Hyperfine Coupling (Hyperfine Interaction)

Hyperfine coupling, also known as **hyperfine interaction**, is one of the most important phenomena observed in Electron Spin Resonance (ESR) spectroscopy. It arises from the magnetic interaction between the magnetic moment of an **unpaired electron** and the magnetic moment of one or more **atomic nuclei** present in the molecule or ion. This interaction causes the single ESR absorption line to split into two or more closely spaced lines, a phenomenon known as **hyperfine splitting**. The pattern of splitting provides valuable information about the number and type of magnetic nuclei surrounding the unpaired electron, their nuclear spin values, and the distribution of electron density within the molecule.

In the absence of hyperfine interaction, an unpaired electron placed in an external magnetic field gives rise to only one ESR absorption signal. However, if the unpaired electron is located near nuclei having non-zero nuclear spin ($I \neq 0$), each possible orientation of the nuclear magnetic moment slightly modifies the magnetic field experienced by the electron. As a result, the electron experiences several slightly different magnetic environments, leading to the splitting of the resonance signal into multiple equally spaced components. Therefore, hyperfine coupling is one of the most useful features of ESR spectroscopy because it provides direct structural information that cannot be obtained from the resonance position alone.

The magnitude of hyperfine interaction depends upon the overlap between the electron cloud and the nucleus. A greater probability of finding the unpaired electron near the nucleus results in stronger hyperfine coupling and consequently larger separation between the split ESR lines. This separation is called the **hyperfine coupling constant**, usually represented by the symbol **A**. The coupling constant is generally expressed in units of gauss (G), millitesla (mT), or megahertz (MHz), depending upon the experimental method.

Origin of Hyperfine Coupling

Every nucleus having a non-zero nuclear spin possesses a magnetic moment. When an unpaired electron is present near such a nucleus, the magnetic field produced by the nucleus either adds to or subtracts from the externally applied magnetic field. Consequently, the effective magnetic field experienced by the electron changes slightly depending on the orientation of the nuclear spin. Since resonance occurs at a magnetic field satisfying the ESR condition, different effective magnetic fields produce different resonance positions, resulting in hyperfine splitting of the ESR signal.

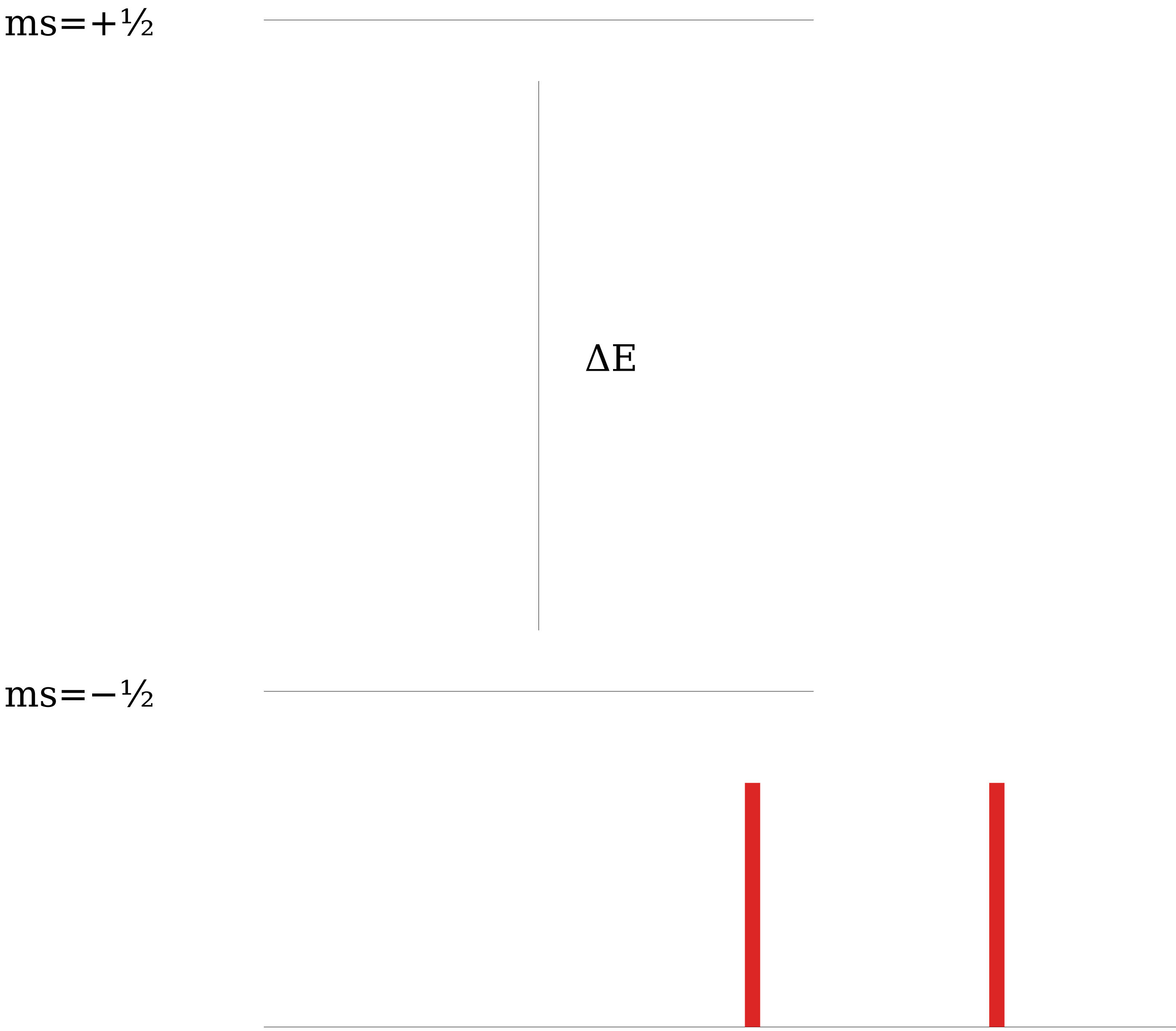
Only nuclei having a non-zero nuclear spin participate in hyperfine interaction. Nuclei with nuclear spin equal to zero do not produce hyperfine splitting because they possess no magnetic moment.

Nuclei Commonly Producing Hyperfine Splitting

Nucleus	Nuclear Spin (I)	Hyperfine Splitting
^{1}H	1/2	Yes
^{14}N	1	Yes
^{13}C	1/2	Yes
^{19}F	1/2	Yes
^{31}P	1/2	Yes
^{16}O	0	No
^{12}C	0	No

Illustration of Hyperfine Splitting

When an unpaired electron interacts with a single proton (^{1}H, I = 1/2), the proton can exist in two possible nuclear spin orientations. Consequently, the ESR signal splits into two equally spaced lines, commonly called a **doublet**.



Two equally spaced ESR lines (D

Similarly, interaction with two equivalent protons produces three equally spaced lines (triplet), while interaction with three equivalent protons produces four equally spaced lines (quartet). Thus, the number of hyperfine lines depends upon the number of equivalent magnetic nuclei and their nuclear spin values.