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Magnetic Resonance

Betul Çalışkan and Ali Cengiz Çalışkan

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Abstract

Magnetic resonance is divided into electron spin resonance (ESR) [electron paramagnetic resonance (EPR)] and nuclear magnetic resonance (NMR) according to the working region in the electromagnetic spectrum. If the studied region is in the microwave region, this resonance type is electron spin resonance. If the region studied is the radio frequency region, then nuclear magnetic resonance is mentioned. ESR and NMR are similar in terms of their basic theorem.

Keywords: electron spin resonance (ESR), electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), microwave frequency, radio frequency

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy examines the interaction of nuclear spins forming an atom with the magnetic field applied to them. Electron spin (paramagnetic) resonance (ESR, EPR) spectroscopy studies the interaction of the electron spins with the applied magnetic field.

The resonance term is used to determine that an external factor is in harmony with the natural frequency of the magnetic system. The natural frequency is the radio frequency (RF) or microwave (MD) frequency, which is in agreement with the Larmor rotation frequency of the magnetic moments in the magnetic field.

The magnetic moment referred to NMR is a nonzero nuclear moment. In other words, NMR deals with nuclei whose spin value is nonzero. The magnetic moment referred to EPR is the magnetic moment of the electron. EPR studies magnetic systems with unpaired electrons.

2. Magnetic resonance spectroscopy (NMR and EPR spectroscopy)

Nuclear magnetic resonance (NMR) was first observed by F. Bloch in 1946. In the same period, the electron spin resonance (ESR) experiment was first performed by YK Zavoisky in 1944.

Magnetic resonance spectroscopy is similar to other types of absorption spectroscopy. Magnetic resonance is based on the interaction of matter with electromagnetic radiation. Electromagnetic radiation for NMR is in the radio frequency domain. For the EPR, it is in the microwave area. As a result of this interaction, the transition from the high energy state to the low energy state leads to an energy release in the amount of (ΔE) [1].

$$\Delta E = h\nu \quad (1)$$

Within the external magnetic field, the magnetic moment of the nucleus or electron makes a precession movement with the Larmor frequency (ω) around the magnetic field. The Larmor precession movement tries to orient the spins or magnetic dipole moments in the direction of the magnetic field. This process is called **the relaxation process** [2].

The state of the system reaching the thermal equilibrium is called relaxation time. Relaxation times are divided into two. The first is T_1 spin-lattice (longitudinal) relaxation time. It affects the z-component of the magnetization vector. T_1 determines the energy flow rate of neighboring molecules (lattice) from the nuclear spin system. It is the time to reach the thermal equilibrium of the neighboring molecules with the nuclear spin system. The second is T_2 spin-spin (transverse) relaxation time. T_2 affects the x and y components of the magnetization vector. The process of reaching thermal equilibrium as the result of the interaction between the spins without transferring energy to the neighboring molecules is called the spin-spin relaxation process. T_2 is related to **the full width at half maximum (fwhm)** ($\Delta\nu_{1/2}$) of the NMR signal.

The orientations of the magnetic moments are in the form of different spin populations at different energy levels. Boltzmann expression is used for low energy state (N_-) and high energy state (N_+) spin populations with temperature effect.

$$\frac{N_-}{N_+} = e^{h\nu/kT} \quad (2)$$

where k is Boltzmann's constant and T is the temperature in K.

The ratio of the magnetic moment to the spin angular momentum is called **the gyromagnetic ratio** (γ). This expression is also equal to the ratio of the Larmor precession frequency to the magnetic field.

$$\vec{\omega} = \gamma \vec{H} \quad (3)$$

where ω is 2π times the precession frequency ($2\pi\nu$) and H is the applied magnetic field.

This expression contains both the resonance condition and the magneton concept. For EPR studies, Bohr magneton is valid whereas for NMR studies nuclear magneton is applied.

