

# Nuclear Magnetic Resonance: An Introduction

Nuclear magnetic resonance or NMR is one of the most widely used discoveries of Modern Physics. NMR is based on the bulk magnetic properties of materials made up of certain isotopes, most notably, protons ( ${}^1_1\text{H}$ ), but encompassing a wide variety of species including  ${}^{13}\text{C}$ ,  ${}^{19}\text{F}$ , and  ${}^{29}\text{Si}$ . NMR is used to measure magnetic fields with exquisite precision. NMR is used in chemical analysis, oil exploration, and, of course, is the basis of MRI — magnetic resonance imaging.

Nuclear magnetic resonance is not just a bulk effect. The dynamics of a nuclear spin subjected to static and time dependent magnetic fields are described by quantum mechanics, and for the case of a spin 1/2 nucleus such as  ${}^1_1\text{H}$ , can be described by classical electrodynamics. Both of these descriptions are useful and important for a full understanding of NMR. Bulk NMR effects are most apparent in the classical context of magnetic materials.

There are currently two NMR experiments available in this lab. Pulsed NMR, demonstrates the dynamics of nuclear spins and is the basis of many modern NMR based instruments. Continuous wave (CW) NMR is based on the bulk features of a sample of nuclear spins. An NMR imaging experiment is currently under development. This chapter serves as the introduction to all of these experiments.

## Reading

Haken and Wolf, Chapter 20

Principles of Magnetic Resonance, C.P. Slichter, Springer Chapters 1-2

## Spin dynamics

Any charged or composite neutral object with non-zero angular momentum has a magnetic moment.<sup>1</sup> For example the electron, a particle with charge  $q = -e$  and spin angular momentum  $\hbar/2$ , that is the electron has spin  $S = 1/2$ . The electron magnetic moment is given by

$$\vec{\mu}_e = g\mu_B \frac{\vec{S}}{S}. \quad (12.1)$$

where  $\mu_B = e\hbar/2mc$  is the Bohr magneton. For the electron  $g \approx 2$ .

A nucleus is not an elementary particle in the sense that the electron is considered a *point* particle. A nucleus is composite, made up of constituent neutrons and protons, both of which are also composite – they are made up of quarks. The magnetic moment of a nucleus arises due to the magnetic moments of all the constituents AND the motions of the charged constituents (protons). For a nucleus labeled by  $A$ , with angular momentum  $\vec{I}$  the nuclear magnetic moment is

$$\vec{\mu}_A = g_A\mu_N \frac{\vec{I}}{I}. \quad (12.2)$$

Here  $\mu_N = 5 \times 10^{-27}$  J/T is the nuclear magneton. The value of  $I$  is determined in experiments that count the effective number of magnetic substates (labeled by  $m_I$ ) of an atomic or nuclear species, for example the Zeeman Experiment. Since  $m_I$  can take on the values

$$m_I = -I, -I + 1, \dots, I - 1, I \quad (12.3)$$

there are  $2I + 1$  magnetic substates and possible values of  $m_I$ . The magnetic moment and therefore  $g$ -factor is determined in a magnetic resonance experiment.

## Classical electrodynamics of a magnetic moment

A nuclear magnetic moment in a magnetic field, which may be static or time dependent, is subject to a torque  $\vec{\tau} = \hbar \frac{d\vec{I}}{dt}$

$$\vec{\tau} = \hbar \frac{d\vec{I}}{dt} = \vec{\mu} \times \vec{B} \quad (12.4)$$

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<sup>1</sup>Generally the total angular momentum of a system is denoted  $\vec{J}$ . Special symbols are reserved for the electron ( $\vec{S}$ ) and the nucleus of an atom ( $\vec{I}$ ).

and

$$\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu} \times \vec{B} \quad (12.5)$$

where  $\gamma = g_A\mu_N/I\hbar$ . For example, consider the case of a static magnetic field  $B_0$  along the  $z$ -axis. Then this equation becomes

$$\begin{aligned} \frac{d\mu_x}{dt} &= \gamma(\mu_y B_0) \\ \frac{d\mu_y}{dt} &= -\gamma(\mu_x B_0) \\ \frac{d\mu_z}{dt} &= 0 \end{aligned}$$

