1. Introduction

Unpaired electrons in atomic or molecular species and atoms possessing unpaired nucleons (odd Z-odd A, even Z-odd A, and odd Z-even A) have magnetic dipole moments. These magnetic moments are associated with spin angular momentum. Magnetic resonance involves the collective macroscopic magnetic properties of these systems and implies correspondence of an external frequency with a natural frequency of the system.

When a system possessing unpaired electrons or nucleons is placed in a static magnetic field, a number of energy levels is differentiated by Zeeman splittings of the quantum states of the magnetic moment. Transitions of the magnetic moment between those levels are induced with an applied radiation at the resonant frequency. Such transitions are indicated by an energy absorption or emission. Detailed information regarding the environment of the atoms and electrons in the material are obtained from the intensities and the frequencies of resonance absorption and emission.

Magnetic resonance of assemblies of unpaired electrons is called either electron paramagnetic resonance (EPR) or electron spin resonance (ESR). The first experimental evidence for macroscopic magnetic resonance transitions between Zeeman levels of bulk CuCl$_2$:2H$_2$O was given by Zavoisky [1]. Cummcer and Halliday [2] employed 2.9 gigahertz (GHz) radiation to examine the magnetic resonance in bulk MnSO$_4$:4H$_2$O. The first hyperfine structure EPR measurements were reported by Penrose [3] who doped magnesium ammonium nitrate hexahydrate with copper (II).

EPR spectroscopy has been used effectively for investigating transition (d electron) ions, inner transition (f electron) ions, stable or unstable mono- and bi-radicals, metal-organic compounds, ground and excited state triple molecules, donors and acceptors in semiconductors, radiation-induced defects, metals and paramagnetic impurities in solids. The general theory and the applications of EPR spectroscopy have been described in detail in review articles and textbooks [4-27].

The first observation of bulk nuclear paramagnetism was made by Lasarev and Schubnikov [28] when measured the static magnetization of solid hydrogen. The first successful nuclear magnetic resonance experiment on bulk material were performed independently by Purcell, Torrey, and Pound [29] and by Boch, Hansen, and Packard [30]. Purcell and his coworkers observed resonance absorption of protons in a hydrocarbon (paraffin) whereas Boch and his colleagues found the proton resonance signal in water.

Nuclear magnetic-resonance spectroscopy (NMR) has been applied to many areas in physics and chemistry which include the elucidation of the intermolecular structure in solids, liquids, and gases, the determination of magnetic fields in single crystals, molecular absorption, diffusion coefficients, and electric field effects. A number of review articles and books treat the general theory, experimental techniques and applications [31-51].

Useful literature surveys of the applications, and advances of ESR and NMR have been given [52]. In addition, symposia to cover special topics and advances in NMR and EPR have been published [53-62]. A continuing series on magnetic resonance has been started [63].

2. Magnetic Properties of Nuclei and Electrons

If it is assumed that a charge $e$, and mass, $m$, are distributed uniformly on a spherical shell which is spinning about a given axis, a magnetic field symmetrical about this axis will be generated by the rotating charge. The charge $e$, rotating at $\omega/2\pi$ revolutions sec$^{-1}$ generates a current $ie\omega/2\pi$. Since the rotating charge behaves as a magnetic dipole whose moment, $\mu$, is given by the product of the current $i$ and the loop cross-sectional area, $\pi r^2$,

$$\mu = i\pi r^2 e \frac{\omega}{2\pi} \text{(omu)}$$

where $c$ represents the velocity of light. The spinning mass generates an angular momentum, $p$, of magnitude $nr \omega$ directed along the axis of rotation. Thus the magnetic moment is colinear and directly proportional to the angular momentum [64]

$$\mu = \frac{e}{2mc}$$

(9.1)

The electron mass is used when unpaired electrons are involved, whereas when unpaired nucleons are present nuclidic masses are required.
The direction of the vectors is determined by the sign of the charge; however, this model does not explain nuclear moments (e.g., neutron). The nuclear model deficiencies suggest a complex structure involving orbital angular momentum and spin angular momentum coupling analogous to that well known for the electron [65].

The proportionality constant between \( \mu \) and \( \mathbf{p} \) is designated \( g \) for the electron and \( g_N \) for nucleon. For free atoms the spectroscopic splitting factor, \( g \), is identical with the Lande \( g \) value; however, this identity does not hold for all magnetic molecules as will be seen later. The nuclear \( g_N \) value or nuclear spectroscopic splitting factor has a characteristic value for each nuclide.

The angular momentum, \( \mathbf{p} \), of any particle or particle system can be expressed in units of \( \hbar \) (Plank's constant divided by \( 2\pi \)). The spin is defined as the largest observable value of the time average of the angular momentum component in a specified direction (\( \mathbf{p} > \mathbf{m}/\hbar = \text{spin} \)). The electron spin is designated by \( S \) whereas the nuclear spin is termed \( I \).

For the nucleus, the general expression for all permitted values of \( \mathbf{p} = m \hbar \), where \( m \) the nuclear magnetic quantum number, has \( (2I + 1) \) values \( I, I - 1, \ldots, 0, I + 1, I \). The lowest lying energy level is characterized by an \( I \) which has a positive integral or half integral value. Then the nuclear magnetic moment is given by

\[
\mu = g_N \frac{e\hbar}{2Mc} \quad I = g_N m_N \chi
\]  

(9.2)

where \( g_N \), the nuclear magneton, has the value 5.05050 \( \times 10^{-11} \) erg gauss\(^{-1} \) for the proton. The term \( g_{p}(e/2M_{c}) \) is often replaced by \( \gamma_{e} \), the magnetic ratios: hence, \( \mu = \gamma_{e} \hbar \). The usual nuclear property tables [31, 32, 34-36, 40, 42, 50] list values of \( \mu \) in nuclear magnetons and \( I \) in units. The magnetic moment of the proton is 2.79277 \( \pm 0.00007 \) nuclear magnetons [66, 67].

Nuclides having spins \( \geq 1 \) do not always have a spherical nuclear charge. The charge asphericity is given by the nuclear electric quadrupole moment, \( Q \), which is defined by the relation

\[
e Q = \int_{s} \rho r^{2}(3 \cos^{2} \theta - 1) \, dr
\]  

(9.3)

where \( \rho \) is the charge density, \( ds \) is a volume element inside the nucleus located a distance \( r \) from the nucleus center and making an angle \( \theta \) with the nuclear spin axis, \( e \) is the protonic charge, and the integration is performed for the state \( I \). Positive \( eQ \) values are observed when the charge distribution is elongated along the spin axis (prolate spheroid) whereas a flattened charge distribution (oblate spheroid) along the spin axis is indicated by a negative \( eQ \) value. The \( Q \) values expressed in barns \( (10^{-24} \text{cm}^{2}) \) vary from 10.2 barns for \( {^{2}}_{7} \text{Li} \) to -1.7 barns for \( {^{18}}_{8} \text{O} \) [68-73].