Magneton is related to the concept of spin magnetic moment (μ_I : the nuclear spin magnetic moment, μ_S : the electron spin magnetic moment). It is a concept related to the ratio between the mass and the charge of a particle having a different spin from zero.

$$\beta = \frac{e\hbar}{2m_e} \quad (4)$$

where β is the Bohr magneton, $\beta=9.2741 \times 10^{-24}$ J/T, e is the charge of the spinning particle, and m_e is the mass of the electron. For the nuclear magneton β_n , this would be:

$$\beta_n = \frac{e\hbar}{2m_p} \quad (5)$$

β_n (nuclear magneton) is much smaller than β (Bohr magneton) since the proton mass (m_p) is 1836 times as great as that of the electron, $\beta_n=5.05 \times 10^{-27}$ J/T. The magneton relates to the basic equation above because:

$$\gamma = \frac{g\beta}{\hbar} \quad (6)$$

where g is a proportionality constant usually referred to as the g -value or g is the spectroscopic splitting constant, and \hbar is Planck's constant divided by 2π . Hence:

$$\frac{\omega}{H} = \frac{g\beta}{\hbar} \quad (7)$$

or

$$\omega\hbar = g\beta H \quad (8)$$

Since ω is $2\pi\nu$, then:

$$h\nu = g\beta H \quad (9)$$

The above expression is called resonance condition in both NMR and ESR [1].

Although many processes are similar in the EPR and NMR experiments, the tools used in the experiments differ. In EPR, it is used in microwave components, such as wave-guide, cavities, and klystron tubes. In NMR, inductances, capacitors, conductors that transmit radio frequency energy, and vacuum tubes are used [2].

2.1. NMR spectroscopy

Magnetic dipole moment of the nucleus:

$$\vec{\mu}_I = \gamma_I \vec{I} \quad (10)$$

$$\vec{\mu}_I = g_n \frac{\beta_n}{\hbar} \vec{I} \quad (11)$$

$$\mu_I = g_n \left(\frac{e\hbar}{2m_p} \right) \frac{1}{\hbar} \left(\sqrt{I(I+1)} \hbar \right) \quad (12)$$

$$\mu_I = g_n \beta_n \sqrt{I(I+1)} \quad (13)$$

Here, I is nuclear spin and g_n is the nuclear g-factor ($g_n=5.5855$).

The interaction between the external magnetic field and the nuclear magnetic moment is given as follows:

$$E = -\vec{\mu}_I \cdot \vec{H}_0 \quad (14)$$

$$E = -\mu_I H_0 \cos\theta \quad (15)$$

where θ is the angle between the dipole and the magnetic field. There are two orientations for a proton with a nuclear spin $1/2$. This indicates the quantum number of magnetic spin, m_I . For $m_I = \pm \frac{1}{2}$, energy takes values $-\frac{1}{2}g_n\beta_n H_0$ and $+\frac{1}{2}g_n\beta_n H_0$ as shown in **Figure 1**.

The nuclear magnetic resonance transition occurs between two energy levels. The transition between the two energy levels constitutes the resonance condition.

$$\Delta E = h\nu = g_n\beta_n H_0 \quad (16)$$

is called **the resonance condition for NMR**.

Nuclear magnetic resonance stays on two important interactions. The first one is **the chemical shift** and the other is **the spin-spin coupling**. A third interaction can also be mentioned. This is **the exchange interaction**. Thus, we can list three important interactions in NMR as follows:

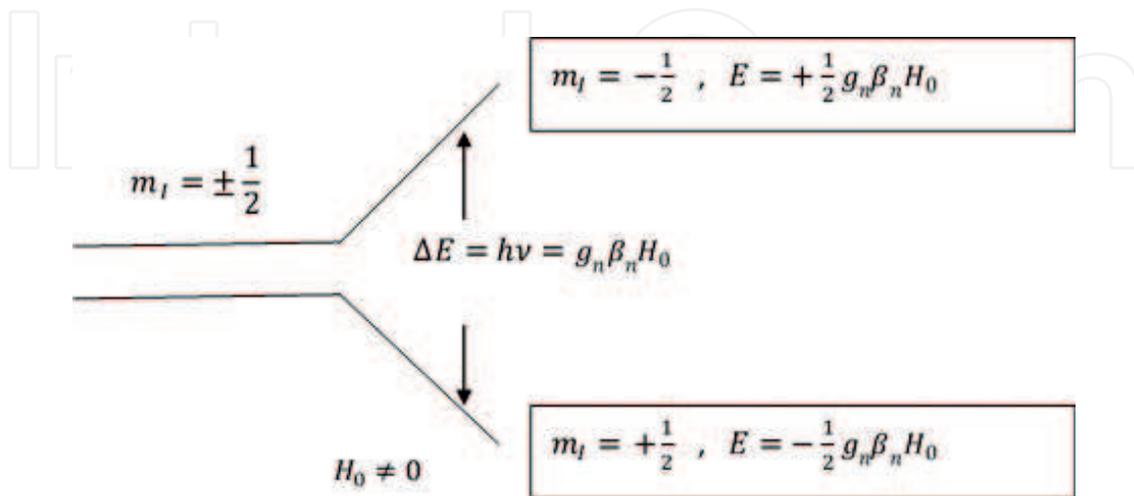


Figure 1 . Nuclear magnetic resonance transition.

