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Undergraduate Studies
Physical chemistry
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Scholar units: 3 units

Lectures of Molecular Spectroscopy

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Lecture No. Six: Magnetic Resonance Spectroscopy

1-Introudction.

2-General properties

3-The Physical Basis.

4-Quantum-mechanical treatment.

5-Active dipole magnetic moment.

1-Introudction:

1945 – Purcell, Torrey, and Pound (Harvard, Cambridge, Massachusetts) detected weak radiofrequency signals generated by the nuclei of atoms in about 1 kg of paraffin wax placed in a magnetic field. Simultaneously, Bloch, Hansen, and Packard (Stanford, Palo Alto, California) independently observed radio signals from atomic nuclei in water in a magnetic field.

Purcell, Torrey, and Pound described NMR as observation of absorption by the nuclear spin system that produces an additional load that changes the quality factor Q of the circuit that drives the resonance. Bloch, Hansen, and Packard described NMR as forced precession of the nuclear magnetization in the applied radio frequency field and the induction of detectable electromotive force in a receiver coil .

Magnetic Resonance Spectroscopy is a branch of spectroscopy that deals with the phenomenon found in assemblies of large number of nuclei of atoms that possess both “magnetic moments” and “angular momentum” is subjected to external magnetic field.

Resonance – Implies that we are in tune with a natural frequency of the nuclear magnetic system in the magnetic field.

What is Spin? A rotating object possesses a quantity called angular momentum given by the right hand thumb rule. Spin is a type of angular momentum that does not vanish even at absolute zero! So a physical motion to represent this type of angular momentum is not with out error. Spin is a fundamental property of electron and nucleus like mass, electric charge, and magnetism.

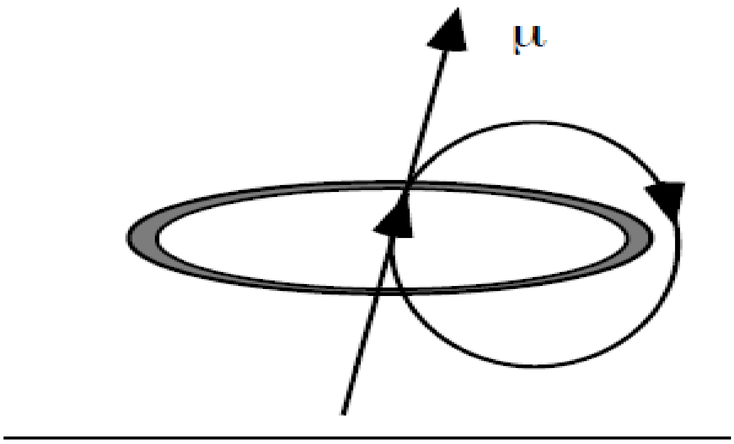
2-General properties :-

- Magnetic Resonance Spectroscopy technique gives a new pathway of energy levels production, were energy levels difference is occurred by the effect of outer magnetic field presence.
- Magnetic resonance are comes out due interaction between outer magnetic field with the nuclear moment of spin for chemical species.
- The radiation energy at radio frequencies is absorbed(is directed to be perpendicular into magnetic field) by resonance of active chemical species to promotion into high energy levels.
- Two general techniques have been found in this area; there are Nuclear magnetic resonance spectroscopy (NMR) and Electron spin Resonance spectroscopy (ESR) or Electron para magnetic resonance spectroscopy (EPR).
- The radio frequency radiation limits in NMR reached 10m-100cm. The radio frequency radiation limits at ESR is reached 100cm-1cm. Both of them techniques are physical change but not chemical change.

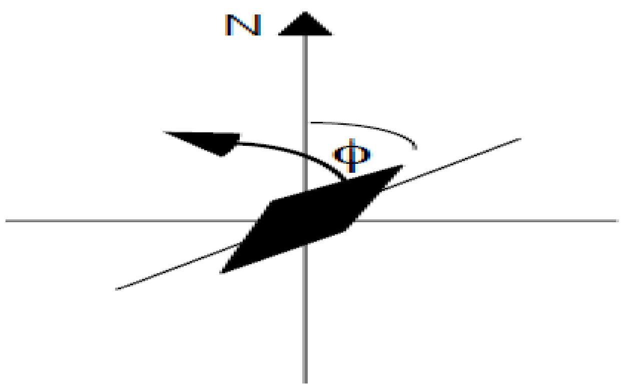
2-The Physical Basis:

Imagine a charge travelling circularly about an axis. As a current that flows through a conducting loop. Such a circular current builds up a magnetic Moment μ whose direction is perpendicular to the plane of the

conducting loop. The faster the charge travels the stronger is the induced magnetic field. In other words, a magnetic dipole has been created.



