

The Magnetic Susceptibility

Any system may be characterized by its response to external stimuli. For example, in electronics the proverbial “black box” is characterized by its measured output voltage when an input current is applied. This transfer impedance, as it is called, provides all the information necessary to understand the operation of the black box. If we know what is in the black box – for example, the detailed arrangement of resistors, diodes, etc. – then we can predict, through analysis, what the transfer impedance will be.

Similarly, a system of charges and currents, such as a crystal, may be characterized by a response function. In this text we shall be concerned mainly with the response of such a system to a magnetic field. In this case the “output” is the magnetization and the response function is the magnetic susceptibility. A complete analysis of the magnetic susceptibility is virtually impossible since the system consists of about 10^{21} particles. Therefore we usually look to a measured susceptibility for clues to the important mechanisms active in the system and then use these to analyze the system. In order to carry out such a program, we must know what possible mechanisms exist and what effect they have on the susceptibility.

Determination of the susceptibility entails evaluation of the magnetization produced by an applied magnetic field. In general, this applied field may depend on space and time. The resulting magnetization will also vary in space and time. If the spatial dependence of the applied field is characterized by a wave vector \mathbf{q} and its time dependence is characterized by a frequency ω , and if we restrict ourselves for the time being to the magnetization with this wave vector and frequency, we obtain the *susceptibility* $\chi(\mathbf{q}, \omega)$. As we shall see shortly, the magnetization is the average magnetic moment. The magnetic moment itself is a well-defined quantity. The problem, however, is the computation of its average value. In order to compute this average it is necessary to know the probabilities of the system being in its various configurations. This information is contained in the distribution function associated with the system.

We shall see in this chapter that the distribution function depends on the total energy, or Hamiltonian, of the system. Therefore the first step in understanding magnetic properties is the identification of those interactions relevant to magnetism. In Chap. 2 the origin of these interactions is discussed, and they are expressed in a form which facilitates their application in later chapters. The reader is asked to keep in mind that Chaps. 1 and 2 both constitute background material for the theoretical development which begins in Chap. 3. The motivation for the material in these first two chapters should become clear as this theory unfolds.

In the absence of time-dependent fields we may assume that the system is in thermal equilibrium. In this case the distribution function is easily obtained. In Chap. 3 this is used to compute the response of noninteracting moments to a static field. This computation leads to the susceptibility $\chi(\mathbf{q}, 0)$. In Chaps. 4 and 5 the response $\chi(\mathbf{q}, 0)$ of an interacting system of moments to a static field is investigated in the random-phase approximation.

In the presence of time-dependent fields the distribution function must be obtained from its equation of motion. In the case of localized moments this consists of solving the *Bloch equations*. For itinerant moments the distribution function is obtained from a *Boltzmann equation*. In Chaps. 6 and 7 these equations are solved for weakly interacting systems to obtain the generalized susceptibility $\chi(\mathbf{q}, \omega)$. Finally, in Chap. 8 the generalized susceptibility associated with strongly interacting systems is investigated. This function is of particular interest because its singularities determine the magnetic-excitation spectrum of the system.

With the development of thin film deposition techniques it became possible to fabricate inhomogeneous magnetic materials, particularly thin films. Chapter 9 describes some of the phenomena associated with such structures.

One of the most powerful techniques for studying the spatial and temporal behavior of magnetic materials is neutron scattering. While pulsed and “cold” sources have expanded the range of neutron studies since the first edition of this book, the scattering description provided in Chap. 10 remains valid.

The next few sections introduce the basic quantities with which we shall be concerned throughout this text. Since these quantities may be defined in various ways, the reader may find it informative to compare other approaches (especially the classic work [1]).

1.1 The Magnetic Moment

Let us begin by discussing the magnetic moment. To see why this particular object is of interest let us consider the classical description of a system of charges and currents. Such a system is governed by Maxwell’s equations. The appropriate forms of these equations in a medium are the so-called *macroscopic Maxwell equations*, which are obtained from the microscopic equations by averaging over a large number of particles, see [2]. The microscopic equation

in which we shall be particularly interested is the one representing Ampere's law, which has the differential form

$$\nabla \times \mathbf{h} = \frac{4\pi}{c} \mathbf{j} + \frac{\partial \mathbf{e}}{\partial t}. \quad (1.1)$$

We define the average fields

$$\begin{aligned} \langle \mathbf{h} \rangle &\equiv \mathbf{B}, \\ \langle \mathbf{e} \rangle &\equiv \mathbf{E}. \end{aligned} \quad (1.2)$$

Here $\langle \dots \rangle$ is a spatial average over a region which is small compared with the size of the sample, yet large enough to contain many atomic systems (the lower limit to the macroscopic domain would typically be 10 nm).

When we write $\mathbf{B}(\mathbf{r})$ or $\mathbf{E}(\mathbf{r})$, the coordinate \mathbf{r} refers to the center of the region over which the average is taken. Thus the first equation of (1.2) might have been written as $\mathbf{B}(\mathbf{r}) = \langle \mathbf{h} \rangle_{\mathbf{r}}$. In this description it is assumed that any spatial variations are large in comparison with interatomic spacings. The actual details of the averaging will be discussed in Sect. 1.2. With this notation the macroscopic version of (1.1) becomes

$$\nabla \times \mathbf{B} = \frac{4\pi}{c} \langle \mathbf{j} \rangle + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t}. \quad (1.3)$$

The objective now is to calculate the average current density. To do this we separate the total current density into two parts, that associated with conduction electrons and that localized at an ionic site. The average value of the conduction electron current density is the *free current density* \mathbf{j}_{free} .

The ionic current density may be further separated into two contributions. First of all, the ion may possess an electric-dipole moment which is characterized by a *dipole charge density* ρ_{dip} . If this charge density is time dependent, there is a *polarization current density* \mathbf{j}_{pol} which satisfies the continuity equation

$$\nabla \cdot \mathbf{j}_{\text{pol}} = -\frac{\partial \rho_{\text{dip}}}{\partial t}. \quad (1.4)$$

Taking the average of this equation and assuming that the average commutes with the time and space derivatives, we obtain

$$\left\langle \sum_{\text{ions}} \mathbf{j}_{\text{pol}} \right\rangle = \frac{\partial \mathbf{P}}{\partial t}, \quad (1.5)$$

where the sum is over those ions within the averaging volume and \mathbf{P} is the electric polarization defined by

$$\left\langle \sum_{\text{ions}} \rho_{\text{dip}} \right\rangle = -\nabla \cdot \mathbf{P}.$$

The second contribution to the ionic current density arises from the internal motion of the ionic electrons. Since this current density \mathbf{j}_{mag} is stationary, $\nabla \cdot \mathbf{j}_{\text{mag}} = 0$. This is the current density responsible for the *magnetic moment* \mathbf{m} of the ion. If the center of mass of the ion is at \mathbf{R} , the magnetic moment is defined as

$$\mathbf{m} = \frac{1}{2c} \int d\mathbf{r} (\mathbf{r} - \mathbf{R}) \times \mathbf{j}_{\text{mag}}. \quad (1.6)$$

A convenient representation for \mathbf{j}_{mag} which has zero divergence and satisfies (1.6) is

$$\mathbf{j}_{\text{mag}} = -c\mathbf{m} \times \nabla f(|\mathbf{r} - \mathbf{R}|), \quad (1.7)$$

where $f(|\mathbf{r} - \mathbf{R}|)$ a smoothly varying function centered at \mathbf{R} which goes to 0 at the ionic radius and is normalized to 1. In Chap. 2 we shall see that this function has a quantum mechanical interpretation. Then

$$\left\langle \sum_{\text{ions}} \mathbf{j}_{\text{mag}} \right\rangle = c \left\langle \sum_{\text{ions}} \nabla f(|\mathbf{r} - \mathbf{R}|) \times \mathbf{m} \right\rangle = c \nabla \times \left\langle \sum_{\text{ions}} f(|\mathbf{r} - \mathbf{R}|) \mathbf{m} \right\rangle. \quad (1.8)$$

The last average in (1.8) is the magnetization \mathbf{M} , defined by

$$\mathbf{M} \equiv \left\langle \sum_{\text{ions}} f(|\mathbf{r} - \mathbf{R}|) \mathbf{m} \right\rangle. \quad (1.9)$$

Combining these results, we may now write (1.3) as

$$\nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{j}_{\text{free}} + \frac{4\pi}{c} \frac{\partial \mathbf{P}}{\partial t} + 4\pi \nabla \times \mathbf{M} + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t}. \quad (1.10)$$

Defining

$$\mathbf{H} = \mathbf{B} - 4\pi \mathbf{M} \quad (1.11)$$

and

$$\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}, \quad (1.12)$$

we have the familiar result

$$\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j}_{\text{free}} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}. \quad (1.13)$$

Thus we see that the magnetization which appears in the macroscopic Maxwell's equations is the average of the ionic magnetic moment density. Since $f(|\mathbf{r} - \mathbf{R}|)$ is normalized to the volume the magnetization is the magnetic moment per unit volume.

As an example of the use of definition (1.6), let us neglect the possibility of nuclear currents and consider only the electron currents within the ion. Then

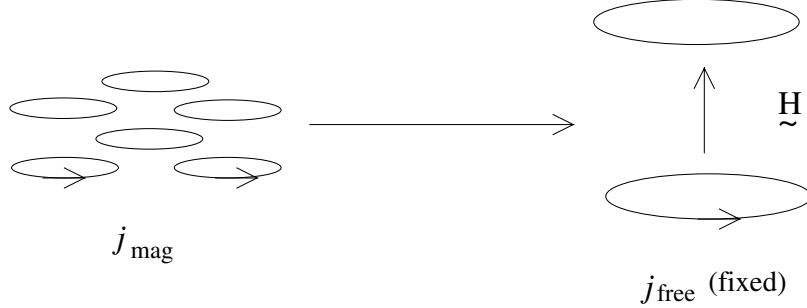


Fig. 1.1. Geometry envisioned in deriving the magnetic energy

$$\mathbf{j}_{\text{mag}}(\mathbf{r}) = \sum_{\alpha} e \mathbf{v}_{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\alpha}), \quad (1.14)$$

where e is the charge on the electron, which is $-|e|$, and \mathbf{v}_{α} is the velocity of the α th electron. From (1.6) we find for the total magnetic moment of the ion

$$\mathbf{m} = \frac{e}{2c} \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{v}_{\alpha}. \quad (1.15)$$

Recalling that the orbital angular momentum of an electron is

$$\mathbf{l}_{\alpha} = \mathbf{r}_{\alpha} \times m \mathbf{v}_{\alpha}, \quad (1.16)$$

we have

$$\mathbf{m} = \sum_{\alpha} \frac{e}{2mc} \mathbf{l}_{\alpha}. \quad (1.17)$$

Since $e = -|e|$, we see that the orbital magnetic moment of an electron is in the opposite direction to its orbital angular momentum.