1. The chemical shift
2. The spin-spin coupling
3. The exchange interaction
 - a. Slow exchange interaction
 - b. Fast exchange interaction

However, the third influence is not taken into consideration. So, we will focus on two interactions.

The effective Hamiltonian expression for NMR consists of the sum of the nuclear Zeeman Hamiltonian and the nuclear spin-spin interaction Hamiltonian terms:

$$\mathcal{H} = -g_n\beta_n \vec{H} \cdot \vec{I} \cdot \vec{S} + \vec{I} \cdot \vec{Q} \cdot \vec{I} \quad (17)$$

Here, \vec{Q} is the quadrupole interaction tensor (interaction between two nuclear spins) interaction tensor [3].

2.1.1. Chemical shift

The electrons surrounding the nucleus of a molecular system show a spherical distribution. The external magnetic field applied on the system creates polarity in the electron distribution in the spherical structure. That is, a current flows through the molecule. This current induces a magnetic field by induction where the core is located. This field is called the internal magnetic field (Figure 2). The internal magnetic field is opposite to the external magnetic field. The total

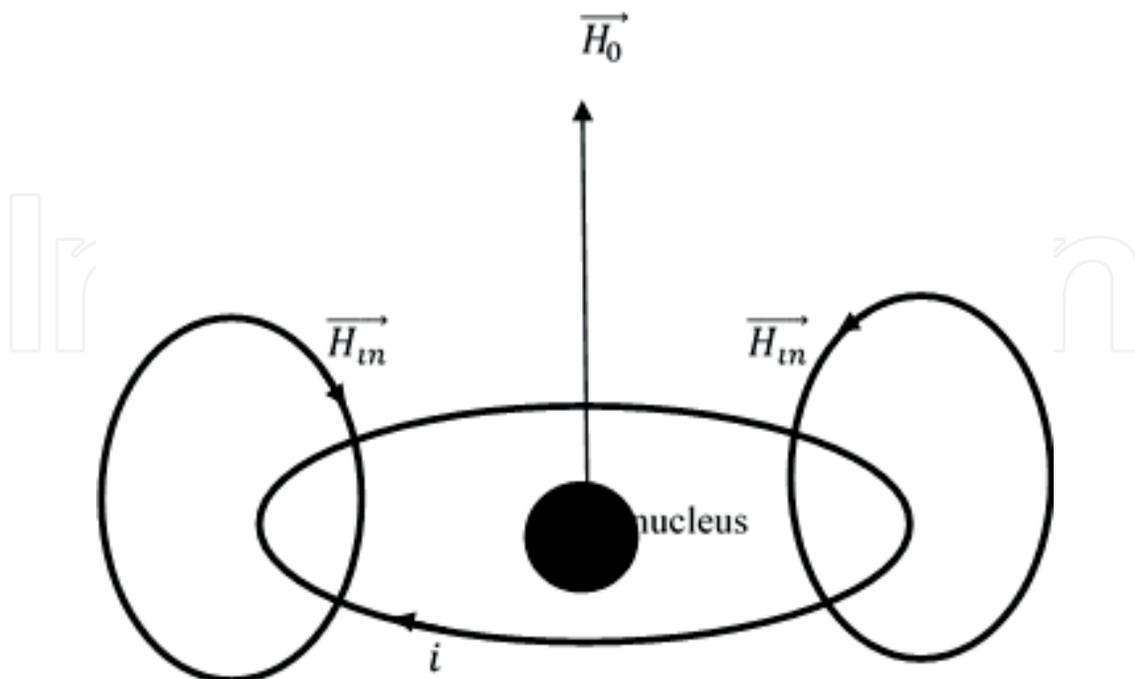


Figure 2. Internal magnetic field and external magnetic field orientation.

magnetic field seen by the nucleus is different from the external magnetic field. This brings about a shift in the resonance frequency of the nucleus. This is called the chemical shift. That is, the electron-nucleus interaction originating from the magnetic field created by moving charges is the chemical shift (**Figure 3**).

