Vivekanand college, Kolhapur (AUTONOMOUS)

Electron Spin Resonance

Lecture by
Miss. S. M. Kumbhar

15/09/2018

Electron Spin Resonance

In this method, use is made of the Zeeman interaction of the magnetic dipoles associated with the electron, when placed in an external magnetic field.

We know that the intrinsic angular momentum (spin) of the electron S couples with the orbital angular momentum of the electron L to give a resultant J and this coupling gives rise to the 'fine structure' of the spectra. Further, under the influence of an external magnetic field (H) each of the level will split into (2j+1) sublevels (Zeeman effect) and the splitting of a level will be

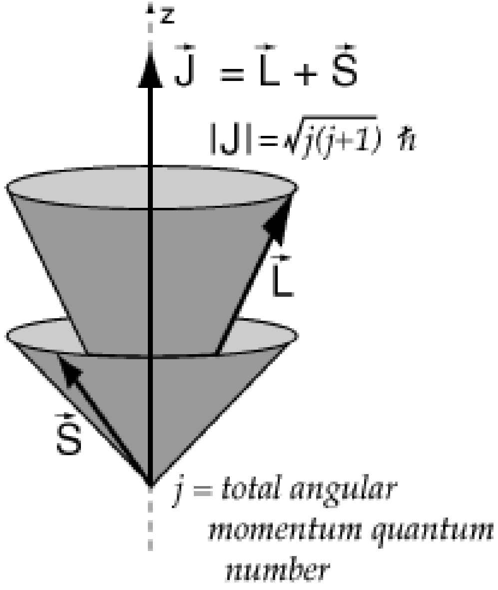
$$\Delta E = (g\mu_0 H)m_j \leftarrow \text{magnetic quantum number}$$

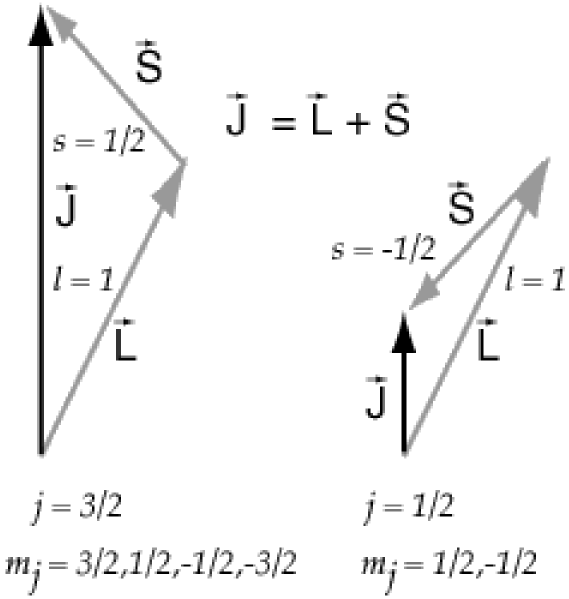
$$\mu_0 = \frac{eh}{4\pi mc} \qquad g = 1 + \frac{j^{*2} + s^{*2} - l^{*2}}{2j^{*2}} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

