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Drawing Single NMR Spins and Understanding Relaxation

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Abstract

How should we draw vectors to represent individual nuclear spins? Vectors in 3D space are merely a way of understanding the mathematics of quantum mechanics, which provides the “true” description of a single spin- $\frac{1}{2}$ nucleus. They are a useful aid to understanding, but there is no single “correct” vector representation, and the different vector models that are used have advantages and disadvantages. Here, we discuss the 2 standard vector models for a nuclear magnetic resonance spin: the up/down or *alignment* model and the *2-cone* model, and we show how they relate to quantum mechanics. We show why both of these models are limited and discuss a third model, the *uniform* model, in which individual spins can be in any orientation. We demonstrate how the uniform model presents a clear and logically coherent description for spins: at equilibrium; following a 90° pulse; and during the subsequent relaxation back to equilibrium. The uniform model is fully consistent with quantum mechanics and leads to an understanding of coherence and relaxation that cannot be obtained from the other 2 models. We suggest that the uniform model is more helpful than the other 2 for most purposes.

Keywords

NMR, single spin, vector model, relaxation, equilibrium, quantum mechanics, alignment, 2 cones

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Nuclear magnetic resonance (NMR) experiments on spin- $\frac{1}{2}$ nuclei with weak scalar coupling can be understood remarkably well using product operators,^{1,2} which provide an explanation of most modern NMR experiments using simple mathematics, and in almost all cases can be represented using simple vector diagrams. There are, however, 2 places where product operators are less useful. One is for thinking about individual nuclear spins and the other is in understanding relaxation. It is not often that we need to think about individual spins, though it is unfortunate that the most common occasion is in introductory NMR courses, which are precisely the places where care needs to be taken to use the most helpful and appropriate models. However, relaxation crops up at all levels, and although the conventional description of relaxation being caused by spins flipping works, it is also rather unsatisfying. The different models in use are all representations of quantum mechanics, so in some sense they are all at least partially correct; however, some are more helpful than others. Here, we present a model which explains both of these aspects of NMR and leads naturally into product operators. We suggest that it should be adopted much more widely.

Introductory NMR courses usually start by describing a single nuclear spin and show how it is affected by a magnetic field. We are all aware that single spins are quantized objects

and we therefore do not expect them necessarily to behave in the same way as classical macroscopic objects. Specifically, most websites and textbooks begin by explaining that in the presence of an applied magnetic field, the nuclear spin will align either parallel or antiparallel to the field. This model is described below as the *alignment* model, and is not the behavior expected for classical magnets, which align only *with* the field. It therefore presents students at the start of their NMR course with a clear example of nuclear spins behaving in an unexpectedly nonclassical manner. This immediately gives students the idea that nuclear spins behave in nonintuitive ways and implies that they are therefore inherently difficult if not incomprehensible. This is not helpful. It is also entirely avoidable.

Very few textbooks take the trouble to explain why this model is limited: Honorable exceptions are *Understanding*

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NMR Spectroscopy by Keeler³ and *Spin Dynamics* by Levitt,⁴ which is considerably more detailed and mathematical. This nonclassical behavior is usually explained as a quantum effect and is not discussed. Many websites and textbooks then go on to describe a second model, with spins precessing in a cone tilted at 54° to the magnetic field (the 2-cone model). This is also a nonclassical behavior and leads to major conceptual problems later, as we shall see.

In all normal applications of NMR, we never observe single spins; we observe populations of very large numbers of spins. Ensembles of spins behave almost entirely in the way expected by classical physics. Ensembles can be well represented using product operators, which represent accurately and completely the behavior of assemblies of spins, including coherences involving more than 1 spin, have a simple vectorial representation,¹ and are therefore an excellent basis for understanding modern multiple-pulse experiments. They are very widely used and are the tools used in the large majority of research applications.² Any vector-based description of an NMR experiment leading to an observable result, from the simplest single-pulse to complex multiple-pulse experiments, is essentially drawing product operators, which work well and form a good model. We are therefore concerned here only with models for *individual* spins.

We start by considering the quantum mechanics equations that describe single nuclear spins, because these are what represent reality and allow us to discuss the different models on a firm theoretical foundation. We then go on to consider the use of each model to discuss how single spins behave at thermal equilibrium, the effect of a 90° pulse, and relaxation, and discuss the advantages and disadvantages of each model, concluding that the uniform model has many advantages and almost no disadvantages. We happily acknowledge that the ideas presented here are not novel or original. Many were expressed clearly by Bloch⁵ and have been propounded by many others since; recently, most clearly by Keeler³ and particularly by Levitt,⁴ from whom many of the equations cited here are obtained, as well as by Hanson,⁶ who makes many of the same arguments as used here and is well worth reading. A detailed analysis has also been set out by Macomber.⁷ Despite these authors' efforts, the alignment and 2-cone models still dominate NMR teaching. This article is an attempt to remedy this, by showing how the uniform model explains many other aspects of NMR better than the other models, in particular relaxation.

