algebraic signs into account because, just as in the classical description the disturbing torque may either decrease or increase the orientational energy, on a quantum treatment the perturbing field may stimulate quantum emission as well as lead to quantum absorption. In either of these events the magnetic state of the atom or molecule has been changed, and for that particular particle magnet B now no longer exactly compensates for the effect of magnet A. Thus there will be a drop in intensity of the beam recorded at the detector. In practice the detector may be a very thin metal strip, not more than 10^{-3} mm wide. The change in deflection of a particle arising from a change in μ_{eff} of the order of a nuclear magneton can therefore result in the particle being lost from the collected beam. We thus see that if the radio frequency is kept fixed and H_C is slowly varied, a sudden drop in collected current, i.e. a resonance, indicates that the radio frequency is coinciding with the Larmor precession frequency at that particular value of H_C. From the equation for ω_L derived in section 8.5.1, we can write

$$\mu_I = \frac{|I|\omega_L}{H_C}.$$

To appreciate the accuracy with which ω_L, and hence μ_I, can be determined we require to know the frequency range in which the resonance may be expected to take place. If we assume that μ_I is of the order of a nuclear magneton, that H_C = 1000 G and I is of the order of unity, then ω_L is found to be approximately 5 MHz. In this frequency range a frequency determination to an accuracy of one part in a million is easily achieved. The accuracy of the dipole-moment measurement will then be determined by the accuracy with which the magnetic field H_C is known. If the magnetic field can be guaranteed to be constant, even although it is not known in absolute value, then very precise comparisons of dipole moments can clearly be made.

An alternative method of procedure known as the *'flop-in' technique* is to adjust magnet B to bring to the detector only those molecules which have undergone a particular change in magnetic state on passing through magnet C. Under these conditions the collected current off resonance will be very small and will rise sharply when the resonance is reached.

The resonance technique was originally developed with a view to investigating magnetic moments using non-paramagnetic systems, i.e. systems in which the electrons make no contribution to the total magnetic moment. One then expects the interpretation to be very simple, involving only the reorientation of the nuclear moment in the field H_C. In Figure 47 is shown the result of such an experiment on the HD molecule. The sharp resonance shown is believed to arise from the reorientation of the proton spin in molecules which are in a zero rotational state. From the figure the resonant field is seen to be 945·8 G. The frequency being 4 MHz, it follows that

$$\mu_p = \frac{\hbar\omega_L}{2H_C} = 14 \times 10^{-31}\ \text{J G}^{-1} = 2{\cdot}77 \text{ nuclear magnetons.}$$

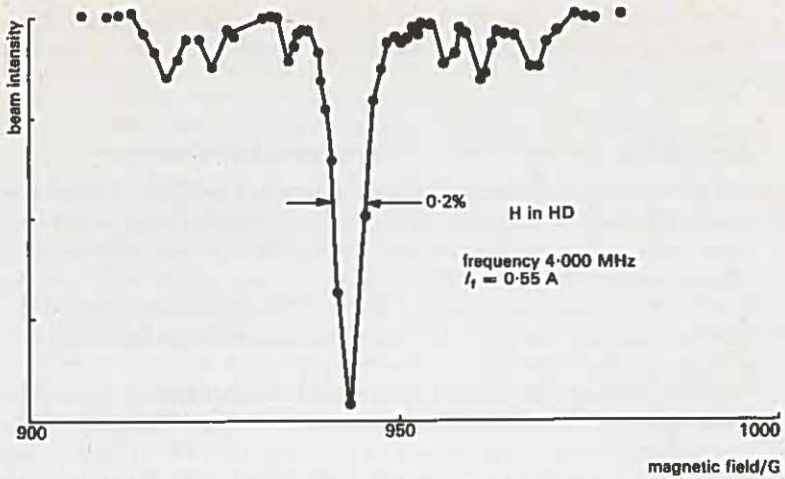

Figure 47 Resonance curve for HD molecules. The largest resonance corresponds to the transition of the proton spin for the zero rotational state

In pressing these measurements to the highest possible accuracy, account had to be taken of diamagnetic circulations induced in the electronic system. This may significantly modify the external magnetic field at the nucleus. Although corrections can be made from atomic theory, the uncertainty in these corrections is quite appreciable relative to the experimental errors.

