



SRI AKILANDESWARI WOMEN'S COLLEGE, WANDIWASH

Electron Spin Resonance Spectroscopy

CLASS : II PG PHYSICS

**DR. V. MARIA VINOSEL
ASSISTANT PROFESSOR
DEPARTMENT OF PHYSICS**

SWAMY ABEDHANADHA EDUCATIONAL TRUST, WANDIWASH



INTRODUCTION:


- Also known as....
- **Electron Paramagnetic Resonance (EPR)**
- **Electron Magnetic Resonance (EMR)**

The molecule which contain unpaired electrons are paramagnetic species or free radical species discovered by ZAVOISKII in 1944.

- It is a non-destructive technique.
- 



What is ESR???

- It is a branch of absorption spectroscopy in which radiation having frequency in microwave region(300Mhz to 300GHz) is absorbed by paramagnetic substance to induce transition between magnetic energy level of electron with unpaired spin.
 - Magnetic energy splitting is done by applying a static magnetic field.
- 

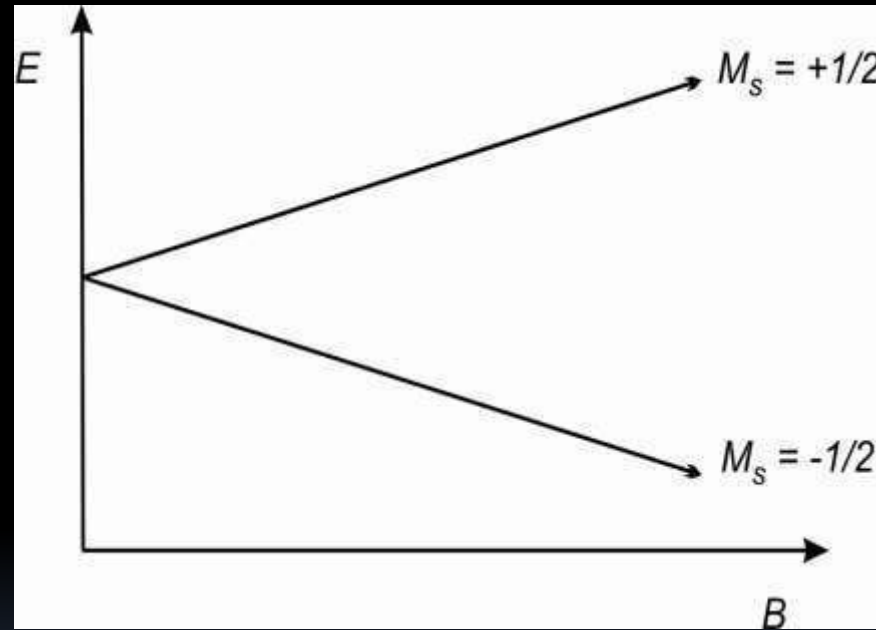
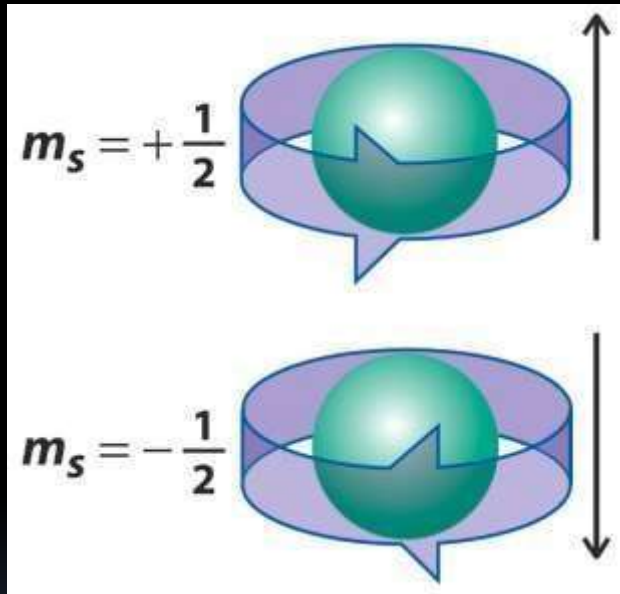
ESR Phenomenon Is Shown By...

