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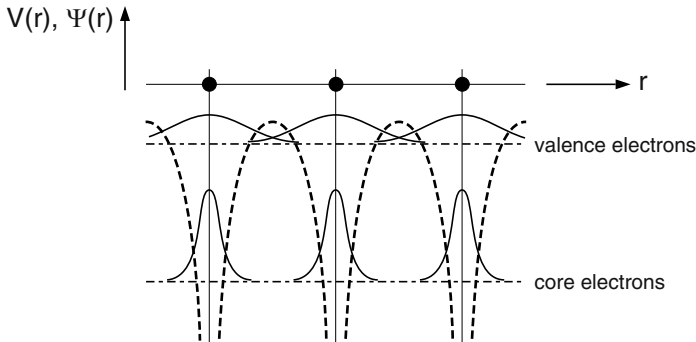
## The Solid as a Many-Particle Problem

As mentioned in Sect. 1.1, we understand the solid as being composed of ions (nuclei and closed electron shells) and valence electrons. A more rigorous approach would start from nuclei and electrons, but a simple consideration of the spatial extension of electrons in different shells of the isolated atoms shows immediately that this is not necessary. The wave functions of electrons in inner shells (the core electrons) with binding energies of hundreds or thousands of eV extend over a distance much smaller than the lattice spacing in a solid, as visualized in Fig. 2.1. In fact, when the atoms are assembled into the configuration of a crystal lattice (or likewise of a molecule, cluster, liquid...) it will be the outermost, weakly bound valence electrons which first experience the presence of their nearest neighbors. They will rearrange from their states in the isolated atoms into those which establish the chemical binding. Together with the electrostatic energy of the ion configuration, this defines the stable structure. Some textbooks on Solid State Theory start with a detailed description of this structure of crystalline solids (e.g., [4, 7, 9, 11]) which is only briefly repeated here. Instead, we follow the approach of [5, 14, 21] with a presentation of the basic Hamiltonian, which defines the solid as a quantum-mechanical many-body problem.

The effectiveness of chemical binding depends on the overlap of the electronic wave functions at neighboring lattice sites and on their coordination number. Thus, metals prefer a close-packed structure, namely the body-centered cubic (bcc) and face-centered cubic (fcc) lattices, with delocalized electrons acting as glue between the positively charged ions (*metallic binding*), while in (binary) ionic crystals, electrons are transferred from the cation to the anion to complete their outer shells (*ionic* or *heteropolar binding*) and form lattices dominated by electrostatic interaction (like the rocksalt structure). Rare gases with closed shell configurations as well as larger molecules form crystalline solids due to the weak *van der Waals*<sup>1</sup> forces and are stable only at low temperatures. Elements of the fourth group of the periodic table

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<sup>1</sup> Johannes Diderik van der Waals 1837–1923, Noble prize in physics 1910.



**Fig. 2.1.** Schematic view of a solid: periodic potential (*dashed line*) and wave functions of core and valence electrons (*solid lines*) drawn at their respective energy levels

share each of their four valence electrons with the four nearest neighbors in directed covalent bonds (*covalent* or *homopolar binding*), which results in the diamond structure. A mixture of covalent and ionic binding, whereby the contribution of the latter increases with the polarity of the material, is typical for the zinc blende structure realized in  $A_3B_5$ ,  $A_2B_6$ , and  $A_1B_7$  compounds. A dominant covalent binding is typical for semiconductors.

In most cases, the distinction between valence and closed shell electrons is justified by the large energy separation, which can be detected by photoelectron spectroscopy (PES [65, 66]). With reference to the heavier elements (including transition-metals and rare-earths) and their compounds, for which *d* states are in the same energy range as the *s* like valence electrons, one should keep in mind, however, that even complete *d* shells can participate in the chemical binding and influence the electronic structure. In Chap. 5, we shall come back to this case but will rely here on a clear separation between closed-shell ions and valence electrons.

## 2.1 The Hamiltonian of the Solid

These introductory considerations about the composition of a solid out of valence electrons and ions justify writing the Hamiltonian as

$$\mathcal{H}_0 = \mathcal{H}_{\text{ion}} + \mathcal{H}_{\text{el}} + \mathcal{H}_{\text{el-ion}}. \quad (2.1)$$

The first term depends only on the coordinates of the ions and reads

$$\mathcal{H}_{\text{ion}} = \sum_{i=1}^{N_I} \frac{\mathbf{P}_i^2}{2M_i} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N_I} V(\mathbf{R}_i - \mathbf{R}_j) \quad (2.2)$$

where  $\mathbf{P}_i$ ,  $\mathbf{R}_i$ , and  $M_i$  denote the momentum, position, and mass of the *i*th ion, respectively, and  $N_I$  is the number of ions in the crystal volume  $V_c$ .

$V(\mathbf{R}_i - \mathbf{R}_j)$  can be a quite general ion-ion interaction potential, but for point-like ions with charge  $Q_i = \text{sign}(Q_i)Z_i e$  and positive integer  $Z_i$ , it will be the Coulomb interaction

$$V(\mathbf{R}_i - \mathbf{R}_j) = \frac{Q_i Q_j}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{R}_j|}. \quad (2.3)$$

Here,  $\epsilon_0$  is the vacuum dielectric constant. The assumption of point-like ions is justified for closed shells with tightly bound electrons. This situation is visualized in Fig. 2.1.

The electron part of  $\mathcal{H}_0$  is given by

$$\mathcal{H}_{\text{el}} = \sum_{l=1}^{N_e} \frac{\mathbf{p}_l^2}{2m} + \frac{1}{2} \sum_{\substack{k,l=1 \\ k \neq l}}^{N_e} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{r}_k|} \quad (2.4)$$

where  $\mathbf{p}_l$  and  $\mathbf{r}_l$  are the momentum and position of the  $l$ th electron,  $m$  is the free electron mass, and  $N_e$  is the number of electrons in the crystal volume. The charge neutrality of the solid requires that

$$\sum_{i=1}^{N_I} Q_i - eN_e = 0. \quad (2.5)$$

The interaction between electrons and ions is described by

$$\mathcal{H}_{\text{el-ion}} = \sum_{l=1}^{N_e} \sum_{i=1}^{N_I} v(\mathbf{r}_l - \mathbf{R}_i) \simeq \sum_{l=1}^{N_e} \sum_{i=1}^{N_I} \frac{Q_i e}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{R}_i|} \quad (2.6)$$

where the last expression is the approximation for point-like ions.

It is conceivable that the physical properties of the system described by  $\mathcal{H}_0$  do not depend on  $N_{I,e}$  as long as these numbers are sufficiently large. These properties will be considered in the thermodynamic limit  $N_{I,e} \rightarrow \infty$ , with the corresponding densities  $N_{I,e}/V_c$  kept constant. This situation, valid for macroscopic solids, is to be distinguished from that of *mesoscopic systems* for which *clusters* are a representative example. The number of their surface ions is comparable with that of the bulk ions with the consequence that their properties depend on the shape defined by the surface. The physics of clusters has become a research field in its own right [32–34]. Nevertheless, it is interesting to note that the properties of macroscopic solids can be thought of as evolving with increasing size from those of clusters as the ratio of the number of surface ions divided by the number of bulk ions goes to zero.

So far the spin of electrons or ions did not appear because neither the kinetic energy nor the Coulomb interaction depends on spin. The expression for the kinetic energy is that of the non-relativistic formulation. In principle, one could have started, e.g., for the electrons, from the relativistic Dirac operator (which is in fact used in band structure theory and becomes relevant for

solids composed of atoms with large  $Z_i$ , see Chap. 5). However, in most cases, it is sufficient to consider just the spin-orbit coupling in the electron part of the Hamiltonian

$$\mathcal{H}_{\text{so}} = \frac{\hbar}{4m^2c^2} \sum_l (\nabla_l V_{\text{eff}}(\mathbf{r}_l) \times \mathbf{p}_l) \cdot \boldsymbol{\sigma}_l \quad (2.7)$$

where  $V_{\text{eff}}(\mathbf{r}_l)$  is the effective single-particle potential, which will be introduced in Chap. 5, and  $\boldsymbol{\sigma}_l$  is the vector of the Pauli spin matrices of the  $l$ th electron. A similar term can be added to the ion part of the Hamiltonian, in order to account for the nuclear spins, if their influence is addressed. But even without spin-orbit coupling, the spin becomes important in the presence of a magnetic field, when the Zeeman term causes removal of spin degeneracy, and, because of the fermion character of the electrons, by considering the Pauli principle, when dealing with the many-particle aspect of the problem (see Chap. 4). Moreover, spin alignment and spin excitation are essential for magnetic properties (see Chap. 6).