What Quantum Mechanics Says

The state of a single spin-1/2 nucleus can be represented by a wavefunction. This wavefunction can take many forms, but the ones that are generally of most interest are those that are

eigenstates (equivalently, eigenfunctions) of the nuclear spin Hamiltonian \mathcal{H} . This is because the eigenstates are solutions to the time-independent Schrödinger equation

$$\mathcal{H} | \Psi \rangle = m | \Psi \rangle \quad (1)$$

where the m are real numbers, the eigenvalues, and describe the *energy* of the system. A single spin-1/2 has 2 eigenstates of angular momentum along the z axis, described as $|\alpha \rangle$ and $|\beta \rangle$. The $|\alpha \rangle$ eigenstate has an eigenvalue of +1/2, and the $|\beta \rangle$ eigenstate has an eigenvalue of -1/2:

$$I_z |\alpha \rangle = +\frac{1}{2} |\alpha \rangle \quad (2)$$

$$I_z |\beta \rangle = -\frac{1}{2} |\beta \rangle \quad (3)$$

This means that when we measure the z angular momentum of a nuclear spin, the only possible values we can observe are either +1/2 (the lower energy) or -1/2. Similarly, when we observe a transition between 2 states, the only observable transition is between the $|\alpha \rangle$ and $|\beta \rangle$ eigenstates.

However, this does not mean that a spin has to be in one of the 2 eigenstates.⁵ In general, any individual spin will have a wavefunction that is a mixture of the 2 eigenstates, often called a superposition state. Its wavefunction is

$$|\Psi \rangle = c_\alpha |\alpha \rangle + c_\beta |\beta \rangle \quad (4)$$

where c_α and c_β are, in general, complex time-dependent coefficients, with the requirement that

$$|c_\alpha|^2 + |c_\beta|^2 = 1 \quad (5)$$

$|c_\alpha|^2$ is a real quantity and is equal to c_α multiplied by its complex conjugate, $c_\alpha^* c_\alpha$. Although $|\alpha \rangle$ and $|\beta \rangle$ are eigenstates of I_z , the superposition states are not. The superposition states evolve with time (in fact, as discussed below, they precess around the z axis at the Larmor frequency).

An observation of the z angular momentum of a spin must give only the value +1/2 or -1/2, with probability $|c_\alpha|^2$ and $|c_\beta|^2$, respectively. This is the result familiar to us from the *Gedankenexperiment* of Schrödinger's cat, that the superposition wavefunction collapses to one of the 2 eigenstates when it is observed. It remains one of the most surprising and nonintuitive features of quantum mechanics. It is, however, worth noting that this is the *only* mysterious feature of quantum mechanics that need concern us when we attempt to picture nuclear spins using the uniform model (including entanglement, which is not a relevant concept for isolated spins-1/2). The consequence of the wavefunction collapse is that the only observable transition between 2 spin states is between pure $|\alpha \rangle$ and $|\beta \rangle$ states, even though most spins are actually in mixed superposition states.

The wavefunctions $|\alpha \rangle$ and $|\beta \rangle$ are only eigenfunctions of the Hamiltonian, and thus of the z angular momentum operator I_z . They are not eigenfunctions of the x and y

angular momentum operators I_x and I_y . Thus if one tries to measure the x angular momentum of a spin that is in the $|\alpha\rangle$ state (corresponding to the operation $I_x|\alpha\rangle$), the result is fundamentally unpredictable. The result is always either $+\frac{1}{2}$ or $-\frac{1}{2}$ (note: *not* zero), but it is impossible to predict which. Indeed, as stressed on page 242 of Levitt,⁴ even the spin itself does not “know” which value will be returned. The same is of course also true for I_y .

Total spin angular momentum is quantized, and takes the value

$$P/\hbar = [R(R+1)]^{\frac{1}{2}} \quad (6)$$

where R is the quantum number. However, the angular momentum along the z axis is given by

$$P_z/\hbar = m \quad (7)$$

with m being another quantum number, which must take values $R, R-1, \dots, -R$. For a spin $-\frac{1}{2}$ nucleus, $R = \frac{1}{2}$ and $m = +\frac{1}{2}$ or $-\frac{1}{2}$. The only way in which equations (6) and (7) can both be satisfied is for the total angular momentum to be at an angle θ to the z axis, such that

$$\cos \theta = m/[R(R+1)]^{\frac{1}{2}} \quad (8)$$

which results in 2 possible angles θ of 54° and $(180-54)^\circ$, the magic angle, as shown below (Section The 2-Cone Model under Comparison of Models: Equilibrium).

Three Models of Individual Spins $-\frac{1}{2}$

The Alignment Model

In this model, spins in the absence of a magnetic field are randomly oriented. When the spins are put into a magnetic field, they become aligned such that they point either with or against the field (Figure 1). Because the up orientation $|\alpha\rangle$ is of lower energy, spin-lattice relaxation will lead to flips of spins between up and down, and thus produce a slightly larger population of up than down. An observation of a sample containing many identical nuclei will yield a

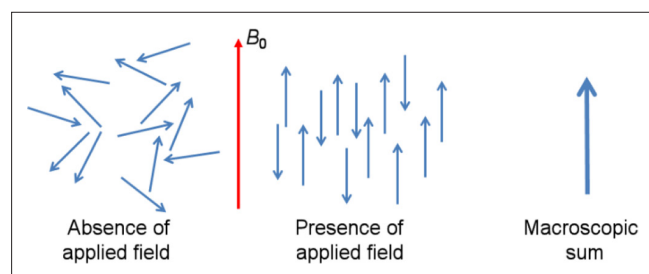


Figure 1. The alignment model. An applied field aligns spins either up or down, with slightly more in the up orientation. The ratio of up to down has been exaggerated for clarity. As explained, this is not what spins actually do.

macroscopic magnetization that is a summation of the individual spins, and thus a net observable magnetization in the $+z$ direction. From this point on, we normally consider only the net magnetization and ignore individual spins. Thus, this model is used only to depict spins at equilibrium and indeed *is only valid in this very limited condition*. It is used very widely, for example, in a number of major NMR and magnetic resonance imaging textbooks,⁸⁻¹⁰ and on the NMR teaching websites of many universities and research institutes. A survey of introductory NMR courses shows that a very large number of courses use this model.

