CHAPTER 1

ELEMENTS OF RESONANCE

1·1 INTRODUCTION

Magnetic resonance is a phenomenon found in magnetic systems that possess both magnetic moments and angular momentum. As we shall see, the term *resonance* implies that we are in tune with a natural frequency of the magnetic system, in this case corresponding to the frequency of gyroscopic precession of the magnetic moment in an external static magnetic field. Because of the analogy between the characteristic frequencies of atomic spectra, and because the magnetic resonance frequencies fall typically in the radio frequency region (for nuclear spins) or microwave frequency (for electron spins), we often use the terms *radio frequency* or *microwave spectroscopy*.

The advantage of the resonance method is that it enables one to select out of the total magnetic susceptibility, a particular contribution of interest—one that may, for example, be relatively very weak. The most spectacular example is, no doubt, the observation of the feeble nuclear paramagnetism of iron against a background of the electronic ferromagnetism. Resonance also permits the gathering of precise, highly detailed magnetic information of a type not obtainable in other ways.

One of the reasons for the impact of magnetic resonance on physics is its ability to give information about processes at the atomic level. In this book we seek to give some of the background necessary or useful to the application of magnetic resonance to the study of solids. Most of the book will be concerned with nuclear resonance, but the final chapters will focus on certain problems particularly important for electron spin resonance. Many of the principles developed in the earlier portions are, of course, equally applicable to nuclear or electron magnetic resonance. Our object is not to tell how to apply magnetic resonance to the study of solids. However, the activity in magnetic resonance has proceeded at such a vigorous pace, pouring out so many new concepts and results, that an author or lecturer faces an enormous task in the selection of material. In this book, we shall use the study of solids as a sort of ultimate goal that will help to delineate the topics for discussion and from which we shall attempt to draw most of the concrete examples of the more formal techniques.

As we remarked above, we are concerned with magnetic systems that possess angular momentum. As examples, we have electron spins, or the nuclei of atoms.

A system such as a nucleus may consist of many particles coupled together so that in any given state, the nucleus possesses a total magnetic moment $\boldsymbol{\mu}$ and a total angular momentum $\mathbf{J}$. In fact the two vectors may be taken as parallel, so that we can write

$$\boldsymbol{\mu} = \gamma \mathbf{J} \tag{1}$$

where γ is a scalar called the "gyromagnetic ratio." For any given state of a nucleus, knowledge of the wave function would in principle enable us to compute both $\boldsymbol{\mu}$ and $\mathbf{J}$. Hence we should find that the quantity γ would vary with the state. Such calculations are beyond the scope of this book.

Of course, in the quantum theory, $\boldsymbol{\mu}$ and $\mathbf{J}$ are treated as (vector) operators. The meaning of the concept of two operators being "parallel" is found by considering the matrix elements of the operators. Suppose we define a dimensionless angular momentum operator, $\mathbf{I}$, by the equation:

$$\mathbf{J} = \hbar \mathbf{I} \tag{2}$$

$\mathbf{I}^2$ then has eigenvalues I which are either integer or half-integer. Any component of $\mathbf{I}$ (for example, I_z) commutes with $\mathbf{I}^2$, so that we may specify simultaneously eigenvalues of both $\mathbf{I}^2$ and I_z. Let us call the eigenvalues I and m, respectively. Of course m may be any of the $2I + 1$ values $I, I - 1, \cdots, -I$. The meaning of Eq. (1) is then that

$$(Im|\mu_{x'}|Im') = \gamma\hbar(Im|I_{x'}|Im') \tag{3}$$

where $\mu_{x'}$ and $I_{x'}$ are components of the operators $\boldsymbol{\mu}$ and $\mathbf{I}$ along the (arbitrary) x'-direction. The validity of this equation is based on the Wigner-Eckart theorem, which we shall discuss in Chapter 6.

We shall, for the remainder of this chapter, give a very brief introduction to some of the basic facts of magnetic resonance, introducing most of the major concepts or questions that we shall explore in later chapters.

1·2 SIMPLE RESONANCE THEORY

We shall wish, in later chapters, to consider both quantum mechanical and classical descriptions of magnetic resonance. The classical viewpoint is particularly helpful in discussing dynamic or transient effects. For an introduction to resonance phenomena, however, we consider a simple quantum mechanical description.

The application of a magnetic field $\mathbf{H}$ produces an interaction energy of the nucleus of amount $-\boldsymbol{\mu} \cdot \mathbf{H}$. We have, therefore, a very simple Hamiltonian:

$$\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{H} \tag{1}$$

Taking the field to be H_0 along the z-direction, we find

$$\mathcal{H} = -\gamma\hbar H_0 I_z \tag{2}$$

The eigenvalues of this Hamiltonian are simple, being only multiples $(\gamma\hbar H_0)$ of the eigenvalues of I_z. Therefore the allowed energies are

$$E = -\gamma\hbar H_0 m \qquad m = I, I - 1, \cdots, -I \tag{3}$$

They are illustrated in Fig. 1.1 for the case $I = 3/2$, as is the case for the nuclei of Na or Cu. The levels are equally spaced, the distance between adjacent ones being $\gamma\hbar H_0$.

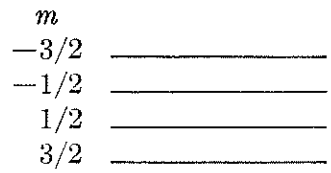

FIG. 1.1. Energy levels of Eq. (3).

One should hope to be able to detect the presence of such a set of energy levels by some form of spectral absorption. What is needed is to have an interaction that can cause transitions between levels. To satisfy the conservation of energy, the interaction must be time dependent and of such an angular frequency ω that

$$\hbar\omega = \Delta E \tag{4}$$

where ΔE is the energy difference between the initial and final nuclear Zeeman energies. Moreover, the interaction must have a non-vanishing matrix element joining the initial and final states.

The coupling most commonly used to produce magnetic resonances is an alternating magnetic field applied perpendicular to the static field. If we write the alternating field in terms of an amplitude H_x^0, we get a perturbing term in the Hamiltonian of

$$\mathcal{H}_{\text{pert}} = -\gamma\hbar H_x^0 I_x \cos\omega t \tag{5}$$

The operator I_x has matrix elements between states m and m', $(m'|I_x|m)$, which vanish unless $m' = m \pm 1$. Consequently the allowed transitions are between levels adjacent in energy, giving

$$\hbar\omega = \Delta E = \gamma\hbar H_0 \tag{6}$$

or

$$\omega = \gamma H_0 \tag{6a}$$

Note that Planck's constant has disappeared from the resonance equation. This fact suggests that the result is closely related to a classical picture. We shall see, in fact, that a classical description also gives Eq. (6a). By studying the two formulations (classical and quantum mechanical), one gains a great deal of added insight.

From Eq. (6a) we can compute the frequency needed to observe a resonance if we know the properties that determine γ. Although such calculations are of basic interest in the theory of nuclear structures, they would take us rather far afield. However, a simple classical picture will enable us to make a correct order-of-magnitude estimate of γ.

Let us compute the magnetic moment and angular momentum of a particle of mass m and charge e moving in a circular path of radius r with period T. The angular momentum is then

$$J = mvr = m\frac{2\pi r^2}{T} \tag{7}$$

while the magnetic moment (treating the system as a current loop of area A carrying current i) is

$$\mu = iA \tag{8}$$

Since $i = (e/c)(1/T)$, we get

$$\mu = \frac{e}{c}\frac{\pi r^2}{T} \tag{9}$$

Comparison of the expressions for μ and J therefore gives us $\gamma = e/2mc$. Besides enabling us to make an order of magnitude estimate of the expected size of γ, for our purposes the important result of this formula is that large masses have low γ's. We expect about a factor of 1,000 lower γ for nuclei than for electrons. In fact, for magnetic fields of 3,000 to 10,000 gauss, electronic systems have a resonance at $\omega/2\pi = 10{,}000$ Mc (the 3 cm microwave region), whereas nuclear systems are typically 10 Mc (a radio frequency). Of course one can always change ω by changing H_0, but in most cases it is advantageous to use as large a magnetic field as possible, since the quanta absorbed are then larger and the resonance is correspondingly stronger.

In later sections, we shall comment somewhat more on typical experimental arrangements.

1·3 ABSORPTION OF ENERGY AND SPIN-LATTICE RELAXATION

We now wish to go a step further to consider what happens if we have a macroscopic sample in which we observe a resonance. For simplicity we consider a system whose nuclei possess spin 1/2 (Fig. 1–2). Since there are many nuclei in our macroscopic sample, we shall specify the number in the two m states $+1/2$ and $-1/2$ by N_+ and N_-, respectively.

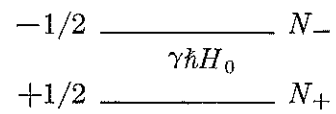

FIG. 1.2. Energy levels for $I = \frac{1}{2}$.

The total number of spins, N, is a constant, but application of an alternating field will cause N_+ or N_- to change as a result of the transitions induced. Let us denote the probability per second of inducing the transition of a spin with $m = +1/2$ to a state $m = -1/2$ by $W_{(+)\to(-)}$. We shall denote the reverse transition by $W_{(-)\to(+)}$. We can then write a differential equation for the change of the population N_+.

$$\frac{dN_+}{dt} = N_- W_{(-)\to(+)} - N_+ W_{(+)\to(-)} \tag{1}$$

Without as yet attempting to compute $W_{(+)\to(-)}$ or $W_{(-)\to(+)}$, we note a famous formula from time-dependent perturbation theory for the probability per second, $P_{a\to b}$, that an interaction $V(t)$ induces a transition from a state (a) with energy E_a to a state (b) whose energy is E_b:

$$P_{a\to b} = \frac{2\pi}{\hbar} |(b|V|a)|^2 \, \delta(E_a - E_b - \hbar\omega) \tag{2}$$

Since $|(a|V|b)|^2 = |(b|V|a)|^2$, we note that $P_{a\to b}$ is the same as the rate $P_{b\to a}$. Such an argument describes many situations and leads to the condition $W_{(+)\to(-)} = W_{(-)\to(+)} \equiv W$.

$$\frac{dN_+}{dt} = W(N_- - N_+) \tag{3}$$

It is convenient to introduce the variable $n = N_+ - N_-$, the difference in population of the two levels. The two variables N_+ and N_- may be replaced by n and N, using the equations

$$\begin{aligned} N &= N_+ + N_- \\ n &= N_+ - N_- \end{aligned} \tag{4}$$

$$\begin{aligned} N_+ &= \tfrac{1}{2}(N + n) \\ N_- &= \tfrac{1}{2}(N - n) \end{aligned} \tag{4a}$$

Substitution of Eq. (4a) into Eq. (3) gives us

$$\frac{dn}{dt} = -2Wn \tag{5}$$

the solution of which is

$$n = n(0)e^{-2Wt} \tag{6}$$

where $n(0)$ is the value of n at $t = 0$. We note that if initially we have a population difference, it will eventually disappear under the action of the induced transitions.

The rate of absorption of energy, dE/dt, is given by computing the number of spins per second that go from the lower energy to the upper, and by subtracting the number that drops down, emitting energy in the process:

$$\frac{dE}{dt} = N_+W\hbar\omega - N_-W\hbar\omega = \hbar\omega Wn \tag{7}$$

Therefore, for a net absorption of energy, n must be non-zero; that is, there must be a population difference. We see that when the upper state is more highly populated than the lower, the net absorption of energy is negative—the system supplies more energy than it receives. This state of affairs is the basis of the oscillators or amplifiers known as *masers* (*m*icrowave *a*mplification by *s*timulated *e*mission of *r*adiation).

We see that if the equations we have put down were complete, the resonant absorption of energy would eventually stop and the resonance would disappear. A more serious difficulty is seen if we assume $W = 0$ (that is, we do not apply the alternating magnetic field). Under these circumstances our equations say that $dN_+/dt = 0$. The populations cannot change. On the other hand, if we applied a static field to a piece of unmagnetized material, we should expect it to become magnetized. The preferential alignment of the nuclear moments parallel to the field corresponds to N_+ being greater than N_-. ($N_- = 0$ would represent perfect polarization, a state we should not expect to find at temperatures above absolute zero.) The process of magnetization of an unmagnetized sample, therefore requires a net number of transitions from the upper to the lower energy state. In the process, the spins give up energy—there is, so to speak, a heat transfer. Therefore there must be some other system to accept the energy. If we ask how big a population

difference will eventually be found, the answer must depend upon the willingness of the other system to continue accepting energy. Speaking in thermodynamic terms, the heat flow will continue until the relative populations N_-/N_+ correspond to the temperature T of the reservoir to which the energy is given.

The final equilibrium populations, N_+^0 and N_-^0, are then given by

$$\frac{N_-^0}{N_+^0} = e^{-\Delta E/kT} = e^{-\gamma\hbar H_0/kT} \tag{8}$$

We must postulate, therefore, that there exists a mechanism for inducing transitions between N_+ and N_-, which arises because of the coupling of the spins to some other system. Let us denote the probability per second that such a coupling will induce a spin transition upward in energy (from $+ \rightarrow -$) by $W_\uparrow$, and the reverse process by $W_\downarrow$. Then we have a rate equation

$$\frac{dN_+}{dt} = +N_-W_\downarrow - N_+W_\uparrow \tag{9}$$

Let us again introduce the variables N and n; but now we no longer can assume equality of the two transition probabilities, since we know such an assumption would not give the preference for downward transitions, which is necessary for the establishment of the magnetization. In fact, since in the steady-state dN_+/dt is zero, Eq. (9) tells us that

$$\frac{N_-^0}{N_+^0} = \frac{W_\uparrow}{W_\downarrow} \tag{10}$$

By using Eq. (8), we find that the ratio of $W_\downarrow$ to $W_\uparrow$ is not unity but rather is

$$\frac{W_\downarrow}{W_\uparrow} = e^{\gamma\hbar H_0/kT} \tag{10a}$$

It is natural to wonder why the argument given to show the equality of $W_{(+)\rightarrow(-)}$ and $W_{(-)\rightarrow(+)}$ does not also apply here. The resolution of this paradox is that the thermal transition requires not only a coupling but also another system in an energy state that permits a transition. We can illustrate by assuming that the reservoir has only two levels whose spacing is equal to that of the nuclear system. If the nucleus and reservoir are initially in the states of Fig. 1.3a given by the

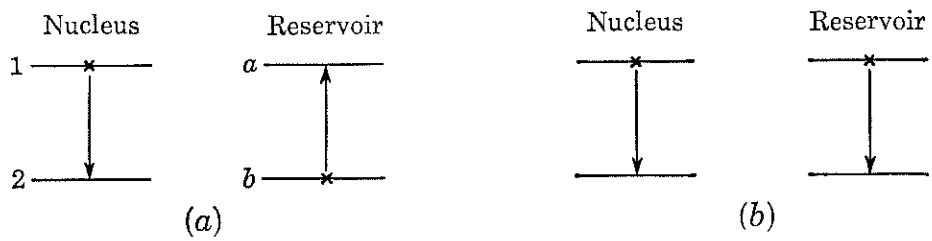

FIG. 1.3. (a) A possible transition. (b) A forbidden transition.

crosses, conservation of energy is satisfied by simultaneous transitions indicated by the arrows. The nucleus may therefore give up energy to the lattice. On the other hand, if both systems are in the upper state (Fig. 1.3b), the simultaneous transition

cannot occur because it does not conserve energy. The rate of transition of the nucleus will therefore depend not only on the matrix elements but *also* on the probability that the reservoir will be in a state that permits the transition.

