

# The Nuclear Emphasis

Atoms are composed of electrons and nuclei – we'll focus almost exclusively on the physical properties of the nucleus and the chemicoelectronic attributes of its environment.

The nucleus exhibits four intrinsic physical properties:

- Mass
- Charge
- Magnetism
- Spin

The *mass* of nuclei accounts for virtually all of the inertial properties and weight of matter.

Electric *charge* accounts for the structure of atoms – the chemical properties of elements depend upon the electric charge of the nucleus.

The result of *nuclear magnetism* is that atoms interact with applied magnetic fields. Nuclear magnetism is a very weak interaction that normally does not affect chemical behavior.

Spin is the most difficult property to describe. Spin is in fact an abstract concept – there is no macroscopic analogy (like mass, or electricity or magnetism). The emergence of the notion of spin is a result of the failure of prevailing (old atomic theory) to explain experimental results.

Spin is a form of *angular momentum*, and in classical physics, objects that rotate possess nonvanishing angular momenta. This is not the case in the microscopic world (the quantum mechanical perspective) and although a convenient way of thinking about spin portrays it as arising from charge motion, it is actually an intrinsic property of matter.

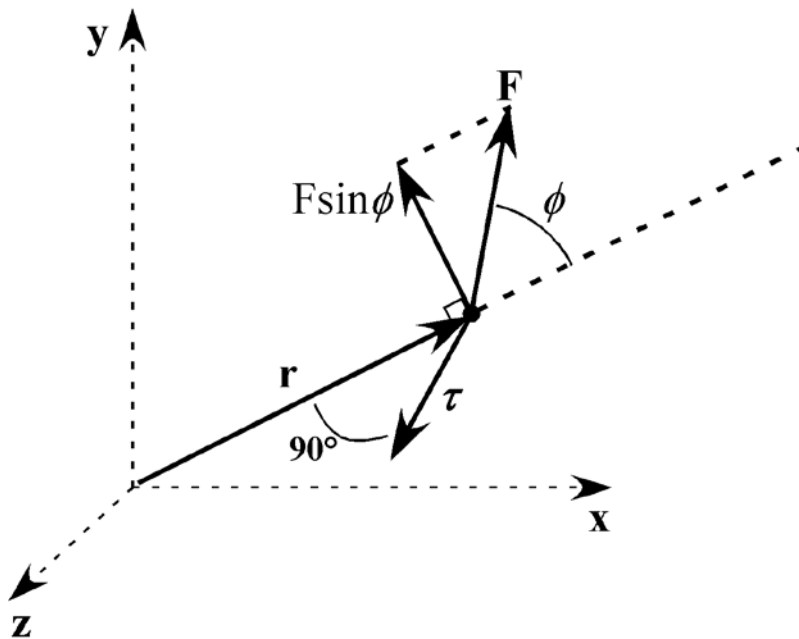
## Classical Angular Momentum

Velocity: 
$$\vec{v} = \frac{d\vec{r}}{dt} \rightarrow \frac{\Delta\vec{r}}{\Delta t}$$

Linear momentum: 
$$\vec{p} = m\vec{v} = m\frac{d\vec{r}}{dt}$$

Force: 
$$\vec{F} = ma = m\frac{d^2\vec{r}}{dt^2} = m\frac{d\vec{v}}{dt} = \frac{d}{dt}(m\vec{v}) = \frac{d}{dt}\vec{p}$$

