Paramagnetic Resonance in Gases at Low Fields

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A classical analysis has been made of the paramagnetic resonance of a gas composed of a collection of magnetic dipoles in an external static magnetic field H_0 for both circularly and linearly polarized radio-frequency fields at right angles to H_0. Assuming that during collisions the dipoles have components only along the H_0 direction one obtains for the circularly polarized case equations similar to those of Bloch with the single parameter τ, the mean time between collisions. The expression for paramagnetic absorption thus obtained suffers from the defect that at zero external field it does not reduce to the Debye formula, as it should. If a Boltzmann distribution of the x and y components of the magnetization is assumed during collisions, the absorption formula is modified and correctly reduces to the Debye formula. For a linearly polarized radio-frequency field, one obtains as the absorption formula the sum of two terms [Eq. (17)]. This again does not reduce to the Debye formula. Introducing a Boltzmann distribution of magnetization during collisions one obtains a corrected formula in which absorption does not vanish at low fields.

I. INTRODUCTION

EXAMINATION of the macroscopic paramagnetic absorption formula of Bloch[1] indicates that it does not reduce to the Debye formula at zero field, as it should and as experiment indicates,[2] but instead predicts zero absorption at zero field. This suggests that it is subject to the same restriction which troubles the Lorentz theory of line broadening for a harmonic oscillator which restriction was eliminated by the revision carried through by Van Vleck and Weisskopf.[3] We have been interested in carrying through in detail a similar revision of the Bloch equations. We consider the case of a gas which is composed of a collection of dipoles with τ the mean time between collisions. Instead of the harmonic oscillator treated by Lorentz and Van Vleck-Weisskopf we follow the precessional motion of the magnetic dipoles in the external field during and between collisions as defined by their equations of motion.

II. THE CIRCULARLY POLARIZED CASE

If the dipole collection is placed in an external field H_0 in the z direction and subjected to a circularly polarized radio-frequency field in the plane at right angles to z, the motion of each dipole is governed by the following differential equations

$$\frac{d\mu_x}{dt}=\gamma[\mu_y H_0+\mu_z H_1 \sin\omega t], \tag{1a}$$

$$\frac{d\mu_y}{dt}=\gamma[\mu_z H_1 \cos\omega t-\mu_x H_0], \tag{1b}$$

$$\frac{d\mu_z}{dt}=\gamma[-\mu_x H_1 \sin\omega t-\mu_y H_1 \cos\omega t], \tag{1c}$$

where μ is the constant magnetic moment of each dipole, μ_x, μ_y, μ_z are the components of μ in the x, y, z direction, H_1 the amplitude of the rf field, γ the gyromagnetic ratio, ω the angular frequency, and $H_x=H_1\cos\omega t$, $H_y=-H_1\sin\omega t$, $H_z=$ the external field H_0. A simple solution of (1) can be obtained by assuming that $\mu_x=\mu_y=0$, $\mu_z=\mu$ during collisions[4] and that μ_x and $\mu_y \ll \mu_z$ between collisions. The latter assumption implies that $\mu_z \sim \mu$ so that μ_z may be considered constant.

The solution of these equations under the above assumptions is

$$\mu_+=Ke^{-i\omega t}+B_1 e^{-i\omega_0 t}, \tag{2a}$$

$$\mu_-=Ke^{i\omega t}+B_2 e^{i\omega_0 t}, \tag{2b}$$

where

$$K=\gamma H_1\mu_z/(\omega_0-\omega),\quad \omega_0=\gamma H_0,\quad \mu_+=\mu_x+i\mu_y,$$

and

$$\mu_-=\mu_x-i\mu_y.$$

If collisions are assumed to occur at the time $t-\theta$, then $\mu_+=\mu_-=0$ at this time. Thus

$$B_1=-Ke^{i(t-\theta)(\omega_0-\omega)},\quad B_2=-Ke^{-i(t-\theta)(\omega_0-\omega)},$$