Thus, if we label the nuclear states 1 and 2 with populations N_1 and N_2, and label the lattice states (a) and (b) with populations N_a and N_b, the number of transitions per second, such as shown in Fig. 1.3a, will be

$$\text{number/sec} = N_1 N_b W_{1b\to 2a} \tag{11}$$

where $W_{1b\to 2a}$ is the probability per second of such a transition under the condition that the nucleus is actually in state 1 and the lattice is actually in state (b). The steady-state condition is found by equating the rate of such transitions to the rate of the inverse transition:

$$N_1 N_b W_{1b\to 2a} = N_2 N_a W_{2a\to 1b} \tag{12}$$

Since the quantum theory requires that $W_{1b\to 2a} = W_{2a\to 1b}$, we see that in thermal equilibrium,

$$\frac{N_1}{N_2} = \frac{N_a}{N_b} \tag{13}$$

That is, the nuclear levels will have the same relative populations as do the lattice's. The nuclear population will therefore be in thermal equilibrium with the lattice's. Note, moreover, that for this simple model, we can compute $W_\uparrow$ and $W_\downarrow$:

$$W_\uparrow = N_a W_{2a\to 1b} \qquad W_\downarrow = N_b W_{1b\to 2a} = N_b W_{2a\to 1b} \tag{14}$$

so that $W_\uparrow$ and $W_\downarrow$ are seen to be unequal.

We now leave our special model and return to Eq. (9). By making the substitutions of Eq. (4a) for N_+ and N_-, we find

$$\frac{dn}{dt} = N(W_\downarrow - W_\uparrow) - n(W_\downarrow + W_\uparrow) \tag{15}$$

which can be rewritten as

$$\frac{dn}{dt} = \frac{n_0 - n}{T_1} \tag{16}$$

where

$$n_0 = N\left(\frac{W_\downarrow - W_\uparrow}{W_\downarrow + W_\uparrow}\right) \qquad \frac{1}{T_1} = (W_\downarrow + W_\uparrow) \tag{17}$$

Since the solution of Eq. (16) is

$$n = n_0 + Ae^{-t/T_1} \tag{18}$$

(where A is a constant of integration), we see that n_0 represents the thermal equilibrium population difference, and T_1 is a characteristic time associated with the approach to thermal equilibrium. T_1 is called the "spin-lattice relaxation time." For example, if we deal with a sample that is initially unmagnetized, the magnetization process is described by an exponential rise to the equilibrium:

$$n = n_0(1 - e^{-t/T_1}) \tag{19}$$

That is, T_1 characterizes the time needed to magnetize an unmagnetized sample.

We may now combine the two rate equations for dn/dt, to find the combined transition rate due to both thermal processes and transitions induced by the applied alternating field:

$$\frac{dn}{dt} = -2Wn + \frac{n_0 - n}{T_1} \tag{20}$$

In the steady state, Eq. (20) tells us that

$$n = \frac{n_0}{1 + 2WT_1} \tag{21}$$

Therefore, as long as $2WT_1 \ll 1$, $n = n_0$, and the absorption of energy from the alternating field does not disturb the populations much from their thermal equilibrium values. The rate of absorption of energy dE/dt is given by

$$\frac{dE}{dt} = n\hbar\omega W = n_0\hbar\omega \frac{W}{1 + 2WT_1} \tag{22}$$

We shall see later that W is proportional to the square of the alternating magnetic field. Therefore Eq. (22) tells us that we can increase the power absorbed by the nuclei by increasing the amplitude of the alternating field, as long as $2WT_1 \ll 1$. However, once W is large enough so that $W \sim 1/2T_1$, this statement is no longer true. The power absorbed levels off despite an increase in W. This effect is called "saturation." Provided one has enough information to compute W (a situation often realized), one can measure T_1 by observing the saturation effect.

We have now seen several quantities that will be important in describing a magnetic resonance. The quantity T_1 will clearly be related to the microscopic details of both the nuclear system and the reservoir. We shall wish to consider what mechanisms may give rise to spin-lattice relaxation, and how to compute T_1 for any assumed mechanism. In the early work on nuclear resonance, it was feared that the spin-lattice relaxation might be so slow that a population excess might not be achieved within reasonable times. The famous Dutch physicist C. J. Gorter, who has made so many of the important discoveries and proposals in connection with magnetic relaxation, was the first person to look for a magnetic resonance in bulk matter.† That he failed was probably due to his bad luck in having a sample which was easily saturated because of its long T_1.

When Purcell, Pound, and Torrey†† first looked for a resonance of protons in paraffin, they allowed the nuclei to sit in the magnetic field H_0 for a long time before even attempting a resonance. They used a value of alternating field sufficiently low to allow them time to observe a resonance even though T_1 were many seconds. Their efforts, as with those of Bloch, Hansen, and Packard,§ were made independently of Gorter's.

We have also seen that the rate of absorption is related to the transition rate W. An estimate of the size of the resonance absorption is basic to a decision about whether or not a resonance might be observed. We shall wish to consider how to calculate W. Moreover, since no resonance line is perfectly sharp, we expect that

† C. J. Gorter and L. J. F. Broer, *Physica*, 9: 591 (1942).
†† E. M. Purcell, H. C. Torrey, and R. V. Pound, *Phys. Rev.*, 69: 37 (1946).
§ F. Bloch, W. W. Hansen, and M. Packard, *Phys. Rev.*, 69: 127 (1946).

the factors governing the width of the spectral line will be of interest. Closely related is the question of what magnetic field to use in the relation $\omega = \gamma H_0$, for the nuclei are never bare. There will be magnetic fields due to electrons as well as due to other nuclei, which must be added to the external field. These fields produce effects of greatest interest, such as the splitting of the proton resonance of ethyl alcohol (CH_3CH_2OH) into three lines of relative intensities 3:2:1. They are also responsible for the fact that there is a nuclear resonance in ferromagnets even in the absence of an applied static magnetic field.

CHAPTER 2

BASIC THEORY

2·1 MOTION OF ISOLATED SPINS—CLASSICAL TREATMENT

We begin our study of the basic theory with a classical description of the motion of a spin in an external magnetic field **H**, assuming that **H** may possibly vary with time. **H** will produce a torque on the magnetic moment $\boldsymbol{\mu}$ of amount $\boldsymbol{\mu} \times \mathbf{H}$. If we applied a magnetic field to an ordinary bar magnet, mounted with bearings so that it could turn at will, the magnet would attempt to line up along the direction of **H**. If **H** were constant in time and if the bearings were frictionless, the magnet would actually oscillate about the equilibrium direction. If the bearings were not frictionless, the oscillations would die out as the magnet gave up energy to the bearings, until eventually it would be lined up along **H**.

When the magnet also possesses angular momentum, the situation is modified, since it now acts like a gyroscope. As we shall see, in the event of frictionless bearings, the moment would remain at fixed angle with respect to **H** (providing **H** is constant in time), but would precess about it. The conversion of energy back and forth between potential energy and kinetic energy would not occur. It would still be true, however, that if the bearings possessed friction, the magnet would eventually become parallel to a static field **H**. As we shall see, the friction corresponds to relaxation processes such as T_1.

The equation of motion of the magnet is found by equating the torque with the rate of change of angular momentum, **J**.

$$\frac{d\mathbf{J}}{dt} = \boldsymbol{\mu} \times \mathbf{H} \tag{1}$$

Since $\boldsymbol{\mu} = \gamma\mathbf{J}$, we may eliminate **J**, getting

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times (\gamma\mathbf{H}) \tag{2}$$

This equation, which holds regardless of whether or not **H** is time dependent, tells us that at any instant the changes in $\boldsymbol{\mu}$ are perpendicular to both $\boldsymbol{\mu}$ and **H**. Refer to Fig. 2.1 and consider the tail of the vector $\boldsymbol{\mu}$ as fixed; the tip of the vector is therefore moving out of the paper. The angle θ between $\boldsymbol{\mu}$ and **H** does not change. If **H** is independent of time, the vector $\boldsymbol{\mu}$ therefore generates a cone.

One can proceed with the solution of Eq. (2) by standard methods of differential equations for various assumed time dependences of **H**. We shall find it most useful for our future work, however, to introduce a special technique: the use of a rotating coordinate system.

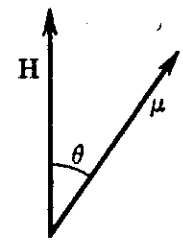

FIG. 2.1. Relation of $\boldsymbol{\mu}$ to **H**.

Consider a vector function of time $\mathbf{F}(t)$, which we may write in terms of its components $F_x(t)$, $F_y(t)$, $F_z(t)$, along a set of rectangular coordinates. In terms of the corresponding unit vectors **i**, **j**, and **k**, we have

$$\mathbf{F} = \mathbf{i}F_x + \mathbf{j}F_y + \mathbf{k}F_z \tag{3}$$

Ordinarily we think of **i**, **j**, and **k** as being constant in time, but we shall wish to be more general. Since their lengths are fixed, they can at most rotate. We shall assume they rotate with an instantaneous angular velocity $\boldsymbol{\Omega}$. Then

$$\frac{d\mathbf{i}}{dt} = \boldsymbol{\Omega} \times \mathbf{i} \tag{4}$$

The time derivative of **F** is therefore

$$\begin{aligned}\frac{d\mathbf{F}}{dt} &= \mathbf{i}\frac{dF_x}{dt} + F_x\frac{d\mathbf{i}}{dt} + \mathbf{j}\frac{dF_y}{dt} + F_y\frac{d\mathbf{j}}{dt} + \mathbf{k}\frac{dF_z}{dt} + F_z\frac{d\mathbf{k}}{dt} \\ &= \mathbf{i}\frac{dF_x}{dt} + \mathbf{j}\frac{dF_y}{dt} + \mathbf{k}\frac{dF_z}{dt} + \boldsymbol{\Omega} \times (\mathbf{i}F_x + \mathbf{j}F_y + \mathbf{k}F_z) \\ &= \frac{\delta\mathbf{F}}{\delta t} + \boldsymbol{\Omega} \times \mathbf{F}\end{aligned} \tag{5}$$

where we have introduced the symbol $\delta\mathbf{F}/\delta t$, representing the time rate of change of **F** with respect to the coordinate system **i**, **j**, **k**. For example, when $\delta\mathbf{F}/\delta t = 0$, the components of **F** along **i**, **j**, and **k** do not change in time.

By making use of Eq. (5), we can rewrite the equation of motion of $\boldsymbol{\mu}$ in terms of a coordinate system rotating with an as yet arbitrary angular velocity $\boldsymbol{\Omega}$:

$$\frac{\delta\boldsymbol{\mu}}{\delta t} + \boldsymbol{\Omega} \times \boldsymbol{\mu} = \boldsymbol{\mu} \times \gamma\mathbf{H} \tag{6}$$

or

$$\frac{\delta\boldsymbol{\mu}}{\delta t} = \boldsymbol{\mu} \times (\gamma\mathbf{H} + \boldsymbol{\Omega}) \tag{7}$$

Equation (7) tells us that the motion of $\boldsymbol{\mu}$ in the rotating coordinate system obeys the same equation as in the laboratory system, *provided* we replace the actual magnetic field **H** by an effective field $\mathbf{H}_e$:

$$\mathbf{H}_e = \mathbf{H} + \frac{\boldsymbol{\Omega}}{\gamma} \tag{8}$$

We can now readily solve for the motion of $\boldsymbol{\mu}$ in a static field $\mathbf{H} = \mathbf{k}H_0$ by choosing $\boldsymbol{\Omega}$ such that $\mathbf{H}_e = 0$. That is, we take $\boldsymbol{\Omega} = -\gamma H_0\mathbf{k}$. Since in this reference frame $\delta\boldsymbol{\mu}/\delta t = 0$, $\boldsymbol{\mu}$ remains fixed with respect to $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$. The motion with respect to the laboratory is therefore that of a vector fixed in a set of axes which themselves rotate at $\boldsymbol{\Omega} = -\gamma H_0\mathbf{k}$. In other words, $\boldsymbol{\mu}$ rotates at an angular velocity $\boldsymbol{\Omega} = -\gamma H_0\mathbf{k}$ with respect to the laboratory. The angular frequency γH_0 is called the "Larmor frequency."

We are struck by the fact that the classical precession frequency $\boldsymbol{\Omega}$ is identical in magnitude with the angular frequency needed for magnetic resonance absorption, as found by elementary quantum theory. Let us therefore look more closely at the quantum mechanical description.

2.2 QUANTUM MECHANICAL DESCRIPTION OF SPIN IN A STATIC FIELD

We have seen that the quantum mechanical description of a spin in a static field gave energies in terms at the quantum number m, which was an eigenvalue of the component of spin, I_z, parallel to the static field H_0. The energies E_m were

$$E_m = -\gamma\hbar H_0 m \tag{1}$$

The corresponding eigenfunctions of the time-independent Schrödinger equation may then be denoted by $u_{I,m}$. The time-dependent solution corresponding to a particular value of m is therefore

$$\Psi_{I,m}(t) = u_{I,m}e^{-(i/\hbar)E_m t} \tag{2}$$

The most general time-dependent solution $\Psi(t)$ is therefore

$$\Psi(t) = \sum_{m=-I}^{+I} c_m u_{I,m}e^{-(i/\hbar)E_m t} \tag{3}$$

where the c_m's are complex constants. We may compute the expectation value of any observable by means of $\Psi(t)$, as we can illustrate with the x-component of magnetic moment:

$$\langle\mu_x(t)\rangle = \int \Psi^*(t)\mu_x\Psi(t)\, d\tau^{\dagger} \tag{4}$$

We have emphasized that the expectation value of μ_x, $\langle\mu_x\rangle$ will vary in time by explicitly writing it as a function of time.

By using the fact that $\mu_x = \gamma\hbar I_x$, and that $\Psi(t)$ is given by Eq. (3), we find

$$\langle\mu_x(t)\rangle = \sum_{m,m'} \gamma\hbar c^*_{m'}c_m(m'|I_x|m)e^{(i/\hbar)(E_{m'}-E_m)t} \tag{5}$$

where

$$(m'|I_x|m) \equiv \int u^*_{Im'}I_x u_{Im}\, d\tau \tag{6}$$

† We write a variable of integration $d\tau$ in the expression for the expectation value, in analogy to that which we would do for a spatial coordinate x, y, z or angular coordinates θ, ϕ. For spin, the notation is to be thought of as a symbolic representation of the scalar product of the two functions $\Psi(t)$ and $\mu_x\Psi(t)$.

is a time-independent matrix element. Expressions similar to Eq. (5) would hold for any operator. We note that the expectation value will in general be time dependent, will consist of a number of terms oscillating harmonically, and that the possible frequencies

$$\frac{E_{m'} - E_m}{\hbar} \tag{7}$$

are just those which correspond to the frequency of absorption or emission between states m and m'. Of course it was the assumption that observable properties of any quantum system had to be given by expressions such as Eq. (5), which was the basis of Heisenberg and Born's formulation of the quantum theory in matrix form.