We shall find it convenient to adopt a more general definition of the magnetic moment than that given by (1.6). This definition is based on the energy of the magnetic system (magnetic energy is discussed in [3] and [4]). The form of the magnetic energy depends upon the definition of the magnetic system. Let us define our magnetic system by the ionic magnetic current density \mathbf{j}_{mag} . This excludes the free currents, \mathbf{j}_{free} , which are assumed to be fixed and are the source of an external field \mathbf{H} in which our magnetic ion is to be located.¹ We now want to know the change in energy of this magnetic system when the field \mathbf{H} is applied or, equivalently, we may think of bringing the currents \mathbf{j}_{mag} in from infinity to a position in the field (see Fig. 1.1).

The energy difference results from the work done by the magnetic currents as they accommodate to the increasing external field. Since the magnetic field itself does no work on moving charges, we must use the induced electric field

¹ The magnetic field \mathbf{H} is understood to be the field in vacuum. Strictly speaking, this is the magnetic induction or flux density, \mathbf{B} . But in vacuum and in cgs units, $\mathbf{B} = \mathbf{H}$. It has become common practice to denote the field in vacuum as \mathbf{H} .

which is present while the external magnetic field is being turned on (due to the relative motion). This is given by

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t}. \quad (1.18)$$

The work done by the magnetic currents in a time δt is

$$\delta W = \int \mathbf{j}_{\text{mag}} \cdot \mathbf{E} d\mathbf{r} \delta t. \quad (1.19)$$

Making use of the representation (1.7) for \mathbf{j}_{mag} , integrating by parts, and then using (1.18), we obtain

$$\delta W = - \int f(|\mathbf{r} - \mathbf{R}|) \mathbf{m} \cdot \delta \mathbf{H} d\mathbf{r}. \quad (1.20)$$

If the field \mathbf{H} is uniform over the ionic dimension, $\delta \mathbf{H}$ may be taken outside the integral. Since \mathbf{m} is just a constant vector and $f(|\mathbf{r} - \mathbf{R}|)$ is normalized to unity,

$$\delta W = -\mathbf{m} \cdot \delta \mathbf{H}. \quad (1.21)$$

This work corresponds to Kittel's "scheme A" for applying the field [4]. Kittel also calculates the work needed to create the magnetized material in zero field in the first place ("scheme B"). The work associated with scheme A is important because this is the work that results in the change in the energy of the system given by its quantum mechanical eigenvalues [4].

Neither of these results give the *total* change in energy of the system when the magnetic material is introduced into the field since they do not include the work done by the source in keeping \mathbf{j}_{free} fixed. Jackson shows that the total change in energy is given by

$$W = \frac{1}{2} \int \mathbf{M} \cdot \mathbf{H}_0 d\mathbf{r},$$

where \mathbf{H}_0 is the field (\mathbf{B}_0) in the absence of the magnetic material, and the $\frac{1}{2}$ arises from an assumed linear relation between \mathbf{M} and \mathbf{B} .

The resulting change in the energy of the magnetic system is $\delta E = W$. Thus from (1.21)

$$\mathbf{m} = -\frac{\partial E}{\partial \mathbf{H}}. \quad (1.22)$$

As an example of the application of this definition, consider the ionic system of electrons which gave rise to the current density of (1.14). In the presence of a uniform field \mathbf{H} , which may be obtained from a vector potential \mathbf{A} by $\mathbf{H} = \nabla \times \mathbf{A}$, the energy of such a system is

$$E = \sum_{\alpha} \frac{1}{2} m v_{\alpha}^2 + \sum_{\alpha} e \phi_{\alpha}, \quad (1.23)$$

where ϕ_α is the ionic potential. We see that the magnetic field \mathbf{H} does not appear explicitly in this energy. However, the velocity is, in fact, a function of the field. In general, the task of finding the field dependence of the total energy of the system is a difficult one. However, in this case the actual field dependence is revealed by expressing the energy in terms of the canonical coordinates of the system. The reason for this is that in a slowly varying uniform field the canonical momentum does not change. When expressed in canonical coordinates, the energy is the same as the Hamiltonian function. For this reason the *Hamiltonian* \mathcal{H} is often used in place of the energy E in definition (1.22).

In Chap. 2 we shall find that the Hamiltonian is

$$\mathcal{H} = \sum_{\alpha} \frac{1}{2m} \left(\mathbf{p}_{\alpha} - \frac{e}{c} \mathbf{A} \right)^2 + \sum_{\alpha} e\phi_{\alpha}. \quad (1.24)$$

With the gauge $\mathbf{A} = \frac{1}{2} \mathbf{H} \times \mathbf{r}$ this becomes

$$\mathcal{H} = \sum_a \frac{p_a^2}{2m} - \sum_a \frac{e}{2mc} (\mathbf{r}_a \times \mathbf{p}_a) \cdot \mathbf{H} + \frac{e^2}{8mc^2} \sum_a (\mathbf{H} \times \mathbf{r}_a)^2 + \sum_a e\phi_a. \quad (1.25)$$

Differentiating with respect to \mathbf{H} and using the fact that the canonical momentum is given by $\mathbf{p}_{\alpha} = m\mathbf{v}_{\alpha} + (e/c)\mathbf{A}$, we obtain (1.15).

1.2 The Magnetization

The magnetization is obtained by averaging the ionic moments over a region of space which is large enough to give such an average a meaning but smaller than spatial variations in the system. In order to perform this average we must know the ionic-current distributions. In general they are not known. In fact, herein lies the principle difficulty in the theory of magnetism. In any real system the motion of charge in one region is governed by the charge and currents throughout the system. Thus we have a many-body problem. Historically, there have been two ways of describing magnetic systems, that of localized moments and that of itinerant moments. The choice between these two descriptions depends on the nature of the material and in many cases is a difficult one to make.

In certain cases the relevant current distributions are localized within a lattice cell. In such cases the ionic magnetic moment is relatively unambiguous. The interaction with external charge and current distributions is then expressed in terms of this moment. This approach leads to the *spin Hamiltonian*, which has proved extremely useful. In other cases we begin by assuming that the current distributions are those associated with free electrons. Thus, although these electrons may extend throughout the lattice, the fact that they may be approximated as a “gas” provides a certain simplification. With these two types of current distributions—that corresponding to very

localized electrons and that corresponding to itinerant electrons—we can proceed to determine the average moment. The computation of averages necessarily relies on the techniques of statistical mechanics. Since this is not the place to develop such techniques, they will be introduced in a rather ad hoc manner. A more thorough derivation may be found in texts on statistical physics [5].

If the system possesses translational invariance, then the statistical average over numerous unit cells of the crystal is equivalent to the time average over one cell. This average is determined by the probability that the system will have some particular current distribution. For example, in the case of a magnetic insulator the average over a cell is an average of the magnetic ion. If this ion consists of h electrons, then, classically, the state of the ion is characterized by the $6h$ coordinates and momenta, $(q_1, \dots, q_{3h}, p_1, \dots, p_{3h})$. The magnetization is obtained by multiplying the magnetic moment, which is a function of all the coordinates and momenta, by the probability that the system is in the state (q_1, \dots, p_1, \dots) and then integrating over all the coordinates and momenta. This probability is determined by the ion's environment, which defines a temperature T . For the most part this will be the temperature of the lattice in which the ions are located. Classically, the equilibrium probability function is the Boltzmann distribution function $\exp(-\beta\mathcal{H}_{\text{ion}})$, where \mathcal{H}_{ion} , is the Hamiltonian for the ion and $\beta = 1/k_B T$. Therefore the equilibrium magnetization associated with N/V ions per unit volume is

$$\mathbf{M} = \frac{N}{V} \langle \mathbf{m} \rangle = \frac{N}{V} \frac{\int \dots \int \mathbf{m} \exp(-\beta\mathcal{H}_{\text{ion}}) dq_1 \dots dp_1 \dots}{\int \dots \int \exp(-\beta\mathcal{H}_{\text{ion}}) dq_1 \dots dp_1 \dots}. \quad (1.26)$$

It is interesting that this classical averaging procedure leads to the conclusion that there can be no magnetism in thermodynamic equilibrium. The reason for this is that the integrals over the momenta in (1.26) run from $-\infty$ to $+\infty$. Therefore adding a vector potential may shift the momentum origin, but it will not affect the limits of integration. Since the vector potential always enters the integrand as an addition to the momentum, it may be transformed away. This is readily seen by considering the partition function Z , which is just the integral of $\exp(-\beta\mathcal{H}_{\text{ion}})$ over phase space,

$$Z = \int_{-\infty}^{\infty} dx dy dz \int_{-\infty}^{\infty} dp_x dp_y dp_z \exp\{-\beta[p_x - (e/c)A_x]^2/2m + \dots\}. \quad (1.27)$$

This function is of importance because the equilibrium thermodynamic properties of the system can be calculated from it. For example, the energy is $E = -\partial \ln Z / \partial \beta$.

We introduce

$$u = p_x - \frac{e}{c}A_x, \dots, \quad (1.28)$$

where, in general, \mathbf{A} may be a function of \mathbf{r} . Then

$$Z = V \int_{-\infty}^{\infty} du dv dw \exp[-\beta(u^2 + v^2 + w^2)/2m], \quad (1.29)$$

which is independent of \mathbf{A} . Therefore the derivative of Z with respect to the field \mathbf{H} , which can be shown to be proportional to the magnetization, is 0. This result, known as *Miss van Leeuwen's theorem*, forces us to consider the discreteness of the eigenvalues of the system and hence its quantum-mechanical nature. This interesting result has the following physical interpretation (see the discussion in [1] Sect. 26). In the presence of a magnetic field the electrons move in circular orbits in the plane perpendicular to the field. Those electrons that complete such orbits contribute a diamagnetic moment. However, those electrons which strike the boundary have their orbits interrupted with the result that they creep around the boundary giving rise to a paramagnetic moment. It turns out that this paramagnetic moment just cancels the diamagnetic moment. Furthermore, it is independent of the size and nature of the boundary.

Quantum mechanically, the magnetic system is described by a Hamiltonian operator \mathcal{H} which has eigenfunctions ψ with eigenvalues E . The total magnetic moment of the system when it is in the state ψ is, according to (1.22),

$$\mathbf{M}V = -\frac{\partial E}{\partial \mathbf{H}}. \quad (1.30)$$

This may be written in a more useful form. First we differentiate the eigenvalue relation

$$(\mathcal{H} - E)\psi = 0 \quad (1.31)$$

with respect to \mathbf{H} to obtain

$$\left(\frac{\partial \mathcal{H}}{\partial \mathbf{H}} - \frac{\partial E}{\partial \mathbf{H}}\right)\psi = -(\mathcal{H} - E)\frac{\partial \psi}{\partial \mathbf{H}}. \quad (1.32)$$

Forming the scalar product with ψ and using the fact that \mathcal{H} is a hermitian operator, i.e., $\mathcal{H}_{ij} = \mathcal{H}_{ji}^*$, we find

$$\begin{aligned} \left\langle \psi \left| \frac{\partial \mathcal{H}}{\partial \mathbf{H}} \right| \psi \right\rangle - \frac{\partial E}{\partial \mathbf{H}} &= -\left\langle \psi \left| (\mathcal{H} - E) \right| \frac{\partial \psi}{\partial \mathbf{H}} \right\rangle \\ &= -\left\langle \frac{\partial \psi}{\partial \mathbf{H}} \left| (\mathcal{H} - E) \right| \psi \right\rangle^* = 0. \end{aligned} \quad (1.33)$$

Therefore

$$\mathbf{M}V = -\left\langle \psi \left| \frac{\partial \mathcal{H}}{\partial \mathbf{H}} \right| \psi \right\rangle. \quad (1.34)$$

This leads us to define a *magnetic-moment operator*

$$\mathcal{M} = -\frac{\partial \mathcal{H}}{\partial \mathbf{H}}. \quad (1.35)$$

Hereafter \mathcal{M} will be understood to be an operator.

