

7.2 Beyond the MF-RPA theory

When the temperature is raised, the available magnetic scattering intensity, from eqn (4.2.7) proportional to $J(J+1)$, is divided more and more equally among the $(2J)!$ different dipolar transitions, and in the high-temperature limit half the intensity is transferred to the emissive part of the spectrum. This means that the different crystal-field excitations become weaker and less dispersive, and correspondingly correlation effects become less important as the temperature is raised. An additional mechanism diminishing the correlation effects at elevated temperatures is the scattering of the excitations against random fluctuations, neglected in the MF-RPA theory. In this theory, all the ions are assumed to be in the same MF state, thus allowing an entirely coherent propagation of the excitations. However, at non-zero temperatures, the occupations of the different crystal-field levels differ from site to site, and these *single-site fluctuations* lead to a non-zero linewidth for the excitations. In fact, if two-ion interactions are important, such fluctuations already exist at zero temperature, as the MF ground state $\prod_i |0_i\rangle$ cannot be the true ground state, because $\sum_i |0_i\rangle\langle 0_i|$ does not commute with the two-ion part of the Hamiltonian. Hence, the occupation n_0 of the 'ground-state' is reduced somewhat below 1 even at $T = 0$. The response functions derived above already predict such a reduction of n_0 but, as discussed earlier in connection with eqn (3.5.23), the MF-RPA theory is not reliable in this order. A more satisfactory account of the influence of fluctuations, both at zero and non-zero temperatures, can only be obtained by calculations which go beyond the MF-RPA.

One way to proceed to higher order is to postpone the use of the RPA decoupling to a later stage in the Green-function hierarchy generated by the equations of motion. Returning to our derivation of the MF-RPA results in Section 3.5; instead of performing the RPA decoupling on the Green function $\langle\langle a_{\nu\xi}(i)a_{\nu'\mu'}(j); a_{rs}(i')\rangle\rangle$, as in eqn (3.5.16), we first apply this decoupling to the higher-order Green functions appearing in

the equation of motion of this function. This method requires rather extensive manipulation, but it is essentially straightforward, and we shall not discuss the details here. It has been applied to the ($J = 1$)-model, corresponding to Pr (Jensen 1982b), and the results may be interpreted by replacing the crystal-field splitting and the exchange coupling by renormalized quantities, while the excitations acquire a linewidth proportional to the fluctuations in the single-site population factors. As may be seen in Fig. 7.3, this *self-consistent RPA* gives a good account of the temperature dependence of the excitations on the hexagonal sites in Pr, and fits the results of Houmann *et al.* (1975b) somewhat better than their MF model. The mode of lowest energy varies very rapidly with

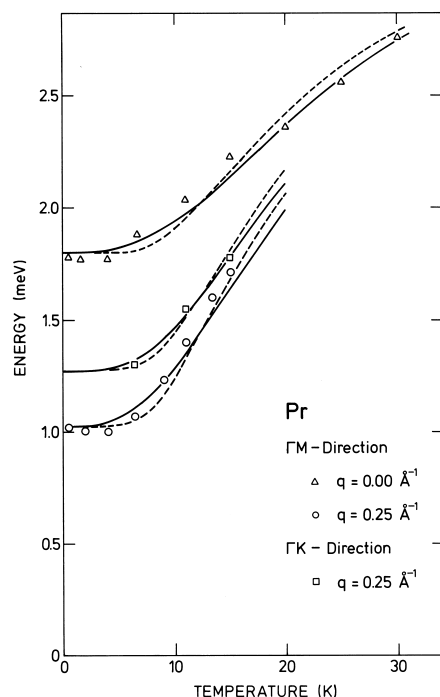


Fig. 7.3. The temperature dependence of the excitation energies at three different wave-vectors for the hexagonal sites in Pr. The dashed lines give the results of a MF calculation, and the full curves are based on the self-consistent RPA. The lowest-lying mode is the incipient soft mode, whose \mathbf{q} and longitudinal polarization correspond to the antiferromagnetic structure which may be induced in Pr by various perturbations.

temperature, but does not become soft, so Pr remains paramagnetic down to very low temperatures. However, these calculations indicate that $R_0 \simeq 0.92$, so that the exchange is very close to the critical value which would drive this *incipient soft mode* to zero energy. As we shall discuss in Section 7.4.1, under these circumstances a variety of perturbations may induce magnetic ordering.

