Magnetic Resonance for Arbitrary Field Strengths

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Starting from a microscopic viewpoint, the steady-state value of the magnetization of a system of moments has been calculated semiclassically and quantum mechanically when the external field has a circularly polarized component perpendicular to the constant component. It is assumed that the only other processes which can change the orientation of the individual moments are strong collisions, and that their average tendency is to produce equilibrium with respect to the instantaneous value of the field. The solutions thus obtained predict a nonzero absorption in zero constant field, and that there is no dependence of g-values on frequency. Further properties of the solutions are discussed. It is also shown that the solutions for the circularly polarized case, as well as Garstens' expression for the absorption coefficient for the linearly polarized case, can be obtained as steady-state solutions of the macroscopic equation

$$d\mathbf{M}/dt=\gamma\mathbf{M}\times\mathbf{H}+\tau^{-1}[\chi_0\mathbf{H}-\mathbf{M}].$$

This equation is a special case of an equation in which longitudina relaxation is assumed to be along and transverse relaxation perpendicular to the instantaneous field. The relation of these results to the question of the general validity of this modified form of Bloch's equation is discussed.

INTRODUCTION

THE phenomenological equations of motion for the magnetization which were devised by Bloch[1] for the description of nuclear magnetic resonance have also been widely used in the analysis of magnetic resonance experiments on paramagnetic, ferromagnetic, and ferrimagnetic materials. In this way, many results of interest concerning the interactions affecting the spin systems have been inferred from the comparison of experimental line shapes with those given by the solutions of Bloch's equations, since the latter depend upon the values of the longitudinal and transverse relaxation times.

Recent measurements of electronic magnetic resonance at low dc fields[2,3] have shown that the experimental results no longer agree even qualitatively with the predictions of Bloch's equations. In particular, the Bloch formula predicts zero absorption at zero field in contrast to the finite absorption found experimentally; this point has been recently emphasized by Garstens.[4] This general failure of Bloch's equations at zero field is not too surprising, since the detailed analysis[5] of the conditions required for the validity of Bloch's equations showed that it is necessary that the applied field be large compared to the line width.

The question then naturally arises as to the proper mode of description of magnetic resonance for arbitrary values of the fields, and, in particular, for very small fields. In general, there are several approaches one can use in attempting to solve this problem. For specific cases, one can start with the microscopic situation and make a direct calculation of the average value of the magnetization in the steady state which results from the final macroscopic balance between the effect of the applied field and the interactions affecting the system which tend to restore the system to a state of thermodynamic equilibrium. Garstens' calculation is essentially of this kind; he considered specifically the role of strong collisions in a paramagnetic gas. The principal disadvantage of this procedure is that it cannot be carried through except for extremely simple cases, and even then, the precise relation of the specific results thus obtained to the general problem is usually not at all clear. On the other hand, one can modify the macroscopic phenomenological equations in some plausible way and then proceed by comparing the predictions of the modified equations with experiment. The suggestions of Codrington, Olds, and Torrey[2] fall into this category; this procedure has the advantage of apparent generality but the principal disadvantage here is that one has no firm basis on which to predict the applicability of these equations to a new set of experimental conditions. Perhaps the most satisfactory, but also the most difficult, procedure would be to follow the general ideas of the treatment used by Wangsness and Bloch for strong fields in that one tries to obtain a general description of the phenomena by a suitable method of averaging the microscopic behavior of the system over all the degrees of freedom which are not of direct interest.

In the present paper, we shall not discuss the problem in its full generality, but rather from a point of view which is a combination of the first two discussed above. First, we shall discuss the case of a paramagnetic gas for which we assume that strong collisions are the only important factors to be considered in addition to the applied field. We shall assume the applied field to consist of a circularly polarized component in the plane perpendicular to the constant component. This problem will be treated both semiclassically and quantum mechanically. After considering some of the specific properties of the solutions obtained in this way, we shall discuss the relation of these and Garstens' results to each other and to the solutions of a more general differential equation. Finally, we shall give a brief discussion of the possibility of extending the treatment

[1] F. Bloch, Phys. Rev. **70**, 460 (1946).
[2] Codrington, Olds, and Torrey, Phys. Rev. **95**, 607 (1954).
[3] Garstens, Singer, and Ryan, Phys. Rev. **96**, 53 (1954).
[4] M. A. Garstens, Phys. Rev. **93**, 1228 (1954).
[5] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).

of Wangsness and Bloch to the case of arbitrary field strengths by using some of the methods used here.

