_4) &= \frac{e^2}{4\pi\epsilon_0} \iint d^3r_1 d^3r_2 \left\langle \mathbf{k}_1^{(1)} \mathbf{k}_2^{(2)} \right| \frac{1}{|\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}|} \cdot \\ &\quad \cdot \left| \mathbf{r}_1^{(1)} \mathbf{r}_2^{(2)} \right\rangle \left\langle \mathbf{r}_1^{(1)} \mathbf{r}_2^{(2)} \right| \mathbf{k}_3^{(1)} \mathbf{k}_4^{(2)} \rangle \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} = \\ &= \frac{e^2}{4\pi\epsilon_0} \iint d^3r_1 d^3r_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left\langle \mathbf{k}_1^{(1)} \mathbf{k}_2^{(2)} \right| \mathbf{r}_1^{(1)} \mathbf{r}_2^{(2)} \rangle \cdot \\ &\quad \cdot \left\langle \mathbf{r}_1^{(1)} \mathbf{r}_2^{(2)} \right| \mathbf{k}_3^{(1)} \mathbf{k}_4^{(2)} \rangle \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} = \\ &= \frac{e^2}{4\pi\epsilon_0} \iint d^3r_1 d^3r_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{\mathbf{k}_1}^*(\mathbf{r}_1) \psi_{\mathbf{k}_2}^*(\mathbf{r}_2) \cdot \\ &\quad \cdot \psi_{\mathbf{k}_3}(\mathbf{r}_1) \psi_{\mathbf{k}_4}(\mathbf{r}_2) \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} . \end{aligned}$$

Making use of Bloch's theorem (2.15), we can furthermore show that in addition,

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{k}_4$$

must hold. We then have:

$$\begin{aligned} v(\mathbf{k}_1\sigma_1, \dots, \mathbf{k}_4\sigma_4) &= \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} \delta_{\mathbf{k}_1+\mathbf{k}_2, \mathbf{k}_3+\mathbf{k}_4} v(\mathbf{k}_1, \dots, \mathbf{k}_4) , \\ v(\mathbf{k}_1, \dots, \mathbf{k}_4) &= \frac{e^2}{4\pi\epsilon_0} \iint d^3r_1 d^3r_2 \psi_{\mathbf{k}_1}^*(\mathbf{r}_1) \psi_{\mathbf{k}_2}^*(\mathbf{r}_2) \cdot \\ &\quad \cdot \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{\mathbf{k}_3}(\mathbf{r}_1) \psi_{\mathbf{k}_4}(\mathbf{r}_2) . \end{aligned} \quad (2.54)$$

For the Coulomb interaction H_{ee} , we thus obtain the following expression:

$$H_{ee} = \frac{1}{2} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ \sigma, \sigma'}} v(\mathbf{k}_1, \dots, \mathbf{k}_4) \delta_{\mathbf{k}_1+\mathbf{k}_2, \mathbf{k}_3+\mathbf{k}_4} a_{\mathbf{k}_1\sigma}^+ a_{\mathbf{k}_2\sigma'}^+ a_{\mathbf{k}_4\sigma'} a_{\mathbf{k}_3\sigma} . \quad (2.55)$$

In the jellium model, the $\psi_{\mathbf{k}}(\mathbf{r})$ are plane waves, so that we still must calculate:

$$\begin{aligned} v_{\alpha}(\mathbf{k}_1, \dots, \mathbf{k}_4) &= \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{V^2} \iint d^3r_1 d^3r_2 \frac{e^{-i(\mathbf{k}_1-\mathbf{k}_3) \cdot \mathbf{r}_1} e^{-i(\mathbf{k}_2-\mathbf{k}_4) \cdot \mathbf{r}_2}}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-\alpha|\mathbf{r}_1-\mathbf{r}_2|} . \end{aligned} \quad (2.56)$$

We set

$$\begin{aligned} \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2; & \mathbf{R} &= \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \\ \iff \mathbf{r}_1 &= \frac{1}{2}\mathbf{r} + \mathbf{R}; & \mathbf{r}_2 &= -\frac{1}{2}\mathbf{r} + \mathbf{R}. \end{aligned} \quad (2.57)$$

and must then solve:

$$\begin{aligned} v_\alpha(\mathbf{k}_1, \dots, \mathbf{k}_4) &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{V} \int d^3R \, e^{-i(\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_4) \cdot \mathbf{R}} \cdot \\ &\quad \cdot \frac{1}{V} \int d^3r \, \frac{1}{r} e^{-\alpha r} e^{-(i/2)(\mathbf{k}_1 - \mathbf{k}_3 - \mathbf{k}_2 + \mathbf{k}_4) \cdot \mathbf{r}} = \\ &= \frac{e^2}{4\pi\epsilon_0} \delta_{\mathbf{k}_1 + \mathbf{k}_2, \mathbf{k}_3 + \mathbf{k}_4} \frac{1}{V} \int d^3r \, \frac{e^{-i(\mathbf{k}_1 - \mathbf{k}_3) \cdot \mathbf{r}} e^{-\alpha r}}{r}. \end{aligned}$$

Using

$$\int d^3r \, \frac{e^{-i\mathbf{q} \cdot \mathbf{r}}}{r} e^{-\alpha r} = \frac{4\pi}{q^2 + \alpha^2}, \quad (2.58)$$

we finally obtain:

$$v_\alpha(\mathbf{k}_1, \dots, \mathbf{k}_4) = \frac{e^2}{\epsilon_0 V [(\mathbf{k}_1 - \mathbf{k}_3)^2 + \alpha^2]} \delta_{\mathbf{k}_1 - \mathbf{k}_3, \mathbf{k}_4 - \mathbf{k}_2}. \quad (2.59)$$

We insert this into (2.55):

$$H_{\text{ee}}^{(\alpha)} = \frac{1}{2} \sum_{\substack{\mathbf{k}, \mathbf{p}, \mathbf{q} \\ \sigma, \sigma'}} v_\alpha(\mathbf{q}) a_{\mathbf{k} + \mathbf{q}\sigma}^+ a_{\mathbf{p} - \mathbf{q}\sigma'}^+ a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma}, \quad (2.60)$$

$$v_\alpha(\mathbf{q}) = \frac{e^2}{\epsilon_0 V (q^2 + \alpha^2)}. \quad (2.61)$$

We consider now the $q = 0$ term of the Coulomb interaction:

$$\begin{aligned} &\frac{1}{2} \frac{e^2}{\epsilon_0 V \alpha^2} \sum_{\substack{\mathbf{k}, \mathbf{p} \\ \sigma, \sigma'}} a_{\mathbf{k}\sigma}^+ a_{\mathbf{p}\sigma'}^+ a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma} = \\ &= \frac{1}{2} \frac{e^2}{\epsilon_0 V \alpha^2} \sum_{\substack{\mathbf{k}, \mathbf{p} \\ \sigma, \sigma'}} (-\delta_{\sigma\sigma'} \delta_{\mathbf{k}\mathbf{p}} n_{\mathbf{k}\sigma} + n_{\mathbf{p}\sigma'} n_{\mathbf{k}\sigma}) = \\ &= \frac{e^2}{2\epsilon_0 V \alpha^2} [-\hat{N} + (\hat{N})^2]. \end{aligned} \quad (2.62)$$

We can see that the second term in (2.62) just compensates the second term in (2.52), i.e. the contributions from H_+ and H_{e+} just cancel. The first term in (2.62) leads to an energy per particle which vanishes in the thermodynamic limit,

$$-\frac{e^2}{2\varepsilon_0 V \alpha^2} \xrightarrow{N \rightarrow \infty; V \rightarrow \infty} 0,$$

and therefore can be left off from the beginning. If we now finally take the limit $\alpha \rightarrow 0$, we find for the

Hamiltonian of the jellium model:

$$H = \sum_{k\sigma} \varepsilon_0(\mathbf{k}) a_{k\sigma}^\dagger a_{k\sigma} + \frac{1}{2} \sum_{\substack{k, p, q \\ \sigma, \sigma'}}^{q \neq 0} v_0(\mathbf{q}) a_{k+q\sigma}^\dagger a_{p-q\sigma'}^\dagger a_{p\sigma'} a_{k\sigma}. \quad (2.63)$$

From (2.26), we have

$$\varepsilon_0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \quad (2.64)$$

as the matrix element of the kinetic energy, and

$$v_0(\mathbf{q}) = \frac{1}{V} \frac{e^2}{\varepsilon_0 q^2} \quad (2.65)$$

as that of the Coulomb interaction.

In addition, we would like to derive a useful alternative representation of H , making use of the

electron density operator:

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \hat{\mathbf{r}}_i). \quad (2.66)$$

This is a single-particle operator. The site of the electron $\hat{\mathbf{r}}_i$ is an operator here, whilst the variable \mathbf{r} is naturally not. From (1.100), we find for $\hat{\rho}$ in the second-quantisation formalism using the Bloch representation:

$$\hat{\rho}(\mathbf{r}) = \sum_{\substack{k, k' \\ \sigma, \sigma'}} \langle k\sigma | \delta(\mathbf{r} - \hat{\mathbf{r}}') | k'\sigma' \rangle a_{k\sigma}^\dagger a_{k'\sigma'}. \quad (2.67)$$

For the matrix element, we need to calculate the following:

$$\begin{aligned}
 \langle \mathbf{k}\sigma | \delta(\mathbf{r}-\hat{\mathbf{r}}') | \mathbf{k}'\sigma' \rangle &= \sum_{\sigma''} \int d^3 r'' \langle \mathbf{k}\sigma | \delta(\mathbf{r}-\hat{\mathbf{r}}') | \mathbf{r}''\sigma'' \rangle \langle \mathbf{r}''\sigma'' | \mathbf{k}'\sigma' \rangle = \\
 &= \sum_{\sigma''} \int d^3 r'' \delta(\mathbf{r}-\mathbf{r}'') \langle \mathbf{k}\sigma | \mathbf{r}''\sigma'' \rangle \langle \mathbf{r}''\sigma'' | \mathbf{k}'\sigma' \rangle = \\
 &= \sum_{\sigma''} \delta_{\sigma\sigma''} \delta_{\sigma''\sigma'} \langle \mathbf{k}\sigma | \mathbf{r}\sigma \rangle \langle \mathbf{r}\sigma | \mathbf{k}'\sigma' \rangle = \\
 &= \delta_{\sigma\sigma'} \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}'}(\mathbf{r}) .
 \end{aligned}$$

If we confine ourselves to plane waves, as in the jellium model, then we have

$$\langle \mathbf{k}\sigma | \delta(\mathbf{r}-\hat{\mathbf{r}}') | \mathbf{k}'\sigma' \rangle = \delta_{\sigma\sigma'} \frac{1}{V} e^{i(\mathbf{k}'-\mathbf{k}) \cdot \mathbf{r}} . \quad (2.68)$$

In terms of (2.67), this means:

$$\hat{\rho}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}, \mathbf{q}, \sigma} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}+\mathbf{q}\sigma} e^{i\mathbf{q} \cdot \mathbf{r}} . \quad (2.69)$$

For the Fourier component of the electron-density operator, we thus find:

$$\hat{\rho}_{\mathbf{q}} = \sum_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}+\mathbf{q}\sigma} . \quad (2.70)$$

One can read off, among other things:

$$\hat{\rho}_{\mathbf{q}}^+ = \hat{\rho}_{-\mathbf{q}}; \quad \hat{\rho}_{\mathbf{q}=0} = \hat{N} . \quad (2.71)$$

With this result, we can express the Hamiltonian of the jellium model in terms of density operators. The kinetic energy remains unchanged:

$$\begin{aligned}
 H_{\text{ce}} &= \frac{1}{2} \sum_{\substack{\mathbf{k}, \mathbf{p}, \mathbf{q} \\ \sigma, \sigma'}}^{q \neq 0} v_0(\mathbf{q}) a_{\mathbf{k}+\mathbf{q}\sigma}^+ a_{\mathbf{p}-\mathbf{q}\sigma'}^+ a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma} = \\
 &= \frac{1}{2} \sum_{\substack{\mathbf{k}, \mathbf{p}\mathbf{q} \\ \sigma, \sigma'}}^{q \neq 0} v_0(\mathbf{q}) a_{\mathbf{k}+\mathbf{q}\sigma}^+ \left\{ -\delta_{\sigma\sigma'} \delta_{\mathbf{k}, \mathbf{p}-\mathbf{q}} + a_{\mathbf{k}\sigma} a_{\mathbf{p}-\mathbf{q}\sigma'}^+ \right\} a_{\mathbf{p}\sigma'} = \\
 &= -\frac{1}{2} \sum_{\mathbf{q}, \mathbf{p}, \sigma}^{q \neq 0} v_0(\mathbf{q}) a_{\mathbf{p}\sigma}^+ a_{\mathbf{p}\sigma} + \frac{1}{2} \sum_{\mathbf{q}}^{q \neq 0} v_0(\mathbf{q}) \sum_{\mathbf{k}\sigma} a_{\mathbf{k}+\mathbf{q}\sigma}^+ a_{\mathbf{k}\sigma} \cdot \\
 &\quad \cdot \sum_{\mathbf{p}, \sigma'} a_{\mathbf{p}-\mathbf{q}\sigma'}^+ a_{\mathbf{p}\sigma} .
 \end{aligned}$$

Thus, all together, the Hamiltonian of the jellium model becomes:

$$H = \sum_{\mathbf{k}\sigma} \varepsilon_0(\mathbf{k}) a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\mathbf{q}}^{q \neq 0} v_0(\mathbf{q}) \{ \hat{\rho}_{\mathbf{q}} \hat{\rho}_{-\mathbf{q}} - \hat{N} \} . \quad (2.72)$$

In order to obtain a certain insight into the *physics* of the model, we now investigate the ground-state energy of the jellium model. To this end, we make use of first-order perturbation theory, which according to the variational principle will in any case give us an upper limit for the ground-state energy. We consider the Coulomb interaction H_{ee} as a *perturbation*; the *unperturbed* system is thus given by

$$H_0 = \sum_{\mathbf{k}\sigma} \varepsilon_0 \mathbf{k} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} \quad (2.73)$$

(**Sommerfeld model**). It can be solved exactly. In the

“**unperturbed**” ground state $|E_0\rangle$,

the N electrons occupy all the states with energies which are not greater than a limiting energy ε_F , which is referred to as the **Fermi energy**:

$$\varepsilon_0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \leq \varepsilon_F = \frac{\hbar^2 k_F^2}{2m} . \quad (2.74)$$

k_F is the **Fermi wavevector**, which can readily be computed as follows: owing to the isotropic energy dispersion

$$\varepsilon_0(\mathbf{k}) = \varepsilon_0(k) , \quad (2.75)$$

the electrons occupy all the states in \mathbf{k} space within a sphere of radius k_F . Since the \mathbf{k} -points are discrete in k space due to the periodic boundary conditions (cf. (2.45)), each \mathbf{k} -point occupies an available

$$\text{grid volume } \Delta k = \frac{(2\pi)^3}{L^3} = \frac{(2\pi)^3}{V} . \quad (2.76)$$

If we now take the spin degeneracy into account, we find the following relation between the electron number N and the Fermi wavevector k_F :

$$N = 2 \frac{1}{\Delta k} \left(\frac{4\pi}{3} k_F^3 \right) = \frac{V}{3\pi^2} k_F^3 .$$

This means that:

$$k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3} , \quad (2.77)$$

$$\varepsilon_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}. \quad (2.78)$$

We can readily compute the mean energy per particle $\bar{\varepsilon}$, finding:

$$\bar{\varepsilon} = \frac{2}{N} \left(\int_{k \leq k_F} d^3k \frac{\hbar^2 k^2}{2m} \right) \frac{1}{\Delta k} = \frac{3}{5} \varepsilon_F. \quad (2.79)$$

We thus have obtained the ground-state energy:

$$E_0 = N\bar{\varepsilon} = \frac{3}{5} N \varepsilon_F. \quad (2.80)$$

We introduce some standard abbreviations:

$$n_e = \frac{N}{V} : \quad \text{mean electron density,} \quad (2.81)$$

$$v_e = \frac{1}{n_e} : \quad \text{mean volume per electron.} \quad (2.82)$$

v_e determines via

$$v_e = \frac{4\pi}{3} (a_B r_s)^3 \quad (2.83)$$

the dimensionless **density parameter** r_s , where

$$a_B = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \text{ \AA} \quad (2.84)$$

is the **Bohr radius**. If we introduce an energy parameter in a similar fashion,

$$1 \text{ ryd} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} = 13.605 \text{ eV}, \quad (2.85)$$

then for the Fermi energy ε_F , we find:

$$\varepsilon_F = \frac{\alpha^2}{r_s^2} [\text{ryd}]; \quad \alpha = \left(\frac{9\pi}{4} \right)^{1/3}. \quad (2.86)$$

Then the *unperturbed* ground-state energy is given by:

$$E_0 = N \frac{2.21}{r_s^2} [\text{ryd}]. \quad (2.87)$$

We now switch on the *perturbation* H_{ee} and compute the energy correction to first order:

$$\varepsilon^{(1)} = \frac{1}{2N} \sum_{\substack{q \neq 0 \\ k, p, q \\ \sigma, \sigma'}} v_0(\mathbf{q}) \left\langle E_0 \left| a_{\mathbf{k}+\mathbf{q}\sigma}^+ a_{\mathbf{p}-\mathbf{q}\sigma'}^+ a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma} \right| E_0 \right\rangle . \quad (2.88)$$

Only those terms contribute for which the annihilation operator acts on states **within** the Fermi sphere, and the creation operator subsequently fills the resulting holes within the Fermi sphere:

1) Direct Term:

$$\mathbf{k} = \mathbf{k} + \mathbf{q}; \quad \mathbf{p} = \mathbf{p} - \mathbf{q} \iff \mathbf{q} = 0 . \quad (2.89)$$

According to our preliminary considerations, terms of this type however do not occur in the sum!

