3.5 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.

3.5.1 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:

$$\mathcal{H} = \sum_i \mathcal{H}_J(J_i) - \frac{1}{2} \sum_{i \neq j} J(ij) \cdot J_i \cdot J_j. \quad (3.5.1)$$

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 $\langle J_i \rangle$ in the Hamiltonian, which may then be written

$$\mathcal{H} = \sum_i \mathcal{H}_{MF}(i) - \frac{1}{2} \sum_{i \neq j} J(ij) (J_i - \langle J_i \rangle) \cdot (J_j - \langle J_j \rangle), \quad (3.5.2)$$

where

$$\mathcal{H}_{MF}(i) = \mathcal{H}_J(J_i) - (J_i - \frac{1}{2} \langle J_i \rangle) \cdot \sum_j J(ij)(J_j). \quad (3.5.3)$$

From the mean-field Hamiltonians $\mathcal{H}_{MF}(i)$, we may calculate $\langle J_i \rangle$ as before. The Hamiltonian (3.5.3) also determines the dynamic susceptibility of the $i$th ion, in the form of a Cartesian tensor $\chi^{\alpha\beta}_i(\omega)$, according to eqns (3.3.4–6), with $\hat{A}$ and $\hat{B}$ set equal to the angular-momentum components $J^{\alpha}_i$. We wish to calculate the linear response $\langle J_i(t) \rangle$ of
the system to a small perturbative field \( h_j(t) = g \mu_B H_j(t) \) (the Zeeman term due to a stationary field is taken as included in \( \mathcal{H}_j(J_j) \)). From (3.5.2), we may extract all terms depending on \( J_j \) and collect them in an effective Hamiltonian \( \mathcal{H}_j \), which determines the time-dependence of \( J_j \). Transformed to the Heisenberg picture, this Hamiltonian is

\[
\mathcal{H}_j(t) = \mathcal{H}_{MF}(i, t) - (J_j(t) - \langle J_j \rangle) \cdot \left( \sum_j \mathcal{J}(ij)(J_j(t) - \langle J_j \rangle) + h_i(t) \right).
\]

We note that a given site \( i \) appears twice in the second term of (3.5.2), and that the additional term \( \langle J_i \rangle \cdot h_i \) has no consequences in the limit when \( h_i \) goes to zero. The differences \( J_j(t) - \langle J_j \rangle \) fluctuate in a virtually uncorrelated manner from ion to ion, and their contribution to the sum in (3.5.4) is therefore small. Thus, to a good approximation, these fluctuations may be neglected, corresponding to replacing \( J_j(t) \) in (3.5.4) by \( \langle J_j(t) \rangle \) (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 \( J_j(t) - \langle J_j \rangle \) 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 (3.5.4) to an ensemble average. If we introduce the RPA in eqn (3.5.4), the only dynamical variable which remains is \( J_i(t) \), and the Hamiltonian becomes equivalent to \( \mathcal{H}_{MF}(i) \), except that the probing field \( h_i(t) \) is replaced by an effective field \( h_i^{\text{eff}}(t) \). With \( \langle J_i(\omega) \rangle \) defined as the Fourier transform of \( \langle J_i(t) \rangle - \langle J_i \rangle \), then, according to eqn (3.1.9),

\[
\langle J_i(\omega) \rangle = \overline{\chi}_i^o(\omega) h_i^{\text{eff}}(\omega),
\]

where the effective field is

\[
h_i^{\text{eff}}(\omega) = h_i(\omega) + \sum_j \mathcal{J}(ij) \langle J_j(\omega) \rangle. \tag{3.5.5}
\]

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

\[
\langle J_i(\omega) \rangle = \sum_j \overline{\chi}(ij, \omega) h_j(\omega). \tag{3.5.6}
\]

The two ways of writing the response should coincide for all \( h_j(\omega) \), which implies that, within the RPA,

\[
\overline{\chi}(ij, \omega) = \overline{\chi}_i^o(\omega) \left( \delta_{ij} + \sum_{jj'} \mathcal{J}(ij') \overline{\chi}(jj', \omega) \right). \tag{3.5.7}
\]
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 $\mathcal{H}_{\text{MF}}(i)$ is the same for all the ions, i.e. $\langle J_i \rangle = \langle J \rangle$ and $\chi^0_i(\omega) = \chi^0(\omega)$, in which case we get the final result

$$\chi(q, \omega) = \left(1 - \chi^0(\omega) J(q)\right)^{-1} \chi^0(\omega).$$

Here 1 is the unit matrix, and we have used the Fourier transform (3.4.2) of $J(ij)$

$$J(q) = \sum_j J(ij) e^{-i q \cdot (R_i - R_j)}.$$  

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 $\chi^0_i(\omega)$ 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 $\beta = 1/k_B T$.

