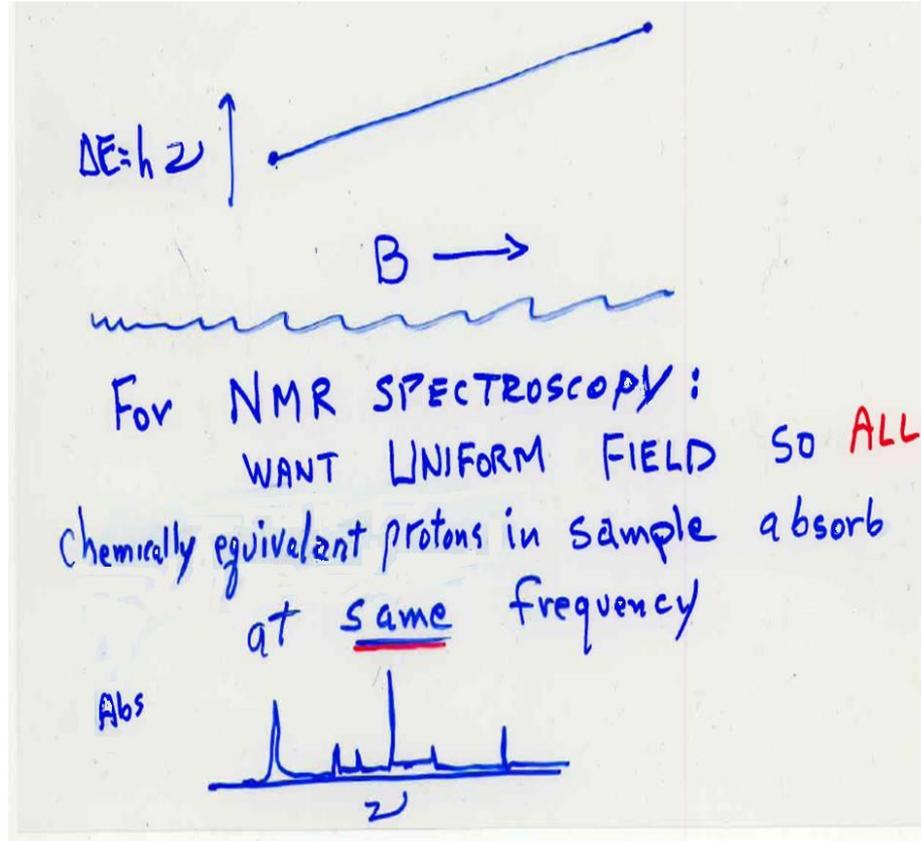


NMR Spectroscopy vs. MRI:

316-17 Lec 41
Mon 20nov17



The applied magnetic field is **same everywhere in sample.**

Field at the nucleus is **reduced** because of **electron density**
so **each chemically distinct H has a slightly different resonant frequency**
i.e., CHEMICAL SHIFT

For MRI (magnetic resonance imaging):

Applied **field is deliberately made to vary across the sample.**

Frequency set to **ONLY MEASURE WATER**

Then, **protons in different parts of sample will resonate at different frequency**

Only because of POSITION;

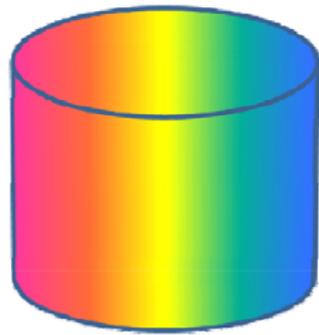
NOT because of different chemical shift

MRI Detects primarily two things:

(1) **amount of water at different positions**

(2) and **direction of diffusion** (more difficult)

Using color to indicate frequency in different parts of the sample



red is low frequency (because *low* field)
blue is high frequency (because *high* field)

Protons in different places absorb different frequencies.