Taking the time derivative of each equation and substituting, you'll find

$$\begin{aligned} \frac{d^2\mu_x}{dt^2} &= -(\gamma B_0)^2 \mu_x \\ \frac{d^2\mu_y}{dt^2} &= -(\gamma B_0)^2 \mu_y \\ \frac{d}{dt}(\mu_x^2 + \mu_y^2) &= 0 \end{aligned}$$

The solution, for  $\mu_x(0) = \mu_T$ , is

$$\mu_x(t) = \mu_T \cos \omega_0 t \quad (12.6)$$

$$\mu_y(t) = -\mu_T \sin \omega_0 t \quad (12.7)$$

$$\mu_z(t) = \text{const.} \quad (12.8)$$

This describes the precession of the magnetic moment about the  $z$ -axis along a cone, with constant  $\mu_z$ . The angular frequency  $\omega_0 = \gamma B_0$  is called the Larmor frequency.

## The Rotating Frame

A lot of what goes on in NMR can be best understood by transforming the situation to a reference frame that is rotating around the  $z$ -axis so that  $\hat{z}^R = \hat{z}$ , and

$$\hat{x} = \hat{x}^R \cos \Omega t - \hat{y}^R \sin \Omega t$$

$$\hat{y} = \hat{x}^R \sin \Omega t + \hat{y}^R \cos \Omega t$$

To begin with, consider such a frame rotating around the  $z$ -axis at the same angular frequency as the precessing magnetic moment  $\mu$  so that  $\Omega = \omega_0$ . In this frame,  $\mu^R$  is stationary – it's as if  $\vec{\mu} \times \vec{B}^R = 0$ ! In fact we will show this mathematically. In particular, we will see that the physics of  $\mu^R$  can be found by setting  $B_z^R = B_0 - \Omega/\gamma$ .

Also consider an oscillating magnetic field, which in the lab frame is given by  $\vec{B}(t) = B_1 \cos \omega t \hat{x} = B_1/2(e^{i\omega t} + e^{-i\omega t})\hat{\phi}$ , where  $\phi$  is the azimuth angle. The oscillating field is therefore equivalent to two rotating fields, one moving with the rotating frame and one rotating in the opposite direction with relative angular frequency  $-2\omega$ . We generally ignore the effects of this “counter rotating” component, which gives rise to small effects called Bloch-Siegert effects. The field  $B(t)$  transformed to the rotating frame is  $\vec{B}^R \approx \frac{B_1}{2}\hat{x}^R + (B_z - \Omega/\gamma)\hat{z}$ . The time dependence of  $\mu^R$  in the rotating frame is given by

$$\frac{d\vec{\mu}_R}{dt} = \gamma \vec{\mu}_R \times \vec{B}_R \quad (12.9)$$

The mathematics of the rotating frame follows from consideration of a system rotating at the angular frequency  $\vec{\Omega}$ . For example, for rotation about the  $z$ -axis,  $\vec{\Omega} = \Omega \hat{z}$ . In this case, the time dependence of the vector  $\vec{\mu}$  in the lab frame becomes

$$\frac{d\vec{\mu}}{dt} = \frac{d\vec{\mu}^R}{dt} + \vec{\Omega} \times \vec{\mu} \quad (12.10)$$

The term  $\frac{d\vec{\mu}^R}{dt}$  is the time derivative of  $\vec{\mu}$  that would be measured IN THE ROTATING FRAME. A special case arises when  $\frac{d\vec{\mu}_R}{dt} = 0$ , *i.e.* the magnetic moment is STATIC in the rotating frame and thus the time dependence of  $\vec{\mu}$  in the lab frame is

$$\frac{d\vec{\mu}}{dt} = \vec{\Omega} \times \vec{\mu} \quad (12.11)$$

In the rotating frame, the motion of  $\vec{\mu}_R$  is found by combining equations 5 and 10:

$$\frac{d\vec{\mu}_R}{dt} = \gamma \vec{\mu} \times \left( \vec{B} + \frac{\vec{\Omega}}{\gamma} \right) \quad (12.12)$$

You can see that this is similar to equation 5 as long as  $\vec{B}$  is replaced by

$$\vec{B}^R = \vec{B} + \frac{\vec{\Omega}}{\gamma} \quad (12.13)$$

The motion of a spin measured in the rotating frame is thus that of a spin in the presence of an effective field  $\vec{B}^R$ .