Since the derivation above was independent of the detailed form of the Hamiltonian and its eigenfunctions, the result (1.35) is quite general. For example, the magnetic-moment operator for a particle governed by the non-relativistic Schrödinger Hamiltonian (1.25) is

$$\mathcal{M}_z = \frac{e}{2mc}(xp_y - yp_x) - \frac{He^2}{4mc^2}(x^2 + y^2) = \frac{e}{2c}(x\dot{y} - y\dot{x}). \quad (1.36)$$

For a relativistic electron governed by the Dirac equation (which will be discussed briefly in Chap. 2) the magnetic moment becomes

$$\mathcal{M}_z = -\frac{e}{2}(\alpha_x y - \alpha_y x). \quad (1.37)$$

Since the α 's are 4×4 matrices acting on negative as well as positive energy states, the physical meaning of the operator is not clear. However, if we apply a transformation to this operator which separates the positive and negative energy states, then we find that an intrinsic spin contribution to the magnetic moment emerges automatically.

To find the magnetization we must take the expectation value of the magnetic moment operator,

$$\langle \mathcal{M} \rangle = \int \psi^* \mathcal{M} \psi \Pi_i d\mathbf{r}_i. \quad (1.38)$$

If we knew the wavefunction ψ this would be straightforward. But the fact that we are describing the system at a temperature T implies that the system is in equilibrium with some temperature bath. Let us describe the system in terms of its eigenfunctions, $\varphi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. The effect of the temperature bath is to cause the system to move through different states k much as a classical system moves through phase space. That is, the wavefunction ψ may be written as a superposition of states,

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) = \sum_k c_k(t) \varphi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (1.39)$$

The expectation value then becomes

$$\langle \mathcal{M} \rangle = \sum_k \sum_{k'} c_k^*(t) c_{k'}(t) \mathcal{M}_{kk'}, \quad (1.40)$$

where

$$\mathcal{M}_{kk'} = \int \varphi_k^* \mathcal{M} \varphi_{k'} \Pi_i d\mathbf{r}_i. \quad (1.41)$$

When we measure the magnetization we actually do a time average,

$$\langle \overline{\mathcal{M}} \rangle = \sum_k \sum_{k'} \overline{c_k^*(t) c_{k'}(t)} \mathcal{M}_{kk'}. \quad (1.42)$$

The quantity $\overline{c_k^*(t)c_{k'}(t)}$ is defined as the statistical density matrix, $\rho_{kk'}$. Thus

$$\langle \overline{\mathcal{M}} \rangle = \text{Tr}(\rho \mathcal{M}). \quad (1.43)$$

If the system is isolated from the temperature bath then the c_k 's are independent of time and $\rho_{kk'} = |c_k|^2 \delta_{kk'}$. The states comprise the microcanonical ensemble. In contact with the temperature bath $\rho_{kk'} = \exp(-\beta E_k) \delta_{kk'}$ and we speak of this weighted set of states as the canonical ensemble. In the presence of time-dependent fields it is necessary to solve for $\rho_{kk'}$ from its equation of motion. From the Schrödinger equations

$$i\hbar \frac{\partial \phi(t)^*}{\partial t} = -\mathcal{H} \phi(t)^*, \quad (1.44)$$

$$i\hbar \frac{\partial \phi(t)}{\partial t} = \mathcal{H} \phi(t), \quad (1.45)$$

we obtain the equations for the expansion coefficients. From our definition of the density matrix, we find that

$$i\hbar \frac{\partial \rho_{k'k}}{\partial t} = - \sum_{k''} \rho_{k'k''} \mathcal{H}_{k''k} + \sum_{k''} \mathcal{H}_{k'k''} \rho_{k''k} \quad (1.46)$$

or

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho]. \quad (1.47)$$

This is often a more convenient approach to the density matrix, for, as we shall see below, when perturbation theory applies, (1.47) may be solved iteratively.

Notice that (1.42) gives the average of the magnetic moment over the entire system. If we are interested in the magnetization at point \mathbf{r} , $\mathbf{M}(\mathbf{r})$ this behavior can be projected out by introducing the Dirac delta function,

$$\mathcal{M}(\mathbf{r}) = \frac{1}{2} \sum_{\alpha} [\boldsymbol{\mu}_{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\alpha}) + \delta(\mathbf{r} - \mathbf{r}_{\alpha}) \boldsymbol{\mu}_{\alpha}]. \quad (1.48)$$

Since the delta functions have dimensions of a reciprocal volume, $\mathcal{M}(\mathbf{r})$ is the magnetic-moment operator per unit volume. Here $\boldsymbol{\mu}_{\alpha}$ is the magnetic-moment operator associated with the α th electron. Notice that since this is a function of \mathbf{r}_{α} and \mathbf{p}_{α} , we must form the symmetric product denoted by $\{\cdots\}$. Therefore the magnetization becomes

$$\mathbf{M}(\mathbf{r}) = \text{Tr}\{\rho \mathcal{M}(\mathbf{r})\}. \quad (1.49)$$

1.3 The Generalized Susceptibility

When we speak of a *susceptibility*, we are usually referring to a medium in which the response is proportional in some sense to the excitation. If the medium is linear, the response is directly proportional to the excitation. If the medium is nonlinear, the proportionality involves higher powers of the excitation. However, if the excitation is very small, the response will be given to a good approximation by the linear susceptibility. Since time- and space-varying magnetic fields are generally quite small, a linear response theory is usually adequate. Nonlinear effects become important in dealing with hysteresis phenomena or high-power absorption in magnetic materials. For the most part, then, we shall be concerned with a linear response theory. In this section we shall define the wave-vector-dependent frequency-dependent linear susceptibility and investigate some of its properties.

Let us consider the magnetization $\mathbf{M}(\mathbf{r}, t)$ associated with a particular magnetic field $\mathbf{H}(\mathbf{r}, t)$. These quantities are related to their Fourier components by

$$\mathbf{M}(\mathbf{r}, t) = \frac{1}{2\pi V} \sum_{\mathbf{k}} \int d\Omega \mathbf{M}(\mathbf{k}, \Omega) e^{i(\mathbf{k} \cdot \mathbf{r} - \Omega t)}, \quad (1.50)$$

$$\mathbf{H}(\mathbf{r}, t) = \frac{1}{2\pi V} \sum_{\mathbf{q}} \int d\omega \mathbf{H}(\mathbf{q}, \omega) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)}. \quad (1.51)$$

To invert these expansions we use the following relations:

$$\int d\mathbf{r} e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} = V \Delta(\mathbf{k} - \mathbf{k}'), \quad (1.52)$$

$$\int dt e^{-i(\Omega - \Omega')t} = 2\pi \delta(\Omega - \Omega'), \quad (1.53)$$

$$\sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} = \frac{V}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} = V \delta(\mathbf{r} - \mathbf{r}'). \quad (1.54)$$

Here $\Delta(\mathbf{k} - \mathbf{k}')$ is the *Kronecker delta function* and $\delta(\mathbf{r} - \mathbf{r}')$ is the *Dirac delta function*.

We now define the generalized wave-vector-dependent frequency-dependent susceptibility by

$$M_\nu(\mathbf{k}, \Omega) = \sum_{\mathbf{q}} \int d\omega \sum_{\mu} \chi_{\nu\mu}(\mathbf{k}, \mathbf{q}; \Omega, \omega) H_\mu(\mathbf{q}, \omega), \quad (1.55)$$

where ν and $\mu = x, y$, or z . This may be written in the more convenient dyadic form

$$\mathbf{M}(\mathbf{k}, \Omega) = \sum_{\mathbf{q}} \int d\omega \chi(\mathbf{k}, \mathbf{q}; \Omega, \omega) \cdot \mathbf{H}(\mathbf{q}, \omega).$$

In general $\chi(\mathbf{k}, \mathbf{q}; \Omega, \omega)$ will depend on the particular form of $\mathbf{H}(\mathbf{r}, t)$, or equivalently, $\mathbf{H}(\mathbf{q}, \omega)$; that is, the susceptibility is a functional of the field. The susceptibility is also a tensor. Furthermore, since the magnetization may be out of phase with the exciting field, the susceptibility is also complex. Substituting this expression into (1.50) gives

$$\mathbf{M}(\mathbf{r}, t) = \frac{1}{2\pi V} \sum_{\mathbf{k}} \int d\Omega \sum_{\mathbf{q}} \int d\omega \chi(\mathbf{k}, \mathbf{q}; \Omega, \omega) \cdot \mathbf{H}(\mathbf{q}, \omega) e^{i(\mathbf{k} \cdot \mathbf{r} - \Omega t)} \quad (1.56)$$

or

$$\begin{aligned} \mathbf{M}(\mathbf{r}, t) = & \int \int d\mathbf{r}' dt' \\ & \times \left\{ \left[\frac{1}{2\pi V} \sum_{\mathbf{k}} \int d\Omega \sum_{\mathbf{q}} \int d\omega \chi(\mathbf{k}, \mathbf{q}; \Omega, \omega) e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') - i\Omega(t - t')} \right] \right. \\ & \left. \times e^{i(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r}' - i(\Omega - \omega)t'} \right\} \cdot \mathbf{H}(\mathbf{r}', t'), \end{aligned} \quad (1.57)$$

where the quantity in braces defines a general spatial-temporal susceptibility density $\chi(\mathbf{r}, \mathbf{r}'; t, t')$.