2) Exchange Term:

$$\sigma = \sigma'; \quad \mathbf{k} + \mathbf{q} = \mathbf{p}; \quad \mathbf{p} - \mathbf{q} = \mathbf{k} . \quad (2.90)$$

This is a typically quantum-mechanical term, which is not classically understandable. It results from the antisymmetrisation principle for the N -particle states:

$$\begin{aligned} \varepsilon^{(1)} &= \frac{1}{2N} \sum_{\substack{q \neq 0 \\ k, q, \sigma}} v_0(\mathbf{q}) \left\langle E_0 \left| a_{\mathbf{k}+\mathbf{q}\sigma}^+ a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}+\mathbf{q}\sigma} a_{\mathbf{k}\sigma} \right| E_0 \right\rangle = \\ &= -\frac{1}{2N} \sum_{\substack{q \neq 0 \\ k, q, \sigma}} v_0(\mathbf{q}) \left\langle E_0 \left| \hat{n}_{\mathbf{k}+\mathbf{q}\sigma} \hat{n}_{\mathbf{k}\sigma} \right| E_0 \right\rangle . \end{aligned} \quad (2.91)$$

Since in the *unperturbed* ground state $|E_0\rangle$, all the states within the Fermi sphere are occupied and all those outside it are unoccupied, it follows that:

$$\varepsilon^{(1)} = -\frac{1}{2N} \sum_{\substack{q \neq 0 \\ k, q, \sigma}} v_0(\mathbf{q}) \Theta(k_F - |\mathbf{k} + \mathbf{q}|) \Theta(k_F - k) . \quad (2.92)$$

In the thermodynamic limit, we can replace the sums by integrals:

$$\sum_k \Rightarrow \frac{1}{\Delta k} \int d^3k = \frac{V}{(2\pi)^3} \int d^3k .$$

After carrying out the summation over spins, we still need to compute:

$$\varepsilon^{(1)} = -\frac{V}{N} \frac{e^2}{\varepsilon_0 (2\pi)^6} \int d^3 k \int d^3 q \frac{1}{q^2} \Theta(k_F - |\mathbf{k} + \mathbf{q}|) \Theta(k_F - k) .$$

The substitution

$$\mathbf{k} \Rightarrow \mathbf{x} = \mathbf{k} + \frac{1}{2}\mathbf{q}$$

leads to

$$\varepsilon^{(1)} = -\frac{V}{N} \frac{e^2}{\varepsilon_0 (2\pi)^6} \int d^3 q \frac{1}{q^2} 2S(q), \quad (2.93)$$

$$S(q) = \frac{1}{2} \int d^3 x \Theta\left(k_F - \left|x + \frac{1}{2}\mathbf{q}\right|\right) \Theta\left(k_F - \left|x - \frac{1}{2}\mathbf{q}\right|\right) . \quad (2.94)$$

For the spherical segment sketched in Fig. 2.2, we clearly need to calculate:

$$S(q) = \Theta\left(k_F - \frac{q}{2}\right) \int_{\frac{q/2}{k_F}}^1 d \cos \vartheta \int_{y(\vartheta)}^{k_F} d\varphi \int dx x^2 ,$$

$$y(\vartheta) = \frac{q/2}{\cos \vartheta} .$$

The integration can be readily carried out:

$$S(q) = \frac{2\pi}{3} \Theta\left(k_F - \frac{q}{2}\right) \left\{ k_F^3 - \frac{3}{4} q k_F^2 + \frac{1}{16} q^3 \right\} . \quad (2.95)$$

The remaining evaluation of (2.93) is then simple:

$$\varepsilon^{(1)} = -\frac{0.916}{r_s} [\text{ryd}] .$$

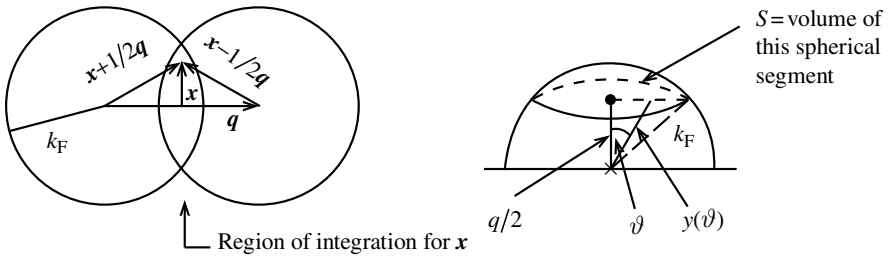
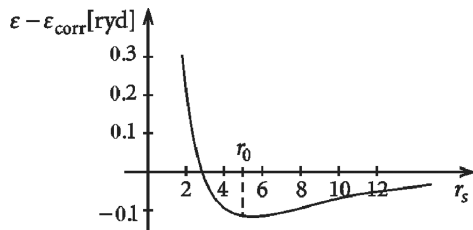


Fig. 2.2 A schematic representation of the integration region for computing the ground-state energy in the jellium model to first order in perturbation theory as in (2.93)

Fig. 2.3 Ground-state energy per particle in the jellium model as a function of the density parameter r_s



This yields finally for the ground-state energy per particle:

$$\frac{1}{N} E_{\min}[\text{ryd}] = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \varepsilon_{\text{corr}} = \varepsilon. \quad (2.96)$$

The first term is the kinetic energy (2.87), the second represents the so-called **exchange energy**. The latter is typical of systems of identical particles and is a direct result of the principle of indistinguishability and thus for Fermions of the Pauli principle. It guarantees that electrons with parallel spins do not approach each other too closely. Every effect which keeps particles of the same charge *at a distance* leads to a reduction of their ground-state energy. This is the reason for the minus sign in (2.96). The last term is called the **correlation energy**. It gives the deviation of the perturbation-theoretical energy from the exact result and is thus naturally unknown. Modern methods of many-body theory lead to the following series (see (5.177)):

$$\varepsilon_{\text{corr}} = \frac{2}{\pi^2} (1 - \ln 2) \ln r_s - 0.094 + O(r_s \ln r_s) [\text{ryd}]. \quad (2.97)$$

The simple jellium model already gives useful results, e.g. $\varepsilon - \varepsilon_{\text{corr}}$ passes through a minimum at

$$\begin{aligned} r_0 &= (r_s)_{\min} = 4.83, \\ (\varepsilon - \varepsilon_{\text{corr}})_{\min} &= -0.095 [\text{ryd}] = -1.29 [\text{eV}]. \end{aligned}$$

This indicates an optimal value of the electron density, which corresponds finally to the energetically most favourable ionic spacing, and thus explains, at least qualitatively, the phenomenon of **metallic bonding**.

2.1.3

The Hubbard Model

The decisive simplification achieved by the jellium model consists of the fact that it treats the ions in a solid merely as a positively-charged, homogeneously distributed background, i.e. the crystalline structure is completely ignored. The Bloch functions then become plane waves (2.44), so that within the framework of this model, the electrons have a constant

occupation probability throughout the entire crystal. The jellium model is thus limited from the start to electrons in *broad* energy bands, i.e. for example to the conduction electrons of the alkali metals, for which these assumptions are valid to a good approximation.

The electrons in *narrow* energy bands have a relatively low mobility and distinct maxima in their occupation probabilities at the locations of the individual lattice ions. Plane waves are naturally not appropriate for the description of such band electrons. A considerably better starting point is the so-called **tight-binding approximation**.

If we assume a strong lattice potential $\hat{V}(\mathbf{r})$ and a low mobility of the band electrons, then in the neighbourhood of the lattice ions, the atomic Hamiltonian

$$H_{\text{at}} = \sum_{i=1}^{N_i} h_{\text{at}}^{(i)} , \quad (2.98)$$

which is the sum of the Hamiltonians for the individual atoms, should yield a fairly reasonable description, that is, it should be quite similar to H_0 as in (2.7):

$$h_{\text{at}}^{(i)} \varphi_n(\mathbf{r} - \mathbf{R}_i) = \varepsilon_n \varphi_n(\mathbf{r} - \mathbf{R}_i) . \quad (2.99)$$

φ_n is an atomic wavefunction, which we can take to be known. The index n symbolises a set of quantum numbers. We are interested in the case that the functions φ_n have only a limited overlap when they are centered at different locations \mathbf{R}_i , \mathbf{R}_j . This results in a low tunneling probability for the electrons from atom to atom and therefore only a weak splitting of the atomic levels in the solid – i.e. a narrow energy band.

For the Hamiltonian of the non-interacting electrons (2.7),

$$H_0 = \sum_{i=1}^{N_e} h_0^{(i)} , \quad (2.100)$$

we use the following approach:

$$h_0 = h_{\text{at}} + V_1(\mathbf{r}) . \quad (2.101)$$

The correction $V_1(\mathbf{r})$ should thus be small in the neighbourhood of the lattice ions, but in contrast relatively large in the intermediate regions, where however the φ_n have dropped to nearly zero. From (2.13), we in fact must solve the following problem:

$$h_0 \psi_{nk}(\mathbf{r}) = \varepsilon_n(\mathbf{k}) \psi_{nk}(\mathbf{r}) . \quad (2.102)$$

The complete solution of this eigenvalue problem appears to be extremely complicated. We therefore use the following trial functions for the Bloch functions $\psi_{nk}(\mathbf{r})$:

$$\psi_{nk}(\mathbf{r}) = \frac{1}{\sqrt{N_i}} \sum_{j=1}^{N_i} e^{ik \cdot \mathbf{R}_j} \varphi_n(\mathbf{r} - \mathbf{R}_j) . \quad (2.103)$$

This *ansatz* obeys the Bloch theorem (2.15), and it is practically exact near the ionic cores ($V_1(\mathbf{r}) \approx 0$), whilst the errors in the interatomic regions are not too great, due to the small overlap of the wavefunctions there. A comparison with (2.29) shows that we have replaced the exact Wannier functions by the atomic wavefunctions. Using (2.102), we now compute approximately the Bloch energies $\varepsilon_n(\mathbf{k})$. To start, the following expressions are strictly valid:

$$\begin{aligned} \int \varphi_n^*(\mathbf{r}) h_0 \psi_{nk}(\mathbf{r}) d^3r &= \varepsilon_n(\mathbf{k}) \int \varphi_n^*(\mathbf{r}) \psi_{nk}(\mathbf{r}) d^3r, \\ \int \varphi_n^*(\mathbf{r}) V_1(\mathbf{r}) \psi_{nk}(\mathbf{r}) d^3r &= (\varepsilon_n(\mathbf{k}) - \varepsilon_n) \int \varphi_n^*(\mathbf{r}) \psi_{nk}(\mathbf{r}) d^3r. \end{aligned}$$

Here, we now apply the *ansatz* (2.103). With the abbreviations

$$v_n = \int d^3r V_1(\mathbf{r}) |\varphi_n(\mathbf{r})|^2, \quad (2.104)$$

$$T_0^{(n)} = \varepsilon_n + v_n, \quad (2.105)$$

$$\alpha_n^{(j)} = \int d^3r \varphi_n^*(\mathbf{r}) \varphi_n(\mathbf{r} - \mathbf{R}_j), \quad (2.106)$$

$$\gamma_n^{(j)} = \int d^3r \varphi_n^*(\mathbf{r}) V_1(\mathbf{r}) \varphi_n(\mathbf{r} - \mathbf{R}_j) \quad (2.107)$$

we obtain:

$$(\varepsilon_n(\mathbf{k}) - \varepsilon_n) = v_n + \frac{1}{\sqrt{N_i}} \sum_j^{\mathbf{R}_j \neq 0} [\gamma_n^{(j)} - (\varepsilon_n(\mathbf{k}) - \varepsilon_n) \alpha_n^{(j)}] e^{i\mathbf{k} \cdot \mathbf{R}_j},$$

where we have presumed that the atomic wavefunctions are normalised. We then find for the Bloch energies:

$$\varepsilon_n(\mathbf{k}) = \varepsilon_n + \frac{v_n + \frac{1}{\sqrt{N_i}} \sum_j^{\neq 0} \gamma_n^{(j)} e^{i\mathbf{k} \cdot \mathbf{R}_j}}{1 + \frac{1}{\sqrt{N_i}} \sum_j^{\neq 0} \alpha_n^{(j)} e^{i\mathbf{k} \cdot \mathbf{R}_j}}. \quad (2.108)$$

The *overlap integrals* $\gamma_n^{(j)}$ and $\alpha_n^{(j)}$ are by assumption for $\mathbf{R}_j \neq 0$ only very small quantities, so that we can with confidence simplify further:

$$\varepsilon_n(\mathbf{k}) = T_0^{(n)} + \gamma_n^{(1)} \sum_{\Delta} e^{i\mathbf{k} \cdot \mathbf{R}_{\Delta}}. \quad (2.109)$$

Δ indicates the nearest neighbours to the atom at the origin of the coordinate system. The sum can as a rule be readily computed. Thus, for a simple **cubic lattice**:

$$\begin{aligned} \mathbf{R}_{\Delta} &= a(\pm 1, 0, 0); \quad a(0, \pm 1, 0); \quad a(0, 0, \pm 1), \\ \varepsilon_n^{\text{s.c.}}(\mathbf{k}) &= T_0^{(n)} + 2\gamma_n^{(1)} (\cos(k_x a) + \cos(k_y a) + \cos(k_z a)). \end{aligned} \quad (2.110)$$

a is the lattice constant, and $T_0^{(n)}$ and $\gamma_n^{(1)}$ are parameters which must be determined experimentally. $\gamma_n^{(1)}$ is determined by the width W of the band:

$$W_n^{\text{s.c.}} = 12 |\gamma_n^{(1)}| . \quad (2.111)$$

The tight-binding approximation, which led to (2.109), is strictly speaking allowed only for so-called s bands. For p -, d -, f -... bands, a certain degree of degeneracy must be taken into account, but we shall not discuss this point further here. In the following, we limit our treatment to s bands and thus leave off the index n from here on.

The Bloch energies, (2.109) or (2.110), now clearly exhibit the influence of the crystal structure. Only for very small $|\mathbf{k}|$ values near the bottom of the band does the parabolic dispersion, which applies within the jellium model, hold approximately, $\varepsilon(\mathbf{k}) \Rightarrow \varepsilon_0(\mathbf{k})/\hbar^2 k^2/2m$.

In second quantisation, H_0 takes the same form as in (2.33):

$$H_0 = \sum_{ij\sigma} T_{ij} a_{i\sigma}^+ a_{j\sigma} . \quad (2.112)$$

The tight-binding approximation permits electronic transitions via the hopping integral

$$T_{ij} = \frac{1}{N_i} \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \quad (2.113)$$

only between nearest-neighbour lattice positions. For the Coulomb interaction of the band electrons, (2.55) of course still applies. The transformation to real space then yields:

$$H_{\text{ee}} = \frac{1}{2} \sum_{\substack{ijkl \\ \sigma, \sigma'}} v(ij; kl) a_{i\sigma}^+ a_{j\sigma'}^+ a_{l\sigma'} a_{k\sigma} , \quad (2.114)$$

where the matrix element is to be computed with atomic wavefunctions:

$$\begin{aligned} v(ij; kl) &= \\ &= \frac{e^2}{4\pi\varepsilon_0} \iint d^3r_1 d^3r_2 \frac{\varphi^*(\mathbf{r}_1 - \mathbf{R}_i) \varphi^*(\mathbf{r}_2 - \mathbf{R}_j) \varphi(\mathbf{r}_2 - \mathbf{R}_l) \varphi(\mathbf{r}_1 - \mathbf{R}_k)}{|\mathbf{r}_1 - \mathbf{r}_2|} . \end{aligned} \quad (2.115)$$

Owing to the small overlap of the atomic wavefunctions which are centered on different lattice positions, the intra-atomic matrix element

$$U = v(ii; ii) \quad (2.116)$$

predominates. Hubbard made the suggestion that the electron-electron interaction therefore be limited to this term:

Hubbard model

$$H = \sum_{ij\sigma} T_{ij} a_{i\sigma}^+ a_{j\sigma} + \frac{1}{2} U \sum_{i,\sigma} \hat{n}_{i\sigma} \hat{n}_{i-\sigma} \quad (2.117)$$

(Notation: $\sigma = \uparrow$ (\downarrow) $\iff -\sigma = \downarrow$ (\uparrow)). The Hubbard model must thus be the simplest model with which one can study the interplay of the kinetic energy, the Coulomb interactions, the Pauli principle and the lattice structure.

The drastic simplifications which led to (2.117) of course entail a correspondingly limited applicability of the model.

The model is used in the discussion of

1. the electronic properties of solids with narrow energy bands (e.g. transition metals),
2. band magnetism (Fe, Co, Ni, ...),
3. metal-insulator transitions ("Mott transitions"),
4. general principles of statistical mechanics,
5. high-temperature superconductivity.

In spite of its simple structure, the exact solution of the Hubbard model has thus far not been achieved. One must still resort to approximate solutions. Examples will be discussed in the following sections.

2.1.4

Exercises

Exercise 2.1.1 A solid contains $N = N'^3$ (N' even) unit cells in the volume $V = L^3$ ($L = aN'$). For the allowed wave vectors, using periodic boundary conditions, the following holds:

$$\mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z); \quad n_{x,y,z} = 0, \pm 1, \pm 2, \dots, \pm \left(\frac{N'}{2} - 1 \right), N'/2.$$

Prove the orthogonality relation

$$\delta_{ij} = \frac{1}{N} \sum_{\mathbf{k}}^{\text{1. BZ}} \exp [i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)].$$

The sum runs over all the wavenumbers within the first Brillouin zone.

Exercise 2.1.2 Based on the fundamental commutation relations for Bloch operators, $a_{k\sigma}^+$, $a_{k\sigma}$, derive the corresponding relations for Wannier operators $a_{i\sigma}^+$, $a_{j\sigma}$.

Exercise 2.1.3 In theoretical solid-state physics, one often has to deal with integrals of the type

$$I(T) = \int_{-\infty}^{+\infty} dx g(x) f_-(x), \quad f_-(x) = \{\exp[\beta(x - \mu)] + 1\}^{-1}.$$

These deviate from their values at $T = 0$

$$I(T = 0) = \int_{-\infty}^{\varepsilon_F} dx g(x)$$

by an expression which is determined almost exclusively by the behaviour of the function $g(x)$ within the *Fermi layer* $(\mu - 2k_B T; \mu + 2k_B T)$, where μ represents the chemical potential. Power series are therefore very promising! Assume that $g(x) \rightarrow 0$ for $x \rightarrow -\infty$, and that $g(x)$ for $x \rightarrow +\infty$ diverges at most as a power of x and is regular within the *Fermi layer*.