Now consider the following: A static field  $\vec{B} = B_0 \hat{z}$  and a resonant oscillating field along the  $x$ -axis in the lab  $\vec{B}(t) = B_1 \cos \omega_0 t$ , where  $\omega_0 = \gamma B_0$ . In the rotating frame,  $B_z^R = 0$ ,  $B_x^R = \frac{B_1}{2}$ , and  $B_y = 0$ . Equation 9 shows that

$$\frac{d\vec{\mu}_x^R}{dt} = 0 \quad (12.14)$$

$$\frac{d\mu_y^R}{dt} = \gamma \mu_x^R * \frac{B_1}{2} \quad (12.15)$$

$$\frac{d\mu_z^R}{dt} = -\gamma \mu_y^R * \frac{B_1}{2} \quad (12.16)$$

with solution

$$\mu_x^R(t) = \text{const.} \quad (12.17)$$

$$\mu_y^R(t) = \mu_T \cos \omega_R t \quad (12.18)$$

$$\mu_z^R(t) = -\mu_T \sin \omega_R t \quad (12.19)$$

The solution shows that  $\vec{\mu}_R$  precesses in a cone about the  $\hat{x}^R$ -axis at the frequency  $\omega_R = \gamma B_1/2$ . This precession is given the name ‘‘Rabi Oscillation,’’ and  $\omega_R$  is called the ‘‘Rabi Frequency.’’

## Nuclear Magnetism

Magnetism in materials is due to an ordered collection of microscopic magnetic dipoles (or magnetic moments), each with a north and south pole. Conventional magnetism arises from the magnetic moments of electrons that are not coupled in spin-up-spin-down pairs in a material. In some cases, most notably oxygen ( $O_2$ ), the atomic electrons in the molecule bind in the configuration of two spins up, called the spin-triplet state. In other cases, for example neutral atoms with odd atomic number  $A$ , the odd number of electrons leaves one or more electrons unpaired in the atoms’ ground state. These systems with net electron spin not equal to zero are called electron paramagnetic. But generally the magnetic moments of atoms or molecules are randomly aligned so that a sample of the material has no net magnetism or magnetic moment. However, for metals such as Fe, Ni, Co, and alloys,

permanent magnetism can arise as the crystalline structure supports an ordering of electron magnetic moments in the bulk material. All permanent magnetic effects exploited in technology, such as magnetic recording media (floppy disks, credit cards), inventory control, refrigerator magnets, solenoids in automobile starters, and a near infinity of other examples, are due to electron magnetism.

Nuclear paramagnetism is the net magnetic moment of the nucleus of an atom and occurs in all isotopes with nuclear spin not equal to zero. Thus all isotopes for which the proton number ( $Z$ ) and/or the neutron number ( $N$ ) is odd have nuclear paramagnetism. The magnetic moment of a paramagnetic nucleus is typically 1000 times less than that of a paramagnetic atom, and nuclear ferromagnetic effects do not exist. As a result, the effects of nuclear magnetism do not affect practical life. However a bulk magnetic moment and magnetization does arise when a sample of nuclear magnets is placed in a magnetic field, and it is this bulk moment that is exploited in NMR and MRI.

The bulk magnetic moment of any sample of atoms with nuclear paramagnetism is

$$\mathcal{M} = P[A]\mu V \quad (12.20)$$

where  $[A]$  is the concentration of atoms,  $PA = C_{\uparrow} - C_{\downarrow}$  is the difference of concentrations of spin-up ( $C_{\uparrow}$ ) and spin-down ( $C_{\downarrow}$ ) nuclear moments, and  $\mu$  is the magnetic moment of each nucleus.  $P$  is called the polarization of the sample, and the concentration  $[A] = C_{\uparrow} + C_{\downarrow}$ . The magnetization concentration or simply magnetization is the magnetic moment per unit volume

$$M = P[A]\mu. \quad (12.21)$$

A nuclear magnetic moment is often expressed in units of the nuclear magneton

$$\mu = g\mu_N \quad (12.22)$$

where

$$\mu_N = \frac{e\hbar}{4\pi m_p} = 5 \times 10^{-27} \text{amp} \cdot \text{m}^2 \quad (12.23)$$

and  $m_p$  is the mass of the proton. A magnetic moment has units of current times area ( $\text{amp}\cdot\text{m}^2 = \text{Joules}/\text{Tesla}$ ). The factors  $g$  for several isotopes are given in table 1.