A more elegant technique for obtaining such results is based on a diagrammatic-expansion technique. The introduction of this method requires a further development and refinement of the mathematical analysis of the Green functions, which falls outside the scope of this book. Nevertheless, we wish to discuss some essential problems connected with the use of the technique for rare earth systems, so we will present it very briefly and refer to the books by Abrikosov *et al.* (1965), Doniach and Sondheimer (1974), and Mahan (1990) for more detailed accounts.

Instead of the *retarded* Green function, introduced in eqn (3.3.12), we consider the Green function defined as the τ -ordered ensemble average: $G_{BA}^\tau(\tau_1 - \tau_2) \equiv -\langle T_\tau \hat{B}(\tau_1) \hat{A}(\tau_2) \rangle$. Here $\hat{B}(\tau)$ is the equivalent of the time-dependent operator in the Heisenberg picture, eqn (3.2.1), with t replaced by $-i\hbar\tau$. The τ -ordering operator T_τ orders subsequent operators in a sequence according to decreasing values of their τ -arguments, i.e. $T_\tau \hat{B}(\tau_1) \hat{A}(\tau_2) = \hat{B}(\tau_1) \hat{A}(\tau_2)$ if $\tau_1 \geq \tau_2$ or $\hat{A}(\tau_2) \hat{B}(\tau_1)$ otherwise. Restricting ourselves to considering the Green function $G_{BA}^\tau(\tau)$ only in the interval $0 \leq \tau \leq \beta$, where $\beta = 1/k_B T$, we may represent it by a Fourier series (corresponding to letting the function repeat itself with the period β):

$$G_{BA}^\tau(\tau) = -\langle T_\tau \hat{B}(\tau) \hat{A} \rangle = \frac{1}{\beta} \sum_n G_{BA}^\tau(i\omega_n) e^{-i\hbar\omega_n\tau} \quad ; \quad \hbar\omega_n = \frac{2\pi n}{\beta}. \quad (7.2.1a)$$

n is an integer and the ω_n are called the *Matsubara frequencies*. The Fourier coefficients are determined by

$$G_{BA}^\tau(i\omega_n) = \int_0^\beta G_{BA}^\tau(\tau) e^{i\hbar\omega_n\tau} d\tau. \quad (7.2.1b)$$

The most important property of the τ -ordered Green function is that it can be calculated by perturbation theory using the *Feynman-Dyson* expansion. By dividing the Hamiltonian into two parts, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$, and denoting the ensemble average with respect to the ‘unperturbed’ Hamiltonian \mathcal{H}_0 by an index ‘0’, it can be shown that

$$G_{BA}^\tau(\tau) = -\frac{\langle T_\tau U(\beta, 0) \hat{B}(\tau) \hat{A}(0) \rangle_0}{\langle U(\beta, 0) \rangle_0}, \quad (7.2.2a)$$

where

$$U(\beta, 0) = 1 - \int_0^\beta \mathcal{H}_1(\tau_1) d\tau_1 + \cdots \\ \cdots + \frac{(-1)^n}{n!} \int_0^\beta \cdots \int_0^\beta T_\tau \mathcal{H}_1(\tau_1) \cdots \mathcal{H}_1(\tau_n) d\tau_1 \cdots d\tau_n + \cdots \quad (7.2.2b)$$

which is suitable for a diagrammatic representation in which the denominator in (7.2.2a) just eliminates all ‘un-linked’ diagrams. Furthermore, it can be shown that the retarded Green function is the analytic continuation of the τ -ordered function to the real axis in the complex ω -plane, or

$$\chi_{BA}(\omega) = - \lim_{\epsilon \rightarrow 0^+} G_{BA}^T(i\omega_n \rightarrow \omega + i\epsilon), \quad (7.2.3)$$

and we shall therefore use the frequency arguments $i\omega_n$ and ω to distinguish between respectively the τ -ordered and the retarded Green function.

Considering the simplest case of the Ising model, we wish to calculate the Fourier transform of $G(ij, \tau) = -\langle T_\tau J_{i\alpha}(\tau) J_{j\alpha} \rangle$. We take \mathcal{H}_0 to be the single-ion crystal-field Hamiltonian, and the perturbation \mathcal{H}_1 is then the two-ion part. With this partition, the ensemble average $\langle \rangle_0$ of a product of operators belonging to different sites is just the product of the averages of the operators, i.e. $\langle J_{i\alpha} J_{j\alpha} \rangle_0 = \langle J_{i\alpha} \rangle_0 \langle J_{j\alpha} \rangle_0$ if $i \neq j$. This concentrates attention on the Green function for a single site $G(ii, i\omega_n)$, for which the perturbation expansion leads to a series corresponding to that considered in the CPA calculation, eqn (5.6.9). The only differences are that $\overline{K}(i, \omega)$ is replaced by the $\alpha\alpha$ -component $K(i\omega_n)$ and, more significantly, that the products $(c_i \chi^o(\omega))^p = c_i (\chi^o(\omega))^p$ are replaced by the $2p$ th order *cumulant* averages or *semi-invariants*

