GENERAL SURVEY

2

THE RESONANCE PHENOMENON

2.1. Use of rotating coordinates

It was shown in § 1.1 that when an atom with angular momentum G and magnetic moment $\mu = \gamma G$ is placed in a magnetic field H, the equation of motion is

$$dG/dt = \mu \wedge H = \gamma G \wedge H \tag{2.1}$$

and the solution is one in which both G and μ precess about H with angular velocity $\omega_L = -\gamma H$. The question arises, what will the motion appear to be to an observer in a rotating coordinate system, the axis of rotation being taken to lie along the field H? If this system is rotating with angular velocity ω relative to a system stationary in the laboratory, then the rate of variation of a vector quantity such as G in the laboratory system (which we denote by dG/dt) is related to its rate of variation in the rotating system (which we denote by DG/Dt) through the equation

$$dG/dt = DG/Dt + \omega \wedge G. \tag{2.2}$$

This may be combined with the equation of motion (2.1) to obtain the equation of motion in the rotating system, which is then

$$DG/Dt = dG/dt - \omega \wedge G = \gamma G \wedge H + G \wedge \omega$$
$$= \gamma G \wedge (H + \omega/\gamma). \tag{2.3}$$

This equation is similar to the original eqn (2.1) except that instead of H we have $(H + \omega/\gamma)$. Thus the motion relative to the rotating system will again be a precession, but with angular velocity

$$\omega' = -\gamma H' = -\gamma(H + \omega/\gamma)$$
$$= \omega_L - \omega. \tag{2.4a}$$

As would be expected, the apparent precession velocity is equal to the difference between ω_L, the angular velocity observed in the stationary system, and ω, the velocity of the rotating coordinate system relative

to the fixed one. This is equivalent to saying that in the rotating system there is an effective magnetic field parallel to the z-axis

$$\mathbf{H}' = \mathbf{H} + \boldsymbol{\omega}/\gamma = \mathbf{H} - \mathbf{H}^*, \tag{2.4b}$$

where $\mathbf{H}^* = -\boldsymbol{\omega}/\gamma$. Clearly, if we choose $\boldsymbol{\omega}$ to be equal to $\boldsymbol{\omega}_L$, the precession vanishes and both $\mathbf{G}$ and $\boldsymbol{\mu}$ are at rest in the rotating system, corresponding to the effective field $\mathbf{H}'$ being zero.

2.2. Magnetic resonance

This result enables us to derive simply the motion of an atom under the combined action of a steady field $\mathbf{H}$, which we suppose to lie
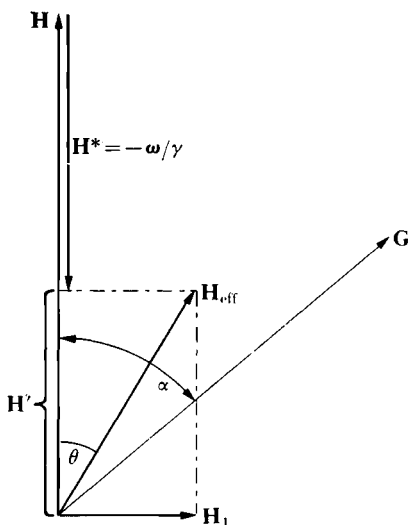

FIG. 2.1. Effective fields in the rotating coordinate system.

along the z-axis of a Cartesian coordinate system, and a field $\mathbf{H}_1$ rotating with angular velocity $\boldsymbol{\omega}$ about the z-axis. It is clear that if we change to a coordinate system that also rotates about the z-axis with angular velocity $\boldsymbol{\omega}$, then the field $\mathbf{H}_1$ will be represented in this system by a constant vector $\mathbf{H}_1$ normal to the z-axis, as in Fig. 2.1. At the same time the constant field $\mathbf{H}$ must be replaced by the effective field $\mathbf{H}' = \mathbf{H} + \boldsymbol{\omega}/\gamma$, which (see eqn (2.4b)) may conveniently be written as $\mathbf{H}' = \mathbf{H} - \mathbf{H}^*$, where $\mathbf{H}^* = -\boldsymbol{\omega}/\gamma$. The couple acting on the magnetic moment, referred to the rotating system, is now

$$\mathbf{DG}/\mathbf{D}t = \gamma \mathbf{G} \wedge (\mathbf{H}' + \mathbf{H}_1) = \gamma \mathbf{G} \wedge \mathbf{H}_{\text{eff}} \tag{2.5}$$

where $\mathbf{H}_{\text{eff}}$ is the resultant of $\mathbf{H}'$ and $\mathbf{H}_1$, added vectorially as shown in Fig. 2.1. This equation of motion is again the same as the original eqn (2.1). Hence referred to the rotating system, $\mathbf{G}$ and $\boldsymbol{\mu}$ will undergo a precession about $\mathbf{H}_{\text{eff}}$ with angular velocity $-\gamma\mathbf{H}_{\text{eff}}$.

We consider first the particular case where $\omega = \omega_L$, so that $\mathbf{H}' = 0$ and $\mathbf{H}_{\text{eff}} = \mathbf{H}_1$, and assume that the rotating field $\mathbf{H}_1$ is switched on suddenly at time $t = 0$, when the magnetic moment $\boldsymbol{\mu}$ is aligned along $\mathbf{H}$. The motion of the magnetic moment is then a precession about $\mathbf{H}_1$ with angular velocity $-\gamma\mathbf{H}_1$, and every half-cycle of this motion it changes from being parallel to $\mathbf{H}$ to being anti-parallel and back again. In the rotating system this rotation takes place in the plane normal to $\mathbf{H}_1$. In general $H_1 \ll H$, so that the precession about $\mathbf{H}_1$ occurs at a much lower velocity than that at which $\mathbf{H}_1$ rotates in the laboratory system. Thus, in the latter system, the motion of $\mathbf{G}$ and $\boldsymbol{\mu}$ consists of a rapid rotation about $\mathbf{H}$ at an angle α to $\mathbf{H}$ which varies slowly from 0 to π and back again.

When the frequency of rotation of $\mathbf{H}_1$ is not equal to the natural precession frequency ω_L, the magnetic moment $\boldsymbol{\mu}$ precesses (in the rotating coordinate frame) about the field $\mathbf{H}_{\text{eff}}$. This field makes an angle θ with $\mathbf{H}$, where

$$\tan\theta = H_1/H' = H_1/(H-H^*) = H_1/(H+\omega/\gamma) \qquad (2.6)$$

and from simple geometrical considerations the value of the angle α at time t (assuming $\alpha = 0$ at $t = 0$) is found to be

$$\cos\alpha = \cos^2\theta + \sin^2\theta\,\cos(\gamma H_{\text{eff}}t)$$
$$= 1 - 2\sin^2\theta\,\sin^2(\tfrac{1}{2}\gamma H_{\text{eff}}t), \qquad (2.7)$$

where

$$\gamma H_{\text{eff}} = \{(\omega-\omega_L)^2 + \gamma^2 H_1^2\}^{\frac{1}{2}}. \qquad (2.8)$$

The maximum value attained by α is clearly 2θ, and if $H_1 \ll H$ (as is normally the case) this value is large only when we are correspondingly close to fulfilling the condition $\omega = \omega_L$. This is clearly a resonance effect, and the possibility of being able to change appreciably the orientation of the magnetic moment $\boldsymbol{\mu}$ with respect to the steady field $\mathbf{H}$ by the application of a relatively small rotating field $\mathbf{H}_1$ constitutes the phenomenon of 'magnetic resonance'. When $\omega = \omega_L$, the magnetic moment $\boldsymbol{\mu}$, assumed to be initially parallel to $\mathbf{H}$, can be completely reversed by application of the rotating field $\mathbf{H}_1$; in the ideal case this will occur no matter how small the value of $\mathbf{H}_1$, though the rate of reversal is of course proportional to $\mathbf{H}_1$.

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Such a change in the orientation of the magnetic moment with respect to **H** (i.e. a change in the value of α) leads to the possibility of the detection of magnetic resonance in one of two ways. In the molecular beam method of Rabi for free particles the re-orientation is detected by the change in path of the molecule in an inhomogeneous field. For matter in the aggregated state, magnetic resonance is usually detected by an electromagnetic method. In a transient method energy must be supplied to or taken from the system of dipoles in order respectively to increase or decrease the average value of the angle α. This represents an interchange of stored energy with the source of electromagnetic radiation. In a steady-state method, power must be supplied in order to maintain the angle α at a value larger than the thermal equilibrium value. This power can be detected either through the extra dissipation it represents in the electromagnetic system, or through its appearance as heat resulting in a rise in temperature in the aggregated state of matter. A magnetic induction method has also been used (Bagguley 1955), in which the signal is induced by the oscillatory magnetic moment of the system arising from the forced precession about **H**, the oscillatory moment increasing as α increases towards $\pi/2$. In spin-echo methods, the observed signal is again induced by either a free or a forced precession of the magnetic moment.

2.3. Quantum-mechanical analysis

The discussion hitherto has been on a classical basis, and an outline of the quantum-mechanical approach will now be given.

When an atom with no nuclear hyperfine interaction is placed in a steady magnetic field **H** (which we take to be parallel to the z-axis), the interaction with its dipole moment is described by the Hamiltonian

$$\mathscr{H} = -\boldsymbol{\mu} \cdot \mathbf{H} = -\gamma\hbar(\mathbf{J} \cdot \mathbf{H}) = -\gamma\hbar H J_z. \qquad (2.9)$$

This equation holds also for the case where **J** reduces simply to **L** or **S**, and also for an atom with no electronic momentum but with nuclear angular momentum if we replace **J** by **I**, provided that the appropriate value of γ is inserted in each case. Hence in this section we may regard **J** as representing an angular momentum, either electronic or nuclear, for an atom with no hyperfine interaction.

The only matrix element of J_z is

$$\langle M| J_z |M \rangle = M, \qquad (2.10)$$

where M is the magnetic quantum number appropriate to J. Hence the

energy in a stationary state is

$$W = -\gamma\hbar H\langle M|\,J_z\,|M\rangle = -\gamma\hbar HM \qquad (2.11)$$

as given by the classical theory.

If now an oscillatory magnetic field is applied in the plane normal to **H**, with components H_x, H_y, there will be an additional perturbation described by the Hamiltonian

$$\mathscr{H}' = -(H_x\mu_x + H_y\mu_y). \qquad (2.12)$$

If the oscillatory field consists of a rotating field with components $H_x = H_1 \cos \omega t$, $H_y = H_1 \sin \omega t$, this can be written as

$$\mathscr{H}' = -\tfrac{1}{2}H_1\{\mu_+ \exp(-i\omega t) + \mu_- \exp(i\omega t)\}, \qquad (2.13)$$

where

$$\mu_+ = \mu_x + i\mu_y, \qquad \mu_- = \mu_x - i\mu_y.$$

Since the perturbation is an oscillatory one we use time-dependent perturbation theory to evaluate its effect. If the overall wave-function is written as a summation over all states $|u_n\rangle$,

$$\psi = \sum_n a_n\,|u_n\rangle\exp(-iW_n t/\hbar),$$

where a_n is the amplitude and W_n the energy of the nth state, then the coefficients a_n obey the relation

$$\frac{\mathrm{d}a_k}{\mathrm{d}t} = (i\hbar)^{-1} \sum_n \mathscr{H}_{kn}a_n \exp\{i(W_k - W_n)t/\hbar\}, \qquad (2.14)$$

where $\mathscr{H}_{kn}$ is the matrix element of the perturbation between the states k and n,

$$\mathscr{H}_{kn} = \langle u_k|\,\mathscr{H}'\,|u_n\rangle.$$

In our case the only matrix elements that arise are those between states M and $M \pm 1$, which are

$$\langle M+1|\,\mu_+\,|M\rangle = \langle M+1|\,\gamma\hbar J_+\,|M\rangle = \gamma\hbar\{J(J+1) - M(M+1)\}^{\frac{1}{2}},$$
$$\qquad (2.15)$$
$$\langle M-1|\,\mu_-\,|M\rangle = \langle M-1|\,\gamma\hbar J_-\,|M\rangle = \gamma\hbar\{J(J+1) - M(M-1)\}^{\frac{1}{2}},$$

which lead to the selection rule $M \leftrightarrow M \pm 1$, or $\Delta M = \pm 1$. If we assume that the system is initially in the state $J_z = M$, so that all the co-efficients a_n are initially zero except a_M, which is unity, then since

