Nuclear Quadrupole Resonance 12

Nuclear Quadrupole Resonance (NQR) is a branch of spectroscopy occurring in the radio-frequency region of the electromagnetic spectrum like nuclear magnetic resonance. Just like any other branch of spectroscopy, this also deals with the coupling between electromagnetic radiation and a set of energy levels, in this case nuclear energy levels.

12.1 THE QUADRUPOLE NUCLEUS

A nucleus with $I > ½$ lack the spherical symmetry along the spin axis. Such nuclei are shaped either elongated or compressed along the spin axis. The former one has a prolate spheroid shape (symmetrical egg) and the latter an oblate spheroid shape (flattened disc). Eventhough the charge density inside a nucleus is uniform, the distorted shape gives rise to a charge distribution which is nonspherical. The electric quadrupole moment eQ is defined by

$$eQ = \int \rho(x, y, z) r^2 (3 \cos^2 \theta - 1) d\tau \qquad (12.1)$$

where $+e$ is the charge on the proton, $\rho(x, y, z)$ is the charge density at (x, y, z), r is the distance of the volume element $d\tau$ from the nucleus and θ is the angle which the radius vector r makes with the nuclear spin axis. The nuclear quadrupole moment eQ, a measure of the departure from spherical symmetry of the nuclear charge, is greater than zero for prolate ones and less than zero for oblate ones (Figure 12.1).

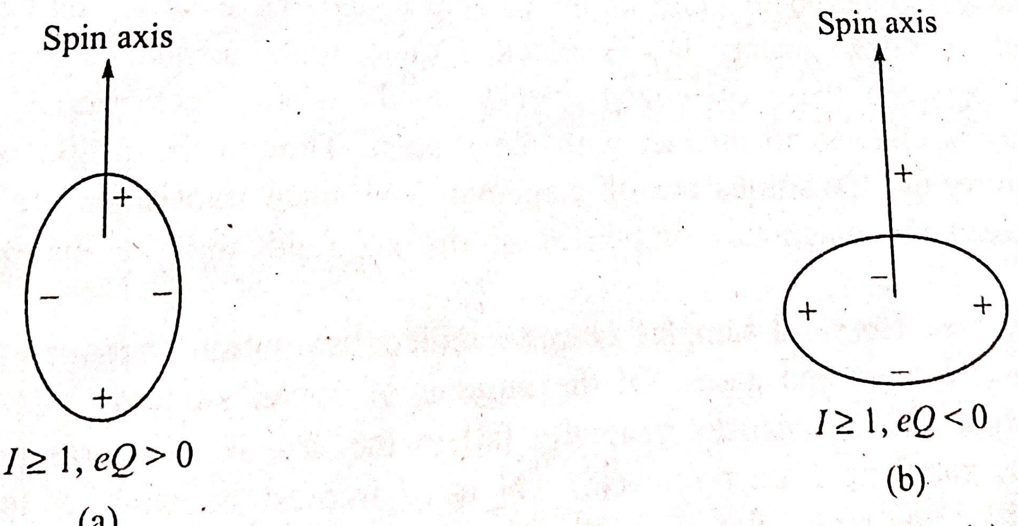

Figure 12.1 Representation of nuclei for quadrupole configurations: (a) $I \geq 1$; $eQ > 0$, (b) $I \geq 1$, $eQ < 0$.

The charges near a nucleus produces an electrostatic potential V at the nucleus. The electric field gradient eq is defined as the second derivative of V and in general it is a tensor with nine components. The components are given by

$$eq_{ij} = \frac{\partial^2 V}{\partial x_i \, \partial x_j}, \qquad x_i, x_j = x, y, z \tag{12.2}$$