If the magnetic medium possesses translational invariance, then this susceptibility must be a function only of the relative coordinate $\mathbf{r} - \mathbf{r}'$. From the expression above we see that this implies that in the wave-vector-dependent susceptibility \mathbf{q} is equal to \mathbf{k} . Furthermore, if the medium is stationary, it can be shown that the temporal dependence is $t - t'$, which implies a monochromatic response to a monochromatic excitation with the same frequency, that is, $\Omega = \omega$. Therefore, when these conditions are satisfied, the susceptibility takes the form

$$\chi(\mathbf{k}, \mathbf{q}; \Omega, \omega) = \chi(\mathbf{q}, \omega) \Delta(\mathbf{k} - \mathbf{q}) \delta(\Omega - \omega).$$

Thus

$$\mathbf{M}(\mathbf{r}, t) = \int \int d\mathbf{r}' dt' \chi(\mathbf{r} - \mathbf{r}', t - t') \cdot \mathbf{H}(\mathbf{r}', t'), \quad (1.58)$$

where

$$\chi(\mathbf{r} - \mathbf{r}', t - t') = \frac{1}{2\pi V} \sum_{\mathbf{q}} \int d\omega \chi(\mathbf{q}, \omega) e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}') - i\omega(t - t')}, \quad (1.59)$$

and its Fourier transform is

$$\chi(\mathbf{q}, \omega) = \int d(t - t') \int d(\mathbf{r} - \mathbf{r}') \chi(\mathbf{r} - \mathbf{r}', t - t') e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}') + i\omega(t - t')}. \quad (1.60)$$

The more general susceptibility is required whenever the presence of impurities destroys the translational invariance. The response of a typical paramagnet is such a case.

Since the susceptibility has such a general nature, it should not be surprising that there are various important theorems involving this quantity. We shall consider three of these now. The first theorem, known as the *Kramers–Kronig relations*, relates the real and imaginary parts of the susceptibility. The second is the *fluctuation-dissipation theorem*, which relates the susceptibility to thermal fluctuations in the magnetization. Finally, we shall present a derivation of the so-called *Onsager relation* that describes the symmetry of the susceptibility tensor.

1.3.1 The Kramers–Kronig Relations

As a consequence of some rather general properties of

$$\chi(\mathbf{q}, \omega) = \chi'(\mathbf{q}, \omega) + i\chi''(\mathbf{q}, \omega),$$

its real part $\chi'(\mathbf{q}, \omega)$ and its imaginary part $\chi''(\mathbf{q}, \omega)$ are connected on the real axis ω by integral relations known as the *Kramers–Kronig relations*, or just as *dispersion relations*. To the electrical engineer, the real and imaginary parts of the response function are related by the Hilbert transform. Let us consider a medium which is *linear* and *stationary* (and translationally invariant, although this is not a necessary condition). Then $\chi(\mathbf{q}, \omega)$ is related to $\chi(\mathbf{r} - \mathbf{r}', t - t')$ by (1.60). If the system obeys the principle of *causality*, then $\chi(\mathbf{r} - \mathbf{r}', t - t') = 0$ for $t < t'$. Hence the time integral in (1.60) runs only from 0 to ∞ ; that is,

$$\chi(\mathbf{q}, \omega) = \int_0^\infty dt \chi(\mathbf{q}, t) e^{i\omega t}. \quad (1.61)$$

Therefore the function $\chi(\mathbf{q}, \omega)$ is a complex function of ω which has no singularities at the ends of the real axis, *provided* that

$$\int_0^\infty \chi(\mathbf{q}, t) dt$$

is finite. This is equivalent to the assumption that the response to a finite excitation is finite. The finite values of $\chi(\mathbf{q}, \omega)$ at the ends of the real axis may be identified with the real part of the susceptibility $\chi'(\mathbf{q}, \infty)$. The fact that $\chi''(\mathbf{q}, \omega)$ vanishes as $\omega \rightarrow \infty$ may be obtained from the following physical argument. As we shall see in Chap. 5, the rate of energy absorption by a magnetic system is proportional to $\omega \chi''(\mathbf{q}, \omega)$. If this is to remain finite as $\omega \rightarrow \infty$, then $\chi''(\mathbf{q}, \omega)$ must go to 0 as $\omega \rightarrow \infty$. This result may also be derived from the finite-response assumption.

There is no reason for the real part of the susceptibility to vanish as $\omega \rightarrow \infty$. Therefore let us define $\lim_{\omega \rightarrow \infty} \chi'(\mathbf{q}, \omega) = \chi(\mathbf{q}, \infty)$. The quantity $\chi(\mathbf{q}, \omega) - \chi(\mathbf{q}, \infty)$ is then a complex function which vanishes at the ends of the real axis. The theory of complex variables tells us that the function

$\chi(\mathbf{q}, z) - \chi(\mathbf{q}, \infty)$, where z is a complex variable, will be analytic in the upper half plane. The residue theorem then says

$$\oint_c \frac{\chi(\mathbf{q}, z) - \chi(\mathbf{q}, \infty)}{z - \omega} dz = 0, \quad (1.62)$$

where the contour C runs from $-\infty$ to $+\infty$ along the real axis and closes in the upper half plane. In terms of its *principal value*, this integral may be written as

$$\mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(\mathbf{q}, \omega') - \chi(\mathbf{q}, \infty)}{\omega' - \omega} d\omega' - i\pi[\chi(\mathbf{q}, \omega) - \chi(\mathbf{q}, \infty)] = 0. \quad (1.63)$$

Equating the real and imaginary parts to 0 separately gives the result

$$\chi'(\mathbf{q}, \omega) - \chi(\mathbf{q}, \infty) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi''(\mathbf{q}, \omega')}{\omega' - \omega} d\omega', \quad (1.64)$$

$$\chi''(\mathbf{q}, \omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi'(\mathbf{q}, \omega') - \chi(\mathbf{q}, \infty)}{\omega' - \omega} d\omega'. \quad (1.65)$$

The usefulness of this result lies in the fact that χ'' is proportional to the absorption spectrum of the medium. Therefore (1.64) tells us, for example, that the static susceptibility may be obtained by integrating over the absorption spectrum. This is, in fact, an experimental technique used to obtain the static susceptibility of certain systems.

Since the response $\mathbf{M}(\mathbf{r}, t)$, is a real quantity, it follows that $\chi'(\mathbf{q}, \omega)$ is an even function of ω while $\chi''(\mathbf{q}, \omega)$ is odd. This enables us to express the Kramers–Kronig relations in terms of integrals over positive frequencies. In particular,

$$\chi''(\mathbf{q}, \omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^{\infty} \frac{\chi'(\mathbf{q}, \omega')}{\omega'^2 - \omega^2} d\omega'. \quad (1.66)$$

The term involving $\chi(\mathbf{q}, \infty)$ vanishes because the principal value of the integral of $1/(\omega'^2 - \omega^2)$ is zero.

1.3.2 The Fluctuation-Dissipation Theorem

It is well known that a colloidal suspension of particles exhibits Brownian motion; that is, the particles move about irregularly because they are being bombarded by the molecules of the liquid. Now, suppose that these particles are charged, and we attempt to accelerate them with an external electric field. Because of the impacts with the molecules, the particles experience a resistive force which is proportional to their velocity. Thus the mechanism that produces the random fluctuations in the position of the particle is also

responsible for its response to an external excitation. The relationship between the response of a system and its thermal fluctuation spectrum is called the *fluctuation-dissipation theorem*. This relationship is a very general one, and we shall consider only its specific application to a magnetic medium.

Let us consider a linearly polarized magnetic field of amplitude $H_\mu \cos(\mathbf{q} \cdot \mathbf{r})$ oscillating at a frequency ω in the μ direction, $H_\mu \cos(\mathbf{q} \cdot \mathbf{r}) \cos \omega t$. Since we have a linear system, the principle of superposition applies. Therefore we may construct the response to an arbitrary field if we know the response to this particular field. The response in the ν direction to such an excitation is given by (1.55). Since

$$\begin{aligned} H_\mu(\mathbf{q}', \omega') = \frac{\pi H_1 V}{2} [\Delta(\mathbf{q}' - \mathbf{q})\delta(\omega' + \omega) + \Delta(\mathbf{q}' - \mathbf{q})\delta(\omega' - \omega) \\ + \Delta(\mathbf{q}' + \mathbf{q})\delta(\omega' + \omega) + \Delta(\mathbf{q}' + \mathbf{q})\delta(\omega' - \omega)] , \end{aligned} \quad (1.67)$$

we obtain

$$\begin{aligned} \mathbf{M}_\nu(\mathbf{k}, \Omega) = \frac{\pi H_1 V}{2} [\chi_{\nu\mu}(\mathbf{k}, \mathbf{q}; \Omega, -\omega) + \chi_{\nu\mu}(\mathbf{k}, \mathbf{q}; \Omega, \omega) \\ + \chi_{\nu\mu}(\mathbf{k}, -\mathbf{q}; \Omega, -\omega) + \chi_{\nu\mu}(\mathbf{k}, -\mathbf{q}; \Omega, \omega)] . \end{aligned} \quad (1.68)$$

Let us now compute $M_\nu(\mathbf{k}, \Omega)$, using the prescription given in Sect. 1.2. The magnetization is

$$\mathbf{M}_\nu(\mathbf{r}, t) = \text{Tr}\{\rho \mathcal{M}_\nu(\mathbf{r})\} . \quad (1.69)$$

Although ρ is a function of time, we shall not display this dependence explicitly, for a reason that will be apparent later. Since the time-varying field now disrupts the thermodynamic equilibrium, we must solve for ρ . We write the total Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 , \quad (1.70)$$

where $\mathcal{H}_1 = - \int d\mathbf{r} \mathcal{M}(\mathbf{r}) \cdot \mathbf{H}(\mathbf{r}, t)$. For the particular field we are considering this becomes

$$\mathcal{H}_1 = -H_1 \int d\mathbf{r} \mathcal{M}_\mu(\mathbf{r}) \cos(\mathbf{q} \cdot \mathbf{r}) \cos \omega t = -\frac{H_1}{2} [\mathcal{M}_\mu(\mathbf{q}) + \mathcal{M}_\mu(-\mathbf{q})] \cos \omega t . \quad (1.71)$$

The equation of motion for the density matrix is

$$\frac{\partial \rho}{\partial t} = \frac{i}{\hbar} [\rho, \mathcal{H}_0 + \mathcal{H}_1] . \quad (1.72)$$

It is now convenient to introduce

$$\rho(t) \equiv \exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right) \rho \exp\left(\frac{-i\mathcal{H}_0 t}{\hbar}\right) . \quad (1.73)$$

Differentiating (1.73) and using (1.72) gives

$$\frac{d\rho(t)}{dt} = \frac{i}{\hbar} \left[\rho(t), \exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right) \mathcal{H}_1 \exp\left(\frac{-i\mathcal{H}_0 t}{\hbar}\right) \right]. \quad (1.74)$$

This has the solution

$$\rho(t) = \rho(-\infty) + \frac{i}{\hbar} \int_{-\infty}^t \left[\rho(t'), \exp\left(\frac{i\mathcal{H}_0 t'}{\hbar}\right) \mathcal{H}_1 \exp\left(\frac{-i\mathcal{H}_0 t'}{\hbar}\right) \right] dt'. \quad (1.75)$$

If the interaction is turned on adiabatically, then $\rho(-\infty) = \rho_0$, which is the equilibrium density matrix $\rho_0 = \exp(-\beta\mathcal{H}_0)/Z$ where $Z = \text{Tr}\{\exp(-\beta\mathcal{H}_0)\}$. Inverting (1.75), using (1.71), and replacing ρ within the commutator by ρ_0 , we have

$$\rho \simeq \rho_0 - i \frac{H_1}{2\hbar} \int_0^\infty \left\{ \rho_0, \exp\left(\frac{-i\mathcal{H}_0 t'}{\hbar}\right) [\mathcal{M}_\mu(\mathbf{q}) + \mathcal{M}_\mu(-\mathbf{q})] \exp\left(\frac{i\mathcal{H}_0 t'}{\hbar}\right) \right\}. \quad (1.76)$$