Accordingly, the nucleus sees the effective magnetic field given by the formula:

$$\vec{H}_{eff} = \vec{H}_0 - \vec{H}_{in} \quad (18)$$

The internal magnetic field is connected to the external magnetic field (Eq. (18))

$$\vec{H}_{in} = \sigma \vec{H}_0 \quad (19)$$

The internal magnetic field is connected to the external magnetic field by **the diamagnetic shielding coefficient** (σ). In NMR, tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, is generally used as a standard sample for comparison. The chemical shift is shown as δ . Its scale is parts per million (ppm).

$$\delta = (\sigma_T - \sigma_X) \cdot 10^6 \text{ ppm} \quad (20)$$

$$\delta = \left(\frac{\omega_X - \omega_T}{\omega_0} \right) \cdot 10^6 \text{ ppm} \quad (21)$$

$$\delta = \left(\frac{H_X - H_T}{H_0} \right) \cdot 10^6 \text{ ppm} \quad (22)$$

2.1.2. Spin-spin coupling

Contrary to the dipole-dipole interaction, it is a new type of interaction that is not dependent on the orientation of the molecule. It is the indirect spin-spin interaction period that occurs through the electrons that form chemical bonds in the molecule. In other words, the interaction of a nucleus with another nucleus through an electron cloud is a spin-spin coupling. The spin of an electron near the A nucleus is S_A and the spin of an electron near the B nucleus is S_B . In

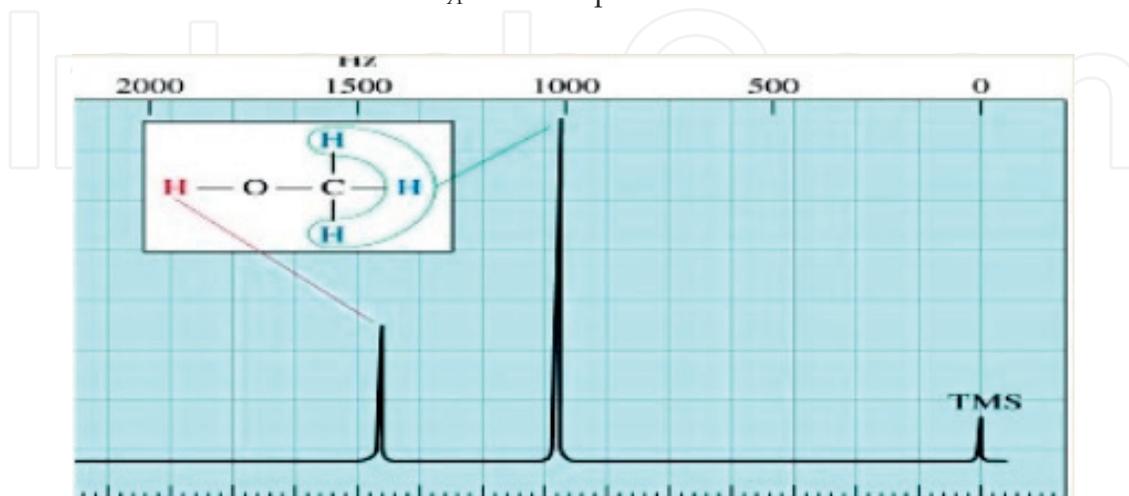


Figure 3. The chemical shift.

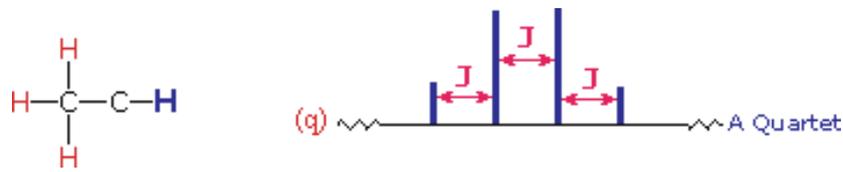


Figure 4. A spin-spin coupling example.

