The line shape theory of nuclear magnetic resonance is presented based on the linear response approximation, in which the retarded Green's function of magnetization vectors plays a central role. To estimate this the corresponding temperature Green's function, which is ordered with respect to the imaginary time, is first investigated with the diagram method, then the desired retarded one is obtained by analytical continuation.

The results obtained are as follows: The main line is Lorentzian at the vicinity of the resonance frequency and is Gaussian at the wings. Satellite lines are also given with similar shapes and reasonable intensities.

§ 1. Introduction

The relaxation phenomenon or the line shape problem is extremely important in the magnetic resonance spectroscopy. This problem was first investigated classically by Bloch, then a beautiful analysis of experimental phenomena was made. The quantum theoretical treatments were also successfully tried: These are, for example, the theory of dipolar broadening by Van Vleck using the moment method, and perturbation treatments by Bloch et al. and by Kubo and Tomita. The last one is the correlation function formalism. As far as we understand, they estimate the time correlation function of the magnetization vector perturbationally up to second order, then conjecture the higher order ones. This treatment seems not fully satisfactory, but is essentially equal to that of the recent many-body theory.

Further investigations, attempting more accurate treatments have been made. Lado et al. obtained a formally accurate expression for the above-mentioned correlation function in terms of a continued fraction. The Green's function approaches have been done by Tomita et al. and by Mansfield. These are similar to each other in the respect that they investigate the retarded Green's function by means of the equation-of-motion method. The difference between these lies in the decoupling procedure. The former approximates the higher-order Green's function with a Gaussian function and the latter with the step function.

Our treatment is based on the linear response theory with the assumption that the external interaction causing transition is weak; however, dipolar interac-
tions between magnetic nuclei, which are responsible for the line shape, are taken into account in selected forms or diagrams to an infinite order.

§ 2. General theory

When a system interacts with the external field, change of any physical quantity of this system $\delta\langle B(t) \rangle$, is expressed, under the assumption that the interaction $\hat{H}^{ex}$ is weak, as

$$ \delta\langle B(t) \rangle = \frac{i}{\hbar} \int_{-\infty}^{t} dt' \text{Tr} \{ \hat{\rho}_0 [\hat{H}_H^{ex}(t'), \hat{B}(t)] \}, $$

where the suffix $H$ represents the Heisenberg picture. In the above $\hat{\rho}_0$ is the grand canonical statistical operator defined by

$$ \hat{\rho}_0 = \exp \{ \beta (Q - \hat{K}) \} $$

in which $\hat{K}$ is the grand canonical Hamiltonian of the system and is written as

$$ \hat{K} = \hat{H} - \mu \hat{N} $$

with the usual Hamiltonian $\hat{H}$, the particle number operator $\hat{N}$ and the chemical potential $\mu$, and $Q$ is the thermodynamic potential relating the grand canonical partition function $Z_\beta$, as

$$ \exp (-\beta Q) = \text{Tr} \exp (-\beta \hat{K}) = Z_\beta. \quad (\beta = 1/k_B T, k_B: \text{Boltzmann constant}) $$

The grand canonical Hamiltonian $\hat{K}$ is divided into two parts:

$$ \hat{K} = \hat{K}_s + \hat{K}_1, $$

where $\hat{K}_s$ consists of three parts; the term describing spatial behavior of the particle $\hat{H}_N$, the Zeeman term $\hat{H}_Z$ and $-\mu \hat{N}$, while $\hat{K}_1$ is the dipolar interaction. These are explicitly written as

$$ \hat{H}_Z = -\hbar \omega_0 \hat{I}_z, \quad \hat{I}_z = \sum_i \hat{I}_i^z, $$

$$ \hat{K}_1 = \mu_N^2 (1/2) \sum_{ij} r_{ij}^2 \left[ \hat{I}_i \cdot \hat{I}_j - 3 \left( \hat{I}_i \cdot r_{ij} \right) \left( \hat{I}_j \cdot r_{ij} \right) / r_{ij}^2 \right], $$

where $r_{ij}$ is the distance between nuclear spins $\hat{I}_i$ and $\hat{I}_j$.