Since matrix elements $(m'|I_x|m)$ vanish unless $m' = m \pm 1$, we see that all the terms of Eq. (5) have an angular frequency of either $+\gamma H_0$ or $-\gamma H_0$. Their sum must also contain just γH_0. The expectation value $\langle \mu_x(t) \rangle$ therefore oscillates in time at the classical precession frequency.

It is convenient at this point to introduce the famous raising and lowering operators I^+ and I^-, defined by the equations

$$\begin{aligned} I^+ &= I_x + iI_y \\ I^- &= I_x - iI_y \end{aligned} \tag{8}$$

We may express I_x or I_y in terms of I^+ and I^- by solving Eq. (8), getting

$$\begin{aligned} I_x &= \frac{1}{2}[I^+ + I^-] \\ I_y &= \frac{1}{2i}[I^+ - I^-] \end{aligned} \tag{9}$$

The operators are called "raising" or "lowering" because of the effect they produce when they operate on a function u_{Im}:

$$\begin{aligned} I^+ u_{I,m} &= \sqrt{I(I+1) - m(m+1)}\, u_{I,m+1} \\ I^- u_{I,m} &= \sqrt{I(I+1) - m(m-1)}\, u_{I,m-1} \end{aligned} \tag{10}$$

I^+ turns $u_{I,m}$ into a function whose m value has been raised by one unit. We see, therefore, that $(m'|I^+|m)$ vanishes unless $m' = m + 1$, while $(m'|I^-|m)$ vanishes unless $m' = m - 1$. Van Vleck has characterized these as "sharper" selection rules than those of the operators I_x or I_y, which may join a state $u_{I,m}$ with either $u_{I,m+1}$ or $u_{I,m-1}$.

In order to gain further insight into the physical significance of the general expression for $\langle \mu_x(t) \rangle$, Eq. (5), we now consider the form it takes for a spin of $\frac{1}{2}$. By using the fact that the diagonal matrix elements of I_x vanish, we get

$$\begin{aligned} \langle \mu_x(t) \rangle = \gamma\hbar[&c^*_{1/2} c_{-1/2} (\tfrac{1}{2}|I_x|-\tfrac{1}{2}) e^{-(i\gamma H_0 t)} \\ &+ c^*_{-1/2} c_{1/2} (-\tfrac{1}{2}|I_x|\tfrac{1}{2}) e^{(i\gamma H_0 t)}] \end{aligned} \tag{11}$$

It is convenient to define a quantity $\omega_0 = \gamma H_0$. As we have seen, ω_0 is the angular frequency we must apply to produce resonance and is also the classical precession frequency. By utilizing the fact that $(\frac{1}{2}|I_x|-\frac{1}{2})$ is the complex conjugate of

$(-\frac{1}{2}|I_x|\frac{1}{2})$, and using the symbol "Re" for "take the real part of," we get

$$\langle \mu_x(t) \rangle = 2\gamma\hbar \mathrm{Re}[c^*_{1/2} c_{-1/2} (\tfrac{1}{2}|I_x|-\tfrac{1}{2}) e^{-i\omega_0 t}] \tag{12}$$

We evaluate the matrix element by means of Eqs. (9) and (10), getting $(\frac{1}{2}|I_x|-\frac{1}{2}) = \frac{1}{2}$.

It is convenient at this point to express the c's in terms of two real, positive quantities a and b, and two other real quantities (which may be positive or negative) α and β:

$$\begin{aligned} c_{1/2} &= a e^{i\alpha} \\ c_{-1/2} &= b e^{i\beta} \end{aligned} \tag{13}$$

The normalization of the wave function gives us $a^2 + b^2 = 1$. These give us

$$\langle \mu_x(t) \rangle = \gamma\hbar ab \cos(\alpha - \beta + \omega_0 t) \tag{14a}$$

Similarly we find

$$\begin{aligned} \langle \mu_y(t) \rangle &= -\gamma\hbar ab \sin(\alpha - \beta + \omega_0 t) \\ \langle \mu_z(t) \rangle &= \gamma\hbar \left(\frac{a^2 - b^2}{2} \right) \end{aligned} \tag{14b}$$

We note that both $\langle \mu_x \rangle$ and $\langle \mu_y \rangle$ oscillate in time at the Larmor frequency γH_0, but that $\langle \mu_z \rangle$ is independent of time. Moreover the maximum amplitudes of $\langle \mu_x \rangle$ and $\langle \mu_y \rangle$ are the same. If we define

$$\langle \boldsymbol{\mu} \rangle \equiv \mathbf{i}\langle \mu_x \rangle + \mathbf{j}\langle \mu_y \rangle + \mathbf{k}\langle \mu_z \rangle \tag{15}$$

and utilize the fact that $\langle \mu_x \rangle^2 + \langle \mu_y \rangle^2 =$ constant, a fact readily verified from Eq. (14), we see that $\langle \boldsymbol{\mu} \rangle$ behaves as does a vector making a fixed angle with the z-direction, precessing in the x-y plane.

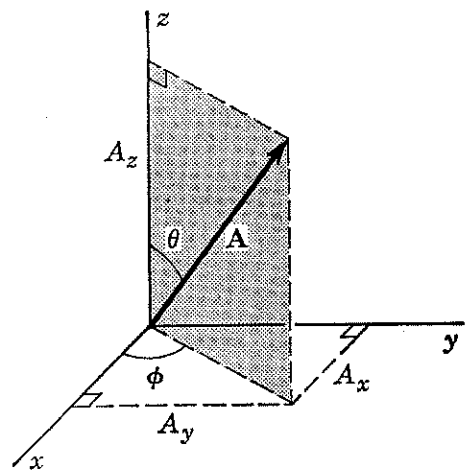

FIG. 2.2. Relationship of the components A_x, A_y, and A_z of a vector **A** to the polar angles θ, ϕ, and the magnitude A.

In terms of polar coordinates θ, ϕ, (see Fig. 2.2), any vector **A** may be written as

$$\begin{aligned} A_x &= \mathrm{A} \sin\theta \cos\phi \\ A_y &= \mathrm{A} \sin\theta \sin\phi \\ A_z &= \mathrm{A} \cos\theta \end{aligned} \tag{16}$$

By means of algebraic manipulation one can show that

$$\langle \mu_x \rangle = \frac{\gamma\hbar}{2} \sin\theta \cos\phi$$

$$\langle \mu_y \rangle = \frac{\gamma\hbar}{2} \sin\theta \sin\phi \tag{17}$$

$$\langle \mu_z \rangle = \frac{\gamma\hbar}{2} \cos\theta$$

provided

$$\phi = \beta - \alpha - \omega_0 t$$

$$a^2 = \frac{1 + \cos\theta}{2} \tag{18}$$

One may look on Eq. (18) as a formal change of variables, of course, but the results of Eq. (17) tell us that there is a simple physical significance; the expectation value of the operator $\boldsymbol{\mu}$ acts as does a vector of length $\gamma\hbar/2$, whose direction is given by the spherical coordinates θ, ϕ. If the orientation is specified at any time, it can be found at future times by recognizing that it precesses at angular velocity ω_0 in the negative ϕ direction. The orientation may be specified quite arbitrarily (by specifying a or b and $\beta - \alpha$). We emphasize that an *arbitrary* orientation can be specified, since sometimes the belief is erroneously held that spins may only be found pointing either parallel or antiparallel to the quantizing field. One of the beauties of the quantum theory is that it contains features of both discreteness and continuity. In terms of the two quantum states with $m = \pm\frac{1}{2}$ we can describe an *expectation* value of magnetization which may go all the way from parallel to antiparallel, including all values in between. Thus a wave function with $a = b$ has an expectation value corresponding to a magnetization lying somewhere in the x-y plane (that is, with vanishing z-component). Just where in the plane it points is given by the complex phase $\alpha - \beta$, as well as the time at which we wish to know the orientation.

It is useful to consider briefly what we should expect for the wave function if we took a sample of many non-interacting spins which were in thermal equilibrium. There will be a wave function for each spin, but in general it will not be in one of the eigenstates ($m = +\frac{1}{2}$ or $m = -\frac{1}{2}$); rather it will be in some linear combination. For a given spin, there will be a particular set of values for a, b, α, β. The values will differ from spin to spin. For example, we have a distribution of the quantity $\alpha - \beta$ that gives the spin orientation in the x-y plane at $t = 0$. If the spins are in thermal equilibrium, the expectation value of the total magnetization must be parallel to the magnetic field. We expect, therefore, that there will be no preference for any one value of $\alpha - \beta$ over any other. That is, the spins will have a random distribution of $\alpha - \beta$. On the other hand, since the spins will be polarized to some extent, we expect to find a larger than b more often than b is larger than a. That is, the average value of a must be larger than the average value of b. Since an observable quantity can be expressed in the form of Eq. (5), we see that we can specify either the individual c_m's or the complex products $c^*_{m'}c_m$, which we shall label $P_{mm'}$ for convenience.

$$P_{mm'} = c^*_{m'}c_m$$

For our example:

$$P_{1/2\ 1/2} = a^2$$
$$P_{-1/2\ -1/2} = b^2$$
$$P_{1/2\ -1/2} = abe^{i(\alpha-\beta)}$$
$$P_{-1/2\ 1/2} = abe^{i(\beta-\alpha)}$$

We may consider the $P_{mm'}$'s to be the elements of a complex matrix P. Notice that the diagonal elements ($m = m'$) give the probabilities of occupation of the various states, while the off-diagonal elements are closely related to the components of magnetic moment perpendicular to the static field. We shall make use in a subsequent section of the average of the matrix P over a statistical ensemble. The statement that in thermal equilibrium the magnetization will be parallel to the field amounts to saying that the average over the ensemble of $P_{mm'}$ for $m' \neq m$ is zero, whereas the average for $m = m'$ is the Boltzmann factor describing the probability of finding the state occupied.

(Of course, in the quantum theory, even for a number of spins with *identical* wave functions, any experiment that counts the number of spins in the various m states will find a statistical distribution not related, however, to temperature.)

2·3 EQUATIONS OF MOTION OF THE EXPECTATION VALUE

The close correspondence of the classical and quantum mechanical treatments is made particularly clear by examination of a differential equation relating the time variations of the expectation values $\langle\mu_x\rangle$, $\langle\mu_y\rangle$, and $\langle\mu_z\rangle$. The equation is based on a well-known formula whose derivation we sketch.

Suppose we have a pair of wave functions $\Psi(t)$ and $\Phi(t)$, both of which are solutions of the same Schrödinger equation:

$$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = \mathcal{H}\Psi \qquad -\frac{\hbar}{i}\frac{\partial\Phi}{\partial t} = \mathcal{H}\Phi \tag{1}$$

Let us have some operator F that has no explicit time dependence. Then

$$\frac{d}{dt}\int \Phi^* F\Psi\, d\tau = \frac{i}{\hbar}\int \Phi^*(\mathcal{H}F - F\mathcal{H})\Psi\, d\tau \tag{2}$$

This equation is readily derived from the fact that

$$\frac{d}{dt}\int \Phi^* F\Psi\, d\tau = \int \frac{\partial\Phi^*}{\partial t} F\Psi\, dt + \int \Phi^* F\frac{\partial\Psi}{\partial t}\, d\tau \tag{3}$$

into which we substitute expressions for the time derivative taken from Eq. (1).†

It is convenient to write Eq. (2) in operator form. There is no problem with the right-hand side: It is simply $(i/\hbar)(\mathcal{H}F - F\mathcal{H})$. For the left-hand side we must define some new notation. We define the operator dF/dt by the equation

$$\int \Phi^* \frac{dF}{dt}\Psi\, d\tau = \frac{d}{dt}\int \Phi^* F\Psi\, d\tau \tag{4}$$

† To prove Eq. (2), one must use the fact that $\mathcal{H}$ is an Hermitian operator. (See discussion in Section 2.5.)

That is to say, dF/dt does *not* mean to take the derivative of F with respect to t. Such a derivative vanishes, since F does not contain the variable t. Rather dF/dt is a symbol that has the meaning of Eq. (4). By using dF/dt in this symbolic sense, we have

$$\frac{dF}{dt} = \frac{i}{\hbar}[\mathcal{H}, F] \tag{5}$$

where $[\mathcal{H}, F]$ is the usual commutator $\mathcal{H}F - F\mathcal{H}$. We may use this formalism to compute the time derivative of the expectation values of μ_x, μ_y, and μ_z. We define the x-, y-, z-axes as being fixed in space but with the z-axis coinciding at an instant with the direction of the magnetic field. (In this way we include both static and time-varying fields.) Then

$$\mathcal{H} = -\gamma\hbar H I_z \tag{6}$$

We shall wish to use the commutation relations for the components of angular momentum, all of which may be obtained by cyclic permutation from

$$[I_x, I_y] = iI_z \tag{7}$$

Then

$$\begin{aligned}\frac{dI_x}{dt} &= \frac{i}{\hbar}[\mathcal{H}, I_x] \\ &= -\gamma H_0 i[I_z, I_x] \\ &= \gamma H_0 I_y\end{aligned} \tag{8a}$$

Similarly,

$$\begin{aligned}\frac{dI_y}{dt} &= -\gamma H_0 I_x \\ \frac{dI_z}{dt} &= 0\end{aligned} \tag{8b}$$

These equations are the component equations of the vector operator equation

$$\frac{d\mathbf{I}}{dt} = \mathbf{I} \times \gamma\mathbf{H} \tag{9}$$

where

$$\frac{d\mathbf{I}}{dt} = \mathbf{i}\frac{dI_x}{dt} + \mathbf{j}\frac{dI_y}{dt} + \mathbf{k}\frac{dI_z}{dt} \tag{10}$$

Therefore, since $\boldsymbol{\mu} = \gamma\hbar\mathbf{I}$, we have the equation for the expectation value of magnetization,

$$\frac{d\langle\boldsymbol{\mu}\rangle}{dt} = \langle\boldsymbol{\mu}\rangle \times \gamma\mathbf{H} \tag{11}$$

which is just the classical equation. In words, Eq. (11) tells us that the expectation value of the magnetic moment obeys the classical equation of motion. Equation (11) was derived for the expectation value of a magnetic moment of a single spin. If we have a group of spins with moments $\boldsymbol{\mu}_k$, for the kth spin, their total magnetic moment $\boldsymbol{\mu}$ is defined as

$$\boldsymbol{\mu} = \sum_k \boldsymbol{\mu}_k \tag{12}$$

If the spins do not interact with one another, it is easy to prove that Eq. (11) also holds true for the expectation value of the total magnetization. Since, in practice we measure the results of a number of spins simultaneously, the experimental measurements of magnetization measure the expectation value of the various components of magnetization. That is, the experimentally determined bulk magnetization is simply the expectation value of the total magnetic moment. Therefore the classical equation correctly describes the dynamics of the magnetization, provided the spins may be thought of as not interacting with one another.

It is important to bear in mind that *Eq. (11) holds true for a time dependent* **H**, *not simply a static one.* Therefore it enables us to use a classical picture for studying the effects produced by alternating magnetic fields. We turn to that in the next section.

2·4 EFFECT OF ALTERNATING MAGNETIC FIELDS

The effect of an alternating magnetic field $H_x(t) = H_{x0} \cos \omega t$ is most readily analyzed by breaking it into two rotating components, each of amplitude H_1, one rotating clockwise and the other counterclockwise.