The resonance technique has been successfully applied to the measurement of a large number of magnetic moments of nuclei whose spins had already been determined.

8.5.3 *The magnetic dipole moment of the neutron*

A technique similar in principle to the above has been applied to neutron beams. By scattering neutrons from a magnetized iron surface, or by transmitting them through thick sheets of magnetized iron, a degree of polarization can be produced in the beam. By this we mean that if n_+ is the number of neutrons with spins parallel to the magnetic field in the iron and n_- the number with spins antiparallel, then

$$P = \frac{n_+ - n_-}{n_+ + n_-}$$

may differ significantly from zero. A second mirror, or a second magnetized sheet, may be used to act as an analyser. The number of neutrons transmitted is then sensitive to any change taking place in the polarization of the beam as it travels between polarizer and analyser. Such a change in polarization can be produced by a long constant magnetic field containing an oscillator coil when the oscillator frequency equals the Larmor precession frequency of the neutron

in the constant field. Alvarez and Bloch (1940) were the first to apply this difficult technique and measured the neutron dipole moment to an accuracy of 1 per cent.

8.5.4 *Application of resonance beam technique to paramagnetic atoms*

The resonance beam technique has been extended to the study of paramagnetic atoms. The much greater values of the magnetic moments being measured permit much lower field strengths to be used. This has the important consequence that magnetic states having practically the same μ_{eff} value in high fields, have in these lower intermediate fields μ_{eff} values sufficiently different to permit transitions between the states to be detected. This technique has greatly extended detailed knowledge of hyperfine structure.

By this method Rabi and his collaborators (1940) studied the moments of several nuclides. One of these was ^{7}Li, for which $J = \frac{1}{2}$, $I = \frac{3}{2}$ leading to $F = 2$ or 1 with M_F values as shown in Figure 48. In strong fields J and I are decoupled and the rules for transitions are $\Delta M_I = 0, \pm 1$; $\Delta M_J = 0, \pm 1$. In medium fields in which J and I remain coupled, the rules are $\Delta F = 0, \pm 1$; $\Delta M_F = 0, \pm 1$. Transitions involving a change in M_F are referred to as π-transitions; those in which M_F is not changed are referred to as σ-transitions. It is to be noted that in the present case of magnetic transitions the convention is the reverse of that used for electric dipole transitions. σ-Transitions occur only if there is an oscillating field component parallel to H_C and can be encouraged by the choice of coil geometry. This can be used to confirm the interpretation. From the observations of the resonant frequencies, the energy differences as a function of magnetic field can be obtained. Interpreting these on the basis of the theory discussed in section 8.1, and illustrated for the present values of J and I in Figure 46, one can make estimates of A and B from which the magnetic dipole and electric quadrupole moments can be calculated.

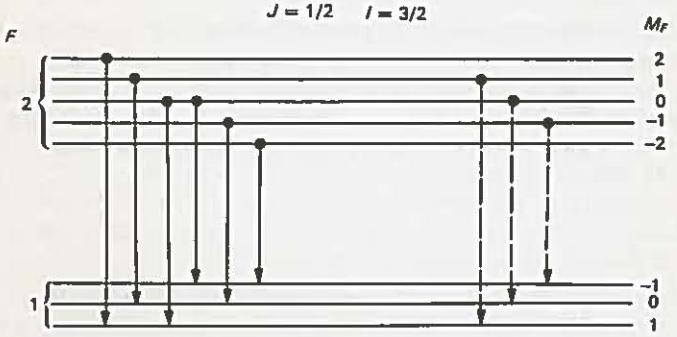

Figure 48 The magnetic levels, at intermediate field, of an h.f.s. doublet of an $S_{\frac{1}{2}}$ state. π-Transitions are shown in full lines, σ-transitions in broken lines

8.5.5 *Magnetic resonant measurements on bulk materials*

We now turn to the second group of resonant experiments which are concerned with the measurement of the moments of nuclei in solid or liquid materials. Whereas, in the beam techniques, the energy changes were being induced and observed in an isolated molecule, in the experiments we now have to discuss the molecules in the sample are in thermal contact with each other. Once more a magnetic field, which we shall here denote by H_0, is applied across the sample and a rotating field H is applied at right angles to H_0.