The dipolar interaction $\hat{K}_1$ is conveniently expressed as

$$ \hat{K}_1 = \sum_{a=-2}^{2} K_{1}^a = (1/2) \sum_{a} \sum_{ij} \phi_{ij}^a \{ ij \}^a $$

in which

$$ \{ ij \}^a = \hat{I}_i^a \hat{I}_j^a, $$

$$ \{ ij \}^1 = \hat{I}_i^+ \hat{I}_j^- + \hat{I}_i^- \hat{I}_j^+, $$

$$ \{ ij \}^0 = \hat{I}_i^z \hat{I}_j^z - (1/4) \{ \hat{I}_i^+ \hat{I}_j^- + \hat{I}_i^- \hat{I}_j^+ \}, $$
\[ \{ij\}_{-1} = \tilde{I}_t^z \tilde{I}_f^z + \tilde{I}_t^+ \tilde{I}_f^- \]
\[ \{ij\}_{-1} = \tilde{I}_t^z \tilde{I}_f^- \]

and

\[ \phi_{ij}^z = (\mu S^2 / \ell_i^3) A^z Y_i^z(\vec{r}) \]
\[ A^z = -(16\pi / 5)^{1/2}, \quad A^{2z} = (6\pi / 5)^{1/2}. \] (10)

Here \( Y_i^z(\vec{r}) \) is the spherical Harmonics and \( \vec{r} = (\theta, \phi) \).

The \( z \) axis being taken along the external static field, the rotating field causing transition lies in the \( xy \) plane and has components \( (H_\perp \cos \omega t, -H_\perp \sin \omega t, 0) \), then \( \tilde{H}_{ex}(t) \) is in common notation written as

\[ \tilde{H}_{ex}(t) = (-1 / 2) h \gamma H_\perp (\tilde{I}_t^z e^{i\omega t} + \tilde{I}_f^z e^{-i\omega t}), \] (11)

where \( \gamma \) is the gyromagnetic ratio.

In order to get second-quantized expressions for these interactions we assume that single-particle states for which \( \hat{K}_0 \) is diagonal is given by

\[ (\hat{H}_N - \hbar \omega_0 \tilde{I}_t^z - \mu) \varphi_k(\vec{r}) |m\rangle = (\epsilon_k - m\hbar \omega_0 - \mu) \varphi_k(\vec{r}) |m\rangle 
\]
\[ = \hbar \omega_{km} \varphi_k(\vec{r}) |m\rangle. \] (12)

By defining the creation and annihilation operators \( \hat{a}_{km}^\dagger \) and \( \hat{a}_{km} \), it follows that

\[ \hat{K}_0 = \sum_{km} \hbar \omega_{km} \hat{a}_{km}^\dagger \hat{a}_{km}, \] (13)

\[ \hat{K}_1 = \frac{1}{2V} \sum_{qk\ell m} \sum_{a=-1}^1 I_a(m_\ell m_\ell; m_\ell m_\ell) \phi^{-a}(q) \hat{a}_{k+a,0,m}^\dagger \hat{a}_{k-a,0,m} \hat{a}_{k,m} \hat{a}_{km}, \] (14)

\[ \tilde{H}_{ex}(t) = (-1 / 2) h \gamma H_\perp \sum_{km} [\langle m-1 | \tilde{I}_t^z | m \rangle \hat{a}_{km,m-1} \hat{a}_{km} e^{-i\omega t} 
\]
\[ + \langle m | \tilde{I}_t^z | m - 1 \rangle \hat{a}_{km}^\dagger \hat{a}_{km,m-1} e^{i\omega t}], \] (15)

where

\[ I_a(m_\ell m_\ell; m_\ell m_\ell) = \langle m_\ell(i) m_\ell(j) | \{ij\}_a | m_\ell(j) m_\ell(i) \rangle. \] (15a)

To get (14), \( \varphi_k(\vec{r}) \) is assumed to be plane wave:

\[ \varphi_k(\vec{r}) = V^{-1/2} e^{i\mathbf{K} \cdot \vec{r}} \quad (V:\ \text{volume}), \] (16)

then \( \phi^{-a}(q) \) is the Fourier component of \( \phi_{ij}^a \). More precisely it is given by

\[ \phi^a(q) = \mu S^2 4\pi A^a Y_i^a(q) \int_D \frac{1}{r} j_a(qr) dr 
\]
\[ \equiv \mu S^2 (4\pi / 3) A^a Y_i^a(q), \quad qD \ll 1, \] (17)

where \( j_a(qr) \) is the second-order spherical Bessel function and the Debye cutoff \( D \), from which \( q \)-dependence of \( \phi^a(q) \) arises, is introduced to avoid divergence of the integral. However, the value of integral is almost constant (nearly equal to 1/3) for small \( qD \), which is actually our case. The summation indicated
by \( \{m\} \) is carried out with respect to a set of \( m_i \) satisfying
\[
m_1 + m_2 - m_3 - m_4 = a,
\]
otherwise \( L_a(m_1 m_2; m_3 m_4) \) vanishes.