and Eqs. (2) become

$$\mu_+=Ke^{-i\omega t}[1-e^{i\theta(\omega-\omega_0)}], \tag{3a}$$

$$\mu_-=Ke^{+i\omega t}[1-e^{-i\theta(\omega-\omega_0)}]. \tag{3b}$$

To average the components of the magnetic moments over varying times of last collision, assuming random occurrence of collisions with the mean time τ between them, we multiply μ_+ and μ_- by $(1/\tau)e^{-\theta/\tau}$ and integrate θ from zero to infinity. We thus obtain

$$\langle\mu_+\rangle=\int_0^\infty \frac{\mu_+}{\tau}e^{-\theta/\tau}d\theta=Ke^{-i\omega t}\left(\frac{(\omega-\omega_0)^2\tau^2-i(\omega-\omega_0)\tau}{1+\tau^2(\omega-\omega_0)^2}\right),$$

$$\langle\mu_-\rangle=\int_0^\infty \frac{\mu_-}{\tau}e^{-\theta/\tau}d\theta=Ke^{i\omega t}\left(\frac{(\omega-\omega_0)^2\tau^2+i(\omega-\omega_0)\tau}{1+\tau^2(\omega-\omega_0)^2}\right).$$

[1] F. Bloch, Phys. Rev. **70**, 460 (1946).
[2] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, New York, 1947).
[3] J. H. Van Vleck and V. F. Weisskopf, Revs. Modern Phys. **17**, 227 (1945).
[4] Such collisions are known as strong collisions since the dipoles have no memory of their orientation before collision (see reference 3). They are also assumed to be adiabatic (occurring in a time short compared to the Larmor period). With these two assumptions it is permissible to use, as we later do, a Boltzmann distribution of magnetization during collisions.

Here the angular brackets around μ_+ and μ_- represent their mean values, so that the total magnetization of the collection of dipoles is obtained by multiplying the mean value by N, the number of dipoles per cm^3. Thus the x and y components of magnetization M_x and M_y are given by the expressions

$$
\begin{aligned}
M_x&=N\frac{\langle\mu_+\rangle+\langle\mu_-\rangle}{2}\\
&=\omega_0\chi_0\tau\frac{(H_1\cos\omega t)\tau(\omega_0-\omega)+H_1\sin\omega t}{1+\tau^2(\omega_0-\omega)^2},\\
M_y&=N\frac{\langle\mu_+\rangle-\langle\mu_-\rangle}{2i}\\
&=\omega_0\chi_0\tau\frac{(-H_1\sin\omega t)\tau(\omega_0-\omega)+H_1\cos\omega t}{1+\tau^2(\omega_0-\omega)^2},
\end{aligned}
\tag{4}
$$

where χ_0 represents the static susceptibility. These are similar to the Bloch equations[1] with T_2 replaced by τ. Thus the imaginary portion of the susceptibility χ'' corresponding to the out of phase component of magnetization is given by

$$\chi''=\tfrac{1}{2}\chi_0\omega_0\tau\frac{1}{1+\tau^2(\omega_0-\omega)^2}. \tag{5}$$

We now lift the restriction μ_x, $\mu_y\ll\mu_z$ (i.e., $\mu_z\sim\mu_0$). If the times between collisions are sufficiently long this restriction will not hold since μ_x, μ_y, μ_z can have all values between $\pm\mu$. We transform Eqs. (1) by means of the definitions[5]

$$\mu_x+i\mu_y=Se^{-i\omega t},\quad \alpha^2=\omega_1^2+\Delta^2,\quad \Delta=\omega-\omega_0,\quad \omega_1=\gamma H_1,$$

into

$$dS/dt=i\Delta S+i\omega_1\mu_z,\quad d\mu_z/dt=\tfrac{1}{2}i\omega_1(S-\bar{S}). \tag{6}$$