We first consider the case of a material containing only diamagnetic molecules having nuclei with non-zero spin. Assume the field H_0 to have been established but the field H not yet applied. The specimen will be affected only to the extent that the nuclei orient themselves at the allowed angles with respect to the direction of H_0. For simplicity we shall assume that the nuclear spin is $I = \frac{1}{2}$, although the arguments can be extended in an obvious way to other values of I. Let μ be the magnetic moment of the nucleus. There will then be a contribution of $-\mu H_0$ to the potential energy of the molecule when the nuclear spin is parallel to H_0 and $+\mu H_0$ when the spin and H_0 are antiparallel. When thermal equilibrium has been established, the populations of these two states are known from thermodynamic theory to be proportional to $\exp(\mu H_0/kT)$ and $\exp(-\mu H_0/kT)$ respectively, k being Boltzmann's constant and T the absolute temperature. Introducing n_+ and n_- to represent these populations we thus have

$$\frac{n_+}{n_-} = e^{2\mu H_0/kT}. \qquad 8.3$$

Let P_1 denote the probability that an individual dipole will in unit time, due to thermal disturbance, make a transition from the lower to the higher energy state (i.e. leave the n_+ population and join the n_-), and let P_2 denote the probability, also per dipole and per unit time, for a transition from the higher to the lower state. Since, when the system is in thermal equilibrium there must be as many transitions into as out of the lower energy state (and similarly for the higher), we must have

$$P_1 n_+ = P_2 n_-.$$

Hence $$\frac{n_+}{n_-} = e^{2\mu H_0/kT} = \frac{P_2}{P_1}.$$

Now suppose the field H to be switched on. The probabilities P_1 and P_2 will both be increased by a constant amount, say P_3, which will represent the probability per unit time that a dipole change its orientation due to interaction with the radio-frequency field. Thus the populations of the states will be altered. If they now be denoted by n'_+ and n'_-, we can write

$$\frac{n'_+}{n'_-} = \frac{P_2 + P_3}{P_1 + P_3} = e^{2\mu H_0/kT'},$$

where we have introduced a new equivalent temperature, T', called the *spin temperature*, differing from T, the thermal temperature, since

$$\frac{n'_+}{n'_-} \neq \frac{n_+}{n_-}.$$

Adding a constant to numerator and denominator of P_2/P_1, which is greater than unity, will bring it closer to unity. Hence $T' > T$ and

$$\frac{n'_+}{n'_-} < \frac{n_+}{n_-}.$$

Thus there will be an increase in the population of the upper state at the expense of a decrease in the population of the lower.

8.5.6 *Nuclear magnetic resonance*

The energy for a transition from lower to upper energy state may now come either from the radio-frequency source driving the coil producing H or from the interaction of the nuclear moment with its surroundings, i.e. from the thermal energy of the specimen, which in this simplified treatment we regard as having infinite thermal capacity. Similarly the energy emitted when a transition from upper to lower state takes place may be delivered to the coil or to the thermal sink. The energy taken from the coil will be proportional to $P_3 n'_+$, while the energy delivered to the coil will be proportional to $P_3 n'_-$. Since n_- is always necessarily less than n'_+, there will be a net absorption of energy from the radio frequency supply. We note that

$$P_1 n'_+ < P_1 n_+ = P_2 n_- < P_2 n_-,$$

as a consequence of the change in population brought about by the application of the radio-frequency field. Thus more thermal energy is released by downward transitions than is absorbed by upward transitions. This surplus energy, which passes to the thermal sink, is of course exactly equal to the energy supplied by the radio-frequency source.

