

# INTRODUCTION TO QUANTUM MECHANICS

OR

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## WHY CHEMISTRY IS DIFFICULT TO LEARN

**Electrons (and photons) DO NOT behave according to Newton's Laws of Motion**

**But, Chemistry is all about electrons**

Feynman, from *Lectures on Physics III* :

“Quantum Mechanics exactly describes the behavior electrons and light.”

“Electrons and light do not behave like anything we have ever seen.”

“There is one lucky break, however—**electrons behave just like light**”

# Understanding Quantum Mechanics?

Richard Feynman lecturing to a lay audience at  
Cornell, *circa*. 1965:

“There was a time when the newspapers said that only twelve men understood the theory of relativity.

I do not believe there ever was such a time...

After they read the paper, quite a lot of people understood the theory of relativity... On the other hand, I think it is safe to say that

*no one “understands” quantum mechanics...*

Feynman’s Admonition:

“Do not keep saying to your self “But how can it be like that?”, because you will get “down the drain” into a blind alley from which nobody has yet escaped. **NOBODY KNOWS HOW IT CAN BE LIKE THAT.** “

--Richard P. Feynman

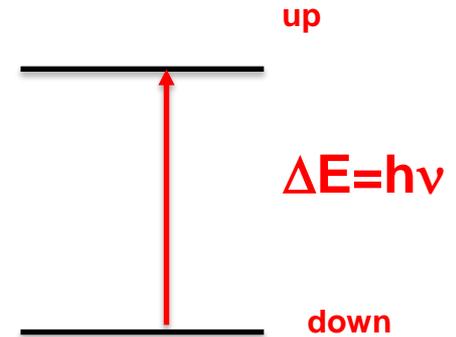
Chapter 6, *The Character of Physical Law*, 23<sup>rd</sup> Printing, 1998

# Now we return to NMR and learn the reality at 300K:

Boltzmann:

Ratio of spin up/spin down:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{k_B T}}$$



Divide energy by Planck's constant x speed of light in cm/sec

$$\text{Ratio of spin up to spin down} \\ \frac{N_2}{N_1} = e^{-\frac{\Delta E}{k_B T}} = e^{-\frac{\Delta E/hc}{k_B T}} = e^{-\frac{0.02 \text{ cm}^{-1}}{0.697 \text{ cm}^{-1} \text{ K} \cdot 300}}$$

$$= e^{-\frac{0.02}{207}} = e^{-0.0001} = 0.9999$$

**At room temperature only 0.01 % more in lowest state than in highest state.**

(about the ratio of the atmospheric pressure between the floor and ceiling in this room!)

Ratio of spin up to spin down:

$$\frac{N_2}{N_1} = e^{\frac{-\Delta E}{k_B T}} = e^{\frac{-\Delta E/hc}{k_B T}} = e^{\frac{-0.02 \text{ cm}^{-1}}{0.697 \text{ cm}^{-1} \text{ K} \cdot 300}} = e^{\frac{-0.02}{207}} = e^{-0.0001} = 0.9999$$

$k_B T$  at 300K = 207  $\text{cm}^{-1}$

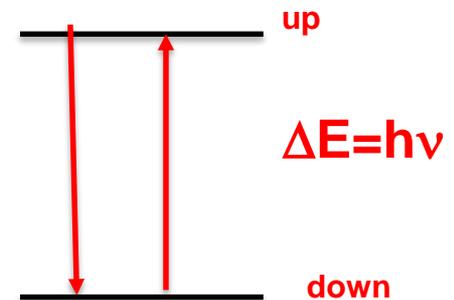
Einstein pointed out that **excitation is stimulated from the high state to low state at same rate as excitation upwards.** i.e., **light shakes things down as well as up!**  
**(predicted LASERS 60 years before they could be created)**

Resonant RADIO FREQUENCY used in NMR is absorbed to increase the population of the higher state, but **ONLY STIMULATES** the loss of the higher state. **NO FLUORESCENCE.** "Spontaneous" emission rate is proportional to **1/frequency cubed.** **The fluorescence lifetime would be 32 YEARS!!!!**

The RADIO FREQUENCY wavelength is  $\sim \frac{1}{2}$  meter, so **Entire all spins feel the same oscillating magnetic field.**

Even with no excitation from radio waves, the spins are **constantly being jolted up and down in energy.**

**This DOES NOT MEAN that they are constantly making instantaneous jumps up and down between the pure spin up and spin down states**



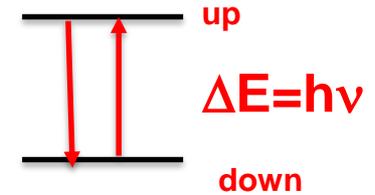
At room temperature only 0.01 % more in lowest state than in highest state

## Quantum Concept: Superposition.

A molecule may be “in” more than one state at once!