$$\mathcal{S}^{(2p)} = \frac{1}{\beta^p} \int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_{2p} \langle T_\tau \prod_{l=1}^{2p} J_{i\alpha}(\tau_l) \rangle_0 \prod_{l=1}^{2p} \exp(i\hbar\omega_n \tau_l), \quad (7.2.4)$$

with the conditions $\sum_l \omega_{nl} = 0$ and $\omega_{n1} = \omega_n$. The lowest-order semi-invariant is $\mathcal{S}^{(2)} = -g(i\omega_n) = 2n_{01} M_\alpha^2 \Delta / [\Delta^2 - (i\hbar\omega_n)^2]$, which is the Fourier transform of $\langle T_\tau J_{i\alpha}(\tau) J_{i\alpha} \rangle_0$, and $-g(i\omega_n \rightarrow \omega) = -g(\omega) = \chi^o(\omega)$. The calculation of the fourth- and higher-order cumulants is more involved. It is accomplished basically by utilizing the invariance of the trace (i.e. of the ensemble average) to a cyclic permutation of the operators, as is discussed, for instance, by Yang and Wang (1974) and Care and Tucker (1977). If the operators are proportional to Bose operators this results in *Wick's theorem*, which here implies that $\mathcal{S}_{\text{Bose}}^{(2p)} = [\mathcal{S}^{(2)}]^p$. The determination of the cumulant averages is facilitated by

expressing the angular-momentum components as linear combinations of the standard-basis operators introduced by eqn (3.5.11). These are not Bose operators, so the ‘contractions’ determined by the commutators of the different operators are not c -numbers, but operators which give rise to new contractions. In the singlet–singlet Ising model, the result is

$$\begin{aligned} G(ii, i\omega_n) &= G(i\omega_n) = g(i\omega_n) \\ &- \frac{1}{n_{01}^2} \left[(n_0 + n_1)g(i\omega_n)K(i\omega_n) + \frac{1}{\beta} \sum_{n'} g(i\omega_{n'})K(i\omega_{n'})u(n, n') \right] g(i\omega_n) \\ &+ \dots \end{aligned} \quad (7.2.5a)$$

with

$$u(n, n') = \frac{g(i\omega_n)}{M_\alpha^2} + \frac{g(i\omega_{n'})}{M_\alpha^2} \frac{(i\hbar\omega_{n'})^2 + \Delta^2}{2\Delta^2} + \frac{1}{2}(n_0 + n_1 - n_{01}^2)\beta. \quad (7.2.5b)$$

The sum over the Matsubara frequencies may be transformed into an integral over real frequencies, but it may be advantageous to keep the frequency sum in numerical calculations. Before proceeding further, we must clarify a few points. The first is that \mathcal{H}_1 cannot, in general, be considered as being ‘small’ compared to \mathcal{H}_0 . However, each time a term involving the two-ion coupling is summed over \mathbf{q} , we effectively gain a factor $1/Z$, where Z is the co-ordination number. Hence, if we use $1/Z$ as a small expansion parameter, the order of the different contributions may be classified according to how many \mathbf{q} -summations they involve. In the equation above, $K(i\omega_{n'})$ is derived from one summation over \mathbf{q} , as in (5.6.17), so the series can be identified as being equivalent to an expansion in $1/Z$. The second point to realize is that it is of importance to try to estimate how the expansion series behaves to infinite order. A truncation of the series after a finite number of terms will produce a response function with incorrect analytical properties. If we consider the corresponding series determining $G(\mathbf{q}, i\omega_n)$, it is clear that any changes in the position of the poles, i.e. energy changes and linewidth phenomena, are reflected throughout the whole series, whereas a (small) scaling of the amplitude of the response function, which might be determined by the first few terms, is not particularly interesting. In other words, what we wish to determine is the first- (or higher-) order correction in $1/Z$ to the denominator of the Green function, i.e. to determine the self-energy $\Sigma(\mathbf{q}, i\omega_n)$, defined by