The difference in population between the upper and lower states, which is critical in the above considerations, is a very small fraction of the total population N. This can be seen to be so because

$$\frac{n_+ - n_-}{N} = \frac{n_+ - n_-}{n_+ + n_-} = \frac{n_+/n_- - 1}{n_+/n_- + 1} = \frac{2\mu H_0/kT - 1}{e^{2\mu H_0/kT} + 1}.$$

Now, for a magnetic moment of one nuclear magneton in a field of 10^4 G at 288 K,

$$\frac{2\mu H_0}{kT} = 2{\cdot}6 \times 10^{-6}.$$

Expanding the exponential function and taking only the first two terms we thus have

$$\frac{n_+ - n_-}{N} \simeq \frac{\mu H_0}{kT} = 1{\cdot}3 \times 10^{-6}.$$

Despite this exceedingly small population difference the consequent net energy absorption by the process outlined is measurable. This effect was first demonstrated by Purcell and his colleagues (1946), using a radio-frequency cavity of volume 850 cm^3 filled with paraffin. The cavity resonated at 29·8 MHz. When an external magnetic field was applied it was found that there was a resonant attenuation of the radio frequency as the magnetic field passed through 7100 G. The Larmor precession frequency of the protons in a field of that strength is thus established to be 29·8 MHz. A much simpler and more compact arrangement than that originally used has proved possible and is shown in Figure 49. A coil wound round a sample container of only a few cubic centimetres capacity is made part of a tuned circuit and incorporated in an apparatus which responds to a change in Q, the electrical selectivity of the circuit. The sample container is filled with water, or alternatively by another liquid under investigation. The radio frequency is kept constant. The field H_0 is then caused to vary slowly over a limited range by a subsidiary coil which carries a current alternating at 50 Hz. A cathode-ray oscilloscope trace, synchronized horizontally to the variation of H_0, can then be used to display the Q-variation vertically and a synchronized picture of the resonance is then achieved.

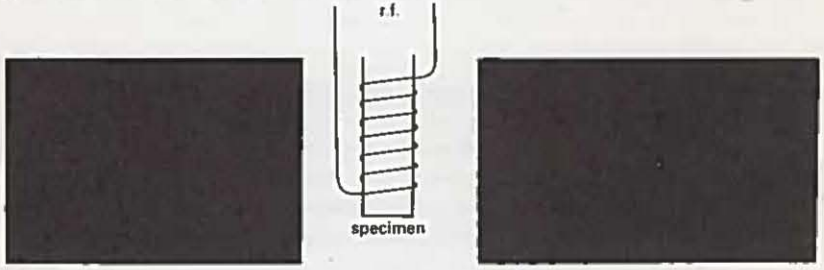

Figure 49 Schematic diagram of nuclear-magnetic-resonance measurement. Radio-frequency power is fed to a coil surrounding the specimen which is immersed in a uniform magnetic field

Apart from its importance in nuclear physics in providing an accurate measurement of the Larmor precession frequency for particular nuclei, and thus permitting an accurate determination of their magnetic moments, this technique has quickly become important in other fields of research. It enables precise comparisons to be made of steady magnetic fields. Providing the magnetic field is constant over the volume of the sample, so that all the protons in the sample have the same Larmor precession frequency, a very sharp resonance is obtained. From the central frequency of the resonance the field can be calculated

in terms of the proton moment. As previously mentioned, frequencies in the range of ten megahertz, which is the relevant frequency for magnetic fields of a few thousand gauss, can readily be measured to one part in a million. Thus magnetic fields can be compared to this order of accuracy.

The technique has also provided considerable insight into the thermal properties of the samples under investigation. If the equilibrium condition is upset, for example by a sudden alteration of H_0, then the new equilibrium condition is approached with a time factor given by $1 - \exp(-t/T_1)$ and T_1 is called the *spin lattice relaxation time*. It is a measure of the tightness of coupling of the nuclear spins with the other degrees of freedom of the system. In a crystal structure T_1 may be of the order of seconds or even minutes. In a liquid it is more likely to be 10^{-2} s. It is greatly affected by the presence of a relatively small number of paramagnetic atoms. Advantage of this can be taken when water is the sample under investigation by adding a small amount of a paramagnetic salt, say manganese sulphate. This has the effect of reducing the relaxation time and sharpening the resonance.