The magnetization is obtained from (1.69). If the system is ordered in the absence of the applied field, then $\text{Tr}\{\rho_0 \mathcal{M}_\nu\} \equiv M_\nu(-\infty)$ is nonzero. The response of such a system is then defined by the difference $M_\nu(\mathbf{r}, t) - M_\nu(-\infty)$ resulting from the applied field. In the following we shall understand $M_\nu(\mathbf{r}, t)$ to be the response to the applied field. Then,

$$\begin{aligned} M_\nu(\mathbf{r}, t) &= -i \frac{H_1}{2\hbar} \\ &\times \text{Tr} \left\{ \int_0^\infty \left\{ \rho_0, \exp\left(\frac{-i\mathcal{H}_0 t'}{\hbar}\right) [\mathcal{M}_\mu(\mathbf{q}) + \mathcal{M}_\mu(-\mathbf{q})] \right. \right. \\ &\times \left. \left. \exp\left(\frac{i\mathcal{H}_0 t'}{\hbar}\right) \right\} \mathcal{M}_\nu(\mathbf{r}) \right\} \cos \omega(t - t') dt'. \end{aligned} \quad (1.77)$$

Taking the Fourier transform of this equation gives

$$\begin{aligned} M_\nu(\mathbf{k}, \Omega) &= -\frac{\pi H_1}{2\hbar} \text{Tr} \left\{ \int_0^\infty [\rho_0, \mathcal{M}_\mu(\mathbf{q}, -t')] \mathcal{M}_\nu(\mathbf{k}) \right\} e^{i\omega t'} dt' \delta(\Omega + \omega) \\ &+ (\text{terms involving } -\mathbf{q} \text{ and } -\omega). \end{aligned} \quad (1.78)$$

Here $\mathcal{M}_\mu(\mathbf{q}, t)$ is defined in a manner identical to (1.73). The delta function involving the frequency results from our having linearized the expression for ρ when we replaced ρ by ρ_0 within the commutator.

If we now commute the integral with the trace in (1.78) and make use of the cyclic invariance of the trace, we have

$$\begin{aligned} &\text{Tr} \left\{ \int_0^\infty [\rho_0, \mathcal{M}_\mu(\mathbf{q}, -t')] \mathcal{M}_\nu(\mathbf{k}) \right\} e^{-i\omega t'} dt' \\ &= \int \langle [\mathcal{M}_\mu(\mathbf{q}, -t'), \mathcal{M}_\nu(\mathbf{k})] \rangle e^{i\omega t'} dt'. \end{aligned} \quad (1.79)$$

By comparing the resulting expression for $M_\nu(\mathbf{k}, \Omega)$ with (1.68) we make the following identification:

$$\chi_{\nu\mu}(\mathbf{k}, \mathbf{q}; \Omega, \omega) = \frac{i}{\hbar V} \int_0^\infty \langle [\mathcal{M}_\nu(\mathbf{k}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle e^{i\omega t} dt \delta(\Omega - \omega). \quad (1.80)$$

Since the \mathbf{q} component of the applied field couples to the $-\mathbf{q}$ component of the magnetization, let us consider $\chi_{\nu\mu}(\mathbf{q}, \mathbf{q}, \omega)$ which we write as $\chi_{\nu\mu}(\mathbf{q}, \omega)$. Therefore,

$$\chi_{\nu\mu}(\mathbf{q}, \omega) = \frac{i}{\hbar V} \int_0^\infty \langle [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle e^{i\omega t} dt. \quad (1.81)$$

The quantity

$$(i/\hbar) \langle [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle,$$

or equivalently

$$\frac{i}{\hbar} \text{Tr}\{[\mathcal{M}_\mu(-\mathbf{q}), \rho_0] \mathcal{M}_\nu(\mathbf{q}, t)\},$$

is referred to in the literature as the *response function* of the system. The susceptibility may also be written as an integral over the full range of time by multiplying the integrand by the theta function $\theta(t)$ which equals 1 for $t > 0$ and 0 for $t < 0$. The product of the response function and this theta function is called the double-time-retarded Green's function and represented by double angular brackets:

$$\langle\langle \mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q}) \rangle\rangle \equiv -i \langle [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle \theta(t).$$

These functions are very useful in calculating thermodynamic properties but are beyond the scope of this monograph.

Since the response function does not have a classical analog and is not a well-defined observable, it is more convenient to relate the susceptibility to the *correlation function* $\langle\{ \mathcal{M}_\nu(\mathbf{q}, t) \mathcal{M}_\mu(-\mathbf{q}) \}\rangle$, where $\{\dots\}$ is the symmetrized product, which is defined by

$$\{ \mathcal{M}_\nu(\mathbf{q}, t) \mathcal{M}_\mu(-\mathbf{q}) \} \equiv \frac{1}{2} [\mathcal{M}_\nu(\mathbf{q}, t) \mathcal{M}_\mu(-\mathbf{q}) + \mathcal{M}_\mu(-\mathbf{q}) \mathcal{M}_\nu(\mathbf{q}, t)],$$

In order to relate the response function to the correlation function let us consider their Fourier transforms,

$$f_{\nu\mu}(\mathbf{q}, \omega) = \frac{i}{\hbar} \int_{-\infty}^\infty \langle [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle e^{i\omega t} dt, \quad (1.82)$$

$$g_{\nu\mu}(\mathbf{q}, \omega) = \int_{-\infty}^\infty \langle \{ \mathcal{M}_\nu(\mathbf{q}, t) \mathcal{M}_\mu(-\mathbf{q}) \} \rangle e^{i\omega t} dt. \quad (1.83)$$

We can rewrite (1.82) by using the following relation:

$$\begin{aligned}
& \int_{-\infty}^{\infty} dt \langle \mathcal{M}_{\mu}(-\mathbf{q}) \mathcal{M}_{\nu}(\mathbf{q}, t) \rangle e^{i\omega t} \\
&= \int_{-\infty}^{\infty} dt \text{Tr} \left\{ \exp(-\beta \mathcal{H}_0) \mathcal{M}_{\mu}(\mathbf{q}) \exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right) \mathcal{M}_{\nu}(\mathbf{q}) \exp\left(\frac{-i\mathcal{H}_0 t}{\hbar}\right) \right\} e^{i\omega t} \\
&= \int_{-\infty}^{\infty} dt \text{Tr} \left\{ \exp(-\beta \mathcal{H}_0) \exp\left(\frac{i\mathcal{H}_0(t - i\hbar\beta)}{\hbar}\right) \mathcal{M}_{\nu}(\mathbf{q}) \right. \\
&\quad \times \exp\left[\frac{-i\mathcal{H}_0(t - i\hbar\beta)}{\hbar}\right] \mathcal{M}_{\mu}(-\mathbf{q}) \left. \right\} e^{i\omega t} \\
&= e^{-\beta\hbar\omega} \int_{-\infty}^{\infty} dt \langle \mathcal{M}_{\nu}(\mathbf{q}, t) \mathcal{M}_{\mu}(-\mathbf{q}) \rangle e^{i\omega t}. \tag{1.84}
\end{aligned}$$

Therefore

$$f_{\nu\mu}(\mathbf{q}, \omega) = \frac{i}{\hbar} (1 - e^{-\beta\hbar\omega}) \int_{-\infty}^{\infty} dt \langle \mathcal{M}_{\nu}(\mathbf{q}, t) \mathcal{M}_{\mu}(-\mathbf{q}) \rangle e^{i\omega t}. \tag{1.85}$$

From the definition of $g_{\nu\mu}$ we see that its relation to $f_{\nu\mu}$ is

$$g_{\nu\mu}(\mathbf{q}, \omega) = (\hbar/2i) \coth(\beta\hbar\omega/2) f_{\nu\mu}(\mathbf{q}, \omega). \tag{1.86}$$

We can also relate $f_{\nu\mu}$ to the susceptibility by separating the time integral as follows:

$$\begin{aligned}
f_{\nu\mu}(\mathbf{q}, \omega) &= \frac{i}{\hbar} \int_0^{\infty} dt \langle [\mathcal{M}_{\nu}(\mathbf{q}, t), \mathcal{M}_{\mu}(-\mathbf{q})] \rangle e^{i\omega t} \\
&\quad + \frac{i}{\hbar} \int_{-\infty}^0 dt \langle [\mathcal{M}_{\nu}(\mathbf{q}, t), \mathcal{M}_{\mu}(-\mathbf{q})] \rangle e^{i\omega t}. \tag{1.87}
\end{aligned}$$

If we now make the transformation $t \rightarrow -t$ in the second integral and use the fact that $\chi_{\mu\nu}(-\mathbf{q}, -\omega) = \chi_{\mu\nu}^*(\mathbf{q}, \omega)$, which follows from (1.81), then

$$f_{\nu\mu}(\mathbf{q}, \omega) = [\chi_{\nu\mu}(\mathbf{q}, \omega) - \chi_{\mu\nu}^*(\mathbf{q}, \omega)]V$$

and

$$g_{\nu\mu}(\mathbf{q}, \omega) = (\hbar V/2i) \coth(\beta\hbar\omega/2) [\chi_{\nu\mu}(\mathbf{q}, \omega) - \chi_{\mu\nu}^*(\mathbf{q}, \omega)].$$

Therefore

$$\int_{-\infty}^{\infty} dt \langle \{\mathcal{M}_{\nu}(\mathbf{q}, t) \mathcal{M}_{\mu}(-\mathbf{q})\} \rangle_s e^{i\omega t} = \hbar V \coth(\beta\hbar\omega/2) \chi_{\nu\mu}''(\mathbf{q}, \omega)_s, \tag{1.88}$$

where the subscript s indicates the symmetric part of the tensor.

This is the result we had set out to find. It tells us that the Fourier transform of the correlation function is proportional to the imaginary part of the susceptibility. The derivation has been presented here in detail because it is a very important relationship, and we shall make frequent reference to this result throughout the text.

The imaginary part of the susceptibility describes the absorptive or lossy, response of the magnetic system. The fluctuation-dissipation theorem therefore relates the fluctuations in the magnetization to energy loss. This is a general result that applies to many systems. One example that may be familiar to the reader is Johnson noise. This is the noise associated with thermal fluctuations in a resistive electrical circuit element. The voltage noise power is given by $\langle v^2 \rangle / R$. Since this power is due to thermal fluctuations it may also be expressed as the unit of thermal energy, $k_B T$, divided by the measurement time, which is the reciprocal of the frequency bandwidth, Δf . A rigorous derivation gives

$$\langle v^2 \rangle = 4k_B T R \Delta f.$$

This form of the fluctuation-dissipation theorem is known as the Nyquist theorem.

