RARE EARTH MAGNETISM AND SUPERCONDUCTIVITY

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ELEMENTS OF RARE EARTH MAGNETISM

1.1 Rare earth atoms

In order to determine the atomic structure of rare-earth atoms, the Schrödinger equation

$$\Big[-\frac{\hbar^2}{2m}\nabla^2 + v_{\rm eff}(\mathbf{r})\Big]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \qquad (1.1.1)$$

must be solved by the Hartree self-consistent procedure, in which, through a process of iteration, the potential

$$v_{\rm eff}(\mathbf{r}) = \int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\rm ext}(\mathbf{r}) + v_{\rm xc}[n(\mathbf{r})]; \qquad n(\mathbf{r}) = \sum_i^Z |\psi_i(\mathbf{r})|^2 \qquad (1.1.2)$$

generates wavefunctions which reproduce itself. Since this potential is spherically symmetric in atoms, the single-particle wavefunctions may be written as the product of a radial function, a spherical harmonic and a spin function

$$\psi_{nlm_lm_s}(\mathbf{r}\sigma) = i^l R_{nl}(r)Y_{lm_l}(\hat{\mathbf{r}})\chi_{m_s}, \qquad (1.1.3)$$

where $\hat{\mathbf{r}}$ is a unit vector in the direction of $\mathbf{r}$, the spin quantum number m_s can take the values $\pm\frac{1}{2}$, and the phase factor i^l is included for later convenience. The radial component satisfies the equation

$$-\frac{\hbar^2}{2m}\frac{d^2[rR_{nl}(r)]}{dr^2} + \Big(v_{\rm eff}(r) + \frac{l(l+1)\hbar^2}{2mr^2} - \varepsilon\Big)[rR_{nl}(r)] = 0. \qquad (1.1.4)$$

Some radial wavefunctions for rare earth atoms are shown in Fig. 1.1. The $4f$ electrons are well embedded within the atom, and shielded by the $5s$ and $5p$ states from the surroundings. The $5d$ and $6s$ electrons form the conduction bands in the metals. The incomplete screening of the increasing nuclear charge along the rare earth series causes the lanthanide contraction of the wavefunctions, which is reflected in the ionic and atomic radii in the solid state. In particular, as illustrated in Fig. 1.1, the $4f$ wavefunction contracts significantly between Ce, which has one $4f$ electron, and Tm, which has one $4f$ hole in the atom, though two in the metallic state. The angular dependences of the $4f$ wavefunctions are depicted in Fig. 1.2. The charge clouds are highly anisotropic, with pronounced multipoles whose magnitudes and signs change dramatically with m_l. As we shall see, this anisotropy is clearly manifested in the magnetic properties of the metals.

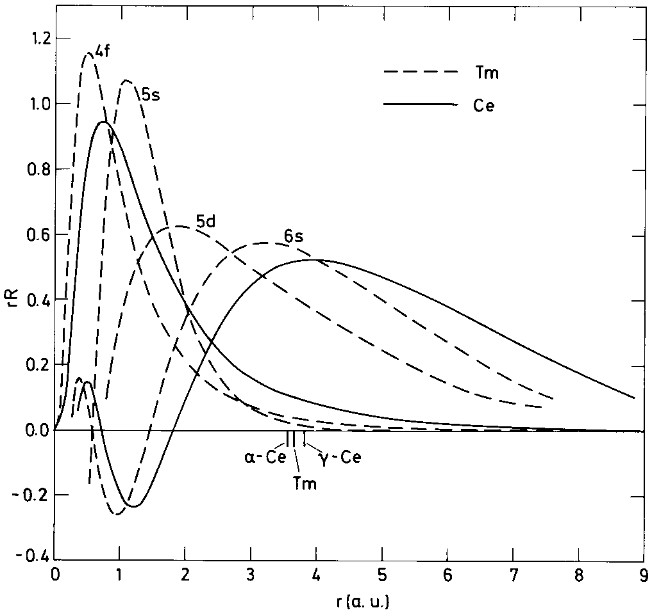

Fig. 1.1. The radial components of atomic wavefunctions for Ce, which has one $4f$ electron, and Tm, which has 13 $4f$ electrons, or one $4f$ hole. The Tm wavefunctions are contracted, relative to those of Ce, due to the incomplete shielding of the greater nuclear charge. As a consequence, the amplitude of the $4f$ wavefunction at the indicated Wigner–Seitz radius is much greater in Ce than in Tm, which has important consequences for the character of the $4f$ states in the metals.

Since they are among the heavier elements, relativistic effects are of substantial importance in the rare earths. These are most straightforwardly taken into account by solving the Dirac equation in the central field, rather than the Schrödinger equation, but it may be more instructive to consider them as perturbations which, to order $(p/mc)^2$, augment the one-electron potential with

$$-\frac{p^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2}\frac{dv}{dr}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2r}\frac{dv}{dr}\,\mathbf{s}\cdot\mathbf{l}. \tag{1.1.5}$$

The first term, which is due to the increase of mass with velocity, reduces the energy of all states by an amount which decreases with l, while the second 'Darwin' term increases the energy of s states only. These effects may both be incorporated into the central field, but the last term couples together the spin and orbital motion in a way that has far-reaching consequences for the magnetic properties.

In the Russell–Saunders coupling scheme, which is an accurate procedure for the $4f$ electrons, the spins $\mathbf{s}_i$ of the individual $4f$ electrons are coupled by the exchange interaction, diagonal in the total spin $\mathbf{S}$ of the incompletely filled subshell, while the Coulomb interaction similarly combines the $\mathbf{l}_i$ into the total orbital momentum $\mathbf{L}$. In terms of the one-electron functions, the wavefunction for the subshell may be written

$$\Psi(LSM_LM_S) = \sum_{m_lm_s} C(LSM_LM_S;m_lm_s)\psi(m_lm_s), \tag{1.1.6}$$

where the $C(LSM_LM_S;m_lm_s)$ are the *Clebsch–Gordan* or *Wigner* coefficients. It is convenient to write this expansion in a representation-independent form, in terms of the state vectors

$$|LSM_LM_S\!> = \sum_{m_lm_s} <\!m_lm_s|LSM_LM_S\!>|m_lm_s\!> . \tag{1.1.7}$$

The exchange and Coulomb interactions are sufficiently large that the magnetic properties at all accessible temperatures are determined by the S and L states of lowest energy. These are found from Hund's rules; S is maximized and, subject to this maximum S value, L is also maximized. This results in the values for the trivalent ions shown in Table 1.1.

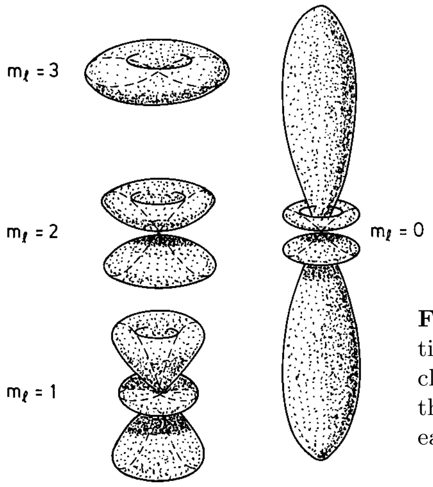

Fig. 1.2. The angular variation of the $4f$ wavefunctions. The interaction of the highly anisotropic charge clouds with the crystalline electric fields gives rise to the large single-ion anisotropies observed in the rare earth metals.

It is a consequence of the *Wigner–Eckart theorem* that the spin–orbit term in (1.1.5) can be written

$$\mathcal{H}_{\rm so} = \pm\zeta(LS)\,\mathbf{S}\cdot\mathbf{L}, \tag{1.1.8}$$

where

$$\zeta(LS) = \frac{\pi}{m^2c^2S}\int rR_{4f}^2(r)\frac{dv}{dr}dr, \tag{1.1.9}$$

and the + and − signs refer respectively to a less or more than half-filled subshell. The spin and orbital angular momenta are thus combined into the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. These states may be written

$$|JM_JLS\!> = \sum_{M_LM_S} <\!LSM_LM_S|JM_JLS\!>|LSM_LM_S\!> . \tag{1.1.10}$$

Because of the sign of (1.1.8), the value of J in the ground state is $L \mp S$, according as the subshell is less or more than half-full. Roughly speaking, $\mathbf{L}$ is always parallel to $\mathbf{J}$, but $\mathbf{S}$ is antiparallel in the first half of the series and parallel in the second half. The energy separation to the first excited multiplet may be determined from the matrix elements of (1.1.8), and is given by

$$\Delta = \zeta(LS)\begin{cases} (J+1) \\ J \end{cases} \tag{1.1.11}$$

again depending on whether the subshell is respectively less or more than half-filled. The values of J in the ground state and of Δ, obtained from spectroscopic measurements on rare earth salts (Dieke 1968), are given in Table 1.1.

Table 1.1. Properties of the tripositive rare earth ions.

$4f^n$	Ion^{+++}	L	S	J	g	$(g-1)^2J(J+1)$	$\Delta(K)$
0	La	0	0	0	—		
1	Ce	3	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{6}{7}$	0.18	3150
2	Pr	5	1	4	$\frac{4}{5}$	0.80	3100
3	Nd	6	$\frac{3}{2}$	$\frac{9}{2}$	$\frac{8}{11}$	1.84	2750
4	Pm	6	2	4	$\frac{3}{5}$	3.20	2300
5	Sm	5	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{2}{7}$	4.46	1450
6	Eu	3	3	0	—		500
7	Gd	0	$\frac{7}{2}$	$\frac{7}{2}$	2	15.75	
8	Tb	3	3	6	$\frac{3}{2}$	10.50	2900
9	Dy	5	$\frac{5}{2}$	$\frac{15}{2}$	$\frac{4}{3}$	7.08	4750
10	Ho	6	2	8	$\frac{5}{4}$	4.50	7500
11	Er	6	$\frac{3}{2}$	$\frac{15}{2}$	$\frac{6}{5}$	2.55	9350
12	Tm	5	1	6	$\frac{7}{6}$	1.17	11950[a]
13	Yb	3	$\frac{1}{2}$	$\frac{7}{2}$	$\frac{8}{7}$	0.32	14800
14	Lu	0	0	0	—		

[a] The lowest excited state in Tm is $^3F_4$ at 8490K.

The magnetization of an assembly of N rare earth atoms or ions is given by the derivative of the free energy with respect to magnetic field:

$$M = -\frac{1}{V}\frac{\partial F}{\partial H} \qquad \text{or, recalling that} \qquad F = -\frac{N}{\beta}\ln\sum_n e^{-\beta E_n(H)}, \tag{1.1.12}$$

where $E_n(H)$ are the atomic energy levels in the field, and $\beta = 1/k_BT$,

$$M = \frac{N}{V}\sum_n -\frac{\partial E_n}{\partial H}e^{-\beta E_n} \Big/ \sum_n e^{-\beta E_n}. \tag{1.1.13}$$

Neglecting the small diamagnetic susceptibility, the magnetic contribution to the Hamiltonian is given by the Zeeman term

$$\mathcal{H}_Z = -\mu_B(\mathbf{L} + g_0\mathbf{S})\cdot\mathbf{H}, \tag{1.1.14}$$

where μ_B is the Bohr magneton. Because of the negative charge on the electron, the angular momentum and the magnetic moment are *antiparallel*. This gives rise to certain difficulties, which are frequently ignored in the literature. We shall circumvent them by taking **L**, **S**, and **J** as signifying the *negative* of the corresponding angular-momentum vector. We shall furthermore from now on take the gyromagnetic ratio g_0 as 2. Second-order perturbation theory then gives the magnetic contribution to the energy:

$$\delta E_n(H) = -\mu_B \mathbf{H}\cdot\!<\!n|\,\mathbf{L}+2\mathbf{S}\,|n\!> + \sum_{m\neq n} \frac{|\!<\!n|\,\mu_B \mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})|m\!>\!|^2}{E_n - E_m}. \tag{1.1.15}$$

Problems of degeneracy are taken care of by using the $|JM_JLS\!>$ basis, whose degeneracy is completely lifted by the field. In this basis, and within a particular JLS-multiplet, the Wigner–Eckart theorem implies that the matrix elements of ($\mathbf{L}$+2$\mathbf{S}$) are proportional to those of **J**, so that

$$<\!JLSM_J|\,\mathbf{L}+2\mathbf{S}\,|JLSM_J'\!> = g(JLS)<\!JLSM_J|\,\mathbf{J}\,|JLSM_J'\!>, \tag{1.1.16}$$

and the proportionality constant, *the Landé factor*, is

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \tag{1.1.17}$$

Within this multiplet, we may write eqn (1.1.16) in the shorthand form $\mathbf{L}+2\mathbf{S} = g\mathbf{J}$, and consider the effective moment on the atom to be

$$\boldsymbol{\mu} = g\mu_B\mathbf{J}. \tag{1.1.18}$$

With the same proviso, we may similarly write

$$\mathbf{L} = (2-g)\mathbf{J} \qquad \text{and} \qquad \mathbf{S} = (g-1)\mathbf{J}. \tag{1.1.19}$$

If J is non-zero, the first-order term in (1.1.15), combined with (1.1.13) gives a magnetization for the ground-state multiplet:

$$M(H,T) = \frac{N}{V} g\mu_B J B_J(\beta g\mu_B JH), \tag{1.1.20}$$

where the *Brillouin function* is

$$B_J(x) = \frac{2J+1}{2J}\coth\frac{2J+1}{2J}x - \frac{1}{2J}\coth\frac{1}{2J}x. \tag{1.1.21}$$

If $g\mu_B JH$ is small compared with k_BT, the susceptibility is constant and given by *Curie's law*:

$$\chi = \frac{M}{H} = \frac{g^2\mu_B^2 J(J+1)}{3k_BT}\frac{N}{V} \equiv \frac{C}{T}, \tag{1.1.22}$$

where C is the *Curie constant.* The second-order non-diagonal term in (1.1.15) gives a paramagnetic contribution to χ which is independent of temperature, provided that the thermal population of the excited states is negligible. This *Van Vleck paramagnetism* is very small in the heavy rare earths, but in the first half of the series it is given by

$$\chi_V = \frac{2\mu_B^2(L+1)S}{3(J+1)\Delta}\frac{N}{V}, \tag{1.1.23}$$

which may be significant, since

$$\frac{\chi_V}{\chi} = \frac{2(L+1)S}{g^2 J(J+1)^2}\frac{k_B T}{\Delta} = \frac{\alpha k_B T}{\Delta}, \tag{1.1.24}$$

where, from Table 1.1, α takes the modest value of 0.19 for Pr, but is 12 for Sm. Since Δ is only 1450 K, the Van Vleck paramagnetism in Sm is significant even at rather low temperatures. In trivalent Eu, $J = 0$ in the ground state and the paramagnetic susceptibility is due entirely to the mixing of the excited states into the ground state by the field, and to the thermal excitation of these states. However, Eu metal is divalent and the ${}^8S_{7/2}$ ionic susceptibility follows Curie's law very closely. The Van Vleck paramagnetism arising from the mixing of states of different J will not play a significant role in our later discussion, but the analogous phenomenon of the mixing of states of different M_J, split by the crystalline electric field in the metal, will be of central importance.

1.2 Magnetic interactions

In the metallic state, the $4f$ electrons on a rare earth ion are subjected to a variety of interactions with their surroundings. These forces may be broadly classified into two categories. The *single-ion interactions* act independently at each ionic site, so that their influence on the state of the $4f$ electrons at a particular site is unaffected by the magnetic state of its neighbours. The corresponding contribution to the Hamiltonian therefore contains sums over terms located at the ionic sites i of the crystal, but without any coupling between different ions. On the other hand, the *two-ion interactions* couple the $4f$-electron clouds at pairs of ions, giving terms which involve two sites i and j.

The charge distribution around an ion produces an electric field, with the local point-symmetry, which acts on the $4f$ electrons and gives rise to the large magnetic anisotropies which are characteristic of the rare earth metals. This *crystal field* makes a contribution to the potential energy

$$v_{\text{cf}}(\mathbf{r}) = \int \frac{e\rho(\mathbf{R})}{|\mathbf{r}-\mathbf{R}|}\, d\mathbf{R}, \tag{1.2.1}$$

where $\rho(\mathbf{R})$ is the charge density of the surrounding electrons and nuclei. If these do not penetrate the $4f$ charge cloud, $v_{\text{cf}}(\mathbf{r})$ is a solution of Laplace's equation, and may be expanded in spherical harmonics as

$$v_{\text{cf}}(\mathbf{r}) = \sum_{lm} A_l^m r^l Y_{lm}(\hat{\mathbf{r}}), \tag{1.2.2}$$

where

$$A_l^m = (-1)^m \frac{4\pi}{2l+1} \int \frac{e\rho(\mathbf{R})}{R^{l+1}} Y_{l-m}(\hat{\mathbf{R}})\, d\mathbf{R}, \tag{1.2.3}$$

which is a special case of the multipole expansion (1.3.7). We can thus look upon (1.2.2) as arising from the interaction of the multipoles $r^l Y_{lm}(\hat{\mathbf{r}})$ of the $4f$ electrons with the appropriate components of the electric field. If part of the charge which is responsible for the crystal field lies within the $4f$ cloud, $v_{\text{cf}}(\mathbf{r})$ can still be expanded in spherical harmonics with the appropriate symmetry, but the coefficients are not generally proportional to r^l, nor to (1.2.3).

As the crystal-field energy is small compared to the spin–orbit splitting, its effects on the eigenstates of the system are adequately accounted for by first-order perturbation theory. Since f electrons cannot have multipole distributions with $l > 6$, the properties of the spherical harmonics ensure that the corresponding matrix elements of (1.2.2) vanish. Even so, the calculation of those that remain from the electronic wavefunctions would be a formidable task, even if the surrounding charge distribution were known, if the ubiquitous Wigner–Eckart theorem did not once again come to the rescue. As first pointed out by Stevens (1952), provided that we remain within a manifold of constant J, in this case the ground-state multiplet, the matrix elements of $v_{\mathrm{cf}}(\mathbf{r})$ are proportional to those of operator equivalents, written in terms of the **J** operators. We may thus replace (1.2.2) by

$$\mathcal{H}_{\mathrm{cf}} = \sum_i \sum_{lm} A_l^m \alpha_l \langle r^l \rangle \left(\frac{2l+1}{4\pi} \right)^{1/2} \widetilde{O}_{lm}(\mathbf{J}_i), \tag{1.2.4}$$

where we have also summed over the ions. The *Stevens factors* α_l depend on the form of the electronic charge cloud through L, S and J, and on l, but not on m. They are frequently denoted α, β, and γ when l is 2, 4, and 6 respectively, and their values for the magnetic rare earth ions are given in Table 1.2. The expectation value $\langle r^l \rangle$ is an average over the $4f$ states. The *Racah operators* $\widetilde{O}_{lm}(\mathbf{J})$ are obtained from the spherical harmonics, multiplied by $(4\pi/2l{+}1)^{1/2}$, by writing them in terms of Cartesian coordinates and replacing (x, y, z) by (J_x, J_y, J_z), with an appropriate symmetrization to take account of the non-commutation of the **J** operators. They have been tabulated for l-values up to 8 by Lindgård and Danielsen (1974).

Table 1.2. Stevens factors for rare earth ions.

Ion^{+++}	$\alpha \times 10^2$	$\beta \times 10^4$	$\gamma \times 10^6$
Ce	−5.71	63.5	0
Pr	−2.10	−7.35	61.0
Nd	−0.643	−2.91	−38.0
Pm	0.771	4.08	60.8
Sm	4.13	25.0	0
Tb	−1.01	1.22	−1.12
Dy	−0.635	−0.592	1.03
Ho	−0.222	−0.333	−1.30
Er	0.254	0.444	2.07
Tm	1.01	1.63	−5.60
Yb	3.17	−17.3	148.0

Following the customary practice, we shall generally use not the Racah operators, which are tensor operators transforming under rotations like spherical harmonics, but the *Stevens operators* $O_l^m(\mathbf{J})$, which transform like the real *tesseral harmonics* T_{lm}. If we define corresponding operators for m zero or positive as:

$$\begin{aligned} T_{l0} &= \widetilde{O}_{l0} \\ T_{lm}^c &= \frac{1}{\sqrt{2}} \big[\widetilde{O}_{l-m} + (-1)^m \widetilde{O}_{lm} \big] \\ T_{lm}^s &= \frac{i}{\sqrt{2}} \big[\widetilde{O}_{l-m} - (-1)^m \widetilde{O}_{lm} \big], \end{aligned} \tag{1.2.5}$$

the Stevens operators for positive and negative m are proportional respectively to T^c_{lm} and $T^s_{l|m|}$. There is some ambiguity in the literature about the proportionality constants, but we have used the standard definitions of the Stevens operators, which are given in Table 1.3. In terms of these operators, we may write the crystal-field Hamiltonian

$$\mathcal{H}_{\rm cf} = \sum_i \sum_{lm} B_l^m O_l^m(\mathbf{J}_i). \tag{1.2.6a}$$

The *crystal-field parameters* B_l^m can in principle be calculated from the charge distribution in the metal, but in practice attempts to do so have met with limited success. The difficulties are two-fold. The charge density on the surroundings of an ion is not easy to determine with the necessary accuracy, and the approximations normally used in the calculation of the electronic structure of a metal, in particular the assumption that the charge distribution in the atomic polyhedron is spherically symmetric, are inadequate for the purpose. Furthermore, a redistribution of the charge within the cell can modify the electric fields experienced by the $4f$ electrons, and such shielding effects are again very difficult to estimate. It is therefore necessary to appeal to relatively crude models, such as the instructive but quite unjustified point-charge model, in which an adjustable charge is placed on each lattice site, or alternatively to regard the B_l^m as parameters to be determined from experiment.

Table 1.3. Stevens operators. $X \equiv J(J+1)$ and $J_\pm \equiv J_x \pm iJ_y$.

$$\begin{aligned}
O_2^2 &= \frac{1}{2}(J_+^2 + J_-^2) \\
O_2^1 &= \frac{1}{2}(J_zJ_x + J_xJ_z) \\
O_2^0 &= 3J_z^2 - X \\
O_2^{-1} &= \frac{1}{2}(J_zJ_y + J_yJ_z) \\
O_2^{-2} &= \frac{1}{2i}(J_+^2 - J_-^2) \\
O_4^4 &= \frac{1}{2}(J_+^4 + J_-^4) \\
O_4^2 &= \frac{1}{4}\big[(7J_z^2 - X - 5)(J_+^2 + J_-^2) + (J_+^2 + J_-^2)(7J_z^2 - X - 5)\big] \\
O_4^0 &= 35J_z^4 - (30X - 25)J_z^2 + 3X^2 - 6X \\
O_4^{-2} &= \frac{1}{4i}\big[(7J_z^2 - X - 5)(J_+^2 - J_-^2) + (J_+^2 - J_-^2)(7J_z^2 - X - 5)\big] \\
O_4^{-4} &= \frac{1}{2i}(J_+^4 - J_-^4) \\
O_6^0 &= 231J_z^6 - (315X - 735)J_z^4 + (105X^2 - 525X + 294)J_z^2 - 5X^3 + 40X^2 - 60X \\
O_6^4 &= \frac{1}{4}\big[(11J_z^2 - X - 38)(J_+^4 + J_-^4) + (J_+^4 + J_-^4)(11J_z^2 - X - 38)\big] \\
O_6^6 &= \frac{1}{2}(J_+^6 + J_-^6)
\end{aligned}$$

Fortunately, the number of such parameters is strongly restricted by symmetry. We shall be concerned almost exclusively with tetragonal structures, and in defining the Stevens operators, we have used a Cartesian system in which the (x, y, z)-directions are along the crystallographic (a, b, c)-axes. For an ion with tetragonal point-symmetry, as in the body centered tetragonal structure of $\mathrm{TmNi_2B_2C}$, the crystal field is specified by 5 parameters:

$$\mathcal{H}_{\mathrm{cf}} = \sum_i \Big[\sum_{l=2,4,6} B_l^0 O_l^0(\mathbf{J}_i) + B_4^4 O_4^4(\mathbf{J}_i) + B_6^4 O_6^4(\mathbf{J}_i) \Big]. \qquad (1.2.6b)$$

The Hamiltonian (1.2.6) lifts the degeneracy of the ionic $|JM_J>$ states and, since it is expressed in terms of $\mathbf{J}$ operators, whose matrix elements between these states may be determined by straightforward calculation, it may readily be diagonalized to yield the crystal-field energies and eigenfunctions. The B_l^m may then be used as adjustable parameters to reproduce the available experimental information on these eigenstates. As an example, we show in Fig. 1.3 the splitting of the nine $|4M_J>$ states in Pr by the crystal fields acting on the hexagonal sites. This level scheme was derived from values of the crystal-field parameters adjusted to account for a variety of experimental phenomena (Houmann *et al.* 1979).

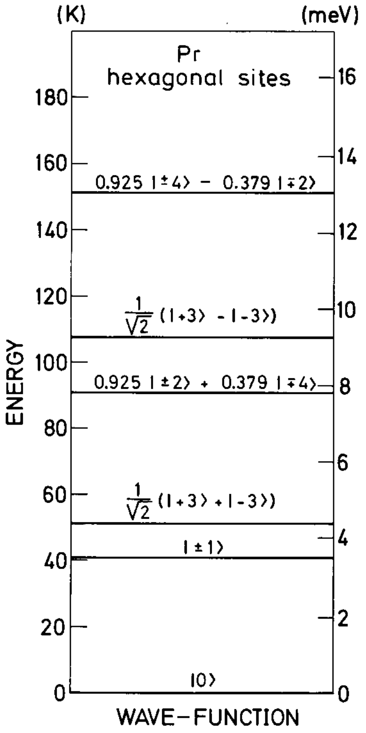

Fig. 1.3. The crystal-field splitting of the nine $|4M_J>$ states on the hexagonal sites in dhcp Pr. The wavefunctions are written in terms of a basis $|M_J>$ corresponding to quantization along the c-direction.

The exchange coupling between a conduction-electron spin $\mathbf{s}$ and the $4f$ spins takes the Heisenberg form

$$\mathcal{H}_{\mathrm{sf}} = -2I\mathbf{s} \cdot \sum_i \mathbf{S}_i. \qquad (1.2.7)$$

It is the two-ion couplings which are primarily responsible for co-operative effects and magnetic ordering in the rare earths, and of these the most important is the *indirect exchange*, by which the moments on pairs of ions are coupled through the intermediary of the conduction electrons. The form of this coupling can be calculated straightforwardly, provided that we generalize (1.2.7) slightly to

$$\mathcal{H}_{\rm sf}(i) = -\frac{2}{N}\int I(\mathbf{r}-\mathbf{R}_i)\,\mathbf{S}_i\cdot\mathbf{s}(\mathbf{r})d\mathbf{r} = -\int \mathbf{H}_i(\mathbf{r})\cdot\boldsymbol{\mu}(\mathbf{r})d\mathbf{r}, \tag{1.2.8}$$

where N is the number of ions, $\mathbf{s}(\mathbf{r})$ is the conduction-electron spin density, and the exchange integral $I(\mathbf{r}-\mathbf{R}_i)$ is determined by the overlap of the $4f$ and conduction-electron charge clouds. This expression can be viewed as arising from the action of the effective inhomogeneous magnetic field

$$\mathbf{H}_i(\mathbf{r}) = \frac{1}{N\mu_B}I(\mathbf{r}-\mathbf{R}_i)\mathbf{S}_i \tag{1.2.9}$$

on the conduction-electron moment density $\boldsymbol{\mu}(\mathbf{r}) = 2\mu_B\mathbf{s}(\mathbf{r})$. The spin at $\mathbf{R}_i$ generates a moment at $\mathbf{r}$, whose Cartesian components are given by

$$\mu_{i\alpha}(\mathbf{r}) = \frac{1}{V}\sum_\beta\int \chi_{\alpha\beta}(\mathbf{r}-\mathbf{r}')H_{i\beta}(\mathbf{r}')d\mathbf{r}', \tag{1.2.10}$$

where $\overline{\overline{\chi}}$ is the nonlocal susceptibility tensor for the conduction electrons and V the volume. This induced moment interacts through $\mathcal{H}_{\rm sf}(j)$ with the spin $\mathbf{S}_j$, leading to a coupling

$$\mathcal{H}(ij) = -\frac{1}{V}\sum_{\alpha\beta}\int\!\!\int H_{j\alpha}(\mathbf{r})\chi_{\alpha\beta}(\mathbf{r}-\mathbf{r}')H_{i\beta}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{1.2.11}$$

If we neglect, for the moment, the spin–orbit coupling of the conduction electrons, and the crystal is unmagnetized, $\chi_{\alpha\beta}$ becomes a scalar. We define the Fourier transforms:

$$\chi(\mathbf{q}) = \frac{1}{V}\int \chi(\mathbf{r})\,e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r} \quad ; \quad \chi(\mathbf{r}) = \frac{V}{(2\pi)^3}\int \chi(\mathbf{q})\,e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{q} \tag{1.2.12}$$

and

$$I(\mathbf{q}) = \frac{1}{V}\int I(\mathbf{r})\,e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}. \tag{1.2.13}$$

Summing over the lattice sites, counting each interaction once only, we find that the indirect-exchange interaction takes the familiar isotropic Heisenberg form:

$$\begin{aligned}\mathcal{H}_{\rm ff} &= -\frac{1}{2}\frac{V}{N^2\mu_B^2}\frac{V}{(2\pi)^3}\sum_{ij}\int \chi(\mathbf{q})I(\mathbf{q})I(-\mathbf{q})\,e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\,\mathbf{S}_i\cdot\mathbf{S}_j d\mathbf{q}\\ &= -\frac{1}{2N}\sum_{\mathbf{q}}\sum_{ij}\mathcal{J}_S(\mathbf{q})\,e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\,\mathbf{S}_i\cdot\mathbf{S}_j = -\frac{1}{2}\sum_{ij}\mathcal{J}_S(ij)\,\mathbf{S}_i\cdot\mathbf{S}_j, \end{aligned}\tag{1.2.15}$$

where

$$\mathcal{J}_S(ij) = \frac{1}{N}\sum_{\mathbf{q}}\mathcal{J}_S(\mathbf{q})\,e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)} \tag{1.2.16}$$

and

$$\mathcal{J}_S(\mathbf{q}) = \frac{V}{N\mu_B^2}|I(\mathbf{q})|^2\chi(\mathbf{q}). \tag{1.2.17}$$

In the presence of an orbital moment, it is convenient to express (1.2.15) in terms of **J** rather than **S**, which we may do within the ground-state multiplet by using (1.2.29) to project **S** on to **J**, obtaining

$$\mathcal{H}_{\rm ff} = -\frac{1}{2}\sum_{ij} \mathcal{J}(ij)\, \mathbf{J}_i \cdot \mathbf{J}_j, \tag{1.2.18}$$

with

$$\mathcal{J}(\mathbf{q}) = (g-1)^2 \Big[\mathcal{J}_S(\mathbf{q}) - \frac{1}{N}\sum_{\mathbf{q}'} \mathcal{J}_S(\mathbf{q}')\Big], \tag{1.2.19}$$

where we have also subtracted the interaction of the ith moment with itself, as this term only leads to the constant contribution to the Hamiltonian; $-\frac{1}{2}(g-1)^2 N \mathcal{J}_S(ii) J(J+1)$. The origin of the indirect exchange in the polarization of the conduction-electron gas by the spin on one ion, and the influence of this polarization on the spin of a second ion, is apparent in the expression (1.2.17) for $\mathcal{J}_S(\mathbf{q})$. As we shall see, it is the Fourier transform $[\mathcal{J}(\mathbf{q}) - \mathcal{J}(\mathbf{0})]$ which may be directly deduced from measurements of the dispersion relations for the magnetic excitations, and its experimentally determined variation with $\mathbf{q}$ in the c-direction for the heavy rare earths is shown in Fig. 1.4.

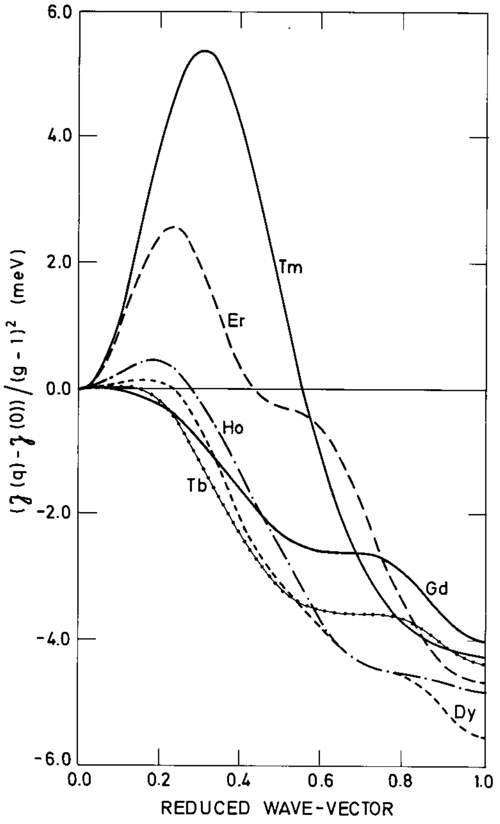

Fig. 1.4. The exchange interaction $\mathcal{J}_S(\mathbf{q}) - \mathcal{J}_S(\mathbf{0})$, determined experimentally in the magnetic heavy rare earth metals. The magnitude of the peak, which stabilizes the observed periodic magnetic structures, increases monotonically with atomic number.

A notable feature is the maximum which, except in Gd, occurs at non-zero $\mathbf{q}$ and, as discussed in the following section, is responsible for stabilizing the periodic magnetic structures in the metals. In the approximation which we have used, the conduction-electron susceptibility is given by

$$\chi(\mathbf{q}) = \frac{2\mu_B^2}{V} \sum_{nn'\mathbf{k}} \frac{f_{n\mathbf{k}} - f_{n'\mathbf{k}-\mathbf{q}}}{\varepsilon_{n'}(\mathbf{k}-\mathbf{q}) - \varepsilon_n(\mathbf{k})}, \tag{1.2.20}$$

where $f_{n\mathbf{k}}$ is the Fermi–Dirac function. It is clear that a large contribution to the sum is made by pairs of electronic states, separated by $\mathbf{q}$, one of which is occupied and the other empty, and both of which have energies very close to the Fermi level. Consequently, parallel or *nesting* regions of the Fermi surface tend to produce peaks, known as *Kohn anomalies*, at the wave-vector $\mathbf{Q}$ which separates them. This conjecture is supported by both positron-annihilation experiments and band structure calculations but, despite extensive efforts, first-principles estimates of $\mathcal{J}(\mathbf{q})$ have not proved particularly successful. $\chi(\mathbf{q})$ may be calculated quite readily from the energy bands (Liu 1978), and exhibits the expected peaks, but the exchange matrix elements which determine $I(\mathbf{q})$ are much less tractable. Lindgård *et al.* (1975) obtained the correct general variation with $\mathbf{q}$ for Gd, but the matrix elements were, not surprisingly, far too large when the screening of the Coulomb interaction was neglected.

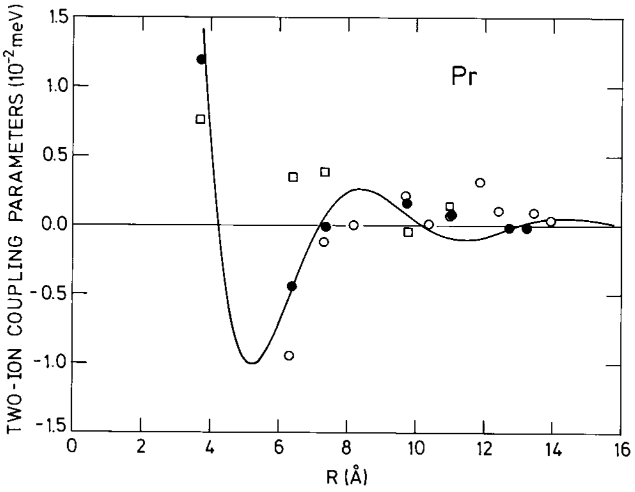

Fig. 1.5. The indirect-exchange interaction between ions on the hexagonal sites in Pr, deduced from measurements of the magnetic excitations at 6 K. The circles represent the isotropic interaction $\mathcal{J}(\mathbf{R})$ between an ion at the origin and those at different sites. The filled symbols are for pairs of ions in the same hexagonal plane, and the open symbols for pairs in different planes. The former are reasonably well described by the simple free-electron model, with an effective value of 1.1 Å^{-1} for $2k_F$, as shown by the full curve. In addition, the exchange incorporates an anisotropic component $\mathcal{K}(\mathbf{R})$, which is smaller, but of comparable magnitude. Its values between pairs of ions in the plane are indicated by the squares. The calculated uncertainties in the exchange interactions are, at the most, of the size of the points.

The Kohn anomalies in $\mathcal{J}(\mathbf{q})$ Fourier transform into *Friedel oscillations* in $\mathcal{J}(\mathbf{R})$, and such oscillations, and the extremely long range of the indirect exchange, are illustrated in the results of Houmann *et al.* (1979) for Pr in Fig. 1.5. As is also shown in this figure, they found that the *anisotropic* component of the coupling is a substantial proportion of the Heisenberg exchange. The anisotropic coupling between the moments on two ions can be written in the general form

$$\mathcal{H}_{\mathrm{JJ}} = -\frac{1}{2}\sum_{ij}\sum_{ll'mm'} \mathcal{K}_{ll'}^{mm'}(ij) O_l^m(\mathbf{J}_i) O_{l'}^{m'}(\mathbf{J}_j), \tag{1.2.21}$$

where the terms which appear in the sum are restricted by symmetry, but otherwise may exhibit a large variety, depending on their origin. The many possible causes of anisotropy have been summarized by Jensen *et al.* (1975). They are usually associated with the orbital component of the moment and are therefore expected to be relatively large when L is large. In addition to contributions due to the influence of the localized $4f$ orbital moment on the conduction electrons (Kaplan and Lyons 1963), and to the magnetization and spin–orbit coupling of the latter (Levy 1969), direct multipolar interactions and two-ion magnetoelastic couplings, for which the coefficients $\mathcal{K}_{ll'}^{mm'}$ depend explicitly on the strain, may be important. A general two-ion coupling which depends only on the dipolar moments of the $4f$ electrons is

$$\mathcal{H}_{\mathrm{dd}} = -\frac{1}{2}\sum_{ij} \mathcal{J}_{\alpha\beta}(ij) J_{i\alpha} J_{j\beta}. \tag{1.2.22}$$

The dispersion relations for the magnetic excitations provide extensive evidence for anisotropy of this form. A special case is the classical *dipole–dipole interaction* for which

$$\mathcal{J}_{\alpha\beta}(ij) = (g\mu_B)^2\, \frac{3(R_{i\alpha} - R_{j\alpha})(R_{i\beta} - R_{j\beta}) - \delta_{\alpha\beta}|\mathbf{R}_i - \mathbf{R}_j|^2}{|\mathbf{R}_i - \mathbf{R}_j|^5}. \tag{1.2.23}$$

Although it is very weak, being typically one or two orders of magnitude less than the exchange between nearest neighbours, the dipole–dipole coupling is both highly anisotropic and extremely long-ranged, and may therefore have important effects on both magnetic structures and excitations. Apart from this example, the anisotropic two-ion couplings are even more difficult to calculate than are the isotropic components, so the strategy which has generally been adopted to investigate them is to assume that all terms in (1.2.21) which are not forbidden by symmetry are present, to calculate their influence on the magnetic properties, and to determine their magnitude by judicious experiments.

