

SPIN ABSORPTION OF SOLIDS

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ABSTRACT

A study of the spin absorption lines of all orders was made. Rules for obtaining the absorption operator of any line were found, and a generalization of the method of moments was obtained. With magnetic dipole-dipole and exchange interactions taken into account, and with the assumption that the Zeeman energy is dominant, the zeroth and the second moments of the following four lines were evaluated without approximations for powders: (1) first Larmor line, parallel field, (2) second Larmor line, parallel field, (3) second Larmor line, perpendicular field, (4) low frequency line, perpendicular field. The contribution of exchange to the second moment was found to be the same for the four cases treated, while the total intensity has the ratio 1:1:1:3/2. Agreement with existing experimental data is good.

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I. INTRODUCTION

The method of moments was developed by Waller (1), Broer (2), Van Vleck (3), and Wright (4). They investigated in particular the energy absorption of a paramagnetic salt in a strong, constant magnetic field, when a weak oscillating field either perpendicular or parallel to the constant field is applied. The atoms in the salt are assumed to interact with the external magnetic field through their spins, and the interaction of the constant magnetic field with the salt can be written as

$$\mathcal{H}_0 = - g\beta H \sum_i S_{zi}, \quad (1)$$

where β is the Bohr magneton, g the gyromagnetic ratio, H the constant magnetic field, S_{zi} the z component of the spin of the i^{th} atom, and the z axis is in the direction of H .

In the absence of other interactions, the z component of the total spin, i.e., $\sum_i S_{zi}$, would be a constant of the motion, and would be specified by the usual total magnetic quantum number M . The energy eigenvalues of the spin system would then be given by $-g\beta HM$. If an oscillating field in the x direction is applied, the perturbation $-g\beta H_{\text{osc}} \sum_i S_{xi}$, with H_{osc} the magnitude of the oscillating field, gives rise to the selection rule $\Delta M = \pm 1$, as the matrix elements of this

perturbation between two eigenstates of the system would vanish unless the initial and the final states have magnetic quantum numbers differing by one unit. As the energy difference between two such states is $\pm g\beta H$, the salt would make transitions and absorb energy from the oscillating field only when the frequency of the field equals the Larmor frequency $\beta gH/h$. If an oscillating field in the z direction is applied, the perturbation $-g\beta H_{\text{osc}} \sum_i S_{zi}$ gives no transitions, since all of its non-diagonal matrix elements vanish. No absorption would then occur.

Now the spins in the salt couple with one another through dipole-dipole and exchange interactions (5), and the complete Hamiltonian of the salt should be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' . \quad (2)$$

where

$$\begin{aligned} \mathcal{H}' = & g^2 \beta^2 \sum_{i>j} \left[r_{ij}^{-3} (\vec{S}_i \cdot \vec{S}_j) - 3 r_{ij}^{-5} (\vec{R}_{ij} \cdot \vec{S}_i)(\vec{R}_{ij} \cdot \vec{S}_j) \right] \\ & + \sum_{i>j} \tilde{A}_{ij} \vec{S}_i \cdot \vec{S}_j . \end{aligned} \quad (3)$$

with \tilde{A}_{ij} the exchange constant. The z component of the total spin is now no longer a constant of the motion. With the assumption that $\mathcal{H}' \ll \mathcal{H}_0$, which is always true for strong enough magnetic fields, the energy eigenvalues would be slightly modified from the values $-Mg\beta H$.

If a perpendicular oscillating field (in the x direction, say) is applied, absorptions would now occur in a small range of frequencies

near $g\beta H h^{-1}$, owing to the modification of the energy eigenvalues. We would therefore observe an absorption line around the Larmor frequency $g\beta H h^{-1}$. The word "around" is used since, as we shall see later, there is a slight shift of the mean frequency of absorption of this line from the Larmor frequency. Furthermore, since the matrix elements of the perturbation between two states with energy differences of approximately $0, 2g\beta H, 3g\beta H, \dots, ng\beta H, \dots$ no longer vanish, as they must in the limit of vanishing dipolar and exchange interactions, there will appear absorption lines around frequencies $0, 2g\beta H h^{-1}, 3g\beta H h^{-1}, \dots, ng\beta H h^{-1}, \dots$ of weaker intensities. Since all eigenstates of the salt have energies differing from one another by amounts of approximately $ng\beta H$, with n any integer (would be exactly $ng\beta H$ in the limit of vanishing dipolar and exchange interactions), the lines listed above are all the absorption lines that will be present.

Similarly, if we apply a parallel oscillating field (in the z direction), we would observe absorption lines centering around $0, g\beta H h^{-1}, 2g\beta H h^{-1}, \dots, ng\beta H h^{-1}$, of weak intensities. From now on we shall call these lines the low frequency, first Larmor, second Larmor, \dots n th Larmor lines, respectively.

Let us study these lines in more detail.

Assume that the spin system is in thermal equilibrium at temperature T . The density matrix is given by

$$\rho = \frac{e^{-\frac{E_k}{KT}}}{\text{Tr}(e^{-\frac{E}{KT}})} \quad (4)$$

The number of atoms in state $|k\rangle$ of energy E_k is given by

$$\rho_k = \frac{N e^{-\frac{E_k}{KT}}}{\text{Tr}(e^{-\frac{E}{KT}})} \quad (5)$$

where N is the total number of atoms present.

For high temperatures we may approximate ρ_k by

$$\rho_k = \frac{N(1 - \frac{E_k}{KT})}{\text{Tr}(1)} = \frac{N(1 - \frac{E_k}{KT})}{(2S + 1)^N} \quad (6)$$

where S is the magnitude of an atomic spin in the salt. The trace of unity is equal to the total number of states of the system, which is $(2S + 1)^N$.

Under the excitation of the oscillating field $H_{\text{osc}} \cos \omega t = \frac{H_{\text{osc}}}{2} (e^{i\omega t} + e^{-i\omega t})$, the energy absorption by the salt per unit time is

$$A(v) = \frac{2\pi}{h} \hbar v \sum_{\substack{j, k, \\ E_j > E_k}} \left\{ \rho(E_k) - \rho(E_j) \right\} \left| \left\langle j \left| \frac{g\beta \vec{H}_{\text{osc}} \cdot \vec{S}}{2} \right| k \right\rangle \right|^2 \delta(E_k - E_j + \hbar v)$$

$$= \frac{2\pi \hbar}{KT} \frac{Ng^2 \beta^2}{(2S+1)^N} \sum_{\substack{j, k, \\ E_j > E_k}} \left| \left\langle j \left| \vec{H}_{\text{osc}} \cdot \vec{S} \right| k \right\rangle \right|^2 v^2 \delta(E_k - E_j + \hbar v) \quad (7)$$

where \vec{S} is the total spin of the system.

Broer (2) then defined the shape function

$$f(\nu) \Delta\nu = \sum_{j, k,} \left| \langle j | S_H | k \rangle \right|^2, \quad \text{for } E_j - E_k = h(\nu - \frac{\Delta\nu}{2}) \quad (8)$$

where S_H is the component of the total spin in the direction of H_{osc} .

It is obvious that $\nu^2 f(\nu)$ is proportional to the energy absorption by the salt from an oscillating field of frequency ν .

Now it is extremely difficult to obtain $f(\nu)$ as a function of ν , for we don't know the eigenstates of \mathcal{H} , and even if we knew them, it would still be formidably difficult to sum the absolute value square of the matrix elements within a small energy range, as is required by equation 8, since there is an incalculable number of states in a salt. However, the moments of $f(\nu)$ of a certain line, defined by

$$\langle \nu^n \rangle_{av} \equiv \int_0^\infty f(\nu) d\nu, \quad (9)$$

$$\langle \nu^n \rangle_{av} \equiv \int_0^\infty \nu^n f(\nu) d\nu / \int_0^\infty f(\nu) d\nu, \quad \text{for } n > 0$$

$$\langle (\nu - \bar{\nu})^n \rangle_{av} \equiv \int_0^\infty (\nu - \bar{\nu})^n f(\nu) d\nu / \int_0^\infty f(\nu) d\nu, \quad \text{for } n > 0$$

where \bar{v} is the mean frequency of a line, can be evaluated with much less effort. Usually the moments about the mean frequency, rather than the moments about the origin, are of physical interests.

Let us demonstrate this by investigating the first Larmor line for a perpendicular oscillating field.

First we rewrite expression 2 in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \equiv \mathcal{H}_0 + \mathcal{H}'_0 + \mathcal{H}'_{-2} + \mathcal{H}'_2 + \mathcal{H}'_{-1} + \mathcal{H}'_1, \quad (10)$$

where

$$\mathcal{H}'_0 = \sum_{i,j \neq} C_{ij} S_{zi} S_{zj} + \sum_{i,j \neq} A_{ij} S_{+i} S_{-j}, \quad (11)$$

$$\mathcal{H}'_{-2} = \sum_{i,j \neq} D_{ij} S_{+i} S_{+j},$$

$$\mathcal{H}'_2 = \sum_{i,j \neq} D_{ij}^* S_{-i} S_{-j},$$

$$\mathcal{H}'_{-1} = \sum_{i,j \neq} E_{ij} S_{+i} S_{zj},$$

$$\mathcal{H}'_1 = \sum_{i,j \neq} E_{ij}^* S_{-i} S_{zj},$$

with

$$A_{ij} = \frac{1}{2} [\tilde{A}_{ij} + \frac{1}{2} g^2 \beta^2 r_{ij}^{-3} (3v_{ij}^2 - 1)] = \frac{1}{2} (\tilde{A}_{ij} + \frac{1}{2} B_{ij}), \quad (12)$$

$$B_{ij} = g^2 \beta^2 r_{ij}^{-3} (3v_{ij}^2 - 1),$$

$$C_{ij} = \frac{1}{2} [X_{ij} - g^2 \beta^2 r_{ij}^{-3} (3\gamma_{ij}^2 - 1)] = \frac{1}{2} (X_{ij} - B_{ij}),$$

$$D_{ij} = 3g^2 \beta^2 r_{ij}^{-3} (\alpha_{ij}^2 - \beta_{ij}^2 - 2i\alpha_{ij}\beta_{ij})/8,$$

$$E_{ij} = -\frac{3}{2} g^2 \beta^2 r_{ij}^{-3} \gamma_{ij} (\alpha_{ij} - i\beta_{ij}),$$

$$\text{and } S_{\underline{+j}} = S_{\underline{xj}} + i S_{\underline{yj}},$$

where α_{ij} , β_{ij} , γ_{ij} are the direction cosines of r_{ij} . Notice that applying $\mathcal{H}'_0 (\mathcal{H}'_{-2}, \mathcal{H}'_2, \mathcal{H}'_{-1}, \mathcal{H}'_1)$ on eigenstates of \mathcal{H}_0 changes this state into a state with magnetic quantum number 0(+2, -2, +1, -1) higher than that of the original state, and hence with energy $0(-2g\beta H, +2g\beta H, -g\beta H, +g\beta H)$ higher than that of the original state.

From this we also conclude that the expectation values of $\mathcal{H}'_2, \mathcal{H}'_1, \mathcal{H}'_{-2}, \mathcal{H}'_{-1}$, with respect to eigenstates of \mathcal{H}_0 , vanish.

Notice also that the Hermitian adjoint of $\mathcal{H}'_1, \mathcal{H}'_2$ are $\mathcal{H}'_{-1}, \mathcal{H}'_{-2}$, while \mathcal{H}'_0 is Hermitian.

Since \mathcal{H}'_0 commutes with \mathcal{H}_0 , we can take the eigenstates of $(\mathcal{H}_0 + \mathcal{H}')$ as the unperturbed states ϕ_j, ϕ_k , and call the eigenstates of the complete Hamiltonian which go over to ϕ_j, ϕ_k in the limit of vanishing dipolar and exchange interactions as $|j\rangle, |K\rangle$.

The transitions which contribute to the first Larmor line occur between states with energy difference approximately equal to $g\beta H$. Therefore we have, for the first Larmor line

$$\int_0^\infty f(v)dv = \sum_{\substack{v \\ jk \approx g\beta Hh^{-1}}} |\langle j | S_x | k \rangle|^2, \quad (13a)$$

$$\int_0^\infty (v - g\beta Hh^{-1})^n f(v)dv = \sum_{\substack{v \\ jk \approx g\beta Hh^{-1}}} (v_{jk} - g\beta Hh^{-1})^n |\langle j | S_x | k \rangle|^2, \quad (13b)$$

where $h\nu_{jk}$ is the energy difference between states $|j\rangle$ and $|k\rangle$ and S_x is the x component of the total spin of the system. The criterion for $v_{jk} \approx g\beta Hh^{-1}$ is that $(v_{jk} - g\beta Hh^{-1})/g\beta Hh^{-1} \ll 1$.

As the first approximation we can substitute $|j\rangle, |k\rangle$ by ϕ_j, ϕ_k in expression 13 thus 13a becomes

$$\int_0^\infty f(v)dv = \sum_{\substack{v \\ jk \approx g\beta Hh^{-1}}} |(\phi_j S_x \phi_k)|^2. \quad (14)$$

Now

$$S_x = \frac{1}{2} S_+ + \frac{1}{2} S_-.$$

As $M_j - M_k = -1$ for all of the matrix elements included in the sum of equation 14, we have

$$(\phi_j S_+ \phi_k) = 0.$$

Expression 14 then becomes

$$\int_0^\infty f(v)dv = \sum_{\substack{v \\ jk \approx g\beta Hh^{-1}}} |(\phi_j \frac{S_-}{2} \phi_k)|^2. \quad (14a)$$

Now $\frac{S_z}{2}$ is a rather selective operator; its matrix element between ϕ_j and ϕ_k vanishes unless $M_j - M_k = -1$, and this condition is satisfied if and only if the corresponding states $|j\rangle$ $|k\rangle$ have an energy difference $h\nu_{jk} \approx g\beta H$. We have now the interesting result that $(\phi_j \frac{S_z}{2} \phi_k)$ is a good approximation to $\langle j | S_x | k \rangle$ when $|j\rangle$, $|k\rangle$ are two states the transition between which contributes to the first Larmor line, and is zero otherwise. Therefore using $\frac{S_z}{2}$ in place of S_x automatically selects out the unwanted matrix elements, and we can, in expression 14, formally sum over all states j and k , since all of the extra terms vanish. Thus expression 14a becomes

$$\int_0^\infty f(\nu) d\nu = \sum_{\substack{\nu \\ jk \approx g\beta H}} \left| \left(\phi_j \frac{S_z}{2} \phi_k \right) \right|^2 = \sum_{j,k} \left| \left(\phi_j \frac{S_z}{2} \phi_k \right) \right|^2$$

$$= \sum_{j,k} \left(\phi_j \frac{S_z}{2} \phi_k \right) \left(\phi_j \frac{S_z}{2} \phi_k \right)^* = \sum_{j,k} \left(\phi_j \frac{S_z}{2} \phi_k \right) \left(\phi_k \frac{S_z}{2} \phi_j \right) = \text{Tr} \left(\frac{S_z}{2} \frac{S_z}{2} \right) , \quad (15)$$

correct to the first approximation.

We see that a series difficult to evaluate is now reduced to the trace of the product of the operator $\frac{S_z}{2}$ with its Hermitian adjoint $\frac{S_z}{2}$. The operator $\frac{S_z}{2}$ will be called the absorption operator for the first Larmor line in a perpendicular field.

Now ϕ_j , ϕ_k are eigenstates of $H_0 + H'_0$, i.e.,

$$(H_o + H'_o) \phi_j = E_j^o \phi_j .$$

$$(H_o + H'_o) \phi_k = E_k^o \phi_k .$$

But E_j^o , E_k^o equal to E_j , E_k , to the approximation of first order perturbation, since from the perturbation theory, the first order corrections to E_j and E_k equal to the matrix elements V_{jj} and V_{kk} , where V is the perturbing potential, which is the sum $(H'_1 + H'_{-1} + H'_2 + H'_{-2})$ in our case, and since all of these matrix elements vanish in our problem.

Hence we have

$$\begin{aligned} V_{jk}(\phi_j \frac{S_z}{2} \phi_k) &= \frac{1}{h} (\phi_j (H_o + H'_o) \frac{S_z}{2} \phi_k) \\ &\quad - (\phi_j \frac{S_z}{2} (H_o + H'_o) \phi_k) \\ &= \frac{1}{h} (\phi_j [H_o + H'_o, \frac{S_z}{2}] \phi_k) . \end{aligned} \quad (16)$$

As $[H_o, \frac{S_z}{2}] = g\beta H \frac{S_z}{2}$, we have

$$(V_{jk} - g\beta H h^{-1})(\phi_j \frac{S_z}{2} \phi_k) = \frac{1}{h} (\phi_j [H'_o, \frac{S_z}{2}] \phi_k) . \quad (17)$$

correct to the first order.