SEMICLASSICAL GAS MODEL: CIRCULARLY POLARIZED FIELD

The general philosophy of calculations based on a strong-collision gas model, and which we shall adopt, is essentially the following: we assume that between collisions only the external field has any effect on the orientation of the magnetic moment associated with a given molecule so that we can follow its changes in orientation exactly between collisions, provided that we can solve the appropriate equation of motion; the collisions are assumed to be so strong and to last such a short time that during a collision the change in orientation produced by the external field can be neglected as compared to that effected by the collision; and that, immediately after a collision, the moment has an orientation completely determined by this last collision. An average over the ensemble representing our gas thus requires an average over the varying times between collisions, and over the orientations of the moments immediately after the last collision. Collisions are therefore the only mechanism we have provided to enable the system of moments to come into thermal equilibrium with its surroundings. If the external field were constant, the average over last collisions must reflect the fact that for the equilibrium state the moments have a Boltzmann distribution with respect to the external field, and thus that the parallel component of the magnetization is given by the classical Langevin function while the transverse components are zero. If we now assume an additional time-varying field to be present, whose period is long compared to the duration of a collision, then the instantaneous field seen by the molecule after collision is the same as that before collision. Therefore, it is reasonable to assume in this case that an average over the orientations after the last collision should correspond to an equilibrium state with respect to the *instantaneous* field at the last collision.

We shall carry this program out only for the case in which the external field $\mathbf{H}$ consists of a constant plus a rotating component perpendicular to it, i.e., we assume that

$$H_z=H_0, \quad H_+=H_x+iH_y=H_1e^{-i\omega t}. \tag{1}$$

The advantage of discussing this case is that the solutions of the equation of motion $d\mathbf{M}/dt=\gamma\mathbf{M}\times\mathbf{H}$ can be obtained exactly[6]; thus we can avoid the difficulties encountered by Garstens for both the circularly and linearly polarized case which resulted from not using an exact description of the motion of the moment between collisions.

If $\boldsymbol{\mu}$ is an individual moment whose last collision occurred at a time t', the values of its components at the time t are given by[6]

$$\mu_+(t)=\mu e^{-i\omega t}\{\cos\phi\,\sin\theta+\tfrac{1}{2}\sin\phi[(\cos\theta-1)e^{i(\alpha\tau'+\eta)} +(\cos\theta+1)e^{-i(\alpha\tau'+\eta)}\}. \tag{2}$$

$$\mu_z(t)=\mu[\cos\phi\,\cos\theta-\sin\phi\,\sin\theta\,\cos(\alpha\tau'+\eta)], \tag{3}$$

where

$$\mu_+=\mu_x+i\mu_y, \tag{4}$$

$$\alpha^2=\Delta^2+\omega_1^2, \quad \tan\theta=\omega_1/\Delta, \tag{5}$$

$$\Delta=\gamma H_0-\omega=\omega_0-\omega, \quad \omega_1=\gamma H_1. \tag{6}$$

In (2) and (3), the time which has elapsed since the last collision is $\tau'=t-t'$, and ϕ and η give the orientation of $\boldsymbol{\mu}$ for $\tau'=0$ in the primed coordinate system of reference 6, i.e., a coordinate system rotating with angular velocity $-\omega\mathbf{k}$, so that the components of the effective field in this system are given by

$$H_{x'}=H_1, \quad H_{y'}=0, \quad H_{z'}=\Delta/\gamma.$$

The situation for $\tau'=0$ is illustrated in Fig. 1(a).

We must, however, perform our averaging over orientations at the last collision in the laboratory system where we have assumed that the collisions tend to result in equilibrium with respect to the instantaneous value of the actual field. We can choose the axes of our laboratory system to coincide with the primed axes at t', and we let φ and ξ give the orientation of $\boldsymbol{\mu}$ with respect to the resultant field $H=(H_0^2+H_1^2)^{\frac{1}{2}}$. This situation is illustrated in Fig. 1(b); we note that $\tan\vartheta=H_1/H_0=\omega_1/\omega_0$. Since both sets of angles give the orientation of the same moment at the same time, we can equate the expressions for $\mu_{x'}$, $\mu_{y'}$, and $\mu_{z'}$ obtained from the two parts of Fig. 1 to get the following relations:

$$\begin{aligned}\cos\varphi\,\sin\vartheta+\sin\varphi\,\cos\xi\,\cos\vartheta &=\cos\phi\,\sin\theta+\sin\phi\,\cos\eta\,\cos\theta,\\ \sin\varphi\,\sin\xi&=\sin\phi\,\sin\eta,\\ \cos\varphi\,\cos\vartheta-\sin\varphi\,\cos\xi\,\sin\vartheta &=\cos\phi\,\cos\theta-\sin\phi\,\cos\eta\,\sin\theta.\end{aligned} \tag{7}$$

From these, we easily find that

$$\begin{aligned}\cos\phi&=\cos\varphi\,\cos(\theta-\vartheta)+\sin\varphi\,\cos\xi\,\sin(\theta-\vartheta);\\ \sin\phi\,\cos\eta&=-\cos\varphi\,\sin(\theta-\vartheta) +\sin\varphi\,\cos\xi\,\cos(\theta-\vartheta),\\ \sin\phi\,\sin\eta&=\sin\varphi\,\sin\xi.\end{aligned} \tag{8}$$

Results which represent averages only over orientations in the laboratory system will be represented by $\langle\ \rangle$; in accordance with our assumption of equilibrium with respect to the instantaneous field, we can now assume that: φ and ξ are independent with respect to averaging; ξ has a random distribution; and, φ is described by a Boltzmann distribution with respect to the resultant field H.