1.3.3 Onsager Relation

Generally, when we probe a magnetic system it is in the presence of a dc field \mathbf{H} . Therefore \mathcal{H}_0 and hence the response function, is a function of this field. In 1931 Onsager pointed out that microscopic reversibility requires the simultaneous reversal of both the magnetic field *and* time. To see this, consider the response function for the susceptibility:

$$\langle [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle = \sum_n \langle n | \rho_0(\mathcal{H}_0) [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] | n \rangle.$$

Let us introduce time reversal through the time reversal operator, T , which satisfies the relation

$$\langle \psi | \varphi \rangle = \langle T\psi | T\varphi \rangle^*. \quad (1.89)$$

Therefore

$$\langle [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle = \sum_n \langle Tn | T\rho_0(\mathcal{H}_0) [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] | n \rangle^*. \quad (1.90)$$

We now insert $T^{-1}T$ between all the factors. If the system is invariant under time reversal then $T\rho_0(\mathcal{H}_0)T^{-1} = \rho_0(\mathcal{H}_0)$, where any magnetic field has been reversed. Let us display this explicitly as $\rho_0(-H)$. We also have factors like $T\mathcal{M}_\nu(\mathbf{q}, t)T^{-1}$. Since the magnetic moment changes sign under time reversal,

$$T\mathcal{M}_\nu(\mathbf{q}, t)T^{-1} = -\mathcal{M}_\nu(\mathbf{q}, -t). \quad (1.91)$$

If we also recognize that the state $T|n\rangle$ is some eigenstate $|m\rangle$, then the sum over n is the same as the sum over m , which can then be relabeled as n . These steps enable us to carry out all the time reversal operations in the expression for the response function above,

$$\langle [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle = \sum_n \langle n | \rho_0(-H) [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] | n \rangle^*. \quad (1.92)$$

To remove the complex conjugation we introduce the Hermitian adjoint 0^\dagger of an arbitrary operator 0 by the relation

$$\langle \psi | 0 | \varphi \rangle^* = \langle \varphi | 0^\dagger | \psi \rangle. \quad (1.93)$$

The first term in the commutator becomes

$$\begin{aligned} (\rho_0(-H) \mathcal{M}_\nu(\mathbf{q}, -t) \mathcal{M}_\mu(-\mathbf{q}))^\dagger &= \mathcal{M}_\mu(-\mathbf{q})^\dagger \mathcal{M}_\nu(\mathbf{q}, -t)^\dagger \rho_0(-H)^\dagger \\ &= \mathcal{M}_\mu(\mathbf{q}) \mathcal{M}_\nu(-\mathbf{q}, -t) \rho_0(-H), \end{aligned} \quad (1.94)$$

where we have used the fact that the magnetic moment and the Hamiltonian are Hermitian operators. We now use the cyclic invariance of the trace to write

$$\begin{aligned} \langle [\mathcal{M}_\nu(\mathbf{q}, t), \mathcal{M}_\mu(-\mathbf{q})] \rangle &= \sum_n \langle n | \rho_0(-H) [\mathcal{M}_\mu(\mathbf{q}), \mathcal{M}_\nu(-\mathbf{q}, -t)] | n \rangle \\ &= \sum_n \langle n | \rho_0(-H) [\mathcal{M}_\mu(\mathbf{q}, t), \mathcal{M}_\nu(-\mathbf{q})] | n \rangle. \end{aligned} \quad (1.95)$$

Therefore we have the relation

$$\chi_{\nu\mu}(\mathbf{q}, \omega, H) = \chi_{\mu\nu}(\mathbf{q}, \omega, -H). \quad (1.96)$$

which is known as the Onsager relation. Note that this tells us immediately that the diagonal components of the susceptibility tensor must be even functions of the field.

1.4 Second Quantization

Magnetism, particularly in metals, is a many-body phenomenon. It is therefore important to incorporate the fermion statistics of the electrons that govern the magnetic behavior. In this section we shall briefly develop the technique of second quantization which facilitates this description. We shall have occasion to use these results later, particularly in setting up the so-called Anderson and Hubbard Hamiltonians.

Let us begin by considering a system of N interacting particles described by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N T(\mathbf{r}_i, \dot{\mathbf{r}}_i) + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N V(\mathbf{r}_i, \mathbf{r}_j) \quad (1.97)$$

The many-body wave function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t)$ satisfies the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = \mathcal{H} \psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t). \quad (1.98)$$

We now expand this wave function in terms of products of single-particle wave functions characterized by quantum numbers E_i ,

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = \sum_{(E_1, \dots, E_N)} c(E_1, \dots, E_N, t) \varphi_{E_1}(\mathbf{r}_1) \varphi_{E_2}(\mathbf{r}_2) \dots \varphi_{E_N}(\mathbf{r}_N), \quad (1.99)$$

where the sum is over all possible sets of quantum numbers. The statistical nature of the particles is contained in the coefficients $c(E_1, \dots, E_N, t)$. For example, if the particles are bosons, the sign of the coefficient is invariant under particle interchange,

$$c(E_1, \dots, E_k, \dots, E_i, \dots, E_N, t) = c(E_1, \dots, E_i, \dots, E_k, \dots, E_N, t), \quad (1.100)$$

and any number of particles may occupy a given state. If the particles are fermions,

$$c(E_1, \dots, E_k, \dots, E_i, \dots, E_N, t) = -c(E_1, \dots, E_i, \dots, E_k, \dots, E_N, t). \quad (1.101)$$

This insures that there may not be more than one particle in a particular state.

Since we shall be concerned mainly with electrons, which are fermions, we shall be faced with the problem of keeping track of the minus sign introduced when two electrons are interchanged. It is to facilitate this bookkeeping that the concept of second quantization is introduced.

The coefficients in the expansion of ψ above are characterized by the set of N quantum numbers. We could just as well, however, have chosen coefficients characterized by the number of electrons in each of the possible states. That is, instead of the set of N numbers $\{E_1, \dots, E_N\}$ we could have used the infinite set of numbers $\{n_1, \dots, n_\infty\}$, where for fermions $n = 0$ or 1 . We must be very careful in making this transcription. For example, suppose that the electron at \mathbf{r}_i is in a state E_i and the electron \mathbf{r}_k is in a state E_k . In this case the occupation-number description would be the same as if the electron at \mathbf{r}_i , were in state E_k and the electron at \mathbf{r}_k were in state E_i . However,

$$c(E_1, \dots, E_k, \dots, E_i, \dots, E_N, t) = -c(E_1, \dots, E_i, \dots, E_k, \dots, E_N, t). \quad (1.102)$$

If we wish to use the occupation-number scheme, we must account for this minus sign. This is done by arbitrarily assigning a certain order to the particular set of quantum numbers $\{E_1, \dots, E_N\}$. Then the relative sign of any permutation of the electrons from this order is automatically given by writing the single-particle wave functions as a *Slater determinant*:

$$\begin{aligned} & c(E_1, \dots, E_N, t) \varphi_{E_1}(\mathbf{r}_1) \dots \varphi_{E_N}(\mathbf{r}_N) \\ & + (\text{all permutations within the set } \{E_1, \dots, E_N\}) \\ & = f(n_1, \dots, n_\infty, t) \begin{vmatrix} \varphi_{E_1}(\mathbf{r}_1) & \dots & \varphi_{E_1}(\mathbf{r}_N) \\ \dots & \dots & \dots \\ \varphi_{E_N}(\mathbf{r}_1) & \dots & \varphi_{E_N}(\mathbf{r}_N) \end{vmatrix} \end{aligned} \quad (1.103)$$

where $f(n_1, \dots, n_\infty, t)$ has the sign and magnitude of the first c . Summing over all sets $\{E_1, \dots, E_N\}$ is equivalent to summing over all combinations of occupied states. Therefore

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = \sum_{n_1, \dots, n_\infty} f(n_1, \dots, n_\infty, t) \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{E_1}(\mathbf{r}_1) & \dots & \varphi_{E_1}(\mathbf{r}_N) \\ \dots & \dots & \dots \\ \varphi_{E_N}(\mathbf{r}_1) & \dots & \varphi_{E_N}(\mathbf{r}_N) \end{vmatrix}. \quad (1.104)$$

The states used in constructing the determinant are, of course, those occupied.

By using this occupation-number description we have succeeded in moving the statistics from the expansion coefficients into the basis functions, which, in fact, form an orthonormal antisymmetric set.

Let us now define an abstract vector space, or *Hilbert space*, spanned by vectors $|n_1, n_2, \dots, n_\infty\rangle$. We introduce operators which satisfy the *anticommutation relations*

$$\{a_i, a_j^\dagger\} \equiv a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}, \quad \{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0. \quad (1.105)$$

From these relations it can be shown that a_i^\dagger creates an entry in position i (provided one does not already exist there) and a_i destroys an entry at i . Therefore we may represent a basis vector of our Hilbert space as

$$|n_1, \dots, n_\infty\rangle = (a_1^\dagger)^{n_1} (a_2^\dagger)^{n_2} (a_\infty^\dagger)^{n_\infty} |0\rangle. \quad (1.106)$$

Now consider operating on this with a_k . If $n_k = 0$, then a_k can be commuted all the way over to the “vacuum”, where it gives 0. If $n_k = 1$, then a_k will commute until it comes to a_k^\dagger .

$$a_k |n_1, \dots, n_k, \dots, n_\infty\rangle = (-1)^{\sum_{i=1}^k n_i} a_k a_k^\dagger \dots (a_\infty^\dagger)^{n_\infty} |0\rangle. \quad (1.107)$$

Here $\sum_k = n_1 + n_2 + \cdots n_{k-1}$ accounts for all the sign changes that a_k left in its wake as it commuted over to a_k^\dagger . We now use $a_k a_k^\dagger = 1 - a_k^\dagger a_k$. In the second term a_k may again commute over to the vacuum to give 0. Thus we are left with

$$a_k |n_1, \dots, n_k, \dots, n_\infty\rangle = \begin{cases} 0 & n_k = 0 \\ (-1)^{\sum_k} |n_1, \dots, n_k - 1, \dots, n_\infty\rangle & n_k = 1. \end{cases} \quad (1.108)$$

Similarly,

$$a_k^\dagger |n_1, \dots, n_k, \dots, n_\infty\rangle = \begin{cases} (-1)^{\sum_k} |n_1, \dots, n_k + 1, \dots, n_\infty\rangle & n_k = 0 \\ 0 & n_k = 1. \end{cases} \quad (1.109)$$

Since it can be shown that $a_k^\dagger a_k$ has the eigenvalue n_k , we can simplify these results by writing

$$\begin{aligned} a_k |n_1, \dots, n_k, \dots, n_\infty\rangle &= (-1)^{\sum_k} \sqrt{n_k} |n_1, \dots, n_k - 1, \dots, n_\infty\rangle, \\ a_k^\dagger |n_1, \dots, n_k, \dots, n_\infty\rangle &= (-1)^{\sum_k} \sqrt{n_k + 1} |n_1, \dots, n_k + 1, \dots, n_\infty\rangle. \end{aligned} \quad (1.110)$$

