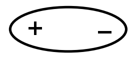
M.Sc. IVSemester
Paper I: General Paper
Unit IV: Nuclear Quadrupole Resonance spectroscopy

NQR spectroscopy was first time discovered by H. G. Dehmelt in 1950. It is observed only in the solid state. It is not observed in the liquid or gaseous state because tumbling of nuclei very fast. It is observed in the radio frequency region. NQR is the extension of NMR spectroscopy. It is help to use the study the electronic environment around the quadrupolor nuclei.

Quadrupole Nuclei:

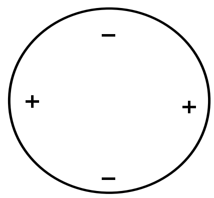
Pole: Accumulative charged centre (either negative or positive) is called pole.

Dipole: The molecule or body which has opposite charge at its terminal of the body is called dipole.

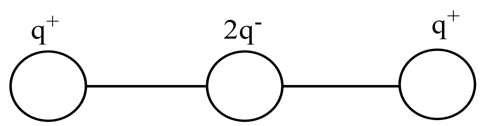


Dipole

Quadrupole: Those bodies which have four charges (two positive and two negative) is called quadrupole.



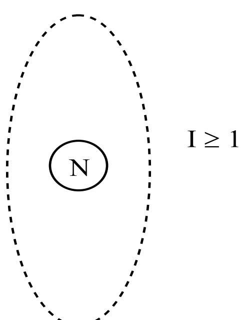
Spherical Quadrupole



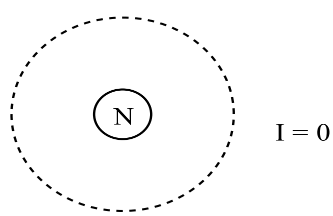
Linear quadrupole

All nuclei having integral and half integral nuclear spins (1, 3/2, 2, 5/2, 3, 7/2 etc.) possess nuclear electric quadrupole moments. These nuclei are referred to as quadrupole nuclei.

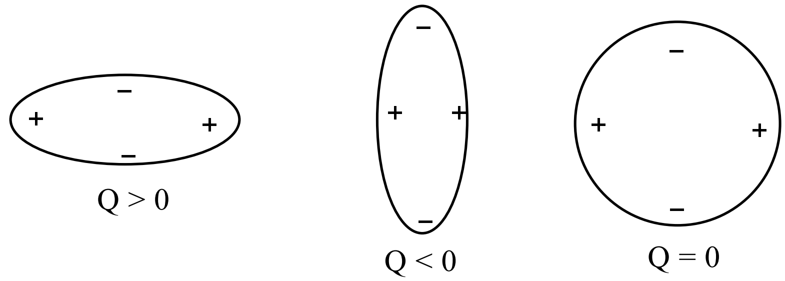
Quadrupole moment: Quantum mechanical consideration of the distribution of nuclear charge shows that nuclei do not have permanent electric dipoles moments, but can have electric quadrupole moments when their electric charges are not spherically symmetric. It is designated as Q or eQ. It is a parameter, used to determine Unsymmetric distribution of electronic charge of spinning nuclei. It is also measure of deviation of nuclear charge distribution from spherical symmetry.



Spherically unsymmetric
non-degerate state

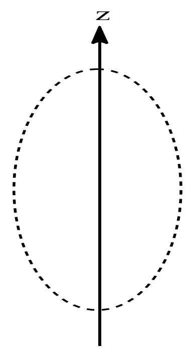


Spherically symmetric
Degerate state

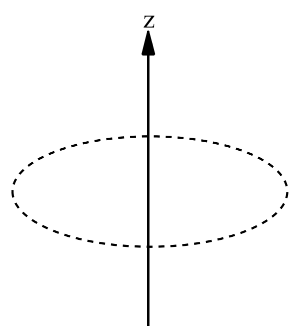


Types of quadrupole moment: It is classified into two categories.

Prolate charge distribution (Q > 0): A prolate charge distribution with its axis parallel to z-axis (elongation along spinning axis) gives rise to positive quadrupole moment. It is egg shaped or cigar shaped.