$(W_{M\pm1} - W_M)/\hbar = \mp\gamma H$, for small values of the perturbation we have approximately

$$\frac{\mathrm{d}a_{M\pm1}}{\mathrm{d}t} = \tfrac{1}{2}i\gamma H_1\langle M\pm1|\ J_\pm\ |M\rangle\exp[i\{(W_{M\pm1}-W_M)\mp\hbar\omega\}t/\hbar]$$

$$= \tfrac{1}{2}i\gamma H_1\langle M\pm1|\ J_\pm\ |M\rangle\exp\{\mp i(\gamma H+\omega)t\}. \qquad (2.16)$$

This is readily integrated, and yields for the probability $(aa^*)_{M\pm1}$ of finding the system in the states $M\pm1$ after a time t

$$(aa^*)_{M\pm1} = (\gamma H_1)^2\langle M\pm1|\ J_\pm\ |M\rangle^2\ \frac{\sin^2\tfrac{1}{2}(\gamma H+\omega)t}{(\gamma H+\omega)^2}$$

$$= (\gamma H_1)^2\langle M\pm1|\ J_\pm\ |M\rangle^2\ \frac{\sin^2\tfrac{1}{2}(\omega-\omega_L)t}{(\omega-\omega_L)^2}\ . \qquad (2.17)$$

The transition probability per unit time w is given by the time derivative $\mathrm{d}(aa^*)/\mathrm{d}t$ integrated over a distribution of Larmor frequencies:

$$w = (\gamma H_1)^2\langle M\pm1|\ J_\pm\ |M\rangle^2 \int\limits_{-\infty}^{+\infty} \frac{\sin\,(\omega-\omega_L)t}{2(\omega-\omega_L)}\,f(\omega_L)\ \mathrm{d}\omega_L$$

$$= (\pi/2)(\gamma H_1)^2\langle M\pm1|\ J_\pm\ |M\rangle^2 f(\omega), \qquad (2.17a)$$

where it is assumed that $f(\omega_L)$ has a wide spectrum, but the only significant contribution to the integral comes from the region where $\omega_L \approx \omega$. The quantity $f(\omega)$, known as the 'shape function', is normalized by the condition

$$\int_0^\infty f(\omega)\ \mathrm{d}\omega = 1, \qquad (2.17b)$$

and describes the distribution of energy levels between which the transition is taking place. For the case of $J = \tfrac{1}{2}$, Rabi (1937) has shown that an exact solution is

$$(aa^*) = \frac{(\gamma H_1)^2}{(\gamma H+\omega)^2+(\gamma H_1)^2}\ \sin^2[\tfrac{1}{2}\{(\gamma H+\omega)^2+(\gamma H_1)^2\}^{\frac{1}{2}}t] \quad (2.18)$$

for the probability of finding the system in the state $M = -\tfrac{1}{2}$ at time t if it was in the state $M = +\tfrac{1}{2}$ at $t = 0$. Since for $J = \tfrac{1}{2}$ the matrix elements of $J_\pm$ are just unity, eqn (2.18) is similar to (2.17) except that an additional term $(\gamma H_1)^2$ is added to $(\gamma H+\omega)^2$.

It is clear from these equations that the probability of a transition is large only if $(\gamma H+\omega)$ is close to zero. This corresponds to the resonance condition deduced from the classical equations, but it is possible to

make a much more detailed correlation between the classical and quantum mechanical approaches, as has been shown, for example, by Rabi, Ramsey, and Schwinger (1954). First, it will be shown that the classical equation of motion (2.1) is valid also in quantum mechanics.

The rate of variation of a quantity such as $\mathbf{G}$ is given by

$$-i\hbar(d\mathbf{G}/dt) = \mathscr{H}\mathbf{G} - \mathbf{G}\mathscr{H}, \tag{2.19}$$

where $\mathscr{H}$ is the Hamiltonian which for our system is

$$\mathscr{H} = -\boldsymbol{\mu}\cdot\mathbf{H} = -\gamma\mathbf{G}\cdot\mathbf{H}.$$

Hence

$$-i\hbar(d\mathbf{G}/dt) = -\gamma\{(\mathbf{G}\cdot\mathbf{H})\mathbf{G} - \mathbf{G}(\mathbf{G}\cdot\mathbf{H})\},$$

which does not vanish because the components of $\mathbf{G}$ do not commute with one another, though they do with $\mathbf{H}$. The bracket on the right-hand side thus has the x-component

$$\begin{aligned}
&G_z H_z G_x - G_x G_z H_z + G_y H_y G_x - G_x G_y H_y \\
&= (G_z G_x - G_x G_z)H_z - (G_x G_y - G_y G_x)H_y \\
&= i\hbar(G_y H_z - G_z H_y)
\end{aligned}$$

by using the commutation relations for the components of $\mathbf{G}$. The last expression is just $i\hbar(\mathbf{G} \wedge \mathbf{H})_x$, so that we obtain again the eqn (2.1),

$$d\mathbf{G}/dt = \gamma\mathbf{G} \wedge \mathbf{H}.$$

Thus we may expect that our classical analysis is valid also in quantum mechanics, and a simple comparison can again be made for the case of $J = \frac{1}{2}$.

The wave-function for this case will, in general, be a linear combination of the wave-functions for the states $|J_z\rangle = +\frac{1}{2}$ and $-\frac{1}{2}$, which can be written as just $|+\rangle$ and $|-\rangle$. A suitable combination with normalized coefficients is

$$\psi = \cos\tfrac{1}{2}\alpha\,|+\rangle + \sin\tfrac{1}{2}\alpha\,|-\rangle,$$

for which the z-component of the magnetic moment is

$$\begin{aligned}
\mu_z &= \langle\psi^*|\,\gamma\hbar J_z\,|\psi\rangle = \tfrac{1}{2}\gamma\hbar(\cos^2\tfrac{1}{2}\alpha - \sin^2\tfrac{1}{2}\alpha) \\
&= \tfrac{1}{2}\gamma\hbar\cos\alpha = \mu\cos\alpha,
\end{aligned}$$

showing that our wave-function corresponds to the magnetic moment lying at an angle α to the z-axis. Thus the angle introduced to give normalized coefficients in the wave-function can be associated with a simple physical quantity.

If the system is in the $|+\rangle$ state at time $t = 0$, then α is initially zero, and the probability of a transition to the $|-\rangle$ state at time t is given by the square of the coefficient of the $|-\rangle$ state, i.e. by $\sin^2\frac{1}{2}\alpha$. From the classical eqn (2.7) one finds

$$\sin^2\tfrac{1}{2}\alpha = \tfrac{1}{2}(1-\cos \alpha)$$
$$= \sin^2\theta \sin^2(\tfrac{1}{2}\gamma H_{\text{eff}}t),$$

which on substitution from eqn (2.8) and use of the relation

$$\sin \theta = H_1/H_{\text{eff}} = (\gamma H_1)/\{(\gamma H + \omega)^2 + (\gamma H_1)^2\}^{\frac{1}{2}}$$

is seen to be identical with the quantum-mechanical eqn (2.18).

2.4. Magnetic resonance in aggregated systems

It has now been shown that the classical equations of motion can be justified on quantum mechanics, and that they provide an easy physical approach to the phenomenon of magnetic resonance. This approach is valid for a simple system, such as an atom with an electronic but no nuclear magnetic moment, or vice versa, but not for a complex system such as an atom with hyperfine structure. This restriction follows from the use of the simple Hamiltonian of eqn (2.9) instead of the complex one (eqn (1.67)). Even in the absence of hyperfine structure, the simple Hamiltonian (2.9) may not be adequate when dealing with aggregated systems, for there may then be other interactions such as quadrupole splittings in the nuclear case, or its equivalent in the electronic case, the so-called fine structure terms (see §§ 3.3–3.6). The classical approach is not then valid, but there are many cases when it is, and it is particularly fruitful in providing a physical picture in many situations in which it is only approximately valid. We shall therefore investigate the solutions of the classical equation which describe the motion of the magnetization in bulk matter.

In an aggregated system of permanent magnetic dipoles it is convenient to think in terms of the magnetization $\mathbf{M}$, or the magnetic moment of the whole system, rather than in terms of individual dipoles. Now the magnetic moment of the whole system is simply the vector resultant of the individual dipoles. Similarly, the angular momentum, $\mathbf{G}$, of the whole system is the vector resultant of the individual momenta $\hbar\mathbf{J}$. Since each individual dipole, $\boldsymbol{\mu}$, is parallel and proportional to its own associated angular momentum vector ($\boldsymbol{\mu} = \gamma\hbar\mathbf{J}$), then for a system of particles which all have identical values of γ we have

$$\mathbf{M} = \gamma\mathbf{G} \qquad (2.20)$$

and the system as a whole will obey the classical equation of motion

$$dG/dt = \gamma G \wedge H$$

which, in order to deal in terms of M instead of G, can be multiplied by γ yielding

$$dM/dt = \gamma M \wedge H. \qquad (2.21)$$

With suitable modifications, this equation is widely used to treat the phenomenon of resonance in cooperative systems (ferro-, antiferro-, or ferri-magnetic). We are concerned with paramagnetic systems where the dipoles interact only weakly with one another; primarily this means systems for which we can write

$$M = \chi_0 H = N \frac{\gamma^2 \hbar^2 J(J+1)}{3kT} H \qquad (2.22)$$

in the high temperature limit where $(\mu H/kT) \ll 1$. Essentially our analysis will consist of finding solutions to eqn (2.21) which will yield the conditions under which magnetic resonance can be observed. As we should expect, this phenomenon is readily observable only when the resonance condition $\omega = -\gamma H$ is fulfilled. We can, however, vary either ω, the angular velocity of the applied rotating field H_1, or the steady field H, to reach resonance. In practice, it is nearly always preferable experimentally to work at fixed frequency and vary the steady field H. This is also the simpler case to analyze since we can make use of rotating coordinate systems as has been done earlier in this chapter. There will be some restriction on the rate at which H is varied, however, as a rapidly changing field will have oscillatory components that introduce transitions between the atomic energy levels. When the field is changed slowly such transitions do not take place, and the change is said to be 'adiabatic'. The condition that this should hold can be found by means of the rotating coordinate system.

Instead of varying the magnitude of H, let us assume that H is constant in magnitude but changing in direction; for simplicity we assume that this change consists of a rotation about the x-axis, with angular velocity ω'. Then, if we change from the laboratory system to one rotating with this velocity, H will be a constant vector in the rotating system, but there will also be an apparent field $H^* = -\omega'/\gamma$ at right angles to H, as in Fig. 2.2. Then the effective field H_{eff} in the rotating system will be the vector sum of H and H^*. If the magnetization was initially parallel to H, then it will start to precess about H_{eff} and hence will not remain closely parallel to H unless the angle between

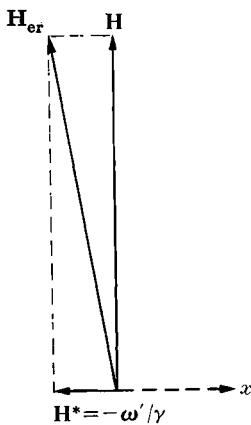FIG. 2.2. Rotation of the field **H** about the x-axis with angular velocity $\boldsymbol{\omega'}$.

H and $\mathbf{H_{eff}}$ in the rotating system is very small. This implies that $H^* \ll H$, or

$$\omega' = |\gamma H^*| \ll |\gamma H|. \tag{2.23}$$

In other words, the Larmor precession frequency in the field H must be very much higher than the frequency of rotation of the field H itself. Then the precessional motion of the magnetization caused by the rotation of **H** will cause it to deviate from being parallel to **H** only by a very small angle, instead of the large angles possible when a rapidly rotating field at the Larmor resonance frequency is applied. Since characteristic electron resonance frequencies lie in the range 10^{10} to 10^{12} Hz, while modulation of the field **H** is seldom used at a frequency much above 10^5 Hz, the adiabatic condition is easily fulfilled under normal conditions.