- Atoms having an odd number of electrons.
- Ions having partly filled inner electron shells.
- Molecule that carry angular momentum of electronic origin.
- Free radicals having unpaired electrons.
- Molecule with paired electrons and zero magnetic field

PRINCIPLE of ESR:

- ESR spectroscopy is based on the absorption of **microwave radiation** by an unpaired electron when it is exposed to a strong magnetic field.
- The electronic energy levels of the atom or molecule will split into different levels.
- The magnitude of the splitting is dependent on the strength of the applied magnetic field.
- The atom or molecule can be excited from one split level to another in the presence of an external radiation of frequency corresponding to the frequency obtained from the difference in energy between the split levels. Such an excitation is called a **magnetic resonance absorption**.
- The magnetic resonance frequency will hence be influenced by the local environment of the atom or molecule.

What causes the Energy levels?



Resulting energy levels of a electron in a magnetic field

Describing the Energy levels:

- Based upon the spin of an electron and its associated magnetic moment.
- For a molecule with one unpaired electron.
 - In the presence of a magnetic field, the two electron spin energy levels are given by,

$$E = gm_B B_0 M_S$$

g = proportionality factor

M_S = electron spin quantum number

(+1/2 or -1/2)

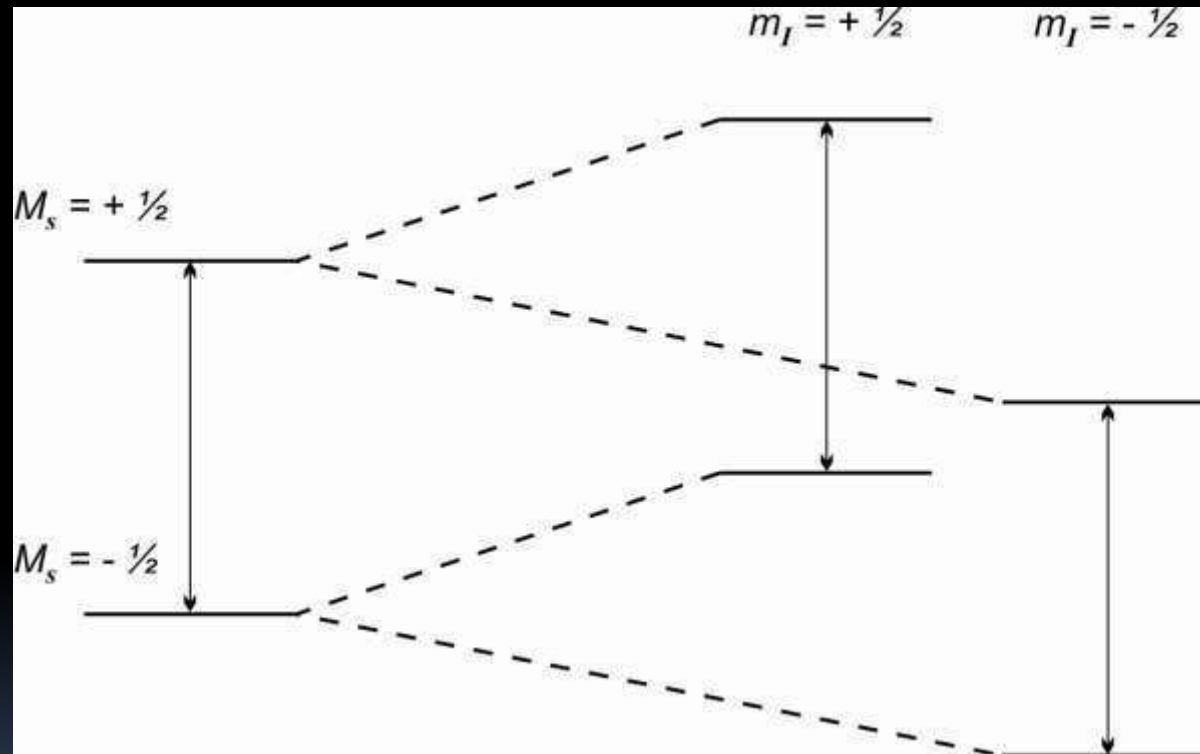
m_B = Bohr magneton

B_0 = Magnetic field

HYPERFINE SPLITTING: (SPIN-SPIN SPLITTING)

- Magnetic resonance can also occur without an external magnetic field from interaction of the electron and nuclear spin. Such resonance produces fine and hyperfine structure of atomic spectra.
- The nuclei of atoms in a molecule or complex often have magnetic moment which produces a local magnetic field at the electron. The interaction between an unpaired electron and nuclei with non zero nuclear spin is called the hyperfine interaction. This leads to splitting of the ESR line and is known as hyperfine spectrum.

