Chapter

Dipolar Interactions: Hyperfine Structure Interaction and Fine Structure Interactions

Betül Çalişkan and Ali Cengiz Çalişkan

Abstract

The interaction between the nuclear spin and the electron spin creates a hyperfine structure. Hyperfine structure interaction occurs in paramagnetic structures with unpaired electrons. Therefore, hyperfine structure interaction is the most important of the fundamental parameters investigated by electron paramagnetic resonance (EPR) spectroscopy. For EPR spectroscopy the two effective Hamiltonian terms are the hyperfine structure interaction and the electronic Zeeman interaction. The hyperfine structure interaction has two types as isotropic and anisotropic hyperfine structure interactions. The zero-field splitting term (electronic quadrupole fine structure), the nuclear Zeeman term, and the nuclear quadrupole interaction term are among the Hamiltonian terms used in EPR. However, their effects are not as much as the term of the hyperfine structure interaction. The zero-field splitting term and the nuclear quadrupole interaction term are the fine structure terms. The interaction of two electron spins create a zero-field splitting, the interaction between the two nucleus spins form the nuclear quadrupole interaction. Hyperfine structure interaction, zero-field interaction, and nuclear quadrupole interaction are subclasses of dipolar interaction. Interaction tensors are available for all three interactions.

Keywords: dipolar interaction hyperfine structure, isotropic hyperfine structure, anisotropic hyperfine structure, the zero-field splitting, the nuclear quadrupole interaction, the electronic Zeeman interaction, the nuclear Zeeman term, EPR

1. Dipolar interactions

Dipolar interaction occurs due to the interaction between the two spins. If one spin becomes an electron spin and the other spin becomes a nucleus spin, this interaction is called a hyperfine structure interaction. If two of the spins are electron spin or both are nucleus spin, this interaction is called fine structure interaction. The dipolar interaction Hamiltonian is expressed as

$$\varkappa = \left[\frac{\overrightarrow{\mu_1}.\overrightarrow{\mu_2}}{r^3} - \frac{3\left(\overrightarrow{\mu_1}.\vec{r}\right)\left(\overrightarrow{\mu_2}.\vec{r}\right)}{r^5}\right] \tag{1}$$

where $\overrightarrow{\mu_1}$ and $\overrightarrow{\mu_2}$ are the magnetic dipole moments for each spin (electron spin or nucleus spin).

1.1 Hyperfine structure interaction

The interaction between the magnetic dipole moment of the nucleus and the magnetic dipole moment of the electron gives the hyperfine structure interaction. There are two types of hyperfine structure interaction. These are isotropic hyperfine interaction and anisotropic hyperfine interaction.

1.1.1 Isotropic hyperfine structure

Isotropic superfine interaction is also known as Fermi contact interaction. The Hamiltonian term of isotropic hyperfine structure interaction is expressed as

$$\varkappa = g_e g_N \beta_e \beta_N \left[\frac{8\pi}{3}\vec{S}.\vec{I}.\delta(r)\right] \tag{2}$$

where g_e = g-value of the electron, g_N = g-value of the nucleus, β_e = Bohr magneton, β_N = nuclear magneton, $\vec{S}$ = electron spin operator, $\vec{I}$ = nuclear spin operator, and $\delta(r)$ = Dirac delta function for the distance between the electron and the nucleus.

In a shorter way, it is expressed as

$$\varkappa = a\vec{S}.\vec{I} \tag{3}$$

The isotropic hyperfine constant is written as

$$a = \frac{8\pi}{3} g_e g_N \beta_e \beta_N \delta(r) \tag{4}$$

Here a is called the isotropic hyperfine constant, $\vec{S}$ is the spin angular momentum of the electron, and $\vec{I}$ is the spin angular momentum of the nucleus.