2.5. Adiabatic rapid passage

We will now discuss a special solution of the equation of motion (2.21) and its implications, before proceeding to the more general case. As before, we assume that the system is subject to a steady magnetic field directed along the z-axis, together with a field H_1 precessing with angular velocity ω in the xy-plane, so that it has components $H'_x = H_1 \cos \omega t$, $H'_y = H_1 \sin \omega t$. A plausible solution might correspond to the magnetization precessing about the z-axis at an angle θ, so that it has components

$$\begin{aligned} M_x &= M \sin \theta \cos \omega t, \\ M_y &= M \sin \theta \sin \omega t, \\ M_z &= M \cos \theta. \end{aligned} \tag{2.24}$$

This corresponds to a steady-state solution, with forced precession at the same angular velocity as that of the applied field. To find whether this satisfies eqn (2.21) it is convenient to work in terms of the quantities

$$M_+ = M_x + iM_y = M \sin \theta \exp(i\omega t),$$
$$M_- = M_x - iM_y = M \sin \theta \exp(-i\omega t), \qquad (2.25)$$
$$M_z = M \cos \theta.$$

In terms of these components the equations of motion become

$$\dot{M}_+ + i\gamma H M_+ = +i\gamma M_z H_1 \exp(i\omega t),$$
$$\dot{M}_- - i\gamma H M_- = -i\gamma M_z H_1 \exp(-i\omega t), \qquad (2.26)$$
$$\dot{M}_z = \tfrac{1}{2}i\gamma\{M_+ \exp(-i\omega t) - M_- \exp(i\omega t)\}H_1.$$

The first two equations in (2.26) (which are complex conjugates) can be integrated at once if M_z is constant, as assumed in (2.25), and substitution from (2.25) into the equation for $\dot{M}_z$ shows that the solutions assumed for M_+, M_- do give $\dot{M}_z = 0$. Hence the equation of motion is satisfied by our solution, and integration gives

$$M_\pm = \frac{\gamma H_1 M_z}{(\gamma H + \omega)} \exp(\pm i\omega t). \qquad (2.27)$$

These are of the form (2.25) provided that we take

$$\tan \theta = \gamma H_1/(\gamma H + \omega)$$
$$= H_1/(H - H^*). \qquad (2.28)$$

The nature of this solution can readily be seen by working in a system of coordinates rotating about $\mathbf{H}$ with angular velocity $\boldsymbol{\omega}$. In this system $\mathbf{H}_1$ is a constant vector perpendicular to $\mathbf{H}$, while parallel to $\mathbf{H}$ the effective field component is $\mathbf{H}' = \mathbf{H} + \boldsymbol{\omega}/\gamma = \mathbf{H} - \mathbf{H}^*$. The magnetization vector $\mathbf{M}$ is also constant in this system, and from (2.28) we see that it is parallel to $\mathbf{H}_{\mathrm{eff}}$, the vector resultant of $(\mathbf{H} - \mathbf{H}^*)$ and $\mathbf{H}_1$.

Let us assume that the steady-state solution (2.24) is attained under the condition $(H - H^*) \gg H_1$, so that θ is initially close to zero, and $\mathbf{M}$ is almost parallel to $\mathbf{H}$. Then, if H is diminished slowly, the angle θ increases and passes through $\pi/2$ at resonance when $H = H^*$, attaining the limiting value π when $H \ll H^*$ and again $\{H_1/(H - H^*)\} \to 0$. The magnetization $\mathbf{M}$ is now reversed in direction and is anti-parallel to $\mathbf{H}$, while at intermediate times when $(H - H^*) \sim H_1$, there is a large precessing magnetization in the xy-plane in the laboratory system. If the specimen is inside a coil of area A which picks up a flux in the

y-direction, a voltage will be induced in the coil of magnitude

$$V = -(4\pi A/c)\dot{M}_y$$
$$= -\omega(4\pi A/c)M \sin \theta \cos \omega t. \qquad (2.29)$$

This is largest when $\theta = \pi/2$, corresponding to H being at the resonance value $H^* = -\omega/\gamma$. Detection of this voltage gives a method of detecting the magnetic resonance and is the essence of the method of nuclear induction.

The solution obtained above was based on the assumption that **H** was constant, but we have presumed that it still holds when **H** is varied 'slowly'. We note that **M** in our solution is always parallel to the effective field $\mathbf{H_{eff}}$ in the rotating coordinate system, and that variation of **H** corresponds to a rotation of $\mathbf{H_{eff}}$ as well as a change in its magnitude, its smallest value being just $\mathbf{H_1}$. From the 'adiabatic condition' discussed in § 2.4, we should expect that **M** will follow $\mathbf{H_{eff}}$ at a small angle when $\mathbf{H_{eff}}$ is rotated provided that the rate of rotation $(d\theta/dt)$ is small compared with $|\gamma H_1|$. Since $\cot \theta = H'/H_1$,

$$d\theta/dt = -\sin^2\theta \, d(\cot \theta)/dt$$
$$= -(H_1^2/H_{eff}^2) \, d(H'/H_1)/dt$$
$$= -(H_1^2/H_{eff}^2) \, d(H/H_1)/dt.$$

The maximum value of H_1/H_{eff} is unity, and hence the adiabatic condition is satisfied provided that

$$\frac{1}{H_1} |dH/dt| \ll \gamma H_1. \qquad (2.30)$$

In words, this means that any change in H in a time of the order $(\gamma H_1)^{-1}$ must be small compared to H_1. We can obtain some idea of the magnitude of this restriction by taking $H_1 = 1$ G. Then for protons, for which $\gamma = 2{\cdot}6 \times 10^4$ rad G^{-1}, $(\gamma H_1)^{-1} = 4 \times 10^{-5}$ s, while for electron spins it is 6×10^{-8} s. Thus H must be varied in such a way that a change of 1 G must take place in a time long compared with either of these, a condition that is readily fulfilled. In terms of the solution of eqns (2.26), this corresponds to $(d\theta/dt)$ being so small that it can be neglected in the differentiation of eqns (2.25).

Since the equation of motion is linear in M, the magnetization does not become infinite during forced resonance, as is commonly the case in other systems without any damping. It means also that the size of M is indeterminate, though if the system of magnetic dipoles is allowed to come to thermal equilibrium at a constant field $\mathbf{H_0}$ by waiting a long

time before commencing the sweep through resonance, then we should expect $\mathbf{M}$ to have its equilibrium value

$$\mathbf{M_0} = \chi_0 \mathbf{H_0}$$

with χ_0 given by eqn (2.22). Then $\mathbf{M}$ is initially parallel to $\mathbf{H}$, and also parallel to $\mathbf{H'} = \mathbf{H} - \mathbf{H^*}$, as assumed above in taking $\theta = 0$ initially, provided that $\mathbf{H_0} > \mathbf{H^*}$. If, on the other hand, the system is allowed to reach thermal equilibrium in a field $\mathbf{H_0}$ that is less than $\mathbf{H^*}$, then $\mathbf{M}$ is initially anti-parallel to $\mathbf{H'} = \mathbf{H} - \mathbf{H^*}$, so that $\theta = \pi$ initially. Then on sweeping through resonance $\mathbf{M}$ is again reversed, but the change in θ is from π to 2π, and the sign of the voltage picked up in the coil (see eqn (2.29)) is the reverse of that in the former case. This is readily seen from the diagrams showing the relative positions of the vectors in the rotating coordinate system in Fig. 2.3.
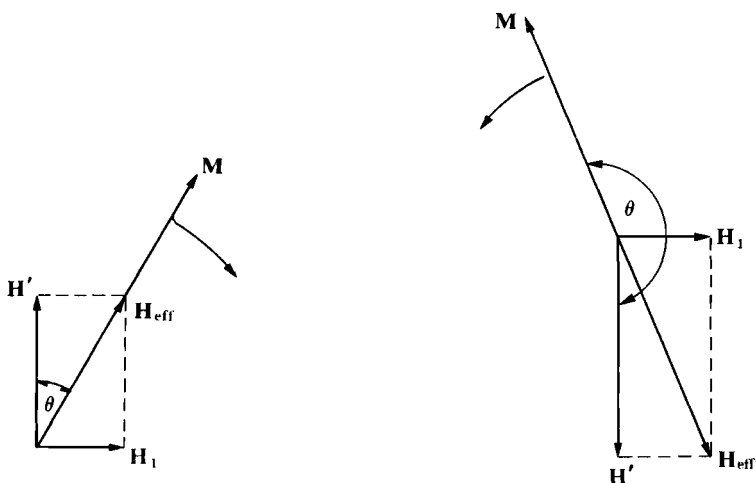
FIG. 2.3. Motion of the magnetic vector in the rotating coordinate system during adiabatic rapid passage.

In this discussion it has been necessary to determine $\mathbf{M}$ by reference to the initial conditions, assuming the system was initially in thermal equilibrium. Such equilibrium is attained by means of relaxation processes, which occupy a finite time. It is clear that if the sweep through resonance occupies a time long compared with the 'relaxation time', reversal of the magnetization will not be attained because the relaxation will tend to restore $\mathbf{M}$ to being parallel to $\mathbf{H}$. Thus there is a lower limit to the rate of sweep through resonance as well as the upper

limit given by the adiabatic condition (eqn (2.30)). When the rate lies between these limits the sweep through resonance is called 'adiabatic rapid passage' through resonance. When the relaxation time τ_1 is much longer than $(\gamma H_1)^{-1}$, [that is, $(\gamma H_1 \tau_1) \gg 1$], it is clearly possible to satisfy both conditions. We note also that this gives a lower limit for the size of H_1, unlike the analysis of § 2.2 in which no damping forces were present.

2.6. Relaxation effects

In view of the restriction that it has been necessary to introduce concerning relaxation effects, it is clearly essential to consider these in more detail before examining the case of slow passage through resonance. This amounts to abandoning the assumption that all changes in orientation or magnitude of the magnetization are due entirely to the external magnetic fields applied.

There are three major internal interactions to be considered. The first of these includes the ligand interaction, which may result simply in a modified form of the Zeeman interaction but may also include 'fine structure' effects (see Chapter 3); it also includes hyperfine interactions between the magnetic electrons and nuclear moments. If these interactions are comparable with or greater than the electronic Zeeman interaction energy, the macroscopic model is seldom applicable. If they are smaller than the electronic Zeeman energy, and only those parts of the interaction Hamiltonian are retained which are diagonal in the representation in which the electronic Zeeman energy has been diagonalized, the macroscopic analysis often gives a useful physical picture that forms a good approximation to the actual motion.

The second and third internal interactions are the effects of thermal agitation and of interaction between the dipoles themselves. These are usually much weaker than the Zeeman interaction with the external fields, but are of importance because of their cumulative effects over long periods of time. Both these effects represent random interactions with the various atomic dipoles, and to this extent our model becomes only 'semi-macroscopic' when they are introduced. However, there is a fundamental difference in that only thermal perturbations can change the energy of the total dipole system (the 'spin system' as it is generally called, though this must be taken to include orbital dipoles in the electronic case), whereas interactions within the spin system (i.e. between the individual dipoles) leave this energy unchanged.

The major part of the energy of the spin system, is, under the

restrictions retained above, the Zeeman energy in the steady field **H**, which is just

$$W = -\mathbf{M} \cdot \mathbf{H} = -M_z H,$$

assuming **H** to be in the z-direction, as before. Major changes in the energy are therefore due to changes in M_z, for which thermal fluctuations must be responsible. If at any time the magnetization component M_z is not equal to its equilibrium value $M_0 = \chi_0 H$, it is not a bad approximation to assume that it will approach this equilibrium value exponentially according to the differential equation

$$\dot{M}_z = -(M_z - M_0)/\tau_1. \tag{2.31}$$

τ_1 is a characteristic time-constant, sometimes called the 'longitudinal' relaxation time, since it governs the changes in M_z, the component parallel to the steady magnetic field, and sometimes the 'spin-lattice' relaxation time, since it is connected with the exchange of energy between the spin system and the lattice in which the dipoles are embedded. We use τ_1 and (below) τ_2 instead of the more usual T_1, T_2 as a more logical nomenclature which avoids confusion with the temperature T.

We now consider the mutual interactions between the dipoles, which are conveniently, if somewhat loosely, described by means of 'local fields'. As above, we assume that the spin system is in an external magnetic field parallel to the z-axis which is much larger than the internal fields. Then the mutual interactions between the dipoles, or spin-spin interactions, cannot affect the longitudinal component M_z of the magnetization, but only the transverse components M_x, M_y.