The *hyperfine interaction* between the $4f$ moment and the nuclear spin $\mathbf{I}$ may be written

$$\mathcal{H}_{\mathrm{hf}} = A\sum_{i} \mathbf{I}_i \cdot \mathbf{J}_i. \tag{1.2.24}$$

Since A is typically of the order of micro-electron-volts, the coupling to the nuclei normally has a negligible effect on the electronic magnetism in the rare earth metals, but it has a decisive influence on the low-temperature magnetic ordering in for instance Pr.

1.3 The dipole–dipole interaction

A general two-ion Hamiltonian involving only the dipolar moments of the $4f$ electrons is

$$\mathcal{H}_{\mathrm{dd}} = -\frac{1}{2}\sum_{ij}\sum_{\alpha\beta} \mathcal{J}_{\alpha\beta}(ij) J_{i\alpha} J_{j\beta}. \tag{1.3.1}$$

The Heisenberg interaction, when expressed in this way, is diagonal, with the form $\mathcal{J}(ij)\delta_{\alpha\beta}$. The most familiar example of an *anisotropic* two-ion coupling is the classical magnetic dipole–dipole interaction, which gives a contribution

$$\Delta\mathcal{J}_{\alpha\beta}(ij) = \frac{N}{V}(g\mu_B)^2 D_{\alpha\beta}(ij), \tag{1.3.2a}$$

where $D_{\alpha\beta}(ij)$ is the dimensionless coupling parameter

$$D_{\alpha\beta}(ij) = \frac{V}{N}\frac{3(R_{i\alpha}-R_{j\alpha})(R_{i\beta}-R_{j\beta}) - \delta_{\alpha\beta}|\mathbf{R}_i-\mathbf{R}_j|^2}{|\mathbf{R}_i-\mathbf{R}_j|^5}, \tag{1.3.2b}$$

recalling that the magnetic moment of the ith ion is $g\mu_B\mathbf{J}_i$. This coupling is weak, being typically one or two orders of magnitude smaller than the indirect exchange between near neighbours, but it is extremely long-range and anisotropic and may therefore have important consequences for the magnetic properties, as we shall discuss in the following.

We wish to calculate the spatial Fourier transform

$$D_{\alpha\beta}(\mathbf{q}) = \frac{1}{N}\sum_i\sum_j D_{\alpha\beta}(ij)\, e^{-i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}. \tag{1.3.3}$$

If $\mathbf{q}$ is along the c-axis, which is a three-fold axis of the hcp lattice, the symmetry dictates that the only non-zero elements of $\mathcal{J}_{\alpha\beta}(\mathbf{q})$ are $\mathcal{J}_{\xi\xi}(\mathbf{q}) = \mathcal{J}_{\eta\eta}(\mathbf{q})$ and $\mathcal{J}_{\zeta\zeta}(\mathbf{q})$. In addition, the condition $\sum_\alpha D_{\alpha\alpha}(\mathbf{q}) = 0$ implies that

$$D_{\zeta\zeta}(\mathbf{q}) = -2D_{\xi\xi}(\mathbf{q}) = -2D_{\eta\eta}(\mathbf{q}) \qquad ; \quad \mathbf{q} \parallel c-\text{axis}, \tag{1.3.4}$$

with the extra stipulation that $\mathbf{q} \neq \mathbf{0}$, in which case the surface of the sample does not contribute. In the limit of long wavelengths, the shape of the sample becomes important, and for convenience we assume it to be an ellipsoid, with the principal axes along the symmetry ξ-, η-, and ζ-axes. We consider first the limit $\mathbf{q} = \mathbf{0}$ where, because the sample is an ellipsoid, the summation over j in (1.3.3) leads to a result independent of i, since an ellipsoid placed in a constant magnetic field has a uniform magnetization throughout its interior. Furthermore, when $\mathbf{r} = \mathbf{R}_i - \mathbf{R}_j$ becomes large, it may be replaced by a continuous variable, and the sum over j may be split into a sum over the lattice points lying within a large sphere plus an integral over the rest of the sample:

$$\sum_j \cdots = \sum_{j\in\text{sphere}} \cdots + \frac{N}{V}\int_{\text{sphere}}^{\text{sample}} \cdots d\mathbf{r}.$$

The value of the integral for the zz-component is

$$\int \frac{1}{r^3}\big(\frac{3z^2}{r^2} - 1\big)d\mathbf{r} = -\int \nabla\cdot\Big(\frac{\mathbf{z}}{r^3}\Big)d\mathbf{r} = \int_{\text{sphere}} \frac{\mathbf{z}\cdot d\mathbf{S}}{r^3} - \int_{\text{sample}} \frac{\mathbf{z}\cdot d\mathbf{S}}{r^3} = \frac{4\pi}{3} - N_z,$$

where $d\mathbf{S}$ is a vectorial surface element of the sphere/sample, and N_ξ is the *demagnetization factor*

$$N_\xi = \int_{\text{sample}} \frac{\hat{\boldsymbol{\xi}}\cdot d\mathbf{S}}{r^2}, \tag{1.3.5}$$

where $\hat{\boldsymbol{\xi}}$ is a unit vector along the ξ-axis. It is easily seen that $N_\xi + N_\eta + N_\zeta = 4\pi$. Hence we obtain

$$D_{\xi\xi}(\mathbf{0}) = \frac{4\pi}{3} + \big[D_{\xi\xi}(\mathbf{0})\big]_L - N_\xi, \tag{1.3.6}$$

plus equivalent results for the other diagonal components. The first term is the *Lorentz factor*, and $\big[D_{\xi\xi}(\mathbf{0})\big]_L$ is the value of the lattice sum over the sphere, satisfying the relations $\big[D_{\zeta\zeta}(\mathbf{0})\big]_L = -2\big[D_{\xi\xi}(\mathbf{0})\big]_L = -2\big[D_{\eta\eta}(\mathbf{0})\big]_L$. In the case of a cubic lattice, the lattice sums vanish by symmetry. This is also true for an hcp lattice with an ideal c/a-ratio, because of the close relationship between the fcc lattice and the ideal hcp lattice. The hcp lattice of the heavy rare earths is slightly distorted, as may be seen from Table 1.2, in which case the lattice sums become non-zero, approximately proportionally to the deviation from the ideal c/a-ratio; $\big[D_{\xi\xi}(\mathbf{0})\big]_L = 1.50\big(c/a - \sqrt{8/3}\,\big)$. Brooks and Goodings (1968) overestimate the anisotropy in the free energy due to the dipole interaction by a factor of two.

When considering the lattice sum determining $D_{\alpha\beta}(\mathbf{q}) - D_{\alpha\beta}(\mathbf{0})$, we may immediately apply the continuum approximation in the long-wavelength limit $2\pi/q \gg a$, and replace the sum with the corresponding integral. In the calculation above at $\mathbf{q} = \mathbf{0}$, this approximation is not directly applicable, because the corresponding integral contains a divergence at the origin, which is however removed in the difference $D_{\alpha\beta}(\mathbf{q}) - D_{\alpha\beta}(\mathbf{0})$. In addition to the condition $q \ll 2\pi/a$, we shall assume that $q \gg 2\pi/L$, or more specifically $q \geq 10/L$ (Keffer 1966), where L is a length dimension of the crystal, in which case the effects of the boundaries on $D_{\alpha\beta}(\mathbf{q})$ are averaged out because of the relatively rapid variation of the exponential factor on the surface. Using these two conditions, we find

$$\begin{aligned} D_{\alpha\beta}(\mathbf{q}) &= D_{\alpha\beta}(\mathbf{0}) + \int \frac{3(\hat{\boldsymbol{\alpha}}\cdot\mathbf{r})(\hat{\boldsymbol{\beta}}\cdot\mathbf{r}) - \delta_{\alpha\beta}\, r^2}{r^5}\big(e^{i\mathbf{q}\cdot\mathbf{r}} - 1\big)d\mathbf{r} \\ &= \big[D_{\alpha\beta}(\mathbf{0})\big]_L + \iint \frac{3(\hat{\boldsymbol{\alpha}}\cdot\mathbf{r})(\hat{\boldsymbol{\beta}}\cdot\mathbf{r}) - \delta_{\alpha\beta} r^2}{r^5}\Big[\sum_{l=0}^{\infty}\,[4\pi(2l+1)]^{1/2}\, i^l\, j_l(qr)Y_{l0}(\theta,\phi)\Big]r^2 dr d\Omega. \end{aligned}$$

The $\mathbf{q}$-independent term in the first integral leads to the same result as in (1.3.6), but without the lattice-sum contribution, and adding $D_{\alpha\beta}(\mathbf{0})$, we are left with the term $\big[D_{\alpha\beta}(\mathbf{0})\big]_L$. The $\mathbf{q}$-dependent exponential is expanded in terms of the spherical Bessel functions, as in (4.1.8), with the polar axis chosen to be parallel to $\mathbf{q}$. The dipole factor in the resulting integral may be written as a linear combination of the spherical harmonics of second rank $Y_{2m}(\theta,\phi)$, multiplied by r^{-3}, ensuring that only the term with $l = 2$ in the sum over l survives the integration over solid angles. Further, if $\hat{\boldsymbol{\alpha}}$ and $\hat{\boldsymbol{\beta}}$ are either parallel or perpendicular to $\mathbf{q}$, only the diagonal components may differ from zero. With $\hat{\boldsymbol{\alpha}}$ and $\hat{\boldsymbol{\beta}}$ both parallel to $\mathbf{q}$, the longitudinal component is

$$\begin{aligned} D_{\parallel}(\mathbf{q}) - \big[D_{\parallel}(\mathbf{0})\big]_L &= \iint [16\pi/5]^{1/2} Y_{20}(\theta,\phi) r^{-3} [4\pi\cdot 5]^{1/2}(-1) j_2(qr) Y_{20}(\theta,\phi) r^2 dr d\Omega \\ &= -8\pi\int_0^\infty \frac{1}{\rho} j_2(\rho)d\rho = -8\pi\Big[-\frac{j_1(\rho)}{\rho}\Big]_0^\infty = -\frac{8\pi}{3}, \end{aligned} \tag{1.3.7}$$

recalling that $j_1(\rho)/\rho \to \frac{1}{3}$ or 0, for respectively $\rho \to 0$ or ∞. This result implies that the two transverse components are

$$D_{\perp}(\mathbf{q}) - \big[D_{\perp}(\mathbf{0})\big]_L = -\tfrac{1}{2}\big\{D_{\parallel}(\mathbf{q}) - \big[D_{\parallel}(\mathbf{0})\big]_L\big\} = \frac{4\pi}{3}; \tag{1.3.8}$$

when $2\pi/L \ll q \ll 2\pi/a$. The dipole-coupling components change from the values given by (1.3.6) to those above within a very narrow range of q, i.e. when q goes from zero to about $10/L$, as shown by the detailed analysis of Keffer (1966). At larger wave-vectors, the variation of $D_{\alpha\beta}(\mathbf{q})$ is smooth and gradual, and it may be described by a few interplanar coupling parameters of the type used for other two-ion interactions. Cohen and Keffer (1955) have calculated the $\mathbf{q}$-dependence for the three cubic Bravais lattices, and their results also determine $D_{\alpha\beta}(\mathbf{q})$, with $\mathbf{q}$ along the c-axis, in the hcp lattice with the ideal c/a-ratio, since this is equivalent to $\mathbf{q}$ along a (111)-direction in the fcc crystal. In the distorted case, with $c/a = 0.963\sqrt{8/3}$ (corresponding to Ho), a numerical calculation gives

$$D_{\xi\xi}(\mathbf{q}) + 0.0216\frac{4\pi}{3} = \left\{0.9185 + 0.0815\cos{(qc/2)} - 0.0006\cos{(qc)}\right\}\frac{4\pi}{3}$$

when $\mathbf{q} \parallel c$-axis and $q \geq 10/L$, so that the $\mathbf{q}$-dependence in the c-direction is very weak, except for the jump at small $\mathbf{q}$, which is illustrated for the example of Ho in Fig. 1.6.

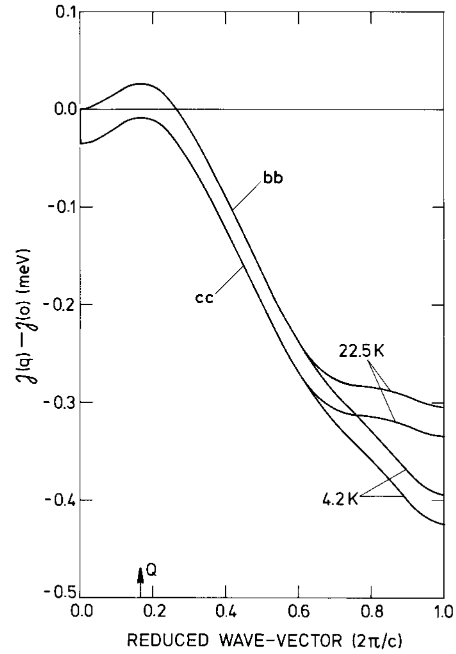

Fig. 1.6. Parallel and perpendicular components of the Fourier transform, for $\mathbf{q}$ along the c-direction, of the two-ion coupling in Ho, deduced from the spin-wave energies. The coupling is assumed to comprise an isotropic indirect-exchange contribution and the classical dipole–dipole interaction, which gives rise to the discontinuity at $\mathbf{q} = \mathbf{0}$ in the parallel component, and stabilizes the cone structure at low temperatures.

In a uniform ferromagnet, the demagnetization factor leads to a positive contribution to the internal energy. Without any external applied field, it is therefore energetically favourable for the system to split up in *domains*, in which the magnetization vector points in different directions, so that the magnetization almost vanishes at the surface. The greater the number of domains, the more effectively the demagnetization contribution may be eliminated, but this tendency is opposed by the cost in energy of the *domain-walls.* It is only the contribution due to the demagnetization factor (as determined by the magnetization at the surface) which is affected by the creation of domains, and in a simple model in which the energy of the domain-walls is neglected, the internal energy per unit volume, due to the dipole coupling and including the Zeeman energy, is

$$U_D + U_Z \simeq -\tfrac{1}{2} D^{\rm eff}_{zz}(\mathbf{0}) M^2 + \tfrac{1}{2} N_z \langle M \rangle^2 - H_A \langle M \rangle .$$

The demagnetization factor is considered separately, so that $D^{\rm eff}_{zz}(\mathbf{0}) = 4\pi/3 + \big[D_{zz}(\mathbf{0}) \big]_L$, and H_A is the field applied in the z-direction. M is the magnetization,

$$M = \frac{N}{V} g \mu_B \langle J_z \rangle \tag{1.3.9}$$

in each domain, whereas $\langle M \rangle$ is the magnetization averaged over the whole crystal. If the *internal field* H_I and the *demagnetization field* H_D are defined by

$$H_I = H_A - H_D \qquad ; \qquad H_D = N_z \langle M \rangle , \tag{1.3.10}$$

the energy is minimized by the conditions; $H_I = 0$ when $\langle M \rangle < M$, and $\langle M \rangle = M$ when $H_I > 0$. As a function of H_I, the magnetization jumps from zero to its ‘saturation’ value at $H_I = 0$.

2

MAGNETIC STRUCTURES

2.1 Mean-field theory of magnetic ordering

The simplest form of Hamiltonian which is adequate to explain the occurrence of most of the observed magnetic structures is

$$\mathcal{H} = \sum_i \mathcal{H}_{\rm cf}(i) - \frac{1}{2}\sum_{ij} \mathcal{J}(ij)\, \mathbf{J}_i \cdot \mathbf{J}_j + \mathcal{H}_{\rm Z}, \tag{2.1.1a}$$

where the first sum is the single-ion crystal-field Hamiltonian (in the case of a hcp lattice)

$$\mathcal{H}_{\rm cf}(i) = \sum_{l=2,4,6} B_l^0 O_l^0(\mathbf{J}_i) + B_6^6 O_6^6(\mathbf{J}_i), \tag{2.1.1b}$$

the two-ion term is assumed to be isotropic, and the Zeeman term is

$$\mathcal{H}_{\rm Z} = -\sum_i \boldsymbol{\mu}_i \cdot \mathbf{H}_i. \tag{2.1.1c}$$

The field may vary spatially, so that we must specify its value on each site, writing $\mathbf{H}_i \equiv \mathbf{H}(\mathbf{R}_i)$, and the magnetic moment on the ith ion is $\boldsymbol{\mu}_i = g\mu_B \mathbf{J}_i$.

The static-susceptibility tensor may be derived as the second derivative of the free energy, and we shall therefore begin by recapitulating a few basic thermodynamic results. The free energy is

$$F = U - TS = -\frac{1}{\beta}\ln Z, \tag{2.1.2}$$

where U is the internal energy, S the entropy, and $\beta = (k_B T)^{-1}$. The partition function is

$$Z = {\rm Tr}\{e^{-\beta\mathcal{H}}\} = \sum_p e^{-\beta E_p}. \tag{2.1.3}$$

Tr indicates the trace over a complete set of states, and the final summation may be performed if the eigenvalues E_p of the Hamiltonian are known. The expectation value of an operator A is

$$\langle A \rangle = \frac{1}{Z}{\rm Tr}\{A e^{-\beta\mathcal{H}}\}. \tag{2.1.4}$$

The derivative of the free energy with respect to a variable x is

$$\frac{\partial F}{\partial x} = -\frac{1}{\beta Z}\frac{\partial Z}{\partial x} = \frac{1}{Z}{\rm Tr}\Big\{\frac{\partial \mathcal{H}}{\partial x} e^{-\beta\mathcal{H}}\Big\} = \Big\langle \frac{\partial \mathcal{H}}{\partial x}\Big\rangle. \tag{2.1.5}$$

This expression is obtained by utilizing the invariance of the trace to the basis used, assuming it to be independent of x and a cyclic permutation of the operators, thus allowing a conventional differentiation of the exponential operator, as may be seen by a Taylor expansion. This result is general, but the exponential operator can only be treated in this simple way in second derivatives if $\partial\mathcal{H}/\partial x$ commutes with the Hamiltonian, which is usually not the case. However, we may be interested only in the leading-order contributions in the limit where β is small, i.e. at *high temperatures.* Expanding in powers of β, we may use the approximation $\exp\{-\beta\mathcal{H}\} \simeq 1-\beta\mathcal{H}+\frac{1}{2}\beta^2\mathcal{H}^2$. In this case, we may proceed as above, and the result is

$$\begin{aligned}\frac{\partial^2 F}{\partial x\partial y} = \Big\langle\frac{\partial^2\mathcal{H}}{\partial x\partial y}\Big\rangle + \beta\Big(\Big\langle\frac{\partial\mathcal{H}}{\partial x}\Big\rangle\Big\langle\frac{\partial\mathcal{H}}{\partial y}\Big\rangle - \Big\langle\frac{\partial\mathcal{H}}{\partial x}\frac{\partial\mathcal{H}}{\partial y}\Big\rangle\Big)\\ -\frac{\beta^2}{2}\Big\langle\Big[\frac{\partial\mathcal{H}}{\partial x},\frac{\partial\mathcal{H}}{\partial y}\Big]\mathcal{H}\Big\rangle + \mathcal{O}(\beta^3),\end{aligned} \tag{2.1.6}$$

where the second- and higher-order terms vanish if one of the derivatives of $\mathcal{H}$ commutes with $\mathcal{H}$ itself.

In many instances, it is more convenient to consider the angular momentum rather than the magnetic moment, with a corresponding field variable $\mathbf{h}_i = g\mu_B\mathbf{H}_i$, so that the Zeeman term (2.1.1*c*) becomes

$$\mathcal{H}_{\mathrm{Z}} = -\sum_i \boldsymbol{\mu}_i\cdot\mathbf{H}_i = -\sum_i \mathbf{J}_i\cdot\mathbf{h}_i. \tag{2.1.7}$$

Since the exchange and anisotropy terms in $\mathcal{H}$ do not depend explicitly on the field, $\partial\mathcal{H}/\partial H_{i\alpha} = -\mu_{i\alpha}$ and, using eqn (2.1.5), we have

$$\langle\mu_{i\alpha}\rangle = -\partial F/\partial H_{i\alpha} \quad \text{or} \quad \langle J_{i\alpha}\rangle = -\partial F/\partial h_{i\alpha}. \tag{2.1.8}$$

Next, we define the non-local susceptibilities

$$\chi^{\mu}_{\alpha\beta}(ij) = \partial\langle\mu_i\rangle/\partial H_{j\beta} = -\partial^2F/\partial H_{i\alpha}\partial H_{j\beta}, \tag{2.1.9a}$$

and similarly

$$\chi^{\mathbf{J}}_{\alpha\beta}(ij) = (g\mu_B)^{-2}\chi^{\mu}_{\alpha\beta}(ij) = -\partial^2F/\partial h_{i\alpha}\partial h_{j\beta}, \tag{2.1.9b}$$

and the corresponding Fourier transforms, e.g.

$$\chi^{\mathbf{J}}_{\alpha\beta}(\mathbf{q}) = \frac{1}{N}\sum_{ij}\chi^{\mathbf{J}}_{\alpha\beta}(ij)e^{-i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)} = \sum_j \chi^{\mathbf{J}}_{\alpha\beta}(ij)e^{-i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}. \tag{2.1.9c}$$

The final equality only applies in a uniform system. If the field is increased by an infinitesimal amount $\delta\mathbf{H}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{R}_i)$, the individual moments are changed by

$$\delta\langle\mu_{i\alpha}\rangle = \sum_j\sum_\beta \chi^{\mu}_{\alpha\beta}(ij)\delta H_\beta(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_j}, \tag{2.1.10a}$$

according to (2.1.9). Hence the added harmonically-varying field introduces one Fourier component in the magnetization:

$$\delta M_\alpha(\mathbf{q}) = \frac{1}{V}\sum_i \delta\langle\mu_{i\alpha}\rangle e^{-i\mathbf{q}\cdot\mathbf{R}_i} = \frac{N}{V}\sum_\beta \chi^{\mu}_{\alpha\beta}(\mathbf{q})\delta H_\beta(\mathbf{q}), \tag{2.1.10b}$$

proportional to the susceptibility at the wave-vector considered. The usual definition of the susceptibility components (per unit volume), as used in Section 1, (1.1.22), is $\delta M_\alpha(\mathbf{q})/\delta H_\beta(\mathbf{q})$. The susceptibility used in (2.1.10*b*) differs from this by the factor

V/N, i.e. we are here considering the susceptibility per atom instead of per unit volume. Furthermore, since we shall not make any further use of $\chi^{\mu}_{\alpha\beta}(\mathbf{q})$, we shall reserve the notation $\chi_{\alpha\beta}(\mathbf{q})$ for the **q**-dependent susceptibility $\chi^{\mathbf{J}}_{\alpha\beta}(\mathbf{q})$, introduced in eqn (2.1.9*b*), throughout the rest of the book. So in terms of the susceptibility per atom, 'in units of $(g\mu_B)^2$', the above equation may be written

$$\delta\langle J_\alpha(\mathbf{q})\rangle = \frac{1}{N}\sum_i \delta\langle J_{i\alpha}\rangle e^{-i\mathbf{q}\cdot\mathbf{R}_i} = \sum_\beta \chi_{\alpha\beta}(\mathbf{q})\delta h_\beta(\mathbf{q}), \tag{2.1.10c}$$

with the upper index **J** in $\chi^{\mathbf{J}}_{\alpha\beta}(\mathbf{q})$ being suppressed from now on.

2.1.1 The high-temperature susceptibility

In order to calculate $\overline{\overline{\chi}}(\mathbf{q})$ in zero field, we shall first use the approximation (2.1.6) to the derivative of the free energy, valid at high temperatures. In this limit $\langle \mathbf{J}_i\rangle = \mathbf{0}$, and only one term in the expansion is non-zero:

$$\chi_{\alpha\beta}(ij) = \beta\mathrm{Tr}\big\{J_{i\alpha}J_{j\beta}(1-\beta\mathcal{H})\big\}/\mathrm{Tr}\big\{1-\beta\mathcal{H}\big\}, \tag{2.1.11}$$

to second order in β. The commutator in the third term on the right-hand side of (2.1.6) is either zero or purely imaginary (if $i=j$ and $\alpha\neq\beta$), showing immediately that the expectation value of this term must vanish in all cases. To first order in β, we obtain from (2.1.11)

$$\chi_{\alpha\beta}(ij) \simeq \beta\mathrm{Tr}\big\{J_{i\alpha}J_{j\beta}\big\}/\mathrm{Tr}\big\{1\big\} = \tfrac{1}{3}J(J+1)\beta\delta_{\alpha\beta}\delta_{ij}\,,$$

using the product of the eigenvectors of $J_{i\alpha}$ as the basis, and recalling that

$$\sum m^2 = \tfrac{1}{3}J(J+1)(2J+1),$$

when m runs from $-J$ to J. In order to calculate the second-order contribution, we shall utilize the general tensor properties of the Stevens operators, which satisfy the orthogonality condition:

$$\begin{aligned} &\mathrm{Tr}\big\{O_l^m(\mathbf{J}_i)O_{l'}^{m'}(\mathbf{J}_j)\big\} = \delta_{ij}\delta_{ll'}\delta_{mm'}\mathrm{Tr}\big\{[O_l^m(\mathbf{J}_i)]^2\big\}\\ \text{and}\qquad &\mathrm{Tr}\big\{O_l^m(\mathbf{J}_i)\big\} = 0, \end{aligned} \tag{2.1.12}$$

when l and l' are both non-zero. O_0^0 is just the identity operator. $J_{i\alpha}$ is a linear combination of $O_1^m(\mathbf{J}_i)$, $m=-1,0,1$, and (2.1.12) then implies that the trace of the Hamiltonian (2.1.1) vanishes, and hence that the denominator in (2.1.11) is $\mathrm{Tr}\{1\} = (2J+1)^N$. For the second-order term in the numerator, we find

$$\begin{aligned}\mathrm{Tr}\big\{J_{i\alpha}J_{j\beta}\mathcal{H}\big\} &= \delta_{ij}B_2^0\mathrm{Tr}\big\{J_{i\alpha}J_{i\beta}O_2^0(\mathbf{J}_i)\big\} - \mathcal{J}(ij)\mathrm{Tr}\big\{J_{i\alpha}J_{j\beta}\mathbf{J}_i\cdot\mathbf{J}_j\big\}\\ &= \delta_{ij}\delta_{\alpha\beta}B_2^0\mathrm{Tr}\big\{J_{i\alpha}^2[3J_{iz}^2 - J(J+1)]\big\} - \delta_{\alpha\beta}\mathcal{J}(ij)\mathrm{Tr}\big\{J_{i\alpha}^2J_{j\alpha}^2\big\},\end{aligned}$$

utilizing that $J_{i\alpha}J_{j\beta}$ is a linear combination of second- and lower-rank tensors for $i=j$, and a product of first-rank tensors for $i\neq j$. When $\alpha = z$ (or ζ), we may readily calculate the first trace, using

$$\sum m^4 = \tfrac{1}{15}J(J+1)(2J+1)(3J^2+3J-1).$$

The traces with $\alpha = x$ or $\alpha = y$ must be equal, and using this equality in the case $\alpha = x$, for instance, we may replace J_x^2 in the trace by $\frac{1}{2}(J_x^2 + J_y^2) \rightarrow \frac{1}{2}J(J+1) - \frac{1}{2}J_z^2$. As the constant term multiplied by $3J_z^2 - J(J+1)$ does not contribute (as $\mathrm{Tr}\{3J_z^2 - J(J+1)\} = 0$), the trace with $\alpha = x$ or y is equal to $-1/2$ times that with $\alpha = z$. Only the single-ion terms contribute to the trace when $i = j$ ($\mathcal{J}(ii)$ is assumed to be zero), and of these only the lowest-rank term B_2^0 appears, to leading order. The two-ion coupling only occurs in the trace, and hence in $\chi_{\alpha\beta}(ij)$, when $i \neq j$, and this contribution may be straightforwardly calculated. To second order in β, the off-diagonal terms are zero, whereas

$$\chi_{\alpha\alpha}(ij) = \delta_{ij}\tfrac{1}{3}J(J+1)\beta\big[1 - \tfrac{2}{5}(3\delta_{\alpha\zeta} - 1)B_2^0(J-\tfrac{1}{2})(J+\tfrac{3}{2})\beta\big] + \big[\tfrac{1}{3}J(J+1)\beta\big]^2\mathcal{J}(ij).$$

Introducing the Fourier transform of the two-ion coupling,

$$\mathcal{J}(\mathbf{q}) = \sum_j \mathcal{J}(ij)e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)}, \tag{2.1.13}$$

we find that, to the order considered, the inverse of the $\mathbf{q}$-dependent susceptibility may be written

$$1/\chi_{\alpha\alpha}(\mathbf{q}) = \frac{3k_BT}{J(J+1)} + (3\delta_{\alpha\zeta} - 1)\frac{6(J-\frac{1}{2})(J+\frac{3}{2})}{5J(J+1)}B_2^0 - \mathcal{J}(\mathbf{q}) + \mathcal{O}(1/T). \tag{2.1.14}$$

The inverse susceptibility in the high-temperature limit thus increases linearly with the temperature, with a slope inversely proportional to the square of the effective paramagnetic moment ($\propto \{J(J+1)\}^{1/2}$). The susceptibilities determined experimentally by magnetization measurements are the bulk values at zero wave-vector. The straight lines found at high temperatures for the inverse-susceptibility components $1/\chi_{\alpha\alpha}(\mathbf{0})$ versus temperature may be extrapolated to lower values, as illustrated in Fig. 2.1. The values at which these lines cross the temperature axis are the *paramagnetic Curie temperatures* $\theta_\parallel$ and $\theta_\perp$, determined respectively when the field is parallel and perpendicular to the c-axis (ζ-axis). The high-temperature expansion then predicts these temperatures to be

$$k_B\theta_\parallel = \tfrac{1}{3}J(J+1)\mathcal{J}(\mathbf{0}) - \tfrac{4}{5}(J-\tfrac{1}{2})(J+\tfrac{3}{2})B_2^0, \tag{2.1.15a}$$

and

$$k_B\theta_\perp = \tfrac{1}{3}J(J+1)\mathcal{J}(\mathbf{0}) + \tfrac{2}{5}(J-\tfrac{1}{2})(J+\tfrac{3}{2})B_2^0. \tag{2.1.15b}$$

Hence the paramagnetic Curie temperatures are determined by the lowest-rank interactions in the Hamiltonian, i.e. those terms for which $l+l' = 2$. The difference between the two temperatures depends only on B_2^0, because of the assumption that the two-ion coupling is an *isotropic* Heisenberg exchange. The mean temperature $(\theta_\parallel + 2\theta_\perp)/3$ is determined by $\mathcal{J}(\mathbf{0})$ which, from (2.1.13), is the algebraic sum of the isotropic two-ion interactions, and this temperature may be measured directly with a polycrystalline sample. The two basal-plane components are found to be equal. This is not just due to the assumption of high temperatures, but is generally valid as long as there is no ordered moment in the basal-plane. In this case, the c-axis is a three-fold symmetry axis, or effectively a six-fold axis, due to the symmetry of the basal-plane anisotropy B_6^6 in the

Hamiltonian. The susceptibility is a second-rank tensor, according to (2.1.9), and it cannot therefore vary under rotation about a three- or six-fold axis.

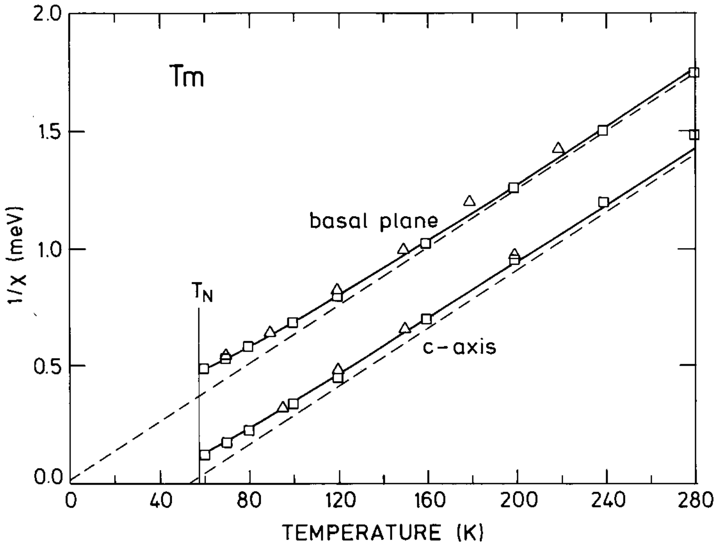

Fig. 2.1. The inverse susceptibility, in atomic units, in Tm above T_N. The full lines depict the results of a mean-field calculation and the dashed lines are extrapolations of the high-temperature limit. Experimental values are also shown. The MF theory predicts a deviation from the high-temperature expression as the ordering temperature is approached from above, because of crystal-field anisotropy effects.

2.1.2 The mean-field approximation

The high-temperature expansion may be extended to higher order in β, but the calculations rapidly become more complex, so we shall instead adopt another approach, the mean-field approximation. In this method, the correlated fluctuations of the moments around their equilibrium values are neglected. In order to introduce $\langle \mathbf{J}_i \rangle$ into the Hamiltonian, we utilize the identity

$$\mathbf{J}_i \cdot \mathbf{J}_j = (\mathbf{J}_i - \langle \mathbf{J}_i \rangle) \cdot (\mathbf{J}_j - \langle \mathbf{J}_j \rangle) + \mathbf{J}_i \cdot \langle \mathbf{J}_j \rangle + \mathbf{J}_j \cdot \langle \mathbf{J}_i \rangle - \langle \mathbf{J}_i \rangle \cdot \langle \mathbf{J}_j \rangle.$$

The MF approximation then consists in neglecting the first term on the right-hand side, which is associated with two-site fluctuations, since $i \neq j$. The Hamiltonian (2.1.1) is then effectively decoupled into a sum of N independent terms for the single sites; $\mathcal{H} \simeq \sum_i \mathcal{H}_{\mathrm{MF}}(i)$, where

$$\mathcal{H}_{\mathrm{MF}}(i) = \mathcal{H}_{\mathrm{cf}}(i) - \mathbf{J}_i \cdot \mathbf{h}_i - \big(\mathbf{J}_i - \tfrac{1}{2}\langle \mathbf{J}_i \rangle\big) \cdot \sum_j \mathcal{J}(ij) \langle \mathbf{J}_j \rangle, \qquad (2.1.16)$$

in the presence of an external magnetic field $\mathbf{h}_i = g\mu_B \mathbf{H}_i$. Introducing the effective field

$$\mathbf{h}_i^{\mathrm{eff}} = \mathbf{h}_i + \sum_j \mathcal{J}(ij) \langle \mathbf{J}_j \rangle, \qquad (2.1.17a)$$

we may write the MF Hamiltonian

$$\mathcal{H}_{\mathrm{MF}}(i) = \mathcal{H}_{\mathrm{cf}}(i) - \mathbf{J}_i \cdot \mathbf{h}_i^{\mathrm{eff}} + \tfrac{1}{2}\langle \mathbf{J}_i \rangle \cdot (\mathbf{h}_i^{\mathrm{eff}} - \mathbf{h}_i). \qquad (2.1.17b)$$

Self-consistent solutions of the MF equations may sometimes be obtained analytically, but numerical methods may be used more generally, provided that the periodicity of the magnetic structure is commensurable with that of the lattice. For an assumed distribution of $\langle \mathbf{J}_j \rangle$, the effective field and hence the MF Hamiltonian for the ith site is calculated. Diagonalizing this Hamiltonian, we may derive the partition function Z_i, the free energy F_i, and the expectation value $\langle \mathbf{J}_i \rangle$ for this site. The last term in (2.1.17b) just adds a constant contribution to F_i, without affecting $\langle \mathbf{J}_i \rangle$. Performing this calculation for all the different ions, we determine the various values of $\langle \mathbf{J}_j \rangle$, and the total free energy is the sum of the F_i. The derived values of $\langle \mathbf{J}_j \rangle$ are used as the input for a new MF Hamiltonian, and this iterative procedure is repeated until self-consistency is attained. The self-consistent solution of the MF Hamiltonian may be one in which $\langle \mathbf{J}_i \rangle$ is non-zero even in zero field, thus describing the occurrence of a spontaneous ordering of the moments.