1.1.2 Anisotropic hyperfine structure

Anisotropic hyperfine interaction is also called dipolar interaction or dipole–dipole interaction. The Hamiltonian term of anisotropic hyperfine structure interaction is expressed as

$$\varkappa = g_e g_N \beta_e \beta_N \left[\frac{3\left(\vec{S}.\vec{r}\right)\left(\vec{I}.\vec{r}\right)}{r^5} - \frac{\vec{S}.\vec{I}}{r^3}\right] \tag{5}$$

More specifically, the expression of the anisotropic hyperfine interaction in the Cartesian coordinate is written as

$$\begin{aligned}\varkappa = g_e g_N \beta_e \beta_N \Bigg[&\frac{(3x^2 - r^2)}{r^5} I_x S_x + \frac{(3y^2 - r^2)}{r^5} I_y S_y + \frac{(3z^2 - r^2)}{r^5} I_z S_z + \frac{3xy}{r^5}\left(I_x S_y + I_y S_x\right) \\ &+ \frac{3yz}{r^5}\left(I_y S_z + I_z S_y\right) + \frac{3xz}{r^5}\left(I_x S_z + I_z S_x\right)\Bigg]\end{aligned} \tag{6}$$

In a shorter way, it is expressed as

$$\varkappa = \vec{S}.\overrightarrow{\overrightarrow{A^0}}.\vec{I} \tag{7}$$

where $\overrightarrow{\overrightarrow{A^0}}$ is called the anisotropic hyperfine coupling tensor. The tensor is expressed in two ways as diagonal elements and non-diagonal elements.
The diagonal elements of the tensor is expressed as

$$A_{ii}^0 = g_e g_N \beta_e \beta_N \left\langle \frac{3i^2 - r^2}{r^5} \right\rangle, i = x, y, z \tag{8}$$

The non-diagonal elements of the tensor is expressed as

$$A_{ij}^0 = g_e g_N \beta_e \beta_N \left\langle \frac{3ij}{r^5} \right\rangle, i, j = x, y, z \tag{9}$$

The sum of the isotropic and anisotropic terms fully expresses the hyperfine structure interaction Hamiltonian and is expressed as

$$\varkappa = a\vec{S}.\vec{I} + \vec{S}.\overrightarrow{\overrightarrow{A^0}}.\vec{I} = \vec{S}.\overrightarrow{\overrightarrow{A}}.\vec{I} \tag{10}$$

where $\overrightarrow{\overrightarrow{A}}$ is the general hyperfine structure tensor.

Figure 1 shows the formation of the hyperfine structure splittings. **Figure 2** shows the formation of an EPR spectrum due to the hyperfine structure splittings.

1.2 Fine structure interaction

The fine structure is seen in two ways. The first is the fine structure interaction between two electron spins. The second is the fine structure interaction between the two nucleus spins. The fine structure interaction between two electron spin is also

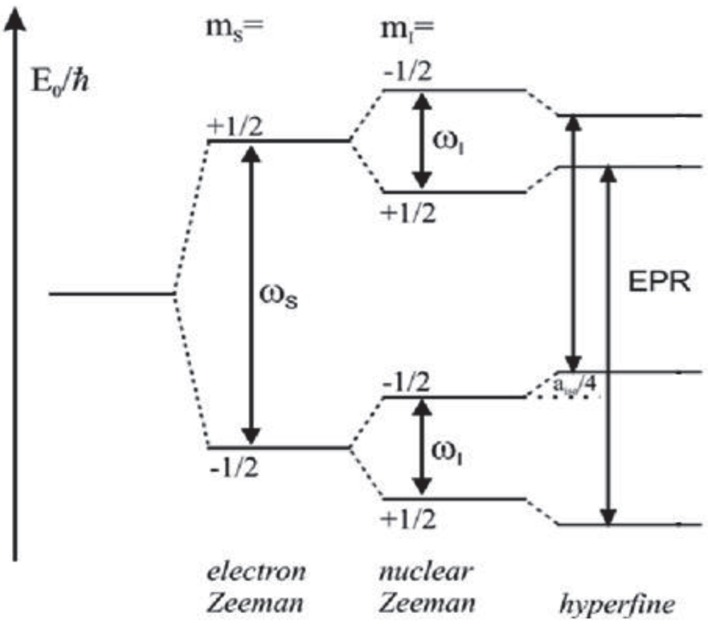


Figure 1.
The formation of the hyperfine structure splittings.