[6] R. K. Wangsness, Am. J. Phys. **21**, 274 (1953). The right side of the expression for μ_y in Eq. (9) of this paper should have a minus sign before it.

Thus, we have

$$\langle \sin\varphi \cos\xi\rangle = \langle \sin\varphi \sin\xi\rangle = 0,$$

and

$$\langle \cos\varphi\rangle = L(\mu H/kT) \simeq \mu H/3kT, \tag{9}$$

where L is the Langevin function. Averaging over Eqs. (8), and using these results, we find that

$$\begin{aligned} \langle \cos\phi\rangle &= \langle \cos\varphi\rangle \cos(\theta-\vartheta), \\ \langle \sin\phi \cos\eta\rangle &= -\langle \cos\varphi\rangle \sin(\theta-\vartheta), \\ \langle \sin\phi \sin\eta\rangle &= 0, \end{aligned} \tag{10}$$

so that

$$\langle \sin\phi e^{\pm i\eta}\rangle = -\langle \cos\varphi\rangle \sin(\theta-\vartheta). \tag{11}$$

Therefore, we see that (2) and (3) become

$$\langle \mu_+(t)\rangle = \mu\langle \cos\varphi\rangle e^{-i\omega t}\{\sin\theta \cos(\theta-\vartheta) + \tfrac{1}{2}\sin(\theta-\vartheta) \times[(1-\cos\theta)e^{i\alpha\tau'} - (1+\cos\theta)e^{-i\alpha\tau'}]\}, \tag{12}$$

$$\langle \mu_z(t)\rangle = \mu\langle \cos\varphi\rangle[\cos\theta \cos(\theta-\vartheta) + \sin\theta \sin(\theta-\vartheta) \cos\alpha\tau']. \tag{13}$$

The second part of our averaging process now involves the average over the intervals τ' using the distribution function $e^{-\tau'/\tau}(d\tau'/\tau)$, where τ is the mean time between collisions. Representing our final averages by $\langle\ \rangle_{Av}$, we find from (12) and (13) that

$$\langle \mu_+(t)\rangle_{Av} = \mu\langle \cos\varphi\rangle e^{-i\omega t}\{\sin\theta \cos(\theta-\vartheta) - [\sin(\theta-\vartheta)(\cos\theta - i\alpha\tau)/(1+\alpha^2\tau^2)]\}, \tag{14}$$

$$\langle \mu_z(t)\rangle_{Av} = \mu\langle \cos\varphi\rangle\{\cos\theta \cos(\theta-\vartheta) + [\sin\theta \sin(\theta-\vartheta)]/(1+\alpha^2\tau^2)\}. \tag{15}$$

If we now multiply these equations by the number of moments per unit volume, N, we will obtain the values of the magnetization components at the time t. From (9), we have $N\mu\langle \cos\varphi\rangle = N\mu^2 H/3kT = \chi_0 H$, where χ_0 is the static susceptibility. From (5), (6), and Fig. 1(b), we also find that

$$\begin{aligned} \cos(\theta-\vartheta) &= (\alpha^2+\omega\Delta)/\gamma\alpha H, \\ \sin(\theta-\vartheta) &= \omega H_1/\alpha H. \end{aligned}$$

Substituting these into (14) and (15), we get

$$M_+(t) = \chi_0 H_1 e^{-i\omega t}\{1+[(\omega\Delta\tau^2 + i\omega\tau)/(1+\alpha^2\tau^2)]\}, \tag{16}$$

$$M_z(t) = (\chi_0/\gamma)\{\omega_0 - (\omega\omega_1^2\tau^2)/(1+\alpha^2\tau^2)\}. \tag{17}$$

We can also obtain expressions for the in- and out-of-phase components of the susceptibility, for, if we write

$$M_+(t) = (\chi' + i\chi'')H_+ = (\chi' + i\chi'')H_1 e^{-i\omega t} \tag{18}$$

we find from (16) that

$$\frac{\chi'}{\chi_0} = 1 + \frac{\omega\Delta\tau^2}{1+\Delta^2\tau^2+\omega_1^2\tau^2}, \tag{19}$$

$$\frac{\chi''}{\chi_0} = \frac{\omega\tau}{1+\Delta^2\tau^2+\omega_1^2\tau^2}. \tag{20}$$

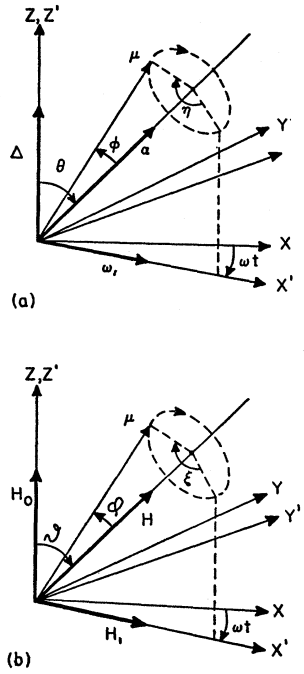

FIG. 1. Orientation of the moment and the field components at the time of the last collision in the coordinate systems used in the text. (*a*) Rotating system. (*b*) Laboratory system.

