The Theory of Nuclear Magnetic Resonance Behind Magnetic Resonance Imaging

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Physics 304
Physics of the Human Body
May 3, 2005
Magnetic resonance imaging (MRI) is a tool utilized in the medical field to produce images of the interior of the human body. It can be used to depict pathological or other physiological alterations of tissues in the body. The main theory behind MRI is based on the principles of nuclear magnetic resonance (NMR). NMR is a technique used by scientists to study the nuclear spin polarization of a material in order to identify information about the sample in question. Initially, NMR was used to produce one-dimensional images but has been adapted to produce both two- and three-dimensional images as well.\textsuperscript{4} Since magnetic resonance imaging relies heavily on the theory of nuclear magnetic resonance, a thorough understanding of what NMR is and how it came about is in order.

Felix Bloch and Edward Mills Purcell demonstrated nuclear magnetic resonance independently in 1946. Both men were jointly awarded the Nobel Prize in 1952 for their discoveries in this field. The drive behind their research was to show that magnetism due to atomic nuclei could be detected in most materials even if the magnetization was weak. Their early work led to the use of NMR to characterize solid-state environments during the period ranging from 1950 to 1970. In the early 1970s, Raymond Damadian demonstrated that the relaxation times of nuclei composing tissues and tumors are different. This led to instituting magnetic resonance as the leading vehicle of detection of diseases.\textsuperscript{2} Since then, magnetic resonance imaging as well as nuclear magnetic resonance research has come a long way, but the basic physics behind NMR has remained the same.

Nuclear magnetic resonance is achieved by placing nuclei in a static magnetic field, $B_0$, thus allowing the spins of the nuclei to align themselves in the direction of the field. A second magnetic field, $B_1$, oscillating at the material’s resonant (or Larmor) frequency of the nuclei allows experimenters to identify certain characteristics pertaining specifically to the material in question. It is this response to the oscillatory field that is utilized in NMR spectroscopy and
MRI. Other things that can be determined in NMR include, but are not limited to, the number of spins of a particular type reflected by the strength of the signal, the chemical shift or the exact gyromagnetic ratio, and the spin lattice (longitudinal) relaxation time, $T_1$, as well as the spin-spin (transverse) relaxation time, $T_2$. To understand this scientific occurrence, it would be best to explain intrinsic nuclear spin and then the idea of polarizing these spins.

The possession of spin angular momentum in a nucleus is what gives rise to the magnetic dipole moment, represented by the formula
\[ \mu = \gamma h I \] (1)
where $\gamma$ is the “gyromagnetic ratio” and $I$ is the spin quantum number. Paired particles, one with a positive spin and one with a negative spin, will have a net spin of 0. Unpaired protons and neutrons will have an overall spin contributing to one half of the spin quantum number, $I$. When $I > 0$, the nucleus will possess this spin angular momentum and, as a result, a magnetic moment, $\mu$. The magnetic moment of the nuclei is what is manipulated in NMR experiments.

If we take, for example, nuclei that possess a spin of 1/2, such as $^1$H (commonly referred to as the proton), we know that the magnetic moment could be an up-spin (+1/2) or a down-spin (-1/2). As it exists naturally, the spins are randomly oriented in such a fashion that approximately half of the spins are up-spins and the rest are down-spins. The premise of nuclear magnetic resonance is to place these randomly oriented nuclei in a static magnetic field, $B_o$, so that the angular momentum of the nuclei aligns itself with the directions of the field. This axis is considered to be the z-direction.

With the spins aligned with the static external field, $B_o$, the energy of the nuclei are no longer the same (before the states were degenerate). The energies differ since one state is aligned with the external field and therefore has a lower energy, but the other’s natural state is opposed to...
the field and is now higher in energy. The energy of the of the magnetic moment when placed in this external field is represented by the formula

$$E = -\mu Bo$$

(2)

To get resonance between states, we apply a radio frequency with the same energy as the difference in energy between these states. This frequency, known as the Larmor or resonant frequency, can be found from the equation

$$\nu = \frac{\Delta E}{h}$$

(3)

therefore the frequency needed to transition between energy levels is given by

$$\nu = \frac{\gamma}{2\pi} B_o$$

(4)

This frequency is what describes the sample that we are looking at since it allows us to select out of the total magnetic susceptibility a particular portion of interest.1,5