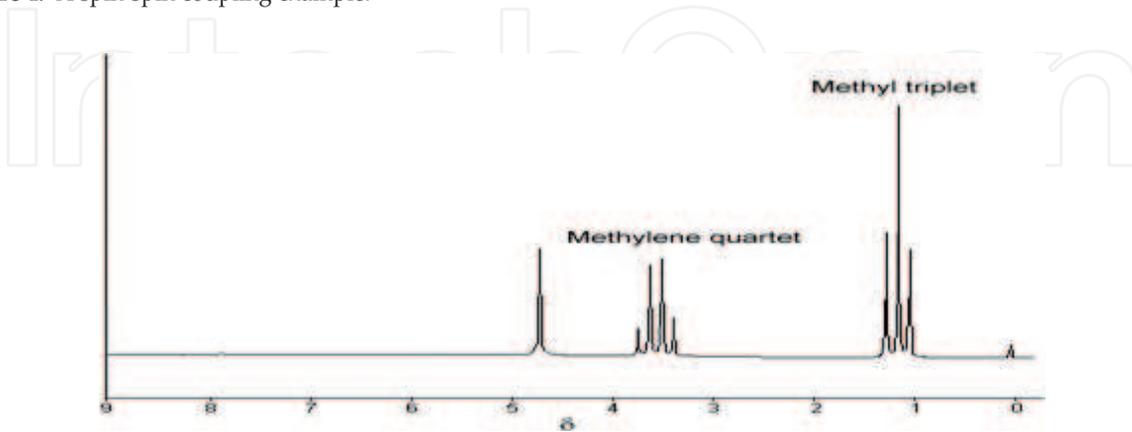


Figure 5. An example of an NMR spectrum.

external magnetic field, the opposite or the same direction of orientation of A and B nuclei with $I = 1/2$ is the spin-spin coupling state of A and B nuclei. The energy of the spin-spin coupling is given as

$$E = \hbar J_{AB} \vec{I}_A \cdot \vec{I}_B \quad (23)$$

J is the spin-spin coupling coefficient.

When a nucleus or nucleus group interacts with n magnetically equivalent nuclei with spin quantum number I , the observed number of splits is $(2nI + 1)$. **Figure 4** shows a spin-spin coupling example and **Figure 5** shows an NMR spectrum example.

2.2. EPR (ESR) spectroscopy

EPR is a magnetic resonance method such as NMR. EPR deals with substance that contains unpaired electrons. These substances are free radicals, triplet excited states, and most transition metal and rare earth species. Among the parameters found in the EPR experiments are the g -factor, the hyperfine structure constant (hf), the nuclear quadrupole coupling constant, and the zero-field splitting constant. However, mostly **the g -factor** and **the hyperfine structure constant** are among the more studied parameters.

For EPR analysis, the sample is placed in a strong magnetic field. The applied electromagnetic radiation is in the microwave area. Due to the interaction between the magnetic moment of the free electron and the external magnetic field, the spin of the electron is directed parallel or antiparallel to the magnetic field. The energy difference between the two orientations gives the resonance condition for EPR.

$$\Delta E = h\nu = g_e\beta H_0 \quad (24)$$

Here, g_e is the free electron g -factor ($g_e = g_s = 2.0023$) and β is Bohr magneton, $\beta = 9.2741 \times 10^{-24}$ J/T. Magnetic dipole moment of the free electron:

$$\vec{\mu}_S = \gamma_S \vec{S} \quad (25)$$

$$\vec{\mu}_S = -g_S \frac{\beta}{\hbar} \vec{S} \quad (26)$$

$$\mu_S = -g_S \left(\frac{e\hbar}{2m_e} \right) \frac{1}{\hbar} \left(\sqrt{S(S+1)}\hbar \right) \quad (27)$$

$$\mu_S = -g_S \beta \sqrt{S(S+1)} \quad (28)$$

where S is the electron spin.

The interaction between the external magnetic field and the magnetic moment of the free electron is given as follows:

$$E = -\vec{\mu}_S \cdot \vec{H}_0 \quad (29)$$

$$E = -\mu_S H_0 \cos\theta \quad (30)$$

where θ is the angle between the dipole and the magnetic field. There are two orientations for a electron spin $1/2$. This indicates the quantum number of magnetic spin, m_S . For $m_S = \pm \frac{1}{2}$ energy takes values $+\frac{1}{2}g_e\beta H_0$ and $-\frac{1}{2}g_e\beta H_0$ as shown in **Figure 6**.

The electron spin resonance transition occurs between two energy levels. The transition between the two energy levels constitutes the resonance condition.

