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Thermodynamic properties and the magnetic neutron scattering cross-section of an atom in a solid

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Abstract. A model of an atom in a magnetic solid is used to investigate theoretically features expected in the cross-section for the magnetic scattering of neutrons by the atom. The atom is assumed to have two nondegenerate magnetic states, envisaged as two states in a crystal-field energy level scheme very well separated in energy from all higher states, and the subject of a Weiss molecular field. It is argued that the thermodynamic quantities which determine the weights attached to elastic and inelastic scattering events, the magnetic moment and isothermal susceptibility, respectively, obey a sum rule, and this is exploited to give the temperature dependence of the weights given, say, the separation in energy of the crystal-field levels and the critical temperature below which there is a spontaneous magnetic moment. A small value of the ratio of the energy separation and critical temperature leads to properties significantly different from those of an ion in a Weiss molecular field and not subjected to a crystal-field potential, for which the magnetic moment as a function of temperature is obtained from a Brillouin function. For this special limit of the parameters analytic expressions are provided for the moment and susceptibility.

1. Introduction

The magnetic properties of some materials are tolerably described, in the first instance, in terms of the individual constituent magnetic atoms, perturbed by their local environments, instead of a more complicated scenario that involves all of the unpaired electrons from all of the atoms. Empirical evidence shows that of many materials which contain atoms from the rare-earth series in the Periodic Table belong to this class of magnetic materials, and the finding can be understood on the grounds that the unpaired electrons occupy an f shell which has a relatively small radius, i.e. f electrons are spatially localized and do not meander throughout the material. In the localized model of a magnetic material the environment of an atom is treated as a perturbation on the f-electron states. The components of the perturbation have a range of strengths, and they are treated accordingly. For rare-earth materials it is often adequate to neglect all perturbations other than the electrostatic field created by the ligand ions (crystal-field potential) and the magnetic field produced by neighbouring magnetic ions [1]. The magnetic field is normally represented by a Weiss molecular field which is proportional to the atomic magnetic moment.

Two recent reports of the findings from interpretations of experimental investigations of a Tb compound [2] and Pr compounds [3] conclude that the magnetic properties of the rare-earth ions, to a large extent, can be described in terms of just two energy states. These are two states from a plethora of crystal-field states included in the numerical analysis of the data, and they differ in energy by a very small amount, Δ, when compared to the energy

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of the next state in the crystal-field energy level scheme. Both teams of investigators used the neutron scattering experimental technique.

The main purpose of this paper is to derive the neutron scattering cross-section for a two-state system, and provide a simple and believable interpretation of its main features. To this end, the temperature dependence of the thermodynamic quantities that determine the weights of elastic and inelastic scattering events are obtained. The method used is new, different from the standard mean-field method for calculating thermodynamic quantities, and akin to the method used to derive the spherical model from the Heisenberg spin Hamiltonian [4].

The model is derived from an isolated, two-state magnetic system, described by the Hamiltonian H_0. To this is added a Weiss molecular-field energy, V, meant to represent the interaction of the system H_0 with its magnetic environment. As normal, V is assumed to be proportional to the total angular momentum of the atom, $\boldsymbol{J}$. With our new method of calculating the thermodynamic properties of $H_0 + V$ the strength of the Weiss molecular field is not explicit in the cross-section, and the two parameters in the model are Δ and the temperature, T_c, at which the spontaneous magnetic moment, μ_0, as a function of increasing temperature, reaches the value zero. The two states of $H_0 + V$ are separated by an energy, ε, that varies with the temperature, and its maximum value is achieved at zero temperature. However, at this temperature and for $\Delta \ll T_c$ the weight attached to the inelastic event, in which the system is excited in energy by an amount ε, is very small compared to the weight attached to the inelastic events at a temperature $T = T_c$ at which $\varepsilon = \Delta$.

