Andrew, Nuclear Magnetic Resonance.

BASIC THEORY

2.1. The resonance condition†

First of all let us consider an isolated nucleus in a steady magnetic field $\mathbf{H}_0$. We will suppose that the nuclear spin number I is greater than zero, so that the nucleus may possess a magnetic moment. From the theory of quantum mechanics we know that the length of the nuclear angular momentum vector is $[I(I+1)]^{\frac{1}{2}}\hbar$, but that the only measurable components of this vector are given by $m\hbar$, where m, the magnetic quantum number, may take any of the $(2I+1)$ values in the series $I, I-1, I-2, \ldots, -(I-1), -I$. This is illustrated for the case of $I=\frac{3}{2}$ in fig. 1, where the angular momentum has just four measurable values along the direction of the applied magnetic field $\mathbf{H}_0$.

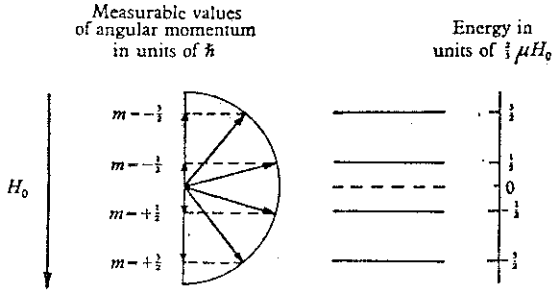

Fig. 1. Diagram showing schematically the four measurable values of angular momentum for a nucleus having spin number $I=\frac{3}{2}$, when placed in a magnetic field $\mathbf{H}_0$. The corresponding four energy levels are also shown.

Corresponding to this quantization of the angular momentum components, the nuclear magnetic moment also has $(2I+1)$ components in proportion. In Chapter 1 we defined μ as the maximum measurable component of the magnetic moment. It must therefore be remembered that the length of the magnetic moment vector is actually $[(I+1)/I]^{\frac{1}{2}}\mu$. However, μ is the quantity which is of phys-

† The approach in the earlier part of this chapter is based upon sections of the classic paper by Bloembergen, Purcell and Pound (1948).

ical interest, and for this reason experimental workers usually derive and state the value of μ from their measurements, and frequently refer to this quantity simply as the 'magnetic moment'. The components of the magnetic moment are given by the $(2I+1)$ values of $m\mu/I$, forming the series μ, $(I-1)\mu/I$, ..., $-(I-1)\mu/I$, $-\mu$. The energy levels of the nuclear magnet in the magnetic field $\mathbf{H}_0$ are therefore given by the $(2I+1)$ values of $-m\mu H_0/I$. These levels also are illustrated in fig. 1 for the case of $I=\frac{3}{2}$, and in the general case show a set of equally spaced levels with separation $\mu H_0/I$ between successive levels. This energy separation is often written as $g\mu_0 H_0$, where μ_0 is the nuclear magneton, and $g\,(=\mu/\mu_0 I)$ is called the *splitting factor* or *g-factor*. This g-factor is in fact the counterpart of the Landé splitting factor in atomic spectroscopy. It will be noticed that the quantity gI is the magnetic moment measured in units of the nuclear magneton.

The selection rule governing transitions between energy levels is the same as for the closely related Zeeman effect; transitions are allowed which cause m to change by ± 1. A quantum of energy can therefore excite transitions between the energy levels if it has the same magnitude as the level spacing:

$$h\nu_0=\frac{\mu}{I}H_0=g\mu_0 H_0, \tag{2.1}$$

where ν_0 is the frequency of the electromagnetic radiation supplying the quanta of energy.

For the proton the value of g is approximately 5·58. Thus, in a typical field of 5000 gauss the resonance frequency given by (2.1) is 21·3 Mc./s. Only the triton ^{3}H has a greater g-factor, corresponding to a frequency of 22·7 Mc./s. in this field, while for most other nuclei which possess a magnetic moment the resonance frequency is greater than 1 Mc./s. in the same field. The frequencies thus fall in a convenient radiofrequency band.

In conventional optical spectroscopy emitted radiation is analyzed, whereas in the nuclear magnetic resonance absorption experiment, as also for molecular beam magnetic resonance, radiation is generated externally and its effect on the atomic system is investigated. Notwithstanding this difference in technique, we may find the necessary condition for observation of the magnetic reson-

ance transitions from the properties of the emission spectrum of the analogous atomic Zeeman effect. Zeeman effect transitions which involve a change in m of ± 1 produce radiation which is circularly

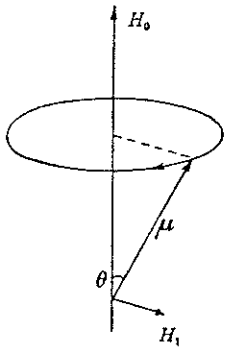

Fig. 2. Diagram illustrating the classical Larmor precession of a magnetic moment μ in a magnetic field $\mathbf{H}_0$.

polarized in the plane perpendicular to the steady magnetic field $\mathbf{H}_0$. In order to excite such transitions in the magnetic resonance experiment, it is therefore necessary to supply radiation with the magnetic vector circularly polarized in a plane perpendicular to the steady magnetic field.

