ON THE TEMPERATURE DEPENDENCE OF THE SHAPE OF MAGNETIC RESONANCE LINES

by

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ABSTRACT

This thesis is devoted to a theoretical study of that temperature dependence of the shape of magnetic resonance lines in solids which remain when the direct effect of lattice vibrations can be neglected. This is the case at sufficiently low temperatures. To discuss the shape of resonance lines the "moment method" is used. This procedure was introduced by Van Vleck (1948) and was used also by Pryce and Stevens (1950) and Usui and Kambe (1952). A line shape function which describes the shape of the resonance lines is defined and the first and second moments of this function are calculated in various approximations. In particular, the question to what extent the standard formula of Van Vleck for the second moment is valid is discussed in great detail. The general formulae are applied to the case of a spherical sample of nickel fluosilicate crystal. From the general discussions and from this special case it follows that the temperature dependence of the characteristics of paramagnetic resonance lines becomes noticeable at liquid helium temperatures and that these characteristics are then also dependent on the shape of the sample.

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Table of Contents

Table of Contents (Cont'd)

Table of Contents (Cont'd)

Chapter I

Introduction and Summary

This thesis is a theoretical investigation in one branch of magnetic phenomena, namely, magnetic resonance. We are concerned in particular with the temperature dependence of the shape of magnetic resonance absorption lines. The formulae we give can refer to electron or nuclear resonance lines.

Let us consider, for definiteness, the case of a paramagnetic salt in the presence of a static magnetic field. In the absence of mutual interactions between the paramagnetic ions and disregarding the effect of lattice vibrations, the resonance line would be "infinitely narrow". (apart from radiation width which is completely negligible). The mutual interaction of the paramagnetic ions and the lattice vibrations both contribute, in general, to the finite width of the line. However, the effect of lattice vibrations decreases with temperature. In this thesis we restrict ourselves to the temperature range for which this effect can be neglected. The effect of the mutual interactions between the paramagnetic ions turns out to be practically independent of temperature except at very low temperatures. It is the theory of this latter temperature effect which is the main topic of this thesis.

In order to discuss the shape of magnetic resonance lines we use the "moment method" which was introduced by Van Vleck (1948) and used also by Pryce and Stevens (1950) and Usui and Kambe (1952). (The idea behind the moment method is to calculate the moments of resonance lines rather than to find analytical expressions for the shape of these lines.) In this classic paper, Van Vleck does not concern himself with the dependence of resonance lines on temperature. To what extent this attitude is valid is, in fact, one of the topics discussed in this thesis. On the other hand, Pryce and Stevens have introduced the temperature into their equations for the moments via Boltzmann factors but when illustrating their general equations they give only temperature independent expressions. Usui and Kambe also introduce the temperature into their equations for the moments via Boltzmann factors. Our procedure, in fact, is quite similar to that used by these latter authors.

We shall now turn to a brief summary of the contents of the remaining chapters. After discussing, in Chapter II, the types of magnetic systems we have under consideration we proceed, in Chapter III, to define a function called the "line shape function" which describes the shape of magnetic resonance lines. We then give expressions for the first and second moments of this line shape function. Before writing these expressions, however, we have performed the so-called "truncation" of the interaction Hamiltonian and of the operator which represents the coupling of the magnetic moment of the sample to the oscillating magnetic field. Then, following Usui and Kambe, we rewrite the first and second moments of this line shape function in a form involving traces over these operators.

In Chapter IV we introduce simplifying assumptions and with their aid we are able to obtain, from our exact equations for the moments, general formulae for the moments in the form given by Pryce and Stevens. Later, in Chapter VI, we apply these formulae to a case more general than the one considered by these authors in section 4 of their paper.

In Chapter V we give sufficient conditions (involving the temperature and the magnitude of the interactions) under which the Van Vleck equation for the second moment is valid. Up to this time there has been no explicit discussion of this point in the literature.

In Chapter VII we give a more refined approximation for the moments than that given in Chapter IV, and in Chapter VIII we apply these more exact formulae to a paramagnetic nickel salt. We give graphs showing the temperature variation of the first and second central moments of the line shape function. From these graphs some general conclusions can be drawn; these have been included in the final, very brief Chapter IX.

Chapter II

Brief Discussion of the Physical System Considered

For the purpose of the discussions in the later sections, we shall consider the following to be the physical situation:

We have a sample, which may be a crystal or a powder, containing identical N "spins". For the general calculations given in the following sections it is not necessary to specify whether we are dealing with electronic systems possessing a magnetic moment or nuclear systems possessing a magnetic moment, that is, the general formulae given can be applied either to the case of paramagnetic resonance or nuclear magnetic resonance. Thus, we shall speak of a "spin" as follows:

1) to refer to an electronic system with arbitrary but fixed spin quantum number S and "g-factor", $\underline{\underline{g}}$, wherein $\underline{\mu} = -\mu_B \, \underline{\underline{g}} \cdot \underline{S}$ where $\underline{\mu}$ = magnetic moment of the electronic system and μ_B = Bohr magneton = $\frac{|e|\hbar}{2mc}$. If the electronic system is an atomic dipole and if no crystalline field is present, then the g-factor will have the form $\underline{\underline{g}} = g\underline{\underline{E}}$ where $\underline{\underline{E}}$ is the unit tensor. Thus, in this case, we have $\underline{\mu} = -g\mu_B \underline{S}$. If the electronic system is an atomic dipole in the presence of a crystalline field, the g-factor will in general become a non-unit tensor $\underline{\underline{g}}$,

2) to refer to a nuclear system with arbitrary but fixed spin quantum number I and nuclear g-factor, $\underline{\underline{g}}_N$, wherein $\underline{\mu} = \mu_N \underline{\underline{g}}_N \cdot \underline{I}$ where $\underline{\mu}$ = magnetic moment of the nuclear system and where μ_N = nuclear magneton $= \frac{|e|\hbar}{2Mc}$. (In general $\underline{\underline{g}}_N$ is a tensor).

We shall speak of a "spin system" as a system of N weakly interacting spins.

We assume that the system of N spins has been placed in a constant magnetic field, $\underline{H}_0$ and a high frequency oscillating magnetic field, $2\underline{H}_1 \cos 2\pi\nu t$. The high frequency magnetic field induces transitions between the energy states of the spin system and experimentally one finds that energy is absorbed from the oscillating magnetic field.

In addition to the interactions within the spin system, there will be interactions between the spin system and the rest of the physical world. These latter interactions will consist of interactions between the spin system and the constant magnetic field, between the spin system and the oscillating magnetic field, and between the spin system and the "lattice", where we consider the lattice to be that part of the physical world not included in the spin system or the two magnetic fields. The relationship between the absorption of energy and the frequency of the oscillating magnetic field will depend on the nature of these interactions.

The procedure in the following chapter will be to define a function which depends on the above interactions and which describes the relationship between the absorption of energy by the spin system and the frequency of the oscillating magnetic field.

Chapter III

Definition of the Line Shape Function and Calculation of its First and Second Moments

3.1 General Discussion

The contents of this section will be devoted to finding the first and second moments of a function which we shall call the "line shape function, $f(\nu)$". Many functions may be used to describe the relationship between the frequency of the oscillating magnetic field and the power absorbed by the spin system. In section 3.2 we shall define the line shape function such that $f(\nu)$ is proportional to the imaginary part of the high frequency susceptibility, $\chi''(\nu)$. Furthermore, we shall define $f(\nu)$ such that $\int_0^\infty f(\nu)\,d\nu = 1$.

To calculate the moments of $f(\nu)$ we shall use a method, first developed by Van Vleck (1948), which demands a knowledge of the Hamiltonian, $\mathfrak{H}$, of the spin system. From the discussion in Chapter II it is apparent that $\mathfrak{H}$ must in general be written as

$$\mathfrak{H} = \mathfrak{H}^{(0)} + \mathfrak{H}^{(1)} + \mathfrak{H}^{(2)} + \mathfrak{H}^{(3)}$$

where the four terms represent the following interactions energies:

$\mathcal{H}^{(0)}$ = spin-magnetic field interaction plus spin-crystalline field interaction when this latter is present.

$\mathcal{H}^{(1)}$ = spin-spin interaction (which may include exchange interactions)

$\mathcal{H}^{(2)}$ = spin- lattice interaction

$\mathcal{H}^{(3)}$ = spin-high frequency magnetic field interaction.

We have, furthermore, that $\mathcal{H}^{(0)} = \sum_{i=1}^{N} \mathcal{H}_i^{(0)}$.

In the following, we shall disregard $\mathcal{H}^{(2)}$ completely. Furthermore, we shall assume that $\mathcal{H}^{(0)} \gg \mathcal{H}^{(1)} + \mathcal{H}^{(3)}$ and $\mathcal{H}^{(1)} \gg \mathcal{H}^{(3)}$ so that, to a first approximation, $\mathcal{H}$ can be written as

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} \qquad (3.1.1)$$

We shall consider $\mathcal{H}^{(0)}$ as the unperturbed energy and $\mathcal{H}^{(1)}$ as the perturbation energy.

Van Vleck (1948) has pointed out, however, that use of (3.1.1) when finding the moments does not allow us easily to compare our results to experimental findings. We must, in fact "truncate" the Hamiltonian. The reasons behind this are rather subtle and for this reason, we shall devote the next section to this point.

Usui and Kambe (1952) have pointed out that in general (for example, when a crystalline field is present) a further truncation is necessary, namely, truncation of the interaction energy $\mathcal{H}^{(3)}$. This point will also be discussed in the next section.

3.2 Truncation of the Hamiltonian, $\mathcal{H}^{(0)}+\mathcal{H}^{(1)}$,
and of the interaction energy, $\mathcal{H}^{(3)}$.

We are considering the Hamiltonian of the spin system to be given by (3.1.1). If the Hamiltonian of the system could be written as $\mathcal{H}^{(0)}$, that is, if all other interactions could be regarded as negligible when compared with $\mathcal{H}^{(0)}$, the energy levels of the system could consist of a large number of highly degenerate levels.

Let us label the eigenstates and eigenvalues of $\mathcal{H}^{(0)}$ by $|\alpha, i^{(0)})$ and E_α where $i=1,2,\ldots,g_\alpha$ and g_α is the degeneracy of the eigenvalue E_α . We recall that we consider that $\mathcal{H}^{(3)}$ induces transitions between the various states of the spin system. As is well known, the probability of a transition being induced by $\mathcal{H}^{(3)}$ between the states $|\alpha, i^{(0)})$ and $|\beta, k^{(0)})$ is proportional to the absolute square of the matrix element '

$$(\alpha, i^{(0)}|\mathcal{H}^{(3)}|\beta, k^{(0)}) \tag{3.2.1}$$

When such a transition takes place the spin system absorbs the energy $|E_\alpha - E_\beta|$.

In practice one usually finds that not all such matrix elements are non-zero but rather that non-zero matrix elements occur only for certain values of α and β .

For example, if (3.2.1) were non-zero only if

$$\left.\begin{array}{l} |\alpha-\beta|=1 \\ \text{and in addition } |E_\alpha - E_{\alpha\pm1}| = \text{constant independent of } \alpha \\ \qquad = h\nu_0 \end{array}\right\} \tag{3.2.2}$$

then the spin system would absorb energy at a single frequency, ν_0 , and $f(\nu)$ would have the simple form

$$f(\nu) = \delta(\nu-\nu_0) \tag{3.2.3}$$

where $\delta(\nu-\nu_0)$ is the familiar Dirac delta function. (Condition (3.2.3) refers to the case when no crystalline field is present.)

When the Hamiltonian of the spin system is written as $\mathcal{H}^{(0)}$, each of the N spins has the same energy values, say, $a_1, a_2, \ldots\ldots, a_R$. The condition (3.2.2) corresponds to the case when

$a_{k+1} - a_k =$ constant for k = 1,2,.....,R-1
and, furthermore, when transitions can occur only between adjacent levels of the individual spins. (3.2.2)

If, on the other hand,

$$a_{k+1} - a_k \neq \text{constant} \tag{3.2.4}$$

(as one usually finds when a crystalline field is present) then the spin system will absorb energy at several different frequencies, say, $\nu_0, \nu_1, \nu_2, \ldots\ldots \nu_r$. In this case $f(\nu)$ would have the form $f(\nu) = \frac{1}{r+1}\sum_{i=1}^{r} \delta(\nu-\nu_i)$

When $\mathcal{H}^{(1)}$ is added to $\mathcal{H}^{(0)}$ the highly degenerate energy values E_α split. The new energies and new eigenstates are given by first order perturbation theory:

$$E_{i_\alpha} = E_\alpha + (\alpha,i|\mathcal{H}^{(1)}|\alpha,i) + \sum_{\beta(\neq\alpha)}\sum_{\ell=1}^{g_\beta} \frac{|(\beta,\ell|\mathcal{H}^{(1)}|\alpha,i)|^2}{E_\alpha - E_\beta} \qquad (3.2.5)$$

$$|i_\alpha) = |\alpha,i) + \sum_{k(\neq i)}\sum_{\beta(\neq\alpha)}\sum_{\ell=1}^{g_\beta} a_{\alpha i;\alpha k;\beta\ell}\,|\alpha,k) + \sum_{\beta(\neq\alpha)}\sum_{\ell=1}^{g_\beta} b_{\alpha i;\beta\ell}\,|\beta,\ell) \qquad (3.2.6)$$

where we use i_α to label the new eigenfunctions and eigenvalues and where

$$a_{\alpha i;\alpha k;\beta\ell} = \frac{(\alpha,k|\mathcal{H}^{(1)}|\beta,\ell)(\beta,\ell|\mathcal{H}^{(1)}|\alpha,i)}{(E_\alpha - E_\beta)\left[(\alpha,i|\mathcal{H}^{(1)}|\alpha,i) - (\alpha,k|\mathcal{H}^{(1)}|\alpha,k)\right]} \qquad (3.2.7)$$

$$b_{\alpha i;\beta\ell} = \frac{(\beta,\ell|\mathcal{H}^{(1)}|\alpha,i)}{E_\alpha - E_\beta} \qquad (3.2.8)$$

The zero order states $|\alpha,i)$ are

$$|\alpha,i) = \sum_{k=1}^{g_\alpha} \Lambda_{\alpha;i,k}\,|\alpha,k^{(0)})$$

where Λ_α is a unitary matrix and has been chosen so that:

1) $(\alpha,i|\mathcal{H}^{(1)}|\alpha,k) = (\alpha,i|\mathcal{H}^{(1)}|\alpha,i)\,\delta_{ik}$

2) $a_{\alpha i;\alpha k;\beta\ell}$ is never infinite.

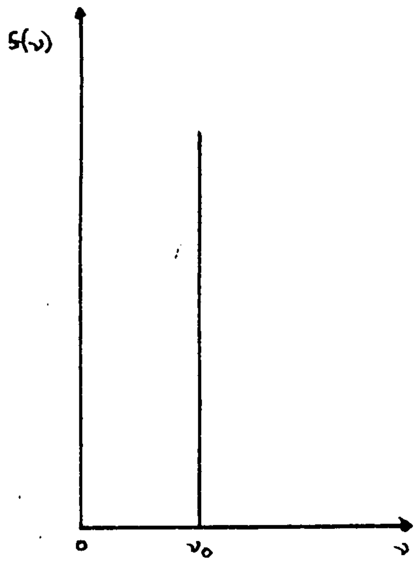
This can always be done.

Now, the probability of $\mathcal{H}^{(3)}$ inducing a transition between $|\rho_\alpha)$ and $|\rho'_\beta)$ is proportional to the absolute square of the matrix element

$$(\rho_\alpha | \mathcal{H}^{(3)} | \rho'_\beta) \tag{3.2.9}$$

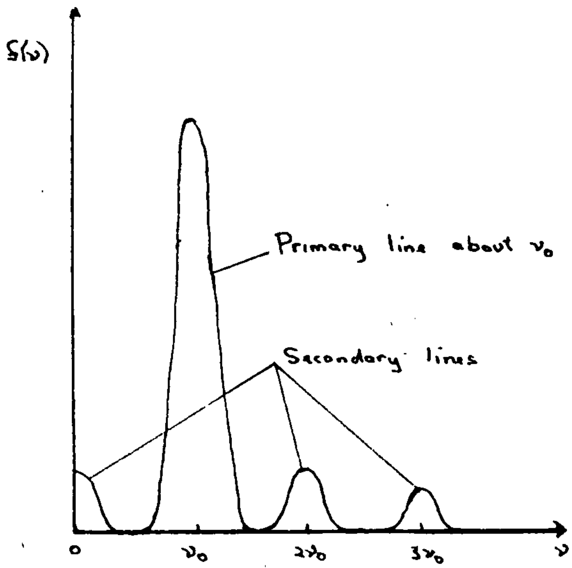
Let us suppose for simplicity that (3.2.2) holds. It is seen immediately that because of the last two terms in (3.2.6), (3.2.9) will be different from zero for many values of α and β. As a result, energy will be absorbed at frequencies many times larger or smaller than ν_0. The function $f(\nu)$ will now consist of several broad overlapping lines and will have several maxima, the number of which depends on $\mathcal{H}^{(1)}$. As can easily be seen, these maxima will occur at multiples of ν_0 when (3.2.2) holds. The following diagrams will illustrate the point:

DIAGRAM I



$\mathcal{H}^{(1)} = 0$ and condition (3.2.2) holding

DIAGRAM II



$\mathcal{H}^{(1)} \neq 0$ and condition (3.2.2) holding

It should be noticed that this phenomenon is not the result of the simple condition (3.2.2) but that it is the result of the fact that to first order the eigenstates of $\mathcal{H}$ are linear combinations of all of the eigenstates of $\mathcal{H}^{(0)}$.

In general, then, when $\mathcal{H}^{(1)}$ is added to $\mathcal{H}^{(0)}$ two things happen to $f(\nu)$. Firstly, the infinitely narrow lines represented by the delta functions broaden and secondly, secondary lines occur. (By secondary lines we mean those lines which occur because of the presence of the last two terms in (3.2.6). We shall refer to those lines which result from the broadening of the delta functions as primary lines. See diagram II.)

Experimentally, one observes one of the primary lines of $f(\nu)$. We seek to characterize $f(\nu)$ by its moments, so that if we are to compare the moments of the experimental curve with the moments of $f(\nu)$ we must then find some way of eliminating the secondary lines from our function $f(\nu)$.

If $a_{\alpha i;\alpha k;\beta\ell}$ and $b_{\alpha i;\beta\ell}$ could be put equal to zero the difficulties would disappear. In this case, when condition (3.2.2) holds, transitions will occur only between those states whose original separation was $h\nu_0$, where by original separation we mean when $\mathcal{H}^{(1)}$ is taken to be zero. The function $f(\nu)$ will then consist of the broadened portion centred about ν_0 , that is, the primary line about ν_0 . In other words, no subsidiary secondary lines will occur.

In general, $a_{\alpha i;\alpha k;\beta\ell}$ and $b_{\alpha i;\beta\ell}$ can be put equal to zero in only one way, namely, by considering the

Hamiltonian of the system to be $\mathcal{H}^{(0)} + \overline{\mathcal{H}^{(1)}}$ instead of $\mathcal{H}^{(0)} + \mathcal{H}^{(1)}$ where $\overline{\mathcal{H}^{(1)}}$ is that part of $\mathcal{H}^{(1)}$ which commutes with $\mathcal{H}^{(0)}$. Then, as is well known, there exists a set of functions which are simultaneous eigenfunctions of $\mathcal{H}^{(0)}$ and $\overline{\mathcal{H}^{(1)}}$. These functions will be the functions $|\alpha,i)$. Because of the orthogonality of these eigenfunctions we see immediately that $a_{\alpha i;\alpha k;\beta\ell}$ and $b_{\alpha i;\beta\ell}$ are zero if $\mathcal{H}^{(1)}$ is replaced by $\overline{\mathcal{H}^{(1)}}$.

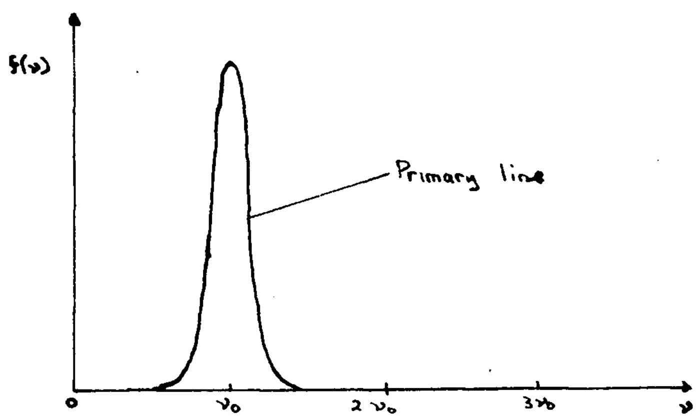
Thus when discussing $f(\nu)$ we shall consider the Hamiltonian of the spin system to be

$$\overline{\mathcal{H}} = \mathcal{H}^{(0)} + \overline{\mathcal{H}^{(1)}} \tag{3.2.10}$$

We shall refer to $\overline{\mathcal{H}}$ as the "truncated Hamiltonian" of the spin system.

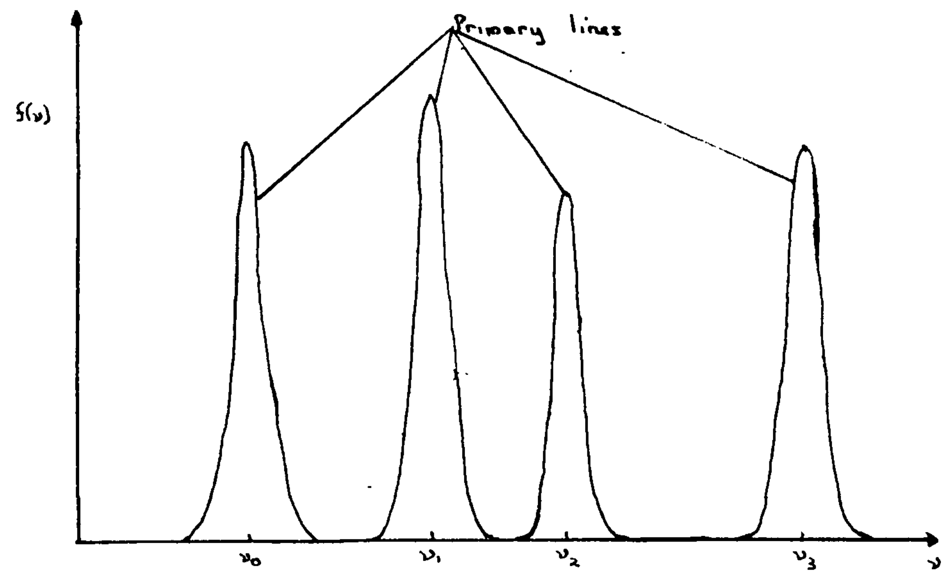
As a result of the truncation of the Hamiltonian, the secondary lines disappear from $f(\nu)$. The function $f(\nu)$ will then have the form

DIAGRAM III



if the Hamiltonian of the system is given by (3.2.10) and condition (3.2.2) holds, or, the form

DIAGRAM IV



if the Hamiltonian of the system is given by (3.2.10) and condition (3.2.4) holds and where $r = 3$.

We have mentioned that experimentally one observes one of the primary lines. If, then, we hope to interpret experimental findings by comparing the moments of the experimental curve and the moments of $f(\nu)$, we must eliminate from our function $f(\nu)$ any of the primary lines in which we are not interested.

For example, if we wish to find the second moment of f( ) about ν_2 then we must eliminate the primary lines about $\nu_0, \nu_1, \nu_3, \nu_4, \ldots, \nu_r$ if we are to compare our theoretical results with the second moment of $f(\nu)$ about ν_2 found experimentally.