The magnetic field measured by the nuclear-magnetic-resonance technique is of course the resultant of the external field and any internal fields in the material. The internal fields depend on the molecular structure, and may differ from the site of one proton to another in the same molecule. The pattern resulting from slightly shifted resonance can be a useful means of identifying the presence of a particular molecular species. As a consequence the technique, which is referred to as nuclear spin resonance (NSR), has already found a role in chemical investigations.

8.5.7 *Nuclear induction*

An alternative and equally sensitive method of detecting the resonance phenomenon discussed in the previous paragraph was developed by Bloch and co-workers in 1946. Two coils are set up with their axes at right angles to the constant field H_0 and to each other, as shown in Figure 50. One coil is fed with radio-frequency current to set up H as before. The other, the detector coil, is connected to a sensitive radio-frequency voltage detector. In the absence of a sample, the coils are accurately positioned to minimize magnetic-flux linkage, so that the signal induced in the detector coil is a minimum. In terms of the concept of two oppositely rotating fields one should rather say that there are two almost equal and opposite signals induced.

Now the sample to be investigated is introduced. We can consider H', the resultant of H_0 and that rotating field H which constitutes the synchronous perturbation, as defining the direction with respect to which the nuclear spins orient themselves. The nuclear dipole moments will have finite components parallel to H and sweeping round with H. These will induce a signal in the detector coil. If the two magnetic substates existing when $I = \frac{1}{2}$ were equally populated, then the net signal would be zero, as there would be as many positive as negative components contributing. In so far as the populations are not equal there will be a resultant signal. This signal is detected and amplified.

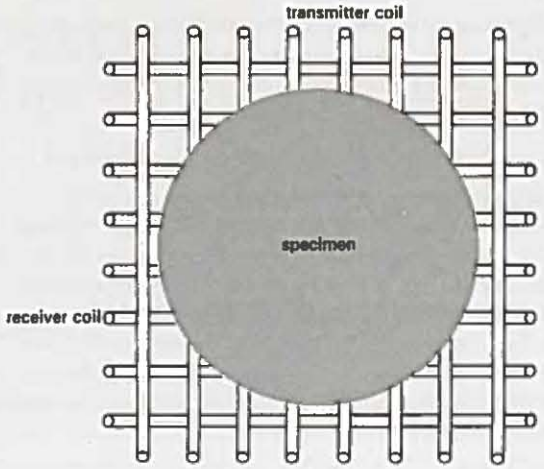

Figure 50 Schematic diagram of nuclear induction experiment. Radio-frequency power is fed to a transmitter coil. A radio-frequency signal is picked up by the receiver coil from nuclei precessing in the presence of a uniform magnetic field applied perpendicularly to the plane of the diagram

With this technique there is the additional information of the phase of the signal in the detector coil with respect to the phase of the voltage applied to the drive coil. This relative phase will depend on the sign of the magnetic moment as it would be altered by 180° if the direction of the Larmor precession were to be reversed.

8.5.8 *The measurement of electric quadrupole moments in bulk materials*

When a nucleus has a quadrupole moment and when it is situated in an internal electric field gradient $\partial^2\phi(0)/\partial z^2$ in the specimen, then there will be an electric quadrupole contribution to the total potential energy. This will give rise to a splitting of the resonances described above. In a crystal, where the electric field gradient is in a direction fixed with respect to the axis of the crystal, this splitting will vary with crystal orientation. Thermal motions giving rise to fluctuations in field gradient will broaden the lines and may make their resolution impossible. Also, where a measurement is possible, it is

$$B = eQ\frac{\partial^2\phi(0)}{\partial z^2}$$

which is measured and $\partial^2\phi(0)/\partial z^2$ is not usually known with any certainty. As pointed out above, the need to know the field gradient can be avoided by limiting the discussion to the ratios of quadrupole moments of two isotopes. By this method Becker (1951) measured the ratio of the quadrupole moments of ^{63}Cu and ^{65}Cu using single crystals of $K_3[Cu(CN)_4]$.