The result of spin-lattice relaxation is that spins populate the up orientation to a greater extent than the down orientation, the difference in populations being given by the Boltzmann distribution, which depends on the energy difference. Because the difference in energy between $|\alpha\rangle$ and $|\beta\rangle$ is very small, the difference in population is also small. In an 11.4 T magnet, the difference in energy is $\nu = 500$ MHz for ^1H , or $E = h\nu = 3.3 \times 10^{-25}$ J. Thus from the Boltzmann distribution

$$\frac{p_1}{p_2} = \exp\left(-\frac{E}{kT}\right) = 0.99992 \quad (9)$$

implying that the excess population in $|\alpha\rangle$ is only about 1 in 12 000. In other words, to a good approximation the spins have equal populations in the 2 states, with a *very* small tendency for them to prefer to be up rather than down.

The 2-Cone Model

This model says that at equilibrium, nuclear spins point, not along the $\pm z$ axis, but at a fixed angle to it, and that they precess around the z axis at the Larmor frequency on the surface of 2 cones (Figure 2). The population difference between the 2 cones is given by the Boltzmann distribution, as above. This model is used even more widely than the alignment

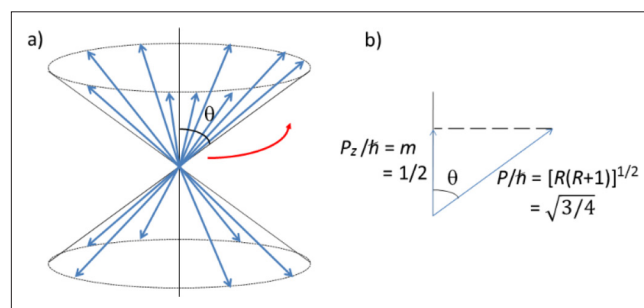


Figure 2. The 2-cone model. (a) There are slightly more spins in the top cone than the bottom one (exaggerated here for clarity). Spins are drawn with a common origin, to make the shape of the distribution clearer. (b) The total spin angular momentum is $\sqrt{3}$ times larger than the angular momentum along the z axis. The half-cone angle is therefore $54^\circ = \cos^{-1}(1/\sqrt{3})$, often described in solid-state nuclear magnetic resonance as the magic angle; many published representations of this model have a cone that is too narrow.

model and can be found in some form in a wide range of textbooks.^{8,10-25} Some books and websites use both models, generally with no hint of a contradiction. In exactly the same way as the alignment model, macroscopic magnetization is the sum of the individual vectors. Because each vector has random phase on the cone, the vector sum is along $+z$, the same as for the alignment model.

An argument often given in support of the 2-cone model derives from the Heisenberg uncertainty principle: The argument runs that because the uncertainty principle says that one cannot know precisely the position and angular momentum of a particle, then spins cannot be pointing directly up or down, and must be at an angle to the z axis, the angle being determined by the magnitude of the uncertainty. This is (more or less) true. As we have seen, if a spin is in a pure $|\alpha\rangle$ eigenstate, its magnitude in (eg,) the x direction is not zero; it is in fact undefined: A measurement of x angular momentum would give a value of $\pm\frac{1}{2}$ with equal probability. The same is true for y . This puts it on the cone. We will have more to say about this in Section The 2-Cone Model Under Comparison of Models: Equilibrium).

The Uniform Model

In the absence of a magnetic field, this model is identical to the other 2 models: Spins point in random directions. They spin around their own axes, but do not precess, because there is no applied field to precess around. The difference is that the presence of a field has no immediate effect on the orientations, although it does cause spins to precess around the applied field (Figure 3). It also causes different orientations to have different energies according to the Boltzmann distribution, dependent on the magnitudes of $|c_\alpha|^2$ and $|c_\beta|^2$. The closer in energy the spin is to the $+z$ axis, the lower the

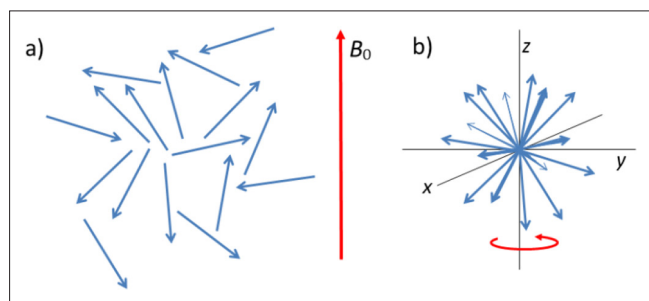


Figure 3. The uniform model. (a) In the absence of an applied field, a nuclear spin can have any orientation. (b) In the presence of an applied field, spins initially retain their orientations in 3 dimensions and precess around the field at the Larmor frequency. The presence of B_0 leads to a slightly lower energy for spins the closer they point to the $+z$ direction. At equilibrium there is therefore a slight tendency for spins to be more up than down (exaggerated for clarity). This figure also depicts the conventional right-handed axis system, in which a positive frequency rotates in the direction from x to y .

