

Principle of Electron Spin Resonance (ESR) Spectroscopy

The principle of Electron Spin Resonance (ESR) spectroscopy is based on the interaction between the magnetic moment of an unpaired electron and an externally applied magnetic field. When a substance containing one or more unpaired electrons is placed in a strong magnetic field, the magnetic moment associated with each unpaired electron interacts with that field. As a result, the single spin state of the electron splits into two energy levels having different energies. If microwave radiation of suitable frequency is allowed to pass through the sample, the electrons present in the lower energy level absorb the radiation and move to the higher energy level. This absorption occurs only when the energy of the microwave radiation is exactly equal to the energy difference between the two spin states. This phenomenon is known as electron spin resonance, and it forms the basis of ESR spectroscopy.

To understand this principle clearly, it is necessary to know why an electron behaves like a tiny magnet and why its energy changes when an external magnetic field is applied. These concepts are explained below.

Electron Spin and Magnetic Moment

Every electron possesses two fundamental properties. The first is its negative electric charge, while the second is an intrinsic property known as **spin**. Electron spin is a quantum mechanical property and should not be interpreted as the physical rotation of the electron about its own axis. Although the word “spin” is used for convenience, it simply represents the intrinsic angular momentum of an electron.

Since a moving electric charge produces a magnetic field, every spinning electron possesses a magnetic moment. Therefore, an electron behaves like a very small bar magnet having two opposite magnetic poles. The magnetic moment associated with an electron is called the **electron spin magnetic moment**. It is this magnetic moment that interacts with the external magnetic field during an ESR experiment.

The magnitude of the magnetic moment is expressed by the relation

$$\mu = -g\mu_B S$$

where,

- μ = magnetic moment of the electron
- g = spectroscopic splitting factor

- μ_B = Bohr magneton
- S = spin angular momentum of the electron

The negative sign indicates that the direction of the magnetic moment is opposite to the direction of the spin angular momentum because an electron carries a negative charge.

Spin Quantum Number

According to quantum mechanics, every electron possesses a spin quantum number,

$$s = \frac{1}{2}$$

The projection of this spin along the direction of an external magnetic field is represented by the spin magnetic quantum number, m_s , which can have only two possible values:

$$m_s = +\frac{1}{2} \quad \text{or} \quad m_s = -\frac{1}{2}$$

These two values represent the only two allowed orientations of the electron spin. No other orientation is permitted. In the absence of an external magnetic field, both orientations possess exactly the same energy and therefore cannot be distinguished from one another.

Behaviour of an Unpaired Electron in the Absence of a Magnetic Field

Consider a paramagnetic substance containing an unpaired electron. When no external magnetic field is applied, the two allowed spin orientations of the electron have identical energies. Since there is no difference in energy between them, neither orientation is more stable than the other. Such states are said to be **degenerate**.

Under these conditions, an electron cannot absorb microwave radiation because absorption of electromagnetic radiation is possible only when two energy levels are separated by a finite amount of energy. Since no energy difference exists between the two spin states in the absence of a magnetic field, resonance cannot occur.

Therefore, merely having an unpaired electron is not sufficient for ESR spectroscopy. A strong external magnetic field is essential to produce energy separation between the spin states. The effect of the magnetic field on these degenerate spin states is discussed in the next section.

Behaviour of an Unpaired Electron in the Presence of an External Magnetic Field

When a paramagnetic substance is placed between the poles of a strong magnet, the unpaired electron no longer behaves in the same manner as it does in the absence of a magnetic field. The external magnetic field interacts with the magnetic moment of the unpaired electron. This interaction changes the energy of the electron depending upon the orientation of its spin with respect to the applied magnetic field.

As discussed earlier, an electron can exist only in two spin orientations represented by the spin magnetic quantum numbers

$$m_s = +\frac{1}{2} \quad \text{and} \quad m_s = -\frac{1}{2}$$

Before the application of the magnetic field, these two spin states possess the same energy and are therefore degenerate. As soon as the magnetic field is applied, this degeneracy disappears. One spin state becomes slightly more stable and acquires lower energy, whereas the other becomes less stable and acquires higher energy.