We shall defer a detailed discussion of these results until a later section, but for the present we can note that they reduce to the correct values for the static case, for when $\omega=0$, $\chi'=\chi_0$, $\chi''=0$, and $M_z=\chi_0 H_0$. As Garstens noted, his results for the circularly polarized case, which can be obtained from the above by dropping the one in (19) and replacing ω by ω_0 in the numerators of (19) and (20), are incorrect in that they do not reduce to the proper values for the static case.

We can also point out here that the maximum value of χ'' occurs when $\Delta=0$, i.e., $\omega_0=\omega$. Thus, for the circularly polarized case, there is no change in g-value with frequency.

QUANTUM-MECHANICAL DERIVATION

In the previous section, we considered the effect of the external field and of collisions upon the magnetization components. In this section, we shall instead consider the effect upon the distribution function, i.e., the density matrix for the spins.

As before,[5] we shall use a representation in which the z component of the spin, I_z, is diagonal with eigenvalues m. In terms of the spin probability amplitudes $a_m(t)$, the components of the density matrix ρ are given by

$$(m|\rho(t)|m') = a_m(t)a_{m'}{}^*(t). \tag{21}$$

We also have the relation

$$\mathfrak{y} = \gamma\hbar\mathbf{I}, \tag{22}$$

so that we can initially confine our considerations to the expectation values of **I**. In fact, the expectation values are given by

$$\langle I_+\rangle=\mathrm{Tr}(I_+\rho)=\textstyle\sum_m(m|I_+|m-1)(m-1|\rho|m),$$
$$\langle I_z\rangle=\mathrm{Tr}(I_z\rho)=\textstyle\sum_m m(m|\rho|m), \tag{23}$$

where

$$(m|I_+|m-1)=[(I+m)(I-m+1)]^{\frac{1}{2}}.$$

Although all of the results describing the effect of the external field alone on ρ which we shall be using have been obtained for arbitrary values of I,[7] we shall restrict our considerations to the case that $I=\frac{1}{2}$ since the formulas become quite cumbersome otherwise. Since then $m=\pm\frac{1}{2}$, we shall let $(+\frac{1}{2}|\rho|+\frac{1}{2})=\rho_{++}$, etc., so that Eqs. (23) simplify to

$$\langle I_+\rangle=\rho_{-+} \quad\text{and}\quad \langle I_z\rangle=\tfrac{1}{2}(\rho_{++}-\rho_{--}). \tag{24}$$

If we now transform from the laboratory system to the primed coordinate system which is rotating so as to keep the resultant field H in the $x'z'$ plane, it is convenient to express everything in terms of the probability amplitudes b_m and the density matrix ρ' in the rotating system. Using the results quoted by Bloch and Rabi[7] for the transformation of the probability amplitudes,

$$b_+=e^{-i\frac{1}{2}\omega t}a_+ \quad\text{and}\quad b_-=e^{i\frac{1}{2}\omega t}a_-,$$

we find that

$$\rho_{++}=\rho_{++}', \quad \rho_{--}=\rho_{--}', \quad \rho_{-+}=e^{-i\omega t}\rho_{-+}',$$

so that the expectation values in the laboratory system given by (24) becomes

$$\langle I_+\rangle=\rho_{-+}'e^{-i\omega t} \quad\text{and}\quad \langle I_z\rangle=\tfrac{1}{2}(\rho_{++}'-\rho_{--}'). \tag{25}$$

In the primed coordinate system, the probability amplitudes at the time t in terms of their values at the time t' are given by[7]

$$b_+(t)=Ab_+^0+Bb_-^0, \quad b_-(t)=Bb_+^0+A^*b_-^0, \tag{26}$$

where

$$A=\cos(\tfrac{1}{2}\alpha\tau')+i\cos\theta\sin(\tfrac{1}{2}\alpha\tau'),$$
$$B=i\sin\theta\sin(\tfrac{1}{2}\alpha\tau'), \tag{27}$$

and where, as before, $\tau'=t-t'$ is the interval since the last collision. Therefore, we find for the elements of ρ' the following:

$$\rho_{-+}'=(A^*)^2\rho_{-+}'^0-B^2\rho_{+-}'^0+A^*B(\rho_{++}'^0-\rho_{--}'^0),$$
$$\rho_{++}'-\rho_{--}'=(AA^*+B^2)(\rho_{++}'^0-\rho_{--}'^0)+2B(A^*\rho_{-+}'^0-A\rho_{+-}'^0), \tag{28}$$

where $\rho_{++}'^0=b_+^0b_+^{0*}$, etc. These results must now be averaged over the state at the last collision and then over the intervals since the last collision.