In order to eliminate the unnecessary primary lines we must introduce another artifice. Instead of considering $\mathcal{H}^{(3)}$

as inducing transitions we shall suppose that $\hat{\mathcal{H}}^{(3)}$ induces transitions, where by the circumflex we mean that we are considering only that part of $\mathcal{H}^{(3)}$ which is relevant to the particular problem under consideration. For example, if we wish to consider only the broadened portion about ν_2, then we only wish to consider transitions between the states $|\alpha, i)$ and $|\beta, k)$ of $\overline{\mathcal{H}}$ wherein $|E_\alpha - E_\beta| = h\nu_2$. In this case, then, we define the operator $\hat{\mathcal{H}}^{(3)}$ such that it has matrix elements

$$(\alpha, i|\,\hat{\mathcal{H}}^{(3)}|\beta, k) = \begin{cases} (\alpha, i|\,\mathcal{H}^{(3)}|\beta, k) & \text{if } |E_\alpha - E_\beta| = h\nu_2 \\ 0 & \text{otherwise} \end{cases}$$

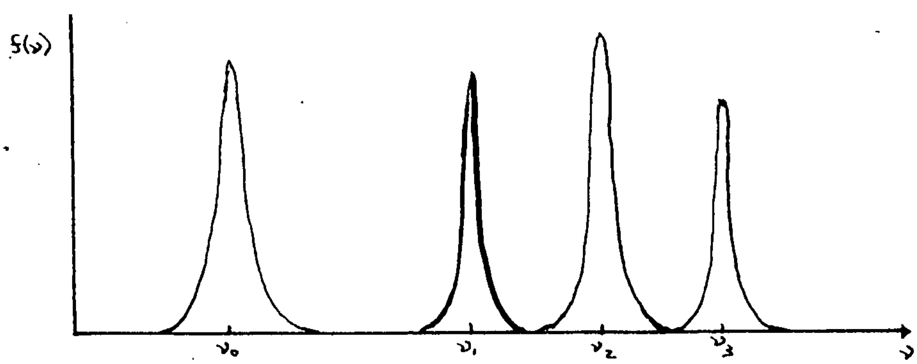
For any other problem it is necessary to redefine $\hat{\mathcal{H}}^{(3)}$. In general, however, the circumflex indicates that the matrix elements

$$(\alpha, i|\,\hat{\mathcal{H}}^{(3)}|\beta, k)$$

can be non-zero only for particular values of α and β.

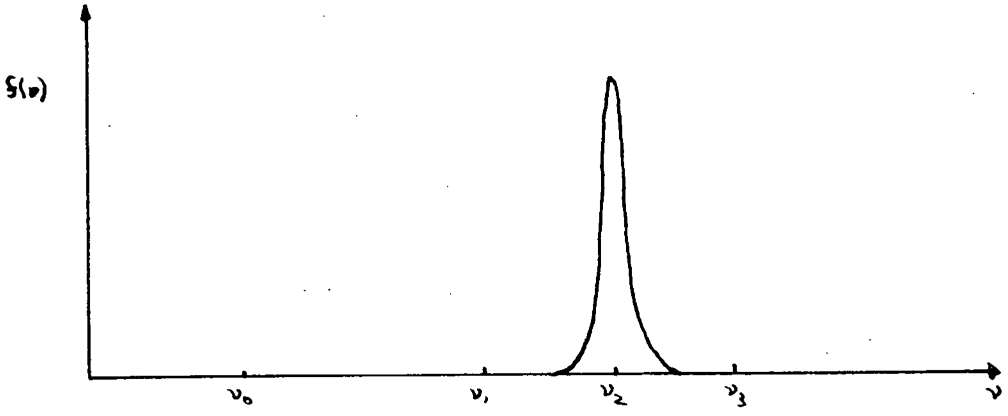
The following diagram will illustrate the point:

DIAGRAM V.



where $\overline{\mathcal{H}} = \mathcal{H}^{(0)} + \overline{\mathcal{H}^{(1)}}$ and $\mathcal{H}^{(3)}$ induces the transitions, but:

DIAGRAM VI.



where $\bar{\mathcal{H}} = \mathcal{H}^{(0)} + \overline{\mathcal{H}^{(1)}}$ and $\hat{\mathcal{H}}^{(3)}$ induces the transitions and where the circumflex means, in this case, that the matrix element

$$(\alpha, i \,|\, \hat{\mathcal{H}}^{(3)} \,|\, \beta, k)$$

can be non-zero only if $|E_\alpha - E_\beta| = h\nu_2$

It should be noticed that in the simple case where (3.2.2) holds, that is, no crystalline field present, it is not necessary to introduce the circumflex over $\mathcal{H}^{(3)}$ since $f(\nu)$ consists of only one primary line.

In general, then, before comparing the moments of $f(\nu)$ with the moments found experimentally we have to do the following two things:

1) truncate the Hamiltonian in order to eliminate the secondary lines from $f(\nu)$,

2) truncate $\mathcal{H}^{(3)}$ in order to eliminate any primary lines from $f(\nu)$ in which we are not interested.

We can now proceed to defining $f(\nu)$ and to calculating its first and second moments. For simplicity, we shall call ν^* the frequency about which the primary line in which we are interested is centered. That is, in what follows, we are considering the primary line at ν^*. Thus, for the purpose of the following discussion, we define $\hat{\mathcal{H}}^{(3)}$ so that

$$(\alpha,i|\hat{\mathcal{H}}^{(3)}|\beta,k) = \left\{ \begin{array}{ll} (\alpha,i|\mathcal{H}^{(3)}|\beta,k) & \text{is } |E_\alpha - E_\beta| = h\nu^* \\ 0 & \text{otherwise} \end{array} \right\} \quad (3.2.11)$$

3.3 Definition of $f(\nu)$ and Calculation of its First and Second Moments

Let us now consider the eigenvalues and eigenfunctions of $\bar{\mathcal{H}}$. We shall label the eigenvalues of $\bar{\mathcal{H}}$ by E_n and the corresponding eigenstates by $|n)$.

If we define a function $g(\nu)$ such that $g(\nu)\Delta\nu$ is the probability that in one second the spin system will absorb energy from the high frequency oscillating magnetic field in the frequency range ν to $\nu+\Delta\nu$ then:

$$g(\nu)\Delta\nu = \sum_n \sum_{n'}^{+\Delta} P(n,n') - \sum_n \sum_{n'}^{-\Delta} P(n,n') \quad (3.3.1)$$

where

$P(n,n')$ = probability that the spin system undergoes a transition from the state $|n)$ to the state $|n')$ in one second

$\sum_n$ = sum over all of the eigenstates of $\bar{\mathcal{H}}$

$\sum_{n'}^{+\Delta}$ = sum over all of those eigenstates of $\bar{\mathcal{H}}$ wherein $h\nu \leq E_{n'} - E_n \leq h(\nu + \Delta\nu)$

$\sum_{n'}^{-\Delta}$ = sum over all of those eigenstates of $\bar{\mathcal{H}}$ wherein $h\nu \leq E_n - E_{n'} \leq h(\nu + \Delta\nu)$

However,

$$\sum_n \sum_{n'}^{-\Delta} P(n, n') = \sum_{n'} \sum_{n}^{-\Delta} P(n', n) = \sum_n \sum_{n'}^{+\Delta} P(n', n)$$

so that
$$g(\nu)\,\Delta\nu = \sum_n \sum_{n'}^{+\Delta} \left\{ P(n, n') - P(n', n) \right\} \qquad (3.3.2)$$

Now, $P(n, n') = a_n p_{nn'}$ where

a_n = probability that the system is initially in the state $|n)$, that is, in the state $|n)$ before the high frequency field is applied.

$p_{nn'}$ = probability that in one second the system undergoes a transition to the state $|n')$ given that the system is initially in the state $|n)$.

From statistical mechanics we have $a_n = Z^{-1} e^{-\frac{E_n}{kT}}$ where

$Z = \sum_n e^{-\frac{E_n}{kT}}$

k = Boltzmann's constant

T = initial temperature of the spin system = lattice temperature

Let us now consider $p_{nn'}$. From standard quantum mechanical theory we have the probability that the perturbing energy $\hat{\mathcal{H}}^{(2)}$ induces a transition between the states $|n)$

and $|n')$ of $\overline{\mathcal{H}}$ in the time $t-t_o$ where at t_o the system is the state $|n)$ is

$$p_{nn'} = \hbar^{-2} \left| \int_{t_o}^{t} (n' | \hat{\mathcal{H}}^{(3)*} | n) \, dt' \right|^2$$

where

$$\hat{\mathcal{H}}^{(3)*} = \exp\left\{\frac{i\overline{\mathcal{H}}(t-t_o)}{\hbar}\right\} \hat{\mathcal{H}}^{(3)} \exp\left\{\frac{-i\overline{\mathcal{H}}(t-t_o)}{\hbar}\right\}$$

Now, in our problem, $\mathcal{H}^{(3)} =$ -(oscillating field)·(magnetic moment)

$= -\underline{H}(t)\cdot\underline{M}$

$= -H(t)M$ where M is the component of $\underline{M}$ in the direction of H(t).

Then, $\hat{\mathcal{H}}^{(3)} = -H(t)\hat{M}$

Now, we can write

$$p_{nn'} = \hbar^{-2} |(n|\hat{M}|n')|^2 \left| \int_{t_o}^{t} e^{2\pi i\nu(t'-t_o)} H(t') \, dt' \right|^2$$

where $\nu = \frac{E_{n'} - E_n}{h}$

If H(t) is resolved into its Fourier components, the energy crossing unit area in the direction of H(t) per unit frequency range about the frequency ν will be, according to classical electrodynamics,

$$E_\nu = \frac{c}{2\pi} \left| \int_{t_o}^{t} e^{2\pi i\nu(t'-t_o)} H(t') \, dt' \right|^2$$

Thus,

$$p_{nn'} = 2\pi c^{-1} \hbar^{-2} |(n|\hat{m}|n')|^2 \; E_\nu$$

Finally, then,

$$P_{nn'} = 2\pi c^{-1} \hbar^{-2} Z^{-1} e^{-\frac{E_n}{kT}} |(n|\hat{m}|n')|^2 \; E_\nu$$

so that

$$g(\nu)\,\Delta\nu = 2\pi c^{-1} \hbar^{-2} Z^{-1} \sum_n \sum_{n'}^{+\Delta} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_n'}{kT}} \right) |(n|\hat{m}|n')|^2 \; E_\nu$$

In order that our results be independent of E_ν , a quantity which depends on experimental conditions, we assume that E_ν is a constant, say U, for all ν . Then:

$$g(\nu)\,\Delta\nu = 2\pi c^{-1} \hbar^{-2} Z^{-1} U \sum_n \sum_{n'}^{+\Delta} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_n'}{kT}} \right) |(n|\hat{m}|n')|^2 \qquad (3.3.3)$$

Now, if $E(\nu)\,\Delta\nu$ is the power absorbed by the spin system from the oscillating magnetic field in the frequency range ν to $\nu+\Delta\nu$ then:

$$E(\nu) = h\nu \; g(\nu)\,\Delta\nu \qquad (3.3.4)$$

But, as is well known (see for example Andrew (1955))

$$E(\nu) = 4\pi\nu \, H_1^2 \, \chi''(\nu) \qquad (3.3.5)$$

where $\chi''(\nu)$ is the imaginary part of the high frequency susceptibility, and where $2H_1$ is the amplitude of the oscillating magnetic field.

Combining equations (3.3.3), (3.3.4) and (3.3.5) we have

$$\chi''(\nu)\Delta\nu = \frac{\pi U}{\hbar c Z H_1^2} \sum_n \sum_{n'}^{+\Delta} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |\langle n|\hat{m}|n'\rangle|^2 .$$

The area under the curve $\chi''(\nu)$ is then

$$\int_0^\infty \chi''(\nu)\,d\nu = \frac{\pi U}{\hbar c Z H_1^2} \sum_n \sum_{n'}^{+} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |\langle n|\hat{m}|n'\rangle|^2$$

where $\sum\limits_{n'}^{+}$ means summation over all states wherein $E_{n'} \geq E_n$

We shall now define a dimensionless quantity $f(\nu)$ which we shall call the line shape function:

$$f(\nu)\Delta\nu = \frac{\chi''(\nu)\Delta\nu}{\int_0^\infty \chi''(\nu)d\nu} = \frac{\sum_n \sum_{n'}^{+\Delta} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |\langle n|\hat{m}|n'\rangle|^2}{\sum_n \sum_{n'}^{+} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |\langle n|\hat{m}|n'\rangle|^2} \qquad (3.3.6)$$

Our line shape function, then, is proportional to the function $\chi''(\nu)$ and furthermore, $\int_0^\infty f(\nu)d\nu = 1.$

The first moment of $f(\nu)$ which is defined as

$$\langle \nu \rangle = \int_0^\infty \nu f(\nu)\,d\nu$$

can be written

$$h\langle \nu \rangle = \frac{\sum_n \sum_{n'} (E_{n'} - E_n)\left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |\langle n|\hat{m}|n'\rangle|^2}{\sum_n \sum_{n'} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |\langle n|\hat{m}|n'\rangle|^2} \qquad (3.3.7)$$

and the second moment of $f(\nu)$ which is defined as

$$\langle \nu^2 \rangle = \int_0^\infty \nu^2 f(\nu)\,d\nu$$

can be written

$$h^2\langle \nu^2 \rangle = \frac{\sum_n \sum_{n'}^{+} (E_{n'} - E_n)^2\left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |\langle n|\hat{m}|n'\rangle|^2}{\sum_n \sum_{n'}^{+} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |\langle n|\hat{m}|n'\rangle|^2} \qquad (3.3.8)$$

We shall calculate these two moments. Evaluating the summations in (3.3.7) and (3.3.8) as they stand would require a knowledge of all of the eigenvalues of $\bar{\mathcal{H}}$, that is, we would be forced to solve the eigenvalue problem $\bar{\mathcal{H}}|n) = E_n|n)$ before continuing. It has been noticed by Waller (1932), Broer (1943), Van Vleck (1948), and others that this arduous task could be avoided by rewriting equations (3.3.7) and (3.3.8) in trace form, that is, as traces over operators. The advantage in doing this is apparent: The trace of an operator is invariant under a similarity transformation and hence the traces can be evaluated using as a basis any functions that can be obtained from the functions $|n)$ by a similarity transformation.

The procedure which we shall use to rewrite (3.3.7) and (3.3.8) in trace form is identical to that given by Usui and Kambe (1952). It will be noticed later that our general formulae for $\langle\nu\rangle$ and $\langle\nu^2\rangle$ are identical to those given by these authors.

Consider, now, the denominator of (3.3.7) and (3.3.8). In order to avoid the rather awkward summation $\sum_{n'}^{+}$, it is convenient to introduce the operators $\hat{m}_+$ and $\hat{m}_-$ which, are defined as

$$(n|\hat{m}_+|n') = \begin{cases} (n|\hat{m}|n') & \text{if } E_n > E_{n'} \\ 0 & \text{otherwise} \end{cases} \tag{3.3.9}$$

$$(n|\hat{m}_-|n') = \begin{cases} (n|\hat{m}|n') & \text{is} \quad E_{n'} > E_n \\ 0 & \text{otherwise} \end{cases} \tag{3.3.10}$$

Thus $\quad (n|\hat{m}|n') = (n|\hat{m}_+|n') + (n|\hat{m}_-|n')$

We can now write

$$\sum_n \sum_{n'}{}^{+} e^{-\frac{E_n}{kT}} |(n|\hat{m}|n')|^2 = \sum_n \sum_{n'}{}^{+} e^{-\frac{E_n}{kT}} (n|\hat{m}|n')(n'|\hat{m}|n) =$$

$$= \sum_n \sum_{n'} e^{-\frac{E_n}{kT}} (n|\hat{m}_-|n')(n'|\hat{m}_+|n) = \sum_n e^{-\frac{E_n}{kT}} (n|\hat{m}_-\hat{m}_+|n)$$

But, $\quad (n|e^{-\frac{\bar{H}}{kT}}|n') = e^{-\frac{E_n}{kT}} \delta_{nn'}$

so that

$$\sum_n e^{-\frac{E_n}{kT}} (n|\hat{m}_-\hat{m}_+|n) = \sum_n \sum_{n'} e^{-\frac{E_n}{kT}} \delta_{nn'} (n'|\hat{m}_-\hat{m}_+|n) =$$

$$= \sum_n \sum_{n'} (n|e^{-\frac{\bar{H}}{kT}}|n')(n'|\hat{m}_-\hat{m}_+|n) = \sum_n (n|e^{-\frac{\bar{H}}{kT}} \hat{m}_-\hat{m}_+|n) =$$

$$= \mathrm{Trace}\left(e^{-\frac{\bar{H}}{kT}} \hat{m}_-\hat{m}_+\right).$$

Similarily,

$$\sum_n \sum_{n'}{}^{+} e^{-\frac{E_{n'}}{kT}} |(n|\hat{m}|n')|^2 = \sum_{n'} e^{-\frac{E_{n'}}{kT}} (n'|\hat{m}_+\hat{m}_-|n') = \sum_{n'} (n'|e^{-\frac{\bar{H}}{kT}} \hat{m}_+\hat{m}_-|n') =$$

$$= \mathrm{Trace}\left(e^{-\frac{\bar{H}}{kT}} \hat{m}_+\hat{m}_-\right).$$

Then, $$\sum_n \sum_{n'}{}^{+} \left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right) |(n|\hat{m}|n')|^2 = \mathrm{Trace}\left(e^{-\frac{\bar{H}}{kT}} [\hat{m}_-, \hat{m}_+]\right) \tag{3.3.11}$$

where, as is customary, $[\hat{m}_-, \hat{m}_+] = \hat{m}_-\hat{m}_+ - \hat{m}_+\hat{m}_-$.

Consider, now, the numerator of (3.3.7). It will immediately be noticed that here it is not necessary to introduce the operators $\hat{m}_+$ and $\hat{m}_-$ since

$$\sum_n \sum_{n'}{}^{+} (E_{n'}-E_n)\left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right)|(n|\hat{m}|n')|^2 = \frac{1}{2}\sum_n \sum_{n'} (E_{n'}-E_n)\left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right)|(n|\hat{m}|n')|^2$$

Now, $\sum_n \sum_{n'} e^{-\frac{E_n}{kT}} (E_{n'}-E_n)|(n|\hat{m}|n')|^2 = \sum_n \sum_{n'} e^{-\frac{E_n}{kT}} \left\{ E_{n'}(n'|\hat{m}|n)(n|\hat{m}|n') - E_n(n|\hat{m}|n')(n'|\hat{m}|n) \right\} =$

$$= \sum_n \sum_{n'} e^{-\frac{E_n}{kT}} \left\{ (n'|\mathcal{H}\hat{m}|n)(n|\hat{m}|n') - (n|\hat{m}|n')(n'|\hat{m}\mathcal{H}|n) \right\} =$$

$$= \sum_n e^{-\frac{E_n}{kT}} \left\{ (n|\hat{m}\mathcal{H}\hat{m} - \hat{m}\hat{m}\mathcal{H}|n) \right\} =$$

$$= \mathrm{Trace}\left(e^{-\frac{\mathcal{H}}{kT}} \hat{m}[\mathcal{H}, \hat{m}] \right).$$

where we have made use of the relationship $E_n \delta_{nn'} = (n|\mathcal{H}|n')$

and its consequences

$$E_n (n|\hat{m}|n') = (n|\mathcal{H}\hat{m}|n')$$

$$E_{n'}(n|\hat{m}|n') = (n|\hat{m}\mathcal{H}|n)$$

Since $\sum_n \sum_{n'} e^{-\frac{E_{n'}}{kT}} (E_{n'}-E_n)|(n|\hat{m}|n')|^2 = -\sum_n \sum_{n'} e^{-\frac{E_n}{kT}} (E_{n'}-E_n)|(n|\hat{m}|n')|^2$

we have

$$\sum_n \sum_{n'} (E_{n'}-E_n)\left(e^{-\frac{E_n}{kT}} - e^{-\frac{E_{n'}}{kT}}\right)|(n|\hat{m}|n')|^2 = 2\,\mathrm{Trace}\left(e^{-\frac{\mathcal{H}}{kT}} \hat{m}[\mathcal{H}, \hat{m}] \right) \qquad (3.3.12)$$

Using (3.3.11) and (3.3.12) we can rewrite (3.3.7) in the form

$$\hbar\langle\nu\rangle = \frac{\mathrm{Trace}\left(e^{-\frac{\mathcal{H}}{kT}}\,\hat{m}[\mathcal{H},\hat{m}]\right)}{\mathrm{Trace}\left(e^{-\frac{\mathcal{H}}{kT}}\,[\hat{m}_-,\hat{m}_+]\right)} \qquad (3.3.13)$$

It will be noticed that the expression given by Usui and Kambe (1952) for $\langle\nu\rangle$ involves

$$\mathrm{Trace}\left(e^{-\frac{\mathcal{H}}{kT}}\,[\hat{m},[\mathcal{H},\hat{m}]]\right)$$

However,

$$\mathrm{Trace}\left(e^{-\frac{\mathcal{H}}{kT}}\,[\hat{m},[\mathcal{H},\hat{m}]]\right) = 2\,\mathrm{Trace}\left(e^{-\frac{\mathcal{H}}{kT}}\,\hat{m}[\mathcal{H},\hat{m}]\right)$$

as can easily be seen by calculating the traces with respect to the functions $|n)$.

Consider, now, the numerator of (3.3.8). It will again be necessary to introduce the operators $\hat{m}_+$ and $\hat{m}_-$:

$$\sum_n\sum_{n'}{}^{+}(E_{n'}-E_n)^2\left(e^{-\frac{E_n}{kT}}-e^{-\frac{E_{n'}}{kT}}\right)|(n|\hat{m}|n')|^2 = \sum_n\sum_{n'}(E_{n'}-E_n)^2\left(e^{-\frac{E_n}{kT}}-e^{-\frac{E_{n'}}{kT}}\right)(n|\hat{m}_-|n')(n'|\hat{m}_+|n)$$

As before, we write

$$\sum_n\sum_{n'} e^{-\frac{E_n}{kT}}(E_{n'}-E_n)^2\,(n|\hat{m}_-|n')(n'|\hat{m}_+|n) =$$

$$= \sum_n\sum_{n'}(n|e^{-\frac{\mathcal{H}}{kT}}|n)\Big\{(n'|\mathcal{H}|n')(n'|\mathcal{H}|n') - 2(n'|\mathcal{H}|n')(n|\mathcal{H}|n)$$

$$+(n|\mathcal{H}|n)(n|\mathcal{H}|n)\Big\}(n|\hat{m}_-|n')(n'|\hat{m}_+|n) =$$

$$= \sum_n \sum_{n'} (n|e^{-\frac{\bar{\mathcal{H}}}{kT}}|n) \Big\{ (n|\hat{m}_- \bar{\mathcal{H}}|n')(n'|\bar{\mathcal{H}}\hat{m}_+|n) - 2(n|\hat{m}_- \bar{\mathcal{H}}|n')(n'|\hat{m}_+ \bar{\mathcal{H}}|n)$$

$$+ (n|\bar{\mathcal{H}}\hat{m}_-|n')(n'|\hat{m}_+\bar{\mathcal{H}}|n)\Big\} =$$

$$= \sum_n (n|e^{-\frac{\bar{\mathcal{H}}}{kT}}|n)(n|\hat{m}_- \bar{\mathcal{H}}\bar{\mathcal{H}}\hat{m}_+ - 2\hat{m}_- \bar{\mathcal{H}}\hat{m}_+\bar{\mathcal{H}} + \bar{\mathcal{H}}\hat{m}_-\hat{m}_+\bar{\mathcal{H}}|n) =$$

$$= \mathrm{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}}\left\{\hat{m}_- \bar{\mathcal{H}}\bar{\mathcal{H}}\hat{m}_+ - 2\hat{m}_- \bar{\mathcal{H}}\hat{m}_+\bar{\mathcal{H}} + \bar{\mathcal{H}}\hat{m}_-\hat{m}_+\bar{\mathcal{H}}\right\}\right).$$

Similarily,

$$\sum_n \sum_{n'} e^{-\frac{E_{n'}}{kT}}(E_{n'}-E_n)^2 (n|\hat{m}_-|n')(n'|\hat{m}_+|n) =$$

$$= \sum_{n'} (n'|e^{-\frac{\bar{\mathcal{H}}}{kT}}|n')(n'|\bar{\mathcal{H}}\hat{m}_+\hat{m}_-\bar{\mathcal{H}} - 2\hat{m}_+\bar{\mathcal{H}}\hat{m}_-\bar{\mathcal{H}} + \hat{m}_+\bar{\mathcal{H}}\bar{\mathcal{H}}\hat{m}_-|n') =$$

$$= \mathrm{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}}\left\{\bar{\mathcal{H}}\hat{m}_+\hat{m}_-\bar{\mathcal{H}} - 2\hat{m}_+\bar{\mathcal{H}}\hat{m}_-\bar{\mathcal{H}} + \hat{m}_+\bar{\mathcal{H}}\bar{\mathcal{H}}\hat{m}_-\right\}\right).$$

Finally, then, we can write the numerator of (3.3.8) in the form:

$$\mathrm{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}}[[\hat{m}_-,\bar{\mathcal{H}}],[\bar{\mathcal{H}},\hat{m}_+]]\right) \qquad (3.3.14)$$

Using (3.3.11) and (3.3.14) we can write $\langle\nu^2\rangle$ as follows:

$$\hbar^2\langle\nu^2\rangle = \frac{\mathrm{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}}[[\hat{m}_-,\bar{\mathcal{H}}],[\bar{\mathcal{H}},\hat{m}_+]]\right)}{\mathrm{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}}[\hat{m}_-,\hat{m}_+]\right)} \qquad (3.3.15)$$

Our equations (3.3.13) and (3.3.15) are identical with those given by Usui and Kambe (1952) for

$$\frac{\hbar \int_0^\infty \nu \chi''(\nu)\, d\nu}{\int_0^\infty \chi''(\nu)\, d\nu} \quad \text{and} \quad \frac{\hbar^2 \int_0^\infty \nu^2 \chi''(\nu)\, d\nu}{\int_0^\infty \chi''(\nu)\, d\nu} \quad \text{respectively.}$$

It should be noted that (3.3.13) and (3.3.15) have been derived without resorting to any assumptions as to the temperature T. These equations are quite general and are valid at all temperatures. Furthermore, they can be applied to the case of paramagnetic resonance or to the case of nuclear magnetic resonance.