Hyperfine Interaction:

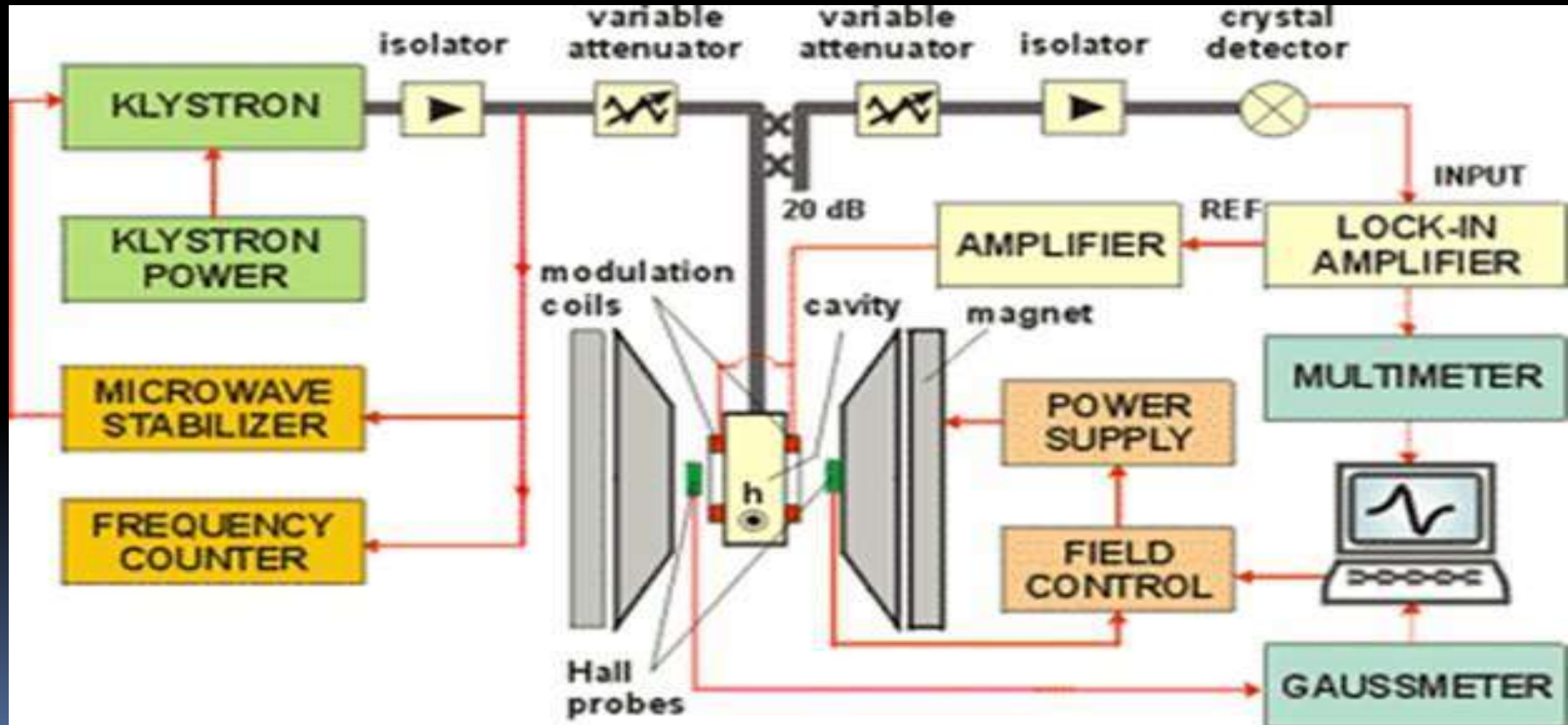


Interaction with a single nucleus of spin $1/2$

INSTRUMENTATION:



SCHEMATIC DIAGRAM OF AN ESR SPECTROMETER:



KLYSTRONS:

- Klystron tube acts as the source of radiation.
- The frequency of the monochromatic radiation is determined by the voltage applied to klystron.
- It is kept at a fixed frequency by an automatic control circuit and provides a power output of about 300 milli watts.