In the neutron scattering cross-section the weight of the elastic event is μ_0^2, and the weight of inelastic events, apart from the detailed-balance factor, is the isothermal susceptibility, χ. The quantity $\mu_0^2 + T\chi$ is a constant (T is the temperature in units of Boltzmann's constant) equal to the saturation moment. Thus, with increasing T there is a transfer of weight from elastic to inelastic events. For $T \geqslant T_c$ one has $\mu_0 = 0$ and the susceptibility obeys the Curie–Weiss law. Below T_c the value of μ_0, and hence χ, depends on the energy-separation parameter Δ. The dependence is very pronounced when the separation is small compared to T_c, and it disappears in the opposite extreme.

The paper is arranged in the following way. Key properties and matrix elements of the model are gathered in section 2. In the following section, the matrix elements are used to calculate the explicit form of the cross-section. Its general properties provide definitions of μ_0 and χ which are translated to algebraic expressions by exploiting the known explicit form of the cross-section. The temperature dependences of these two thermodynamic quantities are determined in section 4 from the result, mentioned above, that the combination $\mu_0^2 + T\chi$ is a constant. The subtle balance of the weights attached to elastic and inelastic events in scattering, and their variation with temperature, is believable because the analysis is made without further approximations. Statistical mechanics has to be applied in a consistent manner. For example, a completeness statement is not to be used; if it is our model is robbed of its interesting thermodynamics, since completeness implies $\Delta = 0$. At the end of our calculation one has derived realistic results for the thermodynamic quantities, using a novel method, and taken a fresh look at the cross-section for scattering neutrons from states of a crystal-field potential. The standard mean-field method for estimating thermodynamic quantities is briefly reviewed in section 5 to better appreciate the method described in section 4. Finally, section 6 contains a discussion of our findings, and a generalization of the model used in the body of the text.

2. Model

The isolated atom, described by H_0, has two nondegenerate eigenstates $|j\rangle$ with $j = 1, 2$, chosen to be purely real. The operation in which all velocities are reversed (time reversal) bestows several important properties to the atom and matrix elements required in our calculation. H_0 can have nondegenerate eigenstates if it is time-even and describes an even number of electrons. For these states diagonal matrix elements of the total angular momentum operator $\boldsymbol{J}$ are zero. This result uses the property of $\boldsymbol{J}$ that it is a time-odd operator, and can be viewed as a generalization of Van Vleck's theorem for quenching orbital angular momentum by a crystal-field potential which totally lifts the degeneracy of the ground state. Off-diagonal matrix elements of $\boldsymbol{J}$ are zero or purely imaginary. This result for off-diagonal matrix elements is valid for time-odd operators and purely real eigenstates (which exist for nondegenerate states); a proof can be constructed with the same mathematical apparatus used in a proof of the generalized Van Vleck theorem. Later, we represent off-diagonal matrix elements of $\boldsymbol{J}$ by $\mathrm{i}\zeta$ and ζ is purely real or zero.

The wave functions and energies of the two states of $H_0 + V$ can be written in terms of the corresponding quantities for H_0. Here, we just record results with a direct bearing on the calculation of the cross-section, and from it μ_0 and χ. As V is proportional to $\boldsymbol{J}$ only its off-diagonal matrix elements are different from zero. The separation of the two energy levels of $H_0 + V$ is

$$\varepsilon = \sqrt{(\Delta^2 + |2\langle 1|V|2\rangle|^2)} \tag{2.1}$$

where Δ is the corresponding quantity for the system described by H_0.

To calculate the neutron cross-section, which is treated in the next section, we need the matrix elements of $\boldsymbol{J}$ calculated with the wave functions of $H_0 + V$. Let us label the two states of $H_0 + V$ by the letters a and b. We find energies

$$\left.\begin{matrix} E_a \\ E_b \end{matrix}\right\} = \tfrac{1}{2}(E_1 + E_2 \pm \varepsilon) \tag{2.2}$$

in which $E_1 - E_2 = \Delta$. For the moment, all matrix elements of J_x and J_y are assumed to be zero; it is argued in section 6 that this assumption does not bear on our main findings, and it is used now to simplify the algebra in our calculations. The matrix element $\langle 1|J_z|2\rangle$ is assumed to be nonzero and have the value $\mathrm{i}\zeta$ where ζ is purely real. The matrix elements required to calculate the cross-section are found to be

$$\langle a|J_z|a\rangle = -\langle b|J_z|b\rangle = \zeta\{1 - (\Delta/\varepsilon)^2\}^{1/2} \qquad \text{and} \qquad \langle a|J_z|b\rangle = -\zeta(\Delta/\varepsilon). \tag{2.3}$$