Torque (vector moment of force): 
$$\vec{\tau} = \vec{r} \times \vec{F}$$



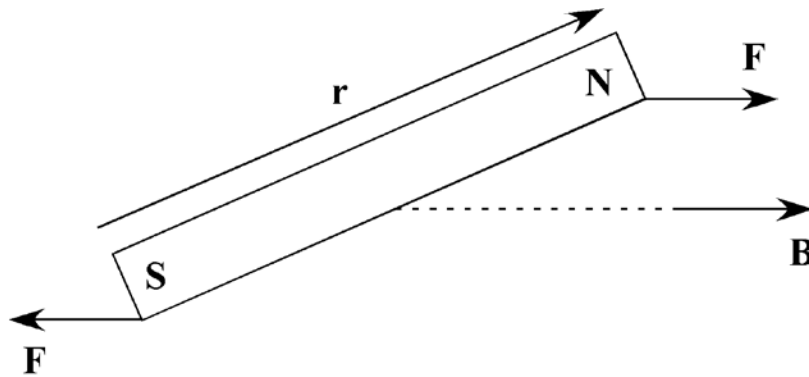
$$\tau = Fr \sin \phi$$

Angular momentum

(moment of linear momentum):  $\vec{P} = \vec{r} \times m \vec{v}$

Torque (again):  $\vec{\tau} = \vec{r} \times \vec{F} = \vec{r} \times \frac{d}{dt}(m \vec{v}) = \frac{d}{dt}(\vec{r} \times m \vec{v}) = \frac{d}{dt} \vec{P}$

Magnetic moment:



Representation of Forces on Magnetic Dipole

Magnetic pole strength:  $q^* = \frac{F}{B}$

Force applied to pole:  $\vec{F} = q^* \vec{B}$

Torque :  $\vec{\tau} = \vec{r} \times \vec{F} = \vec{r} \times q^* \vec{B} = q^* \vec{r} \times \vec{B}$

Definition of the magnetic moment:  $\vec{\mu} = q^* \vec{r}$

Torque (again):  $\vec{\tau} = \vec{\mu} \times \vec{B}$

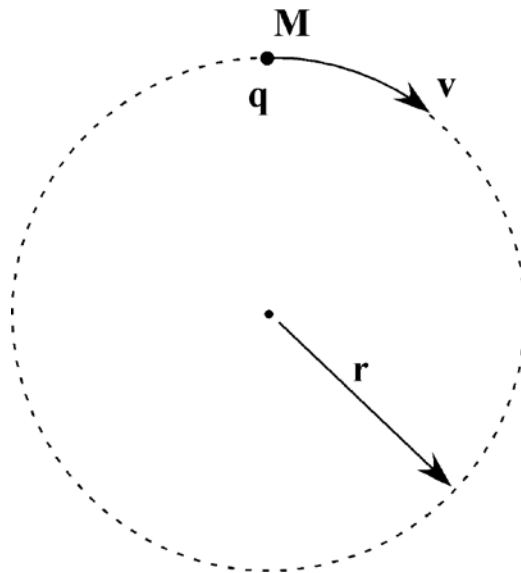
The angular momentum of a charged particle arises from the rotation of the particle of mass,  $m$ , and charge,  $q$ , about an axis.

Consider a charge,  $q$ , moving in a circle of radius,  $r$ , with velocity,  $v$ . The motion produces a current loop, which itself produces a magnetic moment (dipole).

The Biot-Savart Law expresses the relationship between current element and the induced magnetic field:

$$d\vec{B} = k_m \frac{Id\vec{l} \times \hat{r}}{r^2}$$

This expression states that a loop of current will generate a dipolar field.



The period of revolution,  $T$ , is related to the speed of the motion and the radius of the circle by the following expression:

$$T = \frac{2\pi r}{v}$$

The *current* is the ratio of the charge and the period:  $I = \frac{q}{T} = \frac{qv}{2\pi r}$

The *magnetic moment* is equal to the product of the current generated by the moving charge and the area of the circle:

$$\mu = IA = \left(\frac{q}{T}\right) \cdot (\pi r^2)$$

Simple substitution leads to the following expression:

$$\mu = IA = \frac{qv}{2\pi r} \pi r^2 = \frac{1}{2} qvr$$

For the given geometry, and designating the mass associated with the charge to be M, the angular momentum may be written as:

$$P = Mvr = M \frac{2\mu}{q}$$

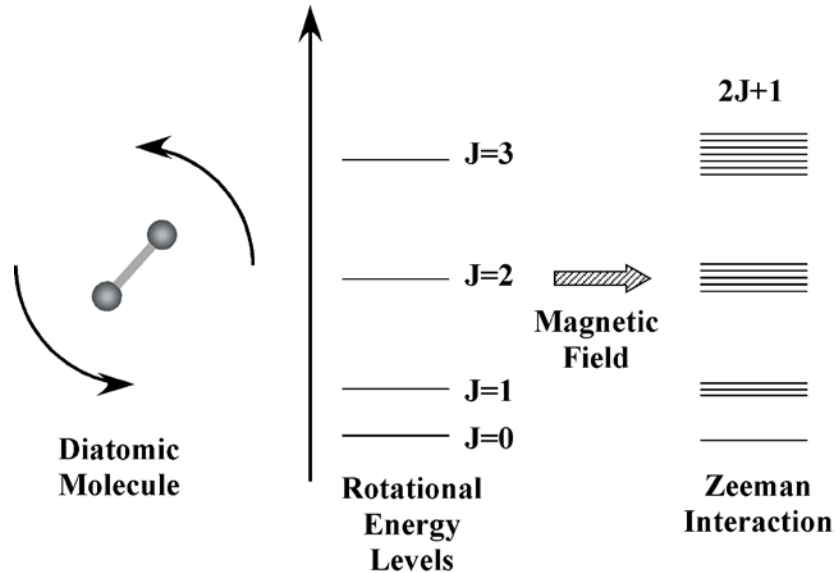
or as it written more commonly,

$$\frac{q}{2M} = \frac{\mu}{P} = \gamma$$

The ratio of the magnetic moment to the angular momentum is represented as  $\gamma$ , and is named the *gyromagnetic ratio*.

# Quantum Mechanical Angular Momentum

Quantum mechanical angular momentum is quantized.



A rotating diatom generates a set of stable rotational states. The total angular momentum,  $L$ , may be calculated as follows:

$$L = [J(J + 1)]^{1/2} \hbar; \quad J = 0, 1, 2, \dots$$

The rotational energy depends upon the square of the total angular momentum:

$$E_J = BJ(J + 1)$$

Additional details of the rotation are specified by the magnetic or azimuthal quantum number,  $M_J$ . The  $M_J$  can assume integer values between  $-J$  and  $J$  as shown below:

$$M_J = -J, -J + 1, \dots, -1, 0, +1, \dots, +J$$

In the absence of applied vector fields, the energy levels of these states is degenerate, however the application of an applied magnetic field will cause these level to become nondegenerate (Zeeman splitting)

## The Concept of Spin

In addition to the magnetic effects produced by actual angular motion, nuclei (and electrons too!) themselves possess magnetic properties, i.e., the spin-quantum number,  $M_s$ .

These magnetic properties are intrinsic however, i.e., they do not depend on the prior history of the system – this intrinsic angular momentum is called *spin* and is symbolized as  $I$ .

Spin angular momentum is a vector quantity which has a magnitude equal to:

$$[I(I + 1)]^{1/2} \hbar$$

Particles with spin have  $2I+1$  sublevels that are degenerate in the absence of applied fields but that become nondegenerate in the presence of electromagnetic fields.

Note that  $I$  may be zero, integer (1,2,3...) or half-integer (1/2, 3/2, 5/2...).

The formal (mathematical) description of spins is very similar to angular momentum. – note the presence of  $\hbar$  in the expression for spin.

Historically, the notion of a charge spinning on an internal axis provided an adequate model for *integer* spin. However, analytical NMR emphasizes observation of nuclei that possess half-integer spin ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{31}\text{P}$ ), which this simple theory cannot describe. A more complete theoretical description of spin was developed by Dirac using the framework of relativistic quantum electrodynamics.

