Magnetic Resonance Researches

Resonances

Nuclear Magnetic Resonance	Electron Spin Resonance

Methods

Continuous Wave Method	Radio Frequency Pulse Method

Spin Resonance- NMR and ESR

• **Spin resonance** is a physical phenomena resulting from the intrinsic angular momentum associated with the spin of the nucleus or electron of an atom.

•**Nuclear magnetic resonance** (NMR) implies that the nuclei of the atoms are in resonance, while **electron spin resonance** (ESR) deals with electrons.

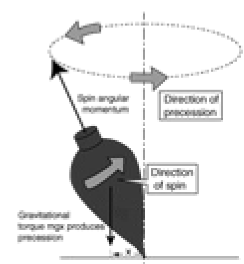
• For particles such as the hydrogen atom nucleus or an electron, which have a quantum spin number, **I, of ½,** there are two possible orientations of the spin axis, described as "spin up" or "spin down".

Spin Resonance- NMR and ESR

- A transition between these two energy levels is caused by the application of radiofrequency (or microwave) radiation, ■ , in a stationary magnetic field of strength B.
- At a specific radiofrequency (or microwave frequency) in relation to the magnetic field strength, the system is said to be in resonance as energy is absorbed by the nucleus or the electron, and the particle is promoted to its higher energy state

Introduction

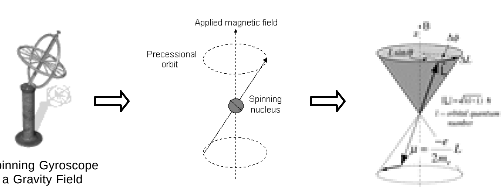
- Spin is a fundamental property of all elementary particles and is typically viewed as the intrinsic angular momentum.
- Both electrons and nuclei possess spin, and these spins precess around the direction defined by an applied magnetic field.
- The frequency of precession scales with the applied field and is roughly 1,000 times faster for electrons.



Theory of Magnetic Resonance

Classical Description

- *Spinning particle precesses around an applied magnetic field*

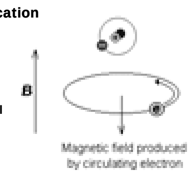


A Spinning Gyroscope in a Gravity Field

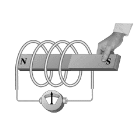
Basic concept in Electro Magnetic Theory

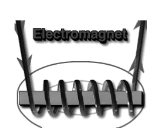
A Direct Application

A moving perpendicular external magnetic field will induce an electric current in a closed loop

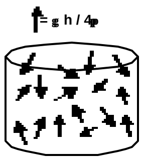


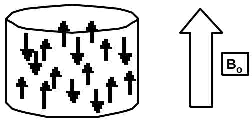
An electric current in a closed loop will create a perpendicular magnetic field





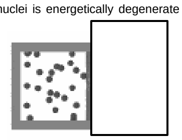
Magnetic Alignment

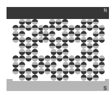




In the absence of external field, each nuclei is energetically degenerate

Add a strong external field (B_o) and the nuclear magnetic moment: aligns with (low energy) against (high-energy)





What is **ESR, EPR OR EMR**?

- **Electron Paramagnetic Resonance (EPR)**
- **Electron Spin Resonance (ESR)**
- **Electron Magnetic Resonance (EMR)**

EPR ~ ESR ~ EMR

What is **ESR, EPR OR EMR**?

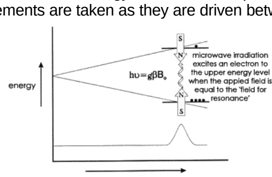
- **Electron spin resonance** (ESR) spectroscopy is a technique for studying chemical species that have one or more unpaired electrons,
  - Such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion.
- The basic physical concepts of ESR are analogous to those of nuclear magnetic resonance (NMR),
  - But it is electron spins that are excited instead of spins of atomic nuclei.
- Because most stable molecules have all their electrons paired, the ESR technique is less widely used than NMR.
  - However, this limitation to paramagnetic species also means that the ESR technique is one of great specificity, since ordinary chemical solvents and matrices do not give rise to ESR spectra.

History - ESR, EPR OR EMR

- Stern and Gerlach (1921-22) - electron magnetic moment quantized
- Pauli (1924) - nuclear moments connected with hyperfine structure in atomic spectra
- Uhlenbeck and Goudsmidt (1925) - linked electron magnetic moment with spin of electron
- Breit and Rabi (1931) described energy level for H· atom, linking nuclear and electron spin angular momentum
- Rabi , Zacharias, Millman, Kusch (1938) first experimental observation of magnetic resonance
- Zavoisky (1945) first EMR on $CuCl_2.2H_2O$ 4.76mT @ 133MHz (World War II - 9 GHz radar)

How does EPR Work?