In applications of magnetic resonance, a static magnetic field,  $\vec{B}_0$ , creates an axis of quantization with “spin-up” and “spin-down” corresponding to

parallel and antiparallel to  $\mathbf{B}_0$ . The static field  $\mathbf{B}_0$  also produces energy level separation for spin 1/2 given by,

$$\Delta E = h\Delta\nu = 2\mu B_0. \quad (12.24)$$

As the magnetic moments and the thermal bath of translational and rotational degrees of freedom exchange energy, an equilibrium is established, and the lower energy state has greater concentration than the higher energy state. The concentration difference is given by

$$\frac{C_\uparrow}{C_\downarrow} = e^{\frac{2\mu B_0}{kT}} \quad (12.25)$$

so that

$$P = \frac{C_\uparrow - C_\downarrow}{C_\uparrow + C_\downarrow} = \frac{e^{\frac{2\mu B_0}{kT}} - 1}{e^{\frac{2\mu B_0}{kT}} + 1} = \frac{e^{\frac{\mu B_0}{kT}} - e^{-\frac{\mu B_0}{kT}}}{e^{\frac{\mu B_0}{kT}} + e^{-\frac{\mu B_0}{kT}}} \quad (12.26)$$

where  $k = 1.38 \times 10^{-23}$  J/°K is Boltzmann's constant. For any reasonable field,  $\frac{\mu B_0}{kT}$  is so small that the exponential can be approximated by

$$e^{\pm \frac{\mu B_0}{kT}} \approx 1 \pm \frac{\mu B_0}{kT} \quad (12.27)$$

so that

$$P \approx \frac{\mu B_0}{kT} \quad (12.28)$$

For the typical magnetic field  $B_0=1.5$  T, and the temperature  $37^\circ$  C = 310° K,  $P \approx 1.1 \times 10^{-5}$ .

The energy level separation

$$\Delta E = h\nu_0 = 2\mu B_0 \quad (12.29)$$

shows that for each magnetic field value, there is a unique characteristic or resonance frequency for the magnetic moments. Energy can be added or extracted from the magnetization of the sample most effectively at this resonant frequency, which corresponds to the splitting of spin-up and spin down. This adding or extracting of energy is the basis of magnetic resonance.

The magnetic resonance frequency for an isolated nuclear magnetic moment is

$$\nu_0 = \frac{2\mu B_0}{h} = \gamma B_0. \quad (12.30)$$

However when the nucleus is imbedded in an atom and the atoms in a sample of material, the actual magnetic field is partially shielded, that is reduced so that the measured frequency is

$$\nu = \nu_0(1 - \alpha) \quad (12.31)$$

where  $\alpha$  is called the chemical shift, which is typically measured in “parts per million” or ppm.

Table 12.1: Magnetic Moments and NMR Frequencies for Several Isotopes.

Isotope	Abundance	$\frac{\mu}{\mu_N}$	$\gamma/2\pi$ (MHz/T)
proton ( $^1\text{H}$ )	99.985%	2.79	42.6
deuteron ( $^2\text{H}$ )	0.015%	0.857	6.53 (spin 1)
$^3\text{He}$	–	-2.13	32.4
$^{13}\text{C}$	1.1%	0.702	10.7
$^{19}\text{F}$	100 %	2.63	40.05
$^{29}\text{Si}$	4.6%	-0.555	8.46
$^{31}\text{P}$	100%	1.13	17.23
$^{129}\text{Xe}$	26.7%	-0.773	11.78

## Quantum Mechanics of NMR

The Hamiltonian for a spin system in a magnetic field is

$$H = -\vec{\mu} \cdot \vec{B} \quad (12.32)$$

where  $\vec{\mu} = \hbar\gamma\vec{I}$  and  $\hbar\gamma = g\mu_N/I$ . Let the  $z$ -axis be along the direction of the static field so that  $\vec{B} = B_0\hat{z}$ . Then

$$H = -\hbar\gamma B_0 I_z \quad (12.33)$$

The eigenfunctions of  $H$  are labeled by  $I$  and  $m_I$ , and the  $2I + 1$  eigenvalues are

$$E(I, m_I) = -\hbar\gamma m_I B_0 \quad (12.34)$$



These span the range from  $-\hbar\gamma IB_0 \dots + \hbar\gamma IB_0$ . The wave function for any state can be expanded in terms of these eigenstates:

$$|\psi\rangle = \sum_{m_I=-I}^{m_I=+I} A(m_I) e^{-im_I\omega_0 t} |I, m_I\rangle \quad \text{where} \quad \sum_{m_I=-I}^{m_I=+I} |A(m_I)|^2 = 1 \quad (12.35)$$

and  $\omega_0 = \gamma B_0$ .