In general, we have

$$V_{jk}^n (\phi_j \frac{S_z}{2} \phi_k) = \frac{1}{h^n} (\phi_j [(H_o + H'_o), [(H_o + H'_o), \dots [(H_o + H'_o), \frac{S_z}{2}], \dots]] \phi_k) . \quad (18)$$

and

$$(\nu_{jk} - g\beta Hh^{-1})^n (\phi_j \frac{S_z}{2} \phi_k) = \frac{1}{h^n} (\phi_j [\mathcal{H}_o' [\mathcal{H}_o' \cdots [\mathcal{H}_o' \frac{S_z}{2}] \cdots]] \phi_k), \quad (18a)$$

where we commute $\frac{S_z}{2}$ with $(\mathcal{H}_o + \mathcal{H}_o')$ or \mathcal{H}_o' for n times. Expression 13b for $n = n_1 + n_2$ can be written as

$$\begin{aligned} \int_0^\infty (\nu - g\beta Hh^{-1})^{n_1+n_2} f(\nu) d\nu &= \sum_{\substack{\nu_{jk} \approx g\beta Hh^{-1}}} (\nu_{jk} - g\beta Hh^{-1})^{n_1+n_2} |\langle j | S_x | k \rangle|^2 \\ &\approx \sum_{j, k} (\nu_{jk} - g\beta Hh^{-1})^{n_1+n_2} \left| (\phi_j \frac{S_z}{2} \phi_k) \right|^2 \\ &\approx \frac{1}{h^n} \text{Tr}([\mathcal{H}_o' [\mathcal{H}_o' \cdots [\mathcal{H}_o' \frac{S_z}{2}] \cdots]] [[\cdots [\frac{S_z}{2}, \mathcal{H}_o] \cdots \mathcal{H}_o' \mathcal{H}_o]]), \end{aligned}$$

where there are n_1 \mathcal{H}_o' 's in the first commutator bracket, and n_2 \mathcal{H}_o 's in the second commutator bracket. In the above process of calculation both $f(\nu)$ and $(\nu - g\beta Hh^{-1})$ are replaced by quantities which are equal to them in the first approximation, hence the expression is correct to the first approximation.

A similar expression, with \mathcal{H}_o' replaced by $\mathcal{H}_o + \mathcal{H}_o'$, gives

$$\int_0^\infty \nu^{n_1+n_2} f(\nu) d\nu, \text{ the } (n_1+n_2)^{\text{th}} \text{ moment about the origin.}$$

In practice the multiple commutator becomes more and more difficult to evaluate as the length increases, and we usually split n as evenly as possible. For instance, if n is an even integer, we take

$n_1 = n_2 = \frac{n}{2}$, and if n is an odd integer, we take $n_1 = (n+1)/2$,

$n_2 = (n-1)/2$.

Let us now summarize the foregoing as follows: the calculation of the moments of the first Larmor line is facilitated by obtaining the absorption operator $\frac{S_-}{2}$, taking the trace of the product of $\frac{S_-}{2}$ with its Hermitian adjoint $\frac{S_+}{2}$ gives the zeroth moment of the line, and taking the trace of the product of suitable multiple commutator between \mathcal{H}_0' and $\frac{S_-}{2}$ with suitable multiple commutator between \mathcal{H}_0' and $\frac{S_+}{2}$ gives higher moments of the line about its mean frequency. Similar expressions for moments about the origin can be obtained if \mathcal{H}_0' above is replaced by $\mathcal{H}_0 + \mathcal{H}_0'$.

Van Vleck (3) used the above method to obtain, after some calculations, the second moment of the first Larmor line in a perpendicular field for a powder as:

$$\begin{aligned} \langle \Delta v^2 \rangle_{av} &\equiv \langle (v - g\beta H/h)^2 \rangle_{av} = \frac{\int_0^\infty (v - g\beta H h^{-1})^2 f(v) dv}{\int_0^\infty f(v) dv} \\ &= \frac{\text{Tr}([\mathcal{H}_0', \frac{S_-}{2}] [\frac{S_+}{2}, \mathcal{H}_0'])}{h^2 \text{Tr}(\frac{S_-}{2} \frac{S_+}{2})} = \frac{3}{5} g^4 \beta^4 h^{-2} S(S+1) \sum_{k \neq j} r_{jk}^{-6}, \end{aligned} \quad (18)$$

the summation is over all other atoms except j , which can be chosen

arbitrarily as long as it is not near the surface of the salt. Expression 18 agrees with the experiments within experimental uncertainties, which are smaller than ten percent.

The absorption line was then assumed to have a Gaussian distribution

$$f(v) = \langle v^0 \rangle_{av} [2\pi \langle v^2 \rangle_{av}]^{-\frac{1}{2}} \exp[-(v - g\beta H h^{-1})^2 / 2(\Delta v^2)_{av}], \quad (19)$$

It was concluded that expression 19 is a close description of the absorption line in case of negligible exchange forces, and is thus useful for nuclear resonance, where exchange does not enter.

Van Vleck also calculated the fourth moment of the first Larmor line in a perpendicular field, and the interested reader can find the rather lengthy expression in his paper (3).

Some low frequency lines were studied by Wright (4). We shall demonstrate her method by reproducing her arguments in obtaining the moments of the low frequency line in a perpendicular field as follows*:

It is necessary to limit the states j, k , appearing in expression 8 in some way to states with energy differences much smaller than $g\beta H$. The problem is to construct, by means of perturbation formulas, an operator from S_x which gives, at least to the first order, the correct matrix element $\langle j | S_x | k \rangle$ between levels with small energy difference

*For an alternative method, see Reference 8.

(small compared to $g\beta H$) and zero matrix elements for other pairs of states. In other words, if ϕ_j, ϕ_k are the states corresponding to $|j\rangle$ and $|k\rangle$, respectively, and if M_j, M_k are their quantum magnetic numbers, respectively, then we want to find an operator O such that $(\phi_j O \phi_k)$ approximately equals $\langle j | S_x | k \rangle$ for $M_j = M_k$ and vanishes otherwise.

To the first order perturbation the state $|j\rangle$ is given by

$$|j\rangle = \phi_j + \sum_{\ell} \sum_{n=1, -1, 2, -2} \frac{(\phi_{\ell} \mathcal{H}_n \phi_j)}{(M_{\ell} - M_j) g\beta H} \phi_{\ell} \quad (20)$$

For states j, k , such that $M_j = M_k$, $(\phi_j | S_x | \phi_k) = 0$, therefore, the first order non-vanishing term in $\langle j | S_x | k \rangle$ for $M_j = M_k$ are

$$\langle j | S_x | k \rangle = \langle j | \frac{S+}{2} + \frac{S-}{2} | k \rangle$$

$$= \left(\phi_j + \sum_{\ell} \sum_{n=1, -1} \frac{(\phi_{\ell} \mathcal{H}_n \phi_j)}{(M_{\ell} - M_j) g\beta H} \phi_{\ell} \right) \left| \frac{S+}{2} + \frac{S-}{2} \right| \phi_k + \sum_{\ell} \sum_{n=1, -1} \frac{(\phi_{\ell} \mathcal{H}_n \phi_k)}{(M_{\ell} - M_k) g\beta H} \phi_{\ell}$$

$$= \sum_{\ell} \frac{(\phi_{\ell} \mathcal{H}_{-1} \phi_j)^*}{(M_{\ell} - M_j) g\beta H} (\phi_{\ell} \frac{S+}{2} \phi_k) + \sum_{\ell} (\phi_j \frac{S-}{2} \phi_{\ell}^*) \frac{(\phi_{\ell} \mathcal{H}_{-1} \phi_k)}{(M_{\ell} - M_k) g\beta H}$$

$$+ \sum_{\ell} (\phi_{\ell} \mathcal{H}_{-1} \phi_k) \frac{(\phi_j \frac{S+}{2} \phi_{\ell}^*)}{(M_{\ell} - M_k) g\beta H} + \sum_{\ell} (\phi_{\ell} \frac{S-}{2} \phi_k) \frac{(\phi_{\ell} \mathcal{H}_1 \phi_j)^*}{(M_{\ell} - M_j) g\beta H}$$

$$\begin{aligned}
 &= \sum_{\ell} \frac{(\phi_j \mathcal{H}_1 \phi_\ell) (\phi_\ell \frac{S+}{2} \phi_k)}{+g\beta H} + \sum_{\ell} \frac{(\phi_j \frac{S-}{2} \phi_\ell) (\phi_\ell \mathcal{H}_{-1} \phi_j)}{+g\beta H} \\
 &+ \sum_{\ell} \frac{(\phi_j \frac{S+}{2} \phi_\ell) (\phi_\ell \mathcal{H}_{-1} \phi_k)}{-g\beta H} + \sum_{\ell} \frac{(\phi_j \mathcal{H}_{-1} \phi_j) (\phi_\ell \frac{S-}{2} \phi_k)}{-g\beta H} \\
 &= \frac{(\phi_j \mathcal{H}_1 \frac{S+}{2} \phi_k)}{g\beta H} - \frac{(\phi_j \mathcal{H}_{-1} \frac{S-}{2} \phi_k)}{g\beta H} \quad (20)
 \end{aligned}$$

$$= (\phi_j O \phi_k) .$$

$$\text{where } O \equiv \left(\mathcal{H}_1 \frac{S+}{2} - \mathcal{H}_{-1} \frac{S-}{2} \right) / g\beta H. \quad (20a)$$

Now it is easily seen that the matrix elements of O are zero for $M_j \neq M_k$. A physical way to see this is by noticing that applying $S+$ to ϕ_k increases the magnetic quantum number by one, and applying \mathcal{H}_1 to ϕ_k decreases the magnetic quantum number by one, so that the successive application of \mathcal{H}_1 and $S+$ leaves the magnetic quantum number unchanged; the same is true for \mathcal{H}_{-1} and $S-$. The orthogonality condition for eigenstates of \mathcal{H}_0 then ensures the vanishing of the afore-mentioned matrix elements. Operator O in expression 20a is therefore the absorption operator for the line.

Hence we have for the moments of this line

$$\begin{aligned}
 \int_0^\infty f(v)dv &= \sum_{E_j \approx E_k} | \langle j, S_x | k \rangle |^2 = \sum_{M_j = M_k} | (\phi_j^* \phi_k) |^2 \\
 &= \sum_{\text{all } j, k} | (\phi_j^* \phi_k) |^2 = \text{Tr}(O O^\dagger) . \tag{21}
 \end{aligned}$$

$$\int_0^\infty v^{n_1+n_2} f(v)dv = \frac{1}{h^{n_1+n_2}} \text{Tr}([H_o^{n_1} [H_o^{n_2} [H_o^{n_3} \dots [H_o^{n_{l-1}} [H_o^{n_l} O^\dagger, H_o^{n_l}] \dots H_o^{n_3}] H_o^{n_2}] H_o^{n_1}] \dots)$$

where there are $n_1 H_o^{n_1}$ in the first commutator and $n_2 H_o^{n_2}$ in the second commutator and where O^\dagger is the Hermitian adjoint of O . Notice here the mean frequency \bar{v} is zero so that it does not appear in expression 21.

Again we see that calculating the moments of this line is facilitated by obtaining the operator O which will be called the absorption operator of this line.

The above is a fairly laborious process and is only applicable for lines where first order perturbation suffices. For lines that require higher order perturbation the derivation would be still more difficult. As the result comes out to be suspiciously simple it is natural to ask whether there is an easier way to handle this problem.

The next section will be devoted to an investigation of this question. It will be shown there that a rule can indeed be found which would enable one to obtain the absorption operator of all lines without much

labor. Furthermore, this rule is not only true for a system with the particular Hamiltonian discussed previously, but is also true for Hamiltonians of all kinds, provided the perturbing part of the complete Hamiltonian is small enough for the perturbation method to be valid.

II. THE ABSORPTION OPERATOR

Let us assume that the Hamiltonian of a system is described by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' . \quad (22)$$

where \mathcal{H}' is the perturbing Hamiltonian small compared to \mathcal{H}_0 .

Let us decompose \mathcal{H}' into its spectrum

$$\mathcal{H}' = \int_{-\infty}^{\infty} \mathcal{H}'(\omega) d\omega , \quad (23)$$

where

$$[\mathcal{H}_0, \mathcal{H}'(\omega)] = \hbar\omega \mathcal{H}'(\omega) . \quad (24)$$

The physical meaning of $\mathcal{H}'(\omega)$ is that it is the part of \mathcal{H}' which, when operating on an eigenstate of \mathcal{H}_0 , will raise the state into a state of eigenvalue $\hbar\omega$ higher than that of the original state.

Under an extremely small perturbing potential $M(t)$, $M(t) \ll \mathcal{H}'$, the probability of transition at time T from one state to another, both eigenstates of \mathcal{H}_0 when $t = 0$, is proportional to the absolute value square of the matrix element

$$\begin{aligned}
 & \int_{-\infty}^T \langle \exp(-i\mathcal{H}T/\hbar) \phi_j | \exp[-i\mathcal{H}(T-t)/\hbar] \mathcal{M}(t) \exp[-i\mathcal{H}t/\hbar] \phi_k \rangle dt \\
 &= \langle \phi_j | \int_{-\infty}^T \exp(i\mathcal{H}t/\hbar) \mathcal{M}(t) \exp(-i\mathcal{H}t/\hbar) dt | \phi_k \rangle. \tag{25}
 \end{aligned}$$

Physically, expression 25 says that the wave function, in state ϕ_k at $t = 0$, propagates to time t with the propagation factor $\exp(-i\mathcal{H}t/\hbar)$; there it is scattered by the potential $\mathcal{M}(t)$, and then propagates to time T with propagation factor $\exp[-i\mathcal{H}(T-t)/\hbar]$. The matrix element is then taken between the resulting wave function and the wave function which is ϕ_j at $t = 0$, and is therefore $\exp(-i\mathcal{H}T/\hbar)\phi_j$ at time T . As the system may be scattered at any time t in the time interval $[-\infty, T]$, a time integral from $-\infty$ to T is taken.