Chapter IV

Derivation of Pryce and Stevens' (1950) Equations for the First and Second Moments Directly From Equations (3.3.13) and (3.3.15)

Another derivation of the first and second moments of a line shape function has been given by Pryce and Stevens (1950). It will be shown in this section that by introducing one simplifying assumption equations (3.3.13) and (3.3.15) can be written in the form given by these authors.

Before proceeding it should be pointed out that Pryce and Stevens have found the first and second moments of the function

$$\frac{E(\nu)\,\Delta\nu}{\int_0^\infty E(\nu)\,d\nu}$$

where $E(\nu)\Delta\nu$ is the power absorbed by the spin system from the oscillating magnetic field in the frequency range ν to $\nu+\Delta\nu$.

But, by (3.3.5)

$$\frac{E(\nu)\,\Delta\nu}{\int_0^\infty E(\nu)\,d\nu} = \frac{\nu\chi''(\nu)\,\Delta\nu}{\int_0^\infty \nu\chi''(\nu)\,d\nu}$$

Pryce and Stevens have assumed in the course of their discussion that $\nu\chi''(\nu) \simeq \nu^*\chi''(\nu)$ where ν^* is the frequency about which the primary line under consideration is centered. In other words, Pryce and Stevens actually calculate the first and second moments of the function

$$\frac{\chi''(\nu)\Delta\nu}{\int_0^\infty \chi''(\nu)d\nu}$$

which is our $f(\nu)$. We should, then, be able to derive the expressions given by Pryce and Stevens directly from our equations (3.3.13) and (3.3.15).

It should be noted that Pryce and Stevens do not consider explicitly the truncation of $\mathfrak{H}$ and $\mathfrak{m}$; they have, instead, introduced projection operators which perform these operations for them. We shall now introduce projection operators which perform the truncations for us so that (3.3.13) and (3.3.15) can be written in terms of $\mathfrak{H}$ and $\mathfrak{m}$ instead of $\bar{\mathfrak{H}}$ and $\hat{\mathfrak{m}}$.

We shall define an operator P_λ , which we shall call a projection operator, such that

$$(\eta, i \,|\, P_\lambda \,|\, \mu, k) = \delta_{\eta\lambda}\, \delta_{\mu\lambda}\, \delta_{ik} \tag{4.1}$$

As a consequence of (4.1) we have $P_\lambda P_{\lambda'} = P_\lambda \delta_{\lambda\lambda'}$ (4.2)

Let us consider the matrix representation of a general operator O with respect to the totality of eigenstates $|\alpha, k)$ of $\mathfrak{H}^{(0)}$. ($\alpha = 1,2,\ldots\ldots,\Omega$ where Ω = the number of different eigenvalues of $\mathcal{H}^{(0)}$; $k = 1,2,\ldots,g_\alpha$ where g_α is the degeneracy of the eigenvalue E_α of $\mathcal{H}^{(0)}$.) The general matrix element of O in this representation is then

$$(\alpha,i|O|\beta,k)$$

Now, the matrix elements of $P_\alpha OP_\beta$ are

$$(\eta,\ell|P_\alpha OP_\beta|\mu,m) = (\alpha,i|O|\beta,k)\,\delta_{\eta\alpha}\,\delta_{\mu\beta} \quad \text{using (4.1)}$$

Clearly, then, the matrix representation of any operator O with respect to the totality of eigenstates of $\mathcal{H}^{(0)}$ can be written in the form

$$O = \sum_{\eta=1}^{\Omega}\sum_{\mu=1}^{\Omega} P_\eta O P_\mu \qquad (4.3)$$

In section 3.2 we introduced the operator $\bar{\mathcal{H}}$ which is that part of $\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}$ which commutes with $\mathcal{H}^{(0)}$. Taking the matrix representations of $\mathcal{H}$ and $\mathcal{H}^{(0)}$ with respect to the states $|\alpha,k)$ and writing $\mathcal{H}$ in the form given by (4.3), we find easily that

$$\Big[\sum_\eta\sum_\mu P_\eta \mathcal{H} P_\mu \;,\; \mathcal{H}^{(0)}\Big] = 0 \qquad \text{if and only if} \quad \mu = \eta$$

That is $$\bar{\mathcal{H}} = \sum_{\mu=1}^{\Omega} P_\mu \mathcal{H} P_\mu \qquad (4.4)$$

Let us now write $\hat{M}$ in terms of projection operators. We recall from section 3.2 that the circumflex was introduced over $\mathcal{U}^{(3)}$ and hence over M in order to eliminate from $f(\nu)$ any of the primary lines in which we are not interested. Here we are interested only in the primary line at ν^* so that we shall define the operator $\hat{M}$ such that it has matrix elements

$$(\alpha,i\,|\,\hat{m}\,|\,\beta,k) = \begin{cases} (\alpha,i\,|\,m\,|\,\beta,k) & \text{if } |E_\alpha - E_\beta| = \hbar\nu^* \\ 0 & \text{otherwise} \end{cases}$$

Consider the operator

$$\sum_{\alpha,\beta} P_\alpha m P_\beta$$

where $\sum_{\alpha,\beta}$ means sum over all values of α and β wherein $|E_\alpha - E_\beta| = \hbar\nu^*$

The matrix elements of $\sum_{\alpha,\beta} P_\alpha MP_\beta$ are then:

$$(\alpha,i\,|\sum_{\alpha,\beta} P_\alpha m P_\beta\,|\,\beta,k) = \begin{cases} (\alpha,i\,|\,m\,|\,\beta,k) & \text{if } |E_\alpha - E_\beta| = \hbar\nu^* \\ 0 & \text{otherwise} \end{cases}$$

Thus we can write

$$\hat{m} = \sum_{\alpha,\beta} P_\alpha m P_\beta \tag{4.5}$$

From (4.5) we can immediately write

$$\hat{m}_+ = \sum\sum_{\alpha<\beta} P_\beta m P_\alpha \tag{4.6}$$

$$\hat{m}_- = \sum_{\alpha<\beta}\sum P_\alpha m P_\beta \tag{4.7}$$

where $\sum_{\alpha<\beta}\sum$ means summation over all values of α and β wherein $E_\beta - E_\alpha = \hbar\nu^*$.(The symbol $\sum_{\alpha<\beta}\sum$ actually denotes a single summation since $E_\beta = E_\alpha + \hbar\nu^*$. We use the notation $\sum_{\alpha<\beta}\sum$ for convenience.)

Strictly speaking, although (4.5) is an exact expression, (4.6) and (4.7) involve the assumption that $\overline{\mathcal{H}^{(1)}}$ is not too large. We have certainly that

$$\hat{m} = \sum_{\alpha<\beta}\sum \left\{ P_\beta m P_\alpha + P_\alpha m P_\beta \right\}$$

and $\hat{m} = \hat{m}_+ + \hat{m}_-$

However, we recall that we have defined $\hat{m}_+$ and $\hat{m}_-$ by equations (3.3.9) and (3.3.10) respectively. To write (4.6) and (4.7) then we require that if

$$\mathcal{H}^{(0)} |\alpha, i) = E_\alpha |\alpha, i)$$

and $$\overline{\mathcal{H}} \; |\alpha, i) = E_{\alpha,i} |\alpha, i)$$

then $E_\alpha < E_\beta$ implies that $E_{\alpha,i} < E_{\beta,k}$ for all i and k.

If $\overline{\mathcal{H}^{(1)}}$ is not too large then this in fact will be true.

In Appendix A we shall rewrite (4.5) in another form. We shall show in Appendix B that equation (6) of Ishiguro, Usui, and Kambe (1952) is a special case of (4.5).

Using (4.4) to (4.7), equations (3.3.13) and (3.3.15) can be transformed into equations containing $\mathcal{H}$ and m rather than $\overline{\mathcal{H}}, \hat{m}, \hat{m}_-,$ and $\hat{m}_+$.

Let us consider the denominator of (3.3.13) and (3.3.15). First,

$$e^{-\frac{\overline{\mathcal{H}}}{kT}} = e^{-\frac{1}{kT}\sum_{\mu} P_\mu \mathcal{H} P_\mu} \qquad \text{by (4.4)}$$

Now, $[\hat{m}_-, \hat{m}_+] = [\sum\sum_{\alpha<\beta} P_\alpha m P_\beta, \sum\sum_{\alpha'<\beta'} P_{\beta'} m P_{\alpha'}] =$ from (4.6) and (4.7)

$$= \sum\sum_{\alpha<\beta} \{ P_\alpha m P_\beta m P_\alpha - P_\beta m P_\alpha m P_\beta \} \qquad \text{using (4.2)}$$

Thus, $e^{-\frac{\overline{\mathcal{H}}}{kT}} [\hat{m}_-, \hat{m}_+] = \sum\sum_{\alpha<\beta} \{ e^{-\frac{1}{kT}\sum_{\mu} P_\mu \mathcal{H} P_\mu} P_\alpha m P_\beta m P_\alpha - e^{-\frac{1}{kT}\sum_{\mu} P_\mu \mathcal{H} P_\mu} P_\beta m P_\alpha m P_\beta \} =$

$$= \sum\sum_{\alpha<\beta} \{ e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} P_\alpha m P_\beta m P_\alpha - e^{-\frac{P_\beta \mathcal{H} P_\beta}{kT}} P_\beta m P_\alpha m P_\beta \}.$$

where we have again used (4.2).

Using (4.2) again and the fact that for any matrices A,B, and C Trace ABC=Trace CAB cyclically, we have:

$$\mathrm{Trace}\, e^{-\frac{\mathcal{H}}{kT}} [\hat{m}_-, \hat{m}_+] = \sum_{\alpha<\beta}\sum \mathrm{Trace}\left(e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} P_\alpha m P_\beta m - e^{-\frac{P_\beta \mathcal{H} P_\beta}{kT}} P_\beta m P_\alpha m \right) \qquad (4.8)$$

Consider, now, the numerator of (3.3.13). Using (4.2), (4.4), and (4.5) we can write

$$[\bar{\mathcal{H}}, \hat{m}] = \sum_{\alpha,\beta} \left\{ P_\alpha \mathcal{H} P_\alpha m P_\beta - P_\alpha m P_\beta \mathcal{H} P_\beta \right\}$$

and

$$\hat{m}[\bar{\mathcal{H}}, \hat{m}] = \sum_{\alpha,\beta} \left\{ P_\beta m P_\alpha \mathcal{H} P_\alpha m P_\beta - P_\beta m P_\alpha m P_\beta \mathcal{H} P_\beta \right\}$$

Thus, Trace $e^{-\frac{\bar{\mathcal{H}}}{kT}} \hat{m}[\bar{\mathcal{H}}, \hat{m}] =$

$$= \sum_{\alpha,\beta} \mathrm{Trace}\, e^{-\frac{P_\beta \mathcal{H} P_\beta}{kT}} \left(P_\beta m P_\alpha \mathcal{H} P_\alpha m P_\beta - P_\beta m P_\alpha m P_\beta \mathcal{H} P_\beta \right) =$$

$$\left.\begin{aligned} = \sum_{\alpha<\beta}\sum \mathrm{Trace} \Big\{ & e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \left(P_\alpha m P_\beta \mathcal{H} P_\beta m - P_\alpha m P_\beta m P_\alpha \mathcal{H} \right) \\ & + e^{-\frac{P_\beta \mathcal{H} P_\beta}{kT}} \left(P_\beta m P_\alpha \mathcal{H} P_\alpha m - P_\beta m P_\alpha m P_\beta \mathcal{H} \right) \Big\} \end{aligned}\right\} \qquad (4.9)$$

Consider, now, the numerator of (3.3.15). Using (4.2), (4.4), (4.6), and (4.7) we can write

$$[\hat{m}_-, \bar{\mathcal{H}}] = \sum_{\alpha<\beta}\sum \left\{ P_\alpha m P_\beta \mathcal{H} P_\beta - P_\alpha \mathcal{H} P_\alpha m P_\beta \right\}$$

and

$$[\bar{\mathcal{H}}, \hat{m}_+] = \sum_{\alpha<\beta}\sum \left\{ P_\beta \mathcal{H} P_\beta m P_\alpha - P_\beta m P_\alpha \mathcal{H} P_\alpha \right\}$$

so that $[[\hat{m}_-, \bar{\mathcal{H}}],[\bar{\mathcal{H}}, \hat{m}_+]] =$

$$\begin{aligned} = \sum_{\alpha<\beta}\sum \Big\{ \big(& P_\alpha m P_\beta \mathcal{H} P_\beta \mathcal{H} P_\beta m P_\alpha - P_\alpha \mathcal{H} P_\alpha m P_\beta \mathcal{H} P_\beta m P_\alpha \\ & - P_\alpha m P_\beta \mathcal{H} P_\beta m P_\alpha \mathcal{H} P_\alpha + P_\alpha \mathcal{H} P_\alpha m P_\beta m P_\alpha \mathcal{H} P_\alpha \big) \\ - \big(& P_\beta \mathcal{H} P_\beta m P_\alpha m P_\beta \mathcal{H} P_\beta - P_\beta \mathcal{H} P_\beta m P_\alpha \mathcal{H} P_\alpha m P_\beta \\ & - P_\beta m P_\alpha \mathcal{H} P_\alpha m P_\beta \mathcal{H} P_\beta + P_\beta m P_\alpha \mathcal{H} P_\alpha \mathcal{H} P_\alpha m P_\beta \big) \Big\} \end{aligned}$$

Thus, $\text{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}} [[\hat{m}_-, \bar{\mathcal{H}}],[\bar{\mathcal{H}}, \hat{m}_+]]\right) =$

$$\left.\begin{aligned} = \sum_{\alpha<\beta}\sum \text{Trace} \Big\{ e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \big(& P_\alpha m P_\beta \mathcal{H} P_\beta \mathcal{H} P_\beta m - P_\alpha \mathcal{H} P_\alpha m P_\beta \mathcal{H} P_\beta m \\ & - P_\alpha m P_\beta \mathcal{H} P_\beta m P_\alpha \mathcal{H} + P_\alpha \mathcal{H} P_\alpha m P_\beta m P_\alpha \mathcal{H} \big) \\ - e^{-\frac{P_\beta \mathcal{H} P_\beta}{kT}} \big(& P_\beta \mathcal{H} P_\beta m P_\alpha m P_\beta \mathcal{H} - P_\beta \mathcal{H} P_\beta m P_\alpha \mathcal{H} P_\alpha m \\ & - P_\beta m P_\alpha \mathcal{H} P_\alpha m P_\beta \mathcal{H} + P_\beta m P_\alpha \mathcal{H} P_\alpha \mathcal{H} P_\alpha m \big) \Big\} \end{aligned}\right\} \quad (4.10)$$

We have now transformed equations (3.3.13) and (3.3.15) into forms containing $\mathcal{H}$ and M rather than $\bar{\mathcal{H}}$, $\hat{m}$, $\hat{m}_-$, and $\hat{M}_+$. It should be noted that no assumptions have been introduced in writing equations (4.8), (4.9), and (4.10).

By introducing one assumption at this point, we shall be able to produce Pryce and Stevens' equations (1), (2), and (3) from our equations (4.8), (4.9), and (4.10) respectively.

Using $\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}$ we can write

$$P_\alpha \mathcal{H} P_\alpha = P_\alpha \mathcal{H}^{(0)} P_\alpha + P_\alpha \mathcal{H}^{(1)} P_\alpha = E_\alpha P_\alpha + P_\alpha \mathcal{H}^{(1)} P_\alpha \tag{4.11}$$

Since $\left[P_\alpha , P_\alpha \mathcal{H}^{(1)} P_\alpha \right] = 0$ we have $e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} = e^{-\frac{E_\alpha P_\alpha}{kT}} e^{-\frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}}$

We now assume that to a first approximation $e^{-\frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}} \simeq 1$

so that

$$e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}} \tag{4.12}$$

This is essentially the assumption used by Pryce and Stevens when deriving their general equations (1), (2), and (3), and by Usui and Kambe at the beginning of section 4 of their paper.

When assumption (4.12) is used (4.8), (4.9) and (4.10) can be written as follows:

$$\mathrm{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}}[\hat{m}_-,\hat{m}_+]\right) \simeq \left(1-e^{-\frac{h\nu^*}{kT}}\right)\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\ P_\alpha m P_\beta m\,. \tag{4.13}$$

$$\left.\begin{aligned}\mathrm{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}}\hat{m}[\bar{\mathcal{H}},\hat{m}]\right) \simeq \left(1-e^{-\frac{h\nu^*}{kT}}\right)\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\big(&P_\beta \mathcal{H} P_\beta m P_\alpha m \\ &- P_\alpha \mathcal{H} P_\alpha m P_\beta m\big)\end{aligned}\right\} \tag{4.14}$$

$$\left.\begin{aligned}&\mathrm{Trace}\left(e^{-\frac{\bar{\mathcal{H}}}{kT}}[[\hat{m}_-,\bar{\mathcal{H}}],[\bar{\mathcal{H}},\hat{m}_+]]\right) \simeq \\ &\simeq \left(1-e^{-\frac{h\nu^*}{kT}}\right)\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\big(P_\beta \mathcal{H} P_\beta \mathcal{H} P_\beta m P_\alpha m \\ &\qquad - 2P_\alpha \mathcal{H} P_\alpha m P_\beta \mathcal{H} P_\beta m \\ &\qquad + P_\alpha \mathcal{H} P_\alpha \mathcal{H} P_\alpha m P_\beta m\big)\end{aligned}\right\} \tag{4.15}$$

Using (4.11) and (4.2) we can write, for example:

$$P_\alpha \mathcal{H} P_\alpha \mathcal{H} P_\alpha = \left(E_\alpha P_\alpha + P_\alpha \mathcal{H}^{(1)} P_\alpha\right)\left(E_\alpha P_\alpha + P_\alpha \mathcal{H}^{(1)} P_\alpha\right) =$$

$$= E_\alpha^2 P_\alpha + 2E_\alpha P_\alpha \mathcal{H}^{(1)} P_\alpha + P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha$$

Finally, then, when approximation (4.12) is valid we have the following relationships holding:

$$h\langle\nu\rangle = h\nu^* + \frac{\sum\sum_{\alpha<\beta} e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}\right)}{\sum\sum_{\alpha<\beta} e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\, P_\alpha \mathfrak{M} P_\beta \mathfrak{M}} \tag{4.16}$$

$$\left.\begin{aligned} h^2\langle\nu^2\rangle = (h\nu^*)^2 &+ 2h\nu^* \frac{\sum\sum_{\alpha<\beta} e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}\right)}{\sum\sum_{\alpha<\beta} e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\, P_\alpha \mathfrak{M} P_\beta \mathfrak{M}} \\ &+ \frac{\sum\sum_{\alpha<\beta} e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - 2 P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} + P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}\right)}{\sum\sum_{\alpha<\beta} e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\, P_\alpha \mathfrak{M} P_\beta \mathfrak{M}} \end{aligned}\right\} \tag{4.17}$$

If we now define $\langle\Delta\nu\rangle$ = the first moment of $f(\nu)$ about ν^* and $\langle\Delta\nu^2\rangle$ = the second moment of $f(\nu)$ about ν^* then

$$\langle\Delta\nu\rangle = \langle\nu\rangle - \nu^*$$

and $$\langle\Delta\nu^2\rangle = \langle\nu^2\rangle - 2\nu^*\langle\Delta\nu\rangle - \nu^{*2}$$

so that

$$h\langle\Delta\nu\rangle = \frac{\sum\sum_{\alpha<\beta} e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}\right)}{\sum\sum_{\alpha<\beta} e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\, P_\alpha \mathfrak{M} P_\beta \mathfrak{M}} \tag{4.18}$$

$$h^2\langle\Delta\nu^2\rangle = \frac{\sum\limits_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - 2P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} + P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}\right)}{\sum\limits_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\,\mathrm{Trace}\, P_\alpha \mathfrak{M} P_\beta \mathfrak{M}} \qquad (4.19)$$

It should be noticed that our $\langle\Delta\nu^2\rangle$ does not give the second moment of $f(\nu)$ about the mean value of ν, that is, $\langle\Delta\nu^2\rangle$ is not the second central moment of $f(\nu)$ since this quantity is given by $\langle\nu^2\rangle - (\langle\nu\rangle)^2$. If $\langle\nu\rangle = \nu^*$, then the second central moment of $f(\nu)$ and $\langle\Delta\nu^2\rangle$ are equal.

Equations (4.18) and (4.19) are identical to the Pryce and Stevens' equations for the first and second moments of $E(\nu) \Big/ \int_0^\infty E(\nu)d\nu$ about the frequency ν^*.

Chapter V

Sufficient Conditions for Van Vleck's (1948) Expression for the Second Moment to be Valid

Another derivation of an expression for the second moment of a line shape function has been given by Van Vleck (1948). Van Vleck has not defined explicitly the line shape function he is considering but we shall show in this chapter that by applying suitable assumptions to our expression (3.3.15), which is the second moment of $f(\nu) = \chi''(\nu) \Big/ \int_0^\infty \chi''(\nu)\,d\nu$, the generalization of Van Vleck's equation (3) can be found.

Van Vleck has considered the special case which we have called condition (3.2.2) that is, the case when no crystalline field is present. He has considered the operator portion of m to be S_x , and he has written the second moment of his line shape function as

$$\hbar^2\langle\nu^2\rangle = -\frac{\text{Trace}\left([\bar{\mathcal{H}}, S_x]\right)^2}{\text{Trace}\left(S_x\right)^2} \tag{5.1}$$

where we use $\bar{\mathcal{H}}$ to denote the truncated Hamiltonian. As we have discussed earlier, it is necessary in general to use $\hat{M}$ rather than M when discussing the problem. In the general case, then, the Van Vleck expression becomes

$$h^2\langle\nu^2\rangle = -\frac{\mathrm{Trace}\left([\bar{\mathcal{H}},\hat{m}]\right)^2}{\mathrm{Trace}\left(\hat{m}\right)^2} \qquad (5.2)$$

It will be shown in Appendix C that S_x and $\hat{S}_x$ are equal when there is no crystalline field and when the magnetic field is parallel to the z-axis.