If the coordinate axes are selected such that the tensor eq is diagonal, then terms such as $\partial^2 V/\partial x\,\partial y$, $\partial^2 V/\partial x\,\partial z$ etc., vanish. In such a principal axes system, the eq tensor is traceless, so that

$$q_{xx} + q_{yy} + q_{zz} = 0 \tag{12.3a}$$

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \tag{12.3b}$$

Hence, out of q_{xx}, q_{yy} and q_{zz} only two are independent. The convention generally followed is that

$$|q_{zz}| \geq |q_{yy}| \geq |q_{xx}| \tag{12.4}$$

If $q_{zz} = q_{yy} = q_{xx}$, the field gradient is spherical and the interaction of quadrupole moment with electronic charge vanishes, leading to degenerate quadrupole levels. If the field has an axial symmetry, q_{zz} lies along the symmetry axis z, $q_{zz} \neq q_{yy} = q_{xx}$. When $q_{zz} \neq q_{yy} \neq q_{xx}$, to measure the departure of the field gradient from axial symmetry, an asymmetry parameter η is introduced which is defined by

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \tag{12.5}$$

In general η varies from 0 to 1, $\eta = 0$ corresponds to axial symmetry whereas $\eta = 1$ to the condition $\partial^2 V/\partial x^2 = 0$, $\partial^2 V/\partial y^2 = -\partial^2 V/\partial z^2$.

12.2 PRINCIPLE OF NUCLEAR QUADRUPOLE RESONANCE

A quadrupolar nucleus will have different nuclear orientations caused by the interaction between the nuclear quadrupole moment of a nucleus and the electric field gradient, giving rise to a set of quantized energy levels. Nuclear quadrupole resonance spectroscopy deals with tran ition between these quantized energy levels when electromagnetic radiation of proper frequency is allowed to interact with the system. Though the origin of the levels are electrical in nature, the transitions are of magnetic type since transitions are induced by the interaction between the magnetic component of the r-f field and the magnetic moment of the nucleus.

NQR is observed for solid samples because molecular motion averages the electric field gradient to zero in liquids and gases. Of the number of nuclei studied, ^{35}Cl and ^{14}N are the most common ones. ^{35}Cl resonances generally fall in the 20–40 MHz range and the signals are not easily saturated by high r-f levels. ^{14}N is of interest because of its different types of bonding in different molecules. For better results, the nucleus under study must have reasonably large value for the nuclear quadrupole moment and natural abundance. Also the chemical bonds associated with it must have an appreciable p character to give a sufficiently large field gradient.

Though both NQR and NMR involve the coupling of r-f field with a set of nuclear energy levels, differences exist between the two. In NMR, the set of nuclear levels are magnetic in origin whereas it is of electrical origin in NQR. In NMR, the splitting between energy levels are proportional to the applied magnetic field and transitions are usually studied by using a fixed frequency oscillator while varying the magnetic field. In NQR as the electric field gradient is a fixed property of the solid, a variable frequency detection system must be used.

12.3 TRANSITIONS FOR AXIALLY SYMMETRIC SYSTEMS

12.3.1 Frequencies of Transitions

For systems having axial symmetry, the Hamiltonian representing the interaction between the nuclear quadrupole moment of the nucleus and the electric field gradient leads to the energy eigenvalues

$$E_m = \frac{e^2 qQ\left[3m_I^2 - I(I+1)\right]}{4I(2I-1)} \tag{12.6}$$

where I is the nuclear spin quantum number, $eq = (\partial^2 V/\partial z^2)$ is the magnitude of the electric field gradient in the direction of the axis of symmetry, eQ is the nuclear quadrupole moment and m_I is the magnetic quantum number which takes the $(2I + 1)$ values

$$m_I = I,\ I - 1,\ \ldots,\ -I$$

The states $+m_I$ and $-m_I$ are degenerate as m_I appears as m_I^2 in the expression. The selection rule for magnetic dipole transition is

$$\Delta m_I = \pm 1 \tag{12.7}$$

The frequency of the $(m_I - 1) \rightarrow m_I$ transition is given by

$$\nu = \frac{3e^2 qQ}{4I(2I-1)h}\,(2\,|m_I| - 1) \tag{12.8}$$

There will be $I - \frac{1}{2}$ transition frequencies for half integral spins and I for integral spins. The NQR frequencies of nuclei usually lie in the range 100 kHz – 1,000 MHz. The expression e^2qQ/h is called the **nuclear quadrupole coupling constant** and has the unit of frequency.