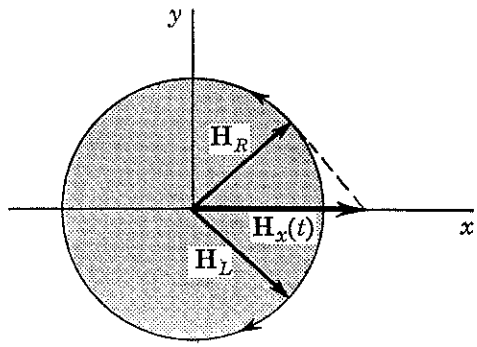

FIG. 2.3. Decomposition of a linear oscillating field into two rotating elements.

We denote the rotating fields by $\mathbf{H}_R$ and $\mathbf{H}_L$:

$$\begin{aligned} \mathbf{H}_R &= H_1[\mathbf{i} \cos \omega t + \mathbf{j} \sin \omega t] \\ \mathbf{H}_L &= H_1[\mathbf{i} \cos \omega t - \mathbf{j} \sin \omega t] \end{aligned} \tag{1}$$

Note that $\mathbf{H}_L$ and $\mathbf{H}_R$ differ simply by a replacement of ω by $-\omega$. Since one component will rotate in the same sense as the precession of the moment, and the other in the opposite sense, one can show that near resonance the counter-rotating component may be neglected. We shall make that approximation in what follows. Alternatively we can assume that we are finding the exact solution of a problem in which the experimental arrangement has produced a rotating field; for example, by use of two identical coils at right angles to each other and with alternating currents 90 degrees out of phase.

We shall assume we have only the field $\mathbf{H}_R$, but this is no loss in generality because the use of a negative ω will convert it to $\mathbf{H}_L$. In order to reserve the symbol ω for a positive quantity, we shall introduce the symbol ω_z, the component of ω along the z-axis. ω_z may therefore be positive or negative. We may, therefore write

$$\mathbf{H}_1 = H_1[\mathbf{i} \cos \omega_z t + \mathbf{j} \sin \omega_z t] \tag{2}$$

which will give us either sense of rotation, depending on the sign of ω_z.

We now ask for the equation of motion of a spin including the effects both of $\mathbf{H}_1(t)$ and of the static field $\mathbf{H}_0 = \mathbf{k}H_0$.

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times \gamma[\mathbf{H}_0 + \mathbf{H}_1(t)] \tag{3}$$

The time dependence of $\mathbf{H}_1$ can be eliminated by using a coordinate system that rotates about the z-direction at frequency ω_z. In such a coordinate system, $\mathbf{H}_1$ will be static. Since the axis of rotation coincides with the direction of $\mathbf{H}_0$, $\mathbf{H}_0$ will also be static. Let us take the x-axis in the rotating frame along $\mathbf{H}_1$. Then Eq. (3) becomes

$$\frac{\delta\boldsymbol{\mu}}{\delta t} = \boldsymbol{\mu} \times [\mathbf{k}(\omega_z + \gamma H_0) + \mathbf{i}\gamma H_1] \tag{4a}$$

Notice that we have encountered two effects in making the transformation of Eq. (3) to Eq. (4). The first is associated with the derivative of the rotating unit vectors and gives the term ω_z. The second is associated with expressing the vectors $\mathbf{H}_0$ and $\mathbf{H}_1$ in terms of their components in the rotating system and gives rise to the conversion of $\mathbf{H}_1$ from a rotating to a static field. Eq. (4) may be rewritten to emphasize that near resonance $\omega_z + \gamma H_0 \cong 0$, by setting $\omega_z = -\omega$, where ω is now positive (we assume here that γ is positive). Then

$$\begin{aligned} \frac{\delta\boldsymbol{\mu}}{\delta t} &= \boldsymbol{\mu} \times \gamma\left[\left(H_0 - \frac{\omega}{\gamma}\right)\mathbf{k} + H_1\mathbf{i}\right] \\ &= \boldsymbol{\mu} \times \mathbf{H}_{\text{eff}} \end{aligned} \tag{4b}$$

where

$$\mathbf{H}_{\text{eff}} = \mathbf{k}\left(H_0 - \frac{\omega}{\gamma}\right) + H_1\mathbf{i}$$

Physically Eq. (4b) states that in the rotating frame, the moment acts as though it experienced effectively a static magnetic field $\mathbf{H}_{\text{eff}}$. The moment therefore precesses in a cone of fixed angle about the direction of $\mathbf{H}_{\text{eff}}$ at angular frequency γH_{eff}. The situation is illustrated in Fig. 2.4 for a magnetic moment which, at $t = 0$, was oriented along the z-direction.

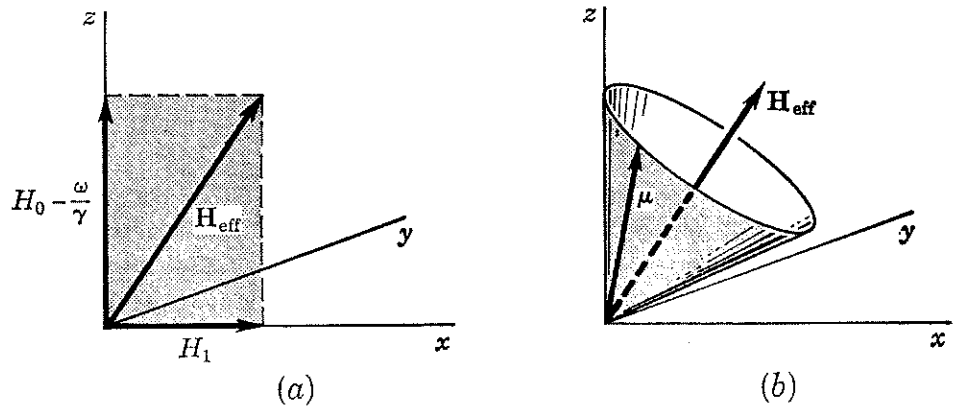

FIG. 2.4. (a) Effective field. (b) Motion of the moment μ in the rotating coordinate system.

We notice that the motion of the moment is periodic. If it is initially oriented along the z-direction, it periodically returns to that direction. As it increases its

angle with the z-direction, its magnetic potential energy in the laboratory reference system changes (in the laboratory system the magnetic energy with respect to H_0 is much larger than that with respect to H_1, so we customarily neglect the latter). However, all the energy it takes to tilt μ away from $\mathbf{H}_0$ is returned in a complete cycle of μ around the cone. There is no net absorption of energy from the alternating field but rather alternately receiving and returning of energy.

Note that if H_0 is above resonance (that is, $H_0 > \omega/\gamma$), the effective field has a positive z-component, but when H_0 lies below the resonance ($H_0 < \omega/\gamma$), the effective field has a negative z-component.

If the resonance condition is fulfilled exactly ($\omega = \gamma H_0$), the effective field is then simply iH_1. A magnetic moment that is parallel to the static field initially will then precess in the y-z plane. That is, it will precess but remaining always perpendicular to $\mathbf{H}_1$. Periodically it will be lined up *opposed* to $\mathbf{H}_0$. If we were to turn on H_1 for a short time (that is, apply a wave train of duration t_w), the moment would precess through an angle $\theta = \gamma H_1 t_w$. If t_w were chosen such that $\theta = \pi$, the pulse would simply invert the moment. Such a pulse is referred to in the literature as a "180 degree pulse." If $\theta = \pi/2$ (90 degree pulse), the magnetic moment is turned from the z-direction to the y-direction. Following the turn-off of H_1, the moment would then remain at rest in the rotating frame, and hence precess in the laboratory, pointing normal to the static field.

These remarks suggest a very simple method of observing magnetic resonance, illustrated in Fig. 2.5. We put a sample of material we wish to study in a coil, the axis of which is oriented perpendicular to $\mathbf{H}_0$. In thermal equilibrium there

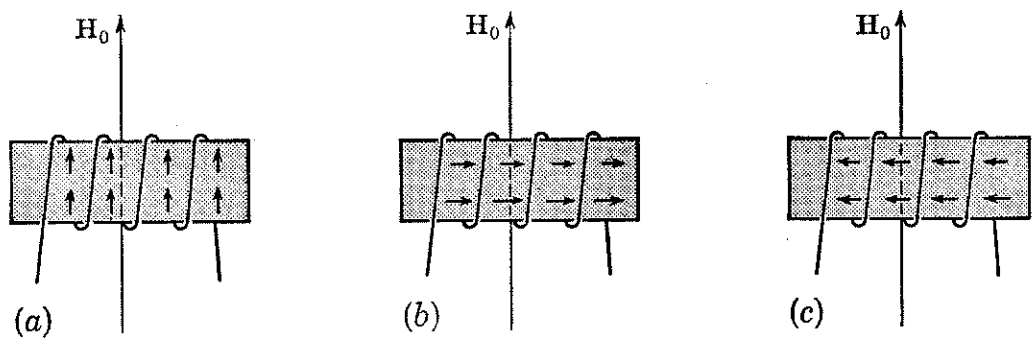

FIG. 2.5. (a) Coil containing sample. In thermal equilibrium an excess of moments is parallel to H_0. (b) and (c) Following a 90-degree pulse, the excess moments precess perpendicular to H_0.

will be an excess of moments pointing along $\mathbf{H}_0$. Application of an alternating voltage to the coil produces an alternating magnetic field perpendicular to H_0. By properly adjusting H_1 and t_w, we may apply a 90 degree pulse. Following the pulse, the excess magnetization will be perpendicular to $\mathbf{H}_0$ and will precess at angular frequency γH_0. As a result, the moments will produce a flux through the coil which will alternate as the spins precess. The resultant induced emf may be observed.

What we have suggested so far would indicate that the induced emf would persist indefinitely, but in practice, the interactions of the spins with their surroundings cause a decay. The decay may last in liquids for many milliseconds, but in solids it is more typically 100 μsec. Even during that short time, however, there are many precession periods. The technique we have described of observing the "free induction decay" (that is, decay "free" of H_1) is a commonly used technique

for observing resonances. It has the great virtue of enabling one to study the resonance signal in the absence of the voltages needed to produce H_1. Since oscillators always generate noise, such a scheme may be advantageous.

One interesting application of the rotating reference frame is to prove the following theorem, which is the basis of another technique for producing resonance signals. Suppose we have a magnetic field $\mathbf{H}_0$ of fixed magnitude whose direction we may vary (no other magnetic field is present). Let the magnetization $\mathbf{M}$ be parallel to $\mathbf{H}_0$ at $t = 0$. We may describe the changing direction of $\mathbf{H}_0$ by an angular velocity $\boldsymbol{\omega}$. Then the theorem states that if

$$\gamma H_0 \gg \omega$$

the magnetization $\mathbf{M}$ will turn with $\mathbf{H}_0$, always remaining aligned along $\mathbf{H}_0$ as $\mathbf{H}_0$ turns.

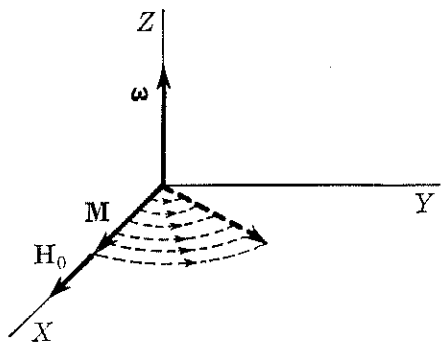

FIG. 2.6. Magnetic field $\mathbf{H}_0$, magnetization $\mathbf{M}$, and angular velocity $\boldsymbol{\omega}$ at $t = 0$.

To prove this theorem, let us assume $\boldsymbol{\omega}$ to be a constant in the z-direction. We can take it perpendicular to $\mathbf{H}_0$, since a component parallel to $\mathbf{H}_0$ produces no

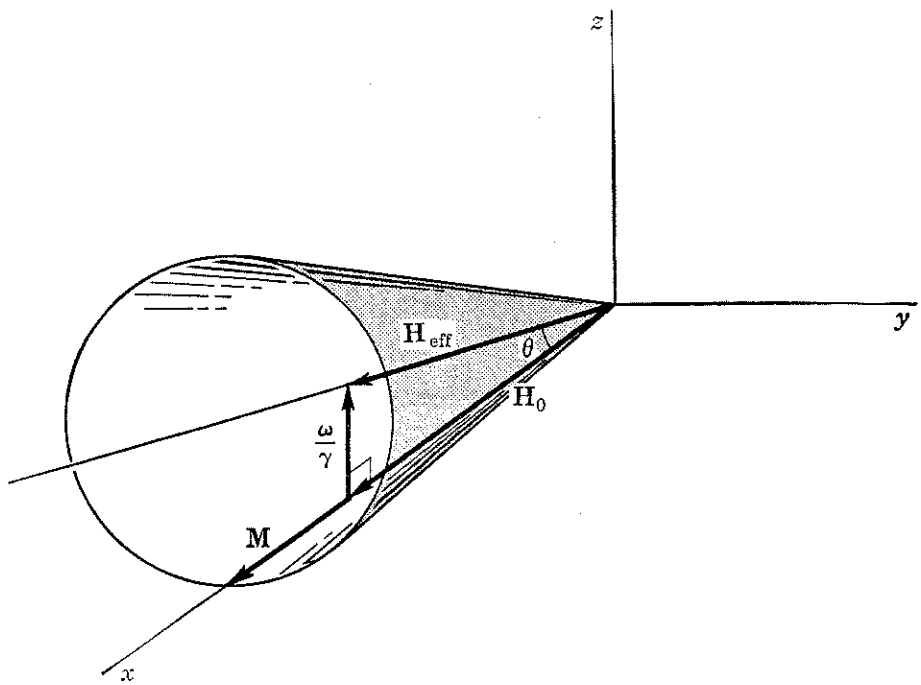

FIG. 2.7. Magnetization $\mathbf{M}$ and effective field $\mathbf{H}_{\text{eff}}$ in the rotating coordinate system x, y, z. The magnetization will precess about the effective field in the cone of angle θ shown.

effect. The relationships are shown in Fig. 2.6 at $t = 0$, with $\mathbf{M}$ and $\mathbf{H}_0$ taken parallel to each other and pointing in the X-direction in the laboratory. If we choose a reference frame x, y, z rotating at angular velcoity $\boldsymbol{\Omega}_R = \boldsymbol{\omega}$, $\mathbf{H}_0$ appears static, but we must add an effective field $\boldsymbol{\Omega}_R/\gamma$. Choosing the z- and Z-axes as parallel, and x to coincide with X at $t = 0$, the effective fields and magnetization at $t = 0$ are shown in Fig. 2.7.

The effective field in the rotating frame is static and given by

$$\mathbf{H}_{\text{eff}} = \mathbf{H}_0 + \frac{\boldsymbol{\Omega}_R}{\gamma}$$

$$= \mathbf{H}_0 + \frac{\boldsymbol{\omega}}{\gamma}$$

$\mathbf{M}$ will precess about $\mathbf{H}_{\text{eff}}$, making an angle θ such that

$$\tan\theta = \frac{\omega}{\gamma H_0} \tag{6}$$

$\mathbf{M}$ will therefore remain within an angle 2θ of $\mathbf{H}_0$. We see that if $\omega/\gamma H_0 \ll 1$, $\mathbf{M}$ and $\mathbf{H}_0$ remain parallel.