Since the interactions between the dipoles do not affect the total energy of the system, in magnetic fields much larger than the local fields they can have no effect on the component M_z of the magnetization, but only on M_x, M_y. For simplicity of analysis it was assumed by Bloch that the effect of these mutual interactions could again be represented by a relaxation time, so that M_x, M_y obey the differential equations

$$\dot{M}_x = -M_x/\tau_2, \qquad \dot{M}_y = -M_y/\tau_2. \tag{2.32}$$

τ_2 is generally known as the 'transverse' relaxation time, and the sense in which the mutual interactions can be treated as giving rise to a relaxation effect will be discussed later.

These relaxation effects may be introduced into the equations of motion by combining eqns (2.26) with (2.31) and (2.32). Since M_+, M_-

will obey equations similar to (2.32), we have

$$\dot{M}_+ + i\gamma H M_+ + M_+/\tau_2 = i\gamma M_z H_1 \exp(i\omega t),$$
$$\dot{M}_- - i\gamma H M_- + M_-/\tau_2 = -i\gamma M_z H_1 \exp(-i\omega t),$$
$$\dot{M}_z + M_z/\tau_1 = \tfrac{1}{2}i\gamma\{M_+ \exp(-i\omega t) - M_- \exp(i\omega t)\}H_1 + M_0/\tau_1.$$

$$(2.33)$$

These equations were first given by Bloch (1946).

It is necessary to point out that while the rate eqn (2.31) defining τ_1 has a wide range of validity, the eqns (2.32) that define τ_2 are valid only for magnetic moments in fast relative motion with respect to each other. They may describe correctly the behaviour of the transverse magnetization of paramagnetic ions or free radicals in liquid solution, or that of conduction electrons in metals and semi-conductors, but in general they will be grossly incorrect in insulating paramagnetic solids. A rate equation such as (2.32) implies that the time dependence of the decaying amplitude of the transverse magnetization is exponential. It can be shown under fairly general assumptions that this decay function is the Fourier transform of the resonance line shape observed with a vanishingly small r.f. field, since the Fourier transform of a decaying exponential $\exp(-t/\tau_2)$ is proportional to the Lorentzian function (where $\Delta\omega = \tau_2^{-1}$)

$$f(\omega) = \frac{1}{\pi}\frac{\tau_2}{1+(\omega-\omega_L)^2\tau_2^2} = \frac{1}{\pi}\frac{\Delta\omega}{(\Delta\omega)^2+(\omega-\omega_L)^2}. \qquad (2.34)$$

Thus the validity of eqns (2.32) would imply that resonance lines always have a Lorentzian shape, which is contradicted by experiment and not to be expected on theoretical grounds.

Whatever the line shape, one may of course somewhat loosely define a time τ_2' by the relation $\tau_2' = (\gamma\,\Delta H)^{-1}$ where ΔH is the line width, but it is preferable to introduce first a distinction between homogeneous and inhomogeneous broadening. We shall say that a line is inhomogeneously broadened if the line width is caused by a distribution across the sample of the Larmor frequencies of the various magnetic moments. The causes of such a distribution are manifold, ranging from a badly inhomogeneous external field to local variation of the gyromagnetic factor γ arising from local imperfections in the crystalline environment of the magnetic dipoles. Whatever the origin, such inhomogeneous broadenings have one feature in common: the loss of phase coherence caused by the fanning out in the equatorial plane of the individual precessing dipoles is not an irreversible phenomenon—there are ways,

known as spin echoes (see § 2.7), whereby phase coherence can be restored.

The problem of phase coherence can be thought of in the following way. In thermal equilibrium the only steady component of the magnetization is M_z, since both M_x and M_y are zero on a time average, though they may fluctuate about this value. This does not imply that the individual dipoles are all necessarily parallel or anti-parallel to the z-axis, but that their components normal to this axis are random and average to zero. Suppose, however, that at some instance there exists a finite value of the magnetization in the equatorial plane. In the presence of a uniform field **H** this will precess about **H** with angular velocity $-\gamma\mathbf{H}$, and since the individual dipoles all precess with this velocity they remain in phase and the magnetization will retain its initial magnitude. This will only be true if the field acting on each dipole is exactly equal to **H**; if the applied field is inhomogeneous, the individual dipoles will precess at different velocities. The mutual interaction of the dipoles produces an effect similar to that of inhomogeneity in **H**, since the local field at individual dipoles then varies by an amount, ΔH, of the order μ/r^3. This gives rise to a spread in the precessional velocity of order $|\gamma|\,\Delta H$, which will cause the dipoles to get out of phase in a time of order

$$\tau_2' \sim (|\gamma|\,\Delta H)^{-1}. \qquad (2.35)$$

For nuclear moments of size $10^{-3}\beta$ at an average separation of 0·2 nm we have $\Delta H \sim 1$ G, and $\tau_2' \sim 10^{-4}$ s. For electronic moments in a moderately dilute paramagnetic salt such as a double sulphate the average distance between dipoles is about 0·6 nm, $\Delta H \sim 50$ G and

$$\tau_2' \sim 10^{-9} \text{ s}. \qquad (2.36)$$

By diluting the salt with an isomorphous diamagnetic salt the value of ΔH can be reduced to a few gauss, or even less than 1 G if the salt contains no nuclear dipole moments of appreciable size, and in this case the value of τ_2' may rise to about 10^{-7} s.

The effect of the mutual interactions cannot be represented entirely as giving rise to inhomogeneity in **H**, since the precessing components of the dipole field give rise to transitions ('spin flips') where one dipole gains energy and another loses it by exchange of a quantum of energy. This process is most effective when the dipoles precess at the same frequency. In such a mutual flip the total value of M_z is conserved, assuming that the external field is much larger than the local fields, so

that the total energy of the system remains unchanged. However there is no such restriction on the total values of M_x or M_y, and the result of such spin flips is a gradual destruction of the phase coherence between the components of the individual dipoles in the xy-plane, so that any precessing magnetization in this plane will gradually decay to zero. In so far as this decay takes place exponentially in time, it can be represented by a transverse relaxation time in an equation such as (2.32). Thus the spin-flip process introduces a 'genuine' transverse relaxation time τ_2. In undiluted salts, the spin-flip process between identical spins increases the line width by a factor $\sim\frac{3}{2}$ (see § 9.7), so that τ_2 is not much greater than τ_2'. In diluted salts where the line width is mainly due to nuclear moments in the host lattice, the true value of τ_2 may be $\sim10^{-5}$ s, corresponding to 'spin packet' widths of order 10^4 Hz.

In non-conducting solids τ_1 is generally much longer than τ_2 for nuclei, but this is not necessarily true for electronic dipoles that are in much more intimate contact with the lattice through the action of thermally modulated electric fields on the translational or orbital motion of the electrons. At low temperatures where thermal fluctuations die out τ_1 becomes large, but at room temperature it may be much shorter for electrons than the value of τ_2' given in eqn (2.36). This does not mean that τ_1 becomes shorter than τ_2, since thermal fluctuations that affect M_z also affect M_x, M_y and result in a τ_2 comparable with τ_1. When the whole of the line width is due to relaxation effects, the resonance line is 'homogeneously broadened'.

We return now to the consideration of the phenomenon of adiabatic rapid passage in the light of our remarks about relaxation effects. The essential feature of the process is that in the rotating frame the magnetization vector follows the effective field $\mathbf{H}_{\text{eff}}$, but since the magnetization is simply the vector sum of the individual dipoles it follows that they must all undergo a similar motion (this does not, of course, imply that they are each parallel to $\mathbf{H}_{\text{eff}}$). The presence of a local field $\Delta\mathbf{H}$ that varies from point to point in the sample means that the field seen by an individual dipole in the rotating frame is $\mathbf{H}_{\text{eff}}+\Delta\mathbf{H}$, and in view of the random nature of $\Delta\mathbf{H}$ the dipoles will not all undergo a similar motion unless $\Delta H \ll H_{\text{eff}}$ always, which means $\Delta H \ll H_1$. If ΔH were a purely longitudinal field, parallel to H, this restriction would not apply since the effect of ΔH would then be merely to change the value of $H' = H - H^*$, so that the individual dipoles pass through the equatorial plane at different times, but all would end anti-parallel

(or parallel) to the external field. If, however, ΔH has transverse components with a frequency dependent spectrum so that there is a genuine transverse relaxation time τ_2, then it is necessary to pass through resonance in a time short compared with τ_2 in order that the transverse magnetization shall not decay appreciably during passage, which must therefore be rapid. In fact spin-flip processes arise from local transverse magnetic fields near the resonance frequency, which appear as constant fields $\Delta H'$ in the rotating system to be added vectorially to $\mathbf{H}_1$. We therefore do require $H_1 \gg \Delta H'$, or

$$\tau_2 = (|\gamma \, \Delta H'|)^{-1} \gg (|\gamma H_1|)^{-1},$$

for adiabatic rapid passage to be effective in reversing the magnetization, and it is thus possible only in heavily diluted salts, where $\tau_2 > 10^{-7}$ s, since at centimetre wavelengths oscillatory fields are not normally greater than about 1 G, for which $(|\gamma H_1|)^{-1}$ is about 10^{-7} s.

Similar restrictions apply to τ_1, but as remarked earlier, if τ_1 is not greater than τ_2 it can be made so by working at lower temperatures, so that the condition $|\gamma H_1 \tau_1| \gg 1$ is readily fulfilled. However, there remains the requirement that the sweep through resonance must be made in a time short compared with τ_1 and τ_2, which is difficult to fulfill unless both are rather long. In addition, any reversed magnetization set up will persist only for a time $\sim \tau_1$. The conditions are, of course, much more easily met in the case of nuclear dipoles.

2.7. Radio-frequency pulses and spin echoes

Reversal of the magnetization such as occurs in adiabatic rapid passage can also be effected by the application of a short pulse of the oscillatory field at the resonance frequency. The situation then is similar to that of the free atom case discussed in § 2.2. Suppose the system is initially in thermal equilibrium in a magnetic field $\mathbf{H}$, and a strong rotating field $\mathbf{H}_1$ at the exact resonance frequency is applied suddenly for a time δt. Then the magnetization $\mathbf{M}$ is initially parallel to $\mathbf{H}$, and in the rotating coordinate system of Fig. 2.1 is normal to $\mathbf{H}_1$. In this system there is no other field, and in time δt, $\mathbf{M}$ will precess about $\mathbf{H}_1$ through an angle $|\gamma| \, H_1 \, \delta t$. If δt is chosen so that $|\gamma| \, H_1 \, \delta t = \pi$, the magnetization will just reach the direction anti-parallel to $\mathbf{H}$ (a '180 degree pulse'), while if δt is half as long, $\mathbf{M}$ is turned to a position normal to $\mathbf{H}_1$ in the equatorial plane (a '90 degree pulse'). It is readily seen that relaxation effects will only be negligible provided that $\delta t \ll \tau_1, \tau_2$; thus the condition $\tau_1, \tau_2 \gg (|\gamma| \, H_1)^{-1}$ applies in this case

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also. If the transverse relaxation time is expressed as a spread in field $\Delta H = (|\gamma|\,\tau_2)^{-1}$, the second and more rigorous of these conditions is readily seen to be $H_1 \gg \Delta H$. In the rotating coordinate system this means that the effective z-component of the field $\mathbf{H}-\mathbf{H}^*$, which is not zero for all parts of the sample if we regard ΔH as being equivalent to an inhomogeneity in $\mathbf{H}$, is small everywhere compared with $\mathbf{H}_1$, so that the precession of $\mathbf{M}$ is about an effective field (the vector resultant of $\mathbf{H}-\mathbf{H}^*$ and $\mathbf{H}_1$) which does not deviate appreciably in direction and magnitude from $\mathbf{H}_1$. This condition is more stringent than that required for adiabatic rapid passage, where a static spread in field of ΔH ('inhomogeneous broadening') only results in dipoles passing through the equatorial plane at different instants of time.