Now, we know that

$$\begin{aligned}
 \exp(i\mathcal{H}t/\hbar) &= \exp[i(\mathcal{H}_0 + \mathcal{H}')t/\hbar] \\
 &= \left\{ 1 + \frac{i}{\hbar} \int_0^t \mathcal{H}'(t_1) dt_1 + \left(\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} \mathcal{H}'(t_2) \mathcal{H}'(t_1) dt_2 \right. \\
 &+ \dots + \left(\frac{i}{\hbar}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} \mathcal{H}'(t_n) \mathcal{H}'(t_{n-1}) \dots \mathcal{H}'(t_1) dt_n \\
 &+ \dots \left. \right\} \exp(i\mathcal{H}_0 t/\hbar), \tag{26}
 \end{aligned}$$

$$\text{where } \mathcal{H}'(t) = \exp(i\mathcal{H}_0 t/\hbar) \mathcal{H} \exp(-i\mathcal{H}_0 t/\hbar), \quad (27)$$

and

$$\begin{aligned} \exp(-i\mathcal{H}t/\hbar) &= \exp[-i(\mathcal{H}_0 + \mathcal{H}')t/\hbar] \\ &= \exp(-i\mathcal{H}_0 t/\hbar) \left\{ 1 - \frac{i}{\hbar} \int_0^t \mathcal{H}'(t_1) dt_1 + \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} \mathcal{H}'(t_1) \mathcal{H}'(t_2) dt_2 \right. \\ &\quad + \dots + \left. \left(-\frac{i}{\hbar}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} \mathcal{H}'(t_1) \mathcal{H}'(t_2) \dots \mathcal{H}'(t_n) dt_n \right. \\ &\quad \left. + \dots \right\}. \end{aligned} \quad (28)$$

We have, from expressions 26 and 28

$$\begin{aligned} &\int_{-\infty}^T \exp(i\mathcal{H}t/\hbar) \mathcal{M}(t) \exp(-i\mathcal{H}t/\hbar) dt \\ &= \int_{-\infty}^T \mathcal{M}(t) dt + \left(\frac{i}{\hbar}\right) \int_{-\infty}^T dt \int_0^t [\mathcal{H}'(t_1), \mathcal{M}(t)] dt_1 \\ &\quad + \left(\frac{i}{\hbar}\right)^2 \int_{-\infty}^T dt \int_0^t dt_1 \int_0^{t_1} [\mathcal{H}'(t_2), [\mathcal{H}'(t_1), \mathcal{M}(t)]] dt_2 + \dots \\ &\quad + \left(\frac{i}{\hbar}\right)^n \int_{-\infty}^T dt \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} [\mathcal{H}'(t_n), [\mathcal{H}'(t_{n-1}), \dots \\ &\quad \quad \quad [\mathcal{H}'(t_1), \mathcal{M}(t)] \dots]] dt_n \\ &\quad + \dots, \end{aligned} \quad (29)$$

where

$$\mathcal{M}(t) = \exp(i\mathcal{H}_0 t/\hbar) \mathcal{U}(t) \exp(-i\mathcal{H}_0 t/\hbar). \quad (30)$$

Without loss of generality, we may assume

$$\mathcal{M}(t) = \mathcal{U} e^{-i\omega t}, \quad (31)$$

where \mathcal{M} is an operator independent of t . Let us decompose \mathcal{M} into its spectrum

$$\mathcal{M} = \int_{-\infty}^{\infty} \mathcal{M}(\omega') d\omega', \quad (32)$$

$$\text{where } [\mathcal{H}_0, \mathcal{M}(\omega')] = \hbar\omega' \mathcal{M}(\omega'). \quad (33)$$

$$\text{Then } \exp(i\mathcal{H}_0 t/\hbar) \mathcal{M}(\omega') \exp(-i\mathcal{H}_0 t/\hbar) = e^{i\omega t} \mathcal{M}(\omega').$$

We therefore have

$$\mathcal{M}(t) = \int_{-\infty}^{\infty} \mathcal{M}(\omega') e^{i(\omega' - \omega)t} d\omega'. \quad (34)$$

Similarly, from expressions 23, 24 and 27, we get

$$\mathcal{H}'(t) = \int_{-\infty}^{\infty} \mathcal{H}'(\omega') e^{-i\omega't} d\omega'. \quad (35)$$

The n^{th} term of the right hand side of expression 29 is therefore equal to

$$\begin{aligned}
 & \left(\frac{i}{\hbar} \right)^n \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} [\mathcal{H}'(\omega_n), [\mathcal{H}'(\omega_{n-1}), \cdots, [\mathcal{H}'(\omega_1), \mathcal{H}(\omega_0)] \cdots]] \\
 & \quad d\omega_n d\omega_{n-1} \cdots d\omega_0 \\
 & \cdot \left\{ \int_{-\infty}^T dt \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \exp[i\omega_n t_n + i\omega_{n-1} t_{n-1} + \cdots + i\omega_1 t_1 + i(\omega_0 - \omega)t] \right\}. \tag{36}
 \end{aligned}$$

As $T \rightarrow \infty$, the dominant term of expression 36 is equal to

$$\begin{aligned}
 & \left(\frac{i}{\hbar} \right)^n \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \frac{[\mathcal{H}'(\omega_n), [\mathcal{H}'(\omega_{n-1}), \cdots, [\mathcal{H}'(\omega_1), \mathcal{H}(\omega_0)] \cdots]]}{(i)^n (\omega_n + \omega_{n-1} + \cdots + \omega_2 + \omega_1)} \\
 & \quad 2\pi (\omega_0 + \omega_1 + \cdots + \omega_n - \omega) \cdot d\omega_0 d\omega_1 d\omega_2 \cdots d\omega_n \\
 & = 2\pi \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \frac{[\mathcal{H}'(\omega_n), [\mathcal{H}'(\omega_{n-1}), \cdots, [\mathcal{H}'(\omega_1), \mathcal{H}(\omega_0)] \cdots]] (\omega_0 + \omega_1 + \cdots + \omega_n - \omega)}{(\hbar\omega_n)(\hbar\omega_n + \hbar\omega_{n-1}) \cdots (\hbar\omega_n + \hbar\omega_{n-1} + \cdots + \hbar\omega_1)} \\
 & \quad d\omega_0 \cdots d\omega_n. \tag{37}
 \end{aligned}$$

The neglected terms in expression 36, as will be discussed in the next section, give higher order corrections to the absorption lines.

The physical meaning of expression 37 is clear: $\mathcal{H}'(\omega_j)$ changes the system to a state with an energy increase of $\hbar\omega_j$, and the successive

applications of $\mathcal{H}'(\omega_n), \mathcal{H}'(\omega_{n-1}), \dots, \mathcal{H}'(\omega_1), \mathcal{H}'(\omega_0)$ change the

system to a state with an energy higher by an amount of

$\hbar(\omega_n + \omega_{n-1} + \dots + \omega_1 + \omega_0)$ than that of the original state, and the law of the conservation of energy demands that this should be equal to the energy absorbed from $\mathcal{H}(t)$, which is $\hbar\omega$. There are many alternative ways to apply a given group of $\mathcal{H}'(\omega_j)$'s and $\mathcal{H}(\omega_0)$, and expression 37 indicates that all of them should be taken into account, with the weighting factor $[(\hbar\omega_n)(\hbar\omega_n + \hbar\omega_{n-1}) \dots (\hbar\omega_n + \dots + \hbar\omega_1)]^{-1}$ for each.

If the spectrum of \mathcal{H}' and \mathcal{H} are discrete, i.e.,

$$\mathcal{H}' = \sum_a \mathcal{H}'(\omega_a) = \sum_a \int_{-\infty}^{\infty} \mathcal{H}'(\omega_a) \delta(\omega - \omega_a) d\omega, \quad (38)$$

and

$$\mathcal{H}(t) = e^{-i\omega t} \sum_{\beta} \mathcal{H}(\omega_{\beta}) = e^{-i\omega t} \sum_{\beta} \int_{-\infty}^{\infty} \mathcal{H}(\omega_{\beta}) \delta(\omega' - \omega_{\beta}) d\omega', \quad (39)$$

then with the omission of the factor 2π , expression 37 is reduced to the form

$$\sum_{a_n} \dots \sum_{\alpha_1} \sum_{\beta} \frac{[\mathcal{H}'(\omega_{a_n}), [\mathcal{H}'(\omega_{a_{n-1}}), \dots, [\mathcal{H}'(\omega_1), \mathcal{H}(\omega_{\beta})] \dots]] \delta(\omega_{a_n} + \dots + \omega_{a_1} + \omega_{\beta} - \omega)}{(\hbar\omega_{a_n})(\hbar\omega_{a_n} + \hbar\omega_{a_{n-1}}) \dots (\hbar\omega_{a_n} + \hbar\omega_{a_{n-1}} + \dots + \hbar\omega_1)}. \quad (40)$$

Let us single out one term of expression 40 and study it more

closely. We see that its matrix elements between ϕ_j and ϕ_k will

vanish unless $\nu_{jk} = \frac{\omega_{a_n} + \dots + \omega_{a_1} + \omega_{\beta}}{2\pi}$. Hence the absorption

operator of a line centering around $\bar{\omega}$ is, in the first approximation, the sum of the lowest order terms in expression 40, with the delta function omitted, which satisfy the condition

$$\omega_{a_n} + \dots + \omega_{a_1} + \omega_{\beta} = \bar{\omega},$$

since the matrix element of this operator, taken between two states ϕ_j, ϕ_k , with $\omega_{jk} = \omega$, closely approximates $\langle j | M | k \rangle$, and is equal to zero otherwise.

The right hand side of expression 29 is now reduced to, aside from a factor of 2π

$$\begin{aligned}
 & \sum_{\beta} M(\omega_{\beta}) \delta(\omega_{\beta} - \omega) + \sum_a \sum_{\beta} \frac{[H'(\omega_a), M(\omega_{\beta})]}{\hbar \omega_a} \delta(\omega_a + \omega_{\beta} - \omega) \\
 & + \sum_{a_1} \sum_{a_2} \sum_{\beta} \frac{[H'(\omega_{a_2}), [H'(\omega_{a_1}), M(\omega_{\beta})]]}{(\hbar \omega_{a_2})(\hbar \omega_{a_1} + \hbar \omega_{a_2})} \delta(\omega_{a_1} + \omega_{a_2} + \omega_{\beta} - \omega) \\
 & + \dots \\
 & + \sum_{a_1} \sum_{a_2} \sum_{a_n} \sum_{\beta} \frac{[H'(\omega_{a_n}), [H'(\omega_{a_{n-1}}), \dots [H'(\omega_{a_1}), M(\omega_{\beta})] \dots]] \delta(\omega_{a_n} + \dots + \omega_{a_1} + \omega_{\beta} - \omega)}{(\hbar \omega_{a_n})(\hbar \omega_{a_n} + \hbar \omega_{a_{n-1}}) \dots (\hbar \omega_{a_n} + \dots + \hbar \omega_{a_1})}
 \end{aligned}
 \tag{61}$$

Let us summarize the foregoing by formulating the rule for obtaining the absorption operator as follows:

(1) Choose the fewest number possible of $\mathcal{H}'(\omega_a)$'s, the successive application of which, together with a chosen $\mathcal{H}(\omega_\beta)$, will give an energy change equal to the mean energy of absorption of the line of interest. (If there are several ways of achieving this that are of the same order, all of them have to be taken into account.)

(2) The absorption operator is the sum of all the multiple commutators of the $\mathcal{H}'(\omega_a)$'s with $\mathcal{H}(\omega_\beta)$, each divided by the weighting factor $(\hbar\omega_{a_n})(\hbar\omega_{a_n} + \hbar\omega_{a_{n-1}}) \cdots (\hbar\omega_{a_n} + \cdots + \hbar\omega_{a_1})$, i.e.,

$$\mathcal{H} = \sum_{a_n} \sum_{a_1} \sum_{\beta} \frac{[\mathcal{H}'(\omega_{a_n}), [\mathcal{H}'(\omega_{a_{n-1}}), \cdots [\mathcal{H}'(\omega_{a_1}), \mathcal{H}(\omega_\beta) \cdots]]]}{(\hbar\omega_{a_n})(\hbar\omega_{a_n} + \hbar\omega_{a_{n-1}}) \cdots (\hbar\omega_{a_n} + \cdots + \hbar\omega_{a_1})} \quad , \quad (42)$$

$$\omega_{a_n} + \cdots + \omega_{a_1} + \omega_\beta = \bar{\omega}$$

where $\frac{\bar{\omega}}{2\pi}$ is the mean absorption frequency of the line of interest.

The moments of a line about the mean frequency can be obtained from appropriate commutators between \mathcal{H}'_0 and the absorption operator, as was indicated in the previous section. Similar expressions can be obtained for the moments about the origin, if \mathcal{H}'_0 is replaced by $\mathcal{H}_0 + \mathcal{H}'_0$.

As an illustration of the employment of this rule, let us proceed to obtain the absorption operators of the absorption lines of a spin system with the Hamiltonian of expressions 2 and 3. First, we find from expression 11 and expression 24 that

$$\mathcal{H}'(ng\beta HH^{-1}) = \mathcal{H}'_n, \quad n = 0, 1, -1, 2, -2. \quad (43)$$

For perpendicular oscillating fields

$$\begin{aligned} \mathcal{M}(t) &= e^{i\omega t} H_{\text{osc}} g\beta S_x \\ &= e^{i\omega t} H_{\text{osc}} g\beta \left(\frac{S_+}{2} + \frac{S_-}{2} \right) . \end{aligned} \quad (44)$$

We shall omit the factor $H_{\text{osc}} g\beta$ in consistency with the notations in the preceding section, and identify $\frac{1}{2} S_+$ and $\frac{1}{2} S_-$ as $\mathcal{M}(-g\beta HH^{-1})$ and $\mathcal{M}(g\beta HH^{-1})$, respectively.

For the first Larmor line in a perpendicular field, $\bar{\omega} = g\beta HH^{-1}$, and the lowest order non-vanishing term in expression 41 is

$$O = \mathcal{M}(g\beta HH^{-1}) \frac{S_-}{2} . \quad (45)$$

This is the absorption operator for this line, in agreement with the previous section.

For the low frequency line in a perpendicular field, these are two lowest order non-vanishing terms in expression 41 which give $\omega_{a_1} + \omega_{a_2} + \dots + \omega_{a_n} + \omega_{\beta} = \bar{\omega} = 0$, i.e., $n = 1$, $\omega_{a_1} = -\omega_{\beta} = \pm g\beta HH^{-1}$, therefore,

$$O = \frac{[\mathcal{H}_1', \frac{1}{2} S_+]}{g\beta H} - \frac{[\mathcal{H}_1', \frac{1}{2} S_-]}{g\beta H} , \quad (46)$$

again in agreement with the previous section.

For the second Larmor line in a perpendicular field, we obtain the absorption operator as

$$O = \frac{[\mathcal{H}_1', \frac{1}{2} S_-]}{g\beta H} . \quad (47)$$

For the third Larmor line in a perpendicular field, the absorption operator is obtained as

$$O = \frac{[\mathcal{H}_1', [\mathcal{H}_1', \frac{1}{2} S_-]]}{(g\beta H)(2g\beta H)} + \frac{[\mathcal{H}_2', [\mathcal{H}_0', \frac{1}{2} S_-]]}{(2g\beta H)(2g\beta H)} + \frac{[\mathcal{H}_2', [\mathcal{H}_2', \frac{1}{2} S_+]]}{(2g\beta H)(4g\beta H)} , \quad (48)$$

The term with the commutator $[\mathcal{H}_0', [\mathcal{H}_2', \frac{1}{2} S_-]]$ is not included, as \mathcal{H}_2' commutes with S_- , so this commutator equals zero.

Next, let us consider the parallel field case; i. e.,

$$\mathcal{M}(t) = e^{-i\omega t} S_z . \quad (49)$$

It is easy to see that \mathcal{M} has only one component in its spectrum, i. e.,

$$S_z = \mathcal{M}(0) , \quad (50)$$

since S_z commutes with \mathcal{H}_0 .

For the first Larmor line in a parallel field, the absorption operator is

$$O = \frac{[\mathcal{H}_1, S_z]}{g\beta H} = \frac{\mathcal{H}_1'}{g\beta H} . \quad (51)$$

For the second Larmor line in a parallel field

$$O = \frac{[\mathcal{H}_2, S_z]}{2g\beta H} = \frac{\mathcal{H}_2'}{g\beta H} . \quad (52)$$

For the third Larmor line in a parallel field

$$O = \frac{[\mathcal{H}_1, [\mathcal{H}_2, S_z]]}{(g\beta H)(3g\beta H)} + \frac{[\mathcal{H}_2, [\mathcal{H}_1, S_z]]}{(2g\beta H)(3g\beta H)} \\ = \frac{[\mathcal{H}_1', \mathcal{H}_2']}{2(g\beta H)^2} . \quad (53)$$

This covers all of the cases up to the third harmonic lines except the low frequency line in a parallel field, which will be discussed in the next section.

The only zeroth order line is the first Larmor line in a perpendicular field. This has the strongest intensity and is most readily observed experimentally. There are four first order lines: (1) low frequency line, perpendicular field, (2) second Larmor line, perpendicular field, (3) first Larmor line, parallel field, (4) second Larmor line, parallel field. Recently it has been possible to measure these

lines with fair precision (6). No experiments have covered higher order lines except the low frequency line in a parallel field, which was studied by Wright (4).

The first Larmor line in a perpendicular field was investigated by Van Vleck (3), who calculated its zeroth, second, and the fourth moments and obtained good agreements with experiment. As the complexity of evaluation increases rapidly with the order of the moments, it has not been feasible to calculate the sixth or even higher moments of this line.

The low frequency line in a perpendicular field was investigated by Wright (4), who calculated its zeroth and second moments. The fourth moment of this line is of the same complexity as the sixth moment of the first Larmor line in a perpendicular field, since this line is of one order higher.

In sections IV, V, VI, VII, all of the four first order lines will be evaluated up to their second moments. Despite Wright's work, the low frequency line in a perpendicular field is also included, since in the past some approximations in evaluation had to be made, owing to the complexity of the problem, but this is no longer necessary if the averaging method introduced by the author is used.

As it turned out, the second moment for the low frequency line in a perpendicular field obtained by the author greatly differs from that obtained by Wright, well over the errors possibly

introduced by the approximations used. It is the author's opinion that algebraic errors were committed by Wright in her work.

Before we turn to detailed investigations of the absorption lines, let us first study the higher order corrections to the absorption in the next section.

III. HIGHER ORDER CORRECTIONS*

We have mentioned that the terms neglected in expression 36 constitute the higher order corrections to the absorption. To be more specific, we shall show that these terms give rise to higher order terms of the absorption operator, shifts of the mean frequencies of the absorption lines, and broadenings, or the higher moments, of the absorption lines. In particular, we shall show that the method of moments demonstrated in the previous sections gives moments correct in the first approximation of perturbation. With the present experimental techniques a second approximation is probably not needed in practice. Yet experimental techniques can improve, and also a clarification of those terms leads to better understanding of the problem.