The spin of the proton and neutron are spin-1/2 particles, but remarkably, there are no simple rules by which to predict the *exact* spin of the nucleus. However, several points are certain:

- i) Isotopes with odd mass numbers have half-integer spin
- ii) Isotopes with even mass numbers have integer spin or are spinless
- iii) If the numbers of protons and neutrons are both even, then the particle is spinless ( $I=0$ ), i.e.,  $^{12}\text{C}$  (6p + 6n),  $^{16}\text{O}$  (8p + 8n) and  $^{56}\text{Fe}$  (26p + 30n)
- iv) If the numbers of protons and neutron are both odd, then the nucleus has integer spin ( $S=1$ ), i.e.,  $^2\text{H}$  (p + n),  $^{10}\text{B}$  (5p+5n),

## Properties of Selected Nuclei

| Isotope           | Spin | Natural Abundance % | Gyromagnetic Ratio<br>$\gamma / \text{s}^{-1} \text{T}^{-1} (\times 10^6)$ | NMR Frequency at 11.7433 T<br>$(\omega_0/2\pi)/\text{MHz}$ |
|-------------------|------|---------------------|--|--|
| $^1\text{H}$      | 1/2  | ~ 100               | 267.522  | 500.000  |
| $^2\text{H}$      | 1    | 0.015               | 41.066   | 76.753   |
| $^3\text{H}$      | 1/2  | 0                   | 285.349  | 533.320  |
| $^{10}\text{B}$   | 3    | 19.9                | 28.747   | 53.718   |
| $^{13}\text{C}$   | 1/2  | 1.1                 | 67.283   | 125.725  |
| $^{14}\text{N}$   | 1    | 99.6                | 19.338   | 36.132   |
| $^{15}\text{N}$   | 1/2  | 0.37                | -27.126  | -50.684  |
| $^{17}\text{O}$   | 5/2  | 0.04                | -36.281  | -67.782  |
| $^{19}\text{F}$   | 1/2  | ~ 100               | 251.815  | 470.470  |
| $^{23}\text{Na}$  | 3/2  | ~ 100               | 70.808   | 132.259  |
| $^{27}\text{Al}$  | 5/2  | ~ 100               | 67.793   | 130.285  |
| $^{31}\text{P}$   | 1/2  | ~ 100               | 108.394  | 202.606  |
| $^{113}\text{Cd}$ | 1/2  | 12.26               | 59.34  | 110.907  |



## NMR in Bulk Materials

Purcell, E.M., Torrey, H.C. and Pound, R.V. Resonance Absorption by Nuclear Magnetic Moments in a Solid. *Phys. Rev.* **69**, 37-38.

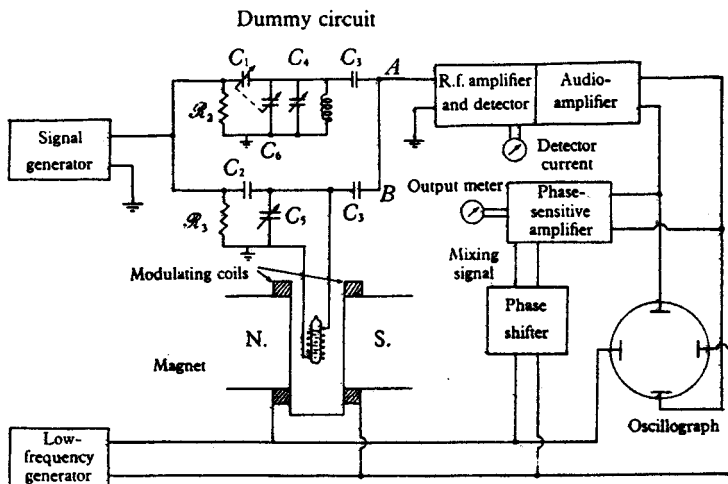


Fig. 10. Schematic diagram of the apparatus of Bloembergen, Purcell and Pound (1948). In a typical arrangement for work at 30 Mc./s. the circuit components were:  $R_1 = R_2 = 50$  ohms (the characteristic impedance of the coaxial cable used);  $C_1 = C_6 = 5$  pF. maximum;  $C_2 = 3$  pF.;  $C_3 = 4$  pF.;  $C_4 = C_5 = 60$  pF. A typical coil consists of 12 turns 18 s.w.g. copper wire wound to give a coil 1.5 cm. long and 0.7 cm. inside diameter.