Having found the self-consistent solution for the angular momenta, we may proceed to calculate the susceptibility. The MF Hamiltonian for the ith site has been diagonalized, and we shall denote the $(2J+1)$ eigenstates by $|\, p >$, with corresponding energy eigenvalues E_p. If the effective field is changed by a small amount $\delta h_\beta^{\mathrm{eff}}$, the Zeeman term $-J_{i\beta}\delta h_\beta^{\mathrm{eff}}$ must be added to the Hamiltonian, and $E_p^{(1)} = E_p - < p \,|\, J_{i\beta} \,|\, p > \delta h_\beta^{\mathrm{eff}}$, to first order in the perturbation, provided that $|\, p >$ is a set which diagonalizes the perturbation within the possibly degenerate subspaces of the zero-field Hamiltonian. The new eigenstates are

$$|\, p^{(1)} > = |\, p > - \delta h_\beta^{\mathrm{eff}} {\sum_{p'}}' |\, p' >< p' \,|\, J_{i\beta} \,|\, p > /(E_p - E_{p'}),$$

where the terms for which $E_p = E_{p'}$ vanish. Using (2.1.3) and (2.1.4), we then have, to first order in $\delta h_\beta^{\mathrm{eff}}$,

$$\begin{aligned}\langle J_{i\alpha}^{(1)} \rangle = \sum_p < p^{(1)} \,|\, J_{i\alpha} \,|\, p^{(1)} > n_p^{(1)} &= \sum_p < p \,|\, J_{i\alpha} \,|\, p > n_p^{(1)} \\ &- \delta h_\beta^{\mathrm{eff}} {\sum_{pp'}}' < p \,|\, J_{i\alpha} \,|\, p' >< p' \,|\, J_{i\beta} \,|\, p > n_p/(E_p - E_{p'}) \\ &- \delta h_\beta^{\mathrm{eff}} {\sum_{pp'}}' < p \,|\, J_{i\beta} \,|\, p' >< p' \,|\, J_{i\alpha} \,|\, p > n_p/(E_p - E_{p'}),\end{aligned}$$

where the last two sums extend over states for which $E_p \neq E_{p'}$. The population factor of the pth level at $\delta h_\beta^{\mathrm{eff}} = 0$ is $n_p = \exp(-\beta E_p)/Z_i$, and $n_p^{(1)}$ is the corresponding factor at the field $\delta h_\beta^{\mathrm{eff}}$. By differentiation, we find

$$\begin{aligned}\partial n_p^{(1)}/\partial(\delta h_\beta^{\mathrm{eff}}) &= \Big\{ < p \,|\, J_{i\beta} \,|\, p > - \sum_{p'} < p' \,|\, J_{i\beta} \,|\, p' > n_{p'} \Big\} \beta n_p \\ &= \Big\{ < p \,|\, J_{i\beta} \,|\, p > - \langle J_{i\beta} \rangle \Big\} \beta n_p.\end{aligned}$$

Introducing this result in the equation above, and interchanging p and p' in the last sum, we obtain finally:

$$\begin{aligned}\chi^o_{\alpha\beta}(i) = \partial\langle J_{i\alpha}\rangle/\partial h^{\text{eff}}_\beta = &\sum_{pp'}^{E_p\neq E_{p'}} \frac{<p\,|\,J_{i\alpha}\,|\,p'><p'\,|\,J_{i\beta}\,|\,p>}{E_{p'}-E_p}(n_p - n_{p'}) \\ &+ \beta \sum_{pp'}^{E_p=E_{p'}} <p\,|\,J_{i\alpha}\,|\,p'><p'\,|\,J_{i\beta}\,|\,p>\, n_p - \beta\langle J_{i\alpha}\rangle\langle J_{i\beta}\rangle.\end{aligned} \tag{2.1.18}$$

The second summation is transformed in such a way that it is no longer necessary for $J_{i\beta}$ to be diagonal within the degenerate subspaces, as required initially. The first term in the susceptibility is the *Van Vleck* contribution, which becomes constant at zero temperature, whereas the second term, the *Curie* contribution, diverges as $1/T$ in the low-temperature limit. The susceptibility deduced above is that determining the response due to a change of the *effective* field, $\delta\langle\mathbf{J}_i\rangle = \overline{\overline{\chi}}^{\,o}(i)\delta\mathbf{h}^{\text{eff}}_i$, whereas we wish to know the response due to a small change of the *external* field. If a small harmonically-varying field $\delta\mathbf{h}_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{R}_i)$ is applied, the effective field, according to (2.1.17*a*), is

$$\delta\mathbf{h}^{\text{eff}}_i = \delta\mathbf{h}_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{R}_i} + \sum_j \mathcal{J}(ij)\overline{\overline{\chi}}^{\,o}(j)\delta\mathbf{h}^{\text{eff}}_j.$$

This equation may be solved by a Fourier transformation if $\overline{\overline{\chi}}^{\,o}(i) = \overline{\overline{\chi}}^{\,o}$ is site-independent, which it is so long as $\langle\mathbf{J}_i\rangle$ is independent of i, as in the high-temperature paramagnetic phase, for example, where $\langle\mathbf{J}_i\rangle = \mathbf{0}$. Neglecting any site-dependence of $\overline{\overline{\chi}}^{\,o}$, and introducing the notation $\delta\mathbf{h}^{\text{eff}}_i = \delta\mathbf{h}^{\text{eff}}_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}_i)$, we get

$$\delta\mathbf{h}^{\text{eff}}_{\mathbf{q}} = \left\{1 - \overline{\overline{\chi}}^{\,o}\mathcal{J}(\mathbf{q})\right\}^{-1}\delta\mathbf{h}_{\mathbf{q}},$$

or, by the definition of the susceptibility,

$$\overline{\overline{\chi}}(\mathbf{q}) = \left\{1 - \overline{\overline{\chi}}^{\,o}\mathcal{J}(\mathbf{q})\right\}^{-1}\overline{\overline{\chi}}^{\,o}. \tag{2.1.19a}$$

In the following, we shall assume that the external magnetic field is zero. With this restriction, $\overline{\overline{\chi}}(\mathbf{q})$ is diagonal in the $(\xi\eta\zeta)$-coordinate system, and the reciprocal susceptibility, in the MF approximation, may be written

$$1/\chi_{\alpha\alpha}(\mathbf{q}) = 1/\chi^o_{\alpha\alpha} - \mathcal{J}(\mathbf{q}). \tag{2.1.19b}$$

In the degenerate case, (2.1.18) implies that $\chi^o_{\alpha\alpha} = \beta J(J+1)/3$. However, if $\mathcal{H}_{\text{cf}}$ is non-zero, the expression (2.1.18) for the susceptibility becomes quite complex. A drastic simplification is achieved by assuming a small value of β. In this high temperature limit, $\overline{\overline{\chi}}^{\,o}$ may be calculated by a procedure equivalent to that used in deriving (2.1.14), except that $\mathcal{J}(ij) = 0$. Hence, to second order in β, we have

$$\chi^o_{\alpha\alpha} \simeq \tfrac{1}{3}J(J+1)\beta\left[1 - \tfrac{2}{5}(3\delta_{\alpha\zeta} - 1)(J - \tfrac{1}{2})(J + \tfrac{3}{2})B^0_2\beta\right]. \tag{2.1.20}$$

Introducing (2.1.20) in (2.1.19), we obtain the same result as previously derived in (2.1.14), demonstrating that the MF approximation is correct in the high-temperature limit. Although the thermal fluctuations increase when the temperature is raised, they also become increasingly uncorrelated. It is the latter effect which is the most pronounced, and the correction to the MF value of the free energy, proportional to the correlation energy of the two-site fluctuations $\mathcal{J}(ij)\{\langle \mathbf{J}_i \cdot \mathbf{J}_j\rangle - \langle \mathbf{J}_i\rangle \cdot \langle \mathbf{J}_j\rangle\}$, decreases with temperature at high temperatures. In the other limit of zero temperature, the correlation effects are much stronger, but the fluctuations themselves are small. We may therefore also expect the MF approximation to be accurate in this limit, and to provide a useful interpolation at intermediate temperatures.

$\overline{\overline{\chi}}^o$ increases steadily with decreasing temperature. If the crystal-field ground state is degenerate, the second sum in (2.1.18) is non-zero and $\overline{\overline{\chi}}^o$ diverges in the zero-temperature limit. Because of the Kramers degeneracy, the ground state is always at least doubly degenerate if $2J$ is odd. When J is an integer, the ground state may be a singlet, in which case $\overline{\overline{\chi}}^o$ saturates at a constant value at zero temperature. Except in this special case, it is always possible to find a temperature where $1/\chi_{\alpha\alpha}(\mathbf{q})$ is zero, corresponding to an infinite $\chi_{\alpha\alpha}(\mathbf{q})$. The largest value of the $\mathbf{q}$-dependent susceptibility is found at the wave-vector $\mathbf{Q}$ at which $\mathcal{J}(\mathbf{q})$ has its maximum. Of the three non-zero components of $\overline{\overline{\chi}}(\mathbf{Q})$, the cc-component is the largest if B_2^0 is negative. If B_2^0 is positive, on the other hand, the two equal basal-plane components are the largest. It is the maximum component of the susceptibility at $\mathbf{q} = \mathbf{Q}$ which first diverges when the system is cooled. This divergence signals that the paramagnetic ground-state becomes unstable against the formation of an ordered state in which the moments are modulated with the wave-vector $\mathbf{Q}$, and point along or perpendicular to the c-direction, depending on whether B_2^0 is respectively negative or positive. Hence, a second-order phase transition takes place at this critical temperature, called the Curie temperature, T_C, or the Néel temperature, T_N, depending on whether $\mathbf{Q} = \mathbf{0}$ or $\mathbf{Q} \neq \mathbf{0}$. Just below T_N, the ordered moment $\langle \mathbf{J}_i\rangle$ is small, and the free energy of the ith ion may be expanded in powers of this moment. In order to establish this expansion, we first consider the Hamiltonian $\mathcal{H}'(i) = \mathcal{H}_{\rm cf}(i) - \mathbf{J}_i \cdot \mathbf{h}$. The corresponding free energy may be written

$$F_i' = F_0/N - \langle \mathbf{J}_i\rangle \cdot \mathbf{h} + \sum_\alpha A_\alpha \langle J_{i\alpha}\rangle^2 + \sum_{\alpha\beta} B_{\alpha\beta} \langle J_{i\alpha}\rangle^2 \langle J_{i\beta}\rangle^2 + \cdots .$$

Except for the field term, this expansion only includes products of components in which the sum of the exponents is even, because of time-reversal symmetry. Using the equilibrium condition $\partial F_i'/\partial\langle J_{i\alpha}\rangle = 0$, and recalling that $\langle J_{i\alpha}\rangle = \chi^o_{\alpha\alpha}(\sigma = 0)h_\alpha$ to leading order, in the zero-field limit, we obtain

$$A_\alpha = \left\{2\chi^o_{\alpha\alpha}(\sigma = 0)\right\}^{-1}, \tag{2.1.21a}$$

where $\chi^o_{\alpha\alpha}(\sigma = 0)$ is the MF susceptibility (2.1.18), in the limit of zero magnetization (field). The susceptibility decreases with increasing magnetization (or field), as described by the fourth-order terms. An order-of-magnitude estimate of $B_{\alpha\beta}$ may be obtained by neglecting $\mathcal{H}_{\rm cf}(i)$. In this case, the magnetization as a function of the field is given by the Brillouin function (1.2.31):

$$\langle J_{i\alpha}\rangle = JB_J(\beta J h_\alpha) \simeq \tfrac{1}{3}J(J+1)\beta h_\alpha \left\{1 - \tfrac{1}{15}(J^2 + J + \tfrac{1}{2})\beta^2 h_\alpha^2\right\},$$

which, in combination with the equilibrium condition for the free energy, determines $B_{\alpha\alpha}$. The off-diagonal terms may be obtained straightforwardly by utilizing the condition that, when $\mathcal{H}_{\rm cf}(i)$ is neglected, the free energy should be invariant with respect to any rotation of the magnetization vector, implying that all the coefficients $B_{\alpha\beta}$ are equal, or

$$B_{\alpha\beta} \approx \frac{9}{20}\frac{J^2+J+\frac{1}{2}}{J^3(J+1)^3}k_BT. \qquad (2.1.21b)$$

The introduction of the crystal-field terms of course modifies this result, but rather little in the high-temperature limit. Under all circumstances, the effective six-fold symmetry around the c-axis implies that $B_{\alpha\beta}$ is symmetric, $B_{\xi\xi} = B_{\eta\eta} = B_{\xi\eta}$, and $B_{\xi\zeta} = B_{\eta\zeta}$, and it also eliminates the possibility that any other fourth-order terms may contribute. The expansion of the free energy of the total system, when the external field is zero, is obtained from the expansion of F'_i, summed over i, by substituting the *exchange* field $\mathbf{h}_i^{\text{eff}} = \sum_j \mathcal{J}(ij)\langle\mathbf{J}_j\rangle$ for $\mathbf{h}$, and adding the 'constant' $\frac{1}{2}\langle\mathbf{J}_i\rangle\cdot\mathbf{h}_i^{\text{eff}}$, so that

$$F = F_0 - \frac{1}{2}\sum_{ij}\mathcal{J}(ij)\langle\mathbf{J}_i\rangle\cdot\langle\mathbf{J}_j\rangle + \sum_i\Big[\sum_\alpha A_\alpha\langle J_{i\alpha}\rangle^2 + \sum_{\alpha\beta}B_{\alpha\beta}\langle J_{i\alpha}\rangle^2\langle J_{i\beta}\rangle^2\Big] \qquad (2.1.22)$$

to fourth order in the magnetization. This expansion of the free energy in terms of the *order parameter(s)* is called the *Landau expansion.*

Assuming the ordered phase to be described by a single wave-vector, we may write

$$\langle J_{i\alpha}\rangle = J\sigma_\alpha\cos(\mathbf{q}\cdot\mathbf{R}_i + \varphi_\alpha), \qquad (2.1.23)$$

where $\sigma_\alpha = \sigma_\alpha(\mathbf{q})$ is the relative magnetization at the wave-vector $\mathbf{q}$. Introducing this into the free-energy expression, and utilizing the condition that $\sum_i\cos(\mathbf{q}'\cdot\mathbf{R}_i + \varphi) = 0$, if $\mathbf{q}'$ is not a reciprocal lattice vector, we find

$$\begin{aligned} f = (F-F_0)/N = \tfrac{1}{4}J^2\sum_\alpha\{2A_\alpha - \mathcal{J}(\mathbf{q})\}\sigma_\alpha^2 \\ + \tfrac{1}{8}J^4\sum_{\alpha\beta}B_{\alpha\beta}\{2+\cos 2(\varphi_\alpha - \varphi_\beta)\}\sigma_\alpha^2\sigma_\beta^2, \end{aligned} \qquad (2.1.24)$$

if $4\mathbf{q}$ is different from a reciprocal lattice vector. The coefficients of the second power are thus $\propto \{2A_\alpha - \mathcal{J}(\mathbf{q})\} = 1/\chi_{\alpha\alpha}(\mathbf{q}, \sigma = 0)$, where the susceptibility is evaluated at zero magnetization. As long as all the second-order coefficients are positive, at any value of $\mathbf{q}$, the free energy is at its minimum when $\sigma_\alpha = 0$, i.e. the system is paramagnetic. The smallest of these coefficients are those at $\mathbf{q} = \mathbf{Q}$, where $\mathcal{J}(\mathbf{q})$ has its maximum. In the heavy rare earths, with the exception of Gd, $\mathbf{Q}$ is non-zero and is directed along the c-axis. Depending on the sign of B_2^0, the magnetic structures occurring in the heavy rare earths may be divided into two classes, which we will discuss in turn.

3

CONDUCTION ELECTRON INTERACTIONS

3.1 The RKKY interaction

As we have already discussed in Section 1.2, the conduction electrons in the rare earth metals act as the medium through which the coupling is established between the $4f$ electrons localized on the ions. In this section, we shall investigate this *RKKY* coupling in more detail, and consider its influence on both the *spin waves* in the ferromagnetic phase, and also on the *conduction electrons* themselves. The indirect-exchange interaction is first derived, and its effects in limiting the *lifetimes* of the spin waves and in *polarizing* the conduction electrons are deduced. The enhancement of the *effective mass* of the conduction electrons by the dynamical magnetic fluctuations is then calculated. Finally, the modification of the *electrical resistivity* by the exchange interaction is discussed, including the *scattering* of the conduction electrons by the spin-wave excitations, and the influence of the magnetic ordering on the conduction-electron band structure. For completeness, we include the effect of *magnetic superzones* in periodic structures in this section.

3.1.1 The indirect-exchange interaction

The starting point for our consideration of the indirect exchange, or RKKY coupling, of the localized moments is the Heisenberg–Dirac exchange between the $4f$ electrons and the conduction electrons. The $4f$-core electrons of the ion at site i are assumed to be described to a good approximation by non-overlapping atomic wavefunctions $\phi_{4f}(\mathbf{r}-\mathbf{R}_i)$. We shall neglect the spin–orbit coupling of the conduction electrons, and assume their wavefunctions to be the Bloch functions

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}} = \psi_{n\mathbf{k}}(\mathbf{r}-\mathbf{R}_i)\, e^{i\mathbf{k}\cdot\mathbf{R}_i}, \qquad (3.1.1)$$

independent of the spin state σ. $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}-\mathbf{R}_i)$ has the periodicity of the lattice, and n is the band index. The Hamiltonian of the conduction electrons in *second quantization* is

$$\mathcal{H}_s = \sum_{n\mathbf{k}\sigma} \varepsilon_{n\mathbf{k}} c^+_{n\mathbf{k}\sigma} c_{n\mathbf{k}\sigma}, \qquad (3.1.2)$$

where the index s is conventionally used for the conduction electrons even though, as we saw in Section 1.3, they have predominantly d character. $c^+_{n\mathbf{k}\uparrow}$ creates and $c_{n\mathbf{k}\uparrow}$ annihilates a spin-up electron in the band-state $(n\mathbf{k})$, and they are Fermi-operators which satisfy the *anticommutation relations*

$$\begin{aligned} \{c_{n\mathbf{k}\sigma}, c^+_{n'\mathbf{k}'\sigma'}\} &\equiv c_{n\mathbf{k}\sigma}c^+_{n'\mathbf{k}'\sigma'} + c^+_{n'\mathbf{k}'\sigma'}c_{n\mathbf{k}\sigma} = \delta_{nn'}\delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'} \\ \{c^+_{n\mathbf{k}\sigma}, c^+_{n'\mathbf{k}'\sigma'}\} &= \{c_{n\mathbf{k}\sigma}, c_{n'\mathbf{k}'\sigma'}\} = 0. \end{aligned} \qquad (3.1.3)$$

An exposition of second quantization may be found, for example, in White (1983). The exchange interaction between a pair of electrons is $-2I\mathbf{s}_1\cdot\mathbf{s}_2$, where I is the exchange integral. If $\mathbf{s}_1$ is the spin of a $4f$ electron at site i, then the sum over all the $4f$ electrons at this site gives

$$\sum_{4f\ el.} -2I\mathbf{s}_1\cdot\mathbf{s}_2 = -2I\mathbf{S}_i\cdot\mathbf{s}_2 = -2I(g-1)\mathbf{J}_i\cdot\mathbf{s}_2,$$

where I is an average value of the exchange integral for the $4f$ electrons, and states other than those in the ground-state J-multiplet are neglected. The spin-density of the conduction electrons at $\mathbf{r}$ may be expressed in second-quantized form so that, for instance,

$$s_{2z}(\mathbf{r}) = \sum_{nn'} \sum_{\mathbf{k}\mathbf{k}'} \psi^*_{n'\mathbf{k}'}(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) \tfrac{1}{2} \big(c^+_{n'\mathbf{k}'\uparrow} c_{n\mathbf{k}\uparrow} - c^+_{n'\mathbf{k}'\downarrow} c_{n\mathbf{k}\downarrow} \big). \tag{3.1.4}$$

The *sf-exchange interaction* is determined by the following exchange integral:

$$\begin{aligned} \int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*_{n'\mathbf{k}'}(\mathbf{r}_1) \phi^*_{4f}(\mathbf{r}_2 - \mathbf{R}_i) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{n\mathbf{k}}(\mathbf{r}_2) \phi_{4f}(\mathbf{r}_1 - \mathbf{R}_i) \\ = \frac{1}{N} I(n'\mathbf{k}', n\mathbf{k}) e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_i}, \end{aligned}$$

with

$$I(n'\mathbf{k}', n\mathbf{k}) = N \int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*_{n'\mathbf{k}'}(\mathbf{r}_1) \phi^*_{4f}(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{n\mathbf{k}}(\mathbf{r}_2) \phi_{4f}(\mathbf{r}_1), \tag{3.1.5}$$

where N is the number of rare earth ions. If there are several $4f$ electrons per ion, $I(n'\mathbf{k}', n\mathbf{k})$ should again be averaged over their wavefunctions. The Hamiltonian $\mathcal{H}_{sf}$, describing the exchange interaction between the conduction electrons and the $4f$ electrons, is then found to be

$$\begin{aligned} \mathcal{H}_{sf} = -\frac{1}{N} \sum_i \sum_{nn'} \sum_{\mathbf{k}\mathbf{k}'} (g-1) I(n'\mathbf{k}', n\mathbf{k}) e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_i} \\ \times \big[(c^+_{n'\mathbf{k}'\uparrow} c_{n\mathbf{k}\uparrow} - c^+_{n'\mathbf{k}'\downarrow} c_{n\mathbf{k}\downarrow}) J_{iz} + c^+_{n'\mathbf{k}'\uparrow} c_{n\mathbf{k}\downarrow} J_i^- + c^+_{n'\mathbf{k}'\downarrow} c_{n\mathbf{k}\uparrow} J_i^+ \big], \end{aligned} \tag{3.1.6}$$

in second quantization.

In the ordered ferromagnetic phase, we may use the MF approximation, in which case

$$\mathcal{H}_{sf}(\mathrm{MF}) = -\sum_{nn'} \sum_{\mathbf{k}} (g-1) I(n'\mathbf{k}, n\mathbf{k}) (c^+_{n'\mathbf{k}\uparrow} c_{n\mathbf{k}\uparrow} - c^+_{n'\mathbf{k}\downarrow} c_{n\mathbf{k}\downarrow}) \langle J_z \rangle. \tag{3.1.7}$$

This Hamiltonian gives rise to both diagonal and off-diagonal contributions to the energies of the conduction electrons. The diagonal energies are

$$\begin{aligned} \varepsilon_{n\mathbf{k}\uparrow} &= \varepsilon_{n\mathbf{k}} - \langle J_z \rangle (g-1) I(n\mathbf{k}, n\mathbf{k}) \\ \varepsilon_{n\mathbf{k}\downarrow} &= \varepsilon_{n\mathbf{k}} + \langle J_z \rangle (g-1) I(n\mathbf{k}, n\mathbf{k}). \end{aligned} \tag{3.1.8}$$

Second-order perturbation theory then gives the energies of the band electrons as

$$\widetilde{\varepsilon}_{n\mathbf{k}\sigma} = \varepsilon_{n\mathbf{k}\sigma} + \langle J_z \rangle^2 (g-1)^2 \sum_{n' \neq n} \frac{|I(n'\mathbf{k}, n\mathbf{k})|^2}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}}}. \tag{3.1.9}$$

This dependence of the energies of the perturbed band-electrons on their state of polarization implies that the electron gas itself develops a non-zero magnetization. In order to calculate this moment, we first note that (3.1.9) corresponds to a replacement of $\mathcal{H}_s + \mathcal{H}_{sf}(\mathrm{MF})$ by an effective Hamiltonian for the band electron,

$$\widetilde{\mathcal{H}}_s = \sum_{n\mathbf{k}\sigma} \widetilde{\varepsilon}_{n\mathbf{k}\sigma} \widetilde{c}^{\,+}_{n\mathbf{k}\sigma} \widetilde{c}_{n\mathbf{k}\sigma}, \tag{3.1.10}$$

where the new Fermi operators are determined in terms of the old by

$$\begin{aligned} c_{n\mathbf{k}\uparrow} &= \widetilde{c}_{n\mathbf{k}\uparrow} + \sum_{n'} U_{\mathbf{k}}(n,n')\widetilde{c}_{n'\mathbf{k}\uparrow} \\ c_{n\mathbf{k}\downarrow} &= \widetilde{c}_{n\mathbf{k}\downarrow} - \sum_{n'} U_{\mathbf{k}}(n,n')\widetilde{c}_{n'\mathbf{k}\downarrow}, \end{aligned} \tag{3.1.11a}$$

to leading order. $U_{\mathbf{k}}(n,n) = 0$ and, for $n' \neq n$,

$$U_{\mathbf{k}}(n,n') = (g-1)\langle J_z \rangle \frac{I(n\mathbf{k}, n'\mathbf{k})}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}}}. \tag{3.1.11b}$$

The (approximately) diagonal form of (3.1.9) implies that the thermal expectation values are

$$\langle \widetilde{c}^{\,+}_{n\mathbf{k}\sigma} \widetilde{c}_{n'\mathbf{k}'\sigma'} \rangle = \delta_{nn'}\delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'}\, f_{n\mathbf{k}\sigma}, \tag{3.1.12a}$$

where

$$f_{n\mathbf{k}\sigma} = \frac{1}{e^{\beta(\widetilde{\varepsilon}_{n\mathbf{k}\sigma} - \mu_F)} + 1} \tag{3.1.12b}$$

is the *Fermi–Dirac distribution function* and μ_F is the chemical potential, equal to the Fermi energy $\widetilde{\varepsilon}_F$ in the temperature regime in which we shall be interested. The moment density is determined by (3.1.4), and introducing the new Fermi operators and using (3.1.12), we obtain

$$\begin{aligned} \langle \mu_z(\mathbf{r}) \rangle_{\text{c.el.}} &= \mu_B \sum_{nn'} \sum_{\mathbf{kk},} \psi^*_{n'\mathbf{k}'}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}) \big(\langle c^+_{n'\mathbf{k}'\uparrow} c_{n\mathbf{k}\uparrow} \rangle - \langle c^+_{n'\mathbf{k}'\downarrow} c_{n\mathbf{k}\downarrow} \rangle \big) \\ &= \mu_B \sum_{nn'} \sum_{\mathbf{k}} \psi^*_{n'\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}) \big[\{ \delta_{nn'} + U^*_{\mathbf{k}}(n',n) \} (f_{n\mathbf{k}\uparrow} - f_{n\mathbf{k}\downarrow}) \\ &\qquad\qquad + U_{\mathbf{k}}(n,n')(f_{n'\mathbf{k}\uparrow} - f_{n'\mathbf{k}\downarrow}) \big]. \end{aligned} \tag{3.1.13}$$

The uniform, averaged part of this moment density can be obtained by an integration of eqn (3.1.13) over space, and remembering that the wavefunctions are orthogonal and normalized, we find the magnetic moment of the conduction electrons per ion to be

$$\langle \mu_z \rangle_{\text{c.el.}} = \mu_B \frac{1}{N} \sum_{n\mathbf{k}} \big(f_{n\mathbf{k}\uparrow} - f_{n\mathbf{k}\downarrow} \big). \tag{3.1.14}$$

We note that, in addition to this uniform polarization of the conduction electrons, there is a spatially non-uniform component of the polarization density with the periodicity of the lattice. This non-uniform component reflects the variation in the electronic density, including the perturbative changes due to the *interband* contributions proportional to $U_{\mathbf{k}}(n,n')$. Furthermore, when the spin–orbit coupling of the conduction electrons is of importance, the interband coupling may induce a positional dependence in the direction of the spin polarization.

In order to obtain order-of-magnitude estimates of the exchange effects, we introduce a reasonable but somewhat crude approximation for the exchange integral, which is due to Overhauser (1963) and has been discussed in detail by Freeman (1972). First we assume that the Coulomb interaction in eqn (3.1.5) is strongly shielded, so that it can be replaced by a δ-function. Next, using plane waves for the Bloch functions, we obtain

$$(g-1)I(n\mathbf{k}', n\mathbf{k}) \approx j(\mathbf{q} = \mathbf{k}' - \mathbf{k}) \propto \int d\mathbf{r} |\phi_{4f}(\mathbf{r})|^2 e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{3.1.15}$$

which is the form factor of the $4f$-electron density, approximately the same as the local moment density (4.1.15). In this simplified model, where the conduction electrons are assumed to be free-electron-like, the interband exchange integrals, in which $n' \neq n$, are obtained by adding reciprocal-lattice vectors $\boldsymbol{\tau}$ to $\mathbf{q}$ in eqn (3.1.15). In this model, we obtain a rigid band-splitting, independent of $\mathbf{k}$, between the spin-down and spin-up bands, of magnitude

$$\Delta = \widetilde{\varepsilon}_{n\mathbf{k}\downarrow} - \widetilde{\varepsilon}_{n\mathbf{k}\uparrow} = 2\langle J_z \rangle j(\mathbf{0}). \tag{3.1.16}$$

Since $j(\mathbf{0})$ has the same sign as $(g-1)$, it is positive in the heavy rare earth metals. If $\mathcal{N}(\varepsilon)$ is the density of electronic states per ion and per spin state in the paramagnetic phase, the shifts of the spin-up and spin-down bands lead to an excess number of spin-up electrons proportional to

$$\overline{\mathcal{N}}(\widetilde{\varepsilon}_F) = \frac{1}{\Delta} \int_{\widetilde{\varepsilon}_F - \frac{\Delta}{2}}^{\widetilde{\varepsilon}_F + \frac{\Delta}{2}} \mathcal{N}(\varepsilon) d\varepsilon, \tag{3.1.17}$$

when the small modification of the density of states due to the interband coupling is neglected, so that $\widetilde{\varepsilon}_F$ is close to the Fermi energy ε_F of the non-magnetic system. In combination with eqn (3.1.14), this result predicts a (positive) augmentation of the ferromagnetic moment of the $4f$ electrons, due to the conduction electrons, of magnitude

$$\langle \mu_z \rangle_{\text{c.el.}} = \mu_B \overline{\mathcal{N}}(\widetilde{\varepsilon}_F) \Delta, \tag{3.1.18}$$

when $k_B T \ll \widetilde{\varepsilon}_F$. The total moment per ion may then be expressed in terms of an effective g-factor:

$$\langle \mu_z \rangle = g\mu_B \langle J_z \rangle + \langle \mu_z \rangle_{\text{c.el.}} = (g + \Delta g)\mu_B \langle J_z \rangle, \tag{3.1.19a}$$

where

$$\Delta g = 2j(\mathbf{0}) \overline{\mathcal{N}}(\widetilde{\varepsilon}_F). \tag{3.1.19b}$$

In the metals, the effective exchange integral $j(\mathbf{0})$ is $\sim (g-1) \times 0.1\,\text{eV}$, leading to an exchange splitting Δ which, in Gd for example, is nearly $1\,\text{eV}$. This relatively large splitting has the consequence that $\overline{\mathcal{N}}(\widetilde{\varepsilon}_F)$ may differ somewhat from the value $\mathcal{N}(\varepsilon_F)$ in the paramagnetic phase. In the hcp metals, the band structure calculations discussed in Section 1.3 reveal that ε_F is near a peak in the density of states due to the d electrons, and that $\mathcal{N}(\varepsilon_F) \simeq 1\,\text{eV}^{-1}$ per spin state per ion, corresponding to an electronic moment of the order of one-tenth of the local moment. In the example of Gd, for which $g = 2$, $\Delta g = 0.18$. The same value of $\Delta g/(g-1)$ accounts fairly well for the conduction-electron contribution to the moments of the other heavy rare earths in Table 1.6, bearing in mind the uncertainties in the experimental results, and the possible effects of the crystal fields in quenching the local moments.

The spin waves in the ferromagnetic phase are decisively influenced by the *sf*-exchange interaction. In order to consider such effects, we introduce the Bose operators acting on the angular-momentum states, as in eqns (5.2.6–8), and find, to first order in $1/J$,

$$\begin{aligned}\mathcal{H}_{sf} \simeq \mathcal{H}_{sf}(\mathrm{MF}) - \frac{1}{N}\sum_{\mathbf{kq}\boldsymbol{\tau}}\sum_{i} j(\mathbf{q}+\boldsymbol{\tau})\, e^{-i\mathbf{q}\cdot\mathbf{R}_i}\Big[&-\delta_{\mathbf{q}\mathbf{0}}(\langle c^+_{\mathbf{k}+\boldsymbol{\tau}\uparrow}c_{\mathbf{k}\uparrow}\rangle \\ - \langle c^+_{\mathbf{k}+\boldsymbol{\tau}\downarrow}c_{\mathbf{k}\downarrow}\rangle)a_i^+a_i + \sqrt{2J}c^+_{\mathbf{k}+\mathbf{q}+\boldsymbol{\tau}\uparrow}c_{\mathbf{k}\downarrow}\, a_i^+ &+ \sqrt{2J}c^+_{\mathbf{k}+\mathbf{q}+\boldsymbol{\tau}\downarrow}c_{\mathbf{k}\uparrow}\, a_i\Big],\end{aligned}$$

using the simplified exchange of eqn (3.1.15), and neglecting effects of third or higher order in $j(\mathbf{q})$ due to $(c^+_{\mathbf{k}'\sigma}c_{\mathbf{k}\sigma} - \langle c^+_{\mathbf{k}'\sigma}c_{\mathbf{k}\sigma}\rangle)a_i^+a_i$. $\mathbf{q}$ is assumed to lie in the primitive Brillouin zone, but no such restriction is placed on $\mathbf{k}$. We note that $c^+_{\mathbf{k}}$ and $c^+_{\mathbf{k}+\boldsymbol{\tau}}$, where $\boldsymbol{\tau}$ is a reciprocal lattice vector, create electrons in different bands in the free-electron model. Introducing the crystal-field Hamiltonian to first order in $1/J$ (eqn (5.2.14) with $\mathcal{J}(ij) = 0$), and the Fourier transforms of the Bose operators (5.2.16), we find that the total magnetic Hamiltonian becomes

$$\begin{aligned}\mathcal{H} = \widetilde{\mathcal{H}}_s + \sum_{\mathbf{q}}&\big[\{A + J\widetilde{\mathcal{J}}(\mathbf{0},0)\}a^+_{\mathbf{q}}a_{\mathbf{q}} + B\tfrac{1}{2}(a_{\mathbf{q}}a_{-\mathbf{q}} + a^+_{\mathbf{q}}a^+_{-\mathbf{q}})\big] \\ &- \sqrt{2J/N}\sum_{\mathbf{kq}\boldsymbol{\tau}} j(\mathbf{q}+\boldsymbol{\tau})\big(c^+_{\mathbf{k}+\mathbf{q}+\boldsymbol{\tau}\uparrow}c_{\mathbf{k}\downarrow}\, a^+_{-\mathbf{q}} + c^+_{\mathbf{k}+\mathbf{q}+\boldsymbol{\tau}\downarrow}c_{\mathbf{k}\uparrow}\, a_{\mathbf{q}}\big),\end{aligned} \tag{3.1.20}$$

where

$$\widetilde{\mathcal{J}}(\mathbf{0},0) = 2j^2(\mathbf{0})\overline{\mathcal{N}}(\widetilde{\epsilon}_F) + \frac{2}{N}\sum_{\mathbf{k},\boldsymbol{\tau}\neq\mathbf{0}} |j(\boldsymbol{\tau})|^2\frac{f_{\mathbf{k}\downarrow} - f_{\mathbf{k}+\boldsymbol{\tau}\uparrow}}{\varepsilon_{\mathbf{k}+\boldsymbol{\tau}} - \varepsilon_{\mathbf{k}}}, \tag{3.1.21}$$

including the ‘interband’ contributions as in (3.1.13). The spin-wave energies may be obtained from the poles in the Green function $\langle\langle a_{\mathbf{q}}\,;\, a^+_{\mathbf{q}}\rangle\rangle$. The equation of motion (3.3.14) for this Green function is determined from $\mathcal{H}$ to be

$$\begin{aligned}\big\{\hbar\omega - A - J\widetilde{\mathcal{J}}(\mathbf{0},0)\big\}&\langle\langle a_{\mathbf{q}}\,;\, a^+_{\mathbf{q}}\rangle\rangle - B\langle\langle a^+_{-\mathbf{q}}\,;\, a^+_{\mathbf{q}}\rangle\rangle \\ &+ \sqrt{2J/N}\sum_{\mathbf{k}\boldsymbol{\tau}} j(-\mathbf{q}-\boldsymbol{\tau})\langle\langle c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}c_{\mathbf{k}\downarrow}\,;\, a^+_{\mathbf{q}}\rangle\rangle = 1.\end{aligned} \tag{3.1.22}$$

The equation of motion of the new Green function $\langle\langle c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}c_{\mathbf{k}\downarrow}\,;\, a^+_{\mathbf{q}}\rangle\rangle$ involves the following commutator:

$$\begin{aligned}[\,c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}c_{\mathbf{k}\downarrow}\,, \mathcal{H}\,] &= \big(\varepsilon_{\mathbf{k}\downarrow} - \varepsilon_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}\big)c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}c_{\mathbf{k}\downarrow} \\ &\quad + \sqrt{2J/N}\sum_{\mathbf{q}'} j(\mathbf{q}')\big(c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}+\mathbf{q}'\downarrow}c_{\mathbf{k}\downarrow} - c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}c_{\mathbf{k}-\mathbf{q}'\uparrow}\big)\, a_{\mathbf{q}'} \\ &\simeq \big(\varepsilon_{\mathbf{k}\downarrow} - \varepsilon_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}\big)c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}c_{\mathbf{k}\downarrow} + \sqrt{2J/N}\, j(\mathbf{q}+\boldsymbol{\tau})\big(f_{\mathbf{k}\downarrow} - f_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}\big)\, a_{\mathbf{q}}\end{aligned} \tag{3.1.23}$$

obtained by applying the anticommutator relations (3.1.3) and, in the second equation, an RPA decoupling of the operator products. It is not necessary here to differentiate between the new and the old Fermi operators, as the differences introduce corrections only in the third order of $|j(\mathbf{q})|$. Introducing this RPA result in the equation of motion for the Green function $\langle\langle c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow} c_{\mathbf{k}\downarrow}\,;\, a^+_{\mathbf{q}}\rangle\rangle$, we obtain

$$\begin{aligned}\big(\hbar\omega - \varepsilon_{\mathbf{k}\downarrow} + \varepsilon_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}\big)&\langle\langle c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow} c_{\mathbf{k}\downarrow}\,;\, a^+_{\mathbf{q}}\rangle\rangle \\ &- \sqrt{2J/N}\, j(\mathbf{q}+\boldsymbol{\tau})\big(f_{\mathbf{k}\downarrow} - f_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}\big)\langle\langle a_{\mathbf{q}}\,;\, a^+_{\mathbf{q}}\rangle\rangle = 0,\end{aligned} \tag{3.1.24}$$

which, in combination with (3.1.22), leads to

$$\big\{\hbar\omega - A - J\widetilde{\mathcal{J}}(\mathbf{0},0) + J\widetilde{\mathcal{J}}(\mathbf{q},\omega)\big\}\langle\langle a_{\mathbf{q}}\,;\, a^+_{\mathbf{q}}\rangle\rangle - B\langle\langle a^+_{-\mathbf{q}}\,;\, a^+_{\mathbf{q}}\rangle\rangle = 1, \tag{3.1.25}$$

where

$$\widetilde{\mathcal{J}}(\mathbf{q},\omega) = \lim_{\varepsilon\to 0^+} \frac{2}{N}\sum_{\boldsymbol{\tau}} |j(\mathbf{q}+\boldsymbol{\tau})|^2 \sum_{\mathbf{k}} \frac{f_{\mathbf{k}\downarrow} - f_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}}{\hbar\omega + i\hbar\varepsilon - \varepsilon_{\mathbf{k}\downarrow} + \varepsilon_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow}}. \tag{3.1.26a}$$

This result may be expressed in terms of the susceptibility of the conduction electrons. Introducing the spin susceptibility per ion, which is the usual magnetic susceptibility times $(2\mu_B)^{-2}V/N$, so that

$$\begin{aligned}\chi^{+-}_{\text{c.el.}}(\mathbf{q},\omega) &= -\frac{1}{N}\int d\mathbf{r}_1 d\mathbf{r}_2 \langle\langle s^+(\mathbf{r}_1)\,;\, s^-(\mathbf{r}_2)\rangle\rangle\, e^{-i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)} \\ &= -\frac{1}{N}\sum_{\mathbf{k}'\mathbf{k}''}\langle\langle c^+_{\mathbf{k}'-\mathbf{q}\uparrow}c_{\mathbf{k}'\downarrow}\,;\, c^+_{\mathbf{k}''+\mathbf{q}\downarrow}c_{\mathbf{k}''\uparrow}\rangle\rangle \\ &= \lim_{\varepsilon\to 0^+}\frac{1}{N}\sum_{\mathbf{k}}\frac{f_{\mathbf{k}\downarrow} - f_{\mathbf{k}-\mathbf{q}\uparrow}}{\hbar\omega + i\hbar\varepsilon - \varepsilon_{\mathbf{k}\downarrow} + \varepsilon_{\mathbf{k}-\mathbf{q}\uparrow}},\end{aligned} \tag{3.1.26b}$$

and neglecting the higher-order corrections to the spin-susceptibility, due to the coupling to the local moments, we can write the above result

$$\widetilde{\mathcal{J}}(\mathbf{q},\omega) = 2\sum_{\boldsymbol{\tau}} |j(\mathbf{q}+\boldsymbol{\tau})|^2 \chi^{+-}_{\text{c.el.}}(\mathbf{q}+\boldsymbol{\tau},\omega), \tag{3.1.26c}$$

where by the relation (3.2.15), $\chi^{+-}_{\text{c.el.}}(\mathbf{q},\omega) = [\chi^{-+}_{\text{c.el.}}(-\mathbf{q},-\omega)]^*$. In general, when the Coulomb interaction cannot be approximated by a δ-function, this factorization is not valid, and the indirect exchange is instead given by

$$\begin{aligned}&\widetilde{\mathcal{J}}(\mathbf{q},\omega) = \\ &\lim_{\varepsilon\to 0^+}\frac{2}{N}\sum_{nn'}\sum_{\mathbf{k}}(g-1)^2|I(n'\mathbf{k}-\mathbf{q},n\mathbf{k})|^2\frac{f_{n\mathbf{k}\downarrow} - f_{n'\mathbf{k}-\mathbf{q}\uparrow}}{\hbar\omega + i\hbar\varepsilon - \varepsilon_{n\mathbf{k}\downarrow} + \varepsilon_{n'\mathbf{k}-\mathbf{q}\uparrow}},\end{aligned} \tag{3.1.27}$$

where $\mathbf{k}$ is now confined to the primitive Brillouin zone.