Let us formally expand \mathcal{M} in a spectrum of $\mathcal{H}_0 + \mathcal{H}'$ rather than that of \mathcal{H}_0 , i.e.,

$$\mathcal{M} = \sum_{\omega'_a} \mathcal{M}(\omega'_a) , \quad (54)$$

where $[\mathcal{H}_0 + \mathcal{H}', \mathcal{M}(\omega'_a)] = \hbar \omega'_a \mathcal{M}(\omega'_a)$,

then we have

$$\exp(i\mathcal{H}t) \mathcal{M} \exp(-i\mathcal{H}t) = \sum_{\omega'_a} \mathcal{M}(\omega'_a) \exp(i\omega'_a t) . \quad (55)$$

*The study made in this section was initiated by the reading of a paper written by Kubo and Tomita (7), after the rest of this work had been completed.

Expression 25 then becomes

$$\begin{aligned}
 & \langle \phi_j | \int_{-\infty}^{\infty} \exp(i\mathcal{H}t/\hbar) e^{-i\omega t} \mathcal{M} \exp(-i\mathcal{H}t/\hbar) dt | \phi_k \rangle \\
 &= \langle \phi_j | \int_{-\infty}^{\infty} \sum_{\omega'_a} e^{-i\omega t} \mathcal{M}(\omega'_a) e^{+i\omega'_a t} dt | \phi_k \rangle \\
 &= 2\pi \sum_{\omega'_a} \langle \phi_j | \mathcal{M}(\omega'_a) | \phi_k \rangle \delta(\omega - \omega'_a), \tag{56}
 \end{aligned}$$

that is, the absorption would occur only when the frequency of the oscillating field is equal to one of the ω'_a 's of the spectrum of \mathcal{M} . Physically we expect that there is a group of ω'_a 's around the mean absorption frequency of each absorption line and that is why we observe an absorption curve around each mean absorption frequency in our experiment.

From expression 56 we have the conclusion that, for an absorption line of mean frequency $\bar{\nu}$, we have

$$\langle \nu^0 \rangle = \sum_{\omega'_a \approx \bar{\nu}} \text{Tr } \mathcal{M}(\omega'_a) \mathcal{M}^*(\omega'_a),$$

and

$$\langle \nu^n \rangle = \sum_{\omega'_a \approx \bar{\nu}} \nu'^n \text{Tr } \mathcal{M}(\omega'_a) \mathcal{M}^*(\omega'_a) / \langle \nu^0 \rangle, \text{ for } n > 0. \tag{57}$$

Expression 57 is exact and no approximation has been made, in contrast with the method given in the preceding section, which gives

answers correct only to the first order.

Now if we expand \mathcal{M} in a spectrum of \mathcal{H}_0 , as we did in the preceding section, we obtain

$$\begin{aligned}
 & \exp(i\mathcal{H}t)\mathcal{M}\exp(-i\mathcal{H}t) \\
 = & \sum_n \sum_{\omega_{a_n}, \omega_{\beta}} \left(\frac{i}{\hbar} \right)^n [\mathcal{H}(\omega_{a_n}), \mathcal{H}(\omega_{a_{n-1}}), \dots, \mathcal{H}(\omega_{a_1}), \mathcal{M}(\omega_{\beta})] \dots] \\
 & \exp(i\omega_{\beta}t) \left\{ \int_0^t dt_1 \dots \int_0^{t_{n-1}} dt_n \exp(i\omega_{a_n}t_n + i\omega_{a_{n-1}}t_{n-1} + \dots + i\omega_{a_1}t_1) \right\}. \tag{58}
 \end{aligned}$$

It was pointed out by Kubo and Tomita (7) that the time integral in expression 58 can be written as

$$\begin{aligned}
 & \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \exp[i(t_1 - t_2)\omega_{a_1} + i(t_2 - t_3)(\omega_{a_1} + \omega_{a_2}) + \dots \\
 & + i(t_{n-1} - t_n) \sum_{l=1}^{n-1} \omega_{a_l} + it_n \sum_{l=1}^n \omega_{a_l}], \tag{59}
 \end{aligned}$$

which is easily seen to be the convolution of the functions $1, \exp(i\omega_{a_1}t), \exp i(\omega_{a_1} + \omega_{a_2})t, \dots$ and $\exp i \sum_{l=1}^n \omega_{a_l} t$. Therefore, it is equal to

$$\frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} \frac{e^{pt}}{p(p-i\omega_{a_1})(p-i\omega_{a_1}-i\omega_{a_2}) \dots (p-i \sum_{l=1}^n \omega_{a_l})} dp, \tag{60}$$

with $\epsilon > 0$

With a change of variable $E = i\hbar p$ in expression 60, we can rewrite expression 58 in the following form:

$$\begin{aligned}
 & \exp(iHt)M \exp(-iHt) \\
 = & \sum_{n=1}^{\infty} \sum_{\omega_{a_1}, \omega_{a_n}} \left[H'(\omega_{a_1}), H'(\omega_{a_{n-1}}), \dots, \left[H'(\omega_{a_1}), M(\omega_{a_n}) \right] \dots \right] \\
 & \frac{\exp(i\omega_{a_n} t)}{-\infty - i\epsilon} \frac{\exp(iEt/\hbar) dE}{E(E - E_{a_1}) (E - E_{a_1} - E_{a_2}) \dots (E - \sum_{l=1}^{n-1} E_{a_l})} \\
 & \quad (61)
 \end{aligned}$$

where the path of integration is taken infinitesimally below the real axis.

It is obvious that if there is a pole of order 2 in the line integral of expression 61, we will obtain a term $Ate^{iE_{\beta}t/\hbar}$ in expression 61, where A is an operator independent of time and E_{β} is the location of the pole. In the same manner, if there is a pole of order $(n+1)$ in the line integral of expression 61, there will be a term $At^n e^{iE_{\beta}t/\hbar}$ in expression 61, where A is a time-independent operator and E_{β} is the location of the pole. Now the transition probability from one state to another under the excitation of M is proportional to the absolute value square of the matrix element of the time integral from $-\infty$ to $+\infty$ of expression 61 taken between these two states, yet the matrix elements arising from the operators $At^n \exp i\omega t$, with $n > 0$, do not even converge.

A comparison of expressions 61 and 55 will show where the trouble lies. They are two different expressions of the same quantity and thus should be equal, yet the exponential functions in expression 55 have argument $i\omega'_a t$ with ω'_a approximately equal to one of the mean absorption frequencies of the absorption lines, while the exponential functions in expression 61 have argument $i\bar{\omega}_n t$, with $\bar{\omega}_n$ the mean absorption frequency of some absorption line.

If we choose a certain $\bar{\omega}_n$ and take all the terms in expression 55 which have ω'_a approximately equal to $\bar{\omega}_n$, and make the following expansion:

$$\begin{aligned}
 & \sum_{\substack{\omega'_a \approx \bar{\omega}_n}} M(\omega'_a) \exp(i\omega'_a t) = \exp(i\bar{\omega}_n t) \sum_{\substack{\omega'_a \approx \bar{\omega}_n}} M(\omega'_a) \exp i(\omega'_a - \bar{\omega}_n)t \\
 & = \exp(i\bar{\omega}_n t) \left\{ \sum_{\substack{\omega'_a \approx \bar{\omega}_n}} M(\omega'_a) + it \sum_{\substack{\omega'_a \approx \bar{\omega}_n}} M(\omega'_a)(\omega'_a - \bar{\omega}_n) + \frac{(it)^2}{2!} \sum_{\substack{\omega'_a \approx \bar{\omega}_n}} M(\omega'_a)(\omega'_a - \bar{\omega}_n)^2 \right. \\
 & \quad \left. + \dots + \frac{(it)^k}{k!} \sum_{\substack{\omega'_a \approx \bar{\omega}_n}} M(\omega'_a)(\omega'_a - \bar{\omega}_n)^k + \dots \right\}, \quad (62)
 \end{aligned}$$

and then collect all of the terms in expression 61 which have the factor $\exp(i\bar{\omega}_n t)$, and express their sum in the following form;

$$\exp(i\bar{\omega}_n t) [g_0(\bar{\omega}_n) + it g_1(\bar{\omega}_n) + \frac{(it)^2}{2!} g_2(\bar{\omega}_n) + \dots + \frac{(it)^k}{k!} g_k(\bar{\omega}_n) + \dots], \quad (63)$$

we arrive at the conclusion that

$$g_0(\bar{\omega}_n) = \sum_{\omega_a' \approx \bar{\omega}_n} M(\omega_a') ,$$

$$g_1(\bar{\omega}_n) = \sum_{\omega_a' \approx \bar{\omega}_n} M(\omega_a') (\omega_a' - \bar{\omega}_n) ,$$

$$g_2(\bar{\omega}_n) = \sum_{\omega_a' \approx \bar{\omega}_n} M(\omega_a') (\omega_a' - \bar{\omega}_n)^2 ,$$

.....

$$g_k(\bar{\omega}_n) = \sum_{\omega_a' \approx \bar{\omega}_n} M(\omega_a') (\omega_a' - \bar{\omega}_n)^k . \quad (64)$$

Now we have

$$\text{Tr}(M(\omega_{a_1}') M^+(\omega_{a_2}')) = 0 \text{ if } \omega_{a_1}' \neq \omega_{a_2}'$$

since if $|i\rangle$ is any eigenstate of \mathcal{H} , $M(\omega_{a_1}') M^+(\omega_{a_2}') |i\rangle$ is an eigenstate of \mathcal{H} with energy $E(\omega_{a_1}' - \omega_{a_2}')$ higher, and as two eigenstates of \mathcal{H} with different energy eigenvalues are orthogonal to each other,

$$\langle i | M(\omega_{a_1}') M^+(\omega_{a_2}') | i \rangle = 0 \text{ for all } i \text{ if } \omega_{a_1}' \neq \omega_{a_2}' .$$

We have the conclusion that

$$\begin{aligned} \text{Tr}(g_{k_1}(\bar{\omega}_n) g_{k_2}^+(\bar{\omega}_n)) &= \sum_{\omega_a' \approx \bar{\omega}_n} (\omega_a' - \bar{\omega}_n)^{k_1+k_2} \text{Tr}(M(\omega_a') M^+(\omega_a')) \\ &= (\delta \Delta \omega)^{k_1+k_2} \cdot \langle \Delta \nu_o \rangle = (2\pi)^{k_1+k_2} \langle \Delta \nu \rangle^{k_1+k_2} \cdot \langle \Delta \nu_o \rangle . \end{aligned} \quad (65)$$

Hence if we take the sum of the terms in expression 61 which have the factor $t^k \exp(i\bar{\omega}_n t)$ and put it in the form $\frac{(it)^k}{k!} \exp(i\bar{\omega}_n t) g_k(\bar{\omega}_n)$, then the trace of the product $g_{k_1}(\bar{\omega}_n) g_{k_2}^+(\bar{\omega}_n)$ is proportional to the $(k_1 + k_2)^{th}$ moment of the absorption line centering around ω_n . This conclusion is somewhat more general than that given by Kubo and Tomita (7), who arrived at their conclusion from examining the correlation function of the spin system, since we can choose any k_1 and k_2 , provided that $k_1 + k_2 = K$, to obtain the K^{th} moment of a line. In practice, we split K as evenly as possible, for the convenience of calculation.

It is easy to see that the sum of the lowest order terms in $g_o(\bar{\omega}_n)$ is the absorption operator in the preceding section, since, according to the previous section, the absorption operator of a line centering around $\bar{\omega}_n$ is

$$O = \sum_{\substack{\omega_{\beta} + \sum_{\ell=1}^n \omega_{a_{\ell}} = \bar{\omega}_n}} \frac{[\mathcal{H}'(\omega_{a_n}), [\mathcal{H}'(\omega_{a_{n-1}}), \dots, [\mathcal{H}'(\omega_{a_1}), \mathcal{M}(\omega_{\beta})] \dots]]}{(\hbar\omega_{a_n})(\hbar\omega_{a_{n-1}} + \hbar\omega_{a_{n-1}}) \dots (\hbar\omega_{a_2} + \hbar\omega_{a_{n-1}} + \dots + \hbar\omega_{a_1})} . \quad (66)$$

where n is the smallest integer for the condition $\omega_{\beta} + \sum_{\ell=1}^n \omega_{a_{\ell}} = \bar{\omega}_n$ to hold. The coefficient of the operator

$[\mathcal{H}'(\omega_{a_n}), [\mathcal{H}'(\omega_{a_{n-1}}), \dots, [\mathcal{H}'(\omega_{a_1}), \mathcal{M}(\omega_{\beta})] \dots]]$ from expression 61 is

$$\frac{\exp(i\omega_{\beta} t)}{2\pi i} \int_{-\infty-i\epsilon}^{\infty-i\epsilon} \frac{\exp(iEt/\hbar) dE}{E(E - E_{a_1})(E - E_{a_1} - E_{a_2}) \dots (E - \sum_{\ell=1}^n E_{a_{\ell}})}$$

and the last pole in the line integral above, i.e., $\sum_{\ell=1}^n E_{\ell}$, gives a term

$$\frac{\exp i(\omega_{\beta} + \sum_{\ell=1}^n \omega_{a_{\ell}})t}{(\sum_{\ell=1}^n E_{a_{\ell}}) \cdots (E_{a_n} + E_{a_{n-1}})(E_{a_n})} = \frac{\exp i \bar{\omega}_n t}{(E_{a_n})(E_{a_n} + E_{a_{n-1}}) \cdots (E_{a_1} + \cdots + E_{a_n})}$$

which belongs to $g_0(\bar{\omega}_n)$ and is in agreement with expression 66. This is one of the lowest order terms of $g_0(\bar{\omega}_n)$ since n is the smallest number for $\omega_{\beta} + \sum_{\ell=1}^n \omega_{a_{\ell}} = \bar{\omega}_n$ to hold.

It is also easy to see that the sum of the lowest order terms in $g_1(\bar{\omega}_n)$ is

$$[\mathcal{H}_0', \mathcal{O}] = \sum_{\ell=1}^n \frac{[\mathcal{H}_0', [\mathcal{H}_0'(\omega_{a_n}), [\mathcal{H}_0'(\omega_{a_{n-1}}) \cdots [\mathcal{H}_0'(\omega_{a_1}), \mathcal{O}(\omega_{\beta})] \cdots]]]}{(\sum_{\ell=1}^n \omega_{a_{\ell}} + \omega_{\beta} = \bar{\omega}_n) (\hbar\omega_{a_n} + \hbar\omega_{a_{n-1}}) \cdots (\sum_{\ell=1}^n \hbar\omega_{a_{\ell}})}$$

for the terms of g_1 always arise from poles of order 2 or higher,

hence the lowest order terms in $g_1(\bar{\omega}_n)$ arise from poles of order 2 at $\sum_{\ell=1}^n \hbar\omega_{a_{\ell}}$.

In general, the sum of the lowest order terms in $g_k(\bar{\omega}_n)$ is $[\mathcal{H}_0', [\mathcal{H}_0', \cdots [\mathcal{H}_0', \mathcal{O}] \cdots]]$, where there are $k \mathcal{H}_0'$'s in the commutator bracket, and where \mathcal{O} is the absorption operator for the line centering around $\bar{\omega}_n$.

This, together with expression 65, establishes the legitimacy of the prescriptions given in the preceding section.

We shall in the following indicate some practical way of obtaining the g functions.

As an illustration, we shall first give the g functions for the first Larmor line in a perpendicular field as follows:

$$\begin{aligned}
 g_o(g\beta H \hbar^{-1}) = & \left(\frac{S_z}{2} + \sum_{\omega_a \neq 0} \frac{[U_a^1, \frac{S_z}{2}]}{(-\hbar\omega_a)} + \sum_{\omega_\beta \neq 0} \frac{[U_a^1, [H_\beta^1, \frac{S_z}{2}]]}{(-\hbar\omega_a)(-\hbar\omega_\beta)} + \sum_{\omega_a \neq 0} \frac{[U_a^1, [U_a^1, \frac{S_z}{2}]]}{(-\hbar\omega_a)^2} \right. \\
 & \left. + \sum_{\omega_\gamma \neq 0} \frac{[U_\gamma^1, [H_\gamma^1, \frac{S_z}{2}]]}{(-\hbar\omega_\gamma)^2} + \dots \right) \\
 & + \left(\frac{U_2^1, \frac{S_z}{2}}{2g\beta H} + \sum_{\omega_a \neq 0} \frac{[U_a^1, [H_2^1, \frac{S_z}{2}]]}{(-\hbar\omega_a)(2g\beta H)} + \frac{[U_o^1, [U_2^1, \frac{S_z}{2}]]}{-(2g\beta H)^2} + \dots \right) \\
 & + \left(\frac{[U_1^1, [H_1^1, \frac{S_z}{2}]]}{(g\beta H)(2g\beta H)} + \dots \right) + \left(\frac{[U_2^1, [H_o^1, \frac{S_z}{2}]]}{(2g\beta H)(2g\beta H)} + \dots \right), \quad (67)
 \end{aligned}$$

correct to the second order.