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 (3.5.8) were presented independently several times in the literature in the early 1970s (Fulde and Perschel 1971, 1972; Haley and Erdős 1972; Purwins et al. 1973; Holden and Buyers 1974). The approach to this problem in the last three references is very similar, and we will now present it, following most closely the account given by Bak (1974).

We start by considering the MF Hamiltonian defined by (3.5.3). The basis in which $\mathcal{H}_{\text{MF}}(i)$ is diagonal is denoted $|\nu_i >$; $\nu = 0, 1, \ldots, 2J$, and we assume that $\mathcal{H}_{\text{MF}}(i)$ is the same for all the ions:

$$\mathcal{H}_{\text{MF}}(i)|\nu_i > = E_\nu |\nu_i >,$$

with $E_\nu$ independent of the site index $i$. The eigenvalue equation defines the standard-basis operators

$$a_{\nu\mu}(i) = |\nu_i > < \mu_i|,$$
in terms of which $H_{\text{MF}}(i) = \sum_{\nu} E_{\nu} a_{\nu\nu}(i)$. Defining the matrix-elements

$$M_{\nu\mu} = \langle \nu | J_i - \langle J_i \rangle | \mu \rangle,$$

we may write

$$J_i - \langle J_i \rangle = \sum_{\nu \mu} M_{\nu \mu} a_{\nu \mu}(i),$$

and hence

$$H = \sum_i \sum_{\nu} E_{\nu} a_{\nu\nu}(i) - \frac{1}{2} \sum_{ij} \sum_{\nu \mu \nu' \mu'} J(ij) M_{\nu \mu} \cdot M_{\nu' \mu'} a_{\nu \mu}(i) a_{\nu' \mu'}(j).$$

We have expressed $H$ in terms of the standard-basis operators, as we now wish to consider the Green functions

$$G_{\nu \mu, rs}(ii', \omega) = \langle \langle a_{\nu \mu}(i) ; a_{rs}(i') \rangle \rangle.$$ According to (3.3.14), their equations of motion are

$$\hbar \omega G_{\nu \mu, rs}(ii', \omega) - \langle \langle [a_{\nu \mu}(i) , H] ; a_{rs}(i') \rangle \rangle = \langle \langle [a_{\nu \mu}(i) , a_{rs}(i')] \rangle \rangle.$$ The MF basis is orthonormal, and the commutators are

$$[a_{\nu \mu}(i) , a_{rs}(i')] = \delta_{ii'} \{ \delta_{\nu \mu} a_{rs}(i) - \delta_{\nu s} a_{r \mu}(i) \},$$

so we obtain

$$\{ \hbar \omega - (E_{\mu} - E_{\nu}) \} G_{\nu \mu, rs}(ii', \omega) + \sum_j J(ij) \sum_{\xi \nu' \mu'} \langle \langle [a_{\nu \xi}(i) M_{\mu \xi} - a_{\xi \mu}(i) M_{\nu \mu'}] \cdot M_{\nu' \mu'} a_{\nu' \mu'}(j) ; a_{rs}(i') \rangle \rangle$$

$$= \delta_{ii'} \{ \delta_{\nu \mu} a_{rs}(i) - \delta_{\nu s} a_{r \mu}(i) \}. (3.5.15)$$

In order to solve these equations, we make an RPA decoupling of the higher-order Green functions:

$$\langle \langle a_{\nu \xi}(i) a_{\nu' \mu'}(j) ; a_{rs}(i') \rangle \rangle_{i \neq j} \simeq$$

$$\langle a_{\nu \xi}(i) \rangle \langle a_{\nu' \mu'}(j) ; a_{rs}(i') \rangle + \langle a_{\nu' \mu'}(j) \rangle \langle a_{\nu \xi}(i) ; a_{rs}(i') \rangle.$$ (3.5.16)