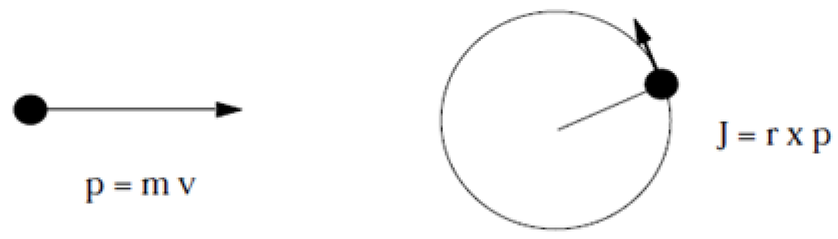
Such dipoles, when placed into a magnetic field, are expected to align with the direction of the magnetic field. In the following they look at a mechanical equivalent represented by a compass needle that aligns within the gravitational field:



When such a compass needle is turned away from the north-pole pointing direction to make an angle φ a force acts on the needle to bring it back. For the case of a dipole moment that has been created by a rotating charge this force is proportional to the strength of the field (**B**) and to the charge (**m**).The torque that acts to rotate the needle may be described as:

$$T=\frac{\delta J}{\delta t}=r*F \qquad .....1$$

J is defined as the *angular momentum* which is the equivalent for rotational movements of the linear momentum.

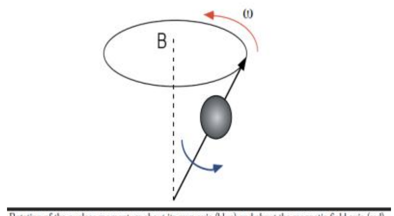


linear momentum. Right: angular momentum

Note that the direction of the momentum is tangential to the direction along which the particle moves. The torque is formed by the vector product between the radius and the momentum and is described by a vector which is perpendicular to both radius and momentum. In fact, it is the axis of rotation which is perpendicular to the plane. The corresponding potential energy is :

$$E_{Pot} = -\int_0^{\varphi} T d\varphi \quad \ldots\ldots 2$$

In contrast to the behavior of a compass needle the nuclear spin does not exactly align with the axis of the external field:



Rotation of the nuclear momentum about its own axis (blue) and about the magnetic field axis (red).

This is a consequence of its rotation about its own axis. This property is called spin. It rotates (spins) about its own axis (the blue arrow) and processes about the axis of the magnetic field B (the red arrow). The frequency of the precession is proportional to the strength of the magnetic field:

$$\omega = \gamma \mathbf{B}$$

The proportionality constant γ is called the gyromagnetic ratio. The frequency ω is expressed in terms of angular velocity. It is specific for the kind of nucleus and therefore has a different value for ^{1}H, ^{13}C, ^{19}F …etc. The precession frequency is

$$\omega_0 = \nu_o 2\pi$$

The relation is called the **Lamor frequency**. In contrast to a compass needle which behaves "classically" in the way that it can adopt a continuous band of energies depending only on the angle φ it makes with the field the corresponding angle φ of the nuclear dipole moment is quantized. Hence, the quantum-mechanical treatment shortly introduce later. Of course, no observe single molecules but look at an ensemble of molecules (usually a huge number of identical spins belonging to different molecules).The sum of the dipole moments of identical spins is called **magnetization**:

$$M=\sum_j \mu i \quad ….3$$

3-Quantum-mechanical treatment:

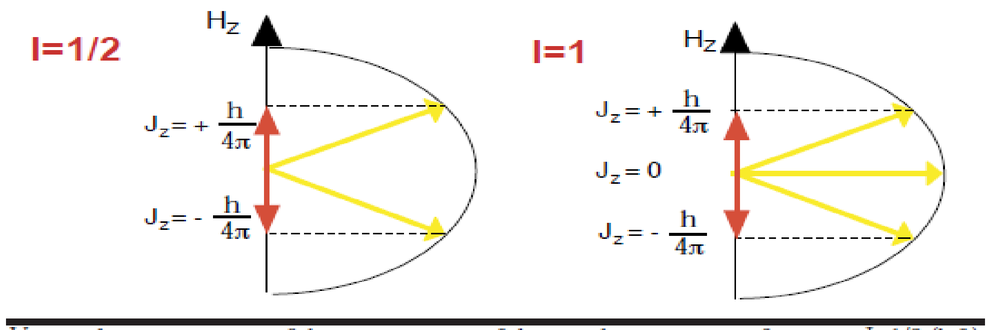
The dipole moment μ of the nucleus is described in quantum-mechanical terms as:

$$\mu = \gamma J \quad ……4$$

Therein, J is the spin angular momentum and γ the gyro magnetic ratio of the spin. When they looking at single spins, will have to use a quantum-mechanical treatment. There in, the z-component of the angular momentum J is quantized and can only take discrete values.

$$J_z = m * \frac{h}{2\pi} \quad …….5$$

Where m is the magnetic quantum number. The latter can adopt values of m = -I, -I+1, …,0,...,I-1, I ,since I being the spin quantum number.