The electron magnetic moment is related to the spin quantum number \( S \) by \( \mu_{e} = -\gamma_{e} S \hbar \). Instead of using \( \gamma_{e} \), the electron magnetic moment is written in terms of the Bohr magneton \( (\mu_{B} = e\hbar/2M_{c}) \) and the spectroscopic splitting factor, \( g_{e} \);

\[
\mu_{e} = -g_{e} \mu_{B} \frac{S}{I}
\]  

(3.4)

where \( g_{e} = 0.93732 \times 10^{-11} \) erg gauss\(^{-1} \) and \( g_{e} = 2.00232 \) [66]. The \( g \) value is a measure of the contribution of the spin and orbital angular momentum of the electron to the total angular momentum and therefore depends on the electron environment. The spin \( S \) refers to the total spin of all unpaired electrons and has a multiplicity \( 2S + 1 \) with values ranging from \( -S \) to \( S \). The Bohr magneton-proton moment ratio is 657.4181 [6]; hence the Bohr magneton-nuclear moment ratio is 1838.2403.

Static Magnetism. The magnetic induction \( \mathbf{B} \) and the magnetic field \( \mathbf{H} \) are related through classical electromagnetics by

\[
B = H + 4\pi M
\]  

(9.5)

where \( M \), the magnetization, is the macroscopic magnetic moment per unit volume. The static magnetic susceptibility, \( x_{s} \), is defined as the ratio of the magnetization to the magnetic field, \( H_{0} \),

\[
x_{s} = \frac{M}{H_{0}}
\]  

(9.6)

When the susceptibility is positive, paramagnetism results whereas diamagnetism is indicated by a negative susceptibility.

When an unpaired electron is placed in a static magnetic field, the potential interaction energy, \( E_{t} \), is given by

\[
E_{t} = -\mu \cdot \mathbf{H}
\]  

(9.7)

The total angular momentum, \( J \), of the electron is related to its magnetic moment by

\[
\mu = g_{e} \mu_{B} J
\]  

(9.8)

When the applied field direction lies along the \( z \) axis, then the resultant Zeeman energy levels are given by

\[
E_{t} = -g_{e} \mu_{B} H_{0} m_{s}
\]  

(9.9)

where \( m_{s} \), the magnetic quantum number, has \( 2J + 1 \) multiplicity ranging in value from \(-J \) to \( J \). Figure 9.1 shows the energy levels for a \( J = \frac{3}{2} \) system.

The probability \( P_{t} \) that an electron within the assembly has a potential energy \( E_{t} \) at a temperature \( T \) is given by the Boltzmann relation

\[
P_{t} = \text{constant} \left( \frac{\exp(-E_{t})}{kT} \right)
\]  

(9.10)

\[
= \sum_{m_{s} = -J}^{J} \exp\left(-g_{e} \mu_{B} H_{0} m_{s}/kT\right)
\]

Boltzmann statistics are applicable since the magnetization is the property of similar, spatially distinguishable particles [74]. The energy when \( H_{0} \) is
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For protons in water at room temperature \( x_0 = 3 \times 10^{-10} \) egs unit, which is considerably smaller than the diamagnetic susceptibility \((-0.719 \times 10^{-4} \) egs unit) of water.

3. Classical Magnetic Resonance Description

When the spinning charged particle is placed in an external magnetic field, \( H_0 \), the magnetic moment experiences a torque \( J \) tending to align it in the direction of the field. The effect of the torque changes the angular momentum, \( \vec{p} \),

\[
\frac{d\vec{p}}{dt} = \vec{\mu} \times \vec{H}
\]

or

\[
\frac{d\vec{M}}{dt} = \gamma (\vec{M} \times \vec{H})
\]

Since the magnetization \( M \) is defined by \( N \langle \mu \rangle \) where \( \langle \mu \rangle \) is the average moment,

\[
\frac{dM_\parallel}{dt} = \gamma (M_\parallel \times H_0)
\]

This equation (9.17) when written in terms of the vector components takes the form:

\[
\frac{dM_z}{dt} = \gamma (M_z H_0 - M_y H_y)
\]

\[
\frac{dM_y}{dt} = \gamma (M_y H_0 - M_x H_x)
\]

\[
\frac{dM_x}{dt} = 0
\]

The solutions of these equations are

\[
M_z = M_0 \sin \alpha \cos (\gamma H_0 t + \phi)
\]

\[
M_y = -M_0 \sin \alpha \sin (\gamma H_0 t + \phi)
\]

\[
M_x = M_0 \cos \alpha
\]

and represent the magnetization precession about \( H_0 \) with an angular frequency \( \omega = \gamma H_0 \) as shown in Fig. 9.2. A special solution \( M_z = \frac{M_0}{2\pi} \) independent of time exists when \( \omega = 0 \) or \( \phi \). The system has a characteristic frequency \( \omega L / 2\pi \), termed the Larmor frequency, which equals 42.577 megahertz (MHz) for protons and 27.99 gigahertz (GHz) for electrons when each is placed in a 10-kilogauss (kG) field.

This system may be excited at the Larmor frequency, \( \omega L / 2\pi \), with a small oscillating field, \( \vec{H}_0 \), applied perpendicular to \( H_0 \). To first order, only the proper circular polarization component will synchronize with the precession frequency [77]; hence a
linear oscillating field, composed of two counterrotating fields, is suitable. To describe this weak field addition, a coordinate system rotating in the $xy$ plane at a frequency $\omega = \omega_0$ to hold $H_1$ constant is convenient \[78\]. Let $\partial M / \partial t$ represent the time variation of $M$ in the rotating coordinate system. Then

$$\frac{d\vec{M}}{dt} = \frac{\partial \vec{M}}{\partial t} - (\vec{M} \times \vec{\omega}) \tag{9.21}$$

in the laboratory coordinates. If $\vec{\omega}$ is along the $z$ axis (Fig. 9.3), then the components of $\vec{M}$ are

$$\frac{d\vec{M}_z}{dt} = \frac{\partial \vec{M}_z}{\partial t}$$
$$\frac{d\vec{M}_x}{dt} = \frac{\partial \vec{M}_x}{\partial t} + \omega \vec{M}_y$$
$$\frac{d\vec{M}_y}{dt} = \frac{\partial \vec{M}_y}{\partial t} - \omega \vec{M}_x \tag{9.22}$$

Thus the magnetization $M'$ in the rotating system has the behavior

$$\frac{\partial \vec{M}'}{\partial t} = \gamma \left( \vec{M}' \times \left( \vec{\omega} + \frac{\vec{\omega}}{\gamma} \right) \right) \tag{9.23}$$

and the rotating system behaves as a stationary system with an effective magnetic field $[\vec{H} + (\vec{\omega}/\gamma)]$. No effective field exists when $\vec{\omega} = \vec{\omega}_0 = -\gamma \vec{H}$. When $H_1$ is directed along the $z$ axis the effective-magnetic-field components are $H_{1z}' = M_z'\sin \omega t + M_y'\cos \omega t$ and

$$H_1 = H_4 - \left( \frac{\omega}{\gamma} \right)$$

The effective magnetic field is directed at an angle

FIG. 9.2. Magnetization precession in a magnetic field.

FIG. 9.3. Relation of rotating and laboratory coordinate systems.

FIG. 9.4. Effective magnetic field in rotating frame.

$\theta$ to $H_4$ when the $z$ axes are superimposed as shown in Fig. 9.4.