In the frequency regime of the spin waves, where $|\hbar\omega|$ is much smaller than the Fermi energy or the exchange splitting Δ, the frequency dependence of $\widetilde{\mathcal{J}}(\mathbf{q},\omega)$ can, to a good approximation, be neglected. The spins of the conduction electrons respond essentially instantaneously to any changes in the state of the local angular momenta, compared with the time-scale of these changes. For a Bravais-lattice, $\widetilde{\mathcal{J}}(\mathbf{q},\omega) \simeq \widetilde{\mathcal{J}}(\mathbf{q},0) = \widetilde{\mathcal{J}}(-\mathbf{q},0)$. A comparison of eqn (3.1.25) with the $1/J$ spin-wave result (5.2.18) shows that $\widetilde{\mathcal{J}}(\mathbf{0},0)\,-$

$\widetilde{\mathcal{J}}(\mathbf{q},0)$ replaces the contribution of the Heisenberg interaction considered in eqn (5.2.1). In this equation, $\mathcal{J}(ii) \equiv 0$ by definition and, since this is not the case for $\widetilde{\mathcal{J}}(ii) = (1/N)\sum_{\mathbf{q}} \widetilde{\mathcal{J}}(\mathbf{q},0)$, $\widetilde{\mathcal{J}}(\mathbf{q},0)$ cannot be associated directly with $\mathcal{J}(\mathbf{q})$. The instantaneous or frequency-independent part of the coupling of $\mathbf{J}_i$ with itself leads to a contribution $\frac{1}{2}N\widetilde{\mathcal{J}}(ii)\langle \mathbf{J}_i \cdot \mathbf{J}_i\rangle$ to the total energy, where $\langle \mathbf{J}_i \cdot \mathbf{J}_i\rangle = J(J+1)$, independently of the magnetic ordering or the temperature. This assertion may be verified (to first order in $1/J$) by a direct calculation of $\langle\mathcal{H}\rangle$ from (3.1.20). For this purpose $\langle c^+_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\uparrow} c_{\mathbf{k}\downarrow} a^+_{\mathbf{q}}\rangle$, for instance, is determined from eqn (3.1.24), but a *self-energy* correction of a factor 1/2 must be included in its contribution to $\langle\mathcal{H}\rangle$. Taking this condition into account, we may finally write

$$\mathcal{J}(\mathbf{q}) = \widetilde{\mathcal{J}}(\mathbf{q},0) - \frac{1}{N}\sum_{\mathbf{q}'} \widetilde{\mathcal{J}}(\mathbf{q}',0). \tag{3.1.28}$$

The exchange interaction between the $4f$ electrons and the conduction electrons thus leads to an effective Heisenberg interaction between the local angular momenta, as given in (5.2.1). This is the RKKY interaction discussed earlier in Section 1.4.

The above calculation has been performed for a Bravais lattice, but the result (3.1.26) is readily generalized to a crystal with a basis of p ions, as the conduction electrons, in the approximation adopted, are not affected by the presence of the basis. If the couplings between the different sublattices are introduced in an equivalent manner to (5.1.1), then

$$\widetilde{\mathcal{J}}_{ss'}(\mathbf{q},\omega) = \frac{2}{p}\sum_{\boldsymbol{\tau}} |j(\mathbf{q}+\boldsymbol{\tau})|^2 \chi^{+-}_{\text{c.el.}}(\mathbf{q}+\boldsymbol{\tau},\omega)\exp\big(i\boldsymbol{\rho}_{ss'}\cdot\boldsymbol{\tau}\big) \tag{3.1.29}$$

replaces (3.1.26c), where $\boldsymbol{\rho}_{ss'}$ is the vector connecting the two sublattices s and s'.

The interaction between the localized moments is effectuated via virtual electron-hole pair-excitations of the conduction electrons. The transmission of any time dependent event may be disturbed in two ways; either by the finite propagation-time of the pairs, or by a decay of the pair states into unbound electron and hole excitations, the so-called *Stoner* excitations. The second effect produces by far the most important correction to the instantaneous interaction, but we shall begin with a discussion of the frequency-dependence of the real part of $\widetilde{\mathcal{J}}(\mathbf{q},\omega)$, due to the finite transmission time. Returning to the simple model leading to (3.1.26), we find that the exchange coupling is proportional to the susceptibility function $\chi^{+-}_{\text{c.el.}}(\mathbf{q},\omega)$, which for unpolarized free electrons is the same as the *Lindhard function* (Lindhard 1954). If corrections of the order k_BT/ε_F are neglected, the real part at zero wave-vector is

$$\begin{aligned}\text{Re}\big[\chi^{+-}_{\text{c.el.}}(\mathbf{0},\omega)\big] &= \frac{1}{N}\sum_{\mathbf{k}} \frac{f_{\mathbf{k}\downarrow} - f_{\mathbf{k}\uparrow}}{\hbar\omega - \varepsilon_{\mathbf{k}\downarrow} + \varepsilon_{\mathbf{k}\uparrow}} \\ &= \frac{1}{N}\sum_{\mathbf{k}} \frac{f_{\mathbf{k}\uparrow} - f_{\mathbf{k}\downarrow}}{\Delta - \hbar\omega} = \overline{\mathcal{N}}(\widetilde{\epsilon}_F)\Big(1 + \frac{\hbar\omega}{\Delta}\Big).\end{aligned} \tag{3.1.30}$$

From this result, we find immediately that the intra-band contribution at zero frequency to $\widetilde{\mathcal{J}}(\mathbf{q}\to\mathbf{0},0)$ in eqn (3.1.26a) is $2j^2(\mathbf{0})\overline{\mathcal{N}}(\widetilde{\epsilon}_F)$, which is the same as in (3.1.21). On the other hand, the interband contributions differ in the two expressions, as the denominator in (3.1.26a) involves the exchange splitting Δ, whereas that in (3.1.21) does not. However, this difference can be neglected, as it is of the order $(\Delta/\varepsilon_F)^2$ times the intra-band contribution, which is beyond the order considered in these calculations.

In fact, since the starting Hamiltonian (3.1.6) is invariant with respect to the choice of z-axis for the electronic spins and the angular momenta, the spin-wave frequency must vanish when $\mathbf{q} \to \mathbf{0}$ and $A = B = 0$, according to the *Goldstone theorem*, which will be discussed in the next chapter. Therefore $\widetilde{\mathcal{J}}(\mathbf{q} \to \mathbf{0}, 0) = \widetilde{\mathcal{J}}(\mathbf{0}, 0)$, and we simply assume that eqn (3.1.26a), with $(\mathbf{q}, \omega) = (\mathbf{0}, 0)$, replaces eqn (3.1.21). In the presence of an external field, Δ in eqn (3.1.16) is increased by an amount $2\mu_B H$, which leads to the extra contribution $\Delta g \mu_B H$ to $\widetilde{\mathcal{J}}(\mathbf{0}, 0)$ in (3.1.21), as the change with field of the interband terms may be neglected. To leading order, $\widetilde{\mathcal{J}}(\mathbf{q} \to \mathbf{0}, 0)$ is not affected by the applied field, so to this order the extra polarization of the conduction electrons, due to an external field, may simply be accounted for by replacing $g\mu_B H$ by $(g + \Delta g)\mu_B H$, both in the Zeeman energy (3.1.19a) and in the spin-wave energy parameters (in A). Writing the susceptibility in eqn (3.1.26b) as the sum of two terms, and replacing $\mathbf{k} - \mathbf{q}$ by $\mathbf{k}$ in the term involving $f_{\mathbf{k}-\mathbf{q}\uparrow}$, we obtain

$$\begin{aligned}
&\mathrm{Re}\big[\chi^{+-}_{\text{c.el.}}(\mathbf{q}, \omega)\big] = \\
&\quad \frac{V}{(2\pi)^3} \frac{2\pi}{N} \int_0^{k_{F\downarrow}} k^2 dk \int_{-1}^{1} d\mu \big[\hbar\omega - \Delta + \frac{(\hbar q)^2}{2m} - \frac{\hbar^2 kq}{m}\mu\big]^{-1} \\
&\quad - \frac{V}{(2\pi)^3} \frac{2\pi}{N} \int_0^{k_{F\uparrow}} k^2 dk \int_{-1}^{1} d\mu \big[\hbar\omega - \Delta - \frac{(\hbar q)^2}{2m} - \frac{\hbar^2 kq}{m}\mu\big]^{-1},
\end{aligned}$$

or

$$\begin{aligned}
&\mathrm{Re}\big[\chi^{+-}_{\text{c.el.}}(\mathbf{q}, \omega)\big] = \\
&\frac{V}{N} \frac{m}{(2\pi\hbar)^2} \Big\{ k_{F\downarrow}(1 - \eta)\mathcal{F}\Big(\frac{q}{2k_{F\downarrow}}(1 - \eta)\Big) + k_{F\uparrow}(1 + \eta)\mathcal{F}\Big(\frac{q}{2k_{F\uparrow}}(1 + \eta)\Big)\Big\}
\end{aligned} \tag{3.1.31a}$$

where we have introduced the function

$$\mathcal{F}(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln\left|\frac{1 + x}{1 - x}\right| \tag{3.1.31b}$$

and the parameter

$$\eta = \frac{\Delta - \hbar\omega}{\varepsilon_F} \left(\frac{k_F}{q}\right)^2. \tag{3.1.31c}$$

The Fermi energy is $\varepsilon_F = (\hbar k_F)^2/2m$, and the wave-vectors of the spin-up and the spin-down electrons at the Fermi surface are

$$k_{F\uparrow} = k_F\big(1 + \frac{\Delta}{2\varepsilon_F}\big)^{\frac{1}{2}} \quad ; \quad k_{F\downarrow} = k_F\big(1 - \frac{\Delta}{2\varepsilon_F}\big)^{\frac{1}{2}}. \tag{3.1.31d}$$

$\eta \to \infty$ in the limit $q \to 0$ and, using $\mathcal{F}(x) = 1/3x^2$ when $|x| \to \infty$, we may re-derive the result (3.1.30). At non-zero q, a numerical analysis shows that, to a good approximation,

$$\mathrm{Re}\big[\chi^{+-}_{\text{c.el.}}(\mathbf{q}, \omega)\big] = \overline{\mathcal{N}}(\widetilde{\epsilon}_F)\Big\{\mathcal{F}\big(\frac{q}{2k_F}\big) + \xi_q \frac{\hbar\omega}{\Delta}\Big\}, \tag{3.1.32}$$

even when Δ/ε_F is as large as 0.5. The parameter ξ_q is equal to 1 at $q = 0$, and peaks at $q = q_0 = k_{F\uparrow} - k_{F\downarrow}$, after which it rapidly decreases ($\xi_q \simeq 0.25$ at $q = 2q_0$). For $\Delta/\varepsilon_F = 0.1$, the maximum value is about 4 and it decreases for increasing values of

Δ, falling to about 3 at $\Delta/\varepsilon_F = 0.4$. Usually q_0 is much smaller than the length of any reciprocal-lattice vector, which means that the frequency dependence of the 'inter-band' term in the real part of $\widetilde{\mathcal{J}}(\mathbf{q},\omega)$ can be neglected. The intra-band contribution is $2|j(\mathbf{q})|^2\overline{\mathcal{N}}(\widetilde{\epsilon}_F)\xi_q\hbar\omega/\Delta$, and using

$$\big\{\hbar\omega + A + J\widetilde{\mathcal{J}}(\mathbf{0},0) - J\widetilde{\mathcal{J}}^*(-\mathbf{q},-\omega)\big\}\langle\langle a^+_{-\mathbf{q}}\,;\,a^+_{\mathbf{q}}\rangle\rangle + B\langle\langle a_{\mathbf{q}}\,;\,a^+_{\mathbf{q}}\rangle\rangle = 0, \tag{3.1.33}$$

which follows by symmetry from eqn (3.1.25), we may determine the spin-wave energies from the real part of $\widetilde{\mathcal{J}}(\mathbf{q},\omega)$ to be

$$\hbar\omega = E'_{\mathbf{q}} = E_{\mathbf{q}}\big[1 + \xi_q\overline{\mathcal{N}}(\widetilde{\epsilon}_F)|j(\mathbf{q})|^2/j(\mathbf{0})\big]^{-1}, \tag{3.1.34a}$$

to first order in $1/J$, with $E_{\mathbf{q}}$ given by (5.2.22). The extra factor, which originates from the frequency dependence of $\chi^{+-}_{\text{c.el.}}(\mathbf{q},\omega)$, differs from 1 by only a few per cent, and its $\mathbf{q}$-dependent contribution could scarcely be distinguished from that of $\mathcal{J}(\mathbf{q})$. However, the presence of this factor at $\mathbf{q} = \mathbf{0}$ means that the energy of the uniform spin-wave mode is no longer determined exclusively by the magnetic anisotropy of the bulk, according to (5.4.12) and (5.4.19), when the magnetoelastic effects are included, but instead the energy gap is

$$E'_{\mathbf{0}} = \frac{1}{N}\left(\frac{\partial^2 F}{\partial\theta^2}\frac{\partial^2 F}{\partial\phi^2}\bigg|_{\overline{\epsilon}}\right)^{\frac{1}{2}}\frac{1}{\langle J_z\rangle(1+\frac{1}{2}\Delta g)}. \tag{3.1.34b}$$

Although this modification is small, it demonstrates that the frequency dependence of $\chi^{+-}_{\text{c.el.}}(\mathbf{q},\omega)$ may cause small deviations between the static anisotropy parameters and those derived from the energy gap, as possibly detected in Tb in the form of a non-zero value of $\delta_6(-)$, defined by eqn (5.4.23a).

The dominant term in the real part of $\chi^{+-}_{\text{c.el.}}(\mathbf{q},\omega)$ is the frequency-independent contribution proportional to $\mathcal{F}(q/2k_F)$. Including only this contribution, and making the rather drastic simplifying assumption that $|j(\mathbf{q}+\boldsymbol{\tau})|$ in eqn (3.1.26c) is a constant $|j_0|$ at all wave-vectors, we may derive the exchange coupling in real space, which then depends only on the distance R between the different ions:

$$\mathcal{J}(R) = 2|j_0|^2\frac{V}{N(2\pi)^3}\int\overline{\mathcal{N}}(\widetilde{\epsilon}_F)\mathcal{F}\big(\frac{q}{2k_F}\big)e^{i\mathbf{q}\cdot\mathbf{R}}d\mathbf{q}.$$

The sum over $\boldsymbol{\tau}$ in (3.1.26c) corresponds to letting q vary between 0 and ∞, and the result is

$$\mathcal{J}(R) = 12\pi\nu|j_0|^2\overline{\mathcal{N}}(\widetilde{\epsilon}_F)\,\frac{\sin(2k_F R) - 2k_F R\cos(2k_F R)}{(2k_F R)^4}\,, \tag{3.1.35}$$

where ν is the number of conduction electrons per ion; $\nu = Vk_F^3/3\pi^2N$. Although this result is not directly applicable to realistic systems, it demonstrates explicitly that the indirect coupling mediated by the conduction electrons is long range, $\mathcal{J}(R) \propto R^{-3}$ for large R, and that it oscillates. The period of the oscillation is here $2\pi/2k_F$ whereas, in a real system, such oscillations may occur as a result of large parallel areas of Fermi surface, the separation of which determines an effective value of $2k_F$. It is interesting that $\mathcal{J}(R)$, derived from the excitation spectrum in Pr and shown in Fig. 1.18 on page 49, is reasonably well described by the above function, especially when $\mathbf{R}$ is in the basal plane, provided that an effective value of $2k_F$ of about $1.1\,\text{Å}^{-1}$ is used.

The magnetic scattering of the electron-hole pairs leads to a damping of the spin waves, which is determined by the imaginary part of the susceptibility (3.1.26*b*). The complementary result to eqn (3.1.31*a*) is then

$$\begin{aligned}&\mathrm{Im}\big[\chi^{+-}_{\mathrm{c.el.}}(\mathbf{q},\omega)\big] = \\ &-\frac{V}{(2\pi)^3}\frac{2\pi}{N}\int_0^\infty k^2dk\int_{-1}^{1}d\mu\,\pi\delta\big(\hbar\omega-\Delta+\frac{(\hbar q)^2}{2m}-\frac{\hbar^2kq}{m}\mu\big)\,f_{\mathbf{k}\downarrow} \\ &+\frac{V}{(2\pi)^3}\frac{2\pi}{N}\int_0^\infty k^2dk\int_{-1}^{1}d\mu\,\pi\delta\big(\hbar\omega-\Delta-\frac{(\hbar q)^2}{2m}-\frac{\hbar^2kq}{m}\mu\big)\,f_{\mathbf{k}\uparrow}.\end{aligned}$$

Because $-1<\mu<1$, the δ-function argument in the first term can only be zero if $\varepsilon_q\equiv(\hbar q)^2/(2m)$ lies between the two roots $\varepsilon_\pm=2\varepsilon_k+\Delta-\hbar\omega\pm2\big[\varepsilon_k(\varepsilon_k+\Delta-\hbar\omega)\big]^{1/2}$. For the second term, the same condition applies, except that the signs of Δ and $\hbar\omega$ are reversed, leading to the extra requirement that $\varepsilon_k>\varepsilon_K=\Delta-\hbar\omega$. If these conditions are satisfied,

$$\begin{aligned}&\mathrm{Im}\big[\chi^{+-}_{\mathrm{c.el.}}(\mathbf{q},\omega)\big] = \\ &-\frac{V}{N(2\pi)^2}\int_0^\infty\frac{\pi m}{\hbar^2q}kf(\varepsilon_k+\tfrac{\Delta}{2})dk+\frac{V}{N(2\pi)^2}\int_K^\infty\frac{\pi m}{\hbar^2q}kf(\varepsilon_k-\tfrac{\Delta}{2})dk,\end{aligned}$$

where $f(\varepsilon)=1/\big[\exp(\varepsilon-\varepsilon_F)+1\big]$. By a suitable change of variables, the two integrals acquire the same limits and the same condition on ε_q, and they may therefore be combined in a single integral:

$$\mathrm{Im}\big[\chi^{+-}_{\mathrm{c.el.}}(\mathbf{q},\omega)\big]=\frac{V}{N(2\pi)^2}\frac{\pi m^2}{\hbar^4q}\int_{\frac{\Delta-\hbar\omega}{2}}^\infty\big\{-f(\varepsilon+\tfrac{\hbar\omega}{2})+f(\varepsilon-\tfrac{\hbar\omega}{2})\big\}d\varepsilon.$$

The integrand is only non-zero in a narrow interval of width $|\hbar\omega|\ll\Delta<\varepsilon_F$ around the Fermi surface, in which case the condition on ε_q can be written $k_{F\uparrow}-k_{F\downarrow}<q<k_{F\uparrow}+k_{F\downarrow}$ (if $\Delta=0$ the lower boundary is replaced by $(\hbar\omega)^2/(4\varepsilon_F)<\varepsilon_q$). With this condition fulfilled,

$$\mathrm{Im}\big[\chi^{+-}_{\mathrm{c.el.}}(\mathbf{q},\omega)\big]=\frac{V}{N(2\pi)^2}\frac{\pi m^2}{\hbar^4q}\hbar\omega,$$

independent of T (as long as $k_BT\ll\varepsilon_F$). Using

$$\mathcal{N}_\sigma(\varepsilon_F)=(V/N)(2\pi\hbar)^{-2}2mk_{F\sigma}\quad;\quad(V/N)(2\pi)^{-2}\,\tfrac{2}{3}(k^3_{F\uparrow}+k^3_{F\downarrow})=\nu,$$

where ν is the number of conduction electrons per ion ($\nu=3$), we may write the result:

$$\begin{aligned}&\mathrm{Im}\big[\chi^{+-}_{\mathrm{c.el.}}(\mathbf{q},\omega)\big]=\frac{\pi}{3\nu}\mathcal{N}_\uparrow(\varepsilon_F)\mathcal{N}_\downarrow(\varepsilon_F)\frac{k_F}{q}\hbar\omega; \qquad (3.1.36)\\ &\qquad\qquad k_{F\uparrow}-k_{F\downarrow}<q<k_{F\uparrow}+k_{F\downarrow},\end{aligned}$$

neglecting corrections of second order in Δ/ε_F. In the zero-frequency limit considered here, q has to exceed the threshold value $q_0=k_{F\uparrow}-k_{F\downarrow}$ before the imaginary part of $\chi^{+-}_{\mathrm{c.el.}}(\mathbf{q},\omega)$ becomes non-zero. This threshold value corresponds to the smallest distance in q-space between an occupied spin-down state and an unoccupied spin-up state, or vice versa, of nearly the same energy ($\simeq \varepsilon_F$). At $q = q_0$, the function makes a discontinuous step from zero to a finite value. The above result, combined with eqn (3.1.26), leads to

$$\mathrm{Im}\big[\widetilde{\mathcal{J}}(\mathbf{q},\omega)\big] = \zeta(\mathbf{q})\hbar\omega, \tag{3.1.37a}$$

with

$$\zeta(\mathbf{q}) = \frac{2\pi}{3\nu}\mathcal{N}_\uparrow(\varepsilon_F)\mathcal{N}_\downarrow(\varepsilon_F)\sum_{\boldsymbol{\tau}}|j(\mathbf{q}+\boldsymbol{\tau})|^2\frac{k_F}{|\mathbf{q}+\boldsymbol{\tau}|}, \tag{3.1.37b}$$

where the sum is restricted to $k_{F\uparrow} - k_{F\downarrow} < |\mathbf{q}+\boldsymbol{\tau}| < k_{F\uparrow} + k_{F\downarrow}$. The imaginary part of $\widetilde{\mathcal{J}}(\mathbf{q},\omega)$ gives rise to a non-zero width in the spin-wave excitations. If the above result is inserted in eqns (3.1.25) and (3.1.33), the denominator of the Green functions may approximately be written $(\hbar\omega)^2 - (E'_{\mathbf{q}})^2 + 2i\Gamma_{\mathbf{q}}\hbar\omega$, where $\Gamma_{\mathbf{q}}$ is half the linewidth of the spin waves at the wave-vector $\mathbf{q}$, and is found to take the form

$$\Gamma_{\mathbf{q}} = J\big[A + J\{\mathcal{J}(\mathbf{0}) - \mathcal{J}(\mathbf{q})\}\big]\,\zeta(\mathbf{q}) = JA_{\mathbf{q}}\,\zeta(\mathbf{q}). \tag{3.1.38}$$

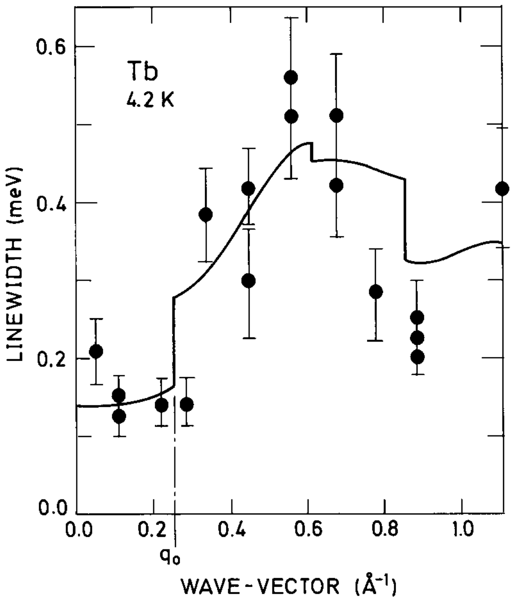

Fig. 3.1. The linewidths of magnons propagating in the c-direction of Tb at 4 K, compared with a theory based upon the nearly-free-electron model. The abrupt changes in the calculated lifetimes are due to the spin-splitting of the Fermi surface.

The lifetimes of the magnons propagating in the c-direction in Tb at 4 K, at which temperature the conduction electrons provide the dominant scattering process, were measured by Bjerrum Møller and Mackintosh (1979). As illustrated in Fig. 3.1, the linewidths are small, but non-zero, at small wave-vectors, rise abruptly at about a quarter of the way to the zone boundary, and fall again at large q. In order to interpret these results rigorously, it would be necessary to use eqn (3.1.27), with the correct band structure for Tb and realistic values for the exchange matrix elements $I(n'\mathbf{k}', n\mathbf{k})$. However, it is possible to obtain a semi-quantitative description by using the simple free-electron expression (3.1.37). As we shall see in the remainder of this section, this model, with an

sf-interaction determined, for example, from the polarization of the conduction electrons (3.1.16–19), gives a surprisingly good account of the real scattering processes involving the interaction between the $4f$ and conduction electrons. Although the dominant d bands are far from parabolic in the rare earths, the nearly-free-electron Fermi surface for a trivalent hcp metal has a sheet with the form of a lens normal to the c-axis (Mackintosh *et al.* 1963), which mimics the Fermi-surface webbing described in Section 1.3, and reproduces a number of observed features. In the calculations of Jensen (1982a), compared with the experimental results in Fig. 5.13, the spin-splitting of this surface gives rise to the critical value q_0 at which the linewidths abruptly increase. The finite lifetimes below this cut-off are due to interband transitions between states on sections of the Fermi surface with opposite spin, which intersect in the primitive Brillouin zone after translation through a reciprocal-lattice vector. These effects will also occur in calculations based on a realistic band structure, whereas the behaviour at higher q is much more dependent on the details of the energy bands.

3.1.2 The mass-enhancement of the conduction electrons

The processes in which the spin waves are scattered by the electron-hole pair excitations of the conduction electrons, and which therefore limit their lifetime, also have consequences for the conduction electrons. The energies of the conduction electrons are changed, and hence also their effective mass at the Fermi surface m^*, as measured directly by cyclotron resonance or the de Haas–van Alphen effect, or as determined from the low-temperature heat capacity. In the zero-temperature limit, the electronic part of the specific heat is

$$C = \gamma T = \frac{m^*}{m}\gamma_0 T \qquad ; \quad \gamma_0 = \tfrac{1}{3}\pi^2 k_B^2 \{\mathcal{N}_\uparrow(\widetilde{\varepsilon}_F) + \mathcal{N}_\downarrow(\widetilde{\varepsilon}_F)\}N, \tag{3.1.39}$$

where $m^* = (m^*_\uparrow + m^*_\downarrow)/2$ in the spin-polarized case. The use of $\widetilde{\varepsilon}_F$ instead of ε_F is meant to indicate that all the effects of the MF Hamiltonian, including the interband couplings in (3.1.7), are assumed to be incorporated in γ_0 or m.

In order to calculate m^*, we shall utilize the Green functions of the conduction electrons. Because these particles are fermions, it is convenient to introduce an alternative type of Green function, in which an anticommutator bracket replaces the commutator bracket occurring in the definition (3.3.12), so that, for instance,

$$G_\uparrow(\mathbf{k}, t-t') \equiv \langle\langle c_{\mathbf{k}\uparrow}(t)\, ; c^+_{\mathbf{k}\uparrow}(t')\rangle\rangle_+ = -\frac{i}{\hbar}\theta(t-t')\langle\{c_{\mathbf{k}\uparrow}(t)\, , c^+_{\mathbf{k}\uparrow}(t')\}\rangle. \tag{3.1.40}$$

The Fourier transform obeys an equation of motion equivalent to eqn (3.3.14a), except that the commutator on the *right*-hand side of this equation is replaced by the anticommutator, or

$$\hbar\omega G_\uparrow(\mathbf{k},\omega) - \langle\langle [\, c_{\mathbf{k}\uparrow}\, , \mathcal{H}\,]\, ; c^+_{\mathbf{k}\uparrow}\rangle\rangle_+ = \langle\{c_{\mathbf{k}\uparrow}\, , c^+_{\mathbf{k}\uparrow}\}\rangle = 1. \tag{3.1.41}$$

If $\mathcal{H}$ is approximated by $\widetilde{\mathcal{H}}_s$, given by eqn (3.1.10), we obtain the non-interacting value of the Green function

$$G_\uparrow(\mathbf{k},\omega) \simeq G^o_\uparrow(\mathbf{k},\omega) = \frac{1}{\hbar\omega - \varepsilon_{\mathbf{k}\uparrow}} \tag{3.1.42}$$

(neglecting the minor difference between ε and $\widetilde{\varepsilon}$), showing that the poles of the Green function determine the energies of the conduction electrons. Considering the total Hamiltonian, in the approximation given by (3.1.20), we have instead

$$(\hbar\omega - \varepsilon_{\mathbf{k}\uparrow})G_\uparrow(\mathbf{k},\omega) + \sqrt{2J/N}\sum_{\mathbf{q}\boldsymbol{\tau}} j(\mathbf{q}+\boldsymbol{\tau})\langle\langle c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a^+_{-\mathbf{q}}\, ; c^+_{\mathbf{k}\uparrow}\rangle\rangle_+ = 1. \tag{3.1.43}$$

The equation of motion of the new Green function is determined from

$$\begin{aligned}
&[\, c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a^+_{-\mathbf{q}} \,,\, \mathcal{H}\,] \\
&= \big\{\varepsilon_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} - A - J\widetilde{\mathcal{J}}(\mathbf{0},0)\big\} c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a^+_{-\mathbf{q}} - B\, c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a_{\mathbf{q}} \\
&\quad - \sqrt{2J/N} \sum_{\mathbf{k}'\boldsymbol{\tau}'} j(-\mathbf{q}-\boldsymbol{\tau}') \Big[c^+_{\mathbf{k}'-\mathbf{q}-\boldsymbol{\tau}'\downarrow} c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} c_{\mathbf{k}'\uparrow} \\
&\qquad\qquad\qquad\qquad + \delta_{\mathbf{k}-\boldsymbol{\tau},\mathbf{k}'-\boldsymbol{\tau}'} \, \langle a^+_{-\mathbf{q}} a_{-\mathbf{q}} \rangle c_{\mathbf{k}+\boldsymbol{\tau}'-\boldsymbol{\tau}\uparrow} \Big],
\end{aligned}$$

using an RPA decoupling procedure to obtain the last term. To proceed further, we have to calculate $\langle\langle c^+_{\mathbf{k}'-\mathbf{q}-\boldsymbol{\tau}'\downarrow} c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} c_{\mathbf{k}'\uparrow} \,;\, c^+_{\mathbf{k}\uparrow} \rangle\rangle_+$ and, within the RPA,

$$\begin{aligned}
&\langle\langle c^+_{\mathbf{k}'-\mathbf{q}-\boldsymbol{\tau}'\downarrow} c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} c_{\mathbf{k}'\uparrow} \,;\, c^+_{\mathbf{k}\uparrow} \rangle\rangle_+ \\
&= \delta_{\mathbf{k}'-\boldsymbol{\tau}',\mathbf{k}-\boldsymbol{\tau}} \, f_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} \langle\langle c_{\mathbf{k}+\boldsymbol{\tau}'-\boldsymbol{\tau}\uparrow} \,;\, c_{\mathbf{k}\uparrow} \rangle\rangle_+ \\
&\quad - \sqrt{2J/N} \frac{j(\mathbf{q}+\boldsymbol{\tau}')\{f_{\mathbf{k}'\uparrow} - f_{\mathbf{k}'-\mathbf{q}-\boldsymbol{\tau}'\downarrow}\}}{\hbar\omega - \varepsilon_{\mathbf{k}'\uparrow} - \varepsilon_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} + \varepsilon_{\mathbf{k}'-\mathbf{q}-\boldsymbol{\tau}'\downarrow}} \langle\langle c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a^+_{-\mathbf{q}} \,;\, c^+_{\mathbf{k}\uparrow} \rangle\rangle_+ .
\end{aligned}$$

Writing $\hbar\omega_1 = \hbar\omega - \varepsilon_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow}$, we obtain from these equations

$$\begin{aligned}
&\big\{\hbar\omega_1 + A + J\widetilde{\mathcal{J}}(\mathbf{0},0) - J\widetilde{\mathcal{J}}^*(\mathbf{q},-\omega_1)\big\} \langle\langle c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a^+_{-\mathbf{q}} \,;\, c^+_{\mathbf{k}\uparrow} \rangle\rangle_+ \\
&\qquad\qquad\qquad + B \langle\langle c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a_{\mathbf{q}} \,;\, c^+_{\mathbf{k}\uparrow} \rangle\rangle_+ \\
&= -\sqrt{2J/N} \sum_{\boldsymbol{\tau}'} j(-\mathbf{q}-\boldsymbol{\tau}') \big(f_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} + \langle a^+_{-\mathbf{q}} a_{-\mathbf{q}} \rangle \big) \langle\langle c_{\mathbf{k}+\boldsymbol{\tau}'-\boldsymbol{\tau}\uparrow} \,;\, c^+_{\mathbf{k}\uparrow} \rangle\rangle_+ .
\end{aligned} \tag{3.1.44}$$

In the sum, the terms with $\boldsymbol{\tau}' \neq \boldsymbol{\tau}$ only lead to higher-order corrections, of the same type as those arising from the difference between $c_{\mathbf{k}\uparrow}$ and $\widetilde{c}_{\mathbf{k}\uparrow}$, and they can be neglected. Calculating $\langle\langle c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a_{\mathbf{q}} \,;\, c^+_{\mathbf{k}\uparrow} \rangle\rangle_+$ in an equivalent way, and introducing the notation:

$$\begin{aligned}
&G_{m1}(\mathbf{q},\omega) = \langle\langle a_{\mathbf{q}} \,;\, a^+_{\mathbf{q}} \rangle\rangle \qquad ; \quad G_{m2}(\mathbf{q},\omega) = \langle\langle a^+_{\mathbf{q}} \,;\, a_{\mathbf{q}} \rangle\rangle = G^*_{m1}(\mathbf{q},-\omega) \\
&G_{m3}(\mathbf{q},\omega) = \langle\langle a^+_{-\mathbf{q}} \,;\, a^+_{\mathbf{q}} \rangle\rangle
\end{aligned} \tag{3.1.45}$$

for the magnon Green functions determined by (3.1.25) and (3.1.33), we obtain

$$\begin{aligned}
&\langle\langle c_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} a^+_{-\mathbf{q}} \,;\, c^+_{\mathbf{k}\uparrow} \rangle\rangle_+ = \sqrt{2J/N}\, j(-\mathbf{q}-\boldsymbol{\tau}) G_\uparrow(\mathbf{k},\omega) \\
&\quad \times \big[\{ f_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} + \langle a^+_{\mathbf{q}} a_{\mathbf{q}} \rangle \} G_{m2}(\mathbf{q},\omega_1) - \langle a_{\mathbf{q}} a_{-\mathbf{q}} \rangle G_{m3}(\mathbf{q},\omega_1) \big].
\end{aligned} \tag{3.1.46}$$

Defining the self-energy of the spin-up electrons by the relation

$$G_\uparrow(\mathbf{k},\omega) = \frac{1}{\hbar\omega - \varepsilon_{\mathbf{k}\uparrow} - \Sigma_\uparrow(\mathbf{k},\omega)}, \tag{3.1.47}$$

and using (3.1.10) to establish that

$$G_m(\mathbf{q},\omega) = \frac{1}{i\pi} \int \frac{G_m(\mathbf{q},\omega')}{\hbar\omega' - \hbar\omega} d(\hbar\omega'),$$

we obtain finally

$$\begin{aligned}\Sigma_\uparrow(\mathbf{k},\omega) = -\frac{2J}{N}\sum_{\mathbf{q}\boldsymbol{\tau}} |j(\mathbf{q}+\boldsymbol{\tau})|^2 \frac{1}{i\pi}\int_{-\infty}^{\infty} \frac{d(\hbar\omega')}{\hbar\omega' - \hbar\omega + \varepsilon_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow}} \\ \times \big[\{f_{\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}\downarrow} + \langle a^+_{\mathbf{q}} a_{\mathbf{q}}\rangle\} G_{m2}(\mathbf{q},\omega') - \langle a_{\mathbf{q}} a_{-\mathbf{q}}\rangle G_{m3}(\mathbf{q},\omega')\big].\end{aligned} \tag{3.1.48}$$

This result corresponds to that deduced by Nakajima (1967), as generalized by Fulde and Jensen (1983).