As mentioned already in Sect. 1.2, we consider a solid primarily for the case of the crystalline periodic order of the ions. Only in Chap. 9, we shall remove this restriction by allowing structural disorder and its effect on the electronic eigenstates and transport. The perfect crystalline configuration – which, in order to simplify the notation, is assumed here to be a Bravais lattice – is characterized by ion positions  $\mathbf{R}_i$  forming a point lattice (see Sect. 1.2)

$$\mathbf{R}_n^0 = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (2.8)$$

where the upper index 0 indicates that these vectors now mark the equilibrium positions, while the actual position of an ion is given by

$$\mathbf{R}_n = \mathbf{R}_n^0 + \mathbf{u}_n \quad (2.9)$$

with a displacement  $\mathbf{u}_n$  accounting for the motion of the ion about its equilibrium position. These displacements will be assumed to be small in comparison with the lattice constant to motivate a separation of the ion-ion potential according to

$$\begin{aligned} V(\mathbf{R}_n - \mathbf{R}_m) &= V(\mathbf{R}_n^0 - \mathbf{R}_m^0 + \mathbf{u}_n - \mathbf{u}_m) \\ &= V(\mathbf{R}_n^0 - \mathbf{R}_m^0) + \delta V(\mathbf{R}_n - \mathbf{R}_m), \end{aligned} \quad (2.10)$$

where  $V(\mathbf{R}_n^0 - \mathbf{R}_m^0)$  is determined by the equilibrium configuration and  $\delta V$  can be explicitly expressed as a Taylor series in the displacements. In the same way we may proceed with the electron-ion potential

$$v(\mathbf{r}_l - \mathbf{R}_n) = v(\mathbf{r}_l - \mathbf{R}_n^0) + \delta v(\mathbf{r}_l - \mathbf{R}_n). \quad (2.11)$$

The Hamiltonian of the solid may now be written as

$$\begin{aligned}
 \mathcal{H}_0 = & \sum_{\mathbf{n}} \frac{\mathbf{P}_{\mathbf{n}}^2}{2M_{\mathbf{n}}} + \frac{1}{2} \sum_{\substack{\mathbf{n}, \mathbf{m} \\ \mathbf{n} \neq \mathbf{m}}} \delta V(\mathbf{R}_{\mathbf{n}} - \mathbf{R}_{\mathbf{m}}) \\
 & + \sum_{l=1}^{N_e} \frac{\mathbf{p}_l^2}{2m} + \frac{1}{2} \sum_{\substack{k, l=1 \\ k \neq l}}^{N_e} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{r}_k|} + \sum_{\mathbf{n}, l} v(\mathbf{r}_l - \mathbf{R}_{\mathbf{n}}^0) \\
 & + \frac{1}{2} \sum_{\substack{\mathbf{n}, \mathbf{m} \\ \mathbf{n} \neq \mathbf{m}}} V(\mathbf{R}_{\mathbf{n}}^0 - \mathbf{R}_{\mathbf{m}}^0) + \sum_{\mathbf{n}, l} \delta v(\mathbf{r}_l - \mathbf{R}_{\mathbf{n}}). \quad (2.12)
 \end{aligned}$$

The first line of (2.12), depending only on the positions and momenta of the heavy constituents of the solid, will be the subject of Chap. 3, the lattice dynamics. In the quantum mechanical version, it is characterized by phonons, the quanta of lattice vibrations, which determine the elastic properties, the specific heat, and the optical properties in the far-infrared spectral range.

The second line, describing the electrons in a static periodic lattice potential and their mutual interaction, will be the starting point of Chaps. 4–7. In Chap. 4, we will present the properties of the homogeneous electron gas (for which the periodic potential will be smeared out into a homogeneous positive charge background defining the jellium model) and learn how to treat the electron–electron interaction. In Chap. 5, the single-particle concepts of band structure, which allow one to distinguish metals from insulators will be introduced. Also, spin dynamics and magnetic properties (Chap. 6) and correlated electron systems (Chap. 7) will be treated, essentially by starting from the second line of (2.12).

The third line of (2.12) contains two contributions. The first one is the electrostatic interaction energy of the ions in their equilibrium configuration, representing a constant energy which becomes important in total energy calculations. For a binary cubic lattice, with a basis consisting of two point-like ions with opposite charge  $\pm Ze$  (e.g., the zinc blende and rocksalt structure), this term can be expressed using

$$\frac{1}{2} \sum_{j \neq i} \text{sign}(Q_i) \text{sign}(Q_j) \frac{(Ze)^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{R}_j|} = \frac{1}{2} \frac{(Ze)^2}{4\pi\epsilon_0 R} \alpha_M, \quad (2.13)$$

where  $|\mathbf{R}_i - \mathbf{R}_j| = R p_{ij}$ , with the nearest neighbor distance  $R$ , and

$$\alpha_M = \sum_{j \neq i} \text{sign}(Q_i) \text{sign}(Q_j) \frac{1}{p_{ij}} \quad (2.14)$$

is the Madelung<sup>2</sup> constant. It is independent of the reference lattice point  $i$  [29]. The second contribution depends on the actual positions of the ions

<sup>2</sup> Erwin Madelung 1881–1972.

and electrons and couples the dynamics of both subsystems, thus giving rise to electron–phonon interaction (Chap. 8). It is important for electron transport properties, relaxation phenomena, and superconductivity.

The structuring of  $\mathcal{H}_0$  as given in (2.12) is by purpose quite suggestive: Without the third line, the electron and ion subsystems are separated and can be considered as independent. We will discuss in the next section the conditions under which such an approximation is justified.

## 2.2 Separating the Motion of Electrons and Ions

In order to describe a solid and its properties, we have to solve the quantum mechanical problem:

$$\mathcal{H}_0 \tilde{\Psi} = i\hbar \dot{\tilde{\Psi}} \quad \text{with} \quad \tilde{\Psi} = \tilde{\Psi}(\{\mathbf{r}_l\}, \{\mathbf{R}_n(t)\}). \quad (2.15)$$

Here,  $\{\mathbf{r}_l\}, \{\mathbf{R}_n(t)\}$  denote the configurations of the electrons and ions of the system, of which the latter is considered time-dependent because of the thermal motion of the ions.

Employing thermodynamic concepts, electrons and ions can be considered as two systems which are in contact as mediated by the last term of (2.12). Let us assume that the thermal equilibrium of the whole system, i.e., electrons and ions have the same temperature and the same average thermal energy per degree of freedom. This can be quantified by the mean values of the kinetic energy and we may write

$$\left\langle \frac{p_l^2}{2m} \right\rangle = \left\langle \frac{P_n^2}{2M} \right\rangle. \quad (2.16)$$

Because of the mass ratio  $m/M \simeq 10^{-4}$ , this equation indicates that the electrons move much faster than the ions. Thus, the electrons will experience any actual configuration of the ions (caused by thermal fluctuation) as a stationary potential to which they adjust instantaneously by adopting the state of lowest energy. This fact can be used to formulate the conditions for separating the motions of ions and electrons.