The explicit transformations to the rotating coordinate system for a positive $\gamma$ are

$$H_{1z} = H_1 \cos \omega t - H_4 \sin \omega t$$
$$M_{1z}' = M_z' \cos \omega t + M_y' \sin \omega t$$

and

$$M_{1y}' = -M_x' \sin \omega t + M_y' \cos \omega t \tag{9.24}$$

Then the time-independent equations for the rotating frame are

$$\frac{\partial M_{1z}'}{\partial t} = \gamma M_{1z}' \left( H_4 - \frac{\omega}{\gamma} \right)$$
$$\frac{\partial M_{1y}'}{\partial t} = -\gamma M_{1y}' \left( H_4 - \frac{\omega}{\gamma} \right) + \gamma H_1 M_{1y}'$$
$$\frac{\partial M_{1x}'}{\partial t} = -\gamma H_1 M_{1z}' \tag{9.25}$$
Now assume $t = 0$ that $M'$ is parallel to $H_0$ and that an oscillating field of amplitude $H_1$ is imposed on the system. At a later time $t$, 

$$M'_t = 2M_t \frac{\sin \theta \cos \theta \sin^2 \left( \frac{\gamma H_0 t}{2} \right)}{(\omega_0 - \omega + \gamma H_0 t)^2}$$

For $P = 0$ then $P_{-I} = \sin \frac{\gamma H_0 t}{2}$ since $H_1 = H_0$ (see Fig. 9.4). This result describes magnetic resonance and indicates that the magnetic moment oscillates between the $z$ and $-z$ directions.

At equilibrium, the relative population of each Zeeman level is given by a Boltzmann distribution

$$N_j / N_i = \exp \frac{-g_B H_0 \gamma_j}{kT}$$

For $I = \frac{1}{2}$ system at room temperature in a magnetic field $H_0 = 10$ kG

$$g_B H_0 / kT = 7 X 10^{-4}$$

In the analogous electron case 

$$N_j / N_i = \exp \frac{-g_B H_0 \gamma_j}{kT} = 1 - \exp \frac{-g_B H_0 \gamma_I}{kT}$$

For $I = \frac{1}{2}$ system at room temperature in $H_0$ of 10 kG. Thus, a net energy absorption will occur during the normal magnetic resonance experiment.

### Quantum Mechanical Behavior (79-81)

A quantum mechanical description of magnetic resonance is required to explain coupled spin systems which are not handled by the classical theory. This analysis will be restricted to a nuclear spin of $I = \frac{1}{2}$ and begins with the Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \mathcal{H} \psi$$

where $\psi$ is the wavefunction and $\mathcal{H}$ is an operator representing the energy of the system. $\mathcal{H}$ is time-independent, then

$$\psi(t) = \psi_0 e^{\frac{iE_0}{\hbar} t}$$

where the wave function $\psi_0$ is time-independent, and $\mathcal{H}_0 = \mathcal{H} \psi_0$ with $\mathcal{H}$ is the system energy and $\mathcal{H}_0$ represents the time-independent Hamiltonian.

The Hamiltonian of a nucleus of $I = \frac{1}{2}$ placed in a magnetic field $H_0$ is

$$\mathcal{H}_0 = -\gamma H_0 I_z$$

and if $H_0 \parallel z$, then $\mathcal{H}_0 = -\gamma H_0 I_z$. The energy, $E_{\pm i/2}$ in a magnetic field is given by

$$E_{\pm i/2} = -\gamma H_0 I_\pm$$

for $m = \pm 1/2$. The two states correspond to spins parallel and antiparallel to $H_0$. The Bohr condition gives the natural frequency of the system

$$\omega = \frac{g_B H_0}{\hbar}$$

Application of an oscillating field requires the solution to the time dependent Schrödinger equation which can be treated as the sum of a time-dependent Hamiltonian $\mathcal{H}_0$ and a time-dependent Hamiltonian $\mathcal{H}_1$. The time-independent solution is $\psi_0 = \mathcal{H} \psi_0$. The wave function $\psi(t)$ can be expanded using time-dependent coefficients $a_n(t)$ in conjunction with the stationary wave functions, $\psi_n$,

$$\psi(t) = \sum_n a_n(t) \psi_n e^{\frac{-iE_n}{\hbar} t}$$

Then the time-dependent Schrödinger equation becomes

$$i\hbar \frac{\partial a_n}{\partial t} \psi_n e^{\frac{-iE_n}{\hbar} t} = \sum_n a_n \mathcal{H}_1 \psi_n e^{\frac{-iE_n}{\hbar} t}$$

Multiplying equation (9.35) by $\psi_n$ and integrating gives

$$\frac{\partial a_n}{\partial t} = \frac{1}{i\hbar} \sum_n a_n \mathcal{H}_1 \psi_n e^{\frac{-iE_n}{\hbar} t}$$

Thw time-dependent part of the Hamiltonian is given by

$$\mathcal{H}_1 = -\gamma H_0 \gamma \psi_n e^{\frac{-iE_n}{\hbar} t}$$

where $\gamma_0 = \frac{g_B H_0}{\hbar}$ and $\mathcal{H}_1 = \psi_n (\gamma_0 \mathcal{H}_0) \psi_n$
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ω in the xy plane.

Then \[ \frac{\partial a_{15}}{\partial t} = \frac{1}{2} q_7 H_1 a_{15} \exp \{ i(\omega_0 - \omega) t \} \]

and \[ \frac{\partial a_{15}}{\partial t} = \frac{1}{2} q_7 H_1 a_{15} \exp \{ -i(\omega_0 - \omega) t \} \]

(9.38)

Taking the second derivative, the differential equation involving \( a_{15} \) is obtained,

\[ \frac{\partial^2 a_{15}}{\partial t^2} + i(\omega_0 - \omega) \frac{\partial a_{15}}{\partial t} + \frac{1}{4} \gamma^2 H_1 a_{15} = 0 \]

The solution of this equation is

\[ a_{15} = A \exp \left( i(\omega_0 - \omega) t \right) + B \exp \left( iP_1 t \right) \]

(9.39)

where \( P_1 \) and \( P_3 \) are determined from

\[ -P_1 = (\omega_0 - \omega) P + \frac{1}{2} \gamma^2 H_1 t = 0 \]

yielding

\[ P_1 = -\frac{i}{2}(\omega_0 - \omega) + \frac{1}{2} \left( \omega_0 - \omega \right)^2 + \gamma^2 H_1 t \]

and

\[ P_3 = \frac{1}{2}(\omega_0 - \omega) - \frac{1}{2} \left( \omega_0 - \omega \right)^2 + \gamma^2 H_1 t \]

For the conditions \( t = 0 \) and \( a_{15} = 0 \), \( B = A \); hence

\[ a_{15} = A \exp \left[ \frac{-i(\omega_0 - \omega) t}{2} \right] \sin \left( \gamma H_1 t \right) \]

(9.40)

where

\[ \gamma H_1 = \left( \omega_0 - \omega \right) + \gamma^2 H_1 t \]

The normalization condition

\[ |a_{15}|^2 + |a_{35}|^2 = 1 \]

determines \( A \). Since

\[ |a_{15}|^2 = a_{15}^* a_{15} = \frac{1}{2} \left( \omega_0 - \omega \right)^2 \left( \omega_0 - \omega \right)^2 + \gamma^2 H_1 t \left( \gamma H_1 t \right)^2 \]

then

\[ A = \frac{\gamma H_1}{\left( \omega_0 - \omega \right)^2 + \gamma^2 H_1 t^2} \]

and

\[ a_{15} = \frac{\gamma H_1}{\left( \omega_0 - \omega \right)^2 + \gamma^2 H_1 t^2} \exp \left[ \frac{-i(\omega_0 - \omega) t}{2} \right] \sin \left( \gamma H_1 t \right) \]

(9.41)

Now the total probability, \( P_{13} \), of finding the nucleus in the \( \frac{1}{2} \) level is

\[ |a_{15}|^2 = a_{15}^* a_{15} \]

\[ P_{13} = \frac{\gamma^2 H_1 t \sin \left( \gamma H_1 t \right)}{\left( \omega_0 - \omega \right)^2 + \gamma^2 H_1 t^2} \]

(9.42)

This equation is identical with the classical solution [Eq. (9.27)]. This development can be extended to higher-order spin systems.