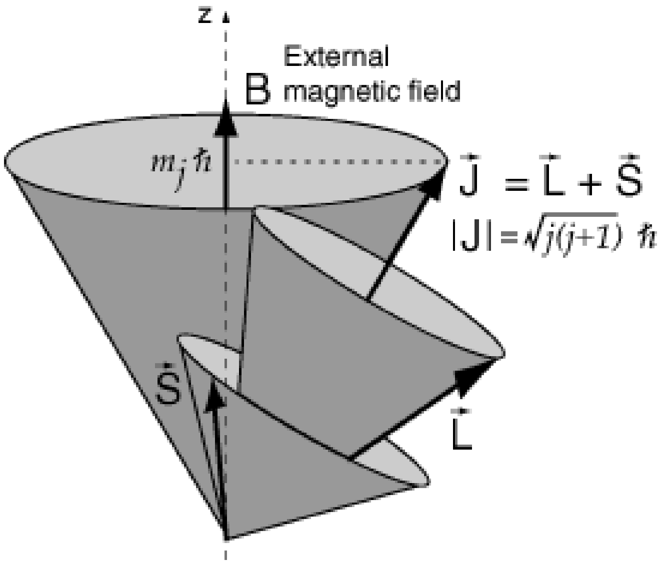
Bohr magneton

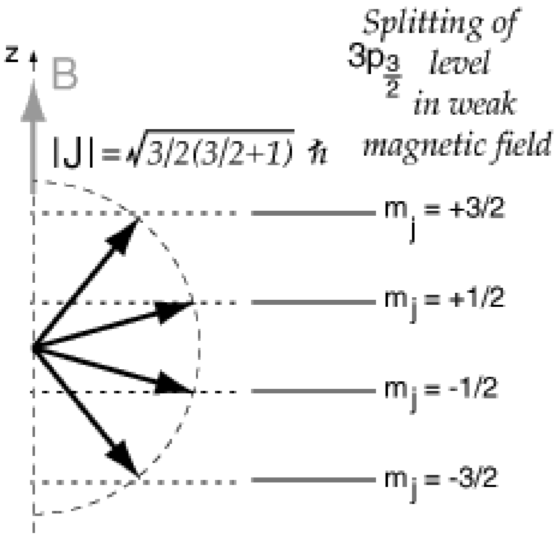
Lande' g-factor

One electron in *2p* sub-shell







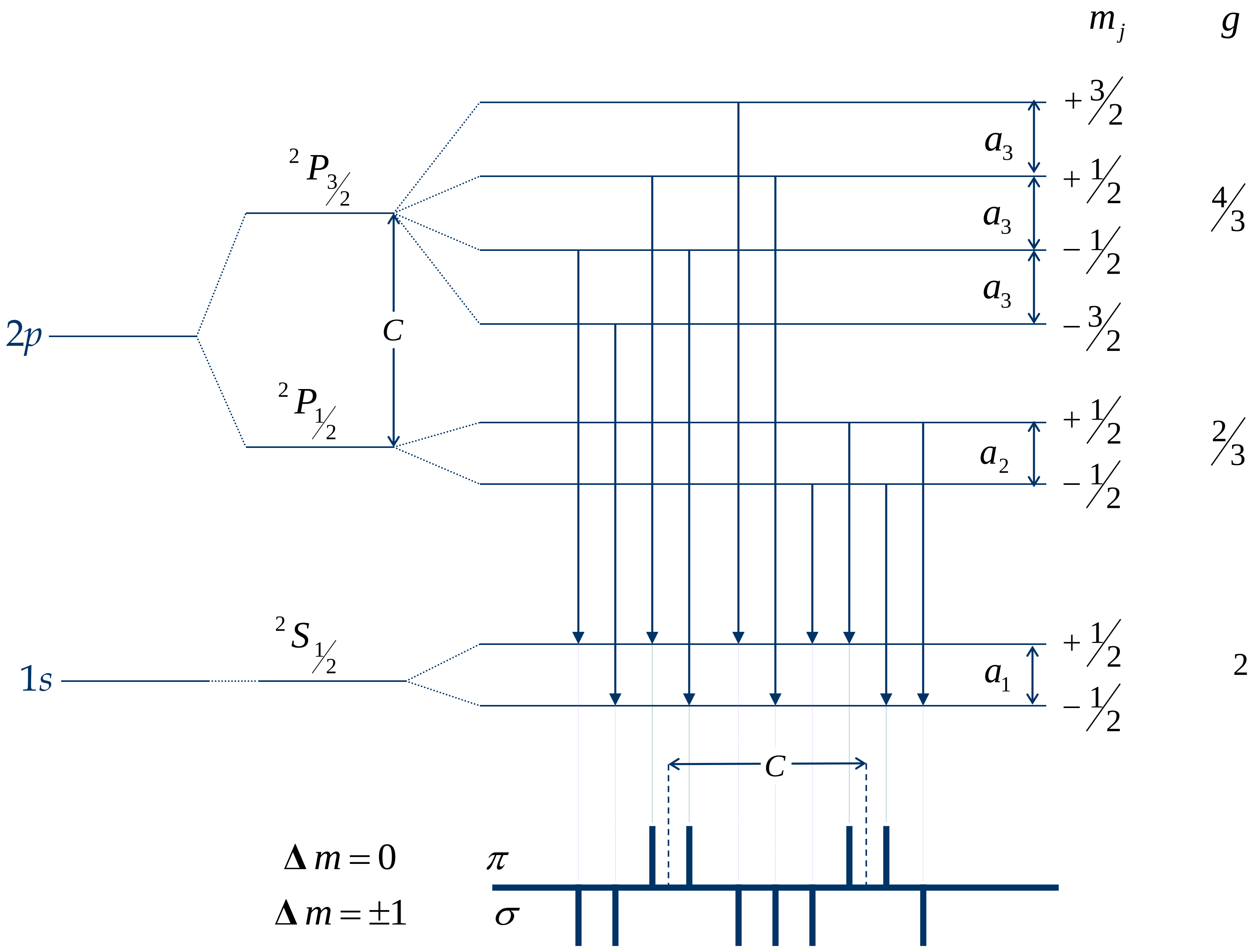


$$g = 1 + \frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$$

$$^{2}P_{3/2} \longrightarrow g = 1 + \frac{\frac{3}{2}\left(\frac{3}{2}+1\right)+\frac{1}{2}\left(\frac{1}{2}+1\right)-1(1+1)}{2\frac{3}{2}\left(\frac{3}{2}+1\right)} = 1 + \frac{\frac{15}{4}+\frac{3}{4}-\frac{8}{4}}{\frac{30}{4}} = 1+\frac{1}{3} = \frac{4}{3}$$

$$^{2}P_{1/2} \longrightarrow g = 1 + \frac{\frac{1}{2}\left(\frac{1}{2}+1\right)+\frac{1}{2}\left(\frac{1}{2}+1\right)-1(1+1)}{2\frac{1}{2}\left(\frac{1}{2}+1\right)} = 1 + \frac{\frac{3}{4}+\frac{3}{4}-\frac{8}{4}}{\frac{6}{4}} = 1-\frac{1}{3} = \frac{2}{3}$$

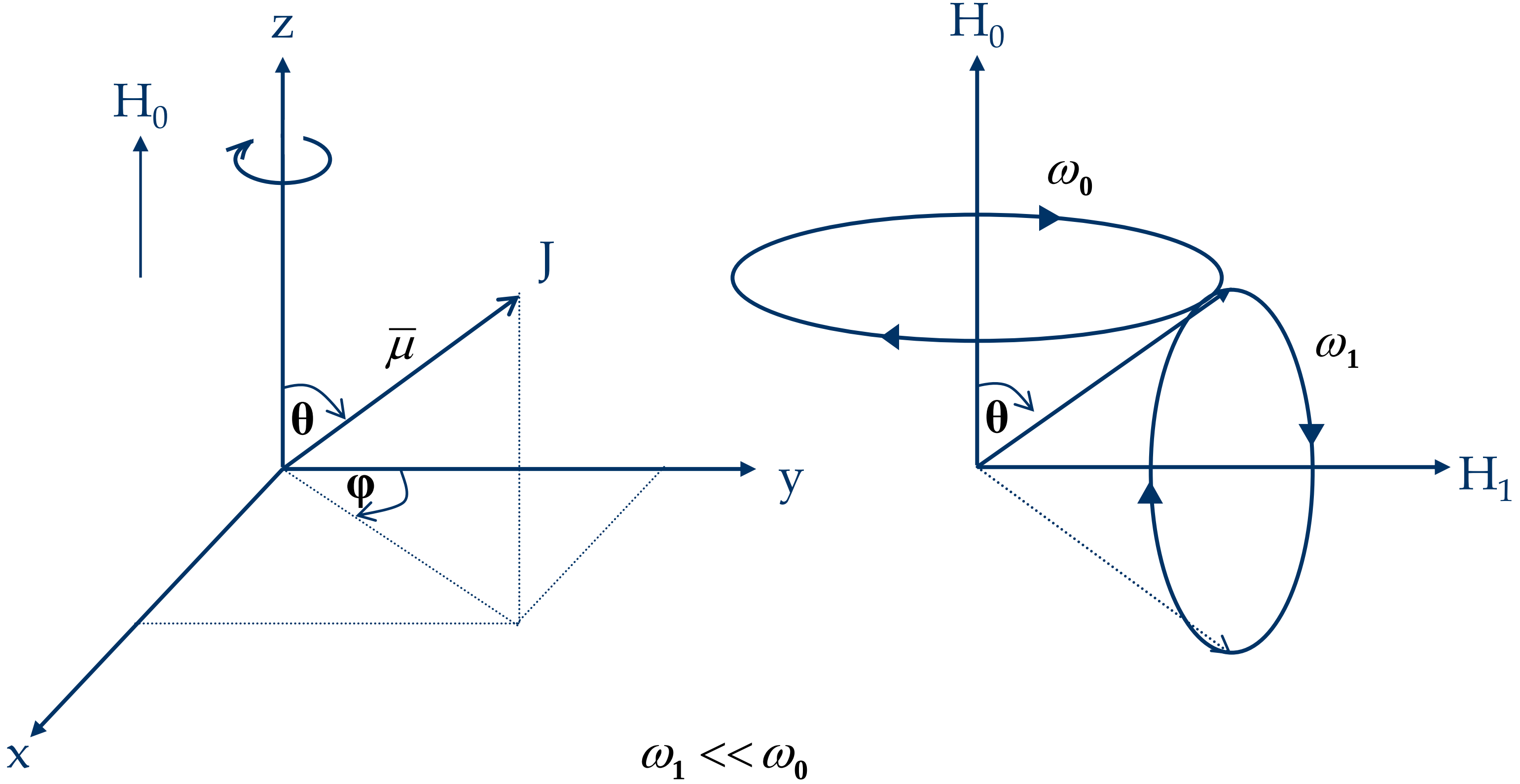
$$^{2}S_{1/2} \longrightarrow g = 1 + \frac{\frac{1}{2}\left(\frac{1}{2}+1\right)+\frac{1}{2}\left(\frac{1}{2}+1\right)-0(0+1)}{2\frac{1}{2}\left(\frac{1}{2}+1\right)} = 1 + \frac{\frac{3}{4}+\frac{3}{4}}{\frac{6}{4}} = 1+1 = 2$$


m_j
g
$+3/2$
a_3
$+1/2$
a_3
$-1/2$
$4/3$
a_3
$-3/2$
$^2P_{3/2}$
C
$2p$
$^2P_{1/2}$
$+1/2$
a_2
$-1/2$
$2/3$
$^2S_{1/2}$
$1s$
$+1/2$
a_1
$-1/2$
2
C
$\Delta m = 0$
π
$\Delta m = \pm 1$
σ