The assumption shown in (16) might be adequate for almost freely moving particles or spatially homogeneous systems.

Now we assume that particles obey the Fermi statistics,
\[
[a_{km}, a_{k'm'}]_+ = \delta_{kk'} \delta_{mm'}.
\]
Our assumption is also open to another choice, the Bose statistics; however neither of them give any difference in the high temperature approximation.

In discussing the line shape of magnetic resonance, the transverse component of the magnetization vector should be considered. Hence putting \( \hat{I}^t \) for \( \hat{B} \) in (1),
\[
\hat{B}_H(t) = \sum_{km} \langle m | \hat{I}^t | m - 1 \rangle a_{km}^\dagger(t) a_{k,m-1}(t),
\]
and retaining the first term of (15) (the reason will be mentioned in a later section), we obtain,
\[
\delta \langle \hat{I}^t(t) \rangle = (-1/2) \gamma H e^{-\gamma t} \int_0^\infty dt' e^{i \omega t'} \sum_{km} \langle m | \hat{I}^t | m - 1 \rangle \langle m - 1 | \hat{I}^t | n \rangle D_{m,n-1}^R(k, k', t') = (-1/2) \gamma H e^{-\gamma t} \int_0^\infty dt' e^{i \omega t'} \sum_{km} \langle m | \hat{I}^t | m - 1 \rangle \langle m - 1 | \hat{I}^t | n \rangle D_{m,n-1}^R(k, k', \omega)
\]
where the last line defines the magnetic susceptibility \( \chi(\omega) \), and \( D_{m,n-1}^R(k, k', t) \) is the retarded Green's function defined by
\[
\delta \langle \hat{I}^t(t) \rangle = \theta(t) \langle \hat{I}^t | \hat{I}^t | \rangle = \sum_{km} \langle m | \hat{I}^t | m - 1 \rangle \langle m - 1 | \hat{I}^t | n \rangle D_{m,n-1}^R(k, k', \omega)
\]
with a step function \( \theta(t) \):
\[
\theta(t) = \begin{cases} 1 & \text{for } t > 0, \\ 0 & \text{for } t < 0. \end{cases}
\]

The retarded Green's function being inadequate for the diagram analysis, the corresponding temperature Green's function, which is ordered in imaginary times, will be introduced as
\[
D_{m,n-1}(k, k', \tau) = \text{Tr} \{ \hat{\rho}_0 [\hat{a}_{km}(\tau) \hat{a}_{k,m-1}(\tau)] \hat{a}_{k',n-1}^\dagger \hat{a}_{k'n}^\dagger \},
\]
where \( T \) is the operator for time ordering with respect to imaginary time \( \tau \).

The Fourier components of \( D^R(t) \) and \( D(\tau) \) are related to with each other in the Lehmann representation as
\[
D_{m,n-1}^R(k, k', \omega) = \hbar \int \frac{d\omega'}{2\pi} \frac{A(\omega')}{\omega - \omega' + i\eta},
\]
\[
D_{m,n-1}(k, k', \nu_n) = \hbar \int \frac{d\omega'}{2\pi} \frac{A(\omega')}{i\nu_n - \omega'},
\]

\( A(\omega') \) is the Lehmann representation of the Fourier component of the magnetization vector.

\( \eta \) is a small positive constant.
where

\[ \mathcal{H}(\omega) = 2\pi e^{\beta\omega} \sum_{n} e^{-\beta K_n} \langle e' | \hat{a}_{n}^{\dagger} \hat{a}_{n} | e \rangle \times [1 - e^{-\beta \hbar}] \delta[\omega - \hbar^{-1}(K_n - K_{n'})]. \]  

(26)

In the above, \( \eta \) is the positive infinitesimal and \( K_n \) the eigenvalue of \( \hat{K} \). Once we obtain integral expressions as in (25) and (26), the analytical continuation of \( \omega \) into the complex plane is trivial.