Having developed the properties of the Hilbert space, we now use the expansion coefficients $f(n_1, \dots, n_\infty, t)$ to define the abstract state vector

$$|\psi(t)\rangle = \sum_{n_1, \dots, n_\infty} f(n_1, \dots, n_\infty, t) |n_1, \dots, n_\infty\rangle. \quad (1.111)$$

The reason for this becomes clear when we consider the equation of motion of this state vector. Taking the time derivative, we have

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = i\hbar \sum_{n_1, \dots, n_\infty} \frac{\partial f(n_1, \dots, n_\infty, t)}{\partial t} |n_1, \dots, n_\infty\rangle. \quad (1.112)$$

To evaluate this we go back to the real-space Schrödinger equation,

$$\begin{aligned} i\hbar \frac{\partial |\psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t)\rangle}{\partial t} &= i\hbar \sum_{(n_1, \dots, n_\infty)} \frac{\partial (n_1, \dots, n_\infty, t)}{\partial t} \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{E_1}(\mathbf{r}_1) & \cdots & \varphi_{E_1}(\mathbf{r}_N) \\ \vdots & & \vdots \\ \varphi_{E_N}(\mathbf{r}_1) & \cdots & \varphi_{E_N}(\mathbf{r}_N) \end{vmatrix}, \\ &= \mathcal{H} \sum_{n_1, \dots, n_\infty} f(n_1, \dots, n_\infty, t) \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{E_1}(\mathbf{r}_1) & \cdots & \varphi_{E_1}(\mathbf{r}_N) \\ \vdots & & \vdots \\ \varphi_{E_N}(\mathbf{r}_1) & \cdots & \varphi_{E_N}(\mathbf{r}_N) \end{vmatrix}. \end{aligned} \quad (1.113)$$

We now multiply through from the left by the conjugate Slater determinant appropriate for some particular set of occupation numbers $\{n_1, \dots, n_\infty\}$. The left-hand side just gives

$$i\hbar \frac{\partial f(n_1, \dots, n_\infty, t)}{\partial t}. \quad (1.114)$$

Consider the one-particle terms of the right-hand side of (1.113), which arise from the $T(\hat{\mathbf{r}}_i)$ term in (1.97). We write the Slater determinant as

$$\frac{1}{\sqrt{N!}} \sum_p (-1)^p P \varphi_{E_1}(\mathbf{r}_1) \varphi_{E_2}(\mathbf{r}_2) \cdots \varphi_{E_N}(\mathbf{r}_N), \quad (1.115)$$

where P is an operator which permutes the order of the electrons and p is the number of such permutations. Then the matrix element becomes

$$\begin{aligned} & \frac{1}{N!} \sum_i \sum_{n'_1, \dots, n'_\infty} \sum_{p, p'} (-1)^{p+p'} f(n'_1, \dots, n'_\infty, t) \\ & \times \int P \varphi_{E_1}^*(\mathbf{r}_1) \cdots T(\hat{\mathbf{r}}_i) P' \varphi_{E'_1}(\mathbf{r}_1) \cdots d\mathbf{r}_1 \cdots d\mathbf{r}_N. \end{aligned} \quad (1.116)$$

Since $T(\hat{\mathbf{r}}_i)$ is a one-particle operator, the set of numbers $\{n'_1, \dots, n'_\infty\}$ cannot differ from the particular set $\{n_1, \dots, n_\infty\}$ by more than two numbers. In particular, let the set $\{n'_1, \dots, n'_\infty\}$ contain the state E_i and the set $\{n_1, \dots, n_\infty\}$ contain the state E_k . The sums over i , p , and p' give $N!$, leaving us with

$$\sum_{k, l} (-1)^{\sum_k + \sum_l} \int d\mathbf{r} \varphi_{E_k}^*(\mathbf{r}) T(\hat{\mathbf{r}}) \varphi_{E_l}(\mathbf{r}) f(n_1, \dots, n_k - 1, n_l + 1, \dots, n_\infty, t). \quad (1.117)$$

Therefore

$$\begin{aligned} i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} &= \sum_{n_1, \dots, n_\infty} \sum_{k, l} \langle k | T | l \rangle \\ &\times f(n_1, \dots, n_k = 0, \dots, n_l = 1, \dots, n_\infty, t) (-1)^{\sum_k + \sum_l} \\ &\times |n_1, \dots, n_k = 1, \dots, n_l = 0, \dots, n_\infty\rangle + (\text{interaction terms}). \end{aligned} \quad (1.118)$$

We now recall from above that

$$\begin{aligned} & (-1)^{\sum_k + \sum_l} |n_1, \dots, n_k, \dots, n_l, \dots, n_\infty\rangle \\ &= a_k^\dagger a_l |n_1, \dots, n_k - 1, \dots, n_l + 1, \dots, n_\infty\rangle. \end{aligned} \quad (1.119)$$

Substituting this into the equation for $\partial|\psi(t)\rangle/\partial t$, we see that the sum over $\{n_1, \dots, n_\infty\}$ just gives $|\psi(t)\rangle$. Carrying through the same arguments for the two-particle interaction terms, we find

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \mathcal{H} |\psi(t)\rangle, \quad (1.120)$$

where

$$\mathcal{H} = \sum_{k,l} \langle k|T|l\rangle a_k^\dagger a_l + \frac{1}{2} \sum_{k,l,s,t} \langle kl|V|st\rangle a_k^\dagger a_l^\dagger a_t a_s. \quad (1.121)$$

Thus we have the important result that in this occupation-number space the state vector $|\psi(t)\rangle$, as defined above, also satisfies a Schrödinger-like equation, with the Hamiltonian expressed in this second-quantized form. It is easy to show that the matrix elements of such second-quantized operators between occupation-number states are the same as the matrix elements of “first-quantized” operators between the usual states.

Since we shall often have occasion to express an operator in second-quantized form, let us develop a prescription for doing this. For this purpose it is convenient to define what is called the *field operator* in our Hilbert space,

$$\psi(\mathbf{r}) = \sum_k \varphi_k(\mathbf{r}) a_k. \quad (1.122)$$

Here again the $\varphi_k(\mathbf{r})$ are a complete set of single-particle states characterized by the quantum numbers k , and a_k is the fermion operator introduced above. To second quantize a one-particle operator such as $T(\mathbf{r}_i)$ we write $\mathbf{r}_i \rightarrow \mathbf{r}$, sandwich this operator between $\psi^\dagger(\mathbf{r})$ and $\psi(\mathbf{r})$, and integrate over all space. For a two-particle operator such as $V(\mathbf{r}_i, \mathbf{r}_j)$ we let $\mathbf{r}_i \rightarrow \mathbf{r}$ and $\mathbf{r}_j \rightarrow \mathbf{r}'$, sandwich it between $\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')$ and $\psi(\mathbf{r}')\psi(\mathbf{r})$, and integrate over $d\mathbf{r}$ and $d\mathbf{r}'$.

1.4.1 Example: The Degenerate-Electron Gas

As an example of the use of this prescription let us second quantize the Hamiltonian for a gas of electrons moving in the field of a uniform positive charge distribution. The total Hamiltonian is

$$\mathcal{H} = \mathcal{H}_{e1-e1} + \mathcal{H}_{e1-n} + \mathcal{H}_{n-n}. \quad (1.123)$$

The electron-electron Hamiltonian is

$$\mathcal{H}_{e1-e1} = \sum_i \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i \neq j} \frac{\exp(-\mu|\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1.124)$$

where a screening factor has been inserted for mathematical convenience. The interaction of the electrons with the positive background due to the nuclei is

$$\mathcal{H}_{e1-n} = -e^2 \sum_i \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} \exp(-\mu|\mathbf{r}_i - \mathbf{r}'|) d\mathbf{r}', \quad (1.125)$$

where $\rho(\mathbf{r})$ is the positive charge density, which for a uniform distribution is

$$\rho(\mathbf{r}) = \frac{N}{V}. \quad (1.126)$$

Thus \mathcal{H}_{e1-n} becomes

$$\mathcal{H}_{e1-n} = -e^2 \left(\frac{N}{V} \right) \sum_i \int \frac{\exp(-\mu|\mathbf{r}_i - \mathbf{r}'|)}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}'. \quad (1.127)$$

If μ^{-1} is much smaller than L , where L is the sample dimension, we may replace the integral over $d\mathbf{r}'$ by one over $d(\mathbf{r}' - \mathbf{r}_i)$, which gives

$$\mathcal{H}_{e1-n} = -e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}. \quad (1.128)$$

Finally, the self-energy of the background charge is

$$\mathcal{H}_{n-n} = -\frac{1}{2}e^2 \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} e^{-\mu|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \frac{e^2}{2} \frac{N^2}{2} \frac{4\pi}{\mu^2}. \quad (1.129)$$

We must now decide what functions to use as a basis for our field operator. Since the eigenfunctions for a gas of *free* electrons are plane waves, we shall use these as our basis. These states are characterized by their wave vector \mathbf{k} and spin quantum number σ . Thus

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}, \sigma} \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \eta_{\sigma} a_{\mathbf{k}\sigma}, \quad (1.130)$$

where

$$\eta_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \eta_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (1.131)$$

Notice that

$$\int \psi^{\dagger}(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = \sum_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma} = N. \quad (1.132)$$

Since the terms \mathcal{H}_{e1-n} and \mathcal{H}_{n-n} do not involve any electron coordinates, they are carried over directly into our Hilbert space. The kinetic energy of the electron-electron Hamiltonian becomes

$$\sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma}. \quad (1.133)$$

For the Coulomb interaction we have

$$\begin{aligned}
& \frac{e^2}{2} \frac{1}{V^2} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} \sum_{\mathbf{k}'',\sigma''} \sum_{\mathbf{k}''',\sigma'''} \int d\mathbf{r} \int d\mathbf{r}' e^{-i(\mathbf{k}\cdot\mathbf{r}+\mathbf{k}'\cdot\mathbf{r}')} \frac{e^{-\mu|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} e^{i(\mathbf{k}'''\cdot\mathbf{r}'+\mathbf{k}''\cdot\mathbf{r})} \\
& \times \eta_{\sigma}^{\dagger}(\mathbf{r}) \eta_{\sigma'}^{\dagger}(\mathbf{r}') \eta_{\sigma'''}(\mathbf{r}') \eta_{\sigma''}(\mathbf{r}) a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}'\sigma'}^{\dagger} a_{\mathbf{k}'''\sigma'''} a_{\mathbf{k}''\sigma''} \\
& = \frac{e^2}{2} \frac{1}{V^2} \sum_{\mathbf{k},\sigma} \sum_{\mathbf{k}',\sigma'} \sum_{\mathbf{k}'',\sigma''} \sum_{\mathbf{k}''',\sigma'''} \delta_{\sigma,\sigma'''} \delta_{\sigma',\sigma''} \int d\mathbf{r} \int d\mathbf{r}' e^{-i(\mathbf{k}+\mathbf{k}'-\mathbf{k}''-\mathbf{k}''')\cdot\mathbf{r}} \\
& \times \frac{e^{i(\mathbf{k}'-\mathbf{k}''')\cdot(\mathbf{r}-\mathbf{r}')} e^{-\mu|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}'\sigma'}^{\dagger} a_{\mathbf{k}'''\sigma'''} a_{\mathbf{k}''\sigma''} . \tag{1.134}
\end{aligned}$$