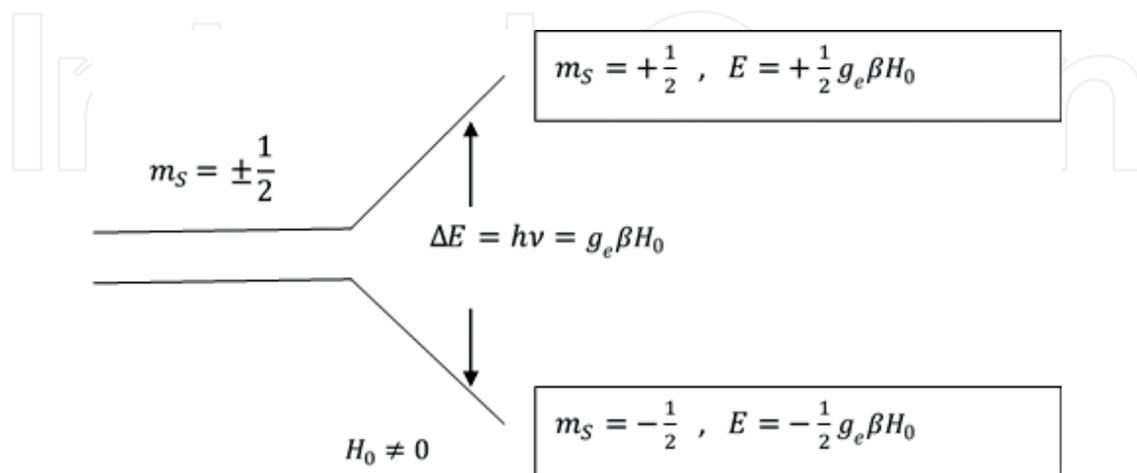


Figure 6. Electron spin resonance transition.

$$\Delta E = h\nu = g_e\beta H_0 \quad (31)$$

is called **the resonance condition for EPR**.

2.2.1. *g-factor*

The unpaired electrons can cause a slight shift in the resonance line due to the internal magnetic field effect. This effect is expressed as a *g*-value shift in the EPR. The largest shifts occur in paramagnetic transition metal ions. The *g*-value parameter in the EPR is identical to the chemical shift parameter in NMR.

To calculate the *g*-value, the values of the microwave frequency and the magnetic field must be known. *g*-value is obtained from the resonance condition.

$$g_e = \frac{h\nu}{\beta H_0} \quad (32)$$

The *g*-value calculation can also be performed using a sample with the known *g*-value as a reference. The reference material for EPR is **diphenylpicrylhydrazyl**. The *g*-value of the standard sample is 2.0036.

$$g = g_{ref} \frac{H_{ref}}{H} \quad (33)$$

2.2.2. *Hyperfine coupling*

The interaction between the unpaired electron and the nucleus is called the hyperfine structure interaction. For hyperfine structure interaction, the nuclear spin value must be different from zero ($I \neq 0$). The hyperfine structure interaction is divided into **the isotropic hyperfine structure interaction (Fermi contact)** and **the anisotropic hyperfine structure interaction (dipole-dipole interaction)**. While the anisotropic interaction is dependent on the orientation of the molecule, the isotropic effect is not dependent on the orientation of the molecule. The symbol of the isotropic hyperfine structure interaction constant is "*a*," whereas the symbol of the anisotropic hyperfine structure interaction constant is "*A*." Usually the Gauss unit is used for hyperfine structure constant. In addition to the Gauss unit, the unit of MHz is also used (1 G \approx 2.8 MHz). The value of *a* is expressed as

$$a = \frac{8\pi}{3} g_e \beta g_n \beta_n |\psi(0)|^2 \quad (34)$$

where $|\psi(0)|^2$ is the probability of finding the electron in the *s*-sphere for the hydrogen atom. For isotropic hyperfine structure interaction, the Hamiltonian is expressed as follows:

$$\mathcal{H} = a \vec{S} \cdot \vec{I} \quad (35)$$

For the anisotropic hyperfine structure interaction, it is expressed as:

$$\mathcal{H} = \vec{S} \cdot \vec{A} \cdot \vec{I} \tag{36}$$

The effective Hamiltonian expression for EPR consists of the sum of the electron Zeeman Hamiltonian and the hyperfine structure interaction Hamiltonian terms:

$$\mathcal{H} = \beta \vec{H} \cdot \vec{g} \cdot \vec{S} + \vec{S} \cdot \vec{A} \cdot \vec{I} \tag{37}$$

where \vec{g} and \vec{A} are in the tensor form. In the resonance case, the average of the diagonal elements of the g-tensor gives the isotropic value of the g-factor.

$$g = \frac{1}{3} \text{Trace}(\vec{g}) \tag{38}$$

In the same way, the average of the diagonal elements of the A-tensor gives isotropic value “a.”

$$a = \frac{1}{3} \text{Trace}(\vec{A}) \tag{39}$$

An example of an EPR spectrum is shown in Figure 7.