Observing (24), we want to evaluate \( \mathcal{D}(r) \) in the following approximate form:

\[ \mathcal{D}(r) = \mathcal{G}(\tau) \mathcal{G}(-\tau), \]

(27)

where \( \mathcal{G}(\tau) \) is the single particle Green's function defined by

\[ \mathcal{G}(\tau) = \mp \text{Tr} \{ \hat{\rho}_0 \mathcal{T} \{ \hat{a}^\dagger(\tau) \hat{a} \} \} \]

(28)

according to \( \tau > 0 \) or \( \tau < 0 \). As to the approximation shown in (27), a discussion will be given in the last section.

The Fourier component of (27) is written as

\[ \mathcal{D}(\nu_i) = (1/\beta \hbar) \sum_{\omega_n} \mathcal{G}(\omega_n) \mathcal{G}(\omega_n - \nu_i), \]

(29)

where it should be noticed that \( \omega_n \), the Fermion frequency, is an odd integer (in unit of \( \pi/\beta \hbar \)), while \( \nu_i \) which is the difference of two Fermion frequencies is an even integer.

Our calculation procedure is as follows: We evaluate \( \mathcal{D}(\nu_i) \) using the diagram method. The selected diagrams give an approximate \( \mathcal{D}(\nu_i) \), from which \( \mathcal{D}_n^\alpha(\omega) \) is obtained through analytical continuation.

\section*{§ 3. Non-interacting system with 1/2 spin}

Now we consider the non-interacting system with \( I = 1/2 \). The result would be trivial, but instructive for the later investigation. The Green's function for this system is

\[ \mathcal{D}_{+-}(k, \tau) = \mathcal{G}_{+-}^0(k, \tau) \mathcal{G}_{++}^0(k, -\tau), \]

(30)

where \( \mathcal{G}_{\alpha\alpha}^0(\tau) \) is the free single particle Green's function and its Fourier component is

\[ \mathcal{G}_{\alpha\alpha}^0(k, \omega_n) = (i\omega_n - \omega_{\alpha\alpha})^{-1}. \]

(31)

Substituting this into (30) and using the well-known frequency sum

\[ \lim_{\tau \to 0} \sum_{\omega_n} e^{i\omega_n \tau} (i\omega_n - \chi) = \mp \beta \hbar / (e^{\beta \hbar^2} + 1) \]

(32)

and identities

\[ \exp(i\beta \hbar \omega_n) = \pm 1, \]

(33)
where the upper (lower) sign refers to the Boson (Fermion), we obtain from (21)

$$\delta \langle I^\dagger (t) \rangle = - \frac{1}{2} \gamma H_{\alpha} e^{-i\omega t} \frac{2 \sinh (\beta \omega_0/2)}{\omega - \omega_0 + i\eta}, \quad (34)$$

where

$$N = \sum_{k} n_k^\delta, \quad n_k^\delta = e^{-\beta (q - p)} \{ e^{\beta \omega_k} + 1 \}^{-1} = n_{k\alpha} \quad (35)$$

under the assumption $\omega_{k\alpha} \gg \omega_0$ and the classical limit $\beta \mu \to -\infty$ for $T \to \infty$.

Then the magnetic susceptibility $\chi(\omega)$ is given by

$$\chi(\omega) = -\gamma N \sinh (\beta \omega_0/2) \left[ P \{ 1/(\omega - \omega_0) \} - i\pi \delta (\omega - \omega_0) \right], \quad (36)$$

where $P$ stands for the principal part. The imaginary part of $\chi(\omega)$ indicates that the line shape is $\delta$ function-like at the resonance frequency $\omega_0$.

§ 4. Interacting system with 1/2 spin

The Green's function $\mathcal{G}$ is written generally as

$$\mathcal{G}_{\alpha\beta} (k, \omega_n) = [\mathcal{G}^0 (k, \omega_n) - \Sigma^* (k, \omega_n)]^{-1}, \quad (37)$$

where $\Sigma^*$ is called the proper self-energy part. In describing $\Sigma^*$, since the line shape problem is now in question, we ignore the first order diagrams which are frequency independent, and retain only a second order diagram (shown in Fig. 1) which is called the ring diagram and is most divergent in the case of the electron gas problem. However it is not performed in this work to sum up all of similar diagrams of higher orders, due to the fact that interactions shown in (8) and (9) have spin-dependent complicate characters.

As is easily checked through direct calculation, the off-diagonal elements of the self-energy parts in spin indices give negligible contributions to the result (an order of $|\Sigma_{\alpha\beta}|^2/\omega_0$, where $\omega_0$ is much larger than $\Sigma^*$ in our case); thus only the diagonal terms are kept.