Consider the stationary Schrödinger<sup>3</sup> equation of the electrons moving in the electrostatic potential, defined by the actual configuration of the ions,

$$(\mathcal{H}_{\text{el}} + \mathcal{H}_{\text{el-ion}}) \Psi_\alpha = \mathcal{E}_{\text{el},\alpha} \Psi_\alpha \quad (2.17)$$

as being solved. The eigensolutions  $\Psi_\alpha(\{\mathbf{r}_l\}, \{\mathbf{R}_n\})$  and energy eigenvalues  $\mathcal{E}_{\text{el},\alpha}(\{\mathbf{R}_n\})$  are characterized by a complete set of quantum numbers  $\alpha$  and depend parametrically on the ion configuration  $\{\mathbf{R}_n\}$ . For a given configuration, the  $\Psi_\alpha$  form a complete set and can be used to expand the solution of the time-dependent problem (2.15) in the form

<sup>3</sup> Erwin Schrödinger 1887–1961, shared in 1933 the Nobel prize in physics with P.A.M. Dirac.

$$\tilde{\Psi}(\{\mathbf{r}_l\}, \{\mathbf{R}_n(t)\}) = \sum_{\alpha} \Phi_{\alpha}(\{\mathbf{R}_n\}, t) \Psi_{\alpha}(\{\mathbf{r}_l\}, \{\mathbf{R}_n\}) \quad (2.18)$$

with the expansion coefficients  $\Phi_{\alpha}$  depending on the ion configuration and on  $t$ . Then the full problem (2.15) reads

$$\mathcal{H}_0 \tilde{\Psi} = \sum_{\alpha} \left[ \underbrace{(\mathcal{H}_{\text{el}} + \mathcal{H}_{\text{el-ion}})}_{=\mathcal{E}_{\text{el},\alpha} \Psi_{\alpha}} \Phi_{\alpha} + \mathcal{H}_{\text{ion}} \Psi_{\alpha} \Phi_{\alpha} \right] = i\hbar \sum_{\alpha} \Psi_{\alpha} \dot{\Phi}_{\alpha}. \quad (2.19)$$

Using the completeness of the  $\Psi_{\alpha}$ , we eliminate the electron coordinates by multiplying from left with  $\Psi_{\beta}^*$  and integrating over all  $\mathbf{r}_l$  to obtain

$$\mathcal{E}_{\text{el},\beta} \Phi_{\beta} + \sum_{\alpha} \int \dots \int \Psi_{\beta}^* \mathcal{H}_{\text{ion}} \Psi_{\alpha} d^3\{\mathbf{r}_l\} \Phi_{\alpha} = i\hbar \dot{\Phi}_{\beta}. \quad (2.20)$$

The operator  $\mathcal{H}_{\text{ion}}$  contains the momentum operators  $\mathbf{P}_n$  which act on the ion coordinates of both  $\Psi_{\alpha}$  and  $\Phi_{\alpha}$ . Thus the integration over electron coordinates in the second term of (2.20) can be performed by writing (as operator equation applied to  $\Phi_{\alpha}$ )

$$\int \dots \int \Psi_{\beta}^* \mathcal{H}_{\text{ion}} \Psi_{\alpha} d^3\{\mathbf{r}_l\} = \sum_{\mathbf{n}} \frac{1}{2M} (2(\mathbf{P}_{\mathbf{n}})_{\beta\alpha} \cdot \mathbf{P}_{\mathbf{n}} + (\mathbf{P}_{\mathbf{n}}^2)_{\beta\alpha}), \quad (2.21)$$

where the matrix elements (for  $\kappa = 1, 2$ )

$$(\mathbf{P}_{\mathbf{n}}^{\kappa})_{\beta\alpha} = \int \dots \int \Psi_{\beta}^*(\{\mathbf{r}_l\}, \{\mathbf{R}_n\}) \mathbf{P}_{\mathbf{n}}^{\kappa} \Psi_{\alpha}(\{\mathbf{r}_l\}, \{\mathbf{R}_n\}) d^3\{\mathbf{r}_l\} \quad (2.22)$$

couple between different electron states  $\Psi_{\alpha}, \Psi_{\beta}$ . When writing the momentum in atomic units (Bohr radius  $a_B = 4\pi\epsilon_0\hbar^2/me^2$  and Rydberg energy  $1 \text{ Ry} = me^4/(4\pi\epsilon_0)^2 2\hbar^2$ ),  $\mathbf{P}_{\mathbf{n}} = \mathbf{P}'_{\mathbf{n}}\hbar/a_B$ , this coupling, expressed in terms of

$$\frac{P^2}{2M} = \frac{m}{M} P'^2 \text{ Ry},$$

is seen to carry a factor  $m/M \ll 1$ , thus representing a small term. If this coupling is neglected, one arrives at the *Born–Oppenheimer*<sup>4</sup> *approximation*. It is sometimes also called *adiabatic approximation* because the electrons follow the (slow) motion of the ions adiabatically, i.e., without changing their eigenstate. Within this approximation, the motion of the electrons is separated from that of the ions, and we may write for these two systems, the equations

$$(\mathcal{H}_{\text{ion}} + \mathcal{E}_{\text{el},\alpha}) \Phi_{\alpha} = i\hbar \dot{\Phi}_{\alpha} \quad (2.23)$$

with

$$\mathcal{H}_{\text{ion}} + \mathcal{E}_{\text{el},\alpha} = \sum_{\mathbf{n}} \frac{\mathbf{P}_{\mathbf{n}}^2}{2M} + \mathcal{E}_{\text{el},\alpha}(\{\mathbf{R}_n\}) + \frac{1}{2} \sum_{\substack{\mathbf{n}, \mathbf{m} \\ \mathbf{n} \neq \mathbf{m}}} V(\mathbf{R}_n - \mathbf{R}_m) \quad (2.24)$$

<sup>4</sup> Max Born 1882–1970, Nobel prize in physics 1954; J. Robert Oppenheimer 1904–1967.

and (see (2.17))

$$(\mathcal{H}_{\text{el}} + \mathcal{H}_{\text{el-ion}}) \Psi_{\alpha} = \mathcal{E}_{\text{el},\alpha} \Psi_{\alpha}. \quad (2.25)$$

Equation (2.23) is the time-dependent Schrödinger equation for the ions which move in the *adiabatic potential*

$$\mathcal{U}_{\alpha}(\{\mathbf{R}_n\}) = \mathcal{E}_{\text{el},\alpha}(\{\mathbf{R}_n\}) + \frac{1}{2} \sum_{\substack{n,m \\ n \neq m}} V(\mathbf{R}_n - \mathbf{R}_m) \quad (2.26)$$

defined by the ion configuration and the energy of the eigenstate  $\alpha$  of the electron system. This problem will be studied in more detail in Chap. 3. Equation (2.25) is the stationary eigenvalue problem of the electron system for a given ion configuration. We will discuss its solution in Chaps. 4–7 with the simplification of always replacing  $\{\mathbf{R}_n\}$  by the equilibrium configuration  $\{\mathbf{R}_n^0\}$ . It should be mentioned that the Born–Oppenheimer approximation does not apply only to solids but also to molecules.

## 2.3 Thermal Expectation Values

One of the important aims of a theory is to explain experimental results and possibly arrive at a quantitative description of measurements. Experiments yield information about physical observables, which in quantum formulation are Hermitian operators  $\hat{A} = \hat{A}^{\dagger}$ . Thus, our theory has to aim at the description of the expectation values  $\langle \hat{A} \rangle$  of such operators. For solids, which are macroscopic thermodynamic systems, they have to be understood as thermal expectation values. Therefore, a brief repetition of the related concepts of statistical mechanics is required.

Simple quantum mechanical systems (e.g., an atom, an oscillator) can be prepared in a state  $|i\rangle$  and the expectation (or mean) value is given by

$$\langle \hat{A} \rangle = \langle i | \hat{A} | i \rangle. \quad (2.27)$$

The state  $|i\rangle$  can be an eigenstate or a mixture of eigenstates and thus, in repeated measurements, the measured values will be sharp (an eigenvalue of  $\hat{A}$ ) or fluctuate around the mean value, respectively. A solid, consisting of many particles, is not a simple system and cannot be prepared in a well defined quantum state. Instead, being a thermodynamic system, the solid can be prepared in a state characterized by a set of thermodynamic variables like temperature  $T$ , particle number  $N$ , volume  $V$ . These thermodynamic quantities specify the state of the solid as a statistical ensemble of quantum mechanical micro-states  $\{|i\rangle, i = 1, \dots, I; T, N, \dots \text{fixed}\}$ , and the experimental values for the observable  $\hat{A}$  are described by the thermal expectation value (or ensemble mean value)

$$\langle \hat{A} \rangle = \frac{1}{I} \sum_{i=1}^I \langle i | \hat{A} | i \rangle. \quad (2.28)$$



Making use of a complete orthonormal set of states  $|n\rangle$  and of the property that factors under the trace operation  $\text{Tr}(\dots) = \sum_n \langle n | \dots | n \rangle$  can be interchanged, we may formulate the expectation or *thermal mean value* as

$$\langle \hat{A} \rangle = \sum_n \langle n | \left( \frac{1}{I} \sum_{i=1}^I |i\rangle \langle i| \right) \hat{A} | n \rangle \quad (2.29)$$

or in short

$$\langle \hat{A} \rangle = \text{Tr} \left( \hat{\rho} \hat{A} \right), \quad (2.30)$$

where

$$\hat{\rho} = \frac{1}{I} \sum_{i=1}^I |i\rangle \langle i| \quad (2.31)$$

is the statistical operator.