As we have seen, the observable in NMR is a transverse component of magnetization, for example  $\mu_x$ . We can express the operator  $\mu_x = \hbar\gamma I_x$  in terms of the raising and lowering operators  $I_+$  and  $I_-$ :

$$\mu_x = \hbar\gamma \frac{I_+ + I_-}{2} \quad (12.36)$$

We therefore want to find

$$\langle \mu_x \rangle = \frac{\hbar\gamma}{2} (\langle \psi | I_+ | \psi \rangle + \langle \psi | I_- | \psi \rangle) \quad (12.37)$$

The raising and lowering operators produce the following results:

$$I_+ |I, m_I\rangle = \sqrt{(I - m_I)(I + m_I + 1)} |I, m_I + 1\rangle \quad (12.38)$$

$$I_- |I, m_I + 1\rangle = \sqrt{(I + m_I + 1)(I - m_I)} |I, m_I\rangle \quad (12.39)$$

Thus  $\langle \mu_x \rangle$  involves the summing over eigenstates from  $m_I = -I$  to  $m_I = I - 1$ . Each term in the sum involves the product  $e^{i(m_I+1)\omega_0 t} e^{-im_I\omega_0 t}$  (for  $I_+$ ) or  $e^{im_I\omega_0 t} e^{-i(m_I+1)\omega_0 t}$  (for  $I_-$ ) and takes the form

$$e^{-i\omega_0 t} \langle I, m_I + 1 | I_+ | I, m_I \rangle \quad \text{or} \quad e^{+i\omega_0 t} \langle I, m_I | I_- | I, m_I + 1 \rangle \quad (12.40)$$

Thus

$$\langle \mu_x \rangle = g\mu_N \frac{e^{-i\omega_0 t} + e^{+i\omega_0 t}}{2} \sum_{m_I=-I}^{m_I=I-1} \sqrt{(I - m_I)(I + m_I + 1)} \quad (12.41)$$

$$= g\mu_N \cos \omega_0 t \sum_{m_I=-I}^{m_I=I-1} \sqrt{(I - m_I)(I + m_I + 1)} \quad (12.42)$$

So the quantum mechanics of NMR describes the oscillation of the transverse,  $x$ , component of  $\mu$  at the frequency  $\omega_0 = \gamma B_0$ . For example, when  $I = 1/2$  (e.g. for protons)  $\hbar\gamma = 2\mu_p$ , where  $\mu_p = g_p\mu_n$ . For protons,  $\gamma = 4.26$  kHz/G.

## Pulsed NMR

Resonance is the exchange of energy between two systems at or near the characteristic resonant frequency of one or both of them. For example, a child on a swing is a system with a resonant frequency, for small oscillations and no dissipation, given by

$$\nu = \sqrt{g/L} \quad (12.43)$$

where  $L$  is the length of the “pendulum” and  $g=9.8$  m/s<sup>2</sup>. When one adds energy to the system by pushing periodically at the resonant frequency, the energy stored in the oscillations, which is proportional to the oscillation amplitude squared, increases. Any mechanical system for which there is some kind of restoring force always directed toward the equilibrium position is an oscillator and has a resonant frequency for small oscillations. (For large oscillations, more complicated behavior leads to anharmonic motion and multiple normal modes.) A discrete system, such as that described by the quantum mechanics of spin 1/2 nuclear magnetic moments, displays analogous resonant behavior, the resonant frequency given by  $\omega_0 = \gamma B_0$ .

Dissipation, the transfer of oscillation amplitude and energy from the oscillations to heat (*i.e.* translation and rotation of molecules) and similar forms of energy, is important in any real physical system. For magnetic moments, dissipation occurs due to the exchange of energy with the thermal motion of atoms or molecules and due to the energy extracted to produce NMR signals.