Combining (29), (31) and (37), we get from (21)

$$\delta \langle \hat{I}^\dagger (t) \rangle = - (1/2) \gamma H_{\alpha} e^{-i\omega t} D_{\alpha\beta} (k, \nu_k) \quad (i \nu_i = \omega + i\eta)
= - (1/2) \gamma H_{\alpha} e^{-i\omega t} (\beta \hbar)^{-1} \sum_{\omega_n} \left[ -i \nu_i + \omega_0 + \Sigma^* (k, \omega_n) - \Sigma^{*+} (k, \omega_n + \nu_i) \right]^{-1}
\times \left[ (i \omega_n - \omega_{k\alpha} - \Sigma^* (k, \omega_n))^{-1} - (i \omega_n - i \nu_i - \omega_{k\alpha} + \Sigma^{*+} (k, \omega_n + \nu_i) \right]^{-1}.$$  

$$\quad \times \left[ 1_{i\nu_i - \omega_{k\alpha} + \eta} \right]. \quad (38)$$

Since the exact frequency sum is impossible due to the $\omega_n$-dependence of $\Sigma^*$, we are obliged to adopt the approximate procedure: that is, considering the $\Sigma^*$ may
be a smooth and slowly varying function of $\omega_n$, we replace $\omega_n$ in $\Sigma^*$ by what is obtained in the absence of $\Sigma^*$. Then a little algebra leads to the expression

$$
\hat{\rho}(t) = (-1/2) \gamma H_R e^{-\frac{1}{2} t} \sum_k e^{-\beta (k_{\perp} - \mu)} 
\times \left\{ \left[ -i \nu_i + \omega_0 + \Sigma^*_{-}(k, \omega_{k-}) - \Sigma^*_+(k, \omega_{k-} - \nu_i) \right]^{-1} - \left[ -i \nu_i + \omega_0 + \Sigma^*_{-}(k, \omega_{k+} + \nu_i) - \Sigma^*_+(k, \omega_{k+} - \nu_i) \right]^{-1} \right\}.
$$

(39)

In deriving the above, the identity (for Boson) of (33) and approximations, for example,

$$
\{ \exp [\beta \hbar \omega_{k-} + \Sigma^*_{-}(k, \omega_{k-})] + 1 \}^{-1} \approx \exp [ -\beta (\epsilon_k - \mu) ]
$$

(40)

are used.

From (39) the susceptibility $\chi'(w)$ is obtained, the imaginary part of which, $\chi''(w)$, suffices to the line shape problem. Considering that the imaginary parts appear from $\Sigma^*_+(k, \omega_{k-} - \nu_i)$ and $\Sigma^*_-(k, \omega_{k+} + \nu_i)$ on substituting $i\nu_i = \omega + i\eta$, we obtain

$$
\chi''(w) = \frac{I}{2} \sum_k e^{-\beta (k_{\perp} - \mu)} \left[ \text{Im} \left( \frac{1}{(\omega - \omega_0 - \text{Re})^2 + \text{Im}^2} \right) - \text{Im}' \left( \frac{1}{(\omega - \omega_0 - \text{Re}')^2 + \text{Im}'^2} \right) \right],
$$

(41)

where short-handed notations $\text{Re}$, $\text{Im}$, $\text{Re}'$ and $\text{Im}'$ are written as

$$
\text{Re} = \Sigma^*_+(k, \omega_{k-} - \nu_i),
\text{Im} = \text{Imaginary Part of } \Sigma^*_+(k, \omega_{k-} + \nu_i),
\text{Re}' = -\Sigma^*_-(k, \omega_{k+} + \nu_i),
\text{Im}' = \text{Imaginary Part of } \Sigma^*_-(k, \omega_{k+} + \nu_i).
$$

(42)

Now we turn to calculate $\text{Im} \Sigma^*_+(k, \omega_{k-} - \nu_i)$ and $\text{Im} \Sigma^*_-(k, \omega_{k+} + \nu_i)$ in more detail. Looking at Fig. 1, we have in general

$$
\Sigma^*_a(k, \omega_n) = -(\beta \hbar^2)^{-1} \sum_{\alpha'} \langle 2\pi \rangle^{-3} \int d^3 p d^3 q \sum_{ab} \phi(q)^{-a} \phi(q)^{-b} \times \sum_{(m)} I_a(m_2, m_3, \alpha') I_b(\beta m_5; m_2 m_1) \mathcal{G}_{m_1}^0(p, \omega_i) \times \mathcal{G}_{m_5}^0(p + q, \omega_n + \nu) \mathcal{G}_{m_4}^0(k - q, \omega_n - \nu).
$$