1. Show that

$$I(T) = - \int_{-\infty}^{+\infty} dx p(x) \frac{\partial}{\partial x} f_-(x)$$

holds, with

$$p(x) = \int_{-\infty}^x dy g(y).$$

2. Use a Taylor series for $p(x)$ around μ (chemical potential) for the following representation of the integral:

$$I(T) = p(\mu) + 2 \sum_{n=1}^{\infty} (1 - 2^{1-2n}) \beta^{-2n} \zeta(2n) g^{(2n-1)}(\mu).$$

Here, $g^{(2n-1)}(\mu)$ is the $(2n - 1)$ -th derivative of the function $g(x)$ at the position $x = \mu$, and $\zeta(n)$ is Riemann's ζ function:

$$\zeta(n) = \sum_{p=1}^{\infty} p^{-n} = \frac{1}{(1-2^{1-n})\Gamma(n)} \int_0^{\infty} du \frac{u^{n-1}}{e^u + 1} .$$

3. Calculate explicitly the first three terms of the series for $I(T)$.

Exercise 2.1.4 The *Sommerfeld model* can explain many electronic properties of the so-called *simple metals* such as Na, K, Mg, Cu, ... to a good approximation. It is defined by the following model assumptions:

- An ideal Fermi gas within the volume $V = L^3$.
 - Periodic boundary conditions on V .
 - A constant lattice potential $V(\mathbf{r}) = \text{const.}$
- Give the eigenstate energies and the eigenfunctions.
 - Calculate the Fermi energy and the Fermi wavevector as functions of the electron density $n = N/V$.
 - How does the average energy per electron depend on the Fermi energy?
 - Determine the electronic density of states $\rho_0(E)$.
 - Make use of the dimensionless density parameter r_s from Eq. (2.83) to compute the ground-state energy E_0 :

$$E_0 = N \frac{2,21}{r_s^2} [\text{ryd}] .$$

Exercise 2.1.5 Discuss some of the thermodynamic properties of the Sommerfeld model which was introduced in Ex. 2.1.4.

- Calculate the temperature dependence of the mean occupation number of a single-particle level.
- How are the total particle number N and the internal energy $U(T)$ related to the density of states $\rho_0(E)$?
- Verify, using the Sommerfeld series from Ex. 2.1.2, that the following relation holds for the chemical potential μ :

$$\mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right] .$$

- Compute to a precision of $(k_B T/\varepsilon_F)^4$ the internal energy $U(T)$ and the specific heat c_V of the itinerant metal electrons.

5. Calculate and discuss the entropy

$$S = \frac{\partial}{\partial T} (k_B T \ln \Xi) .$$

Test the Third Law! Ξ is the grand canonical partition function.

Exercise 2.1.6

1. Transform the operator for the electron density

$$\hat{\rho} = \sum_{i=1}^N \delta(\mathbf{r} - \hat{\mathbf{r}}_i)$$

to the second quantisation with Wannier states as the single-particle basis.

2. Derive, using the result of 1, the relation between the electron number and the electron density operator.
 3. What form does the electron density operator from part 1 take in the special case of the jellium model?

Exercise 2.1.7 Represent the operator for the electron density

$$\hat{\rho} = \sum_{i=1}^N \delta(\mathbf{r} - \hat{\mathbf{r}}_i)$$

in the formalism of second quantisation using field operators.

Exercise 2.1.8 Transform the Hamiltonian of the jellium model into second quantisation using Wannier states as a single-particle basis.

Exercise 2.1.9 Making use of the electron density operator

$$\hat{\rho} = \sum_{i=1}^N \delta(\mathbf{r} - \hat{\mathbf{r}}_i) ,$$

one can calculate the so-called density correlation

$$G(\mathbf{r}, t) = \frac{1}{N} \int d^3 r' \langle \rho(\mathbf{r}' - \mathbf{r}, 0) \rho(\mathbf{r}', t) \rangle$$

as well as the dynamic structure factor

$$S(\mathbf{q}, \omega) = \int d^3r \int_{-\infty}^{+\infty} dt G(\mathbf{r}, t) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} .$$

The expression

$$S(\mathbf{q}) = \int_{-\infty}^{+\infty} d\omega S(\mathbf{q}, \omega)$$

is termed the static structure factor,
whilst the static pair distribution function $g(\mathbf{r})$ is defined by

$$G(\mathbf{r}, 0) = \delta(\mathbf{r}) + ng(\mathbf{r}) \quad (n = N/V) .$$

1. Show that for the density correlation,

$$G(\mathbf{r}, t) = \frac{1}{NV} \sum_{\mathbf{q}} \langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}}(t) \rangle e^{-i\mathbf{q} \cdot \mathbf{r}}$$

holds. What is the meaning of $G(\mathbf{r}, t)$?

2. Verify the expression

$$ng(\mathbf{r}) = \frac{1}{N} \sum_{i,j}^{i \neq j} \langle \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(0)) \rangle .$$

Consider an appropriate physical interpretation here, also.

3. Prove the following relations for the structure factor:

$$S(\mathbf{q}, \omega) = \frac{1}{N} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}}(t) \rangle ,$$

$$S(\mathbf{q}) = \frac{2\pi}{N} \langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}} \rangle .$$

4. Show that at $T = 0$, the following holds:

$$S(\mathbf{q}, \omega) = \frac{2\pi}{N} \sum_n | \langle E_n | \rho_{\mathbf{q}}^+ | E_0 \rangle |^2 \delta \left[\omega - \frac{1}{\hbar} (E_n - E_0) \right] .$$

$|E_n\rangle$ are the eigenstates of the Hamiltonian, and $|E_0\rangle$ is its ground state.

Exercise 2.1.10

1. Use the general results from Ex. 2.1.9 to determine the static structure factor $S(\mathbf{q})$ with the exact eigenstates of the Sommerfeld model. Sketch its q dependence.
2. Compute also the static pair distribution function $g(\mathbf{r})$. Sketch and discuss its r dependence.

Exercise 2.1.11 Compute in the *tight-binding* approximation the Bloch energies $\varepsilon(\mathbf{k})$ for the body-centered cubic and for the face-centered cubic lattice structures.

Exercise 2.1.12 Show that the *tight-binding* approach for the electronic wavefunctions $\varphi_{n\mathbf{k}}(\mathbf{r})$ obeys the Bloch theorem.

2.2

Lattice Vibrations

In Sect. 2.1, the lattice ions were assumed to be motionless and only the excitations of the electronic system were investigated. Following a programme as in (2.6) we now want to discuss the subsystem of the ions in more detail; i.e. the Hamiltonian of (2.3) will now be at the centre of attention.

If energy is transferred to a single lattice ion, e.g. by a particle collision, it will be rapidly distributed over the whole lattice as a result of the strong ion-ion interactions. The local excitation will become a **collective excitation**, in which finally all the lattice sites participate. It is therefore expedient to use collective coordinates, which are still to be defined, in the mathematical description instead of ion coordinates. In this representation, the lattice vibrations can then be quantised. The corresponding quanta are called **phonons**.

2.2.1

The Harmonic Approximation

The restoring forces required for lattice vibrations are the **bonding forces**, which can have rather diverse physical origins. Qualitatively, the pair potential $V_i(|\mathbf{R}_\alpha - \mathbf{R}_\beta|)$ however always has the same form. The potential minimum defines the equilibrium distance $R_{\alpha\beta}^{(0)}$. The so-called **harmonic approximation** consists in the end in treating the potential curve

approximately as a parabola, which seems reasonable for small excursions from the equilibrium distance. We shall next discuss this point more quantitatively.

Our starting point will be a Bravais lattice with a basis containing p atoms, which we describe as in (2.9) by

$$\mathbf{R}_s^m = \mathbf{R}^m + \mathbf{R}_s \quad (2.118)$$

with $s = 1, 2, \dots, p$ and $\mathbf{m} \equiv (m_1, m_2, m_3)$; $m_i \in \mathbb{Z}$,

$$\mathbf{R}^m = \sum_{i=1}^3 m_i \mathbf{a}_i . \quad (2.119)$$

Let

$\mathbf{x}_s^m(t)$ be the momentary position of the (\mathbf{m}, s) -th atom, and
 $\mathbf{u}_s^m(t)$ be the displacement of the (\mathbf{m}, s) -th atom from equilibrium.

As a result, we find:

$$\mathbf{x}_s^m(t) = \mathbf{R}_s^m + \mathbf{u}_s^m(t) . \quad (2.120)$$

The **kinetic energy** of the lattice ions is then given by:

$$H_{i,\text{kin}} = \frac{1}{2} \sum_{\substack{\mathbf{m} \\ s, i}} M_s \left(\frac{d\mathbf{u}_{s,i}^m}{dt} \right)^2 , \quad i = x, y, z . \quad (2.121)$$

For the **potential energy**, we write:

$$H_{ii} = V(\{\mathbf{x}_s^m\}) = V(\{\mathbf{R}_s^m + \mathbf{u}_s^m\}) . \quad (2.122)$$

Here, the quantity

$$V_0 = V(\{\mathbf{R}_s^m\}) \quad (2.123)$$

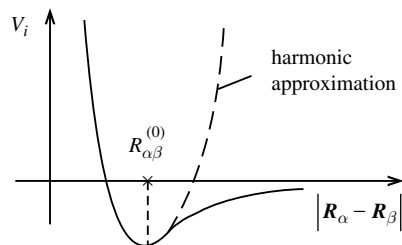


Fig. 2.4 Illustration of the harmonic approximation for the pair potential in a solid

represents the so-called **binding energy**. We expand V around the equilibrium position:

$$V(\{\mathbf{x}_s^m\}) = V_0 + \sum_{\substack{\mathbf{m} \\ s,i}} \varphi_{\mathbf{m},s,i} u_{s,i}^m + \frac{1}{2} \sum_{\substack{\mathbf{m} \\ s,i}} \sum_{\substack{\mathbf{n} \\ t,j}} \varphi_{\mathbf{m},s,i}^{n,t,j} u_{s,i}^m u_{t,j}^n + O(u^3) . \quad (2.124)$$

The **harmonic approximation** now consists of neglecting the remainder $O(u^3)$. The displacements u are as a rule less than 5% of the lattice spacing, so that the harmonic approximation is quite appropriate. Higher-order, so-called **anharmonic terms**, are therefore initially not of interest.

For the partial derivatives φ in (2.124), we find:

$$\varphi_{\mathbf{m},s,i} \equiv \left. \frac{\partial V}{\partial x_{s,i}^{\mathbf{m}}} \right|_0 = 0 . \quad (2.125)$$

This is the definition of the equilibrium position. The second derivatives form a

matrix of the atomic force constants

$$\varphi_{\mathbf{m},s,i}^{n,t,j} \equiv \left. \frac{\partial^2 V}{\partial x_{t,j}^{\mathbf{n}} \partial x_{s,i}^{\mathbf{m}}} \right|_0 . \quad (2.126)$$

For a better understanding of this important matrix, the following statement is useful:

$-\varphi_{\mathbf{m},s,i}^{n,t,j} u_{t,j}^n$ is the force in the i direction, which acts on the (\mathbf{m},s) -th atom, when the (\mathbf{n},t) -th atom is displaced in the j direction by $u_{t,j}^n$, and all the other atoms remain fixed.

The harmonic approximation thus corresponds to a linear force law, as in a harmonic oscillator:

$$M_s \ddot{u}_{s,i}^{\mathbf{m}} = - \frac{\partial V}{\partial u_{s,i}^{\mathbf{m}}} = - \sum_{\substack{\mathbf{n} \\ t,j}} \varphi_{\mathbf{m},s,i}^{n,t,j} u_{t,j}^n . \quad (2.127)$$

The force-constant matrix has a few obvious symmetries. It follows directly from its definition that:

$$\varphi_{\mathbf{m},s,i}^{n,t,j} \equiv \varphi_{\mathbf{n},t,j}^{\mathbf{m},s,i} . \quad (2.128)$$

On translating the whole solid body by $\Delta \mathbf{x} = (\Delta x_1, \Delta x_2, \Delta x_3)$, the forces naturally remain unchanged. It therefore follows from

$$-\sum_j \Delta x_j \sum_{n,t} \varphi_{m,s,i}^{n,t,j} = 0$$

that the relation

$$\sum_{n,t} \varphi_{m,s,i}^{n,t,j} = 0 \quad (2.129)$$

holds. Finally, the translational symmetry yields:

$$\varphi_{m,s,i}^{n,t,j} = \varphi_{s,i}^{t,j}(\mathbf{n} - \mathbf{m}) . \quad (2.130)$$

To solve (2.127), we first take a trial solution of the form:

$$u_{s,i}^m = \frac{\hat{u}_{s,i}^m}{\sqrt{M_s}} e^{-i\omega t} . \quad (2.131)$$

This gives the eigenvalue equation

$$\omega^2 \hat{u}_{s,i}^m = \sum_{\substack{n \\ t,j}} D_{m,s,i}^{n,t,j} \hat{u}_{t,j}^n \quad (2.132)$$

for the real and symmetric matrix

$$D = \frac{\varphi}{\sqrt{M_s M_t}} . \quad (2.133)$$

It has $3pN$ real eigenvalues $(\omega_{s,i}^m)^2$. The eigenvalues $\omega_{s,i}^m$ are thus likewise real or purely imaginary. Only the real eigenvalues represent *physical* solutions. Making use of the translational symmetry (2.130), the dimensionality of the eigenvalue problem is reduced from $3pN$ to $3p$:

$$\omega^2 c_{s,i} = \sum_{t,j} K_{i,j}^{s,t} c_{t,j} . \quad (2.134)$$

Here, we have used the following definitions:

$$u_{s,i}^m = \frac{c_{s,i}}{\sqrt{M_s}} \exp[i(\mathbf{q} \cdot \mathbf{R}_m - \omega t)] , \quad (2.135)$$

$$K_{i,j}^{s,t}(\mathbf{q}) = \sum_p \frac{\varphi_{0,s,i}^{p,t,j}}{\sqrt{M_s M_t}} \exp(i\mathbf{q} \cdot \mathbf{R}^p) . \quad (2.136)$$

Equation (2.134) is an eigenvalue equation for the matrix K with $3p$ eigenvalues:

$$\omega = \omega_r(\mathbf{q}), \quad r = 1, 2, \dots, 3p. \quad (2.137)$$

Crystals are anisotropic. The **dispersion branches** $\omega_r(\mathbf{q})$ therefore have to be determined for each direction $\mathbf{q}/|\mathbf{q}|$ as functions of $q = |\mathbf{q}|$. Details can be found for the standard example of a *diatomic, linear chain* in the textbook literature of solid-state physics. One finds there (Ex. 2.2.1):

$$3 \text{ acoustic branches} \iff \omega(q = 0) = 0,$$

$$3(p - 1) \text{ optical branches} \iff \omega(q = 0) \neq 0.$$

Owing to the periodic boundary conditions, the wavenumbers \mathbf{q} are discrete. If \mathbf{G} is an arbitrary vector in the reciprocal lattice, then because of $\exp(i\mathbf{G} \cdot \mathbf{R}^m) = 1$, we have:

$$\omega_r(\mathbf{q} + \mathbf{G}) = \omega_r(\mathbf{q}). \quad (2.138)$$

This means that one needs only consider wavenumbers \mathbf{q} within the first Brillouin zone. Time-reversal invariance of the equations of motion finally leads to:

$$\omega_r(\mathbf{q}) = \omega_r(-\mathbf{q}). \quad (2.139)$$

For each of the $3p$ ω_r values, Eq. (2.134) has a solution

$$c_{s,i} = \varepsilon_{s,i}^{(r)}(\mathbf{q}), \quad (2.140)$$

which can be chosen so that the orthonormality relation

$$\sum_{s,i} \varepsilon_{s,i}^{(r)*}(\mathbf{q}) \varepsilon_{s,i}^{(r')}(\mathbf{q}) = \delta_{r,r'} \quad (2.141)$$

is fulfilled. The general solution of the equation of motion (2.127) is thus finally found to be:

$$u_{s,i}^m(t) = \frac{1}{\sqrt{NM_s}} \sum_{r=1}^{3p} \sum_{\mathbf{q}}^{\text{1.BZ}} Q_r(\mathbf{q}, t) \varepsilon_{s,i}^{(r)}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}^m}. \quad (2.142)$$

Here, we have included the time factor $\exp(-i\omega_r(\mathbf{q})t)$ within the coefficients $Q_r(\mathbf{q}, t)$. With

$$\frac{1}{N} \sum_m \exp(i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}^m) = \delta_{\mathbf{q}, \mathbf{q}'},$$

we find the **normal coordinates** $Q_r(\mathbf{q}, t)$

$$Q_r(\mathbf{q}, t) = \frac{1}{\sqrt{N}} \sum_{\substack{\mathbf{m} \\ s, i}} \sqrt{M_s} u_{s, i}^{\mathbf{m}}(t) \varepsilon_{s, i}^{(r)*}(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{R}^{\mathbf{m}}}, \quad (2.143)$$

which obey the equation of motion of the harmonic oscillator

$$\ddot{Q}_r(\mathbf{q}, t) + \omega_r^2(\mathbf{q}) Q_r(\mathbf{q}, t) = 0. \quad (2.144)$$

2.2.2

The Phonon Gas

The harmonic approximation of the previous sections gives the following expression for the Lagrange function $L = T - V$ of the ion system:

$$L = \frac{1}{2} \sum_{\substack{\mathbf{m} \\ s, i}} M_s (\dot{u}_{s, i}^{\mathbf{m}})^2 - \frac{1}{2} \sum_{\substack{\mathbf{m}, s, i \\ \mathbf{n}, t, j}} \varphi_{\mathbf{m}, s, i}^{\mathbf{n}, t, j} u_{s, i}^{\mathbf{m}} u_{t, j}^{\mathbf{n}}. \quad (2.145)$$