According to our basic assumption, the average over the states at the last collision should correspond to an equilibrium distribution with respect to the instantaneous resultant field H of Fig. 1(b). If we use c_+ and c_- as the probability amplitudes in the system whose z'' axis lies along H and whose y'' axis coincides with y', we can therefore assume that there exists complete incoherence in the relative phases of c_+ and c_-. If we let averages over the states at last collision be represented by $(\ )_c$, our basic assumption therefore is equivalent to the relations

$$(c_+c_-)_c=(c_+^*c_-)_c=(c_+^*c_-^*)_c=(c_+c_-^*)_c=0,$$
$$(c_+c_+^*-c_-c_-^*)_c=\tanh(\mu H/kT)\simeq\mu H/kT=\kappa. \tag{29}$$

Since the systems in which the b's and c's are used differ by a rotation about the y' axis by the angle ϑ, the relation between the amplitudes is given by[7]

$$b_+^0=c_+\cos\tfrac{1}{2}\vartheta-c_-\sin\tfrac{1}{2}\vartheta, \quad b_-^0=c_+\sin\tfrac{1}{2}\vartheta+c_1\cos\tfrac{1}{2}\vartheta,$$

and therefore, we find that

$$(\rho_{-+}'^0)_c=(\rho_{+-}'^0)_c=\tfrac{1}{2}\kappa\sin\vartheta, \quad (\rho_{++}'^0-\rho_{--}'^0)_c=\kappa\cos\vartheta,$$

so that (28) becomes:

$$(\rho_{-+}')_c=\kappa[\tfrac{1}{2}\sin\vartheta((A^*)^2-B^2)+\cos\vartheta A^*B]$$
$$=\tfrac{1}{2}\kappa\{\sin\theta\cos(\theta-\vartheta)+\tfrac{1}{2}\sin(\theta-\vartheta)\times[(1-\cos\theta)e^{i\alpha\tau'}-(1+\cos\theta)e^{-i\alpha\tau'}]\}, \tag{30}$$

$$(\rho_{++}'-\rho_{--}')_c=\kappa[\cos\vartheta(AA^*+B^2)+\sin\vartheta B(A^*-A)]$$
$$=\kappa[\cos\theta\cos(\theta-\vartheta)+\sin\theta\sin(\theta-\vartheta)\cos\alpha\tau']. \tag{31}$$

The next step would now be to average these results over the intervals since the last collision. We do not, however, have to carry this through as we can now easily see that we will get the same results as before. For, if we now wanted to get a result to compare with that of the last section at an equivalent stage such as (12), we see from (22) and (25), we can get $\langle\mu_+(t)\rangle$ by multiplying (30) by $\gamma\hbar e^{-i\omega t}$. Then the factor in front of the braces of (30) becomes, except for $e^{-i\omega t}$, $\frac{1}{2}\gamma\hbar\kappa=\mu\kappa=\mu^2H/kT=\chi_0H/N$ where χ_0 is the static susceptibility appropriate to spin $\frac{1}{2}$. Since we showed in the last section that $\mu\langle\cos\varphi\rangle=\chi_0H/N$, if we now compare the form of (30) and (12) we see that we will be led to exactly the same final result upon averaging (30) over τ' as we were from (12). Similarly, since the terms in the brackets of (31) are the same as (13), an average of (31) over τ' will lead to the same final results as did (13). Thus, we see that Eqs. (16)–(20) will also be obtained by this quantum-mechanical calculation.

PROPERTIES OF THE RESULTS FOR THE CIRCULARLY POLARIZED CASE

The quantities of principal interest to us in this section are the susceptibilities

$$\frac{\chi'}{\chi_0}=1+\frac{\omega\Delta\tau^2}{1+\alpha^2\tau^2}, \quad \frac{\chi''}{\chi_0}=\frac{\omega\tau}{1+\alpha^2\tau^2}. \tag{32}$$

[7] F. Bloch and I. I. Rabi, Revs. Modern Phys. **17**, 237 (1945).

We note first of all that for zero constant field ($\omega_0=0$) they become

$$\frac{\chi'}{\chi_0}=\frac{1+(\omega_1\tau)^2}{1+(\omega\tau)^2+(\omega_1\tau)^2},\quad \frac{\chi''}{\chi_0}=\frac{\omega\tau}{1+(\omega\tau)^2+(\omega_1\tau)^2}. \tag{33}$$

We see that $\chi''\neq 0$ so that there is an absorption at zero field as there should be and, in fact, if the rotating field is sufficiently weak, i.e., $(\omega_1\tau)^2\ll 1$, χ'' reduces correctly to the Debye formula $\chi_0\omega\tau/(1+\omega^2\tau^2)$.

For extremely large fields ($\Delta\to\infty$), we also find that these formulas reduce to the reasonable values $\chi'\to\chi_0$ and $\chi''\to 0$.

As mentioned before, χ'' has its maximum value for $\Delta=0$ (resonance), and we have

$$\chi'_{\rm res}=\chi_0,\quad \chi''_{\rm res}=\chi_0\omega\tau/(1+\omega_1^2\tau^2).$$

It is interesting to see that χ' is not zero when χ'' is a maximum, but rather is equal to the static value of the susceptibility.