The lower energy state corresponds to the electron whose magnetic moment is aligned parallel to the applied magnetic field, while the higher energy state corresponds to the electron whose magnetic moment is aligned in the opposite direction. Although the energy difference produced between these two states is very small, it is sufficiently large to permit absorption of microwave radiation.

Zeeman Splitting

The splitting of a single spin energy level into two separate energy levels under the influence of an external magnetic field is known as the **Zeeman effect**. The two energy levels produced are collectively referred to as **Zeeman levels**, while the energy difference between them is called **Zeeman splitting**.

The magnitude of this splitting depends directly upon the strength of the applied magnetic field. If the magnetic field is increased, the separation between the two energy levels also increases. Conversely, if the magnetic field is decreased, the energy difference becomes smaller.

Therefore, the applied magnetic field determines the amount of energy required for an electron to move from the lower energy level to the higher energy level.

Energy of an Electron in a Magnetic Field

The interaction energy of the magnetic moment of an electron with the applied magnetic field is given by

$$E = -\mu B_0$$

where,

- E = interaction energy
- μ = magnetic moment of the electron
- B_0 = strength of the external magnetic field

The magnetic moment of an electron is represented by

$$\mu = -g\mu_B S$$

Substituting this value into the energy equation,

$$E = -(-g\mu_B S)B_0$$

or,

$$E = g\mu_B S B_0$$

Since only the component of spin along the direction of the magnetic field contributes to the interaction energy, the spin angular momentum is replaced by the spin magnetic quantum number, m_s .

Hence,

$$E = g\mu_B m_s B_0$$

Calculation of the Two Spin Energy Levels

An electron possesses only two allowed values of the spin magnetic quantum number. Therefore, two different energy levels are obtained.

Lower Energy Level

For

$$m_s = -\frac{1}{2}$$

the energy is

$$E_1 = g\mu_B \left(-\frac{1}{2} \right) B_0$$

or

$$E_1 = -\frac{1}{2}g\mu_B B_0$$

This represents the lower energy state occupied by the majority of electrons under ordinary conditions.

Higher Energy Level

For

$$m_s = +\frac{1}{2}$$

the energy becomes

$$E_2 = g\mu_B \left(+\frac{1}{2} \right) B_0$$

or

$$E_2 = +\frac{1}{2}g\mu_B B_0$$

This is the higher energy state. Only a small number of electrons occupy this level because it is less stable than the lower energy level.

Energy Difference Between the Two Spin States

The separation between the two Zeeman levels is obtained by subtracting the lower energy from the higher energy.

$$\Delta E = E_2 - E_1$$

Substituting the values of the two energy levels,

$$\Delta E = \left(+\frac{1}{2}g\mu_B B_0 \right) - \left(-\frac{1}{2}g\mu_B B_0 \right)$$

Removing the brackets,

$$\Delta E = \frac{1}{2}g\mu_B B_0 + \frac{1}{2}g\mu_B B_0$$

Therefore,

$$\boxed{\Delta E = g\mu_B B_0}$$

This equation shows that the energy difference between the two spin states is directly proportional to the strength of the applied magnetic field. A stronger magnetic field produces greater Zeeman splitting, whereas a weaker magnetic field produces a smaller energy separation.

The next step is to determine the condition under which an electron can absorb microwave radiation and move from the lower energy level to the higher energy level. This leads to the derivation of the fundamental resonance condition of ESR spectroscopy.

Resonance Condition

The Zeeman effect produces two spin energy levels separated by an energy difference of

$$\Delta E = g\mu_B B_0$$

The existence of two energy levels alone does not produce an ESR spectrum. A transition between these levels takes place only when the electron absorbs electromagnetic radiation having energy exactly equal to the energy difference between them.