The fact that the magnetization follows the direction of the magnetic field when the field changes direction sufficiently slowly is described by the term *adiabatic*.

By utilizing this principle, one can turn to the case of a rotating magnetic field H_1 of frequency ω, perpendicular to a static field H_0. If one starts far below resonance, the magnetization is nearly parallel to the effective field in the rotating frame, $\sqrt{H_1^2 + [(\omega/\gamma) - H_0]^2}$. As one approaches resonance, both magnitude and direction of the effective field change, but if resonance is approached sufficiently slowly, $\mathbf{M}$ will remain parallel to $\mathbf{H}_{\text{eff}}$ in the rotating frame according to the theorem we have just proved. Thus, exactly at resonance, the magnetization will lie along H_1, making a 90 degree angle with H_0 (Fig. 2.8).

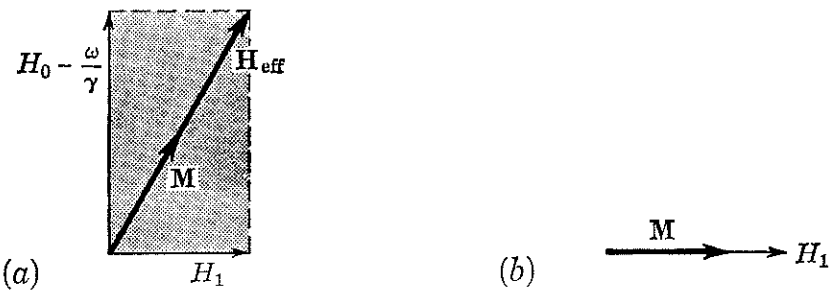

FIG. 2.8. (a) Magnetization $\mathbf{M}$ and effective field $\mathbf{H}_{\text{eff}}$ in the rotating frame, with $\mathbf{M}$ parallel to $\mathbf{H}_{\text{eff}}$. (b) The situation exactly at resonance, having approached resonance slowly, with $\mathbf{M}$ parallel to $\mathbf{H}_0$ when H_0 was far above resonance.

If one were to continue on through the resonance, the magnetization would end up by pointing in the negative z-direction. This technique of inverting $\mathbf{M}$ is very useful experimentally and is called "adiabatic inversion."

2·5 EXPONENTIAL OPERATORS

It will be useful to consider the quantum mechanical equivalent of the rotating coordinate transformation, but to do so, we shall need to employ several useful relations. We review them here for the convenience of the reader.

Suppose we have two wave functions, Φ and Ψ, that satisfy appropriate boundary conditions and have other satisfactory properties for some region of space, and suppose we have an operator F. F may be, for example, a component of spin. The operator is said to be Hermitian when

$$\int \Phi^* F \Psi \, d\tau = \int (F\Phi)^* \Psi \, d\tau \tag{1}$$

where the integrals are over the region of space designated. To prove that an operator is Hermitian requires some statement about the conditions Ψ and Φ are to satisfy, as well as a definition of the region. For example, if F is an operator involving derivatives, the proof that it is Hermitian may involve transforming the volume integral to a surface integral and requiring the integrand of the surface integral to vanish on the surface of the region.

Hermitian operators are important because their expectation values and eigenvalues are real. Therefore any operator that corresponds to a physically observable quantity must be Hermitian. Thus the operators I_x, I_y, and I_z are Hermitian. If they are Hermitian, it is easy to show from Eq. (1) that the operators $I^+ = I_x + iI_y$ and $I^- = I_x - iI_y$ are not.

In the theory of functions, it is useful to define the exponential function of the complex variable z:

$$e^z = 1 + z + \frac{z^2}{2!} + \frac{z^3}{3!} + \cdots$$

the power series converging for all z.

We define the function

$$e^F = 1 + F + \frac{F^2}{2!} + \frac{F^3}{3!} + \cdots$$

similarly, where F is now an operator. We shall be particularly interested in the function

$$e^{iF} = 1 + iF + \frac{(iF)^2}{2!} + \frac{(iF)^3}{3!} + \cdots \tag{2}$$

By using the series expansion, one can show that if F is Hermitian, e^{iF} is not. In fact

$$\int (e^{iF}\Phi)^* \Psi \, d\tau = \int \Phi^* e^{-iF} \Psi \, d\tau \tag{3}$$

The exponential function of operators obeys some of the same algebra as does the function of ordinary number, but as usual with operators, care must be taken whenever two non-commuting operators are encountered. Thus, if A and B are two operators, one can verify by means of the series expansion that

$$Ae^{iB} = e^{iB}A \tag{4a}$$

only if A and B commute. Likewise,

$$e^{i(A+B)} = e^{iA}e^{iB} \tag{4b}$$

only if A and B commute.

If A and B do not commute, another useful equation may still hold. Let us define C as the commutator of A and B:

$$[A, B] = AB - BA \equiv C$$

Suppose that C commutes with both A and B:

$$[A, C] = 0$$
$$[B, C] = 0$$

Then

$$e^{(A+B)} = e^{A}e^{B}e^{-C/2} = e^{C/2}e^{B}e^{A}$$

This theorem is proved in Appendix A.

Use of the exponential function provides a particularly simple method for obtaining a formal solution of Schrödinger's equation if the Hamiltonian does not depend explicitly on time. That is, if $\Psi(t)$ is the solution of

$$-\frac{\hbar}{i}\frac{\partial\Psi(t)}{\partial t} = \mathcal{H}\Psi(t) \tag{5}$$

then we can express $\Psi(t)$ in terms of its value at $t = 0$, $\Psi(0)$, by the equation

$$\Psi(t) = e^{-(i/\hbar)\mathcal{H}t}\Psi(0) \tag{6}$$

Equation (6) may be verified by direct substitution into Equation (5). If, for example, we consider the motion of a spin in a magnetic field so that $\mathcal{H} = -\gamma\hbar H_0 I_z$

$$\Psi(t) = e^{-(i/\hbar)(-\gamma\hbar H_0 I_z)t}\Psi(0) \tag{7}$$
$$= e^{i\omega_0 t I_z}\Psi(0)$$

where $\omega_0 = \gamma H_0$.

We know that H_0 produces a rotation of the magnetic moment at angular velocity $\boldsymbol{\Omega}$ given by $\boldsymbol{\Omega} = -\gamma H_0\mathbf{k}$. We shall call such a rotation "negative," since the component of angular velocity along the z-axis is negative. It is logical to suppose, then, that $\Psi(t)$ must correspond to the function $\Psi(0)$, referred, however, to axes rotated in the negative direction through an angle $\omega_0 t$. Thus $e^{-iI_z\phi}\Psi(0)$ should correspond to a function identical to $\Psi(0)$ referred to axes rotated through the positive angle ϕ. If we compute the expectation value or matrix elements of, for example, I_x, we find

$$\int \Psi^*(t) I_x \Psi(t)\, d\tau = \int (e^{i\omega_0 t I_z}\Psi(0))^* I_x e^{i\omega_0 t I_z}\Psi(0)\, d\tau$$
$$= \int \Psi^*(0) e^{-i\omega_0 t I_z} I_x e^{i\omega_0 t I_z}\Psi(0)\, d\tau \tag{8a}$$
$$= \int \Psi^*(0) I_{x'}(t)\Psi(0)\, d\tau$$

where

$$I_{x'}(t) \equiv e^{-i\omega_0 t I_z} I_x e^{i\omega_0 t I_z} \tag{8b}$$

The last line defines the operator $I_{x'}$. We can give a simple interpretation of Eq. (8) as follows:

The first integral, which gives $\langle I_x(t) \rangle$, corresponds to a precessing angular momentum arising from the effect on a time-independent operator I_x of a time-dependent function $\Psi(t)$. The last integral describes the effect on a time-dependent operator $I_{x'}(t)$ of a wave function $\Psi(0)$, which is independent of time. Since the precession is in the negative sense, the first integral involves a fixed operator and a wave function fixed with respect to axes that rotate in the negative sense. Therefore the last integral must describe an operator rotating in the *positive* sense with respect to the "fixed" wave function $\Psi(0)$.

It is a simple matter to show that $I_{x'}$ is related to I_x through a rotation of axes. Let us consider

$$e^{-iI_z\phi} I_x e^{iI_z\phi} = f(\phi) \tag{9}$$

We wish to find $f(\phi)$, to see what meaning we can ascribe to it. Of course we could simply expand the exponentials, and using the commutation laws, try to reduce the function to something tractable. A simpler method is to show first that $f(\phi)$ satisfies a simple differential equation and then solve the equation. We have

$$\frac{df}{d\phi} = e^{-iI_z\phi}(-iI_zI_x + iI_xI_z)e^{iI_z\phi} \tag{10}$$

But, since $[I_z, I_x] = iI_y$,

$$\frac{df}{d\phi} = e^{-iI_z\phi} I_y e^{iI_z\phi} \tag{11}$$

Likewise

$$\begin{aligned} \frac{d^2f}{d\phi^2} &= e^{-iI_z\phi}(-iI_zI_y + iI_yI_z)e^{iI_z\phi} \\ &= -e^{-iI_z\phi}(I_x)e^{iI_z\phi} = -f \qquad \text{or} \qquad \frac{d^2f}{d\phi^2} + f = 0 \end{aligned} \tag{12}$$

Therefore

$$f(\phi) = A\cos\phi + B\sin\phi$$

where we must evaluate the constants of integrations. (As we shall see, the "constants" are actually operators.) Clearly, $A = f(0)$, but from Eq. (9), $f(0) = I_x$.

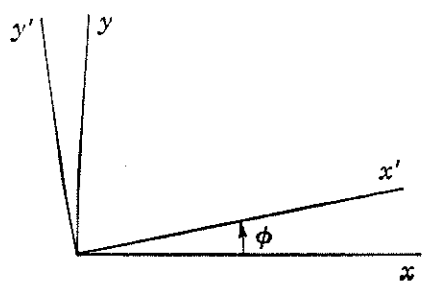

FIG. 2.9. Relation of axes x, y to x', y' and the angle ϕ.

Likewise, $B = f'(0) = I_y$, using Eq. (11). In this way we get

$$\begin{aligned} I_{x'} &\equiv e^{-iI_z\phi} I_x e^{iI_z\phi} = I_x \cos\phi + I_y \sin\phi \\ I_{y'} &\equiv e^{-iI_z\phi} I_y e^{iI_z\phi} = -I_x \sin\phi + I_y \cos\phi \\ I_{z'} &\equiv e^{-iI_z\phi} I_z e^{iI_z\phi} = I_z \end{aligned} \tag{13}$$

The quantities $I_{x'}$, $I_{y'}$, and $I_{z'}$ are clearly the components of angular momentum along a set of axes x', y', z' rotated with respect to x, y, z, as shown in Fig. 2.9. Therefore we see that we can use the exponential operator $e^{iI_z\phi}$ to generate rotations.

2·6 QUANTUM MECHANICAL TREATMENT OF A ROTATING MAGNETIC FIELD

We shall now use the exponential operators to perform the quantum mechanical equivalent of the classical "rotating coordinate" transformation. We shall consider a magnetic field H_1, which rotates at angular velocity ω_z, in addition to the static field $\mathbf{k}H_0$. The total field $\mathbf{H}(t)$ is then

$$\mathbf{H}(t) = \mathbf{i}H_1 \cos\omega_z t + \mathbf{j}H_1 \sin\omega_z t + \mathbf{k}H_0 \tag{1}$$

and the Schrödinger equation

$$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = -\boldsymbol{\mu}\cdot\mathbf{H}\Psi = -\gamma\hbar[H_0 I_z + H_1(I_x \cos\omega_z t + I_y \sin\omega_z t)]\Psi \tag{2}$$

By using Eq. (13) of the preceding section, we can write the Hamiltonian of Eq. (2) as

$$\mathcal{H} = -\gamma\hbar[H_0 I_z + H_1 e^{-i\omega_z t I_z} I_x e^{i\omega_z t I_z}] \tag{3}$$

We are tempted to try to "remove" the operator $e^{i\omega_z t I_z}$ from I_x and transfer it onto Ψ, much as the reverse of the steps of Eq. (8) of the preceding section. Accordingly we let

$$\Psi' = e^{i\omega_z t I_z}\Psi \tag{4}$$

or

$$\Psi = e^{-i\omega_z t I_z}\Psi'$$

The physical interpretation of Eq. (4) is that Ψ and Ψ' differ by a rotation of axes through an angle $\omega_z t$ (a rotating coordinate transformation).

Then

$$\frac{\partial\Psi}{\partial t} = -i\omega_z I_z e^{-i\omega_z t I_z}\Psi' + e^{-i\omega_z t I_z}\frac{\partial\Psi'}{\partial t} \tag{5}$$

We may substitute Eqs. (4) and (5) into Eq. (3), multiply both sides from the left by $e^{i\omega_z t I_z}$, and obtain

$$-\frac{\hbar}{i}\frac{\partial\Psi'}{\partial t} = -[\hbar(\omega_z + \gamma H_0)I_z + \gamma\hbar H_1 I_x]\Psi' \tag{6}$$

In Eq. (6) the time dependence of $\mathbf{H}_1(t)$ has been eliminated. In fact we recognize

it as representing the coupling of the spins with an effective *static* field

$$\mathbf{k}\left(H_0 + \frac{\omega_z}{\gamma}\right) + \mathbf{i}H_1$$

the effective field of our classical equations. The spins are therefore quantized along the effective field in the rotating coordinate system, the energy spacing being $\gamma\hbar H_{\text{eff}}$.

The wave function Ψ' given by Eq. (4) is related to the function Ψ by a coordinate rotation, the "forward" motion of I_x relative to a stationary Ψ having been replaced by a stationary I_x and "backward" rotating Ψ'. As usual, resonance occurs when $\omega_z \approx -\gamma H_0$. If we define the transformed Hamiltonian $\mathcal{H}'$ by

$$\mathcal{H}' = -[(\hbar\omega_z + \gamma\hbar H_0)I_z + \gamma\hbar H_1 I_x] \tag{7}$$

we can formally solve Eq. (6):

$$\Psi'(t) = e^{-(i/\hbar)\mathcal{H}'t}\Psi'(0) \tag{8a}$$

whence, using Eq. (4),

$$\Psi(t) = e^{-i\omega_z t I_z}e^{-(i/\hbar)\mathcal{H}'t}\Psi'(0) \tag{8b}$$

[Note that at $t = 0$, $\Psi(0) = \Psi'(0)$.]

Equation (8b) gives us a particularly compact way to express the solution of Schrödinger's equation when a rotating field is present.