The transition probability between two energy states \( m \) and \( n \) is given by \( P_{mn} \alpha \left( \gamma_{11} f_1(t) \right) \) which is nonzero only when \( m = n \pm 1 \); thus the first-order selection rule for nuclear levels is \( \Delta m = \pm 1 \) [38, 79, 81, 82]. The first-order selection rule for many electronic Zeeman transitions is also \( \Delta m = \pm 1 \); however, other effects, e.g., crystal electric field, sufficiently mix the wave functions of the levels, thereby permitting \( \Delta m = \pm 1 \) transitions to occur.

5. Spin Lattices and Spin-Spin Relaxation

Both the classical and quantum mechanical solutions for magnetic resonance predict sharp absorption and emission lines. Actual lines are broadened by either homogeneous or inhomogeneous mechanisms.

Homogeneous broadening mechanisms include:

1. Dipole-dipole interactions between like spins
2. Spin-lattice relaxation
3. Notional narrowing by local field fluctuations
4. Spin interactions with the exciting field
5. Diffusion of excitation through the spin system.

Examples of inhomogeneous broadening mechanisms are:

1. ESR hyperfine interactions
2. Anisotropic broadening
3. Dipolar and electric quadrupolar coupling to unlike spins

The homogeneous broadening mechanisms (1) and (2) act as magnetization damping terms, and their concepts in terms of a nuclear spin system are presented below.

Spin-lattice Relaxation. Nuclear spins interact with their surroundings, but the magnitude of the interaction usually permits distinguishing between the temperature of the spin system and the lattice (bath) temperature. Absorption of energy at resonance tends to equalize the populations of the two levels involved, but heat flow from the spin system to the lattice via lattice vibrations (phonons) restores thermal equilibrium following resonance.

The Boltzmann distribution of a spin system in a magnetic field, \( H_0 \), is characterized by a spin temperature \( T_s \) [83, 84] such that

\[ \frac{N_s}{N_n} = \exp \left( \frac{-E_n - E_s}{kT_s} \right) \]

(9.43)

where \( N_s \) and \( N_n \) are the populations of the nth and mth nuclear Zeeman levels. The magnetization, \( M_n \), at thermal equilibrium as given by Curie's law

\[ M_s = \frac{C H_s}{T_s} \]

(3.44)

where \( C = \frac{N \gamma^2 H^2 (I + 1)}{3k} \) defines the lattice temperature, \( T_s \). When \( T_s \neq T_l \), a semi-equilibrium population distribution occurs where the spin system has internal equilibrium, but it is not in thermal equilibrium with the lattice; hence \( M_s = C H_0 / T_l \).

A positive spin temperature occurs when \( M_s \) is parallel to \( H_0 \) and the level populations decrease with increasing energy. When \( M_s \) is antiparallel to \( H_0 \), the spin temperature is negative, indicating that the populations of the Zeeman levels increase with increasing energy. This situation is possible since antiparallel
magnetization gives the state of greatest internal energy to the spin system. In many instances, the nuclear magnetization growth or decay rate is a single exponential and the time constant, \( T_1 \), is termed the spin-lattice relaxation time. Thus

\[
\frac{dM_z}{dt} = \left[ M_0 - M_L \right] \frac{1}{T_1}
\]

or in terms of the spin temperature

\[
\frac{d}{dt} \left( \frac{1}{T} \right) = \frac{1}{T_1} \left( \frac{1}{T} - \frac{1}{T_0} \right).
\]

(9.45)

The spin-lattice relaxation process can be described by an increase or decrease of a spin system temperature as thermal equilibrium is approached.

Another way of developing the spin-lattice relaxation involves the rate of change of the population difference between two Zeeman levels. Consider a nuclear spin of \( \frac{1}{2} \) in a magnetic field \( H_s \). Let \( w_{\pm} \) represent the probability of \( + \rightarrow - \) transition, and \( N_\pm \) are the spin populations of the \( m_1 = \frac{1}{2} \) and \( m_1 = -\frac{1}{2} \) respectively; then according to the principle of detailed balancing the level populations \( N_+, N_- \) are given by the Boltzmann distribution

\[
N_\pm = \exp \left[ \frac{\Delta E}{kT} \right]
\]

(9.46)

Therefore,

\[
\frac{dN_+}{dt} = 2N_- w_- - 2N_+ w_+ = 2w_+ \left[ N_- \left( 1 + \frac{\gamma H_z}{kT} \right) - N_+ \right]
\]

(9.48)

Then to first order

\[
\frac{\gamma H_z}{kT} \Delta n = \frac{N_+ - N_-}{2} \frac{\gamma H_z}{kT} = \Delta n_0
\]

(9.49)

where \( \Delta n_0 \) is the population difference when thermal equilibrium between the lattice and spin system exists. Now

\[
\frac{d\Delta n}{dt} = 2w_+ (\Delta n_0 - \Delta n)
\]

(9.50)

which has the solution

\[
\Delta n = (\Delta n_0 - n_0) \exp (-2W_+ t)
\]

(9.51)

where \( n_0 \) is the initial value for \( n \). The time constant \( (2W)^{-1} \) is defined as the spin-lattice relaxation time, \( T_1 \). Thermal or longitudinal relaxation have been used interchangeably with spin-lattice relaxation.

The spin-lattice relaxation time can be written in terms of the magnetization by multiplying (9.51) by \( \mu_0 \)

\[
\mu_0 \frac{dM_z}{dt} = 2W_+ \left[ N_- \left( 1 + \frac{\gamma H_z}{kT} \right) - N_+ \right]
\]

(9.52)

Since \( \mu(N_+ - N_-) = \mu n = M_0 \) and then the fundamental equation results,

\[
\frac{dM_z}{dt} = 2W_+ (M_0 - M_L)
\]

(9.53)

where \( T_1 = (2W)^{-1} \) and \( W \) is the transition probability for absorption.

**Spin-Spin Relaxation.** Each magnetic moment interacts with the local magnetic field,

\[
\left[ H_\perp \approx \frac{\mu}{r^3} (3 \cos^2 \theta - 1) \right]
\]

(9.54)

produced by neighboring nuclei. For hydrogen \( (\mu = 1.41 \times 10^{-12} \text{ cm}^2 \text{ G}) \) this local field is 1 gauss for a nearest neighbor distance of 1 A. In the presence of an external magnetic field, \( H_0 \), the magnetic moment of nucleus \( f \) in a solid directed parallel to \( H_0 \) will be constant, if the time-dependent effects produced by precessing neighbor moments \( g \) are ignored. The mean-square local field at the \( f \) nucleus due to the remaining nuclei is

\[
\langle \sum \langle H_{g,I}^2 \rangle \rangle = \sum \langle \mu_{g,I}^2 \rangle \left( 1 - 3 \cos^2 \theta_{g,I} \right)^2
\]

(9.55)

If all \( g \) nuclei are alike but differ from nucleus \( j \)

\[
\langle \mu_{g,I}^2 \rangle = \left( \frac{\gamma f}{\gamma g} \right) \langle I(I+1) \rangle \gamma^2 \theta^2
\]

and

\[
\langle \Delta H_{f}^2 \rangle = \langle (H - H_f)^2 \rangle
\]

(9.56)

when nuclei \( g \) and nucleus \( f \) have the same moment. Then Eq. (9.56) must be multiplied by \( \gamma_f^2 \) since a nucleus \( g \) precessing in the field \( H_0 \) gives a resonant time-dependent field at nucleus \( f \) and vice versa, with the result that simultaneous spin flips, \( \Delta m_f = \pm 1 \) and \( \Delta m_g = \mp 1 \), occur. This moment reorientation (flip-flop) conserves total energy and limits the lifetime of the spin in an energy level, thereby contributing to the line broadening.