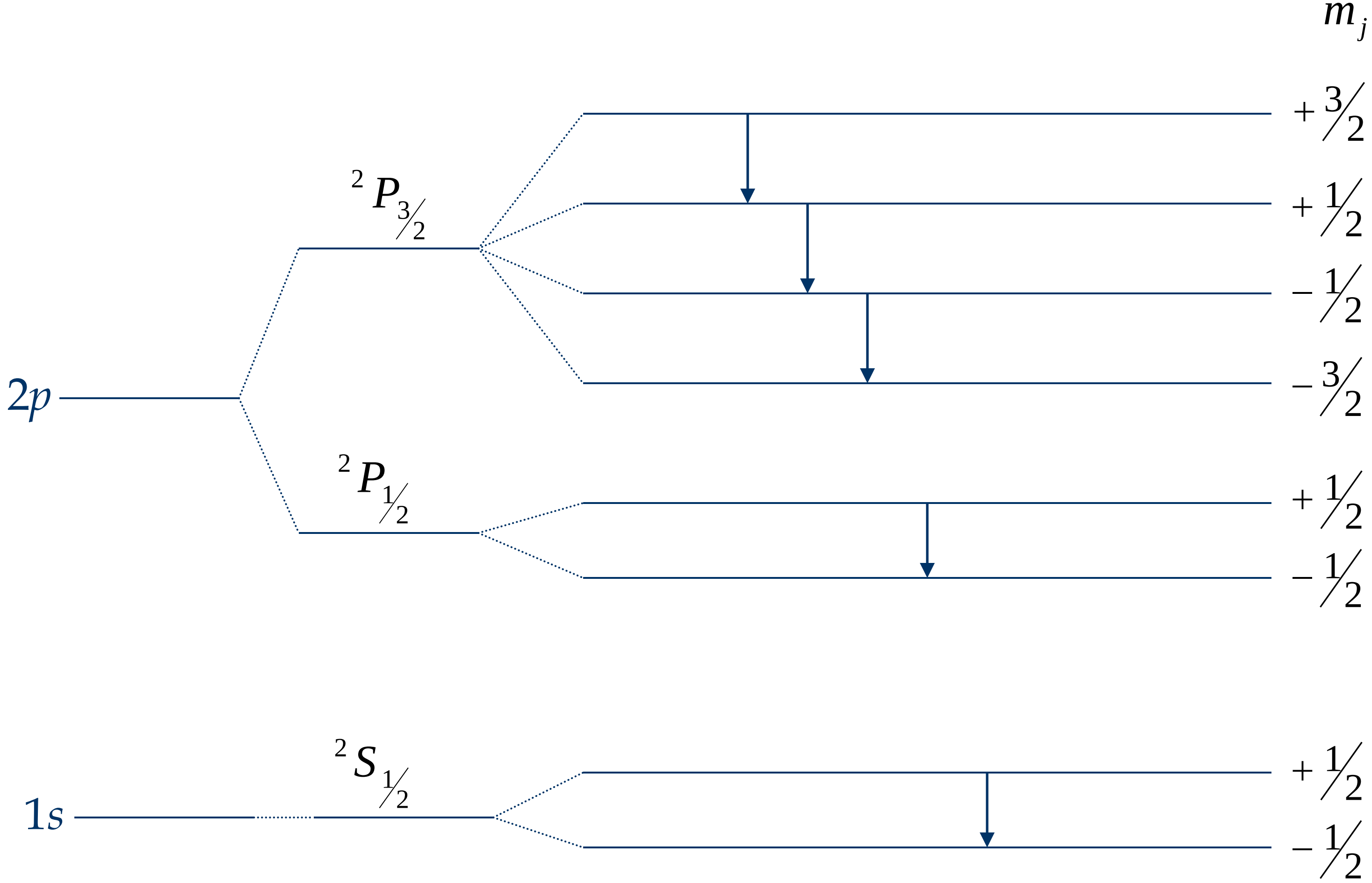
As can be seen, the splitting is not same for all levels; it depends on the J and L of the level ($s=½$ always for one electron). However, the sublevels will split equally by an amount

$$\Delta E = g\mu_0 H = h\nu_0$$

where ν_0 is the frequency of the system. Now if the electron is subjected to a perturbation by an oscillating magnetic field with its direction perpendicular to the static magnetic field and its frequency ν_1 such that the quantum $h\nu_1$ is equal to $E=h\nu_0$, we say that there is a resonance between ν_1 and ν_0. This will induce transition between neighbouring sublevels (mj = ±1) and in turn will absorb energy from oscillating field. Thus, at resonance, we get a peak due to the absorption of energy by the system.



Precession of magnetic moment μ when placed in a magnetic field



m_j
$+3/2$
$+1/2$
$-1/2$
$-3/2$
$+1/2$
$-1/2$
$+1/2$
$-1/2$
$^2P_{3/2}$
$2p$
$^2P_{1/2}$
$^2S_{1/2}$
$1s$

In Atomic Spectroscopy, we do not observe the transitions between sublevels with different m (a_1, a_2 and a_3), because they do not satisfy the selection rules $\Delta L = \pm 1$. Instead the splitting of a level is observed through small change in frequency of the radiation emitted in the transition between widely distant levels. It is clear that, if we could directly measure the frequency corresponding to a transition between the sublevels of the same state, a much more precise knowledge of the energy splitting would be obtained.

TECHNIQUE:

If we consider a free electron and substitute the proper value of constants in the equation:

g=2.00, μ_0 =0.927 X 10^{-20} erg/gauss & h =6.625 X 10^{-27} erg sec,

we get $g\mu_0 H_0 = h\nu_0$

$$\frac{\nu_0}{H_0} = \frac{g\mu_0}{h} = \frac{2.00\times 0.927\times 10^{-20}}{6.625\times 10^{-27}} = 0.2798\times 10^{7} = 2.8\times 10^{6} = 2.8\,MHz/gauss$$

That is ESR can be observed at radio frequencies in a magnetic field of a few gauss or in the microwave region in a magnetic field of a few kilogauss. The latter alternate has many advantages: improved signal-to-noise ratio, high resolution etc. and is always preferred for accurate work, though it is very sophisticated and expensive.