Field increasing in x



Resonant frequency ν_r increasing in x

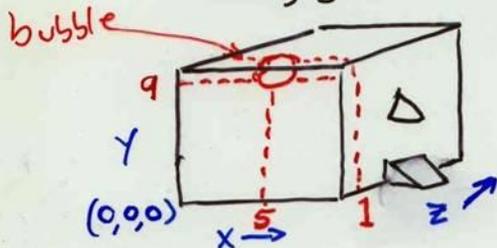


Field increasing in z

Resonant frequency ν_r increasing in z

MRI - Magnetic Resonance Imaging.

Consider a $10 \times 10 \times 10$ inch "Beaker" of water with "nose", "jaw", and "tumor" ← bubble of air.

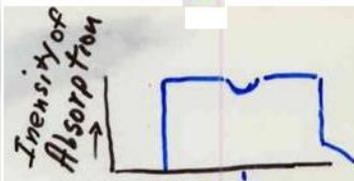
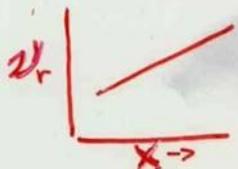
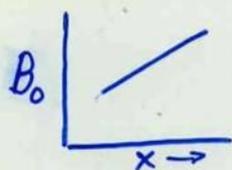


"Tumor" is located at:

$$\begin{aligned} x &= 5 \\ y &= 9 \\ z &= 1 \end{aligned}$$

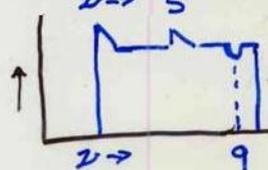
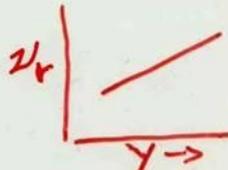
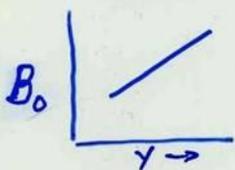
Take 3 spectra with magnetic field gradient $\leftarrow B_0$ along $x, y,$ or z .

Remember, $\nu_r \leftarrow$ resonant frequency for water. proportional to magnetic field strength

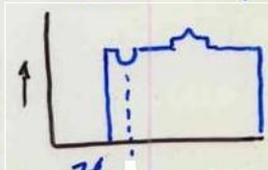
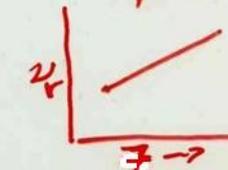
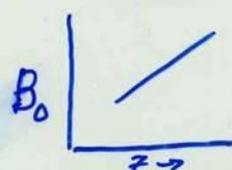


Gradient

X

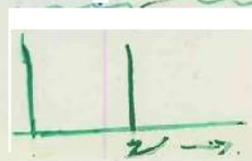
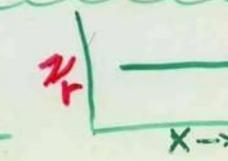
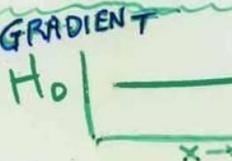


Y



Z

NO GRADIENT

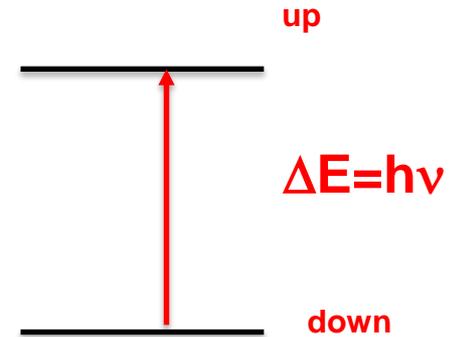


Now we return to NMR and learn the reality at 300K:

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

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

$$= e^{-\frac{0.02 \text{ cm}^{-1}}{209.1 \text{ cm}^{-1}}} = e^{-0.0001} = 0.9999$$

$$= e^{-\frac{0.02}{209}} = e^{-0.0001} = 0.9999$$

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:

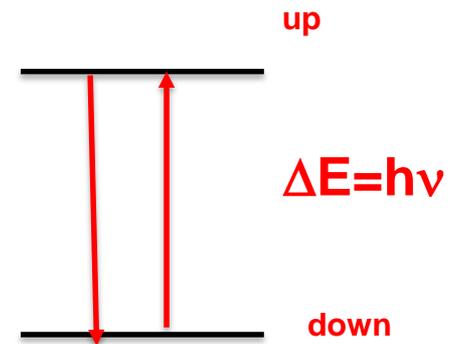
$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{k_B T}} = e^{-\frac{\Delta E/hc}{k_B T/hc}} = e^{-\frac{0.02 \text{ cm}^{-1}}{0.697 \text{ cm}^{-1} \text{ K}^{-1} \cdot 300 \text{ K}}}$$

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

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

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

(predicted LASERS 60 years before they could be created)



Resonant frequency is RADIO FREQUENCY;

Wavelength is $\sim \frac{1}{2}$ meter, so

Entire sample literally feels oscillating magnetic field.

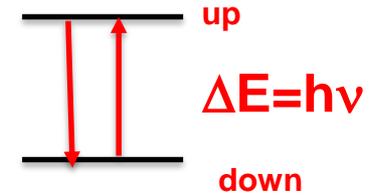
At room temperature only 0.01 % more in lowest state than in highest state

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.

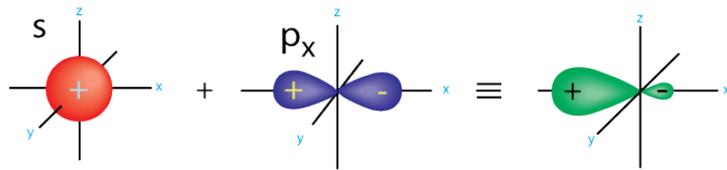
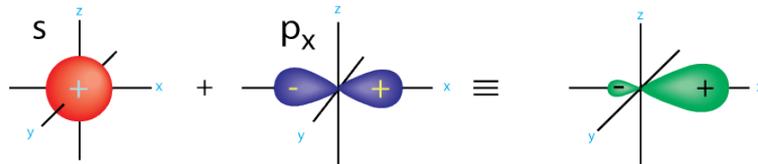


$$\Psi_{total} = c_{up} \Psi_{up} e^{-i \frac{2\pi E_{up} time}{h}} + c_{down} \Psi_{down} e^{-i \frac{2\pi E_{down} time}{h}}$$

Ψ_{up} and Ψ_{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

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



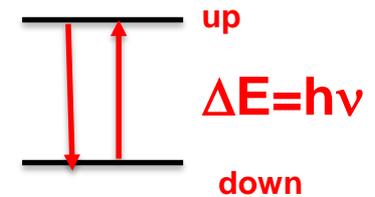
The electron density would oscillate back and forth, and would be in **RESONANCE** with high frequency light

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.



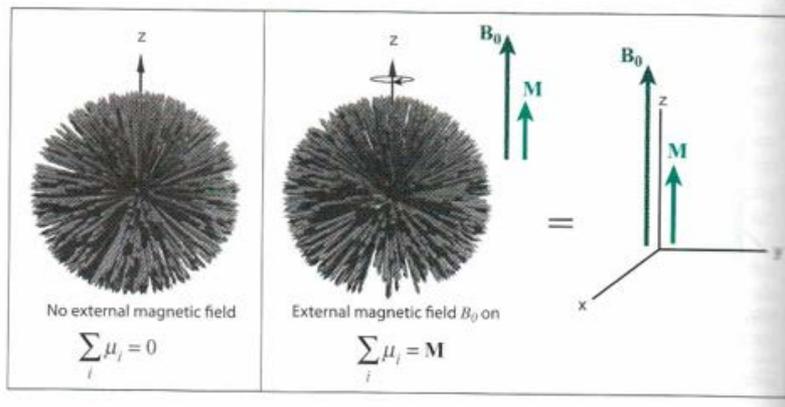
$$\Psi_{total} = c_{up} \Psi_{up} e^{-i \frac{2\pi E_{up} time}{h}} + c_{down} \Psi_{down} e^{-i \frac{2\pi E_{down} time}{h}}$$

Ψ_{up} and Ψ_{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 μ_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.’