We wish to represent L in normal coordinates. We rearrange, making use of:

$$\frac{1}{N} \sum_{\mathbf{m}} \exp[i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}^{\mathbf{m}}] = \begin{cases} 1, & \text{if } \mathbf{q} - \mathbf{q}' = 0 \text{ or } \mathbf{G}, \\ 0 & \text{otherwise,} \end{cases} \quad (2.146)$$

$$\left[Q_r(\mathbf{q}, t) \varepsilon_{s, i}^{(r)}(\mathbf{q}) \right]^* = Q_r(-\mathbf{q}, t) \varepsilon_{s, i}^{(r)}(-\mathbf{q}). \quad (2.147)$$

Equation (2.147) must hold, so that the displacements $u_{s, i}^{\mathbf{m}}$ are real. We have already used Eq. (2.146) in various contexts.

$$\begin{aligned} \frac{1}{2} \sum_{\substack{\mathbf{m} \\ s, i}} M_s (\dot{u}_{s, i}^{\mathbf{m}})^2 &= \frac{1}{2} \sum_{\substack{\mathbf{m} \\ s, i}} M_s \frac{1}{N M_s} \sum_{\mathbf{q}, \mathbf{q}'} \sum_{r, r'} \dot{Q}_r(\mathbf{q}, t) \dot{Q}_{r'}(\mathbf{q}', t) \varepsilon_{s, i}^{(r)}(\mathbf{q}) \cdot \\ &\quad \cdot \varepsilon_{s, i}^{(r')}(\mathbf{q}') e^{i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{R}^{\mathbf{m}}} = \\ &= \frac{1}{2} \sum_{\mathbf{q}} \sum_{r, r'} \dot{Q}_r(\mathbf{q}, t) \dot{Q}_{r'}(-\mathbf{q}, t) \sum_{s, i} \varepsilon_{s, i}^{(r)}(\mathbf{q}) \varepsilon_{s, i}^{(r')}(-\mathbf{q}) = \\ &= \frac{1}{2} \sum_{\mathbf{q}, r} \dot{Q}_r^*(\mathbf{q}, t) \dot{Q}_r(\mathbf{q}, t). \end{aligned} \quad (2.148)$$

In an analogous manner, we find the potential energy:

$$\begin{aligned}
 & \frac{1}{2} \sum_{\substack{\mathbf{m}, s, i \\ \mathbf{n}, t, j}} \varphi_{\mathbf{m}, s, i}^{\mathbf{n}, t, j} u_{s, i}^{\mathbf{m}} u_{t, j}^{\mathbf{n}} = \\
 &= \frac{1}{2N} \sum_{\substack{\mathbf{m}, s, i \\ \mathbf{n}, t, j}} \varphi_{\mathbf{m}, s, i}^{\mathbf{n}, t, j} \frac{1}{\sqrt{M_s M_t}} \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \sum_{r, r'} Q_r(\mathbf{q}, t) Q_{r'}(\mathbf{q}', t) \cdot \\
 & \quad \cdot \varepsilon_{s, i}^{(r)}(\mathbf{q}) \varepsilon_{t, j}^{(r')}(\mathbf{q}') e^{i\mathbf{q} \cdot \mathbf{R}^m} e^{i\mathbf{q}' \cdot \mathbf{R}^n} = \\
 &= \frac{1}{2N} \sum_{\substack{s, i \\ \mathbf{n}, t, j}} \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \sum_{r, r'} Q_r(\mathbf{q}, t) Q_{r'}(\mathbf{q}', t) \varepsilon_{s, i}^{(r)}(\mathbf{q}) \varepsilon_{t, j}^{(r')}(\mathbf{q}') \cdot \\
 & \quad \cdot \sum_{\mathbf{m}} \frac{\varphi_{s, i}^{t, j}(\mathbf{n} - \mathbf{m})}{\sqrt{M_s M_t}} e^{i\mathbf{q} \cdot (\mathbf{R}^m - \mathbf{R}^n)} e^{i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{R}^n} = \\
 &= \frac{1}{2} \sum_{\substack{s, i \\ t, j}} \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \sum_{r, r'} Q_r(\mathbf{q}, t) Q_{r'}(\mathbf{q}', t) \varepsilon_{s, i}^{(r)}(\mathbf{q}) \varepsilon_{t, j}^{(r')}(\mathbf{q}') \cdot \\
 & \quad \cdot K_{i, j}^{s, t}(\mathbf{q}) \frac{1}{N} \sum_{\mathbf{n}} e^{i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{R}^n} = \\
 &= \frac{1}{2} \sum_{s, i} \sum_{\mathbf{q}} \sum_{r, r'} Q_r(\mathbf{q}, t) Q_{r'}(-\mathbf{q}, t) \varepsilon_{s, i}^{(r)}(\mathbf{q}) \sum_{t, j} K_{ij}^{s, t}(\mathbf{q}) \varepsilon_{t, j}^{(r')}(-\mathbf{q}) = \\
 &= \frac{1}{2} \sum_{\mathbf{q}} \sum_{r, r'} \omega_r^2(-\mathbf{q}) Q_r(\mathbf{q}, t) Q_{r'}(-\mathbf{q}, t) \sum_{s, i} \varepsilon_{s, i}^{(r)}(\mathbf{q}) \varepsilon_{s, i}^{(r')}(-\mathbf{q}) = \\
 &= \frac{1}{2} \sum_{\mathbf{q}, r} \omega_r^2(\mathbf{q}) Q_r(\mathbf{q}, t) Q_r^*(\mathbf{q}, t) .
 \end{aligned} \tag{2.149}$$

All together, we then have for the Lagrange function:

$$L = \frac{1}{2} \sum_{r, \mathbf{q}} \{ \dot{Q}_r^*(\mathbf{q}, t) \dot{Q}_r(\mathbf{q}, t) - \omega_r^2(\mathbf{q}) Q_r^*(\mathbf{q}, t) Q_r(\mathbf{q}, t) \} . \tag{2.150}$$

The momenta which are canonically conjugate to the normal coordinates,

$$\Pi_r(\mathbf{q}, t) = \frac{\partial L}{\partial \dot{Q}_r} = \dot{Q}_r^*(\mathbf{q}, t) , \tag{2.151}$$

are required to formulate the classical Hamilton function:

$$H = \frac{1}{2} \sum_{r, \mathbf{q}} \{ \Pi_r^*(\mathbf{q}, t) \Pi_r(\mathbf{q}, t) + \omega_r^2(\mathbf{q}) Q_r^*(\mathbf{q}, t) Q_r(\mathbf{q}, t) \} . \tag{2.152}$$

This is a notable result, since by transforming to the normal coordinates, we have shown that the Hamilton function decomposes into a sum of $3pN$ non-coupled, linear harmonic oscillators.

The next step is the **quantisation** of the classical variables. The displacements $u_{s,i}^m$ and the momenta $M_s \dot{u}_{s,i}^m$ now become operators with the fundamental commutation relations:

$$[u_{s,i}^m, u_{t,j}^n]_- = [M_s \dot{u}_{s,i}^m, M_t \dot{u}_{t,j}^n]_- = 0, \quad (2.153)$$

$$[M_s \dot{u}_{s,i}^m, u_{t,j}^n]_- = \frac{\hbar}{i} \delta_{m,n} \delta_{s,t} \delta_{i,j}. \quad (2.154)$$

By substitution, we find from them the commutation relations for the normal coordinates and their canonically conjugated momenta. With (2.143) and (2.153), we immediately obtain:

$$[Q_r(\mathbf{q}), Q_{r'}(\mathbf{q}')]_- = [\Pi_r(\mathbf{q}), \Pi_{r'}(\mathbf{q}')]_- = 0. \quad (2.155)$$

For the third relation, we make use of (2.154):

$$\begin{aligned} [\Pi_r(\mathbf{q}), Q_{r'}(\mathbf{q}')]_- &= \frac{1}{N} \sum_{\substack{\mathbf{m} \\ s,i}} \sum_{\substack{\mathbf{n} \\ t,j}} \sqrt{M_s M_t} \varepsilon_{s,i}^{(r)}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}^m} \\ &\quad \cdot \varepsilon_{t,j}^{(r')*}(\mathbf{q}') e^{-i\mathbf{q}' \cdot \mathbf{R}^n} \frac{1}{M_s} [M_s \dot{u}_{s,i}^m, u_{t,j}^n] = \\ &= \frac{\hbar}{i} \frac{1}{N} \sum_{\substack{\mathbf{m} \\ s,i}} e^{i(\mathbf{q}-\mathbf{q}') \cdot \mathbf{R}^m} \varepsilon_{s,i}^{(r)}(\mathbf{q}) \varepsilon_{s,i}^{(r')*}(\mathbf{q}') = \\ &= \frac{\hbar}{i} \sum_{s,i} \varepsilon_{s,i}^{(r)}(\mathbf{q}) \varepsilon_{s,i}^{(r')*}(\mathbf{q}') \delta_{\mathbf{q},\mathbf{q}'} . \end{aligned}$$

With (2.141), it finally follows that:

$$[\Pi_r(\mathbf{q}), Q_{r'}(\mathbf{q}')]_- = \frac{\hbar}{i} \delta_{\mathbf{q},\mathbf{q}'} \delta_{r,r'}. \quad (2.156)$$

We now introduce new operators b_{qr} and b_{qr}^+ :

$$Q_r(\mathbf{q}) = \sqrt{\frac{\hbar}{2\omega_r(\mathbf{q})}} \{b_{qr} + b_{-qr}^+\}, \quad (2.157)$$

$$\Pi_r(\mathbf{q}) = i\sqrt{\frac{1}{2}\hbar\omega_r(\mathbf{q})} \{b_{qr}^+ - b_{-qr}\}. \quad (2.158)$$

We can read off directly:

$$Q_r^+(-\mathbf{q}) = Q_r(\mathbf{q}); \quad \Pi_r^+(-\mathbf{q}) = \Pi_r(\mathbf{q}). \quad (2.159)$$

The inverses of (2.157) and (2.158) are given by:

$$b_{qr} = (2\hbar\omega_r(\mathbf{q}))^{-1/2} \left\{ \omega_r(\mathbf{q}) Q_r(\mathbf{q}) + i \Pi_r^+(\mathbf{q}) \right\}, \quad (2.160)$$

$$b_{qr}^+ = (2\hbar\omega_r(\mathbf{q}))^{-1/2} \left\{ \omega_r(\mathbf{q}) Q_r^+(\mathbf{q}) - i \Pi_r(\mathbf{q}) \right\}. \quad (2.161)$$

We compute the commutation relations:

$$\begin{aligned} [b_{qr}, b_{q'r'}]_- &= \\ &= (4\hbar^2 \omega_r(\mathbf{q}) \omega_{r'}(\mathbf{q}'))^{-1/2} \cdot \\ &\cdot \left\{ i\omega_r(\mathbf{q}) [Q_r(\mathbf{q}), \Pi_{r'}^+(\mathbf{q}')]_- + i\omega_{r'}(\mathbf{q}') [\Pi_r^+(\mathbf{q}), Q_{r'}(\mathbf{q}')]_- \right\} = \\ &= (4\hbar^2 \omega_r(\mathbf{q}) \omega_{r'}(\mathbf{q}'))^{-1/2} \cdot \\ &\cdot \left\{ i\omega_r(\mathbf{q}) \left(-\frac{\hbar}{i} \delta_{rr'} \delta_{\mathbf{q}, -\mathbf{q}'} \right) + i\omega_{r'}(\mathbf{q}') \left(\frac{\hbar}{i} \delta_{rr'} \delta_{-\mathbf{q}, \mathbf{q}'} \right) \right\} = \\ &= 0, \\ [b_{qr}, b_{q'r'}^+]_- &= \\ &= (4\hbar^2 \omega_r(\mathbf{q}) \omega_{r'}(\mathbf{q}'))^{-1/2} \cdot \\ &\cdot \left\{ -i\omega_r(\mathbf{q}) [Q_r(\mathbf{q}), \Pi_{r'}(\mathbf{q}')]_- + i\omega_{r'}(\mathbf{q}') [\Pi_r^+(\mathbf{q}), Q_{r'}^+(\mathbf{q}')]_- \right\} = \\ &= (4\hbar^2 \omega_r(\mathbf{q}) \omega_{r'}(\mathbf{q}'))^{-1/2} \cdot \\ &\cdot \left\{ -i\omega_r(\mathbf{q}) \left(-\frac{\hbar}{i} \delta_{r, r'} \delta_{\mathbf{q} \mathbf{q}'} \right) + i\omega_{r'}(\mathbf{q}') \left(\frac{\hbar}{i} \delta_{r, r'} \delta_{-\mathbf{q}, -\mathbf{q}'} \right) \right\} = \\ &= \delta_{rr'} \delta_{\mathbf{q} \mathbf{q}'} . \end{aligned}$$

b_{qr} and b_{qr}^+ are thus **Bosonic operators**:

$$[b_{qr}, b_{q'r'}]_- = [b_{qr}^+, b_{q'r'}]_- = 0, \quad (2.162)$$

$$[b_{qr}, b_{q'r'}^+]_- = \delta_{\mathbf{q} \mathbf{q}'} \delta_{rr'}. \quad (2.163)$$

We are now in a position to quantise the Hamilton function:

$$H = \sum_{\mathbf{q}, r} \frac{1}{2} \left\{ \Pi_r^+(\mathbf{q}) \Pi_r(\mathbf{q}) + \omega_r^2(\mathbf{q}) Q_r^+(\mathbf{q}) Q_r(\mathbf{q}) \right\} =$$

$$\begin{aligned}
&= \frac{1}{4} \sum_{qr} \hbar \omega_r(\mathbf{q}) \left\{ (b_{qr} - b_{-qr}^+) (b_{qr}^+ - b_{-qr}) + (b_{qr}^+ + b_{-qr}) (b_{qr} + b_{-qr}^+) \right\} = \\
&= \frac{1}{4} \sum_{qr} \hbar \omega_r(\mathbf{q}) \left\{ b_{qr} b_{qr}^+ + b_{-qr}^+ b_{-qr} + b_{qr}^+ b_{qr} + b_{-qr} b_{-qr}^+ \right\} = \\
&= \frac{1}{4} \sum_{qr} \hbar \omega_r(\mathbf{q}) \left\{ 2b_{qr}^+ b_{qr} + 2b_{-qr}^+ b_{-qr} + 2 \right\} .
\end{aligned}$$

We can also make use of (2.139) and then obtain within the harmonic approximation the **Hamiltonian for the quantised vibrations of the ion lattice**:

$$H = \sum_{qr} \hbar \omega_r(\mathbf{q}) \left\{ b_{qr}^+ b_{qr} + \frac{1}{2} \right\} . \quad (2.164)$$

We are dealing here with a system of $3pN$ non-coupled harmonic oscillators.

In Eqs. (2.157) and (2.158), we suppressed the time dependence of the normal coordinates Q_r and their canonical momenta. As set out in (2.142), it is given simply by:

$$Q_r(\mathbf{q}t) = Q_r(\mathbf{q}) e^{-i\omega_r(\mathbf{q})t} . \quad (2.165)$$

This implies according to (2.157) that:

$$b_{qr}(t) = b_{qr} e^{-i\omega_r(\mathbf{q})t} . \quad (2.166)$$

We wish to show that this result agrees with

$$b_{qr}(t) = \exp\left(\frac{i}{\hbar} H t\right) b_{qr} \exp\left(-\frac{i}{\hbar} H t\right) . \quad (2.167)$$

To this end, we first prove the assertion

$$b_{qr} H^n = \{\hbar \omega_r(\mathbf{q}) + H\}^n b_{qr} , \quad (2.168)$$

using the method of complete induction:

$n = 1$:

$$\begin{aligned}
[b_{qr}, H]_- &= \sum_{q', r'} \hbar \omega_{r'}(\mathbf{q}') [b_{qr}, b_{q'r'}^+ b_{q'r'}]_- = \hbar \omega_r(\mathbf{q}) b_{qr} \\
&\Rightarrow b_{qr} H = (\hbar \omega_r(\mathbf{q}) + H) b_{qr} .
\end{aligned}$$

$n \Rightarrow n + 1$:

$$\begin{aligned}
b_{qr} H^{n+1} &= (b_{qr} H^n) H = (\hbar \omega_r(\mathbf{q}) + H)^n b_{qr} H = \\
&= (\hbar \omega_r(\mathbf{q}) + H)^{n+1} b_{qr} .
\end{aligned}$$

This proves the assertion in (2.168). It then follows that:

$$\begin{aligned} b_{qr} \exp\left(\frac{-i}{\hbar} H t\right) &= \sum_{n=0}^{\infty} \frac{(-i/\hbar)^n}{n!} t^n b_{qr} H^n = \\ &= \exp\left[-\frac{i}{\hbar} (\hbar\omega_r(\mathbf{q}) + H) t\right] b_{qr}. \end{aligned}$$

After insertion into (2.167), we find the result (2.166). The two relations are therefore equivalent.

The essential result of this section is (2.164). This makes it clear that the energy of the lattice vibrations is quantised. The elementary quantum $\hbar\omega_r(\mathbf{q})$ is interpreted as the energy of the quasi-particle **phonon**. In detail, one makes the following associations:

- b_{qr}^+ : Creation operator for a (\mathbf{q}, r) phonon,
- b_{qr} : Annihilation operator for a (\mathbf{q}, r) phonon,
- $\hbar\omega_r(\mathbf{q})$: Energy of the (\mathbf{q}, r) phonon.

Phonons are Bosons! Each vibrational state can therefore be occupied by arbitrarily many phonons.

The harmonic approximation which underlies this section models the ion lattice as a non-interacting **phonon gas**. The terms neglected in the series expansion (2.124) for the potential V , which are of third or higher order in the displacements $u_{s,i}^m$ (*anharmonicity* of the lattice), can be interpreted as a coupling, i.e. an interaction between the phonons. They are important for the description of effects such as thermal expansion, the approach to thermal equilibrium, heat conductivity, the high-temperature behaviour of c_p , c_v , etc.

2.2.3

Exercises

Exercise 2.2.1 Consider a linear chain composed of two different types of atoms (masses m_1 , m_2) alternating along the chain:

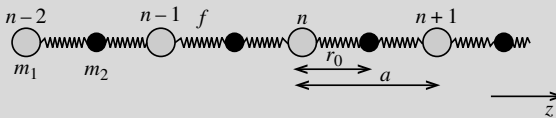


Fig. 2.5 Model of the linear diatomic chain

The interaction between the atoms can be taken to a good approximation to be limited to nearest neighbours. Within the harmonic approximation (linear force law),

the coupling between neighbouring atoms can be expressed in terms of a force constant f .