The average effective mass of the spin-up electrons at the Fermi surface is determined by

$$\frac{1}{m^*_\uparrow} = \frac{1}{\hbar^2 \mathbf{k}} \frac{\partial \mathcal{E}_{\mathbf{k}\uparrow}}{\partial \mathbf{k}}\bigg|_{k=k_{F\uparrow}},$$

averaged over the direction of $\mathbf{k}$. Here $\mathcal{E}_{\mathbf{k}\uparrow} = \varepsilon_{\mathbf{k}\uparrow} + \mathrm{Re}\big[\Sigma_\uparrow(\mathbf{k},\mathcal{E}_{\mathbf{k}\uparrow})\big]$ is the corrected energy of the spin-up electrons. We can neglect the explicit $\mathbf{k}$-dependence of $\Sigma_\uparrow(\mathbf{k},\omega)$ in comparison to its frequency dependence, disregarding terms of the order $E_{\mathbf{q}}/\varepsilon_F$ in the derivative of $\mathcal{E}_{\mathbf{k}\uparrow}$, so that

$$\frac{\partial \mathcal{E}_{\mathbf{k}\uparrow}}{\partial \mathbf{k}} = \frac{\partial \varepsilon_{\mathbf{k}\uparrow}}{\partial \mathbf{k}} + \frac{1}{\hbar}\frac{\partial}{\partial\omega}\mathrm{Re}\big[\Sigma_\uparrow(\mathbf{k},\omega)\big]\bigg|_{\hbar\omega=\mathcal{E}_{\mathbf{k}\uparrow}} \frac{\partial \mathcal{E}_{\mathbf{k}\uparrow}}{\partial \mathbf{k}},$$

or

$$\frac{m^*_\uparrow}{m} = 1 - \frac{1}{\hbar}\frac{\partial}{\partial\omega}\mathrm{Re}\big[\Sigma_\uparrow(\mathbf{k}_{F\uparrow},\omega)\big]\bigg|_{\hbar\omega=\mathcal{E}_F}, \tag{3.1.49}$$

averaged over the Fermi surface. Within the same approximation, the terms in eqn (3.1.48) proportional to the magnon correlation-functions can be neglected and, to leading order, $\hbar\omega = \mathcal{E}_F$ in the ω-derivative may be replaced by $\varepsilon_{\mathbf{k}\uparrow}$, with $\mathbf{k} = \mathbf{k}_{F\uparrow}$. In the limit of zero temperature, the free-electron model then gives

$$\begin{aligned}\frac{m^*_\uparrow}{m} = 1 + \frac{2J}{N}\sum_{\mathbf{q}\boldsymbol{\tau}} |j(\mathbf{q}+\boldsymbol{\tau})|^2 \frac{1}{\pi}\int_{-\infty}^{\infty} d(\hbar\omega') \\ \times \tfrac{1}{2}\int_{-1}^{1} d\mu \frac{\mathrm{Im}\big[G_{m2}(\mathbf{q},\omega')\big]}{\big(\hbar\omega' + \Delta + \frac{(\hbar|\mathbf{q}+\boldsymbol{\tau}|)^2}{2m} - \frac{\hbar^2 k|\mathbf{q}+\boldsymbol{\tau}|}{m}\mu\big)^2},\end{aligned}$$

subject to the conditions that $k = k_{F\uparrow}$ and $|\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}| < k_{F\downarrow}$. These conditions imply that $k_{F\uparrow} - k_{F\downarrow} < |\mathbf{q}+\boldsymbol{\tau}| < k_{F\uparrow} + k_{F\downarrow}$, and that the lower bound -1 of the μ-integral is replaced by $(\hbar^2 q^2 + 2m\Delta)/(2\hbar^2 k_{F\uparrow}|\mathbf{q}+\boldsymbol{\tau}|)$. Because $\mathrm{Im}\big[G_{m2}(\mathbf{q},\omega')\big]$ is odd in ω', the contribution due to the upper bound in the μ-integral can be neglected (it is of the order $\hbar\omega'/\varepsilon_F$). Since

$$\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\mathrm{Im}\big[G_{m2}(\mathbf{q},\omega')\big]}{\hbar\omega'} d(\hbar\omega') = \mathrm{Re}\big[G_{m2}(\mathbf{q},0)\big] = -\frac{A_{\mathbf{q}}}{E^2_{\mathbf{q}}},$$

the average mass-enhancement of the spin-up electrons at the Fermi surface is

$$\frac{m^*_\uparrow}{m} = 1 + \frac{\mathcal{N}_\downarrow(\varepsilon_F)}{2k_{F\uparrow}k_{F\downarrow}}\int_{k_{F\uparrow}-k_{F\downarrow}}^{k_{F\uparrow}+k_{F\downarrow}} dq \int \frac{d\Omega_{\mathbf{q}}}{4\pi}\, q|j(\mathbf{q})|^2 \frac{2JA_{\mathbf{q}}}{E^2_{\mathbf{q}}}, \tag{3.1.50}$$

and, by symmetry, $m^*_\downarrow/m$ is given by the same expression, except that $\mathcal{N}_\downarrow(\varepsilon_F)$ is replaced by $\mathcal{N}_\uparrow(\varepsilon_F)$. We note that the mass-enhancement only depends on the static part of the susceptibility, i.e. $G_{m2}(\mathbf{q},0)$, and that the magnitude of the mass-renormalization is intimately related to the linewidth of the spin waves derived above in eqn (3.1.38). Utilizing this connection, we can write the specific heat, in the zero-temperature limit,

$$C = \frac{\pi^2}{3} k_B^2 T \left[\mathcal{N}_\uparrow(\varepsilon_F) + \mathcal{N}_\downarrow(\varepsilon_F) + \frac{1}{N} \sum_{\mathbf{q}} \frac{2\Gamma_{\mathbf{q}}}{\pi E_{\mathbf{q}}^2} \right] N, \tag{3.1.51}$$

where again the $\mathbf{q}$-sum only extends over the primitive Brillouin zone. With typical values of $E_{\mathbf{q}}\mathcal{N}(\varepsilon_F) \approx 0.01$ and $2\Gamma_{\mathbf{q}}/E_{\mathbf{q}} \approx 0.05$, this expression predicts a doubling of the linear term in the heat capacity due to the interaction between the conduction electrons and the spin waves, which therefore has an appreciable effect on the effective mass of the electrons near the Fermi surface. More detailed analyses (Nakajima 1967; Fulde and Jensen 1983) show that the deformation of the electronic bands is pinned to the Fermi surface, and occurs within a narrow interval with a width corresponding to the spin-wave energies. This implies that, even if the electronic energies $\varepsilon_{\mathbf{k}\sigma}$ appearing in the magnon Green-functions were replaced with $\mathcal{E}_{\mathbf{k}\sigma}$, due to higher-order processes, this modification would not be of much importance. The total electronic heat capacity is $C_e = \sum_{\mathbf{k}\sigma} \mathcal{E}_{\mathbf{k}\sigma} df_{\mathbf{k}\sigma}/dT$, when the imaginary part of the self-energy is neglected. The extra contribution due to the coupling to the spin waves is linear only at the lowest temperatures ($k_BT < 0.05E_{\mathbf{q}}$), after which it increases more rapidly than linearly to its maximum at $k_BT \simeq 0.15E_{\mathbf{q}}$. Above $k_BT \simeq 0.3E_{\mathbf{q}}$, this contribution becomes negative and finally dies out when $k_BT \approx E_{\mathbf{q}}$. This variation with temperature was described by Fulde and Jensen (1983), and has been discussed in the context of the phonon interaction by Grimvall (1981). The bosons (magnons and phonons) do not contribute directly to the linear term in the heat capacity, which is thus a characteristic phenomenon of the Fermi gas. However, the departure from the linear variation when $k_BT > 0.05E_{\mathbf{q}}$ may be influenced by the spin-wave contribution

$$\begin{aligned} C_m &= \sum_{\mathbf{q}} \frac{1}{\pi} \int_{-\infty}^{\infty} d(\hbar\omega) \frac{2\Gamma_{\mathbf{q}}(\hbar\omega)^3}{\left\{(\hbar\omega)^2 - E_{\mathbf{q}}^2(T)\right\}^2 + \left\{2\Gamma_{\mathbf{q}}\hbar\omega\right\}^2} \frac{d}{dT}\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right) \\ &\simeq \sum_{\mathbf{q}} E_{\mathbf{q}}(T) \frac{d}{dT}\left(n_{\mathbf{q}} + \tfrac{1}{2}\right) + \frac{\pi^2}{3} k_B^2 T \sum_{\mathbf{q}} \frac{2\Gamma_{\mathbf{q}}}{\pi E_{\mathbf{q}}^2} \left[\frac{2}{5y^2} + \frac{4}{7y^4} + \cdots \right]_{y=\beta E_{\mathbf{q}}/2\pi}, \end{aligned} \tag{3.1.52}$$

to first order in $\Gamma_{\mathbf{q}}/E_{\mathbf{q}}$. The first term is the RPA spin-wave contribution (5.3.3) derived before, which dominates strongly at elevated temperatures. However, in the low-temperature limit, the second term is of the same order of magnitude as the non-linear corrections to eqn (3.1.51). For comparison, the last term in this equation is multiplied by the factor $\left[1 + 3/(5y^2) + 5/(7y^4) + \cdots\right]$ when the higher-order temperature effects are included. The additional contribution due to the non-zero linewidth of the bosons is normally not considered in the literature. It may be added to the pure electronic contribution derived by Fulde and Jensen (1983), by replacing $yL'(y)$ with $2yL'(y) + L(y)$ in their eqn (17*a*). The mass-enhancement effect increases proportionally to the inverse of $E_{\mathbf{q}}$ ($\Gamma_{\mathbf{q}} \propto A_{\mathbf{q}}$). On the other hand, the interval in which the linear variation occurs is diminished correspondingly, requiring a more careful consideration of the higher-order modifications.

In the metals, the itinerant electrons also interact with the phonons, and this leads to an entirely equivalent enhancement of their mass. This effect has been calculated for the whole rare earth series by Skriver and Mertig (1990), who find an increase of the band mass due to coupling to the phonons of typically about 35% for the heavy elements. Assuming the different contributions to be additive, we may write the total mass-enhancement

$$\frac{m^*}{m} = 1 + \lambda_{\text{tot}} = 1 + \lambda_{\text{sw}} + \lambda_{\text{ph}} + \lambda_{\text{c}} \tag{3.1.53}$$

as a sum of contributions from the interactions with the spin waves and the phonons, and from the possible exchange and Coulomb interactions within the electron gas itself (λ_{c}). Although the different correlation effects may increase the effective mass derived from band structure calculations by a factor of two or more, it is difficult to isolate this enhancement in heat capacity measurements, because of the quite narrow temperature interval where a truly linear behaviour can be anticipated. This interval is bounded below because of the nuclear spins, which may give large contributions to the heat capacity in the mK-range. The upper bound is due partly to the higher-order temperature effects, but most importantly to the disturbance by the normal boson contributions, approximately proportional to $T^{\alpha}\exp(-E_{\mathbf{0}}/k_BT)$ and T^3 for the magnons and the phonons respectively, which completely dominate the heat capacity at elevated temperatures. Because of this limitation, the most reliable method of determining the mass-enhancement is by measuring the temperature dependence of the dHvA effect, which also allows a separation of the contributions from the different sheets of the Fermi surface. Using this method, and comparing with the results of band structure calculations, Sondhelm and Young (1985) found values of λ_{tot} varying between 0.2 and 1.1 for Gd. The theoretical results of Fulde and Jensen (1983) lie within this range, but these measurements point to the necessity of discriminating between states of different symmetry in considering the mass-enhancement of the conduction electron gas.

3.1.3 Magnetic contributions to the electrical resistivity

The electrical resistivity of a metal can be calculated by solving the *Boltzmann equation.* We shall not discuss the theory of transport properties in detail here, but instead refer to the comprehensive treatments of Ziman (1960), and Smith and Højgaard Jensen (1989). The non-equilibrium distribution function $g_{\mathbf{k}\sigma}$, generated by the application of an external electric field $\mathbf{E}$, is written in terms of the equilibrium distribution function, and is determined by the Boltzmann equation:

$$g_{\mathbf{k}\sigma} = f_{\mathbf{k}\sigma} + f_{\mathbf{k}\sigma}(1 - f_{\mathbf{k}\sigma})\psi_{\mathbf{k}\sigma}, \quad \text{where} \quad \frac{\partial g_{\mathbf{k}\sigma}}{\partial \mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} = \left.\frac{dg_{\mathbf{k}\sigma}}{dt}\right|_{\text{coll}}. \tag{3.1.54}$$

The electrical current-density is then determined as

$$\mathbf{j} = \overline{\overline{\sigma}} \cdot \mathbf{E} = -\frac{e}{V}\sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}(1 - f_{\mathbf{k}\sigma})\psi_{\mathbf{k}\sigma},$$

with $\hbar\mathbf{v}_{\mathbf{k}\sigma} = \partial\varepsilon_{\mathbf{k}\sigma}/\partial\mathbf{k}$. In the linear regime, the left-hand side of the Boltzmann equation is

$$\frac{\partial g_{\mathbf{k}\sigma}}{\partial \mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} \simeq -\frac{\partial f_{\mathbf{k}\sigma}}{\partial \varepsilon_{\mathbf{k}\sigma}} e\mathbf{v}_{\mathbf{k}\sigma} \cdot \mathbf{E} = e\beta f_{\mathbf{k}\sigma}(1 - f_{\mathbf{k}\sigma})\mathbf{v}_{\mathbf{k}\sigma} \cdot \mathbf{E}.$$

The collision term on the right-hand side is

$$\left.\frac{dg_{\mathbf{k}\sigma}}{dt}\right|_{\text{coll}} = \sum_{\mathbf{k}'\sigma'} \big[g_{\mathbf{k}'\sigma'}(1 - g_{\mathbf{k}\sigma})W(\mathbf{k}'\sigma', \mathbf{k}\sigma) - g_{\mathbf{k}\sigma}(1 - g_{\mathbf{k}'\sigma'})W(\mathbf{k}\sigma, \mathbf{k}'\sigma')\big],$$

where $W(\mathbf{k}\sigma, \mathbf{k}'\sigma')$ is the probability per unit time for an electronic transition from an occupied state $|\mathbf{k}\sigma\!>$ to an unoccupied state $|\mathbf{k}'\sigma'\!>$. Linearizing the collision term, and using the principle of detailed balance, so that this term must vanish if $g_{\mathbf{k}\sigma} = f_{\mathbf{k}\sigma}$, we may reduce the Boltzmann equation to

$$e\beta f_{\mathbf{k}\sigma}(1-f_{\mathbf{k}\sigma})\mathbf{v}_{\mathbf{k}\sigma}\cdot\mathbf{E} = -\sum_{\mathbf{k}'\sigma'}(1-f_{\mathbf{k}\sigma})f_{\mathbf{k}'\sigma'}W(\mathbf{k}'\sigma',\mathbf{k}\sigma)\big(\psi_{\mathbf{k}\sigma}-\psi_{\mathbf{k}'\sigma'}\big).$$

It is possible to find an upper bound on the resistivity from this equation, with the use of a variational principle. Defining $\hat{\mathbf{u}}$ to be a unit vector along one of the principal axes of the resistivity tensor,

$$\rho_{uu} \leq \frac{V}{2\beta e^2}\frac{\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}(1-f_{\mathbf{k}'\sigma'})f_{\mathbf{k}\sigma}W(\mathbf{k}\sigma,\mathbf{k}'\sigma')\big(\phi_{\mathbf{k}\sigma}-\phi_{\mathbf{k}'\sigma'}\big)^2}{\big[\sum_{\mathbf{k}\sigma}\mathbf{v}_{\mathbf{k}\sigma}\cdot\hat{\mathbf{u}}\,(1-f_{\mathbf{k}\sigma})f_{\mathbf{k}\sigma}\,\phi_{\mathbf{k}\sigma}\big]^2}, \qquad (3.1.55)$$

where $\phi_{\mathbf{k}\sigma}$ is an arbitrary trial function, and where the equality applies if $\phi_{\mathbf{k}\sigma} = \psi_{\mathbf{k}\sigma}$. In the case of the free-electron model, the Boltzmann equation possesses an exact solution, $\psi_{\mathbf{k}\sigma} \propto \mathbf{k}\cdot\hat{\mathbf{u}}$, if the scattering is purely elastic. As discussed, for instance, by Hessel Andersen *et al.* (1980), this trial function is still useful for treating possible inelastic scattering mechanisms, at least as long as the resistivity is dominated by elastic impurity scattering, so we shall use $\phi_{\mathbf{k}\sigma} = \mathbf{k}\cdot\hat{\mathbf{u}}$.

In the Born approximation, the transition probability per unit time is given by the Golden Rule (4.1.1), which we may here write

$$W(\mathbf{k}\sigma,\mathbf{k}'\sigma') = \frac{2\pi}{\hbar}\sum_{if}P_i|\!<\!\mathbf{k}\sigma; i\,|\,\mathcal{H}_{\mathrm{int}}\,|\,\mathbf{k}'\sigma'; f\!>\!|^2\delta(\hbar\omega+E_i-E_f),$$

where $\hbar\omega = \varepsilon_{\mathbf{k}\sigma}-\varepsilon_{\mathbf{k}'\sigma'}$. Instead of basing the derivation of the magnetic resistivity on the linearized spin-wave expression (3.1.20) for $\mathcal{H}_{\mathrm{int}}$, we shall be somewhat more general and use $\mathcal{H}_{sf}$ from eqn (3.1.6) as the interaction Hamiltonian. We assume that the system is uniform, paramagnetic or ferromagnetically ordered, continue to utilize the simple free-electron model, and replace $(g-1)I(n'\mathbf{k}', n\mathbf{k})$ by $j(\mathbf{k}'-\mathbf{k}+\boldsymbol{\tau})$. The MF part (3.1.7) of the Hamiltonian may lead to a modification $\varepsilon_{\mathbf{k}\sigma} \to \widetilde{\varepsilon}_{\mathbf{k}\sigma}$ of the electronic band-states, but we can neglect this difference to leading order, and since the MF Hamiltonian does not lead to transitions between electronic states, we can replace J_{iz} by $\hat{J}_{iz} = J_{iz} - \langle J_z\rangle$ in $\mathcal{H}_{\mathrm{int}}$, and obtain

$$\begin{aligned}
W(\mathbf{k}\sigma,\mathbf{k}'\sigma') &= \int_{-\infty}^{\infty} d(\hbar\omega)\delta(\hbar\omega-\varepsilon_{\mathbf{k}\sigma}+\varepsilon_{\mathbf{k}'\sigma'})\\
&\times\frac{2\pi}{\hbar}\sum_{if}P_i\frac{1}{N^2}\sum_{jj'}|j(\mathbf{k}'-\mathbf{k})|^2e^{-i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}\\
&\times\Big\{<\!i\,|J^-_{j'}|\,f\!><\!f\,|J^+_j|\,i\!>\,\delta_{\sigma\uparrow}\delta_{\sigma'\downarrow}+<\!i\,|J^+_{j'}|\,f\!><\!f\,|J^-_j|\,i\!>\,\delta_{\sigma\downarrow}\delta_{\sigma'\uparrow}\\
&\qquad+<\!i\,|\hat{J}_{j'z}|\,f\!><\!f\,|\hat{J}_{jz}|\,i\!>\,(\delta_{\sigma\uparrow}\delta_{\sigma'\uparrow}+\delta_{\sigma\downarrow}\delta_{\sigma'\downarrow})\Big\}\delta(\hbar\omega+E_i-E_f),
\end{aligned}\qquad (3.1.56)$$

accounting explicitly for the condition on $\hbar\omega$ by the integral over the first δ-function. Using the same procedure as in the calculation of the neutron-scattering cross-section, when going from (4.1.16) to (4.2.1–3), we may write this:

$$\begin{aligned}W(\mathbf{k}\sigma,\mathbf{k}'\sigma') =&\frac{2}{N\hbar}\int_{-\infty}^{\infty} d(\hbar\omega)\delta(\hbar\omega-\varepsilon_{\mathbf{k}\sigma}+\varepsilon_{\mathbf{k}'\sigma'})\frac{1}{1-e^{-\beta\hbar\omega}}|j(\mathbf{k}-\mathbf{k}')|^2\\ &\times\big\{\chi''_{-+}(\mathbf{k}-\mathbf{k}',\omega)\delta_{\sigma\uparrow}\delta_{\sigma'\downarrow}+\chi''_{+-}(\mathbf{k}-\mathbf{k}',\omega)\delta_{\sigma\downarrow}\delta_{\sigma'\uparrow}\\ &\qquad+\chi''_{zz}(\mathbf{k}-\mathbf{k}',\omega)(\delta_{\sigma\uparrow}\delta_{\sigma'\uparrow}+\delta_{\sigma\downarrow}\delta_{\sigma'\downarrow})\big\}.\end{aligned}$$

Introducing this expression into (3.1.55), and using $\phi_{\mathbf{k}\sigma}=\mathbf{k}\cdot\hat{\mathbf{u}}$ and $\mathbf{k}'=\mathbf{k}-\mathbf{q}-\boldsymbol{\tau}$, we proceed as in the derivation of eqn (3.1.36) for $\mathrm{Im}\big[\chi^{+-}_{\mathrm{c.el.}}(\mathbf{q},\omega)\big]$, obtaining

$$\begin{aligned}&\frac{1}{N}\sum_{\mathbf{k}} f_{\mathbf{k}\downarrow}(1-f_{\mathbf{k}-\mathbf{q}\uparrow})\delta(\hbar\omega-\varepsilon_{\mathbf{k}\downarrow}+\varepsilon_{\mathbf{k}-\mathbf{q}\uparrow})=\\ &\frac{V}{N(2\pi)^2}\int_0^{\infty}dk\,k^2\int_{-1}^{1}d\mu f(\varepsilon_{\mathbf{k}\downarrow})\big\{1-f(\varepsilon_{\mathbf{k}\downarrow}-\hbar\omega)\big\}\delta\big(\hbar\omega-\Delta+\varepsilon_q-\mu\frac{\hbar^2qk}{m}\big)\\ &=\frac{V}{N(2\pi)^2}\int_{\frac{\Delta}{2}}^{\infty}d\varepsilon\,\frac{m^2}{\hbar^4q}f(\varepsilon)\big\{1-f(\varepsilon-\hbar\omega)\big\}\;=\;\frac{V}{N(2\pi)^2}\frac{m^2}{\hbar^4q}\frac{\hbar\omega}{e^{\beta\hbar\omega}-1},\end{aligned}$$

where $k_{F\uparrow}-k_{F\downarrow}<q<k_{F\uparrow}+k_{F\downarrow}$ (when $k_BT\ll\varepsilon_F$). The denominator in (3.1.55) may be calculated in a straightforward fashion and is $[N\nu/(\hbar\beta)]^2$, and we finally obtain the following expression for the resistivity, or rather its upper limit:

$$\begin{aligned}\rho_{uu}(T)\simeq\rho_0&\frac{3}{(4k_{F\uparrow}k_{F\downarrow})^2\overline{j_u^2}}\int_{k_{F\uparrow}-k_{F\downarrow}}^{k_{F\uparrow}+k_{F\downarrow}}dq\int\frac{d\Omega_{\mathbf{q}}}{4\pi}\int_{-\infty}^{\infty}d(\hbar\omega)\\ &\times|j(\mathbf{q})|^2\big(\mathbf{q}\cdot\hat{\mathbf{u}}\big)^2q\frac{\beta\hbar\omega}{\sinh^2(\beta\hbar\omega/2)}\frac{1}{\pi}\sum_\alpha\chi''_{\alpha\alpha}(\mathbf{q},\omega),\end{aligned}\qquad(3.1.57a)$$

where

$$\rho_0=\frac{3}{2}\frac{V}{N}\frac{\pi m}{\hbar e^2\varepsilon_F}\overline{j_u^2}=\frac{m}{ne^2}\frac{\pi}{\hbar}\{\mathcal{N}_\uparrow(\varepsilon_F)+\mathcal{N}_\downarrow(\varepsilon_F)\}\overline{j_u^2},\qquad(3.1.57b)$$

$n=\nu N/V$ is the electron density, and

$$\overline{j_u^2}=4\frac{3}{(2k_F)^4}\int_0^{2k_F}dq\int\frac{d\Omega_{\mathbf{q}}}{4\pi}|j(\mathbf{q})|^2\big(\mathbf{q}\cdot\hat{\mathbf{u}}\big)^2q.\qquad(3.1.57c)$$

For cubic symmetry, ρ_{uu} is independent of u and $\big(\mathbf{q}\cdot\hat{\mathbf{u}}\big)^2$ can be replaced by $q^2/3$. In the high-temperature limit, we have

$$\begin{aligned}&\frac{1}{\pi}\int_{-\infty}^{\infty}d(\hbar\omega)\frac{\beta\hbar\omega}{\sinh^2(\beta\hbar\omega/2)}\sum_\alpha\chi''_{\alpha\alpha}(\mathbf{q},\omega)\simeq\\ &\frac{1}{\pi}\int_{-\infty}^{\infty}d(\hbar\omega)\frac{4}{\beta\hbar\omega}\sum_\alpha\chi''_{\alpha\alpha}(\mathbf{q},\omega)=\frac{4}{\beta}\sum_\alpha\chi'_{\alpha\alpha}(\mathbf{q},0)=4J(J+1),\end{aligned}$$

recalling that $\chi'_{\alpha\alpha}(\mathbf{q},0)=\frac{1}{3}\beta J(J+1)$ in this limit. This result shows that the magnetic resistivity saturates at temperatures which are so high that the ions are uniformly distributed over the states in the ground-state J-multiplet, since the condition $k_BT\ll\varepsilon_F$ is always satisfied:

$$\rho_{uu}(T)\rightarrow J(J+1)\,\rho_0\qquad\text{for}\quad T\rightarrow\infty,\qquad(3.1.58)$$

and $J(J+1)\,\rho_0$ is called the saturation value of the *spin-disorder* resistivity. Since ρ_0 contains the factor $(g-1)^2$, the spin-disorder resistivity is proportional to the de Gennes factor, as observed (Legvold 1972). If the crystal-field splitting of the energy levels is neglected, this factor also determines the relative magnitudes of the contributions of magnetic rare earth-impurities to the resistivity of a non-magnetic host (Kasuya 1959). However, in analysing the measurements of Mackintosh and Smidt (1962) of the resistivity changes produced by small amounts of heavy rare earths in Lu, Hessel Andersen (1979) found that such crystal-field effects are indeed important at 4 K.

In a metal, the total collision rate $W(\mathbf{k}\sigma, \mathbf{k}'\sigma')$ in eqn (3.1.55) is actually the sum of contributions from several scattering mechanisms. If the trial function for elastic impurity-scattering still leads to a result reasonably close to that determined by the exact solution of the Boltzmann equation, then (3.1.55) implies that the different scattering mechanisms contribute additively to the total resistivity, in accordance with *Matthiessen's rule*:

$$\rho_{\text{total}}(T) = \rho_{\text{imp}} + \rho_{\text{m}}(T) + \rho_{\text{ph}}(T). \tag{3.1.59}$$

Here ρ_{imp} is the residual resistivity due to elastic scattering of the electrons from impurities and from lattice defects. $\rho_{\text{m}}(T)$ is the contribution, calculated above, due to the magnetic excitations, whereas $\rho_{\text{ph}}(T)$ is the equivalent term due to the phonons. The two last terms, associated with the excitations in the metal, vanish in the limit of zero temperature, so that $\rho_{\text{total}}(T=0) = \rho_{\text{imp}}$. The problem of distinguishing between the magnetic and phonon scattering can be approximately solved by estimating the latter from the temperature dependence of the resistivity of Lu, which has an electronic structure and phonon spectrum very similar to those of the magnetic heavy rare earths, but no magnetic moment. Using this method, Mackintosh (1963) was able to show that the magnetic scattering in Tb increases as $\exp(-E_{\mathbf{0}}/k_BT)$ at low temperatures, where the spin-wave energy gap $E_{\mathbf{0}}/k_B$ was estimated to be about 20 K, a value which was subsequently verified by neutron scattering. This analysis was refined by Hessel Andersen and Smith (1979), who used the free-electron model to show that the magnetic resistivity associated with the scattering by spin waves with an isotropic dispersion relation $E_{\mathbf{q}} = E_{\mathbf{0}} + \hbar^2 q^2/2m_{\text{sw}}$ is given by

$$\rho_{\text{m}}(T) = \frac{J}{4}\frac{m_{\text{sw}}^2}{m^2}\frac{E_{\mathbf{0}}k_BT}{\varepsilon_F^2}e^{-E_{\mathbf{0}}/k_BT}\big(1 + 2\frac{k_BT}{E_{\mathbf{0}}} + \tfrac{1}{2}e^{-E_{\mathbf{0}}/k_BT} + \cdots\big)\,\rho_0, \tag{3.1.60}$$

approximating the lower cut-off $k_{F\uparrow} - k_{F\downarrow}$ by 0 in (3.1.57a). A numerical calculation, utilizing the measured spin-wave energies and including one scaling parameter for the magnetic scattering and one for the phonon scattering, gave the excellent fit shown in Fig. 3.2. The disordered electric quadrupole moments of the $4f$-charge distributions can also provide a mechanism for the scattering of the conduction electrons. This is normally very difficult to distinguish from the magnetic scattering, but in TmSb, where the exchange interaction is relatively small and the electric quadrupoles large, the latter appear to dominate the electrical resistivity at low temperatures (Hessel Andersen and Vogt 1979).

Even though $k_BT \ll \varepsilon_F$, the residual resistivity ρ_{imp} is only independent of temperature as long as the ground-state properties of the electron gas remain unchanged. If the resistivity of the unpolarized electrons is $\rho^0_{\text{total}}(T)$ and their density of states at the Fermi surface is $\mathcal{N}(\varepsilon_F)$, the polarization (3.1.16) of the conduction electrons in the ferromagnetic state leads to a scaling of the *total* resistivity, which according to eqn

(3.1.55) is

$$\rho_{\text{total}}(T) = \big\{1 + \zeta(T)\big\}\rho^0_{\text{total}}(T) \quad ; \; \zeta(T) = \frac{\mathcal{N}_\uparrow(\widetilde{\varepsilon}_F) + \mathcal{N}_\downarrow(\widetilde{\varepsilon}_F)}{2\mathcal{N}(\varepsilon_F)} - 1. \qquad (3.1.61)$$

In $\rho^0_{\text{total}}(T)$, the residual resistivity is temperature independent and the magnetic contribution is determined by the above result, if $\mathcal{N}_\sigma(\varepsilon_F)$ in (3.1.57*b*) is replaced by its paramagnetic value $\mathcal{N}(\varepsilon_F)$. The modification $\zeta(T)$, due to the polarization of the conduction electrons, depends on the temperature via the magnetization, and $\zeta(T) \propto \langle J_z \rangle^2$ at small magnetization.

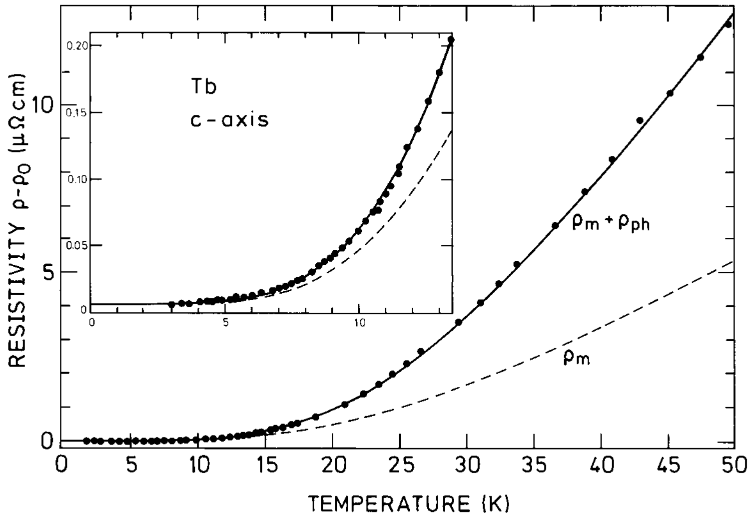

Fig. 3.2. A comparison of the measured and calculated resistivity of a Tb single crystal, as a function of temperature, after Hessel Andersen and Smith (1979). The residual resistivity has been subtracted from the experimental results. The full line includes the calculated contributions from both the magnon scattering and the phonons. The rapid increase around 20 K is predominantly due to the excitation of magnons across the energy gap.

The most important effect on the resistivity produced by the spin-polarization of the electronic states results from the change in the density of states at the Fermi surface, taken into account by $\zeta(T)$ in (3.1.61). Since the other modification, the appearance of $k_{F\sigma}$ instead of the paramagnetic value k_F in (3.1.57*b*), generally only causes a minor correction to the value of the integral in this equation, the magnetic contribution to $\rho^0_{\text{total}}(T)$ is approximately independent of the spin-polarization, in this model. However, the spin-polarization in the real metals may be sufficiently great to alter the topology of the Fermi surface, as discussed in Section 1.4, so that the resistivity may change abruptly with temperature or magnetic field. Under these circumstances, the resistivity must be calculated from first principles, using a realistic model of the spin-polarized energy bands. The zz-contribution should be treated separately, as the q-integral for this case should go from 0 to $2k_F$, even when the electron spins are polarized, since no spin-flip is involved in the scattering process. This modification is, however, unimportant as the dominating contributions, in the ordered phase, arise from the perpendicular spin-wave components of the susceptibility.

The above results also apply, to a good approximation, when the moments are ordered antiferromagnetically, if the value of $\zeta(T)$ is calculated for a spatial modulation of the moments. The spin-polarization of the band electrons is determined by the MF Hamiltonian, and assuming $\langle J_{iz}\rangle = \langle J_z\rangle \cos(\mathbf{Q}\cdot\mathbf{R}_i)$, we may replace (3.1.7) by

$$\begin{aligned}\mathcal{H}_{sf}(\mathrm{MF}) = -\sum_{nn'}\sum_{\mathbf{k}\mathbf{k}'}(g-1)I(n'\mathbf{k}', n\mathbf{k})\big(c^+_{n'\mathbf{k}'\uparrow}c_{n\mathbf{k}\uparrow} - c^+_{n'\mathbf{k}'\downarrow}c_{n\mathbf{k}\downarrow}\big)\\ \times\tfrac{1}{2}\big(\delta_{\mathbf{k}',\mathbf{k}+\mathbf{Q}+\boldsymbol{\tau}} + \delta_{\mathbf{k}',\mathbf{k}-\mathbf{Q}+\boldsymbol{\tau}}\big)\langle J_z\rangle,\end{aligned} \qquad (3.1.62)$$

showing that the modulated moments induce a coupling between the band electrons at the wave-vectors $\mathbf{k}$ and $\mathbf{k}\pm\mathbf{Q}+\boldsymbol{\tau}$. In the same way as the periodic lattice potential lifts the degeneracy of the band states at the Brillouin-zone boundaries (passing through $\mathbf{k}=\boldsymbol{\tau}/2$), the above MF Hamiltonian gives rise to energy gaps at the *superzone boundaries*, the planes perpendicular to, and passing through, the vectors $\mathbf{k}_s = (\pm\mathbf{Q}+\boldsymbol{\tau})/2$. If $\mathbf{k}_s$ is along the c-axis, the value of the energy gap δ is $(g-1)|I(n\mathbf{k}, n-\mathbf{k})|\langle J_z\rangle$ in the nth band. The importance of the superzone gaps for the resistivity was first pointed out by Mackintosh (1962), and detailed theories were developed by Elliott and Wedgwood (1963) and Miwa (1963). These theories utilized the free-electron model and the *relaxation time* approximation, $dg_{\mathbf{k}\sigma}/dt|_{\mathrm{coll}} = -(g_{\mathbf{k}\sigma} - f_{\mathbf{k}\sigma})/\tau_{\mathbf{k}\sigma}$, giving a conductivity

$$\sigma_{uu} = \frac{e^2\beta}{V}\sum_{\mathbf{k}\sigma}\tau_{\mathbf{k}\sigma}\big(\mathbf{v}_{\mathbf{k}\sigma}\cdot\hat{\mathbf{u}}\big)^2 f_{\mathbf{k}\sigma}\big(1-f_{\mathbf{k}\sigma}\big)$$

or, if the relaxation time $\tau_{\mathbf{k}\sigma}$ is assumed to be constant over the Fermi surface,

$$\sigma_{uu} \simeq \frac{e^2\tau}{(2\pi)^3\hbar^2}\sum_\sigma\int_{\varepsilon_{\mathbf{k}\sigma}=\varepsilon_F}\left(\frac{\partial\varepsilon_{\mathbf{k}\sigma}}{\partial k_u}\right)^2\frac{1}{|\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}\sigma}|}dS, \qquad (3.1.63)$$

where dS is a surface element of the Fermi surface. Even without detailed calculations, this expression shows that the conductivity may be reduced substantially if the superzone gaps are able to eliminate significant areas of the Fermi surface. Furthermore, the Fermi-velocity factor puts different weight on the various regions of the Fermi surface in the different components of the conductivity tensor. If $\mathbf{k}_s$ is parallel to the c-axis, as in the heavy rare earths, and if its length is close to that of the Fermi wave-vector in the c-direction, only the cc-component of the conductivity is appreciably affected by the superzone boundary. For instance, an internal field of 2 kOe in the basal plane of Ho at 4 K, which eliminates the superzone energy gaps by inducing a transition from the cone to ferromagnetic ordering, increases the conductivity along the c-axis by about 30%, while decreasing the b-axis component by only about 1% (Mackintosh and Spanel 1964). As illustrated in Fig. 3.3, the anomalous increase in the resistivity in the helical phase of Tb is eliminated by a magnetic field which is large enough to suppress this structure, leaving only a weak maximum similar to that observed in Gd, which has been ascribed to critical scattering of the conduction electrons by magnetic fluctuations (de Gennes and Friedel 1958). This anomalous increase is not observed in the basal plane and the resistivity is little affected by a magnetic field (Hegland *et al.* 1963).

The theoretical calculations of the superzone effects within the free-electron model give a semi-quantitative account of the experimental observations, with a small number of adjustable parameters. For example, a superzone boundary normal to the c-axis, which intersects the Fermi surface, gives a positive contribution to $\zeta_{cc}(T)$ in (3.1.61) which is proportional to δ/ε_F, while $\zeta_{bb}(T)$ decreases like $(\delta/\varepsilon_F)^2$. Bearing in mind the analogy between the real and free-electron Fermi surfaces mentioned above, this corresponds well with the observations in, for example, Ho. In addition, the model calculations suggest that the superzone gaps are important for the value of the ordering wave-vector $\mathbf{Q}$, at which the exchange energy has its maximum (Elliott and Wedgwood 1964; Miwa 1965), by predicting a gradual reduction of the length of $\mathbf{Q}$ with the increase of the size of the superzone gaps, which are proportional to $\langle J_z\rangle$ below the Néel temperature. Hence the exchange coupling $\mathcal{J}(\mathbf{q})$ is somewhat dependent on the magnetization, because the nearly elastic intra-band contributions to the exchange interaction depend on the density of states near the Fermi surface, as is also true in the ferromagnetic case, according to (3.1.21).

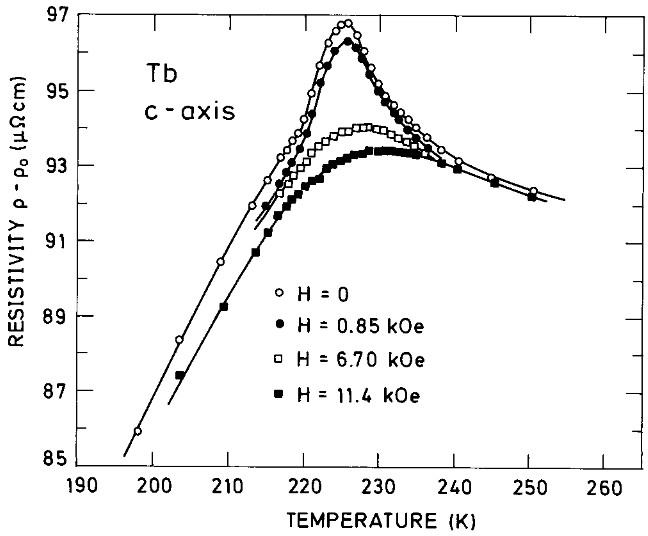

Fig. 3.3. The c-axis resistivity of Tb in the vicinity of $T_N = 230\,\mathrm{K}$, after Hegland *et al.* (1963). As the helical ordering develops, the magnetic superzones cause a sharp increase in the resistivity, which disappears at $T_C = 220\,\mathrm{K}$. The superzones may also be eliminated by a magnetic field in the b-direction, which suppresses the helical structure.