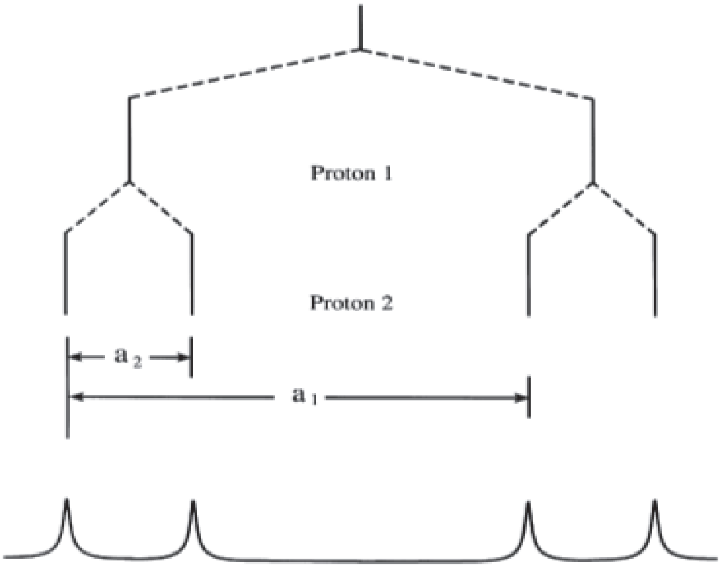


Figure 2.
The formation of an EPR spectrum due to the hyperfine structure splittings.

referred to as zero-field interaction or zero-field splitting. The interaction between two nuclear spin is called nuclear quadrupole interaction.

1.2.1 Zero-field splitting (interaction)

This interaction between two electron spins is the dipolar interaction. When writing Hamiltonian for zero-field interaction, the magnetic dipole moments in Eq. (1) are arranged for two electron spins. In this case, the Hamiltonian of the zero-field splitting is written as

$$\varkappa = g_e{}^2\beta_e{}^2\left[\frac{\overrightarrow{S_1}.\ \overrightarrow{S_2}}{r^3} - \frac{3\left(\overrightarrow{S_1}.\vec{r}\right)\left(\overrightarrow{S_2}.\vec{r}\right)}{r^5}\right] \tag{11}$$

More specifically, the expression of the anisotropic hyperfine interaction in the Cartesian coordinate is written as

$$\begin{aligned}\varkappa = g_e{}^2\beta_e{}^2\Bigg[&\frac{(r^2-3x^2)}{r^5}S_{1x}S_{2x} + \frac{(r^2-3y^2)}{r^5}S_{1y}S_{2y} + \frac{(r^2-3z^2)}{r^5}S_{1z}S_{2z}\\ &-\frac{3xy}{r^5}\left(S_{1x}S_{2y}+S_{1y}S_{2x}\right) - \frac{3yz}{r^5}\left(S_{1y}S_{2z}+S_{1z}S_{2y}\right) - \frac{3xz}{r^5}\left(S_{1z}S_{2x}+S_{1x}S_{2z}\right)\Bigg]\end{aligned} \tag{12}$$

In a shorter way, it is expressed as

$$\varkappa = \overrightarrow{S_1}.\overset{\rightrightarrows}{D}.\overrightarrow{S_2} \tag{13}$$