1. Describe the chain as a linear Bravais lattice with a diatomic basis. Determine the primitive translations and the vectors of the (reciprocal) lattice as well as the first Brillouin zone.
2. Formulate the equation of motion for longitudinal lattice vibrations.
3. Justify and make use of the trial solution

$$u_{\alpha}^n = \frac{c_{\alpha}}{\sqrt{m_{\alpha}}} \exp [i (q R^n - \omega t)]$$

for the displacement of the (n, α) -th atom from its equilibrium position.

4. Sketch the dispersion branches for a qualitative discussion. Investigate in particular the special cases $q = 0, +\pi/a, -\pi/a, 0 < q \ll \pi/a$.

Exercise 2.2.2 Compute the density of states $D(\omega)$ of the linear chain:

$$D(\omega)d\omega = \text{The number of eigenfrequencies in the interval } (\omega; \omega + d\omega).$$

Use appropriate periodic boundary conditions. How does $D(\omega)$ depend on the *group velocity* $v_g = d\omega/dq_z$? Give a qualitative sketch of $D(\omega)$!

Exercise 2.2.3 Compute the density of states $D(\omega)$ for the lattice vibrations of a three-dimensional crystal. The crystal has the primitive translations $\mathbf{a}_i, i = 1, 2, 3$, which are not necessarily orthogonal.

1. Introduce periodic boundary conditions on a parallelepiped with the edges $N_i \mathbf{a}_i, i = 1, 2, 3$. Express the allowed wavenumbers in terms of the primitive translations of the reciprocal lattice.
2. Calculate the grid volume in \mathbf{q} space, which contains one and only one wavevector.
3. Express the density of states for one dispersion branch $\omega_r(\mathbf{q})$ in terms of a volume integral in \mathbf{q} space.
4. Make use of the group velocity to find an alternative representation of the density of states:

$$v_g^{(r)} = \left| \Delta_{\mathbf{q}} \omega_r(\mathbf{q}) \right| .$$

5. What is the expression for the overall density of states?

Exercise 2.2.4 The so-called Debye model for the lattice vibrations of a pure Bravais lattice ($p = 1$, monatomic basis) makes use of the following two assumptions:

1. A linear, isotropic approximation for the acoustic branches:

$$\omega_r = \bar{v}_r q.$$

2. Replacement of the Brillouin zone by a sphere of the same volume.

Due to 2., there must be a limiting frequency ω_r^D (the Debye frequency). Calculate it! Derive the density of states $D_D(\omega)$ corresponding to this model.

Exercise 2.2.5

1. Calculate in the harmonic approximation the internal energy $U(T) = \langle H \rangle$ ($\langle \dots \rangle$: thermal average) of the lattice vibrations of a three-dimensional crystal. Discuss the limiting cases of high and low temperatures (Hint: $\langle b_{qr}^\dagger b_{qr} \rangle \Rightarrow$ Bose-Einstein distribution).
2. Use the Debye model (Ex. 2.2.4) to compute the specific heat at low temperatures.

2.3

The Electron-Phonon Interaction

Having discussed in Sect. 2.1 the crystal electrons and in Sect. 2.2 the lattice ions, essentially with no mutual coupling, or at most coupled in a very simple manner via H_{e+} (2.50), we now examine the interaction between these two subsystems in more detail. Within our general model of the solid state (2.1), we will now consider the operator H_{ei} .

2.3.1

The Hamiltonian

Our starting point is the operator (2.5):

$$H_{ei} = \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_i} V_{ei}(\mathbf{r}_j - \mathbf{x}_\alpha) = H_{ei}^{(0)} + H_{e-p}. \quad (2.169)$$

The interaction $H_{\text{ei}}^{(0)}$ of the electrons with the rigid ion lattice was already included in our model H_0 for the crystal electrons (see (2.7)). $H_{\text{e-p}}$ is the electron-phonon interaction *per se*.

Following the considerations of the previous section, we know that every lattice vibration is characterised by the states defined by the wavenumber \mathbf{q} and the branch r of the dispersion spectrum $\omega_r(\mathbf{q})$. The electron-phonon interaction thus implies the

absorption and emission of (\mathbf{q}, r) phonons.

The conceivable **elementary processes** can be shown graphically in a simple way (see Fig. 2.6).

All the interactions can be composed out of these four elementary processes. They should therefore be reflected in a corresponding model Hamiltonian.

We assume that in these interactions, the ion is displaced as a rigid body and is not deformed, which is of course by no means to be taken for granted. Deformations of the ions however represent *higher-order* effects. In the framework of the *harmonic approximation* for the lattice vibrations, we expand the interaction energy V_{ei} up to the first non-vanishing term. It is in this case the linear term:

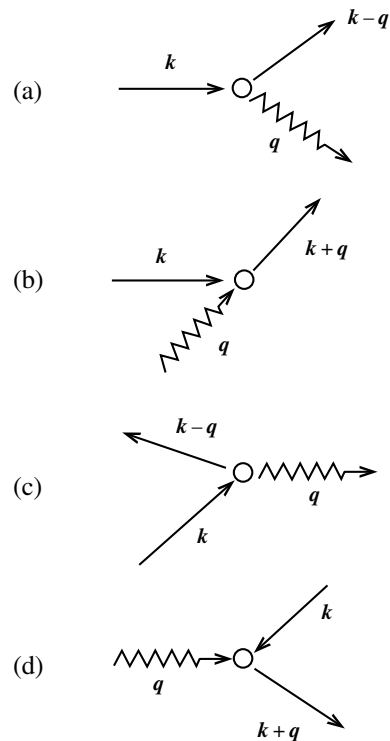


Fig. 2.6 Elementary processes of the electron-phonon interaction; *straight arrows* stand for electrons, *wavy arrows* for phonons: (a) Phonon emission by an electron; (b) Phonon absorption by an electron; (c) Phonon emission from electron-hole recombination; (d) Creation of an electron-hole pair by phonon annihilation

$$\begin{aligned}
V_{\text{ei}}(\mathbf{r}_j - \mathbf{x}_s^m) &\equiv V_{\text{ei}}(\mathbf{r}_j - \mathbf{R}_s^m - \mathbf{u}_s^m) = \\
&= V_{\text{ei}}(\mathbf{r}_j - \mathbf{R}_s^m) - \mathbf{u}_s^m \cdot \nabla V_{\text{ei}} + O(u^2) .
\end{aligned} \tag{2.170}$$

The first term leads to $H_{\text{ei}}^{(0)}$ and was already taken into account in the treatment of the crystal electrons (see Sect. 2.1) e.g. in the Bloch energies $\varepsilon(\mathbf{k})$. The second term contains the actual electron-phonon interaction. We assume singly-charged ions, ($N_e = N_i = N$), and use expression (2.142) for the displacements \mathbf{u}_s^m :

$$\begin{aligned}
H_{\text{e-p}} &= - \sum_{j=1}^N \sum_{\mathbf{m}, s} \sum_{r=1}^{3p} \sum_{\mathbf{q}}^{\text{1.BZ}} \frac{1}{\sqrt{NM_s}} Q_r(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_m} \cdot \\
&\quad \cdot \boldsymbol{\varepsilon}_s^{(r)}(\mathbf{q}) \cdot \nabla V_{\text{ei}}(\mathbf{r}_j - \mathbf{R}_s^m) .
\end{aligned} \tag{2.171}$$

$Q_r(\mathbf{q})$ is already familiar from (2.157) in second quantisation. We still have to transform the electronic part. In ∇V_{ei} , the electronic variable \mathbf{r}_j appears. We choose the Fourier representation for V_{ei} :

$$V_{\text{ei}}(\mathbf{r}_j - \mathbf{R}_s^m) = \sum_{\mathbf{p}} V_{\text{ei}}^{(s)}(\mathbf{p}) e^{i\mathbf{p} \cdot (\mathbf{r}_j - \mathbf{R}_s^m)} . \tag{2.172}$$

Note that in this representation, \mathbf{p} – as a wavenumber – is a variable and not an operator. Operator properties apply only to \mathbf{r}_j .

$$\nabla V_{\text{ei}}(\mathbf{r}_j - \mathbf{R}_s^m) = i \sum_{\mathbf{p}} V_{\text{ei}}^{(s)}(\mathbf{p}) \mathbf{p} e^{i\mathbf{p} \cdot (\mathbf{r}_j - \mathbf{R}_s^m)} . \tag{2.173}$$

For the second quantisation of this single-electron operator, we choose the Bloch representation:

$$\sum_{j=1}^N \nabla V_{\text{ei}}(\mathbf{r}_j - \mathbf{R}_s^m) = \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \sigma, \sigma'}} \langle \mathbf{k}\sigma | \nabla V_{\text{ei}} | \mathbf{k}'\sigma' \rangle a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}'\sigma'} . \tag{2.174}$$

We compute the matrix element:

$$\begin{aligned}
\langle \mathbf{k}\sigma | e^{i\mathbf{p} \cdot \hat{\mathbf{r}}} | \mathbf{k}'\sigma' \rangle &= \delta_{\sigma\sigma'} \int d^3r \langle \mathbf{k} | e^{i\mathbf{p} \cdot \hat{\mathbf{r}}} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{k}' \rangle = \\
&= \delta_{\sigma\sigma'} \int d^3r e^{i\mathbf{p} \cdot \mathbf{r}} \langle \mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{k}' \rangle = \\
&= \delta_{\sigma\sigma'} \int d^3r e^{i\mathbf{p} \cdot \mathbf{r}} \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}'}(\mathbf{r}) .
\end{aligned}$$

For the Bloch functions, we use (2.16):

$$\langle \mathbf{k}\sigma | e^{i\mathbf{p}\cdot\mathbf{r}} | \mathbf{k}'\sigma' \rangle = \delta_{\sigma\sigma'} \int d^3r e^{i(\mathbf{p}-\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}} u_{\mathbf{k}}^*(\mathbf{r}) \cdot u_{\mathbf{k}'}(\mathbf{r}) . \quad (2.175)$$

The amplitude function $u_{\mathbf{k}}(\mathbf{r})$ which reflects the periodicity of the lattice is not to be confused with the displacements \mathbf{u}_s^m . Inserting (2.175) into (2.174), we now find the following intermediate result:

$$\begin{aligned} \sum_{j=1}^N \nabla V_{\text{ei}}(\mathbf{r}_j - \mathbf{R}_s^m) &= i \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \mathbf{p}, \sigma}} V_{\text{ei}}^{(s)}(\mathbf{p}) \mathbf{p} e^{-i\mathbf{p}\cdot\mathbf{R}^m} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}'\sigma} \cdot \\ &\cdot \int d^3r e^{i(\mathbf{p}-\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}} u_{\mathbf{k}}^*(\mathbf{r}) u_{\mathbf{k}'}(\mathbf{r}) . \end{aligned} \quad (2.176)$$

The product of the displacements has the periodicity of the lattice, owing to (2.17). The integral can therefore be nonzero only for $\mathbf{k} = \mathbf{k}' + \mathbf{p}$. Inserting into (2.171) then yields the following result (making use of

$$\frac{1}{N} \sum_m e^{i(\mathbf{q}-\mathbf{p})\cdot\mathbf{R}^m} = \sum_{\mathbf{K}} \delta_{\mathbf{p}, \mathbf{q}+\mathbf{K}} , \quad (2.177)$$

where \mathbf{K} is a vector in the reciprocal lattice):

$$\begin{aligned} H_{\text{e-p}} &= - \sum_{s,r} \sum_{\mathbf{q}, \mathbf{k}', \mathbf{K}, \sigma} i \sqrt{\frac{N}{M_s}} Q_r(\mathbf{q}) V_{\text{ei}}^{(s)}(\mathbf{q} + \mathbf{K}) \cdot \\ &\cdot (\mathbf{e}_s^{(r)}(\mathbf{q}) \cdot (\mathbf{q} + \mathbf{K})) a_{\mathbf{k}'+\mathbf{q}+\mathbf{K}\sigma}^+ a'_{\mathbf{k}\sigma} \cdot \\ &\cdot \int d^3r u_{\mathbf{k}'+\mathbf{q}+\mathbf{K}}^*(\mathbf{r}) u_{\mathbf{k}'}(\mathbf{r}) . \end{aligned}$$

We now use (2.157) for the normal coordinates $Q_r(\mathbf{q}, t)$, and define as an abbreviation the

Matrix element of the electron-phonon coupling

$$\begin{aligned} T_{\mathbf{k}, \mathbf{q}, \mathbf{K}}^{(s,r)} &= -i \sqrt{\frac{\hbar N}{2M_s \omega_r(\mathbf{q})}} V_{\text{ei}}^{(s)}(\mathbf{q} + \mathbf{K}) [\mathbf{e}_s^{(r)}(\mathbf{q}) \cdot (\mathbf{q} + \mathbf{K})] \cdot \\ &\cdot \int d^3r u_{\mathbf{k}+\mathbf{q}+\mathbf{K}}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) . \end{aligned} \quad (2.178)$$

Then the Hamiltonian for the electron-phonon interaction is given by:

$$H_{\text{e-p}} = \sum_{k\sigma} \sum_{\mathbf{q}, \mathbf{K}} \sum_{s,r} T_{\mathbf{k}, \mathbf{q}, \mathbf{K}}^{(s,r)} (b_{\mathbf{q}r} + b_{-\mathbf{q}r}^+) a_{\mathbf{k}+\mathbf{q}+\mathbf{K}\sigma}^+ a_{\mathbf{k}\sigma}. \quad (2.179)$$

Upon emission (creation) of a $(-\mathbf{q}, r)$ phonon, or upon absorption (annihilation) of a (\mathbf{q}, r) phonon, the wavenumber \mathbf{k} of the electron becomes $\mathbf{k} + \mathbf{q} + \mathbf{K}$. One therefore defines the

$\hbar(\mathbf{q} + \mathbf{K})$: **quasi-(crystal)-momentum of the phonons,**

where \mathbf{q} originates in the first Brillouin zone, whilst \mathbf{K} can be an arbitrary reciprocal-lattice vector. In (2.179), \mathbf{K} is fixed by the requirement

$$\mathbf{k} + \mathbf{q} + \mathbf{K} \in \text{the first Brillouin zone.}$$

We distinguish between:

$$\begin{aligned} \mathbf{K} = \mathbf{0}: & \quad \text{normal processes,} \quad \text{and} \\ \mathbf{K} \neq \mathbf{0}: & \quad \text{umklapp processes.} \end{aligned}$$

The complicated matrix element (2.178) can be greatly simplified if the following assumptions can be made:

1. A simple Bravais lattice: $p = 1 \Rightarrow \sum_s$ is omitted,
2. Only normal processes: $\mathbf{K} = \mathbf{0} \Rightarrow \sum_{\mathbf{K}}$ is omitted,
3. The phonons are uniquely longitudinally or transversally polarised:

$$\begin{aligned} \boldsymbol{\varepsilon}^{(r)}(\mathbf{q}) \cdot \mathbf{q} & \begin{cases} \neq 0 : & \text{longitudinal,} \\ = 0 : & \text{transverse.} \end{cases} \end{aligned}$$

Under these assumptions, only the longitudinal acoustic phonons interact with the electrons. With the matrix element

$$T_{\mathbf{k}, \mathbf{q}} = -i \sqrt{\frac{\hbar N}{2M\omega(\mathbf{q})}} V_{\text{ei}}(\mathbf{q}) [\boldsymbol{\varepsilon}(\mathbf{q}) \cdot \mathbf{q}] \int d^3r u_{\mathbf{k}+\mathbf{q}}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}), \quad (2.180)$$

the electron-phonon interaction can be simplified to:

$$H_{\text{e-p}} = \sum_{\mathbf{k}\mathbf{q}\sigma} T_{\mathbf{k}\mathbf{q}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+) a_{\mathbf{k}+\mathbf{q}\sigma}^+ a_{\mathbf{k}\sigma}. \quad (2.181)$$

2.3.2

The Effective Electron-Electron Interaction

The elementary processes sketched in Fig. 2.6 may be combined into additional, more complex types of coupling. In particular, phonon-induced electron-electron interactions can be described. Figure 2.7 symbolises a process in which a (\mathbf{k}, σ) electron emits a \mathbf{q} phonon, which is then absorbed by a (\mathbf{k}', σ') electron. The spin of the electron is of course not involved in this process. The first electron deforms the lattice in its immediate neighbourhood, i.e. as a negatively-charged particle, it displaces the positively-charged ions slightly. *Deformation* means abstractly always absorption or emission of phonons. A second electron “sees” this lattice deformation and reacts to it. The result is thus an effective electron-electron interaction, which naturally has nothing to do with the usual Coulomb interaction and can therefore be either attractive or repulsive. In the case of an attractive interaction, it can lead to the formation of electron pairs (**Cooper pairs**) with an accompanying decrease in the ground-state energy. This process forms the basis for conventional superconductivity. We consider the electron-phonon interaction in the form (2.181) and neglect electron-electron as well as phonon-phonon interactions. The matrix element T_{kq} (2.180) can be computed for simplicity with plane waves, which also eliminates the \mathbf{k} -dependence ($u_{\mathbf{k}}(\mathbf{r}) \Rightarrow 1/\sqrt{V}$):

$$T_q = -i \sqrt{\frac{\hbar N}{2M\omega(\mathbf{q})}} V_{\text{ei}}(\mathbf{q}) [\boldsymbol{\varepsilon}(\mathbf{q}) \cdot \mathbf{q}] . \quad (2.182)$$

One can see from (2.172) that

$$V_{\text{ei}}^*(\mathbf{q}) = V_{\text{ei}}(-\mathbf{q})$$

must hold. Due to (2.147), we also can assume

$$[\boldsymbol{\varepsilon}(\mathbf{q}) \cdot \mathbf{q}]^* = \boldsymbol{\varepsilon}(-\mathbf{q}) \cdot \mathbf{q} ,$$

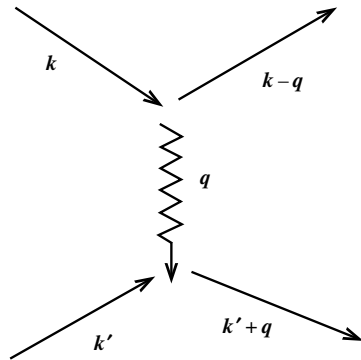


Fig. 2.7 Elementary process of the phonon-induced effective electron-electron interaction

so that

$$T_q^* = T_{-q} \quad (2.183)$$

follows. We now investigate whether the following model Hamiltonian contains terms representing an effective electron-electron interaction, as presumed:

$$H = \sum_{k\sigma} \varepsilon(k) a_{k\sigma}^+ a_{k\sigma} + \sum_q \hbar\omega(q) b_q^+ b_q + \sum_{kq\sigma} T_q (b_q + b_{-q}^+) a_{k+q\sigma}^+ a_{k\sigma} . \quad (2.184)$$

We carry out an appropriate **canonical transformation** and try to eliminate linear terms in H_{e-p} .

$$\begin{aligned} \tilde{H} &= e^{-S} H e^S = \left(1 - S + \frac{1}{2} S^2 + \dots\right) H \left(1 + S + \frac{1}{2} S^2 + \dots\right) = \\ &= H + [H, S]_- + \frac{1}{2} [[H, S]_-, S]_- + \dots, \\ \tilde{H} &= e^{-S} H e^S = H_0 + H_{e-p} + [H_0, S]_- + [H_{e-p}, S]_- + \frac{1}{2} [[H_0, S]_-, S]_- + \dots \end{aligned} \quad (2.185)$$

We take H_{e-p} to be a small perturbation. S should be of the same order of magnitude. We therefore neglect all the terms in the expansion (2.185) which are of higher than quadratic order in S or H_{e-p} . H_0 combines the first two terms in (2.184).