We can illustrate the use of the wave function of Eq. (8b) by computing the time dependence of the expectation value of μ_z. Of course we know already what the result must be, since we have proved that the classical picture applies. Let us for simplicity assume that H_1 is applied exactly at resonance. Then, from Eq. (7),

$$\mathcal{H}' = -\gamma\hbar H_1 I_x \tag{9}$$

Then we have, using Eqs. (8b) and (9),

$$\begin{aligned}\langle\mu_z(t)\rangle &= \int \Psi^*(t)\mu_z\Psi(t)\,d\tau \\ &= \gamma\hbar\int (e^{-i\omega_z t I_z}e^{+i\gamma H_1 I_x t}\Psi(0))^* I_z(e^{-i\omega_z t I_z}e^{+i\gamma H_1 I_x t}\Psi(0))\,d\tau\end{aligned} \tag{10}$$

If we define ω_1,

$$\omega_1 \equiv \gamma H_1 \tag{11}$$

and use the fact that I_x and I_z are Hermitian, we get

$$\begin{aligned}\langle\mu_z(t)\rangle &= \gamma\hbar\int \Psi^*(0)e^{-i\omega_1 t I_x}e^{i\omega_z t I_z}I_z e^{-i\omega_z t I_z}e^{i\omega_1 t I_x}\Psi(0)\,d\tau \\ &= \gamma\hbar\int \Psi^*(0)e^{-i\omega_1 t I_x}I_z e^{i\omega_1 t I_x}\Psi(0)\,d\tau\end{aligned} \tag{12}$$

By using Eq. (13) of Section 2.6, we can write

$$e^{-i\omega_1 t I_x}I_z e^{i\omega_1 t I_x} = -I_y \sin\omega_1 t + I_z\cos\omega_1 t \tag{13}$$

Substituting in Eq. (12) we get

$$\langle \mu_z(t) \rangle = -\langle \mu_y(0) \rangle \sin \omega_1 t + \langle \mu_z(0) \rangle \cos \omega_1 t \tag{14}$$

If the magnetization lies along the z-axis at $t = 0$ so that $\langle \mu_y(0) \rangle = 0$, we get

$$\langle \mu_z(t) \rangle = \langle \mu_z(0) \rangle \cos \gamma H_1 t \tag{15}$$

Thus the z-magnetization oscillates in time at γH_1, corresponding to the precession of $\langle \boldsymbol{\mu} \rangle$ about H_1 in the rotating reference frame. It is important to note that in this picture, which neglects all interactions of spins with one another or the lattice, the magnetization continues oscillating between $+\langle \mu_z(0) \rangle$ and $-\langle \mu_z(0) \rangle$ indefinitely. This behavior is very different from that which we should expect from a time-independent transition probability such as we assumed in Chapter 1. The time-independent transitions occur only if some physical process spoils the coherent precession about H_1 in the rotating reference frame.

2·7 BLOCH EQUATIONS

Both quantum mechanical and classical descriptions of the motion of noninteracting spins have in common a periodic motion of the magnetization in the rotating frame. For example, if $\gamma H_0 = \omega$ and if the magnetization is parallel to the static field at $t = 0$, the magnetization precesses around H_1 in the rotating frame, becoming alternately parallel and antiparallel to the direction of the static field. Viewed from the laboratory frame, the magnetization is continuously changing its orientation with respect to the large static field. However, the energy that must be supplied to turn the spins from parallel to antiparallel to the static field is recovered as the spins return to being parallel to the static field. Thus there is no cumulative absorption over long times but rather an alternate absorption and recovery. The situation is reminiscent of that we described in the first chapter prior to introduction of the coupling to a thermal reservoir. (We note that there the system, however, simply equalized populations, whereas our present model predicts an alternating reversal of populations. The two models must therefore be based on differing assumptions.)

Without contact to a reservoir, we have no mechanism for the establishment of the magnetization. By analogy to the equation

$$\frac{dn}{dt} = \frac{n_0 - n}{T_1} \tag{1}$$

and recognizing that $M_z = \gamma \hbar n/2$, we expect that it would be reasonable for M_z to be established according to the equation

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \tag{2}$$

where M_0 is the thermal equilibrium magnetization. In terms of the static magnetic susceptibility χ_0 and the static magnetic field H_0, we have

$$M_0 = \chi_0 H_0 \tag{3}$$

We combine Eq. (2) with the equation for the driving of $\mathbf{M}$ by the torque to get

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} + \gamma(\mathbf{M} \times \mathbf{H})_z \tag{4}$$

Furthermore we wish to express the fact that in thermal equilibrium under a static field, the magnetization will wish to be parallel to H_0. That is, the x- and y-components must have a tendency to vanish. Thus

$$\begin{aligned} \frac{dM_x}{dt} &= \gamma(\mathbf{M} \times \mathbf{H})_x - \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= \gamma(\mathbf{M} \times \mathbf{H})_y - \frac{M_y}{T_2} \end{aligned} \tag{5}$$

We have here introduced the same relaxation time T_2 for the x- and y-directions, but have implied that it is different from T_1. That the transverse rate of decay may differ from the longitudinal is reasonable if we recall that, in contrast to the longitudinal decay, the transverse decay conserves energy in the static field. Therefore there is no necessity for transfer of energy to a reservoir for the transverse decay. (This statement is not strictly true and gives rise to important effects when saturating resonances in solids, as has been described by Redfield.)

On the other hand, the postulate of the particular (exponential) form of relaxation we have assumed must be viewed as being rather arbitrary. It provides a most useful postulate to describe certain important effects, but must not be taken too literally. According to Eq. (5), under the influence of a static field the transverse components would decay with a simple exponential. (This result is readily seen by transforming to a frame rotating at γH_0, where the effective field vanishes.)

A possible simple mechanism for T_2 for a solid in which each nucleus has nearby neighbors arises from the spread in precession rates produced by the magnetic field that one nucleus produces at another. If the nearest neighbor distance is r, we expect a typical nucleus to experience a local field $H_{\text{loc}} \sim \mu/r^3$ (due to the neighbors) either aiding or opposing the static field. As a result, if all nuclei were precessing in phase at $t = 0$, they would get out of step. In a time τ such that $\gamma H_{\text{loc}}\tau \cong 1$, there would be significant dephasing, and the vector sum of the moments would have thus diminished significantly. Since τ must therefore be comparable to T_2, a rough estimate for T_2 on this model is

$$T_2 = \frac{1}{\gamma H_{\text{loc}}} = \frac{r^3}{\gamma\hbar} \tag{6}$$

often about 100 μsec for nuclei. Equations (4) and (5) were first proposed by Felix Bloch and are commonly referred to as the "Bloch equations." Although they have some limitations, they have nevertheless played a most important role in understanding resonance phenomena, since they provide a very simple way of introducing relaxation effects.

2·8 SOLUTION OF THE BLOCH EQUATIONS FOR LOW H_1

At this stage we shall be interested in the solution of the Bloch equations for low values of the alternating field, values low enough to avoid saturation. We

immediately transform to the coordinate frame rotating at ω_z, taking H_1 along the x-axis and denoting $H_0 + (\omega_z/\gamma)$ by h_0. Then

$$\frac{dM_z}{dt} = -\gamma M_y H_1 + \frac{M_0 - M_z}{T_1} \tag{1a}$$

$$\frac{dM_x}{dt} = +\gamma M_y h_0 - \frac{M_x}{T_2} \tag{1b}$$

$$\frac{dM_y}{dt} = \gamma[M_z H_1 - M_x h_0] - \frac{M_y}{T_2} \tag{1c}$$

Since M_x and M_y must vanish as $H_1 \to 0$, we realize from Eq. (1a) that in a steady state, M_z differs from M_0 to order H_1^2. We therefore replace M_z by M_0 in Eq. (1c). The solution is further facilitated by introducing $M_+ = M_x + iM_y$. By adding Eq. (1b) to i times Eq. (1c), we get

$$\frac{dM_+}{dt} = -M_+\alpha + i\gamma M_0 H_1 \tag{2}$$

where

$$\alpha = \frac{1}{T_2} + \gamma h_0 i \tag{3}$$

Therefore

$$M_+ = Ae^{-\alpha t} + \frac{i\gamma M_0 H_1}{(1/T_2) + i\gamma h_0} \tag{4}$$

If we neglect the transient term and substitute $M_0 = \chi_0 H_0$, and define $\omega_0 = \gamma H_0$, $\omega_z = -\omega$, we get

$$\begin{aligned} M_x &= \chi_0(\omega_0 T_2)\,\frac{(\omega_0 - \omega)T_2}{1 + (\omega - \omega_0)^2 T_2^2}\,H_1 \\ M_y &= \chi_0(\omega_0 T_2)\,\frac{1}{1 + (\omega - \omega_0)^2 T_2^2}\,H_1 \end{aligned} \tag{5}$$

Equations (5) show that the magnetization is a constant in the rotating reference frame, and therefore is rotating at frequency ω in the laboratory. In a typical experimental arrangement we observe the magnetization by studying the emf it induces in a fixed coil in the laboratory. If the coil is oriented with its axis

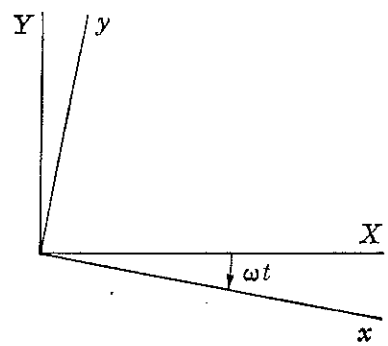

FIG. 2.10. Rotating axes x, y relative to laboratory axes X, Y.

along the X-direction in the laboratory, we can calculate the emf from knowledge of the time-dependent component of magnetization M_X along the X-direction.

By referring to Fig. 2.10, we can relate the laboratory component M_X to the components M_x and M_y in the rotating frame. Thus

$$M_X = M_x \cos \omega t + M_y \sin \omega t \tag{6}$$

If we write the magnetic field as being a linear field,

$$H_X(t) = H_{X0} \cos \omega t \qquad 2H_1 = H_{X0} \tag{7}$$

then we see that both M_x and M_y are proportional to H_{X0}, and we can write

$$M_X(t) = [\chi' \cos \omega t + \chi'' \sin \omega t]H_{X0} \tag{8}$$

defining the quantities χ' and χ''. By using Eqs. (5) and (8), we get

$$\chi' = \frac{\chi_0}{2} \omega_0 T_2 \frac{(\omega_0 - \omega)T_2}{1 + (\omega - \omega_0)^2 T_2^2}$$

$$\chi'' = \frac{\chi_0}{2} \omega_0 T_2 \frac{1}{1 + (\omega - \omega_0)^2 T_2^2} \tag{8a}$$

It is convenient to regard both $M_X(t)$ and $H_X(t)$ as being the real parts of complex functions $M_X^C(t)$ and $H_X^C(t)$. Then, defining the complex susceptibility χ by

$$\chi = \chi' - i\chi'' \tag{9}$$

and writing

$$H_X^C(t) = H_{X0} e^{i\omega t} \tag{10}$$

we find

$$M_X^C(t) = \chi H_X^C(t) \tag{11}$$

or

$$M_X(t) = \mathrm{Re}[\chi H_{X0} e^{i\omega t}] \tag{11a}$$

Although Eqs. (7) and (11a) were arrived at by considering the Bloch equations, they are in fact quite general. Any resonance is characterized by a complex susceptibility expressing the linear relationship between magnetization and applied field.

Ordinarily, if a coil of inductance L_0 is filled with a material of susceptibility χ_0, the inductance is increased to $L_0(1 + 4\pi\chi_0)$, since the flux is increased by the factor $1 + 4\pi\chi_0$ for the same current. In a similar manner the complex susceptibility produces a flux change. The flux is not only changed in magnitude but *also* in phase. By means of Eqs. (8) through (11), it is easy to show that the inductance at frequency ω is modified to a new value L, given by

$$L = L_0[1 + 4\pi\chi(\omega)] \tag{12}$$

where $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$. It is customary in electric circuits to use the symbol j for $\sqrt{-1}$. However, in order to avoid the confusion of using two symbols for the same quantity, we use only i.†

† In practice, the sample never completely fills all space, and we must introduce the "filling factor" q. Its calculation depends on a knowledge of the spatial variation of the alternating field. Then Eq. (12) becomes

$$L = L_0[1 + 4\pi q\chi(\omega)]$$

Denoting the coil resistance in the absence of a sample as R_0, the coil impedance Z becomes

$$\begin{aligned} Z &= iL_0\omega(1 + 4\pi\chi' - i4\pi\chi'') + R_0 \\ &= iL_0\omega(1 + 4\pi\chi') + L_0\omega 4\pi\chi'' + R_0 \end{aligned} \tag{13}$$

The real part of the susceptibility χ' therefore changes the inductance, whereas the imaginary part, χ'', modifies the resistance. The fractional change in resistance $\Delta R/R_0$ is

$$\frac{\Delta R}{R_0} = \frac{L_0\omega}{R_0} 4\pi\chi'' = 4\pi\chi''Q \tag{14}$$

where we have introduced the so-called quality factor Q, typically in a range of 50 to 100 for radio frequency coils or 1,000 to 10,000 for microwave cavities.

Assuming uniform magnetic fields occupying a volume V, the peak stored magnetic energy produced by an alternating current, whose peak value is i_0, is

$$\frac{1}{2} L_0 i_0^2 = \frac{1}{8\pi} H_{X0}^2 V \tag{15}$$

The average power dissipated in the nuclei $\overline{P}$ is

$$\overline{P} = \tfrac{1}{2} i_0^2 \Delta R = \tfrac{1}{2} i_0^2 L_0 \omega 4\pi\chi'' \tag{16}$$

By substituting from Eq. (15), we find

$$\overline{P} = \tfrac{1}{2}\omega H_{X0}^2 \chi'' V \tag{17}$$

This equation provides a simple connection between the power absorbed, χ'', and the strength of the alternating field. We shall use it as the basis of a calculation of χ'' from atomic considerations, since the power absorbed can be computed in terms of such quantities as transition probabilities. Since χ' and χ'' are always related, as we shall see shortly, a calculation of χ'' will enable us to compute χ'. Moreover, we recognize that the validity of Eq. (17) does not depend on the assumption of the Bloch equations.

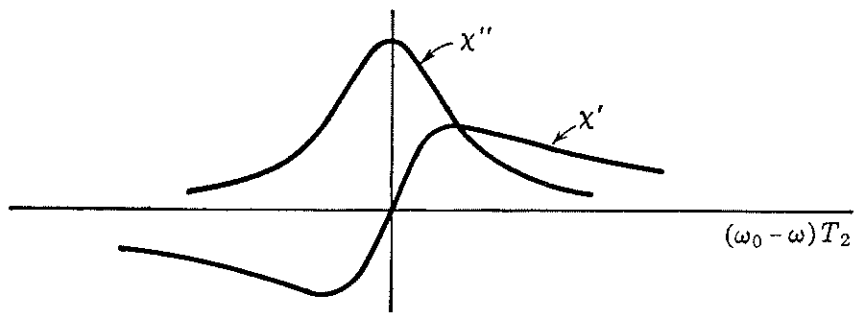

FIG. 2.11. χ' and χ'' from the Bloch equations plotted versus $x \equiv (\omega_0 - \omega)T_2$.

The particular functions χ' and χ'', which are solutions of the Bloch equations, are frequently encountered. They are shown in the graph of Fig. 2.11. The term *Lorentzian line* is often applied to them.

At this time we should point out that we have computed the magnetization produced in the X-direction by an alternating field applied in the X-direction. Since the magnetization vector rotates about the Z-direction, we see that there will also be magnetization in the Y-direction. To describe such a situation, we may consider χ to be a tensor, such that

$$M^C_{\alpha'}(t) = \chi_{\alpha'\alpha} H_{\alpha 0} e^{i\omega t} \qquad \begin{matrix} \alpha = X, Y, Z \\ \alpha' = X, Y, Z \end{matrix}$$

In general we shall be interested in χ_{XX}.