energy is; thus the energy of the spin is dependent on $\cos \theta$, where θ is the angle between the direction of the spin angular momentum and the $+z$ axis. This means that the populations of different orientations depend also on $\cos \theta$ (as a result of relaxation, in a time of the order of T_1), with a very slight excess close to the $+z$ axis and a very slight deficit close to the $-z$ axis (Figure 3). As for the other 2 models, the summed macroscopic magnetization is along the $+z$ axis.

We now proceed to look at how the different models explain the most common situations relevant to single spins.

Comparison of Models: Equilibrium

The Alignment Model

The beauty of the alignment model is that it makes it immediately obvious that there are 2 energy levels for a spin $-\frac{1}{2}$ nucleus, and that NMR observes the transition between them (Figure 4). (Although it is worth noting that NMR does not in fact observe a transition, it observes the precession of magnetization in the xy plane.) It is also easy to see that there is a difference in population between the 2 levels, dependent on the Boltzmann distribution. Thus, as a teaching tool it is simple and direct.

The problem is that as soon as we start to look deeper, we see that the alignment model is a drastic oversimplification. In fact, spins do *not* occupy only the $|\alpha\rangle$ and $|\beta\rangle$ eigenstates: Most spins are in superposition states. The model has therefore avoided an important but confusing quantum reality (the collapse of the wavefunction on observation), but at the cost of an unnecessary oversimplification, and a limitation to

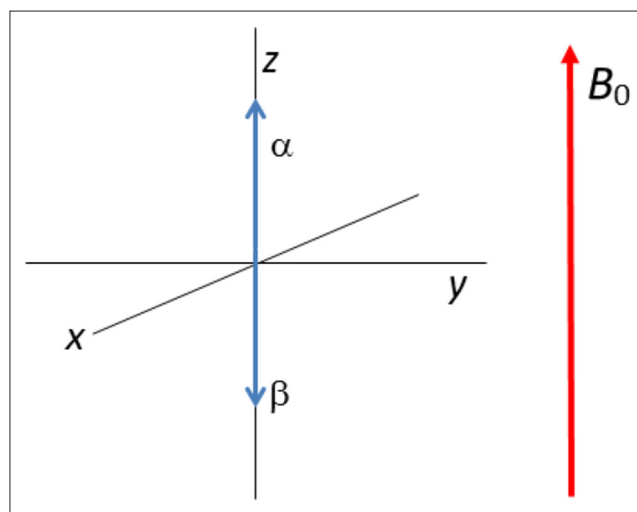


Figure 4. The alignment model, referred to a common origin. All spins are in one of the 2 pure states $|\alpha\rangle$ and $|\beta\rangle$, with a slight excess in the "up" state $|\alpha\rangle$. A nuclear magnetic resonance transition involves a flip of an individual spin from $|\alpha\rangle$ to $|\beta\rangle$ (or $|\beta\rangle$ to $|\alpha\rangle$).

treating spins only at equilibrium. Its value as a teaching aid is therefore questionable. The question has been debated since the very early days of NMR. As early as 1964, Slichter wrote²⁶

Sometimes the belief is erroneously held that spins may only be found pointing either parallel or antiparallel to the quantizing field ... We emphasize that an *arbitrary* orientation can be specified.

The 2-Cone Model

The 2-cone model is the model that is used to introduce most NMR spectroscopists to the subject, and for many of us it is so fundamental a picture that it feels almost blasphemous to criticize it. It has a number of elegant features. Like the alignment model, it illustrates 2 states with a single transition between them. It shows spins precessing around the applied field, and it can therefore be used to explain the concepts of phase and coherence. It can also be used to explain both T_1 and T_2 relaxations.

The origin of the idea of spins being at a fixed angle to the applied field is explained particularly clearly in Harris,¹⁸ and comes from the comparison of total angular momentum and angular momentum along the z axis discussed in equations (6) to (8)(Figure 2). Because the total angular momentum is larger than the angular momentum along the z axis by a factor of $\sqrt{3}$, then it has to be tilted at the magic angle $[\cos^{-1}(\frac{1}{\sqrt{3}})]$ to the z axis. If it is tilted away from the z axis, then it “must” be precessing; hence, it “obviously” (though as it turns out, erroneously) precesses in a cone around the z axis. A more detailed discussion of the quantum mechanics is presented in Supporting Information.

As a brief summary, the upper cone represents a pure $|\alpha\rangle$ state, and the lower cone represents a pure $|\beta\rangle$ state. This means that the 2-cone model has the same problem as the alignment model, that it depicts all spins in their eigenstates, whereas in fact most spins are in superposition states. Furthermore, spins in pure eigenstates have stationary wavefunctions, and cannot give rise to observable NMR signals. (Compare to Figure 7, which has the same problem.)