The precession frequency for \( \langle H_f \rangle \) from the Larmor equation is

\[
\Delta \omega = \frac{\mu \langle H_f \rangle}{I_h}
\]

If the nuclear moments are precessing in phase at a time \( t \) then the time \( \Delta \omega^{-1} \) is required for the moments to get out of phase. These local field effects limit the phase memory lifetime of a spin state. Hence, the spin-spin or transverse relaxation time is defined as the characteristic time \( T_2 \), required for the precessing spins to lose phase. Since local field variations give a range of absorption frequencies a line width of the order of \( H_{\text{Lineal}} \) is obtained. Usually the line shape function \( g(\omega) \) is defined such that \( T_2 = \tau g(\omega)_{\text{max}} \).

6. **Bloch Phenomenological Equations.**

Bloch [86, 87] introduced a set of phenomenological equations which describe the interaction of the macro-
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The steady-state solutions for these equations are

\[ u = M_x \frac{yH_z T_2 (\omega_s - \omega)}{1 + T_1 (\omega_s - \omega)^2 + yH_z^2 T_1 T_2} \]
\[ v = -M_y \frac{yH_z T_2 (\omega_s - \omega)}{1 + T_1 (\omega_s - \omega)^2 + yH_z^2 T_1 T_2} \]
\[ M_z = M_y \frac{1 + T_1 (\omega_s - \omega)^2 + yH_z^2 T_1 T_2}{1 + T_1 (\omega_s - \omega)^2 + yH_z^2 T_1 T_2} \]
\[ M_y = \frac{1}{2} M_x \frac{yH_z T_2 (\omega_s - \omega)}{1 + T_1 (\omega_s - \omega)^2 + yH_z^2 T_1 T_2} \]
\[ M_x = \frac{1}{2} M_y \frac{yH_z T_2 (\omega_s - \omega)}{1 + T_1 (\omega_s - \omega)^2 + yH_z^2 T_1 T_2} \]

Since both \( M_x \) and \( M_y \) contain a term in phase with \( H_z (2H_z \cos \omega \omega) \) and a term out of phase with \( H_x (2H_z \sin \omega \omega) \), Bloch suggested the use of complex susceptibility, \( \chi = \chi' + i \chi'' \).

Thus

\[ M_x = \chi' (2H_z \cos \omega \omega) + \chi'' (2H_z \sin \omega \omega) \]
\[ M_y = \chi' (2H_z \cos \omega \omega) - \chi'' (2H_z \sin \omega \omega) \]

where

\[ \chi' = \frac{1}{2} \chi_x T_2 (\omega_s - \omega) \]
\[ \chi'' = \frac{1}{2} \chi_x T_2 (\omega_s - \omega) \]

Figure 9.5 shows the dispersion \( \chi' \) and absorption \( \chi'' \) components as functions of the dimensionless product

\[ \frac{\omega_1}{T_1} \]

FIG. 9.5. Absorption (\( \chi'' \)) and dispersion (\( \chi' \)) Lorentzian line shapes.

\[ T_1 (\omega_s - \omega) \] It is the spin temperature equal to the lattice temperature, then \( \chi'' \) can be written in terms of the line function \( g(\omega) \) as

\[ \chi'' = \frac{1}{2} \chi_x \omega_0 g(\omega) \]

Thus

\[ g(\omega) = \frac{2T_1}{1 + T_1 (\omega_s - \omega)^2} \]

which is the Lorentzian line shape characteristic of a damped harmonic oscillator. Line shapes are not always approximated by a Lorentzian-type curve and hence limits the Bloch formalism. The spin-lattice relaxation theory (90) predicts a Lorentzian line shape but the spin-spin relaxation theory (91) indicates a Gaussian line shape.

Homogeneous broadening yields Lorentzian line shapes whereas Gaussian line shapes occur when inhomogeneous broadening is involved. Some mag-
netic resonance line shapes can be fitted by a combination of the Lorentzian and Gaussian functions.

The rate of energy absorption per unit volume, \( A \), is given by

\[
A = \frac{\omega}{2\pi} \int_0^\infty 2H \cos \omega t \left( \frac{d\gamma H}{dt} \right) dt
\]

\[
= \frac{\omega}{2\pi} \int_0^\infty 4H \gamma H \cos \omega t \left( -\gamma H \cos \omega t + \gamma'' H \cos \omega t \right) dt
\]

\[
= 2\omega H_1 \gamma'' H_2 \sin \omega t
\]

(9.65)

This equation indicates that energy absorbed by the spin system from the oscillating field is proportional to the \( \gamma'' \) magnetization component.

The conditions under which the Bloch equations apply [87] are:

1. The effect of all other spins upon a given spin is equivalent to that of a “bath” in thermodynamic equilibrium.
2. The “bath” temperature remains constant.
3. \( \gamma H_1, T, T_1, T_2 \ll \gamma H_0 \) and \( \gamma H_\text{magn.} \).
4. The spin-bath interaction can be expanded in multipoles.
5. When two unpaired spins occur, \( kT \gg \hbar \omega_n \) or for more than two unpaired spins, the quadrupole coupling, \( \epsilon Q \ll \hbar \omega_n \).

The steady-state solution of the Bloch equations assumes that thermal equilibrium exists between the magnetization and the oscillating field. Thus the rate of passage through resonance influences the resulting line shape. The slow-passage condition \( (d/dt)[(H_0 - H)/H] \ll (T_1 T_2)^{-1} \) is required for the steady-state solution and the true line shape is observed when \( dH/dt \ll \gamma (\Delta H)^2 \), where \( \Delta H \) is the line width at half maximum. The adiabatic rapid-passage condition, where \( \gamma H \gg (d/dt)[(H_0 - H)/H] \gg (T_1 T_2)^{-1} \), may be employed to observe weak signals or long relaxation times. Other transient response effects which occur during resonance passage have been described in detail [88, 92-96].

When \( \gamma H_1, T, T_1, T_2 \approx 1 \), the resonance width increases and the resonance height decreases; at sufficiently high amplitudes of \( H_1 \), no resonance absorption is observed because the energy-level populations have been equalized or the resonance is saturated. The term \( 1 + \gamma H_1, T, T_1, T_2 \) is called the saturation factor. The absorption mode \( \gamma'' \) saturates rapidly when \( H_1 \geq (T_1 T_2)^{-1} \), but the dispersion mode requires higher \( H_1 \) values for saturation [97].

7. Magnetic Resonance Spectrometers

The essential components of a magnetic resonance spectrometer are (1) 3 magnet to provide \( H_0 \), (2) a generator at the appropriate frequency to provide \( H_1 \), and (3) a detector to indicate the resonant condition.