The first term of each parenthesis is an energy conserving term which gives one spin flip, and its weighting factor obeys the prescription in the previous section. Some of the other terms do not give the correct spin flip. This is because the magnetic quantum number is actually not a good quantum number in the presence of the dipolar and exchange interactions. These other terms can be obtained from the energy conserving terms by taking commutators of $H_{a_n}^1, H_{a_{n-1}}^1, \dots, H_{a_1}^1$ with the energy conserving terms, with the weighting factor

$\left[\left(-\sum_{k=1}^n \hbar \omega_{a_k} \right) \left(-\sum_{k=1}^{n-1} \hbar \omega_{a_k} \right) \cdots \left(-\hbar \omega_{a_1} - \hbar \omega_{a_2} \right) \left(-\hbar \omega_{a_1} \right) \right]^{-1}$ for each. If some of the factors are equal to zero, it does not actually give an infinite weighting factor. An examination of expression 61 gives us the conclusion that a term with such weighting factor arises from a pole in the line integral with order higher than the first. Since the residue of a function $f(E)$ at a pole E_0 of order $(K+1)$ is $\frac{1}{K!} \frac{d^K}{dE^K} (E-E_0)^{K+1} f(E) \Big|_{E=E_0}$, and since

$$(uv)^{(K)} = u^{(K)} v + \binom{K}{1} u^{(K-1)} v^{(1)} + \cdots + \binom{K}{\gamma} u^{(K-\gamma)} v^{(\gamma)} + \cdots$$

$$+ \binom{K}{K-1} u^{(1)} v^{(K-1)} + u v^{(K)},$$

with $\binom{K}{\gamma} = \frac{K!}{(K-\gamma)! \gamma!}$ and $h^{(\gamma)} = \frac{d^\gamma h}{dE^\gamma}$, by putting

$u = e^{\frac{iEt}{\hbar}}$, $v = [E(E-E_{a_1}) \cdots (E-\sum_{k=1}^n E_{a_k})]^{-1}$ in expression 61, we

see that this pole has as its residue a polynomial of order K in t . The constant term in the polynomial, which is equal to

$\frac{1}{K!} \frac{d^K}{dE^K} [E(E-E_{a_1}) \cdots (E-\sum_{k=1}^n E_{a_k}) (E-E_0)^{-K}]^{-1}$ evaluated at E_0 , is the

true weighting factor for the commutator.

In practice, we simply write down the weighting factor of a commutator bracket according to the prescriptions given, and if a zero factor is encountered, we put it aside; after the complete expression has been written down, we add an E to each factor, differentiate the expression thus obtained K times, where K is the number of zero factors

put aside, divide it by $K!$ and then set $E = 0$.

For example, the fourth term in expression 67, i.e., the term of $[\mathcal{H}'_0, [\mathcal{H}'_0, \frac{S_z}{2}]]$, has the coefficient $\frac{1}{(-\hbar\omega_0)(-0)}$, according to the previous prescription, therefore, the weighting factor of this term is

$$\frac{1}{1!} \left. \frac{d}{dE} \frac{1}{(E - \hbar\omega_0)} \right|_{E=0} = \frac{-1}{(\hbar\omega_0)^2} .$$

and the eighth term in expression 67, i.e., the term $[\mathcal{H}'_0, [\mathcal{H}'_2, \frac{S_z}{2}]]$, has the coefficient $\frac{1}{(-0)(2g\beta H)}$ by the previous prescription, so the weighting factor of this term should be

$$\frac{1}{1!} \left. \frac{d}{dE} (E - 2g\beta H)^{-1} \right|_{E=0} = \frac{-1}{(2g\beta H)^2} .$$

We also easily obtain the g_1 function for the first Larmor line in a perpendicular field as

$$g_1(g\beta H \hbar^{-1}) = \frac{1}{\hbar} \left([\mathcal{H}'_0, \frac{S_z}{2}] + \sum_{\substack{\omega \neq 0 \\ \gamma}} \frac{[\mathcal{H}'_\gamma, [\mathcal{H}'_0, \frac{S_z}{2}]]}{-\hbar\omega_\gamma} + \dots \right) + \frac{1}{\hbar} \left(\sum_{\substack{\omega \neq 0 \\ \gamma}} \frac{[\mathcal{H}'_\gamma, [\mathcal{H}'_2, \frac{S_z}{2}]]}{(2g\beta H)} + \dots \right) + \frac{1}{\hbar} \left(\sum_{\substack{\omega \neq 0 \\ \gamma}} \frac{[\mathcal{H}'_\gamma, [\mathcal{H}'_{-2}, \frac{S_z}{2}]]}{(+\hbar\omega_\gamma)} + \dots \right), \quad (68)$$

correct to the second order.

The first term of each parenthesis is an energy conserving term. If we write its coefficient according to the prescription for obtaining the coefficient of an absorption operator, exactly one zero factor will

appear. Throwing away this zero factor gives us the weighting factor for this term in g_1 . The energy non-conserving terms are obtained by the same prescription as before, i.e., commute $\mathcal{H}_{a_n}^{\dagger}, \mathcal{H}_{a_{n-1}}^{\dagger}, \dots, \mathcal{H}_{a_1}^{\dagger}$, with the energy conserving terms, with the weighting factor

$$[(-\sum_{\ell=1}^n E_{a_\ell})(-\sum_{\ell=1}^{n-1} E_{a_\ell}) \cdots (-E_{a_1} - E_{a_2})(-E_{a_1})]^{-1}$$

for each, and with differentiation as described above, if necessary.

We obtain, for instance, the line shift of the first Larmor line as

$$\frac{\langle v - g\beta H h^{-1} \rangle}{\langle v \rangle} = \frac{\text{Tr}(g_1(g\beta H h^{-1}) g_0^{\dagger}(g\beta H h^{-1}))}{2\pi \text{Tr}(g_0(g\beta H h^{-1}) g_0^{\dagger}(g\beta H h^{-1}))}$$

which can be easily evaluated to the first order as $\frac{1}{3} \frac{\Delta v_0^2}{g\beta H h^{-1}}$ where Δv_0^2 is the second moment of the first Larmor line in a perpendicular field, to the first order. The detail is omitted.

The absorption operator for the low frequency line in a parallel field will now be given. The lowest order, energy conserving term is S_z , yet this term gives diagonal elements only; since in $f(v)$ we include only non-diagonal matrix elements which give transitions that can be experimentally detected, this term should not be included. The next order, energy conserving term is

$$O = \sum_{\gamma} \frac{[\mathcal{H}^{\dagger}, [\mathcal{H}^{\dagger}, S_z]]}{\omega_{\gamma} - (\hbar\omega_{\gamma})^2}$$

$$= \frac{[\mathcal{H}_2, \mathcal{H}_{-2}]}{(\text{gSH})^2} + \frac{2[\mathcal{H}_1, \mathcal{H}_{-1}]}{(\text{gSH})^2} .$$

where the differentiation method has been applied.

In general, $\hbar^k g_k^{(2)}$ can be obtained by the following prescription:

(1) Find all of the energy conserving terms which give exactly k zero factors in the denominators for the coefficients if the prescription for the absorption operator is used. Throwing away the zeroes gives the weighting factor for this energy-conserving commutator bracket of $\hbar^k g_k$.

(2) All of the other terms are obtained by forming multiple commutator brackets of $\mathcal{H}_a^{'}$'s with the energy conserving terms \mathcal{O}_E , i.e., $[\mathcal{H}_{a_n}^{'}, [\mathcal{H}_{a_{n-1}}^{'}, \dots, [\mathcal{H}_{a_1}^{'}, \mathcal{O}_E] \dots]]$ with the coefficient

$\left[\left(-\sum_{l=1}^N \hbar \omega_{a_l} \right) \left(-\sum_{l=1}^{N-1} \hbar \omega_{a_l} \right) \dots \left(-\hbar \omega_{a_1} \right) \right]^{-1}$ for each. If there are K zero factors in this coefficient, throw them away and obtain the value of

$$\frac{1}{K!} \frac{d^K}{dE^K} f(E)$$

evaluated at $E = 0$ where the function $f(E)$ is the coefficient of the whole commutation bracket, with the zero factors thrown out and with an E inserted in all of the factors. This value is the weighting factor for this commutation bracket of $\hbar^k g_k$.

These prescriptions can be easily proved. But as the proof involves only simple algebra and is rather lengthy, it probably is easier for the reader to work it out himself, if interested, rather than to read a proof of it.

IV. MOMENTS OF THE SECOND LARMOR LINE
IN A PERPENDICULAR FIELD

The absorption operator for this line is given as

$$O = \frac{[\mathcal{H}_1, \frac{1}{2} S_z]}{g\beta H} = -\frac{\sum_{i,j \neq} E_{ij}^* S_{-i} S_{-j}}{2g\beta H} . \quad (69)$$

The Hermitian conjugate of O is readily found from expression 69 as

$$O^+ = -\frac{\sum_{i,j \neq} E_{ij} S_{+j} S_{+i}}{2g\beta H} . \quad (70)$$

Making use of Appendix A, we obtain

$$\langle v^O \rangle = \text{Tr}(OO^+) = \frac{2}{9} \frac{S^2(S+1)^2}{g^2 \beta^2 H^2} \sum_{i,j} |E_{ij}|^2 . \quad (71)$$

The commutator $[\mathcal{H}_1, O]$ is found to be

$$\begin{aligned} [\mathcal{H}_1, O] &= \left[\sum_{i,j \neq} C_{ij} S_{zi} S_{zj} + \sum_{i,j \neq} A_{ij} S_{+i} S_{-j} , -\frac{\sum_{i,j \neq} E_{ij}^* S_{-i} S_{-j}}{2g\beta H} \right] \\ &= 2 \sum_{i,j, m \neq} (C_{ij} E_{jm}^* - A_{ij} E_{im}^*) S_{zi} S_{-j} S_{-m} / g\beta H + \sum_{i,j \neq} C_{ij} E_{ij}^* S_{zi} S_{-i} S_{-j} / g\beta H \\ &+ \sum_{i,j \neq} C_{ij} E_{ij}^* S_{-i} S_{zi} S_{-j} / g\beta H - 2 \sum_{i,j \neq} A_{ij} E_{ij}^* S_{zi} S_{-j} S_{-i} / g\beta H . \end{aligned} \quad (72)$$

The commutator $[O^+, \mathcal{H}_1]$ is the Hermitian adjoint of expression

72. As A_{ij} , C_{ij} are real, we have

$$[\mathcal{O}^+, \mathcal{H}_o^i] = 2 \sum_{i,j,m} (C_{ij} E_{jm} - A_{ij} E_{im}) S_{zi} S_{+j} S_{+m} / g\beta H + \sum_{i,j} C_{ij} E_{ij} S_{+i} S_{zi} S_{+j} / g\beta H$$

$$+ \sum_{i,j} C_{ij} E_{ij} S_{zi} S_{+i} S_{+j} / g\beta H - 2 \sum_{i,j} A_{ij} E_{ij}^* S_{zi} S_{+j}^2 / g\beta H. \quad (73)$$

Making use of Appendix A, we obtain

$$\text{Tr}([\mathcal{H}_o^i \mathcal{O}] [\mathcal{P}^+, \mathcal{H}_o^i]) = \frac{16}{27} \frac{S^3 (S+1)^3}{g^2 \beta^2 H^2} \sum_{i,j,m} (C_{ij} E_{jm}^* - A_{ij} E_{im}^*) (C_{im} E_{jm} - A_{im} E_{ij})$$

$$+ \frac{16}{27} \frac{S^3 (S+1)^3}{g^2 \beta^2 H^2} \sum_{i,j,m} C_{ij} E_{jm}^* - A_{ij} E_{im}^* \cdot 2$$

$$+ \frac{4S^2 (S+1)^2 [4S(S+1)-3]}{45 g^2 \beta^2 H^2} \sum_{i,j} (2A_{ij}^2 + C_{ij}^2) |E_{ij}|^2. \quad (74)$$

The triple sums of expression 74 are added together to give

$$\frac{16S^3 (S+1)^3}{27g^2 \beta^2 H^2} \sum_{i,j,m} [(A_{ij}^2 + C_{ij}^2) |E_{im}|^2 + A_{ij} A_{im} E_{im}^* E_{ij}]$$

$$- 2 \text{Re} (A_{ij} C_{ij} E_{im} E_{jm}^*) + C_{ij} C_{im} |E_{mj}|^2 - 2 \text{Re} (C_{ij} A_{im} E_{jm}^* E_{ij}). \quad (75)$$

We are going to evaluate the moments for a powder.

For powder, we average the terms of expression 74 over the direction of the constant magnetic field.* The first term of expression 75 is averaged to be

*See Appendix B.

$$\begin{aligned}
 & \frac{s^3(s+1)^3 g^2 \beta^2}{H^2} \left\{ \frac{4}{45} \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-6} + \frac{4g^2 \beta^2}{315} \sum_{i,j \neq} \tilde{A}_{ij}^2 r_{ij}^{-9} \right. \\
 & \left. + \frac{2}{63} g^4 \beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{ij}^{-6} (1 + 3 \cos^2 \theta_i - 3 \cos^4 \theta_i) \right\}. \quad (76)
 \end{aligned}$$

The second term of expression 75 is averaged to be

$$\begin{aligned}
 & \frac{s^3(s+1)^3 g^2 \beta^2}{H^2} \left\{ -\frac{2}{45} \sum_{i,j \neq} \tilde{A}_{ij}^2 r_{ij}^{-6} - \frac{4}{315} g^2 \beta^2 \sum_{i,j \neq} \tilde{A}_{ij}^2 r_{ij}^{-9} \right. \\
 & \left. + \frac{g^4 \beta^4}{630} \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-6} (1 - 12 \cos^2 \theta_i + 15 \cos^4 \theta_i) \right\}, \quad (77)
 \end{aligned}$$

where we have made use of the fact that

$$\sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{mj} r_{ij}^{-3} r_{mj}^{-3} (3 \cos^2 \theta_j - 1) = \sum_{\substack{i \neq j \\ m \neq j}} \tilde{A}_{ij} \tilde{A}_{mj} r_{ij}^{-3} r_{mj}^{-3} (3 \cos^2 \theta_j - 1)$$

$$- \sum_{\substack{i \neq j \\ m=i}} \tilde{A}_{ij} \tilde{A}_{mj} r_{ij}^{-3} r_{mj}^{-3} (3 \cos^2 \theta_j - 1) = \sum_{\substack{i \neq j \\ m \neq j}} \tilde{A}_{ij} \tilde{A}_{mj} r_{ij}^{-3} r_{mj}^{-3} (3 \cdot \frac{1}{3} - 1)$$

$$- \sum_{i \neq j} \tilde{A}_{ij}^2 r_{ij}^{-6} (3-1) = -2 \sum_{i \neq j} \tilde{A}_{ij}^2 r_{ij}^{-6}, \text{ for lattices with cubic symmetry.}$$

The sum of the third and the fifth terms of expression 75 gives

an average value of

$$\begin{aligned}
 & \frac{s^3(s+1)^3 g^2 \beta^2}{H^2} \left\{ -\frac{2}{45} \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1) + \frac{4g^2 \beta^2}{315} \sum_{i,j,m \neq} \right. \\
 & \left. \tilde{A}_{ij} r_{mj} r_{im}^{-6} (3 \cos^2 \theta_m - 1) \right\}
 \end{aligned}$$

$$\begin{aligned}
 & -\frac{2}{45} \sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{mj} r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1) + \frac{2g \beta^4}{315} \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} \\
 & \quad (9 \cos^2 \theta_m + 3 \cos^2 \theta_i \cos^2 \theta_j - 4) \Big). \quad (78)
 \end{aligned}$$