Van Vleck's derivation for the second moment appeared before those of Pryce and Stevens, and Usui and Kambe. The methods used by these latter authors, and by us in Chapter III, merely involve a more refined approach to the problem. The most important point to notice is that (5.2) does not contain the temperature, T, whereas (3.3.15) does. In deriving his general expression, Van Vleck has not taken into account the Boltzmann factors which we introduced in (3.3.8) and which gave rise to the factor $e^{-\frac{\mathcal{H}}{kT}}$ in (3.3.15). There seems to be no doubt, however, that for sufficiently high temperatures the Van Vleck method, that is, equation (5.2), yields correct results. In fact, Usui and Kambe (1952) have applied their general equations to the special case considered by Van Vleck (that is, no crystalline field and energy levels of each spin equidistant) and found that if $\frac{h\nu^*}{kT} \ll 1$, then their results are identical with those given by Van Vleck. Secondly, Ishiguro, Usui, and Kambe (1951) have applied (5.2) to the case where a crystalline field is present and have stated that the results so obtained have also been found when the Pryce and Stevens' equations (1) and (3) are applied to this case and are restricted to sufficiently high temperatures. We have checked this independently.

From the foregoing discussion it would appear that by applying suitable approximations to (3.3.15) it should be possible to arrive at (5.2), that is, it should be possible to give sufficient conditions under which (5.2) yields valid results for the second moment. There has, however, been no explicit discussion of this point in the literature. The remainder of this section, then, will be devoted to finding such conditions.

For the present, we shall find under which conditions the expression

$$h^2\langle\nu^2\rangle = \frac{\sum_n \sum_{n'} (E_{n'}-E_n)^2 \, |\langle n|\hat{m}|n'\rangle|^2}{\sum_n \sum_{n'} |\langle n|\hat{m}|n'\rangle|^2} \qquad (5.3)$$

which is equivalent to (5.2), is a valid approximation of (3.3.8), which is equivalent to (3.3.15). We shall see that the following two assumptions are sufficient if (5.3) is to be a valid approximation of (3.3.8):

1) $\mathcal{H}^{(0)} \gg \overline{\mathcal{H}^{(1)}}$ and $e^{-\frac{\overline{\mathcal{H}^{(1)}}}{kT}} \simeq 1$ so that to a first approximation the exponentials in (3.3.8) can be replaced by their values when $\overline{\mathcal{H}^{(1)}} = 0$.

2) The temperature is high enough so that $|E_\alpha - E_\beta| \ll kT$ for all values of α and β.

Let us now perform these calculations. We recall from Chapter III that the functions $|\alpha, i)$ are the simultaneous eigenfunctions of $\mathcal{H}^{(0)}$ and $\overline{\mathcal{H}}$. In equation (3.3.8), then, we shall put $|n) = |\alpha, i)$ and $E_n = E_{\alpha,i}$ where $E_{\alpha,i} = E_\alpha + (\alpha, i|\overline{\mathcal{H}^{(1)}}|\alpha, i)$. Thus, (3.3.8) can be written:

$$\hbar^2\langle\nu^2\rangle = \frac{\sum_{\alpha=1}^{\Omega}\sum_{\beta=1}^{\Omega}\sum_{i=1}^{g_\alpha}\sum_{\ell=1}^{g_\beta}\left(E_{\beta,\ell}-E_{\alpha,i}\right)^2\left(e^{-\frac{E_{\alpha,i}}{kT}}-e^{-\frac{E_{\beta,\ell}}{kT}}\right)|(\alpha,i|\hat{m}|\beta,\ell)|^2}{\sum_{\alpha=1}^{\Omega}\sum_{\beta=1}^{\Omega}\sum_{i=1}^{g_\alpha}\sum_{\ell=1}^{g_\beta}\left(e^{-\frac{E_{\alpha,i}}{kT}}-e^{-\frac{E_{\beta,\ell}}{kT}}\right)|(\alpha,i|\hat{m}|\beta,\ell)|^2} =$$

$$\simeq \frac{\sum_\alpha\sum_\beta\left(e^{-\frac{E_\alpha}{kT}}-e^{-\frac{E_\beta}{kT}}\right)\sum_i\sum_\ell\left(E_{\beta,\ell}-E_{\alpha,i}\right)^2|(\alpha,i|\hat{m}|\beta,\ell)|^2}{\sum_\alpha\sum_\beta\left(e^{-\frac{E_\alpha}{kT}}-e^{-\frac{E_\beta}{kT}}\right)\sum_i\sum_\ell|(\alpha,i|\hat{m}|\beta,\ell)|^2}$$

using the first assumption above.

$$= \frac{\left(1-e^{-\frac{\hbar\nu^*}{kT}}\right)\sum_{\alpha,\beta}e^{-\frac{E_\alpha}{kT}}\sum_i\sum_\ell\left(E_{\beta,\ell}-E_{\alpha,i}\right)^2|(\alpha,i|m|\beta,\ell)|^2}{\left(1-e^{-\frac{\hbar\nu^*}{kT}}\right)\sum_{\alpha,\beta}e^{-\frac{E_\alpha}{kT}}\sum_i\sum_\ell|(\alpha,i|m|\beta,\ell)|^2}$$

using the definition of M (see Chapter III).

$$= \frac{\sum_{\alpha}\sum_{\beta} e^{-\frac{E_\alpha}{kT}} \sum_{i}\sum_{\ell} (E_{\beta,\ell} - E_{\alpha,i})^2 |(\alpha,i|\hat{m}|\beta,\ell)|^2}{\sum_{\alpha}\sum_{\beta} e^{-\frac{E_\alpha}{kT}} \sum_{i}\sum_{\ell} |(\alpha,i|\hat{m}|\beta,\ell)|^2}$$

$$\simeq \frac{\sum_{\alpha}\sum_{\beta}\sum_{i}\sum_{\ell} (E_{\beta,\ell} - E_{\alpha,i})^2 |(\alpha,i|\hat{m}|\beta,\ell)|^2}{\sum_{\alpha}\sum_{\beta}\sum_{i}\sum_{\ell} |(\alpha,i|\hat{m}|\beta,\ell)|^2}$$

using the second assumption above.

Thus, we have that when the above two assumptions are applied to (3.3.8) we get

$$\hbar^2 \langle \nu^2 \rangle = \frac{\sum_{\alpha=1}^{\Omega}\sum_{\beta=1}^{\Omega}\sum_{i=1}^{g_\alpha}\sum_{\ell=1}^{g_\beta} (E_{\beta,\ell} - E_{\alpha,i})^2 |(\alpha,i|\hat{m}|\beta,\ell)|^2}{\sum_{\alpha=1}^{\Omega}\sum_{\beta=1}^{\Omega}\sum_{i=1}^{g_\alpha}\sum_{\ell=1}^{g_\beta} |(\alpha,i|\hat{m}|\beta,\ell)|^2}$$

which is identical except for the notation with equation (5.3).

We have shown that by applying two assumptions to our equation (3.3.8), equation (5.3) can be found. However, it should immediately be noticed that the second assumption is most unreasonable. The energy difference between the highest and the lowest values of E_α is at least $N\hbar\nu^+$ so that the second assumption implies that $T \gg \frac{N\hbar\nu^*}{k} \simeq 10^{23}\ {}^{\circ}K$. Since it has been shown that (5.2) yields experimentally valid results for T approximately equal room temperature, it would be desirable to show that assumption 2) can be replaced by a much weaker condition. This will be done in the remainder of this chapter. It will turn out that temperatures much below room temperature are sufficiently high for the validity of the Van Vleck method (as has been generally assumed).

It will be recalled that (4.17) was obtained from (3.3.15) by introducing one assumption, namely, (4.12). This is identical with the assumption 1) given above. Therefore, in order to find conditions to replace assumption 2), we can simply find under what conditions (5.2) is a valid approximation for (4.17).

In order to compare equations (4.17) and (5.2), it will be convenient to rewrite (5.2) in a form containing $\mathcal{H}$ and M rather $\bar{\mathcal{H}}$ and $\hat{M}$, that is, we shall substitute (4.4) and (4.5) into (5.2). Thus,

$$\mathrm{Trace}\,(\hat{m})^2 = \mathrm{Trace} \sum_{\alpha,\beta} \sum_{\alpha',\beta'} P_\alpha m P_\beta P_{\alpha'} m P_{\beta'} = \qquad \text{using (4.5)}$$

$$= \sum_{\alpha,\beta} \mathrm{Trace}\, P_\alpha m P_\beta m = 2 \sum_{\alpha<\beta}\sum \mathrm{Trace}\, P_\alpha m P_\beta m$$

$$\mathrm{Trace}\left([\bar{\mathcal{H}},\hat{m}]\right)^2 = \mathrm{Trace}\Big(\sum_{\alpha,\beta}\{P_\alpha \mathcal{H} P_\alpha m P_\beta - P_\alpha m P_\beta \mathcal{H} P_\beta\}\Big)^2 = \qquad \text{using (4.4) and (4.5)}$$

$$= -2 \sum_{\alpha<\beta}\sum \mathrm{Trace}\left(P_\beta \mathcal{H} P_\beta \mathcal{H} P_\beta m P_\alpha m - 2 P_\alpha \mathcal{H} P_\alpha m P_\beta \mathcal{H} P_\beta m + P_\alpha \mathcal{H} P_\alpha \mathcal{H} P_\alpha m P_\beta m\right).$$

Thus,

$$\hbar^2\langle\nu^2\rangle = \frac{\sum\sum_{\alpha<\beta} \text{Trace}\left(P_\beta \mathcal{H} P_\beta \mathcal{H} P_\beta \mathfrak{m} P_\alpha \mathfrak{m} - 2P_\alpha \mathcal{H} P_\alpha \mathfrak{m} P_\beta \mathcal{H} P_\beta \mathfrak{m} + P_\alpha \mathcal{H} P_\alpha \mathcal{H} P_\alpha \mathfrak{m} P_\beta \mathfrak{m}\right)}{\sum\sum_{\alpha<\beta} \text{Trace}\ P_\alpha \mathfrak{m} P_\beta \mathfrak{m}}$$

Using equations (4.11) and (4.2) we have, finally:

$$\left.\begin{aligned} \hbar^2\langle\nu^2\rangle = (\hbar\nu^*)^2 + 2\hbar\nu^* \frac{\sum\sum_{\alpha<\beta} \text{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{m} P_\alpha \mathfrak{m} - P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{m} P_\beta \mathfrak{m}\right)}{\sum\sum_{\alpha<\beta} \text{Trace}\ P_\alpha \mathfrak{m} P_\beta \mathfrak{m}} \\ + \frac{\sum\sum_{\alpha<\beta} \text{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{m} P_\alpha \mathfrak{m} - 2P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{m} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{m} + P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{m} P_\beta \mathfrak{m}\right)}{\sum\sum_{\alpha<\beta} \text{Trace}\ P_\alpha \mathfrak{m} P_\beta \mathfrak{m}} \end{aligned}\right\} \quad (5.4)$$

We see that equation (5.4) is identical to (4.17) but with the Boltzmann factors, $e^{-\frac{E_\alpha}{kT}}$, replaced by unity in this last equation. As before, it seems that the procedure can only be justified if $T \gg \frac{N\hbar\nu^*}{k}$. We shall see that this is not the case.

The procedure now, will be to consider (4.17) for the case when we can write:

$$\hat{\mathfrak{m}} = \sum_{i=1}^{N} m_i \quad (5.5)$$

$$\mathcal{H}^{(1)} = \sum\sum_{1\le i<j\le N} \mathcal{H}_{ij}^{(1)} \quad (5.6)$$

where $\mathcal{H}^{(1)}_{ij}$ is symmetrical in i and j

and, then, in our results to replace all exponentials containing the temperature by unity. The results so obtained will be identical to those found if (5.4) had been used. We shall then give conditions under which the replacing of these exponentials by unity is valid. (The restrictions (5.5) and (5.6) are definitely not severe. If we speak of a "system of spins", that is, if we look upon the spins as separate physical entities, then we must be able to write (5.5). Secondly, most forces of interest in this field, for example, dipole-dipole forces or exchange forces, can be written as two-body forces, that is, in the form given by (5.6)).

It will prove very inconvenient to perform the calculations at this time; this will be done in detail in Chapter VI. We shall, then, only state the conditions under which (5.2) yields a valid approximation for the second moment of $f(\nu)$: We suppose that condition (4.12) holds. Then, if the energy values of the unperturbed spin are non-degenerate and are labelled a_1, a_2, a_3, ... a_R (where the phrase "energy levels of the unperturbed spin" means the energy values each of the N spins has when the Hamiltonian of the system is considered to be $\mathcal{H}^{(0)}$), and if $\mathfrak{m}$ and $\mathcal{H}^{(1)}$ can be written the forms (5.5) and (5.6) respectively, then, if Q pairs of the energy values a_1, a_2, a_3, ...,a_R have energy separation $h\nu^*$, equation (5.2) yields a valid approximation for the second moment of $f(\nu)$ if

$$\frac{a_{max.} - a_{min.}}{kT} \ll \frac{1}{4} \tag{5.7}$$

Chapter VI

An Application of Equations (4.18) and (4.19)

We shall now apply equations (4.18) and (4.19) to the case when the unperturbed spin has R energy values a_1, a_2, a_3, .., a_R which are all non-degenerate. We shall suppose that Q pairs of these energy values have energy separation $\hbar\nu^*$. Before proceeding it will be convenient to establish a method of labelling the energy levels of the unperturbed spin.

The energy level systems of the unperturbed spin is such that Q pairs of levels have energy separation $\hbar\nu^*$. We can always construct a set of Q positive integers (1,x,y,....,z) where $1<x<y<\cdots\cdots<z\leq R-1$ and a second set of positive integers $(z+2, z+3, \ldots\ldots\ldots, R)$ such that

$$a_2-a_1 = a_{x+1}-a_x = a_{y+1}-a_y = \cdots\cdots = a_{z+1}-a_z = \hbar\nu^*$$

and for any r in the set $(z+2, z+3, \ldots\ldots, R)$, $|a_\rho - a_r| \neq \hbar\nu^*$ for $\rho = 1,2,\ldots, R$. That is, if s is in the set (1,x,y,....) then $a_{s+1}-a_s = \hbar\nu^*$ and if s is not in the set (1,x,y,....) then $|a_\rho - a_s| \neq \hbar\nu^*$ for $\rho=1,2,\ldots, R$. (It should be noticed that if $z=R-1$ then the second set is the null set.)

The following example should illustrate this method of labelling the energy levels of the unperturbed spin. (For convenience we shall call the set of Q positive integers

(1,x,y,...,) the set G.) Let us suppose that the energy level system for the unperturbed spin is given by Diagram VII:

Diagram VII

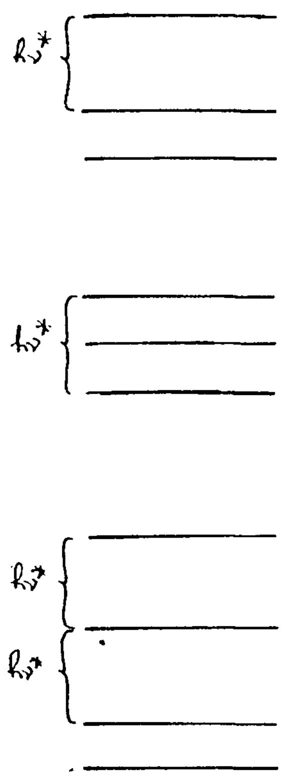
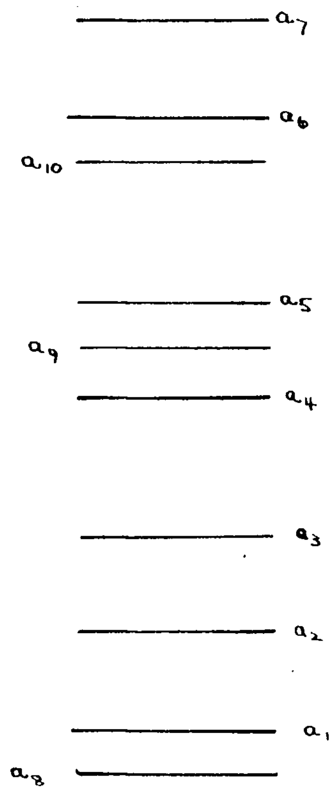


Diagram VIII



We have R = 10 and Q = 4. Using the above method the labels of the energy levels are given in Diagram VIII. We see that the set $\mathcal{G}$ is (1,2,4,6) and the second set is (8,9,10) and that $a_2 - a_1 = a_3 - a_2 = a_5 - a_4 = a_7 - a_6 = h\nu^*$
and $|a_p - a_r| \neq h\nu^*$ for $p = 1,2,\dots,10$ and $r = 8,9,10$.

Let us first of all evaluate the traces in (4.18) and (4.19) with respect to the eigenfunctions of $\mathcal{H}^{(0)}$, $|\mu,i)$. (μ = 1,2,....,Ω ; i = 1,2,.....,g_μ , the degeneracy of E_μ.):

$$\text{Trace } P_\alpha M P_\beta M = \sum_{\mu=1}^{\Omega}\sum_{i=1}^{g_\mu} (\mu,i|P_\alpha m P_\beta m|\mu,i) =$$

$$= \sum_{i=1}^{g_\alpha} (\alpha,i|P_\alpha m P_\beta m|\alpha,i) = \qquad \text{by } (4.1)$$

$$= \sum_{i=1}^{g_\alpha}\sum_{\mu=1}^{\Omega}\sum_{k=1}^{g_\mu}\sum_{\eta=1}^{\Omega}\sum_{\ell=1}^{g_\eta}\sum_{\rho=1}^{\Omega}\sum_{q=1}^{g_\rho} (\alpha,i|P_\alpha|\mu,k)(\mu,k|m|\eta,\ell)(\eta,\ell|P_\beta|\rho,q)(\rho,q|m|\alpha,i) =$$

$$= \sum_{i=1}^{g_\alpha}\sum_{k=1}^{g_\beta} |(\alpha,i|m|\beta,k)|^2 \qquad (6.1)$$

$$\text{Trace } P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta m = \sum_{\mu=1}^{\Omega}\sum_{i=1}^{g_\mu} (\mu,i|P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta m|\mu,i) =$$

$$= \sum_{i=1}^{g_\alpha}\sum_{k=1}^{g_\alpha}\sum_{j=1}^{g_\beta} (\alpha,i|\mathcal{H}^{(1)}|\alpha,k)(\alpha,k|m|\beta,j)(\beta,j|m|\alpha,i) \qquad (6.2)$$

$$\text{Trace } P_\beta \mathcal{H}^{(1)} P_\beta m P_\alpha m = \sum_{i=1}^{g_\beta}\sum_{k=1}^{g_\beta}\sum_{j=1}^{g_\alpha} (\beta,i|\mathcal{H}^{(1)}|\beta,k)(\beta,k|m|\alpha,j)(\alpha,j|m|\beta,i) \qquad (6.3)$$

$$\text{Trace } P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta m =$$

$$= \sum_{i=1}^{g_\alpha}\sum_{k=1}^{g_\alpha}\sum_{j=1}^{g_\beta}\sum_{\ell=1}^{g_\alpha} (\alpha,i|\mathcal{H}^{(1)}|\alpha,k)(\alpha,k|\mathcal{H}^{(1)}|\alpha,\ell)(\alpha,\ell|m|\beta,j)(\beta,j|m|\alpha,i) \qquad (6.4)$$

$$\text{Trace } P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta m P_\alpha m =$$

$$= \sum_{i=1}^{g_\beta}\sum_{k=1}^{g_\beta}\sum_{j=1}^{g_\alpha}\sum_{\ell=1}^{g_\beta} (\beta,i|\mathcal{H}^{(1)}|\beta,k)(\beta,k|\mathcal{H}^{(1)}|\beta,\ell)(\beta,\ell|m|\alpha,j)(\alpha,j|m|\beta,i) \qquad (6.5)$$

$$\text{Trace } P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta \mathcal{H}^{(1)} P_\beta m =$$

$$= \sum_{i=1}^{g_\alpha}\sum_{k=1}^{g_\alpha}\sum_{j=1}^{g_\beta}\sum_{\ell=1}^{g_\beta} (\alpha,i|\mathcal{H}^{(1)}|\alpha,k)(\alpha,k|m|\beta,\ell)(\beta,\ell|\mathcal{H}^{(1)}|\beta,j)(\beta,j|m|\alpha,i) \qquad (6.6)$$

We must now find some way to perform the summations in the above equations and the summations in (4.18) and (4.19). The method which we use will be essentially the same as that used by Pryce and Stevens (1950). This will now be discussed.

Let us denote the unperturbed eigenfunctions of the t^{th} spin by $|r)_t$ and the corresponding eigenvalue by a_r so that

$$\mathcal{H}_t^{(0)}|r)_t = a_r|r)_t \qquad t = 1,2,\ldots,N \qquad r = 1,2,\ldots\ldots,R \tag{6.7}$$

An eigenfunction of $\mathcal{H}^{(0)} = \sum_{t=1}^{N} \mathcal{H}_t^{(0)}$ can then be written in the form $|a)_1 \times |b)_2 \times |c)_3 \times \cdots\cdots \times |d)_N$.
For example,

$$\mathcal{H}^{(0)}|a)_1 \times |b)_2 \times |c)_3 \times \cdots\cdots \times |d)_N = E_\mu |a)_1 \times |b)_2 \times |c)_3 \times \cdots \times |d)_N \quad \text{if} \quad a_a + a_b + a_c + \cdots\cdots + a_d = E_\mu .$$

It should be noticed that equations (6.1) to (6.6) remain true if $|\mu,i)$ is replaced by $|a)_1 \times |b)_2 \times |c_3) \times \cdots \times |d)_N$ where $a_a + a_b + a_c + \cdots\cdots + a_d = E_\mu$ since the functions $|\mu,i)$, which diagonalize $\mathcal{H}^{(1)}$, are obtained by taking linear combinations of all functions of the form $|a)_1 \times |b)_2 \times |c_3) \times \cdots \times |d)_N$ where $a_a + a_b + a_c + \cdots\cdots + a_d = E_\mu$. For this reason we shall change the meaning of the symbol $|\mu,i)$; from now on, this symbol will mean

$$|\mu,i) = |a)_1 \times |b)_2 \times |c)_3 \times \cdots\cdots \times |d)_N \tag{6.8}$$

where $\quad a_a + a_b + a_c + \cdots + a_d = E_\mu$ (6.9)

This should lead to no confusion.

Now, we can write

$$E_\mu = \sum_{r=1}^{R} n_r a_r \tag{6.10}$$

where $\quad 0 \leq n_r \leq N \quad$ for $\quad r = 1, 2, \ldots, R$

and where $\quad \sum_{r=1}^{R} n_r = N$ (6.11)

Furthermore, the degeneracy g_μ of E_μ is

$$g_\mu = \frac{N!}{\prod_{r=1}^{R} n_r!} \qquad \text{when} \quad \sum_{r=1}^{R} n_r a_r = E_\mu \tag{6.12}$$

Thus, any eigenfunction $|\mu, i)$ of $\mathcal{H}^{(0)}$ can be characterized by two sets of integers. The first set of R integers $(n_1, n_2, n_3, \ldots . n_R)$, where $0 \leq n_r \leq N$ for $r = 1, 2, \ldots, R$ and where $\sum_{r=1}^{R} n_r = N$, tells us the eigenvalue to which the function belongs, that is, gives us the μ-value. The second set of N integers $(a, b, c, \ldots, d)$, where

$1 \leq a \leq R \;,\; 1 \leq b \leq R \;,\; 1 \leq c \leq R \;,\; \ldots \ldots \;,\; 1 \leq d \leq R$

specifies the particular eigenfunction, that is, the i-value.

We can, then, replace

$$\sum_{i=1}^{g_\mu} \qquad \text{by} \qquad \sum_{(a,b,c,\ldots,d)}^{\mu} \tag{6.13}$$

where $\sum^{\mu}_{(a,b,c,\dots,d)}$ means summation over all combinations of the N integers wherein $a_a + a_b + a_c + \cdots + a_d = E_\mu$. Further, we can replace

$$\sum_{\mu=1}^{\Omega} \qquad \text{by} \qquad \sum_{\substack{\sum_{r=1}^{R} n_r = N \\ (0 \leqslant n_r \leqslant N)}} \tag{6.14}$$

where $\sum_{\substack{\sum_{r=1}^{R} n_r = N \\ (0 \leqslant n_r \leqslant N)}}$ means summation over all integers $n_1, n_2, \dots, n_R$ wherein $0 \leqslant n_r \leqslant N$ for $r = 1,2,\dots,R$ such that $\sum_{r=1}^{R} n_r = N$.