Permanent magnets [98, 99], electromagnets [43], and superconducting solenoids [100] have been used in magnetic resonance spectrometers and the particular choice depends on the intended application. High-resolution NMR spectral measurements requiring extremely high homogeneity can be made with any of the above magnets; however, the electromagnet is preferred for ESR measurement where large field variations are desired. Significant signal-strength enhancement can be obtained with higher magnetic fields; therefore, the high field strengths which can be attained with superconducting solenoids may be used for low abundant nuclides or low spin concentrations. To traverse the resonance line, either frequency sweeping [101] or magnetic-field sweeping [43] as a function of time is required.

When signal-to-noise improvement is required e.g., wide lines or low spin concentrations, a small sinusoidal modulation, \( \omega_m \), is applied to the magnetic field [102]; then

\[
H = H_0 + H_m \cos \omega t
\]

For wide NMR lines \( \nu_m \approx 10-10^2 \) hertz whereas \( 10^3-10^4 \) hertz is employed in EPR spectroscopy. In conjunction with magnetic-field modulation, a narrowband amplifier and phase-sensitive detector are used. In this case, the first derivative, \( d\gamma/\gamma_0 \), or \( d\gamma'/dH_0 \), is obtained.

NMR spectrometers can be divided into three major types: the double-coil type, the bridge type, and the marginal oscillator. The double-coil NMR spectrometer [30] shown in Fig. 9.6 is widely used.

![Fig. 9.6. Schematic diagram of the double-coil spectrometer used by Bloch, Hansen, and Packard [30].](image)

In this spectrometer, the sample is placed inside the receiver coil with its axis perpendicular to both the transmitter coil and to the magnetic-field direction. Control of the radio-frequency leakage from the transmitter coil permits selection of either the absorption or dispersion magnetization component. Off resonance, no voltage is induced in the receiver coil, but at resonance the radiation emitted by the excited nuclei returning to lower energy levels induces a voltage \( E_r \) on the turn receiver coil,

\[
E_r = 4\pi A dM_r/dt
\]

where \( A \) is the sample cross section. This voltage change is diode-detected and amplified for oscilloscope or recorder presentation.

In the bridge-type [29] NMR spectrometer a single inductance coil in a tuned \( LC \) circuit serves as both the transmitter and receiver coil. Off resonance, the radio-frequency voltage arriving at the amplifier is balanced out with an r-f bridge. Susceptibility component selection is made by unbalancing the bridge in the proper phase. This bridge unbalance must be significantly larger than the resonance signal for pure
mode selection. At resonance the energy absorbed from the tuned circuit by the sample further unbalances the bridge and gives a voltage identical to that of the double-coil spectrometer. A double-bridge NMR spectrometer [103] providing both amplitude and phase balance minimizes fluctuations associated with large $H_1$ levels and gives better mode selection.

The sample coil of the marginal oscillator spectrometer [101-106] forms part of a tuned circuit, which controls the oscillator frequency by regenerative feedback. In the marginal condition the feedback circuit time constant is sufficient to maintain nearly constant oscillation amplitude; however, at resonance, the long time constant does not permit the generator to follow the energy absorption. The great advantages of this spectrometer are pure absorption mode detection, high sensitivity, and the case of frequency changes.

ESR spectrometers have operated in the frequency range 1 MHz [107, 108] to 158.5 GHz [109]. However, the usual commercial spectrometers operate at X band (8.2-12.4 GHz), K band (18-26.5 GHz), and L band (26.5-40 GHz) or Q band (33-50 GHz) because of increased sensitivity and higher resolution at microwave frequencies.

Two major types [12, 15, 16, 110] of ESR spectrometers, transmission and reflection, are used. In the transmission spectrometer, the sample is placed in the waveguide between the microwave generator (usually a reflex klystron) and the detector. At resonance, the microwave energy absorption is determined with a simple silicon crystal diode or bolometer. A block diagram of a reflection-type ESR spectrometer is shown in Fig. 9.7. Microwaves pass from the stabilized klystron, through arm 1 of the magic tee to a high quality factor reflection cavity in which the sample is located. By mechanically and electronically tuning the frequency of the klystron, its operating mode can be matched to the resonant frequency of the reflection cavity. After being properly tuned to the cavity, the klystron is frequency- or phase-stabilized at the cavity resonant frequency. Off resonance the cavity will have a representative quality factor, $Q$, which is given by

$$Q = \frac{\text{total stored energy}}{\text{power lost per cycle}} = \frac{\omega L}{R}$$

At resonance additional power is lost to the sample resulting in a decreased $Q$. This decrease, $dQ$, is given by

$$dQ = -4\pi\eta Q^2 f$$

where $\eta$ is the filling factor which is the fraction of the coil volume occupied by the sample. Three general types of detectors [111-113] can be used: (1) bolometer, (2) crystal diode, and (3) superheterodyne, in the third arm of the magic tee to detect the resonance. Usually additional amplification is provided before the resonance is recorded.

The experimental methods for measuring relaxation processes are basically the same for both NMR [40, 44, 50, 56, 114, 115] and EPR [116-120]. These methods can be divided into saturation methods and pulse methods. The saturation methods can be divided into three techniques: the direct, the progressive or steady-state saturation, and the polarization reversal. In the direct method [44] $\xi$ is increased to produce saturation and then suddenly it is reduced to a small value. The observed signal recovery follows a single exponential in many cases.

The progressive-saturation technique [44] depends on the saturation factor $(1 - \gamma \frac{\xi}{2} T_1T_2)^{-1}$. At a low $H_1$ value $T_2$ is evaluated from the line width. The signal amplitude as a function of $H_1$ decreases

FIG. 9.7. Block diagram of a typical reflection cavity electron spin resonance spectrometer.
rapidly when \( \gamma H_1 \cdot \mathbf{T}_3 = 1 \). Then \( \mathbf{T}_3 \) can be evaluated from \( \mathbf{T}_2 \) and the value of \( H_1 \) at the sample.

The polarization-reversal method [114-121] employs an adiabatic fast passage through resonance plus a large \( H_1 \) field to reverse \( H_i \), from the \( z \) to \(-z\) direction. As equilibrium the return signal \((-d\mathbf{x}''/\mathbf{d}H)\) will have the opposite sign and the same amplitude as the forward signal \((d\mathbf{x}''/\mathbf{d}H)\). The signal amplitude depends on the time above and below resonance and is proportional to the magnetization at each passage. Thus \( \mathbf{T}_3 \) can be evaluated from the signal amplitudes at two different sweep frequencies or by using unequal time intervals above and below resonance.

Two pulse methods, often referred to as the incoherent and coherent techniques, are used for accurate relaxation-time measurements. Incoherent techniques usually refer to relaxation measurements which invoke magnetization recovery from single high-power \( H_1 \) pulses. Most electron spin relaxation measurements are performed with the saturation recovers method [116, 117] because of experimental difficulties associated with a microwave spin echo spectrometer [119, 120].

The spin echo method [89] is an example of a coherent technique for relaxation measurements. In this method the magnetization is rotated away from the direction of static field with a timed series of pulses of amplitude and duration such that

\[ \gamma \mathbf{H}_1 \cdot \mathbf{d}_\omega = \frac{\pi}{\omega} (90^\circ \text{ pulse}) \]

[89] or a combination of a \( 90^\circ \) pulse and a \( 180^\circ \) pulse [122]. In the latter case a signal (the echo) will occur at time \( 2\tau \) where \( \tau \) is the time interval between pulses. The echo amplitude, \( A \), is given by

\[ A = \exp \left( - \frac{2\tau}{\tau_T} - k \frac{(2\tau)^3}{3} \right) \]

where \( k = 2\gamma^2 \gamma' \gamma'^{\prime} D \) with \( D \) being the diffusion coefficient and \( G \) being the magnetic-field gradient, \( \gamma' \), can be obtained from a \( 180^\circ - 90^\circ \) sequence [122] or a series of \( 90^\circ \) pulses spaced at variable time intervals [89, 123].