The fourth term of expression 75 is averaged to be

$$\begin{aligned}
 & \frac{s^3 (s+1)^3 g^2 \beta^2}{H^2} \left[\frac{2}{45} \sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{im} r_{mj}^{-6} - \frac{4}{315} g^2 \beta^2 \sum_{i,j,m \neq} \tilde{A}_{ij} r_{im}^{-3} r_{mj}^{-6} (3 \cos^2 \theta_m - 1) \right. \\
 & \left. + \frac{8}{315} g^4 \beta^4 \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} (-2 + 3 \cos^2 \theta_i + 3 \cos^2 \theta_m - 3 \cos^2 \theta_i \cos^2 \theta_j) \right]. \quad (79)
 \end{aligned}$$

The double sums in expression 74 are also averaged over the direction of the constant magnetic field and give

$$\begin{aligned}
 & g^2 \beta^2 H^{-2} s^2 (s+1)^2 [0.08 s(s+1) - 0.06] \sum_{i,j \neq} \tilde{A}_{ij}^2 r_{ij}^{-6} \\
 & + \frac{3}{175} s^2 (s+1)^2 \left[\frac{4}{3} s(s+1) - 1 \right] g^6 \beta^6 H^{-2} \sum_{i,j \neq} r_{ij}^{-12}. \quad (80)
 \end{aligned}$$

From expressions 76-80, we obtain the second moment of the second Larmor line in a perpendicular field as

$$\begin{aligned}
 & \langle \Delta v^2 \rangle = \frac{\text{Tr}(\mathcal{H}_0^{\dagger} \cdot \mathcal{O})(\mathcal{O}^{\dagger} \cdot \mathcal{H}_0^{\dagger})}{h^2 \text{Tr}(\mathcal{O} \mathcal{O}^{\dagger})} \\
 & = (h^2 \sum_{i,j \neq} r_{ij}^{-6})^{-1} \frac{2}{3} s(s+1) \left[2 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-6} - \sum_{i,j \neq} \tilde{A}_{ij}^2 r_{ij}^{-6} - \sum_{m,i,j \neq} \tilde{A}_{ij}^2 r_{im}^{-3} r_{jm}^{-3} \right. \\
 & \quad \left. (3 \cos^2 \theta_m - 1) \right]
 \end{aligned}$$

$$\begin{aligned}
& - \frac{A_{ij} A_{mj} r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1)}{m, i, j} + \frac{A_{ij} A_{im} r_{mj}^{-6}}{m} \\
& + [1.8 - 1.35 S^{-1} (S+1)^{-1} \frac{r_{ij}^{-6} A_{ij}^{-2}}{i, j}] \\
& + (h^2 \frac{r_{ij}^{-6}}{i, j})^{-1} S(S+1) [g^4 \beta^4 \frac{r_{ij}^{-6} r_{im}^{-6}}{i, j, m} (\frac{1}{2} + \frac{8}{7} \cos^2 \theta_i - \frac{15}{14} \cos^4 \theta_i) \\
& + g^4 \beta^4 \frac{r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3}}{i, j, m} (2 \cos^2 \theta_m - \frac{6}{7} \cos^2 \theta_i \cos^2 \theta_j - \frac{3}{7} + \frac{3}{7} \cos^2 \theta_i) \\
& + g^4 \beta^4 (\frac{12}{35} S(S+1) - \frac{9}{35}) \frac{r_{ij}^{-12}}{i, j}] . \tag{81}
\end{aligned}$$

The second bracket of the right side of expression 81 is the dipolar contribution and the first bracket of the right side of expression 81 is the exchange contribution. Notice that no approximations have been made yet.

With the usual assumption that the exchange constant A_{ij} is zero unless i and j are nearest neighbors, and is equal to A in that case, we obtain, for a simple cubic lattice,

$$\langle \Delta \nu^2 \rangle = [1.08 - 0.04 S^{-1} (S+1)^{-1} + (1.07 - 0.13 S^{-1} (S+1)^{-1}) A^2 d^6 \beta^{-4} g^{-4}] \Delta \nu_0^2 . \tag{82}$$

and for a body centered cubic lattice,

$$\langle \Delta \nu^2 \rangle = [1.13 - 0.04 S^{-1} (S+1)^{-1} + (1.14 - 0.08 S^{-1} (S+1)^{-1}) A^2 d^6 \beta^{-4} g^{-4}] \Delta \nu_0^2 . \tag{83}$$

where d is the distance between two nearest lattice points in a lattice and $\Delta\nu_0^2$ is the second moment of the first Larmor line for a perpendicular field, i.e.,

$$\begin{aligned}
 \Delta\nu_0^2 &= 3 g^4 \beta^4 h^{-2} S(S+1) \sum_{i \neq j} r_{ij}^{-6} / 5 \\
 &= 5.04 S(S+1) g^4 \beta^4 h^{-2} d^{-6}, \text{ for simple cubic lattices} \\
 &= 7.37 S(S+1) g^4 \beta^4 h^{-2} d^{-6}, \text{ for body centered cubic lattices} \\
 &\quad (84)
 \end{aligned}$$

The zeroth moment of this line for a powder is obtained by averaging expression 71 with respect to the orientation with the magnetic field,

$$\begin{aligned}
 \langle \nu^0 \rangle &= \frac{1}{15} S^2 (S+1)^2 g^2 \beta^2 H^{-2} \sum_{i \neq j} r_{ij}^{-6} \\
 &= 0.56 S^2 (S+1)^2 N g^2 \beta^2 H^{-2} d^{-6}, \quad (85)
 \end{aligned}$$

$$\begin{aligned}
 &\text{for a simple cubic lattice} \\
 &= 0.82 S^2 (S+1)^2 g^2 \beta^2 H^{-2} d^{-6}, \quad (86)
 \end{aligned}$$

for a body centered cubic lattice, where a factor $(2S+1)^N$ is omitted in compliance with the conventions in the literature.

This factor actually cancels a similar factor in expression 7.

It is interesting to note that the cross terms between dipolar and exchange energies, or the terms linear in A , drop out after the averaging process.

V. MOMENTS OF THE FIRST LARMOR LINE IN
A PARALLEL FIELD

The absorption operator for this line is given as

$$\mathcal{O} = \frac{[\mathcal{H}_1, S_z]}{g\beta H} = \frac{\sum_{i,j \neq} E_{ij}^* S_{-i} S_z j}{g\beta H} . \quad (87)$$

The commutator $[\mathcal{H}_1, \mathcal{O}]$ is calculated to be

$$[\mathcal{H}_1, \frac{\sum_{i,j \neq} E_{ij}^* S_{-i} S_z j}{g\beta H}] = \frac{1}{g\beta H} \left[-2 \sum_{i,j,m \neq} (C_{ij} E_{jm}^* - A_{ij} E_{im}^*) S_{zi} S_{-j} S_{zm} \right. \\ - \sum_{i,j,m \neq} A_{ij} (E_{mi}^* - E_{mj}^*) S_{+i} S_{-m} S_{-j} - 2 \sum_{i,j \neq} C_{ij} E_{ij}^* S_{zi}^2 S_{-j} \\ \left. + 2 \sum_{i,j \neq} A_{ij} E_{ij}^* S_{zi} S_{zj} S_{-j} - \sum_{i,j \neq} A_{ij} E_{ij}^* S_{-j}^2 S_{+i} + \sum_{i,j \neq} A_{ij} E_{ij}^* S_{+i} S_{-i} S_{-j} \right] . \quad (88)$$

From expression 87, we readily obtain the zeroth moment of this line as

$$\langle v^0 \rangle = \frac{2}{9} \frac{S^2 (S+1)^2}{g^2 \beta^2 H^2} \sum_{i,j \neq} |E_{ij}|^2 . \quad (89)$$

This is exactly equal to expression 71. We thus see that the zeroth moment of this line is the same as that of the second Larmor line in a perpendicular field, whether we have a powder or not.

From expression 88, we get

$$\begin{aligned}
 \text{Tr}([\mathcal{H}_o^1, \mathcal{O}] [\mathcal{O}^{\dagger}, \mathcal{H}_o^1]) = & \frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \sum_{i,j,m \neq} \left\{ (C_{ij}E_{jm} - A_{ij}E_{im}) \right\}^2 \\
 & + (C_{ij}E_{jm} - A_{ij}E_{im})(C_{mj}E_{ij}^* - A_{mj}E_{im}^*) + A_{ij}^2 |E_{mj} - E_{im}|^2 + C_{ij}C_{mj}E_{ij}^*E_{mj}^* \\
 & + A_{ij}A_{mj}(E_{mj} - E_{im})(E_{ij}^* - E_{im}^*) + A_{ij}A_{im}E_{ij}^*E_{im}^* - 2A_{jm}C_{ij}E_{jm}E_{ij} \\
 & + \frac{S^2(S+1)^2[4S(S+1)-3]}{15g^2\beta^2H^2} \sum_{i,j \neq} A_{ij}^2 E_{ij}^2 + \frac{S^2(S+1)^2[14S(S+1)-3]}{H^2g^2\beta^2} \sum_{i,j \neq} B_{ij}^2 E_{ij}^2
 \end{aligned} \tag{90}$$

The triple sums of expression 90 total to

$$\begin{aligned}
 & \frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \sum_{i,j,m \neq} \left\{ (C_{ij}^2 + 3A_{ij}^2) |E_{im}|^2 - 2A_{ij}(A_{ij} + C_{ij})E_{im}E_{jm}^* \right. \\
 & + (C_{ij}C_{mj} + A_{ij}A_{mj} + \frac{9B_{ij}B_{mj}}{16}) E_{ij}^*E_{jm} + 2A_{ij}A_{jm} |E_{im}|^2 \\
 & \left. - 2A_{ij}(C_{mj} + A_{mj})E_{im}E_{ij}^* \right\} .
 \end{aligned} \tag{91}$$

We shall evaluate expression 90 for a powder.

The first term of expression 91, after averaging over the orientations, gives

$$\frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ \frac{3}{10} g^4 \beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-6} + \frac{3}{280} g^6 \beta^6 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{ij}^{-3} r_{im}^{-6} (3 \cos^2 \theta_i - 1) \right. \\ \left. + \frac{3}{40} g^8 \beta^8 \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-6} (1 + 3 \cos^2 \theta_i - 3 \cos^4 \theta_i) \right\}. \quad (92)$$

The second term of expression 91, after averaging over the orientations, gives

$$\frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ -\frac{3}{20} g^4 \beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1) \right. \\ - \frac{3}{280} g^6 \beta^6 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-3} r_{jm}^{-3} r_{ij}^{-3} (3 \cos \theta_i \cos \theta_j \cos \theta_m - 1) \\ \left. + \frac{3}{140} g^8 \beta^8 \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} (-2 + 3 \cos^2 \theta_m + 3 \cos^2 \theta_i - 3 \cos^2 \theta_i \cos^2 \theta_j) \right\}. \quad (93)$$

The third terms of expression 91 is averaged to be

$$\frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ -\frac{3}{20} g^4 \beta^4 \sum_{i,j \neq} \tilde{A}_{ij}^2 r_{ij}^{-6} - \frac{3}{280} g^6 \beta^6 \sum_{i,j,m \neq} \tilde{A}_{mj}^2 r_{ij}^{-6} r_{mj}^{-3} (3 \cos^2 \theta_j - 1) \right. \\ \left. + \frac{3}{80} g^8 \beta^8 \sum_{i,j,m \neq} r_{ij}^{-6} r_{mj}^{-6} (1 - 12 \cos^2 \theta_j + 15 \cos^4 \theta_j) \right\}. \quad (94)$$

The fourth term of expression 91 is averaged to give

$$\begin{aligned}
 & \frac{8S^3(S+1)^3}{27g_\beta^2 H^2} \left\{ \frac{3}{20} g_\beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{mj} r_{im}^{-6} + \frac{3}{140} g_\beta^6 \sum_{i,j,m \neq} \tilde{A}_{ij} r_{mj}^{-3} r_{jm}^{-6} \right. \\
 & \quad \left. (3 \cos^2 \theta_m - 1) \right. \\
 & + \frac{3}{140} g_\beta^8 \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} (-2 + 3 \cos^2 \theta_i + 3 \cos^2 \theta_m - 3 \cos^2 \theta_i \cos^2 \theta_j) \} . \\
 & \quad (95)
 \end{aligned}$$

The fifth term of expression 91 is averaged to give

$$\begin{aligned}
 & \frac{8S^3(S+1)^3}{27g_\beta^2 H^2} \left\{ -\frac{3}{20} g_\beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{mj} r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1) \right. \\
 & - \frac{3}{140} g_\beta^6 \sum_{i,j,m \neq} \tilde{A}_{ij} r_{mj}^{-6} r_{im}^{-3} (3 \cos^2 \theta_m - 1) \\
 & + \frac{3}{280} g_\beta^6 \sum_{i,j,m \neq} \tilde{A}_{mj} r_{ij}^{-3} r_{im}^{-3} r_{jm}^{-3} (3 \cos \theta_i \cos \theta_j \cos \theta_m - 1) \\
 & \left. + \frac{1}{35} \frac{3}{16} g_\beta^8 \sum_{i,j,m \neq} r_{mj}^{-3} r_{ij}^{-6} r_{mi}^{-3} (4 + 15 \cos^2 \theta_i \cos^2 \theta_j - 12 \cos^2 \theta_i - 3 \cos^2 \theta_m) \right\} . \\
 & \quad (96)
 \end{aligned}$$

The double sums of expression 90, after averaging over the orientation of the magnetic field, give

$$\begin{aligned}
 & \frac{g_\beta^6 S^2 (S+1)^2}{H^2} [0.04 S(S+1) - \frac{0.06}{7}] \sum_{i,j \neq} r_{ij}^{-12} \\
 & + S^2 (S+1)^2 [0.08 S(S+1) - 0.06] g_\beta^4 \sum_{i,j \neq} \tilde{A}_{ij}^2 r_{ij}^{-6} . \\
 & \quad (97)
 \end{aligned}$$

From expressions 90-97, we obtain the second moment of this line as

$$\begin{aligned}
 \langle \Delta \nu^2 \rangle &= \frac{\text{Tr}([\mathcal{H}_0^{\dagger} \mathcal{O}] [\mathcal{O}^{\dagger}, \mathcal{H}_0^{\dagger}])}{h^2 \text{Tr } \mathcal{O} \mathcal{O}^{\dagger}} \\
 &= (h^2 \sum_{i,j \neq} r_{ij}^{-6})^{-1} S(S+1) g^4 \beta^4 \left[\sum_{i,j,m \neq} r_{mj}^{-3} r_{ij}^{-6} r_{mi}^{-3} \left(-\frac{2}{7} + \frac{\cos^2 \theta_m}{2} + \frac{2 \cos^2 \theta_i}{7} - \frac{3}{14} \right. \right. \\
 &\quad \left. \left. \cos^2 \theta_i \cos^2 \theta_j \right) \right. \\
 &\quad \left. + \sum_{i,j,m \neq} r_{ij}^{-6} r_{mj}^{-6} \left(\frac{1}{2} - \cos^2 \theta_j + \frac{3}{2} \cos^4 \theta_j \right) + (0.6S(S+1) - \frac{9}{70}) \sum_{i,j \neq} r_{ij}^{-12} \right] \\
 &\quad + \langle \Delta \nu_A^2 \rangle. \tag{98}
 \end{aligned}$$

The term $\langle \Delta \nu_A^2 \rangle$ denotes the exchange contribution to the second moment of this line, and is found to be exactly equal to the exchange contribution to the second moment of the second Larmor line in a perpendicular field. As is found in the next two sections, the exchange contribution to the second moment for all of the four lines investigated here is the same.

For a simple cubic lattice

$$\langle \Delta \nu^2 \rangle = [0.89 - 0.02 S^{-1} (S+1)^{-1} + (1.07 - 0.13 S^{-1} (S+1)^{-1}) A^2 d^6 \beta^{-4} g^{-4}] \Delta \nu_0^2, \tag{99}$$

and for a body-centered cubic lattice

$$\langle \Delta v^2 \rangle = \left[0.77 - 0.01 S^{-1} (S+1)^{-1} + [1.14 - 0.08 S^{-1} (S+1)^{-1}] A^2 d^6 \beta^{-4} g^{-4} \right] \Delta v_o^2, \quad (100)$$

where Δv_o^2 is given by expression 84. Notice that it depends on the kind of lattice the powder has, and has different numerical values in expressions 99 and 100.