This equation is correct in the limit where two-ion correlation effects can be neglected, i.e. when the ensemble averages are determined by the MF Hamiltonian. The decoupling is equivalent to the approximation made above, when $J_j(t)$ in (3.5.4) was replaced by $\langle J_j(t) \rangle$. The thermal expectation value of a single-ion quantity $\langle a_{\nu \mu}(i) \rangle$ is independent of $i$, and to leading order it is determined by the MF Hamiltonian:

$$\langle a_{\nu \mu} \rangle \simeq (a_{\nu \mu})_0 = \frac{1}{Z} \text{Tr} \left\{ e^{-\beta H_{\text{MF}}} a_{\nu \mu} \right\} = \delta_{\nu \mu} n_{\nu},$$ (3.5.17)
and correspondingly \((\mathbf{J})\) in (3.5.12) is assumed to take the MF value \((\mathbf{J})_0\). Here \(Z\) is the partition function of the MF Hamiltonian, and thus \(n_\nu\) is the population factor of the \(\nu\)th MF level. With the two approximations (3.5.16) and (3.5.17), and the condition that \(\sum_{\nu'=\mu'}(\mathbf{M}_{\nu'=\mu'} a_{\nu'=\mu'}(j))_0 = (\mathbf{J}_j - (\mathbf{J})_0)_0 = 0\) by definition, (3.5.15) is reduced to a closed set of equations by a Fourier transformation:

\[
\{\hbar \omega - (E_\mu - E_\nu)\} G_{\nu\mu,rs}(q, \omega) + \sum_{\nu'\mu'} J(q)(n_\nu - n_\mu) M_{\nu'=\mu'} \cdot M_{\nu'=\mu'} G_{\nu'=\mu',rs}(q, \omega) = (n_\nu - n_\mu) \delta_{\nu\mu} \delta_{rs}.
\]  

(3.5.18)

We now show that these equations lead to the same result (3.5.8) as found before. The susceptibility, expressed in terms of the Green functions, is

\[
\chi(q, \omega) = -\sum_{\nu, \mu, rs} M_{\nu\mu} M_{rs} G_{\nu\mu,rs}(q, \omega).
\]  

(3.5.19)

\(M_{\nu\mu} M_{rs}\) is the dyadic vector-product, with the \((\alpha/\beta)\)-component given by \((M_{\nu\mu} M_{rs})_{\alpha\beta} = (M_{\nu\mu})_{\alpha} (M_{rs})_{\beta}\). Further, from eqns (3.3.4–6), the MF susceptibility is

\[
\chi(q, \omega) = \sum_{\nu, \mu} \frac{M_{\nu\mu} M_{\mu'}}{E_\mu - E_\nu - \hbar \omega} (n_\nu - n_\mu) + \sum_{\nu, \mu} M_{\nu\mu} M_{\mu'/\nu} \delta_{\nu,0}. 
\]  

(3.5.20)

Multiplying (3.5.18) by \(M_{\nu\mu} M_{rs}/(E_\mu - E_\nu - \hbar \omega)\), and summing over \((\nu, \mu, rs)\), we get (for \(\omega \neq 0\))

\[
\chi(q, \omega) - \chi(q, \omega) J(q) \chi(q, \omega) = \chi(q, \omega),
\]  

(3.5.21)

in accordance with (3.5.8). Special care must be taken in the case of degeneracy, \(E_\mu = E_\nu\), due to the resulting singular behaviour of (3.5.18) around \(\omega = 0\). For \(\omega \neq 0\), \(G_{\nu\mu,rs}(q, \omega)\) vanishes identically if \(E_\mu = E_\nu\), whereas \(G_{\nu\mu,rs}(q, \omega = 0)\) may be non-zero. The correct result, in the zero frequency limit, can be found by putting \(E_\mu - E_\nu = \delta\) in (3.5.18), so that \(n_\nu - n_\mu = n_\nu (1 - e^{-\beta \delta}) \approx \beta n_\nu \delta\). Dividing (3.5.18) by \(\delta\), and taking the limit \(\delta \to 0\), we obtain in the degenerate case \(E_\nu = E_\mu\):

\[
-G_{\nu\mu,rs}(q, 0) - \beta \sum_{\nu'\mu'} J(q)n_{\nu'} M_{\nu'} \cdot M_{\nu'\mu'} G_{\nu'\mu',rs}(q, 0) = \beta n_\nu \delta_{\mu r} \delta_{rs}.
\]  

(3.5.22)

Since \(\chi(q, \omega)\) does not depend on the specific choice of state-vectors in the degenerate case, (3.5.22) must also apply for a single level, i.e. when \(\mu = \nu\). It then follows that (3.5.18), when supplemented with (3.5.22),
ensures that (3.5.21) is also valid at \( \omega = 0 \), as (3.5.22) accounts for the elastic contributions due to \( \mathcal{M}^e(\omega) \), proportional to \( \delta_{\omega,0} \). This zero-frequency modification of the equations of motion was derived in this context in a slightly different way by Lines (1974a).