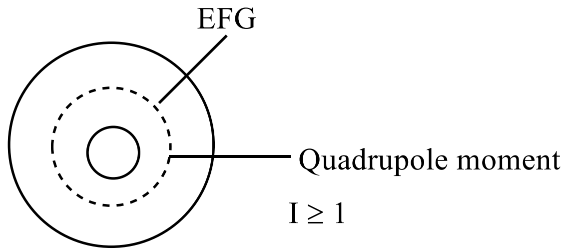


Oblate charge distribution (Q < 0): An oblate charge distribution with its axis horizontal to z-axis (flattened or spheroid along spinning axis) gives rise to negative quadrupole moment. It is knob shaped.



Note: Quadrupole moment is a measure of the departure from sphericity being positive for egg shaped and negative for tangerine shaped nuclei. Q is zero for spherical nuclei for which the spin I = 0 or ½.

Electric field gradient (EFG): It is parameter measure the rate of change of electric field at atomic nuclei generated by electronic charge distribution and by nearby electronic density. It is denoted by q. Quadrupole nuclei possess nuclear quadrupole moment which interact with electric field gradient (EFG), created at the nuclei by a symmetric distribution of charge arising from the extra nuclear electrons or the non-bonding electrons.



Nuclear quadrupole resonance

Only two parameters are needed to specify the EFG. An important quantity, the asymmetry parameter η (degree of deviation) is defined as

$$\eta = \frac{(q_{xx} - q_{yy})}{q_{zz}}$$

Asymmetry parameter η lies between 0 and 1, i.e. $0 < \eta < 1$.

i. If $q_{xx} = q_{yy} = q_{zz}$ then EFG is said to spherical. In this case there is no interaction of the nuclear quadrupole moment Q, with the electronic charge distribution. Hence no resonance occurs.
ii. If $q_{xx} = q_{yy} \neq q_{zz}$ then EFG is axial symmetry around z-axis.
iii. If $q_{xx} \neq q_{yy} \neq q_{zz}$ then EFG is said to be nonsymmetric. It gives complex spectrum.

Coupling constant: The product of quadrupole moment eQ (or Q) and EFG (q) i.e. e^2Qq is called nuclear quadrupole coupling constant (QCC). Coupling constant value observed in range of 3 MHz to 500MHz.

$$QCC = e^2Q \times q$$

i. Non-bonding electrons in the valence shell of the atom being investigated make the biggest contribution. Thus atoms with one, two or three lone pairs usually show very large value of QCC.
ii. The next largest contribution arises from the electrons in the bonds to the ligands. Since these are shared with the ligand atoms, their average distance from the quadrupole nucleus is greater than that of the non-bonding electrons.
iii. When arrangement of bonds has symmetry less than cube, there will be a contribution to EFG. For instance, there is an EFG at the nucleus of the M atom in the molecule MAB5 which depends upon the difference in the nature of the M-A and M-B bonds.
iv. In a molecule, the electronic structure near a nucleus depends on the hybridization of the bonding orbital and the ionic character of the bond.

e^2Qq_{mol} of halogen atom to that measure or in the isolated atom e^2Qq_{atom} is given by

$$e^2Qq_{mol} = [1 - s + d - i(1 - s - d)]\, e^2Qq_{atom}$$

Where s and d denote the amount of s and d character of the bonding orbital and i is the ionic character of the bond. If π-bond is also present, then

$$e^2Qq_{mol} = [1 - s + d - i - \pi)]\, e^2Qq_{atom}$$

Theory of NQR: If a nuclei possessing nuclear quadrupole moment or having a non-spherical charge distribution is placed in an inhomogeneous electric field, the potential energy V of the quadrupole will vary, depending on the orientation of the quadrupole moment with field. In an inhomogeneous electric field, the interaction is between the nuclear quadrupole moment and the EFG at the nucleus.

$$q_{xx} = \frac{d^2V}{dx^2}, q_{yy} = \frac{d^2V}{dy^2}, q_{zz} = \frac{d^2V}{dz^2},$$