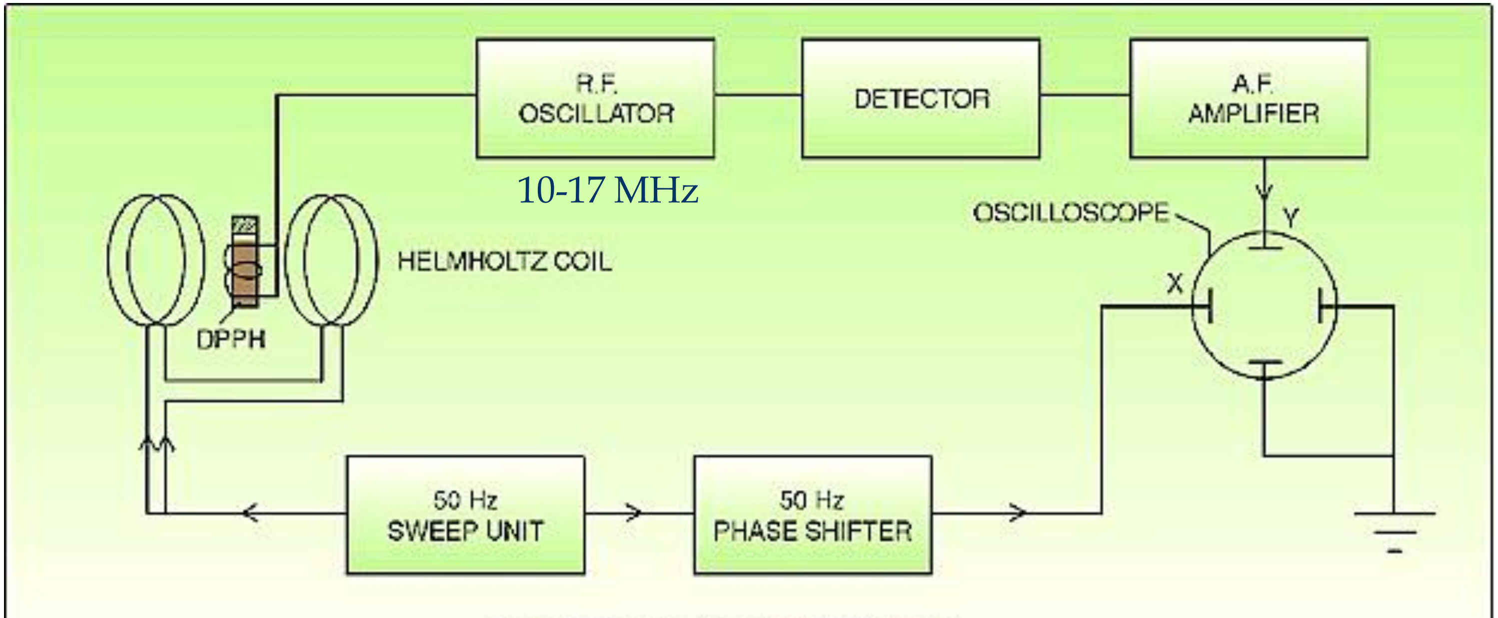
However, if the basic understanding of the subject is the main criteria as is usually the requirement of class room experiments, the observation of ESR in low magnetic field and in a radio frequency region makes it a lot simple, inexpensive and within the reach of every post-graduate laboratory.

EXPERIMENTAL TECHNIQUE:

This method is based on a determination of the change in a load factor of the oscillatory circuit due to paramagnetic losses.

The sample under investigation is placed in an induction coil, which is the component of the tank circuit of the oscillator (generator). When there is a absorption of a power from generator, the watt load (Δw) on the generator changes. This change of Δw is proportional to the change in base current ΔI_b or collector current ΔI_c of the generator. The change ΔI_c is detected with the conventional circuits. To make the detection simple and more sensitive, the magnetic field and hence the Larmour's frequency of the sample is modified with a low frequency field 50 Hz in the present set up.

Block diagram of ESR set up



10-17 MHz

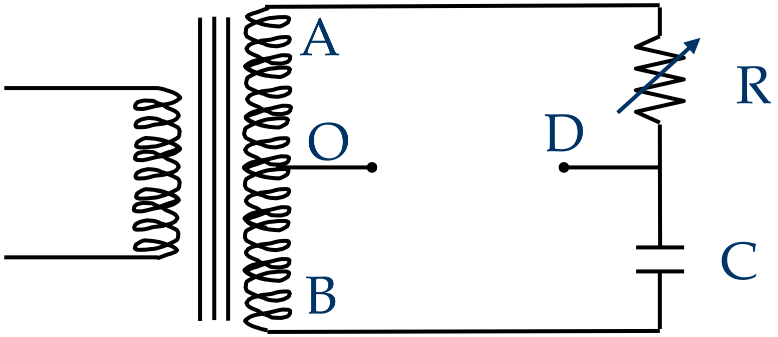
Fig. 1 Block diagram of the ESR set-up

1. Basic Circuit

The first stage of the ESR circuit consists of a critically adjusted radio frequency oscillator having frequency range of approximately 10 – 17 MHz. A sample is kept in the tank circuit of this oscillator, which in turn, is placed in the 50 Hz magnetic field, generated by the Helmholtz coils. At resonance, I.e. when frequency of the oscillation equal to the Larmour frequency of the sample, the oscillator amplitude registers a dip due to the absorption os power by sample. This obviously, occurs periodically – four times in each complete cycle of the Helmholtz coils supply voltage. Which is then detected by using a diode detector and amplified by a chain of three low noise, high gain audio frequency amplifiers of excellent stability. A Sensitivity control is provided in the amplifier to suit the input requirement of any oscilloscope.

2. Phase shifter

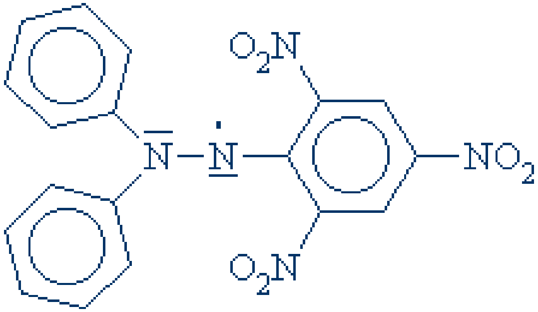
In order to make is possible to use an ordinary displaying–type oscilloscope, a phase shifter is provided. This can compensate the undetermined phase difference which is introduced in the amplification stage of the ordinary oscilloscope.



3. Test Sample

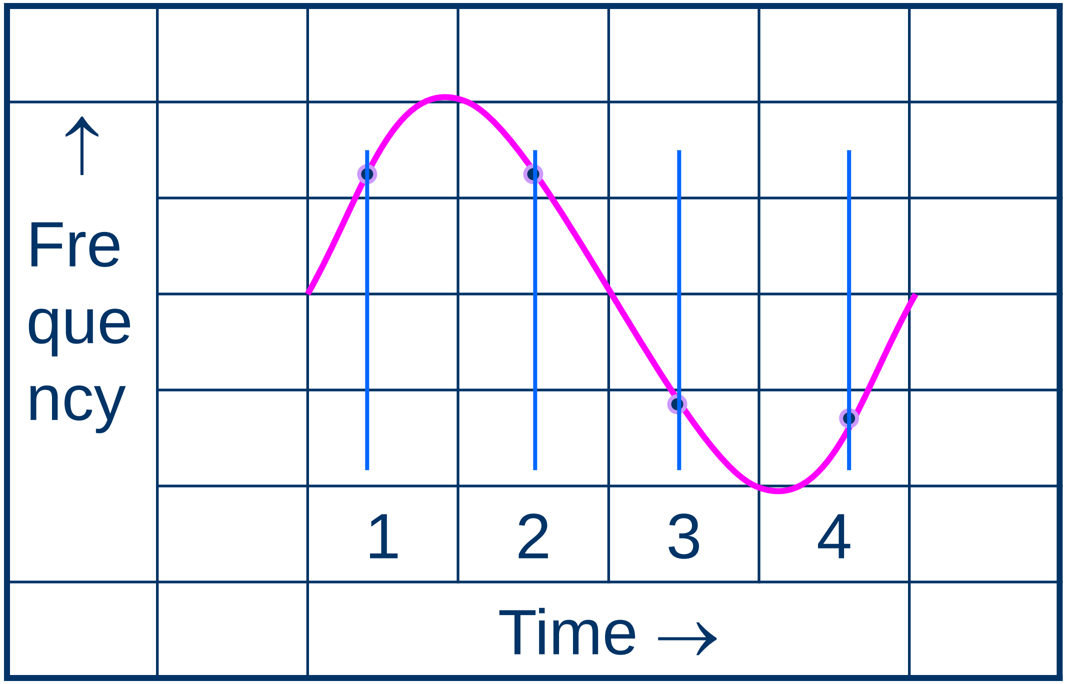
A test sample Diphenyl Picryl Hydrazyl (DPPH) is placed in a plastic tube, which itself is in the induction coils. DPPH is a free radical and is widely used as a standard for ESR measurement.