Although eqns (3.5.18) and (3.5.22) only lead to the result (3.5.8), derived previously in a simpler manner, the equations of motion clarify more precisely the approximations made, and they contain more information. They allow us to keep track in detail of the different transitions between the MF levels, which may be an advantage when performing actual calculations. Furthermore, the set of Green functions \( G_{\nu\mu,rs}(q,\omega) \) is complete, and hence any magnetic single- or two-ion response function may be expressed as a linear combination of these functions.

In the derivation of the RPA result, we utilized two approximate equations, (3.5.16) and (3.5.17). The two approximations are consistent, as both equations are correct if two-ion correlation effects are negligible. However, the RPA Green functions contain implicitly two-ion correlations and, according to (3.3.7), we have in the linear response theory:

\[
\langle a_{\nu\mu}(i)a_{rs}(j) \rangle - \langle a_{\nu\mu}(i) \rangle \langle a_{rs}(j) \rangle = \frac{1}{N} \sum_q e^{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{-1}{1 - e^{-\beta \bar{\mathcal{h}}\omega}} G''_{\nu\mu,rs}(q,\omega) d(\bar{\mathcal{h}}\omega),
\]

(3.5.23)

where, by the definition (3.2.11b),

\[
G''_{\nu\mu,rs}(q,\omega) = \frac{1}{2i} \lim_{\epsilon \to 0^+} \left\{ G_{\nu\mu,rs}(q,\omega + i\epsilon) - G_{rs,\nu\mu}(-q, -\omega + i\epsilon) \right\}.
\]

Equation (3.5.23), with \( i = j \), might be expected to give a better estimate of the single-ion average \( \langle a_{\nu\mu} \rangle \) than that afforded by the MF approximation used in (3.5.17). If this were indeed the case, the accuracy of the theory could be improved by using this equation, in a self-consistent fashion, instead of (3.5.17), and this improvement would maintain most of the simplicity and general utility of the RPA theory. Unfortunately, such an improvement seems to occur only for the Heisenberg ferromagnet discussed previously, and the nearly-saturated anisotropic ferromagnet, which we will consider later. Equation (3.5.23) allows different choices of the Green functions \( G_{\nu\mu,rs}(q,\omega) \) for calculating \( \langle a_{\nu\nu} \rangle \), and the results in general depend on this choice. Furthermore, (3.5.23) may lead to non-zero values for \( \langle a_{\nu\mu}(i)a_{rs}(i) \rangle \), when \( \mu \neq r \), despite the fact that \( \langle \mu_i | r_i \rangle = 0 \) by definition. The two-ion correlation effects which are neglected by the RPA decoupling in (3.5.18) might be as important, when using eqn (3.5.23) with \( i = j \), as those effects which are accounted for by the RPA. Nevertheless, it might be possible that certain choices
of the Green functions, or a linear combination of them, would lead to
an accurate determination of $\langle a_{\nu} \rangle$ (the most natural choice would be to
use $G_{\nu_0,0_0}^\nu(q,\omega)$). However, a stringent justification of a specific choice
would require an analysis of the errors introduced by the RPA decou-
pling. We conclude that a reliable improvement of the theory can only
be obtained by a more accurate treatment of the higher-order Green
functions than that provided by the RPA. General programs for ac-
complishing this have been developed, but they have only been carried
through in the simplest cases, and we reserve the discussion of these
analyses to subsequent sections, where a number of specific systems are
considered.

3.5.2 MF-RPA theory of the Heisenberg ferromagnet
We conclude this chapter by applying the RPA to the Heisenberg model,
thereby demonstrating the relation between (3.5.8) and the results pre-
sented in the previous section. In order to do this, we must calculate
$\chi^o_0(\omega)$. The eigenstates of the MF Hamiltonian (3.4.4b) are $|S^z = M>$,
with $M = -S, -S + 1, \cdots, S$, and we neglect the constant contribution
to the eigenvalues