The agreement obtained between simple model calculations of the variation of $\mathbf{Q}$ and that observed experimentally is surprisingly good, to some extent fortuitously so. The band electrons are far from free-electron-like in the rare earth metals, and the approximation in which $I(n'\mathbf{k}', n\mathbf{k})$ is replaced by $j(\mathbf{k}' - \mathbf{k} + \boldsymbol{\tau})$ is rather crude. The effective free-electron model, with $j(\mathbf{q})$ proportional to a form factor $\left[1 + (A\,q)^2\right]^{-1}$ where $A \approx 0.2\,\text{Å}$ and $2k_F \approx 2.8\,\text{Å}^{-1}$, leads to a maximum in $\mathcal{J}(\mathbf{q})$ at $\mathbf{q} \simeq 0.3\,\text{Å}^{-1}$ parallel to the c-axis, in the paramagnetic phase. In this model, $\frac{1}{N}\sum_{\mathbf{q}} \widetilde{\mathcal{J}}(\mathbf{q})$ is found to be an order of magnitude larger than $\mathcal{J}(\mathbf{0})$, and the same is the case with the interband contributions ($\boldsymbol{\tau} \neq \mathbf{0}$) to the exchange interaction, compared to the intra-band contributions. However, various estimates indicate that all these terms are of the same order of magnitude. Lindgård *et al.* (1975) have made the only existing *ab initio* calculation of $\mathcal{J}(\mathbf{q})$ in a rare earth metal, considering the simplest case of Gd, and they obtained a reasonable account of the dependence on wave-vector, even though the magnitude differed by as much as a factor of four from that determined experimentally. Their calculations show that the exchange integral is dominated by the contributions of the d-like band electrons, as is the density of states at the Fermi surface. Although the effective free-electron model is not adequate for determining the exchange interaction, other quantities derived above which depend on real scattering processes close to the Fermi surface (i.e. the contributions to the spin-wave linewidths, the mass enhancement, and the resistivity), may be more trustworthy, particularly if the actual density of states of the band electrons is substituted for the free-electron value. This should especially be true for the linewidth and mass-enhancement, but the strong polarization effect (3.1.60) on the resistivity in the ferromagnetic phase, for which the maximum effect occurs in Gd, with $\zeta(T)$ approaching -0.5 in the zero temperature limit (Fulde and Jensen 1983), may be somewhat exaggerated, because the conductivity is strongly influenced by the sp-band electrons.

4

THE SUPERCONDUCTING PHASE

4.1 The susceptibility of a superconductor

4.1.1 The Bardeen–Cooper–Schrieffer model

The Hamiltonian of the conduction electrons in second quantization is, in the superconducting phase,

$$\mathcal{H}_{\rm el} = \sum_{\mathbf{k}\sigma} \xi_{\mathbf{k}}\, c^+_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} - \sum_{\mathbf{k}} \Delta\big(c^+_{\mathbf{k}\uparrow} c^+_{-\mathbf{k}\downarrow} + c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}\big), \tag{4.1.1}$$

when considering only a single band and neglecting a possible **k**-dependence of the superconducting energy gap Δ. In this expression the energy of the electrons, $\varepsilon_{\mathbf{k}}$ has been replaced by the energy relatively to the chemical potential μ; i.e. $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu$, and it is assumed that $\xi_{-\mathbf{k}} = \xi_{\mathbf{k}}$. The introduction of the chemical potential is required, because the term proportional to Δ does not conserve the number of particles. $c^+_{\mathbf{k}\uparrow}$ creates and $c_{\mathbf{k}\uparrow}$ annihilates a spin-up electron in the **k**-state, and they are Fermi-operators which satisfy the anticommutation relations

$$\begin{aligned} \{c_{\mathbf{k}\sigma}, c^+_{\mathbf{k}'\sigma'}\} &\equiv c_{\mathbf{k}\sigma} c^+_{\mathbf{k}'\sigma'} + c^+_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma} = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'} \\ \{c^+_{\mathbf{k}\sigma}, c^+_{\mathbf{k}'\sigma'}\} &= \{c_{\mathbf{k}\sigma}, c_{\mathbf{k}'\sigma'}\} = 0. \end{aligned} \tag{4.1.2}$$

The BCS-Hamiltonian in eqn (4.1.1) may be diagonalized by introducing two new Fermi-operators, $\gamma_{\mathbf{k}}$ and $\delta_{\mathbf{k}}$, according to (Bogoliubov transformation)

$$c_{\mathbf{k}\uparrow} = u^*_{\mathbf{k}}\gamma_{\mathbf{k}} + v_{\mathbf{k}}\delta^+_{\mathbf{k}} \qquad ; \qquad c_{\mathbf{k}\downarrow} = u^*_{-\mathbf{k}}\delta_{-\mathbf{k}} - v_{-\mathbf{k}}\gamma^+_{-\mathbf{k}} \tag{4.1.3a}$$

and the Hermitean conjugates

$$c^+_{\mathbf{k}\uparrow} = u_{\mathbf{k}}\gamma^+_{\mathbf{k}} + v^*_{\mathbf{k}}\delta_{\mathbf{k}} \qquad ; \qquad c^+_{\mathbf{k}\downarrow} = u_{-\mathbf{k}}\delta^+_{-\mathbf{k}} - v^*_{-\mathbf{k}}\gamma_{-\mathbf{k}}, \tag{4.1.3b}$$

where

$$\{\gamma_{\mathbf{k}}, \gamma^+_{\mathbf{k}'}\} = \{\delta_{\mathbf{k}}, \delta^+_{\mathbf{k}'}\} = \delta_{\mathbf{k}\mathbf{k}'} \qquad \text{with} \qquad |u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1, \tag{4.1.4}$$

whereas all other anticommutators are zero. Introducing (4.1.3) in (4.1.1) then the “off-diagonal” contributions vanish if

$$\Delta(v^2_{\mathbf{k}} - u^2_{\mathbf{k}}) + 2\xi_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} = 0. \tag{4.1.5}$$

Multiplying this equation with $\Delta/u^2_{\mathbf{k}}$ and solving the quadratic equation, then

$$\Delta\frac{v_{\mathbf{k}}}{u_{\mathbf{k}}} = E_{\mathbf{k}} - \xi_{\mathbf{k}} \qquad \text{where} \qquad E_{\mathbf{k}} = \sqrt{\xi^2_{\mathbf{k}} + \Delta^2}, \tag{4.1.6}$$

and using the condition in (4.1.4) we get

$$|v_{\mathbf{k}}|^2 = 1 - |u_{\mathbf{k}}|^2 = \frac{1}{2}\left(1 - \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}}\right) \tag{4.1.8}$$

implying that the Hamiltonian may be written:

$$\mathcal{H}_{\mathrm{el}} = \sum_{\mathbf{k}} \Big[\big\{ \xi_{\mathbf{k}} \left(|u_{\mathbf{k}}|^2 - |v_{\mathbf{k}}|^2 \right) + \Delta \big(u^*_{\mathbf{k}} v_k + u_{\mathbf{k}} v^*_{\mathbf{k}} \big) \big\} \big(\gamma^+_{\mathbf{k}} \gamma_{\mathbf{k}} + \delta^+_{\mathbf{k}} \delta_{\mathbf{k}} \big) \\ + 2\xi_{\mathbf{k}} |v_{\mathbf{k}}|^2 - \Delta (u^*_{\mathbf{k}} v_k + u_{\mathbf{k}} v^*_{\mathbf{k}}) \Big]$$

or

$$\mathcal{H}_{\mathrm{el}} = \sum_{\mathbf{k}} \left(\xi_{\mathbf{k}} - E_{\mathbf{k}} \right) + \sum_{\mathbf{k}} E_{\mathbf{k}} \big(\gamma^+_{\mathbf{k}} \gamma_{\mathbf{k}} + \delta^+_{\mathbf{k}} \delta_{\mathbf{k}} \big). \tag{4.1.9}$$

The first term is the ground state energy and the second sum gives the increase in energy above the ground state in terms of the number operators of the two kinds of quasiparticles annihilated by $\gamma_{\mathbf{k}}$ and $\delta_{\mathbf{k}}$, where

$$\langle \gamma^+_{\mathbf{k}} \gamma_{\mathbf{k}} \rangle = \langle \delta^+_{\mathbf{k}} \delta_{\mathbf{k}} \rangle = f(E_{\mathbf{k}}) = \frac{1}{e^{\beta E_{\mathbf{k}}} + 1}. \tag{4.1.10}$$

In the BCS-theory the energy gap is determined self-consistently in terms of the (average) electron–phonon matrix element g

$$\Delta = \frac{g}{N} \sum_{\mathbf{k}} \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle = \frac{g}{N} \sum_{\mathbf{k}} u^*_{\mathbf{k}} v_{\mathbf{k}} \langle \delta_{\mathbf{k}} \delta^+_{\mathbf{k}} - \gamma^+_k \gamma_{\mathbf{k}} \rangle = \frac{g}{N} \sum_{\mathbf{k}} \frac{\Delta}{2E_{\mathbf{k}}} \Big[1 - 2f(E_{\mathbf{k}}) \Big]. \tag{4.1.11}$$

4.1.2 The electronic susceptibility of the BCS-superconductor

The electronic susceptibility is, according to (3.1.26b), determined by

$$\chi^{+-}(\mathbf{q}, \omega) = -\frac{1}{N} \sum_{\mathbf{k}\mathbf{k}'} \langle\langle c^+_{\mathbf{k}-\mathbf{q}\uparrow} c_{\mathbf{k}\downarrow} \,;\, c^+_{\mathbf{k}'+\mathbf{q}\downarrow} c_{\mathbf{k}'\uparrow} \rangle\rangle \tag{4.1.12}$$

and the equation of motion is, according to eqn (A.3.14),

$$\hbar\omega \langle\langle \hat{B} \,;\, \hat{A} \rangle\rangle_\omega - \langle\langle \,[\, \hat{B} \,,\, \mathcal{H} \,] \,;\, \hat{A} \rangle\rangle_\omega = \langle \,[\, \hat{B} \,,\, \hat{A} \,]\, \rangle. \tag{4.1.13}$$

The vector Green function defined by $\hat{A} = \sum_{\mathbf{k}'} c^+_{\mathbf{k}'+\mathbf{q}\downarrow} c_{\mathbf{k}'\uparrow}$ and the four components

$$\hat{B} = \Big(c^+_{\mathbf{K}\uparrow} c_{\mathbf{k}\downarrow} \;,\; c^+_{\mathbf{K}\uparrow} c^+_{-\mathbf{k}\uparrow} \;,\; c_{-\mathbf{K}\downarrow} c_{\mathbf{k}\downarrow} \;,\; c_{-\mathbf{K}\downarrow} c^+_{-\mathbf{k}\uparrow} \Big) \tag{4.1.14}$$

is introduced. Here $\mathbf{K}$ denotes $\mathbf{k} - \mathbf{q}$. The use of $\mathcal{H} = \mathcal{H}_{\mathrm{el}}$ given by (4.1.1) then leads to the following matrix equation

$$\begin{pmatrix} \hbar\omega - \xi_{\mathbf{k}} + \xi_{\mathbf{K}} & -\Delta & -\Delta & 0 \\ -\Delta & \hbar\omega + \xi_{\mathbf{k}} + \xi_{\mathbf{K}} & 0 & -\Delta \\ -\Delta & 0 & \hbar\omega - \xi_{\mathbf{k}} - \xi_{\mathbf{K}} & -\Delta \\ 0 & -\Delta & -\Delta & \hbar\omega + \xi_{\mathbf{k}} - \xi_{\mathbf{K}} \end{pmatrix} \langle\langle \hat{B} \,;\, \hat{A} \rangle\rangle = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{pmatrix} \tag{4.1.15}$$

The anticommutator relations imply that the four thermal expectation values of the commutators on the right hand side are:

$$\begin{aligned} b_1 &= \langle c^+_{\mathbf{K}\uparrow} c_{\mathbf{K}\uparrow} \rangle - \langle c^+_{\mathbf{k}\downarrow} c_{\mathbf{k}\downarrow} \rangle \quad ; \quad & b_2 &= \langle c^+_{-\mathbf{K}\downarrow} c^+_{\mathbf{K}\uparrow} \rangle - \langle c^+_{\mathbf{k}\downarrow} c^+_{-\mathbf{k}\uparrow} \rangle \\ b_3 &= \langle c_{-\mathbf{K}\downarrow} c_{\mathbf{K}\uparrow} \rangle - \langle c_{\mathbf{k}\downarrow} c_{-\mathbf{k}\uparrow} \rangle \quad ; \quad & b_4 &= \langle c^+_{-\mathbf{K}\downarrow} c_{-\mathbf{K}\downarrow} \rangle - \langle c^+_{-\mathbf{k}\uparrow} c_{-\mathbf{k}\uparrow} \rangle \end{aligned} \tag{4.1.16}$$

Introducing the quasiparticles operators and using that only the expectation values of the number operators are non-zero, eqn (4.1.10), we get

$$\begin{aligned} b_1 = b_4 &= -\frac{\xi_{\mathbf{K}}}{2E_{\mathbf{K}}}\Big(1-2f(E_{\mathbf{K}})\Big) + \frac{\xi_{\mathbf{k}}}{2E_{\mathbf{k}}}\Big(1-2f(E_{\mathbf{k}})\Big) \\ b_2 = -b_3 &= -\frac{\Delta}{2E_{\mathbf{K}}}\Big(1-2f(E_{\mathbf{K}})\Big) + \frac{\Delta}{2E_{\mathbf{k}}}\Big(1-2f(E_{\mathbf{k}})\Big) \end{aligned} \tag{4.1.17}$$

The determinant $D(\omega)$ of the 4×4 matrix on the left hand side of eqn (4.1.15) is

$$\begin{aligned} D(\omega) &= (\hbar\omega)^4 - 2\big(\xi_{\mathbf{K}}^2 + \xi_{\mathbf{k}}^2 + 2\Delta^2\big)(\hbar\omega)^2 + \big(\xi_{\mathbf{K}}^2 - \xi_{\mathbf{k}}^2\big)^2 \\ &= \big[(\hbar\omega)^2 - \big(E_{\mathbf{K}} + E_{\mathbf{k}}\big)^2\big]\big[(\hbar\omega)^2 - \big(E_{\mathbf{K}} - E_{\mathbf{k}}\big)^2\big] \end{aligned} \tag{4.1.18}$$

The response we want to calculate is the first component of the vector Green function in eqn (4.1.15). Defining $T(\omega)$ as the numerator in $\big[\langle\langle \hat{B}\,;\,\hat{A}\rangle\rangle\big]_1 = T(\omega)/D(\omega)$, and using $b_4 = b_1$ and $b_3 = -b_2$, then

$$T(\omega) = \big(\hbar\omega - \xi_{\mathbf{K}} + \xi_{\mathbf{k}}\big)\big[\big(\omega^2 - (\xi_{\mathbf{K}} + \xi_{\mathbf{k}})^2\big)\, b_1 - 2\Delta(\xi_{\mathbf{K}} + \xi_{\mathbf{k}})\, b_2\big] \tag{4.1.19}$$

Instead of calculating $\chi^{+-}(\mathbf{q},\omega)$ we rather want to calculate one of the Cartesian components and due to symmetry (no preferred direction),

$$\begin{aligned} \chi^{\alpha\alpha}(\mathbf{q},\omega) &= \tfrac{1}{2}\big[\chi^{xx}(\mathbf{q},\omega) + \chi^{yy}(\mathbf{q},\omega)\big] = \tfrac{1}{4}\big[\chi^{+-}(\mathbf{q},\omega) + \chi^{-+}(\mathbf{q},\omega)\big] \\ &= \tfrac{1}{4}\big[\chi^{+-}(\mathbf{q},\omega) + \big\{\chi^{+-}(\mathbf{q},-\omega)\big\}^*\big] = -\frac{1}{4N}\sum_{\mathbf{k}} \frac{T(\omega) + T(-\omega)}{D(\omega)} \end{aligned} \tag{4.1.20}$$

At zero frequency the result is

$$\chi^{\alpha\alpha}(\mathbf{q},0) = -\frac{1}{2N}\sum_{\mathbf{k}} \frac{\big(\xi_{\mathbf{K}}^2 - \xi_{\mathbf{k}}^2\big)\big[(\xi_{\mathbf{K}} + \xi_{\mathbf{k}})\, b_1 + 2\Delta\, b_2\big]}{\big(E_{\mathbf{K}}^2 - E_{\mathbf{k}}^2\big)^2} =$$

$$\frac{1}{2N}\sum_{\mathbf{k}} \left[\frac{\big(E_{\mathbf{k-q}}^2 + \xi_{\mathbf{k-q}}\xi_{\mathbf{k}} + \Delta^2\big)\big[1-2f(E_{\mathbf{k-q}})\big]}{2E_{\mathbf{k-q}}\big(E_{\mathbf{k-q}}^2 - E_{\mathbf{k}}^2\big)} - \frac{\big(E_{\mathbf{k}}^2 + \xi_{\mathbf{k-q}}\xi_{\mathbf{k}} + \Delta^2\big)\big[1-2f(E_{\mathbf{k}})\big]}{2E_{\mathbf{k}}\big(E_{\mathbf{k-q}}^2 - E_{\mathbf{k}}^2\big)}\right]$$

Replacing the component superscripts with an s, indicating that this is the susceptibility in the superconducting phase, the result at zero frequency may be written

$$\begin{aligned} \chi^s(\mathbf{q}) = &\frac{1}{2N}\sum_{\mathbf{k}} \frac{f(E_{\mathbf{k}}) - f(E_{\mathbf{k-q}})}{E_{\mathbf{k-q}} - E_{\mathbf{k}}} \\ &+\frac{1}{2N}\sum_{\mathbf{k}} \left[\frac{1-2f(E_{\mathbf{k-q}})}{2E_{\mathbf{k-q}}} - \frac{1-2f(E_{\mathbf{k}})}{2E_{\mathbf{k}}}\right] \frac{\xi_{\mathbf{k-q}}\xi_{\mathbf{k}} + \Delta^2 - E_{\mathbf{k-q}}E_{\mathbf{k}}}{E_{\mathbf{k-q}}^2 - E_{\mathbf{k}}^2} \end{aligned} \tag{4.1.21}$$

In the limit $\Delta \to 0$ and $E_{\mathbf{k}} \to |\xi_{\mathbf{k}}|$ this expression reduces to the usual electronic susceptibility of the normal phase,

$$\lim_{\Delta\to 0} \chi^s(\mathbf{q}) = \chi^n(\mathbf{q}) = \frac{1}{2N}\sum_{\mathbf{k}} \frac{f(\xi_{\mathbf{k}}) - f(\xi_{\mathbf{k-q}})}{\xi_{\mathbf{k-q}} - \xi_{\mathbf{k}}} \tag{4.1.22}$$

[consider separately each of the four cases for the choice of sign of $\xi_{\mathbf{k}-\mathbf{q}}$ and $\xi_{\mathbf{k}}$ in (4.1.21) and utilize $f(-\xi_{\mathbf{k}}) = 1 - f(\xi_k)$]. This result implies also that the susceptibility is not influenced by the superconducting energy gap, whenever $|\mathbf{q}|$ is large, because then Δ can be neglected in comparison with the energy difference between $\xi_{\mathbf{k}}$ and $\xi_{\mathbf{k}-\mathbf{q}}$ (at most $\mathbf{k}$ values in the sum). At zero temperature the Fermi functions vanish, $f(E_{\mathbf{k}}) = 0$ as $E_{\mathbf{k}} > 0$, and

$$\chi_0^s(\mathbf{q}) = \frac{1}{8N} \sum_{\mathbf{k}} \frac{(\xi_{\mathbf{k}-\mathbf{q}} - \xi_{\mathbf{k}})^2 - (E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}})^2}{E_{\mathbf{k}-\mathbf{q}} E_{\mathbf{k}} \big(E_{\mathbf{k}-\mathbf{q}} + E_{\mathbf{k}}\big)} \qquad (T = 0) \tag{4.1.23}$$

In the limit of $\mathbf{q} \to \mathbf{0}$ the numerator vanishes whereas the denominator stays non-zero. Hence, at zero temperature in the superconducting phase, the susceptibility is zero at zero wave vector. This is the equivalent phenomenon of the Meissner effect, reflecting that the superconducting ground state is a singlet. The screening becomes less perfect if the spin moments are oscillating, and is eliminated if the length scale of the oscillations is much shorter than the correlation length ξ. The presence of the superconducting energy gap is only of importance for the electrons near the Fermi surface of the normal metal. Assuming the Fermi surface to be a sphere and a linear variation of the energies close to the Fermi energy, we may use $\xi_{\mathbf{k}} \simeq \hbar v_F(|\mathbf{k}| - k_F)$, in which case $\varepsilon_F = \hbar v_F k_F$. In general the Fermi velocity $\hbar v_F = |\nabla \xi_{\mathbf{k}}|$ depends on $\mathbf{k}$, however, in order to analyze the qualitative behavior of the susceptibility, v_F may be assumed to be a constant, and eqn (4.1.23) may be written

$$\chi_0^s(\mathbf{q})/\chi_0^n(\mathbf{0}) = \int_0^\infty z^2 dz \int_{-1}^1 d\mu \, \frac{\big[u(z,\mu) - z + 1\big]^2 - \big[U(z,\mu) - V(z)\big]^2}{8\, U(z,\mu) V(z) \big[U(z,\mu) + V(z)\big]}$$

The variables in the integral are $\mu = \cos\theta$ and $z = k/k_F$, and the functions are

$$\begin{aligned} u(z,\mu) &= \sqrt{z^2 + r^2 - 2zr\mu} - 1 \quad &;& \quad r = |\mathbf{q}|/k_F \\ V(z) &= \sqrt{(z-1)^2 + d^2} \quad &;& \quad d = \Delta/\varepsilon_F \\ U(z,\mu) &= \sqrt{u^2(z,\mu) + d^2} && \end{aligned}$$

The normal susceptibility at zero wave vector (and temperature) is $\chi_0^n(\mathbf{0}) = \mathcal{N}(\varepsilon_F)/2$, where the density of states at the Fermi energy (per atom and per spin state) in the present model is $4\pi V k_F^3/[(2\pi)^3 N \varepsilon_F]$. The integral is complicated but may be handled numerically. At the smallest values of q the susceptibility increases as q^2, but in a large interval (as long as $0 < q \ll k_F$) the result is

$$\chi_0^s(\mathbf{q})/\chi_0^n(\mathbf{0}) \simeq 0.99 \frac{q}{q + 1.5\, q_0} \qquad ; \quad q_0 = \frac{\pi \Delta}{\hbar v_F} \approx \frac{1}{\xi} \tag{4.1.24}$$

where ξ is the superconducting correlation length. Hence, the susceptibility of the superconductor starts out at zero and approaches the value in the normal phase at q of the order of $10\xi^{-1}$.

In the limit of $\mathbf{q} \to \mathbf{0}$ we may use the expansion $\xi_{\mathbf{k}-\mathbf{q}} \simeq \xi_{\mathbf{k}} - \mathbf{q} \cdot \nabla \xi_{\mathbf{k}}$ and it is easily seen that the second sum in eqn (4.1.21) is of second order in $\mathbf{q}$ and only the first term contribute, i.e.

$$\chi^s(\mathbf{0}) = -\frac{1}{2N} \sum_{\mathbf{k}} \frac{\partial f(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}} = -\frac{1}{2N} \sum_{\mathbf{k}} f'(E_{\mathbf{k}}) \tag{4.1.25}$$

This is zero at zero temperature, in accordance with the result obtained above, however, at finite temperatures, the susceptibility starts to increase because the thermally exited quasiparticles can be polarized by a uniform exchange field. The expression in the normal phase is similar, except that $E_{\mathbf{k}}$ is replaced by $\xi_{\mathbf{k}}$, and using $-\partial f(\xi_{\mathbf{k}})/\partial \xi_k = \delta(\xi_{\mathbf{k}} - \varepsilon_F)$ in the zero temperature limit, the result is $\chi_0^n(\mathbf{0}) = \mathcal{N}(\varepsilon_F)/2$, as used above. In order to calculate the temperature variation of $\chi^s(\mathbf{0})$ we need to know the temperature dependence of $\Delta = \Delta(T)$. In the standard BCS-theory Δ is determined from eqn (4.1.11) leading to

$$\frac{1}{\mathcal{N}(\varepsilon_F)g} = \ln\left(\frac{2\hbar\omega_D}{\Delta(0)}\right) = \int_0^{\hbar\omega_D} dx \frac{\tanh \frac{1}{2}\beta(x^2+\Delta^2)^{\frac{1}{2}}}{(x^2+\Delta^2)^{\frac{1}{2}}} \tag{4.1.26}$$

where $\Delta(0) = 1.764\, k_B T_c$. The sum itself may be written as the integral (assuming $T \ll T_F$)

$$\chi^s(\mathbf{0})/\chi_0^n(\mathbf{0}) = 2\int_0^\infty dx\, \frac{e^{\sqrt{x^2+(\beta\Delta)^2}}}{\left[e^{\sqrt{x^2+(\beta\Delta)^2}}+1\right]^2} \tag{4.1.27}$$

The integral vanishes exponentially, $\propto \exp[-\Delta(0)/k_B T]$, at low temperatures and approaches 1 linearly when $T \to T_c$. The result is shown in Fig. 4.1.

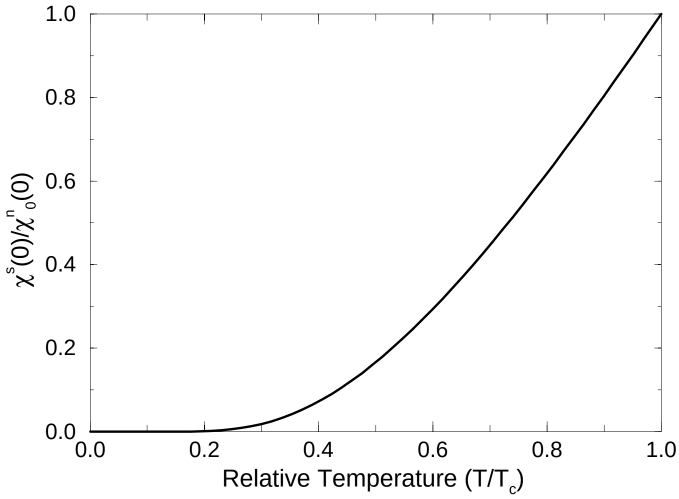

Fig. 4.1. The temperature dependence of the electronic susceptibility in the superconducting phase relatively to the normal phase value.

In the type-I superconductor the internal field is zero, whereas an applied field may penetrate into the bulk of the superconductor in the type-II case. The presence of a field introduces the Zeeman term in the electron Hamiltonian

$$\mathcal{H}_Z = h\sum_{\mathbf{k}} \left(c^+_{\mathbf{k}\uparrow}c_{\mathbf{k}\uparrow} - c^+_{\mathbf{k}\downarrow}c_{\mathbf{k}\downarrow}\right) \tag{4.1.28}$$

assuming the field $h = \mu_B H$ to be along the z axis. This term does not change the diagonalization condition (4.1.5) and the final Hamiltonian is found to be

$$\mathcal{H}_{\text{el}} = \sum_{\mathbf{k}} \left(\xi_{\mathbf{k}} - E_{\mathbf{k}}\right) + \sum_{\mathbf{k}} \Big[\big(E_{\mathbf{k}}+h\big)\gamma^+_{\mathbf{k}}\gamma_{\mathbf{k}} + \big(E_{\mathbf{k}}-h\big)\delta^+_{\mathbf{k}}\delta_{\mathbf{k}}\Big]. \tag{4.1.29}$$

Any other effects of the field on the superconducting state is accounted for implicitly, via a change of $\xi_{\mathbf{k}}$ and (and via the equation (4.1.11) determining the superconducting energy gap Δ). The susceptibility components parallel and perpendicular to the field become slightly different:

$$\chi^s_{\|} = -\frac{1}{4N}\sum_{\mathbf{k}} \big[f'(E_{\mathbf{k}}+h) + f'(E_{\mathbf{k}}-h)\big] \quad ; \quad \chi^s_{\perp} = -\frac{1}{4N}\sum_{\mathbf{k}} \frac{f(E_{\mathbf{k}}+h) - f(E_{\mathbf{k}}-h)}{h}\,. \tag{4.1.30}$$

These results[1] imply that h cancels out to leading order and the second order effects are negligible except in the close neighbourhood of T_c. In the case of TmNi$_2$B$_2$, the value of $T_c \simeq 11$ K corresponds to $\Delta(0) = 1.7$ meV, and at the field of 20 kOe (the order of H_{c2}), $h \simeq 0.12$ meV is a factor of 15 smaller than the superconducting energy gap.

In a type-I superconductor an external applied field is screened from the bulk as determined by the penetration depth λ. This also means that the classical dipole–dipole coupling between localized moments placed in a superconducting medium is screened (S.N. Klausen, Thesis, 1999). The interaction in equation (1.3.2) is changed into

$$D_{\alpha\beta}(ij) = \frac{V}{N}\frac{(3+3w+w^2)(R_{i\alpha}-R_{j\alpha})(R_{i\beta}-R_{j\beta}) - \delta_{\alpha\beta}(1+w+w^2)|\mathbf{R}_i-\mathbf{R}_j|^2}{|\mathbf{R}_i-\mathbf{R}_j|^5}\,e^{-w} \tag{4.1.31}$$

where $w = \lambda/|\mathbf{R}_i - \mathbf{R}_j|$. The screening implies that the surface effects (and thus also the discontinuities at zero wave vector) are cancelled. The demagnetization factor in eqn (1.3.6) disappears, but instead 4π is subtracted due to the supercurrents

$$D_{\xi\xi}(\mathbf{0}) = -\frac{8\pi}{3} + \big[\tilde{D}_{\xi\xi}(\mathbf{0})\big]_L \tag{4.1.32}$$

where the tilde indicates that the lattice sum $\big[\tilde{D}_{\xi\xi}(\mathbf{0})\big]_L$ should be calculated using the screened interaction, however, this modification may be neglected as long as λ is much larger than the lattice parameters. The screening does not affect the long wavelength behaviour of the parallel component, which is still determined by eqn (1.3.7). This means that the longitudinal component is continuous and stays constant in the long wavelength limit, whereas the two transverse components are

$$D_{\perp}(\mathbf{q}) = -\frac{8\pi}{3} + \big[\tilde{D}_{\perp}(\mathbf{0})\big]_L + 4\pi\frac{(\lambda q)^2}{1+(\lambda q)^2} \qquad ; \qquad |\mathbf{q}| \ll \frac{2\pi}{a} \tag{4.1.33}$$

instead of eqn (1.3.8). Hence, the transverse components change (continuously) from the modified value at zero wave vector to the normal-phase value when q is a few times larger than λ^{-1}.

In the type-II superconductor the superconducting order parameter is only much affected within the core of the flux lines leaving the screening of the (spin–spin) susceptibility at zero wave vector more or less unchanged (S.N. Klausen, Thesis, 1999). In contrast, the shielding effects due to the supercurrents become less effective the larger the external field, and may be neglected close to the upper critical field, where the internal field only shows a slight spatial variation.

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[1] The parallel susceptibility may also be derived from $4N\chi_{\|} = -\partial^2 F/\partial h^2$, where $F = \langle\mathcal{H}\rangle - ST$ and $-ST = \beta^{-1}\sum_{\mathbf{k}}\sum_{x=E_{\mathbf{k}}\pm h}\big\{f(x)\ln f(x) + [1-f(x)]\ln[1-f(x)]\big\}$.

4.1.3 Modulated RKKY magnetic ordering and the BCS model

The presence of a modulated ordering $\langle J_z(\mathbf{R}_i)\rangle = \langle J_z\rangle \cos(R_i{\cdot}\mathbf{Q})$ introduces the following term in the Hamiltonian

$$\begin{aligned}\mathcal{H}_{sf}(\mathrm{MF}) &= \sum_{\mathbf{k}} A\big(c^+_{\mathbf{k}+\mathbf{Q}\uparrow}c_{\mathbf{k}\uparrow} + c^+_{\mathbf{k}-\mathbf{Q}\uparrow}c_{\mathbf{k}\uparrow} - c^+_{\mathbf{k}+\mathbf{Q}\downarrow}c_{\mathbf{k}\downarrow} - c^+_{\mathbf{k}-\mathbf{Q}\downarrow}c_{\mathbf{k}\downarrow}\big)\\ \text{where}\qquad & A = -\tfrac{1}{2}(g-1)I\langle J_z\rangle\end{aligned} \tag{4.1.34a}$$

corresponding to eqn (3.1.62), when assuming that the RKKY-interaction is determined by a constant coupling parameter I. The interaction is only important when $\mathbf{k} \approx -\mathbf{k}\pm\mathbf{Q}$ or $\mathbf{k} \approx \pm\mathbf{Q}/2$, in which case it couples two electronic states which are nearly degenerated. Defining the z-axis in reciprocal space (not necessarily the same as the z-axis in spin space) to be along $\mathbf{Q}$, then the higher-order coupling terms are neglected by truncating the Hamiltonian into

$$\mathcal{H}_{sf}(\mathrm{MF}) = \sum_{0<k_z<Q} A\big(c^+_{\mathbf{k}-\mathbf{Q}\uparrow}c_{\mathbf{k}\uparrow} + c^+_{-\mathbf{k}+\mathbf{Q}\uparrow}c_{-\mathbf{k}\uparrow} - c^+_{\mathbf{k}-\mathbf{Q}\downarrow}c_{\mathbf{k}\downarrow} - c^+_{-\mathbf{k}+\mathbf{Q}\downarrow}c_{-\mathbf{k}\downarrow}\big). \tag{4.1.34b}$$

Instead of using the operator technique of section 4.1.1 we shall introduce a new (hole) excitation operator $d^+_{\mathbf{k}\downarrow} = c_{\mathbf{k}\downarrow}$ and adding the magnetic term (4.1.34) to the Hamiltonian of the superconducting electrons, eqn (4.1.1.), the total Hamiltonian may be written:

$$\begin{aligned}\mathcal{H} = {}& \sum_{\mathbf{k}} \xi_{\mathbf{k}}\,\big(c^+_{\mathbf{k}\uparrow}c_{\mathbf{k}\uparrow} + 1 - d^+_{\mathbf{k}\downarrow}d_{\mathbf{k}\downarrow}\big) - \sum_{\mathbf{k}} \Delta\big(c^+_{\mathbf{k}\uparrow}d_{-\mathbf{k}\downarrow} + d^+_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}\big)\\ &+ \sum_{0<k_z<Q} A\big(c^+_{\mathbf{k}-\mathbf{Q}\uparrow}c_{\mathbf{k}\uparrow} + c^+_{-\mathbf{k}+\mathbf{Q}\uparrow}c_{-\mathbf{k}\uparrow} + d^+_{\mathbf{k}\downarrow}d_{\mathbf{k}-\mathbf{Q}\downarrow} + d^+_{-\mathbf{k}\downarrow}d_{-\mathbf{k}+\mathbf{Q}\downarrow}\big).\end{aligned} \tag{4.1.35}$$

Notice that the signs of the last two terms in the A-coupling sum are changed, because of the anticommutator relation $\{d_{\mathbf{k}\sigma}, d^+_{\mathbf{k}'\sigma'}\} = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'}$. We shall consider a certain $\mathbf{k}$ vector, assuming $0 < k_z < Q$, and define four states through the operator relations $c^+_{\mathbf{k}\uparrow} = |1><0|$, $d^+_{-\mathbf{k}\downarrow} = |2><0|$, $d^+_{-\mathbf{k}+\mathbf{Q}\downarrow} = |3><0|$, $c^+_{\mathbf{k}-\mathbf{Q}\uparrow} = |4><0|$, and the Hermitean conjugated, $c_{\mathbf{k}\uparrow} = |0><1|$, etc., implying that for instance $c^+_{\mathbf{k}-\mathbf{Q}\uparrow}c_{\mathbf{k}\uparrow} = |4><1|$. (The fifth state $|0>$ signifies that there is no electron/hole in the four states.) These four states span a subspace of the Hamiltonian as given by the following matrix

$$\mathcal{H}(\mathbf{k}) = \begin{pmatrix} \xi_{\mathbf{k}} & -\Delta & 0 & A\\ -\Delta & -\xi_{-\mathbf{k}} & A & 0\\ 0 & A & -\xi_{-\mathbf{k}+\mathbf{Q}} & -\Delta\\ A & 0 & -\Delta & \xi_{\mathbf{k}-\mathbf{Q}} \end{pmatrix} \tag{4.1.36}$$

This matrix may be diagonalized analytically [see Nass *et al.*, Phys. Rev. Lett. **46**, 614 (1981)], however, the expressions for the eigenvectors become very complex, so we shall instead do a perturbation calculation. Considering the transformation

$$\begin{aligned}|x_1> &= u\,|1> + v\,|4> \quad ; \quad |x_4> = u\,|4> - v\,|1>\\ |x_2> &= u\,|2> - v\,|3> \quad ; \quad |x_3> = u\,|3> + v\,|2>\end{aligned} \tag{4.1.37a}$$

with

$$u^2 + v^2 = 1 \qquad ; \qquad u^2 - v^2 = \Omega_{\mathbf{k}}^{-1} \qquad ; \qquad uv = \frac{A}{(\xi_{\mathbf{k}} - \xi_{\mathbf{k}-\mathbf{Q}})\Omega_{\mathbf{k}}} \tag{4.1.37b}$$

and the parameters

$$\epsilon_{\mathbf{k}} = \tfrac{1}{2}\big(\xi_{\mathbf{k}} + \xi_{\mathbf{k-Q}}\big) + \tfrac{1}{2}\big(\xi_{\mathbf{k}} - \xi_{\mathbf{k-Q}}\big)\Omega_{\mathbf{k}} \quad ; \quad \Omega_{\mathbf{k}} = \left[1 + \frac{4A^2}{\big(\xi_{\mathbf{k}} - \xi_{\mathbf{k-Q}}\big)^2}\right]^{\frac{1}{2}} \tag{4.1.38}$$

then the Hamiltonian in the $|x_n>$ basis is

$$\mathcal{H}(\mathbf{k}) = \begin{pmatrix} \epsilon_{\mathbf{k}} & -\Delta\Omega_{\mathbf{k}}^{-1} & -2uv\Delta & 0 \\ -\Delta\Omega_{\mathbf{k}}^{-1} & -\epsilon_{\mathbf{k}} & 0 & 2uv\Delta \\ -2uv\Delta & 0 & -\epsilon_{\mathbf{Q-k}} & -\Delta\Omega_{\mathbf{k}}^{-1} \\ 0 & 2uv\Delta & -\Delta\Omega_{\mathbf{k}}^{-1} & \epsilon_{\mathbf{Q-k}} \end{pmatrix} \tag{4.1.39}$$