12.3.2 Half Integral Spins

For nuclei having spin $I = \frac{3}{2}$ (^{35}Cl, ^{79}Br) Eq. (12.8) allows only a single transition of frequency,

$$\nu = \frac{e^2 qQ}{2h} \tag{12.9}$$

For nuclei with spin $I = \frac{5}{2}$ (^{127}I, ^{121}Sb), there will be three levels and two transitions.

They are

$$\nu_1 = \frac{3}{20h} e^2qQ, \quad \nu_2 = \frac{6}{20h} e^2qQ \tag{12.10}$$

The energy levels and transitions are illustrated in Figure 12.2. The order of the levels may change depending on the sign of q or eQ

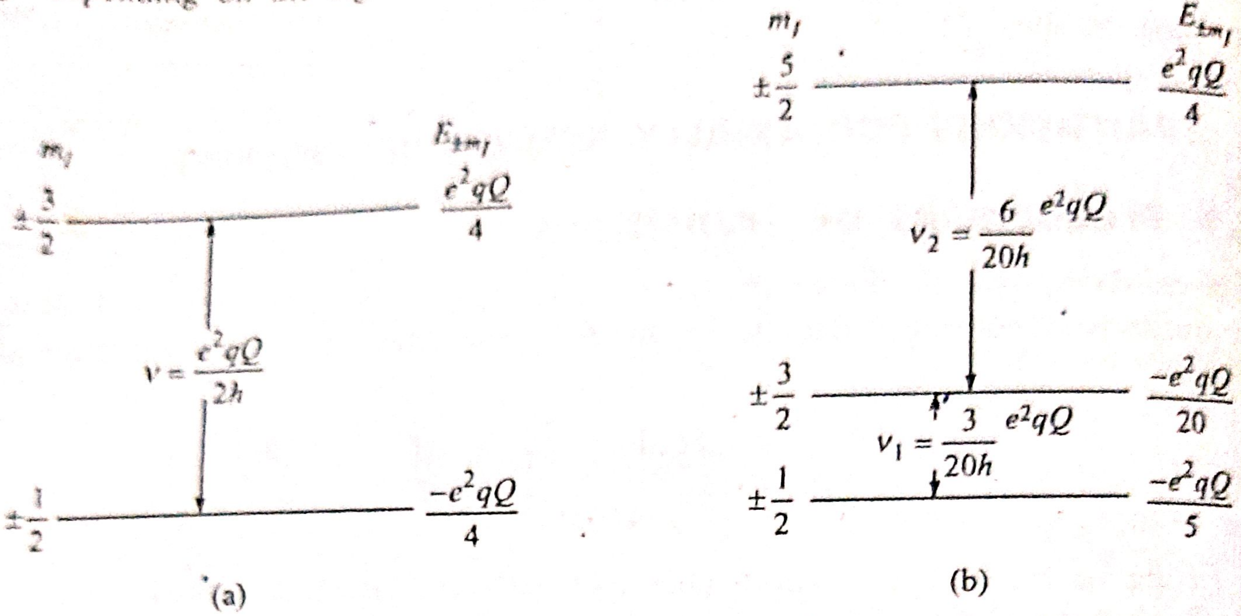

Figure 12.2 Energy levels and transitions for (a) $I = 3/2$, (b) $I = 5/2$.

12.3.3 Integral Spins

For integral spins, the energy expression Eq. (12.6) leads to $(I + 1)$ doubly degenerate and one non-degenerate levels. A single resonance line results for nuclei having $I = 1$ (^{14}N, ^{6}Li), the frequency of which is given by

$$\nu = \frac{3e^2qQ}{4h} \tag{12.11}$$

The energy levels and transition for $I = 1$ case is illustrated in Figure 12.3.