Let us repeat the important properties of the statistical operator:

1. It is Hermitian:  $\hat{\rho} = \hat{\rho}^\dagger$
2. It is positive semi-definite:  $\langle \psi | \hat{\rho} | \psi \rangle = \frac{1}{I} \sum_i |\langle \psi | i \rangle|^2 \geq 0$ , for arbitrary  $|\psi\rangle$
3. It is normalized:  $\text{Tr} \hat{\rho} = \frac{1}{I} \sum_{n,i} \langle n | i \rangle \langle i | n \rangle = \frac{1}{I} \sum_i \langle i | (\sum_n |n\rangle \langle n|) | i \rangle = 1$  in any representation.

These properties qualify  $\hat{\rho}$  as the operator of probability distributions. It satisfies the eigenvalue equation

$$\hat{\rho} |n\rangle = p_n |n\rangle \quad (2.32)$$

with the eigenvalue

$$p_n = \langle n | \hat{\rho} | n \rangle = \frac{1}{I} \sum_i |\langle i | n \rangle|^2, \quad (2.33)$$

which quantifies the probability of finding the state  $|n\rangle$  in the ensemble of micro-states  $\{|i\rangle \dots\}$ .

In thermal equilibrium, one has

$$\dot{\hat{\rho}} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}] = 0, \quad (2.34)$$

where  $\hat{H}$  is the Hamiltonian of the system in which the states  $|i\rangle$  are realized (in our case that of the solid). In the representation of eigenstates of  $\hat{H}$ , the statistical operator, which commutes with  $\hat{H}$ , is diagonal (Problem 2.1).

The following statistical ensembles are of importance in solid state physics and will be used throughout the book:

1. The canonical ensemble with fixed temperature  $T$  and particle number  $N$  ( $\beta = 1/k_B T$  where  $k_B$  is the Boltzmann<sup>5</sup> constant):

$$\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}} \quad (2.35)$$

with the canonical partition function  $Z = \text{Tr}(e^{-\beta \hat{H}})$ . In the energy representation  $\hat{\rho}$  becomes  $p_n = Z^{-1} \exp(-\beta E_n)$ .

2. The grand-canonical ensemble with fixed temperature  $T$  and variable particle number  $N$ :

$$\hat{\rho}_G = \frac{1}{Z_G} e^{-\beta(\hat{H} - \mu \hat{N})} \quad (2.36)$$

with the grand-canonical partition function  $Z_G = \text{Tr}\{e^{-\beta(\hat{H} - \mu \hat{N})}\}$ , where  $\hat{N}$  is the particle number operator and  $\mu$  the chemical potential. In the energy representation,  $\hat{\rho}_G$  becomes  $p_n = Z_G^{-1} \exp(-\beta(E_n - \mu N_n))$ , where  $N_n$  is the particle number in the state  $|n\rangle$ .

In the next section, the thermal expectation values of observables will be evaluated, especially for thermal equilibrium formulated in terms of eigenstates of the Hamiltonian  $\mathcal{H}_0$  (see (2.12)). A particular situation is obtained for very low temperatures, at which the thermal expectation value becomes the ground state expectation value (Problem 2.2). When considering the number operator as observable for a system in thermal equilibrium, one obtains the well-known distribution functions of the Fermi–Dirac<sup>6</sup> or Bose–Einstein<sup>7</sup> statistics (depending on the system), and of their high-temperature limit, the Maxwell distribution (Problem 2.3).

## 2.4 Theory of Linear Response

Any experiment constitutes a perturbation of the system under investigation: By scattering light or particles, we obtain information on the structure of the solid or of its characteristic excitations; by applying an electric or magnetic field, we study the transport or magnetic properties; by probing with light, we detect the optical properties. If we do this to characterize the material, these perturbations have to be weak and must not change the system properties. This defines the regime of *linear response*.

The system (in our case the solid) plus the external perturbation applied to investigate its properties, is described by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + V_{\text{ext}}. \quad (2.37)$$

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<sup>5</sup> Ludwig Boltzmann 1844–1906.

<sup>6</sup> Enrico Fermi 1901–1954, Nobel prize in physics 1938; Paul Adrien Maurice Dirac 1902–1984, Nobel prize in physics 1933.

<sup>7</sup> Satyendra Nath Bose 1894–1974; Albert Einstein 1879–1955, Nobel prize in physics 1922.

**Table 2.1.** Examples of observables used in the response formalism

$\hat{A}, \hat{B}$	$V_{\text{ext}}$	$F$	Response function
Electric current density	$-\mathbf{j} \cdot \mathbf{A}$	Electric field	Electric conductivity
Dielectric polarization	$-\mathbf{P} \cdot \mathbf{E}$	Electric field	Dielectric function
Magnetic polarization	$-\mathbf{m} \cdot \mathbf{H}$	Magnetic field	Magnetic susceptibility
Heat current density	$-\mathbf{v} \cdot \nabla T$	Temp. gradient	Heat conductivity

$\mathcal{H}_0$  is the Hamiltonian (2.12) of the unperturbed solid and the perturbation, (assumed for simplicity as being independent of space variables) can be written as.

$$V_{\text{ext}}(t) = -\hat{B}F(t). \quad (2.38)$$

Here,  $\hat{B}$  is an observable and  $F(t)$ , a (in general, time-dependent) scalar function. We may distinguish between dynamic (time-dependent) and static (time-independent) perturbations. Consider the measurement of an observable  $\hat{A}$ . The measured values can be described by

$$\langle \hat{A} \rangle_t = \text{Tr} \left( \hat{\rho} \hat{A} \right) = \int dt' R(t, t') F(t'). \quad (2.39)$$

They are ruled by a linear response function  $R(t, t')$ , which is expected to depend on  $\hat{A}$  and  $\hat{B}$ . It will turn out to be a correlation function of these observables as shown later in this section. But before doing this, let us look at the examples of experimental situations listed in Table 2.1 together with their translation into the response formalism.

To determine the electric conductivity as a material property of a solid one has to design a measurement of the electric current density  $\mathbf{j}$  by exposing the sample to an electric field, which can be formulated as the time-derivative of the vector potential  $\mathbf{A}$ . The perturbation results from the minimal coupling according to which the particle momenta in  $\mathcal{H}_0$  are replaced by  $\mathbf{p} + e\mathbf{A}$  which, to lowest order in  $\mathbf{A}$ , leads to  $V_{\text{ext}}(t) = -\mathbf{j} \cdot \mathbf{A}(t)$  with the electric current density  $\mathbf{j} = -e \sum_l \mathbf{p}_l / m$ . Thus the electric conductivity is a current–current (or velocity–velocity) correlation function. Due to the vector character of  $\mathbf{j}$  and  $\mathbf{A}$ , the response function is a second rank tensor. Likewise, the dielectric function, characterizing the optical and dielectric properties, follows from measuring the dielectric polarization by probing with an electric field as perturbation. The dielectric function will turn out to be a correlation function between polarizations (or electric dipole moments). A similar situation leads to the magnetic susceptibility. A heat current is caused by a temperature gradient; its measurement provides the heat conductivity.