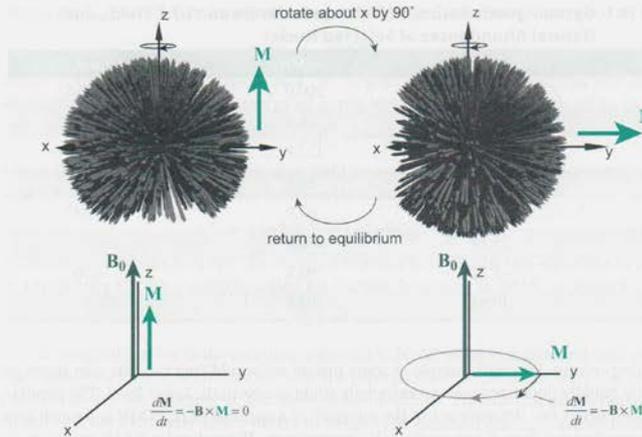


The lines pointing in all directions give an idea of the proportion of spin up and spin down for each of the spins.

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

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.

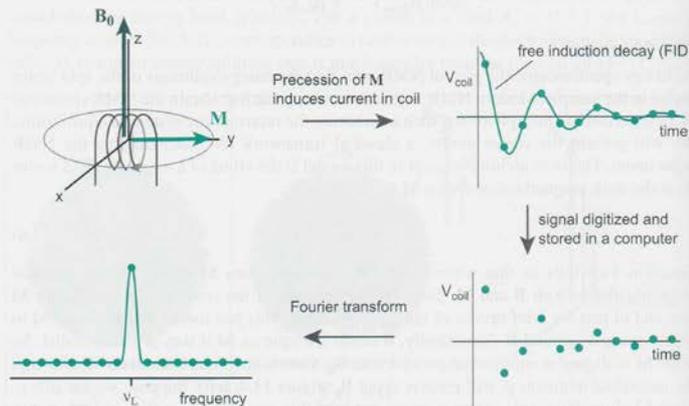


angle between B_0 and M , and so M must rotate around B_0 according to Eq. 14.6. This motion is termed precession, and the frequency of the precession is exactly the Larmor frequency that we wish to know. In order to detect the Larmor precession frequency of M , a coil is placed around the sample along 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.



A very short pulse contains many frequencies. That is, it may be expressed as a linear combination of many cosine and sine waves. i.e., its **Fourier Transform** has frequencies.

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

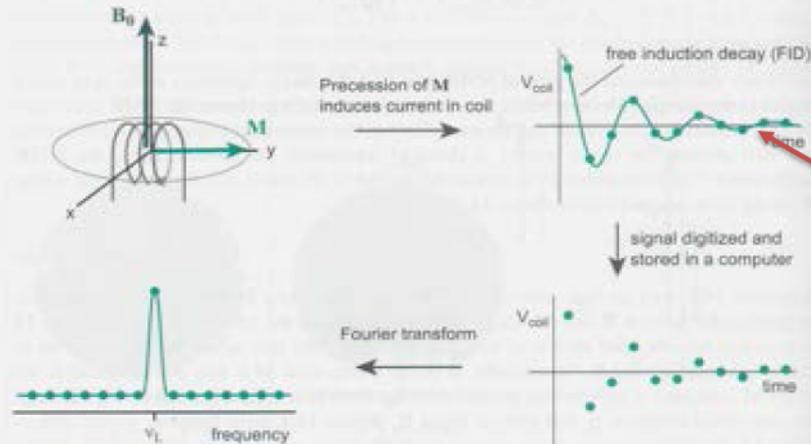
The whole magnet will tip by an angle proportional to how long the pulse is on.

very short pulse contains many frequencies

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

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.