According to Planck's quantum theory, the energy associated with electromagnetic radiation is given by

$$E = h\nu$$

where,

- h = Planck's constant (6.626×10^{-34} J s)
- ν = Frequency of microwave radiation

For resonance absorption to occur, the energy of the microwave radiation must be exactly equal to the energy separation produced by the external magnetic field. Therefore,

$$h\nu = \Delta E$$

Substituting the value of ΔE ,

$$h\nu = g\mu_B B_0$$

This equation is known as the **fundamental resonance condition of ESR spectroscopy**. It forms the basis of every ESR experiment.

The equation shows that resonance is observed only when the microwave energy matches the energy required for an electron to move from the lower spin state to the higher spin state. If the microwave energy is smaller or greater than this value, no absorption occurs and no ESR signal is obtained.

How Resonance is Produced in an ESR Spectrometer

In practical ESR spectroscopy, the microwave source generally operates at a fixed frequency. Instead of changing the frequency continuously, the magnetic field is varied gradually. As the magnetic field increases, the energy difference between the two spin states also increases. At a particular value of the magnetic field, the condition

$$h\nu = g\mu_B B_0$$

is satisfied. At this instant, electrons present in the lower energy state absorb microwave radiation and undergo transition to the higher energy state. The absorbed energy is detected electronically and appears as an ESR signal.

After excitation, the electrons do not remain permanently in the higher energy state. They soon return to the lower energy state by releasing the absorbed energy to the surroundings. This process is known as **relaxation**. Continuous absorption and relaxation enable the spectrometer to record a stable ESR spectrum.

Selection Rule

According to quantum mechanics, not every transition between energy levels is permitted. Electron spin transitions can occur only when they satisfy the selection rule.

$$\Delta m_s = \pm 1$$

This means that during resonance the spin magnetic quantum number must change by one unit. Thus, an electron may undergo the transition

$$-\frac{1}{2} \longrightarrow +\frac{1}{2}$$

after absorbing microwave radiation. Any transition that does not satisfy this condition is forbidden and normally does not appear in the ESR spectrum.

Conditions Required for ESR Spectroscopy

For successful observation of an ESR spectrum, the following conditions must be fulfilled.

1. Presence of Unpaired Electrons

The sample must contain one or more unpaired electrons. Molecules containing only paired electrons are diamagnetic and therefore do not produce ESR spectra.

2. Application of an External Magnetic Field

A strong and uniform magnetic field is necessary to remove the degeneracy of the spin states and produce Zeeman splitting.

3. Microwave Radiation

The sample must be irradiated with microwave radiation whose energy is capable of producing transitions between the two spin states.

4. Resonance Condition

The resonance condition

$$h\nu = g\mu_B B_0$$

must be satisfied. Only then does microwave absorption take place.

ESR Active and ESR Inactive Species

The presence or absence of unpaired electrons determines whether a substance is ESR active or ESR inactive.

ESR Active Species	Reason
Cu^{2+}	Contains one unpaired electron ($3d^9$)
Mn^{2+}	Contains five unpaired electrons ($3d^5$)
Fe^{3+}	Contains five unpaired electrons ($3d^5$)
Cr^{3+}	Contains three unpaired electrons ($3d^3$)
NO molecule	Odd-electron molecule
Organic and inorganic free radicals	Contain one unpaired electron

ESR Inactive Species	Reason
H ₂ O	All electrons are paired
NaCl	Diamagnetic compound
CO ₂	No unpaired electrons
CH ₄	All electrons are paired
Zn ²⁺ compounds	3d ¹⁰ electronic configuration

Summary of the Principle

The principle of ESR spectroscopy is based on the interaction between the magnetic moment of an unpaired electron and an external magnetic field. The magnetic field removes the degeneracy of the two spin states and produces Zeeman splitting. When microwave radiation of appropriate frequency is supplied, electrons absorb energy and move from the lower energy state to the higher energy state. This absorption takes place only when the resonance condition,

$$h\nu = g\mu_B B_0$$

is satisfied. The absorption of microwave energy is detected and recorded as the ESR spectrum. Thus, ESR spectroscopy serves as a powerful technique for studying paramagnetic substances containing unpaired electrons.