Although there are two quantum “**energy levels**”:  
spin up and spin down, there is a continuous mixture.

The spins are all in **superposition** states.



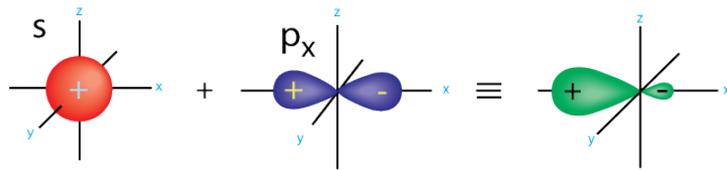
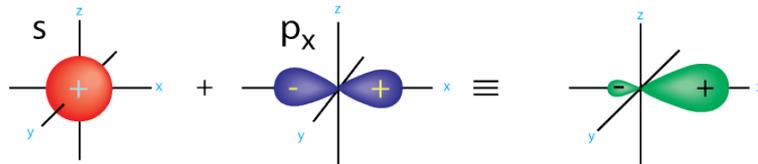
$$\Psi_{total} = c_{up} \Psi_{up} e^{-i \frac{2\pi E_{up} \text{time}}{h}} + c_{down} \Psi_{down} e^{-i \frac{2\pi E_{down} \text{time}}{h}} = \cos(2\pi\nu t) + i\sin(2\pi\nu t)$$

**This is a hybrid  
“orbital of spin”**

$\Psi_{up}$  and  $\Psi_{down}$  are “orbitals” i.e., wavefunctions for the nuclear spin.

If the temperature = **1 billion K**, the SAME would be said of the 1s and 2p orbitals of the H atom

$$\Psi_{total} = c_{1s} \Psi_{1s} e^{-i \frac{2\pi E_{1s} \times \text{time}}{h}} + c_{2p} \Psi_{2p} e^{-i \frac{2\pi E_{2p} \times \text{time}}{h}}$$

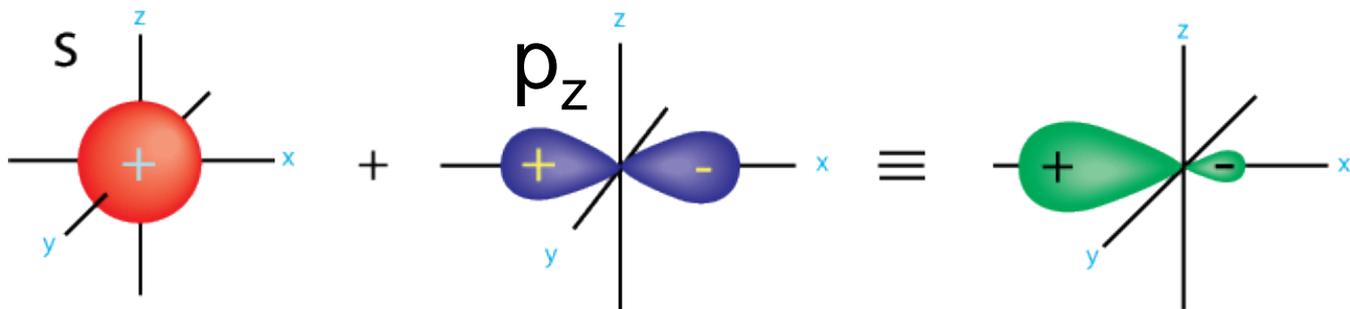
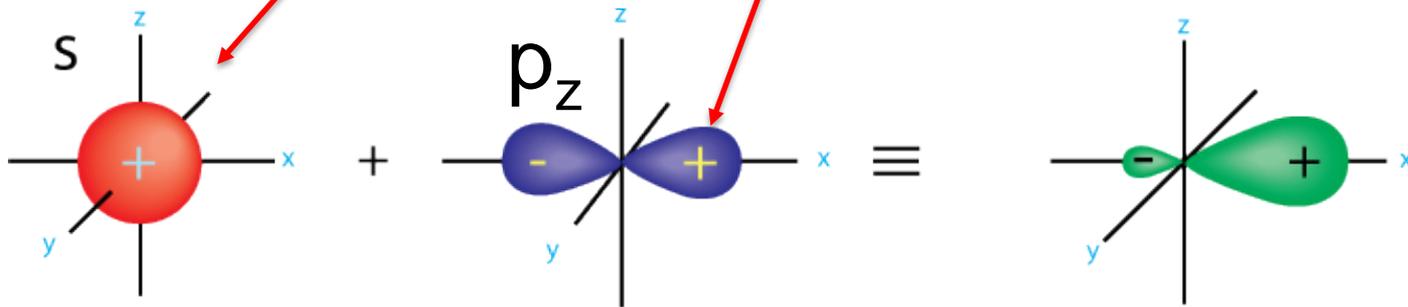