When the second magnetic field, $B_1$, is applied, it is applied perpendicularly to the material. This field oscillates at the Larmor frequency, $\nu$, found from the equation above. When applied, this causes the spin to precess at the same frequency and tilt away from the z-direction of the static magnetic field, $M_o$. The spin tilts to a new magnetization, $M_z$. The angle of rotation depends on the length of time the field is applied, represented by $\tau$, and the magnitude of the applied field, $B_1$. This rotation is given by

$$\theta(\tau) = 2\pi \gamma \tau B_1.$$

(5)

It is convenient to consider the frame of reference as rotating about the z-axis at the precession frequency. With the setup, the magnetization vector appears to be stationary in the rotating frame. Therefore the transverse magnetization can be referred to simply as $M_y$ instead of a sinusoidal function in the non-rotating frame. This component of magnetization can be detected
by measuring the current induced in the solenoid providing the oscillatory field perpendicular to
the material.\textsuperscript{2}

After placing a material in the static magnetic field, $B_o$, the $B_1$ field can either be pulsed
with a certain delay or continuously agitated. The latter, known as continuous wave pulsing, is
what is normally applied in NMR experimentation. This creates a buildup of polarization instead
of allowing the spins to immediately begin relaxing as does delayed pulsing.\textsuperscript{3} First an
explanation of delayed pulsed and relaxation times is needed before explaining various ways to
increase polarization.

When delay pulsing the perpendicular, oscillatory field, $B_1$, at resonance, three
phenomena can be specifically observed by the experimenter. First, the transverse magnetization
that was employed by the pulsed field $B_1$ decays and the nuclei return to equilibrium, in the
direction of $B_o$. Decaying means that $\theta(\tau)$ goes to zero. The spin lattice relaxation time, known
as $T_1$, characterizes $M_z$’s return to its equilibrium value of $M_o$. This decay process back to
equilibrium is demonstrated through the equation

$$M_z = M_o ( 1 - e^{-\tau/T_1} ). \tag{6}$$

The second phenomenon that occurs after applying both fields is the dephasing of the net
magnetization, $M_y$, into the xy plane away from the y axis. The dephasing occurs because each
spin packet experiences a slightly different field and rotates at its own frequency. As more time
passes, a greater phase difference occurs. Therefore, the transverse magnetization fans out from
its alignment with $B_1$. $T_2^*$ describes the transverse magnetization’s return to equilibrium and can
be determined by the formula

$$M_y = M_o e^{-\tau/T_2^*}. \tag{7}$$

Finally, the spin-spin relaxation time, or $T_2$, is the time it takes for the precessing
magnetization around the static field to decay. This decay is independent of $T_1$ and may be
enhanced by such processes as dipole-dipole coupling between spins. $T_2$ can be found using the equation

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma^* \Delta B_o$$

The relaxations times, $T_1$, $T_2$, and $T_2^*$, vary from material to material. This is what makes NMR so useful. NMR can be utilized to find these decay times, and from there, materials can be identified. Things that stay constant regardless of the sample is that $T_2$ is always less than or equal to $T_1$, and relaxation times get longer as $B_o$ is increased.$^1,^5$

Now that it is understood what intrinsic nuclear spin is and how it can be manipulated by the two magnetic fields, the explanation of polarization can be embarked upon. As stated before, placing nuclei in the static magnetic field, $B_o$, allows unpaired spins of the nuclei to align themselves in the direction of the field. How many spins align depends on the strength of the field, the temperature, and the spins themselves. The difference between spins aligned in the direction of the field and spins anti-aligned with the field in the scope of the total number of spins gives rise to the polarization of the material and is represented by the equation

$$P = \frac{N^\uparrow - N^\downarrow}{N^\uparrow + N^\downarrow}$$

$N^\uparrow$ denotes the number of spins aligned with the external magnetic field while $N^\downarrow$ denotes the number of spins not aligned with the field. A positive polarization means that there are more spins aligned with the field, as is obvious from the equation above. The reverse is true for a negative polarization.$^3$

The strength of the field, the temperature of the system, and the magnetic moment of the spins will all affect the polarization of the material. Intrinsically, a higher magnetic moment leads to a higher natural polarization. Polarization of the material also increases with an increase
of the external magnetic field and/or a decrease in temperature. The natural resting polarization of a material located in a constant magnetic field at a constant temperature (without the second field, $B_1$) is known as thermal equilibrium (TE) polarization. These values can be related with the polarization equation

$$P = \tanh \left( \frac{\mu B_o}{kT} \right)$$

for the polarization of spin $\frac{1}{2}$ particles. In this equation, $\mu$ is the magnetic moment, $B_o$ is the value of the magnetic field, $k$ is Boltzmann’s constant, and $T$ is the lattice temperature. It is known that at very low temperatures such as ~1.5K and a magnetic field of 5 Tesla, electron polarization is greater than 95% and proton polarization is ~0.5%.