$$G(\mathbf{q}, i\omega_n) = \frac{g(i\omega_n)}{1 + g(i\omega_n)\{\mathcal{J}_{\alpha\alpha}(\mathbf{q}) + \Sigma(\mathbf{q}, i\omega_n)\}}, \quad (7.2.6)$$

assuming the MF-RPA response function to be the starting point. A systematic prescription for calculating the Green function to any finite

order in $1/Z$ has been given by Stinchcombe (1973), see also Vaks *et al.* (1968). The zero-order result is obtained by the ‘boson’ approximation $\mathcal{S}^{(2p)} \simeq [\mathcal{S}^{(2)}]^p$. As is apparent from (7.2.5a), this corresponds to the replacement of the second and subsequent terms on the r.h.s. by the infinite series generated by $-g(i\omega_n)K(i\omega_n)G(i\omega_n)$, leading to an equation for the single-site Green function which is the equivalent to the *Dyson equation* for bosons (or fermions), or to the CPA equation with $c = 1$. The \mathbf{q} -dependent Green function may be obtained from the single-site function by the same procedure as in the CPA case, eqns (5.6.10–17). In this approximation, the final Green function is that given by the MF-RPA, corresponding to $\Sigma(\mathbf{q}, i\omega_n) = 0$ in (7.2.6). This does not involve any \mathbf{q} -summation and may therefore be classified as the $(1/Z)^0$ -order result. In the *cumulant-expansion*, developed by Stinchcombe (1973) and others, the difference $\mathcal{S}^{(4)} - (\mathcal{S}^{(2)})^2$ is included, to the next order in $1/Z$, as an additional *vertex* appearing in the interaction chain-diagrams of $G(\mathbf{q}, i\omega_n)$, independently of the appearance of the $\mathcal{S}^{(2)}$ -vertices. A different approach, which is made possible by the isolation of the single-site Green function in (7.2.5a), is to generalize this equation once more, so that it becomes a Dyson equation, by replacing $g(i\omega_n)$ with $G(i\omega_n)$ in the second term on the r.h.s. of (7.2.5a), retaining the correct coefficient in this term. The effective-medium equation (5.6.13), with $c = 1$, is valid to first order in $1/Z$, so that

$$G(\mathbf{q}, i\omega_n) = \frac{G(i\omega_n)}{1 + G(i\omega_n)\{\mathcal{J}_{\alpha\alpha}(\mathbf{q}) - K(i\omega_n)\}} \quad (7.2.7a)$$

and, in combination with the Dyson equation for the single-site Green function, this leads to a \mathbf{q} -dependent Green function derived from

$$\begin{aligned} \Sigma(\mathbf{q}, i\omega_n) = \Sigma(i\omega_n) = \\ \frac{1}{n_{01}^2} \left[(n_0 + n_1 - n_{01}^2)K(i\omega_n) + \frac{1}{\beta g(i\omega_n)} \sum_{n'} g(i\omega_{n'})K(i\omega_{n'})u(n, n') \right], \end{aligned} \quad (7.2.7b)$$

where $K(i\omega_n)$ is determined self-consistently, as in (5.6.17),

$$K(i\omega_n) = \sum_{\mathbf{q}} \mathcal{J}_{\alpha\alpha}(\mathbf{q})G(\mathbf{q}, i\omega_n) / \sum_{\mathbf{q}} G(\mathbf{q}, i\omega_n). \quad (7.2.7c)$$

The result obtained in this way is close to that derived by Galili and Zevin (1987) using a more elaborate renormalization procedure, but in addition to the simplifications attained by utilizing the effective-medium approximation, the procedure which we have adopted has allowed us to achieve a fully self-consistent result. We note that, in the application

of the equations of motion, the population factors take the realistic values which may be calculated from eqn (3.5.23) using the more accurate Green functions, whereas the population factors here are by definition the unperturbed MF values. This means that the renormalization of the different RPA parameters predicted by the real part of $\Sigma(\omega)$ includes the possible effects on the population factors. $\Sigma(\omega)$ is the continuation of $\Sigma(i\omega_n)$ on to the real frequency-axis, and the imaginary part of $\Sigma(\omega)$, which is equal to $(n_0 + n_1 - n_{01}^2)/n_{01}^2$ times $\text{Im}[K(\omega)]$, since the sum in (7.2.7b) is real, predicts a non-zero linewidth for the crystal-field excitations. Introducing the spectral density of the excited states, at positive energies $E = \hbar\omega$,