In generalizing (2.39) to also include dependence on space variables, we may write

$$\langle \hat{A}(\mathbf{r}) \rangle_t = \int dt' \int d^3 r' R(\mathbf{r}, t; \mathbf{r}', t') F(\mathbf{r}', t'). \quad (2.40)$$

For homogeneous systems, the response function depends only on  $\mathbf{r} - \mathbf{r}'$  and, therefore, a spatially harmonic external perturbation of the form  $F(\mathbf{r}', t') = F_{\mathbf{q}}(t') \exp(i\mathbf{q} \cdot \mathbf{r}')$  leads to the same spatial dependence of the observable, which in brief means

$$\langle \hat{A}_{\mathbf{q}} \rangle_t = \int dt' R(\mathbf{q}; t, t') F_{\mathbf{q}}(t') \quad (2.41)$$

with  $R(\mathbf{q}; t, t')$  being the Fourier transform of  $R(\mathbf{r} - \mathbf{r}'; t, t')$ .

Let us return to the task of finding an expression for the thermal expectation value of  $\hat{A}$ , which is linear in the perturbing field  $F(t)$  for the system described by the Hamiltonian  $\mathcal{H}$  of (2.37). In view of (2.39), the dependence on the field enters through the statistical operator, which contains the system Hamiltonian including the external perturbation. Without this perturbation, the system is in equilibrium, and the statistical operator satisfies the equation of motion (in the following the  $\hat{\cdot}$ -sign, indicating operators, is dropped)

$$[\mathcal{H}_0, \rho_0] = i\hbar \dot{\rho}_0 = 0. \quad (2.42)$$

If the perturbation is switched on, the system is driven out of the thermal equilibrium described by  $\rho_0$ , and the statistical operator will become time-dependent:

$$\rho_0 \rightarrow \rho(t) = \rho_0 + \Delta\rho(t). \quad (2.43)$$

In order to find the deviation  $\Delta\rho(t)$  from equilibrium, caused by the perturbation, we have to solve the equation of motion for  $\rho(t)$ :

$$[\mathcal{H}, \rho(t)] = i\hbar \dot{\rho}(t). \quad (2.44)$$

Looking for the first order perturbation correction to the equilibrium distribution, we rewrite this equation as

$$\begin{aligned} [\mathcal{H}_0 + V_{\text{ext}}, \rho_0 + \Delta\rho(t)] &= [\mathcal{H}_0, \rho_0] + [\mathcal{H}_0, \Delta\rho(t)] \\ &+ [V_{\text{ext}}, \rho_0] + [V_{\text{ext}}, \Delta\rho(t)] = i\hbar \dot{\rho}(t) \end{aligned} \quad (2.45)$$

and keep only those terms, which are of first order in the perturbation (i.e., we neglect  $[V_{\text{ext}}, \Delta\rho]$ ) to write

$$[V_{\text{ext}}, \rho_0] \simeq i\hbar \left\{ \frac{\partial}{\partial t} \rho(t) - \frac{1}{i\hbar} [\mathcal{H}_0, \Delta\rho(t)] \right\}. \quad (2.46)$$

By multiplying from left and right with the proper exponentials we change from the Schrödinger into the interaction picture (indicated by an overbar), which for the deviation from the equilibrium distribution reads

$$\Delta\bar{\rho}(t) = e^{\frac{i}{\hbar}\mathcal{H}_0 t} \Delta\rho(t) e^{-\frac{i}{\hbar}\mathcal{H}_0 t}. \quad (2.47)$$

Note, that the time dependence of  $\Delta\rho(t)$  on the *rhs* (in the Schrödinger picture) is that of the external field, while that on the *lhs* also includes the time

evolution due to  $\mathcal{H}_0$ . In the interaction picture, the equation of motion for the first order correction  $\Delta\bar{\rho}$  to the equilibrium distribution reads

$$i\hbar \frac{\partial}{\partial t} \Delta\bar{\rho}(t) = e^{\frac{i}{\hbar}\mathcal{H}_0 t} [V_{\text{ext}}(t), \rho_0] e^{-\frac{i}{\hbar}\mathcal{H}_0 t}. \quad (2.48)$$

It is an inhomogeneous linear differential equation indicating a linear relation between  $\Delta\bar{\rho}(t)$  and the external perturbation  $V_{\text{ext}}$ . By direct integration one finds

$$\Delta\bar{\rho}(t) = \frac{1}{i\hbar} \int_{-\infty}^t e^{\frac{i}{\hbar}\mathcal{H}_0 t'} [V_{\text{ext}}(t'), \rho_0] e^{-\frac{i}{\hbar}\mathcal{H}_0 t'} dt', \quad (2.49)$$

and in the Schrödinger picture

$$\Delta\rho(t) = \frac{1}{i\hbar} \int_{-\infty}^t e^{-\frac{i}{\hbar}\mathcal{H}_0(t-t')} [V_{\text{ext}}(t'), \rho_0] e^{\frac{i}{\hbar}\mathcal{H}_0(t-t')} dt', \quad (2.50)$$

which is explicitly a linear expression in the external perturbation.

Let us now calculate the thermal expectation value of the observable  $A$  (the index  $t$  indicates the possible time dependence)

$$\langle A \rangle_t = \text{Tr}((\rho_0 + \Delta\rho(t))A) = \text{Tr}(\rho_0 A) + \text{Tr}(\Delta\rho(t)A). \quad (2.51)$$

The first term is the thermal expectation value of  $A$  of the unperturbed system (i.e., in equilibrium), which may be written  $A_0$ . The second term, depending on the perturbation (2.38), can be transformed in several steps by exploiting the meaning of the trace operation:

$$\begin{aligned} \langle A \rangle_t &= A_0 + \frac{i}{\hbar} \int_{-\infty}^t \text{Tr} \left( e^{-\frac{i}{\hbar}\mathcal{H}_0(t-t')} [BF(t'), \rho_0] e^{\frac{i}{\hbar}\mathcal{H}_0(t-t')} A \right) dt' \\ &= A_0 + \frac{i}{\hbar} \int_{-\infty}^t \text{Tr} (A(t-t') \{BF(t')\rho_0 - \rho_0 BF(t')\}) dt' \\ &= A_0 + \frac{i}{\hbar} \int_{-\infty}^t \text{Tr} (\rho_0 \{A(t-t')B - BA(t-t')\}) F(t') dt'. \end{aligned} \quad (2.52)$$

In the first step, we applied a cyclic permutation of operators under the trace operation, in the second step we introduced the interaction picture for the observable  $A$  written as  $A(t-t')$ , and in the last step, we extracted the scalar factor  $F(t')$  (note, that it is not an operator) and performed a cyclic permutation in the second term. We may now write  $B = B(0)$  because, for vanishing time argument, the Schrödinger picture coincides with the interaction picture. Moreover, the upper limit of the integral can be shifted to infinity when the integrand is multiplied by the unit step function  $\theta(t-t')$ . Thus we find

$$\langle A \rangle_t = A_0 + \frac{i}{\hbar} \int_{-\infty}^{\infty} \theta(t-t') \langle [A(t-t'), B(0)] \rangle_0 F(t') dt' \quad (2.53)$$

which has the form of (2.39). The expectation value  $\langle \dots \rangle_0$  under the integral is to be taken with the statistical operator  $\rho_0$  in the equilibrium. The usual writing is by taking the Fourier transform

$$\begin{aligned}\Delta A(\omega) &= \int_{-\infty}^{+\infty} e^{i\omega t} (\langle A \rangle_t - A_0) dt \\ &= \frac{i}{\hbar} \int \int_{-\infty}^{+\infty} dt dt' e^{i\omega(t-t')} \theta(t-t') \langle [A(t-t'), B(0)] \rangle_0 e^{i\omega t'} F(t').\end{aligned}$$

Finally, by changing the two time integrations with the substitution  $t - t' = \tau$  we have

$$\Delta A(\omega) = \frac{i}{\hbar} \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \theta(\tau) \langle [A(\tau), B(0)] \rangle_0 \int_{-\infty}^{+\infty} dt' e^{i\omega t'} F(t') \quad (2.54)$$

and

$$\Delta A(\omega) = \chi_{AB}(\omega) F(\omega). \quad (2.55)$$

This is the linear response of the system when measuring the observable  $\hat{A}$  (now using the  $\hat{\cdot}$ -sign again) by applying a (time-dependent) perturbation  $-\hat{B}F(\omega)$ . It is expressed as the Fourier transform of the difference between the thermal expectation value of  $\hat{A}$  and its equilibrium value and written as a product of the perturbing field and a response function or susceptibility

$$\chi_{AB}(\omega) = \frac{i}{\hbar} \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \theta(\tau) \langle [\hat{A}(\tau), \hat{B}(0)] \rangle_0. \quad (2.56)$$

The response function is completely defined by the unperturbed system (in our case the solid in thermal equilibrium) and describes a material property of the solid. It is a correlation function between the measured observable  $\hat{A}$  and the observable  $\hat{B}$  appearing in the perturbation. As will be seen later, the observables  $\hat{A}$  and  $\hat{B}$  are Hermitian adjoints of each other. The time dependent integrand with the step function warrants the causality between perturbation and response. This characteristic structure will be identified later (Sect. 7.1) as that of a retarded Green function. Having anticipated a periodic time dependence of the perturbation with the frequency  $\omega$ , we obtain the response depending on  $\omega$  (dynamical response). The special case of  $\omega = 0$  refers to the static response.