In general, the Hamiltonian of the zero-field splitting is written as

$$\varkappa = \vec{S}.\overset{\rightrightarrows}{D}.\vec{S} \tag{14}$$

where $\overset{\rightrightarrows}{D}$ is called the zero-field splitting tensor or the spin–spin coupling tensor. The tensor is expressed in two ways as diagonal elements and non-diagonal elements. The diagonal elements of the tensor is expressed as

$$D_{ii} = {g_e}^2{\beta_e}^2\left\langle\frac{r^2 - 3i^2}{r^5}\right\rangle, i = x, y, z \tag{15}$$

The non-diagonal elements of the tensor is expressed as.

$$D_{ij} = {g_e}^2{\beta_e}^2\left\langle\frac{3ij}{r^5}\right\rangle, i, j = x, y, z \tag{16}$$

The zero-field splittings for s = 1/2, s = 1, and s = 3/2 are shown in **Figure 3**.

1.2.2 Nuclear quadrupole interaction

The interaction between the nucleus spins is known as the nuclear quadrupole interaction. The effects of nuclear quadrupole interaction can be observed on the energy levels of the hyperfine structure for a nucleus with $I \geq 1$. The Hamiltonian of the nuclear quadrupole interaction is expressed as

$$\varkappa = \frac{eQ}{6I(2I-1)}\sum_{\alpha,\beta=x,y,z} V_{\alpha\beta}\left\{\frac{3}{2}\left(I_\alpha I_\beta + I_\beta I_\alpha\right) - \delta_{\alpha\beta}I^2\right\} \tag{17}$$

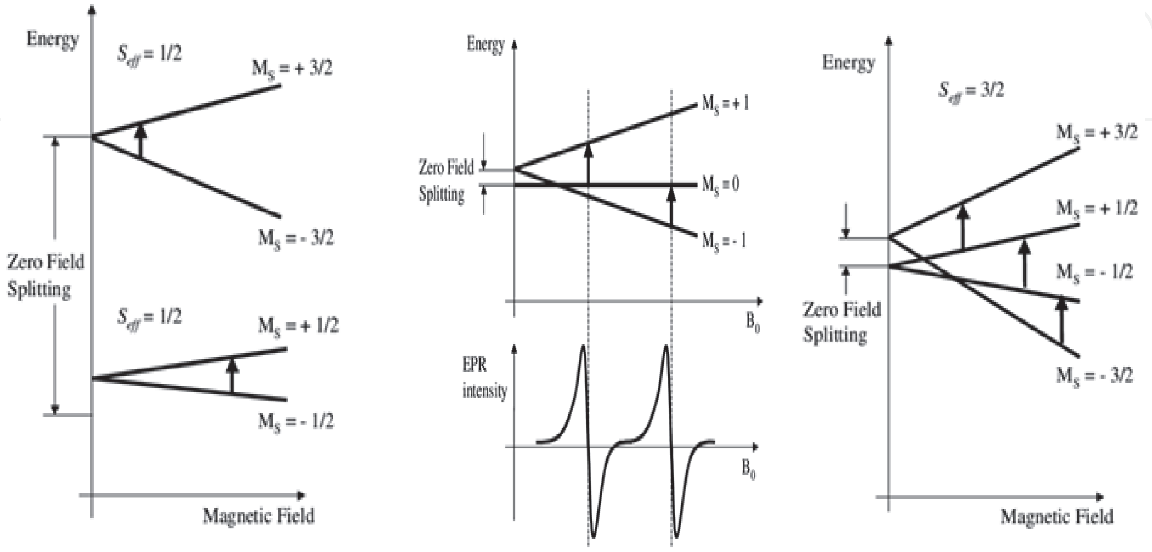
where $V_{\alpha\beta}$ is the component of the field gradient tensor and eQ is the nuclear quadrupole moment, and it is a measure of the deviation of charge distribution from spherical symmetry. The nuclear quadrupole moment is expressed as

$$eQ = \int \rho_N\left(3z^2 - r^2\right)dV \tag{18}$$

where e is the proton charge, ρ_N is the distribution function of the nuclear charge, z is the z-coordinate of the charge element a distance r from the origin. The integral was taken over the volume of the nucleus.