For S , we take the *ansatz*

$$S = \sum_{kq\sigma} T_q (x b_q + y b_{-q}^+) a_{k+q\sigma}^+ a_{k\sigma} \quad (2.186)$$

and fix the parameters x and y in such a way that

$$H_{e-p} + [H_0, S]_- \stackrel{!}{=} 0 \quad (2.187)$$

holds. If we can do this correctly, then the effective operator \tilde{H} is given by:

$$\tilde{H} \approx H_0 + \frac{1}{2} [H_{e-p}, S]_- . \quad (2.188)$$

We first compute the commutator:

$$[H_0, S]_- = [H_e, S]_- + [H_p, S]_- .$$

Here,

$$\begin{aligned}
[H_e, S]_- &= \\
&= \sum_{p, \sigma'} \sum_{kq\sigma} \varepsilon(\mathbf{p}) T_q \left[a_{p\sigma'}^+ a_{p\sigma'}, (xb_q + yb_{-q}^+) a_{k+q\sigma}^+ a_{k\sigma} \right]_- = \\
&= \sum_{\substack{p, k, q \\ \sigma, \sigma'}} \varepsilon(\mathbf{p}) T_q (xb_q + yb_{-q}^+) \left[a_{p\sigma'}^+ a_{p\sigma'}, a_{k+q\sigma}^+ a_{k\sigma} \right]_- = \\
&= \sum \varepsilon(\mathbf{p}) T_q (xb_q + yb_{-q}^+) \delta_{\sigma\sigma'} \left(\delta_{p, k+q} a_{p\sigma'}^+ a_{k\sigma} - \delta_{kp} a_{k+q\sigma}^+ a_{p\sigma'} \right) = \\
&= \sum_{kq\sigma} T_q (\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k})) a_{k+q\sigma}^+ a_{k\sigma} (xb_q + yb_{-q}^+) .
\end{aligned}$$

We have repeatedly made use of the fact that the creation and annihilation operators for electrons and phonons are of course mutually commuting.

$$\begin{aligned}
[H_p, S]_- &= \sum_p \sum_{kq\sigma} \hbar\omega(\mathbf{p}) T_q \left[b_p^+ b_p, (xb_q + yb_{-q}^+) \right]_- a_{k+q\sigma}^+ a_{k\sigma} = \\
&= \sum_p \sum_{kq\sigma} \hbar\omega(\mathbf{p}) T_q (-x\delta_{qp} b_p + y\delta_{-qp} b_p^+) a_{k+q\sigma}^+ a_{k\sigma} = \\
&= \sum_{kq\sigma} T_q \hbar\omega(\mathbf{q}) (-xb_q + yb_{-q}^+) a_{k+q\sigma}^+ a_{k\sigma} .
\end{aligned}$$

All together, we obtain:

$$\begin{aligned}
[H_0, S]_- &= \sum_{kq\sigma} T_q \left\{ x (\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) - \hbar\omega(\mathbf{q})) b_q + \right. \\
&\quad \left. + y (\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) + \hbar\omega(\mathbf{q})) b_{-q}^+ \right\} a_{k+q\sigma}^+ a_{k\sigma} .
\end{aligned} \tag{2.189}$$

Equation (2.187) can thus be obtained using the following parameters x and y :

$$x = \{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q}) + \hbar\omega(\mathbf{q})\}^{-1} , \tag{2.190}$$

$$y = \{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q}) - \hbar\omega(\mathbf{q})\}^{-1} . \tag{2.191}$$

In the last step, we have inserted the expression for S thus obtained into (2.188). The essential task is the computation of the following commutator:

$$\begin{aligned}
&\left[(b_{q'} + b_{-q'}^+) a_{k'+q'\sigma'}^+ a_{k'\sigma'}, (xb_q + yb_{-q}^+) a_{k+q\sigma}^+ a_{k\sigma} \right]_- = \\
&= (b_{q'} + b_{-q'}^+) (xb_q + yb_{-q}^+) \left[a_{k'+q'\sigma'}^+ a_{k'\sigma'}, a_{k+q\sigma}^+ a_{k\sigma} \right]_- + \\
&+ \left[(b_{q'} + b_{-q'}^+), (xb_q + yb_{-q}^+) \right]_- a_{k'+q'\sigma'}^+ a_{k'\sigma'} a_{k+q\sigma}^+ a_{k\sigma} .
\end{aligned}$$

Only the last term leads to an effective electron-electron interaction. We thus concentrate exclusively on this term:

$$\begin{aligned} \left[(b_{q'} + b_{-q'}^+), (xb_q + yb_{-q}^+) \right]_- &= x \left[b_{-q'}^+, b_q \right]_- + y \left[b_{q'}, b_{-q}^+ \right]_- = \\ &= -x\delta_{q',-q} + y\delta_{q',-q} . \end{aligned} \quad (2.192)$$

This yields the following contribution to \tilde{H} :

$$\begin{aligned} \tilde{H}_{\text{eff}} &= \frac{1}{2} \sum_{\substack{kq\sigma \\ k'q'\sigma'}} T_q T_q (y - x) \delta_{q',-q} a_{k'+q'\sigma'}^+ a_{k'\sigma'} a_{k+q\sigma}^+ a_{k\sigma} = \\ &= \frac{1}{2} \sum_{\substack{kq\sigma \\ k'\sigma'}} T_{-q} T_q (y - x) \left(a_{k+q\sigma}^+ a_{k'-q\sigma'}^+ a_{k'\sigma'} a_{k\sigma} + \delta_{k',k+q} \hat{n}_{k\sigma} \right) . \end{aligned}$$

The final term is uninteresting in this context. However, we can see that the electron-phonon interaction brings about a term of the following form:

$$\tilde{H}_{\text{ee}} = \sum_{kpq\sigma,\sigma'} |T_q|^2 \frac{\hbar\omega(\mathbf{q})}{(\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}))^2 - (\hbar\omega(\mathbf{q}))^2} a_{k+q\sigma}^+ a_{p-q\sigma'}^+ a_{p\sigma'} a_{k\sigma} . \quad (2.193)$$

This interaction is

$$\begin{aligned} \text{repulsive, when } & (\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}))^2 > (\hbar\omega(\mathbf{q}))^2 , \\ \text{attractive, when } & (\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}))^2 < (\hbar\omega(\mathbf{q}))^2 . \end{aligned}$$

The latter effect explains the stability of Cooper pairs, and thus forms the basis for our understanding of superconductivity.

2.3.3

Exercises

Exercise 2.3.1 The initial idea of the BCS theory of superconductivity is the correlation of conduction electrons through virtual phonon exchange into so-called **Cooper pairs**, each consisting of two electrons with oppositely-directed wavevectors and spins,

$$(\mathbf{k} \uparrow, -\mathbf{k} \downarrow) ,$$

which form a bound state. Define suitable creation and annihilation operators for the Cooper pairs! Compute the associated fundamental commutation relations! Are Cooper pairs Bosons?

Exercise 2.3.2 The normal electron-phonon interaction generates an effective electron-electron interaction induced by phonon exchange, which under certain circumstances can also be attractive (Sect. 2.3.2). Consider the following model:

- N interaction-free electrons in states $k \leq k_F$, all states with $k > k_F$ unpopulated \iff a filled Fermi sphere |FS).
- Two additional electrons with oppositely-directed wavevectors and spins (Cooper pair, see Ex. 2.3.1) interact according to

$$V_k(\mathbf{q}) = \begin{cases} -V, & \text{if } |\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k})| \leq \hbar\omega_D, \\ 0, & \text{otherwise} \end{cases}$$

(ω_D : Debye frequency).

- Formulate the model Hamiltonian.
- Justify the *ansatz*

$$|\psi\rangle = \sum_{\mathbf{k}, \sigma} \alpha_{\sigma}(\mathbf{k}) a_{\mathbf{k}\sigma}^+ a_{-\mathbf{k}-\sigma}^+ |\text{FS}\rangle$$

for the Cooper-pair state and show that

$$\alpha_{\sigma}(\mathbf{k}) = -\alpha_{-\sigma}(-\mathbf{k})$$

must hold.

- Verify that due to the normalisation of $|\psi\rangle$ and |FS> the following relation must hold:

$$\sum_{\mathbf{k}, \sigma}^{k > k_F} |\alpha_{\sigma}(\mathbf{k})|^2 = 1.$$

Exercise 2.3.3 Consider again the *Cooper model* defined in Ex. 2.3.2 with the *ansatz* $|\psi\rangle$ for the *Cooper-pair state*:

- Show that for the expectation value of the kinetic energy in the state $|\psi\rangle$, the following holds:

$$\langle \psi | T | \psi \rangle = 2 \sum_{\mathbf{k}, \sigma}^{k > k_F} \varepsilon(\mathbf{k}) |\alpha_{\sigma}(\mathbf{k})|^2 + 2 \sum_{\mathbf{k}}^{k < k_F} \varepsilon(\mathbf{k}).$$

- Show that for the expectation value of the potential energy in the state $|\psi\rangle$, the following holds:

$$\langle \psi | V | \psi \rangle = 2 \sum_{\mathbf{k}, \mathbf{q}, \sigma}^{k, |\mathbf{k}+\mathbf{q}| > k_F} V_k(\mathbf{q}) \alpha_{\sigma}^*(\mathbf{k} + \mathbf{q}) \alpha_{\sigma}(\mathbf{k}).$$

Exercise 2.3.4 Consider still further the *Cooper model* defined in Ex. 2.3.2 with the ansatz $|\psi\rangle$ for the *Cooper-pair state*:

1. Determine the *optimum* expansion coefficients $\alpha_{\sigma}(\mathbf{k})$ by minimising the energy calculated in Ex. 2.3.3, $E = \langle\psi|H|\psi\rangle$. Note the side condition from Ex. 2.3.2, 3, which follows from the normalisation of $|\psi\rangle$.
2. Show that the energy of the Cooper pair is less than the energy of two non-interacting electrons at the Fermi edge. What conclusions can you draw from this?

Hint: summations over \mathbf{k} can often be advantageously converted into simpler integrals over energy by making use of the *free* Bloch density of states:

$$\rho_0(\varepsilon) = \frac{1}{N} \sum_{\mathbf{k}} \delta(\varepsilon - \varepsilon(\mathbf{k}))$$

Exercise 2.3.5 On the BCS theory of superconductivity (Phys. Rev. **108**, 1175 (1957)): The BCS model suppresses from the beginning all those interactions which give the same contributions in the normal and the superconducting phase. It considers only the attractive part of the phonon-induced electron-electron interaction. As test states for a variational calculation of the BCS ground-state energy (\Longleftrightarrow difference between the ground-state energies in the normal and the superconducting phases), products of Cooper-pair states are used, since according to Ex. 2.3.4, the latter lead to an energy decrease:

$$|\text{BCS}\rangle = \left[\prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} b_{\mathbf{k}}^+) \right] |0\rangle, \quad |0\rangle : \quad \text{particle vacuum,}$$

$b_{\mathbf{k}}^+ = a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+$: *Cooper-pair creation operator* (see Ex. 2.3.1). The coefficients $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ can be taken to be real.

1. Show that due to the normalisation of the state $|\text{BCS}\rangle$,

$$u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1$$

must hold.

2. Calculate the following expectation values:

$$\langle \text{BCS} | b_{\mathbf{k}}^+ b_{\mathbf{k}} | \text{BCS} \rangle; \quad \langle \text{BCS} | b_{\mathbf{k}}^+ b_{\mathbf{k}} b_{\mathbf{p}}^+ b_{\mathbf{p}} | \text{BCS} \rangle;$$

$$\langle \text{BCS} | b_{\mathbf{k}}^+ b_{\mathbf{k}} (1 - b_{\mathbf{p}}^+ b_{\mathbf{p}}) | \text{BCS} \rangle; \quad \langle \text{BCS} | b_{\mathbf{p}}^+ b_{\mathbf{k}} | \text{BCS} \rangle.$$

Exercise 2.3.6 On the BCS theory of superconductivity (Phys. Rev. **108**, 1175 (1957)): The BCS model of superconductivity limits itself, as explained in Ex. 2.3.5, to treating the attractive contribution to the phonon-induced electron-electron interaction (see Ex. 2.3.2). Using the variational expression $|\text{BCS}\rangle$ from Ex. 2.3.5, an upper limit to the ground-state energy can be calculated.

1. Justify the model Hamiltonian:

$$H_{\text{BCS}} = \sum_{\mathbf{k}, \sigma} t(\mathbf{k}) a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma} - V \sum_{\mathbf{k}, \mathbf{p}}^{k \neq p} b_{\mathbf{p}}^{\dagger} b_{\mathbf{k}};$$

$$t(\mathbf{k}) = \varepsilon(\mathbf{k}) - \mu .$$

2. Calculate:

$$E = \langle \text{BCS} | H_{\text{BCS}} | \text{BCS} \rangle .$$

3. Show that for the *gap parameter*

$$\Delta_{\mathbf{k}} = V \sum_{\mathbf{p}}^{\neq \mathbf{k}} u_{\mathbf{p}} v_{\mathbf{p}} ,$$

the minimum condition for $E = E(\{v_{\mathbf{k}}\})$ leads to the result:

$$\Delta_{\mathbf{k}} = \frac{V}{2} \sum_{\mathbf{p}}^{\neq \mathbf{k}} \Delta_{\mathbf{p}} (t^2(\mathbf{p}) + \Delta_{\mathbf{p}}^2)^{-1/2} .$$

4. Express $v_{\mathbf{k}}^2$, $u_{\mathbf{k}}^2$, $E_0 = (E(\{v_{\mathbf{k}}\}))_{\min}$ in terms of $\Delta_{\mathbf{k}}$ and $t(\mathbf{k})$.

Exercise 2.3.7 In order to derive the effective electron-electron interaction \tilde{H} from the actual electron-phonon interaction H , a canonical transformation (2.185)

$$\tilde{H} = e^{-S} H e^S ,$$

is carried out. Why must $S^{\dagger} = -S$ be required? Is this requirement fulfilled by the solutions (2.186), (2.190), (2.191)?

2.4

Spin Waves

The concepts of many-body theory have a particularly rich field of application in the area of magnetism. For this in fact rather old phenomenon, there is thus far no complete theory. Model concepts are necessary, and they are adapted to particular manifestations of magnetism. We develop the most important of these in this section.

2.4.1

Classification of Magnetic Solids

Using the magnetic susceptibility

$$\chi = \left(\frac{\partial M}{\partial H} \right)_T \quad (M : \text{magnetisation}) , \quad (2.194)$$

the various magnetic phenomena can be divided roughly into three classes:

diamagnetism, paramagnetism, and “collective” magnetism.

In the case of

1) Diamagnetism

In diamagnetism, we are dealing basically with a purely inductive effect. The applied magnetic field H induces magnetic dipoles which are, according to Lenz's rule, opposed to the field which induces them. A negative susceptibility is thus typical of diamagnets:

$$\chi^{\text{dia}} < 0; \quad \chi^{\text{dia}}(T, H) \approx \text{const} . \quad (2.195)$$

Diamagnetism is naturally a property of **all** materials. One therefore refers to a diamagnet only when there is no *additional* paramagnetism or *collective* magnetism present which would overcompensate the relatively weak diamagnetism.

The decisive precondition for

2) Paramagnetism

In paramagnetism is the existence of **permanent** magnetic moments, which can be oriented by the applied field H in competition with the thermal motion of the elementary magnets. It is thus typified by:

$$\chi^{\text{para}} > 0; \quad \chi^{\text{para}}(T, H) \stackrel{\text{i.g.}}{=} \chi^{\text{para}}(T) . \quad (2.196)$$

The permanent moments can be

2a) localised moments

which result from electron shells which are only partly filled. If these are sufficiently well shielded from **environmental influences** by outer, filled shells, then the electrons of the

unfilled shell will not contribute to an electric current in the solid, but rather will remain localised in the region of their *mother ion*. Prominent examples are the $4f$ electrons of the **rare earths**. An incompletely filled electronic shell has as a rule a resultant magnetic moment. Without an applied magnetic field, the moments are statistically distributed over all directions, so that the solid as a whole has no net moment. In an applied field, the moments become oriented, and their magnetic susceptibility follows the so-called **Curie law** at temperatures which are not too low:

$$\chi^{\text{para}}(T) \approx \frac{C}{T} \quad (C = \text{const}) . \quad (2.197)$$

Such a system is called a **Langevin paramagnet**.