For more detailed discussion, it is convenient to write (32) in terms of a set of dimensionless variables

$$x=\omega\tau,\quad x_0=\omega_0\tau,\quad x_1=\omega_1\tau, \tag{34}$$

$$r=x_0/x=\omega_0/\omega, \tag{35}$$

so that resonance corresponds to $r=1$. In addition, we introduce a parameter ϵ, which is a convenient measure of the combined effect of the frequency and amplitude of the rotating field, and which is defined by

$$\epsilon=[(1+x_1^2)/x^2]^{\frac{1}{2}}. \tag{36}$$

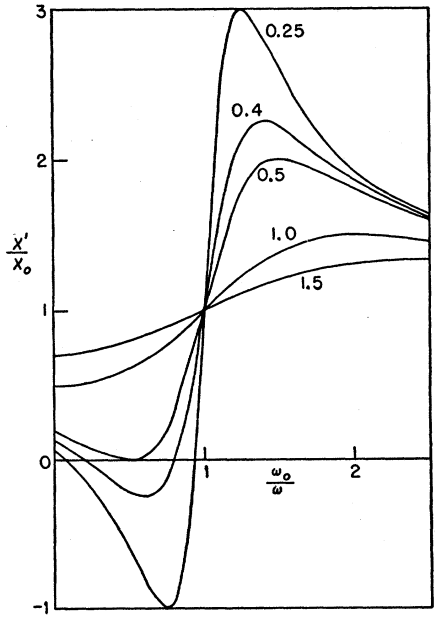

FIG. 2. Real part of susceptibility *vs* applied field when transverse field is circularly polarized. The numbers near the peaks are the values of the parameter ϵ which measures the combined effect of frequency and amplitude.

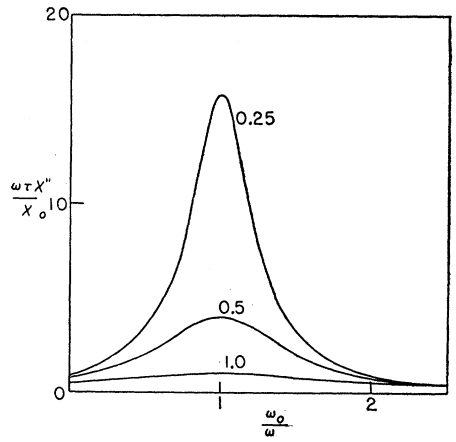

FIG. 3. Imaginary part of susceptibility *vs* applied field when transverse field is circularly polarized. The numbers near the peaks are the values of the parameter ϵ which measures the combined effect of frequency and amplitude.

In this notation, $1+\alpha^2\tau^2=x^2[(r-1)^2+\epsilon^2]$, and (32) becomes

$$\frac{\chi'}{\chi_0}=1+\frac{(r-1)}{(r-1)^2+\epsilon^2},\quad x\left(\frac{\chi''}{\chi_0}\right)=\frac{1}{(r-1)^2+\epsilon^2}. \tag{37}$$

These forms are more useful in performing numerical calculations.

One easily finds that the points at which χ'' is equal to half its maximum value are $r=1\pm\epsilon$, or $(\omega_0)_{\frac{1}{2}}=\omega(1\pm\epsilon)$. It also turns out that these are the same as the points at which χ' has its maximum and minimum values. In fact, we have, for $(\omega_0)_{\rm max}=\omega(1+\epsilon)$,

$$(\chi'/\chi_0)_{\rm max}=1+1/2\epsilon$$

and for $(\omega_0)_{\rm min}=\omega(1-\epsilon)$,

$$(\chi'/\chi_0)_{\rm min}=1-1/2\epsilon.$$

Thus, except for the case discussed below, the maximum and minimum values of χ' are equally above and below χ_0. If $\epsilon<\frac{1}{2}$, $(\chi')_{\rm min}$ is negative; if $\epsilon>\frac{1}{2}$, $(\chi')_{\rm min}$ is positive, while for $\epsilon=\frac{1}{2}$, $(\chi')_{\rm min}=0$, $(\chi')_{\rm max}=2\chi_0$, $(\omega_0)_{\rm min}=\frac{1}{2}\omega$, and $(\omega_0)_{\rm max}=\frac{3}{2}\omega$. If $\epsilon>1$, however, the above formula would indicate that $(\omega_0)_{\rm min}$ is negative; this means, of course, that for $\epsilon>1$, the minimum value of χ' corresponds to the value for $\omega_0=0$ and is greater than the value $1-(1/2\epsilon)$ given by the above formula.

It is possible for χ' to go through or become zero, but only if $\epsilon\leqslant\frac{1}{2}$. If $\epsilon<\frac{1}{2}$, χ' is zero at the frequencies given by

$$\omega_{0z}^{\pm}=\tfrac{1}{2}\omega[1\pm(1-4\epsilon^2)^{\frac{1}{2}}],$$

while if $\epsilon=\frac{1}{2}$, the two zeros coincide and equal the value $\omega/2$ found above for $(\omega_0)_{\rm min}$. On the other hand, if $\epsilon>\frac{1}{2}$, χ' is always positive.