VI. MOMENTS OF THE SECOND LARMOR LINE
IN A PARALLEL FIELD

The absorption operator for this line is

$$O = \frac{[\mathcal{H}_2, S_z]}{2g\beta H} = \frac{\sum_{i,j \neq}^* D_{ij}^* S_{-i} S_{-j}}{g\beta H} . \quad (101)$$

The zeroth moment of this line is given by

$$\langle v^0 \rangle = \text{Tr}(OO^t) = \frac{8}{9} \frac{S^2(S+1)^2}{g^2 \beta^2 H^2} \sum_{i,j \neq}^* |D_{ij}^*|^2 . \quad (102)$$

For powder, we average expression 102 with respect to the orientation and obtain

$$\langle v^0 \rangle = \frac{1}{15} S^2(S+1)^2 g^2 \beta^2 H^{-2} \sum_{i,j \neq}^* r_{ij}^{-6} . \quad (103)$$

We observe that this is exactly equal to expression 85, i.e., the zeroth moments for the three lines calculated are equal for powder.

As expression 101 will be equal to expression 69 if we substitute D_{ij}^* for $-\frac{E_{ij}^*}{2}$ in expression 69, we can obtain $\text{Tr}([\mathcal{H}_o^t O] P^t \mathcal{H}_o^t)$ for this line by substituting $-2D_{ij}^*$ for $+E_{ij}^*$ in expression 74. Thus we have

$$\begin{aligned}
 \text{Tr}([\mathcal{H}_0^{\dagger} \mathcal{O}] [\mathcal{O}^{\dagger} \mathcal{H}_0^{\dagger}]) = & \frac{64}{27} \frac{S^3(S+1)^3}{27g^2\beta^2H^2} \sum_{i,j,m \neq} (A_{ij}^{\dagger} D_{im}^{\dagger} - C_{ij}^{\dagger} D_{jm}^{\dagger})(A_{im}^{\dagger} D_{ij}^{\dagger} - C_{im}^{\dagger} D_{jm}^{\dagger}) \\
 & + \frac{64}{27} \frac{S^3(S+1)^3}{g^2\beta^2H^2} \sum_{i,j,m \neq} |A_{ij}^{\dagger} D_{im}^{\dagger} - C_{ij}^{\dagger} D_{jm}^{\dagger}|^2 \\
 & + \frac{16S^2(S+1)^2[4S(S+1)-3]}{45g^2\beta^2H^2} \sum_{i,j \neq} (2A_{ij}^2 + C_{ij}^2) |D_{ij}|^2. \tag{104}
 \end{aligned}$$

The triple sums of expression 104 are added together to give

$$\begin{aligned}
 \frac{64S^3(S+1)^3}{27g^2\beta^2H^2} \sum_{i,j,m \neq} & \left\{ (A_{ij}^2 + C_{ij}^2) |D_{im}|^2 + A_{ij}^{\dagger} A_{im}^{\dagger} D_{im}^{\dagger} D_{ij}^{\dagger} \right. \\
 & \left. - 2 \text{Re}(A_{ij}^{\dagger} C_{ij}^{\dagger} D_{im}^{\dagger} D_{jm}^{\dagger}) + C_{ij}^{\dagger} C_{im}^{\dagger} |D_{mj}|^2 - 2 \text{Re}(C_{ij}^{\dagger} A_{im}^{\dagger} D_{jm}^{\dagger} D_{ij}^{\dagger}) \right\}. \tag{105}
 \end{aligned}$$

For powder, we again average expression 104 with respect to the orientation. The first term of expression 105 then gives

$$\begin{aligned}
 \frac{64S^3(S+1)^3}{27g^2\beta^2H^2} & \left\{ \frac{3}{80} g^4 \beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-6} + \frac{3}{128} \frac{g^8 \beta^8}{7} \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-6} \right. \\
 & (7-6\cos^2\theta_i + 3\cos^4\theta_i) \\
 & \left. + \frac{3}{560} g^6 \beta^6 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{ij}^{-3} r_{im}^{-6} (3\cos^2\theta_i - 1) \right\}. \tag{106}
 \end{aligned}$$

The second term of expression 105 is averaged over to give

$$\begin{aligned}
 & \frac{64S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ \frac{3}{320} g^4\beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{im} r_{ij}^{-3} r_{im}^{-3} (3 \cos^2 \theta_i - 1) \right. \\
 & - \frac{3}{560} g^6\beta^6 \sum_{i,j,m \neq} \tilde{A}_{im} r_{ij}^{-6} r_{im}^{-3} (3 \cos^2 \theta_i - 1) \\
 & \left. + \frac{3}{256} \frac{g^8\beta^8}{35} \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-6} (15 \cos^4 \theta_i - 6 \cos^2 \theta_i - 1) \right\}. \quad (107)
 \end{aligned}$$

The third term of expression 105 is averaged out to give

$$\begin{aligned}
 & \frac{64S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ -\frac{3}{160} g^4\beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij} r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1) \right. \\
 & + \frac{9}{256} g^6\beta^6 \sum_{i,j,m \neq} r_{ij}^{-3} r_{im}^{-3} r_{jm}^{-3} \tilde{A}_{ij} \left(-\frac{16 \cos^2 \theta_i}{35} - \frac{8 \cos^2 \theta_m}{35} + \frac{8}{21} \right) \\
 & \left. + \frac{3}{35} \frac{1}{32} g^8\beta^8 \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} [1 + 6 \cos^2 \theta_m - 6 \cos^2 \theta_i + 3 \cos^2 \theta_i \cos^2 \theta_j] \right\}. \quad (108)
 \end{aligned}$$

The fourth term of expression 105 is averaged out to give

$$\begin{aligned}
 & \frac{64S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ \frac{3}{160} g^4\beta^4 \sum_{i,j,m \neq} \tilde{A}_{mj} \tilde{A}_{im} r_{ij}^{-6} + \frac{3g^6\beta^6}{280} \sum_{i,j,m \neq} \tilde{A}_{im} r_{mj}^{-3} r_{ij}^{-6} \right. \\
 & (3 \cos^2 \theta_j - 1) \\
 & \left. + \frac{9g^8\beta^8}{256} \sum_{i,j,m \neq} r_{ij}^{-6} r_{mj}^{-3} r_{im}^{-3} \left(\frac{8}{105} + \frac{16}{35} \cos^2 \theta_m - \frac{16}{35} \cos^2 \theta_i + \frac{8}{35} \cos^2 \theta_i \cos^2 \theta_j \right) \right\}. \quad (109)
 \end{aligned}$$

The fifth term of expression 105 is averaged out to give

$$\begin{aligned}
& \frac{64S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ -\frac{3}{160}g^4\beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{r}_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_j - 1) \right. \\
& - \frac{3}{280} g^6 \beta^6 \sum_{i,j,m \neq} \tilde{A}_{im} \tilde{r}_{ij}^{-6} r_{jm}^{-3} (3 \cos^2 \theta_j - 1) \\
& - \frac{3}{32} \frac{g^6 \beta^6}{35} \sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{r}_{ij}^{-3} r_{im}^{-3} r_{jm}^{-3} (-6 \cos^2 \theta_i - 3 \cos^2 \theta_m + 5) \\
& + \frac{9}{64} g^8 \beta^8 \sum_{i,j,m \neq} \tilde{r}_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} \left(\frac{1}{7} \cos^2 \theta_i \cos^2 \theta_j - \frac{1}{35} \cos^2 \theta_i \right. \\
& \left. - \frac{1}{35} \cos^2 \theta_j - \frac{1}{105} \right). \tag{110}
\end{aligned}$$

The double sums of expression 104, after averaging over the orientation, give

$$\frac{g^2 \beta^2 S^2 (S+1)^2 H^{-2}}{350} [4S(S+1)-3] \cdot \left(7 \sum_{i,j \neq} \tilde{A}_{ij}^2 r_{ij}^{-6} + 2g^4 \beta^4 \sum_{i,j \neq} r_{ij}^{-12} \right). \tag{111}$$

The second moment of this line is given by

$$\begin{aligned}
\langle \Delta v^2 \rangle &= (h^2 \sum_{i,j \neq} r_{ij}^{-6})^{-1} S(S+1) \left\{ \frac{g^4 \beta^4}{28} \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-6} (23 - 22 \cos^2 \theta_i + 15 \cos^4 \theta_i) \right. \\
& + \frac{g^4 \beta^4}{7} \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} (1 + 9 \cos^2 \theta_i \cos^2 \theta_j + 8 \cos^2 \theta_m - 10 \cos^2 \theta_i) \\
& \left. + \frac{[12 - 9S^{-1}(S+1)^{-1}]}{35} g^4 \beta^4 \sum_{i,j \neq} r_{ij}^{-12} \right\} + \langle \Delta v_A^2 \rangle. \tag{112}
\end{aligned}$$

It is again found that the exchange contribution to the second moment is equal to that in the two previous cases.

For a simple cubic lattice, it is evaluated that

$$\langle \Delta v^2 \rangle = [1.38 - 0.04 S^{-1} (S+1)^{-1} + (1.07 - 0.13 S^{-1} (S+1)^{-1}) \chi A^2 d^6 g^{-4} \beta^{-4}] \Delta v_0^2 , \quad (113)$$

and for a body-centered cubic lattice

$$\langle \Delta v^2 \rangle = [1.39 - 0.03 S^{-1} (S+1)^{-1} + (1.14 - 0.08 S^{-1} (S+1)^{-1}) \chi A^2 d^6 g^{-4} \beta^{-4}] \Delta v_0^2 . \quad (114)$$

VII. MOMENTS OF THE LOW FREQUENCY LINE
IN A PERPENDICULAR FIELD

The absorption operator for this line is

$$\begin{aligned}
 O &= \frac{[\mathcal{H}_1, \frac{1}{2} S_-]}{-g\beta H} + \frac{[\mathcal{H}_1, \frac{1}{2} S_+]}{g\beta H} \\
 &= \frac{\sum_{i,j \neq} (E_{ij} + E_{ij}^*) S_{+i} S_{-j}}{2g\beta H} - \frac{\sum_{i,j \neq} (E_{ij} + E_{ij}^*) S_{zi} S_{zj}}{g\beta H} . \quad (115)
 \end{aligned}$$

Now, $\text{Tr}(OO^+)$ includes absorption as well as emission in this case, and the zeroth moment is only a half of it; therefore,

$$\langle v^0 \rangle = \frac{1}{2} \text{Tr}(OO^+) = \frac{1}{6} S^2 (S+1)^2 H^{-2} g^{-2} \beta^{-2} \sum_{i,j \neq} |F_{ij}|^2 , \quad (116)$$

where $F_{ij} \equiv E_{ij} + E_{ij}^*$.

The commutator $[\mathcal{H}_0, O]$ is evaluated to be

$$\begin{aligned}
 [\mathcal{H}_0, O] &= \frac{1}{g\beta H} \left\{ \sum_{i,j,m \neq} [F_{ij} (C_{im} - C_{mj}) + A_{mj} F_{im} - A_{im} F_{mj} - 2A_{ij} \cdot \right. \\
 &\quad \left. (F_{mj} - F_{mi}) S_{+i} S_{-j} S_{zm}] \right. \\
 &\quad \left. + \sum_{i,j \neq} (C_{ij} + 2A_{ij}) F_{ij} S_{zj} S_{-j} S_{+i} \cdot \sum_{i,j \neq} (C_{ij} + 2A_{ij}) S_{-i} S_{+j} S_{zm} \right\} . \quad (117)
 \end{aligned}$$

and

$$\text{Tr}([\mathcal{H}_o^\dagger \mathcal{O}] [\mathcal{O}^\dagger \mathcal{H}_o^\dagger] =$$

$$\begin{aligned} & \frac{4S^3(S+1)^3}{27g^2\beta^2H^2} \sum_{i,j,m \neq} \left| F_{ij}(C_{im} - C_{mj}) + A_{mj}F_{im} - A_{im}F_{mj} - 2A_{ij}(F_{mj} - F_{mi}) \right|^2 \\ & + \frac{2S^2(S+1)^2[4S(S+1)-3]}{45g^2\beta^2H^2} \sum_{i,j \neq} (2A_{ij} + C_{ij})^2 |F_{ij}|^2. \end{aligned} \quad (118)$$

The triple sums in expression 118 add up to

$$\begin{aligned} & \frac{4S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ \sum_{i,j,m \neq} (2C_{jm}^2 + 10A_{jm}^2)F_{ij}^2 - (8A_{jm}^2 + 4A_{jm}C_{jm})F_{im}F_{ij} \right. \\ & + (8A_{im}A_{jm} - 2C_{im}C_{jm})F_{ij}^2 + (8A_{ij}C_{im} - 2A_{ij}A_{im})F_{im}F_{ij} \\ & \left. - (8A_{ij}A_{mj} + 8A_{ij}C_{mj} - 4C_{ij}A_{mj})F_{ij}F_{im} \right\}. \end{aligned} \quad (119)$$

We shall calculate the moments for a powder.

The first term in expression 119 is averaged to be

$$\begin{aligned} & \frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ -\frac{9}{10}g^4\beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-6} - \frac{9g^6\beta^6}{140} \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{ij}^{-3} r_{im}^{-6} (3\cos^2\theta_i - 1) \right. \\ & \left. + \frac{27g^8\beta^8}{140} \sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-6} (1 + 3\cos^2\theta_i - 3\cos^4\theta_i) \right\}. \end{aligned} \quad (120)$$

The second term in expression 119 is averaged to give

$$\frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ -\frac{9}{20} g^4 \beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1) \right. \\ \left. - \frac{27}{8} g^6 \beta^6 \sum_{i,j,m} \tilde{A}_{ij}^2 r_{im}^{-3} r_{jm}^{-3} r_{ij}^{-3} \left(-\frac{1}{21} + \frac{\cos^2 \theta_m + \cos^2 \theta_i + \cos^2 \theta_j}{35} \right) \right\}. \quad (121)$$

The third term in expression 119 is averaged to give

$$\frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ \frac{9}{20} g^4 \beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{mj} r_{im}^{-6} \right. \\ \left. + \frac{9}{70} g^6 \beta^6 \sum_{i,j,m \neq} \tilde{A}_{ij} r_{mj}^{-3} r_{im}^{-6} (3 \cos^2 \theta_m - 1) \right\}. \quad (122)$$

The fourth term in expression 119 is averaged to give

$$\frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ -\frac{9}{20} g^4 \beta^4 \sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{ij}^{-6} + \frac{9g^6 \beta^6}{140} \sum_{i,j,m \neq} \tilde{A}_{mj} r_{ij}^{-6} r_{mj}^{-3} (3 \cos^2 \theta_j - 1) \right. \\ \left. - \frac{8i}{32} g^8 \beta^8 \sum_{i,j,m \neq} r_{ij}^{-6} r_{mj}^{-6} \left(\frac{2}{105} - \frac{8}{35} \cos^2 \theta_j + \frac{2}{7} \cos^4 \theta_j \right) \right\}. \quad (123)$$

The fifth term in expression 119 is averaged to be

$$\frac{8S^3(S+1)^3}{27g^2\beta^2H^2} \left\{ -\frac{9}{20} \sum_{i,j,m \neq} g^4 \beta^4 \tilde{A}_{ij} \tilde{A}_{mj} r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1) \right. \\ \left. - \frac{9}{70} g^6 \beta^6 \sum_{i,j,m} \tilde{A}_{ij} r_{mj}^{-6} r_{im}^{-3} (3 \cos^2 \theta_m - 1) \right. \\ \left. + \frac{27}{8} g^6 \beta^6 \sum_{i,j,m} \tilde{A}_{mj} r_{ij}^{-3} r_{im}^{-3} r_{mj}^{-3} \left(-\frac{1}{21} + \frac{\cos^2 \theta_i + \cos^2 \theta_j + \cos^2 \theta_m}{35} \right) \right\}. \quad (124)$$

The double sums in expression 118 are averaged to give.

$$g^2 \beta^2 \frac{S^2(S+1)^2}{h^2} [0.24S(S+1)-0.18] \sum_{i,j \neq} r_{ij}^{-6} . \quad (125)$$

From expressions 118-124, we obtain the second moment for this line as

$$\begin{aligned} \langle \Delta v^2 \rangle &= \left(h^2 \sum_{i,j \neq} r_{ij}^{-6} \right)^{-1} S(S+1) g^4 \beta^4 \sum_{i,j,m \neq} \frac{3}{14} r_{ij}^{-6} r_{im}^{-6} (1+8 \cos^2 \theta_j - 9 \cos^4 \theta_j) \\ &+ \langle \Delta v_A^2 \rangle . \end{aligned} \quad (126)$$

Again, the exchange contribution to the second moment is equal to that of the previous three cases.