The electron density would oscillate back and forth, and would be in **RESONANCE** with high frequency light

$$\Psi_{1,0,0} = \Psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\Psi_{2,0,0} = \Psi_{2s} = \frac{1}{4\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$\Psi_{2,1,0} = \Psi_{2p} = \frac{1}{4\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \cos \theta$$

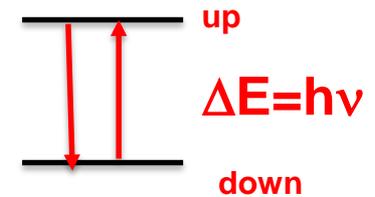


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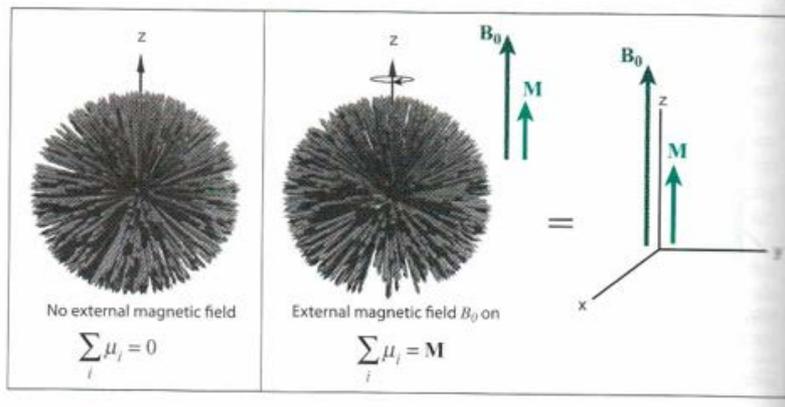
$$\Psi_{total} = c_{up} \Psi_{up} e^{-i \frac{2\pi E_{up} time}{h}} + c_{down} \Psi_{down} e^{-i \frac{2\pi E_{down} time}{h}}$$

$\Psi_{up}$  and  $\Psi_{down}$  are “orbitals” i.e., wavefunctions for the nuclear spin.

The **Time Dependent** Schrodinger Equation says that the individual parts **oscillate** at a frequency given by their energy/Plancks constant & cause **PRECESSION**

The **squares** of the coefficients gives probability to observe in the **up or down** state  
i.e.,  **$c_{up}^2 + c_{down}^2 = 1$**