The solution of the Schrodinger wave equation for a quadrupolar nucleus having both the integral and half-integral spin ($I \geq 1$) gives the following expression for NQR energy levels:

$$E_{m_I} = \frac{e^2Qq}{4I(2I-1)} [3m_{I^2} - I(I+1)]$$

$$E_{m_I} = A\, [3m_{I^2} - I(I+1)]$$

$$\text{Where } A = \frac{e^2Qq}{4I(2I-1)}$$

The above equation hold for an axially symmetric EFG i.e. $\eta = 0$

Splitting in NQR spectra:

Example: $_7N^{14}$: ($I = 1$) then $m_I = -1, 0, 1$

$$E_{-1} = \frac{e^2Qq}{4 \times 1(2 \times 1 - 1)} [3(-1)^2 - 1(1+1)]$$

$$E_{-1} = \frac{e^2Qq}{4} [3-2]$$

$$E_{-1} = \frac{e^2Qq}{4}$$

$$E_{+1} = \frac{e^2Qq}{4 \times 1(2 \times 1 - 1)} [3(1)^2 - 1(1+1)]$$

$$E_{+1} = \frac{e^2Qq}{4} [3-2]$$

$$E_{+1} = \frac{e^2Qq}{4}$$

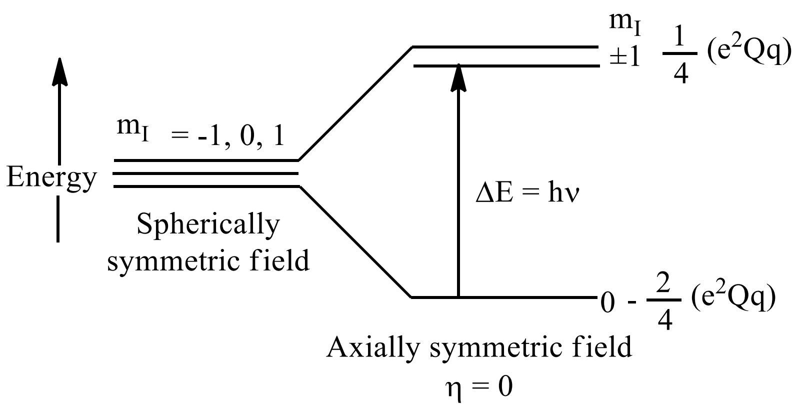
$$E_{\pm 1} = \frac{e^2Qq}{4}$$

$$E_0 = \frac{e^2Qq}{4 \times 1(2 \times 1 - 1)} [3(0)^2 - 1(1+1)]$$

$$E_0 = \frac{e^2Qq}{4} [-2]$$

$$E_0 = -\frac{2}{4} e^2Qq$$

Note: Selection rule $\Delta m_I = \pm 1$, gives only one NQR frequency



$$\Delta E = h\nu$$

$$\nu = \frac{\Delta E}{h}$$

$$\nu\,(0 \rightarrow \pm 1) = (E_{\pm 1} - E_0)/h = \frac{e^2Qq}{4} - \left(-\frac{2}{4}\,e^2Qq\right) = \frac{3}{4}\,e^2Qq$$

$_5$**B**^{11}**:** $I = \frac{3}{2}$ so that $m_I = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

$$E_{-3/2} = \frac{e^2Qq}{4\times\frac{3}{2}(2\times\frac{3}{2}-1)}\,[3\left(-\frac{3}{2}\right)^2 - \frac{3}{2}\left(\frac{3}{2}+1\right)]$$

$$E_{-3/2} = \frac{e^2Qq}{4\times\frac{3}{2}(3-1)}\,[3\times\frac{9}{4} - \frac{3}{2}\left(\frac{5}{2}\right)]$$