The Uniform Model

In the uniform model, all spins have magnitude $\frac{1}{2}$, and precess around the z axis at the Larmor frequency, except for spins aligned exactly along $\pm z$. There is an increase in spin density in going from the $-z$ axis up toward the $+z$ axis, in line with the Boltzmann distribution. The uniform model explains precession, phase, and energy distributions well and is consistent with the quantum mechanics.

It is worth noting that at absolute zero, all spins would align with the field (as seen with a macroscopic bar magnet), because this is the lowest energy. It is the fact that thermal

energy is much larger than the difference in energy between the spin states that leads to magnetization being distributed almost completely randomly in space.

Comparison of Models: The Effect of a 90° Pulse

The Alignment Model

The alignment model only considers individual spins to be along the $\pm z$ axis. It is therefore not possible to consider the effect of a 90° pulse in this model at the level of individual spins. Explanations that use the alignment model sum the magnetizations from individual spins and move straight to the macroscopic magnetization in order to discuss 90° pulses.

The 2-Cone Model

Macroscopically, we expect that a 90° pulse in the xy plane rotates equilibrium magnetization away from the z axis onto the transverse xy plane. In order to understand this at the level of a single spin, we need to return to quantum mechanics.

A 90° pulse along the y axis (in the rotating frame) acts on $|\alpha\rangle$ to give the superposition state

$$\frac{1}{\sqrt{2}} \left| \alpha \right\rangle + \frac{1}{\sqrt{2}} \left| \beta \right\rangle$$

The coefficients c_α and c_β are equal in magnitude, consistent with a spin in the xy plane. This superposition state is not an eigenstate of I_z , but it is an eigenstate of I_x , because

$$I_x \left(\frac{1}{\sqrt{2}} \left| \alpha \right\rangle + \frac{1}{\sqrt{2}} \left| \beta \right\rangle \right) = \frac{1}{2} \left(\frac{1}{\sqrt{2}} \left| \alpha \right\rangle + \frac{1}{\sqrt{2}} \left| \beta \right\rangle \right) \quad (10)$$

We are therefore justified in calling this state $|+x\rangle$, that is, magnetization in the $+x$ direction. Thus, the quantum mechanics agrees with our macroscopic intuitive picture: A 90° _{y} pulse acting on a single spin in the $|\alpha\rangle$ state rotates it to the x axis. In fact, quantum mechanics is consistent with a pulse of any angle causing the appropriate rotation around the pulse axis, exactly as we would expect macroscopically.

In an analogous way to what we saw for $|\alpha\rangle$, operating on this $|+x\rangle$ state with I_z or I_y gives values randomly of $\pm\frac{1}{2}$. Therefore, just as we could draw $|\alpha\rangle$ as a cone around the z axis, so we can draw $|+x\rangle$ as a cone around the x axis (Figure 5).

When the radiofrequency (rf) pulse is turned off, the magnetization precesses around the applied field with an angular velocity ω , corresponding to the Larmor frequency. We can represent this in several different ways. The most obvious is simply as a vector rotating in the xy plane; or, following the 2-cone model, as a pair of horizontal cones precessing in the xy plane (Figure 6). However, the most common “2-cone” representation is to revert to the Hamiltonian view (a

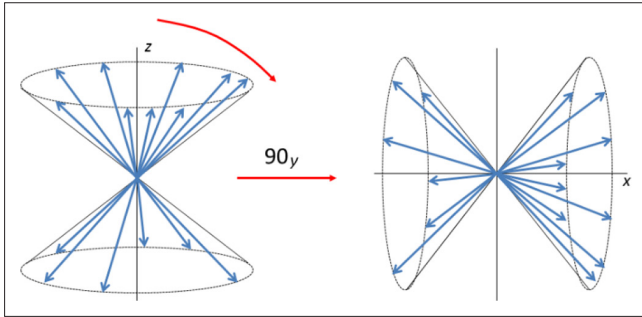


Figure 5. In the 2-cone model, a 90_y° pulse rotates the 2 cones from $\pm z$ to $\pm x$.

sensible representation because usually we are interested in the energies of the system, which implies quantization in the z direction), in which case the magnetization is drawn distributed equally on both cones, but with a defined phase, in this case along $+x$ (Figure 7a). If the system is expanded to contain several spins, this gives rise to a picture in which spins are “bunched up” on one side of the cone (Figure 7b). The bunching up of the spins can also be expressed as having the spins coherently in phase.

The 2-cone model thus leads to a confusing overall picture (Figure 8): Spins on a vertical cone are rotated into the horizontal by a 90° pulse, and then magically and instantaneously rearrange themselves back onto the original vertical cones, but bunched up on one side. Each of these stages is a reasonable representation of the quantum mechanics, but the overall scheme looks, to say the least, unlikely. It is therefore sensible to abandon the 2-cone model before this point.