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

denoting the MF expectation-value (3.4.5a) of $S^z$ by $\langle S^z \rangle_0$. According
to (3.3.4a), we then have (only terms with $\alpha = M + 1$ and $\alpha' = M$
contribute):

$$\chi^o_+(-\omega) = \sum_{M = -S}^{S-1} \frac{<M + 1 | S^+ | M> <M | S^- | M + 1>}{E_M - E_{M+1} - \hbar \omega} (n_{M+1} - n_M)$$

$$= \frac{1}{Z} \sum_{-S}^{S-1} \frac{S(S + 1) - M(M + 1)}{\Delta - \hbar \omega} \left( e^{\beta(M+1)\Delta} - e^{\beta M \Delta} \right)$$

$$= \frac{1}{\Delta - \hbar \omega} \frac{1}{Z} \sum_{-S}^{S-1} \left( S(S + 1) - (M - 1)M \right) e^{\beta M \Delta}$$

$$= \frac{1}{\Delta - \hbar \omega} \frac{1}{Z} \sum_{-S}^{S-1} \left( S(S + 1) - M(M + 1) \right) e^{\beta M \Delta}$$

$$= \frac{1}{\Delta - \hbar \omega} \frac{1}{Z} \sum_{-S}^{S} 2Me^{\beta M \Delta} = \frac{2\langle S^z \rangle_0}{\Delta - \hbar \omega},$$

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
We note here that with \( (\omega + i\epsilon) \) vs. \( \omega \) and letting \( \epsilon \to 0^+ \), are both purely imaginary. Of the remaining components in \( \chi \), only \( \chi_{zz}^\omega(\omega) \) is non-zero, and it comprises only an elastic contribution

\[
\chi_{zz}^\omega(\omega) = \beta (\delta S^z)^2 \delta_{\omega 0}, \quad \text{with} \quad (\delta S^z)^2 = \langle (S^z)^2 \rangle_0 - \langle S^z \rangle_0^2. \tag{3.5.25}
\]

By a straightforward manipulation, this leads to

\[
\chi_{xx}(q, \omega) = \frac{\chi_{xx}(\omega) - |\mathcal{X}^0(\omega)\mathcal{J}(q)|}{1 - \{\chi_{xx}(\omega) + \chi_{yy}(\omega)\} \mathcal{J}(q) + |\mathcal{X}^0(\omega)\mathcal{J}^2(q)|},
\]

where the determinant is

\[
|\mathcal{X}^0(\omega)| = \chi_{xx}(\omega)\chi_{yy}(\omega) - \chi_{xy}(\omega)\chi_{yx}(\omega) = \frac{\langle S^z \rangle_0^2}{\Delta^2 - \langle \hbar \omega \rangle^2}.
\]

By a straightforward manipulation, this leads to

\[
\chi_{xx}(q, \omega) = \frac{E_q^0 \langle S^z \rangle_0}{(E_q^0)^2 - \langle \hbar \omega \rangle^2}, \tag{3.5.26a}
\]

with

\[
E_q^0 = \Delta - \langle S^z \rangle_0 \mathcal{J}(q) = \langle S^z \rangle_0 \{\mathcal{J}(0) - \mathcal{J}(q)\}. \tag{3.5.26b}
\]

The same result is obtained for \( \chi_{yy}(q, \omega) \). We note that (3.5.26a) should be interpreted as

\[
\chi_{xx}(q, \omega) = \frac{1}{2} \langle S^z \rangle_0 \lim_{\epsilon \to 0^+} \left( \frac{1}{E_q^0 - i\hbar \omega - i\hbar \epsilon} + \frac{1}{E_q^0 + i\hbar \omega + i\hbar \epsilon} \right). \]

This result is nearly the same as that deduced before, eqns (3.4.10–11), 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 to the previous results, we find that

$$
\chi_{zz}(q, \omega) = \frac{\chi_{zz}^0(\omega)}{1 - \chi_{zz}^0(\omega) J(q)} = \frac{\beta (\delta S^z)^2}{1 - \beta (\delta S^z)^2 J(q)} \delta_{\omega,0}, \quad (3.5.27a)
$$

and the corresponding correlation function is

$$
S_{zz}(q, \omega) = 2\pi \hbar \frac{(\delta S^z)^2}{1 - \beta (\delta S^z)^2 J(q)} \delta(\hbar \omega). \quad (3.5.27b)
$$

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 (3.3.18b) indicates that the second moment $(\langle \hbar \omega \rangle^2)_{zz}$ is non-zero, when $q \neq 0$ 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 that applied previously, it has the advantage that it is easily generalized, particularly by numerical methods, to models with single-ion anisotropy, i.e. where $H_J(J_i)$ in (3.5.1) is non-zero. The simplicity of the RPA result (3.5.8), or of the more general expression (3.5.7), 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.