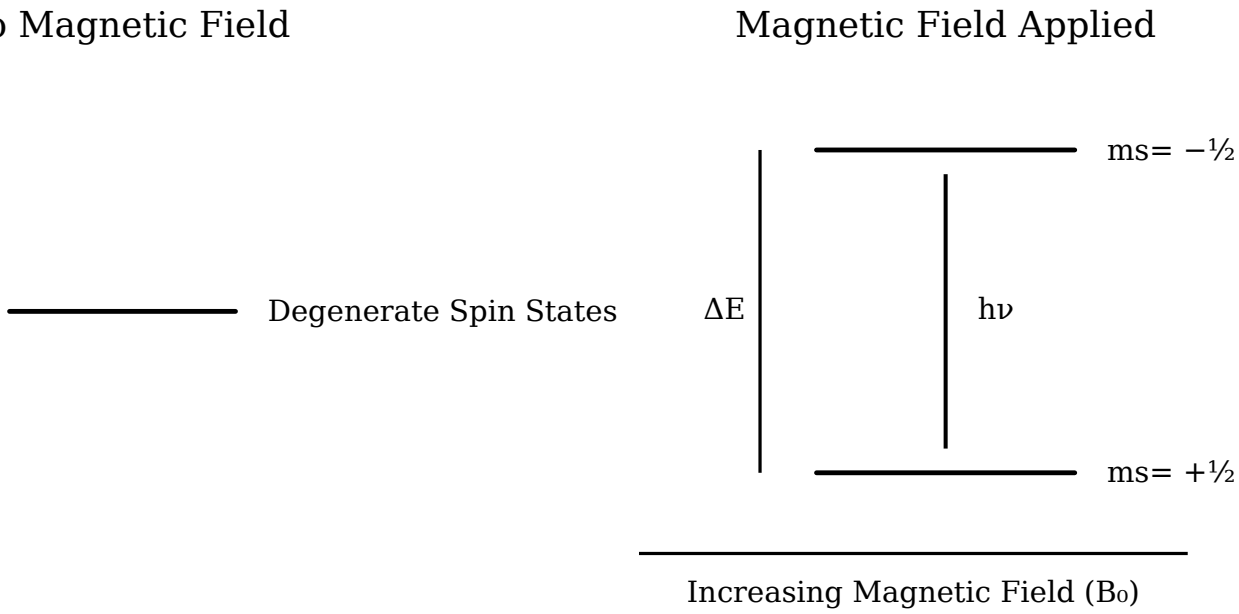
Principle of Electron Spin Resonance (ESR) Spectroscopy

Electron Spin Resonance (ESR) spectroscopy, also known as Electron Paramagnetic Resonance (EPR) spectroscopy, is a magnetic resonance spectroscopic technique used for the investigation of chemical species containing one or more unpaired electrons. The technique is based on the interaction between the magnetic moment of an unpaired electron and an externally applied magnetic field. When a paramagnetic substance is placed in a magnetic field, the degeneracy of the electron spin states is removed and two distinct energy levels are produced. If electromagnetic radiation in the microwave region is applied and its energy exactly matches the energy difference between these two spin states, the unpaired electron absorbs the radiation and undergoes a transition from the lower energy state to the higher energy state. This phenomenon is known as electron spin resonance.

Every electron possesses an intrinsic property known as spin. Associated with this spin is a magnetic moment, due to which the electron behaves like a tiny magnet. In the absence of an external magnetic field, the two possible orientations of the electron spin possess the same energy and are therefore degenerate. On application of a magnetic field, these spin states split into two separate energy levels through the Zeeman effect. The energy difference between these levels depends directly upon the strength of the applied magnetic field. When microwave radiation having energy equal to this energy difference is supplied, resonance absorption occurs. Thus, ESR spectroscopy measures the absorption of microwave radiation by unpaired electrons in the presence of an external magnetic field.

Only paramagnetic substances exhibit ESR spectra because they contain one or more unpaired electrons. In diamagnetic substances, all electrons are paired and their magnetic moments cancel each other, resulting in zero net magnetic moment. Since there is no unpaired electron available to interact with the applied magnetic field, diamagnetic substances do not absorb microwave radiation under ESR conditions. Consequently, ESR spectroscopy is applicable only to paramagnetic atoms, molecules, free radicals, transition metal ions, coordination compounds and crystal defects containing unpaired electrons.

The resonance condition in ESR spectroscopy is achieved by keeping either the microwave frequency constant while varying the magnetic field, or by keeping the magnetic field constant while varying the microwave frequency. In modern ESR spectrometers, the microwave frequency is generally maintained constant, whereas the magnetic field is gradually varied until resonance occurs. At the resonance point, maximum absorption of microwave energy takes place, producing the characteristic ESR spectrum. The position, intensity and splitting of the absorption signal provide valuable information regarding the electronic environment of the unpaired electron, the neighbouring magnetic nuclei and the molecular structure of the paramagnetic species.



Characteristics of ESR Spectroscopy

- ESR spectroscopy is a magnetic resonance spectroscopic technique.
- It detects species containing one or more unpaired electrons.
- It uses microwave radiation as the source of electromagnetic energy.
- A strong external magnetic field is essential for resonance.
- Only paramagnetic substances produce ESR spectra.
- The position and splitting of ESR signals provide information about the electronic structure and molecular environment.

- ESR spectroscopy is widely used for the study of free radicals, transition metal complexes, biological systems and solid-state defects.

Examples of ESR Active Species

Species	Reason for ESR Activity
H	Contains one unpaired electron.
CH_3•	Free radical with one unpaired electron.
OH•	Reactive oxygen radical.
NO	Odd-electron molecule.
Cu^{2+}	d^9 electronic configuration.
Mn^{2+}	High-spin d^5 configuration.
Fe^{3+}	High-spin d^5 configuration.
$[Ni(H_2O)_6]^{2+}$	Paramagnetic coordination complex.