Nuclear Quadrupole Resonance (NQR)

What is NQR?

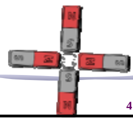
- Nuclear quadrupole resonance or NQR is a technique related to nuclear magnetic resonance (NMR) which is used to detect atoms whose nuclei have a nuclear quadrupole moment
- In NMR, nuclei with spin ≥ 1/2 have a magnetic dipole moment so that their energies are split by a magnetic field, allowing resonance absorption of energy related to the difference between the ground state energy and the excited state.

What is NQR?

- In NQR, on the other hand, nuclei with spin ≥ 1, such as ^{14}N, ^{35}Cl and ^{63}Cu, also have an electric quadrupole moment so that their energies are split by an electric field gradient, created by the electronic bonds in the local environment.

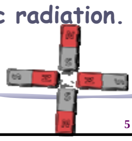
Quadrupole

- A quadrupole is one of a sequence of configurations of electric charge or gravitational mass that can exist in ideal form, but it is usually just part of a multipole expansion of a more complex structure reflecting various orders of complexity.
- To make a magnetic quadrupole we could place two identical bar magnets parallel to each other such that the North pole of one is next to the South of the other and vice versa.



Quadrupole

- The result is a configuration like that in the figure with North poles in place of the positive charges and South in place of negative.
- Such a configuration would have no dipole moment, and its field will decrease at large distances faster than that of a dipole.
- Again, a changing magnetic quadrupole moment will lead to the production of electromagnetic radiation.



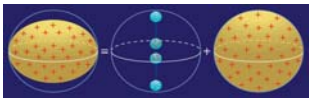
Orbital Symmetry

- Unlike NMR where a powerful external magnetic field is needed, quadrupole resonance takes advantage of a material´s natural electric field gradient
- The electrical gradients are available within certain assymentrical atomic nuclei.

Orbital Symmetry

- These gradients are due to the distribution of the electrical charge and *do therefore strongly depend on the chemical structure*
- Why do some atomic nuclei have an electric quadrupole moment? Physicists would say because they have a spin quantum number greater than 1/2.
- A more intuitive explanation is because the positive electric charge these nuclei carry is not distributed with perfect spherical symmetry

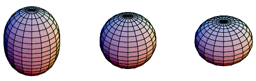
Orbital Symmetry



- Nuclear quadrupole resonance requires that the nuclei under scrutiny display electric quadrupole moments. Such quadrupole moments arise when the distribution of positive electric charge in the nucleus is not perfectly spherical.
  - For example, a slightly oblate (pumpkin-like) distribution of positive charge (*left*) can be thought of as the sum of a quadrupolar distribution (*center*) and a spherical distribution (*right*).

Orbital Symmetry

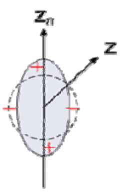
- Consider for a moment a spherical nucleus with its positive charge distributed uniformly throughout.
- Now squeeze that nucleus in your mind's eye so that what was originally shaped like a basketball is flattened into a pumpkin.
- A pumpkin of positive charge can be thought of, to a rough approximation, as being the sum of a sphere of positive charge and two oppositely directed electric dipoles, one at the top and one at the bottom.
- That is, the only requirement for an electric quadrupole moment is that the nucleus be squashed (or stretched) along one axis.



Orbital Symmetry

Torque Acting on the Nucleus

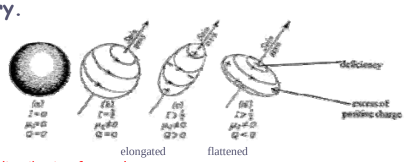
- Visualize quadrupole moment as two anti-parallel electric dipoles
- In a uniform electric field, net torque on the nucleus is zero
- An axial symmetric electric field gradient $\frac{\partial E_z}{\partial z} = -eq$
- produces a net turning torque proportional to $|e^2qQ|$



Q > 0

Electric quadrupole moment (EQM)

- eQ = electric quadrupole moment, EQM
- If I > ½, Nucleus has EQM. EQM measures deviation of nuclear charge distribution from spherical symmetry.