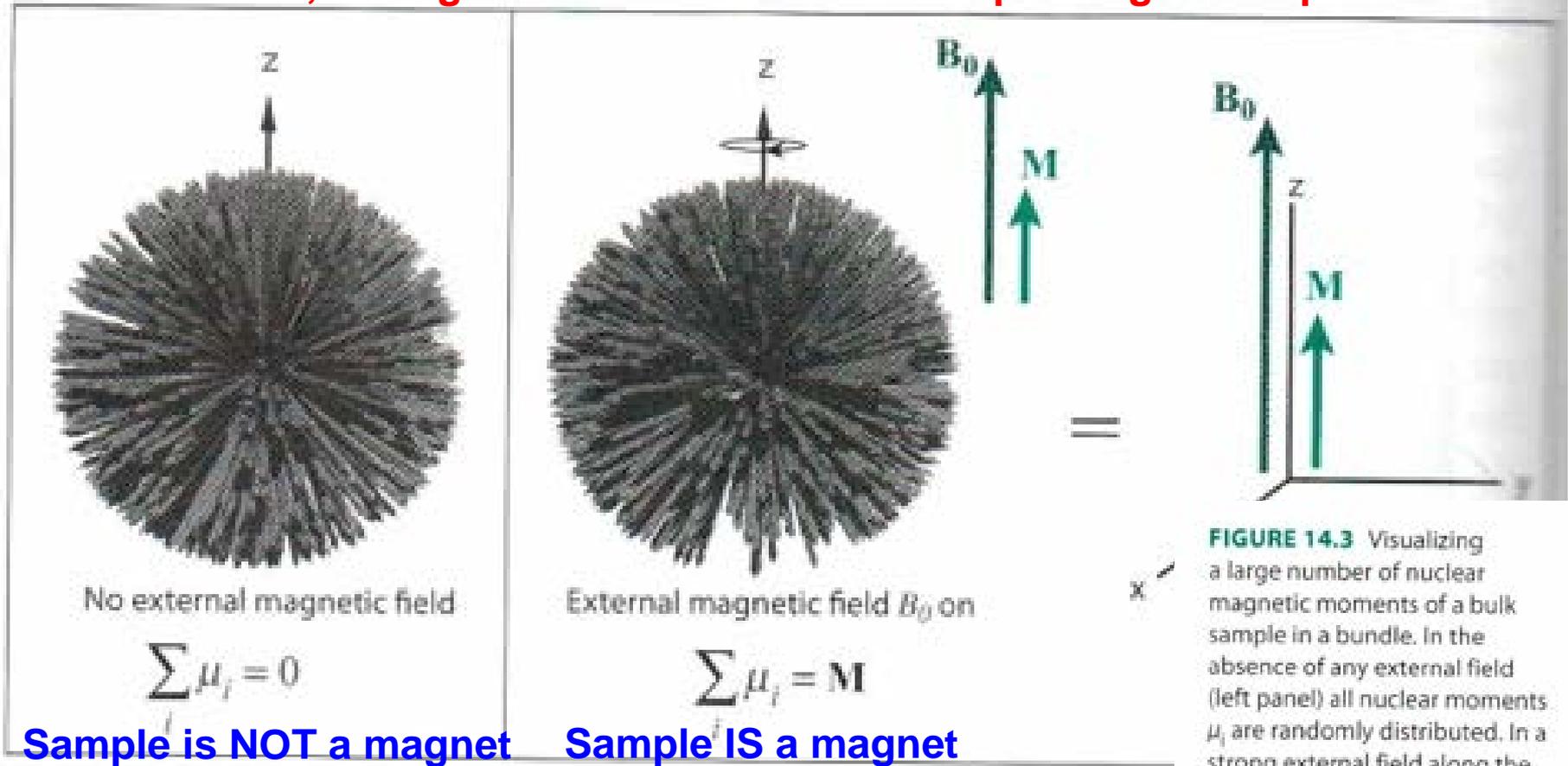
**FIGURE 14.3** Visualizing a large number of nuclear magnetic moments of a bulk sample in a bundle. In the absence of any external field (left panel) all nuclear moments  $\mu_i$  are randomly distributed. In a strong external field along the z-axis ( $B_0$ , right panel), the individual moments are very weakly biased towards the z-axis (the bias is exaggerated 100 fold in the right panel). A vector sum of all of the individual moments reveals the bulk magnetization  $M$  parallel to  $B_0$ . As we discuss shortly, the individual nuclear moments rotate around  $B_0$ , a motion termed ‘precession.’



The lines pointing in all directions give an idea of the proportion of spin up and spin down for each of the spins.