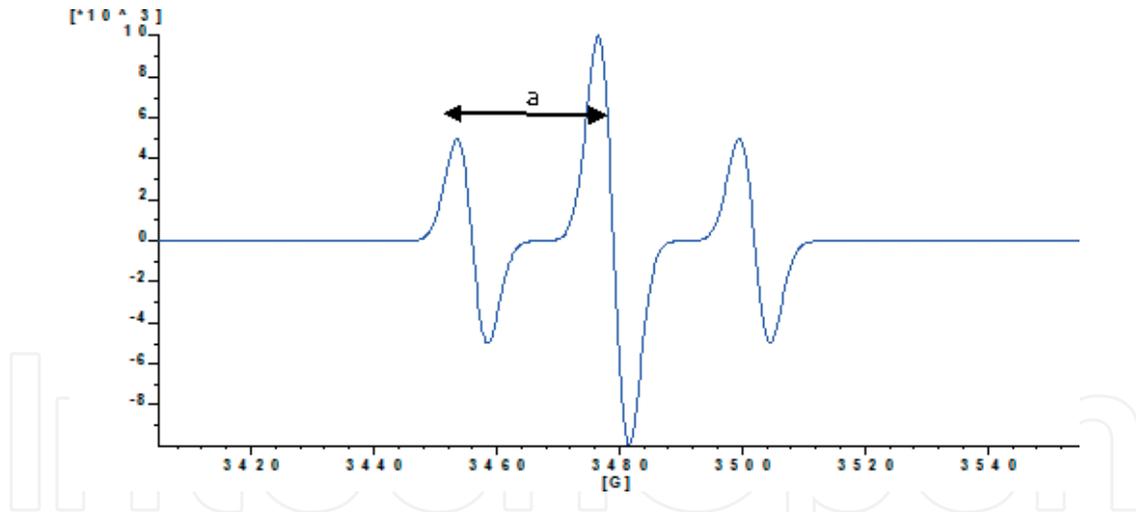


Figure 7. An example of an EPR spectrum and the measurement of the “a” value. If there are n equivalent nuclei, the spectrum shows 2nI + 1 splits. Here, the nuclei with the same hyperfine structure constant as the equivalent nuclei expression are meant. If the nuclear spin is 1/2, the number of lines and the relative intensity are given by the binomial theorem (Figure 8). The line-to-line spacing gives a hyperfine structure constant [4–6].

n° of H	1	1	1	1	1	1	1	1	1
1									
2									
3									
4									
5									

Figure 8. The Pascal triangle.

The difference between the hyperfine structure splitting of two inequivalent protons and the hyperfine structure splitting of two equivalent protons is shown in **Figures 9** and **10**, respectively.