Charge distribution for nucleus,

(a) which does not spin (i.e. I=0),

(b) which has I= ½

(c) and (d) where I > ½

Electric-Field Gradient

- The intrinsic electric quadrupole moment of the nucleus and the electric-field gradient imposed from outside together create distinct energy states.
- This result is analogous to the multiple energy states in NMR, where the critical ingredients were the intrinsic magnetic dipole moment of the nucleus and a magnetic field imposed from the **outside**.

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Electric-Field Gradient

- The key difference between NMR and NQR is the definition of "**outside**."
- In NMR, the outside magnetic field arises because the experimenter has invested considerable effort in setting it up, perhaps using a superconducting electromagnet.
- Since unlike NMR, NQR is done in an environment without a static (or DC) magnetic field, it is sometimes called "**zero field NMR**".

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Electric-Field Gradient

- In NQR, the required electric field (or, more precisely, the required electric-field gradient) comes free:
  - It reflects the local arrangement of electrons around the nucleus under study.
  - That arrangement, in turn, depends not only on the nature of the atom but also on its chemical environment.
- This feature accounts for one of the chief benefits of NQR -- the method is exquisitely sensitive to chemistry.

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Electric-Field Gradient

- Any nucleus with more than one unpaired nuclear particle (protons or neutrons) will have a quadrupolar charge distribution.
- The NQR effect results from the interaction of **this quadrupole** with an **electric field gradient** supplied by the **non-uniform distribution** electron density (from bonding electrons).
- So the technique is very sensitive to the nature of the bonding around the nucleus.

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Electric-Field Gradient

- Spinning nuclear charge has **electric field**, extends outside nucleus.
- Interacts with non-spherical (asymmetric) charge distribution caused by :

nonbonding electrons (lone pairs, p, d)

v

bonding electrons

v

low symmetry environment, charges on neighbouring ions

- So nucleus orients in certain quantized directions with respect to this field, with different energy.

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Electric-Field Gradient

non-homogeneous electric field

electric quadrupole

- Magnitude of asymmetric electric field indicated by **EFG, electric field gradient** along z: $eq = -d^2V/dz^2 = V_{zz}$.
- Interaction between EQM and EFG measured by their product e^2Qq : quadrupole coupling constant, QCC.
- The different orientations cause - interaction with rotational levels, J
  - transitions between nuclear spin levels

nqr spectra (no external field) — nmr spectra (external field applied)

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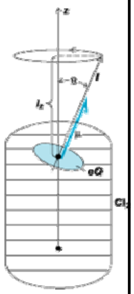
Nuclear Quadrupole Resonance

Interaction of ^{35}Cl nucleus with the electric field of a Cl_2 molecule.

- In the simplest case, for example, ^{35}Cl in solid Cl_2, NQR is associated with the precession of the angular momentum I (and the nuclear magnetic dipole moment μ) of the nucleus,
  - depicted in the illustration as a flat ellipsoid of rotation, around the symmetry axis (taken as the z axis) of the Cl_2 molecule fixed in the crystalline solid.
- The precession, with constant angle θ between the nuclear axis and symmetry axis of the molecule, is due to the torque which the inhomogeneous molecular electric field exerts on the nucleus of electric quadrupole moment eQ.
- The absorption occurs classically when the frequency of the rf field and that of the precessing motion of the angular momentum coincide.



Ionic character (I.C.)

Quadrupole coupling constant (QCC) used to estimate electron configuration of atom, and % ionic character of a bond.
e.g. Cl_2 and ClI compare with 2 reference values:

$$\text{I.C.} = \frac{(\text{QCC})_{\text{obs}} - (\text{QCC})_0}{(\text{QCC})_0}$$

Example 1
Calculate % I.C. of Cl-I bond if
$(QCC)_0$ = 110 MHz for ^{35}Cl `
$[e^2qQ/h](^{35}Cl)$ = 82.5 MHz

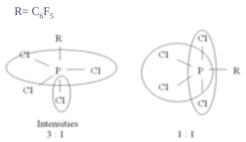
Example 2
$(QCC)_0$ (^{127}I) = 2293 MHz
QCC (^{127}I) in I-Cl = 2992 MHz
Calculate I.C. of ICl bond.