8. Characteristics of NMR Spectra

Solids. Nuclear resonances of solids are both homogeneously and inhomogeneously broadened. The major line broadening mechanisms are:

1. Dipole-dipole
2. Electric quadrupole
3. Electron-coupled spin-spin interactions

For \( I = \frac{1}{2} \), the dipole-dipole coupling gives an \( H \), component at each nucleus of \( H_1 \pm H_2 \), where \( H_1 \) is the local magnetic field [Eq. (9.66)] caused by neighboring nuclei. This magnetic [36, 124] intersection has the form

\[ \sum_{j \neq k} \left( \frac{\mathbf{m}_j \cdot \mathbf{m}_k - 3(\mathbf{m}_j \cdot \mathbf{h}_j)(\mathbf{m}_k \cdot \mathbf{h}_k)}{r_{jk}^3} \right) \]  

(9.66)

and predicts that for a single crystal sample having isolated pairs of nuclei two equally intense resonance lines separated by \( 3\gamma \mathbf{H}_1 G \cos^2 \theta - 1 \) occur. This approach also applies to polycrystalline samples although averaging over all \( \theta \) values causes appreciable resonance overlap.

When more complicated grouping of nuclei occur, the NMR line often is unresolved. Useful information can be obtained from this structureless line by the Van Vleck moment method [85] which expresses the internuclear distances in crystals in terms of the second and fourth moment. The general second moment for both like and unlike spins is

\[ <(\Delta H)^2>_{nm} = \frac{3}{4} \gamma'^{\prime} \frac{I(I + 1)}{N} h^2 \sum_{j \neq k} (3 \cos^2 \theta_{ij} - 1)^2 \gamma'^{\prime 2} \]

\[ \frac{1}{3} \gamma'^{\prime 2} \frac{I(I + 1)}{N} \sum_{j \neq k} (3 \cos^2 \theta_{ij} - 1)^2 \gamma'^{\prime 2} \]  

(9.67)

Bond distances in crystals can be evaluated when one bond length of the crystal is unknown [36, 47, 127]. When an axial symmetric electric field gradient \( \partial^2 V / \partial z^2 \) due to nuclear electric quadrupole coupling \( eQ \), exists at the nucleus, the interaction energy is

\[ \frac{eQ}{4(2I - 1) \partial^2 V} \left[ 3m^2 - I(I + 1) \right] \]  

(9.68)

which must be added to the magnetic field nuclear moment energy [69, 73]. This electric field gradient introduces asymmetry in the nuclear Zeeman splittings, thereby allowing observation of \( 2I \) resonances instead of the single resonance characteristic of nuclei on which the quadrupole moment is relaxed.

The effective second moment in solids is reduced by motion of lattice points about an equilibrium position as well as molecular group vibration and rotation [20, 26, 46]. For free rotation a time average of all \( \theta \) values (Eq. (9.67)) over all azimuthal angles is made. This averaging process increases the fourth moment but does not affect the second moment [128]. When the line width is much smaller than the rotation frequency the resonance tails become broadened beyond detection and an effective second-moment decrease results. Motional narrowing induced by increased temperature has been used to study phase transformations, tunneling, and hindered rotational barriers. In addition rapid rotation of solid samples at an axis inclined at \( \cos^{-1} 1/\sqrt{3} \) to \( H_1 \) provides motional narrowing which permits resolution of nonequivalent site resonances [120-131]. The theory of motional narrowing in solids is directly applicable to the random Brownian motion of liquids [103].

Although rapid random motion averages the direct dipole-dipole coupling to zero, the resonance frequencies for identical nuclei located in chemically
nonequivalent sites differ. Differences in the time average magnetic field at the nucleus are caused by

1. Interactions of the nucleus with the electrons of the same atom or molecular species
2. Nuclear interactions with other atoms or molecular species
3. Bulk susceptibility effects

Thus these shielding mechanisms depend on the chemical environment of the nucleus and hence resonance position differences between nonequivalent sites are called chemical shifts [132, 133]. The interaction Hamiltonian for a set of nuclei $\gamma_i$ is given by

$$X_0 = \sum_i \gamma_i h_i d_i$$  \hspace{1cm} (9.69)

Calculations of atomic shielding constants agree favorably with experimental resonance shifts [50, 134], but calculations of shielding constants for molecules require knowledge of the energies and wave functions of all excited electronic states which are not usually available [50]. Hence a relative chemical shift, $\delta$, for molecules is used, where

$$\delta = H_s - H_R$$

\hspace{1cm} x 10^6  \hspace{1cm} (9.70)

$H_s$ is the magnetic field for the sample and $H_R$ is the resonance field for a reference compound. Tables of these relative NMR chemical shifts for many nuclei have been presented [32, 40-42, 50, 59, 63, 133, 136]. Chemical shifts as large as 10^6 parts per million have been measured for diamagnetic cobalt compounds but the usual range is 10-1,000 ppm.

The NMR spectrum of a molecule containing chemically nonequivalent groups, will exhibit multiplet resonance structure caused by indirect spin-spin coupling transmitted between nuclei by the bonding electrons. This indirect coupling may be represented as an additional Hamiltonian involving scalar products Of all pairs of nuclei,

$$X_1 = \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

\hspace{1cm} (9.71)

where $J_{ij}$ is the magnetic-field-independent spin-spin coupling constant. General procedures for the analysis of complex NMR spectra in terms of coupling constants and chemical shifts have been presented [40, 50, 63, 137-140].

Metals. Comparison of the Cu^+ NMR resonances for Cu and CuCl shows the Cu resonance at a higher magnetic field [141, 142]. This shift is proportional to the field strength but the relative shift

$$\frac{H_{\text{metal}} - H_{\text{reference \ sli}}}{H_{\text{reference \ sli}}} = \frac{\Delta H}{H}$$

\hspace{1cm} (the Knight shift) is independent of the field. Furthermore, Knight shifts do not depend on moments of different isotopes. They arise principally from the contact interaction between the nuclear magnetic moment and the spin magnetization field of the s conduction electrons. The shift is proportional to the spin magnetization density [143] or

$$\frac{\Delta H}{H} = \frac{\gamma_e}{3} \chi_{\text{vol}} < |\psi(0)|^2 > \gamma_e$$

\hspace{1cm} (9.72)

where $\chi$ is the volume spin susceptibility and $< |\psi(0)|^2 > \gamma_e$ is the probability density [47] at the nucleus for s conduction electrons of energies $E_e$ averaged over the Fermi surface. Knight-shift measurements for pure solid and liquid metals [45], intermetallics [144], alloys (single-phase, multi-phase, and ordered) [45] and superconductors [145] have provided useful information for characterization [45] of these materials.

Acoustic Wave-Spin Interaction [146-148]

One of the mechanisms responsible for spin-lattice relaxation of nuclear systems is the indirect or Raman interaction process which invokes two high-frequency lattice vibrations. In this process one phonon is absorbed by the spin system and another phonon is emitted after de-exciting the spin system. The frequency difference between these phonons is $\pm 2\gamma_e$ or $2\gamma_e$ where $\gamma_e$ is the Larmor frequency. This inelastic phonon scattering process is highly probable since the frequencies, $\omega$, of most of the thermal phonons are larger than the resonant frequency.