Figures 2 and 3 show calculated curves of (χ'/χ_0) and $x(\chi''/\chi_0)$ as functions of r for various values of ϵ. They clearly show the existence of absorption for zero

H_0 and the change in the character of the curves as discussed above for increasing values of ϵ. Experimentally, this could be obtained under suitable conditions by increasing ω_1 for a fixed value of ω.

The value of M_z as given by (17) never changes appreciably from the value $\chi_0 H_0$ except for very large ω_1. The value of M_z at resonance is

$$(M_z)_{\text{res}}=\chi_0 H_0/(1+\omega_1^2\tau^2).$$

RELATION OF THESE RESULTS TO A GENERAL EQUATION OF MOTION

As was discussed, it would be of interest to have a general equation of motion for the magnetization, possibly a suitably modified form of Bloch's equation, which is a more accurate description of resonance phenomena for arbitrary fields, particularly at low fields. In the previous sections we derived expressions for the susceptibilities which do reduce to what are felt to be the correct forms at low fields. If we could now show that these susceptibilities can also be derived from a general equation under the same conditions as used in the previous sections rather than necessitating the type of detailed calculation we have actually used, this would furnish a limited theoretical support from the microscopic point of view for the validity of the macroscopic equation.

Briefly stated, the basic assumption in our derivation was that the effect of the strong collisions was the tendency to establish equilibrium with respect to the instantaneous value of the field. This is similar to the suggestion of Codrington, Olds, and Torrey[2] that Bloch's equation be altered by assuming that longitudinal relaxation takes place along the instantaneous field while transverse relaxation is perpendicular to it. We shall now show that our specific results can be obtained from an equation of this type.

If we let T_1 and T_2 be the usual longitudinal and transverse relaxation times, respectively, then the equation of motion suggested by Codrington, Olds, and Torrey would have the form

$$\frac{d\mathbf{M}}{dt}=\gamma\mathbf{M}\times\mathbf{H}+\frac{1}{T_1}\left[\chi_0\mathbf{H}-\frac{(\mathbf{M}\cdot\mathbf{H})}{H^2}\mathbf{H}\right]-\frac{1}{T_2}\left[\mathbf{M}-\frac{(\mathbf{M}\cdot\mathbf{H})}{H^2}\mathbf{H}\right]$$

or

$$\frac{d\mathbf{M}}{dt}=\gamma\mathbf{M}\times\mathbf{H}+\frac{\chi_0\mathbf{H}}{T_1}-\frac{\mathbf{M}}{T_2}+\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{(\mathbf{M}\cdot\mathbf{H})}{H^2}\mathbf{H}. \quad (38)$$

If we let $M_+=M_x+iM_y$ then (38) is equivalent to

$$\dot{M}_+=-\left(i\gamma H_z+\frac{1}{T_2}\right)M_+ +\left[i\gamma M_z+\frac{\chi_0}{T_1}+\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{\mathbf{M}\cdot\mathbf{H}}{H^2}\right]H_+, \quad (39)$$

$$\dot{M}_z=\frac{i\gamma}{2}(M_+H_+^*-M_+^*H_+) -\frac{M_z}{T_2}+\left[\frac{\chi_0}{T_1}+\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{\mathbf{M}\cdot\mathbf{H}}{H^2}\right]H_z. \quad (40)$$

If we now assume that $\mathbf{H}$ has the constant and circularly polarized components given by (1), we can find a steady state solution of (39) and (40) of the form

$$M_+=(\chi_-'+i\chi_-'')H_1e^{-i\omega t}, \quad M_{z-}=\text{const.} \quad (41)$$

When (41) is substituted in (39) and (40), we find that

$$\chi_-'=\chi_0 D_-[1+(\alpha^2+\omega\Delta)T_2^2], \quad (42)$$

$$\chi_-''=\chi_0 D_-\omega T_2, \quad (43)$$

$$M_{z-}=(\chi_0/\gamma)D_-[\omega_0(1+\alpha^2T_2^2)-\omega\omega_1^2T_2^2], \quad (44)$$

where

$$(1/D_-)=1+\alpha^2T_1T_2 -T_2(T_1-T_2)(\omega_1^2+\omega_0\Delta)^2/(\omega_0^2+\omega_1^2). \quad (45)$$

Now in the case of gases, where strong collisions provide the relaxation mechanism, it is known[5] that there is no longer any real distinction between T_1 and T_2. In order to compare these results with those of previous sections, therefore, we should consider the case that $T_1=T_2=\tau$; then we see at once that (42)–(44) reduce exactly to the corresponding expressions in (17), (19), and (20). In other words, the results obtained by the earlier detailed calculations can most simply be obtained as the steady-state solution of the equation to which (38) reduces when $T_1=T_2=\tau$; namely,

$$\frac{d\mathbf{M}}{dt}=\gamma\mathbf{M}\times\mathbf{H}+\frac{1}{\tau}[\chi_0\mathbf{H}-\mathbf{M}]. \quad (46)$$