Pulses of this kind are used in spin-echo techniques, originated by Hahn (1950). After the magnetization has reached thermal equilibrium in a field $\mathbf{H}$, so that $\mathbf{M}$, like $\mathbf{H}$, lies along the z-axis, a '90 degree pulse' is applied by means of an oscillatory field at the resonance frequency. If, in the rotating coordinate system, $\mathbf{H}_1$ is taken to lie along the x-axis, then after the pulse the magnetization vector $\mathbf{M}$ lies in the equatorial plane, parallel to the y-axis if γ is positive, and anti-parallel to the y-axis if γ is negative. There is now no field in the rotating frame, apart from a small spread in field due to the local field or other inhomogeneity which has a steady component ΔH in the rotating frame along the z-axis. The effect of this is to cause the dipoles to fan out in the equatorial plane with angular velocity $-\gamma\,\Delta H$, with resulting diminution in the net magnetization. If at a time τ after the first pulse is applied, a '180 degree pulse' of oscillatory field is turned on, the result is to turn all the individual dipoles in the equatorial plane through $180°$ about $\mathbf{H}_1$. Thus a dipole that had deviated in time τ by an angle $\delta' = -\gamma\,\Delta H\tau$ from the y-axis is turned to an angle

$$\pi - \delta' = \pi - (-\gamma\,\Delta H\tau) = \pi + \gamma\,\Delta H\tau.$$

Under the action of the local field it will subsequently precess in the equatorial plane with angular velocity $-\gamma\,\Delta H$, so that after a further time τ it will reach an angle $(\pi + \gamma\,\Delta H\tau) - \gamma\,\Delta H\tau = \pi$. Thus at time 2τ after the first pulse all dipoles are at the same angle, and a macroscopic magnetization is reconstructed in the equatorial plane which is observed as a pulse on the oscilloscope (see Fig. 2.4). The process can be repeated by applying further $180°$ pulses at times 3τ, 5τ, etc., so that pulsed signals appear at times 4τ, 6τ, etc. as well as 2τ. The amplitude of successive pulses decays because of relaxation effects, and the method
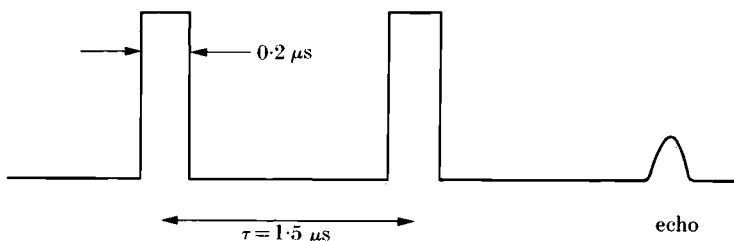
FIG. 2.4. Typical spin echo sequence for electron spin resonance (after Kiel and Mims 1967). Two pulses of r.f. power are applied at an interval of $1 \cdot 5 \, \mu s$. The r.f. field at the sample during each pulse is about $0 \cdot 5$ G; for $g = 2$, $\gamma H_1 \approx 10^7$ rad s^{-1} so that $\gamma H_1 t \approx 2$ for a pulse of duration $0 \cdot 2 \, \mu s$. The spin echo is detected by a superheterodyne receiver. Note that pulse lengths other than 90° followed by 180° (that described in the text) are often used in practice. In the work of Kiel and Mims the spin echo method is used as a sensitive detector in measurements of τ_1.

gives therefore a measurement of the 'genuine' relaxation time τ_2. It can also be applied to the measurement of τ_1.

2.8. Solution of the macroscopic equations for slow passage

In the case of very slow passage through resonance, which is the case commonly encountered in electronic magnetic resonance, another limiting solution of the Bloch equations can easily be found. Essentially we assume that passage is so slow that at all times steady-state conditions prevail, and again look for a solution of eqns (2.33) where $\dot{M}_z = 0$, so that M_z is constant. Then the equations are readily integrable, giving the complex conjugate solutions

$$\left. \begin{array}{l} M_+ = \dfrac{\gamma H_1 M_z \exp(+\mathrm{i}\omega t)}{\omega + \gamma H - \mathrm{i}/\tau_2}\,, \\[3mm] M_- = \dfrac{\gamma H_1 M_z \exp(-\mathrm{i}\omega t)}{\omega + \gamma H + \mathrm{i}/\tau_2}\,. \end{array} \right\} \qquad (2.37)$$

Substitution back into (2.33) gives the value of M_z:

$$\frac{M_z}{M_0} = \frac{1 + (\omega - \omega_L)^2 \tau_2^2}{1 + (\omega - \omega_L)^2 \tau_2^2 + \gamma^2 H_1^2 \tau_1 \tau_2} \qquad (2.38)$$

whence

$$\frac{M_\pm}{M_0} = \frac{\{(\omega - \omega_L)\tau_2 \pm \mathrm{i}\}\gamma H_1 \tau_2 \exp(\pm \mathrm{i}\omega t)}{1 + (\omega - \omega_L)^2 \tau_2^2 + \gamma^2 H_1^2 \tau_1 \tau_2}\,, \qquad (2.39)$$

where, as before, the symbol ω is$_L$ used for the Larmor angular velocity $-\gamma H$. These equations show that because of the term $\{(\omega - \omega_L)\tau_2\}^2$ M_z remains practically equal to M_0 except at resonance, and even then

the departure is small unless $\gamma^2 H_1^2 \tau_1 \tau_2 > 1$. The whole solution corresponds to the magnetization vector precessing about H with angular velocity ω, but tipped at an angle θ to H such that

$$\tan \theta = \frac{|M_{\pm}|}{M_z} = \frac{\gamma H_1 \tau_2}{\{1 + (\omega - \omega_L)^2 \tau_2^2\}^{\frac{1}{2}}} \,. \tag{2.40}$$

If, as in most experiments, H is varied slowly and ω is kept constant, it is convenient to express these quantities in terms of magnetic field. Using $H^* = -(\omega/\gamma)$ for the resonance field at frequency ω, and $\Delta H = -(\gamma \tau_2)^{-1}$, we have

$$\tan \theta = \frac{H_1}{\{(\Delta H)^2 + (H - H^*)^2\}^{\frac{1}{2}}} \,, \tag{2.41}$$

while the equatorial component $M \sin \theta$ of the magnetization leads the rotating field H_1 by an angle ϵ such that

$$\tan \epsilon = \{\tau_2(\omega - \omega_L)\}^{-1} = \Delta H / (H^* - H). \tag{2.42}$$

We have already seen that in a paramagnetic substance with electronic dipoles ΔH is fairly large ($\sim 10^2$ G) unless the substance is heavily diluted. Thus, for ordinary values of H_1, $\tan \theta$ is very small even at resonance, for which $\tan \theta = (H_1/\Delta H)$, so that the angle θ at which $\mathbf{M}$ precesses round $\mathbf{H}$ is small. The value of ϵ varies from 0 for $H^* \ll H$, through $-\pi/2$ for $H^* = H$ to $-\pi$ for $H^* \gg H$. This behaviour is similar to that usually found for the phase angle in forced resonance, and we can express the oscillatory part of the magnetization in terms of a complex susceptibility χ such that

$$M_+ = \chi H_1 \exp(i\omega t). \tag{2.43}$$

Then, since $M_0 = \chi_0 H$,

$$\frac{\chi}{\chi_0} = \frac{\gamma H \tau_2 \{(\omega - \omega_L)\tau_2 + i\}}{1 + (\omega - \omega_L)^2 \tau_2^2 + \gamma^2 H_1^2 \tau_1 \tau_2} \,. \tag{2.44}$$

The real and imaginary parts of $\chi = \chi' - i\chi''$ can be expressed in terms either of fields or of frequencies (writing $\Delta\omega = \tau_2^{-1}$), giving in the latter case (since $\gamma H = -\omega_L$)

$$\left. \begin{aligned} \frac{\chi'}{\chi_0} &= \frac{\omega_L(\omega_L - \omega)}{(\omega - \omega_L)^2 + (\Delta\omega)^2 + \gamma^2 H_1^2 (\Delta\omega)\tau_1} \,, \\ \frac{\chi''}{\chi_0} &= \frac{\omega_L \, \Delta\omega}{(\omega - \omega_L)^2 + (\Delta\omega)^2 + \gamma^2 H_1^2 (\Delta\omega)\tau_1} \,. \end{aligned} \right\} \tag{2.45}$$

Thus χ' is zero at resonance, while at other frequencies it is positive or negative (see Fig. 2.5) according to whether ω_L is greater or less than
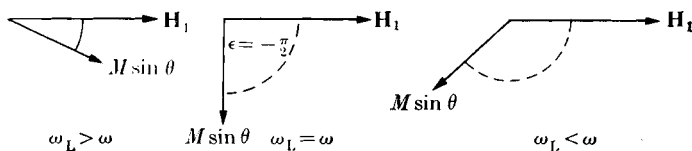
FIG. 2.5. Position of the equatorial component $M \sin \theta$ of the magnetization $\mathbf{M}$, relative to $\mathbf{H}_1$ in the rotating frame, on either side of resonance. When the natural resonance frequency ω_L is numerically larger than the applied frequency ω, the phase angle ϵ given by

$$\tan \epsilon = \Delta\omega/(\omega - \omega_L) \qquad (2.42a)$$

lies between 0 and $-\pi/2$; at resonance it is just equal to $-\pi/2$, and $\chi' = 0$; as ω is increased above ω_L, the angle ϵ moves towards $-\pi$. In terms of magnetic field, the same pattern is followed, starting with $H > H^*$ and decreasing H through the resonance value H^*.

In eqn (2.42a), all angular velocities have the same sign (usually positive for electronic dipoles) provided that $\mathbf{H}_1$ rotates in the same sense as the natural sense of precession of the atomic dipoles. If it rotates in the opposite sense, then the quantities ω, ω_L add numerically and the value of ϵ is always close to zero. Note that $\mathbf{M}$ deviates in the direction corresponding to an incipient precession about $\mathbf{H}_1$.

the applied ω. The imaginary part of the susceptibility is a maximum at resonance, and provided that $\gamma^2 H_1^2 \tau_1 \ll \Delta\omega$, one has at resonance

$$\frac{\chi''}{\chi_0} = \frac{\omega_L}{\Delta\omega}, \qquad (2.46)$$

showing that the imaginary part of the susceptibility is much greater than the static susceptibility provided that the line width is small compared with the resonance frequency, i.e. that the lines are fairly sharp.

The condition that was introduced in deducing eqn (2.46) involves the spin-lattice relaxation time τ_1, and is the same condition as is required to make the departure of M_z from M_0 negligible even at resonance. It is readily shown that at resonance

$$\frac{|M|}{M_0} = \frac{\{1 + \gamma^2 H_1^2 \tau_2^2\}^{\frac{1}{2}}}{1 + \gamma^2 H_1^2 \tau_1 \tau_2} \qquad (2.47)$$

so that M can never be greater than M_0. It can, however, be significantly smaller than M_0 for large amplitudes of the rotating field H_1. This is because the spin system is absorbing energy from the rotating field at a rate

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \left\{ H_x \frac{\mathrm{d}M_x}{\mathrm{d}t} + H_y \frac{\mathrm{d}M_y}{\mathrm{d}t} \right\}_{\mathrm{av}} = \omega \chi'' H_1^2, \qquad (2.48)$$

and this absorption of power raises the temperature of the spin system to the point where $(\mathrm{d}W/\mathrm{d}t)$ is equal to the rate at which energy

is transferred from the spin system to the lattice. Hence M falls below the equilibrium value M_0, which is appropriate to the spin system being at the same temperature as the lattice, and the temperature rise in the spin system with increasing H_1 will be greater, the longer τ_1 and τ_2. If $H_1 = 1$ G, and $\gamma = 10^7$ rad G^{-1}, $\tau_2 = 10^{-9}$ s as for an ordinary paramagnetic, then there will be no significant temperature rise in the spin system unless $\tau_1 \geqslant 10^{-5}$ s, a value that is ordinarily attained only at low temperatures.

This phenomenon is known as 'dynamic saturation'; in experiments where resonance is detected by means of the energy absorbed from the rotating field it limits the gain that can be achieved through increasing H_1. At resonance the size of the precessing component $\chi''H_1$ of the magnetization in the equatorial plane, which is $\pi/2$ out of phase with the rotating field, is given by

$$\frac{\chi''H_1}{M_0} = -\frac{\gamma H_1 \tau_2}{1 + \gamma^2 H_1^2 \tau_1 \tau_2}, \tag{2.49}$$

which passes through a maximum at $|\gamma H_1| = (\tau_1 \tau_2)^{-\frac{1}{2}}$. This maximum arises because the angle θ at which the vector $\mathbf{M}$ precesses about $\mathbf{H}$ increases as $\mathbf{H_1}$ increases (eqn (2.40)), but the magnitude of the vector shrinks as saturation sets in. The absorbed energy $\mathrm{d}W/\mathrm{d}t$ given by (2.48) can be written, using (2.49) and (2.38), as (at resonance)

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{M_0 H}{\tau_1}\left(\frac{\gamma^2 H_1^2 \tau_1 \tau_2}{1 + \gamma^2 H_1^2 \tau_1 \tau_2}\right) = \frac{M_0 H}{\tau_1}\left(\frac{M_0 - M_z}{M_0}\right), \tag{2.50}$$

where the quantity $s = (M_0 - M_z)/M_0$ is sometimes known as the 'saturation parameter'. As H_1 is increased without limit, the value of $\mathrm{d}W/\mathrm{d}t$ tends to the limiting value $(M_0 H/\tau_1)$, which is independent of H_1 and τ_2. This limit occurs because the temperature of the spin system rises and hence χ'' falls as H_1 increases, the temperature adjusting itself to a value such that the rate at which heat is absorbed is just equal to the rate at which it is transferred to the lattice; the latter becomes the controlling factor.

