Resonant frequency is RADIO FREQUENCY; Wavelength is ~ ½ meter, so **Entire sample literally feels oscillating magnetic field.**

Einstein pointed out that **excitation is stimulated from the high state to low state at same rate as excitation upwards.**

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 the there are two quantum “energy levels”: spin up and spin down, there is a continuous mixture. The spins are all in superposition states.

$$\Psi_{\text{total}} = c_{\uparrow} \Psi_{\uparrow} e^{-i \frac{2\pi E_{\uparrow}}{h} \text{time}} + c_{\downarrow} \Psi_{\downarrow} e^{-i \frac{2\pi E_{\downarrow}}{h} \text{time}}$$

$$\Psi_{\uparrow}$$ and $$\Psi_{\downarrow}$$ 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., $$c_{\uparrow}^2 + c_{\downarrow}^2 = 1$$

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 $$c_{\uparrow}$$ and $$c_{\downarrow}$$ give direction.
Each spin 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.

The whole magnet will tip by an angle proportional to how long the pulse is on.

TWO RELAXATION TIMES, T1 and T2:

Returning to Boltzmann energy equilibrium is T1

Returning to degeneracy (phase) equilibrium is T2.

http://en.wikipedia.org/wiki/Spin_echo
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. (1st order rate constant is $1/T_1$)

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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.
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

$T_2$ 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???????
INTRODUCTION TO QUANTUM MECHANICS
OR
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...*

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, 23rd Printing, 1998*
In other words, \( h \) is an experimentally derived constant.
No theory predicts \( h \)

Around **1905**, Max Planck was working hard on trying to understand this behavior. Classical mechanics **worked fine at the LONG wavelengths but NOT at short wavelengths.**

Planck found that if energy of matter was quantized so that \( \Delta E = h\nu = h\frac{c}{\lambda} \)
then **classical mechanics predicted the curves perfectly!!!!**
Planck **varied** \( h \) and found that **6.62 x 10^{-34} gave a perfect match to experiment.**

In other words, \( h \) is an **experimentally derived** constant.
So was born the **FIRST QUANTUM CONCEPT:** Energy is quantized!

Classical thinking does not work for light. $\Delta E = h\nu$

If the structure of the atom were known in 1905 this would have been much more evident.

The mystery could be stated as a very striking problem obvious to chemists.

**THE ELECTRON WILL NOT FALL TO THE NUCLEUS!!!**
despite ENORMOUS Coulomb force.

The *lowest* energy state (1s orbital) of the hydrogen atom.

![Proton and electron](image)

Probability slice through the 1s orbital. The blue line is the square of the wavefunction (orbital).

Most probable point is AT NUCLEUS.
**Most probable DISTANCE is AT Bohr radius**