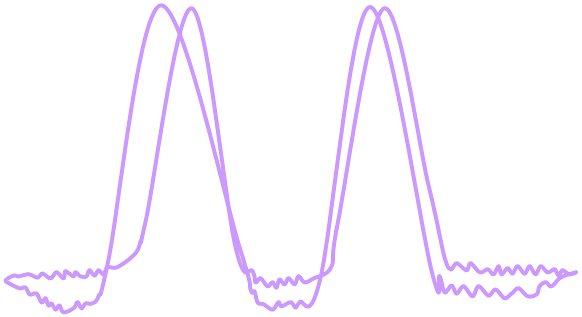
2,2-di(4-tert-octylphenyl)-1-picrylhydrazyl

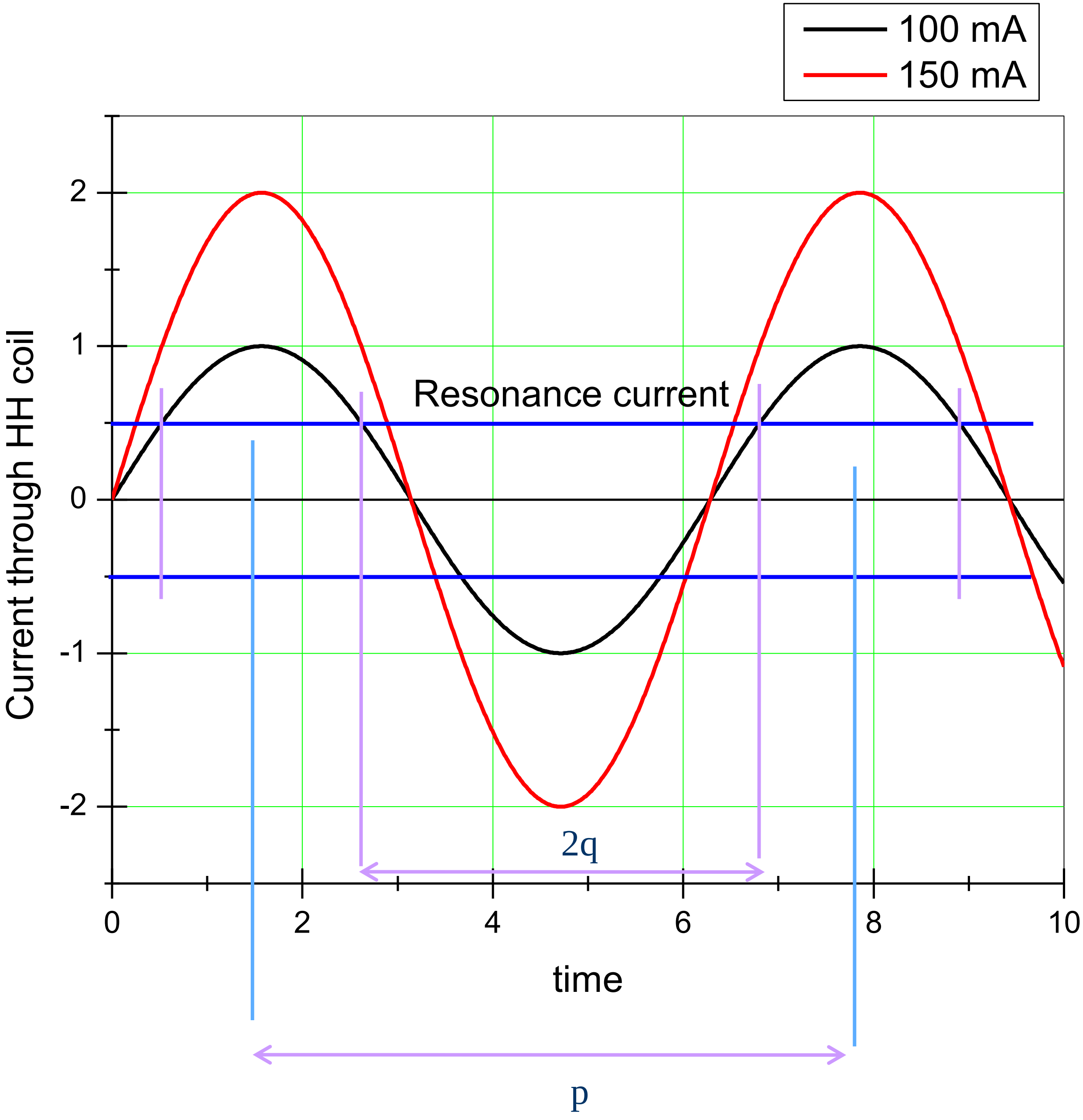


Origin of 4 peaks

The spin precesses with Lamour's frequency ($w_0=eH_0/2mc$) and hence varies in magnitude and direction due to variation of magnetic field $\mathbf{H}_0$ which is due to an alternating current in the Helmholtz coil.






100 mA
150 mA
Current through HH coil
2
1
0
-1
-2
Resonance current
2q
0
2
4
6
8
10
time
p

Aim: To determine Lande’s splitting factor (‘g’) by ESR spectrometer.

Apparatus: Radio Frequency Oscillator, ESR spectrometer, Helmholtz Coil, Sample; DPPH (Di Phynl Picryl Hydroxyl) etc.