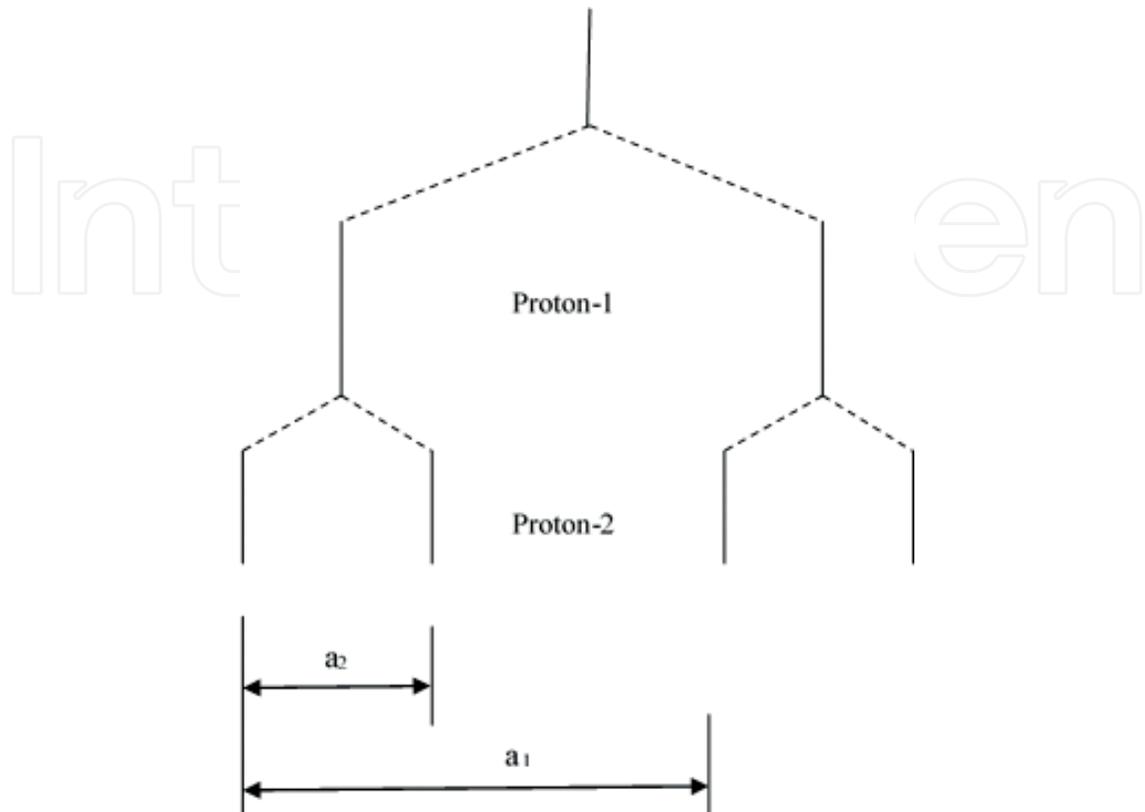


Figure 9. The hyperfine structure splitting of two inequivalent protons ($a_1 \neq a_2$).

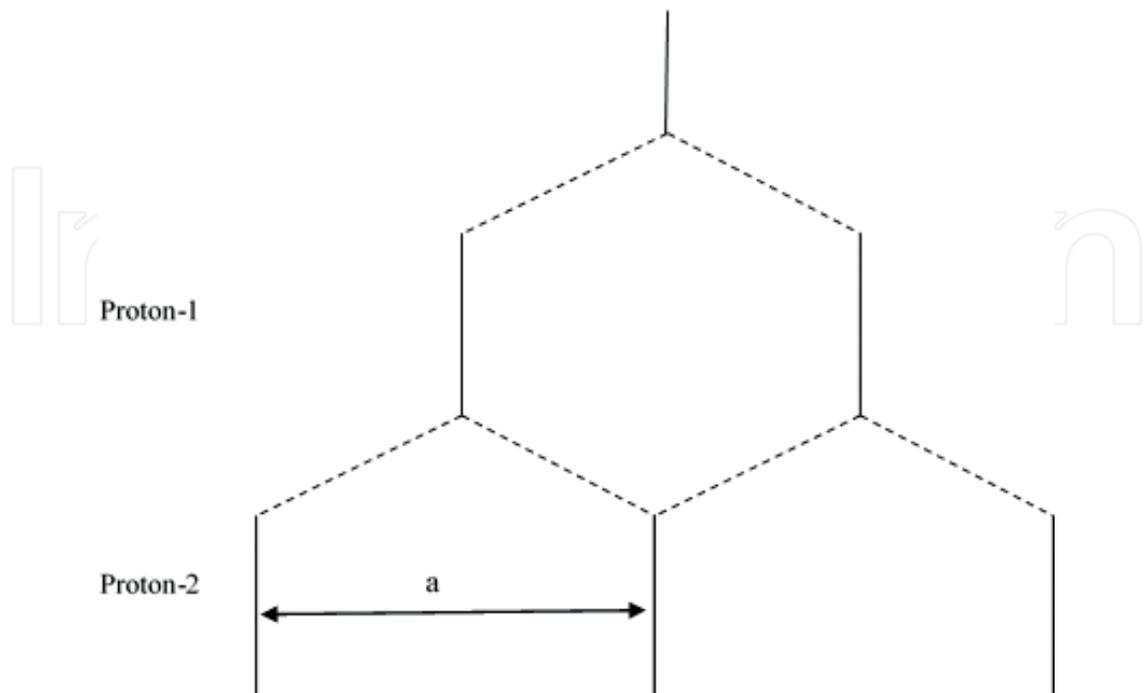


Figure 10. The hyperfine structure splitting of two equivalent protons ($a_1 = a_2$).

The hyperfine structure interaction in the EPR is identical to the spin-spin coupling interaction in NMR.

3. Conclusion

EPR and NMR form the magnetic resonance spectroscopy. EPR and NMR depend on the same basic principles. However, these two experimental methods differ because of the differences in the physical quantities between the electron and the nucleus. These differences stand out in terms of charge, mass, and magnetons (Bohr magneton or nuclear magneton).

Author details

Betul Çalışkan^{1*} and Ali Cengiz Çalışkan²

*Address all correspondence to: bcaliska@gmail.com

1 Department of Physics, Faculty of Arts and Science, Pamukkale University, Kinikli, Denizli, Turkey

2 Department of Chemistry, Faculty of Science, Gazi University, Ankara, Turkey

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