The relative signs of  $c_{up}$  and  $c_{down}$  give **direction**

**Resultant i.e., average of about  $10^{20}$  individual spin magnetic dipoles**



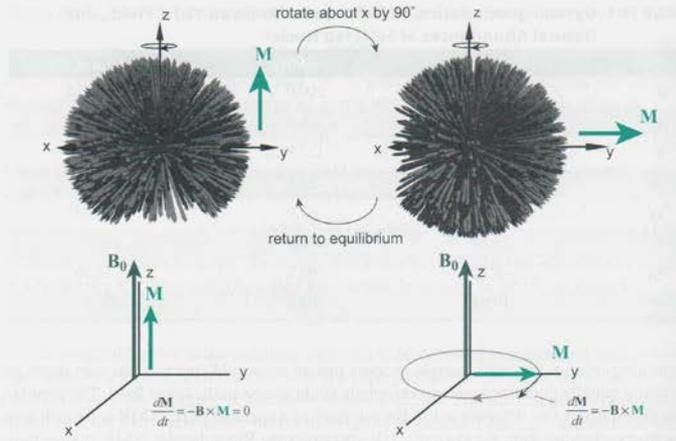
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**Exaggerated depiction of the .01 % fewer spin down (high energy) spins.**

**Note that all energies and directions are possible!!**

# Result of an very short, INTENSE pulse of radio frequency light

**FIGURE 14.4** Schematic of the behavior of both individual and bulk magnetic moments that are parallel (left) or perpendicular (right) to the  $B_0$  field. At equilibrium (left) the individual moments precess but  $M$  does not. If the nuclei have been perturbed, then both the individual and bulk moments precess (right panel). The dynamics of the bulk magnetization  $M$  are always due to the average behavior of a large number of nuclear spins.

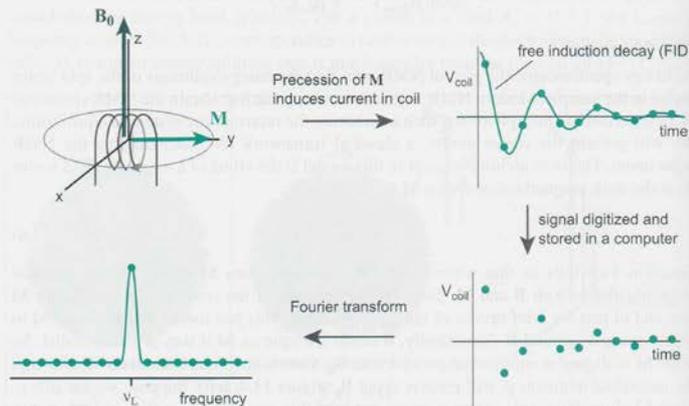


angle between  $B_0$  and  $M$ , and so  $M$  must rotate around  $B_0$  according to Eq. 14.6. This motion is termed precession, and the frequency of the precession is exactly the Larmor frequency that we wish to know. In order to detect the Larmor precession frequency of  $M$ , a coil is placed around the sample along the  $y$ -axis (figure 14.5). The coil experiences an oscillating magnetic field due to the linearly oscillating  $y$  component of the precessing vector  $M$

$$M_y(t) = M \cos(2\pi\nu t)e^{-t/T_2}, \quad (14.7)$$

where  $T_2$  is a time constant governing the loss of the magnetization in the  $xy$ -plane. The vector will precess at the Larmor frequency and will return to be aligned along the positive

**FIGURE 14.5** Signal detection in an NMR experiment. The precessing bulk magnetization  $M$  induces an oscillating current in the coil which may be detected and digitized using electronic test equipment.



Each spin is precessing.

Tipping because the applied pulse can only interact with those individual spins that are **in phase** with the pulse—a small percentage of the many spins. (These have been **coherently** excited. A transient state of **coherence** was created.