The transformation has removed the A-terms in the matrix but introduced the new off-diagonal terms, $\pm 2uv\Delta$. However, as we shall see below, these terms may be neglected to leading order. Doing that the remaining part may be diagonalized straightforwardly by the following transformation

$$\begin{aligned} |y_1> &= r_{\mathbf{k}}|x_1> + s_{\mathbf{k}}|x_2> \quad ; \quad |y_2> = r_{\mathbf{k}}|x_2> - s_{\mathbf{k}}|x_1> \\ |y_3> &= r_{\mathbf{Q-k}}|x_3> - s_{\mathbf{Q-k}}|x_4> \quad ; \quad |y_4> = r_{\mathbf{Q-k}}|x_4> + s_{\mathbf{Q-k}}|x_3> \end{aligned} \tag{4.1.40a}$$

where

$$r_{\mathbf{k}}^2 + s_{\mathbf{k}}^2 = 1 \quad ; \quad r_{\mathbf{k}}^2 - s_{\mathbf{k}}^2 = \frac{\epsilon_{\mathbf{k}}}{\mathcal{E}_{\mathbf{k}}} \quad ; \quad r_{\mathbf{k}}s_{\mathbf{k}} = -\frac{\Delta}{2\mathcal{E}_{\mathbf{k}}\Omega_{\mathbf{k}}} \tag{4.1.40b}$$

and

$$\mathcal{E}_{\mathbf{k}} = \epsilon_{\mathbf{k}}\left[1 + \Big(\frac{\Delta}{\epsilon_{\mathbf{k}}\Omega_{\mathbf{k}}}\Big)^2\right]^{\frac{1}{2}}. \tag{4.1.41}$$

The eigenvalues $\mathcal{E}_n$ of the states $|y_n>$ are $\mathcal{E}_{\mathbf{k}}$, $-\mathcal{E}_{\mathbf{k}}$, $-\mathcal{E}_{\mathbf{Q-k}}$, and $\mathcal{E}_{\mathbf{Q-k}}$, respectively for $n = 1$, 2, 3, and 4. The four eigenstates contribute to the **k**-sum in eqn (4.1.11) by

$$\begin{aligned} \Delta &= 2\frac{g}{N}\sum_{k_z>0}\sum_{n} <y_n|2><1|y_n> f(\mathcal{E}_n) \\ &= 2\frac{g}{N}\sum_{k_z>0}\Big(u^2 r_{\mathbf{k}}s_{\mathbf{k}}\big[f(\mathcal{E}_{\mathbf{k}}) - f(-\mathcal{E}_{\mathbf{k}})\big] - v^2 r_{\mathbf{Q-k}}s_{\mathbf{Q-k}}\big[f(\mathcal{E}_{\mathbf{Q-k}}) - f(-\mathcal{E}_{\mathbf{Q-k}})\big]\Big) \end{aligned}$$

A replacement of $\mathbf{Q-k}$ by $\mathbf{k}$ in the last term does not change v^2 or $\Omega_{\mathbf{k}}$, and we get

$$\Delta = 2\frac{g}{N}\sum_{k_z>0}(u^2 - v^2)r_{\mathbf{k}}s_{\mathbf{k}}\big[f(\mathcal{E}_{\mathbf{k}}) - f(-\mathcal{E}_{\mathbf{k}})\big] = -2\frac{g}{N}\sum_{k_z>0}\frac{\Delta}{2\mathcal{E}_{\mathbf{k}}\Omega_{\mathbf{k}}^2}\big[f(\mathcal{E}_{\mathbf{k}}) - f(-\mathcal{E}_{\mathbf{k}})\big] \tag{4.1.42}$$

and using $f(-\mathcal{E}_{\mathbf{k}}) = 1 - f(\mathcal{E}_{\mathbf{k}})$ the result may be written

$$\Delta = 2\frac{g}{N}\sum_{k_z>0}\frac{\Delta}{2E_{\mathbf{k}}\Omega_{\mathbf{k}}^2}\big[1 - 2f(E_{\mathbf{k}})\big] \quad ; \quad E_{\mathbf{k}} = |\mathcal{E}_{\mathbf{k}}| \tag{4.1.43}$$

In comparison with the original gap equation (4.1.11) the energies $E_{\mathbf{k}}$ are changed via the replacement of $\xi_{\mathbf{k}}$ with $\epsilon_{\mathbf{k}}$ and the factor $\Omega_{\mathbf{k}}^{-2}$ has appeared. At $k = \pm\mathbf{Q}/2$ the energies are $\epsilon_{\mathbf{Q}/2} = \xi_{\mathbf{Q}/2} \pm A$, and if the energy gap $2|A|$ is small in comparison with the Debye energy $\hbar\omega_D$ the effects due to the modification of $E_{\mathbf{k}}$ are of second order in A/ε_F and thus negligible. The factor $\Omega_{\mathbf{k}}^{-2}$ may be accounted for by replacing the density of states close to the Fermi surface, $\mathcal{N}(\varepsilon_F)$ in (4.1.26), by

$$\mathcal{N}_{\text{eff}}(\varepsilon_F) = \mathcal{N}(\varepsilon_F) \sum_{k_z>0} \Omega_{\mathbf{k}}^{-2} \delta(\epsilon_{\mathbf{k}}) \Big/ \sum_{k_z>0} \delta(\xi_{\mathbf{k}}). \tag{4.1.44}$$

The density of states itself is changed only in the second order of A/ε_F (neglecting the special case of $Q \approx 2k_F$), and $\delta(\epsilon_{\mathbf{k}})$ may be replaced by $\delta(\xi_{\mathbf{k}})$. Referring to the free electron model we may assume $\xi_{\mathbf{k}-\mathbf{Q}} = \xi_{\mathbf{k}} - (2k_z - Q)Q\varepsilon_F/k_F^2$ implying that

$$\Omega_{\mathbf{k}}^{-2} = \frac{1}{1 + \frac{4A^2}{(\xi_{\mathbf{k}} - \xi_{\mathbf{k}-\mathbf{Q}})^2}} = 1 - \frac{1}{1 + \frac{(\xi_{\mathbf{k}} - \xi_{\mathbf{k}-\mathbf{Q}})^2}{4A^2}} = 1 - \frac{1}{1 + X^2}$$

where

$$X = X(k_z) = \frac{(2k_z - Q)Q\varepsilon_F}{2|A|\, k_F^2}$$

Using $\xi_{\mathbf{k}} \propto k_\perp^2 + k_z^2$ and integrating with respect to $k_\perp$ the delta function in eqn (4.1.44) disappears and we are left with an integral with respect to k_z from 0 to k_F, or

$$\mathcal{N}_{\text{eff}}(\varepsilon_F) \Big/ \mathcal{N}(\varepsilon_F) = 1 - \frac{1}{k_F} \int_{X(0)}^{X(k_F)} \frac{1}{1 + X^2} \frac{dk_z}{dX} dX$$

dk_z/dX is a constant and assuming $|A| \ll \varepsilon_F$ the lower limit may be replaced by $-\infty$, whereas the upper limit depends on the value of Q. If $Q > 2k_F$ then $X(k_F) \approx -\infty$ and the integral vanishes (to leading order in A). If $Q < 2k_F$ the upper limit may be replaced by ∞ and the result is

$$\mathcal{N}_{\text{eff}}(\varepsilon_F) = \mathcal{N}(\varepsilon_F) \Big(1 - \pi \frac{k_F}{Q} \frac{|A|}{\varepsilon_F} \Big), \tag{4.1.45}$$

This important result shows that the effective density of states in the gap equation (4.1.26) is reduced linearly with the magnitude $2|A|$ of the energy gaps. Those responsible for this effect are the energy gaps produced by the magnetic ordering at the positions where the "superzone boundaries" (the planes normal to the vectors $\pm\mathbf{Q}/2$) cut through the Fermi surface. According to the truncation condition, A is assumed non-zero only as long as $k_z < Q$, and the upper limit of the integral should rather be $X(Q)$ if $Q < k_F$, however, it is clear that this restriction is unimportant as long as $|A| \ll \varepsilon_F$.

The off-diagonal terms $\pm 2uv\Delta$ in (4.1.39) are important when $\xi_k - \xi_{\mathbf{k}-\mathbf{Q}} \approx 0$ where $|2uv| \to 1$ and $\Omega_{\mathbf{k}} \to 0$. Considering this situation, i.e. neglecting the off-diagonal terms $-\Delta\Omega_{\mathbf{k}}^{-1}$ in (4.1.39), the Hamiltonian may be diagonalized. The procedure is the same as above and the result is that the gap equation (4.1.42) is replaced by

$$\Delta \simeq -2\frac{g}{N} \sum_{k_z>0} \left\{ \frac{\Delta}{2\mathcal{E}_{\mathbf{k}}\Omega_{\mathbf{k}}^2} + \frac{\Delta(1 - \Omega_{\mathbf{k}}^{-2})}{\xi_{\mathbf{k}} + \xi_{\mathbf{k}-\mathbf{Q}}} \Big[1 + \frac{4\Delta^2(1 - \Omega_{\mathbf{k}}^{-2})}{(\xi_{\mathbf{k}} + \xi_{\mathbf{k}-\mathbf{Q}})^2} \Big]^{-1/2} \right\} \big[f(\mathcal{E}_{\mathbf{k}}) - f(-\mathcal{E}_{\mathbf{k}}) \big] \tag{4.1.46}$$

At the Fermi surface, $\xi_{\mathbf{k}} = 0$ implying $\xi_{\mathbf{k}} + \xi_{\mathbf{k}-\mathbf{Q}} = -(2k_z - Q)Q\varepsilon_F/k_F^2 = -2|A|X$. This shows that the additional contribution in (4.1.45) is odd in X and therefore that this term cancels out when integrated with respect to X. Hence to leading order the density of states in the superconducting energy gap equation is reduced linear with $|A|$ according to eqn (4.1.45). If $|A|$ is not small in comparison with the Debye energy $\hbar\omega_D$ the modifications of the energy bands due to $|A|$ have to be included. Nass *et al.* [Phys. Rev. Lett. **46**, 614 (1981)] have performed numerical model calculations (including a diagonalization of the four times four matrix) and they find that the reduction of the superconducting condensation energy becomes even more pronounced in this situation.

The electron-phonon interaction may induce an alternative superconducting state than the one considered above. In order to discuss the more general situation we turn our attention to the original electron-phonon Hamiltonian in the simplified version, where the coupling constant g is assumed to be a constant, only non-zero at energies smaller than the Debye energy

$$\begin{aligned}\mathcal{H}_{\mathrm{el-ph}} &= -\frac{g}{N}\sum_{\mathbf{q}}\sum_{\mathbf{k},\mathbf{k}'} c^+_{\mathbf{k}+\mathbf{q}\uparrow} c^+_{\mathbf{k}'\downarrow} c_{\mathbf{k}'+\mathbf{q}\downarrow} c_{\mathbf{k}\uparrow} \\ &\simeq -\frac{g}{N}\sum_{\mathbf{q}}\sum_{\mathbf{k},\mathbf{k}'} \Big[\langle c^+_{\mathbf{k}+\mathbf{q}\uparrow} c^+_{\mathbf{k}'\downarrow}\rangle c_{\mathbf{k}'+\mathbf{q}\downarrow} c_{\mathbf{k}\uparrow} + c^+_{\mathbf{k}+\mathbf{q}\uparrow} c^+_{\mathbf{k}'\downarrow}\langle c_{\mathbf{k}'+\mathbf{q}\downarrow} c_{\mathbf{k}\uparrow}\rangle\Big]\end{aligned} \tag{4.1.47}$$

Assuming $\mathbf{q} = -\mathbf{k} - \mathbf{k}'$ this Hamiltonian may be rearranged so as to produce the coupling term in (4.1.1). There are also other pairing possibilities. These have never been observed and they would normally be less stable than the normal Cooper pairs. However, the presence of the magnetic ordering at the wave vector $\mathbf{Q}$ makes it of interest to consider also $\mathbf{q} = -\mathbf{k} - \mathbf{k}' \pm \mathbf{Q}$. Using the same way of truncating the Hamiltonian as in eqn (4.1.35) the result is

$$\begin{aligned}\mathcal{H}_{\mathrm{el-ph}} &= -\sum_{\mathbf{k}} \Delta\big(c^+_{\mathbf{k}\uparrow} c^+_{-\mathbf{k}\downarrow} + c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}\big) \\ &- \sum_{0<k_z<Q} \big(\Delta_{\mathbf{Q}} c^+_{-\mathbf{k}+\mathbf{Q}\uparrow} c^+_{\mathbf{k}\downarrow} + \Delta_{-\mathbf{Q}} c^+_{\mathbf{k}-\mathbf{Q}\uparrow} c^+_{-\mathbf{k}\downarrow} + \Delta^*_{\mathbf{Q}} c_{\mathbf{k}\downarrow} c_{-\mathbf{k}+\mathbf{Q}\uparrow} + \Delta^*_{-\mathbf{Q}} c_{-\mathbf{k}\downarrow} c_{\mathbf{k}-\mathbf{Q}\uparrow}\big)\end{aligned} \tag{4.1.48}$$

The first sum, where Δ is assumed to be real and to be determined as in eqn (4.1.11), describes the normal BCS superconducting state. The two other energy-gap parameters are determined self-consistently by the similar conditions

$$\Delta_{\mathbf{Q}} = \frac{g}{N}\sum_{\mathbf{k}'}\langle c_{\mathbf{k}'\downarrow} c_{-\mathbf{k}'+\mathbf{Q}\uparrow}\rangle \quad ; \quad \Delta_{-\mathbf{Q}} = \frac{g}{N}\sum_{\mathbf{k}'}\langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'-\mathbf{Q}\uparrow}\rangle \tag{4.1.49}$$

The inversion symmetry implies that $|\Delta_{\mathbf{Q}}| = |\Delta_{-\mathbf{Q}}|$, whereas the phases of the two parameters may differ from each other. The two types of pairs do not interfere directly, but a non-zero value of one of the order parameter, Δ or $|\Delta_{\mathbf{Q}}|$, reduces the available parameter space for the other one, and thus we expect that only one of the two order parameters may develop. When $\Delta = 0$ there are two different cases to consider. One is $\Delta_{-\mathbf{Q}} = -\Delta^*_Q$, which ordering turns out to be distorted by the antiferromagnetic order parameter A in much the same way as derived above in the case of the usual Cooper-pair ordering. The other case to consider is $\Delta_{-\mathbf{Q}} = \Delta^*_Q$, and assuming the order parameter to be real, the coupling matrix corresponding to eqn (4.1.36) is

$$\mathcal{H}(\mathbf{k}) = \begin{pmatrix} \xi_{\mathbf{k}} & 0 & -\Delta_{\mathbf{Q}} & A \\ 0 & -\xi_{-\mathbf{k}} & A & -\Delta_{\mathbf{Q}} \\ -\Delta_{\mathbf{Q}} & A & -\xi_{-\mathbf{k}+\mathbf{Q}} & 0 \\ A & -\Delta_{\mathbf{Q}} & 0 & \xi_{\mathbf{k}-\mathbf{Q}} \end{pmatrix} \tag{4.1.50}$$

Introducing the same (u, v)-transformation as given by the eqns (4.1.37)–(4.1.38) the Hamiltonian in the $|x_n>$ basis is

$$\mathcal{H}(\mathbf{k}) = \begin{pmatrix} \epsilon_{\mathbf{k}} & 0 & -\Delta_{\mathbf{Q}} & 0 \\ 0 & -\epsilon_{\mathbf{k}} & 0 & -\Delta_{\mathbf{Q}} \\ -\Delta_{\mathbf{Q}} & 0 & -\epsilon_{\mathbf{Q}-\mathbf{k}} & 0 \\ 0 & -\Delta_{\mathbf{Q}} & 0 & \epsilon_{\mathbf{k}-\mathbf{Q}} \end{pmatrix} \tag{4.1.51}$$

Hence the antiferromagnetic ordering has no direct influence on the $\Delta_{\mathbf{Q}}$ coupling, except that the electron energies are changed from $\xi_{\mathbf{k}}$ to $\epsilon_{\mathbf{k}}$. The Hamiltonian may now be diagonalized exactly by performing the transformation

$$\begin{aligned} |y_1> &= r_{\mathbf{k}}|x_1> + s_{\mathbf{k}}|x_3> \quad ; \quad |y_3> = r_{\mathbf{k}}|x_3> - s_{\mathbf{k}}|x_1> \\ |y_2> &= r_{\mathbf{Q}-\mathbf{k}}|x_2> - s_{\mathbf{Q}-\mathbf{k}}|x_4> \quad ; \quad |y_4> = r_{\mathbf{Q}-\mathbf{k}}|x_4> + s_{\mathbf{Q}-\mathbf{k}}|x_2> \end{aligned} \tag{4.1.52a}$$

where

$$r_{\mathbf{k}}^2 + s_{\mathbf{k}}^2 = 1 \quad ; \quad r_{\mathbf{k}}^2 - s_{\mathbf{k}}^2 = \Phi_{\mathbf{k}}^{-1} \quad ; \quad r_{\mathbf{k}} s_{\mathbf{k}} = -\frac{\Delta_{\mathbf{Q}}}{(\xi_{\mathbf{k}} + \xi_{\mathbf{k}-\mathbf{Q}})\Phi_{\mathbf{k}}} \tag{4.1.52b}$$

and

$$\mathcal{E}_{\mathbf{k}} = \frac{\xi_{\mathbf{k}} - \xi_{\mathbf{k}-\mathbf{Q}}}{2}\,\Omega_{\mathbf{k}} + \frac{\xi_{\mathbf{k}} + \xi_{\mathbf{k}-\mathbf{Q}}}{2}\,\Phi_{\mathbf{k}} \quad ; \quad \Phi_{\mathbf{k}} = \left[1 + \frac{4\Delta_{\mathbf{Q}}^2}{(\xi_{\mathbf{k}} + \xi_{\mathbf{k}-\mathbf{Q}})^2}\right]^{\frac{1}{2}} \tag{4.1.53}$$

when introducing the original energies. The self-consistent equation determining the energy gap is

$$\begin{aligned} \Delta_{\mathbf{Q}} &= 2\frac{g}{N}\sum_{k_z>0}\sum_{n} <y_n|3><1|y_n>\, f(\mathcal{E}_n) \\ &= 2\frac{g}{N}\sum_{k_z>0}\Big(u^2 r_{\mathbf{k}} s_{\mathbf{k}}\big[f(\mathcal{E}_{\mathbf{k}}) - f(-\mathcal{E}_{\mathbf{Q}-\mathbf{k}})\big] + v^2 r_{\mathbf{Q}-\mathbf{k}} s_{\mathbf{Q}-\mathbf{k}}\big[f(\mathcal{E}_{\mathbf{Q}-\mathbf{k}}) - f(-\mathcal{E}_{\mathbf{k}})\big]\Big), \end{aligned}$$

where $r_{\mathbf{Q}-\mathbf{k}} s_{\mathbf{Q}-\mathbf{k}} = r_{\mathbf{k}} s_{\mathbf{k}}$ and we finally get

$$\Delta_{\mathbf{Q}} = 2\frac{g}{N}\sum_{k_z>0} r_{\mathbf{k}} s_{\mathbf{k}}\big[f(\mathcal{E}_{\mathbf{k}}) - f(-\mathcal{E}_{\mathbf{k}})\big] = -2\frac{g}{N}\sum_{k_z>0}\frac{\Delta_{\mathbf{Q}}}{(\xi_{\mathbf{k}} + \xi_{\mathbf{k}-\mathbf{Q}})\Phi_{\mathbf{k}}}\big[f(\mathcal{E}_{\mathbf{k}}) - f(-\mathcal{E}_{\mathbf{k}})\big]. \tag{4.1.54}$$

Hence the only influence of the antiferromagnetic order parameter is the factor $\Omega_{\mathbf{k}}$ in the energy expression, eqn (4.1.53), which is only different from 1 in the close neighbourhood of the superzone boundaries at $\mathbf{k} = \pm\mathbf{Q}/2$.

A

LINEAR RESPONSE THEORY

A.1 The generalized susceptibility

A response function for a macroscopic system relates the change of an ensemble-averaged physical observable $\langle \hat{B}(t)\rangle$ to an external force $f(t)$. For example, $\hat{B}(t)$ could be the angular momentum of an ion, or the magnetization, and $f(t)$ a time-dependent applied magnetic field. As indicated by its name, the applicability of linear response theory is restricted to the regime where $\langle \hat{B}(t)\rangle$ changes linearly with the force. Hence we suppose that $f(t)$ is sufficiently weak to ensure that the response is linear. We further assume that the system is in thermal equilibrium *before* the external force is applied.

When the system is in thermal equilibrium, it is characterized by the density operator

$$\rho_0 = \frac{1}{Z} e^{-\beta\mathcal{H}_0} \qquad ; \quad Z = \mathrm{Tr}\, e^{-\beta\mathcal{H}_0}, \tag{A.1.1}$$

where $\mathcal{H}_0$ is the (effective) Hamiltonian, Z is the (grand) partition function, and $\beta = 1/k_BT$. Since we are only interested in the linear part of the response, we may assume that the weak external disturbance $f(t)$ gives rise to a linear time-dependent perturbation in the total Hamiltonian $\mathcal{H}$:

$$\mathcal{H}_1 = -\hat{A}\, f(t) \qquad ; \quad \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1, \tag{A.1.2}$$

where $\hat{A}$ is a constant operator, as for example $\sum_i J_{zi}$, associated with the Zeeman term when $f(t) = g\mu_B H_z(t)$ (the circumflex over A or B indicates that these quantities are quantum mechanical operators). As a consequence of this perturbation, the density operator $\rho(t)$ becomes time-dependent, and so also does the ensemble average of the operator $\hat{B}$:

$$\langle \hat{B}(t)\rangle = \mathrm{Tr}\{\rho(t)\, \hat{B}\}. \tag{A.1.3}$$

The linear relation between this quantity and the external force has the form

$$\langle \hat{B}(t)\rangle - \langle \hat{B}\rangle = \int_{-\infty}^{t} \phi_{BA}(t-t')\, f(t')dt', \tag{A.1.4}$$

where $\langle \hat{B}\rangle = \langle \hat{B}(t=-\infty)\rangle = \mathrm{Tr}\{\rho_0\, \hat{B}\}$; here $f(t)$ is assumed to vanish for $t \to -\infty$. This equation expresses the condition that the differential change of $\langle \hat{B}(t)\rangle$ is proportional to the external disturbance $f(t')$ and the duration of the perturbation $\delta t'$, and further that disturbances at different times act independently of each other. The latter condition implies that the *response function* ϕ_{BA} may only depend on the time difference $t-t'$. In (A.1.4), the response is independent of any future perturbations. This causal behaviour may be incorporated in the response function by the requirement

$$\phi_{BA}(t-t') = 0 \qquad \text{for} \quad t' > t, \tag{A.1.5}$$

in which case the integration in eqn (A.1.4) can be extended from t to $+\infty$.

Because ϕ_{BA} depends only on the time difference, eqn (A.1.4) takes a simple form if we introduce the Fourier transform

$$f(\omega) = \int_{-\infty}^{\infty} f(t)\, e^{i\omega t} dt, \tag{A.1.6a}$$

and the reciprocal relation

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega)\, e^{-i\omega t} d\omega. \tag{A.1.6b}$$

In order to take advantage of the causality condition (A.1.5), we shall consider the Laplace transform of $\phi_{BA}(t)$ (the usual s is replaced by $-iz$):

$$\chi_{BA}(z) = \int_{0}^{\infty} \phi_{BA}(t)\, e^{izt} dt. \tag{A.1.7a}$$

$z = z_1 + iz_2$ is a complex variable and, if $\int_0^\infty |\phi_{BA}(t)|\, e^{-\epsilon t} dt$ is assumed to be finite in the limit $\epsilon \longrightarrow 0^+$, the converse relation is

$$\phi_{BA}(t) = \frac{1}{2\pi} \int_{-\infty+i\epsilon}^{\infty+i\epsilon} \chi_{BA}(z)\, e^{-izt} dz \qquad ; \quad \epsilon > 0. \tag{A.1.7b}$$

When $\phi_{BA}(t)$ satisfies the above condition and eqn (A.1.5), it can readily be shown that $\chi_{BA}(z)$ is an analytic function in the upper part of the complex z-plane ($z_2 > 0$).

In order to ensure that the evolution of the system is uniquely determined by $\rho_0 = \rho(-\infty)$ and $f(t)$, it is necessary that the external perturbation be turned on in a smooth, adiabatic way. This may be accomplished by replacing $f(t')$ in (4) by $f(t')\, e^{\epsilon t'}$, $\epsilon > 0$. This force vanishes in the limit $t' \longrightarrow -\infty$, and any unwanted secondary effects may be removed by taking the limit $\epsilon \longrightarrow 0^+$. Then, with the definition of the 'generalized' Fourier transform

$$\langle \hat{B}(\omega) \rangle = \lim_{\epsilon \to 0^+} \int_{-\infty}^{\infty} \Big(\langle \hat{B}(t) \rangle - \langle \hat{B} \rangle \Big)\, e^{i\omega t}\, e^{-\epsilon t} dt, \tag{A.1.8}$$

eqn (A.1.4) is transformed into

$$\langle \hat{B}(\omega) \rangle = \chi_{BA}(\omega)\, f(\omega), \tag{A.1.9a}$$

where $\chi_{BA}(\omega)$ is the boundary value of the analytic function $\chi_{BA}(z)$ on the real axis:

$$\chi_{BA}(\omega) = \lim_{\epsilon \to 0^+} \chi_{BA}(z = \omega + i\epsilon). \tag{A.1.9b}$$

$\chi_{BA}(\omega)$ is called the frequency-dependent or *generalized susceptibility* and is the Fourier transform, as defined by (A.1.8), of the response function $\phi_{BA}(t)$.

The mathematical restrictions (A.1.5) and (A.1.7) on $\phi_{BA}(t)$ have the direct physical significance that the system is respectively causal and stable against a small perturbation. The two conditions ensure that $\chi_{BA}(z)$ has no poles in the upper half-plane. If this were not the case, the response $\langle \hat{B}(t) \rangle$ to a small disturbance would diverge exponentially as a function of time.

The absence of poles in $\chi_{BA}(z)$, when z_2 is positive, leads to a relation between the real and imaginary part of $\chi_{BA}(\omega)$, called the *Kramers–Kronig dispersion relation.* If $\chi_{BA}(z)$ has no poles within the contour $\mathcal{C}$, then it may be expressed in terms of the Cauchy integral along $\mathcal{C}$ by the identity

$$\chi_{BA}(z) = \frac{1}{2\pi i} \int_{\mathcal{C}} \frac{\chi_{BA}(z')}{z' - z} dz'.$$

The contour $\mathcal{C}$ is chosen to be the half-circle, in the upper half-plane, centred at the origin and bounded below by the line parallel to the z_1-axis through $z_2 = \epsilon'$, and z is a point lying within this contour. Since $\phi_{BA}(t)$ is a bounded function in the domain $\epsilon' > 0$, then $\chi_{BA}(z')$ must go to zero as $|z'| \to \infty$, whenever $z_2' > 0$. This implies that the part of the contour integral along the half-circle must vanish when its radius goes to infinity, and hence

$$\chi_{BA}(z) = \lim_{\epsilon' \to 0^+} \frac{1}{2\pi i} \int_{-\infty + i\epsilon'}^{\infty + i\epsilon'} \frac{\chi_{BA}(\omega' + i\epsilon')}{\omega' + i\epsilon' - z} d(\omega' + i\epsilon').$$

Introducing $z = \omega + i\epsilon$ and applying ‘Dirac’s formula’:

$$\lim_{\epsilon \to 0^+} \frac{1}{\omega' - \omega - i\epsilon} = \mathcal{P}\frac{1}{\omega' - \omega} + i\pi\delta(\omega' - \omega),$$

in taking the limit $\epsilon \to 0^+$, we finally obtain the Kramers–Kronig relation ($\mathcal{P}$ denotes the principal part of the integral):

$$\chi_{BA}(\omega) = \frac{1}{i\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\chi_{BA}(\omega')}{\omega' - \omega} d\omega', \qquad (A.1.10)$$

which relates the real and imaginary components of $\chi(\omega)$.

A.2 Response functions

In this section, we shall deduce an expression for the response function $\phi_{BA}(t)$, in terms of the operators $\hat{B}$ and $\hat{A}$ and the unperturbed Hamiltonian $\mathcal{H}_0$. In the preceding section, we assumed implicitly the use of the Schrödinger picture. If instead we adopt the Heisenberg picture, the wave functions are independent of time, while the operators become time-dependent. In the Heisenberg picture, the operators are

$$\hat{B}(t) = e^{i\mathcal{H}t/\hbar}\, \hat{B}\, e^{-i\mathcal{H}t/\hbar}, \qquad (A.2.1)$$

corresponding to the equation of motion

$$\frac{d}{dt}\hat{B}(t) = \frac{i}{\hbar}[\, \mathcal{H}\, ,\, \hat{B}(t)\,] \qquad (A.2.2)$$

(assuming that $\hat{B}$ does not depend explicitly on time). Because the wave functions are independent of time, in the Heisenberg picture, the corresponding density operator ρ_H must also be. Hence we may write (A.1.3)

$$\langle \hat{B}(t) \rangle = \mathrm{Tr}\big\{\rho(t)\, \hat{B}\big\} = \mathrm{Tr}\big\{\rho_H\, \hat{B}(t)\big\}. \qquad (A.2.3)$$

Introducing (A.2.1) into this expression, and recalling that the trace is invariant under a cyclic permutation of the operators within it, we obtain

$$\rho(t) = e^{-i\mathcal{H}t/\hbar}\,\rho_H\, e^{i\mathcal{H}t/\hbar},$$

or

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}[\,\mathcal{H}\,,\,\rho(t)\,]. \tag{A.2.4}$$

The equation of motion derived for the density operator, in the Schrödinger picture, is similar to the Heisenberg equation of motion above, except for the change of sign in front of the commutator.

The density operator may be written as the sum of two terms:

$$\rho(t) = \rho_0 + \rho_1(t) \qquad \text{with} \quad [\,\mathcal{H}_0\,,\,\rho_0] = 0, \tag{A.2.5}$$

where ρ_0 is the density operator (A.1.1) of the thermal-equilibrium state which, by definition, must commute with $\mathcal{H}_0$, and the additional contribution due to $f(t)$ is assumed to vanish at $t \to -\infty$. In order to derive $\rho_1(t)$ to leading order in $f(t)$, we shall first consider the following density operator, in the *interaction picture*,

$$\rho_I(t) \equiv e^{i\mathcal{H}_0 t/\hbar}\,\rho(t)\, e^{-i\mathcal{H}_0 t/\hbar}, \tag{A.2.6}$$

for which

$$\begin{aligned}\frac{d}{dt}\rho_I(t) &= e^{i\mathcal{H}_0 t/\hbar}\left\{\frac{i}{\hbar}[\,\mathcal{H}_0\,,\,\rho(t)\,] + \frac{d}{dt}\rho(t)\right\} e^{-i\mathcal{H}_0 t/\hbar}\\ &= -\frac{i}{\hbar}e^{i\mathcal{H}_0 t/\hbar}\,[\,\mathcal{H}_1\,,\,\rho(t)\,]\,e^{-i\mathcal{H}_0 t/\hbar}.\end{aligned}$$

Because $\mathcal{H}_1$ is linear in $f(t)$, we may replace $\rho(t)$ by ρ_0 in calculating the linear response, giving

$$\frac{d}{dt}\rho_I(t) \simeq -\frac{i}{\hbar}\big[\,e^{i\mathcal{H}_0 t/\hbar}\,\mathcal{H}_1\,e^{-i\mathcal{H}_0 t/\hbar}\,,\,\rho_0\,\big] = \frac{i}{\hbar}[\,\hat{A}_0(t)\,,\,\rho_0\,]f(t),$$

using (A.2.5) and defining

$$\hat{A}_0(t) = e^{i\mathcal{H}_0 t/\hbar}\,\hat{A}\,e^{-i\mathcal{H}_0 t/\hbar}.$$

According to (A.2.6), taking into account the boundary condition, the time-dependent density operator is

$$\begin{aligned}\rho(t) &= e^{-i\mathcal{H}_0 t/\hbar}\left(\int_{-\infty}^{t}\frac{d}{dt'}\rho_I(t')dt' + \rho_0\right)e^{i\mathcal{H}_0 t/\hbar}\\ &= \rho_0 + \frac{i}{\hbar}\int_{-\infty}^{t}[\,\hat{A}_0(t'-t)\,,\,\rho_0\,]\,f(t')dt',\end{aligned} \tag{A.2.7}$$

to first order in the external perturbations. This determines the time dependence of, for example, $\hat{B}$ as

$$\begin{aligned}\langle\hat{B}(t)\rangle - \langle\hat{B}\rangle &= \mathrm{Tr}\big\{\,(\rho(t)-\rho_0)\;\hat{B}\big\}\\ &= \frac{i}{\hbar}\,\mathrm{Tr}\Big\{\int_{-\infty}^{t}[\,\hat{A}_0(t'-t)\,,\,\rho_0\,]\,\hat{B}\,f(t')dt'\Big\}\end{aligned}$$

and, utilizing the invariance of the trace under cyclic permutations, we obtain, to leading order,

$$\begin{aligned}\langle \hat{B}(t)\rangle - \langle \hat{B}\rangle &= \frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{Tr}\big\{\rho_0\,[\,\hat{B}\,,\,\hat{A}_0(t'-t)\,]\big\}\,f(t')dt' \\ &= \frac{i}{\hbar}\int_{-\infty}^{t} \langle\,[\,\hat{B}_0(t)\,,\,\hat{A}_0(t')\,]\,\rangle_0\,f(t')dt'.\end{aligned} \qquad (A.2.8)$$

A comparison of this result with the definition (A.1.4) of the response function then gives

$$\phi_{BA}(t-t') = \frac{i}{\hbar}\theta(t-t')\langle\,[\,\hat{B}(t)\,,\,\hat{A}(t')\,]\,\rangle, \qquad (A.2.9)$$

where the unit step function, $\theta(t) = 0$ or 1 when $t < 0$ or $t > 0$ respectively, is introduced in order to ensure that ϕ_{BA} satisfies the causality principle (A.1.5). In this final result, and below, we suppress the index 0, but we stress that both the variations with time and the ensemble average are thermal-equilibrium values determined by $\mathcal{H}_0$, and are unaffected by the external disturbances. This expression in terms of microscopic quantities, is called *the Kubo formula* for the response function (Kubo 1957, 1966).

The expression (A.2.9) is the starting point for introducing a number of useful functions:

$$K_{BA}(t) = \frac{i}{\hbar}\langle\,[\hat{B}(t)\,,\,\hat{A}\,]\,\rangle = \frac{i}{\hbar}\langle\,[\hat{B}\,,\,\hat{A}(-t)\,]\,\rangle \qquad (A.2.10)$$

is also called a response function. $\hat{A}$ is a shorthand notation for $\hat{A}(t=0)$. The inverse response function $K_{AB}(t)$, which determines $\langle \hat{A}(t)\rangle$ caused by the perturbation $\mathcal{H}_1 = -f(t)\hat{B}$, is

$$K_{AB}(t) = \frac{i}{\hbar}\langle\,[\hat{A}(t)\,,\,\hat{B}\,]\,\rangle = -K_{BA}(-t),$$

and $K_{BA}(t)$ can be expressed in terms of the corresponding causal response functions as

$$K_{BA}(t) = \begin{cases} \phi_{BA}(t) & \text{for} \quad t > 0 \\ -\phi_{AB}(-t) & \text{for} \quad t < 0. \end{cases}$$

The susceptibility is divided into two terms, the reactive part

$$\chi'_{BA}(z) = \chi'_{AB}(-z^*) \equiv \frac{1}{2}\big\{\chi_{BA}(z) + \chi_{AB}(-z^*)\big\}, \qquad (A.2.11a)$$

and the absorptive part

$$\chi''_{BA}(z) = -\chi''_{AB}(-z^*) \equiv \frac{1}{2i}\big\{\chi_{BA}(z) - \chi_{AB}(-z^*)\big\}, \qquad (A.2.11b)$$

so that

$$\chi_{BA}(z) = \chi'_{BA}(z) + i\chi''_{BA}(z) \qquad (A.2.11c)$$

and, according to the Kramers–Kronig relation (A.1.10),

$$\chi'_{BA}(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\chi''_{BA}(\omega')}{\omega'-\omega}d\omega' \quad ; \quad \chi''_{BA}(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\chi'_{BA}(\omega')}{\omega'-\omega}d\omega'. \qquad (A.2.11d)$$

In these equations, $\chi_{AB}(-\omega)$ is the boundary value obtained by taking $z = \omega + i\epsilon$, i.e. as $\lim_{\epsilon\to 0^+}\chi_{AB}(-z^* = -\omega + i\epsilon)$, corresponding to the condition that $\chi_{AB}(-z^*)$, like $\chi_{AB}(z)$, is analytic in the upper half-plane. The appropriate Laplace transform of $K_{BA}(t)$ with this property is

$$\begin{aligned} K_{BA}(z) &= \int_{-\infty}^{\infty} K_{BA}(t)\, e^{i(z_1 t + i z_2 |t|)} dt \\ &= \int_0^{\infty} \phi_{BA}(t)\, e^{izt} dt - \int_0^{\infty} \phi_{AB}(t)\, e^{-iz^* t} dt. \end{aligned}$$

Hence

$$K_{BA}(z) = 2i\, \chi''_{BA}(z). \tag{A.2.12}$$

Next we introduce the dynamic *correlation function*, sometimes referred to as the *scattering function*. It is defined as follows:

$$S_{BA}(t) \equiv \langle \hat{B}(t)\, \hat{A} \rangle - \langle \hat{B} \rangle \langle \hat{A} \rangle = \langle \hat{B}\, \hat{A}(-t) \rangle - \langle \hat{B} \rangle \langle \hat{A} \rangle, \tag{A.2.13}$$

and is related to the response function introduced earlier by

$$K_{BA}(t) = \frac{i}{\hbar} \big\{ S_{BA}(t) - S_{AB}(-t) \big\}. \tag{A.2.14}$$

The different response functions obey a number of symmetry relations, due to the invariance of the trace under a cyclic permutation of the operators. To derive the first, we recall that the Hermitian conjugate of an operator is defined by

$$(< \alpha |\, \hat{B}\, | \alpha' >)^* = < \alpha' |\, \hat{B}^\dagger\, | \alpha > .$$

If we assume that a certain set of state vectors $|\, \alpha >$ constitutes a diagonal representation, i.e. $\mathcal{H}_0 |\, \alpha > = E_\alpha |\, \alpha >$, then it is straightforward to show that

$$\langle \hat{B}(t)\, \hat{A} \rangle^* = \langle \hat{A}^\dagger(-t)\, \hat{B}^\dagger \rangle,$$

leading to the symmetry relations

$$K^*_{BA}(t) = K_{B^\dagger A^\dagger}(t)$$

and

$$\chi^*_{BA}(z) = \chi_{B^\dagger A^\dagger}(-z^*). \tag{A.2.15}$$

Another important relation is derived as follows:

$$\begin{aligned} \langle \hat{B}(t)\, \hat{A} \rangle &= \frac{1}{Z} \mathrm{Tr} \left\{ e^{-\beta \mathcal{H}_0}\, e^{i \mathcal{H}_0 t/\hbar}\, \hat{B}\, e^{-i \mathcal{H}_0 t/\hbar}\, \hat{A} \right\} \\ &= \frac{1}{Z} \mathrm{Tr} \left\{ e^{i \mathcal{H}_0 (t + i\beta\hbar)/\hbar}\, \hat{B}\, e^{-i \mathcal{H}_0 (t + i\beta\hbar)/\hbar}\, e^{-\beta \mathcal{H}_0}\, \hat{A} \right\} \\ &= \frac{1}{Z} \mathrm{Tr} \left\{ e^{-\beta \mathcal{H}_0}\, \hat{A}\, \hat{B}(t + i\beta\hbar) \right\} = \langle \hat{A}\, \hat{B}(t + i\beta\hbar) \rangle, \end{aligned}$$

implying that

$$S_{BA}(t) = S_{AB}(-t - i\beta\hbar). \tag{A.2.16}$$

In any realistic system which, rather than being isolated, is in contact with a thermal bath at temperature T, the correlation function $S_{BA}(t)$ vanishes in the limits $t \to \pm\infty$, corresponding to the condition $\langle \hat{B}(t=\pm\infty)\,\hat{A}\rangle = \langle\hat{B}\rangle\langle\hat{A}\rangle$. If we further assume that $S_{BA}(t)$ is an analytic function in the interval $|t_2| \leq \beta$ of the complex t-plane, then the Fourier transform of (A.2.16) is

$$S_{BA}(\omega) = e^{\beta\hbar\omega}\, S_{AB}(-\omega), \tag{A.2.17}$$

which is usually referred to as being the *condition of detailed balance.* Combining this condition with the expressions (A.2.12) and (A.2.14), we get the following important relation between the correlation function and the susceptibility:

$$S_{BA}(\omega) = 2\hbar \frac{1}{1-e^{-\beta\hbar\omega}} \chi''_{BA}(\omega), \tag{A.2.18}$$

which is called the *fluctuation–dissipation theorem.* This relation expresses explicitly the close connection between the spontaneous fluctuations in the system, as described by the correlation function, and the response of the system to external perturbations, as determined by the susceptibility.