Block diagram:

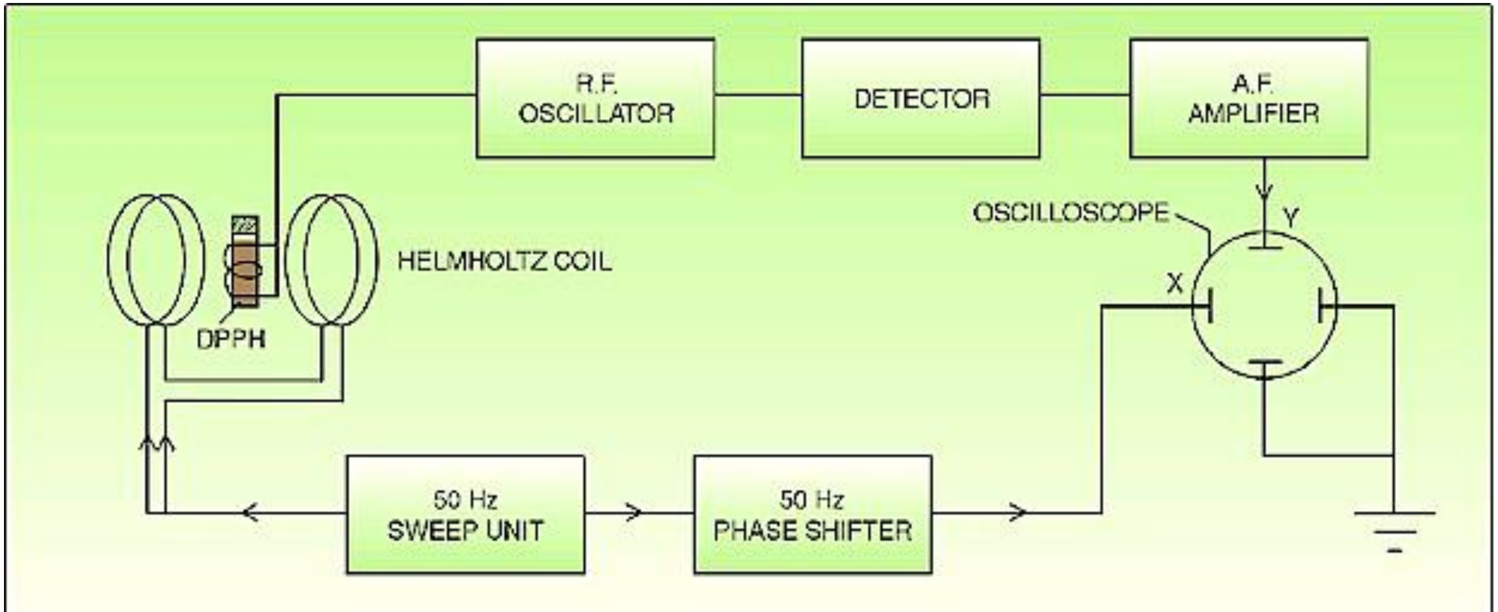


Fig. 1 Block diagram of the ESR set-up

Electron Spin Resonance Spectrometer


20 MHz DUAL TRACE OSCILLOSCOPE
ELECTRON SPIN RESONANCE SPECTROMETER
Model : ESR-104
153
mA
SCIENTIFIC EQUIPMENT
ROORKEE
FREQUENCY
R.F. OSC.
R.F. OSCILLATOR
ESR Coil

Formula:

$$g = \frac{h\nu_o}{\mu_o H_o}$$

$$g = 2.002319304386$$

g – Lande’s splitting factor

h – Plank’s Constant = 6.625 x 10^{-27}

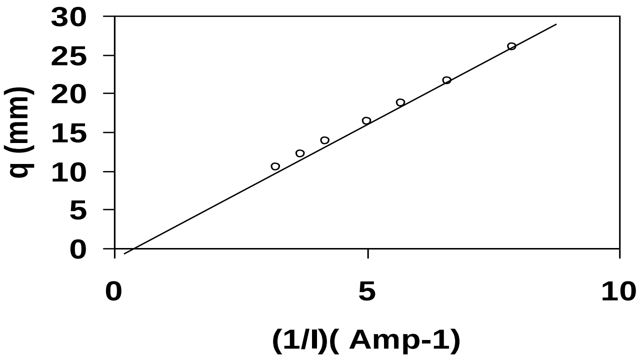
ν_o – Resonant frequency in Hz

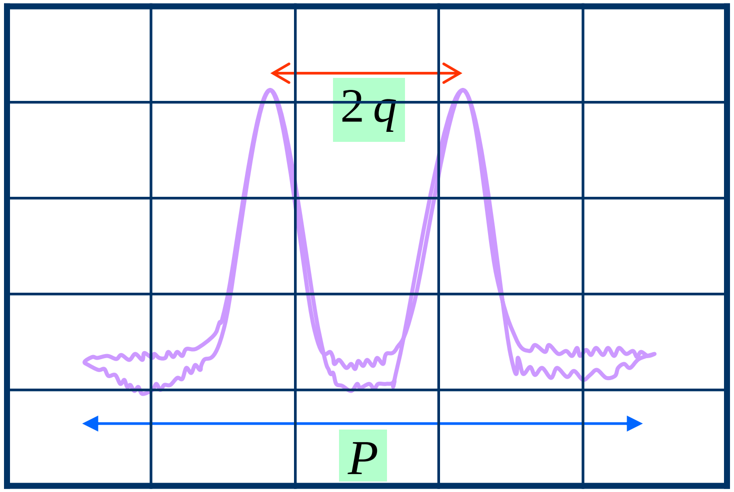
μ_o – Bohr magneton = 0.927 x 10-27 erg / gauss

H_o – Magnetic field on sample at resonance in gauss

$$H_o = H_{pp} \times \frac{qI}{P} \quad ; \; H_{pp} = 168$$

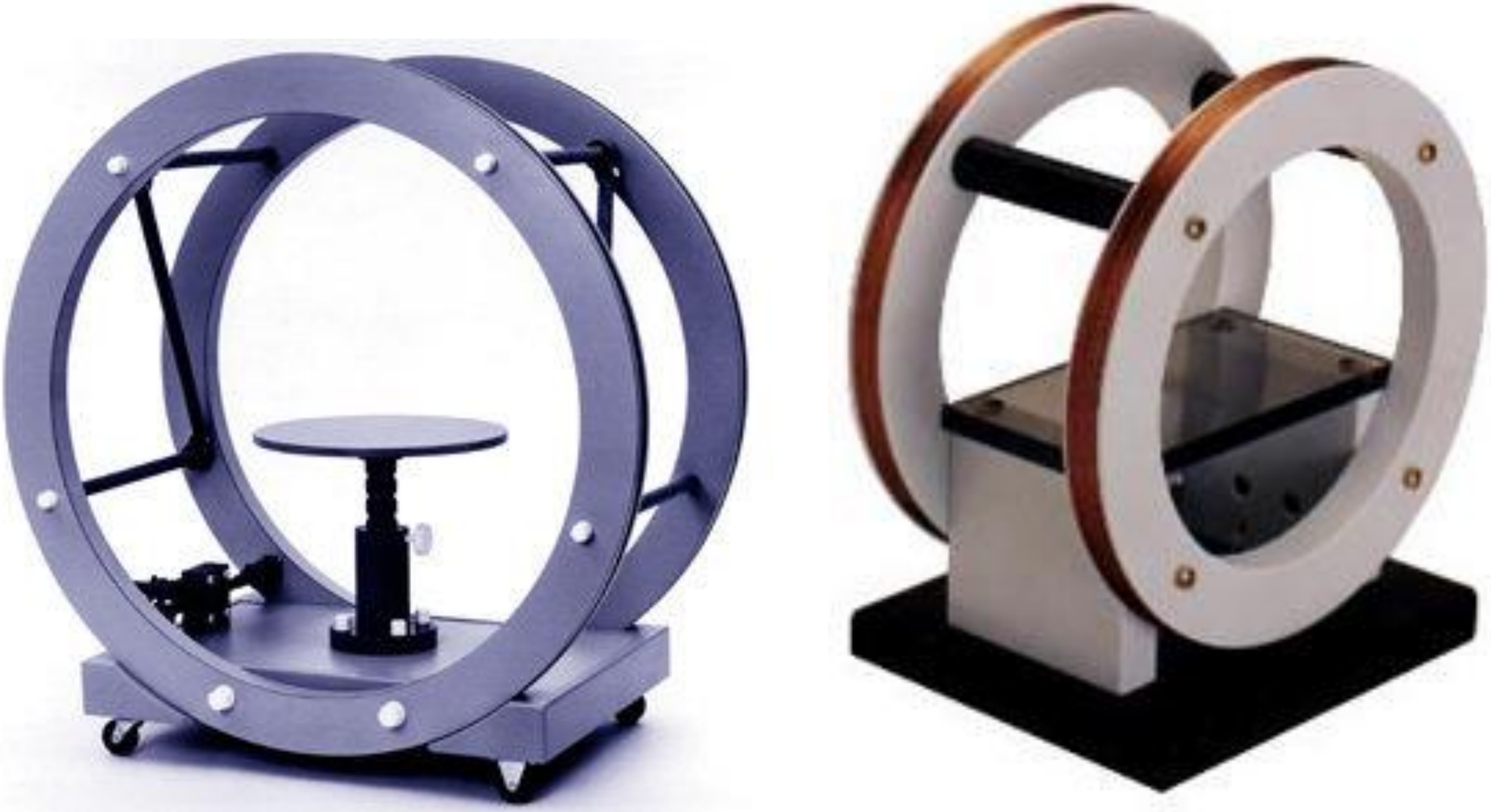
Graph between 1/I vs. 'q'