For example, we can write

$$\sum_{\mu=1}^{\Omega} \sum_{i=1}^{g_\mu} 1. \quad \text{as} \sum_{\substack{\sum_{r=1}^{R} n_r = N \\ (0 \leqslant n_r \leqslant N)}} \sum^{\mu}_{(a,b,c,\dots,d)} 1. = \sum_{\substack{\sum_{r=1}^{R} n_r = N \\ (0 \leqslant n_r \leqslant N)}} \frac{N!}{\prod_{r=1}^{R} n_r!} = R^N.$$

Let us now consider the meaning of $\sum\sum_{\alpha < \beta}$. We recall that $\sum\sum_{\alpha<\beta}$ means summation over all values of α and β wherein $E_\beta - E_\alpha = h\nu^*$. Since E_α and E_β can be labelled by the sets of R integers $(n_1, n_2, \dots, n_R)$ and $(n'_1, n'_2, \dots, n'_R)$ respectively, the condition $E_\beta - E_\alpha = h\nu^*$ and the condition $\sum_{r=1}^{R} n_r = \sum_{r=1}^{R} n'_r = N$ imply that some restrictions must be placed on these 2R integers. We must, in fact, have

$$\left.\begin{array}{lll} 1 \leqslant n_g \leqslant N & & \text{for at least one g in the set } G \\ 0 \leqslant n_r \leqslant N & & \text{for } r \neq g \end{array}\right\} \tag{6.15}$$

and

$$\left.\begin{aligned} n'_g &= n_g - 1 \\ n'_{g+1} &= n_{g+1} + 1 \\ n'_r &= n_r \qquad \text{for } r \neq g, g\ 1. \end{aligned}\right) \qquad (6.16)$$

$$\text{Then } E_\beta - E_\alpha = \sum_{r=1}^{R} (n'_r - n_r) a_r =$$
$$= (n'_g - n_g) a_g + (n'_{g+1} - n_{g+1}) a_{g+1} =$$
$$= a_{g+1} - a_g =$$
$$= h\nu^*$$

Thus, $\sum_{\alpha<\beta}\sum$ means summation over all values of the integers $(n_1, n_2, \ldots, n_R)$

where $\sum_{r=1}^{R} n_r = N$ and where $\begin{cases} 1 \leq n_g \leq N \text{ for some } g \text{ in the set } G \text{ of } Q \text{ positive integers.} \\ 0 \leq n_r \leq N \text{ for } r \neq g \end{cases}$

We can now write (6.1) to (6.6) in a more convenient form. For simplicity in writing we shall write

$$|\mu, i) = |a, b, c, \ldots, d)$$

rather than the more cumbersome form given by (6.8). Using this and (6.13) we can write

$$\text{Trace } P_\alpha m P_\beta m = \sum_{(a,b,c,\ldots)}^{\alpha} \sum_{(a',b',c',\ldots)}^{\beta} (a,b,c,\ldots|m|a',b',c',\ldots)(a',b',c',\ldots|m|a,b,c,\ldots) \qquad (6.17)$$

$$\left.\begin{aligned}\text{Trace } P_\alpha \mathfrak{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M} &= \sum^{\alpha}_{(a,b,c,\dots)} \sum^{\alpha}_{(a',b',\dots)} \sum^{\beta}_{(a'',b'',\dots)} (a,b,c,\dots|\mathfrak{H}^{(1)}|a',b',c',\dots)\times \\ &\times (a',b',c',\dots|\mathfrak{M}|a'',b'',c'',\dots)(a'',b'',c'',\dots|\mathfrak{M}|a,b,c,\dots)\end{aligned}\right\}\quad (6.18)$$

$$\left.\begin{aligned}\text{Trace } P_\beta \mathfrak{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} &= \sum^{\beta}_{(a,b,c,\dots)} \sum^{\beta}_{(a',b',c',\dots)} \sum^{\alpha}_{(a'',b'',c'',\dots)} (a,b,c,\dots|\mathfrak{H}^{(1)}|a',b',c',\dots)\times \\ &\times (a',b',c',\dots|\mathfrak{M}|a'',b'',c'',\dots)(a'',b'',\dots|\mathfrak{M}|a,b,c,\dots)\end{aligned}\right\}\quad (6.19)$$

$$\left.\begin{aligned}\text{Trace } P_\alpha \mathfrak{H}^{(1)} P_\alpha \mathfrak{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M} &= \sum^{\alpha}_{(a,b,c,\dots)} \sum^{\alpha}_{(a',b',c',\dots)} \sum^{\alpha}_{(a'',b'',c'',\dots)} \sum^{\beta}_{(a''',b''',c''',\dots)} (a,b,c,\dots|\mathfrak{H}^{(1)}|a',b',c',\dots)\times \\ &\times (a',b',c',\dots|\mathfrak{H}^{(1)}|a'',b'',c'',\dots)(a'',b'',c'',\dots|\mathfrak{M}|a''',b''',c''',\dots)(a''',b''',c''',\dots|\mathfrak{M}|a,b,c,\dots)\end{aligned}\right\}\quad (6.20)$$

$$\left.\begin{aligned}\text{Trace } P_\beta \mathfrak{H}^{(1)} P_\beta \mathfrak{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} &= \sum^{\beta}_{(a,b,c,\dots)} \sum^{\beta}_{(a',b',\dots)} \sum^{\beta}_{(a'',b'',c'',\dots)} \sum^{\alpha}_{(a''',b''',c''',\dots)} (a,b,c,\dots|\mathfrak{H}^{(1)}|a',b',c',\dots)\times \\ &\times (a',b',c',\dots|\mathfrak{H}^{(1)}|a'',b'',c'',\dots)(a'',b'',c'',\dots|\mathfrak{M}|a''',b''',c''',\dots)(a''',b''',c''',\dots|\mathfrak{M}|a,b,c,\dots)\end{aligned}\right\}\quad (6.21)$$

$$\left.\begin{aligned}\text{Trace } P_\alpha \mathfrak{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{H}^{(1)} P_\beta \mathfrak{M} &= \sum^{\alpha}_{(a,b,c,\dots)} \sum^{\alpha}_{(a',b',c',\dots)} \sum^{\beta}_{(a'',b'',c'',\dots)} \sum^{\beta}_{(a''',b''',c''',\dots)} (a,b,c,\dots|\mathfrak{H}^{(1)}|a',b',c',\dots)\times \\ &\times (a',b',c',\dots|\mathfrak{M}|a'',b'',c'',\dots)(a'',b'',c'',\dots|\mathfrak{H}^{(1)}|a''',b''',c''',\dots)(a''',b''',c''',\dots|\mathfrak{M}|a,b,c,\dots)\end{aligned}\right\}\quad (6.22)$$

Now, let us write m and $\mathcal{H}^{(1)}$ in the forms given by (5.5) and (5.6) respectively, that is,

$$m = \sum_{j=1}^{N} m_j \qquad (5.5)$$

$$\left.\begin{aligned} \mathcal{H}^{(1)} = \sum\sum_{1 \le i < j \le N} \mathcal{H}_{ij}^{(1)} \quad \text{where } \mathcal{H}_{ij}^{(1)} \text{ is symmetrical in} \\ i \text{ and } j \end{aligned}\right\} \qquad (5.6)$$

Before proceeding to evaluate (6.17) to (6.22) using (5.5) and (5.6) it will be convenient to establish the following convention:

We shall use the letter a to refer to the states of the 1st spin
b to refer to the states of the 2nd spin
e to refer to the states of the i^{th} spin
f to refer to the states of the j^{th} spin
g to refer to the states of the k^{th} spin
h to refer to the states of the l^{th} spin

Dashes will be used to distinguish different states of the same spin.

Substituting (5.5) into, for example, (6.17) yields matrix elements of the form $(a',b',c',\ldots|m_j|a,b,c,\ldots)$.

But $m_j|a,b,c,\ldots) = |a)_1 \times |b)_2 \times \ldots \times m_j|f)_j \times \ldots$

so that $(a',b',c',\ldots|m_j|a,b,c,\ldots) = (a'|a)(b'|b)\ldots(f'|m_j|f)\ldots =$

$$= (f'|m_j|f)\,\delta_{a'a}\,\delta_{b'b}\ldots$$

because of the orthonormality of the eigenfunctions.

But, if $a_{a'} + a_{b'} + a_{c'} + \cdots = E_\beta$ and $a_a + a_b + a_c + \cdots = E_\alpha$

then for $a' = a$, $b' = b$, $c' = c$, ... $\quad E_\beta - E_\alpha = a_{f'} - a_f$
$= h\nu^*$ if and only if f is in the set G and $f' = f+1$.

(We shall in future use $f \in G$ to mean "f is in the set G" and $f \notin G$ to mean "f is not in the set G".)

Thus, if

$$\mathcal{H}^{(0)}|a',b',c',\ldots) = E_\beta |a',b',c'\ldots) \text{ and } \mathcal{H}^{(0)}|a,b,c,\ldots) = E_\alpha |a,b,c,\ldots)$$

then
$$(a',b',c',\ldots|m_j|a,b,c,\ldots) = \begin{cases} (f+1|m_j|f)\,\delta_{a'a}\,\delta_{b'b}\ldots\delta_{e'e}\,\delta_{f',f+1}\ldots & \text{for } f \in G \\ 0 & \text{for } f \notin G \end{cases} \quad (6.23)$$

and
$$(a,b,c,\ldots|m_j|a',b',c',\ldots) = \begin{cases} (e|m_j|e+1)\,\delta_{a'a}\,\delta_{b'b}\ldots\delta_{e',e+1}\,\delta_{f'f}\ldots & \text{for } e \in G \\ 0 & \text{for } e \notin G \end{cases} \quad (6.24)$$

so that

$$(a,b,c,\ldots e,\ldots f,\ldots|m_i|a',b',c',\ldots,e',\ldots f'\ldots)(a',b',c'\ldots e'\ldots f'\ldots|m_j|a,b,c,\ldots,e,\ldots,f,\ldots) =$$
$$= (e|m_i|e+1)(f+1|m_j|f)\;\delta_{a'a}\,\delta_{b'b}\ldots\delta_{e',e+1}\,\delta_{e',e}\,\delta_{f'f}\,\delta_{f',f+1}\ldots$$

$= 0$ if $i \neq j$

Thus Trace $P_\alpha \mathfrak{M} P_\beta \mathfrak{M} = \sum_{i=1}^{N} \text{Trace } P_\alpha m_i P_\beta m_i$

and from (6.17), Trace $P_\alpha m_i P_\beta m_i = \sum_{(a,b,c,\ldots)}^{\alpha} |(e|m_i|e+1)|^2$ where $e \in G$.

But $\sum^{\alpha}_{(a,b,c,\dots)}$ means summation over all combinations of the N integers a,b,...,e,.....

Thus, $\sum^{\alpha}_{(a,b,c,\dots)} |(e|m_j|e+1)|^2 = \sum_{e\in G} |(e|m_j|e+1)|^2 \dfrac{(N-1)!}{n_1!n_2!\cdots(n_e-1)!\dots\dots n_R!}$

where $a_a+a_b+a_c+\cdots+a_e+\cdots = \sum_{r=1}^{R} n_r a_r = E_\alpha$

and where $\sum_{e\in G}$ means summation over all Q integers in the set G.

Then, Trace $P_\alpha m_j P_\beta m_j = \sum_{e\in G} |(e|m_j|e+1)|^2 \dfrac{(N-1)!}{n_1!n_2!\dots(n_e-1)!\cdots n_R!}$

Now, $\sum_{\alpha<}\sum_{\beta} e^{-\frac{E_\alpha}{kT}}$ Trace $P_\alpha m_j P_\beta m_j =$

$$= \sum_{\alpha<}\sum_{\beta} e^{-\frac{1}{kT}(n_1a_1+n_2a_2+\cdots+n_ea_e+\cdots+n_Ra_R)} \sum_{e\in G} |(e|m_j|e+1)|^2 \frac{(N-1)!}{n_1!n_2!\cdots(n_e-1)!\cdots n_R!} \qquad (6.25)$$

where $\sum_{\alpha<}\sum_{\beta}$ has been explained before.

Because of the term $(n_e-1)!$ in the denominator of (6.25) which is ∞ if $n_e=0$, we can take the summation over all values of the integers $(n_1,n_2,n_3,\dots,n_R)$ where $0\leq n_r\leq R$ for all r.

Thus, $$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \text{ Trace } P_\alpha m_j P_\beta m_j =$$

$$= \sum_{\substack{n_1+n_2+\cdots+n_R=N \\ (0\le n_r\le N)}} e^{-\frac{1}{kT}(n_1a_1+n_2a_2+\cdots+n_Ra_R)} \sum_{\ell\in G} |(\ell|m_j|\ell+1)|^2 \frac{(N-1)!}{n_1!\,n_2!\cdots(n_\ell-1)!\cdots n_R!} =$$

$$= \sum_{\ell\in G} |(\ell|m_j|\ell+1)|^2 e^{-\frac{a_\ell}{kT}} \sum_{\substack{n_1+n_2+\cdots+n_R=N \\ (0\le n_r\le N)}} \frac{(N-1)!}{n_1!\,n_2!\cdots(n_\ell-1)!\cdots n_R!} e^{-\frac{1}{kT}[n_1a_1+n_2a_2+\cdots+(n_\ell-1)a_\ell+\cdots+n_Ra_R]}$$

Since $(n_\ell-1)! = \infty$ if $n_\ell=0$ we have

$$\sum_{\substack{n_1+n_2+\cdots+n_\ell+\cdots+n_R=N \\ (0\le n_r\le N)}} \frac{(N-1)!}{n_1!\,n_2!\cdots(n_\ell-1)!\cdots n_R!} e^{-\frac{1}{kT}[n_1a_1+n_2a_2+\cdots+(n_\ell-1)a_\ell+\cdots+n_Ra_R]} =$$

$$= \sum_{\substack{n_1+n_2+\cdots+(n_\ell-1)+\cdots+n_R=N-1 \\ \left(\begin{smallmatrix}1\le n_\ell\le N \\ 0\le n_r\le N-1\ r\ne\ell\end{smallmatrix}\right)}} \frac{(N-1)!}{n_1!\,n_2!\cdots(n_\ell-1)!\cdots n_R!} e^{-\frac{1}{kT}[n_1a_1+n_2a_2+\cdots+(n_\ell-1)a_\ell+\cdots+n_Ra_R]} =$$

$$= \sum_{\substack{n_1+n_2+\cdots+n_\ell+\cdots+n_R=N-1 \\ (0\le n_r\le N-1)}} \frac{(N-1)!}{n_1!\,n_2!\cdots n_\ell!\cdots n_R!} e^{-\frac{1}{kT}(n_1a_1+n_2a_2+\cdots+n_\ell a_\ell+\cdots+n_Ra_R)}$$

But

$$\left\{ \sum_{r=1}^{R} e^{-\frac{a_r}{kT}} \right\}^{N-1} = \sum_{\substack{n_1+n_2+\cdots+n_R=N-1 \\ (0\leq n_r \leq N-1)}} \frac{(N-1)!}{n_1!\,n_2!\cdots n_R!}\, e^{-\frac{1}{kT}(n_1a_1+n_2a_2+\cdots+n_Ra_R)} \tag{6.26}$$

so that

$$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \,\mathrm{Trace}\, P_\alpha m_i P_\beta m_i = A^{N-1} \sum_{\ell\in G} |(\ell|m_i|\ell+1)|^2 e^{-\frac{a_\ell}{kT}}$$

where $$A = \sum_{r=1}^{R} e^{-\frac{a_r}{kT}} \tag{6.27}$$

Now, $(\ell|m_i|\ell+1) = (\ell|m|\ell+1)$ for $i = 1, 2, \ldots, N$ (6.28)

since we are considering N identical spins.

Then Trace $P_\alpha \mathfrak{M} P_\beta \mathfrak{M} = N\,\mathrm{Trace}\, P_\alpha m P_\beta m$.

Finally, then, using (6.28) we get

$$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \,\mathrm{Trace}\, P_\alpha \mathfrak{M} P_\beta \mathfrak{M} = N A^{N-1} \sum_{\ell\in G} |(\ell|m|\ell+1)|^2 e^{-\frac{a_\ell}{kT}}. \tag{6.29}$$

Let us now consider Trace $P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}$. Using (5.5) and (5.6) we can write

$$\text{Trace } P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta m = \sum_i \sum_{j(\neq i)} \left\{ \left(\mathcal{H}^{(1)}_{ij} m_i m_i \right)_\alpha + \left(\mathcal{H}^{(1)}_{ij} m_i m_j \right)_\alpha \right\} +$$

$$+ \sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} \left\{ \left(\mathcal{H}^{(1)}_{ij} m_i m_k \right)_\alpha + \left(\mathcal{H}^{(1)}_{ij} m_k m_i \right)_\alpha \right\} +$$

$$+ \sum_{i<j} \sum \sum_{k(\neq i,j)} \left(\mathcal{H}^{(1)}_{ij} m_k m_k \right)_\alpha + \sum_{i<j} \sum \sum_{k(\neq i,j)} \sum_{\substack{l \\ (\neq i,j,k)}} \left(\mathcal{H}^{(1)}_{ij} m_k m_l \right)_\alpha .$$

where we write Trace $P_\alpha \mathcal{H}^{(1)}_{ij} P_\alpha m_p P_\beta m_q = \left(\mathcal{H}^{(1)}_{ij} m_p m_q \right)_\alpha$

Using (6.18), (6.23), and (6.24) we have

$$\left(\mathcal{H}_{ij} m_i m_i \right)_\alpha = \sum_{e \in G} \sum_{f=1}^{R} (e,f|\mathcal{H}^{(1)}_{ij}|e,f)\, |(e|m|e+1)|^2 \frac{(N-2)!}{n_1!\, n_2! \cdots (n_e-1)! \cdots (n_f-1)! \cdots n_R!}$$

Thus, $\displaystyle\sum_\alpha \sum_{<\beta} e^{-\frac{E_\alpha}{kT}} \left(\mathcal{H}_{ij} m_i m_i \right)_\alpha =$

$$= \sum_{e \in G} \sum_{f=1}^{R} (e,f|\mathcal{H}^{(1)}_{ij}|e,f)\, |(e|m|e+1)|^2 \sum_{\substack{n_1+n_2+\cdots+n_R=N \\ (0 \le n_r \le N)}} \frac{(N-2)!}{n_1!\, n_2! \cdots (n_e-1)! \cdots (n_f-1)! \cdots n_R!} \times$$

$$\times\, e^{-\frac{1}{kT}(n_1 a_1 + n_2 a_2 + \cdots + n_R a_R)} .$$

But $$\sum_{\substack{n_1+n_2+\cdots+n_R=N \\ (0\le n_r\le N)}} \frac{(N-2)!}{n_1!\,n_2!\cdots(n_\ell-1)!\cdots(n_\xi-1)!\cdots n_R!}\, e^{-\frac{1}{kT}\left(n_1a_1+n_2a_2+\cdots+n_Ra_R\right)} =$$

$$= e^{-\frac{a_\ell+a_\xi}{kT}} \sum_{\substack{n_1+n_2+\cdots+(n_\ell-1)+(n_\xi-1)+\cdots+n_R=N-2 \\ \left(\begin{array}{l} 1\le n_\ell\le N-1 \\ 1\le n_\xi\le N-1 \\ 0\le n_r\le N-2 \quad r\ne \ell,\xi \end{array}\right)}} \frac{(N-2)!}{n_1!\,n_2!\cdots(n_\ell-1)!\,(n_\xi-1)!\cdots n_R!}\, e^{-\frac{1}{kT}\left[n_1a_1+n_2a_2+\cdots+(n_\ell-1)a_\ell+(n_\xi-1)a_\xi+\cdots+n_Ra_R\right]} =$$

$$= e^{-\frac{a_\ell+a_\xi}{kT}} \sum_{\substack{n_1+n_2+\cdots+n_\ell+n_\xi+\cdots+n_R=N-2 \\ (0\le n_r\le N-2)}} \frac{(N-2)!}{n_1!\,n_2!\cdots n_\ell!\cdots n_\xi!\cdots n_R!}\, e^{-\frac{1}{kT}\left(n_1a_1+n_2a_2+\cdots+n_\ell a_\ell+n_\xi a_\xi+\cdots+n_Ra_R\right)} =$$

$$= e^{-\frac{a_\ell+a_\xi}{kT}} A^{N-2}.$$

Thus $$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\left(\mathcal{H}^{(1)}_{ij}\, m_i m_j\right)_\alpha =$$

$$= A^{N-2}\sum_{\ell\in G}\sum_{\xi=1}^{R} e^{-\frac{a_\ell+a_\xi}{kT}} \left|(\ell|m|\ell+1)\right|^2 \left(\ell,\xi\left|\mathcal{H}^{(1)}_{ij}\right|\ell,\xi\right) \tag{6.30}$$

Similarily, $$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\left(\mathcal{H}^{(1)}_{ij}\, m_i m_j\right) =$$

$$= A^{N-2}\sum_{\ell\in G}\sum_{\xi\in G} e^{-\frac{a_{\ell+1}+a_\xi}{kT}} (\ell|m|\ell+1)(\xi+1|m|\xi)\left(\ell+1,\xi\left|\mathcal{H}^{(1)}_{ij}\right|\ell,\xi+1\right) \tag{6.31}$$

$$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \left(\mathcal{H}^{(1)}_{ij}\, m_k m_k\right)_\alpha =$$

$$= A^{N-3} \sum_{e=1}^{R} \sum_{f=1}^{R} \sum_{g\in G} e^{-\frac{a_e+a_f+a_g}{kT}} \left|(g|m_k|g+1)\right|^2 \left(e,f\,|\mathcal{H}^{(1)}_{ij}|\,e,f\right). \tag{6.32}$$

$$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \left(\mathcal{H}^{(1)}_{ij}\, m_j m_k\right)_\alpha = 0 = \sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \left(\mathcal{H}^{(1)}_{ij}\, m_k m_j\right)_\alpha \tag{6.33}$$

$$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \left(\mathcal{H}_{ij}\, m_k m_k\right)_\alpha = 0 \tag{6.34}$$

and, $\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \left(\mathcal{H}^{(1)}_{ij}\, m_j m_j\right)_\beta =$

$$= A^{N-2} \sum_{e\in G} \sum_{f=1}^{R} e^{-\frac{a_e+a_f}{kT}} \left|(e|m|e+1)\right|^2 \left(e+1,f\,|\mathcal{H}^{(1)}_{ij}|\,e+1,f\right). \tag{6.35}$$

$$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}} \left(\mathcal{H}^{(1)}_{ij}\, m_i m_j\right)_\beta =$$

$$= A^{N-2} \sum_{e\in G} \sum_{f\in G} e^{-\frac{a_{e+1}+a_f}{kT}} (e+1|m|e)(f|m|f+1)\left(e,f+1\,|\mathcal{H}^{(1)}_{ij}|\,e+1,f\right) \tag{6.36}$$

$$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\left(\mathcal{L}^{(1)}_{ij}\, m_k m_k\right)_\beta =$$

$$= A^{N-3}\sum_{e=1}^{R}\sum_{f=1}^{R}\sum_{g\in G} e^{-\frac{a_e+a_f+a_g}{kT}}\,\left|(g|m_k|g+1)\right|^2 \left(e,f\left|\mathcal{L}^{(1)}_{ij}\right|e,f\right). \qquad (6.37)$$

$$\left.\begin{aligned}\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\left(\mathcal{L}^{(1)}_{ij}\, m_j m_k\right)_\beta &= \sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\left(\mathcal{L}^{(1)}_{ij}\, m_k m_i\right)_\beta = \sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\left(\mathcal{L}_{ij}\, m_k m_l\right)_\beta = \\ &= 0.\end{aligned}\right\}(6.38)$$

where we use Trace $P_\beta \mathcal{L}^{(1)}_{ij} P_\beta m_p P_\alpha m_q = \left(\mathcal{L}^{(1)}_{ij}\, m_p m_q\right)_\beta$

Using (6.30) to (6.38) we have

$$\sum_{\alpha<\beta}\sum e^{-\frac{E_\alpha}{kT}}\left(P_\beta \mathcal{L}^{(1)} P_\beta m P_\alpha m - P_\alpha \mathcal{L}^{(1)} P_\alpha m P_\beta m\right) =$$

$$= A^{N-2}\sum_{e\in G}\sum_{f\in G} e^{-\frac{a_f}{kT}}\left(e^{-\frac{a_e}{kT}} - e^{-\frac{a_{e+1}}{kT}}\right)\Lambda_{1,1}(e,f) + A^{N-2}\sum_{e\in G}\sum_{f=1}^{R} e^{-\frac{a_e+a_f}{kT}}\,\Lambda_{1,2}(e,f) \qquad (6.39)$$

where

$$\Lambda_{1,1}(e,f) = (e|m|e+1)(f+1|m|f)\sum_i\sum_{j(\neq i)}\left(e+1,f\left|\mathcal{L}^{(1)}_{ij}\right|e,f+1\right) \qquad (6.40)$$

$$\Lambda_{1,2}(e,f) = |(e|m|e+1)|^2 \sum_{i} \sum_{j(\neq i)} \left\{ (e+1,f|\mathcal{H}_{ij}^{(1)}|e+1,f) - (e,f|\mathcal{H}_{ij}^{(1)}|e,f) \right\} \tag{6.41}$$

In writing the above we have used

$$(e,f|\mathcal{H}_{ij}^{(1)}|e',f') = (f,e|\mathcal{H}_{ij}^{(1)}|f',e') \quad \text{for all } e,f,e',f' \tag{6.42}$$

since $\mathcal{H}_{ij}^{(1)}$ is symmetrical in i and j.