$$\mathcal{N}(E) = \frac{2}{N} \sum_{\mathbf{q}} \frac{\text{Im}[G(\mathbf{q}, E/\hbar)]}{\pi E G(\mathbf{q}, 0)} \simeq \frac{1}{N} \sum_{\mathbf{q}} \delta(E_{\mathbf{q}} - E),$$

which may be compared with (3.3.17), we find that, at frequencies where $|g(\omega)K(\omega)|$ is small compared to one,

$$\text{Im}[K(\omega)] \simeq \pi n_{01} M_{\alpha}^2 \mathcal{N}(\hbar\omega) \Delta / \hbar\omega g^2(\omega),$$

corresponding to a linewidth $2\Gamma_{\mathbf{q}}$ of the excitation at \mathbf{q} , half of which is

$$\Gamma_{\mathbf{q}} \simeq \frac{n_0 + n_1 - n_{01}^2}{n_{01}^2} \left(\frac{\Delta^2 - E_{\mathbf{q}}^2}{2E_{\mathbf{q}}} \right)^2 \pi \mathcal{N}(E_{\mathbf{q}}). \quad (7.2.8a)$$

The linewidth is proportional to the density of states and to the squared energy-difference between the excitation and the crystal-field level (proportional to $\mathcal{J}_{\alpha\alpha}^2(\mathbf{q})$), where the \mathbf{q} -dependences of the two factors roughly balance each other. When $E_{\mathbf{q}}$ is close to Δ , this result is no longer valid. Instead, at $\hbar\omega = \tilde{\Delta}$, where $\tilde{\Delta}$ is the effective crystal-field splitting determined by $\text{Re}[\Sigma(\tilde{\Delta}/\hbar)] = -1/g(\tilde{\Delta}/\hbar)$, we find that $\text{Re}[K(\tilde{\Delta}/\hbar)] = 0$ and

$$\Gamma_{\mathbf{q}}(E_{\mathbf{q}} = \tilde{\Delta}) \simeq \frac{n_0 + n_1 - n_{01}^2}{n_{01}^2} \frac{1}{\pi \mathcal{N}(\tilde{\Delta})}. \quad (7.2.8b)$$

The first result (7.2.8a) for $\Gamma_{\mathbf{q}}$, but not (7.2.8b), agrees with that obtained by the cumulant-expansion method of Stinchcombe (1973) and others. One modification which appears when this method is used is that $K(\omega)$ in (7.2.7b) is replaced by $K(\omega)\{1 - G(\omega)K(\omega)\}$. This is a $(1/Z)^2$ -correction, which however becomes important when $\hbar\omega \approx \Delta$, and in this theory $\Gamma_{\mathbf{q}}(E_{\mathbf{q}} = \Delta) = 0$, in contrast to the result (7.2.8b). In order to decide which of the two procedures leads to the most trustworthy results, we have to some extent to rely on the effective-medium

approximation. It is known (Yonezawa 1968) that the cumulant expansion, in solving the dilute RPA equation (5.6.8), includes all terms proportional to $P_2(ij) = \langle c_i c_j \rangle - c^2$, but that this occurs at the expense of ‘self-containedness’, leading to unphysical features in the final results. Compared to this, the CPA neglects some of the products of $P_2(ii)P_2(jj)$ for neighbouring sites, which are of the order $(1/Z)^2$ (see the discussion following (5.6.17)), but it is self-contained and the results are well-behaved and accurate if Z is not small, as discussed by Elliott *et al.* (1974). Hence, referring to the analyses of the dilute systems, we expect the effective-medium approximation to be more adequate than the unrestricted cumulant expansion in the first order of $1/Z$. More importantly, the Hartree–Fock decoupling of the higher-order cumulants, i.e. $\mathcal{S}^{(6)} = (\mathcal{S}^{(2)})^3 + 3\mathcal{S}^{(2)}\{\mathcal{S}^{(4)} - (\mathcal{S}^{(2)})^2\}$ to first order in $1/Z$, which is one of the basic ideas behind the cumulant-expansion method considered here, does not appear to be a good approximation. The effective-medium model is not solved ‘exactly’, as this would require a determination of the whole series for $G(i\omega_n)$ in (7.2.5a), but a consideration of the second- and higher-order diagrams in this series indicates that the Dyson-equation generalization is much more reasonable. The sum rules, like (3.3.18) or the ‘monotopic restriction’ discussed by Haley and Erdős (1972), are satisfied to the considered order in $1/Z$. This is obviously true for the unrestricted cumulant expansion, but it also holds for the effective-medium approximation, as this is derived directly from the behaviour of the single sites. One may ask (Galili and Zevin 1987) whether there exists any other ‘conservation law’ which permits a more stringent distinction between the various possibilities. For this purpose, we propose to use the condition that the resultant Green function should be independent of adding the following constant to the Hamiltonian:

$$\Delta\mathcal{H} = -\lambda \sum_i \mathbf{J}_i \cdot \mathbf{J}_i = -N \lambda J(J+1), \quad (7.2.9)$$

corresponding to a replacement of $\mathcal{J}(\mathbf{q})$ by $\mathcal{J}(\mathbf{q}) + \lambda$. This change does not affect the effective-medium equation (5.6.9), other than by adding the constant to $\mathcal{J}(\mathbf{q})$, so $K(i\omega_n)$ is still determined by (7.2.7c), with λ added on the r.h.s. A replacement of $K(i\omega_n)$ by $K(i\omega_n) + \lambda$ in (7.2.5a) does not make any difference, as $(1/\beta) \sum_{n'} g(i\omega'_n) u(n, n') = -g(i\omega_n)$ when $n_0 + n_1 = 1$, so that $J_{i\alpha} J_{i\alpha}$ is a constant. The additions of λ to both $J(\mathbf{q})$ and $K(i\omega_n)$ cancel out in the \mathbf{q} -dependent Green function expressed in terms of the single-site Green function, as may be seen from (7.2.7a), so that the final result is independent of λ . This is not the case when the unrestricted cumulant expansion is used. Formally, the occurrence of λ is a $(1/Z)^2$ -effect, but this is an unphysical feature which is a serious defect, since λ may assume an arbitrary value. This

variational test is related to the sum rules (like that considered in eqn (4.2.7) or below), but it has the advantage that it applies directly to the \mathbf{q} -dependent Green function without involving any additional summations with respect to \mathbf{q} or ω_n . For a final comparison of the two methods, we may utilize the fact that the single-site series can be summed exactly in an Ising system with no crystal-field splitting. The result is $G(\omega) = -\beta\delta_{\omega 0}\langle J_\alpha^2 \exp\{\frac{1}{2}\beta K(0)J_\alpha^2\}\rangle_0 / \langle \exp\{\frac{1}{2}\beta K(0)J_\alpha^2\}\rangle_0$, which coincides with that deduced by Lines (1974b, 1975) from his *correlated effective-field* theory. When $J = 1/2$, the above method produces the correct result $G(0) = g(0) = -\beta/4$. For the ($J = 1$)-Ising model, $G(0) = -2\beta[2 + \exp\{-\frac{1}{2}\beta K(0)\}]^{-1}$, which may be compared with the prediction $G(0) = -2\beta[3 - \frac{1}{2}\beta K(0)]^{-1}$ of eqns (7.2.5-7). On the other hand, the unrestricted cumulant expansion, to first order in $1/Z$, leads to spurious contributions of second and higher powers in $K(0)$ and, for instance, suggests a second-order term in the denominator of $G(0)$ which is a factor of 14 larger than the correct value. We note that corrections to the effective-medium theory only appear in the order $(1/Z)^3$ in the *single-site* Green function. This comparison is discussed in more detail by Jensen (1984), in a paper where the $1/Z$ -expansion, in the effective-medium approximation, is combined with the CPA, thereby removing some of the difficulties encountered in the RPA and mentioned at the end of Section 5.6.

In a crystal-field system, the single-site fluctuations lead to a non-zero linewidth of the excitations, to first order in $1/Z$. This reflects the relative importance of corrections to the RPA, compared to spin-wave systems. In the latter, the excitation operators are, to a good approximation, Bose operators, neglecting the 'kinematic' effects, which means that a non-zero linewidth only appears in the second-order of $1/Z$. The linewidth $2\Gamma_{\mathbf{q}}$ derived above is exponentially small at low temperatures, but becomes important when $k_B T \approx \Delta$. The linewidth as a function of ω , $\Gamma_{\mathbf{q}}(\omega) \propto \text{Im}[K(\omega)]$, is only non-zero as long as $\hbar\omega$ lies within the excitation energy-band, which roughly corresponds to that determined by the RPA. This means that the linewidth, in this approximation, begins to decrease at higher temperatures when the RPA-excitation band becomes sufficiently narrow. The behaviour in both limits is modified by higher-order effects. Within the framework of the $1/Z$ -expansion, the effective-medium approximation ceases to be valid in second order. The leading-order scattering effects are due to the single-site fluctuations and, if the interactions are long-range, the correlation of the fluctuations on neighbouring sites only leads to minor modifications (provided that the system is not close to a second-order phase transition). In this kind of system, the effective-medium method should be satisfactory, and in order to avoid the complications encountered in more elaborate theo-