This requirement of circular polarization is just what one would expect by classical argument. If a magnetic dipole μ is placed in a magnetic field $\mathbf{H}_0$ as shown in fig. 2, the dipole precesses about the direction of the applied field. The rate of precession is given by the well-known Larmor angular frequency

$$\omega_0 = \gamma \mathbf{H}_0, \tag{2.2}$$

where γ is the gyromagnetic ratio of the dipole. Suppose now that an additional small magnetic field $\mathbf{H}_1$ is applied at right angles to $\mathbf{H}_0$, in the plane containing μ and $\mathbf{H}_0$. The dipole will experience a couple $(\mu \wedge \mathbf{H}_1)$ tending to increase the angle θ between μ and $\mathbf{H}_0$. If the small field $\mathbf{H}_1$ is made to rotate about $\mathbf{H}_0$ as axis in synchronism with the precession of the dipole, this couple will cause the angle θ to increase steadily. If, on the other hand, $\mathbf{H}_1$ rotates with an angular frequency different from the Larmor precessional frequency, or in opposite sense, the couple $(\mu \wedge \mathbf{H}_1)$ will vary in magnitude and direction according to the relative phases of the two

motions, and will merely produce small perturbations of the precessional motion with no net effect. A resonance therefore occurs when the angular frequency $2\pi\nu$ of the rotating field is equal to the angular frequency of Larmor precession, namely, when

$$2\pi\nu = 2\pi\nu_0 = \omega_0 = \gamma H_0. \tag{2.3}$$

When it is remembered that the nuclear gyromagnetic ratio γ is given by $\mu/I\hbar$, it is seen that this classical resonance condition agrees exactly with that derived from the quantum theory (2.1). Moreover, we see that as with quantum theory, so also classically, a condition for observation of the resonance is that the electromagnetic radiation be circularly polarized with the magnetic vector rotating in a plane perpendicular to the steady magnetic field.

The agreement between the results of the classical and the quantum theory viewpoints allows a number of features of the nuclear magnetic resonance phenomenon to be discussed rather simply in terms of a classical vector model of the nucleus.

Although the generation of a high-frequency rotating magnetic field is quite practicable (see §4.2), it is usually much simpler to provide a linearly oscillating field. Fortunately, for most purposes

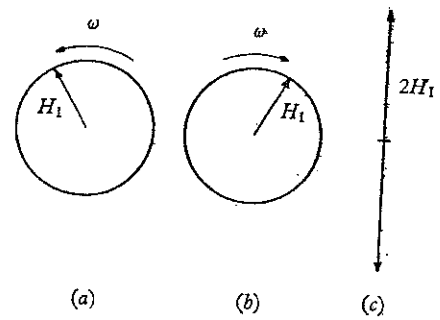

Fig. 3. If the two equal vectors H_1, shown in (*a*) and (*b*) rotating in opposite senses, are superimposed, the resultant (*c*) is a linear vibration of amplitude $2H_1$. The steady field $\mathbf{H}_0$ is taken normal to the diagram.

linear polarization is quite adequate, since, as in the theory of rotatory polarization in optically active crystals, a linearly oscillating field may be regarded as the superimposition of two rotating fields. Thus, as shown in fig. 3, if the linearly oscillating field has amplitude $2H_1$, it may be decomposed into two circularly polarized fields,

each of amplitude H_1, but rotating in opposite senses in a plane perpendicular to $\mathbf{H}_0$. Resonance will be obtained with the component which has the correct sense, the other component having negligible effect. It is not generally possible to tell which component is utilized, and it is not usually necessary to know this. The information is only of importance when it is desired to find the sign of μ; from (2.2) one sees that it is the sign of the gyromagnetic ratio γ, and therefore of μ, which determines the sense of the Larmor precession. This question is discussed more fully in §4.2.

2.2. Spin-lattice relaxation time

Let us now consider an assembly of identical atomic nuclei in the presence of a steady magnetic field $\mathbf{H}_0$. For simplicity we will at first suppose that the nuclear spin number is $\frac{1}{2}$. It will further be assumed that there is only a weak coupling between the nuclear magnets. This allows us to neglect to a first approximation the magnetic interaction between the nuclei, and so to take the energy levels discussed in the previous section for an isolated nucleus as those for each nucleus in the assembly. At the same time some coupling between the nuclei has to be assumed so that the assembly may be considered to be in thermal equilibrium at a temperature T_s.

Since we are concerned with resonance in matter in its normal physical and chemical states, the assembly of nuclei must be present in their usual role as central particles in atomic systems. We shall, however, suppose that the interaction of the nuclear magnets with the remainder of the system is even smaller. If this assumption is to be reasonable we must exclude for the present atomic and molecular systems which possess a permanent magnetic dipole moment; in fact, apart from the feeble paramagnetism produced by the nuclei, the material concerned must be diamagnetic. The material in which the nuclear magnets are embedded is generally referred to as the 'lattice', whether it be solid, liquid or gas.

Since $I=\frac{1}{2}$, each nucleus has two possible energy levels separated by a gap of $2\mu H_0$. If we now apply radiation of the resonant frequency polarized in a direction perpendicular to $\mathbf{H}_0$, transitions between the two levels take place. From the simple theory of the Einstein coefficients (Einstein, 1917) we know that the probability of transitions upwards by absorption is equal to the probability of