Then, using (6.29) and (6.39), we can write (4.18) as follows:

$$h\langle\Delta\nu\rangle = \frac{\sum_{e\in G}\sum_{f\in G} e^{-\frac{a_f}{kT}}\left(e^{-\frac{a_e}{kT}} - e^{-\frac{a_{e+1}}{kT}}\right)\Lambda_{1,1}(e,f) + \sum_{e\in G}\sum_{f=1}^{R} e^{-\frac{a_e+a_f}{kT}}\Lambda_{1,2}(e,f)}{NA\sum_{e\in G} e^{-\frac{a_e}{kT}}\Lambda_0(e)} \tag{6.43}$$

where $\quad \Lambda_0(e) = |(e|m|e+1)|^2 \qquad (6.44)$

Evaluation of (6.20) to (6.22) involves the same methods as used above. It should only be necessary then to give the results of our calculations.

After using equations (5.5), (5.6), (6.28), and (6.42) we have found that:

$$\sum_{\alpha<}\sum_{\beta} e^{-\frac{E_\alpha}{kT}} \operatorname{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{m} P_\alpha \mathfrak{m} - 2 P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{m} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{m} + P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{m} P_\beta \mathfrak{m}\right) =$$

$$= A^{N-2}\left\{\sum_{e\in G}\sum_{f\in G} e^{-\frac{a_f}{kT}}\left(e^{-\frac{a_e}{kT}} + e^{-\frac{a_{e+1}}{kT}}\right)\Lambda_{2,1}(e,f) + \sum_{e\in G}\sum_{f=1}^{R} e^{-\frac{a_e+a_f}{kT}}\Lambda_{2,2}(e,f)\right\}$$

$$+A^{N-3}\left\{\sum_{e\in G}\sum_{f\in G}\sum_{g\in G} e^{-\frac{a_f}{kT}}\left(e^{-\frac{a_e}{kT}} - e^{-\frac{a_{e+1}}{kT}}\right)\left(e^{-\frac{a_g}{kT}} - e^{-\frac{a_{g+1}}{kT}}\right)\Lambda_{2,3}(e,f,g)\right.$$

$$+\sum_{e\in G}\sum_{f\in G}\sum_{g=1}^{R} e^{-\frac{a_f+a_g}{kT}}\left(e^{-\frac{a_e}{kT}} - e^{-\frac{a_{e+1}}{kT}}\right)\Lambda_{2,4}(e,f,g)$$

$$\left.+\sum_{e\in G}\sum_{f=1}^{R}\sum_{g=1}^{R} e^{-\frac{a_e+a_f+a_g}{kT}}\Lambda_{2,5}(e,f,g)\right\} \tag{6.45}$$

where:

$$\Lambda_{2,1}(e,f) = \sum_{i}\sum_{j(\neq i)}\left\{\sum_{a+b=e+f+1}(e|m|e+1)(f+1|m|f)(e+1,f|\mathcal{H}_{ij}^{(1)}|a,b)(a,b|\mathcal{H}_{ij}^{(1)}|e,f+1)\right\}$$

$$\Lambda_{2,2}(e,f) = \sum_{i} \sum_{j(\neq i)} \Big\{ \sum_{a+b=e+f} |(e|m|e+1)|^2 \, |(e,f|\mathcal{H}^{(1)}_{ij}|a,b)|^2 + \sum_{a+b=e+f+1} |(e|m|e+1)|^2 |(e+1,f|\mathcal{H}^{(1)}_{ij}|a,b)|^2$$

$$-2 \sum_{\substack{a+b=e+f \\ a\in G}} \{ (a|m|a+1)(e+1|m|e)(e,f|\mathcal{H}^{(1)}_{ij}|a,b)(a+1,b|\mathcal{H}^{(1)}_{ij}|e+1,f)$$

$$+ (a|m|a+1)(e+1|m|e)(e,f|\mathcal{H}^{(1)}_{ij}|b,a)(b,a+1|\mathcal{H}^{(1)}_{ij}|e+1,f) \} \Big\}$$

$$\Lambda_{2,3}(e,f,g) = \sum_{i} \sum_{j(\neq i)} \sum_{k(\neq i,j)} (e|m|e+1)(f+1|m|f)(e+1,g|\mathcal{H}^{(1)}_{ij}|e,g+1)(f,g+1|\mathcal{H}^{(1)}_{jk}|f+1,g)$$

$$\Lambda_{2,4}(e,f,g) = \sum_{i} \sum_{j(\neq i)} \sum_{k(\neq i,j)} (e|m|e+1)(f+1|m|f)(e+1,f|\mathcal{H}^{(1)}_{ij}|e,f+1)\big[(e+1,g|\mathcal{H}^{(1)}_{jk}|e+1,g)$$

$$+ (f+1,g|\mathcal{H}^{(1)}_{jk}|f+1,g) - (e,g|\mathcal{H}^{(1)}_{jk}|e,g) - (f,g|\mathcal{H}^{(1)}_{jk}|f,g) \big]$$

$$\Lambda_{2,5}(e,f,g) = \sum_{i} \sum_{j(\neq i)} \sum_{k(\neq i,j)} |(e|m|e+1)|^2 \big[(e+1,f|\mathcal{H}^{(1)}_{ij}|e+1,f) - (e,f|\mathcal{H}^{(1)}_{ij}|e,f) \big] \times$$

$$\times \big[(e+1,g|\mathcal{H}^{(1)}_{jk}|e+1,g) - (e,g|\mathcal{H}^{(1)}_{jk}|e,g) \big]$$

where we use :

$\sum\limits_{a+b=e+f}$ to mean summation over all positive integers a and b wherein $a_a + a_b = a_e + a_f$.

$\sum\limits_{\substack{a+b=e+f \\ a\in G}}$ to mean summation over all positive integers a and b wherein $a_a + a_b = a_e + a_f$ and where furthermore $a \in G$.

$\sum\limits_{a+b=e+f+1}$ to mean summation over all positive integers a and b wherein $a_a + a_b = a_{e+1} + a_f$.

Now, using (6.29) and (6.45) we can write (4.18) as follows:

$$
\begin{aligned}
\hbar^2\langle\Delta\nu^2\rangle = {} & \frac{\sum\limits_{e\in G}\sum\limits_{f\in G} e^{-\frac{a_f}{kT}}\left(e^{-\frac{a_e}{kT}} + e^{-\frac{a_{e+1}}{kT}}\right)\Lambda_{2,1}(e,f) + \sum\limits_{e\in G}\sum\limits_{f=1}^{R} e^{-\frac{a_e+a_f}{kT}}\Lambda_{2,2}(e,f)}{NA\sum\limits_{e\in G} e^{-\frac{a_e}{kT}}\Lambda_0(e)} \\
& + \frac{\sum\limits_{e\in G}\sum\limits_{f\in G}\sum\limits_{g\in G} e^{-\frac{a_f}{kT}}\left(e^{-\frac{a_e}{kT}} - e^{-\frac{a_{e+1}}{kT}}\right)\left(e^{-\frac{a_g}{kT}} - e^{-\frac{a_{g+1}}{kT}}\right)\Lambda_{2,3}(e,f,g)}{NA^2\sum\limits_{e\in G} e^{-\frac{a_e}{kT}}\Lambda_0(e)} \\
& + \frac{\sum\limits_{e\in G}\sum\limits_{f\in G}\sum\limits_{g=1}^{R} e^{-\frac{a_f+a_g}{kT}}\left(e^{-\frac{a_e}{kT}} - e^{-\frac{a_{e+1}}{kT}}\right)\Lambda_{2,4}(e,f,g)}{NA^2\sum\limits_{e\in G} e^{-\frac{a_e}{kT}}\Lambda_0(e)} \\
& + \frac{\sum\limits_{e\in G}\sum\limits_{f=1}^{R}\sum\limits_{g=1}^{R} e^{-\frac{a_e+a_f+a_g}{kT}}\Lambda_{2,5}(e,f,g)}{NA^2\sum\limits_{e\in G} e^{-\frac{a_e}{kT}}\Lambda_0(e)}
\end{aligned}
\tag{6.46}
$$

Equation (4.17) can now be written as follows:

$$h^2\langle\nu^2\rangle = (h\nu^*)^2 + 2h\nu^*\left[\,h\langle\Delta\nu\rangle\right] + h^2\langle\Delta\nu^2\rangle \tag{6.47}$$

where $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ are given by (6.43) and (6.46).

Equation (6.47) is a valid expression for the second moment of $f(\nu)$ whenever the following hold:

1) Condition (4.12) holds, that is,

$$e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} = e^{-\frac{E_\alpha P_\alpha}{kT}}\, e^{-\frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}$$

2) $\mathcal{H}^{(1)} = \sum\sum_{1\le i<j\le N}$ and $\mathcal{H}^{(1)}_{ij}$ symmetric in i and j

3) $\mathfrak{M} = \sum_{i=1}^{N} m_i$

4) There are N identical spins and each unperturbed spin has R energy values each of which is non-degenerate and Q pairs of which have energy separation $h\nu^*$.

We have pointed out in the last chapter that the Van Vleck method yields the same results as does (4.17) when all the exponentials containing the temperature in this latter expression are replaced by unity.

Replacing all exponentials containing the temperature by unity in (6.47), which is identical with (4.17) when the above conditions hold, yields:

$$k^2\langle \nu^2\rangle = (k\nu^*)^2 + \frac{2k\nu^*\sum_{\ell\in G}\sum_{\xi=1}^{R}\Lambda_{1,2}(\ell,\xi)}{NR\sum_{\ell\in G}\Lambda_0(\ell)}$$

$$+\frac{2\sum_{\ell\in G}\sum_{\xi\in G}\Lambda_{2,1}(\ell,\xi)+\sum_{\ell\in G}\sum_{\xi=1}^{R}\Lambda_{2,2}(\ell,\xi)}{NR\sum_{\ell\in G}\Lambda_0(\ell)}$$

$$+\frac{\sum_{\ell\in G}\sum_{\xi=1}^{R}\sum_{g=1}^{R}\Lambda_{2,5}(\ell,\xi,g)}{NR^2\sum_{\ell\in G}\Lambda_0(\ell)} \qquad (6.48)$$

Let us consider under which conditions this step is justified. The term

$$\frac{\sum_{\ell\in G}\sum_{\xi\in G}\left(e^{-\frac{a_\ell+a_\xi}{kT}}+e^{-\frac{a_{\ell+1}+a_\xi}{kT}}\right)\Lambda_{2,1}(\ell,\xi)}{NA\sum_{\ell\in G}e^{-\frac{a_\ell}{kT}}\Lambda_0(\ell)}$$

for example, can be written

$$\frac{\sum_{\ell\in G}\sum_{\xi\in G}\left(\frac{e^{-\frac{a_\ell+a_\xi}{kT}}}{A^2}+\frac{e^{-\frac{a_{\ell+1}+a_\xi}{kT}}}{A^2}\right)\Lambda_{2,1}(\ell,\xi)}{N\sum_{\ell\in G}\left(\frac{e^{-\frac{a_\ell}{kT}}}{A}\right)\Lambda_0(\ell)}$$

But, $A = \sum_{r=1}^{R} e^{-\frac{a_r}{kT}}$ so that $\frac{e^{-\frac{a_\ell}{kT}}}{A} = \left[\sum_{r=1}^{R} e^{-\frac{(a_r - a_\ell)}{kT}} \right]^{-1}$

Now, we define $\delta = \frac{a_{max.} - a_{min.}}{kT}$ so that

$$R\, e^{-\delta} \leq \sum_{r=1}^{R} e^{-\frac{a_r - a_\ell}{kT}} \leq R\, e^{+\delta}$$

Thus, $\frac{e^{-\delta}}{R} \leq \frac{e^{-\frac{a_\ell}{kT}}}{A} \leq \frac{e^{+\delta}}{R}$

We can then write

$$\frac{e^{-3\delta}}{R}\left\{\frac{2\sum_{\ell\in G}\sum_{\xi\in G}\Lambda_{2,1}(\ell,\xi)}{N\sum_{\ell\in G}\Lambda_0(\ell)}\right\} \leq \frac{\sum_{\ell\in G}\sum_{\xi\in G}\left(e^{-\frac{a_\ell+a_\xi}{kT}} + e^{-\frac{a_{\ell+1}+a_\xi}{kT}}\right)\Lambda_{2,1}(\ell,\xi)}{NA\sum_{\ell\in G} e^{-\frac{a_\ell}{kT}}\Lambda_0(\ell)} \leq \frac{e^{+3\delta}}{R}\left\{\frac{2\sum_{\ell\in G}\sum_{\xi\in G}\Lambda_{2,1}(\ell,\xi)}{N\sum_{\ell\in G}\Lambda_0(\ell)}\right\}$$

If, now, $\delta \ll \frac{1}{3}$ so that $e^{\pm 3\delta} \simeq 1$ then

$$\frac{\sum_{\ell\in G}\sum_{\xi\in G}\left(e^{-\frac{a_\ell+a_\xi}{kT}} + e^{-\frac{a_{\ell+1}+a_\xi}{kT}}\right)\Lambda_{2,1}(\ell,\xi)}{NA\sum_{\ell\in G} e^{-\frac{a_\ell}{kT}}\Lambda_0(\ell)} \simeq \frac{2\sum_{\ell\in G}\sum_{\xi\in G}\Lambda_{2,1}(\ell,\xi)}{NR\sum_{\ell\in G}\Lambda_0(\ell)}$$

Similarily, the other terms in (6.47) can be investigated. We found that if $\delta \ll \frac{1}{4}$ then (6.48) is a valid approximation of (6.47).

Thus, we have shown that the Van Vleck method, that is, equation (5.2) yields a valid approximation for the second moment of f(ν) for the case when each of the N identical unperturbed spins has R energy values, $a_1, a_2, \ldots, a_R$, all of which are non-degenerate and Q pairs of which have energy separation $h\nu^*$, if:

1) Condition (4.12) holds
2) $\mathcal{H}^{(1)} = \sum\sum_{1 \le i < j \le N} \mathcal{H}^{(1)}_{ij}$; and $\mathcal{H}^{(1)}_{ij}$ symmetrical in i ahd j
3) $m = \sum_{i=1}^{N} m_i$
4) $\frac{a_{max.} - a_{min.}}{kT} \ll \frac{1}{4}$

In Chapters V and VI we have considered condition (4.12) to hold, that is, we have assumed that

$$e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} = e^{-\frac{E_\alpha P_\alpha}{kT}} e^{-\frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}$$

In the next chapter we shall find expressions for $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ when

$$e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}\left(1 - \frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}\right)$$

We shall show then that the temperature independent terms in these new expressions for $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ are not identical with those found by replacing all exponentials containing the temperature by unity in (4.18) and (4.19) respectively. It will be shown that if $\overline{\mathcal{H}^{(1)}}$ cannot be regarded as negligible when compared with $\mathcal{H}^{(0)}$, then the Van Vleck method does not yield a valid approximation for $h^2\langle\nu^2\rangle$.

Chapter VII

Expressions for $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ When

$e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}\left(1 - \frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}\right)$.

(7;1) General Formulae

The expressions for $h\langle\nu\rangle$ and $h^2\langle\nu^2\rangle$ with which we are concerned are given by

$$h\langle\nu\rangle = \frac{C}{B} \tag{7.1.1}$$

$$h^2\langle\nu^2\rangle = \frac{D}{B} \tag{7.1.2}$$

where B = right hand side of equation (4.8)

C = right hand side of equation (4.9)

D = right hand side of equation (4.10)

It should be noticed first that when we put $\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}$ then we can write:

$h\langle\Delta\nu\rangle$ = (right hand side of (7.1.1) when $\mathcal{H}$ is replaced by $\mathcal{H}^{(1)}$ everywhere except in the exponentials in (7.1.1)), and,

$h^2\langle\Delta\nu^2\rangle$ = (right hand side of (7.1.2) when $\mathcal{H}$ is replaced by $\mathcal{H}^{(1)}$ everywhere except in the exponentials in (7.1.2)).

(See Chapter IV for definition of $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$.)

Let us now take

$$e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} = e^{-\frac{E_\alpha P_\alpha}{kT}} e^{-\frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}} \left(1 - \frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}\right) \tag{7.1.3}$$

in these expressions for $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$. Then using (4.2) and the fact that Trace ABC = Trace CAB for any matrices A, B, C we get

$$h\langle\Delta\nu\rangle = \frac{C'}{B'} \tag{7.1.4}$$

$$h^2\langle\Delta\nu^2\rangle = \frac{D'}{B'} \tag{7.1.5}$$

where

$$B' = \sum_{\alpha<\beta}\sum \left(e^{-\frac{E_\alpha}{kT}} - e^{-\frac{E_\beta}{kT}}\right) \text{Trace } P_\alpha \mathfrak{M} P_\beta \mathfrak{M} + \frac{1}{kT} \sum_{\alpha<\beta}\sum \Big\{ e^{-\frac{E_\beta}{kT}} \text{Trace } P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - e^{-\frac{E_\alpha}{kT}} \text{Trace } P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M} \Big\}$$

$$C' = \sum_{\alpha<\beta}\sum \left(e^{-\frac{E_\alpha}{kT}} - e^{-\frac{E_\beta}{kT}}\right) \text{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}\right)$$
$$+ \frac{1}{kT} \sum_{\alpha<\beta}\sum \Big\{ e^{-\frac{E_\beta}{kT}} \text{Trace } P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} + e^{-\frac{E_\alpha}{kT}} \text{Trace } P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}$$
$$- \left(e^{-\frac{E_\alpha}{kT}} + e^{-\frac{E_\beta}{kT}}\right) \text{Trace } P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} \Big\}$$

$$D' = \sum_{\alpha<\beta}\sum \left(e^{-\frac{E_\alpha}{kT}} - e^{-\frac{E_\beta}{kT}}\right) \text{Trace}\Big(P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - 2 P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M}$$
$$+ P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M}\Big)$$
$$+ \frac{1}{kT} \sum_{\alpha<\beta}\sum \Big\{ e^{-\frac{E_\beta}{kT}} \text{Trace}\Big(P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathfrak{M} - 2 P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M}$$
$$+ P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M}\Big)$$
$$- e^{-\frac{E_\alpha}{kT}} \text{Trace}\Big(P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathfrak{M} - 2 P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M}$$
$$+ P_\alpha \mathcal{H}^{(1)} P_\alpha \mathfrak{M} P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta \mathfrak{M}\Big) \Big\}$$

Two points should be mentioned concerning equations (7.1.4) and (7.1.5). Firstly, the expansion indicated by Pryce and Stevens (1950) on page 48 of their paper yields expressions which are slightly cruder than (7.1.4) and (7.1.5). Secondly, taking $e^{-\frac{E_\alpha}{kT}} \simeq 1 - \frac{E_\alpha}{kT}$ then letting $T \rightarrow \infty$ in (7.1.4) and (7.1.5) yields expressions which are different from those found when this procedure is repeated with (4.18) and (4.19) which are the expressions we found for $h\langle \Delta\nu \rangle$ and $h^2\langle \Delta\nu^2 \rangle$ respectively when $e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}$. For example, taking $e^{-\frac{E_\alpha}{kT}} \simeq 1 - \frac{E_\alpha}{kT}$ then letting $T \rightarrow \infty$ in (4.18) yields:

$$h\langle \Delta\nu \rangle = \frac{\sum\sum_{\alpha<\beta} \text{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta m P_\alpha m - P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta m\right)}{\sum\sum_{\alpha<\beta} \text{Trace}\, P_\alpha m P_\beta m} \tag{7.1.6}$$

whereas taking $e^{-\frac{E_\alpha}{kT}} \simeq 1 - \frac{E_\alpha}{kT}$ then letting $T \rightarrow \infty$ in (7.1.4) yields

$$h\langle \Delta\nu \rangle = \frac{\left[h\nu^* \sum\sum_{\alpha<\beta} \text{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta m P_\alpha m - P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta m\right) + \sum\sum_{\alpha<\beta} \text{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta \mathcal{H}^{(1)} P_\beta m P_\alpha m - 2 P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta \mathcal{H}^{(1)} P_\beta m + P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta m\right)\right]}{h\nu^* \sum\sum_{\alpha<\beta} \text{Trace}\, P_\alpha m P_\beta m + \sum\sum_{\alpha<\beta} \text{Trace}\left(P_\beta \mathcal{H}^{(1)} P_\beta m P_\alpha m - P_\alpha \mathcal{H}^{(1)} P_\alpha m P_\beta m\right)} \tag{7.1.7}$$

Similarly, when this procedure is carried out on equations (4.19) and (7.1.5) the resulting expressions will be temperature independent in each case but they will not be eqqal.

In other words, if we apply, for example, equations (4.18) and (7.1.4) to a special case (as we do in the next chapter) the results for high temperatures will not agree. The reason for this is that in writing (7.1.6) we have employed the approximation $\mathcal{H}^{(0)} \gg \mathcal{H}^{(1)}$;

we have taken $e^{-\frac{P_\alpha \mathcal{H}^{(0)} P_\alpha}{kT}} = e^{-\frac{E_\alpha P_\alpha}{kT}} \simeq 1 - \frac{E_\alpha P_\alpha}{kT}$

and $e^{-\frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}} \simeq 1$. In writing (7.1.7) we have not used the assumption that $\mathcal{H}^{(0)} \gg \mathcal{H}^{(1)}$; we have taken $e^{-\frac{E_\alpha P_\alpha}{kT}} \simeq 1 - \frac{E_\alpha P_\alpha}{kT}$ and $e^{-\frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}} \simeq 1 - \frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}$. If, in fact, $\mathcal{H}^{(0)} \gg \mathcal{H}^{(1)}$ then we should find that the difference between the results obtained using (7.1.6) and (7.1.7) is small. In the application in Chapter VIII we show that this in fact is true.

7.2 Application of (7.1.4) to the case considered in Chapter VI

We shall now rewrite equation (7.1.4) in a more convenient form for the case when m and $\mathcal{H}^{(1)}$ can be written in the forms given by (5.5) and (5.6) respectively, and when each unperturbed spin has R energy values $a_1, a_2, a_3, \ldots\ldots, a_R$, all of which are non-degenerate and Q pairs of which have energy separation $h\nu^*$.