These have the solution

$$
\begin{aligned}
\mu_z&=A\cos(\alpha t+B)+C,\\
S-\bar{S}&=(2iA\alpha/\omega_1)\sin(\alpha t+B),\\
S+\bar{S}&=(2\Delta A/\omega_1)\cos(\alpha t+B)+D,
\end{aligned}
\tag{7}
$$

where A, B, C, and D are the constants of integration. If we now assume that at time $t-\theta$, $\mu_x=\mu_y=0$, $\mu_z=\mu$, then $S=(\mu_x+i\mu_y)e^{i\omega(t-\theta)}=0$, and

$$
\begin{aligned}
\mu_z&=\mu=A\cos[\alpha(t-\theta)+B]+C,\\
S-\bar{S}&=0=\frac{2iA\alpha}{\omega_1}\sin[\alpha(t-\theta)+B],\\
S+\bar{S}&=0=\frac{2\Delta A}{\omega_1}\cos[\alpha(t-\theta)+B]+D
\end{aligned}
\tag{8}
$$

[5] W. J. Archibald, Am. J. Phys. **20**, 368 (1952).

From these and the relationship $\mu_x^2+\mu_y^2+\mu_z^2=\mu^2$, the four constants of integration can be evaluated as

$$A=\mu\omega_1^2/\alpha^2,\quad B=-\alpha(t-\theta),\quad C=\mu\Delta^2/\alpha^2,$$
$$D=-2\Delta A/\omega_1.$$

substituting these back into (7) we obtain

$$
\begin{aligned}
\mu_z&=(\mu/\alpha^2)(\omega_1^2\cos\alpha\theta+\Delta^2),\\
S-\bar{S}&=(2i\omega_1\mu/\alpha)\sin\alpha\theta,\\
S+\bar{S}&=(2\Delta\mu\omega_1/\alpha^2)(\cos\alpha\theta-1).
\end{aligned}
\tag{9}
$$

To obtain the mean value of these quantities we must now average them over varying times of last collision assuming again a random occurrence of collisions with mean time τ between them. Thus

$$\langle S-\bar{S}\rangle=\int_0^\infty\frac{1}{\tau}(S-\bar{S})e^{-\theta/\tau}d\theta=\frac{2i\omega_1\mu\tau}{1+\alpha^2\tau^2}$$

$$\langle S+\bar{S}\rangle=\int_0^\infty\frac{1}{\tau}(S+\bar{S})e^{-\theta/\tau}d\theta=-\frac{2\Delta\mu\omega_1\tau^2}{1+\alpha^2\tau^2}.$$

From these, since

$$\langle\mu_x+i\mu_y\rangle=\tfrac{1}{2}e^{-i\omega t}(\langle S-\bar{S}\rangle+\langle S+\bar{S}\rangle),$$

we obtain

$$\langle\mu_x\rangle=\frac{\omega_1\mu\tau}{1+\alpha^2\tau^2}(\sin\omega t-\Delta\tau\cos\omega t),$$

from which

$$M_x=N\langle\mu_x\rangle=\chi_0\omega_0\tau\frac{(\omega_0-\omega)\tau H_1\cos\omega t+H_1\sin\omega t}{1+\tau^2(\omega_0-\omega)^2+\gamma^2H_1^2\tau^2}. \tag{10}$$

We thus note the appearance of the saturation term $\gamma^2H_1^2\tau^2$ as a result of lifting the restrictions on μ_x, μ_y, μ_z.[6]