The matrix element of the angular momentum operator between the two states of H_0, $\langle 1|J_z|2\rangle = \mathrm{i}\zeta$, can be expressed in terms of other parameters in the model, as we will demonstrate. Our model does not invoke a completeness statement that, among other things, implies

$$\langle a|J_z^2|a\rangle = \langle b|J_z^2|b\rangle = \zeta^2 \tag{2.4}$$

and $\Delta = 0$.

It remains to specify V. A Weiss molecular-field description of the magnetic environment is provided by the choice

$$V = \boldsymbol{\lambda} \cdot \boldsymbol{J} \tag{2.5}$$

where $\boldsymbol{\lambda}$ is a coupling parameter.

3. The neutron scattering cross-section

The magnetic neutron cross-section is derived from the so-called dipole approximation to the magnetic scattering amplitude [5]. In this approximation the cross-section, in units of 0.29 barns, is

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E'} = \left(\frac{k'}{k}\right)\{\tfrac{1}{2}gF(\boldsymbol{K})\}^2\sin^2\theta\sum_{\mu,\mu'}p_\mu\langle\mu|J_z|\mu'\rangle\langle\mu'|J_z|\mu\rangle\delta(\omega+E_\mu-E_{\mu'}). \tag{3.1}$$

Here, $\boldsymbol{K} = (\boldsymbol{k}-\boldsymbol{k}')$ is at an angle θ to the axis of quantization, which we have labelled the z-axis. The vector $\boldsymbol{K}$ is the change in the wave vector of the neutron created by the scattering event, and ω is the concomitant change in the energy ($\hbar = 1$) of the neutron. The delta function in (3.1) expresses the conservation of energy for a scattering event. The labels μ, μ' refer to the states of $H_0 + V$, g is the Landé factor, and $F(\boldsymbol{K})$ is the atomic form factor. The quantity p_μ is the Boltzmann population factor for the state labelled μ, and $\sum p_\mu = 1$.

For a two-state atom (3.1) reduces to

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E'} = \left(\frac{k'}{k}\right)\{\tfrac{1}{2}F(\boldsymbol{K})\sin\theta\}^2\{\mu_0^2\delta(\omega)+\tfrac{1}{2}\omega\chi\{1+n(\omega)\}[\delta(\omega+\varepsilon)+\delta(\omega-\varepsilon)]\}. \tag{3.2}$$

From general considerations about information in the cross-section the weights of the elastic and inelastic contributions to the cross-section are known to be thermodynamic properties of the atom; explicit results for the two-state atom are given below. First, the weight of the purely elastic line is proportional to μ_0^2 where μ_0 is the magnetic moment of the atom. This has a saturation value, denoted by μ, at zero temperature, and decreases with increasing temperature until it vanishes at the critical temperature. The inelastic processes, which contribute when the energy of the neutron changes in the scattering event by $\pm\varepsilon$, contain the standard detailed-balance factor

$$\omega[1+n(\omega)] = \omega/\{1-\exp(-\omega/T)\} \tag{3.3}$$

where T is the temperature (in units of Boltzmann's constant). The thermodynamic quantity, χ, is the magnetic susceptibility.

The thermodynamic quantities are dervied by using the results of the previous section and we find the expressions

$$\mu_0 = g\zeta\{1-(\Delta/\varepsilon)^2\}^{1/2} \tag{3.4}$$

and

$$\chi = g^2(2/\varepsilon)(\Delta\zeta/\varepsilon)^2\tanh(\varepsilon/2T). \tag{3.5}$$