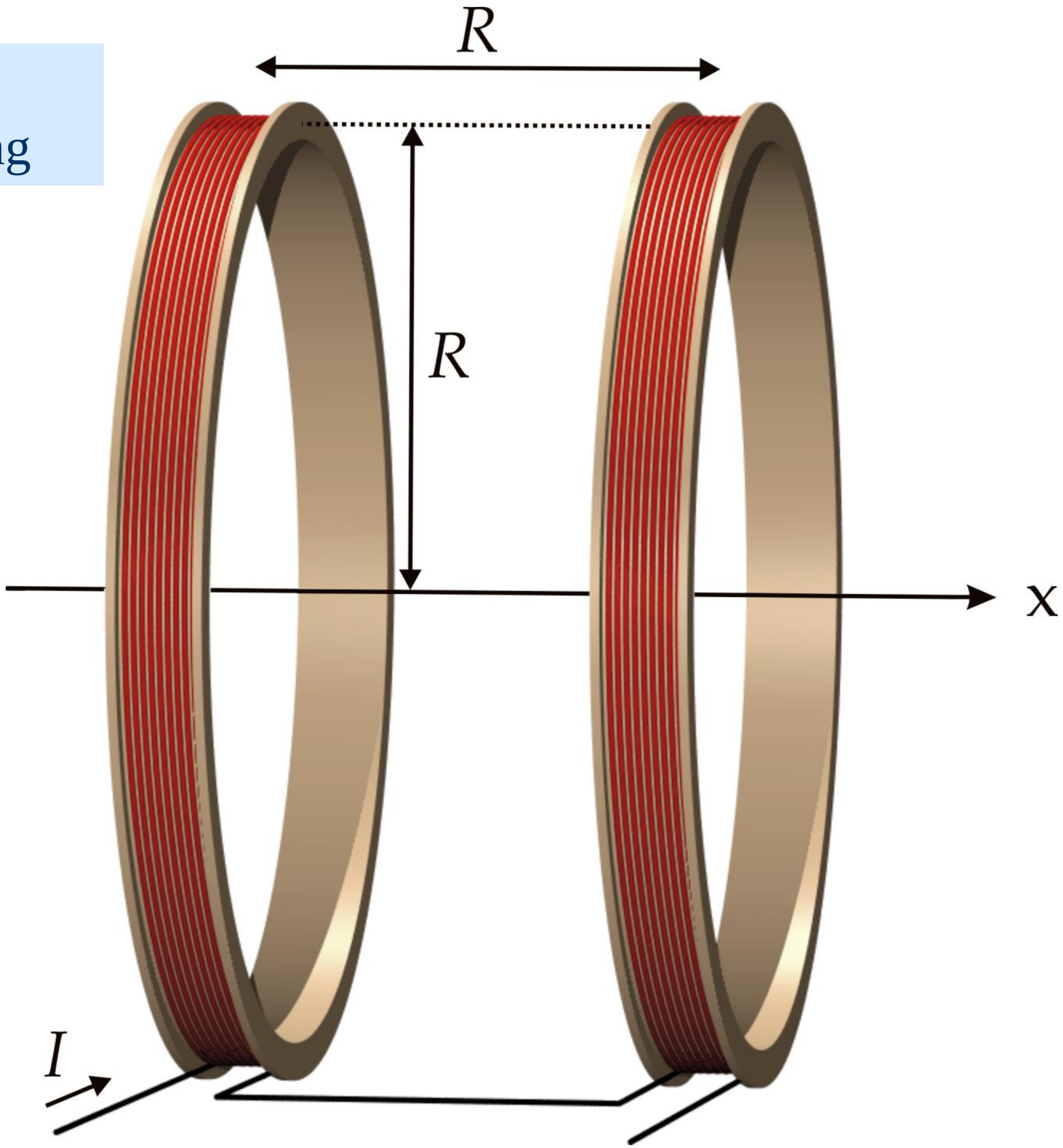


Observation Table

No.	Current I (mA)	Distance between peaks (2q) … cm	q … cm	Current I . A	1/I … A^{-1}
1.	150	5.6			
2.	160	5.2			
3.	170	4.8			
4.	180	4.6			
5.	190	4.4			
6.	200	4.0			