$$E_{-3/2} = \frac{e^2Qq}{2\times3\times2}\,[\frac{27}{4} - \frac{15}{4}]$$

$$E_{-3/2} = \frac{e^2Qq}{12}\times\frac{12}{4}$$

$$E_{-3/2} = \frac{1}{4}\,e^2Qq$$

$$E_{+3/2} = \frac{e^2Qq}{4\times\frac{3}{2}(2\times\frac{3}{2}-1)}\,[3\left(\frac{3}{2}\right)^2 - \frac{3}{2}\left(\frac{3}{2}+1\right)]$$

$$E_{+3/2} = \frac{e^2Qq}{4\times\frac{3}{2}(3-1)}\,[3\times\frac{9}{4} - \frac{3}{2}\left(\frac{5}{2}\right)]$$

$$E_{+3/2} = \frac{e^2Qq}{2\times3\times2}\,[\frac{27}{4} - \frac{15}{4}]$$

$$E_{+3/2} = \frac{e^2Qq}{12}\times\frac{12}{4}$$

$$E_{+3/2} = \frac{1}{4}\,e^2Qq$$

$$E_{-1/2} = \frac{e^2Qq}{4\times\frac{3}{2}(2\times\frac{3}{2}-1)}\,[3\left(-\frac{1}{2}\right)^2 - \frac{3}{2}\left(\frac{3}{2}+1\right)]$$

$$E_{-1/2} = \frac{e^2Qq}{4\times\frac{3}{2}(3-1)}\,[3\times\frac{1}{4} - \frac{3}{2}\left(\frac{5}{2}\right)]$$

$$E_{-1/2} = \frac{e^2Qq}{2 \times 3 \times 2} [\frac{3}{4} - \frac{15}{4}]$$

$$E_{-1/2} = \frac{e^2Qq}{12} \times \left(-\frac{12}{4}\right)$$

$$E_{-1/2} = -\frac{1}{4} e^2Qq$$

$$E_{+1/2} = \frac{e^2Qq}{4 \times \frac{3}{2}(2 \times \frac{3}{2} - 1)} [3\left(\frac{1}{2}\right)^2 - \frac{3}{2}\left(\frac{3}{2} + 1\right)]$$

$$E_{+1/2} = \frac{e^2Qq}{4 \times \frac{3}{2}(3 - 1)} [3 \times \frac{1}{4} - \frac{3}{2}\left(\frac{5}{2}\right)]$$

$$E_{+1/2} = \frac{e^2Qq}{2 \times 3 \times 2} [\frac{3}{4} - \frac{15}{4}]$$

$$E_{+1/2} = \frac{e^2Qq}{12} \times \left(-\frac{12}{4}\right)$$

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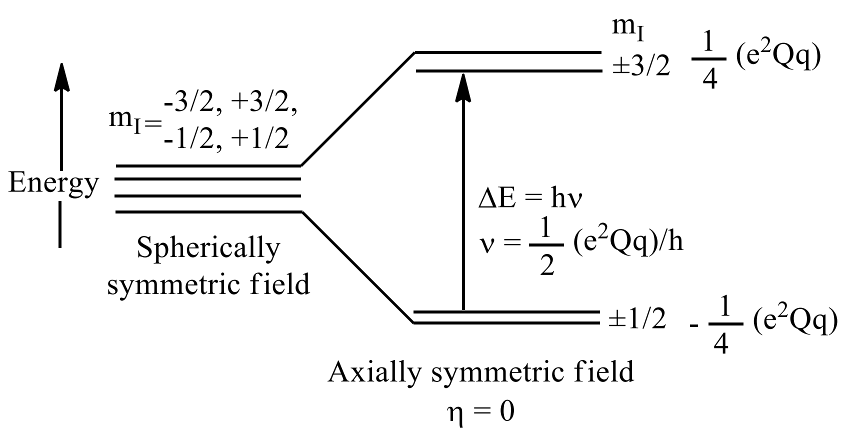
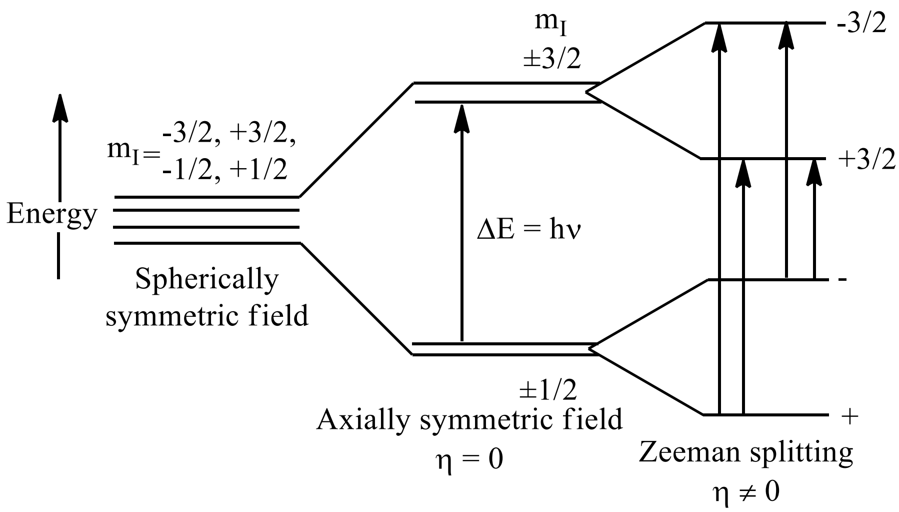