A typical, and the simplest, NMR experiment begins with a sample in a magnetic field  $\vec{B}_0 \hat{z}$ . The small excess of spin-up moments (for  $\mu$  positive) along leads to a bulk magnetic moment in the sample  $\mathcal{M}$ . A pulse of oscillating magnetic field at the resonance frequency ( $B_x(t) = B_1 \cos \omega_0 t$ ) is applied along the  $x$ -axis for a duration  $\tau$ . The result is a Rabi oscillation about  $\hat{x}_R$ , the  $x$ -axis in the rotating frame, by an angle  $\theta = \frac{1}{2}\gamma B_1 \tau$  (The pulse duration  $\tau$  should be much longer than  $1/\omega_0$ , but much shorter than the dissipation times described below.) When  $B_1$  and  $\tau$  are chosen so that  $\theta = 90^\circ = \pi/2$  radians, the term used is a pi-over-two pulse. Of course any angle  $\theta$  is possible.

A  $\pi/2$  pulse is special because just after the pulse, at  $t = 0$ ,  $\mathcal{M}$  has no component along the  $z$ -axis. All of the magnetization has been rotated into the transverse plane. Magnetization is generally described by the two components  $M_L$  (along the  $z$ -axis) and  $M_T$  (transverse, that is in the  $x$ - $y$

plane). The total magnetization is  $M = \sqrt{M_L^2 + M_T^2}$ , and  $M_x = M_T \cos \omega t$ .

After a  $\pi/2$  pulse, the magnetization precesses about the  $z$ -axis, at the Larmor frequency  $\omega_0 = \gamma B_0(1-\alpha)$ . The precessing magnetization produces a magnetic field that can be detected with a pick-up coil. In which the voltage is produced by Faraday induction. The voltage induced for each turn of the coil is

$$V(t) = V_0 \sin(\omega_0 t) \quad (12.44)$$

with

$$V_0 = \omega_0 \phi_M = \omega k M_T \quad (12.45)$$

where  $k$  is a constant that depends on the shape and size of the coil and sample, their relative position, and the properties of the electronic circuit that includes the coil.

A typical signal is not constant in amplitude, rather it decays due to a combination of dissipation, random fluctuation of the phases of individual magnetic moments, and spatial dependence of the Larmor frequency due to the unavoidable non-uniformity of  $\mathbf{B}_0$ . In many cases, the decay of the signal amplitude can be described by an exponential with a time constant  $T_2^*$  so that

$$V(t) = V_0 e^{-t/T_2^*} \sin(\omega t). \quad (12.46)$$

However if non-uniformity of  $\mathbf{B}_0$  dominates and diffusion of atoms from one part of the sample to another is not large, the decay is decidedly non-exponential as you can observe in the laboratory.

For exponential decay,  $T_2^*$  can be separated into individual contributions

$$\frac{1}{T_2^*} = \frac{1}{2} \frac{1}{T_1} + \frac{1}{T_2} + \frac{1}{T_2^B} \quad (12.47)$$

Here we introduce the time constant  $T_1$ . This is the time constant for  $M_0$  recovery to thermal equilibrium – the so called saturation recovery time. The contribution to decay of  $M_T$  due to phase fluctuations is  $T_2$ . Both  $T_1$  and  $T_2$  are intrinsic properties of the sample and depend on temperature, density, magnetic impurities, and the nature of the material. These intrinsic properties are used to provide contrast in medical imaging applications.

The time constants  $T_1$  for  $M_0$  and  $T_2$  for  $M_T$  (*i.e.*  $M_x$  and  $M_y$  are incorporated into the equations of motion for the magnetization. These follows from the combination of equations 11.5 with 11.21:

$$\frac{dM_x}{dt} = \gamma(M_y B_z - M_z B_y) - \frac{M_x}{T_2} \quad (12.48)$$

$$\frac{dM_y}{dt} = \gamma(M_z B_x - M_x B_z) - \frac{M_y}{T_2} \quad (12.49)$$

$$\frac{dM_z}{dt} = \gamma(M_x B_y - M_y B_x) - \frac{M_z}{T_1} \quad (12.50)$$

This set of equations is called the Bloch equations and is fundamental to NMR. The Bloch equations have been adapted to the behavior of atomic electric dipoles in the presence of time dependent electric field of light. These “Optical Bloch Equations” provide a similar description including Rabi Oscillations,  $T_1$  and  $T_2$ .