Bloch, F., Hansen, W.W. and Packard, M. (1946) Nuclear Induction. *Phys. Rev.* **69**, 127.

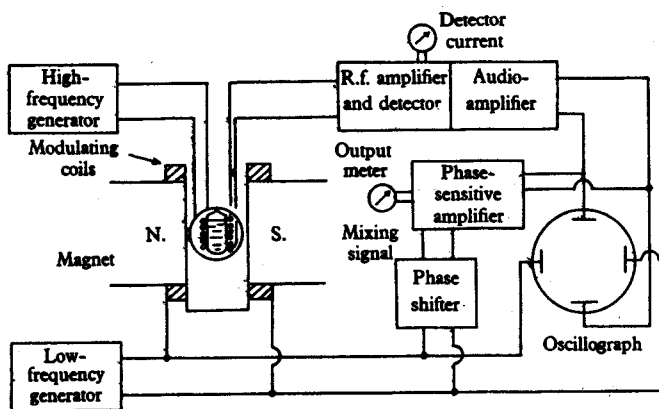


Fig. 15. Schematic diagram of apparatus for the nuclear induction method.

## Development of Pulsed RF Methods

Torrey, H.C. (1949) Transient Nutations in Nuclear Magnetic Resonance. *Phys. Rev.* **76**, 1059-1068.

Hahn, E.L. (1950) Spin Echoes. *Phys. Rev.* **80**, 580.

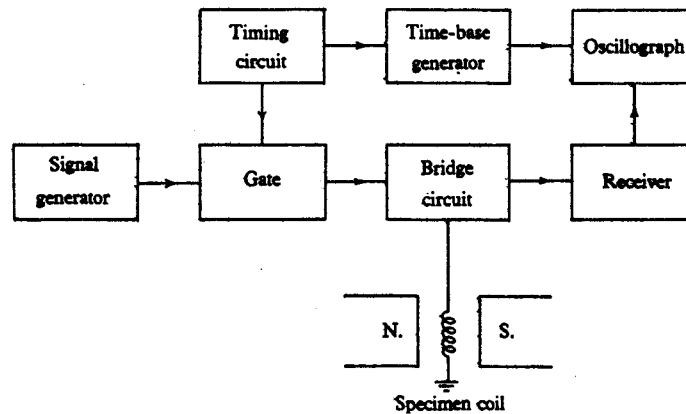
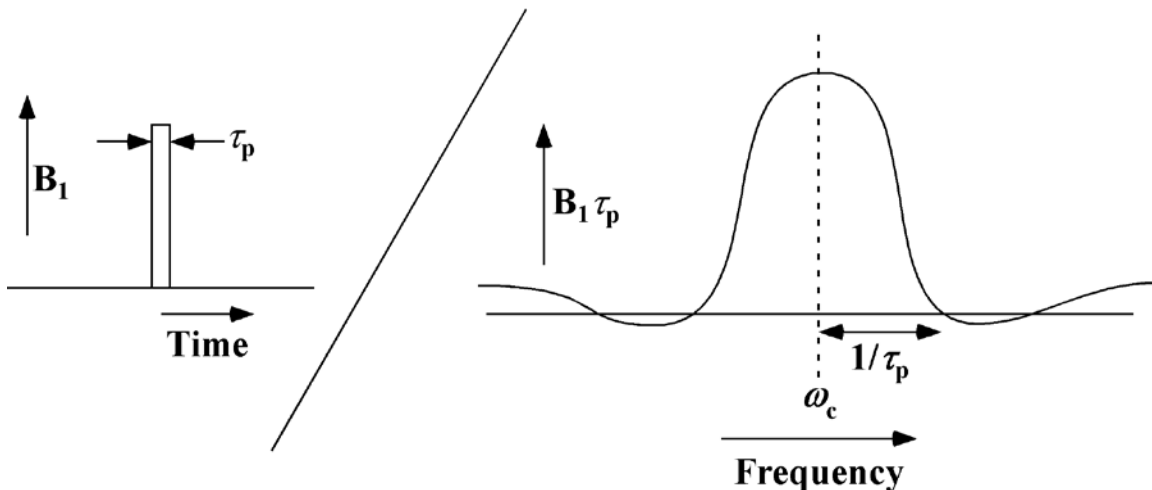


Fig. 19. A schematic diagram of the apparatus for pulse methods.