Since the calculations are similar to those given in Chapter VI only the results will be given. We have found that in this case (7.1.4) can be written:

$$h\langle \Delta\nu \rangle = \frac{X}{Y} \qquad (7.2.1)$$

where

$$X = A^{-1}\sum_{e\in G}\sum_{f\in G}\left(e^{-\frac{a_e}{kT}}-e^{-\frac{a_{e+1}}{kT}}\right)\left(e^{-\frac{a_f}{kT}}-e^{-\frac{a_{f+1}}{kT}}\right)\Lambda_{1,1}(e,f) + A^{-1}\sum_{e\in G}\sum_{f=1}^{R}\left(e^{-\frac{a_e}{kT}}-e^{-\frac{a_{e+1}}{kT}}\right)e^{-\frac{a_f}{kT}}\Lambda_{1,2}(e,f)$$

$$+\frac{1}{kT}\Bigg\{A^{-1}\sum_{e\in G}\sum_{f\in G}e^{-\frac{a_{e+1}+a_f}{kT}}\Lambda_{4,1}(e,f)$$

$$+A^{-1}\sum_{e\in G}\sum_{f=1}^{R}\left\{e^{-\frac{a_e+a_f}{kT}}\Lambda_{4,2}(e,f)+e^{-\frac{a_{e+1}+a_f}{kT}}\Lambda_{4,3}(e,f)\right\}$$

$$+A^{-2}\sum_{e\in G}\sum_{f\in G}\sum_{g=1}^{R}\Bigg\{\left(e^{-\frac{a_{e+1}}{kT}}-e^{-\frac{a_e}{kT}}\right)e^{-\frac{a_f+a_g}{kT}}\Lambda_{4,4}(e,f,g)$$

$$+\left(e^{-\frac{a_e}{kT}}-e^{-\frac{a_{e+1}}{kT}}\right)e^{-\frac{a_{f+1}+a_g}{kT}}\Lambda_{4,5}(e,f,g)\Bigg\}$$

$$+A^{-2}\sum_{e\in G}\sum_{f=1}^{R}\sum_{g=1}^{R}\left\{\left(e^{-\frac{a_{e+1}}{kT}}\Lambda_{4,6}(e,f,g)-e^{-\frac{a_e}{kT}}\Lambda_{4,7}(e,f,g)\right)e^{-\frac{a_f+a_g}{kT}}\right\}$$

$$+A^{-3}\sum_{e\in G}\sum_{f\in G}\sum_{g=1}^{R}\sum_{h=1}^{R}\left(2e^{-\frac{a_{e+1}+a_f}{kT}}-e^{-\frac{a_{e+1}+a_{f+1}}{kT}}-e^{-\frac{a_e+a_f}{kT}}\right)e^{-\frac{a_g+a_h}{kT}}\Lambda_{4,8}(e,f,g,h)$$

$$+A^{-3}\sum_{e\in G}\sum_{f=1}^{R}\sum_{g=1}^{R}\sum_{h=1}^{R}\left(e^{-\frac{a_e}{kT}}-e^{-\frac{a_{e+1}+a_f}{kT}}\right)e^{-\frac{a_f+a_g+a_h}{kT}}\Lambda_{4,9}(e,f,g,h)\Bigg\} \qquad (7.2.2)$$

$$Y = \sum_{e\in G}\left(e^{-\frac{a_e}{kT}}-e^{-\frac{a_{e+1}}{kT}}\right)\Lambda_0(e) +$$

$$+\frac{1}{kT}\Bigg\{A^{-1}\sum_{e\in G}\sum_{f=1}^{R}\left(e^{-\frac{a_{e+1}}{kT}}\Lambda_{3,1}(e,f)+e^{-\frac{a_e}{kT}}\Lambda_{3,2}(e,f)\right)e^{-\frac{a_f}{kT}} +$$

$$+A^{-2}\sum_{\ell\in G}\sum_{f=1}^{R}\sum_{g=1}^{R}\left(e^{-\frac{a_{\ell+1}}{kT}}-e^{-\frac{a_\ell}{kT}}\right)e^{-\frac{a_f+a_g}{kT}}\Lambda_{3,3}(\ell,f,g)\Bigg\} \qquad (7.2.3)$$

We have given $\Lambda_0(\ell)$, $\Lambda_{1,1}(\ell,f)$, and $\Lambda_{1,2}(\ell,f)$ before. (see Chapter VI). The other Λ's are as follows:

$$\Lambda_{3,1}(\ell,f)=\sum_i\sum_{j(\neq i)}|(\ell|m|\ell+1)|^2(\ell+1,f|\mathcal{H}^{(1)}_{ij}|\ell+1,f)$$

$$\Lambda_{3,2}(\ell,f)=-\sum_i\sum_{j(\neq i)}|(\ell|m|\ell+1)|^2(\ell,f|\mathcal{H}^{(1)}_{ij}|\ell,f)$$

$$\Lambda_{3,3}(\ell,f,g)=\sum_{i<j}\sum_{k(\neq i,j)}|(\ell|m_k|\ell+1)|^2(f,g|\mathcal{H}^{(1)}_{ij}|f,g)=(N-2)\sum_{i<j}\sum|(\ell|m|\ell+1)|^2(f,g|\mathcal{H}^{(1)}_{ij}|f,g)$$

$$\Lambda_{4,1}(\ell,f)=2\sum_i\sum_{j(\neq i)}(\ell|m|\ell+1)(f+1|m|f)\sum_{a+b=\ell+f+1}(\ell+1,f|\mathcal{H}^{(1)}_{ij}|a,b)(a,b|\mathcal{H}^{(1)}_{ij}|\ell,f+1)$$

$$\Lambda_{4,2}(\ell,f)=\sum_i\sum_{j(\neq i)}\Big\{|(\ell|m|\ell+1)|^2\sum_{a+b=\ell+f}|(\ell,f|\mathcal{H}^{(1)}_{ij}|a,b)|^2+$$

$$-\Big[\sum_{\substack{a+b=\ell+f\\ a\in G}}\Big\{(\ell,f|\mathcal{H}^{(1)}_{ij}|a,b)(a+1,b|\mathcal{H}^{(1)}_{ij}|\ell+1,f)(a|m|a+1)(\ell+1|m|\ell)+$$

$$+(\ell,f|\mathcal{H}^{(1)}_{ij}|b,a)(b,a+1|\mathcal{H}^{(1)}_{ij}|\ell+1,f)(a|m|a+1)(\ell+1|m|\ell)\Big\}\Big]\Big\}.$$

$$\Lambda_{4,3}(\ell,f)=\sum_i\sum_{j(\neq i)}\Big\{|(\ell|m|\ell+1)|^2\sum_{a+b=\ell+f+1}|(\ell+1,f|\mathcal{H}^{(1)}_{ij}|a,b)|^2+$$

$$-\Big[\sum_{\substack{a+b=e+f\\ a\in G}} \Big\{ (e,f|\mathcal{H}^{(1)}_{ij}|a,b)(a+1,b|\mathcal{H}^{(1)}_{ij}|e+1,f)(a|m|a+1)(e+1|m|e)$$

$$+ (e,f|\mathcal{H}^{(1)}_{ij}|b,a)(b,a+1|\mathcal{H}^{(1)}_{ij}|e+1,f)(a|m|a+1)(a+1|m|e)\Big\}\Big]\Big\}.$$

$$\Lambda_{4,4}(e,f,g) = \sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} (e|m|e+1)(f+1|m|f)(e+1,f|\mathcal{H}^{(1)}_{ij}|e,f+1)\big[(e,g|\mathcal{H}^{(1)}_{jk}|e,g)+(f,g|\mathcal{H}^{(1)}_{jk}|f,g)\big]$$

$$\Lambda_{4,5}(e,f,g) = \sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} (e|m|e+1)(f+1|m|f)(e+1,f|\mathcal{H}^{(1)}_{ij}|e,f+1)\big[(e+1,g|\mathcal{H}^{(1)}_{jk}|e+1,g)+(f+1,g|\mathcal{H}^{(1)}_{jk}|f+1,g)\big]$$

$$\Lambda_{4,6}(e,f,g) = \sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} |(e|m|e+1)|^2\big[(e+1,f|\mathcal{H}^{(1)}_{ij}|e+1,f)-(e,f|\mathcal{H}^{(1)}_{ij}|e,f)\big]\big[(e+1,g|\mathcal{H}^{(1)}_{jk}|e+1,g)+(f,g|\mathcal{H}^{(1)}_{jk}|f,g)\big]$$

$$\Lambda_{4,7}(e,f,g) = -\sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} |(e|m|e+1)|^2\big[(e+1,f|\mathcal{H}^{(1)}_{ij}|e+1,f)-(e,f|\mathcal{H}^{(1)}_{ij}|e,f)\big]\big[(e,g|\mathcal{H}^{(1)}_{jk}|e,g)+(f,g|\mathcal{H}^{(1)}_{jk}|f,g)\big]$$

$$\Lambda_{4,8}(e,f,g,h) = \sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} \sum_{l(\neq i,j,k)} (e|m|e+1)(f+1|m|f)(e+1,f|\mathcal{H}^{(1)}_{ij}|e,f+1)(g,h|\mathcal{H}^{(1)}_{kl}|g,h)$$

$$\Lambda_{4,9}(e,f,g,h) = \sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} \sum_{l(\neq i,j,k)} |(e|m|e+1)|^2\big[(e,f|\mathcal{H}^{(1)}_{ij}|e,f)-(e+1,f|\mathcal{H}^{(1)}_{ij}|e+1,f)\big](g,h|\mathcal{H}^{(1)}_{kl}|g,h).$$

Equation (7.1.5) could also be written in this form but the labour involved would be quite considerable. In the next chapter we shall restrict ourselves to applying equation (7.2.1) to a particular physical system.

Chapter VIII

Calculation of $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ for the Magnetic Resonance Absorption by a Spherically-shaped Nickel Fluosilicate Crystal when the Magnetic Field is in the Direction of the Optic Axis.

Magnetic resonance absorption by a crystal of nickel fluosilicate ($NiSiF_6 \cdot 6H_2O$) has been observed by Holden, Kittel, and Yager (1949) and by Penrose andStevens (1950), and theoretical expressions for the mean square absorption frequencies of two absorption lines has been found by Ishiguro, Usui, and Kambe (1951) (hereafter referred to as I.U.K.) using the Van Vleck method (see equation (5.2)). In this chapter we shall give $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ as functions of the temperature. That is, we shall apply equations (6.43), (6.46), and (7.2.1) to this special case. It should be recalled that equations (6.43) and (6.46) for $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ respectively have been derived on the basis of the assumption that $e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}$. Equation (7.2.1) for $h\langle\Delta\nu\rangle$ has been derived as the assumption that $e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}\left(1-\frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}\right)$.

The structure of nickel fluosilicate crystal and the relevance of this structure for the quantum mechanical problem in question was first discussed by Becquerel and Opechowski (1939) (see also I.U.K.) and will not be repeated here. The main points of interest are

1) each paramagnetic Ni^{++} ion is in the presence of a crystalline field,

2) each Ni^{++} ion has effective spin S = 1 so that
R = number of energy levels of each unperturbed ion = 3,

3) the energy levels of each unperturbed ion are not equidistant so that the set G defined in Chapter VI consists of the single term, 1.

Thus, when applying equation (6.43), (6.46) and (7.2.1) to this case we take, for example,

$$\sum_{\ell \in G} \sum_{s=1}^{R} e^{-\frac{a_\ell + a_s}{kT}} \Lambda_{1,2}(\ell, s) =$$

$$= \sum_{\ell \in G} \sum_{s=1}^{R} e^{-\frac{a_\ell + a_s}{kT}} \sum_i \sum_{j(\neq i)} \left\{ (\ell+1, s | \mathcal{H}_{ij}^{(1)} | \ell+1, s) - (\ell, s | \mathcal{H}_{ij}^{(1)} | \ell, s) \right\} |(\ell | m | \ell+1)|^2 =$$

$$= e^{-\frac{a_1}{kT}} |(1|m|2)|^2 \sum_{s=1}^{3} e^{-\frac{a_s}{kT}} \sum_i \sum_{j(\neq i)} \left\{ (2,s | \mathcal{H}_{ij}^{(1)} | 2,s) - (1,s | \mathcal{H}_{ij}^{(1)} | 1,s) \right\}.$$

That is $\sum_{\ell \in G}$ reduces to one term in this case.

The expressions for $\hbar\langle\Delta\nu\rangle$ and $\hbar^2\langle\Delta\nu^2\rangle$ contain matrix elements of $\mathcal{H}_{ij}^{(1)}$, where $\sum\sum_{1 \le i < j \le N} \mathcal{H}_{ij}^{(1)} = \mathcal{H}^{(1)}$, the spin-spin interaction energy. If $\mathcal{H}^{(1)}$ = (exchange energy) + (dipolar energy) then

$$\mathcal{H}^{(1)} = \sum\sum_{i<j} \tilde{A}_{ij} \underline{S}_i \cdot \underline{S}_j + \sum\sum_{i<j} \frac{\mu_B^2}{r_{ij}^3} \left[(\underline{\underline{g}}\,\underline{S}_i \cdot \underline{\underline{g}}\,\underline{S}_j) - 3 r_{ij}^{-2} (\underline{\underline{g}}\,\underline{S}_i \cdot \underline{r}_{ij})(\underline{\underline{g}}\,\underline{S}_j \cdot \underline{r}_{ij}) \right] \quad (8.1)$$

where $\underline{\underline{g}}\,\underline{S}_i = g_\perp(S_{x_i} + S_{y_i}) + g_\parallel S_{z_i}$

If $\mathcal{H}^{(0)} = \sum_{i=1}^{N} \mathcal{H}_i^{(0)}$ where $\mathcal{H}_i^{(0)} = -\delta S_{z_i}^2 - g_\parallel \mu_B H S_{z_i}$ ($\delta > 0$: this should not be confused with the δ used in Chapter VI) then the only matrix elements of $\mathcal{H}^{(1)}$ occurring in the expressions for $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ are those of the operator

$$\overline{\mathcal{H}^{(1)}} = \sum_{i<j}\sum \left\{ A_{ij}\ \underline{S}_i \cdot \underline{S}_j \ + \ B_{ij}\, S_{z_i} S_{z_j} \right\} \tag{8.2}$$

where

$$A_{ij} = \tilde{A}_{ij} + g_\perp^2 \mu_B^2 r_{ij}^{-3}\left[\tfrac{3}{2}\gamma_{ij}^2 - \tfrac{1}{2}\right]$$

$$B_{ij} = -\left(2g_\parallel^2 + g_\perp^2\right)\mu_B^2 r_{ij}^{-3}\left[\tfrac{3}{2}\gamma_{ij}^2 - \tfrac{1}{2}\right]$$

and where we use γ_{ij} as the direction cosine of $\underline{r_{ij}}$ relative to the z-axis. (I.U.K. have taken $g_\perp = g_\parallel = g$ in their expression for $\overline{\mathcal{H}^{(1)}}$. At high temperatures, the exchange contribution to $h^2\langle\Delta\nu^2\rangle$ is dominant so that the resulting error is small. They have also truncated $(S_{x_i}S_{x_j} + S_{y_i}S_{y_j})$; this does not appear necessary.)

Using (8.2) we have found that (6.43) and (6.46), which are the expressions for $h\langle\Delta\nu\rangle$ and $h^2\langle\Delta\nu^2\rangle$ we found when $e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}$, become respectively:

$$h\langle\Delta\nu\rangle = \frac{1}{N}\sum_i \sum_{j(\neq i)} \left\{ -A_{ij}\left(\frac{e^{-\frac{a_2}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right) - B_{ij}\left(\frac{e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right) \right\} \tag{8.3}$$

$$\begin{aligned} h^2\langle\Delta\nu^2\rangle = {} & \frac{1}{N}\sum_i \sum_{j(\neq i)} \left\{ A_{ij}^2 \left(\frac{e^{-\frac{a_2}{kT}} + 2e^{-\frac{a_3}{kT}}}{A}\right) + B_{ij}^2\left(\frac{e^{-\frac{a_1}{kT}} + e^{-\frac{a_3}{kT}}}{A}\right) + 2A_{ij}B_{ij}\left(\frac{e^{-\frac{a_3}{kT}}}{A}\right) \right\} \\ & + \frac{1}{N}\sum_i \sum_{j(\neq i)} \sum_{k(\neq i j)} \left\{ A_{ij}A_{jk}\left(\frac{e^{-\frac{a_2}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right)^2 + B_{ij}B_{jk}\left(\frac{e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right)^2 \right. \\ & \left. + 2A_{ij}B_{jk}\left(\frac{e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right)\left(\frac{e^{-\frac{a_2}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right) \right\} \end{aligned} \tag{8.4}$$

Using (8.2) we have found that (7.2.1), which is the expression for $h\langle\Delta\nu\rangle$ we found when $e^{-\frac{P_a \mathcal{H} P_a}{kT}} \simeq e^{-\frac{E_a P_a}{kT}}\left(1 - \frac{P_a \mathcal{H}^{(1)} P_a}{kT}\right)$ becomes:

$$h\langle\Delta\nu\rangle = \frac{a + \frac{b}{kT}}{c + \frac{d}{kT}} \simeq \frac{a}{c} + \frac{1}{kT}\left(\frac{b}{c} - \frac{ad}{c^2}\right) \tag{8.5}$$

where

$$a = |(1|m|2)|^2 A^{N-2}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_2}{kT}}\right)\sum_i \sum_{j(\neq i)} \left\{ -A_{ij}\left(e^{-\frac{a_2}{kT}} - e^{-\frac{a_3}{kT}}\right) - B_{ij}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}\right)\right\}$$

$$b = |(1|m|2)|^2 A^{N-2}\sum_i \sum_{j(\neq i)} \left\{ A_{ij}^2\left(e^{-\frac{a_1+a_2}{kT}} + e^{-\frac{a_1+a_3}{kT}} + e^{-\frac{a_2+a_3}{kT}}\right) + A_{ij}B_{ij}\left(e^{-\frac{2a_1}{kT}} + 2e^{-\frac{a_1+a_3}{kT}} - e^{-\frac{a_1+a_2}{kT}}\right)\right.$$

$$\left. + B_{ij}^2\left(e^{-\frac{2a_1}{kT}} + e^{-\frac{a_1+a_3}{kT}}\right)\right\}$$

$$+ |(1|m|2)|^2 A^{N-3}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}\right)\sum_i \sum_{j(\neq i)} \sum_{k(\neq ij)} \left\{ A_{ij}A_{jk}\left(e^{-\frac{a_1+a_2}{kT}} + e^{-\frac{a_2+a_3}{kT}} - 2e^{-\frac{a_1+a_3}{kT}}\right)\right.$$

$$\left. + 2A_{ij}B_{jk}\left(e^{-\frac{2a_1}{kT}} + e^{-\frac{a_2+a_3}{kT}} - 2e^{-\frac{a_1+a_3}{kT}}\right) + B_{ij}B_{jk}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}\right)\left(2e^{-\frac{a_1}{kT}} - e^{-\frac{a_2}{kT}}\right)\right\}$$

$$+ |(1|m|2)|^2 A^{N-4}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_2}{kT}}\right)\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}\right)^2 \frac{1}{2}\sum_i \sum_{j(\neq i)} \sum_{k(\neq ij)} \sum_{\ell(\neq ijk)} \left\{ A_{ij}A_{k\ell}\left(e^{-\frac{a_2}{kT}} - e^{-\frac{a_3}{kT}}\right)\right.$$

$$\left. + A_{ij}B_{k\ell}\left(e^{-\frac{a_1}{kT}} + e^{-\frac{a_2}{kT}} - 2e^{-\frac{a_3}{kT}}\right) + B_{ij}B_{k\ell}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}\right)\right\}$$

$$c = N\,|(1|m|2)|^2 A^{N-1}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_2}{kT}}\right).$$

$$d = -|(1|m|2)|^2 A^{N-2}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}\right) e^{-\frac{a_1}{kT}} \sum_i \sum_{j(\neq i)} A_{ij}$$

$$- |(1|m|2)|^2 A^{N-3}\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_2}{kT}}\right)\left(e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}\right)^2 \left(\frac{N-2}{2}\right) \sum_i \sum_{j(\neq i)} A_{ij} \;.$$

In the above $\quad A = \sum_{r=1}^{3} e^{-\frac{a_r}{kT}}$.

As $T \to \infty$, the right hand side of $(8.3) \to 0$. On the other hand, as $T \to \infty$, $\frac{a}{c} \to 0$ and $\left(\frac{b}{c} - \frac{ad}{c^2}\right) \to Q\left(\frac{kT}{h\nu^*}\right)$ where Q a constant which goes to zero as $\overline{\mathcal{H}^{(1)}}$ goes to zero. Thus, the right hand side of $(8.5) \to \frac{Q}{h\nu^*}$ as $T \to \infty$. The difference, then, in the results found using (7.1.6) and (7.1.7) is $\frac{Q}{h\nu^*}$ which goes to zero as $\overline{\mathcal{H}^{(1)}}$ goes to zero.

In applying (8.3) to (8.5) to nickel fluosilicate we shall take the z-axis to be the optic axis, and, for simplicity, we shall approximate the lattice of the nickel ions by a simple cubic lattice. (It is, in fact, a slightly distorted simple cubic lattice.) This approximation has also been made by I.U.K. We shall, furthermore, take

$$\sum_i \sum_{j(\neq i)} r_{ij}^{-3}\left[\frac{3}{2}\,\gamma_{ij}^2 - \frac{1}{2}\right] = 0 \qquad (8.6)$$

This holds, as is well-known, for a spherically shaped crystal. We shall also take

$$\tilde{A}_{ij} = \begin{cases} \tilde{A} & \text{if i and j are nearest neighbours (Each ion has six nearest neighbours in a simple cubic lattice)} \\ 0 & \text{otherwise.} \end{cases} \tag{8.7}$$

As a consequence of (8.6) and (8.7) we have

$$\sum_i \sum_{j(\neq i)} \tilde{A}_{ij} r_{ij}^{-3}\left[\tfrac{3}{2}\gamma_{ij}^2 - \tfrac{1}{2}\right] = \sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} \tilde{A}_{ij} r_{jk}^{-3}\left[\tfrac{3}{2}\gamma_{jk}^2 - \tfrac{1}{2}\right] = \sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} \sum_{\ell(\neq i,j,k)} \tilde{A}_{ij} r_{k\ell}^{-3}\left[\tfrac{3}{2}\gamma_{k\ell}^2 - \tfrac{1}{2}\right] = 0.$$

and

$$\sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} r_{ij}^{-3} r_{jk}^{-3}\left[\tfrac{3}{2}\gamma_{ij}^2 - \tfrac{1}{2}\right]\left[\tfrac{3}{2}\gamma_{jk}^2 - \tfrac{1}{2}\right] = -\sum_i \sum_{j(\neq i)} r_{ij}^{-6}\left[\tfrac{3}{2}\gamma_{ij}^2 - \tfrac{1}{2}\right]^2$$

$$\sum_i \sum_{j(\neq i)} \sum_{k(\neq i,j)} \sum_{\ell(\neq i,j,k)} r_{ij}^{-3} r_{k\ell}^{-3}\left[\tfrac{3}{2}\gamma_{ij}^2 - \tfrac{1}{2}\right]\left[\tfrac{3}{2}\gamma_{k\ell}^2 - \tfrac{1}{2}\right] = 2\sum_i \sum_{j(\neq i)} r_{ij}^{-6}\left[\tfrac{3}{2}\gamma_{ij}^2 - \tfrac{1}{2}\right]^2$$

Finally, then, (6.43), (6.46) and (7.2.1) become respectively:

$$h\langle\Delta\nu\rangle = -6\tilde{A}\left(\frac{e^{-\frac{a_2}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right) \tag{8.8}$$

$$h^2\langle\Delta\nu^2\rangle = 6\tilde{A}^2\left[\frac{e^{-\frac{a_2}{kT}} + 2e^{-\frac{a_3}{kT}}}{A} + 5\left(\frac{e^{-\frac{a_2}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right)^2\right]$$

$$+0.626\mu_B^4 d^{-6}\left[g_\perp^4\left\{1 - \left(\frac{e^{-\frac{a_1}{kT}} - e^{-\frac{a_2}{kT}}}{A}\right)^2\right\} + 4g_\parallel^4\left\{\left(\frac{e^{-\frac{a_1}{kT}} + e^{-\frac{a_3}{kT}}}{A}\right) - \left(\frac{e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right)^2\right\}\right.$$

$$\left. + 4g_\parallel^2 g_\perp^2\left\{\left(\frac{e^{-\frac{a_1}{kT}}}{A}\right) - \left(\frac{e^{-\frac{a_1}{kT}} - e^{-\frac{a_3}{kT}}}{A}\right)\left(\frac{e^{-\frac{a_1}{kT}} - e^{-\frac{a_2}{kT}}}{A}\right)\right\}\right] \tag{8.9}$$