## 2.5 Kubo's Formulas: Response Functions

The general concept of linear response has been developed in an earlier paper by Ryogo Kubo[67] and can be found in some text books (e.g., [9, 13, 18]). In this section, we restrict ourselves to the response functions of importance in solid state physics, some of which have already been mentioned in Table 2.1.

*1. Dielectric Susceptibility:* When exposing a piece of matter to an electric field, the matter will be polarized, i.e., it responds by shifting positive and

negative charges against each other or by aligning existing electric dipoles which, without the field, are randomly oriented. The polarization or electric dipole density  $\mathbf{P} = \mathbf{M}^E/V$  (here  $V$  is the volume) is given by the relation

$$\mathbf{P} = \chi^E \cdot \mathbf{E}, \quad (2.57)$$

which has the form of (2.55). The dielectric susceptibility  $\chi^E$  is a symmetric second rank tensor. Its principal values depend on the crystal structure of the solid as will be seen later. This tensor property allows the two vectors  $\mathbf{P}$  and  $\mathbf{E}$  to have different directions and to describe birefringence. This is the case in solids with axial anisotropy, while in cubic crystals the principal values of  $\chi^E$  are equal to each other.

In order to formulate the dielectric susceptibility as a correlation function as in (2.56), we have to identify the two observables  $\hat{A}$  and  $\hat{B}$ . The perturbation is the potential energy of the electric dipole moment  $\mathbf{M}^E$  in the applied electric field  $\mathbf{E}(t)$

$$V_{\text{ext}}(t) = -\mathbf{M}^E \cdot \mathbf{E}(t) = -\sum_j M_j^E E_j(t). \quad (2.58)$$

We find the observable  $\hat{B}$  to be one of the components of the electric dipole moment and the scalar field  $F(t)$  to be the corresponding component of the applied electric field. The observable to be measured for investigating the dielectric susceptibility (or one of its tensor components) is a component of the electric dipole density, say  $P_i$ , and we may write (2.53) in the form

$$\langle P_i \rangle_t - P_{i0} = \sum_j \frac{i}{\hbar V} \int_{-\infty}^{+\infty} \theta(t-t') \langle [M_i^E(t-t'), M_j^E(0)] \rangle_0 E_j(t') dt' \quad (2.59)$$

and obtain after Fourier transformation, the response function

$$\chi_{ij}^E(\omega) = \frac{i}{\hbar V} \int_{-\infty}^{+\infty} e^{i\omega\tau} \theta(\tau) \langle [M_i^E(\tau), M_j^E(0)] \rangle_0 d\tau. \quad (2.60)$$

This is the Kubo formula for the *dielectric susceptibility*, which is a correlation function of components of the electric dipole moment. The contribution of the crystal lattice to the dielectric susceptibility will be described in more detail in Sect. 3.5. We mention in passing that systems with  $P_{i0} \neq 0$  are called ferroelectric; their configuration of electrons and ions allows for a spontaneous dielectric polarization.

**2. Magnetic Susceptibility:** Magnetic properties of matter can be characterized by the response of the system to an applied magnetic field  $\mathbf{B}$ . The measured quantity will be the magnetization  $\mathbf{M} = \mathbf{m}/V$ , which in complete analogy to the dielectric case is the magnetic dipole density. Making use of this analogy, we may write the perturbation  $V_{\text{ext}}(t) = -\mathbf{m} \cdot \mathbf{B}(t)$  and identify the observable  $\hat{A}$  with a component of the magnetization and the observable  $\hat{B}$  with a

component of the magnetic dipole moment to write the Kubo formula for the *magnetic susceptibility*

$$\chi_{ij}^M(\omega) = \frac{i}{\hbar V} \int_{-\infty}^{+\infty} e^{i\omega\tau} \theta(\tau) \langle [m_i(\tau), m_j(0)] \rangle_0 d\tau. \quad (2.61)$$

It is a correlation function between the components of the magnetic dipole moment.

In Chap. 6, we shall express the magnetic dipole moment in terms of the electron spin operators  $\mathbf{S}_l$  as

$$\mathbf{m} = g\mu_B \sum_l \mathbf{S}_l, \quad (2.62)$$

with the Landé<sup>8</sup>  $g$  factor and the Bohr<sup>9</sup> magneton  $\mu_B$ . For this case, the magnetic susceptibility

$$\chi_{ij}^M(\omega) = \frac{i}{\hbar V} g^2 \mu_B^2 \sum_{ll'} \int_{-\infty}^{+\infty} e^{i\omega\tau} \theta(\tau) \langle [S_{l,i}(\tau), S_{l',j}(0)] \rangle_0 d\tau. \quad (2.63)$$

turns out to be a correlation function between the components of the electron spin operator or in short, a spin–spin correlation function.

*3. Dielectric Function:* The dielectric function (or frequency dependent dielectric constant) is known from electrodynamics; it connects the displacement field with the electric field according to

$$\mathbf{D}(\mathbf{q}, \omega) = \varepsilon_0 \varepsilon(\mathbf{q}, \omega) \mathbf{E}(\mathbf{q}, \omega). \quad (2.64)$$

The space and time dependence of the quantities are specified by the wave vector  $\mathbf{q}$  and the frequency  $\omega$ , respectively. Depending on the experimental situation, one distinguishes between the response to a longitudinal or transverse perturbation. Let us consider here, the case of probing the dielectric system with an external test charge, which exerts a longitudinal electric field. This scenario is typical for a scattering experiment. It is intuitively clear that the charges of the dielectric will rearrange in the presence of the test charge, and this rearrangement is quantified by an induced charge density  $en_{\text{ind}}$ . The fields are determined by their respective charges via Poisson's equation. For the displacement field, these are the external charges  $en_{\text{ext}}(\mathbf{q}, \omega)$  (the Fourier transform of the external charge density  $en_{\text{ext}}(\mathbf{r}, t)$ )

$$i\mathbf{q} \cdot \mathbf{D}(\mathbf{q}, \omega) = en_{\text{ext}}(\mathbf{q}, \omega) \quad (2.65)$$

and for the electric field, in addition the induced charges (due to polarization in the presence of the external charge)  $en_{\text{ind}}(\mathbf{q}, \omega)$

<sup>8</sup> Alfred Landé 1888–1975.

<sup>9</sup> Niels Bohr 1885–1962, Nobel prize in physics 1922.



$$\mathbf{i}\mathbf{q} \cdot \mathbf{E}(\mathbf{q}, \omega) = \frac{e}{\varepsilon_0} (n_{\text{ext}}(\mathbf{q}, \omega) + n_{\text{ind}}(\mathbf{q}, \omega)). \quad (2.66)$$

It is straightforward to eliminate the fields from (2.64) to (2.66) and to write

$$n_{\text{tot}}(\mathbf{q}, \omega) = n_{\text{ind}}(\mathbf{q}, \omega) + n_{\text{ext}}(\mathbf{q}, \omega) = \frac{n_{\text{ext}}(\mathbf{q}, \omega)}{\varepsilon(\mathbf{q}, \omega)}. \quad (2.67)$$

The last relation is the standard expression for the *dielectric screening* of a test charge in dielectric matter. In general, for time-dependent processes, it depends on  $\omega$ , and describes dynamical screening.