**The whole magnet will tip by an angle proportional to how long the pulse is on because certain spins are driven from low to high energy and certain others are driven from high to low energy**

TWO RELAXATION TIMES,  $T_1$  and  $T_2$ :

Returning to Boltzmann energy equilibrium is  $T_1$

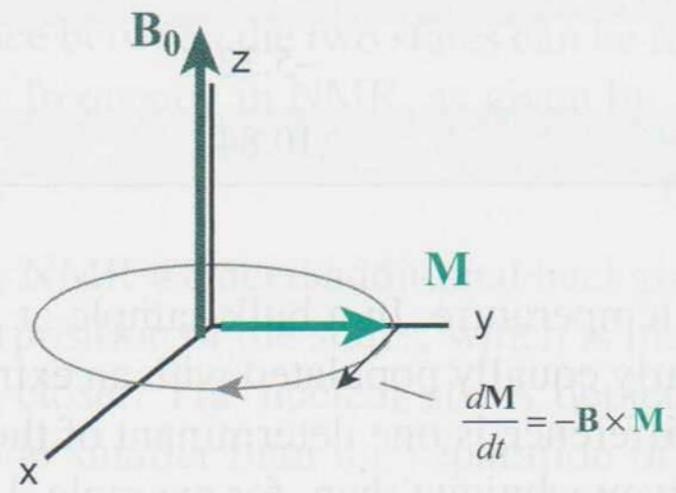
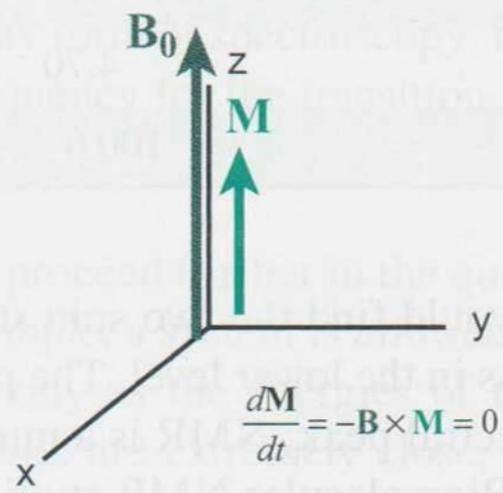
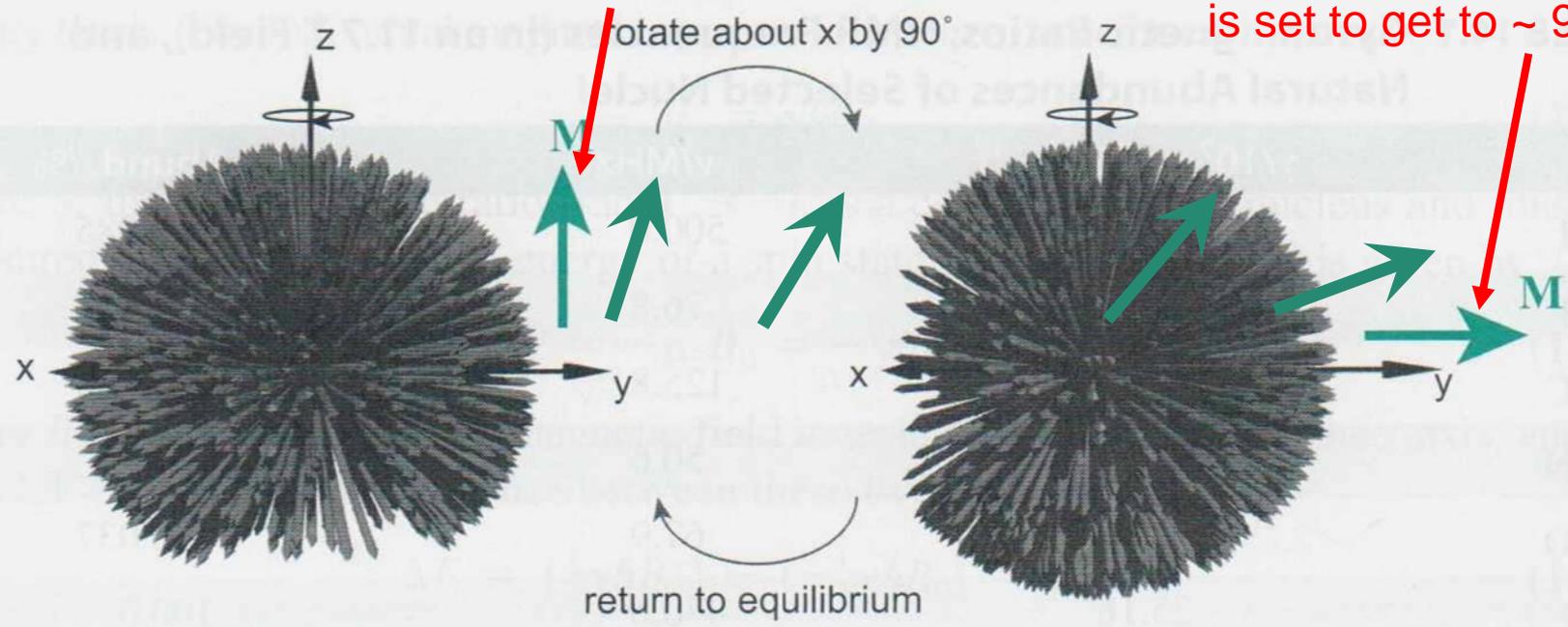
Disordering of COHERENCE (dephasing) is  $T_2$ .