The calculations above do not depend on the starting assumption that $\hat{B}$ (or $\hat{A}$) is a physical observable, i.e. that $\hat{B}$ should be equal to $\hat{B}^\dagger$. This has the advantage that, if the Kubo formula (A.2.9) is taken to be the starting point instead of eqn (A.1.4), the formalism applies more generally.

A.3 Energy absorption and the Green function

In this section, we first present a calculation of the energy transferred to the system by the external perturbation $\mathcal{H}_1 = -\hat{A}\, f(t)$ in (A.1.2), incidentally justifying the names of the two susceptibility components in (A.2.11). The energy absorption can be expressed in terms of $\chi_{AA}(\omega)$ and, without loss of generality, $\hat{A}$ may here be assumed to be a Hermitian operator, so that $\hat{A} = \hat{A}^\dagger$. In this case, $f(t)$ is real, and considering a harmonic variation

$$f(t) = f_0 \cos(\omega_0 t) = \tfrac{1}{2} f_0 \left(e^{i\omega_0 t} + e^{-i\omega_0 t}\right) \quad \text{with} \quad f_0^* = f_0,$$

then

$$f(\omega) = \pi f_0 \{\delta(\omega-\omega_0) + \delta(\omega+\omega_0)\}, \quad \text{as} \quad \int_{-\infty}^{\infty} e^{i(\omega-\omega_0)t} dt = 2\pi\delta(\omega-\omega_0),$$

and we have

$$\langle \hat{A}(t)\rangle - \langle\hat{A}\rangle = \tfrac{1}{2} f_0 \left\{\chi_{AA}(-\omega_0)\, e^{i\omega_0 t} + \chi_{AA}(\omega_0)\, e^{-i\omega_0 t}\right\}.$$

The introduction of $\hat{A} = \hat{B} = \hat{A}^\dagger$ in (A.2.15), and in the definition (A.2.11), yields

$$\begin{aligned} \chi'_{AA}(\omega)^* &= \chi'_{AA}(\omega) = \chi'_{AA}(-\omega) \\ \chi''_{AA}(\omega)^* &= \chi''_{AA}(\omega) = -\chi''_{AA}(-\omega), \end{aligned} \tag{A.3.1}$$

and these symmetry relations allow us to write

$$\langle \hat{A}(t)\rangle - \langle\hat{A}\rangle = f_0 \left\{\chi'_{AA}(\omega_0)\cos(\omega_0 t) + \chi''_{AA}(\omega_0)\sin(\omega_0 t)\right\}.$$

The part of the response which is in phase with the external force is proportional to $\chi'_{AA}(\omega_0)$, which is therefore called the reactive component. The rate of energy absorption due to the field is

$$Q = \frac{d}{dt}\langle \mathcal{H}\rangle = \langle \partial\mathcal{H}/\partial t\rangle = -\langle \hat{A}(t)\rangle\, \partial f/\partial t,$$

which shows that the *mean* dissipation rate is determined by the out-of-phase response proportional to $\chi''_{AA}(\omega)$:

$$\overline{Q} = \tfrac{1}{2} f_0^2\, \omega_0\, \chi''_{AA}(\omega_0) \tag{$A.3.2$}$$

and $\chi''_{AA}(\omega)$ is therefore called the absorptive part of the susceptibility.

If the eigenvalues E_α and the corresponding eigenstates $|\alpha>$ for the Hamiltonian $\mathcal{H}(=\mathcal{H}_0)$ are known, it is possible to derive an explicit expression for $\chi_{BA}(\omega)$. According to the definition (A.2.10),

$$\begin{aligned} K_{BA}(t) = \frac{i}{\hbar}\frac{1}{Z}\mathrm{Tr}\Big\{ e^{-\beta\mathcal{H}}\,[\,e^{i\mathcal{H}t/\hbar}\,\hat{B}\,e^{-i\mathcal{H}t/\hbar}\,,\,\hat{A}\,]\Big\} = \\ \frac{i}{\hbar}\frac{1}{Z}\sum_{\alpha\alpha'} e^{-\beta E_\alpha}\,\big\{ e^{iE_\alpha t/\hbar} < \alpha|\hat{B}|\alpha'> e^{-iE_{\alpha'}t/\hbar} < \alpha'|\hat{A}|\alpha > \\ - < \alpha|\hat{A}|\alpha'> e^{iE_{\alpha'}t/\hbar} < \alpha'|\hat{B}|\alpha > e^{-iE_\alpha t/\hbar}\big\}. \end{aligned}$$

Interchanging α and α' in the last term, and introducing the population factor

$$n_\alpha = \frac{1}{Z}\,e^{-\beta E_\alpha} \qquad ; \quad Z = \sum_{\alpha'} e^{-\beta E_{\alpha'}}, \tag{$A.3.3a$}$$

we get

$$K_{BA}(t) = \frac{i}{\hbar}\sum_{\alpha\alpha'} < \alpha|\hat{B}|\alpha'>< \alpha'|\hat{A}|\alpha > (n_\alpha - n_{\alpha'})\, e^{i(E_\alpha - E_{\alpha'})t/\hbar}, \tag{$A.3.3b$}$$

and hence

$$\begin{aligned} \chi_{BA}(\omega) &= \lim_{\epsilon\to 0^+}\int_0^\infty K_{BA}(t)\, e^{i(w+i\epsilon)t}dt \\ &= \lim_{\epsilon\to 0^+}\sum_{\alpha\alpha'}\frac{< \alpha|\hat{B}|\alpha'>< \alpha'|\hat{A}|\alpha >}{E_{\alpha'} - E_\alpha - \hbar\omega - i\hbar\epsilon}\,(n_\alpha - n_{\alpha'}), \end{aligned} \tag{$A.3.4a$}$$

or equivalently

$$\begin{aligned} \chi_{AB}(-\omega) &= \lim_{\epsilon\to 0^+}\chi_{AB}(-\omega + i\epsilon) \\ &= \lim_{\epsilon\to 0^+}\sum_{\alpha\alpha'}\frac{< \alpha|\hat{A}|\alpha'>< \alpha'|\hat{B}|\alpha >}{E_{\alpha'} - E_\alpha + \hbar\omega - i\hbar\epsilon}\,(n_\alpha - n_{\alpha'}). \end{aligned} \tag{$A.3.4b$}$$

An interchange of α and α' shows this expression to be the same as ($A.3.4a$), with ϵ replaced by $-\epsilon$. The application of Dirac's formula then yields the absorptive part of the susceptibility ($A.2.11b$) as

$$\chi''_{BA}(\omega) = \pi\sum_{\alpha\alpha'} < \alpha|\hat{B}|\alpha'>< \alpha'|\hat{A}|\alpha > (n_\alpha - n_{\alpha'})\,\delta\big(\hbar\omega - (E_{\alpha'} - E_\alpha)\big) \tag{$A.3.5$}$$

(equal to $K_{BA}(\omega)/2i$ in accordance with (A.2.12)), whereas the reactive part $(A.2.11a)$ is

$$\chi'_{BA}(\omega) = \sum_{\alpha\alpha'}^{E_\alpha \neq E_{\alpha'}} \frac{<\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha>}{E_{\alpha'} - E_\alpha - \hbar\omega}(n_\alpha - n_{\alpha'}) + \chi'_{BA}(el)\,\delta_{\omega 0}, \qquad (A.3.6a)$$

where

$$\delta_{\omega 0} \equiv \lim_{\epsilon\to 0^+} \frac{i\epsilon}{\omega + i\epsilon} = \begin{cases} 1 & \text{if} \quad \omega = 0 \\ 0 & \text{if} \quad \omega \neq 0, \end{cases}$$

and the elastic term $\chi'_{BA}(el)$, which only contributes in the static limit $\omega = 0$, is

$$\chi'_{BA}(el) = \beta\Big\{ \sum_{\alpha\alpha'}^{E_\alpha = E_{\alpha'}} <\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha> n_\alpha \;-\; \langle\hat{B}\rangle\langle\hat{A}\rangle \Big\}. \qquad (A.3.6b)$$

We remark that $\chi'_{BA}(\omega)$ and $\chi''_{BA}(\omega)$ are often referred to respectively as the real and the imaginary part of $\chi_{BA}(\omega)$. This terminology is not valid in general, but only if the matrix-element products are real, as they are if, for instance, $\hat{B} = \hat{A}^\dagger$. The presence of the elastic term in the reactive response requires some additional consideration. There are no elastic contributions to $K_{BA}(t)$, nor hence to $\chi''_{BA}(\omega)$, because $n_\alpha - n_{\alpha'} \equiv 0$ if $E_\alpha = E_{\alpha'}$. Nevertheless, the appearance of an extra contribution at $\omega = 0$, not obtainable directly from $K_{BA}(t)$, is possible because the energy denominator in (A.3.4) vanishes in the limit $|\omega + i\epsilon| \to 0$, when $E_\alpha = E_{\alpha'}$. In order to derive this contribution, we consider the equal-time correlation function

$$\begin{aligned} S_{BA}(t=0) &= \langle(\hat{B} - \langle\hat{B}\rangle)(\hat{A} - \langle\hat{A}\rangle)\rangle \\ &= \sum_{\alpha\alpha'} <\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha> n_\alpha \;-\; \langle\hat{B}\rangle\langle\hat{A}\rangle \end{aligned} \qquad (A.3.7a)$$

which, according to the fluctuation–dissipation theorem (A.2.18), should be

$$S_{BA}(t=0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} S_{BA}(\omega)\,d\omega = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{1}{1 - e^{-\beta\hbar\omega}}\,\chi''_{BA}(\omega) d(\hbar\omega). \qquad (A.3.7b)$$

Introducing (A.3.5), the integration is straightforward, except in a narrow interval around $\omega = 0$, and we obtain

$$S_{BA}(t=0) = \sum_{\alpha\alpha'}^{E_\alpha \neq E_{\alpha'}} <\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha> n_\alpha + \lim_{\gamma\to 0^+}\int_{-\gamma}^{\gamma} \frac{\chi''_{BA}(\omega)}{\pi\beta\omega} d\omega$$

after replacing $1 - e^{-\beta\hbar\omega}$ with $\beta\hbar\omega$ in the limit $\omega \to 0$. A comparison of this expression for $S_{BA}(t=0)$ with $(A.3.7a)$ shows that the last integral has a definite value:

$$\lim_{\gamma\to 0^+}\int_{-\gamma}^{\gamma} \frac{\chi''_{BA}(\omega)}{\pi\beta\omega} d\omega = \sum_{\alpha\alpha'}^{E_\alpha = E_{\alpha'}} <\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha> n_\alpha \;-\; \langle\hat{B}\rangle\langle\hat{A}\rangle. \qquad (A.3.8)$$

The use of the Kramers–Kronig relation (A.1.10), in the form of (A.2.11d), for calculating $\chi'_{BA}(0)$ then gives rise to the extra contribution

$$\chi'_{BA}(el) = \lim_{\gamma \to 0^+} \frac{1}{\pi} \int_{-\gamma}^{\gamma} \frac{\chi''_{BA}(\omega)}{\omega} d\omega \tag{A.3.9}$$

to the reactive susceptibility at zero frequency, as anticipated in (A.3.6b). The zero-frequency result, $\chi_{BA}(0) = \chi'_{BA}(0)$, as given by (A.3.6), is the same as the conventional isothermal susceptibility (2.1.18) for the magnetic moments, where the elastic and inelastic contributions are respectively the Curie and the Van Vleck terms. This elastic contribution is discussed in more detail by, for instance, Suzuki (1971).

The results (A.3.4–6) show that, if the eigenstates of the Hamiltonian are discrete and the matrix-elements of the operators $\hat{B}$ and $\hat{A}$ between these states are well-defined, the poles of $\chi_{BA}(z)$ all lie on the real axis. This has the consequence that the absorptive part $\chi''_{BA}(\omega)$ (A.3.5) becomes a sum of δ-functions, which are only non-zero when $\hbar\omega$ is equal to the *excitation* energies $E_{\alpha'} - E_\alpha$. In such a system, no spontaneous transitions occur. In a real macroscopic system, the distribution of states is continuous, and only the ground state may be considered as a well-defined discrete state. At non-zero temperatures, the parameters of the system are subject to fluctuations in space and time. The introduction of a non-zero probability for a spontaneous transition between the 'levels' α and α' can be included in a phenomenological way by replacing the energy difference $E_{\alpha'} - E_\alpha$ in (A.3.4) by $(E_{\alpha'} - E_\alpha) - i\,\Gamma_{\alpha'\alpha}(\omega)$, where the parameters, including the energy difference, usually depend on ω. According to the general stability and causality requirements, the poles of $\chi_{BA}(z)$ at $z = z_{\alpha'\alpha} = (E_{\alpha'} - E_\alpha) - i\,\Gamma_{\alpha'\alpha}$ must lie in the lower half-plane, implying that $\Gamma_{\alpha'\alpha}$ has to be positive (or zero). In the case where $|E_{\alpha'} - E_\alpha| \gg \Gamma_{\alpha'\alpha}$, the ω-dependence of these parameters is unimportant, and the δ-function in (A.3.5) is effectively replaced by a *Lorentzian*:

$$\begin{aligned} \chi''_{BA}(\omega) \simeq \sum_{\alpha\alpha'} & \frac{< \alpha|\hat{B}|\alpha' >< \alpha'|\hat{A}|\alpha >}{(E_{\alpha'} - E_\alpha - \hbar\omega)^2 + \Gamma^2_{\alpha'\alpha}} \, \Gamma_{\alpha'\alpha}(n_\alpha - n_{\alpha'}) \\ & + \frac{\hbar\omega\Gamma_0}{(\hbar\omega)^2 + \Gamma_0^2} \, \chi'_{BA}(el), \end{aligned} \tag{A.3.10}$$

with a *linewidth*, or more precisely FWHM (full width at half maximum), of $2\Gamma_{\alpha'\alpha}$. In (A.3.10), we have added the *quasi-elastic* response due to a pole at $z = -i\,\Gamma_0$, which replaces the one at $z = 0$. The corresponding reactive part of the susceptibility is

$$\begin{aligned} \chi'_{BA}(\omega) \simeq \sum_{\alpha\alpha'} & \frac{< \alpha|\hat{B}|\alpha' >< \alpha'|\hat{A}|\alpha >}{(E_{\alpha'} - E_\alpha - \hbar\omega)^2 + \Gamma^2_{\alpha'\alpha}} (E_{\alpha'} - E_\alpha - \hbar\omega)(n_\alpha - n_{\alpha'}) \\ & + \frac{\Gamma_0^2}{(\hbar\omega)^2 + \Gamma_0^2} \, \chi'_{BA}(el). \end{aligned} \tag{A.3.11}$$

The non-zero linewidth corresponds to an exponential decay of the oscillations in the time dependence of, for instance, the correlation function:

$$S_{BA}(t) \sim e^{-iz_{\alpha'\alpha}t/\hbar} = e^{-i(E_{\alpha'} - E_\alpha)t/\hbar} \, e^{-\Gamma_{\alpha'\alpha}t/\hbar}.$$

The absorption observed in a *resonance* experiment is proportional to $\chi''_{AA}(\omega)$. A peak in the absorption spectrum is interpreted as an *elementary* or *quasi-particle excitation*, or as a *normal mode* of the dynamic variable $\hat{A}$, with a *lifetime* $\tau = \hbar/\Gamma_{\alpha'\alpha}$. A pole at $z = -i\Gamma_0$ is said to represent a *diffusive mode*. Such a pole is of particular importance for those transport coefficients determined by the low-frequency or hydrodynamic properties of the system. Kubo (1957, 1966) gives a detailed discussion of this subject. As we shall see later, the differential scattering cross-section of, for example, neutrons in the Born-approximation is proportional to a correlation function, and hence to $\chi''(\omega)$. This implies that the presence of elementary excitations in the system leads to peaks in the intensity of scattered neutrons as a function of the energy transfer. Finally, the dynamic correlation-functions are related directly to various thermodynamic second-derivatives, such as the compressibility and the magnetic susceptibility, and thereby indirectly to the corresponding first-derivatives, like the specific heat and the magnetization. Consequently, most physical properties of a macroscopic system near equilibrium may be described in terms of the correlation functions.

As a supplement to the response function $\phi_{BA}(t-t')$, we now introduce the *Green function*, defined as

$$\begin{aligned} G_{BA}(t-t') &\equiv \langle\langle \hat{B}(t)\,;\,\hat{A}(t')\rangle\rangle \\ &\equiv -\frac{i}{\hbar}\theta(t-t')\langle\,[\,\hat{B}(t)\,,\,\hat{A}(t')\,]\,\rangle = -\phi_{BA}(t-t'). \end{aligned} \qquad (A.3.12)$$

This Green function is often referred to as the *double-time* or the *retarded* Green function (Zubarev 1960), and it is simply our previous response function, but with the opposite sign. Introducing the Laplace transform $G_{BA}(z)$ according to (A.1.7), we find, as before, that the corresponding Fourier transform is

$$\begin{aligned} G_{BA}(\omega) \equiv \langle\langle \hat{B}\,;\,\hat{A}\rangle\rangle_\omega &= \lim_{\epsilon\to 0^+} G_{BA}(z=\omega+i\epsilon) \\ &= \lim_{\epsilon\to 0^+}\int_{-\infty(0)}^{\infty} G_{BA}(t)\,e^{i(\omega+i\epsilon)t}dt = -\chi_{BA}(\omega). \end{aligned} \qquad (A.3.13)$$

We note that, if $\hat{A}$ and $\hat{B}$ are dimensionless operators, then $G_{BA}(\omega)$ or $\chi_{BA}(\omega)$ have the dimensions of inverse energy.

If $t' = 0$, the derivative of the Green function with respect to t is

$$\begin{aligned} \frac{d}{dt}G_{BA}(t) &= -\frac{i}{\hbar}\Big(\delta(t)\langle\,[\,\hat{B}(t)\,,\,\hat{A}\,]\,\rangle + \theta(t)\langle\,[\,d\hat{B}(t)/dt\,,\,\hat{A}\,]\,\rangle\Big) \\ &= -\frac{i}{\hbar}\Big(\delta(t)\langle\,[\,\hat{B}\,,\,\hat{A}\,]\,\rangle - \frac{i}{\hbar}\theta(t)\langle\,[\,[\,\hat{B}(t)\,,\,\mathcal{H}\,]\,,\,\hat{A}\,]\,\rangle\Big). \end{aligned}$$

A Fourier transformation of this expression then leads to the *equation of motion* for the Green function:

$$\hbar\omega\langle\langle \hat{B}\,;\,\hat{A}\rangle\rangle_\omega - \langle\langle\,[\,\hat{B}\,,\,\mathcal{H}\,]\,;\,\hat{A}\rangle\rangle_\omega = \langle\,[\,\hat{B}\,,\,\hat{A}\,]\,\rangle. \qquad (A.3.14a)$$

The suffix ω indicates the Fourier transforms (A.3.13), and $\hbar\omega$ is shorthand for $\hbar(\omega+i\epsilon)$ with $\epsilon\to 0^+$. In many applications, $\hat{A}$ and $\hat{B}$ are the same (Hermitian) operator, in which case the r.h.s. of $(A.3.14a)$ vanishes and one may proceed to the second derivative. With the condition that $\langle\,[\,[\,[\,\hat{A}(t)\,,\,\mathcal{H}\,]\,,\,\mathcal{H}\,]\,,\,\hat{A}\,]\,\rangle$ is $-\langle\,[\,[\,\hat{A}(t)\,,\,\mathcal{H}\,]\,,\,[\,\hat{A}\,,\,\mathcal{H}\,]\,]\,\rangle$, the equation of motion for the Green function $\langle\langle\,[\,\hat{A}\,,\,\mathcal{H}\,]\,;\,\hat{A}\rangle\rangle_\omega$ leads to

$$(\hbar\omega)^2\langle\langle \hat{A}\,;\,\hat{A}\rangle\rangle_\omega + \langle\langle\,[\,\hat{A}\,,\,\mathcal{H}\,]\,;\,[\,\hat{A}\,,\,\mathcal{H}\,]\,\rangle\rangle_\omega = \langle\,[\,[\,\hat{A}\,,\mathcal{H}\,]\,,\,\hat{A}\,]\,\rangle. \qquad (A.3.14b)$$

The pair of equations (A.3.14) will be the starting point for our application of linear response theory.

A.4 The random-phase approximation

Earlier in this chapter, we have demonstrated that many experimentally observable properties of solids can be expressed in terms of two-particle correlation functions. Hence it is of great importance to be able to calculate these, or the related Green functions, for realistic systems. We shall therefore consider the determination of the generalized susceptibility for rare earth magnets, using the random-phase approximation which was introduced in the last section, and conclude the chapter by applying this theory to the simple Heisenberg model, in which the single-ion anisotropy is neglected.

A.4.1 The generalized susceptibility in the RPA

The starting point for the calculation of the generalized susceptibility is the (effective) Hamiltonian for the angular momenta which, as usual, we write as a sum of single- and two-ion terms:

$$\mathcal{H} = \sum_i \mathcal{H}_{\rm J}(\mathbf{J}_i) - \tfrac{1}{2} \sum_{i \neq j} \mathcal{J}(ij)\, \mathbf{J}_i \cdot \mathbf{J}_j . \qquad (A.4.1)$$

For our present purposes, it is only necessary to specify the two-ion part and, for simplicity, we consider only the Heisenberg interaction. As in Section 2.2, we introduce the thermal expectation values $\langle \mathbf{J}_i \rangle$ in the Hamiltonian, which may then be written

$$\mathcal{H} = \sum_i \mathcal{H}_{\rm MF}(i) - \tfrac{1}{2} \sum_{i \neq j} \mathcal{J}(ij)\, (\mathbf{J}_i - \langle \mathbf{J}_i \rangle) \cdot (\mathbf{J}_j - \langle \mathbf{J}_j \rangle), \qquad (A.4.2)$$

where

$$\mathcal{H}_{\rm MF}(i) = \mathcal{H}_{\rm J}(\mathbf{J}_i) - \big(\mathbf{J}_i - \tfrac{1}{2} \langle \mathbf{J}_i \rangle\big) \cdot \sum_j \mathcal{J}(ij) \langle \mathbf{J}_j \rangle . \qquad (A.4.3)$$

From the mean-field Hamiltonians $\mathcal{H}_{\rm MF}(i)$, we may calculate $\langle \mathbf{J}_i \rangle$ as before. The Hamiltonian (A.4.3) also determines the dynamic susceptibility of the ith ion, in the form of a Cartesian tensor $\overline{\overline{\chi}}{}_i^o(\omega)$, according to eqns (A.3.4–6), with $\hat{A}$ and $\hat{B}$ set equal to the angular-momentum components $J_{i\alpha}$. We wish to calculate the linear response $\langle \mathbf{J}_i(t) \rangle$ of the system to a small perturbative field $\mathbf{h}_j(t) = g\mu_B \mathbf{H}_j(t)$ (the Zeeman term due to a stationary field is taken as included in $\mathcal{H}_{\rm J}(\mathbf{J}_i)$). From (A.4.2), we may extract all terms depending on $\mathbf{J}_i$ and collect them in an effective Hamiltonian $\mathcal{H}_i$, which determines the time-dependence of $\mathbf{J}_i$. Transformed to the Heisenberg picture, this Hamiltonian is

$$\mathcal{H}_i(t) = \mathcal{H}_{\rm MF}(i,t) - \big(\mathbf{J}_i(t) - \langle \mathbf{J}_i \rangle\big) \cdot \Big(\sum_j \mathcal{J}(ij) (\mathbf{J}_j(t) - \langle \mathbf{J}_j \rangle) + \mathbf{h}_i(t) \Big). \qquad (A.4.4)$$

We note that a given site i appears twice in the second term of (A.4.2), and that the additional term $\langle \mathbf{J}_i \rangle \cdot \mathbf{h}_i$ has no consequences in the limit when $\mathbf{h}_i$ goes to zero. The differences $\mathbf{J}_j(t) - \langle \mathbf{J}_j(t) \rangle$ fluctuate in a virtually uncorrelated manner from ion to ion, and their contribution to the sum in (A.4.4) is therefore small. Thus, to a good approximation, these fluctuations may be neglected, corresponding to replacing $\mathbf{J}_j(t)$ in (A.4.4) by $\langle \mathbf{J}_j(t) \rangle$ (when $j \neq i$). This is just the random-phase approximation (RPA), introduced in the previous section, and so called on account of the assumption that $\mathbf{J}_j(t) - \langle \mathbf{J}_j(t) \rangle$ may be described in terms of a random phase-factor. It is clearly best justified when the fluctuations are small, i.e. at low temperatures, and when many sites contribute to the sum, i.e. in three-dimensional systems with long-range interactions. The latter condition reflects the fact that an increase in the number of (nearest) neighbours improves the resemblance of the sum in (A.4.4) to an ensemble average. If we introduce the RPA in eqn (A.4.4), the only dynamical variable which remains is $\mathbf{J}_i(t)$, and the Hamiltonian becomes equivalent to $\mathcal{H}_{\mathrm{MF}}(i)$, except that the probing field $\mathbf{h}_i(t)$ is replaced by an effective field $\mathbf{h}_i^{\mathrm{eff}}(t)$. With $\langle \mathbf{J}_i(\omega)\rangle$ defined as the Fourier transform of $\langle \mathbf{J}_i(t)\rangle - \langle \mathbf{J}_i\rangle$, then, according to eqn (A.1.9),

$$\langle \mathbf{J}_i(\omega)\rangle = \overline{\overline{\chi}}{}_i^{o}(\omega)\mathbf{h}_i^{\mathrm{eff}}(\omega),$$

where the effective field is

$$\mathbf{h}_i^{\mathrm{eff}}(\omega) = \mathbf{h}_i(\omega) + \sum_j \mathcal{J}(ij)\langle \mathbf{J}_j(\omega)\rangle. \tag{A.4.5}$$

This may be compared with the response determined by the two-ion susceptibility functions of the system, defined such that

$$\langle \mathbf{J}_i(\omega)\rangle = \sum_j \overline{\overline{\chi}}(ij,\omega)\,\mathbf{h}_j(\omega). \tag{A.4.6}$$

The two ways of writing the response should coincide for all $\mathbf{h}_j(\omega)$, which implies that, within the RPA,

$$\overline{\overline{\chi}}(ij,\omega) = \overline{\overline{\chi}}{}_i^{o}(\omega)\Big(\delta_{ij} + \sum_{j'} \mathcal{J}(ij')\,\overline{\overline{\chi}}(j'j,\omega)\Big). \tag{A.4.7}$$

This self-consistent equation may be solved under various conditions. For convenience, we shall consider here only the uniform case of a ferro- or paramagnet, where $\mathcal{H}_{\mathrm{MF}}(i)$ is the same for all the ions, i.e. $\langle \mathbf{J}_i\rangle = \langle \mathbf{J}\rangle$ and $\overline{\overline{\chi}}{}_i^{o}(\omega) = \overline{\overline{\chi}}{}^{o}(\omega)$, in which case we get the final result

$$\overline{\overline{\chi}}(\mathbf{q},\omega) = \big\{1 - \overline{\overline{\chi}}{}^{o}(\omega)\mathcal{J}(\mathbf{q})\big\}^{-1}\,\overline{\overline{\chi}}{}^{o}(\omega). \tag{A.4.8}$$

Here 1 is the unit matrix, and we have used the Fourier transform of $\mathcal{J}(ij)$

$$\mathcal{J}(\mathbf{q}) = \sum_j \mathcal{J}(ij)\, e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)}. \tag{A.4.9}$$

In the RPA, the effects of the surrounding ions are accounted for by a time-dependent molecular field, which self-consistently enhances the response of the isolated ions. The above results are derived from a kind of hybrid MF-RPA theory, as the single-ion susceptibility $\overline{\overline{\chi}}{}_i^{o}(\omega)$ is still determined in terms of the MF expectation values. A self-consistent RPA theory might be more accurate but, as we shall see, gives rise to further problems. At high temperatures (or close to a phase transition), the description of the dynamical behaviour obtained in the RPA is incomplete, because the thermal fluctuations introduce damping effects which are not included. However, the static properties may still be described fairly accurately by the above theory, because the MF approximation is correct to leading order in $\beta = 1/k_BT$.

The RPA, which determines the excitation spectrum of the many-body system to leading order in the two-ion interactions, is simple to derive and is of general utility.

Historically, its applicability was appreciated only gradually, in parallel with the experimental study of a variety of systems, and results corresponding to eqn (A.4.8) were presented independently several times in the literature in the early 1970s (Fulde and Perschel 1971, 1972; Haley and Erdös 1972; Purwins *et al.* 1973; Holden and Buyers 1974). The approach to this problem in the last three references is very similar.

A.4.2 MF-RPA theory of the Heisenberg ferromagnet

We conclude this chapter by applying the RPA to the Heisenberg model, thereby demonstrating the relation between (A.4.8) and the results presented in the previous section. In order to do this, we must calculate $\overline{\overline{\chi}}^o(\omega)$. The eigenstates of the MF Hamiltonian $(A.4.4b)$ are $|S^z = M>$, with $M = -S, -S+1, \cdots, S$, and we neglect the constant contribution to the eigenvalues

$$E_M = -M\mathcal{J}(\mathbf{0})\langle S^z\rangle_0 = -M\Delta \qquad \text{with} \quad \Delta = \mathcal{J}(\mathbf{0})\langle S^z\rangle_0,$$

denoting the MF expectation-value $(A.4.5a)$ of S^z by $\langle S^z\rangle_0$. According to $(A.3.4a)$, we then have (only terms with $\alpha = M+1$ and $\alpha' = M$ contribute):

$$\begin{aligned}
\chi^o_{+-}(\omega) &= \sum_{M=-S}^{S-1} \frac{<M+1|S^+|M><M|S^-|M+1>}{E_M - E_{M+1} - \hbar\omega}\,(n_{M+1} - n_M) \\
&= \frac{1}{Z}\sum_{-S}^{S-1} \frac{S(S+1) - M(M+1)}{\Delta - \hbar\omega}\left(e^{\beta(M+1)\Delta} - e^{\beta M\Delta}\right) \\
&= \frac{1}{\Delta - \hbar\omega}\frac{1}{Z}\Big(\sum_{-S+1}^{S}\big\{S(S+1) - (M-1)M\big\}e^{\beta M\Delta} \\
&\qquad\qquad - \sum_{-S}^{S-1}\big\{S(S+1) - M(M+1)\big\}e^{\beta M\Delta}\Big) \\
&= \frac{1}{\Delta - \hbar\omega}\frac{1}{Z}\sum_{-S}^{S} 2Me^{\beta M\Delta} \;=\; \frac{2\langle S^z\rangle_0}{\Delta - \hbar\omega},
\end{aligned}$$

as all the sums may be taken as extending from $-S$ to S. Similarly $\chi^o_{-+}(\omega) = \chi^o_{+-}(-\omega)$, whereas $\chi^o_{++}(\omega) = \chi^o_{--}(\omega) = 0$, from which we obtain

$$\chi^o_{xx}(\omega) = \chi^o_{yy}(\omega) = \frac{1}{4}\left\{\chi^o_{+-}(\omega) + \chi^o_{-+}(\omega)\right\} = \frac{\Delta\langle S^z\rangle_0}{\Delta^2 - (\hbar\omega)^2}, \tag{A.4.24a}$$

and

$$\chi^o_{xy}(\omega) = -\chi^o_{yx}(\omega) = \frac{i}{4}\left\{\chi^o_{+-}(\omega) - \chi^o_{-+}(\omega)\right\} = \frac{i\hbar\omega\langle S^z\rangle_0}{\Delta^2 - (\hbar\omega)^2}. \tag{A.4.24b}$$

We note here that $\chi^o_{xy}{}'(\omega)$ and $\chi^o_{xy}{}''(\omega)$, obtained by replacing ω by $\omega + i\epsilon$ and letting $\epsilon \to 0^+$, are both purely imaginary. Of the remaining components in $\overline{\overline{\chi}}^o(\omega)$, only $\chi^o_{zz}(\omega)$ is non-zero, and it comprises only an elastic contribution

$$\chi^o_{zz}(\omega) = \beta\,(\delta S^z)^2\delta_{\omega 0}, \qquad \text{with} \quad (\delta S^z)^2 \equiv \langle (S^z)^2\rangle_0 - \langle S^z\rangle_0^2. \tag{A.4.25}$$

Because $\chi^o_{\pm z}(\omega) = 0$, the RPA equation (A.4.8) factorizes into a 2×2 (xy)-matrix equation and a scalar equation for the zz-component. Inverting the (xy)-part of the matrix $\{1 - \overline{\overline{\chi}}{}^o(\omega)\, \mathcal{J}(\mathbf{q})\}$, we find

$$\chi_{xx}(\mathbf{q},\omega) = \frac{\chi^o_{xx}(\omega) - |\overline{\overline{\chi}}{}^o(\omega)|\, \mathcal{J}(\mathbf{q})}{1 - \{\chi^o_{xx}(\omega) + \chi^o_{yy}(\omega)\}\, \mathcal{J}(\mathbf{q}) + |\overline{\overline{\chi}}{}^o(\omega)|\, \mathcal{J}^2(\mathbf{q})},$$

where the determinant is

$$|\overline{\overline{\chi}}{}^o(\omega)| = \chi^o_{xx}(\omega)\chi^o_{yy}(\omega) - \chi^o_{xy}(\omega)\chi^o_{yx}(\omega) = \frac{\langle S^z\rangle_0^2}{\Delta^2 - (\hbar\omega)^2}.$$

By a straightforward manipulation, this leads to

$$\chi_{xx}(\mathbf{q},\omega) = \frac{E^0_{\mathbf{q}}\langle S^z\rangle_0}{(E^0_{\mathbf{q}})^2 - (\hbar\omega)^2}, \tag{$A.4.26a$}$$

with

$$E^0_{\mathbf{q}} = \Delta - \langle S^z\rangle_0 \mathcal{J}(\mathbf{q}) = \langle S^z\rangle_0 \{\mathcal{J}(\mathbf{0}) - \mathcal{J}(\mathbf{q})\}. \tag{$A.4.26b$}$$

The same result is obtained for $\chi_{yy}(\mathbf{q},\omega)$. We note that ($A.4.26a$) should be interpreted as

$$\chi_{xx}(\mathbf{q},\omega) = \tfrac{1}{2}\langle S^z\rangle_0 \lim_{\epsilon\to 0^+} \left(\frac{1}{E^0_{\mathbf{q}} - \hbar\omega - i\hbar\epsilon} + \frac{1}{E^0_{\mathbf{q}} + \hbar\omega + i\hbar\epsilon} \right).$$

This result is nearly the same as that deduced by a self-consistent procedure, except that the RPA expectation-value $\langle S^z\rangle$ is replaced by its MF value $\langle S^z\rangle_0$, reflecting the lack of self-consistency in this analysis. As a supplement we find that

$$\chi_{zz}(\mathbf{q},\omega) = \frac{\chi^o_{zz}(\omega)}{1 - \chi^o_{zz}(\omega)\, \mathcal{J}(\mathbf{q})} = \frac{\beta(\delta S^z)^2}{1 - \beta(\delta S^z)^2\, \mathcal{J}(\mathbf{q})}\, \delta_{\omega 0}, \tag{$A.4.27a$}$$

and the corresponding correlation function is

$$S_{zz}(\mathbf{q},\omega) = 2\pi\hbar \frac{(\delta S^z)^2}{1 - \beta(\delta S^z)^2\, \mathcal{J}(\mathbf{q})} \delta(\hbar\omega). \tag{$A.4.27b$}$$

The zz-response vanishes in the zero-temperature limit and, in this approximation, it is completely elastic, since $(\delta S^z)^2$ is assumed independent of time. However, this assumption is violated by the dynamic correlation-effects due to the spin waves. For instance, the $(n = 1)$-sum-rule ($A.3.18b$) indicates that the second moment $\langle(\hbar\omega)^2\rangle_{zz}$ is non-zero, when $\mathbf{q} \neq \mathbf{0}$ and $T > 0$, which is not consistent with a spectral function proportional to $\delta(\hbar\omega)$.

Although this procedure leads to a less accurate analysis of the Heisenberg ferromagnet than the self-consistent procedure, it has the advantage that it is easily generalized, particularly by numerical methods, to models with single-ion anisotropy, i.e. where $\mathcal{H}_{\mathrm{J}}(\mathbf{J}_i)$ in (A.4.1) is non-zero. The simplicity of the RPA result (A.4.8), or of the more general expression (A.4.7), furthermore makes it suitable for application to complex systems. As argued above, its validity is limited to low temperatures in systems with relatively large coordination numbers. However, these limitations are frequently of less importance than the possibility of making quantitative predictions of reasonable accuracy under realistic circumstances. Its utility and effectiveness will be amply demonstrated in subsequent chapters.