We can also find the steady-state solution of (39)–(40) for the other sense of circular polarization. If we assume the external field now has the components

$$H_z=H_0, \quad H_+=H_1e^{i\omega t}, \quad (47)$$

and assume a solution of the form

$$M_+=(\chi_+'+i\chi_+'')H_1e^{i\omega t}, \quad M_{z+}=\text{const.}$$

we find that χ_+', χ_+'', and M_{z+} are given exactly by simply replacing ω by $-\omega$ everywhere in the corresponding results (42)–(45) obtained for the other case. For example, we find that

$$\chi_+''=-\chi_0 D_+\omega T_2, \quad (48)$$

where

$$(1/D_+)=1+[(\omega_0+\omega)^2+\omega_1^2]T_1T_2 -T_2(T_1-T_2)[\omega_1^2+\omega_0(\omega_0+\omega)]^2/(\omega_0^2+\omega_1^2). \quad (49)$$

The linearly polarized case for which $H_x=2H_1\cos\omega t$, $H_y=0$ is very difficult to solve exactly. For our present purposes, it will be sufficient to restrict our considerations of the linearly polarized case to the simpler

equation (46). We can get an approximate steady-state solution if we assume H_1 to be small enough so that we can neglect the product M_xH_x. We then find that a solution of the equation corresponding to (40) is

$$M_{zl}=\chi_0 H_0=\text{const.}$$

The corresponding equation (39) then becomes simply

$$\dot{M}_{+l}=-\left(i\omega_0+\frac{1}{\tau}\right)M_{+l}+\chi_0\left(i\omega_0+\frac{1}{\tau}\right)\times H_1(e^{i\omega t}+e^{-i\omega t}) \quad (50)$$

since $H_+=2H_1\cos\omega t$.

Equation (50) can be easily integrated directly to find the steady-state value of M_{+l} which we see will be proportional to H_1. But the linear form of (50) suggests that we should be able to write M_{+l} as the sum of the solutions we found for the two circularly polarized cases when $T_1=T_2=\tau$, provided that we neglect the quantity $(\omega_1\tau)^2$. This can be verified directly to be the case and therefore we can write

$$M_{+l}=(\chi_-'+i\chi_-'')H_1e^{-i\omega t}+(\chi_+'+i\chi_+'')H_1e^{i\omega t},$$

or

$$M_{xl}=2H_1[\tfrac{1}{2}(\chi_-'+\chi_+')\cos\omega t+\tfrac{1}{2}(\chi_-''-\chi_+'')\sin\omega t],$$

$$M_{yl}=2H_1[\tfrac{1}{2}(\chi_-''+\chi_+'')\cos\omega t-\tfrac{1}{2}(\chi_-'-\chi_+')\sin\omega t]. \quad (51)$$

The only term which will contribute to the energy absorption is the coefficient of $2H_1\sin\omega t$ in the expression for M_{xl}, and this can be written in the normal manner as χ_l''. Thus, from (51), (43), and (48), we get

$$\chi_l''=\tfrac{1}{2}(\chi_-''-\chi_+'')=\tfrac{1}{2}\chi_0\omega\tau\left[\frac{1}{1+(\omega_0-\omega)^2\tau^2}+\frac{1}{1+(\omega_0+\omega)^2\tau^2}\right], \quad (52)$$

which is exactly the expression obtained by Garstens for the linearly polarized case[4] and is known to agree well with experiment.[3] Since Garstens, Singer, and Ryan always used extremely small amplitudes for their oscillating field, one could not expect their experiments to show the effects of the additional terms $(\omega_1\tau)^2$ which will likely appear in a less approximate solution of (46).

The general origin of Garstens' expression for χ_l'' is now less obscure since we have just shown it to be obtainable from an approximate steady-state solution of the general equation of motion (46) in which both relaxation times are taken to be equal.

DISCUSSION

In general, the fact that our results for the circularly polarized case and that of Garstens for the linearly polarized case, which were derived by suitable averaging over the microscopic states, can be obtained as solutions of the macroscopic equation (46) provide support for the feeling that (46) and hence the more general equation (38) will provide a valid description of magnetic resonance phenomena for a wide range of experimental conditions. In order to specify these conditions in detail, we would obviously require a more elaborate analysis than given here. It seems likely that this task could be carried through, at least for the circularly polarized case, by transforming to a properly chosen rotating coordinate system in which the external field has effectively been eliminated, as we did in previous sections by means of the simple transformation equations for spin $\frac{1}{2}$, and then by proceeding along lines similar to those used before.[5]

It has been common practice to use equations of the Bloch form as a basis of discussion of line shapes and relaxation times in ferromagnetic and ferrimagnetic resonance experiments. One of the qualitative results obtained here is the definite indication that g-values obtained by the usual method of finding the field at which the peak of the absorption curve occurs should depend on whether one is using a linearly or circularly polarized field, and it would be interesting if this should also be the case for ferromagnetic and ferrimagnetic materials. This point is currently being investigated experimentally by Dr. T. R. McGuire of this Laboratory.

Note added in proof.—Since this article was submitted, I have learned from private communications that similar conclusions about the necessity of considering the interactions as tending to produce equilibrium with respect to the instantaneous field have been independently arrived at by E. P. Gross, J. Kaplan, and P. Weiss.