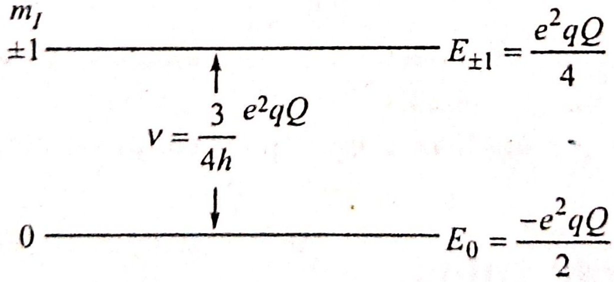

Figure 12.3 Energy levels and transition for $I = 1$.

From simple considerations, it can be shown that intensity of NQR line becomes a maximum when the *r-f* field is perpendicular to the symmetry axis and vanishes when it is parallel. Therefore, a study of the dependence of the intensity of the quadrupole lines on the direction of the *r-f* field with respect to axes fixed in the crystal helps one to determine the axis of symmetry of the field gradient tensor. The experimental observation of transitions in a system also helps one to determine the quadrupole coupling constant e^2qQ/h.

12.4 TRANSITIONS FOR NONAXIALLY SYMMETRIC SYSTEMS

When the field gradient is not axial ($\eta \neq 0$), the energy levels and transition frequencies are more complex. In large number of systems, though the nucleus under investigation is situated in axially symmetric position in free molecule, the axial symmetry is destroyed within the crystal lattice due to intermolecular interaction. Even in simple systems, the double bond character of bonds often leads to departure from axial symmetry in the field gradient.

12.4.1 Half Integral Spins

Formulation of exact solutions beyond $I = \frac{3}{2}$ will be difficult and will involve complicated expressions. Such systems are handled by using series approximations when η is small or by using numerical methods. For $I = \frac{3}{2}$, some of the off diagonal matrix elements of the Hamiltonian are not zero and evaluation of the energy eigenvalues gives the secular equation.

$$E^2 - 3\left(\frac{e^2qQ}{12}\right)^2 \eta^2 - 9\left(\frac{e^2qQ}{12}\right)^2 = 0 \qquad (12.12)$$

The two roots of this equation are:

$$E_{\pm 3/2} = \frac{3e^2qQ}{12}\left(1+\frac{\eta^2}{3}\right)^{1/2} \qquad (12.13)$$

$$E_{\pm 1/2} = \frac{-3e^2qQ}{12}\left(1+\frac{\eta^2}{3}\right)^{1/2} \qquad (12.14)$$

The selection rule $\Delta m_I = \pm 1$ leads to a single transition having frequency ν given by

$$\nu = \frac{e^2qQ}{2h}\left(1+\frac{\eta^2}{3}\right)^{1/2} \qquad (12.15)$$

The transition is represented in Figure 12.4. As there is only one frequency, it is not possible to determine both the nuclear quadrupole coupling constant e^2qQ/h and the asymmetry

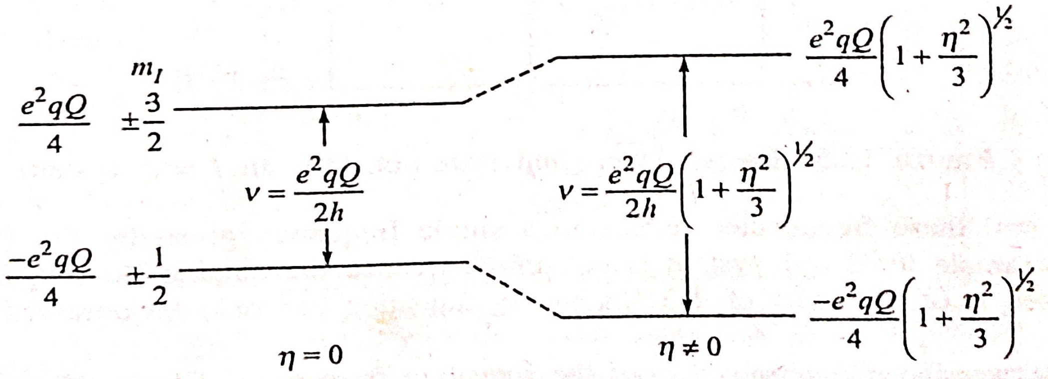

Figure 12.4 Energy levels and transition for $I = 3/2$, $\eta \neq 0$. The one for $\eta = 0$ is given for comparison.