2·9 RELATIONSHIP BETWEEN TRANSIENT AND STEADY-STATE RESPONSE OF A SYSTEM AND OF THE REAL AND IMAGINARY PARTS OF THE SUSCEPTIBILITY

Suppose, to avoid saturation, we deal with sufficiently small magnetic fields. The magnetic system may then be considered linear. That is, the magnetization produced by the sum of two weak fields when applied together is equal to the sum of the magnetization produced by each one alone. (We shall not include the static field H_0 as one of the fields, but may find it convenient to consider small *changes* in the static field.) In a similar manner, an ordinary electric circuit is linear, since the current produced by two voltage sources simultaneously present is the sum of the currents each source would produce if the other voltage were zero.

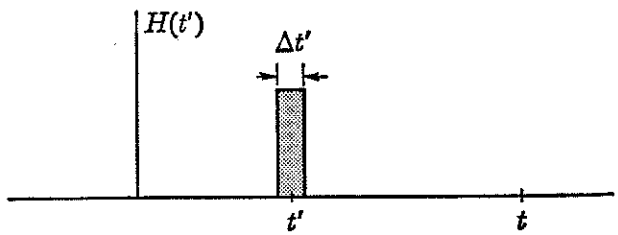

FIG. 2.12. Pulse of magnetic field.

Let us think of the magnetization $\Delta M(t)$ produced at a time t and due to a magnetic field $H(t')$ of duration $\Delta t'$ at an earlier time (see Fig. 2.12). As a result of the linearity condition we know that $\Delta M(t) \propto H(t')$. It is also $\propto \Delta t'$ as long as $\Delta t' \ll t - t'$, since two pulses slightly separate in time must produce the same effect as if they were applied simultaneously.

Therefore we may express the proportionality by writing

$$\Delta M(t) = m(t - t')H(t')\,\Delta t' \tag{1}$$

where $m(t - t')$ is a "constant" for a given t and t', which, however, must depend on how long $(t - t')$ after the pulse of field we wish to know the magnetization. The total magnetization at time t is obtained by integrating Eq. (1) over the history of the magnetic field $H(t')$:

$$M(t) = \int_{-\infty}^{t} m(t - t')H(t')\,dt' \tag{2}$$

Note that $m(t - t') = 0$ if $t' > t$, since the effect cannot precede the cause.

To understand just what $m(t - t')$ is, let us assume $H(t')$ is a δ-function at $t = 0$. Then the magnetization at $t > 0$ (which we shall denote by M_δ) is

$$M_\delta(t) = \int_{-\infty}^{t} m(t - t')\, \delta(t')\, dt' = m(t) \tag{3}$$

That is, $m(t)$ is the response to a δ-function at $t = 0$. Knowledge of $m(t)$ enables us to determine from Eq. (2) the magnetization resulting from a magnetic field of arbitrary time variation.

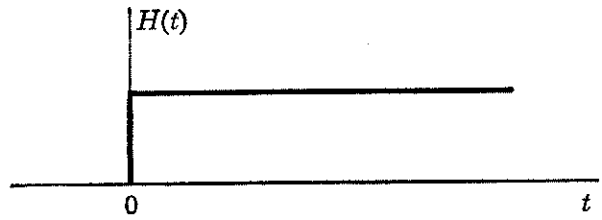

FIG. 2.13. Step function.

If a unit step were applied at $t = 0$ (Fig. 2.13), we should have magnetization, which we shall denote as M_{step}:

$$M_{\text{step}}(t) = \int_0^t m(t - t')\, dt' = \int_0^t m(\tau)\, d\tau \tag{4}$$

By taking the derivative of Eq. (4), we find

$$m(t) = \frac{d}{dt}\,(M_{\text{step}}) \tag{5}$$

Equation (5) therefore shows us that knowledge of $M_{\text{step}}(t)$ enables us to compute $m(t)$.

For example, suppose we discuss the magnetization of a sample following application of a unit magnetic field in the z-direction for a system obeying the Bloch equations. We know from the Bloch equations that

$$M_z(t) = \chi_0[1 - e^{-t/T_1}] = M_{\text{step}} \tag{6}$$

Therefore, using Eq. (5),

$$m(t) = \frac{\chi_0}{T_1}\, e^{-t/T_1} \tag{7}$$

Note that in any real system, the magnetization produced by a step is bounded, so that

$$\int_0^\infty m(\tau)\, d\tau \tag{8}$$

converges.

Suppose we apply an alternating magnetic field. We shall write it as complex for simplicity:

$$H_X^C(t) = H_{X0} e^{i\omega t} \tag{9}$$

Then

$$M_X^C(t) = \int_{-\infty}^{t} m(t - t')H_{X0}e^{i\omega t'}\,dt'$$
$$= H_{X0}e^{i\omega t}\int_{-\infty}^{t} m(t - t')e^{i\omega(t'-t)}\,dt' \tag{10}$$
$$= H_{X0}e^{i\omega t}\int_{0}^{\infty} m(\tau)e^{-i\omega\tau}\,d\tau$$

Comparison with Eq. (11) of the preceding section shows that

$$\chi = \int_0^\infty m(\tau)e^{-i\omega\tau}\,d\tau$$
$$\chi' = \int_0^\infty m(\tau)\cos\omega\tau\,d\tau \tag{11}$$
$$\chi'' = \int_0^\infty m(\tau)\sin\omega\tau\,d\tau\dagger$$

It is simple to show, using the integral representation of the δ function,

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ixt}\,dt \tag{12}$$

that

$$m(\tau) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \chi(\omega)e^{i\omega\tau}\,d\omega \tag{13}$$

That is, $m(\tau)$ and $\chi(\omega)$ are Fourier transforms of each other. Knowledge of one completely determines the other. One may attempt to predict the properties of

† Strictly speaking, we should turn on the alternating field adiabatically and consider the limit of slower and slower turn-on. Thus we can take

$$H_X^C(t) = H_{X0}e^{i\omega t}e^{st}$$

As $t \to -\infty$, this function goes to zero. We compute the limit as $s \to 0$. Thus

$$M_X^C(t) = \int_{-\infty}^{t} m(t - t')H_{X0}e^{i\omega t'}e^{st'}dt'$$
$$= H_{X0}e^{i\omega t}e^{st}\int_{-\infty}^{t} m(t - t')e^{i\omega(t'-t)}e^{s(t'-t)}\,dt'$$
$$= H_{X0}e^{(i\omega+s)t}\int_0^\infty m(\tau)e^{-(s+i\omega)\tau}\,d\tau$$

and

$$\chi(\omega) = \lim_{s\to 0}\int_0^\infty m(\tau)e^{-(s+i\omega)\tau}\,d\tau$$

The advantage of this definition is that it has meaning for the case of a "lossless resonator" (magnetic analogue of an undamped harmonic oscillator), in which a sudden application of a field would excite a transient that would never die out.

resonance lines either by analyzing the response to an alternating signal or by analyzing the transient response. Kubo and Tomita,† for example, base their general theory of magnetic resonance on the transient response, calculating the response of the system to a step.

Examination of Eq. (11) enables us to say something about χ' and χ'' at both zero and infinite frequencies. Clearly, χ'' vanishes at $\omega = 0$, since sin 0 vanishes, but χ' does not vanish at $\omega = 0$. Moreover, if $m(\tau)$ is a finite, reasonably continuous function whose total integral $\int_0^\infty m(\tau)\, d\tau$ is bounded, both χ' and χ'' will go to zero as $\omega \to \infty$, since the oscillations of the sin $\omega\tau$ or cos $\omega\tau$ will "average" the integrand to zero. Actually we may permit $m(\tau)$ to be infinite at $\tau = 0$. We can see this by thinking of $\int_0^t m(\tau)\, d\tau$, the response to a step. We certainly do not expect the response to a step to be discontinuous at any time other than that when the step is discontinuous ($t = 0$). Therefore $m(\tau)$ can have at most an integrable infinity at $t = 0$, since the response must be bounded. We shall represent this by a δ-function. Thus, if

$$m(\tau) = m_1(\tau) + c_1\, \delta(\tau) \tag{14}$$

where $m_1(\tau)$ has no δ-function, we get

$$\chi'(\omega) = \int_0^\infty m_1(\tau) \cos \omega\tau\, d\tau + c_1 \tag{15}$$

The integral vanishes as $\omega \to \infty$, leaving us $c_1 = \chi'(\infty)$. It is therefore convenient to subtract the δ-function part from $m(\tau)$, which amounts to saying that

$$\chi(\omega) - \chi'(\infty) = \int_0^\infty m(\tau) e^{-i\omega\tau}\, d\tau \tag{16}$$

where *now* $m(\tau)$ has no δ-function part.

[Of course no physical system could have a magnetization that follows the excitation at infinite frequency. However, if one were rather making a theorem about permeability μ, $\mu(\infty)$ is *not* zero. We keep $\chi'(\infty)$ to emphasize the manner in which such a case would be treated.]

We wish now to prove a theorem relating χ' and χ'', the so-called Kramers-Kronig theorem. To do so, we wish to consider χ to be a function of a complex variable $z = x + iy$. The real part of z will be the frequency ω, but we use the symbol x for ω to make the formulas more familiar. Therefore

$$\begin{aligned} \chi(z) - \chi'(\infty) &= \int_0^\infty m(\tau) e^{-iz\tau}\, d\tau \\ &= \int_0^\infty m(\tau) e^{y\tau} e^{-ix\tau}\, d\tau \end{aligned} \tag{17}$$

Since an integral is closely related to a sum, we see that $\chi(z)$ is essentially a sum of exponentials of z. Since each exponential is an analytic function of z, so is the integral, providing nothing too bizarre results from integration.

† R. Kubo and K. Tomita, *J. Phys. Soc. Japan*, 9: 888 (1954).

To prove that $\chi(z) - \chi'(\infty)$ is an analytic function of z, one may apply the Cauchy derivative test, which says that if

$$\chi(z) - \chi'(\infty) \equiv u + iv \tag{18}$$

where u and v are real, u and v must satisfy the equations

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y} \qquad \text{and} \qquad \frac{\partial v}{\partial x} = -\frac{\partial u}{\partial y} \tag{19}$$

From Eq. (17) we have

$$\begin{aligned} u &= \int_0^\infty m(\tau) \cos x\tau \, e^{y\tau} \, d\tau \\ v &= -\int_0^\infty m(\tau) \sin x\tau \, e^{y\tau} \, d\tau \end{aligned} \tag{20}$$

giving

$$\begin{aligned} \frac{\partial u}{\partial x} &= -\int_0^\infty m(\tau)\tau \sin x\tau \, e^{y\tau} \, d\tau = \frac{\partial v}{\partial y} \\ \frac{\partial u}{\partial y} &= \int_0^\infty m(\tau)\tau \cos x\tau \, e^{y\tau} \, d\tau = -\frac{\partial v}{\partial x} \end{aligned} \tag{21}$$

which satisfy the Cauchy relations, *provided* it is permissible to take derivatives under the integral sign. There are a variety of circumstances under which one can do this, and we refer the reader to the discussion in E. W. Hobson's book†. For our purposes, the key requirement is that the integrals in both Eqs. (20) and (21) must not diverge. This prevents us in general from considering values of y that are too positive. For any reasonable $m(\tau)$ such as that of Eq. (7), the integrals will be convergent for $y \leq 0$, so that $\chi(z) - \chi'(\infty)$ will be analytic on the real axis and in the lower half of the complex z-plane.

Whenever we use functions $m(\tau)$ that are *not* well behaved, we shall also imply that they are to be taken as the limit of a well-behaved function. (Thus an absorption line that has zero width is physically impossible, but may be thought of as the limit of a very narrow line.)

The presence of the term $e^{y\tau}$ tells us that

$$|\chi(z) - \chi'(\infty)| \to 0 \qquad \text{as} \qquad y \to -\infty$$

We already know that

$$|\chi(z) - \chi'(\infty)| \to 0 \qquad \text{as} \qquad x \to \pm\infty$$

Therefore $\chi(z) - \chi'(\infty)$ is a function that is analytic for $y \leq 0$ and goes to zero as $|z| \to \infty$ in the lower half of the complex plane.

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† E. W. Hobson, *The Theory of Functions of a Real Variable and the Theory of Fourier's Series.* Cambridge University Press, 1926, p. 353 ff.

Let us consider a contour integral along the path of Fig. 2.14 of the function

$$\frac{\chi(z') - \chi'(\infty)}{z' - \omega}$$

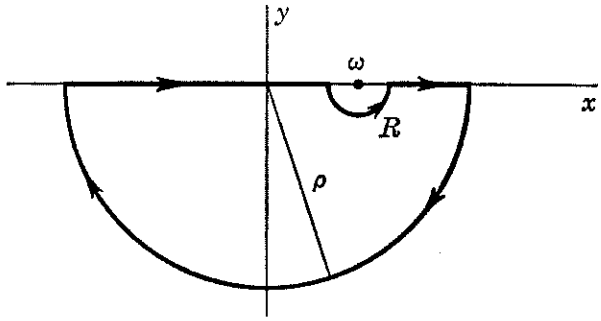

FIG. 2.14. Contour integral.

By Cauchy's integral theorem this integral vanishes, since $\chi(z)$ has no poles inside the contour.

$$\int_C \frac{\chi(z') - \chi'(\infty)}{z' - \omega}\, dz' = 0 \tag{22}$$

Since $|\chi(z') - \chi'(\infty)|$ goes to zero on the large circle of radius ρ, that part of the integral gives zero contribution. There remains the contribution on the real axis plus that on the circle $z' - \omega = Re^{i\phi}$. Thus

$$\int_{-\infty}^{\omega-R} \frac{\chi(\omega') - \chi'(\infty)}{\omega' - \omega}\, d\omega' + \int_{\pi}^{2\pi} \frac{[\chi(\omega') - \chi'(\infty)]}{Re^{i\phi}}\, Rie^{i\phi} d\phi + \int_{\omega+R}^{+\infty} \frac{\chi(\omega') - \chi'(\infty)}{\omega' - \omega} = 0 = P\int_{-\infty}^{+\infty} \frac{\chi(\omega') - \chi'(\infty)}{\omega' - \omega}\, d\omega' + \pi i[\chi(\omega) - \chi'(\infty)] \tag{23}$$

where the symbol P stands for taking the principal part of the integral (that is, takes the limit of the sum of the integrals $\int_{-\infty}^{\omega-R}$ and $\int_{\omega+R}^{+\infty}$ as $R \to 0$ simultaneously in the two integrals).

Solving for the real and imaginary parts, we find

$$\chi'(\omega) - \chi'(\infty) = \frac{1}{\pi} P\int_{-\infty}^{+\infty} \frac{\chi''(\omega')}{\omega' - \omega}\, d\omega'$$
$$\chi''(\omega) = \frac{1}{\pi} P\int_{-\infty}^{+\infty} \frac{\chi'(\omega') - \chi'(\infty)}{\omega' - \omega}\, d\omega' \tag{24}$$

These are the famous Kramers-Kronig equations. Similar equations can be worked out for analogous quantities such as the dielectric constant or the electrical susceptibility.