A few more comments about μ_0 and χ are appropriate at this juncture. The magnetic moment vanishes at the temperature, T_c, at which the energy separation $\varepsilon = \Delta$. The temperature dependence of μ_0 is one of the subjects of the next section. It can be shown, using (3.4) and (5.1), for example, that

$$g\langle J_z\rangle = -\mu_0\tanh(\varepsilon/2T). \tag{3.6}$$

This admits the interpretation that μ_0 is the local magnetic moment of an isolated ion, and $g\langle J_z\rangle$ is the bulk magnetic moment. The difference between the two moments is created by thermal fluctuations, which vanish at zero temperature. Regarding the susceptibility, its presence in the cross-section is required by the general theory of scattering, or equivalently linear response theory [5]; one knows from the theory that the frequency sum rule in $1/\omega$ applied to the inelastic events in the cross-section gives the isothermal susceptibility (apart

from a factor 2). Finally, let us note that the structure of the cross-section (3.2) is quite independent of the method used to estimate the thermodynamic quantities, which is taken up in the next sections. Of course, the structure of (3.2) does reflect the properties assumed of our model, and notably the existence of two magnetic states and the absence of processes involving the transverse components of the angular momentum; cf. section 6.

4. Thermodynamic properties

We will proceed to the determination of the thermodynamic properties of the system by calculating the thermal average value of $\boldsymbol{J}\cdot\boldsymbol{J}$, using a method which has many features in common with the spherical model description of static spin correlations, including a partial account of quantum effects present at low temperatures [1, 4]. If all states of the magnetic atom are taken into account, i.e. completeness is imposed, one can equate $\boldsymbol{J}\cdot\boldsymbol{J}$ and $J(J+1)$, so $\langle\boldsymbol{J}\cdot\boldsymbol{J}\rangle$ is a constant independent of the temperature. We propose that the same result holds in our model, which is physically plausible, of course, and a corollary of the choice $\Delta \neq 0$.

Only one term in $\langle\boldsymbol{J}\cdot\boldsymbol{J}\rangle$ is nonzero because the assumption $\langle 1|J_\alpha|2\rangle = 0$ for $\alpha = x$ or y means $\langle J_\alpha^2\rangle = 0$; cf. (5.1). Average values of products of J_α are obtained from the partition function

$$2\exp\{-(E_1+E_2)/2T\}\cosh(\varepsilon/2T)$$

by differentiating it the requisite number of times with respect to λ_α which appears in ε [1]. From the second derivative of the partition function we find the estimate

$$g^2\langle J_z^2\rangle = \mu_0^2 + T\chi \tag{4.1}$$

where μ_0 and χ are defined in (3.4) and (3.5). From (3.5) evaluated at $T = 0$,

$$\chi = 2(g\zeta\Delta)^2/\varepsilon^3 \qquad T = 0. \tag{4.2}$$

Since the susceptibility at $T = 0$ is bounded the result (4.1) evaluated at this temperature tells us the constant on the left-hand side is the saturation moment, μ, and for an arbitrary temperature we take

$$\mu^2 = \mu_0^2 + T\chi. \tag{4.3}$$

This result can be interpreted as a sum rule on weights attached to elastic and inelastic events in the cross-section (3.2), or an equation of state for the thermodynamic quantities μ_0 and χ. In the context of scattering by the atom, the content of (4.3) is expressed by the observation that total scattering, over all possible events, is a constant independent of the temperature.

It is of interest to compare (4.2) with the value of the susceptibility at T_c. To this end it is useful to introduce some reduced variables. Let $x = \Delta/2T_c$ and $y = (\mu/g\zeta)^2$, which are related by

$$y = (\tanh x)/x \leqslant 1. \tag{4.4}$$

This relation follows from (4.3) evaluated for $T = T_c$. Writing $\chi = \chi(T)$, the ratio of the susceptibilities $T = 0$ and $T = T_c$ is

$$\{\chi(0)/\chi(T_c)\} = (1-y)^{3/2}/(xy). \tag{4.5}$$

In the limit $x \ll 1$

$$\{\chi(0)/\chi(T_c)\} \to 0.192\,x^2$$

Table 1. Various quantities are shown as functions of the reduced temperature (T/T_c). Results are for $x = 0.30$ for which $y = 0.97$. The results in brackets, alongside the results for the reduced magnetic moment, are the reduced magnetic moments obtained from a Brillouin function, equation (4.7).