- An electron has a spin, which gives it a magnetic property known as a magnetic moment.
- When an external magnetic field is supplied, the paramagnetic electrons can either orient in a direction parallel or antiparallel to the direction of the magnetic field .
- This creates two distinct energy levels for the unpaired electrons and measurements are taken as they are driven between the two levels.

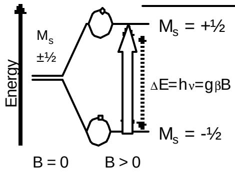


Scope of EMR

- Free radicals & multiple electron systems - triplets and biradicals.
- Transition metal (d,f) ions and their clusters
- Point defects - F (trapped e$^-$), V- ('positive hole') centers
- Conducting electrons
- Electronic excited states

Summary

Electron Paramagnetic Resonance (EPR)
Electron Spin Resonance (ESR)
Electron Magnetic Resonance (EMR)
EPR ~ ESR ~ EMR



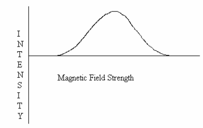
h	**Planck's constant 6.626196 x 10-27 erg.sec**
ν	**frequency (GHz or MHz)**
g	**g-factor (approximately 2.0)**
β	**Bohr magneton (9.2741 x 10-21 erg.Gauss-1)**
B	**magnetic field (Gauss or mT)**

EPR is the resonant absorption of microwave radiation by paramagnetic systems in the presence of an applied magnetic field

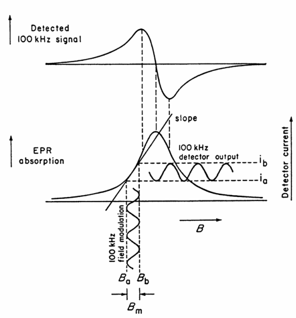
The EPR spectrum

- A 1st derivative spectrum is obtained from the unpaired electron

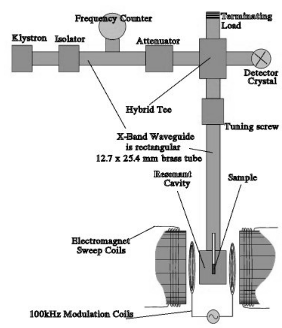
  $h\nu = gB\beta_0$
- **g** is a characteristic of the chemical environment of the unpaired electron; for free radicals it is near 2.00; can vary widely for transition metal centers
- Complicated/enhanced by hyperfine interactions with nuclei with non-zero spin



The EPR spectrum



The ESR Spectrometer



The g factor

- A ***g*-factor** (also called ***g* value** or **dimensionless magnetic moment**) is a dimensionless quantity which characterizes the magnetic moment and gyromagnetic ratio of a particle or nucleus.
- It is essentially a proportionality constant that relates the observed magnetic moment ì of a particle to the appropriate angular momentum quantum number and the fundamental quantum unit of magnetism, the Bohr magneton.

  ***h*ν = gì$_B$B$_0$**
- The shift in g is akin to the chemical shift of NMR. It is a dimensionless constant and equal to 2.002319 for an unbound electron.

The g factor

- The local induced field comes from the orbital motion of electrons, spin-orbit coupling mixes ***S (total spin momentum),*** *L (total orbital momentum)* and ***J (resultant momentum)*** and shifts g, the shift can can be g<2 or g>2. g is thus characteristic of different electronic structures and is also known as the Landé splitting factor.

$$g = 1 + \frac{J(J+1) + S(S+1) - L(l+1)}{2J(J+1)}$$

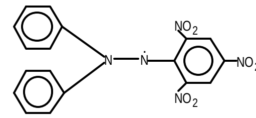
- Light atoms, *i.e.* 'organic' and first row transition metals with a single unpaired electron can have g close to 2.0.
- Heavier atoms, and molecules or atoms with more than one unpaired electron can have g-values very different from 2

g Values

Species	g-value
Flavin semiquinone, ubiquinone, ascorbate, etc :	2.0030 - 2.0050
Nitroxide spin labels and traps	2.0020 - 2.0090
sulphur radicals S-S, S-H	2.02 - 2.06
MoV (in aldehyde oxidase)	1.94
Cu^{2+}	2.0 - 2.4
Fe^{3+} (low spin)	1.4 - 3.1
Fe^{3+} (high spin)	2.0 - 10

Calibration

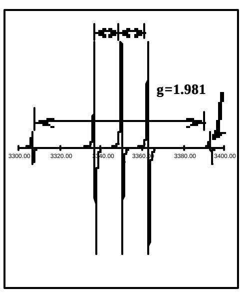
- In order to calculate the number of unpaired electrons in the sample, comparison is made with a standard sample having a known number of unpaired electrons.
- The most widely used standard is 1,1-diphenyl-2-picryl-hydrazyl free radical (DPPH).