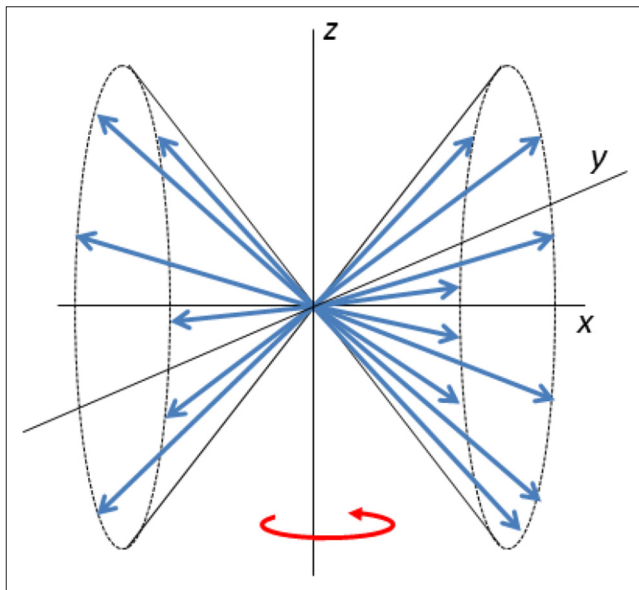


Figure 6. In the 2-cone model, after a 90° pulse is turned off, the free precession of magnetization can be represented as 2 horizontal cones rotating around the z axis.

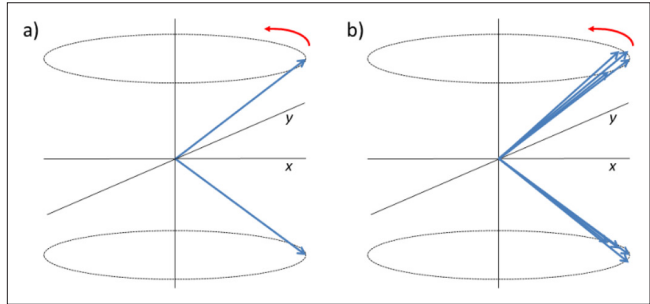


Figure 7. An alternative (and more common) representation than that shown in Figure 6 of free precession in the xy plane within the 2-cone model. Magnetization is represented as 2 vectors of equal magnitude, one on each cone, starting at $+x$ and precessing around the z axis. This can be shown (a) as a single spin split evenly between both cones, or more commonly (b) as an ensemble of spins, bunched up around the $+x$ axis.

Despite this, most textbooks use the model, though they resolve the paradox in different ways. Some simply leave the rotated cones where they are.^{20,25} Some have the rotated cone somehow resolving into something like the original one.^{15,27} The majority draw the spins after a pulse bunched up on one side of the cones, without any clear mechanism for them to have got there.^{10,12,19,25}

The Uniform Model

At equilibrium, spins are distributed around the sphere, with a slight excess in the $+z$ direction. An rf pulse acts on each spin independently and rotates it around the rf field.⁶ Thus, for example, a 90_x° pulse changes the distribution of spins such that, starting from the position in which there is a slight excess in the $+z$ direction and a slight deficit in the $-z$ direction, there is now a slight excess in the $-y$ direction and a slight deficit in the $+y$ direction (Figure 9). After the 90° rotation around the x axis caused by the rf pulse, the spins continue their free precession around the z axis. When the individual magnetizations are summed, the consequence is a bulk magnetization that has been rotated by 90° onto the $-y$ axis, and subsequently precesses in the xy plane.

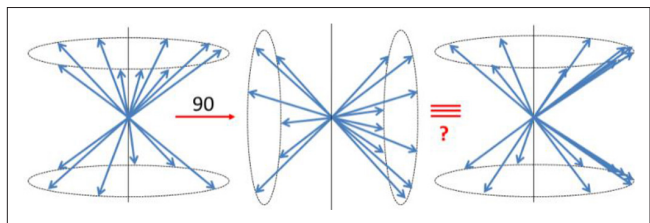


Figure 8. The 2-cone model leads to a confusing overall picture for the effect of a 90° pulse and the subsequent free precession, in which spins seem to have to move instantaneously from x -quantized cones to z -quantized cones, and thus to completely different orientations in space.

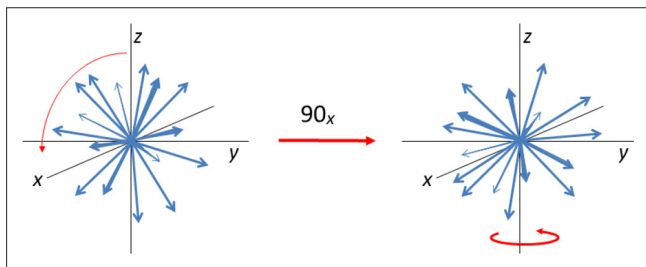


Figure 9. In the uniform model, a 90° pulse rotates all spins by 90° around the direction of the applied radiofrequency field. The pulse is rotating at the Larmor frequency, that is, it is an x pulse in the rotating frame, which rotates magnetization in the direction from $+z$ to $-y$. Before the pulse, there are slightly more spins along $+z$ than $-z$, and after the pulse, there are slightly more spins in the $-y$ than the $+y$ direction. Magnetization subsequently continues to precess around the z axis. Here and elsewhere, we use the standard right-hand rule convention, which says that a pulse in the $+x$ direction rotates $+z$ to $-y$.