T/T_c	μ_0/μ		$\chi(T)/\chi(T_c)$	Δ/ε
0.0	1.0	(1.0)	0.017	0.17
0.4	0.995	(0.986)	0.026	0.20
0.6	0.988	(0.907)	0.040	0.23
0.8	0.968	(0.711)	0.079	0.30
0.9	0.931	(0.525)	0.148	0.40
0.95	0.867	(0.379)	0.261	0.52
0.99	0.606	(0.173)	0.639	0.80

and this means, for the case in hand, that the weight of the inelastic contribution to the cross-section is relatively weak at a temperature small compared to T_c. For $T = 0$ and $x \to 0$ one finds that the energy separation is independent of Δ and it achieves the value $\varepsilon = 2T_c\sqrt{3}$.

To calculate thermodynamic quantities in the range of temperatures up to T_c it proves useful to introduce a third reduced variable, $z = \varepsilon/2T_c$. The sum rule (4.3) expressed in terms of the reduced variables is

$$y = 1 + (x/z)^2\{(\tau/z)\tanh(z/\tau) - 1\} \tag{4.6}$$

where $\tau = (T/T_c)$. The magnetic moment is obtained from (3.4) using the values of y and $\Delta/\varepsilon = x/z$, and the corresponding value of the susceptibility follows immediately from (4.3). By way of an illustration, table 1 contains values of μ_0/μ, $\chi(T)/\chi(T_c)$ and Δ/ε as a function of T/T_c for the particular case $x = \Delta/2T_c = 0.30$.

Looking at the values in table 1 of μ_0 it is evident that they are significantly different from those obtained from a standard mean-field method. To quantify this observation we include in the table values of m that satisfy the mean-field equation (Brillouin function)

$$m = \tanh(m/\tau). \tag{4.7}$$

The moment μ_0 vanishes as T approaches T_c with a power-law dependence, namely

$$\mu_0 \propto (1 - \tau)^{1/2} \qquad \tau \to 1$$

and m possesses the same temperature dependence. The difference between μ_0 and m is in the amplitude factors, and for μ_0 we find that this strongly depends on the value of $x = \Delta/2T_c$, for small values of x. In the latter case

$$\mu_0^2 \propto \{1 - (\Delta/\varepsilon)^2\}/y = (5/x^2)(1 - \tau). \tag{4.8}$$

Hence, a small value of x enhances the magnitude of μ_0, for a given value of τ. In the opposite extreme, $x \to \infty$, we find that μ_0 is independent of x. The corresponding values of χ are obtained from (4.3). A small value of x reduces χ, and enhances μ_0, and we find for $x \ll 1$ and τ close to unity

$$\chi(T) = \chi(T_c)\{1 - 5(1 - \tau)/x^2\}. \tag{4.9}$$

For large values of x the susceptibility is independent of x, at the same level of approximation in $1 - \tau$.

5. The mean-field method

It is to be noted that in the previous treatment of the thermodynamic properties of our model no use is made of $\langle J_z \rangle$. Instead, thermodynamic properties are obtained from an equation which is derived from $\langle \boldsymbol{J} \cdot \boldsymbol{J} \rangle$. In this respect, the treatment of the thermodynamic properties is similar to the spherical model approximation for the static correlation functions of a Heisenberg magnet, while basing the thermodynamic properties on an equation for $\langle J_z \rangle$ using $\lambda \propto \langle J_z \rangle$ is the standard mean-field method [6]. Of course, the essential difference between the two methods is the assumption in the mean-field method that λ is proportional to $\langle J_z \rangle$, whereas in our method λ is not explicit in the values that we derive for the magnetic moment and the susceptibility. The use of $\lambda \propto \langle J_z \rangle$ is physically motivated, scilicet the Weiss molecular field. For completeness, and to facilitate a comparison of the two methods, we briefly describe the standard mean-field method applied to our model system.