ries, we confine ourselves to the $(1/Z)^2$ -corrections which can be determined within this approximation. This provides a better estimate of the effects due to the single-site fluctuations, but neglects the possible \mathbf{q} -dependence of the self-energy. The correct $(1/Z)^2$ -terms in the effective-medium theory are obtained by introducing $\mathcal{S}^{(6)}$ in the third term of the single-site series in eqn (7.2.5). This calculation has been carried out by Jensen *et al.* (1987) for the ($J = 1$)-singlet–doublet case, and the most important effect of the second-order terms is to replace the MF population-factors in (7.2.7b) by approximately the actual population of the excitonic states. Furthermore, $\Gamma_{\mathbf{q}}(\omega)$ becomes non-zero outside the excitation band, and it stays non-zero (although small) in the $T = 0$ limit.

The ($J = 1$)-case has been analysed by Yang and Wang (1975), to first order in $1/Z$, and Bak (1975) independently derived the linewidth and applied the result to Pr. Psaltakis and Cottam (1982) have considered the ($J = 1$)-model in the ordered phase, in the presence of uniaxial anisotropy, where the ‘kinematic’ effects cannot be neglected. In the paramagnetic singlet–doublet XY -model, the $(1/Z)$ -results are close to those derived above for the Ising model. If the xx - and yy -couplings are assumed to be equal, it is found, to a good approximation, that $n_0 + n_1$ in eqn (7.2.7b) is replaced by $n_0 + 2n_1 = 1$, and that the frequency sum in this equation is multiplied by a factor $3/2$. If $\mathcal{J}_{zz}(\mathbf{q})$ is non-zero, it gives rise to additional contributions to the average \mathbf{q} -independent self-energy. Furthermore, it also leads to a \mathbf{q} -dependent contribution, even in the first order of $1/Z$. This occurs because the odd-rank cumulants (corresponding to half-integral p in (7.2.4)) involving all three components may be non-zero. The lowest-rank odd cumulant which is non-zero is $\langle T_{\tau} J_{ix}(\tau_1) J_{iy}(\tau_2) J_{iz}(\tau_3) \rangle_0$. Although this formally leads to a $(1/Z)$ -contribution to the \mathbf{q} -dependent part of $\Sigma(\mathbf{q}, \omega)$, which is not immediately compatible with the effective-medium results above, this should be a minor term in systems with long-range interactions and, if Δ is positive, its importance is much reduced at low temperatures under all circumstances.

The results of calculations of the lifetimes of the long-wavelength magnetic optical-modes in Pr, based on eqn (7.2.7), are compared with the experimental results of Houmann *et al.* (1979) in Fig. 7.4. This theory predicts very nearly the same temperature dependence of the energies as does the self-consistent RPA; the excitation depicted in Fig. 7.4 is the uppermost mode in Fig. 7.3. The theory to first order in $1/Z$ accounts very well for the temperature dependence of the energies, lifetimes, and intensities of these excitations, without adjustable parameters. The low temperature results are similar to those of Bak (1975), but the experiments at the highest temperatures in Fig. 7.4 are more

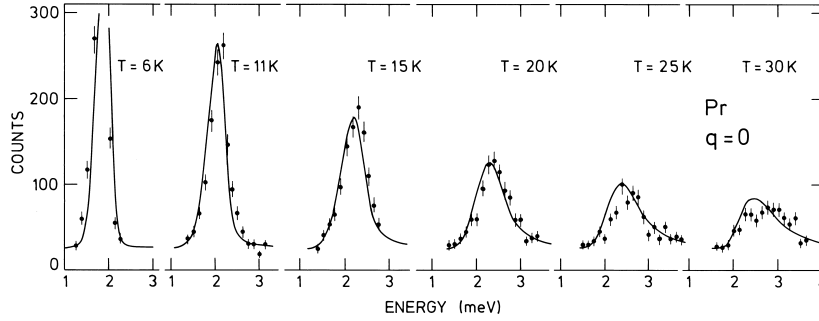


Fig. 7.4. The temperature dependence of the neutron-scattering intensities for the $\mathbf{q} = 0$ magnetic optical-mode on the hexagonal sites of Pr. The instrumental resolution and the overall scaling of the intensity are extracted from the experimental results at 6 K, and thereafter used unchanged in the calculations, which are based on a $1/Z$ -expansion, as described in the text.

accurately described by the effective-medium theory developed above, than by his unrestricted cumulant expansion.