After the 90° pulse, there is a (very weak) correlation between the time-dependent orientations of spins across the sample. There is a tendency for more spins to be pointing in the $-y$ direction, and fewer spins in the $+y$ direction; this alignment that is originally in the $\pm y$ direction has a subsequent time dependence that precesses around the z axis. The term used in NMR to denote this correlation is *coherence*: Coherence (in this context) is simply the very slight correlation between the time-dependent orientations of different spins in the sample. The uniform model therefore leads to a very straightforward interpretation of the concept of coherence, and why this is related to the phase of the spins. It is a simple consequence of the 90° pulse and requires no *deus ex machina*, as it does in the 2-cone model.

Comparison of Models: Relaxation

Spin-lattice relaxation is the process by which spins reach thermal equilibrium in the z direction, whereas transverse relaxation is the process by which spins attain a uniform phase distribution in the transverse plane. The alignment model cannot comment on transverse relaxation, because there is no xy component to magnetization in this model. The alignment and 2-cone models explain spin-lattice relaxation as a flipping of a spin from up to down (or down to up), or equivalently as a flip from one cone to the other. The uniform model has an interestingly different (and more helpful) interpretation, as we shall see.

NMR textbooks show that spontaneous relaxation is very slow, and relaxation has to be stimulated by local magnetic fields that fluctuate at the appropriate frequency. For spin-lattice relaxation this is typically the Larmor frequency (plus sums and differences of Larmor frequencies of the 2 spins). Thus, dipole-dipole spin-lattice relaxation is stimulated when one spin has a neighboring dipole (=spin) that is

moving relative to it within the transverse plane at the Larmor frequency. A neighboring dipole that is moving at the Larmor frequency in the transverse plane is in fact providing an on-resonance pulse. Thus, all models require the neighboring dipole to act as a local on-resonance pulse, in order to rotate the spin from up to down or vice versa. In order to explore this further, we need to think a little about resonance, and in particular the distinction between on-resonance and off-resonance.

Pulses provide a torque, which acts to rotate a spin around the pulse axis. Spins precess rapidly around the z axis. This means that as a pulse rotates a spin away from the z axis, the direction of the magnetic field component supplied by the pulse needs to track the direction of the spin as it precesses, to ensure that the pulse continues to rotate the spin down toward the xy plane. We normally draw spins in the rotating frame, a frame that rotates at exactly the Larmor frequency. In this frame, spins have zero precession frequency, and a pulse that is exactly on-resonance also remains in a fixed direction. It is therefore easy to see that a pulse along the y axis (in the rotating frame, meaning a pulse that is actually rotating around the z axis at the Larmor frequency but starting at y) simply rotates a spin from $+z$ down to $+x$ (Figure 10, route a). In contrast, an off-resonance pulse rotates around the z axis as it acts. The speed of rotation of the pulse axis is significant compared to the rate of rotation of the spin around the pulse axis, and consequently the spin does not move in a plane perpendicular to the pulse, as it does with an on-resonance pulse, but moves in a curved path, in fact rotating around a tilted axis (Figure 10, routes b and c). As the pulse becomes more and more off-resonance, the tilted axis moves closer and closer to the z axis, so that a very off-resonance field has essentially no effect on the spin.

In the alignment and 2-cone models, spin-lattice relaxation requires a complete transition from one spin state to another, that is, a 180° flip of a spin. It is not obvious what physical process is “really happening” during this flip and what the role of the neighboring dipole is. The uniform model, however, provides an interesting and insightful answer. We are familiar with the idea that a 180° spin flip can be achieved by a coherent on-resonance pulse (ie, a 180° pulse), though significantly this is actually a rotation that leads to a flipped state. In the context of relaxation, it can also be achieved by a local dipole that happens to be rotating at the right on-resonance frequency for long enough to cause a flip. In standard textbook accounts, this on-resonance concept is often expressed as requiring the spectral density function $J(\omega)$ at the Larmor frequency to be large enough. The drawback with picturing a spin flip as an on-resonance rotation is that the local magnetic field created by a nearby dipole is very weak. For example, a proton at a distance of 0.2 nm [2 Å] gives rise to a local field of about 30 kHz. Thus, in order to cause a 180° flip, it would need to be active for $1/(2 \times 3 \times 10^4)$ s or 17 μ s. This is very much longer than the correlation time, which for small molecules is much shorter than