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# Resultant i.e., average of about $10^{20}$ individual spin magnetic dipoles

Before microsecond Pulse of radio frequency

Pulse power and duration is set to get to  $\sim 90^\circ$



very short pulse contains many frequencies

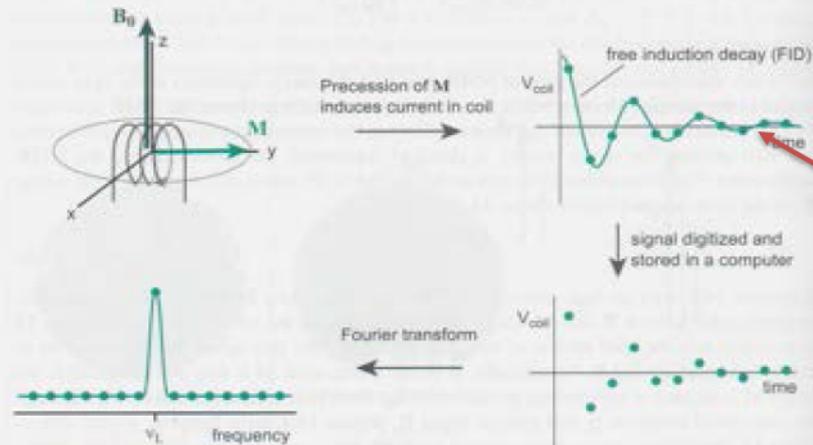
**Intense pulse of radio freq.** in coil perpendicular changes ratio of up/down from .9999 to 1.0 Causes **coherent motion** of the 0.0001 excess spin up. So sample magnet points horizontally. Creates signal in receiver coil (not shown).

Entropy makes sample return to **most probable state** (Boltzmann distribution). Time to do so is called the  **$T_1$  relaxation time**. (1<sup>st</sup> order rate constant is  $1/T_1$ )