Application of a coherent acoustic phonon beam will modulate one of the internal interactions, thereby exchanging energy with the spin system, e.g., coupling 25.33 MHz acoustic waves to $\text{K}_3\text{MnF}_3$ causes $\Delta H_{\text{L}}$ transitions in the $\text{K}_3\text{MnF}_3$ NMR line [149].

9. Characteristics of EPR Spectra

EPR spectra are described by the spin Hamiltonian [4, 150-152] $X_0$, which is essentially the system energy written in terms of the system parameters. The spin Hamiltonian can be divided into an electronic part $X_e$, and a nuclear part $X_n$. The electronic part $X_e$ is given by

$$X_e = \mu_B \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$

\hspace{1cm} (9.73)

and the nuclear part $X_n$ is given by

$$X_n = \frac{\mathbf{S} \cdot \mathbf{T} \cdot \mathbf{\mathbf{T}} + \mathbf{P} \cdot \mathbf{T} - \mathbf{P} \cdot \mathbf{\mathbf{T}}}{2\hbar \gamma_e} = \mathbf{g} \mu_B \mathbf{H} \cdot \mathbf{T}$$

\hspace{1cm} (9.74)

The first term of $X_n$ describes the Zeeman splitting. The second term of $X_n$ represents both the magnetic-dipole interaction between electrons and second order effects of spin orbit coupling. The first term of $X_n$ is the hyperfine interaction and nuclear quadrupolar coupling is represented by the second term. The other terms of $X_e$ and $X_n$ represent the magnetic-field interactions with the electron and nucleus respectively.

For the case of a single electron with zero orbital angular momentum in a magnetic field,

$$X_n = \mu_B \mathbf{H}$$

\hspace{1cm} (9.75)

with $\mathbf{g}$ being near $g_e$, the spin-only value. Quenching of orbital angular momentum is characteristic of most
organic monoradicals [22-26, 153, 154]. When spin-orbit coupling is present, mixing of higher orbital states occurs, thereby causing an effective anisotropic magnetic moment. For this case the Zeeman interaction is written in terms of its components,

\[ \mathbf{J} = \mu g (g_S S_z + g_I I_z) \]

where \( g_S \) and \( g_I \) are the principal values of the \( g \) tensor and \( S_z \) and \( I_z \) refer to effective spin components. In the simple case of axial symmetry in a crystal only two \( g \) components, \( g_1 = g_2 \) (parallel component) and \( g_2 = g_2 \) (perpendicular component) are required. The \( g \) value in a direction making an angle \( \theta \) with the symmetry axis is

\[ g = (g_1 \cos^2 \theta + g_2 \sin^2 \theta) \]

Where spin-orbit coupling or crystal field effects are present, \( g \) values differing from \( g_0 \) are observed [13, 14, 17-19, 21-27].

Initial splittings of the effective spin levels of ions or biradicals in crystals often occur. The strong asymmetric electric field of the crystal interacting through the spin-orbit coupling is largely responsible for this zero field splitting. The second part of \( \mathbf{J} \), the fine structure term, \( \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \), expresses this interaction.

A twofold degeneracy always exists for a half-integral spin system in a crystal field (Kramer's rule), but for an integral spin system this level degeneracy may be resolved. For an axially symmetric crystal field

\[ \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} = D[S_1^2 - \frac{1}{3} S(S + 1)] \]

and for crystals with lower symmetry

\[ \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} = D[S_1^2 - \frac{1}{3} S(S + 1)] + E(S_1^2 - S_1^2) \]

Thus for \( S = \frac{3}{2} \) the zero field splitting between \( E_{3/2} \) and \( E_{1/2} \) for an axially symmetric crystal and \( 2D(1/2^2 + 3E_1^2) \) for lower symmetry crystals; when \( S = 1 \) the axially symmetric zero field splitting, \( E_{1/2} - E_{1/2} = 0 \), whereas \( E_{1/2} - E_{1/2} = 2E \) and \( E_{1/2} - E_{1/2} = D - E \)

for positive \( D \) and \( E \) values when lower crystal symmetries are involved. In the presence of both an applied magnetic field and a crystal field level crossing occurs and because of wave function mixing \( \Delta M > \pm 1 \) transitions are allowed.

The hyperfine term of \( \mathbf{J} \) can be expressed as

\[ \mathbf{S} \cdot \mathbf{T} \cdot \mathbf{T} = A (S_1^1 + B (I_1 S_1^1 + I_1 S_1^1)) \]

where \( A \) and \( B \) measure the hyperfine splitting parallel and perpendicular to the crystal axis. The effect of the hyperfine interaction is to split the electron resonance line into \( 2I + 1 \) lines which to first order have the same separation. The resonance multiplicity serves to identify the coupling nucleus or nuclei, and information on the electron density in the molecule [26] is obtained from the separation.

The second term of \( \mathbf{J} \) represents the nuclear electric quadrupole hyperfine interaction and to first order, it causes no change in the hyperfine resonance positions. However, it often is responsible for "forbidden" transitions which appear near the central resonance of the EPR spectrum. When small hyperfine interactions occur, the nuclear Zeeman term may give observable direct field effects by which the nuclear spin flips during an electron resonance [155].

Detailed procedural methods for deriving the spin Hamiltonian parameters from observed EPR spectral data have been developed [4, 6, 14-20, 25-27, 156], and the parameter values for various ions and biradicals have been listed [4-27].

10. Masers

Continuous high-gain microwave amplification by stimulated emission of radiation uses at least three unevenly spaced Zeeman levels of a magnetically dilute paramagnetic ion \( S \geq 1 \) at 4.2 K [157]. In the three-level spin system the populations of the upper and lower energy levels are saturated by high-amplitude microwaves of the appropriate energy. When a weak microwave signal of energy equal to the separation between the upper and middle energy levels (or the middle and lower energy levels) is received by the hot spin system transitions from the higher to the lower energy level occur, thereby amplifying the triggering signal. Microwave signals or other energies do not affect the spin system. Since the separation between Zeeman levels is readily varied with the magnetic field, masers covering a wide frequency range are possible provided proper microwave or other saturating pumps are available. When the Zeeman level separation of the pumped levels approximates the zero field splitting, a decrease in the wave function mixing occurs which decreases the transition probability between the levels. Therefore the frequency tunability of the maser crystal is limited. When the spin-lattice interaction between pump levels is strong (short \( T_1 \)), these levels will not saturate and thus will limit the amplifier gain.

Two types of solid-state masers, the regenerative reflection cavity maser and the nonregenerative traveling-wave maser have been developed. In the cavity maser, the energy emitted by the maser crystal increases the microwave field traveling through the structure and thus increases the rate of emission from the crystal. Consequently, the maser gain bandwidth product \( (G B) \) is constant for the cavity maser. The energy emitted by a slow wave element of a traveling-wave maser increases the microwave field traveling through the structure and thus increases the rate of energy emission from succeeding active elements without reacting with the original element. Therefore, the gain of the traveling-wave maser is a function of its length and the \( G B \) is not constant. The noise temperatures for masers are \( \sim 10^{15} \) and electronic gains of \( \sim 10^8 \) dB/in. are observed for traveling-wave masers, whereas \( G B \) products of 40-250 MHz are obtained for cavity masers [158-162].

References


References
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