In general, the nuclear quadrupole interaction Hamiltonian is written as

$$\varkappa = \vec{I}\,.\,\overset{\rightarrow}{\vec{P}}\,.\,\vec{I} \tag{19}$$



(a) (b) (c)

Figure 3.
The zero-field splittings for (a) s = 1/2, (b) s = 1, and (c) s = 3/2.

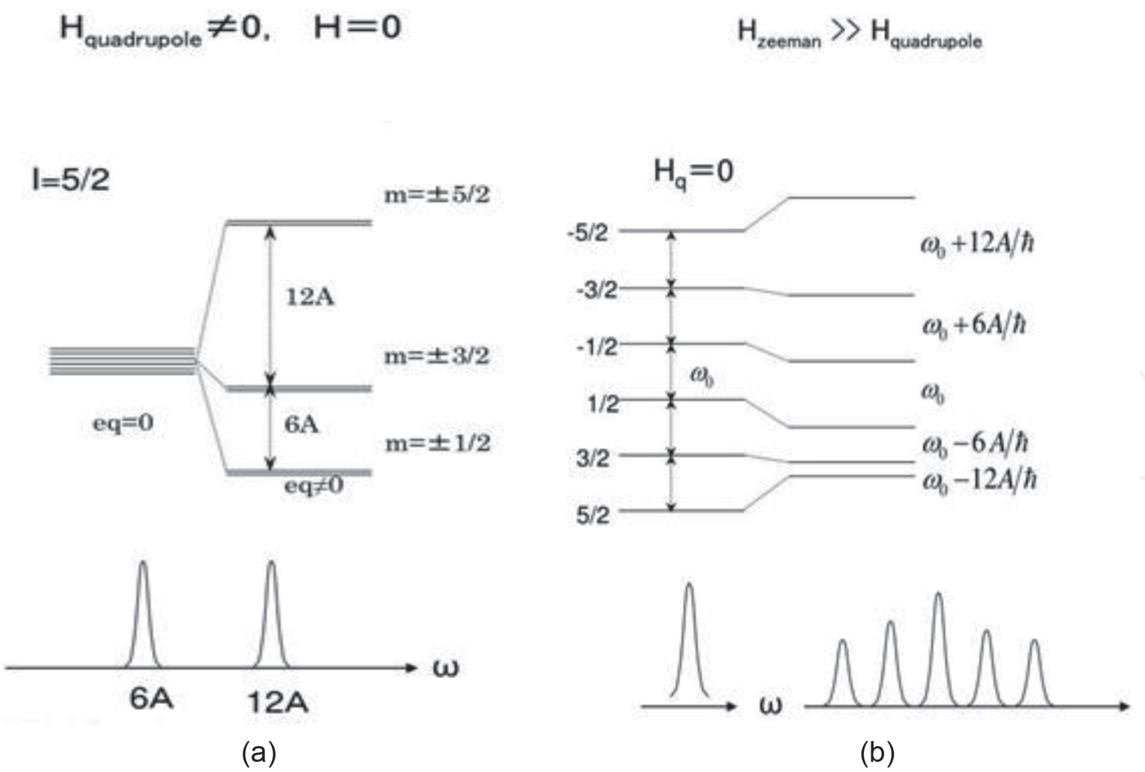


Figure 4.
The nuclear quadrupole splittings for (a) $H_{quadrupole} \neq 0$*,* $H = 0$ *and (b) for* $H_{Zeeman} \gg H_{quadrupole}$*.*

where $\overrightarrow{\overrightarrow{P}}$ is called the nuclear quadrupole coupling tensor.

The nuclear quadrupole splittings are shown in **Figure 4**.