Vectorial representation of the z-component of the angular momentum for a spin I=1/2 (left)

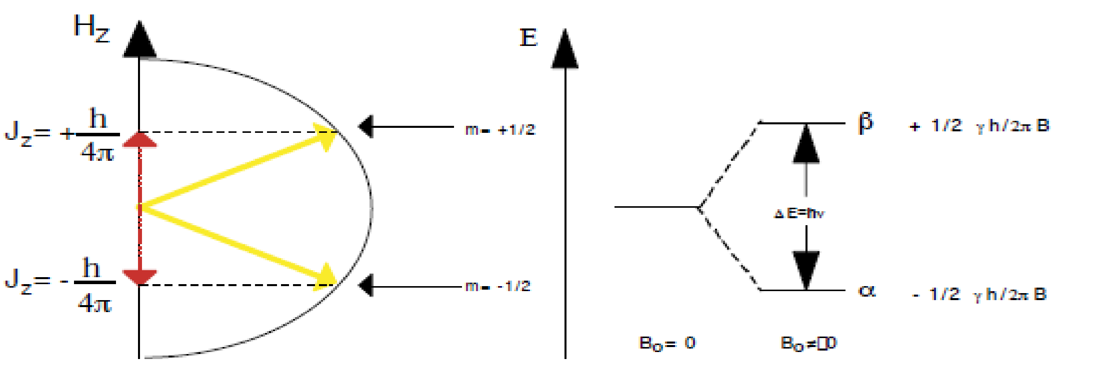
For I=1/2 nuclei, **m** can only be +1/2 or -1/2, giving rise to two distinct energy levels. For spins with I =1, nuclei will have three different values for J_z are allowed:

$$E_{pot}= \mu zB = \gamma J B\ldots\ldots6$$

The energy difference ΔE_{pot}, which corresponds to the two states with m=±1/2, is then

$$E_{pot}= \gamma * \frac{h}{2\pi} * B\ldots\ldots7$$

(The quantum-mechanical selection rule states that only transition with Δm=±1 are allowed):



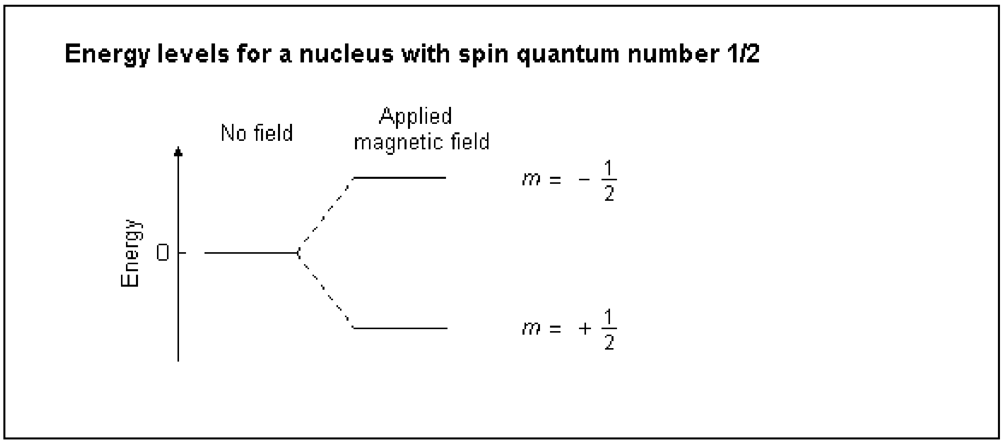
Energy levels of the α- and β- states of I=1/2 nuclei

4-Active dipole magnetic moment:

The active dipole magnetic is represented by magnetic moment (**μ**).Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin. The general rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.
2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, and 3).

The overall spin, I, is important. Quantum mechanics tells us that a nucleus of spin I will have 2I + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a magnetic quantum number, m.



When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that the lower energy level will contain slightly more nuclei than the higher level. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels. Nuclear spin may be related to the nucleon composition of a nucleus in the following manner:

1. Odd mass nuclei (i.e. those having an odd number of nucleons) have fractional spins. Examples are I = 1/2 (^{1}H, ^{13}C, ^{19}F), I = 3/2 (^{11}B) &I = 5/2 (^{17}O).
2. Even mass nuclei composed of odd numbers of protons and neutrons have integral spins. Examples are I = 1 (^{2}H, ^{14}N).
3. Even mass nuclei composed of even numbers of protons and neutrons have zero spin (I = 0). Examples are ^{12}C, and ^{16}O.
4. Spin 1/2 nuclei have a spherical charge distribution, and their NMR behavior is the easiest to understand.
5. Other spin nuclei have non spherical charge distributions and may be analyzed as prolate or oblate spinning bodies.
6. All nuclei with non-zero spins have magnetic moments (**μ**), while the non-spherical nuclei also have an electric Quadra pole moment (**eQ**).

Some characteristic properties of selected nuclei are given in the following table.

Isotope	Natural % Abundance	Spin (I)	Magnetic Moment (μ)*	Magneto gyro Ratio (γ)†
^{1}H	99.9844	1/2	2.7927	26.753
^{2}H	0.0156	1	0.8574	4,107
^{11}B	81.17	3/2	2.6880	--
^{13}C	1.108	1/2	0.7022	6,728
^{17}O	0.037	5/2	-1.8930	-3,628
^{19}F	100.0	1/2	2.6273	25,179
^{29}Si	4.700	1/2	-0.5555	-5,319
^{31}P	100.0	1/2	1.1305	10,840

* **μ** in units of nuclear magnetos = $5.05078 \cdot 10^{-27}$ JT^{-1}

† γ in units of 10^{7}rad T^{-1} sec^{-1}