One easily finds

$$\langle J_\alpha \rangle = -\frac{1}{2}\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}\lambda_\alpha}\right)\tanh(\varepsilon/2T). \tag{5.1}$$

For our model, the right-hand side vanishes for all Cartesian components except $\alpha = z$, and $\langle 1|V|2\rangle = \lambda_z \langle 1|J_z|2\rangle$. The standard mean-field method is obtained by taking λ_z to have the form

$$\lambda_z = -\lambda_0 \langle J_z \rangle. \tag{5.2}$$

Using this relation in (5.1) yields an equation for the temperature dependence of the gap energy, namely

$$\varepsilon = 2\lambda_0 \zeta^2 \tanh(\varepsilon/2T). \tag{5.3}$$

This equation requires ε to vanish at a temperature which is larger than T_c. For $T = T_c$ one has $\varepsilon = \Delta$, and using these values in (3.5) and (5.3) we find [6]

$$g^2 = \lambda_0 \chi(T_c) \tag{5.4}$$

which determines the coupling parameter at T_c in terms of $\chi(T_c)$.

Other features of the mean-field method applied to our model are conveniently expressed in terms of the temperature, T_*, at which ε in (5.3) is zero. One finds

$$T_* = \lambda_0 \zeta^2 \tag{5.5}$$

$$\varepsilon_0 = (\varepsilon/2T_*) = \tanh(\varepsilon_0 T_*/T) \tag{5.6}$$

and (3.6) becomes

$$\mu_0 = -g\langle J_z \rangle/\varepsilon_0. \tag{5.7}$$

Note that (5.5) implies that λ_0 is a constant which is independent of the temperature. At absolute zero $\varepsilon_0 = 1$. The temperature dependence of μ_0 obtained by the mean-field method is similar to that obtained by our method. In particular, equation (5.7) approaches zero at the critical temperature with the power-law dependence displayed in (4.8), and the only difference is the factor 5 in (4.9) is replaced by the factor 3.

To complete the physical picture on which the mean-field method rests we relate λ_0 to the strength of the exchange parameters in a Heisenberg interaction between spin operators, $\{\boldsymbol{S}_j\}$, located at sites labelled by the index j. Denoting the exchange parameter for two sites i and j by $I(i, j)$, which has the property $I(j, j) = 0$, the Heisenberg interaction is

$$-\sum_{i,j} I(i, j)\boldsymbol{S}_i \cdot \boldsymbol{S}_j = -(g-1)^2 \sum_{i,j} I(i, j)\boldsymbol{J}_i \cdot \boldsymbol{J}_j \tag{5.8}$$

and the mean-field energy parameter is [6]

$$\lambda_0 = 2(g-1)^2 \sum_j I(i,j). \tag{5.9}$$

The results (5.4) and (5.9) relate the susceptibility, measured at T_c, to the strength of the exchange parameters.

6. Discussion

We have calculated the neutron cross-section for a magnetic ion that has two nondegenerate energy levels separated by a small energy Δ. The environment of the ion exerts a Weiss molecular field and the potential is taken to be proportional to the total angular momentum, $\boldsymbol{J}$. The cross-section for this simple model can be calculated without approximation. The second aspect of our study is the calculation of the thermodynamic quantities in the cross-section, which are the weights attached to the elastic and inelastic scattering events. We have demonstrated that a sum rule for the weights, which is an exact statement, permits the calculation of the thermodynamic quantities in terms of Δ and the critical temperature, say. Moreover, the weights admit a physical interpretation; the weight attached to the elastic event is the square of the magnetic moment, and the corresponding quantity for inelastic events is the isothermal susceptibility.

The model can be viewed as an abstraction from a full crystal-field model, and it will be of value when Δ is small compared to the energy of the second excited state in the crystal-field energy level scheme. A case in point is the rare-earth magnet studied by Staub *et al* [2]. They estimate that the ratio of the energy of the second level to Δ is approximately 5×10^3, and $x = \Delta/2T_c \sim 0.007$ where T_c is the temperature below which there is a spontaneous magnetic moment. For this set of parameters, we predict a separation in energy of the two states at zero temperature $\varepsilon = 1.64$ meV, which then decreases with increasing temperature, by a factor of 0.004, to its value $\varepsilon = \Delta$ at T_c. The small weight attached to the transition at zero temperature, which we find to be proportional to x^2, and an instrument resolution larger than Δ contrive in the execution of the neutron scattering experiment to render the transition unobservable. One of the compounds studied by Blaise *et al* [3] might also be realistically described by our model. For $PrFe_2Ge_2$ the ratio of the energy of the second level in the crystal-field scheme to Δ is $\sim$14, and $x = 0.37$. The interpretation of the scattering experiment provided by the authors is in accord on several fronts with our findings. For example, the weight attached to the transition with energy ε shows a substantial decrease in moving from the paramagnetic state down to $T = 0.2T_c$, and there is a concomitant increase in ε by a factor of three.