(43)

We investigate as follows: (a) Only the diagonal parts of $\Sigma^*$ in spin indices are retained, (b) $\phi^{-a}(q)$ and $\phi^{-b}(q)$ are given by (17), (c) expressions as (31) are used for the $\mathcal{G}_a$'s, (d) after partial-fraction expansions frequency sums are carried out, (e) approximations as (35) are employed, (f) the classical limit is taken.

Then it follows that

$$
\Sigma^*_a(k, \omega_n) = \sum_a \sum_{(m)} [I_a(m_2, m_3, \alpha') \langle 2\pi \rangle^{-3} \int d^3 p d^3 q |\phi(q)^{-a}|^2 \mathcal{N}_p^0]
$$

(44)
From this form it is obvious that

$\text{Im} \Sigma_{++}^{*}(k, \omega_{k}) = \text{Im} \Sigma_{--}^{*}(k, \omega_{k}) = 0$.

(45)

In calculating $\Sigma_{++}^{*}(k, \omega_{k} - \omega - i\eta)$ we note that the energy term in (44) becomes

$$-\omega - i\eta + \omega_{p} - \omega_{p+q} - \omega_{k-q} - \omega_{k},$$

using (18). Thus we obtain

$$\text{Im} \Sigma_{++}^{*}(k, \omega_{k} - \omega - i\eta) = \sum_{a} \sum_{(m_{2}, m_{2}')} |I_{a}(m_{1}m_{2}; m_{3} + +)|^{2} \pi^{-2}(2\pi)^{-a} \int \int d^{3}p |\phi(q)|^{-a} |^{2} n_{p}^{0} \times \Delta \delta[\omega - h^{-1}(\epsilon_{k} + \epsilon_{p} - \epsilon_{p+q} - \epsilon_{k-q}) - (\omega_{l} + \omega_{l} + \omega_{l})].$$

(47)

Since our system has a response with wave length much longer than the scale of system, we would be allowed to put $k \rightarrow 0$ and $q \rightarrow 0$ in the above, so that in the argument of $\delta$ function

$$\epsilon_{k} + \epsilon_{p} - \epsilon_{p+q} - \epsilon_{k-q} \approx (-h^{2}/m)p \cdot q.$$  (47a)

Now the spatial part integration with respect to $p$ can be carried out in (47) with great care because the integration limit is from 0 to $\infty$, followed by the elementary integration of angular part. As to integration with respect to $q$, only the angular part is made. Thus we obtain

$$\text{Im} \Sigma_{++}^{*}(k, \omega_{k} - \omega - i\eta) = \frac{1}{18\pi^{2}} \frac{m^{4} \mu_{s}^{4}}{h^{6}} e^{\beta\mu} \sum_{a} \sum_{(m_{2}, m_{2}')} |A_{a}(m_{1}m_{2}; m_{3} + +)|^{2} \int dq q \cdot e^{-\beta(m(u_{d} - u_{d} + a_{d})^{2}/2q^{2}}.$$  (48)

Similarly it follows that

$$\text{Im} \Sigma_{--}^{*}(k, \omega_{k} + \omega + i\eta) = \frac{-1}{18\pi^{2}} \frac{m^{4} \mu_{s}^{4}}{h^{6}} e^{\beta\mu} \sum_{a} |A_{a}(m_{1}m_{2}; m_{3} + -)|^{2} \int dq q \cdot e^{-\beta(m(u_{d} - u_{d} + a_{d})^{2}/2q^{2}}.$$  (48a)

The values of $I_{a}(m_{1}m_{2}; m_{3} + a)$ in these expressions are tabulated in Table I.