If we again treat \mathbf{r} and $\mathbf{r}-\mathbf{r}'$ as independent variables, the integrations may be carried out separately to give

$$\begin{aligned}
& \frac{e^2}{2} \frac{1}{V} \sum_{\mathbf{k},\sigma} \sum_{\mathbf{k}',\sigma'} \sum_{\mathbf{k}'',\sigma''} \sum_{\mathbf{k}''',\sigma'''} \delta_{\sigma,\sigma'''} \delta_{\sigma',\sigma''} \Delta(\mathbf{k}+\mathbf{k}'-\mathbf{k}''-\mathbf{k}''') \\
& \times \frac{4\pi}{(\mathbf{k}'-\mathbf{k}''')^2 + \mu^2} a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}'\sigma'}^{\dagger} a_{\mathbf{k}'''\sigma'''} a_{\mathbf{k}''\sigma''} . \tag{1.135}
\end{aligned}$$

If we define $\mathbf{k}'-\mathbf{k}''' \equiv \mathbf{q}$ and collect all the terms, we obtain the total second-quantized Hamiltonian,

$$\begin{aligned}
\mathcal{H} &= \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma} + \frac{e^2}{2V} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{\mathbf{q}} \sum_{\sigma,\sigma'} \frac{4\pi}{q^2 + \mu^2} \\
& \times a_{\mathbf{k}-\mathbf{q},\sigma}^{\dagger} a_{\mathbf{k}'+\mathbf{q},\sigma'}^{\dagger} a_{\mathbf{k}',\sigma'} a_{\mathbf{k},\sigma} - \frac{e^2 N^2}{2V} \frac{4\pi}{\mu^2} . \tag{1.136}
\end{aligned}$$

It is convenient to introduce an equivalent electron radius \mathbf{r}_0 by

$$\frac{4}{3} \pi r_0^3 = \frac{V}{N} . \tag{1.137}$$

This is made dimensionless by dividing it by the Bohr radius $a_0 = \hbar^2/m\epsilon^2$. We also define $r_0/a_0 = r_s$ and $V/r_0^3 \equiv \Omega$. Since 1 Rydberg $= m\epsilon^4/\hbar^2 = e^2/2a_0$, the Hamiltonian expressed in Rydbergs is

$$\begin{aligned}
\mathcal{H} &= \frac{1}{r_s^2} \sum_{\mathbf{k},\sigma} (r_0 \mathbf{k})^2 a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma} + \frac{1}{r_s \Omega} \sum_{\mathbf{k},\sigma} \sum_{\mathbf{k}',\sigma'} \sum_{\mathbf{q}} \frac{4\pi}{r_0^2 (q^2 + \mu^2)} \\
& \times a_{\mathbf{k}-\mathbf{q},\sigma}^{\dagger} a_{\mathbf{k}'+\mathbf{q},\sigma'}^{\dagger} a_{\mathbf{k}',\sigma'} a_{\mathbf{k},\sigma} - \frac{N^2}{r_s \Omega} \frac{4\pi}{(r_0 \mu)^2} . \tag{1.138}
\end{aligned}$$

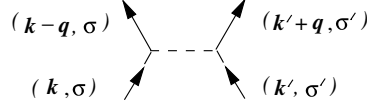
Notice that the electron-electron interaction for $\mathbf{q} = 0$ gives a term proportional to N^2 , which cancels the contribution from the positive background,

plus a term proportional to N , which vanishes by virtue of the condition $\mu^{-1} \ll L$. Thus we finally have

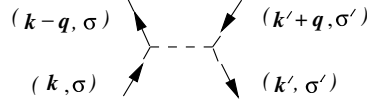
$$\mathcal{H} = \sum_{\mathbf{k}, \sigma} \epsilon_{\mathbf{k}} a_{\mathbf{k}, \sigma}^{\dagger} a_{\mathbf{k}, \sigma} + \sum_{\mathbf{k}, \sigma} \sum_{\mathbf{k}', \sigma'} \sum_{\mathbf{q} \neq 0} V(\mathbf{q}) a_{\mathbf{k}-\mathbf{q}, \sigma}^{\dagger} a_{\mathbf{k}'+\mathbf{q}, \sigma'}^{\dagger} a_{\mathbf{k}', \sigma'} a_{\mathbf{k}, \sigma}, \quad (1.139)$$

where $\epsilon_{\mathbf{k}} \equiv (r_0 k / r_s)^2$ and $V(\mathbf{q}) \equiv 4\pi / [r_s \Omega(r_0 q)^2]$.

Aside from its advantages for handling particle statistics, the second-quantization formalism also lends itself readily to graphical interpretation. For example, the interaction term above corresponds to the destruction of two particles in states (\mathbf{k}, σ) and (\mathbf{k}', σ') and the creation of two particles in states $(\mathbf{k}' + \mathbf{q}, \sigma')$ and $(\mathbf{k} - \mathbf{q}, \sigma)$. This may be represented as



In general, we shall also have particle-hole interactions which have the form



We shall see that long-range magnetic order may be characterized as a coherent electron-hole state just as superconductivity is characterized as a coherent electron-electron state.

1.4.2 Example: The Zeeman Interaction

Finally, let us apply this second quantization prescription to the interaction of an electron spin with a magnetic field $H \cos(\mathbf{q} \cdot \mathbf{r})$. In the next chapter we shall show that this interaction has the form

$$\mathcal{H} = \mu_B \sigma_z H \cos(\mathbf{q} \cdot \mathbf{r}),$$

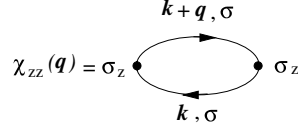
where μ_B is the Bohr magneton and σ_z the Pauli matrix

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

In terms of the field operators (1.122) this becomes

$$\mathcal{H} = \frac{1}{2} \mu_B H \sum_{\mathbf{k}} (a_{\mathbf{k}+\mathbf{q}, \uparrow}^{\dagger} a_{\mathbf{k} \uparrow} - a_{\mathbf{k}+\mathbf{q}, \downarrow}^{\dagger} a_{\mathbf{k} \downarrow} + a_{\mathbf{k}-\mathbf{q}, \uparrow}^{\dagger} a_{\mathbf{k} \uparrow} + a_{\mathbf{k}-\mathbf{q}, \downarrow}^{\dagger} a_{\mathbf{k} \downarrow}).$$

Since $\mathcal{H}_0 = 0$ in this simple example, $\sigma_z(t) = \sigma_z$ and the calculation of the longitudinal susceptibility using (1.81) simply involves terms of the form $\langle a_{k\uparrow}^\dagger a_{k+q\uparrow} a_{k+q,\uparrow}^\dagger a_{k\uparrow} \rangle$. This has the diagrammatic representation



In more complex systems it is convenient to characterize various approximations in terms of their diagrammatic representations.

Problems

1.1. The current density j associated with a wave function ψ is given by

$$j = e \operatorname{Re} \left(\psi^* \frac{\hbar}{im} \nabla \psi \right).$$

Assuming a hydrogenic wave function of the form

$$\psi(r-R) = R_{n\ell}(r-R) Y_\ell^m(\theta, \varphi)$$

calculate the magnetic moment from (1.6).

1.2. Consider a two-dimensional harmonic oscillator with the Hamiltonian

$$\mathcal{H} = \frac{1}{2m} (p_x^2 + m^2 \omega^2 x^2) + \frac{1}{2m} (p_y^2 + m^2 \omega^2 y^2).$$

Introduce the operators

$$a_\mu = \left(\frac{m\omega}{2\hbar} \right)^{\frac{1}{2}} \mu + i(2m\hbar\omega)^{-\frac{1}{2}} p_\mu$$

$$a_\mu^\dagger = \left(\frac{m\omega}{2\hbar} \right)^{\frac{1}{2}} \mu - i(2m\hbar\omega)^{-\frac{1}{2}} p_\mu, \quad (\mu = x, y)$$

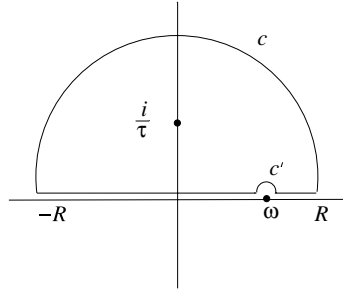
- Compute the commutation relation $[a_\mu, a_\mu^\dagger]$ recalling $[\mu, p_\mu] = i\hbar$.
- Express the Hamiltonian in terms of the operators a_μ, a_μ^\dagger .
- Let $|n_\mu\rangle$ be an eigenvector of $a_\mu^\dagger a_\mu$ with eigenvalue n_μ . The spectrum of these eigenvalues consists of the set of non-negative integers. Sketch the lowest lying eigenvalues of the oscillator indicating any degeneracies.
- Treat the second term in (1.25) as a perturbation and calculate its affect on the first excited state.

1.3. If $\chi'(\omega) = \frac{1}{1+\omega^2\tau^2}$ find $\chi''(\omega)$ from the relation (1.65).

Hint: The principal value is given by

$$\begin{aligned} & \lim_{R \rightarrow \infty} \left[\int_{-R}^{\omega-\epsilon} \frac{\chi'}{\omega' - \omega} d\omega' + \int_{\omega+\epsilon}^R \frac{\chi'}{\omega' - \omega} d\omega' \right] \\ &= \oint \frac{\chi'}{\omega' - \omega} d\omega' - \int_c \frac{\chi'}{\omega' - \omega} d\omega' - \int_{c'} \frac{\chi'}{\omega' - \omega} d\omega', \end{aligned}$$

where the contour of integration is shown in the figure on page 31. Show that the form (1.66) gives the same answer.



1.4. Consider a gas of electrons. The particle density is

$$\rho(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i).$$

The dynamic form factor is defined as

$$S(\mathbf{q}, \omega) = \sum_n |\langle n | \rho_{\mathbf{q}}^\dagger | 0 \rangle|^2 \delta(\omega - \omega_{n0}),$$

where the states $|n\rangle$ are the eigenstates of the electron system. We shall show later that the scattering of electrons or neutrons from a metal is proportional to this form factor.

(a) Second quantize

$$\rho_{\mathbf{q}}^\dagger = \int d^3r \rho(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}}$$

in terms of normalized free electron plane wave states.

(b) Evaluate the form factor $S_0(\mathbf{q}, \omega)$ for a free electron system characterized by a Fermi sphere of radius k_F .

Quantum Theory of Magnetism
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2007, XII, 362 p. 174 illus., Hardcover

ISBN: 978-3-540-65116-1