The significance of these equations is that there are restrictions placed, for example, on the dispersion by the absorption. One cannot dream up arbitrary $\chi'(\omega)$

and $\chi''(\omega)$. To phrase alternately, we may say that knowledge of χ'' for all frequencies enables one to compute the χ' at any frequency. Note in particular that for a narrow resonance line, assuming $\chi'(\infty) = 0$, the static susceptibility χ_0 is given by

$$\begin{aligned}\chi_0 = \chi'(0) &= \frac{1}{\pi} P\int_{-\infty}^{+\infty} \frac{\chi''(\omega')}{\omega'}\, d\omega' \\ &= \frac{2}{\pi}\frac{1}{\omega_0}\int_0^{+\infty} \chi''(\omega')\, d\omega'\end{aligned} \tag{25}$$

The integral of $\chi''(\omega')$ is essentially the area under the absorption curve. We see that it may be computed if the static susceptibility is known.†

As an example, suppose

$$\chi''(\omega) = c[\delta(\omega - \Omega) - \delta(-\omega - \Omega)] \tag{26}$$

The first term corresponds to absorption at frequency Ω. The second term simply makes χ'' an odd function of ω. For this function, what is $\chi'(\omega)$?

$$\begin{aligned}\chi'(\omega) - \chi'(\infty) &= \frac{1}{\pi} P\int_{-\infty}^{+\infty} \frac{c[\delta(\omega' - \Omega) - \delta(-\omega' - \Omega)]\, d\omega'}{\omega' - \omega} \\ &= \frac{c}{\pi}\left[\frac{1}{\Omega - \omega} - \frac{1}{-\Omega - \omega}\right] = \frac{c}{\pi}\left[\frac{1}{\Omega - \omega} + \frac{1}{\Omega + \omega}\right]\end{aligned} \tag{27}$$

where we have used the fact that $\delta(x) = \delta(-x)$.††

Of course, near resonance ($\omega \cong \Omega$), only the first term is large. The function is shown in Fig. 2.15.

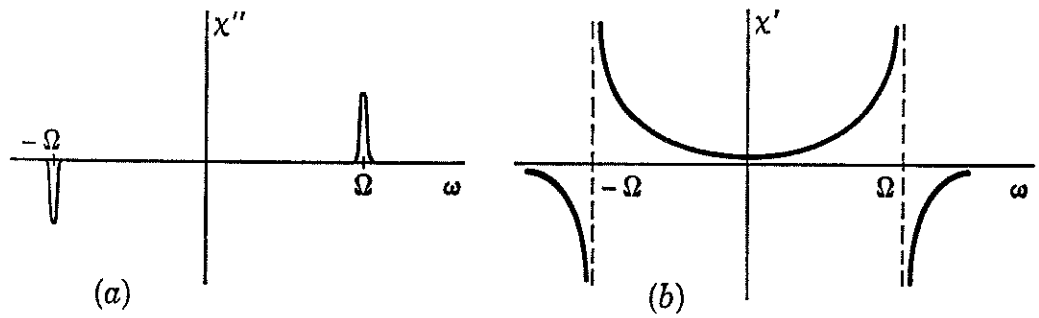

FIG. 2.15. (a) Absorption spectrum. (b) Corresponding dispersion spectrum.

† Of course, if we are talking about a magnetic resonance experiment with the static field in the z-direction and the alternating field in the x-direction, we are discussing χ_{xx}. Then $\chi'(0)$ of Eq. (25) is $\chi'_{xx}(0)$, whereas χ_0 is usually thought of as relating the total magnetization M_0 to the field H_0, which produces it, and is thus $\chi'_{zz}(0)$. However, a small static field H_x in the x-direction simply rotates M_0, giving

$$M_x = M_0 \frac{H_x}{H_0} = \chi'_{zz}(0) H_x$$

Thus $\chi'_{xx}(0) = \chi'_{zz}(0) = \chi_0$.

†† That the Dirac δ-function is an even function of x follows from evaluating $\int_{-\infty}^{+\infty} f(x)\, \delta(-x)\, dx$ and changing variables to $x' = -x$, which shows this equals $\int_{-\infty}^{+\infty} f(-x')\, \delta(x')\, dx' = f(0) = \int_{-\infty}^{+\infty} f(x)\, \delta(x)\, dx$. Thus $\delta(x) = \delta(-x)$.

2·10 ATOMIC THEORY OF ABSORPTION AND DISPERSION

We shall now turn to obtaining expressions for the absorption and dispersion in terms of atomic properties such as the wave functions, matrix elements, and energy levels of the system under study. We shall compute χ'' directly and obtain χ' from the Kramers-Kronig equations.

We make the connection between the macroscopic and the microscopic properties by computing the average power absorbed, $\overline{P}$, from an alternating magnetic field $H_{x0} \cos \omega t$. From Eq. (17) of Section 2.8 we have

$$\overline{P} = \frac{\omega}{2} \chi'' H_{x0}^2 V \tag{1}$$

in a volume V. It will be convenient henceforth to refer everything to a unit volume. (We shall have to remember this fact when we compute the atomic expressions in particular cases.)

On the other hand, the alternating field couples to the magnetic moment μ_{xk} of the kth spin. Therefore, in our Hamiltonian we shall have a time-dependent perturbation $\mathcal{H}_{\text{pert}}$ of

$$\begin{aligned} \mathcal{H}_{\text{pert}} &= -\sum_k \mu_{xk} H_{x0} \cos \omega t \\ &= -\mu_x H_{x0} \cos \omega t \end{aligned} \tag{2}$$

where μ_x is the x-component of the total magnetic moment

$$\mu_x \equiv \sum_k \mu_{xk} \tag{3}$$

In the absence of the perturbation, the Hamiltonian will typically consist of the interactions of the spins with the external static field and of the coupling $\mathcal{H}_{jk}$ between spins j and k. Thus

$$\mathcal{H} = -\sum_k \mu_{zk} H_0 + \sum_{j,k} \mathcal{H}_{jk} \tag{4}$$

We shall denote the eigenvalues of energy of this many-spin Hamiltonian as E_a, E_b, and so on, with corresponding many-spin wave functions as $|a)$ and $|b)$. See Fig. 2.16. Because of the large number of degrees of freedom there will be a quasi-continuum of energy levels.

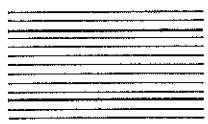

FIG. 2.16. Eigenvalues of energy.

The states $|a)$ and $|b)$ are eigenstates of the Hamiltonian. The most general wave function would be a linear combination of such eigenstates:

$$\Psi = \sum_a c_a |a) e^{-(i/\hbar) E_a t} \tag{5}$$

where the c_a's are complex constants. The square of the absolute value of c_a gives the probability, $p(a)$, of finding the system in the eigenstate a:

$$p(a) = |c_a|^2$$

If the system is in thermal equilibrium, all states will be occupied to some extent, the probability of occupation, $p(a)$, being given by the Boltzmann factor

$$p(E_a) = \frac{e^{-E_a/kT}}{\sum_{E_c} e^{-E_c/kT}} \tag{6}$$

where the sum E_c goes over the entire eigenvalue spectrum. The denominator is just the classical partition function, Z, inserted to guarantee that the total probability of finding the system in any of the eigenstates is equal to unity; that is,

$$\sum_{E_a} p(E_a) = 1$$

We can compute the absorption rate $\overline{P}_{ab}$, due to transitions between states a and b in terms of W_{ab}, the probability per second that a transition would be induced from a to b if the system were entirely in state a initially:

$$\overline{P}_{ab} = \hbar\omega W_{ab}[p(E_b) - p(E_a)] \tag{7}$$

The terms $p(E_b)$ and $p(E_a)$ come in because the states $|a)$ and $|b)$ are only fractionally occupied.

The calculation of the transition probability W_{ab} is well known from elementary quantum mechanics. Suppose we have a time-dependent perturbation $\mathcal{H}_{\text{pert}}$ given by

$$\mathcal{H}_{\text{pert}} = Fe^{-i\omega t} + Ge^{i\omega t} \tag{8}$$

where F and G are two operators. In order that $\mathcal{H}_{\text{pert}}$ will be Hermitian, F and G must be related so that for all states $|a)$ or $|b)$,

$$(a|F|b) = (b|G|a)^* \tag{9}$$

Under the action of such a perturbation we can write that W_{ab} is time independent and is given by the formula

$$W_{ab} = \frac{2\pi}{\hbar} |(a|F|b)|^2 \, \delta(E_a - E_b - \hbar\omega) \tag{10}$$

provided certain conditions are satisfied: We do not ask for details that appear on a time scale shorter than a certain characteristic time τ. It must be possible to find such a time, which will satisfy the conditions that (1) the populations change only a small amount in τ and (2) the possible states between which absorption can occur must be spread in energy continuously over a range ΔE such that $\Delta E \gg \hbar/\tau$.

These conditions are violated if the perturbation matrix element $|(a|F|b)|$ exceeds the line width, as it does when a very strong alternating field is applied. We can see this point as follows: The quantity ΔE may be taken as the line width. We have, then, that $\Delta E < |(a|F|b)|$. But under these circumstances one can show

that the populations change significantly in a time of order $\hbar/|(a|F|b)|$. Thus to satisfy the condition 1 that the populations change only a small amount during τ, τ must be chosen less than $\hbar/|(a|F|b)|$. This gives us

$$|(a|F|b)| < \frac{\hbar}{\tau}$$

But, by hypothesis,

$$\Delta E < |(a|F|b)|$$

Therefore

$$\Delta E < \frac{\hbar}{\tau}$$

which violates condition 2 above. Thus it is not possible to satisfy both conditions, and the transition probability is not independent of time.

This example shows why we did not get a simple time-independent rate process in Section 2.6, since for that problem, the energy levels in the absence of H_1 are perfectly sharp ($\Delta E = 0$), $|(a|F|b)| > \Delta E$.

In our formula for W_{ab} we use the δ-function. This implies that we shall eventually sum over a quasi-continuum of energy states. In writing the transition probability, it is preferable to use the δ-function form to the integrated form involving density of states in order to keep track of quantum numbers of individual states.

By summing over all states with $E_a > E_b$, we find

$$\begin{aligned}\overline{P} &= \frac{2\pi}{\hbar}\frac{H_{x0}^2}{4}\hbar\omega \sum_{E_a>E_b} [p(E_b) - p(E_a)]\,|(a|\mu_x|b)|^2\,\delta(E_a - E_b - \hbar\omega) \\ &= \frac{\omega}{2}\chi''H_{x0}^2\end{aligned} \tag{11}$$

Therefore

$$\chi''(\omega) = \pi \sum_{E_a>E_b} [p(E_b) - p(E_a)]\,|(a|\mu_x|b)|^2\,\delta(E_a - E_b - \hbar\omega) \tag{12}$$

As long as $E_a > E_b$, only positive ω will give absorption because of the δ-function in Eq. (12). Removal of the restriction $E_a > E_b$ extends the meaning of $\chi''(\omega)$ formally to negative ω. Note that since $p(E_b) - p(E_a)$ changes sign when a and b are interchanged, $\chi''(\omega)$ is an odd function of ω, as described in the preceding section.

$$\chi''(\omega) = \pi \sum_{E_a,E_b} [p(E_b) - p(E_a)]\,|(a|\mu_x|b)|^2\,\delta(E_a - E_b - \hbar\omega) \tag{13}$$

Assuming $\chi'(\infty) = 0$ for our system, we can easily compute $\chi'(\omega)$, since

$$\begin{aligned}\chi'(\omega) &= \frac{1}{\pi} P\int_{-\infty}^{+\infty} \frac{\chi''(\omega')}{\omega' - \omega}\,d\omega' \\ &= \pi \sum_{E_a,E_b} [p(E_b) - p(E_a)]\,|(a|\mu_x|b)|^2\,\frac{1}{\pi} P\int_{-\infty}^{+\infty} \frac{\delta(E_a - E_b - \hbar\omega')}{\omega' - \omega}\,d\omega'\end{aligned} \tag{14}$$

or, evaluating the integral,

$$\chi'(\omega) = \sum_{E_a, E_b} [p(E_b) - p(E_a)] \, |(a|\mu_x|b)|^2 \, \frac{1}{E_a - E_b - \hbar\omega} \tag{15}$$

By using the fact that a and b are dummy indices, one may also rewrite Eq. (15) to give

$$\chi'(\omega) = \sum_{E_a, E_b} p(E_b) |(a|\mu_x|b)|^2 \left[\frac{1}{E_a - E_b - \hbar\omega} + \frac{1}{E_a - E_b + \hbar\omega} \right] \tag{15a}$$

The quanta $\hbar\omega$ correspond crudely to the energy required to invert a spin in the static field. This energy is usually much smaller than kT. For nuclear moments in strong laboratory fields ($\sim 10^4$ gauss), T must be as low as 10^{-3} °K so that $\hbar\omega$ will be as large as kT. This fact accounts for the difficulty in producing polarized nuclei. For electrons, $kT \sim \hbar\omega$ at about 1°K in a field of 10^4 gauss. Therefore we may often approximate

$$E_a - E_b \ll kT \tag{16}$$

We may call this the "high-temperature approximation." By using Eq. (6) and Eq. (16), we have

$$\begin{aligned} p(E_b) - p(E_a) &= \frac{e^{-E_a/kT}[e^{(E_a - E_b)/kT} - 1]}{Z} \\ &= \frac{e^{-E_a/kT}}{Z} \left(\frac{E_a - E_b}{kT} \right) \end{aligned} \tag{17}$$

Substitution of Eq. (17) into Eq. (13) together with recognition that $E_a - E_b = \hbar\omega$, owing to the δ-functions, gives

$$\chi''(\omega) = \frac{\hbar\omega\pi}{kTZ} \sum_{E_a, E_b} e^{-E_a/kT} |(a|\mu_x|b)|^2 \, \delta(E_a - E_b - \hbar\omega) \tag{18}$$

Another expression for $\chi''(\omega)$ is frequently encountered. It is the basis, for example, of P. W. Anderson's theory of motional narrowing [*J. Phys. Soc. Japan*, **9**: 316 (1954)]. We discuss it in Appendix B because a proper discussion requires reference to some of the materials in Chapters 3 and 5.

It is important to comment on the role of the factors $e^{-E_a/kT}$. If one is dealing with water, for example, the proton absorption lines are found to be quite different at different temperatures. Ice, if cold enough, possesses a resonance several kilocycles broad, whereas the width of the proton resonance in liquid water is only about 1 cycle. Clearly the only difference is associated with the relative mobility of the H_2O molecule in the liquid as opposed to the solid. The position coordinates of the protons therefore play an important role in determining the resonance. Formally we should express this fact by including the kinetic and potential energies of the atoms as well as the spin energies in the Hamiltonian. Then the energies E_a and E_b contain contributions from both spin and positional coordinates. Some states $|a)$ correspond to a solid, some to a liquid. The factor $e^{-E_a/kT}$ picks out the type of "lattice" wave functions or states that are representative of the temperature, that is, whether the water molecules are in liquid, solid, or gaseous phase.

Commonly the exponential factor is omitted from the expression for χ'', but the states $|a)$ and $|b)$ are chosen to be representative of the known state. The classic papers of Gutowsky and Pake, on the effect of hindered molecular motion on the width of resonance, use such a procedure.

Evaluation of χ'' by using Eq. (18) would require knowledge of the wave functions and energy levels of the system. As we shall see, we rarely have that information, but we shall be able to use Eq. (18) to compute the so-called moments of the absorption line. We see that the only frequencies at which strong absorption will occur must correspond to transitions among states between which the magnetic moment has large matrix elements.