Regarding the magnetic moment one has the exact identity (3.6) that relates the bulk and local moments, from which one deduces $-g\langle J_z\rangle/\mu_0 \leqslant 1$ and the equality is achieved at zero temperature. Physically the difference between the two moments can be ascribed to thermal fluctuations (absent in the classical limit). A very similar phenomenon is observed in the study of an isolated quantum harmonic oscillator, of interest in the interpretation of Mössbauer spectra, which has thermodynamic properties, e.g. a Debye–Waller factor, that are different from those obtained for an assembly of oscillators. A physical interpretation of the ratio $-g\langle J_z\rangle/\mu_0$ can be made in terms of the average energy of $H_0 + V$. The latter, measured with respect to the midpoint of the two levels in H_0 which are separated by an energy Δ, is found to be

$$-(\varepsilon/2)\tanh(\varepsilon/2T).$$

Referring back to the identity (3.6) one can therefore interpret the ratio of the magnetic moments as proportional to the variance in the average energy of the two states in $H_0 + V$.

Finally, let us consider what happens to our findings when we generalize the model by lifting the restriction that the transverse components of $\boldsymbol{J}$ are quenched. Let the matrix elements $\langle 1|J_\alpha|2\rangle = \mathrm{i}\zeta_\alpha$, with $\alpha = x$, y or z, be different from zero. The sum rule (4.3) is changed only in so much as ζ_z^2 in μ_0^2 and χ is replaced by

$$\sum_\alpha \zeta_\alpha^2.$$

Hence, in the discussion of thermodynamic properties that stem from the sum rule the variable y is

$$y = (\mu/g)^2 \Big/ \sum_\alpha \zeta_\alpha^2.$$

Since this is the only change necessitated by the generalization of our model one concludes that the generalization does not change the thermodynamic properties. Next, we consider the change to the neutron scattering cross-section. In (3.1)

$$\sin^2\theta \langle\mu|J_z|\mu'\rangle\langle\mu'|J_z|\mu\rangle$$

is replaced by

$$\sum_{\alpha,\beta}(\delta_{\alpha,\beta} - \hat{K}_\alpha\hat{K}_\beta)\langle\mu|J_\alpha|\mu'\rangle\langle\mu'|J_\beta|\mu\rangle$$

in which $\hat{K}_\alpha$ is the α-component of the unit vector $\hat{\boldsymbol{K}} = \boldsymbol{K}/|\boldsymbol{K}|$. On carrying through the calculation of the cross-section, the change with respect to (3.2) is that $\sin^2\theta|\langle 1|J_z|2\rangle|^2$ is replaced by

$$\sum_{\alpha,\beta}(\delta_{\alpha,\beta} - \hat{K}_\alpha\hat{K}_\beta)\langle 1|J_\alpha|2\rangle^*\langle 1|J_\beta|2\rangle.$$

Now, the materials investigated are often in the form of powders, and not single crystals. In this case, it is appropriate to average the cross-section over the orientations of $\boldsymbol{K}$ relative to the crystal axes. If the atomic form factor is independent of the direction of $\boldsymbol{K}$, to a good approximation, the orientational average amounts to no more than averaging the foregoing combination of matrix elements, and the answer is

$$\frac{2}{3}\sum_\alpha \zeta_\alpha^2 = \frac{2}{3}(\mu/g)^2/y.$$

We conclude that the thermodynamic properties of the cross-section are completely determined by the sum rule, which is the case with the simpler model that we have used as a vehicle for our discussion in the preceding sections.

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