parameter η simultaneously. This difficulty which is unique for $I = \frac{3}{2}$ systems can be solved by investigating the spectrum in the presence of a weak magnetic field.

12.4.2 Integral Spins

The introduction of asymmetry removes the degeneracy in m_I for integer spin systems. For nuclei of spin $I = 1$, the secular equation for energy reduces to

$$\begin{vmatrix} A_1 - E & 0 & A_1\eta \\ 0 & -2A_1 - E & 0 \\ A_1\eta & 0 & A_1 - E \end{vmatrix} = 0 \tag{12.16}$$

where

$$A_1 = \frac{e^2qQ}{4} \tag{12.17}$$

The energy levels are then given by

$$E_0 = -2A_1 \tag{12.18}$$

$$E_{\pm 1} = A_1(1 \pm \eta) \tag{12.19}$$

The energy levels and allowed transitions are shown in Figure 12.5. For comparison $I = 1$, $\eta = 0$ case is also included. The frequencies of the three transitions are given by

$$\nu_0 = \frac{1}{2}\frac{e^2qQ}{h}\eta \tag{12.20}$$

$$\nu_\pm = \frac{3}{4}\frac{e^2qQ}{h}\left(1 \pm \frac{\eta}{3}\right) \tag{12.21}$$

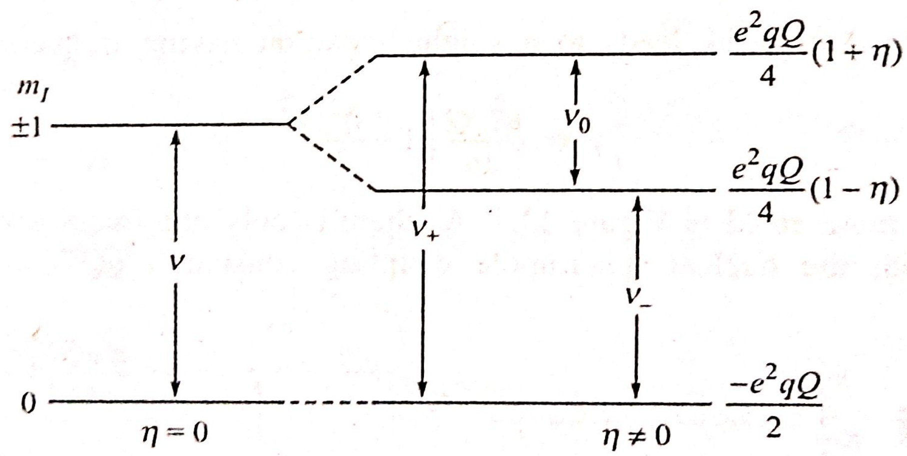

Figure 12.5 Energy levels and transitions for an $I = 1$ system.

When $\eta = 0$ these frequencies reduce to a single frequency given by Eq. (12.11). The familiar example for $I = 1$ system is that of ^{14}N. Since the quadrupole coupling constant for nitrogen is of the order of 4 MHz, the ν_0 transition can only be observed when η is large.

The experimental determination of the transition frequencies allows the calculation of quadrupole coupling constant and the asymmetry parameter η except for $I = \frac{3}{2}$.