Uses of NQR

- NQR has been used principally for investigating the electronic structure of molecules
- Information regarding hybridization and the ionic character of the bond can be determined by comparing the quadrupole coupling constant in atomic and molecular state in the same nuclei
- Study of the structure of charge transfer complexes
- Detection of crystal imperfections
  - small imperfections destroy symmetry of internal electric field, lead to splitting or broadening of NQR lines.
- Confirmation of nuclear spin Q. N. of an isotope from observed NQR lines.

Uses of NQR

Evaluation of QCC
Information
- about EFG of nuclei
- about ionic character of bond
- about structures of molecules from intensities and numbers of lines.



both 2 geometrically distinct sets of Cl

obs. NQR spectrum for ^{35}Cl :
ν/MHz 33.480 34.380 34.290 25.300
Which structure is likely ?

Uses of NQR

- This technique is suitable for detecting land mines, an application for which it would be difficult to project a uniform magnetic field into the ground.
- Although many different technical measures are available to search for land mines and other kinds of hidden explosives (including trained dogs, electronic metal detectors and ground-penetrating radar), instruments based on nuclear quadrupole resonance offer some special advantages.

Uses of NQR

- In particular, they are highly discriminating, being able to sense the presence of various **nitrogen-rich** compounds used in explosives.
- Nuclear quadrupole resonance offers the possibility of being applied to other tasks as well, including the nondestructive evaluation of materials.

Nuclear Quadrupole Resonance

- Unlike NMR where a powerful external magnetic field is needed, quadrupole resonance takes advantage of a material´s natural electric field gradient,
  - i.e. the electrical gradients available within certain assymentrical atomic nuclei.
- These gradients are due to the distribution of the electrical charge and *do therefore strongly depend on the chemical structure*
  - they will be different for RDX, for TNT, etc.

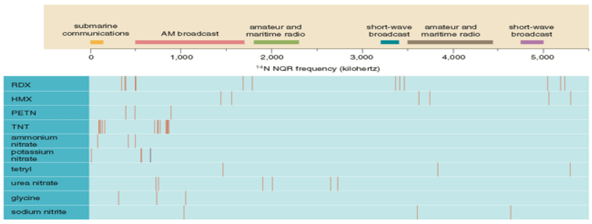
Bulk Explosives Detection Methods

- When a low-intensity RF signal of the correct frequency is applied to the explosive, usually in the range 0.5 to 6 MHz, the energy state of some of the ^{14}N nuclei can be altered.
- After the RF stimulation is removed, the nuclei can return to their original state, releasing energy and producing a characteristic radio signal. The signal can be detected using a special radio reciever and be measured for analysis of the compounds present.

Bulk Explosives Detection Methods

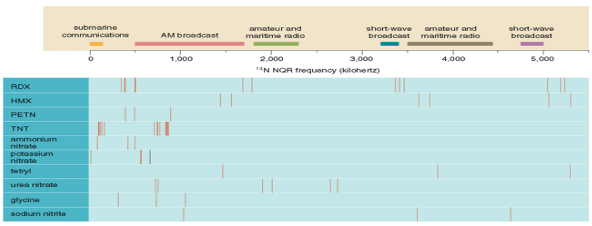
- Detecting the presence of explosives becomes similar to tuning a radio to a particular station and detecting the signal, and the uniqueness of a molecule´s electric field allows NQR technology to be highly compound specific.
- This high selectivity is partly a disadvantage, as it is not straightforward to build a highly specific multichannel system necessary to cover a wide range of target substances, and the precise frequencies drift with temperature.

Bulk Explosives Detection Methods



- Common explosive compounds each produce a unique set of spectral lines when investigated for nuclear quadrupole resonance. The frequencies of almost all of those lines depend on the chemical environment of the nitrogen atoms contained in these compounds and on their crystalline arrangement. (The single purple line shown for potassium nitrate reflects a resonance of potassium-39.)

Bulk Explosives Detection Methods



- Nitrogen-bearing compounds that are innocuous, such as glycine and sodium nitrite, also experience nuclear quadrupole resonance, but their spectral lines are distinct from those used in uncovering explosives. The resonances employed for detecting explosives do, however, overlap with various radio-communication bands (*top*).