III. THE LINEARLY POLARIZED CASE

If the radio-frequency field is linearly polarized, then the equations of motion to be solved are

$$
\begin{aligned}
d\mu_x/dt&=\gamma\mu_yH_0,\\
d\mu_y/dt&=\gamma(2\mu_zH_1\cos\omega t-\mu_xH_0),
\end{aligned}
\tag{11}
$$

with $H_x=2H_1\cos\omega t$, $H_y=0$, and $H_z=H_0$ representing the external field. We again make the assumption that collisions are frequent so that $\mu_z\sim\mu$. If $\mu_+=\mu_x+i\mu_y$, then (11) reduces to

$$d\mu_+/dt+i\gamma H_0=2i\gamma\mu H_1\cos\omega t. \tag{12}$$

[6] If the saturation term is small compared to 1 the previous equation reduces to Eq. (4). It is of interest to ask what the saturation term means in the collision broadening picture. Thus, if in Eq. (7) one sets $\Delta=0$ (i.e., resonance), then $\alpha=\gamma H_1$. The time taken for μ_z to change from its extreme positive to its extreme negative value is then $1/\gamma H_1$. If $\tau\ll1/\gamma H_1$, collisions occur much more frequently than the flip frequency, thus preventing the dipoles from diverging much from their collision values $\mu_x=\mu_y=0$, $\mu_z=\mu$, and reducing the solution for M_x to that previously obtained [i.e., Eq. (4)].

The solution of this equation is

$$\mu_+=\int_{-\infty}^{t}dt'(2i\gamma\mu H_1\cos\omega t')\times\exp\left(-\int_{t'}^{t}i\gamma H_0dt''\right)+C_1e^{-i\omega_0t}$$
$$=2i\gamma\mu H_1\frac{i\gamma H_0\cos\omega t+\omega\sin\omega t}{(i\gamma H_0)^2+\omega^2}+C_1e^{-i\omega_0t}. \quad (13)$$

C_1 may again be evaluated by assuming that $\mu_+=0$ at the time $(t-\theta)$. Then

$$\mu_+=\frac{2\gamma\mu H_1}{\omega_0^2-\omega^2}\{\omega_0\cos\omega t-i\omega\sin\omega t-[\omega_0\cos\omega(t-\theta)-i\omega\sin\omega(t-\theta)]e^{-i\omega_0\theta}\}, \quad (14)$$

and

$$\langle\mu_+\rangle=\int_0^\infty\frac{\mu_+}{\tau}e^{-\theta/\tau}d\theta$$
$$=\frac{2\gamma\mu H_1}{\tau(\omega_0^2-\omega^2)}\left\{\tau\omega_0\cos\omega t-i\omega\tau\sin\omega t-\omega_0\cos\omega t\frac{\tau(1+i\tau\omega_0)}{(1+i\tau\omega_0)^2+\omega^2\tau^2}-\omega_0\sin\omega t\frac{\omega\tau^2}{(1+i\tau\omega_0)^2+\omega^2\tau^2}+i\omega\sin\omega t\frac{\tau(1+i\tau\omega_0)}{(1+i\tau\omega_0)^2+\omega^2\tau^2}-i\omega\cos\omega t\frac{\omega\tau^2}{(1+i\tau\omega_0)^2+\omega^2\tau^2}\right\}. \quad (15)$$

The imaginary component of the susceptibility can now be evaluated using the μ_x component of μ_+ in (15) and the formula for the total absorption of energy per unit volume per second

$$A_0=\frac{\omega}{2\pi}\int_{t=0}^{t=2\pi/\omega}\mathbf{H}\cdot d\mathbf{M}=\frac{\omega}{2\pi}\int_0^{2\pi/\omega}H_xdM_x$$
$$=\frac{N\omega}{2\pi}\int_0^{2\pi/\omega}2H_1\cos\omega t\,d\langle\mu_x\rangle=2H_1^2\omega\chi''.$$

Substituting from (15) into the latter expression one obtains for χ'':

$$\chi''=\tfrac{1}{2}\chi_0\omega_0\tau\left(\frac{1}{1+\tau^2(\omega_0-\omega)^2}-\frac{1}{1+\tau^2(\omega_0+\omega)^2}\right), \quad (16)$$

which can be written in the equivalent but more suggestive form

$$\chi''=\tfrac{1}{2}\chi_0\omega_0\tau\left(\frac{2\omega\omega_0\tau^2}{1+\tau^2(\omega_0+\omega)^2}\right)\times\left(\frac{1}{1+\tau^2(\omega_0-\omega)^2}+\frac{1}{1+\tau^2(\omega_0+\omega)^2}\right). \quad (17)$$