NQR transition in $_5B^{11}$

$$\nu\left(\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}\right), \Delta E = \frac{1}{2} (e^2Qq)/h$$

Zeeman Effect in NQR spectra: The determination of both e^2Qq and η for the special case of I = 3/2, which yields only one NQR frequency, can be done by using Zeeman Effect. The applied magnetic field removes the degeneracy of the ±1/2 and ±3/2 energy sublevels. It is theoretically found that whereas the -3/2 sublevel is raised in energy and the +3/2 sublevel is lowered, exactly similar splitting does not occur for the doubly degenerate sublevels. There occurs considerable mixing of state so that the +1/2 sublevel partakes of some character of -1/2 sublevel and vice versa. The resulting sublevels are designated as + and -, respectively. The Zeeman splitting for the case I = 3/2 is shown below.



The $\Delta m_I = \pm 1$ transitions between the mixed states $\Psi_{\pm}$ and the $\Psi_{\pm 3/2}$ states give rise to the following four frequencies.

$$\nu_{\alpha} \equiv \nu\left(+ \rightarrow +\frac{3}{2}\right), \nu_{\alpha'} \equiv \nu\left(- \rightarrow +\frac{3}{2}\right), \ \nu_{\beta} \equiv \nu\left(+ \rightarrow +\frac{1}{2}\right), \ \nu_{\beta'} \equiv \nu\left(- \rightarrow +\frac{1}{2}\right)$$

The four frequencies are symmetric about the pure NQR frequency. The inner pair of lines ν_{α} and $\nu_{\alpha'}$ has equal intensity. Likewise, the outer pair of lines ν_{β} and $\nu_{\beta'}$ has equal intensity, However the α, α′ pair is more intense than the β, β′ pair.

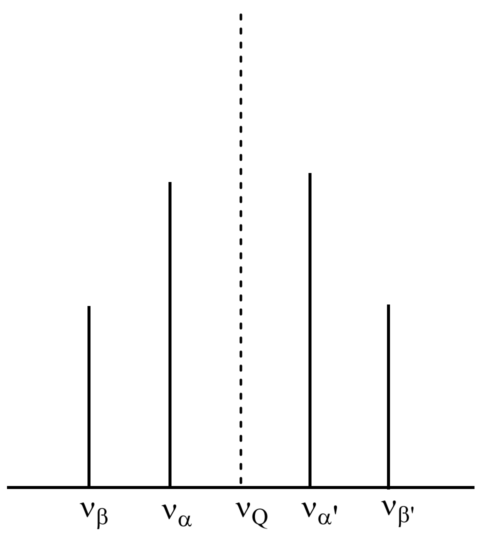


Fig: The four frequencies for I = 3/2 in the presence of Zeeman field