Pure quadrupole resonances have also been observed when a perturbing magnetic field applied perpendicular to the axis of the electric field in the absence of a field H_0 has induced transitions leading to absorption of radio-frequency power.

8.5.9 *The measurements of quadrupole moments by paramagnetic resonances*

The technique of Purcell described in section 8.5.6 has been applied to paramagnetic atoms. The much larger magnetic moment of the atom places the Larmor frequencies, and hence the resonant frequencies, in the microwave range. The effect of the nuclear spin is then to produce hyperfine splitting in the atomic resonances. By observing the degree of splitting as a function of H_0, diagrams of the type encountered in optical hyperfine splitting (see Figure 43, p. 137) are constructed. By comparing these with the theory of hyperfine splitting outlined above, the effect of the quadrupole moment can be detected and values of B estimated.

8.6 Summary

Spins of nuclei can be measured by several techniques and can be regarded as very well established for ground states of stable nuclei. In some cases the techniques can be applied to give a direct measurement of spin for unstable nuclei of suitably long half-life.

Magnetic moments can be measured with high precision, a precision limited in practice by the accuracy with which the internal and induced field produced by the orbital electrons at the nucleus can be calculated.

With respect to quadrupole moments the situation is very much less satisfactory. In certain cases B can be measured directly; in other cases it can be measured as a deviation of hyperfine structure from that expected on the basis of magnetic dipole moments alone. However, the deduction of Q from B is very uncertain because of the lack of knowledge of the internal electric field gradients at the nucleus. The ratio of Q for two isotopes is known with better accuracy on the assumption that the internal electric field gradient is the same for both isotopes.

As we shall see later, information about both electric and magnetic moments of nuclei comes from the study of transitions between their excited states. It is to that source that at present one has to look for better information about the electric quadrupole moment.

Values of spins, magnetic dipole moments and quadrupole moments for stable nuclei are listed in Appendix A.

Chapter 9
The Collective Model

9.1 Introduction

We recall that the discussion of section 6.10 showed that a good account of the ground-state spin of nuclei can be given in terms of the shell model. In that account it is assumed that nucleons of the same kind form pairs, their angular momenta coupling so that the resultant angular momentum of the pair is zero. In the case of (even, even) nuclei there is complete pairing and hence the spin predicted by the model is zero. This, without known exception, is in agreement with measured spins. In the case of odd-A nuclei there is always a nucleon of one type left unpaired. The nuclear spin then is assumed to arise entirely from the motion of this unpaired nucleon. In the case of (odd, odd) nuclei there is an unpaired nucleon of each kind and the nuclear spin has a contribution from the motion of each of these. The satisfactory agreement of this account of nuclear spins with experimental observations argues strongly for the validity of the shell model.

The attempt to extend the ideas of the shell model to explain magnetic dipole moments met, as we saw in section 7.3, with only limited success. It is true that (even, even) nuclei have zero magnetic moment, as well as zero spin, as would be expected on the assumption that the nucleons form pairs. However, in the case of odd-A nuclei, we see from Figures 31 and 32 (pp. 110–12) that, with few exceptions, the measured magnetic dipole moments are significantly smaller than the 'single-particle' predictions. One must conclude that in these cases the paired nucleons in the 'core' are not exactly compensating each others' magnetic moments but are making a contribution to the total dipole moment, this despite the fact that they do compensate each others' angular momentum. It is however to be noted that the main contribution to the magnetic moment still arises from the single particle.

The situation *vis-à-vis* the predictions of the shell model and the experimental facts is less satisfactory when we turn to electric quadrupole moments. The quadrupole moment is taken as a measure of the departure of the charge distribution from spherical symmetry. If a nucleus has a closed shell of protons it has no total angular momentum and hence no distinctive axis. It is therefore expected to exhibit spherical symmetry of charge. If we now take the case of one proton outside a closed shell then, unless that proton be in an s-state, its equivalent charge distribution will not be spherically symmetric and a nuclear electric quadrupole moment would be expected to result. Consider now a second