The permanent magnetic moments of a paramagnet can however also be the

2b) itinerant moments

of quasi-free conduction electrons, of which each carries a moment of one Bohr magneton ($1\mu_B$). In this case, one refers to **Pauli paramagnetism**, whose susceptibility is to first order temperature **independent** as a result of the Pauli principle.

Dia- and paramagnetism can be regarded as essentially understood. They are more or less properties of individual atoms, and thus not typical many-body phenomena. Here, we are interested only in

3) “Collective” Magnetism

“Collective” magnetism results from a characteristic interaction which is understandable only in terms of quantum mechanics, the *exchange interaction* between permanent magnetic dipole moments. These permanent moments can again be

localised (Gd, EuO, Rb₂ MnCl₄)

or else they can be

itinerant (Fe, Co, Ni) .

The exchange interaction leads to a

critical temperature T^* ,

below which the moments order **spontaneously**, i.e. without an applied magnetic field. Above T^* , they behave as in a *normal* paramagnet. The susceptibility for $T < T^*$ is in general a complicated function of the applied field and the temperature, which in addition depends on the previous treatment (history) of the sample:

$$\chi^{KM} = \chi^{KM}(T, H, \text{history}) \quad (T \leq T^*) . \quad (2.198)$$

Collective magnetism can be divided into three major subclasses:

3a) Ferromagnetism

In this case, the critical temperature is referred to as

$$T^* = T_C: \quad \text{Curie temperature.}$$

At $T = 0$, all the moments are oriented parallel to one another (*ferromagnetic saturation*). This ordering decreases with increasing temperature. In the range $0 < T < T_C$, however, a preferred axis persists, i.e. a **spontaneous magnetisation** of the sample is still present; it then vanishes at T_C . Above T_C , the system is paramagnetic with a characteristic high-temperature behaviour of its susceptibility, which is called the **Curie-Weiss law**:

$$\chi(T) = \frac{C}{T - T_C} \quad (T \gg T_C) . \quad (2.199)$$

3b) Ferrimagnetism

The lattice in this case is composed of *two* ferromagnetic sublattices A and B with differing spontaneous magnetisations:

$$M_A \neq M_B: \quad M_A + M_B = M \neq 0 \quad \text{for } T < T_C. \quad (2.200)$$

3c) Antiferromagnetism

This is a special case of ferrimagnetism. Below a critical temperature, which in this case is termed

$$T^* = T_N: \quad \text{the Néel temperature ,}$$

the two sublattices order ferromagnetically with opposite but equal spontaneous magnetisations:

$$T < T_N: \quad |M_A| = |M_B| \neq 0; \quad M = M_A + M_B \equiv 0 . \quad (2.201)$$

Above T_N , the system is normally paramagnetic, with a linear high-temperature behaviour of the inverse susceptibility, as in a ferromagnet:

$$\chi(T) = \frac{C}{T - \Theta} \quad (T \gg T_N) . \quad (2.202)$$

Θ is called the **paramagnetic Curie temperature**. As a rule, it is negative.

2.4.2

Model Concepts

Models are indispensable owing to the lack of a complete theory of magnetism; they relate specifically to particular magnetic phenomena. Here, we refer exclusively to col-

lective magnetism. The collective magnetism of insulators and of metals must be treated separately.

1) Insulators

Magnetism is produced by localised magnetic moments which are due to incompletely filled electronic shells ($3d$ -, $4d$ -, $4f$ - or $5f$ -) in the atoms.

Examples:

Ferromagnets:	CrBr ₃ , K ₂ CuF ₄ , EuO, EuS, CdCr ₂ Se ₄ , Rb ₂ CrCl ₄ , ...
Antiferromagnets:	MnO, EuTe, NiO, RbMnF ₃ , Rb ₂ MnCl ₄ , ...
Ferrimagnets:	MO · Fe ₂ O ₃ (M = divalent metal ion such as Fe, Ni, Cd, Mg, Mn, ...)

These substances are described quite realistically by the so-called

Heisenberg model

$$H = - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j . \quad (2.203)$$

Each localised magnetic moment is associated with an angular momentum \mathbf{J}_i (magneto-mechanical parallelism):

$$\mathbf{m}_i = \mu_B (\mathbf{L}_i + 2\mathbf{S}_i) \equiv \mu_B g_J \cdot \mathbf{J}_i . \quad (2.204)$$

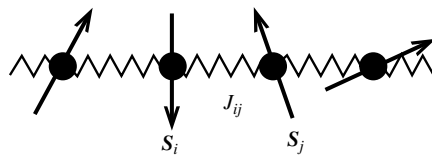
\mathbf{L}_i is here the orbital contribution, \mathbf{S}_i the spin contribution, and g_J is the Landé g -factor. Due to

$$\mathbf{S}_i = (g_J - 1) \mathbf{J}_i , \quad (2.205)$$

the exchange interaction between the moments can be formulated as an interaction between their associated spins. The index i refers to the lattice site. The coupling constants J_{ij} are called **exchange integrals**.

The Heisenberg Hamiltonian (2.203) is to be understood as an *effective* operator. The spin-spin interaction ($\mathbf{S}_i \cdot \mathbf{S}_j$), applied to corresponding spin states, *simulates* the contribution of the exchange matrix elements of the Coulomb interaction (cf. (2.90)), which is presumed to be at the origin of the spontaneous magnetisation.

Fig. 2.8 Model of a ferromagnet with localised magnetic moments. J_{ij} are the exchange integrals



Although the Heisenberg model works well for the magnetic insulators, it is practically useless for the description of magnetic metals.

2) Metals

It is expedient to subdivide this topic into those magnetic metals in which the magnetism and the electrical conductivity are due to the same group of electrons, and those in which these properties can be ascribed to different groups of electrons. In the former case, one refers to

2a) Band magnetism

Prominent representatives of this class are Fe, Co and Ni. A quantum-mechanical exchange interaction causes a spin-dependent band shift below $T < T_C$. Since the two spin subbands are each filled with electrons up to the common Fermi energy E_F , it follows that

$$N_{\uparrow} > N_{\downarrow} \quad (T < T_C) ,$$

and thus a spontaneous magnetic moment is observed. It is found that band magnetism is possible especially with narrow energy bands, and it is therefore thought that the phenomenon can be explained by the **Hubbard model** which was discussed in Sect. 2.1.

2b) “Localised” magnetism

The prototype of this class is the $4f$ metal Gd. Its magnetism is carried by localised $4f$ moments, which can be described realistically by the Heisenberg model (2.203). The electric current in Gd is carried by quasi-free, mobile conduction electrons, which can be understood with the aid of e.g. the jellium model (Sect. 2.1.2), or also with the Hubbard model (Sect. 2.1.3). Interesting phenomena result from an interaction between the localised $4f$ moments and the itinerant conduction electrons. It can for example lead to an effective coupling of the $4f$ moments and thus can amplify the collective magnetism. It can however also contribute to the electrical resistance via scattering of the conduction electrons from the local moments. An appropriate model is the so-called

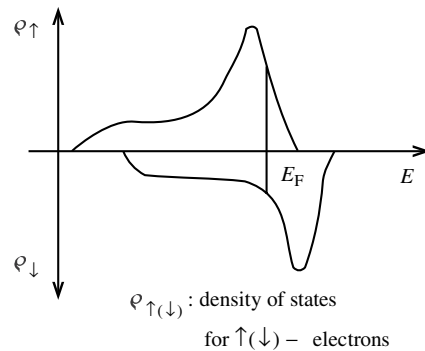


Fig. 2.9 Exchange splitting of the density of states of a ferromagnet below its Curie temperature. The states up to the Fermi energy E_F are all occupied by electrons

s-f (s-d) model

$$H = H \text{ (Hubbard, jellium)} + H \text{ (Heisenberg)} - g \sum_i \sigma_i \cdot S_i . \quad (2.206)$$

σ is the spin operator for the conduction electrons at the site \mathbf{R}_i , and g is a corresponding coupling constant.

2.4.3**Magnons**

There are interesting analogies between the lattice vibrations treated in Sect. 2.2 and the elementary excitations in a ferromagnet. The oscillations of the lattice ions about their equilibrium positions can be decomposed into normal modes with quantised amplitudes. The unit of quantisation is called the **phonon**. The oscillations in a ferromagnet corresponding to the normal modes are called

spin waves,

following Bloch, and their unit of quantisation is the

magnon.

We want to analyse these excitations within the framework of the Heisenberg model (2.203) in more detail. With the usual conventions

$$J_{ij} = J_{ji}; \quad J_{ii} = 0; \quad J_0 = \sum_i J_{ij} = \sum_j J_{ij} \quad (2.207)$$

and the well-known spin operators

$$\mathbf{S}_j = (S_j^x, S_j^y, S_j^z), \quad (2.208)$$

$$S_j^\pm = S_j^x \pm i S_j^y, \quad (2.209)$$

$$S_j^x = \frac{1}{2} (S_j^+ + S_j^-); \quad S_j^y = \frac{1}{2i} (S_j^+ - S_j^-), \quad (2.210)$$

we can decompose the scalar product in the Heisenberg Hamiltonian into its components:

$$\begin{aligned} \mathbf{S}_i \cdot \mathbf{S}_j &= \frac{1}{2} (S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z \\ \Rightarrow H &= - \sum_{i,j} J_{ij} (S_i^+ S_j^- + S_i^- S_j^+) - \frac{1}{\hbar} g_J \mu_B B_0 \sum_i S_i^z. \end{aligned} \quad (2.211)$$

Compared to (2.203), we have added to the Hamiltonian a Zeeman term, in order to take account of the interaction of the local moments with the applied magnetic field $B_0 = \mu_0 H$.

It is often expedient to make use of the spin operators in \mathbf{k} space:

$$S^\alpha(\mathbf{k}) = \sum_i e^{-i\mathbf{k} \cdot \mathbf{R}_i} S_i^\alpha, \quad (2.212)$$

$$S_i^\alpha = \frac{1}{N} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_i} S^\alpha(\mathbf{k}), \quad (2.213)$$

with $(\alpha = x, y, z, +, -)$.

From the commutation relations in real space,

$$[S_i^x, S_j^y]_- = i\hbar \delta_{ij} S_i^z \quad \text{and cyclic permutations}, \quad (2.214)$$

$$[S_i^z, S_j^\pm]_- = \pm\hbar \delta_{ij} S_i^\pm, \quad (2.215)$$

$$[S_i^+, S_j^-]_- = 2\hbar \delta_{ij} S_i^z, \quad (2.216)$$

the commutation relations in \mathbf{k} space follow immediately:

$$[S^+(\mathbf{k}_1), S^-(\mathbf{k}_2)]_- = 2\hbar S^z(\mathbf{k}_1 + \mathbf{k}_2), \quad (2.217)$$

$$[S^z(\mathbf{k}_1), S^\pm(\mathbf{k}_2)]_- = \pm\hbar S^\pm(\mathbf{k}_1 + \mathbf{k}_2), \quad (2.218)$$

$$(S^+(\mathbf{k}))^+ = S^-(\mathbf{k}). \quad (2.219)$$

With the wavenumber-dependent exchange integrals,

$$J(\mathbf{k}) = \frac{1}{N} \sum_{i,j} J_{ij} e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}, \quad (2.220)$$

we can then rewrite the Hamiltonian (2.211) in terms of wavenumbers:

$$\begin{aligned} H = & -\frac{1}{N} \sum_{\mathbf{k}} J(\mathbf{k}) \left\{ S^+(\mathbf{k}) S^-(\mathbf{k}) + S^z(\mathbf{k}) S^z(-\mathbf{k}) \right\} - \\ & -\frac{1}{\hbar} g_J \mu_B B_0 S^z(\mathbf{0}). \end{aligned} \quad (2.221)$$

The ground state $|S\rangle$ of a Heisenberg ferromagnet corresponds to an overall parallel orientation of all the spins. We first compute its energy eigenvalue. The effect of the spin operators on $|S\rangle$ is immediately clear:

$$S_i^z |S\rangle = \hbar S |S\rangle \Rightarrow S^z(\mathbf{k}) |S\rangle = \hbar N S |S\rangle \delta_{\mathbf{k},0}, \quad (2.222)$$

$$S_i^+ |S\rangle = 0 \Rightarrow S^+(\mathbf{k}) |S\rangle = 0. \quad (2.223)$$

It thus follows that:

$$\begin{aligned}
 & -\frac{1}{N} \sum_{\mathbf{k}} J(\mathbf{k}) S^+(\mathbf{k}) S^-(\mathbf{k}) |S\rangle = \\
 & = -\frac{1}{N} \sum_{\mathbf{k}} J(\mathbf{k}) \left[S^-(\mathbf{k}) S^+(\mathbf{k}) + 2\hbar S^z(\mathbf{0}) \right] |S\rangle = \\
 & = -2N\hbar^2 S J_{ii} |S\rangle = 0, \\
 & -\frac{1}{N} \sum_{\mathbf{k}} J(\mathbf{k}) S^z(\mathbf{k}) S^z(-\mathbf{k}) |S\rangle = \\
 & = -\hbar N S \frac{1}{N} J(\mathbf{0}) S^z(\mathbf{0}) |S\rangle = -N J_0 \hbar^2 S^2 |S\rangle.
 \end{aligned}$$

This yields the **ground state energy** E_0 of the Heisenberg ferromagnet:

$$\begin{aligned}
 H |S\rangle &= E_0 |S\rangle, \\
 E_0 &= -N J_0 \hbar^2 S^2 - N g_J \mu_B B_0 S.
 \end{aligned} \tag{2.224}$$

We now show that the state

$$S^-(\mathbf{k}) |S\rangle$$

is likewise an eigenstate of H . To do so, we calculate the following commutator:

$$\begin{aligned}
 & [H, S^-(\mathbf{k})]_- \\
 &= -\frac{1}{N} \sum_{\mathbf{p}} J(\mathbf{p}) \left\{ [S^+(\mathbf{p}), S^-(\mathbf{k})]_- S^-(\mathbf{p}) + \right. \\
 & \quad \left. + S^z(\mathbf{p}) [S^z(-\mathbf{p}), S^-(\mathbf{k})]_- + [S^z(\mathbf{p}), S^-(\mathbf{k})]_- S^z(-\mathbf{p}) \right\} - \\
 & \quad - \frac{1}{\hbar} g_J \mu_B B_0 [S^z(\mathbf{0}), S^-(\mathbf{k})] = \\
 &= -\frac{1}{N} \sum_{\mathbf{p}} J(\mathbf{p}) \left\{ 2\hbar S^z(\mathbf{k} + \mathbf{p}) S^-(\mathbf{p}) - \hbar S^z(\mathbf{p}) S^-(\mathbf{k} - \mathbf{p}) - \right. \\
 & \quad \left. - \hbar S^-(\mathbf{k} + \mathbf{p}) S^z(-\mathbf{p}) \right\} + g_J \mu_B B_0 S^-(\mathbf{k}) = \\
 &= g_J \mu_B B_0 S^-(\mathbf{k}) - \frac{1}{N} \sum_{\mathbf{p}} J(\mathbf{p}) \left\{ -2\hbar^2 S^-(\mathbf{k}) + \right. \\
 & \quad \left. + 2\hbar S^-(\mathbf{p}) S^z(\mathbf{k} + \mathbf{p}) + \hbar^2 S^-(\mathbf{k}) - \hbar S^-(\mathbf{k} - \mathbf{p}) S^z(\mathbf{p}) - \right. \\
 & \quad \left. - \hbar S^-(\mathbf{k} + \mathbf{p}) S^z(-\mathbf{p}) \right\}.
 \end{aligned}$$

Due to

$$J_{ii} = \frac{1}{N} \sum_{\mathbf{p}} J(\mathbf{p}) = 0 \quad (2.225)$$

we finally find:

$$\begin{aligned} [H, S^-(\mathbf{k})]_- &= g_J \mu_B B_0 S^-(\mathbf{k}) - \frac{\hbar}{N} \sum_{\mathbf{p}} J(\mathbf{p}) \left\{ 2S^-(\mathbf{p}) S^z(\mathbf{k} + \mathbf{p}) - \right. \\ &\quad \left. - S^-(\mathbf{k} - \mathbf{p}) S^z(\mathbf{p}) - S^-(\mathbf{k} + \mathbf{p}) S^z(-\mathbf{p}) \right\}. \end{aligned} \quad (2.226)$$

The application of this commutator to the ground state $|S\rangle$ yields:

$$[H, S^-(\mathbf{k})]_- |S\rangle = \hbar\omega(\mathbf{k}) (S^-(\mathbf{k}) |S\rangle), \quad (2.227)$$

$$\hbar\omega(\mathbf{k}) = g_J \mu_B B_0 + 2S\hbar^2 (J_0 - J(\mathbf{k})). \quad (2.228)$$

Here, we have also made use of $J(\mathbf{k}) = J(-\mathbf{k})$. Our assertion that $S^-(\mathbf{k})|S\rangle$ is an eigenstate of H can now be readily demonstrated:

$$\begin{aligned} H (S^-(\mathbf{k}) |S\rangle) &= S^-(\mathbf{k}) H |S\rangle + [H, S^-(\mathbf{k})]_- |S\rangle = \\ &= E(\mathbf{k}) (S^-(\mathbf{k}) |S\rangle), \end{aligned} \quad (2.229)$$

$$E(\mathbf{k}) = E_0 + \hbar\omega(\mathbf{k}). \quad (2.230)$$

If we presume the ground state $|S\rangle$ to be normalised, then it follows that:

$$\langle S | S^+(-\mathbf{k}) S^-(\mathbf{k}) |S\rangle = \langle S | (2\hbar S^z(\mathbf{0}) + S^-(\mathbf{k}) S^+(-\mathbf{k})) |S\rangle = 2\hbar^2 N S.$$

We thus have the following important final result: The

normalised single-magnon state

$$|\mathbf{k}\rangle = \frac{1}{\hbar\sqrt{2SN}} S^-(\mathbf{k}) |S\rangle \quad (2.231)$$

is an eigenstate belonging to the the energy

$$E(\mathbf{k}) = E_0 + \hbar\omega(\mathbf{k}).$$

This corresponds to the **excitation energy**

$$\hbar\omega(\mathbf{k}) = g_J \mu_B B_0 + 2S\hbar^2 (J_0 - J(\mathbf{k})) \quad (2.232)$$

which is ascribed to the quasi-particle **magnon**. The magnetic field term $g_J \mu_B B_0$ contains more information. One can see from it that the magnetic moment of the sample in the state $|\mathbf{k}\rangle$ has been modified relative to the ground state $|S\rangle$ only by a term $g_J \mu_B$. The magnon thus has a spin of $S = 1$:

magnons are Bosons!