$$M_x(t) = M \cos(2\pi\nu t) e^{-t/T_2} \quad (14.7)$$

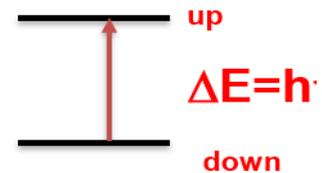
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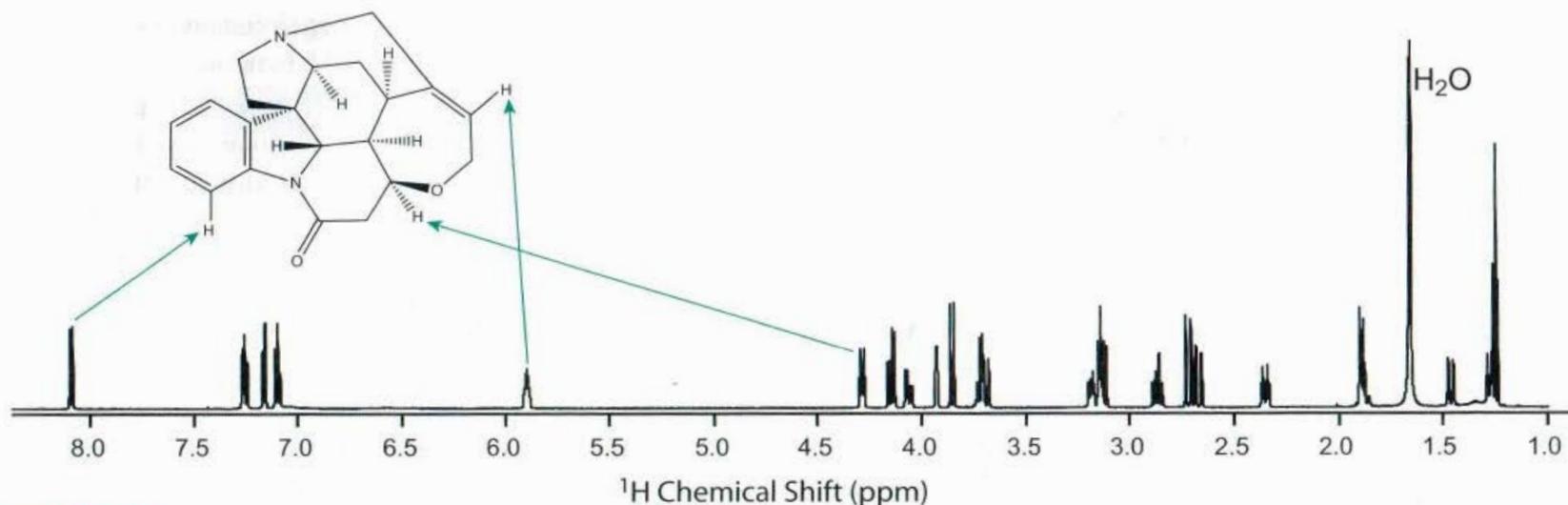


**Fourier transform of these oscillations give the entire NMR spectrum**

Another very important relaxation is the called the  $T_2$  relaxation time which comes from the dephasing of the individual spins due to collisions. The ordering caused by the pulse causing the net dipole of the spins to add up to a vector pointing in the  $y$  direction initially, and direction rotating at a frequency given by  $(E_{up} - E_{down})/h$  is ruined by the thermal motion. But the energy is not lost so quickly. The phase information is not lost! A second pulse twice as long as the first will reverse the phases and therefore the direction of rotation. Those vectors that lagged behind will be leading the pack, and all will reach the “finish line” simultaneously. Almost all the signal comes back for a brief time. This is called a **“SPIN ECHO”**. Please go to: [http://en.wikipedia.org/wiki/Spin\\_echo](http://en.wikipedia.org/wiki/Spin_echo) for nice visual demos.



Analyzing the frequencies making up the decaying oscillations (Fourier Transforming the oscillations) provides the spectrum.



**FIGURE 14.1** The  $^1\text{H}$  NMR spectrum of strychnine (5 mM, 600 MHz) in deuteriochloroform ( $\text{CDCl}_3$ ) illustrates the ability of NMR to obtain richly detailed information on complex molecules with atomic resolution. Each H atom gives a distinct signal with a characteristic position, splittings and relative intensity that is determined by the structure of the molecule. All signals are assigned, and a few representative assignments are shown on the figure (for clarity, not all H atoms are depicted). Complete assignments are performed with the aid of multidimensional NMR experiments. A residual signal from protonated chloroform ( $\text{CHCl}_3$ ) has been digitally removed, while dissolved  $\text{H}_2\text{O}$  is noted.

**T1** is called **“spin lattice relaxation time”**.

This simply means that the thermal motion of solvent creates some oscillating magnetic fields that are in resonance, thus causing transitions.

Another type of relaxation is the T2 relaxation time, called **“spin-spin relaxation”**

[http://en.wikipedia.org/wiki/Spin%E2%80%93spin\\_relaxation](http://en.wikipedia.org/wiki/Spin%E2%80%93spin_relaxation)

$T_2$  relaxation generally proceeds more rapidly than  $T_1$  relaxation.

Different samples and different biological tissues have different  $T_2$ .

Fluids have the longest  $T_2$ s (~5000 ms for [protons](#)),

and water based tissues are in the 40–200 [ms](#) range,

while fat based tissues are in the 10–100 ms range.

Amorphous solids have  $T_2$ s in the 1-10 ms range,

crystals have  $T_2$ s around the 0.05 ms range.

**What is the pattern?????**

[http://en.wikipedia.org/wiki/Spin\\_echo](http://en.wikipedia.org/wiki/Spin_echo)