For a simple cubic lattice, the second moment is evaluated as

$$\langle \Delta v^2 \rangle = \left\{ 0.47 + [1.07 - 0.13S^{-1}(S+1)^{-1}] A^2 d^6 g^{-4} \beta^{-4} \right\} \Delta v_0^2 , \quad (127)$$

and for a body-centered cubic lattice, the second moment is evaluated as

$$\langle \Delta v^2 \rangle = \left\{ 0.64 + [1.14 - 0.08S^{-1}(S+1)^{-1}] A^2 d^6 g^{-4} \beta^{-4} \right\} \Delta v_0^2 . \quad (128)$$

The zeroth moment of this line for powder is evaluated to be 1.5 times that of the previous three cases.

VIII. COMPARISON WITH EXPERIMENT

Experiments (6) were performed on nuclear spin systems of lithium, sodium and aluminum. Since the exchange constant for a nuclear spin system is negligible, these experiments provide a check for the dipole-dipole contribution to the moments only.

The experimental method is briefly described as follows:

The nuclear spin system is put under a strong magnetic field for a period of time long compared to the nuclear spin-lattice relaxation time. For metals which were used in the past experiments it was necessary to work in the temperature range of 1° Kelvin, in order to obtain a spin-lattice relaxation time of the order of seconds. After the spin system has reached equilibrium the spin temperature is measured and the magnetic field is adiabatically turned down to a small value in about 10 milliseconds. An oscillating field is then applied to the system for a time period T_o , and at the end of the period the field is adiabatically raised to its original value and the spin temperature is again measured. The increase of spin temperature after this process is due to the absorption of energy from the oscillating magnetic field. By varying T_o , a relaxation time at field H_o may be obtained. By comparing this relaxation time with the spin lattice relaxation time obtained when the oscillating field is absent, the energy absorbed by the spin system from the oscillating magnetic field may be determined.

From this we can obtain the shape function $f(v)$.

The experiments were performed on spin systems with body-centered cubic lattices, and the results are summarized in Table 1.

No experimental verification of the exchange contribution to the second moments has been obtained.

The agreement with experiments seems to be reasonably good except for the second moment of the low frequency line in a perpendicular field, where, owing to the difficulties in resolving this line from the first Larmor line, the uncertainty is too large for predictions.

Table 1

Line of Interests	Theory	Experiment	$\langle \Delta v^2 \rangle_{\Delta v}$
$2g\beta\mu_{\text{H}}^{-1} (\perp)$	$\frac{1}{15} s^2 (s+1)^2 g^2 \beta^2 \mu_{\text{H}}^2 - 2 \sum_{i,j \neq} r_{ij}^{-6}$	$\frac{1+0.2}{15} s^2 (s+1)^2 g^2 \beta^2 \mu_{\text{H}}^2 - 2 \sum_{i,j \neq} r_{ij}^{-6}$	$1.1 \langle \Delta v^2 \rangle_0$ $(1.3 \pm 0.3) \langle \Delta v^2 \rangle_0$
$2g\beta\mu_{\text{H}}^{-1} (\parallel)$	$\frac{1}{15} s^2 (s+1)^2 g^2 \beta^2 \mu_{\text{H}}^2 - 2 \sum_{i,j \neq} r_{ij}^{-6}$	$\frac{1+0.2}{15} s^2 (s+1)^2 g^2 \beta^2 \mu_{\text{H}}^2 - 2 \sum_{i,j \neq} r_{ij}^{-6}$	$1.4 \langle \Delta v^2 \rangle_0$ $(1.5 \pm 0.3) \langle \Delta v^2 \rangle_0$
$g\beta\mu_{\text{H}}^{-1} (\parallel)$	$\frac{1}{15} s^2 (s+1)^2 g^2 \beta^2 \mu_{\text{H}}^2 - 2 \sum_{i,j \neq} r_{ij}^{-6}$	$\frac{1+0.2}{15} s^2 (s+1)^2 g^2 \beta^2 \mu_{\text{H}}^2 - 2 \sum_{i,j \neq} r_{ij}^{-6}$	$0.8 \langle \Delta v^2 \rangle_0$ $(1.0 \pm 0.3) \langle \Delta v^2 \rangle_0$
0 (\perp)	$\frac{1}{10} s^2 (s+1)^2 g^2 \beta^2 \mu_{\text{H}}^2 - 2 \sum_{i,j \neq} r_{ij}^{-6}$		$0.64 \langle \Delta v^2 \rangle_0$ $(0.7 \sim 1.5) \langle \Delta v^2 \rangle_0$

APPENDIX A

Traces of various products of spin components are listed in this appendix. For the convenience of computation in this paper, the components S_+, S_-, S_z of an atomic spin are used instead of S_x, S_y, S_z , where $S_+ \equiv S_x + iS_y$ is an operator which raises the z component of the atomic spin by one unit, and $S_- \equiv S_x - iS_y$ is an operator which lowers it by one unit. The trace of a product of spin components would therefore vanish unless there are equal numbers of S_+ and S_- in the product. For instance,

$$\text{Tr}(S_+S_+) = \text{Tr}(S_-S_-) = \text{Tr}(S_zS_-S_-) = \text{Tr}(S_zS_+S_+) = 0. \quad (1)$$

The non-vanishing traces that are relevant to our previous calculations are

$$\text{Tr}(S_+S_-) = \frac{2}{3} S(S+1)(2S+1)^N, \quad (2)$$

$$\text{Tr}(S_+S_-S_z) = -\text{Tr}(S_-S_+S_z) = \frac{1}{3} S(S+1)(2S+1)^N, \quad (3)$$

$$\text{Tr}(S_+^2 S_-^2) = \frac{2S(S+1)}{15} [4S(S+1)-3](2S+1)^N, \quad (4)$$

$$\text{Tr}(S_+S_-S_+S_-) = \frac{4S(S+1)}{15} [2S(S+1)+1](2S+1)^N, \quad (5)$$

$$\text{Tr}(S_z^2 S_+S_-) = \frac{S(S+1)}{15} [2S(S+1)+1](2S+1)^N, \quad (6)$$

$$\text{Tr}(S_zS_-S_zS_+) = \frac{2S(S+1)}{15} [S(S+1)-2](2S+1)^N, \quad (7)$$

where S is the magnitude of an atomic spin, and $(2S+1)^N$, which is

equal to the trace of unity, is the total number of states in a spin system, with N the number of spins in the system.

The factor $(2S+1)^N$ in the above expressions is always omitted in the literature, since the same factor was omitted in expression 8. Including both would make them cancel each other, with no change in result.

APPENDIX B

For a powder, the orientation of the crystal axes with respect to the constant magnetic field is random. Therefore, in expressions such as 75, which involve products of α_{ij} , β_{ij} , γ_{ij} , we have to average over the orientation of the crystal axis with respect to the constant magnetic field.

We take these lattice points i , m , j with fixed distance between them (see Fig. 1). The three angles

θ_i , θ_j , θ_m are hence fixed, yet the orientation of the triangle with the magnetic field is arbitrary. We take a coordinate system and obtain the following average values:

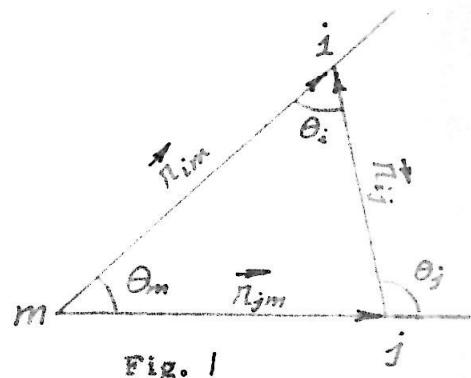


Fig. 1

$$\langle \gamma_{im} \gamma_{jm} \rangle_{av} = \frac{1}{3} \cos \theta_m, \quad (1)$$

$$\langle \gamma_{im} \gamma_{ij} \gamma_{jm} \rangle_{av} = 0, \quad (2)$$

$$\langle \gamma_{im}^2 \gamma_{ij} \gamma_{jm} \rangle_{av} = (\cos \theta_j + 2 \cos \theta_i \cos \theta_m) / 15, \quad (3)$$

$$\langle \gamma_{im}^2 \gamma_{jm}^2 \rangle_{av} = (1 + 2 \cos^2 \theta_m) / 15, \quad (4)$$

$$\langle \gamma_{im}^2 \gamma_{ij}^2 \gamma_{jm}^2 \rangle_{av} = (2 \cos^2 \theta_i + 2 \cos^2 \theta_j + 2 \cos^2 \theta_m - 1) / 35, \quad (5)$$

$$\langle \gamma_{im}^3 \gamma_{jm} \rangle_{av} = \cos \theta_m / 5, \quad (6)$$

$$\langle \gamma_{im}^3 \gamma_{jm}^2 \rangle_{av} = (2 \cos^2 \theta_i \cos \theta_m + \cos \theta_m + 2 \cos \theta_i \cos \theta_j) / 35 , \quad (7)$$

$$\langle \gamma_{im}^3 \gamma_{jm}^3 \rangle_{av} = (2 \cos^3 \theta_m + 3 \cos \theta_m) / 35 , \quad (8)$$

$$\langle \gamma_{im}^4 \gamma_{jm}^2 \rangle_{av} = (1 + 4 \cos^2 \theta_m) / 35 , \quad (9)$$

$$\langle \gamma_{im}^4 \gamma_{ij} \gamma_{jm} \rangle_{av} = (\cos \theta_j + 4 \cos \theta_i \cos \theta_m) / 35 , \quad (10)$$

$$\langle \gamma_{im}^4 \gamma_{ij}^2 \gamma_{jm}^2 \rangle_{av} = (12 \cos^2 \theta_i + 12 \cos^2 \theta_m + 10 \cos^2 \theta_j - 7 + 8 \cos^2 \theta_i \cos^2 \theta_m) / 315 , \quad (11)$$

$$\langle \gamma_{im}^4 \gamma_{jm}^4 \rangle_{av} = (8 \cos^4 \theta_m + 24 \cos^2 \theta_m + 3) / 315 , \quad (12)$$

$$\langle (\alpha_{ij} \beta_{jm} - \beta_{ij} \alpha_{jm})^2 \rangle_{av} = \frac{1}{3} \sin^2 \theta_j , \quad (13)$$

$$\langle \gamma_{im}^2 (\alpha_{ij} \beta_{jm} - \beta_{ij} \alpha_{jm})^2 \rangle_{av} = \sin^2 \theta_j / 15 , \quad (14)$$

$$\langle \gamma_{im}^2 (\alpha_{im} \beta_{jm} - \beta_{im} \alpha_{jm})^2 \rangle_{av} = \sin^2 \theta_m / 15 , \quad (15)$$

$$\langle \gamma_{im}^4 (\alpha_{ij} \beta_{jm} - \beta_{ij} \alpha_{jm})^2 \rangle_{av} = \sin^2 \theta_j / 35 , \quad (16)$$

$$\langle \gamma_{im}^2 \gamma_{ij}^2 (\alpha_{ij} \beta_{jm} - \beta_{ij} \alpha_{jm})^2 \rangle_{av} = (1 + 2 \cos^2 \theta_i) \sin^2 \theta_j / 105 , \quad (17)$$

$$\langle \gamma_{im}^2 \gamma_{ij}^2 (\alpha_{ij} \beta_{im} - \beta_{ij} \alpha_{im})^2 \rangle_{av} = (1 + 2 \cos^2 \theta_i) \sin^2 \theta_i / 105 . \quad (18)$$

The following identity is sometimes needed

$$\cos \theta_i \cos \theta_m \cos \theta_j = -\frac{1}{2} + \frac{1}{2} [\cos^2 \theta_i + \cos^2 \theta_m + \cos^2 \theta_j] \text{ for}$$

$$\theta_j = \theta_i + \theta_m . \quad (19)$$

APPENDIX C

Four series over a simple cubic lattice were computed to within one percent of accuracy,

$$\sum_{i,j \neq \pm} r_{ij}^{-6} = 8.40 N d^{-6}, \quad (1)$$

$$\sum_{i,j \neq \pm} r_{ij}^{-12} = 6.20 N d^{-12}, \quad (2)$$

$$\sum_{i,j,m \neq \pm} r_{ij}^{-6} r_{im}^{-6} \cos^4 \theta_i = 12.16 N d^{-12}, \quad (3)$$

$$\begin{aligned} \sum_{i,j,m \neq \pm} r_{ij}^{-6} r_{jm}^{-6} \cos^2 \theta_j &= \sum_{i \neq j} r_{ij}^{-6} r_{jm}^{-6} \cos^2 \theta_j - \sum_{i \neq j} r_{ij}^{-12} \\ &= \frac{\sum_{i \neq j, j \neq m} r_{ij}^{-6} r_{jm}^{-6}}{3} - \sum_{i \neq j} r_{ij}^{-12} = \frac{(\sum_{i,j \neq \pm} r_{ij}^{-6})^2}{3} - \sum_{i,j \neq \pm} r_{ij}^{-12} \\ &= 17.32 d^{-12}, \end{aligned} \quad (4)$$

where N is the total number of lattice points in the lattice and d the lattice constant.

The following four series for a simple cubic lattice were obtained by summing all the terms from the lattice points within distance $2d$ from the origin. The error is admittedly large, and is estimated to be around 25%. However, in the calculation of this paper, the contribution

from terms involving these sums tends to cancel, and as a result, the over-all accuracy is about two or three percent.

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} \cos^2 \theta_m = 14.74 N d^{-12}, \quad (5)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} \cos^2 \theta_i = 10.37 N d^{-12}, \quad (6)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} \cos^2 \theta_i \cos^2 \theta_j = 3.17 N d^{-12}, \quad (7)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} = 29.9 N d^{-12}. \quad (8)$$

The following four sums involving the exchange constant for a simple cubic lattice were evaluated. With the usual assumption that \tilde{A}_{ij} is zero unless i and j are nearest neighbors, all the four sums were obtained exactly.

$$\sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{im} r_{mj}^{-6} = 99 A^2 N d^{-6} / 32, \quad (9)$$

$$\sum_{i,j,m} \tilde{A}_{im} \tilde{A}_{ij} r_{mj}^{-3} = 9.23 A^2 N d^{-3}, \quad (10)$$

$$\sum_{i,j,m \neq} \tilde{A}_{im} \tilde{A}_{ij} r_{mj}^{-3} \cos^2 \theta_j = 4.99 A^2 N d^{-3}, \quad (11)$$

$$\sum_{i,j,m \neq} A_{ij}^2 r_{im}^{-6} = 50.4 N A^2 d^{-6}. \quad (12)$$

The following sum was also computed. Owing to the slowness of convergence the accuracy is not good, but again its contribution to the total sum is small and the over-all accuracy is not greatly affected.

$$\sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m - 1) = 22.8 N A^2 d^{-6}. \quad (13)$$

With the same accuracies discussed previously, the following series for a body-centered-cubic lattice were also computed.

$$\sum_{i,j \neq} r_{ij}^{-6} = 12.29 N d^{-6}, \quad (14)$$

$$\sum_{i,j \neq} r_{ij}^{-12} = 9.11 N d^{-12}, \quad (15)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-6} \cos^2 \theta_i = 41.2 N d^{-12}, \quad (16)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-6} \cos^4 \theta_i = 22.3 N d^{-12}, \quad (17)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} \cos^2 \theta_m = 36.57 N d^{-12}, \quad (18)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} \cos^2 \theta_i \cos^2 \theta_j = 27.46 N d^{-12}, \quad (19)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} \cos^2 \theta_i \cos^2 \theta_j = 9.78 N d^{-12}, \quad (20)$$

$$\sum_{i,j,m \neq} r_{ij}^{-6} r_{im}^{-3} r_{jm}^{-3} = 79.27 N d^{-12}, \quad (21)$$

$$\sum_{i,j,m \neq} \tilde{A}_{ij} \tilde{A}_{im} r_{mj}^{-6} = 11.52 N A^2 d^{-6}, \quad (22)$$

$$\sum_{i,j,m \neq} \tilde{A}_{im} \tilde{A}_{ij} r_{mj}^{-3} = 22.08 N A^2 d^{-3}, \quad (23)$$

$$\sum_{i,j,m \neq} \tilde{A}_{im} \tilde{A}_{ij} r_{mj}^{-3} \cos^2 \theta_j = 9.865 N A^2 d^{-3}, \quad (24)$$

$$\sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-6} = 90.32 N A^2 d^{-6}, \quad (25)$$

$$\sum_{i,j,m \neq} \tilde{A}_{ij}^2 r_{im}^{-3} r_{jm}^{-3} (3 \cos^2 \theta_m^{-1}) = 35.8 N A^2 d^{-6}. \quad (26)$$

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