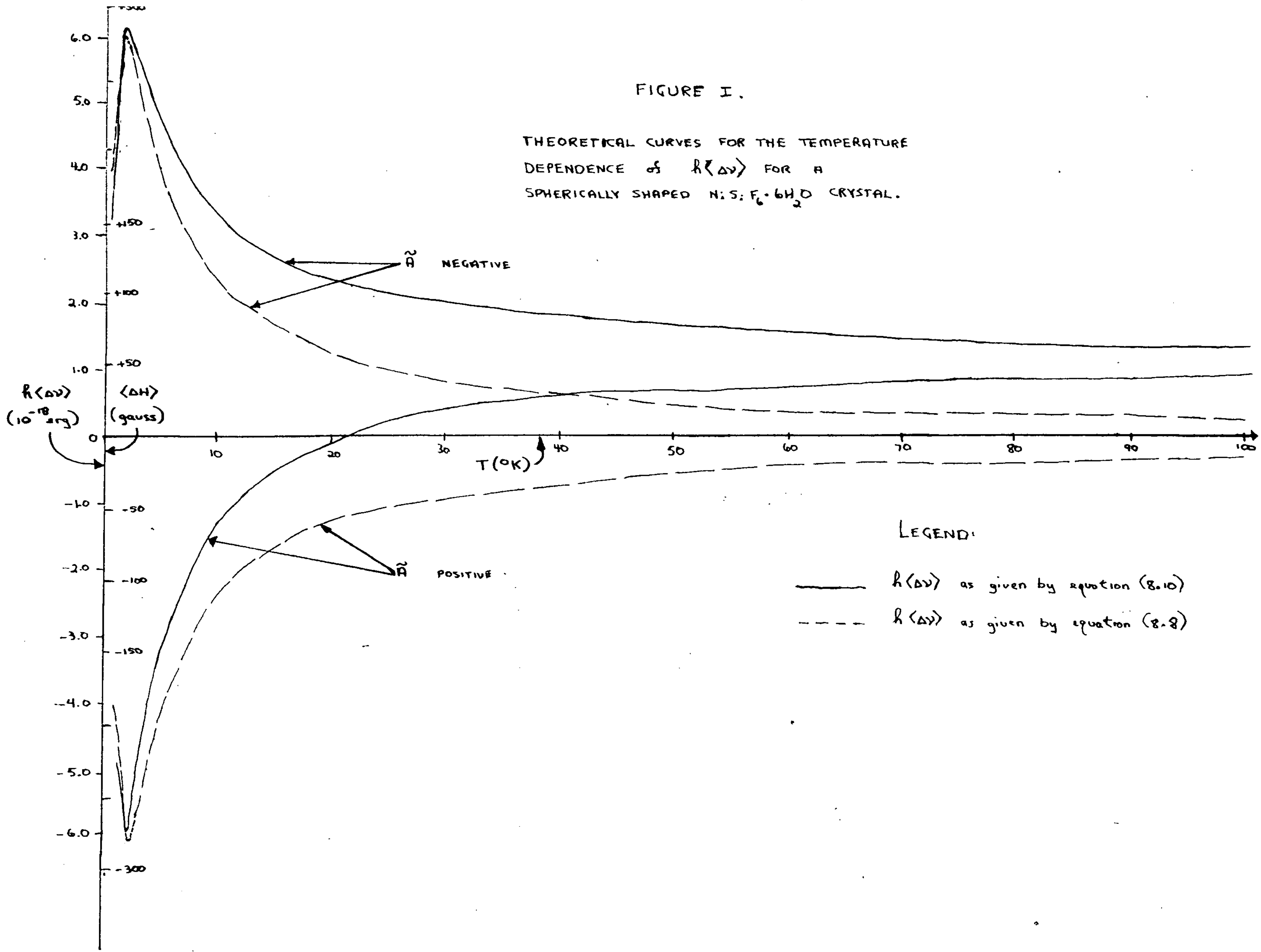
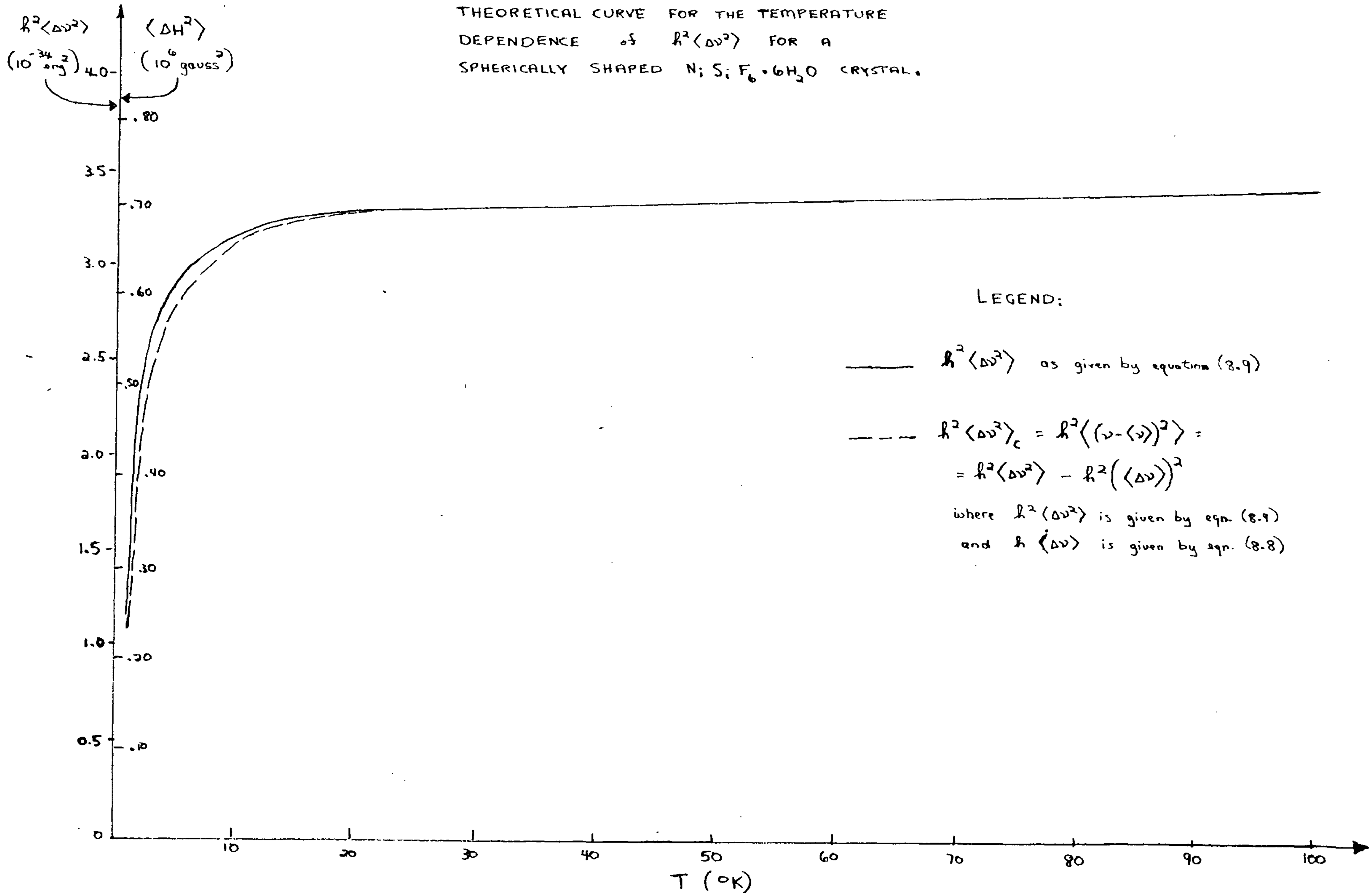


FIGURE I.

THEORETICAL CURVES FOR THE TEMPERATURE DEPENDENCE of $h\langle\Delta\nu\rangle$ FOR A SPHERICALLY SHAPED $NiSiF_6 \cdot 6H_2O$ CRYSTAL.

FIGURE II.

THEORETICAL CURVE FOR THE TEMPERATURE DEPENDENCE of $\hbar^2 \langle \Delta\nu^2 \rangle$ FOR A SPHERICALLY SHAPED $NiSiF_6 \cdot 6H_2O$ CRYSTAL.



$$
\begin{aligned}
\hbar\langle\Delta\nu\rangle = & -6\tilde{A}\left(\frac{e^{-\frac{a_3}{kT}}-e^{-\frac{a_2}{kT}}}{A}\right) \\
& +\frac{1}{kT}\Bigg\{6\tilde{A}^2\Bigg[\frac{e^{-\frac{a_1+a_2}{kT}}+e^{-\frac{a_1+a_3}{kT}}+e^{-\frac{a_2+a_3}{kT}}}{\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_2}{kT}}\right)A}+\frac{\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_3}{kT}}\right)\left(5e^{-\frac{a_2+a_3}{kT}}-4e^{-\frac{a_1+a_3}{kT}}-e^{-\frac{a_1+a_2}{kT}}\right)}{\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_2}{kT}}\right)A^2} \\
& \qquad -\frac{5\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_3}{kT}}\right)^2\left(e^{-\frac{a_2}{kT}}-e^{-\frac{a_3}{kT}}\right)}{A^3}\Bigg] \\
& +0.626\mu_B^4 d^{-6}\Bigg[\frac{4g_{\parallel}^4 e^{-\frac{a_1}{kT}}\left(e^{-\frac{a_1}{kT}}+e^{-\frac{a_3}{kT}}\right)+2g_{\parallel}^2 g_{\perp}^2 e^{-\frac{a_1}{kT}}\left(e^{-\frac{a_1}{kT}}+e^{-\frac{a_2}{kT}}\right)+g_{\perp}^4 e^{-\frac{a_2}{kT}}\left(2e^{-\frac{a_1}{kT}}+e^{-\frac{a_3}{kT}}\right)}{\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_2}{kT}}\right)A} \\
& \qquad -\frac{4g_{\parallel}^4\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_3}{kT}}\right)^2\left(2e^{-\frac{a_1}{kT}}-e^{-\frac{a_2}{kT}}\right)+4g_{\parallel}^2 g_{\perp}^2 e^{-\frac{a_1}{kT}}\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_3}{kT}}\right)}{A^2} \\
& \qquad +\frac{4g_{\parallel}^4\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_3}{kT}}\right)^3+2g_{\parallel}^2 g_{\perp}^2\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_2}{kT}}\right)\left(e^{-\frac{a_1}{kT}}-e^{-\frac{a_3}{kT}}\right)^2}{A^3}\Bigg]\Bigg\}
\end{aligned}
\tag{8.10}
$$

where we have taken $\sum_i \sum_{j(\neq i)} r_{ij}^{-6}\left[\frac{3}{2}\gamma_{ij}^2-\frac{1}{2}\right]^2 = 0.626\,N\,d^{-6}$ (d is the virtual lattice constant), which is a result obtained by I.K.U.

The three energy values of each unperturbed nickel ion are $\pm g_{\parallel}\mu_B H-\delta$, 0 . As an illustration of equations (8.8) to (8.10) we have plotted graphs (see Figures I and II) for the case when

$a_1 = -g_{\parallel}\mu_B H-\delta$

$a_2 = 0$

$a_3 = +g_{\parallel}\mu_B H-\delta$

That is, we have taken $\hbar\nu^* = +g_{\parallel}\mu_B H+\delta$. We have taken H = a constant = 12 kilogauss, $g_{\parallel} = 2.36$, $g_{\perp} = 2.29$, and $d = 6.21$ Å .The quantity δ is a function of temperature and we have taken its values from the experimental data of Penrose and Stevens (1950). The absolute value of the quantity $\tilde{A}$ has been estimated by I.K.U. to be $|\tilde{A}| = 7.5 \times 10^{-18}$ ergs for this transition. We have also used this value.

We have, in Figure I, plotted as the ordinate $\hbar\langle\Delta\nu\rangle$ in ergs and $\langle\Delta H\rangle$ in gauss. The relationship between these quantities is $\hbar\langle\Delta\nu\rangle = g_{\parallel}\mu_B\langle\Delta H\rangle$. Similarily, on Figure II, we have plotted as the ordinate $\hbar^2\langle\Delta\nu^2\rangle$ in ergs^2 and $\langle\Delta H^2\rangle$ in gauss^2. The relationship between these quantities is $\hbar^2\langle\Delta\nu^2\rangle = g_{\parallel}^2\mu_B^2\langle\Delta H^2\rangle$. It should also be noticed that on Figure II we have plotted $\hbar^2\langle\Delta\nu^2\rangle$ and $\hbar^2\langle\Delta\nu^2\rangle_C$ where $\langle\Delta\nu^2\rangle_C = \langle(\nu - \langle\nu\rangle)^2\rangle$, that is, $\langle\Delta\nu^2\rangle_C$ is the second central moment of $f(\nu)$. It can easily be shown that $\langle\Delta\nu^2\rangle_C = \langle\Delta\nu^2\rangle - (\langle\Delta\nu\rangle)^2$.

As we mentioned in Chapter VII, the high temperature results for $\hbar\langle\Delta\nu\rangle$ as given by this application of (4.18) and (7.1.4), that is, as given by (6.43) and (7.2.1), do not agree (see Figure I). We have chosen H to be quite large in the above example and, as expected, the difference in the results for

$$\hbar\langle\nu\rangle = \hbar\nu^* + \hbar\langle\Delta\nu\rangle \qquad (8.11)$$

is small at high temperatures.

For T = 100°K, (8.11) and (6.43) yield (if, for example, $\tilde{A}$ is negative):

$$\hbar\langle\nu\rangle = 30.02\times10^{-17}\text{ erg} + 0.02\times10^{-17}\text{ erg} = 30.04\times10^{-17}\text{ erg}$$

whereas, for T = 100°K, (8.11) and (7.2.1) yield (if, for example, $\tilde{A}$ is negative):

$$\hbar\langle\nu\rangle = 30.02\times10^{-17}\text{ erg} + 0.12\times10^{-17}\text{ erg} = 30.14\times10^{-17}\text{ erg}$$

The difference even at $100^{\circ}K$ is indeed small.

In the next chapter we shall very briefly mention some of the conclusions that can be drawn from this application to a particular physical system.

Chapter IX

In this chapter we shall very briefly outline some of our conclusions. The following general remarks are apparent from the application in Chapter VIII of our general formulae:

1) The dependence on temperature of the characteristics of nuclear magnetic resonance lines is negligible even down to much less than $1^{\circ}K$.
2) The dependence on temperature of the characteristics of paramagnetic resonance lines should be observable at liquid helium temperatures, that is, it should be possible to observe a change in the resonance frequency and the shape of paramagnetic resonance lines as the temperature of the sample is lowered from room temperature to liquid helium temperatures.
3) Both the resonance frequency and the shape of the resonance line depend slightly on the shape of the sample.

We can also make a few remarks from Figures I and II which pertain in particular to the spherically shaped sample of nickel fluosilicate which we considered in Chapter VIII: Below $20^{\circ}K$, when the energy difference, δ , is approximately constant with temperature, keeping one of ν or H constant and varying the other, one should find that as the temperature is lowered, the mean value of the variable quantity changes. If the mean value increases, then $\tilde{A}$, the exchange coefficient, is negative; if the mean value decreases, then $\tilde{A}$ is positive. Coupled with this shift in the mean value of the variable quantity will be a decrease in the width of the resonance line.

Our calculations have also shown that $k\langle\Delta\nu\rangle$ attains an extreme value between 1°K and 2°K (see Figure I). It should be noted that the extreme value occurs in both of our expressions for $k\langle\Delta\nu\rangle$. That is, we find an extreme value for $k\langle\Delta\nu\rangle$ when we take $e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}$ and when we take $e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}\left(1 - \frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT}\right)$

The physical reason for this is not apparent; at these very low temperatures, however, it is highly probable that neither of these approximations is valid. This could be checked, of course, by finding the expression in this case for $k\langle\Delta\nu\rangle$ when we take $e^{-\frac{P_\alpha \mathcal{H} P_\alpha}{kT}} \simeq e^{-\frac{E_\alpha P_\alpha}{kT}}\left(1 - \frac{P_\alpha \mathcal{H}^{(1)} P_\alpha}{kT} + \frac{P_\alpha \mathcal{H}^{(1)} P_\alpha \mathcal{H}^{(1)} P_\alpha}{2\,(kT)^2}\right)$.

This would involve considerable labour and has not been undertaken in this thesis.

Appendix A

Writing of $\hat{m} = \sum\sum_{\alpha<\beta} \{ P_\alpha m P_\beta + P_\beta m P_\alpha \}$

in another general form.

Let us suppose that equation (5.5) holds and that, as in Chapter VI, each of the N identical unperturbed spins has R energy values, all of which are non-degenerate and Q pairs of which have energy separation $\hbar\nu^*$. We shall show here that in this case

$$\hat{m} = \sum_{i=1}^{N} \sum\sum_{\alpha<\beta} \{ P_\alpha m_i P_\beta + P_\beta m_i P_\alpha \} = \sum_{i=1}^{N} \sum_{\ell \in G} \{ P_{\ell_i} m_i P_{\ell+1_i} + P_{\ell+1_i} m_i P_{\ell_i} \} \tag{A.1}$$

where $\sum\sum_{\alpha<\beta}$ and $\sum_{\ell \in G}$ have been discussed previously and where we write, as is customary,

$$P_{\ell_i} m_i P_{\ell+1_i} = 1 \times 1 \times 1 \times \cdots \cdots \times 1 \times \underbrace{P_\ell m P_{\ell+1}}_{i^{th}\ \text{place}} \times 1 \times \cdots \times 1.$$

The operator P_{ℓ_i} is such that:

1) $P_{\ell_i} P_{\ell'_i} = P_{\ell_i} \delta_{\ell'\ell}$ (A.2)

2) $\sum_{\ell=1}^{R} P_{\ell_i} = I_i$, the identity operator (A.3)

3) $P_{\ell_i} |\ell')_i = |\ell)_i \delta_{\ell\ell'}$ where $\mathcal{H}_i^{(0)} |\ell)_i = a_\ell |\ell)_i$ (A.4)

It should be recalled that $E_\alpha = \sum_{r=1}^{R} n_r a_r$ where $\sum_{r=1}^{R} n_r = N$ and where $n_\ell \geq 1$ for some $\ell \in G$, and that $E_\beta = E_\alpha + \hbar\nu^*$. Now, it should be possible to write the operator P_α in terms of the R operators $P_\ell \; (\ell = 1, 2, \ldots, R)$. In fact, we can write P_α as a sum of $\frac{N!}{\prod_{r=1}^{R} n_r!}$ terms each of which consists of the direct product of $n_1 P_1'$s, $n_2 P_2'$s, $n_3 P_3'$s, ..., $n_R P_R'$s. The different terms in the expression for P_α correspond to the different combinations of the $n_1 P_1'$s, ..., $n_R P_R'$s. Similarily P_β can be written as a sum of $\sum_{\ell \in G} \frac{N!}{n_1! n_2! \cdots (n_\ell - 1)! (n_{\ell+1}+1)! \cdots n_R!}$ terms.

Let us consider $P_\alpha m_i P_\beta$. From the above discussion we see that $P_\alpha m_i P_\beta$ consists of

$$\left(\frac{N!}{n_1! n_2! \cdots n_R!}\right)\left(\sum_{\ell \in G} \frac{N!}{n_1! n_2! \cdots (n_\ell - 1)! (n_{\ell+1}+1)! \cdots n_R!}\right)$$

terms. Because of (A.2), however, not all of these terms are non-zero. There can, in fact, be at most

$$\sum_{\ell \in G} \frac{(N-1)!}{n_1! n_2! \cdots (n_\ell - 1)! (n_{\ell+1}+1)! \cdots n_R!}$$

non-zero terms in $P_\alpha m_i P_\beta$.

Thus, $\sum\sum_{\alpha < \beta} P_\alpha m_i P_\beta$ will consist of $Q R^{N-1}$ terms. Using (A.3) it is possible to group the R^{N-1} terms corresponding to each of the Q values of ℓ into one term of the form

$$1 \times 1 \times 1 \times \cdots \times 1 \times P_\ell m_i P_{\ell+1} \times 1 \times \cdots \times 1$$

Finally, then $\sum_{\alpha<\beta}\sum P_\alpha m_j P_\beta = \sum_{\ell \in G} P_{\ell_j} m_j P_{\ell+1_j}$

Similarily $\sum_{\alpha<\beta}\sum P_\beta m_j P_\alpha = \sum_{\ell \in G} P_{\ell+1_j} m_j P_{\ell_j}$

Thus we can write

$$\hat{m} = \sum_{j=1}^{N} \hat{m}_j = \sum_{j=1}^{N} \sum_{\ell \in G} \left\{ P_{\ell_j} m_j P_{\ell+1_j} + P_{\ell+1_j} m_j P_{\ell_j} \right\}$$

Appendix B

Rewriting of $\hat{m} = \sum\sum_{\alpha<\beta} \{ P_\alpha m P_\beta + P_\beta m P_\alpha \}$ in the form given by Ishiguro, Usui, and Kambe (1951)

Using $m = S_x$ we have from (A.1)

$$\hat{S}_x = \sum_{i=1}^{N} \sum_{\ell \in G} \{ P_{\ell_i} S_{x_i} P_{\ell+1_i} + P_{\ell+1_i} S_{x_i} P_{\ell_i} \} \tag{B.1}$$

If, now, Q consists of only the integer unity, that is, only one pair of levels of the unperturbed spin with separation $\hbar\nu^*$, we have from (B.1):

$$\hat{S}_x = \sum_{i=1}^{N} \{ P_{1_i} S_{x_i} P_{2_i} + P_{2_i} S_{x_i} P_{1_i} \} \tag{B.2}$$

Equation (B.2) is identical with equation (6) of Ishiguro, Usui, and Kambe (1951). They have, however, labelled the energy levels of the unperturbed spin whose energy separation is $\hbar\nu^*$ by + and o whereas we use the integers 1 and 2.

Appendix C

Showing that $\hat{S}_x = S_x$ when there is no crystalline field and when the magnetic field is parallel to the Z axis.

Let us suppose that the set G is the set of integers (1,2,3,....,R-1). This corresponds to the case when condition (3.2.2) holds, that is, when the energy levels of each unperturbed spin are equidistant and when transitions occur only between adjacent levels. Then, from (B.1) we have:

$$\hat{S}_{x_i} = \sum_{\ell=1}^{R-1} \left\{ P_{\ell_i} S_{x_i} P_{\ell+1_i} + P_{\ell+1_i} S_{x_i} P_{\ell_i} \right\} \tag{C.1}$$

If $\mathcal{H}_i^{(0)} |\ell)_i = a_\ell |\ell)_i$ then, using (A.4) and (C.1) we have

$$_i(\ell'|\hat{S}_{x_i}|\ell'')_i = {}_i(\ell|S_{x_i}|\ell+1)_i \, \delta_{\ell',\ell} \, \delta_{\ell'',\ell+1} + {}_i(\ell+1|S_{x_i}|\ell)_i \, \delta_{\ell',\ell+1} \, \delta_{\ell'',\ell}$$

$$\text{for } \ell = 1,2,3,\ldots,R-1$$

It is well known, however, that if $|\ell)_i$ denotes an eigenfunction of S_{z_i} then:

$$_i(\ell'|S_{x_i}|\ell'')_i = {}_i(\ell|S_{x_i}|\ell+1)_i \, \delta_{\ell',\ell} \, \delta_{\ell'',\ell+1} + {}_i(\ell+1|S_{x_i}|\ell)_i \, \delta_{\ell',\ell+1} \, \delta_{\ell'',\ell}$$

Thus, if $[\mathcal{H}_i^{(o)}, S_{z_i}] = 0$, then

$$ {}_i(a'|\hat{S}_{x_i}|a'')_i = {}_i(a'|S_{x_i}|a'')_i $$

Since we are concerned with the traces of operators in equation (5.2), we can replace $\hat{S}_x$ with S_x if

1) Q consists of the set (1,2,3,...R-1) ie condition (3.2.2) holds

2) $[\mathcal{H}_i^{(o)}, S_{z_i}] = 0$

These two conditions are satisfied for the case considered by Van Vleck (1948) and hence it was not necessary for him to use $\hat{S}_x$ instead of S_x .

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