We may read this relation also from the viewpoint of linear response: The system responds to the external or test charge by building up the total charge density  $en_{\text{tot}}(\mathbf{q}, \omega)$  with the inverse dielectric function as the response function. In order to cast it into the form of (2.56), we identify the observable  $\hat{A}$  as the charge density operator

$$e\hat{n}(\mathbf{r}) = e \sum_{\mathbf{q}} \hat{n}_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \quad (2.68)$$

or its Fourier transform, the operator of density fluctuations  $\hat{n}_{\mathbf{q}}$ . The time dependent induced density fluctuations are given by

$$n_{\text{ind}}(\mathbf{q}, t) = \langle \hat{n}_{\mathbf{q}} \rangle_t - n_0. \quad (2.69)$$

The perturbation is caused by the charge density of the external (or test) charge

$$en_{\text{ext}}(\mathbf{r}, t) = e \sum_{\mathbf{q}'} n_{\text{ext}}(\mathbf{q}', t) e^{i\mathbf{q}' \cdot \mathbf{r}} \quad (2.70)$$

with the interaction energy

$$\begin{aligned} V_{\text{ext}}(t) &= \frac{-e^2}{4\pi\varepsilon_0} \int \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\hat{n}(\mathbf{r}) n_{\text{ext}}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{-e^2}{4\pi\varepsilon_0} \sum_{\mathbf{q}\mathbf{q}'} \hat{n}_{\mathbf{q}} n_{\text{ext}}(\mathbf{q}', t) \int \int d^3\mathbf{r} d^3\mathbf{r}' \frac{e^{i(\mathbf{q} \cdot \mathbf{r} + \mathbf{q}' \cdot \mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (2.71)$$

The double integral can be expressed in terms of the Fourier transform, and one obtains

$$V_{\text{ext}}(t) = - \sum_{\mathbf{q}} v_{\mathbf{q}} \hat{N}_{-\mathbf{q}} N_{\text{ext}}(\mathbf{q}, t), \quad (2.72)$$

where  $v_{\mathbf{q}} = e^2/V\varepsilon_0 q^2$  is the Fourier transform of the Coulomb potential (see Appendix),  $\hat{N}_{-\mathbf{q}} = V\hat{n}_{-\mathbf{q}}$  and  $N_{\text{ext}}(\mathbf{q}, t) = Vn_{\text{ext}}(\mathbf{q}, t)$ . By identifying  $\hat{N}_{-\mathbf{q}}$  as the observable  $\hat{B}$  and  $n_{\text{ext}}(\mathbf{q}, t)$  as the scalar time dependent field  $F(t)$  of the general response formalism, we may now write

$$n_{\text{ind}}(\mathbf{q}, \omega) = v_{\mathbf{q}} \frac{i}{\hbar} \int_{-\infty}^{+\infty} e^{i\omega\tau} \theta(\tau) \langle [\hat{N}_{\mathbf{q}}(\tau), \hat{N}_{-\mathbf{q}}(0)] \rangle_0 n_{\text{ext}}(\mathbf{q}, \omega) d\tau. \quad (2.73)$$

In comparison with (2.67), we find as the Kubo formula for the *inverse dielectric function*

$$\frac{1}{\varepsilon(\mathbf{q}, \omega)} = 1 + v_{\mathbf{q}} \frac{i}{\hbar} \int_{-\infty}^{+\infty} e^{i\omega\tau} \theta(\tau) \langle [\hat{N}_{\mathbf{q}}(\tau), \hat{N}_{-\mathbf{q}}(0)] \rangle_0 d\tau. \quad (2.74)$$

It is a correlation function of the number (or density) fluctuations and will be discussed in more detail in Chap. 4 as *energy-loss function*.

As further examples, one may consider the tensor components of the electric conductivity  $\sigma_{\mu\nu}(\omega)$  (Problem 2.4) or the thermal conductivity mentioned in Table 2.1. The response concept can be generalized beyond the linear regime by considering higher order terms in the external perturbation (Problem 2.5). The corresponding response functions describe the nonlinear properties of the material, which become important, for instance, in the response of a solid to intense laser light (nonlinear optics) or strong electric fields (nonlinear transport) [68].

## 2.6 Properties of Response Functions

Because response functions will be used throughout the book, some of their properties have to be compiled at the beginning [64, 69, 70]. Response functions  $\chi_{AB}(\omega)$  of the general form (2.56) are complex valued functions for real frequencies. If they are considered in the complex frequency plane with  $z = \omega + i\delta$ , they represent analytic functions in the upper half-plane. The analyticity is a consequence of the causal connection between the perturbation and its effect on the system as expressed by the unit step function under the integral. Due to this property, Cauchy's theorem holds, which reads

$$\chi_{AB}(z) = \frac{1}{2\pi i} \oint \frac{\chi_{AB}(z')}{z' - z} dz', \quad (2.75)$$

where the contour integral is along the real axis and closes along the great semicircle in the upper half-plane. Assuming that  $\chi_{AB}(z')$  vanishes sufficiently rapidly at infinity, the semicircle does not contribute to the integral, and we have

$$\chi_{AB}(z) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\chi_{AB}(\omega')}{\omega' - z} d\omega'. \quad (2.76)$$

This relation can be evaluated for real  $z$  with

$$\lim_{\Gamma \rightarrow 0} \frac{1}{\omega' - \omega - i\Gamma} = \mathcal{P} \left( \frac{1}{\omega' - \omega} \right) + i\pi\delta(\omega' - \omega), \quad (2.77)$$

where  $\mathcal{P}$  denotes the principal part. Using (2.77) in (2.76) and rearranging terms gives

$$\chi_{AB}(\omega) = \frac{1}{i\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\chi_{AB}(\omega')}{\omega' - \omega} d\omega'. \quad (2.78)$$

By separating this relation into real and imaginary part,

$$\chi_{AB}(\omega) = \text{Re}\chi_{AB}(\omega) + i\text{Im}\chi_{AB}(\omega), \quad (2.79)$$

one finds the *dispersion* or *Kramers–Kronig*<sup>10</sup> relations

$$\text{Re}\chi_{AB}(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\text{Im}\chi_{AB}(\omega')}{\omega' - \omega} d\omega' \quad (2.80)$$

$$\text{Im}\chi_{AB}(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\text{Re}\chi_{AB}(\omega')}{\omega' - \omega} d\omega' \quad (2.81)$$

which are a consequence of causality. The real and imaginary parts of the susceptibility are also called the dissipative and absorptive parts, respectively.

The meaning of these relations can be illustrated by considering the imaginary part of a susceptibility of the form  $\text{Im}\chi(\omega') \sim (\delta(\omega_0 - \omega') - \delta(\omega_0 + \omega'))$  (as will be shown in Chap. 3, this describes the absorption (and emission) of a harmonic oscillator with eigenfrequency  $\omega_0$ ). For this case, the real part of  $\chi(\omega)$  takes the form  $1/(\omega_0^2 - \omega^2)$ , characteristic for the anomalous dispersion of an oscillator (Problem 2.6).

According to the structure of (2.56), the susceptibility is the Fourier transform of an object of the more general form

$$G_{AB}(\tau) = -\frac{i}{\hbar} \theta(\tau) \langle [\hat{A}(\tau), \hat{B}(0)]_{\pm} \rangle \quad (2.82)$$

which is a *retarded Green*<sup>11</sup> *function*. Depending on whether  $\hat{A}$ ,  $\hat{B}$  are fermion or boson operators, one has to take the anti-commutator  $[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$  or the commutator  $[\hat{A}, \hat{B}]_- = \hat{A}\hat{B} - \hat{B}\hat{A}$ , respectively. Note, that a response function  $\chi_{AB}$  is always written in terms of the commutator. The thermal expectation value is evaluated for the system Hamiltonian (in case of a response function it is the one without external perturbation).

The retarded Green function  $G_{AB}(\tau)$  can be decomposed into the correlation functions  $C_{AB}^>(\tau) = \langle \hat{A}(\tau)\hat{B}(0) \rangle$  and  $C_{AB}^<(\tau) = \langle \hat{B}(0)\hat{A}(\tau) \rangle$

$$G_{AB}(\tau) = -\frac{i}{\hbar} \theta(\tau) (C_{AB}^>(\tau) \pm C_{AB}^<(\tau)). \quad (2.83)$$

Its Laplace transform, to which the Fourier transform reduces because of the step function in  $G_{AB}(\tau)$ ,

<sup>10</sup> Hendrik Anton Kramers 1894–1952; Ralph de Laer Kronig 1904–1995.