Once the oscillating field $B_1$ is applied, the natural polarization of the material can increase only so far. Doping is a method for increasing the overall polarization of the material. One method of polarization involving doping is known as dynamic nuclear polarization, or DNP. Materials are doped either chemically or through irradiation, and while chemical doping is a decent method, doping through irradiation is more prevalent. Once doped, there are extra electrons to either align themselves or anti-align themselves with the material’s intrinsic spins. Thus there are four probable states: down-up ($\downarrow\uparrow$), up-up ($\uparrow\uparrow$), down-down ($\downarrow\downarrow$), or up-down ($\uparrow\downarrow$) (taking the first spin to be the proton and the second to be the electron). The energy of these states denotes the probability of being in each state, with the more probable state being the lower energy state. These states are listed in order of decreasing energy, making the last state the most probable one. Forced transitions between states is the underlying theory of DNP, and if these four were the actual states of the system, there would be forbidden transitions between the states ($\uparrow\downarrow$) to ($\downarrow\uparrow$) and ($\downarrow\downarrow$) to ($\uparrow\uparrow$). Due to other factors, the actual states of the system are a combination of states, still totaling four states but these forbidden transitions now occur. Thus
there are six transitions: two nuclear spin flip (NMR transitions) where the proton flips, two electron spin flips (EPR transitions) and the two previously forbidden transitions. Figure 1 below quantitatively depicts these transitions.³

![Diagram](image)

**Figure 1 – This diagram shows the transitions between states involved in polarization enhancement through Dynamic Nuclear Polarization (DNP).³**

Once doped and placed in a constant magnetic field and temperature, the material’s spins are in their natural states. The material is then hit with microwaves at a frequency (adding energy to the system) represented by the equation below

\[ \nu = \frac{(\mu_p + \mu_e)B}{h} \]  \hspace{1cm} (11)

These added frequencies cause the transitions among the states to take place. When this happens, both the spin of the protons and the spin of the electrons are flipped. The relaxation time of the electron spin is much, much less than the proton, so the electron transitions back to a state of lower energy in order to be used once again to flip another proton. This act is repeated
many times, causing more and more protons to align, thus causing the polarization of the material to increase. The polarity of the polarization (positive or negative) is the result of the microwave frequency added to the system as shown by the equation above. 

When it comes to actually measuring this value of polarization, continuous wave nuclear magnetic resonance is utilized. Continuous wave can be employed by either applying a constant frequency while the magnetic field is varied or by keeping the magnetic field constant while the frequency is varied. As explained above, microwaves at a frequency represented by Equation 3 are applied. Thus, the material is situated in a magnetic field of known strength. To measure the polarization of this material, a series resonant LCR circuit is employed, where the inductor (L) is located within or surrounding the material. The circuit is tuned so that it resonates with the same frequency as the resonant or Larmor frequency of the nuclei being. The circuit then spans over a window of frequencies. At resonance, there is a voltage peak which is known as the Q curve. This peak corresponds to the nuclei being polarized, because the peak in power results from certain nuclei either 1) aligning themselves with the field and giving off energy to the system or 2) anti-aligning themselves with the field which requires energy from the system. The Q curve is then subtracted from the overall signal of the material, and resulting curve can be used to determine the polarization of the material. The area under this curve is linearly related to the polarization. Using a calibration constant determined from the earlier temperature equilibrium (TE) polarization, we are able to convert the area under the curve into the polarization value. 

An example of a proton signal can be seen in Figure 2 below.
In conclusion, nuclear magnetic resonance is achieved by placing a sample material in a static magnetic field and allowing the intrinsic nuclear spins of the material to align themselves with the field. A second oscillating field is then applied to this material. Through doping and continuous wave application, these nuclear spins are polarized. The resulting polarization passes as current though an NMR coil, and this current shows up as a peak whose area linearly relates to the polarization of the spins. These basic principles compose the underlying theory of nuclear magnetic resonance that allows magnetic resonance imaging to take place. An understanding of NMR is important, because improvements in NMR research will be directly reflected in the usage in MRI’s. Research underway includes the search for higher polarizable materials that are safe for humans, so that the resolution of MRI’s can be vastly improved. While the physics of NMR may remain unchanged, there is no limit to where nuclear magnetic resonance and magnetic resonance imaging can go.
References