Calibration

Use well known standard eg Mn^{2+} for which $I=5/2$

- Doped into MgO at high dilution ($I=0$ for ^{24}Mg)
- Separation of two Mn^{2+} lines is 8.69 mT
- Therefore $a_N = 1.30$ mT and $g= 2.0057$ for $[(O_3S)_2NO]^{2-}$



Spectral Splittings

Among chemists, the following terminology has evolved to describe spectra:

- **Fine structure**
- **Hyperfine structure**
- **Superhyperfine structure**
- **Spin-spin structure**

Spectral Splittings

- **FINE STRUCTURE** refers to that part of a spectrum caused by the splitting of energy levels, and spectral lines, due to **interactions among electrons in a single atom or molecule.**
  - The interactions originate in the s = 1/2 quantum number for electrons.
- **Hyperfine structure** refers to that part of a spectrum caused by the splitting of energy levels, and spectral lines, due to an unpaired electron interacting with a nucleus having I 0.
  - The electron and nucleus (nuclei) are on the same atom or within the same molecule.
- **Superhyperfine structure** refers to that part of a spectrum caused by the splitting of energy levels, and spectral lines, due to an unpaired electron interacting with a nucleus having I 0.
  - The electron and nucleus (nuclei) are on different atoms or different molecules.
- **Spin-spin structure** refers to that part of a spectrum caused by the splitting of energy levels, and spectral lines, due to interactions among nuclei having I 0.
  - This phenomenon is especially important in NMR spectra

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Hyperfine Interactions

- **Hyperfine coupling** refers to the interaction between an electron in an atom or molecule and one or more atomic nuclei.
- Every electron has an intrinsic magnetic moment and a spin quantum number s = ½. For hyperfine coupling to occur, an electron must interact with an atomic nucleus having a spin quantum number I 0.
- Hyperfine interactions can be measured, among other ways, in atomic and molecular spectra and in electron paramagnetic resonance spectra of free radicals and transition-metal ions

Hyperfine Interactions

- The unpaired electron may exist in only two spin states, +1/2 and –1/2, and is expected to give rise to only a single resonance line.
- These two spin states, may interact with the magnetic moments of nuclei with which the unpaired electron may be wholly or partially associated.
- This interaction causes a further splitting of the resonance line into several lines.
- The transitions between these sublevels of the +1/2 and –1/2 spin states of the unpaired electron result in a number of resonance lines.

Hyperfine Interactions

- The extent of interaction is represented as the hyperfine splitting constant, indicated as “A” or “**a**”,
- The number of lines is given by the equation 2nI+1 where **n** is the number of chemically identical nuclei interacting with the unpaired electron, and I is the spin number of the interacting nuclei.
  - so I = ½ gives 2 lines, etc.
- The relative intensities of the components of the peaks are given by the coefficients of the expression **$(a+b)^n$** in the expanded form.

Hyperfine splitting

- **The relative intensities are given by Pascal's triangle for I = ½**

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1
1 7 21 35 35 21 7 1

Hyperfine coupling constant

- Hyperfine interaction usually results in splitting of lines in an ESR spectrum.
- The interaction energy between the electron spin and a magnetic nucleus is characterized by the **hyperfine coupling constant**
- *This is represented by*
  - **A** with units of energy (Joule)
  - **a** with unit of Magnetic Field (Gauss, Tesla)

Interactions of Single Proton

$I=½$, $M_I=±½$

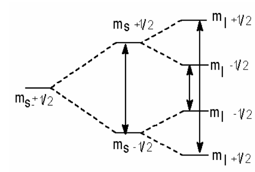
- At the electron there will be one of the two local fields contributed by the proton. For each value of electron spin angular momentum quantum number M_S, the nuclear spin angular momentum quantum number M_I can have the values ±½ giving rise to four different energy levels. The ESR spectrum of hydrogen atom will therefore contain two peaks.

$$E = g\beta H M_S + a M_S M_I$$

- Allowed Transitions are

$\Delta M_S = ±1$, $\Delta M_I = 0$

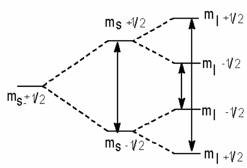
$$E_{+½,+½} = ½ g\beta H + ¼a$$
$$E_{+½,-½} = ½ g\beta H - ¼a$$
$$E_{-½,-½} = -½ g\beta H + ¼a$$
$$E_{-½,+½} = -½ g\beta H - ¼a$$



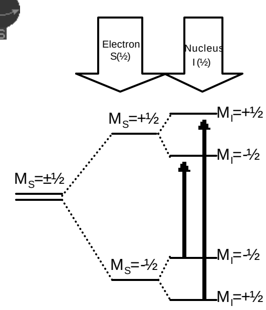
Interactions of Single Proton

From the quantitative expressions for the energy levels of hydrogen atom, in a magnetic field three things are evident

- The equality of splitting of each $M_S=±½$ states.
- The ordering of the M_I levels is reversed in the lower set of levels as compared to the upper set.
- Transitions occur between same values of M_I.



Hyperfine Coupling



Selection Rule
$\Delta M_S = ±1$; $\Delta M_I = 0$

S=½;
I=½
Doublet