In the simple treatment of § 1.11 we saw that saturation sets in when $2w_e \tau_1 \approx 1$. We can compare this result with the treatment given in this section by using eqns (2.17a) and (2.34). For a system with $J = \frac{1}{2}$ the matrix element $\langle M \pm 1| J_{\pm} |M\rangle = 1$, and exactly at resonance ($\omega = \omega_L$) the value of the shape function is $f(\omega) = \tau_2/\pi$. Hence

$$2w_e \tau_1 = 2(\pi/2)(\gamma H_1)^2(\tau_2/\pi)\tau_1 = \gamma^2 H_1^2 \tau_1 \tau_2,$$

which is just the quantity that occurs in the saturation parameter at resonance (cf. eqn (2.50)).

It may also be helpful to give some numerical values. If we take $H_1 = 0\cdot1$ G as being typical of an electron resonance experiment in which $\gamma = 10^7$ rad G^{-1} with $J = \frac{1}{2}$, we find that saturation sets in when $\gamma^2 H_1^2 \tau_1 \tau_2 = 10^{12} \tau_1 \tau_2 \approx 1$. Thus in a concentrated salt for which $\tau_2 = 10^{-9}$ s ($\Delta H \approx 100$ G), saturation occurs only if $\tau_1 \geqslant 10^{-3}$ s. On the other hand, in an inhomogeneously broadened dilute paramagnetic for which $\tau_2 = 10^{-5}$ s in a spin packet, saturation requires only $\tau_1 \geqslant 10^{-7}$ s; since τ_2 cannot be longer than τ_1, saturation would set in at $\tau_2 = \tau_1 = 10^{-6}$ s. For a nuclear paramagnet $\gamma_n = 10^4$ rad G^{-1}, and if we take $H_1 = 1$ G in this case, and $\Delta H = (\gamma_n \tau_2)^{-1} = 10$ G in a solid lattice, saturation occurs if $\tau_1 \geqslant 10^{-3}$ s.

2.9. Intensity and line width

The classical analysis using the macroscopic equations gives an excellent approach to magnetic resonance, particularly because it gives a simple physical picture. It is rather less applicable to electronic paramagnetic than to nuclear paramagnetic substances because the case where the only major interaction is that with the external applied field **H** tends to be the exception rather than the rule. In a solid paramagnetic the energy levels in zero magnetic field are commonly split by crystal field effects as well as nuclear interactions, and even where these are absent, the behaviour of the energy levels in an applied field depends on the angle that this field makes with the crystal axes. In these circumstances a quantum-mechanical approach is essential, and the resonance spectrum can only be interpreted in terms of a 'spin Hamiltonian' where the effects of interaction between the paramagnetic ion and the crystal lattice are included. The relation between the spectrum and this spin Hamiltonian is considered in the next chapter, but it is appropriate to derive here a formula for the intensity of the lines by quantum-mechanical methods. This approach is similar to that given by Bloembergen, Purcell, and Pound (1948) for the nuclear case, with a slight extension.

The number of transitions per second between levels of energy W_i and W_j which are induced by an oscillatory field of amplitude H_1 and angular frequency ω is

$$w_{ij} = \frac{\pi H_1^2}{2\hbar^2} |\mu_{ij}|^2 f(\omega). \tag{2.51}$$

This equation is similar to (2.17a) except that a more general expression, $|\mu_{ij}|^2$, has been introduced for the square of the magnetic dipole matrix element between the states i and j. The 'shape function' $f(\omega)$ is a function of the applied frequency ω, the resonance frequency ω_0, and a parameter describing the line width; it is normalized as in eqn (2.17b).

The oscillating field induces transitions between states i and j with equal probability in either direction, and in each transition the energy change is $\hbar\omega$. There will, in general, be an absorption of energy since the state of lower energy normally has the greater population, and the total number of transitions in either direction is proportional to the population of the initial state. The net absorption of energy per second (assuming no significant departure from thermal equilibrium) is

$$\mathrm{d}W/\mathrm{d}t = w_{ij}(\hbar\omega)(N_i-N_j) = N_i w_{ij}(\hbar\omega)\{1-\exp(-\hbar\omega/kT)\},$$

where N_i, N_j are the populations of lower and upper states respectively. From eqn (2.51) we have then

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{N_i \pi\omega H_1^2}{2\hbar} \{1-\exp(-\hbar\omega/kT)\} |\mu_{ij}|^2 f(\omega). \qquad (2.52a)$$

For a simple ground doublet, the total number of ions is

$$N = N_i+N_j = N_i\{1+\exp(-\hbar\omega/kT)\}$$

and

$$\frac{\mathrm{d}W}{\mathrm{d}t} = N \tanh(\hbar\omega/2kT) \frac{\pi\omega H_1^2}{2\hbar} |\mu_{ij}|^2 f(\omega). \qquad (2.52b)$$

In many experiments $(\hbar\omega/kT) \ll 1$ (it would be equal to unity for radiation of wave number 1 cm^{-1} at a temperature of $1\cdot43°$K), so that $\{1-\exp(-\hbar\omega/kT)\} \approx \hbar\omega/kT$, and the power absorbed in a transition between states i, j is

$$\frac{\mathrm{d}W}{\mathrm{d}t} = N_i \frac{\pi\omega^2 H_1^2}{2kT} |\mu_{ij}|^2 f(\omega). \qquad (2.52c)$$

Circularly polarized radiation

Combining eqns (2.48) and (2.52c), we find for the imaginary part of the susceptibility, when circularly polarized radiation is used,

$$\chi_{ij}'' = \frac{N_i \pi\omega \, |\mu_{ij}|^2 f(\omega)}{2kT} . \qquad (2.53)$$

This formula is a general one, and it may be compared with that derived from the macroscopic equations on a classical basis for the case of a rotating magnetic field. For this comparison we must assume that

all the states have the same energy in zero magnetic field, so that for a system with angular momentum J the partition function

$$Z = \sum \exp(-W_j/kT)$$

may be approximated by $Z = 2J+1$, and $N_i = N/(2J+1)$, where N is the total number of spins. For a rotating field the matrix elements of μ_{ij} are $(\gamma\hbar)$ times those of $|J_{\pm}|$ between states $M\pm1$ and M, as given in eqns (2.15), and hence we have for the transition $M \leftrightarrow M-1$

$$\chi''_{M,M-1} = \frac{N\pi\omega\gamma^2\hbar^2\{J(J+1)-M(M-1)\}f(\omega)}{2(2J+1)kT} . \tag{2.54}$$

The macroscopic equations are applicable to a substance where all the transitions occur at the same frequency, since the energy levels are separated by equal amounts $\gamma\hbar H$ as given by eqn (2.11). Hence (2.54) must be summed over all transitions; using the relation

$$\sum_{-(J-1)}^{J} \{J(J+1)-M(M-1)\} = \tfrac{2}{3}J(J+1)(2J+1)$$

and eqn (2.22), we have

$$\chi'' = \frac{N\pi\omega\gamma^2\hbar^2 J(J+1)f(\omega)}{3kT} = \pi\omega\chi_0 f(\omega). \tag{2.55}$$

With a suitable choice for $f(\omega)$, to which we shall return later, this is similar to eqns (2.45) derived from the macroscopic theory.

In practice it is seldom that a circularly polarized oscillatory field is used in electronic magnetic resonance apart from exceptional cases where the sign of the magnetogyric ratio γ is of importance in deciding the nature of the electronic ground state. We shall therefore consider briefly the modification to the theory required for a linearly polarized oscillatory field.

Linearly polarized oscillatory field

If the oscillatory magnetic field is of amplitude H_1 and is linearly polarized along a direction whose direction cosines are (l_1, m_1, n_1) with respect to the Cartesian axes x, y, z, the interaction with the magnetic dipole moment may be written as

$$\begin{aligned}
\mathscr{H}_1 &= -(l_1\mu_x+m_1\mu_y+n_1\mu_z)H_1 \cos \omega t \\
&= -\tfrac{1}{2}(l_1\mu_x+m_1\mu_y+n_1\mu_z)H_1\{\exp(i\omega t)+\exp(-i\omega t)\}. \quad (2.56)
\end{aligned}$$

Then if μ_{ij} is the matrix element of the dipole moment

$$\mu_{ij} = \langle u_j| (l_1\mu_x+m_1\mu_y+n_1\mu_z) |u_i\rangle$$

between states i and j, the power absorbed (dW/dt) is given by eqn (2.52a). As before, we shall assume that the steady magnetic field is directed along the z-axis, so that the transition probabilities involve only the matrix elements of μ_+, μ_-. The dipole moment operator for the linear oscillatory field may be written as

$$\tfrac{1}{2}(l_1-im_1)\mu_+ + \tfrac{1}{2}(l_1+im_1)\mu_- + n_1\mu_z$$

and the square of the matrix element for the transition $M \leftrightarrow M-1$ is

$$|\mu_{ij}|^2 = \tfrac{1}{4}(l_1^2+m_1^2)\langle M-1| \,\mu_-\, |M\rangle^2. \tag{2.57}$$

It is clear that this will have its maximum value if $l_1^2+m_1^2 = 1$, that is, if the oscillatory field is in the xy-plane, normal to the direction of the steady field. If this condition is satisfied, and we choose the direction of the x-axis so that it coincides with that of H_1, the oscillatory Hamiltonian reduces to

$$\mathscr{H}_1 = -\tfrac{1}{4}\gamma\hbar H_1(J_++J_-)\{\exp(i\omega t)+\exp(-i\omega t)\}. \tag{2.58}$$

This differs from the equivalent eqn (2.13) for a rotating field in two respects: the operators J_+, J_- are each multiplied both by $\exp(i\omega t)$ and by $\exp(-i\omega t)$, so that transitions can be induced irrespective of the sign of γ, and the amplitude of the perturbation is only half as large as for a rotating field. These differences correspond just to the fact that a linearly polarized field $H_1 \cos \omega t$ can be decomposed into two circularly polarized fields each of amplitude $\tfrac{1}{2}H_1$ but rotating in opposite sense with the same numerical value of the angular velocity ω. Of these two, only the component that rotates in the same sense as that in which the magnetization is precessing will be effective in inducing transitions. Since the amplitude of this component is only half as great as before, we would expect the induced precessing magnetization to be only half as great, and the complex susceptibility likewise to be halved. This is confirmed by carrying through the computation of χ''.

In the case of a linearly polarized field we have, instead of eqn (2.48),

$$\frac{dW}{dt} = \tfrac{1}{2}\omega\chi''H_1^2, \tag{2.59}$$

so that from eqn (2.52c)

$$\chi''_{ij} = \frac{\pi N_i \omega \, |\mu_{ij}|^2 f(\omega)}{kT}, \tag{2.60}$$

where N_i is the number of atoms in the lower of the two states between which a transition is taking place. For the transition $M \leftrightarrow M-1$, on

using eqns (2.57) or (2.58) and inserting the matrix element of μ_- or J_- from eqn (2.15), we have

$$\chi''_{M,M-1} = \frac{N_i \pi \omega \gamma^2 \hbar^2 \{J(J+1) - M(M-1)\} f(\omega)}{4kT}. \qquad (2.61)$$

For an electronic transition, the value of γ is usually negative, so that the lower state is $M-1$, for which

$$N_i = N_{M-1} = N \exp(-W_{M-1}/kT)/Z. \qquad (2.62)$$

For a simple ion, as considered earlier in this section, all the transitions are superposed, and at high temperatures where $\hbar\omega \ll kT$, the exponential has a value close to unity and $Z \to 2J+1$. Then, on summing over all transitions, we have

$$\chi'' = \tfrac{1}{2}\pi\omega\chi_0 f(\omega), \qquad (2.63)$$

which is just half as great as the corresponding expression (2.55) for the case of a rotating field.