Substituting (48) and (48a) into (41), we obtain

$$\chi''(\omega) = \frac{1}{60\pi} \frac{m^{2} \mu_{s}^{4}}{h^{6}} \mu_{s}^{6} N \Bigg\{ [\omega - (\omega_{d} - Re^{2}) + \text{Im}^{2}]^{-1} \sum_{a} B_{+}^{a} \int dq q \cdot e^{-\beta(m(u_{d} - u_{d} + a_{d})^{2}/2q^{2}}$$

$$- [\omega - (\omega_{d} - Re^{2}) + \text{Im}^{2}]^{-1} \sum_{a} B_{-}^{a} \int dq q \cdot e^{-\beta(m(u_{d} - u_{d} + a_{d})^{2}/2q^{2}} \Bigg\}.$$  (49)
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Table I. Numerical factors in Eqs. (48), (48a) and (49).

| $a$  | $|L_a(m_1m_2; m_3+)|^2$ | $|L_a(m_1m_2; m_3-)|^2$ | $B_a^+$ | $B_a^-$ |
|------|------------------------|------------------------|--------|--------|
| 2    | 0                      | 1                      | 0      | 4      |
| 1    | 1/4                    | 3/4                    | 1      | 3      |
| 0    | 3/16                   | 3/16                   | 2      | 2      |
| −1   | 3/4                    | 1/4                    | 3      | 1      |
| −2   | 1                      | 0                      | 4      | 0      |

in which the values of $B_a^a$ are also given in Table I. The remaining integration with respect to $q$ is reduced to the integral logarithms, from which the Debye cutoff parameter $D$ would appear (the integration limit should be from 0 to $1/D$). However, as we have made so many assumptions and so many approximations to arrive here, we would rather stop calculation at this stage and be satisfied with the general aspects given by (49).

We conclude as follows:

1. The main line close to the resonance frequency $\omega_0$ (terms giving shift may be expected to be small) is Lorentzian at the vicinity of $\omega_0$, and is Gaussian at the wings.

2. We have satellite lines at $\omega \approx 0$ and $\omega \approx 2\omega_0$, whose intensities are proportional to $1/\omega_0^2$ and $1/(2\omega_0)^2$ compared to that of the main line, respectively.

3. The ratio of line width of the secular part to the whole is determined simply to be

$$B^a/\sum_a B_a = 2/10$$

which, to our regret, deviates from the so-called $3/10$-rule.

§ 5. Discussion

So far we have presented a new type of theory of line shape in magnetic resonance. Though calculation procedure looks a little tedious we believe that the physical structure is fairly transparent. Our fundamental idea lies in quantization of Hamiltonians, given in (13) ~ (15). The technique to rewrite the angular momentum operators in terms of the particle creation and annihilation operators is a simple matter from mathematical viewpoints. However we would suggest the physical contents involved in this technique beyond mathematics. Instead of thinking about the spin system only, we treat particles bearing spins and finally pick out the spin part which is really desired. The result is necessarily related to the particle properties, i.e., mass, momentum and the Debye cutoff parameter (which corresponds to the impact parameter in the collision theory). The Gaussian part of the line shape, as seen in the course of calculation, originates from $n_s^0$. In our Green’s function theory every step is manipulated by
physically meaningful terms, so that it is naturally expected that the line shape should be interpreted in terms of such as the particle number and energy spectrum in this case. We might say that the usual theories, even Kubo and Tomita's could not present explanations for this point in fully satisfactory ways.

Whether particles are Fermion or Boson (see assumption (19)) seems significantly important in the extremely low temperature case. It is known that the structure of magnetic spectrum is restricted, at the very low temperature, by the particle statistics.\(^{10}\)

As shown at the end of the last section, we have reproduced almost all of the current results. Our failure in obtaining the 3/10-rule is really unexpected. The reason is not clear, but a little discussion will be given in connection with diagrams omitted in the present treatment.

We have pointed out that Eq. (27) is an approximation for the real \(\mathcal{D}\), which will be better described by involving the ladder diagrams. However it is seen that the second order ladder diagram, which is given by putting \(p = k\) in Fig. 1, makes no effect to the line shape. From this viewpoint we may be allowed to disregard the ladder diagrams of any order.

It is abandoned to collect ring diagrams (shown in Fig. 2) in this work due to the complex character of interactions. Observing the third order diagram in Fig. 2, we have a relation for \(a\), \(b\) and \(c\) which specify the type of interaction,

\[
a + b + c = 0
\]

Such relations probably make our procedure of adopting only the second order diagram dangerous and also make the diagram collection quite difficult.

The present theory, due to its general scheme, will be easily applied to other fields of spectroscopy only with a slight modification, for instance, with replacement of the coupling constant in the interaction Hamiltonian.

**Acknowledgement**

The authors would like to express their gratitude to Professor M. Kimura for valuable discussions.
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