Another interesting result can be found from the expectation value of the local spin operator S_i^z in the single-magnon state $|\mathbf{k}\rangle$:

$$\begin{aligned}
 \langle \mathbf{k} | S_i^z | \mathbf{k} \rangle &= \\
 &= \frac{1}{2SN\hbar^2} \langle S | S^+(-\mathbf{k}) S_i^z S^-(\mathbf{k}) | S \rangle = \\
 &= \frac{1}{2SN^2\hbar^2} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{R}_i} \langle S | S^+(-\mathbf{k}) S^z(\mathbf{q}) S^-(\mathbf{k}) | S \rangle = \\
 &= \frac{1}{2SN^2\hbar^2} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{R}_i} \langle S | S^+(-\mathbf{k}) (-\hbar S^-(\mathbf{k} + \mathbf{q}) + S^-(\mathbf{k}) S^z(\mathbf{q})) | S \rangle = \\
 &= \frac{1}{2SN^2\hbar^2} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{R}_i} \{ -2\hbar^2 \langle S | S^z(\mathbf{q}) | S \rangle + \hbar N S \delta_{\mathbf{q}, \mathbf{0}} 2\hbar \langle S | S^z(\mathbf{0}) | S \rangle \} = \\
 &= \frac{1}{2SN^2\hbar^2} \{ -2\hbar^2 N \hbar S + 2\hbar^2 N S N \hbar S \} = \\
 &= \hbar S - \frac{\hbar}{N} .
 \end{aligned}$$

We thus have the notable result

$$\langle \mathbf{k} | S_i^z | \mathbf{k} \rangle = \hbar \left(S - \frac{1}{N} \right) \quad \forall i, \mathbf{k} . \quad (2.233)$$

The right-hand side is not dependent on i and \mathbf{k} . That means that the spin deviation $1\hbar$ in the single-magnon state $|\mathbf{k}\rangle$ is uniformly distributed over all the lattice sites \mathbf{R}_i . As compared to the completely ordered ground state $|S\rangle$, with

$$\langle S | S_i^z | S \rangle = \hbar S \quad \forall i , \quad (2.234)$$

we find a deviation of the local spin per lattice site of \hbar/N . This leads immediately to the concept of a **spin wave**, which implies just this **collective** excitation $|\mathbf{k}\rangle$. Every existing spin wave thus implies for the entire lattice a spin deviation of exactly one unit of angular momentum. The spin wave is characterised by its wavevector \mathbf{k} , which can be visualised in a semiclassical vector model as follows: The local spin \mathbf{S}_i precesses about the z -axis with an axial angle which has just the right value so that the projection of the spins of length $\hbar S$ onto the z -axis has the value $\hbar(S - 1/N)$. The precessing spins have a fixed, constant

phase shift from lattice site to lattice site corresponding to $k = 2\pi / \lambda$. They thus clearly define a wave.

2.4.4

The Spin-Wave Approximation

The Heisenberg model (2.211) is not exactly solvable for the general case. In order to arrive at an approximate solution, it is often expedient to transform the somewhat *unwieldy* spin operators to creation and annihilation operators in the second quantisation:

Holstein-Primakoff transformation:

$$S_i^+ = \hbar \sqrt{2S} \varphi(n_i) a_i, \quad (2.235)$$

$$S_i^- = \hbar \sqrt{2S} a_i^+ \varphi(n_i), \quad (2.236)$$

$$S_i^z = \hbar (S - n_i). \quad (2.237)$$

Here, the following abbreviations were used:

$$n_i = a_i^+ a_i; \quad \varphi(n_i) = \sqrt{1 - \frac{n_i}{2S}}. \quad (2.238)$$

By insertion, one can verify that the commutation relations for the spin operators (2.214), (2.215), and (2.216) are fulfilled if and only if the creation and annihilation operators a_i^+ , a_i are **Bosonic operators**:

$$\begin{aligned} [a_i, a_j]_- &= [a_i^+, a_j^+]_- = 0, \\ [a_i, a_j^+]_- &= \delta_{ij}. \end{aligned} \quad (2.239)$$

The corresponding Fourier transforms

$$a_q = \frac{1}{\sqrt{N}} \sum_i e^{-iq \cdot R_i} a_i; \quad a_q^+ = \frac{1}{\sqrt{N}} \sum_i e^{iq \cdot R_i} a_i^+ \quad (2.240)$$

can be interpreted as magnon annihilation or creation operators. The model Hamiltonian (2.211) then takes on the following form as a result of the transformation:

$$H = E_0 + 2S\hbar^2 J_0 \sum_i n_i - 2S\hbar^2 \sum_{i,j} J_{ij} \varphi(n_i) a_i a_j^+ \varphi(n_j) - \hbar^2 \sum_{i,j} J_{ij} n_i n_j. \quad (2.241)$$

Here, E_0 is the ground-state energy (2.224). A disadvantage of the Holstein-Primakoff transformation is obvious: working explicitly with H required us to carry out an expansion

of the square root in $\varphi(n_i)$:

$$\varphi(n_i) = 1 - \frac{n_i}{4S} - \frac{n_i^2}{32S^2} - \dots \quad (2.242)$$

This means that H in principle consists of infinitely many terms. The transformation is thus only reasonable when there is a physical justification for terminating the infinite series. Since n_i can be interpreted as the operator for the magnon number at the site \mathbf{R}_i , but at low temperatures only a few magnons are excited, in such a case one can limit n_i to only its lowest powers. The simplest approximation in this sense is the so-called **spin-wave approximation**:

$$H^{\text{SW}} = E_0 + 2S\hbar^2 \sum_{i,j} (J_0 \delta_{ij} - J_{ij}) a_i^+ a_j \quad (2.243)$$

After the transformation to wavenumbers, H^{SW} is diagonal

$$H^{\text{SW}} = E_0 + \sum_{\mathbf{k}} \hbar\omega(\mathbf{k}) a_{\mathbf{k}}^+ a_{\mathbf{k}} \quad (2.244)$$

with $\hbar\omega(\mathbf{k})$ as in (2.232). In this low-temperature approximation, the ferromagnet is thus described as a *gas* of non-interacting magnons. According to the rules of statistical mechanics, the mean magnon number $\langle n_{\mathbf{k}} \rangle$ at $T > 0$ is then given by the Bose-Einstein distribution function:

$$\langle n_{\mathbf{k}} \rangle = \frac{1}{\exp(\beta\hbar\omega(\mathbf{k})) - 1} \quad (2.245)$$

Then we find for the magnetisation of the ferromagnet:

$$M(T, H) = g_J \mu_B \frac{N}{V} \left(S - \frac{1}{N} \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle \right) \quad (2.246)$$

At low temperatures, this result is experimentally confirmed to high precision.

2.4.5

Exercises

Exercise 2.4.1 Derive the corresponding relations, using the commutation relations of the spin operators in real space, for the wavenumber-dependent spin operators (i.e. in reciprocal space):

$$S^\alpha(\mathbf{k}) = \sum_{\mathbf{i}} e^{-i\mathbf{k} \cdot \mathbf{R}_i} S_i^\alpha \quad .$$

Exercise 2.4.2 Reformulate the Heisenberg-model Hamiltonian,

$$H = - \sum_{i,j} J_{ij} \left(S_i^+ S_j^- + S_i^z S_j^z \right) - g_J \frac{\mu_B}{\hbar} B_0 \sum_i S_i^z ,$$

making use of the \mathbf{k} -space spin operators from Ex. 2.4.1.

Exercise 2.4.3 Carry out the Holstein-Primakoff transformation on the Heisenberg model Hamiltonian from (Ex. 2.4.2).

Exercise 2.4.4 In the *spin-wave approximation*, the spontaneous magnetisation of a Heisenberg ferromagnet at low temperatures is given by:

$$\frac{M_0 - M_S(T)}{M_0} = \frac{1}{NS} \sum_{\mathbf{q}} \frac{1}{\exp[\beta \hbar \omega(\mathbf{q})] - 1} \quad . \quad (\text{s. (2.246)})$$

$M_0 = g_J \mu_B S \frac{N}{V}$ is the saturation magnetisation and

$$\hbar \omega(\mathbf{q}) = 2S\hbar^2 (J_0 - J(\mathbf{q}))$$

is the magnon energy. Prove Bloch's $T^{3/2}$ law:

$$\frac{M_0 - M_S(T)}{M_0} \sim T^{3/2} .$$

Hints:

- Transform the summation over \mathbf{q} into an integral.
- Keep in mind that at low temperatures, it suffices to use the magnon energies in the form which is valid for small q -values:

$$\hbar \omega(\mathbf{q}) = \frac{D}{2S\hbar^2} q^2 ,$$

and that it is allowed to extend the integration over q to the entire q -space rather than limiting it to the first Brillouin zone.

Exercise 2.4.5 Let the following be given:

$$H: \text{ Hamiltonian with } H|n\rangle = E_n|n\rangle; \quad W_n = \frac{\exp(-\beta E_n)}{\text{Tr}[\exp(-\beta H)]},$$

A, B, C : arbitrary operators.

1. Show that

$$(A, B) = \sum_{n, m}^{E_n \neq E_m} \langle n | A^+ | m \rangle \langle m | B | n \rangle \frac{W_m - W_n}{E_n - E_m}$$

represents a (semidefinite) scalar product.

2. Show that with $B = [C^+, H]_-$, the following relations hold:

$$(A, B) = \langle [C^+, A^+]_- \rangle; \quad (B, B) = \langle [C^+, [H, C]_-]_- \rangle \geq 0,$$

$$(A, A) \leq \frac{1}{2} \beta \langle [A, A^+]_+ \rangle.$$

3. Prove the Bogoliubov inequality using 2.:

$$\frac{\beta}{2} \langle [A, A^+]_+ \rangle \langle [[C, H]_-, C^+]_- \rangle \geq |\langle [C, A]_- \rangle|^2.$$

Exercise 2.4.6

1. Show that for the scalar product defined in Ex. 2.4.5, $(H, H) = 0$ holds when H is the Hamiltonian of the system.
2. Let C be an operator which commutes with the Hamiltonian H . Show that for C , the Bogoliubov relation from Ex. 2.4.5 can be taken as an equation.

Exercise 2.4.7 Discuss the isotropic Heisenberg model:

$$H = - \sum_{i, j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - b B_0 \sum_i S_i^z \exp(-i \mathbf{K} \cdot \mathbf{R}_i); \quad b = \frac{g_J \mu_B}{\hbar}.$$

The wavevector \mathbf{K} is a help in distinguishing different magnetic configurations. Thus, $\mathbf{K} = 0$ leads to ferromagnetism. We assume that

$$Q = \frac{1}{N} \sum_{i, j} |\mathbf{R}_i - \mathbf{R}_j|^2 |J_{ij}| < \infty,$$

which is not a major limitation of generality. For the magnetisation, we then have:

$$M(T, B_0) = b \frac{1}{N} \sum_i \exp(i \mathbf{K} \cdot \mathbf{R}_i) \langle S_i^z \rangle .$$

In the case of an antiferromagnet, ($\mathbf{K} = (1/2)\mathbf{Q}$, \mathbf{Q} : the smallest reciprocal lattice vector), M represents the **sublattice** magnetisation.

1. Choose

$$A = S^-(-\mathbf{k} - \mathbf{K}); \quad C = S^+(\mathbf{k})$$

and then prove that

- a) $\langle [C, A]_- \rangle = \frac{2\hbar N}{b} M(T, B_0)$,
- b) $\sum_k \langle [A, A^+]_+ \rangle \leq 2\hbar^2 N S(S+1)$,
- c) $\langle [[C, H]_-, C^+]_- \rangle \leq 4N\hbar^2 (|B_0 M| + \hbar^2 k^2 Q S(S+1))$.

2. Prove the **Mermin-Wagner theorem** (Phys. Rev. Lett. **17**, 1133 (1966)), using the Bogoliubov inequality, (Ex. 2.4.5): **In the $d = 1$ - and $d = 2$ -dimensional, isotropic Heisenberg model, there can be no spontaneous magnetisation for ($T \neq 0$).**

a) Show that the following holds in this connection:

$$S(S+1) \geq \frac{M^2 v_d \Omega_d}{\beta \hbar^2 b^2 (2\pi)^d} \int_0^{k_0} dk \frac{k^{d-1}}{|BM| + \hbar^2 k^2 Q S(S+1)} .$$

Here, k_0 is the radius of a sphere which lies completely within the Brillouin zone, Ω_d is the surface area of the d -dimensional unit sphere ($\Omega_1 = 1$, $\Omega_2 = 2\pi$, $\Omega_3 = 4\pi$), and $v_d = V_d / N_d$ is the specific volume of the d -dimensional system in the thermodynamic limit.

b) Verify for the **spontaneous magnetisation** that:

$$M_S(T) = \lim_{B_0 \rightarrow 0} M(T, B_0) = 0 \quad \text{for } T \neq 0 \text{ and } d = 1 \text{ and } 2 .$$

2.5

Self-Examination Questions

For Section 2.1

1. Which eigenvalue equation leads to the Bloch functions and the Bloch energies?
2. What is stated by Bloch's Theorem?
3. What are the orthogonality and completeness relations for Bloch functions?
4. Give the Hamiltonian H_0 for non-interacting crystal electrons in second quantisation for the Bloch representation, for the real-space representation with field operators, and for the Wannier representation.
5. What are the commutation relations for Bloch operators $a_{k\sigma}^+$, $a_{k\sigma}$ and for Wannier operators $a_{i\sigma}^+$, $a_{i\sigma}$?
6. When does a Bloch function become a plane wave?
7. What is meant by a *hopping integral*?
8. What relationship exists between Bloch and Wannier operators?
9. Which assumptions define the jellium model?
10. Justify the necessity of a *convergence-producing* factor in the Coulomb integrals of the jellium model.
11. What is the Hamiltonian of the jellium model? What is the effect of the *homogeneously distributed* positive ion charges?
12. How is the operator for the electron density written in the formalism of second quantisation if plane waves are used as a single-particle basis?
13. What relationship exists between the electron density operator and the particle number operator?
14. Formulate the Hamiltonian of the jellium model using the electron density operator.
15. Define the concepts of Fermi energy and Fermi wavevector.
16. What is meant by the *direct term* and the *exchange term* in the Coulomb interaction of the jellium model?
17. Give the two leading terms in the expansion of the ground-state energy of the jellium model in terms of the dimensionless density parameter r_s , and interpret them.
18. What is meant by *correlation energy*?
19. Why is the jellium model not useful for the description of electrons in narrow energy bands?
20. Describe the so-called *tight-binding approximation*.
21. What are the decisive simplifications which finally lead to the Hubbard model?
22. What is the Hamiltonian of the Hubbard model?
23. Which physical parameters mainly influence the statements of the Hubbard model?
24. Name some of the important areas of application of the Hubbard model.

For Section 2.2

1. Why is it reasonable in the description of lattice vibrations to use collective coordinates instead of the ion coordinates?
2. How can the *harmonic approximation* be justified?
3. How is the *matrix of the atomic force constants* defined? What is the meaning of its elements?
4. Name some of the obvious symmetries of the force-constant matrix.
5. Justify the terms *acoustic* and *optical dispersion branch*.
6. What equation of motion is obeyed by the so-called *normal coordinates*? How are they related to the real displacements of the ions?
7. How is the Lagrangian function of the ion system written in terms of the normal coordinates?
8. What are the momenta which are canonically conjugate to the normal coordinates?
9. Give the classical Hamilton function of the ion system. Interpret it.
10. State the commutation relations for the normal coordinates and for the momenta which are canonically conjugate to them.
11. How are the creation and annihilation operators b_{qr}^+ , b_{qr} related to the normal coordinates and their canonically conjugated momenta?
12. Why are b_{qr} and b_{qr}^+ Bosonic operators?
13. Give the Hamiltonian for the ion system in the harmonic approximation in terms of the creation and annihilation operators b_{qr} and b_{qr}^+ .
14. What is a *phonon*?

For Section 2.3

1. Describe the elementary processes which lead to an electron-phonon interaction.
2. Which approximation for the electron-phonon interaction corresponds to the harmonic approximation for the lattice vibrations?
3. Which operator combination defines the electron-phonon interaction within the formalism of second quantisation?
4. What is meant by normal and umklapp processes?
5. Describe how the elementary processes of the electron-phonon interaction can be combined.
6. Which method of theoretical physics allows us to recognise that the electron-phonon interaction contains terms describing an effective phonon-induced electron-electron interaction?
7. Can this effective electron-electron interaction also be attractive?

For Section 2.4

1. Which physical quantity would appear to be particularly suited for the classification of magnetic solids?
2. Why is diamagnetism a property of **all** materials?
3. What is the decisive precondition for the occurrence of paramagnetism and collective magnetism?
4. What distinguishes Langevin paramagnetism from Pauli paramagnetism?
5. Comment on the Curie law.
6. Into which three major subclasses can collective magnetism be subdivided?
7. What is the Hamiltonian of the Heisenberg model? For which class of magnetic substances is the model suited?
8. When does one speak of *band magnetism*?
9. Which magnetic materials are described by the s-f (or s-d) model?
10. Sketch the derivation of the so-called *single-magnon state*

$$|\mathbf{k}\rangle = (\hbar^2 2SN)^{-1/2} S^-(\mathbf{k}) |S\rangle \quad (|S\rangle \iff \text{ferromagnetic saturation})$$

as an eigenstate of the Heisenberg Hamiltonian.

11. What is the spin of magnons?
12. What is the expectation value of the local spin operator S_i^z in the single-magnon state $|\mathbf{k}\rangle$? Interpret the result.
13. Explain the concept of a *spin wave*.
14. Formulate the Holstein-Primakoff transformation of the spin operators.
15. What is meant by the *spin-wave approximation*? Under which conditions is it justified?



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