This expression for χ'' satisfies the Kramers–Kronig relations, one of which reduces to

$$\chi_0 = \frac{2}{\pi} \int_0^\infty \frac{\chi''(\omega)\, d\omega}{\omega}. \qquad (2.64)$$

It is readily seen that this equation is satisfied through the normalization of $f(\omega)$ introduced by eqn (2.17b). In this connection it should be noted that the macroscopic eqns (2.45) do not satisfy the Kramers–Kronig relations except in the limit of small H_1 (see Portis 1953); this arises from the presence of the term in H_1 in the denominator of eqns (2.45). As already discussed in § 2.8, this term is connected with saturation effects in which the temperature of the spin system rises above that of the lattice because of the absorption of energy from the oscillatory field; this makes the magnetization non-linear with applied oscillatory field, contrary to one of the assumptions on which the Kramers–Kronig relations are based. Saturation effects have, of course, been neglected in the derivation of formulae for χ'' in the present section (§ 2.9).

The question of an appropriate formula for the line shape in electron paramagnetic resonance will not be discussed in detail here. The problem of the line shape due to spin-spin interaction is considered in Chapter 9, but when the line shape is determined by spin lattice interaction (or 'collisions with phonons'), or another true relaxation

process, an appropriate formula for $f(\omega)$ should be the collision broadening formula of Van Vleck and Weisskopf (1945),

$$f(\omega) = \frac{1}{\pi}\left\{\frac{\Delta\omega}{(\omega-\omega_L)^2+(\Delta\omega)^2}+\frac{\Delta\omega}{(\omega+\omega_L)^2+(\Delta\omega)^2}\right\}. \qquad (2.65)$$

Here the second term (which is absent from eqn (2.34), but which is needed to make $\int_0^\infty f(\omega)\,d\omega = 1$ exactly) can be regarded as arising from the presence of an oscillatory field component rotating in the opposite sense to that required for resonance; correspondingly, the formula allows for reversal of the applied magnetic field H (negative values of ω_L), when linearly polarized oscillatory fields are used. It also gives a suitable form for the line shape near $H = 0$ (compare Fig. 2.6), and in
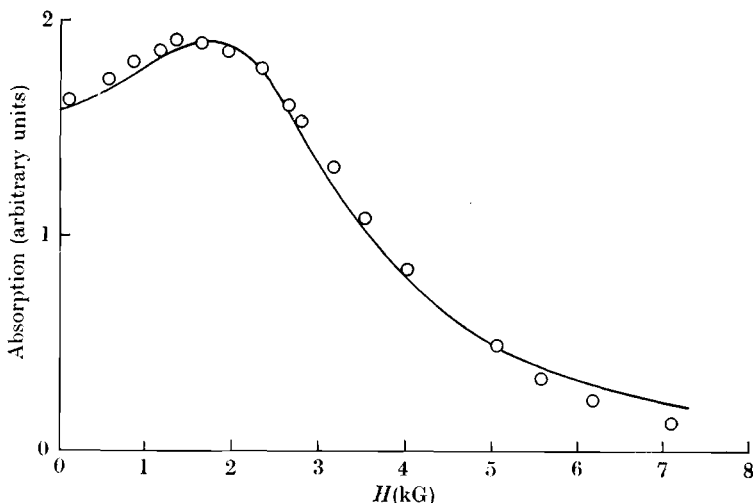

FIG. 2.6. Line shape in $Co(NH_4)_2(SO_4)_2$, $6H_2O$ at $90°K$ and $\bar{\nu} = 0.3$ cm^{-1}.

the limit of $\omega_L = 0$ (or $\omega_L \ll \Delta\omega$, corresponding to $H \ll \Delta H$), the combination of eqns (2.63) and (2.65) gives

$$\chi'' = \chi_0\frac{\omega\,\Delta\omega}{\omega^2+(\Delta\omega)^2}, \qquad (2.66)$$

the formula used in low-frequency measurements on paramagnetic relaxation (see Gorter 1947).

In both eqns (2.65) and (2.66) the effects of saturation by a high-intensity oscillatory magnetic field have been omitted (cf. Karplus and Schwinger (1948) for the case of saturation in microwave gas spectroscopy).

2.10. Spectrometer sensitivity

We now consider in a simple way the practical aspects of the detection of magnetic resonance in an electronic paramagnetic salt, including the important question of spectrometer sensitivity. For simplicity we restrict the discussion to linearly polarized oscillatory fields, since these are almost invariably used in practice. If the paramagnetic sample is subjected to such a linearly polarized magnetic field $H_1 \cos \omega t$, the power absorbed by it is given by eqn (2.59),

$$\mathrm{d}W/\mathrm{d}t = \tfrac{1}{2}\omega\chi''H_1^2, \tag{2.59}$$

where χ'' is the imaginary part of the complex susceptibility of the sample. To make H_1^2 as large as possible, the sample is placed in a tuned circuit or resonant cavity, in which the power dissipated through resistive and other non-magnetic losses may be written

$$\frac{1}{Q_0}\,\omega\,\frac{H_1^2}{8\pi}\,V, \tag{2.67}$$

where Q_0 is the 'quality factor' of the unloaded cavity. The quantity V is the 'effective volume' of the cavity, defined by the fact that $V(H_1^2/8\pi)$ is the total energy stored in the cavity, related to H_1, the amplitude of the oscillatory magnetic field at the sample. The important quantity for the detection of magnetic resonance is the ratio of the power absorbed by magnetic resonance in the sample to that otherwise dissipated in the cavity. From the above equations this ratio is

$$\text{fractional power loss in magnetic resonance} = 4\pi\chi''Q_0/V. \tag{2.68}$$

It is clear that this quantity can be maximized by making Q_0 as large as possible, and keeping the effective volume V as small as possible. The latter is achieved partly by making the actual cavity volume as small as possible, and partly by locating the sample at the position of maximum H_1. As far as the geometry of the cavity is concerned, higher values of (Q_0/V) are achieved by keeping the cavity small; for example, a cavity one-half wavelength long is better than a cavity $n/2$ wavelengths long, since the small gain in Q_0 in the larger cavity is much outweighed by the increase in V. A smaller value of V can be obtained by using a cavity filled with a low-loss dielectric of high permittivity, but this usually has practical difficulties.

The size of the effect on the cavity at resonance can be estimated as follows. At a frequency of 10 GHz (a wavelength of 3 cm), the values for a typical cavity resonator are $Q_0 = 5000$, $V = 3$ cm³. The power

absorbed in the crystal due to magnetic resonance will then equal that dissipated in the cavity (i.e. the Q will be halved at resonance) by a sample for which χ'' is about 5×10^{-5}. This value can be related to the static susceptibility by using eqn (2.63) and taking $f(\omega) = (\pi \, \Delta\omega)^{-1}$ from eqn (2.65) for a reasonably narrow line at resonance. This gives

$$\chi'' = \chi_0 \{ \omega / (2 \, \Delta\omega) \}. \tag{2.69}$$

For a reasonably dilute paramagnetic salt such as a tutton salt (typical formula $M^{2+}K_2(SO_4)_2, 6H_2O$) the volume per gram-ion of paramagnetic ion M^{2+} is close to 200 cm³. If the magnetic ions have effective spin $S = \frac{1}{2}$ and $g = 2$, the line width ΔH is about 100 G and the resonant field H at 10 GHz is a little over 3000 G. Thus $(\omega/\Delta\omega) = (H/\Delta H)$ is roughly 30, and the gram-ionic susceptibility is

$$\chi_0 = 0 \cdot 375/T \text{ (per gram-ion)}$$

so that at room temperature ($T = 300°K$) we have

$$\chi'' = 0 \cdot 018 \text{ (per gram-ion)}.$$

Hence the value of $\chi'' = 5 \times 10^{-5}$ required above to halve the cavity Q needs about 3×10^{-3} gram-ion or 0·6 cm³ of salt at room temperature. Such a sample clearly provides an effect that is very readily detectable and increases inversely with the temperature of the sample. In fact serious detuning of the cavity will occur owing to the anomalous variation in χ' through resonance, and a distorted shape of resonance curve will result unless the cavity is continuously retuned.

Electromagnetic detection

A prime advantage of electron paramagnetic resonance is its ability to detect effects caused by rather small quantities of magnetic ions, and we now consider the ultimate sensitivity that can be achieved. This does not depend on the details of the spectrometer, and we therefore consider a simple lumped-parameter equivalent circuit. A power source of voltage V_1, with internal resistance R_1, is coupled through a mutual inductance M_1 to a tuned circuit of series resistance r, as in Fig. 2.7. The power level in the tuned circuit is detected by an output coupling of mutual inductance M_2 to a voltage detector of input resistance R_2, the voltage across which is V_2. When magnetic resonance occurs in a paramagnetic sample placed in the tuned circuit, the additional power loss is represented by an extra resistance δr. Since we are interested in
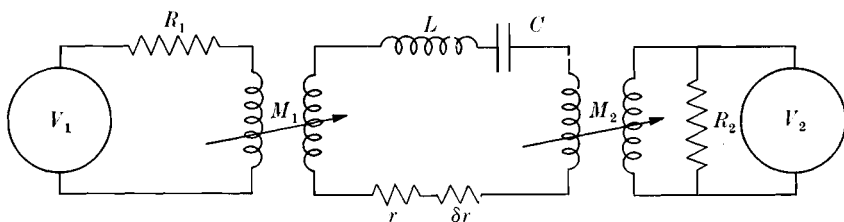
FIG. 2.7. Simple equivalent circuit for 'transmission' spectrometer. A voltage source V_1, with internal resistance R_1, is coupled through M_1 to a tuned circuit in which the magnetic resonance absorption contributes an extra resistance δr. The tuned circuit is coupled through M_2 to a detector of resistance R_2. When M_1, M_2 are adjusted to give the maximum sensitivity (largest change in V_2 for a given δr), the extra resistances coupled into the tuned circuit through input and output are together just equal to r, so that the loaded Q is just half the unloaded Q_0.

the ultimate sensitivity, we are concerned with values of $\delta r \ll r$, and we can write, from eqn (2.68),

$$\delta r/r = 4\pi\chi''Q_0/V. \tag{2.70}$$

Our problem is to relate the change in V_2 to δr, assuming that the source voltage V_1 is constant. In fact we shall specify the source by its 'available power' $P_1 = V_1^2/4R_1$, which is the maximum power it can deliver into a load matched to its internal resistance R_1. If we write $r_1 = \omega^2 M_1^2/R_1$, $r_2 = \omega^2 M_2^2/R_2$, where r_1, r_2 are the resistances coupled into the tuned circuit, then at resonance in the tuned circuit it is easily shown that

$$\frac{V_2}{\sqrt{R_2}} = \frac{2\sqrt{(P_1)}\sqrt{(r_1 r_2)}}{(r_1 + r_2 + r)} \tag{2.71}$$

and hence that

$$\frac{|\delta V_2|}{\sqrt{R_2}} = \frac{2\sqrt{(P_1)}\sqrt{(r_1 r_2)}}{(r_1 + r_2 + r)^2} \delta r. \tag{2.72}$$

We wish to maximize δV_2 by adjusting the input and output couplings, which is equivalent to finding the optimum values of r_1, r_2. These occur at $r_1 = r_2 = r/2$, and the maximum value of δV_2 is then

$$\frac{|\delta V_2|}{\sqrt{R_2}} = \tfrac{1}{4}\sqrt{(P_1)}\frac{\delta r}{r}. \tag{2.73}$$

This maximum occurs when the loaded Q of the cavity is just half the unloaded Q_0, since it requires $(r_1 + r_2 + r) = 2r$. We can see how this maximum arises by re-writing (2.72) in terms of the power $P_2 = V_2^2/R_2$ reaching the detector. The value of $\sqrt{P_2}$ is given by (2.71), so that