Both the circularly and linearly polarized expressions for χ'' thus vanish as the external field H_0 or ω_0 approaches zero, the linearly polarized one doing so much more rapidly according to (17). Since neither formula shows any zero field absorption as they should, the assumption that the x and y components vanish during collision appears to be the one to be modified. Assuming a Boltzmann distribution for the x and y components of magnetization after collision[3] we correct C_1 in Eq. (13). This correction to C_1 for the linearly polarized case, to be added to the solution (14) is given by the expression

$$\Delta C_1e^{-i\omega_0(t-\theta)}=\frac{\int\int\mu e^{-\mu H\cos\theta'/kT}\cos\theta'd\Omega}{\int\int e^{-\mu H\cos\theta'/kT}d\Omega}=\frac{2\chi_0H_1}{N}\cos\omega(t-\theta),$$

where $-\mu H\cos\theta'$ represents the potential energy of the magnetic moment μ in the field $H=2H_1\cos\omega(t-\theta)$ and θ' is the angle between μ and the x axis. Thus

$$\Delta C_1e^{-i\omega_0t}=(2\chi_0H_1/N)\cos\omega(t-\theta)e^{-i\omega_0\theta}.$$

A correction ΔC_2, corresponding to the integration constant C_2 in the solution of the equation defining μ_-, similar to that which defines μ_+, is given by

$$\Delta C_2e^{i\omega_0t}=(2\chi_0H_1/N)\cos\omega(t-\theta)e^{i\omega_0\theta}.$$

The correction to μ_x is obtained by adding ΔC_1 and ΔC_2, i.e.,

$$\Delta\mu_x=\tfrac{1}{2}(\Delta C_1e^{-i\omega_0t}+\Delta C_2e^{i\omega_0t})=(2\chi_0H_1/N)\cos\omega(t-\theta)\cos\omega_0\theta.$$

If this is averaged over θ with the weighting factor $(1/\tau)e^{-\theta/\tau}$ we obtain

$$\langle\Delta\mu_x\rangle=\text{Real Part}\left\{\frac{\chi_0H_1}{\tau N}\int_0^\infty e^{i\omega(t-\theta)}\times(e^{i\omega_0\theta}+e^{-i\omega_0\theta})e^{-\theta/\tau}d\theta\right\}$$
$$=\frac{\chi_0H_1}{\tau N}\left(\frac{(1/\tau)\cos\omega t-(\omega_0-\omega)\sin\omega t}{(1/\tau)^2+(\omega_0-\omega)^2}+\frac{(1/\tau)\cos\omega t+(\omega_0+\omega)\sin\omega t}{(1/\tau)^2+(\omega_0+\omega)^2}\right).$$

Since as the expression for the total absorption of energy A_0 indicates, only the sine terms in $\langle\Delta\mu_x\rangle$ contribute to the absorption, we select those and obtain as the correction to χ'':

$$\langle\Delta\chi''\rangle = -\tfrac{1}{2}\chi_0\tau\left(\frac{\omega_0-\omega}{1+\tau^2(\omega_0-\omega)^2}-\frac{\omega_0+\omega}{1+\tau^2(\omega_0+\omega)^2}\right),$$

yielding, when added to (16), the revised expression for χ'':

$$\chi''=\tfrac{1}{2}\chi_0\omega\tau\left(\frac{1}{1+\tau^2(\omega_0-\omega)^2}+\frac{1}{1+\tau^2(\omega_0+\omega)^2}\right). \quad (18)$$

In effect ω_0 in the coefficient of (16) has been replaced by ω and the sign between the two terms has been changed. If now ω_0 is allowed to approach zero, χ'' approaches the expression:

$$\chi''=\chi_0\omega\tau/(1+\tau^2\omega^2),$$

which is the Debye formula for zero field absorption.