An analysis of the $1/Z$ -corrections to the MF-RPA theory for the singlet-triplet model does not exist in the literature, to our knowledge. We shall not attempt such an analysis here, but we will discuss one aspect, that the elastic response due to the triplet states is predicted to be a diffusive peak of non-zero width, to first order in $1/Z$, within the effective-medium approximation. In order to consider this matter, we can omit the singlet and use instead the ($J = 1$) Heisenberg model, corresponding to the above model with $\Delta = 0$. In this case, the diagonal components of the single-site Green function are

$$G(i\omega_n) = -\frac{2}{3}\beta\left\{1 - \frac{1}{6}\beta K(0)\right\}\delta_{n0} + \frac{4}{3(i\hbar\omega_n)^2}\{K(0) - K(i\omega_n)\} + \dots \quad (7.2.10)$$

to first order in $1/Z$. In zero order, the response is purely elastic and $K(i\omega_n) \propto \delta_{n0}$. If this is introduced into (7.2.10), the second term predicts an inelastic contribution to $G(\omega)$, which further diverges proportionally to ω^{-2} in the zero-frequency limit. This divergence indicates that the elastic peak must broaden out to a Lorentzian, with a non-zero half-width Γ , as in (3.3.10–11), corresponding to the replacement of $(\hbar\omega)^2$ in the denominator by $(\hbar\omega)^2 + \Gamma^2$, when the higher-order terms in the series are included. The classification of $K(i\omega_n \neq 0)$ as a higher-order term in the series (7.2.9) is not consistent with a simple Lorentzian,

and a more appropriate form turns out to be

$$G(\omega) = G(0) \left(\frac{i\Gamma}{\hbar\omega + i\Gamma} \right)^2 = G(0) \frac{\Gamma^2 [\Gamma^2 - (\hbar\omega)^2 + 2i\hbar\omega\Gamma]}{[\Gamma^2 + (\hbar\omega)^2]^2}. \quad (7.2.11a)$$

The real and imaginary parts of this retarded Green function are connected by the Kramers–Kronig relation, and the expansion in powers of Γ agrees with (7.2.10), when

$$G(0) = -\frac{2}{3}\beta \left\{ 1 - \frac{1}{6}\beta K(0) \right\} \quad \text{and} \quad \Gamma = \sqrt{2K(0)/\beta}. \quad (7.2.11b)$$

In the high-temperature limit, $K(0) \simeq (2\beta/3N) \sum_{\mathbf{q}} \mathcal{J}^2(\mathbf{q})$, and hence Γ is independent of T in this limit. The most important reason for choosing the Green function given by (7.2.11a) is that it satisfies the sum rule:

$$\begin{aligned} -\frac{1}{\beta} \sum_n \sum_{\alpha=x,y,z} G(i\omega_n) &= -3 \frac{1}{\pi} \int_0^\infty d(\hbar\omega) \operatorname{Im}[G(\omega)] \coth(\beta\hbar\omega/2) \\ &= J(J+1) = 2, \end{aligned} \quad (7.2.12)$$

to the degree of accuracy with which $G(0)$ is determined (this is the same sum rule considered in (4.2.7)). The original expansion series satisfies this sum rule, to first order in $1/Z$, but this property is not easily conserved if a Lorentzian is chosen. The problem with the Lorentzian (with approximately the same Γ as above) is that it decreases only slowly with ω , and the tails lead to a divergence of the integral in (7.2.12), unless a high-frequency cut-off is introduced. In this system, there is no natural frequency-scale setting such a cut-off, and the only reasonable way of determining it is through the sum-rule itself, which is rather unsatisfactory.

In addition to the equations of motion and the Feynman–Dyson linked-cluster-expansion method discussed here, there are other many-body perturbation techniques which may be useful for analysing this kind of system. The most important supplementary theories are those based on the Mori technique (Mori 1965; Huber 1978; Ohnari 1980), or similar projection-operator methods (Becker *et al.* 1977; Micnas and Kishore 1981). However, no matter which theory is used, it cannot circumvent the essential complication of crystal-field systems; the more single-ion levels which are important, the greater is the complexity of the dynamical behaviour. This principle is illustrated by the fact that the methods discussed above have not yet been extended to systems with more than two levels, singlet or degenerate, per site.