(2.72) becomes

$$\frac{|\delta V_2|}{\sqrt{R_2}} = \sqrt{P_2}\,\frac{\delta r}{(r_1+r_2+r)} \quad \text{or} \quad \frac{|\delta V_2|}{V_2} = \frac{\delta r}{(r_1+r_2+r)}, \qquad (2.74)$$

which shows that the fractional voltage change $(\delta V_2/V_2)$ at the detector is just equal to the fractional change in the 'loaded Q', which is $\delta r/(r_1+r_2+r)$. As we increase the coupling, V_2 rises and so initially does δV_2, but ultimately the increase in V_2 becomes less important than the fall in the loaded Q because of the heavier coupling. By combining eqns (2.70) and (2.73) we find that under optimum coupling conditions

$$|\delta V_2|/\sqrt{R_2} = \sqrt{(P_1)}(\pi\chi''Q_0/V). \qquad (2.75)$$

If the detector has an equivalent noise temperature T_N and bandwidth df, the signal output will be equal to the noise output when

$$|\delta V_2|/\sqrt{R_2} = (kT_N\,\mathrm{d}f)^{\frac{1}{2}}, \qquad (2.76)$$

and if this is regarded as the minimum signal detectable, we find that

$$(\chi'')_{\min} = \left(\frac{V}{\pi Q_0}\right)\left(\frac{kT_N\,\mathrm{d}f}{P_1}\right)^{\frac{1}{2}}. \qquad (2.77)$$

To gain an idea of the order of magnitude implied by this equation we insert some numerical values. Taking (as before) $Q_0 = 5000$, $V = 3$ cm³, together with $P_1 = 40$ mW, $\Delta f = 1$ Hz, and $T_N = 3000°$K, we find

$$(\chi'')_{\min} = 2\times10^{-13}. \qquad (2.78)$$

When working at the limit of sensitivity we are likely to be dealing with highly diluted salts; for convenience we take $\Delta H = 1$ G (i.e. line width $= 2$ G right across at half intensity) and $H = 3000$ G (the resonance field for a salt with $g = 2$ at about 9 GHz frequency). From eqn (2.69) we then obtain

$$(\chi_0)_{\min} \approx 10^{-16}, \qquad (2.79)$$

which for a system of spins $S = \frac{1}{2}$ requires some $3\times10^{-16}T$ moles at temperature T, or about 10^9 spins at $4°$K.

In making this calculation we have assumed that the detector is not overloaded by the power P_2 incident on it, which under the optimum coupling conditions assumed above is $P_1/4$. If it is necessary to keep P_2 to some maximum value less than $P_1/4$, then obviously it is better to loosen the coupling to the cavity so as to increase the loaded Q rather than to insert attenuation by means of a lossy device before or after

the cavity since, from (2.74),

$$|\delta V_2|/V_2 = \delta(1/Q).$$

The means by which we can improve the sensitivity are rather obvious from eqn (2.77). Assuming T_N and P_1 already have the best attainable values, we can reduce the band width df. In considering the choice of frequency we combine (2.77) with (2.69) to obtain

$$(\chi_0)_{\mathrm{min}} = \left(\frac{2\Delta\nu}{\nu}\right)\left(\frac{V}{\pi Q_0}\right)\left(\frac{kT_N\,\mathrm{d}f}{P_1}\right)^{\frac{1}{2}}. \qquad (2.80)$$

If we can scale the cavity in proportion to the wavelength, V varies as ν^{-3} and Q_0 as $\nu^{-\frac{1}{2}}$, so that $(\chi_0)_{\mathrm{min}}$ varies as $\nu^{-\frac{7}{4}}$, giving a big improvement at higher frequencies, even allowing for rather poorer values of T_N and P_1. This improvement assumes that we do not simultaneously have to scale the size of the sample in order to accommodate it in the cavity. In more precise language, the improvement is real for a sample that is so small that it can be contained in the smallest wavelength cavity without affecting the scaling argument. If we can use a larger sample of the same material at longer wavelengths, so that we have a constant filling factor, it is more realistic to discuss the quantity $(\chi_0/V)_{\mathrm{min}}$, which refers to the minimum value of the volume susceptibility. This varies only as $\nu^{-\frac{1}{4}}$, so that allowing for poorer values of T_N and P_1 there is little gain in sensitivity at higher frequencies.

For a paramagnetic substance where resonance is observed in the ground levels we have χ'' proportional to T^{-1} so that we always gain by reducing the temperature provided that the spin-lattice relaxation time does not become so long that we must reduce P_1 in order to avoid dynamic saturation effects. When $h\nu$ becomes larger than kT, χ_0 approaches a constant value (equivalent to static saturation of the sample in the steady magnetic field), but this occurs only at temperatures where the spin-lattice relaxation time is also likely to be long because of the drop in the number of phonons of energy $h\nu$ (see Chapter 10).

Dynamic saturation effects set a more fundamental limit than the possible detector overload mentioned above, since the value of χ'' falls at high values of H_1^2. The optimum then occurs when $1 = \gamma^2 H_1^2\tau_1\tau_2$, (see eqn (2.49)), since from eqn (2.75) we need to maximize $\chi''\sqrt{P_1}$, which for a given coupling is equivalent to maximizing $\chi''H_1$. With the coupling conditions assumed in (2.73) the power dissipated in the

cavity is $P_1/2$, and hence from (2.67) we have

$$P_1 = \frac{1}{Q_0}\, \omega\, \frac{H_1^2}{4\pi}\, V = \frac{\omega V}{4\pi Q_0}\frac{1}{\gamma^2 \tau_1 \tau_2}$$

$$= \frac{V}{4\pi Q_0}\frac{H\,\Delta H}{\tau_1}, \qquad (2.81)$$

since $|(\omega/\gamma)| = H$ and $|(1/\gamma\tau_2)| = \Delta H$.

Using the same numerical values as for eqn (2.79) we find

$$P_1\ (\mathrm{erg\ s^{-1}}) = 0\cdot15/\tau_1,$$

which means that P_1 must be limited to a smaller value than 40 mW $= 4 \times 10^5$ erg s^{-1} unless τ_1 is shorter than about 4×10^{-7} s. This is quite a severe restriction. For example, the value of $H_1 = 0\cdot1$ G used in § 2.8 corresponds to $P_1 = 3$ mW, a level at which saturation sets in for $\Delta H = 1$ G unless τ_1 is shorter than about 5×10^{-6} s. If we have an inhomogeneously broadened line for which the true $\tau_2 = 10^{-5}$ s, corresponding to a spin packet width $\Delta H = 10^{-2}$ G, saturation of the spin packet would occur for a value of P_1 as small as 10^{-2} mW even if τ_1 were as short as τ_2.

The situation can be improved (but only marginally) by using a looser input coupling to the cavity to reduce H_1. In terms of the power P_c dissipated in the cavity, (2.74) becomes, since $P_c/P_2 = \surd(r/r_2)$,

$$\frac{|\delta V_2|}{\surd R_2} = \surd P_c \sqrt{\left(\frac{r_2}{r}\right)}\frac{1}{(r_1+r_2+r)}\,\delta r, \qquad (2.82)$$

which is optimized for a given value of P_c by making $r_2 = r+r_1$ (matching the detector to the loaded cavity) and then adjusting the input coupling to make r_1 as small as possible consistent with a given value of P_c. If then $r_1 \ll r$, the optimum output coupling condition becomes essentially $r_2 = r$, so that the detector is just matched to the unloaded cavity.

Bolometer detection

In the previous section we have assumed that the detector was linear in its response to the incident voltage (or amplitude of the microwave radiation). We consider now a bolometer system, in which the microwave power is absorbed in a suitable element and detected through the rise in temperature of this element, which is proportional to the magnitude of the incident power. The analysis is based on that of Schmidt and Solomon (1966).

If the bolometer has thermal capacity C and thermal time constant

τ, its response to an incident power P_2 is determined by the equation

$$C\{\mathrm{d}T/\mathrm{d}t)+(T/\tau)\} = P_2. \tag{2.83}$$

If P_2 is time-dependent (e.g. modulated) with frequency f, the bolometer will respond fully only if $f\tau \ll 1$. If the bolometer is in thermal equilibrium at temperature T_0, it undergoes temperature fluctuations δT, whose mean square value is

$$\langle \delta T^2 \rangle = (k/C)T_0^2, \tag{2.84}$$

where k is Boltzmann's constant. In a narrow band $\mathrm{d}f$ of frequencies near the modulation frequency f, the fluctuations have the mean square value

$$\langle \delta T^2 \rangle_f = (k/C)T_0^2 \frac{4\tau\,\mathrm{d}f}{1+f^2\tau^2} \tag{2.85}$$

and when $f\tau \ll 1$ this can be written as

$$\langle \delta T^2 \rangle_f = (k/C)T_0^2(4\tau\,\mathrm{d}f). \tag{2.86}$$

This temperature fluctuation is equivalent to a fluctuation P_n in the incident power of magnitude

$$P_n = (C/\tau)\langle \delta T^2 \rangle_f^{\frac{1}{2}}$$
$$= (4kCT_0^2\,\mathrm{d}f/\tau)^{\frac{1}{2}},$$

and this can be written in the form

$$P_n = (4kT_0P_0\,\mathrm{d}f)^{\frac{1}{2}}, \tag{2.87}$$

where $P_0 = CT_0/\tau$ is a useful parameter with the dimensions of a power that characterizes the sensitivity of the bolometer. The value of P_n obviously sets a lower limit to the changes in incident power that can be detected by the bolometer. Very much lower values of P_n can be obtained by operating the bolometer below room temperature, partly because T_0 occurs in (2.87) but more particularly because P_0 is greatly reduced because of the rapid fall in the heat capacity C as the temperature is reduced. At $4°\mathrm{K}$ it is not difficult to make $P_0 = 10^{-3}$ W, which with unit band width $\mathrm{d}f = 1$ Hz gives $P_n = 5 \times 10^{-13}$ W.

We take this value of the 'thermal noise power' P_n to be the smallest detectable amount of power P_2 incident on the bolometer. In an ideal system the spin-resonance sample acts as its own bolometer, the power absorbed through the magnetic resonance effect appearing as heat in the sample. The highest sensitivity is obtained by making the power absorption as large as possible by increasing H_1, and we must allow for

saturation effects. From eqn (2.50) we have

$$P_2 = \frac{dW}{dt} = \frac{M_0 H}{\tau_1} \frac{\gamma^2 H_1^2 \tau_1 \tau_2}{1 + \gamma^2 H_1^2 \tau_1 \tau_2}, \tag{2.50}$$

which approaches a limiting value as we increase H_1. An experiment where this is advantageous is the spin resonance of conduction electrons in a semiconductor, where the spin system relaxes through the motion of the conduction electrons, and the magnetic absorption results in a heating of the conduction electrons which can be detected as a change in the resistance of the specimen. In such a system τ_1 is short, and $\tau_1 = \tau_2$. If we write $\gamma\tau_1 = \gamma\tau_2 = (\Delta H)^{-1}$, then since $M_0 = \chi_0 H$ we have

$$P_2 = \frac{\chi_0 H^2}{\tau_1}\left(\frac{H_1^2}{(\Delta H)^2 + H_1^2}\right). \tag{2.88}$$

If we can make $H_1 \gg \Delta H$, the term in parentheses becomes unity, and on setting $P_2 = P_n$ we have for the limiting sensitivity

$$(\chi_0)_{\min} = \left(\frac{\tau_1}{H^2}\right)(4kT_0 P_0 \, df)^{\frac{1}{2}}. \tag{2.89}$$

This assumes, as in (2.50), that we are using circularly polarized radiation. If, as is more likely, we use linearly polarized radiation, the value of (2.88) should be multiplied by a factor $\frac{1}{2}$, and (2.89) becomes

$$(\chi_0)_{\min} = \left(\frac{2\tau_1}{H^2}\right)(4kT_0 P_0 \, df)^{\frac{1}{2}}. \tag{2.90}$$

In a typical example $\Delta H = 1$ G, corresponding to $\tau_1 = 5 \times 10^{-8}$ s. Then at a resonance frequency of 10 GHz, H is approximately 3000 G, and using the value $P_n = 5 \times 10^{-13}$ W given above for $T_0 = 4°$K and $df = 1$ Hz, we have

$$(\chi_0)_{\min} = 10^{-20},$$

which for a sample with $g = 2$ at $4°$K requires only about 10^5 spins. This very high sensitivity is obtained only for a system with a very short value of τ_1, such as conduction electrons. From eqns (2.89) or (2.90) we see that $(\chi_0)_{\min}$ varies as H^{-2} or as the inverse square of the resonance frequency, so that such a bolometer method of detection is advantageous at millimetre wavelengths but of little use for nuclear magnetic resonance.