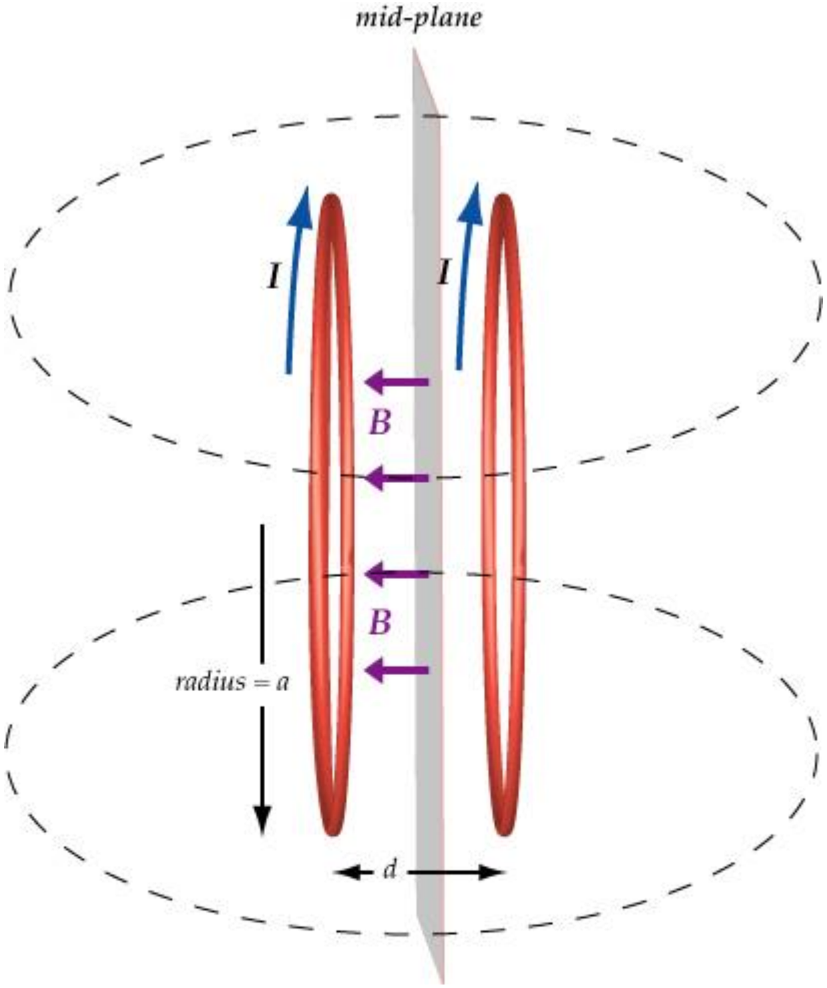


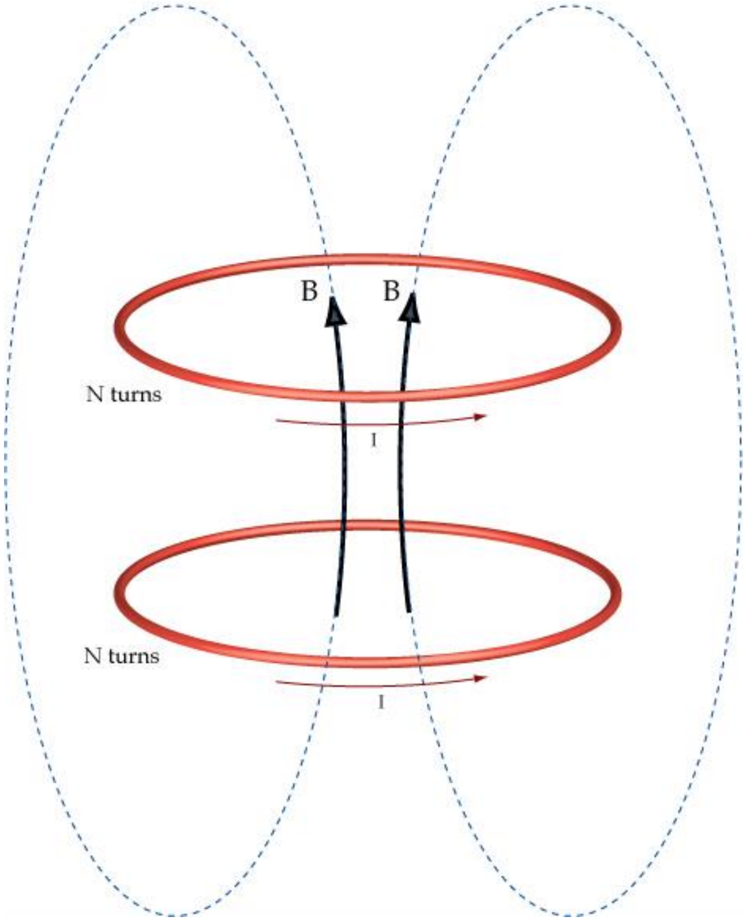
Helmholtz coil schematic drawing

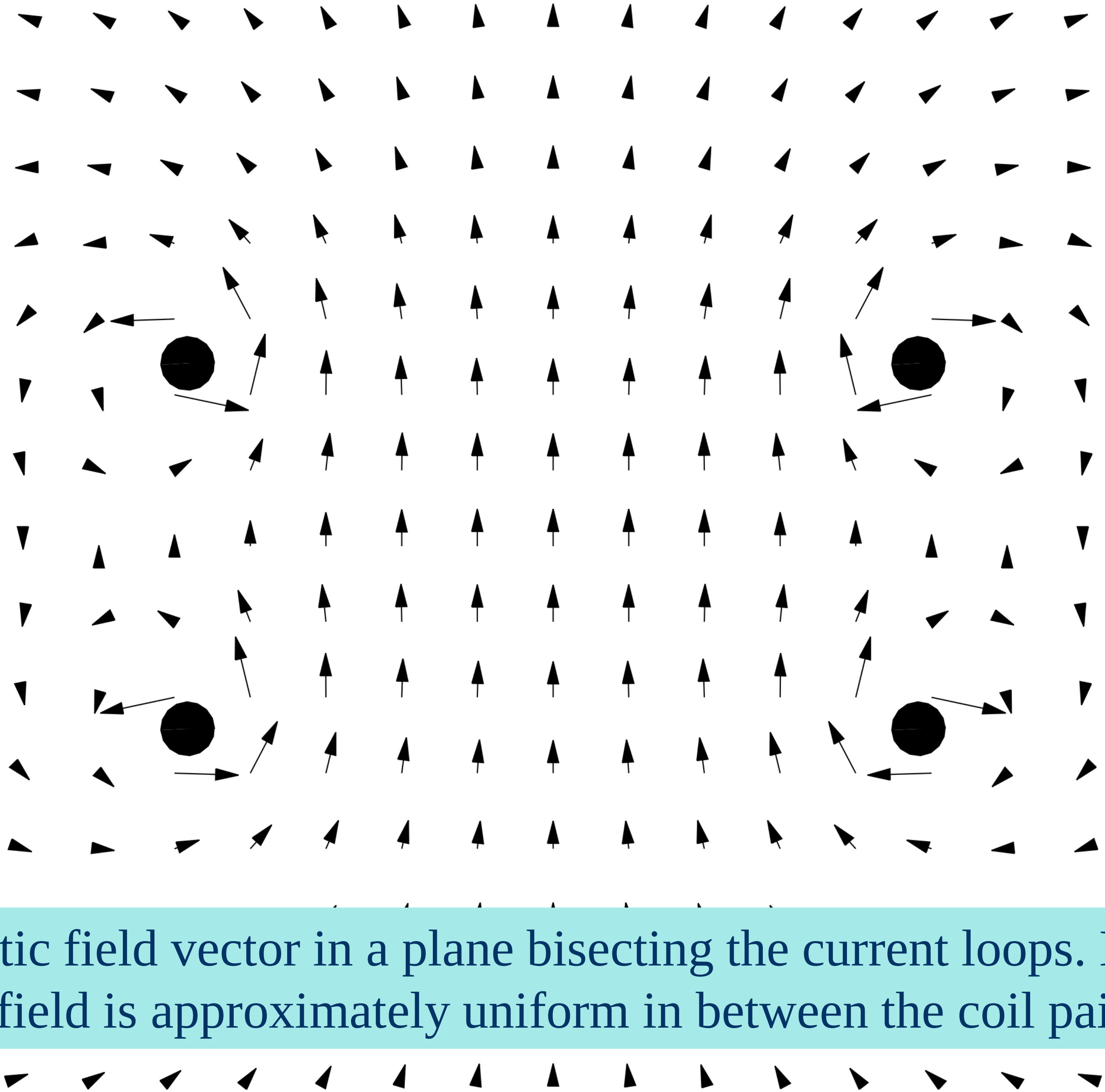


Helmholtz Coils

B = magnetic field (tesla)
I = current (amperes)







Magnetic field vector in a plane bisecting the current loops. Note the field is approximately uniform in between the coil pair.

THANK YOU