2. Effective Hamiltonian terms in electron paramagnetic resonance spectroscopy

The hyperfine structure Hamiltonian term, electron Zeeman Hamiltonian term, nuclear Zeeman Hamiltonian term, the term of the zero-field splitting, and the term of the nuclear quadrupole interaction are Hamiltonian terms in EPR Spectroscopy. However, in EPR spectroscopy, the electron Zeeman term and the hyperfine structure term are effective Hamiltonian terms. Therefore, the effect of the terms other than the electron Zeeman term and the hyperfine structure term is not taken into account, since the effect is minimal compared to these two terms. The electron Zeeman term and the nuclear Zeeman term have not been mentioned before. Therefore, it will be explained briefly below.

The electron Zeeman interaction occurs as a result of the interaction of the magnetic dipole moment caused by the spin of the electron with the applied magnetic field:

$$\varkappa = -\overrightarrow{\mu_s}.\overrightarrow{H} \tag{20}$$

$$\varkappa = -\left(\gamma_s \overrightarrow{S}\right).\overrightarrow{H} \tag{21}$$

where γ_s is the gyromagnetic ratio of electron spin and is written as.

$$\gamma_s = -\frac{g_s \beta_e}{\hbar} = -g_s \beta_e \ (\text{in the atomic unit system}, \hbar = 1) \tag{22}$$

where g_s is the spectroscopic splitting factor of the electron spin and is written as

$$g_s = 2 \tag{23}$$

$$\varkappa = -\left(-g_s\beta_e\vec{S}\right).\vec{H} \tag{24}$$

$$\varkappa = g_s\beta_e\vec{S}.\vec{H} \tag{25}$$

The nuclear Zeeman interaction occurs as a result of the interaction of the magnetic dipole moment caused by the spin of the nucleus with the applied magnetic field:

$$\varkappa = -\vec{\mu_I}.\vec{H} \tag{26}$$

$$\varkappa = -\left(\gamma_I\vec{I}\right).\vec{H} \tag{27}$$

where γ_I is the nuclear gyromagnetic ratio and is written as.

$$\gamma_I = \frac{g_I\beta_N}{\hbar} = g_I\beta_N \ \left(\text{in the atomic unit system}, \hbar = 1\right) \tag{28}$$

where g_I is the spectroscopic splitting factor of the nucleus spin and is written as

$$g_I = 1 \tag{29}$$

$$\varkappa = -\left(g_I\beta_N\vec{I}\right).\vec{H} \tag{30}$$

$$\varkappa = -g_I\beta_N\vec{I}.\vec{H} \tag{31}$$

The general spin Hamiltonian for EPR spectroscopy can be written as

$$\varkappa = g_s\beta_e\vec{S}.\vec{H} + \vec{S}.\overrightarrow{\vec{A}}.\vec{I} - g_I\beta_N\vec{I}.\overrightarrow{H} + \vec{I}.\overrightarrow{\vec{P}}.\vec{I} + \vec{S}.\overrightarrow{\vec{D}}.\vec{S} \tag{32}$$

The effective spin Hamiltonian for EPR spectroscopy can be written as [1–9].

$$\varkappa = g_s\beta_e\vec{S}.\vec{H} + \vec{S}.\overrightarrow{\vec{A}}.\vec{I} \tag{33}$$

3. Conclusion

Dipolar interaction can be seen in three ways. These are the hyperfine structure interaction, the zero-field splitting interaction, and the nuclear quadrupole interaction. Each interaction involves the interaction of two spins. The interaction between a nucleus spin and an electron spin is mentioned in the hyperfine structure interaction. The interaction of two electron spins is mentioned in the zero-field splitting interaction. The interaction of two nuclear spins is mentioned in the nuclear quadrupole interaction. The last two interactions are also known as fine structure interactions.

The hyperfine structure interaction is an important interaction for EPR spectroscopy. In EPR spectroscopy, the effect of the hyperfine structure interaction is taken into account together with the electron Zeeman interaction [10–24]. In addition, nuclear Zeeman interaction, the zero-field interaction, and the nuclear quadrupole interaction have an effect on EPR spectroscopy. However, their effects are negligible.

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