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).

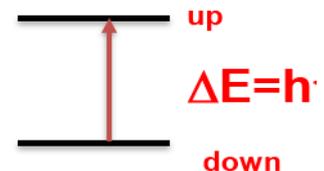
Entropy makes sample return to **most probable state** (Boltzmann distribution). Time to do so is called the **T_1 relaxation time**. (1st order rate constant is $1/T_1$)

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 for nice visual demos.

http://en.wikipedia.org/wiki/Spin_echo



This is the **Fourier Transform** of the “free induction decay” from Figure 14.5

These are amounts and frequencies that when summed give the free induction decay from the short intense pulse of radio frequency

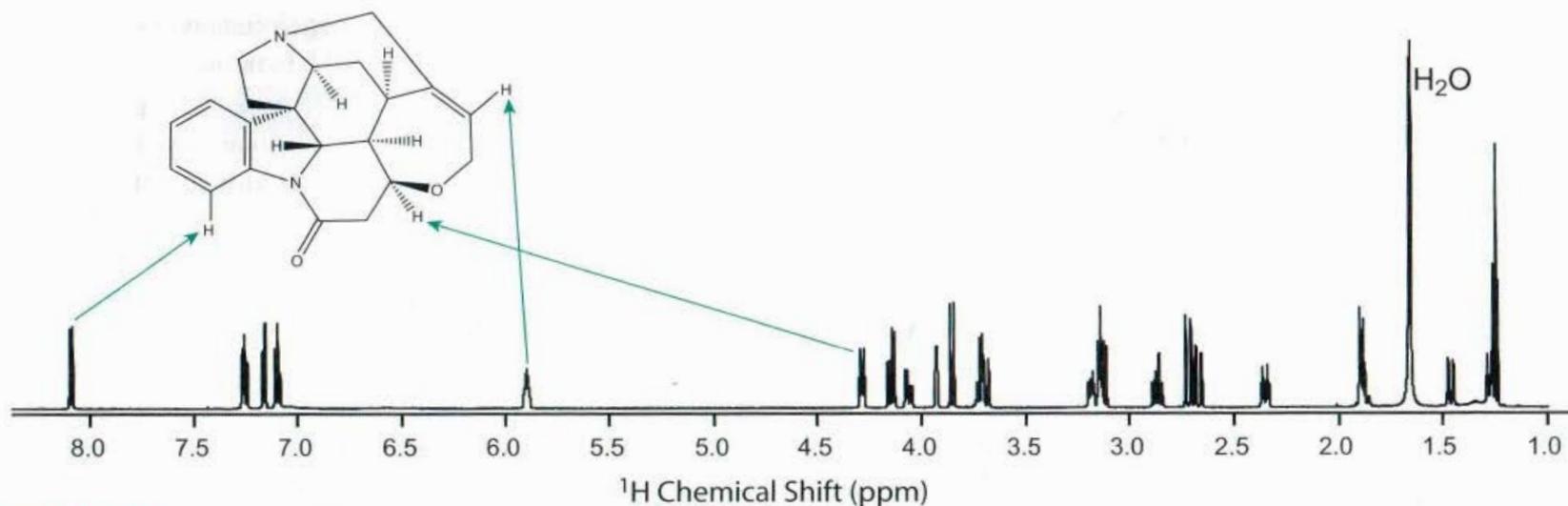


FIGURE 14.1 The ¹H NMR spectrum of strychnine (5 mM, 600 MHz) in deuteriochloroform (CDCl₃) illustrates the ability of NMR to obtain richly detailed information on complex molecules with atomic resolution. Each H atom gives a distinct signal with a characteristic position, splittings and relative intensity 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 (CHCl₃) has been digitally removed, while dissolved H₂O is noted.