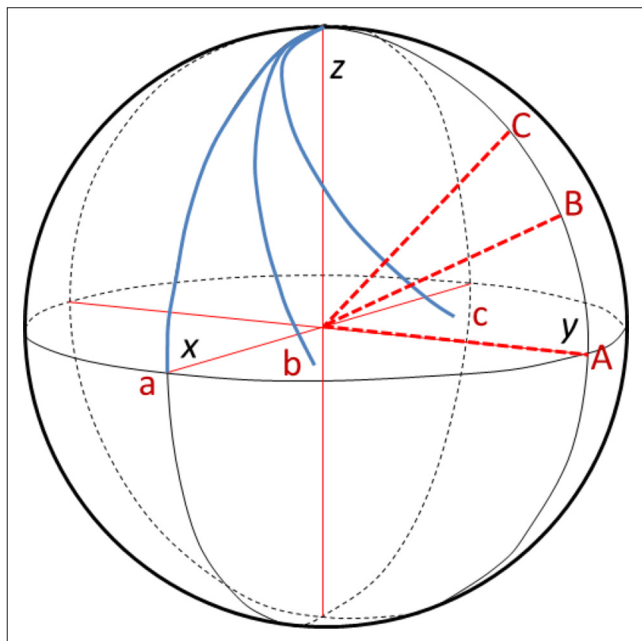


Figure 10. The effect of an off-resonant pulse. An on-resonant 90°_y pulse rotates magnetization from $+z$ to $+x$ (position *a*), this being a rotation around the y axis (marked *A*). An off-resonant pulse is a rotation around an axis that moves away from $+y$ during the pulse: The net effect is a rotation around a tilted axis. Thus when the 90° pulse is off-resonant by half the radiofrequency (rf) field strength, the tilted axis runs through *B* and causes magnetization to rotate to point *b*, whereas when the 90° pulse is off-resonant by the rf field strength, the tilted axis runs through *C* and causes magnetization to rotate to point *c*. For comparison, a typical ^1H pulse has a 90° pulse length of about 10 μs , corresponding to an rf field strength of 25 kHz. The trajectory to *c* would therefore correspond to a pulse 25 kHz off-resonance or 50 ppm on a 500 MHz spectrometer. As discussed in the text, this is also approximately the maximum possible strength of a dipole-dipole interaction. Figure adapted from Keeler,³ with permission.

a nanosecond. In other words, the general mechanism of dipole-dipole relaxation is clear, although in detail it is difficult to see how a neighboring spin would be able to cause a rotation of more than a small fraction of a degree before collisions would lead to a change in the molecular tumbling, and thus prevent further spin rotation.

In the uniform model, this is not a problem. Spins are not just in the pure $|\alpha\rangle$ and $|\beta\rangle$ eigenstates, but adopt all possible orientations. This implies that spin-lattice relaxation will in general not require a change between pure $|\alpha\rangle$ and $|\beta\rangle$ eigenstates, but merely a relative change in $|c_\alpha|^2$ and $|c_\beta|^2$: Overall relaxation is a summation of a large number of small changes, rather than a few large-scale changes. In other words, relaxation simply requires a change in the angle between the spin and the z axis. This is exactly what is achieved by a neighboring dipole that is moving at the Larmor frequency and thus acts as an on-resonant pulse, the difference being that in the uniform model *any* amount of

rotation contributes to relaxation. It is worth noting that standard relaxation theory discusses relaxation as if spin flips happen in one single large change. There is no contradiction with the model discussed here of multiple small steps, because any change in z magnetization, however small, requires a change in $|c_\alpha|^2$ and $|c_\beta|^2$, and thus a transition between $|\alpha\rangle$ and $|\beta\rangle$ states.

In summary, all 3 models have a very similar explanation for relaxation. The insights afforded by the uniform model are that the nearby dipole does not need to cause a complete transition between $|\alpha\rangle$ and $|\beta\rangle$ states, but merely a change in the orientation of a spin; and that this change in orientation can be treated without loss of rigor as a short on-resonance pulse. A similar argument holds for transverse relaxation: The nearby dipole merely needs to cause a change in the angle around the z axis. This explains how a weak dipole with randomly varying tumbling frequency is still capable of stimulating relaxation. Such insight is harder to extract from the alignment and 2-cone models, because they exaggerate the importance of the eigenstates.

The Uniform Model and the Larmor Frequency

So far, we have seen that the uniform model provides a picture of the underlying quantum mechanics that is more satisfactory than that provided by the alignment and 2-cone models, as regards to equilibrium magnetization, the effect of a 90° pulse, and relaxation. The uniform model provides one further helpful insight. The Larmor frequency comes up twice in accounts of NMR. It is the frequency at which spins precess around the z axis, but it is also the energy difference between the $|\alpha\rangle$ and $|\beta\rangle$ eigenstates. Why are these 2 necessarily the same? What is the connection between these 2 apparently different phenomena? The answer (as we have just seen) is that the transfer of energy during a transition between 2 energy states is a resonant phenomenon: The gain or loss of energy of the nuclear spin has to be on-resonance, which, by the definition of on-resonance, means that it has to be at the same frequency as the precession rate.

This discussion shows how the uniform model leads to a clearer understanding of resonance, and why the word “resonance” is such a key part of nuclear magnetic resonance.

Conclusion

We have examined 3 models of nuclear spins $-\frac{1}{2}$. The alignment model has the advantage of simplicity, but implies that spins can only be in one of the 2 eigenstates, and do not precess at equilibrium. It provides no insight into pulses or precession. The 2-cone model provides a better (though inaccurate) picture of phase and precession, and is an answer to a somewhat obscure difficulty (the difference in magnitude between total spin angular momentum and spin angular momentum along the z axis), although it also implies that

spins can only be in one of the 2 eigenstates, and leads to a confused picture following a 90° pulse. In contrast, the uniform model provides a perfect correspondence with the quantum mechanics for the examples considered here, and has no contradiction with classical behavior, meaning that it can be used to follow through from equilibrium, the effect of a 90° pulse, and subsequent precession and relaxation, without requiring adjustment or a change of model. It also provides a more satisfactory description of coherence, relaxation, and resonance than the other 2 models: an important point given the importance of relaxation to modern NMR. We therefore suggest that it is a better model and should be preferred for teaching of basic NMR.

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Supplemental Material

Supplemental material for this article is available online.

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