12.5 NQR INSTRUMENTATION

12.5.1 General Considerations

Nuclear quadrupole resonance deals with transition between the energylevels caused by the interaction of the quadrupole moment of a nucleus with the electric field gradient at the nucleus due to the nearby charges. The transitions are induced by the interaction between the magnetic moment of the nucleus and the magnetic field component of an applied *r-f* field. Crossed coil detection is not possible as in NMR since the $\pm\, m_I$ degeneracy causes a net cancellation of the nuclear induction in a direction perpendicular to the axis of the transmitting coil. When a small magnetic field is applied, the $\pm m_I$ degeneracy is lifted and the cross coil method can be used as a component of nuclear induction appears normal to the axis of the driving coil. However, the method has the disadvantage that the frequency cannot be varied easily over a wide range since both coils have to be tuned simultaneously. The quadrupole frequencies to be detected range from as low as a few to as high as 1000 MHz. Hence, during the search for the detection of resonance absorption, the applied frequency must be changed continuously maintaining reasonable stability and sensitivity. Moreover, because of the smaller spin-lattice relaxation times of quadrupole nuclei, experiments require much larger r-f power than magnetic resonance experiments.

Three different methods are generally used for the detection of NQR frequencies:

(i) Super-regenerative oscillators
(ii) Regenerative continuous wave oscillators, and
(iii) Pulsed r-f or spin echo method.

In the first two, an r-f oscillator is used to act both as exciter of the nuclei and detector. In the third method, separate transmitter and receiver carry out these functions.

12.5.2 Regenerative Continuous Wave Oscillator Method

Regenerative continuous wave oscillator is somewhat simpler than super-regenerative oscillator method. A method of this type was first developed by Pound and Knight. A block diagram of this arrangement is illustrated in Figure 12.6.

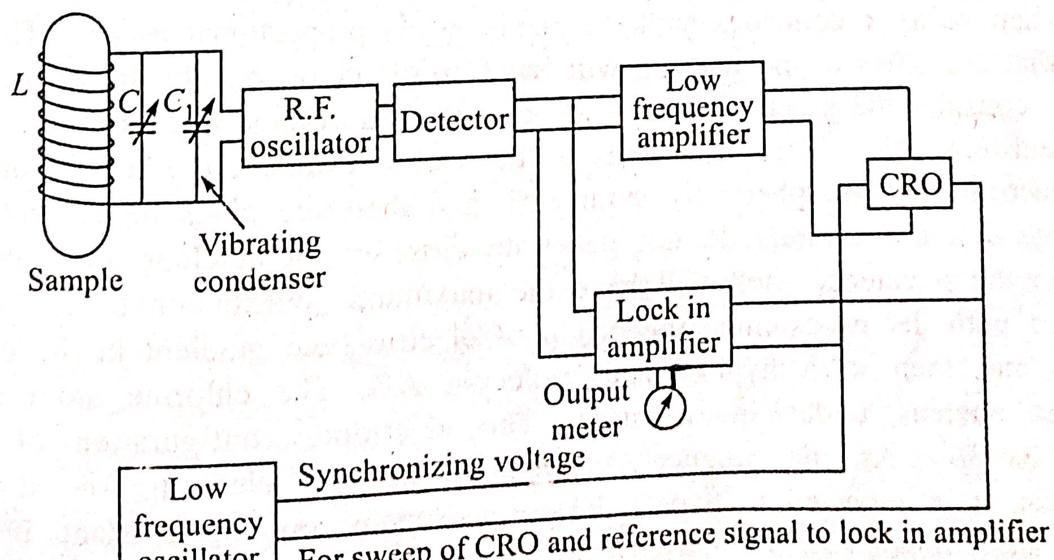

Figure 12.6 Block diagram of a regenerative continuous wave oscillor-detector arrangement to observe NQR.

The sample is placed in the inductance L which is tuned to the transition frequency using the large capacitor C. Changes in frequency over a limited range is effected by changing the capacitance C. Using the LC circuit as the oscillating element with electronic feedback, the voltage level of oscillation becomes a function of nuclear absorption. The applied frequency is modulated about the resonant frequency by varying the small capacitor C_1 sinusoidally. The signal may be presented in an oscilloscope or the derivative of the signal can be recorded by the help of a narrow band lock in the system followed by a recorder.