## CW NMR

The resonant exchange of energy between the nuclear spins’ magnetization and the thermal bath, often called the lattice, can also be observed in a continuous wave (CW) measurement. Consider the resonant LCR “tank” circuit tuned to a resonant frequency  $\omega$ . (The term tank circuit comes from the old days of radio and radar. It’s a circuit that stores electromagnetic energy!) A multi-loop NMR coil is the inductor,  $L$ , and  $R$  is the NMR coil resistance. A voltage  $V(t) = V_0 \cos \omega_0 t$ , provided by a separate electronic oscillator, is tuned to the resonant frequency of the circuit.

The circuit can be analyzed by elementary application of Kirchoff’s laws with the complex impedance given by the combination of  $R$  and the reactance of the capacitor and inductor. The current in the circuit is

$$\frac{I(t) = V_0}{Z \cos(\omega_0 t + \phi)} \quad (12.51)$$

where  $Z = \sqrt{R^2 + (X_L - X_C)^2}$  and  $\phi = \arctan \frac{X_L - X_C}{R}$ , and the voltage measured across the capacitor is

$$V_C = I(t) * X_C = V_0 \sin \omega_0 t * \left( \frac{Q}{((\omega - \omega_0)^2 + \gamma^2/4)} \right) \quad (12.52)$$

where the damping factor is  $\gamma = R/L$ . The quality factor of the circuit is  $Q = \omega/\gamma$ .

This analysis assumes that the only source of dissipation is ohmic heating in wires, which have finite resistance  $R$ . Consider, however what happens

when a sample with nuclear magnetization is placed in the core of the inductor windings. If the driving signal  $V(t)$  is far from the nuclear magnetic resonance frequency,  $\gamma B_0$ , there is little effect. If, however, we tune  $B_0$  so that  $\omega_0 \approx \gamma B_0$ , the nuclear magnetization can absorb energy from the tank circuit causing the spins to “flip” from the low energy state to the high energy state. This energy is continuously transferred to the thermal reservoir (or lattice) and appears as heat – it is another form of dissipation of the energy stored in the tank circuit! Thus the damping of the circuit is increased by the presence of the spin and  $\gamma$  and  $Q$  are affected. The observable result is a decrease in  $I(t)$  and the measured  $V_C(t)$ . Actually the change in  $V_C$  is tiny compared to  $V_C$  and can only be detected by *sweeping*  $B_0$  back and forth across the resonance and only once the baseline is compensated. These experimental techniques are used in the lab on CW NMR.

The effects of the nuclear magnetization on the inductance of the tank circuit can be expressed in terms of the magnetic susceptibility of the circuit. The self inductance of a multi-turn coil depends on how effective the flux produced by the current in each winding is coupled (or threaded) through all the other loops of the coil. The coil of an inductor is often wound on core of magnetic material in order to capture the lines of magnetic flux. In this case, the inductance depends on the susceptibility of the magnetic material. Recall the definition of inductance:

$$LI = N\Phi$$

where  $\Phi$  is the magnetic flux through each of  $N$  identical loops. If there is no paramagnetic material present, the flux is that produced by the current in the coil:

$$\Phi = \int_{\text{loop}} \vec{B} \cdot \vec{A}.$$

If magnetic materials are present, the magnetic field  $\vec{B}$  produced by current in the windings has an effect on the magnetization  $\vec{M}$  of the material and the total magnetic flux becomes

$$\Phi = (1 + q\chi) \int_{\text{loop}} \mu_0 \vec{B} \cdot d\vec{A}$$

So that the inductance becomes

$$L = L_0(1 + q\chi)$$

where  $\chi$  is the susceptibility, and  $q$  is called the filling factor, a measure of how much of the flux passes through the sample.

The susceptibility is a measure of the magnetic polarizability of the material - that is the magnetization induced by the magnetic field produced by the current in loops. The magnetic susceptibility also depends on frequency (this is called dispersion), and damping due to the coupling of the magnetic moments to the thermal reservoir. The damping is therefore expressed as an imaginary component of the susceptibility:

$$\chi(\omega) = \chi' - i\chi''.$$

The real part of  $\chi$  ( $\chi'$ ) changes the inductance and the imaginary part ( $\chi''$ ) changes the resistance and therefore the damping in a CW NMR measurement.