WAVE GUIDE OR WAVEMETER:

- The wave meter is put in between the oscillator and attenuator to know the frequency of microwaves produced by klystron oscillator.
- The wave meter is usually calibrated in frequency unit (megahertz) instead of wavelength. Wave guide is a hollow, rectangular brass tube. It is used to convey the wave radiation to the sample and crystal.

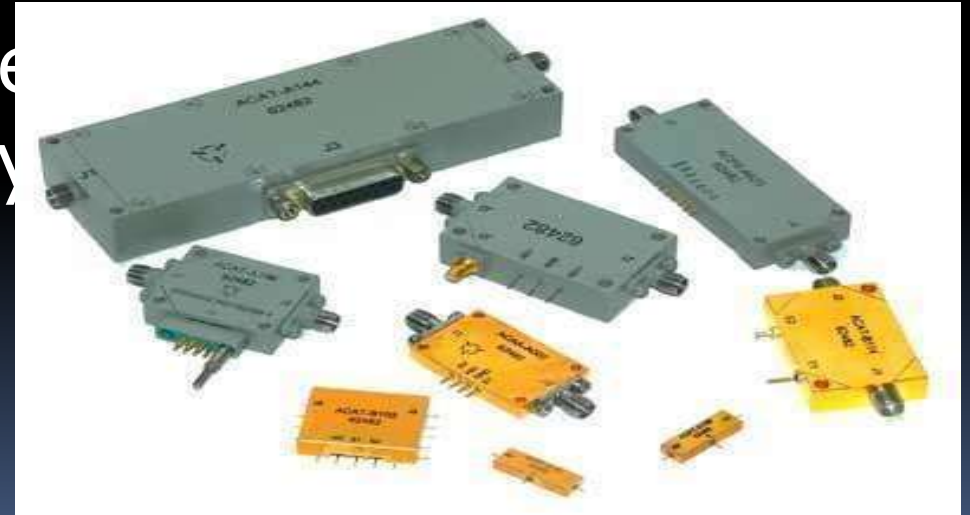


ATTENUATORS:

- The power propagated down the wave guide may be continuously **decreased by inserting a piece of resistive material into the wave guide.**
- The piece is called variable attenuator and used in the power divider to attenuate the sample power to be measured.



Analog



Digital

ISOLATORS:

- It is a non-reciprocal device which minimizes vibrations in the frequency of microwaves produced by klystron oscillator.
- Isolators are used to prevent the reflection of microwave power back into the radiation source.
- It is a strip of **ferrite material** which allows micro waves in one direction only.
- It also is being **stabilizing the frequency** of the klystron.



SAMPLE CAVITIES:

- The heart of the ESR spectrometer is the resonant sample cavity.
- In most of the ESR spectrometers, dual sample cavities are generally used.
- This is done for simultaneous observation of a sample and a reference material.
- Since magnetic field interact with sample to cause spin resonance the sample is placed where the intensity of magnetic field is greatest.



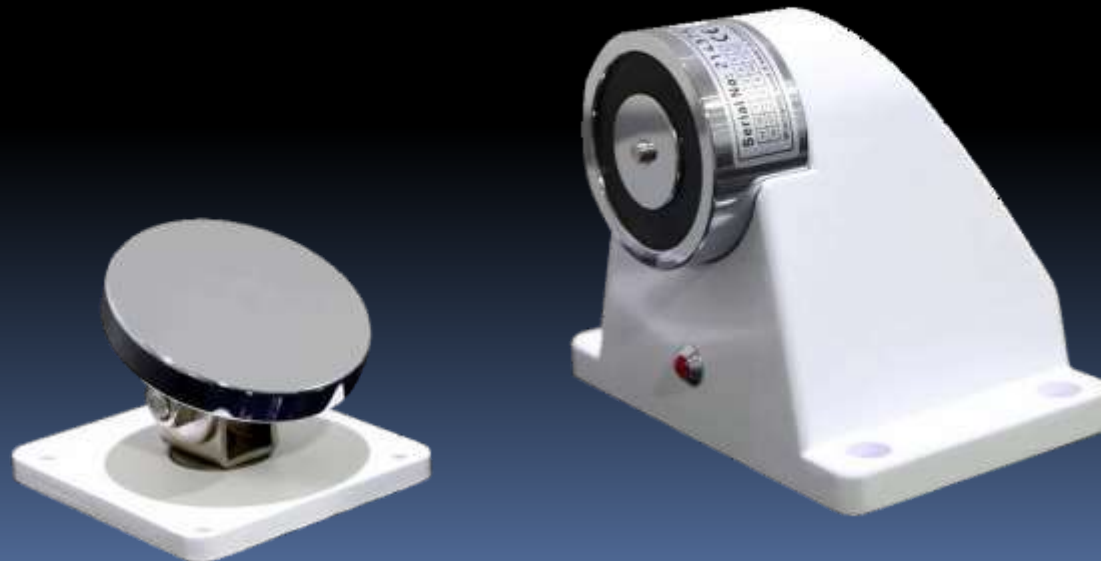
COUPLERS AND MATCHING SCREWS:

- The various components of the microwave assembly to be coupled together by making use of irises or slots of various sizes.



CRYSTAL DETECTORS AND HOLDERS:

- A Silicon crystal detectors, which converts the radiation in D.C., has widely been used as a detector of microwave radiation.
- Microwave Bridge such as magic T and hybrid ring variety are most common.



MAGNET SYSTEM:

- The resonant cavity is placed between the poles pieces of an electromagnet.
- An electro magnet capable of producing magnetic field of at least **5000 gauss** is required for ESR.
- The field should be stable and uniform over the sample volume.
- The stability of field is achieved by energizing the magnet with a highly regulated power supply.

MODULATION COIL:

- The modulation of the signal at a frequency consistent with good signal noise ratio in the crystal detector is accomplished by a small alternating variation of the magnetic field.
- The variation is produced by supplying an AC modulation coil oriented with respect the same direction as the magnetic field.
- If the modulation is of **low frequency (400 cycles or less)**, the coils can be mounted outside the cavity



DISPLAY DEVICES:

- In order to adjust the spectrometer and to observe the signal, a cathode ray oscilloscope has been employed. A strip chart or X-Y recorder is used for recording the signal.
- EPR spectra are usually displayed in derivative form to improve the signal-to-noise ratio.



How does it work???

- ❑ The sample is placed in a resonant cavity which admits microwaves through an iris.
- ❑ The cavity is located in the middle of an electromagnet and helps to amplify the weak signals from the sample.
- ❑ Numerous types of solid-state diodes are sensitive to microwave energy.
- ❑ Absorption lines are detected when the **separation of the energy levels is equal to the energy of the incident microwave.**

APPLICATIONS:

All application of ESR is based on three aspects, which are:

- Study of free radicals,
- Investigation of molecules in the triple state, and
- Study of inorganic compounds.

❖ The various applications of ESR spectroscopy are grouped into two categories:-

1. Analytical applications.
2. Biological applications.



Analytical Applications:

- Mn^{+2} ions can be measured and detected even when present in trace quantities.
- The method is very rapid and can be measured in aqueous solution over the range from 10^{-6} M to 0.1M.
- ESR method has proved to be a rapid and convenient method for determination of Vanadium in petroleum products.
- ESR can also be used to estimate Cu(II), Cr(II), Gadolinium(III), Fe(III) and Ti(III).

Biological Applications:

- From the ESR studies of variety of biological system such as, leaves, seeds, and tissue preparation are done. It is found that a definite, correlation exists between the concentration of *free radicals* and the metabolic activity of the plant material.
- ESR has studied the presence of *free radicals* in healthy and diseased tissues.
- Most of the oxidative enzymes function via one electron redox reaction.
- Much of the ESR work on photosynthesis has been carried out with photosynthetic bacteria.

REFERENCES:

- www.slideshare.net
- <http://web.mit.edu/specclab/www/PDF/DCIF-EPR-training-no3.pdf>
- <http://www.rsic.iitb.ac.in/esr.html>
- <http://www.pharmatutor.org/articles/instrumentation-electron-spin-resonance-spectroscopy>
- Google Search Engine.
- Google Images for the image of instruments and its respective schematic diagrams.

THANK YOU!!!