Figure 1 is a logarithmic plot, of the relative variation $\Delta g/g$ of g from its free spin value as a function of $\omega\tau$, obtained from Eq. (18) by maximizing χ'' as a function of $\omega_0\tau$ for constant $\omega\tau$. This is in conformity with experiment, the field $H_0=\omega_0/\gamma$ being the variable parameter used in determining the maximum of χ'' for different constant frequencies ω. τ is assumed to be constant over the observed range of frequencies and field. $\Delta g/g$ is then defined as the deviation of ω_0 at maximum χ'' from ω divided by ω. For $\omega\tau>1$ an inverse fourth power variation with $\omega\tau$ is indicated. This diminishes as $\omega\tau$ approaches the value 1 and then increases again when $\omega\tau<1$. Of interest is the disappearance of a maximum in absorption when $\omega\tau$ is less than 0.58.

No measurements have been made in paramagnetic gases at low enough fields to check the above formula. At this laboratory,[7] however, this variation of g as a function of frequency at low fields, has been measured in the free radical diphenyl-picryl-hydrazyl in the range $1<\omega\tau<2$. The inverse variation of $\Delta g/g$ with $\omega\tau$ was found to be slightly larger than fourth power. This appears to be consistent with the values indicated by Fig. 1.

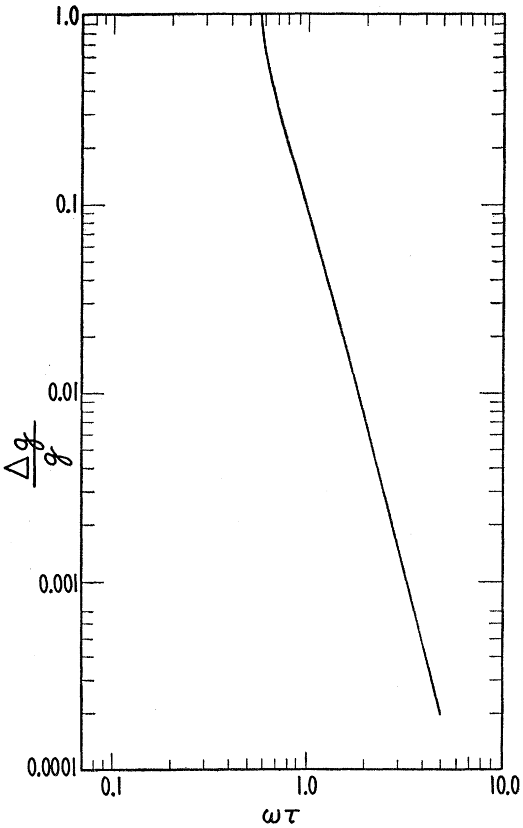

FIG. 1. Variation of g from the free-spin value. The slope measures n in $\Delta g/g\sim 1/(\omega\tau)^n$.

SUMMARY

An analysis has been made of the motion of magnetic dipoles in a gas immersed in a magnetic field H_0 and a cross rf field either circularly or linearly polarized. In the first case, assuming zero x and y components of magnetization during collision, the usual Bloch equation for absorption is obtained; in the second the difference between two Bloch type terms is found. Both, however, predict no absorption at zero field. By assuming a Boltzmann distribution during collisions one obtains for the linearly polarized case the sum of two terms which show zero field absorption and reduce correctly to the Debye formula. The absorption formula thus derived predicts a change of g from the free spin value varying inversely with $\omega\tau$ from the fourth power when $\omega\tau>1$, decreasing as $\omega\tau$ approaches the value 1 and then increasing as $\omega\tau$ sinks below 1. This is verified approximately for diphenyl-picryl-hydrazyl in the range $1<\omega\tau<2$.

[7] A. H. Ryan and L. S. Singer (private communication).