An RF pulse is a short (submicrosecond to several milliseconds) interval of radiofrequency energy delivered at a discrete carrier frequency.

The effect is broadband in the frequency domain as shown below (and as will be calculated in the following section).



The RF Pulse generates a transient nutation of macroscopic magnetization that undergoes free precession as shown in the following figure

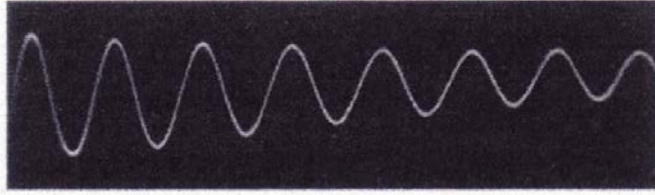


FIG. 4. Proton resonance in glycerine (exact resonance).  
Sweep time = 0.01 sec.,  $H_1 = 0.17$  gauss,  $\nu_0 = 9.0$  mc/sec.

# NMR as an Analytical Tool

## Demonstration of the Chemical Shift

Arnold, J.T., Dharmatti, S.S. and Packard, M.E. (1951) Chemical Effects on Nuclear Induction Signals from Organic Compounds. *J. Chem. Phys.* **19**, 507.

Meyer, L.H., Saika, A. and Gutowsky, H.S. (1953) Electron Distribution in Molecules. III. The Proton Magnetic Resonance Spectra of Simple Organic Compounds. *J. Am. Chem. Soc.* **75**, 4567-4573.

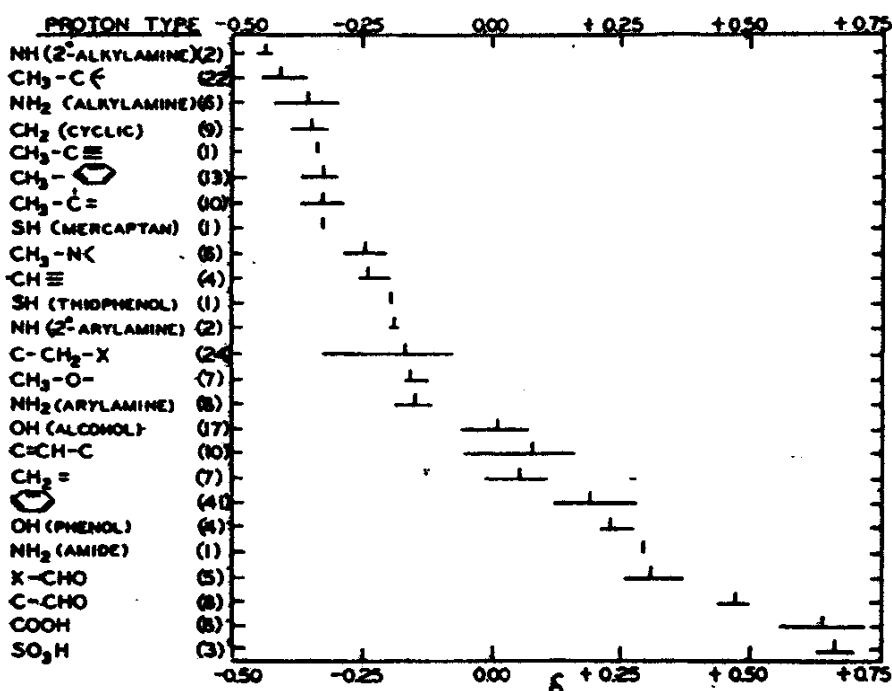


Figure 19 Correlation chart for proton chemical shifts in various organic functional moieties, published by Meyer, Saika, and Gutowsky.<sup>76</sup> (Reproduced by permission of the American Chemical Society)