<sup>11</sup> George Green 1793–1841.

$$\begin{aligned}
G_{AB}(z) &= \int_0^\infty e^{iz\tau} G_{AB}(\tau) d\tau \\
&= -\frac{i}{\hbar} \int_0^\infty d\tau e^{iz\tau} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} (C_{AB}^>(\omega) \pm C_{AB}^<(\omega)) \quad (2.84)
\end{aligned}$$

can be expressed in terms of the Fourier transforms  $C_{AB}^>(\omega)$  and  $C_{AB}^<(\omega)$  of the correlation functions. After performing the time integration, one finds the *spectral representation* of the Green function

$$G_{AB}(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\rho_{AB}(\omega')}{\omega' - z} d\omega' \quad (2.85)$$

with the *spectral function*

$$\rho_{AB}(\omega) = -\frac{1}{2\hbar} (C_{AB}^>(\omega) \pm C_{AB}^<(\omega)). \quad (2.86)$$

The upper(lower) sign refers to expressions formed with fermion(boson) operators. The spectral representation (2.85) can be used to express  $\rho_{AB}(\omega)$  in terms of the Green function

$$\rho_{AB}(\omega) = \frac{1}{2i} \lim_{\Gamma \rightarrow 0} (G_{AB}(\omega + i\Gamma) - G_{AB}(\omega - i\Gamma)) \quad (2.87)$$

which, under the conditions given below, is real valued.

Some properties of the spectral function  $\rho_{AB}(\omega)$  can be obtained by writing the time-dependent correlation functions in the energy or spectral representation (using eigenstates  $|n\rangle$ ,  $|m\rangle$  of the system Hamiltonian  $H$ )

$$\begin{aligned}
C_{AB}^>(\tau) &= \langle e^{\frac{i}{\hbar} H \tau} \hat{A} e^{-\frac{i}{\hbar} H \tau} \hat{B} \rangle \\
&= \sum_{nm} p_n A_{nm} B_{mn} e^{\frac{i}{\hbar} (E_n - E_m) \tau}. \quad (2.88)
\end{aligned}$$

Here  $p_n$  is the statistical factor,  $E_n$ ,  $E_m$  are the eigenvalues of  $H$  and  $A_{nm}$ ,  $B_{mn}$  the matrix elements of  $\hat{A}$  and  $\hat{B}$ . The Fourier transform of  $C_{AB}^>(\tau)$  is given by

$$C_{AB}^>(\omega) = \sum_{nm} p_n A_{nm} B_{mn} 2\pi \delta(\hbar\omega + E_n - E_m). \quad (2.89)$$

Similarly we find

$$C_{AB}^<(\omega) = \sum_{nm} p_m B_{mn} A_{nm} 2\pi \delta(\hbar\omega + E_n - E_m). \quad (2.90)$$

The following relations hold for the correlation functions:

$$C_{AB}^>(\omega) = C_{BA}^<(-\omega) \quad (2.91)$$

$$C_{AB}^<(\omega) = e^{-\beta\hbar\omega} C_{AB}^>(\omega). \quad (2.92)$$

The first of these relations is obtained by interchanging  $n$  and  $m$  under the sum in (2.89) and (2.90). The second is found by using the ratio  $p_m/p_n = \exp(-\beta\hbar\omega)$  of the statistical factors. (This relation holds not only for the canonical ensemble, but also for the grand-canonical ensemble if the operators  $\hat{A}$  and  $\hat{B}$  do not change the particle numbers.) Because of (2.91), the spectral function has the property

$$\rho_{AB}(-\omega) = \pm \rho_{BA}(\omega), \quad (2.93)$$

which in connection with (2.85), implies  $G_{AB}(-z) = \mp G_{BA}(z)$ , where again, the upper(lower) sign refers to the quantity defined for fermion(boson) operators. For  $\hat{B} = \hat{A}^\dagger$ , and using (2.89), (2.90), and (2.92) we may write  $\rho_{BA}(\omega)$  in the form

$$\rho_{AA^\dagger} = -\frac{\pi}{\hbar} (1 \pm e^{-\beta\hbar\omega}) \sum_{m,n} p_n A_{nm} A_{mn} \delta(\hbar\omega + E_n - E_m), \quad (2.94)$$

to see with  $A_{mn} = A_{nm}^*$  that it is real, and with (2.87) that  $\rho_{AA^\dagger}(\omega) = \text{Im}\{G_{AA^\dagger}(\omega)\}$ . In the special case of Hermitian operators,  $\hat{B} = \hat{A}$ , one has  $\text{Im}\{G_{AA}(-\omega)\} = -\text{Im}\{G_{AA}(\omega)\}$ . Using (2.92), the correlation function  $C_{AB}^>(\omega)$  can be expressed also as

$$C_{AB}^>(\omega) = -2\hbar \frac{\rho_{AB}(\omega)}{1 \pm e^{-\beta\hbar\omega}} \quad (2.95)$$

and its Fourier transform is

$$\langle A(\tau)B(0) \rangle = -\frac{\hbar}{\pi} \int_{-\infty}^{+\infty} e^{-i\omega\tau} \frac{\rho_{AB}(\omega)}{1 \pm e^{-\beta\hbar\omega}} d\omega. \quad (2.96)$$

Let us finally specialize to the case of  $G_{AB}$  being a response function with  $\hat{B} = \hat{A}^\dagger$  and consider the case  $\tau = 0$ . Then with  $\rho_{AA^\dagger}(\omega) = -\text{Im} \chi_{\hat{A}\hat{A}^\dagger}(\omega)$  the last relation takes the form

$$\langle \hat{A}\hat{A}^\dagger \rangle = \frac{\hbar}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im} \chi_{\hat{A}\hat{A}^\dagger}(\omega)}{1 - e^{-\beta\hbar\omega}} d\omega, \quad (2.97)$$

which connects the imaginary (or dissipative) part of the response function with a quantity that describes the fluctuations in the observable  $\hat{A}$  and is therefore known as the *dissipation-fluctuation theorem*.

Due to the hermiticity of the operators  $\hat{A}$  and  $\hat{B}$  and the appearance of their commutator in the response function, its imaginary part fulfills the relations

$$\text{Im} \chi_{AB}(-\tau) = -\text{Im} \chi_{BA}(\tau) \quad (2.98)$$

$$\text{Im} \chi_{AB}(-\omega) = -\text{Im} \chi_{BA}(\omega) \quad (2.99)$$

and with

$$\chi_{AB}^*(\omega) = \chi_{AB}(-\omega), \quad (2.100)$$

the response  $\Delta A(\omega)$  in (2.55) is real as required for an observable.

## Problems

- 2.1 Formulate the matrix representation of the statistical operator with the eigenstates of the system Hamiltonian and show that it is diagonal.
- 2.2 Show that the thermal expectation value of an observable reduces for  $T = 0$  K to the expectation value of this observable in the ground state of the system.
- 2.3 Calculate the thermal expectation value of the particle number operator for a system of (free) fermions in thermal equilibrium to find the Fermi–Dirac distribution. Do the same for a system of bosons to obtain the Bose–Einstein distribution. Consider the high temperature limit.
- 2.4 In order to derive the Kubo formula for the electric conductivity  $\sigma_{\mu\nu}(\omega)$ , identify the observables  $\hat{A}$  and  $\hat{B}$  in (2.56). Keep in mind which quantity is measured in transport experiments, and how the coupling between electrons and the electromagnetic field is described.
- 2.5 Develop the concept of nonlinear response by considering (as in perturbation theory) corrections to the equilibrium distribution  $\Delta\rho = \Delta\rho_1 + \Delta\rho_2 + \dots$  of increasing order in the external perturbation. Find the structure of the lowest order nonlinear response function for the observable  $\hat{A}$  due to the perturbation  $V_{\text{ext}}$  (2.38).
- 2.6 Let the imaginary part of a response function be of the form  $\text{Im}\chi_{AB}(\omega) = \chi_0(\delta(\omega_0 - \omega) - \delta(\omega_0 + \omega))$ . Calculate the real part of the response function using (2.80).



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