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

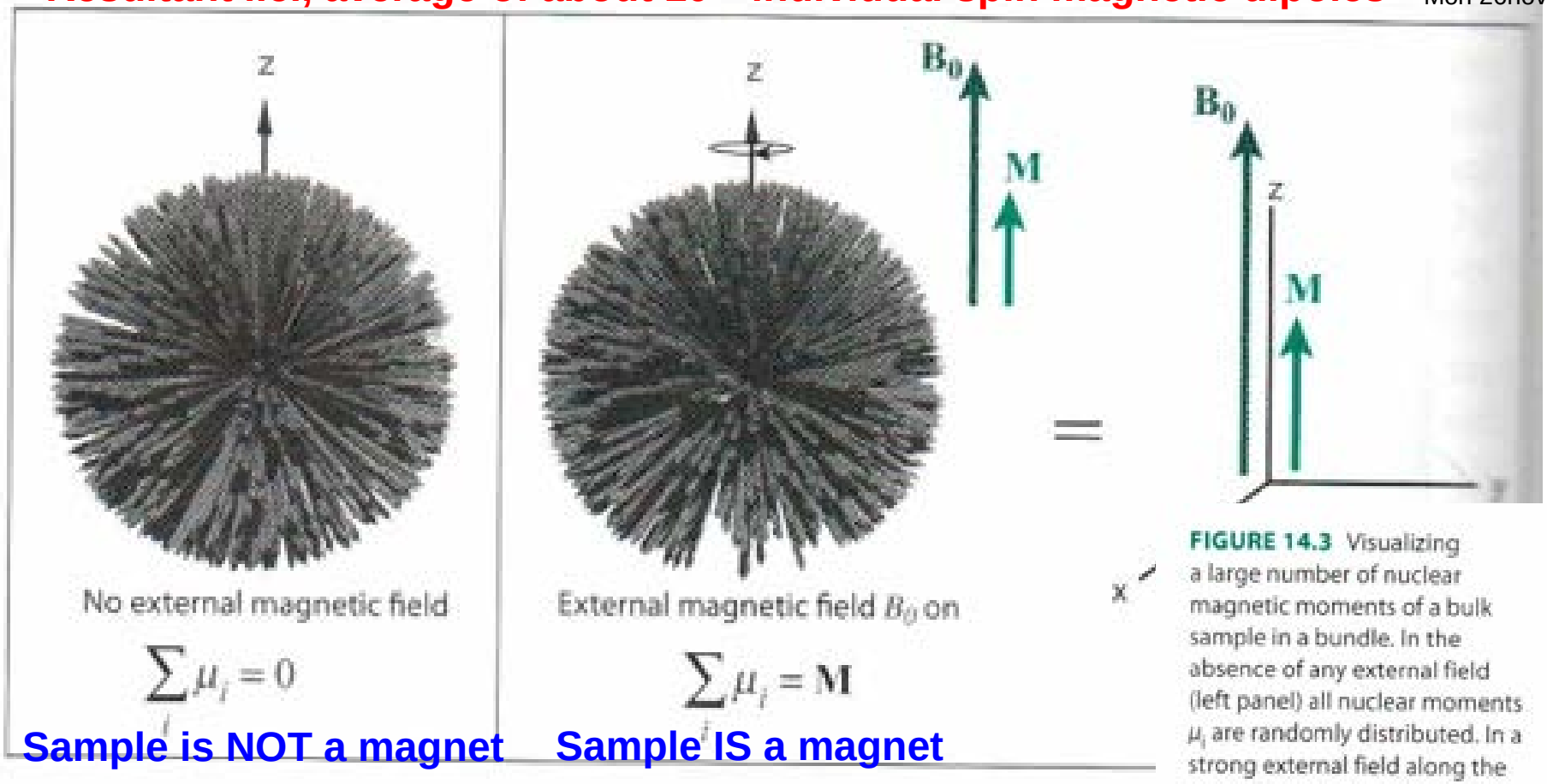


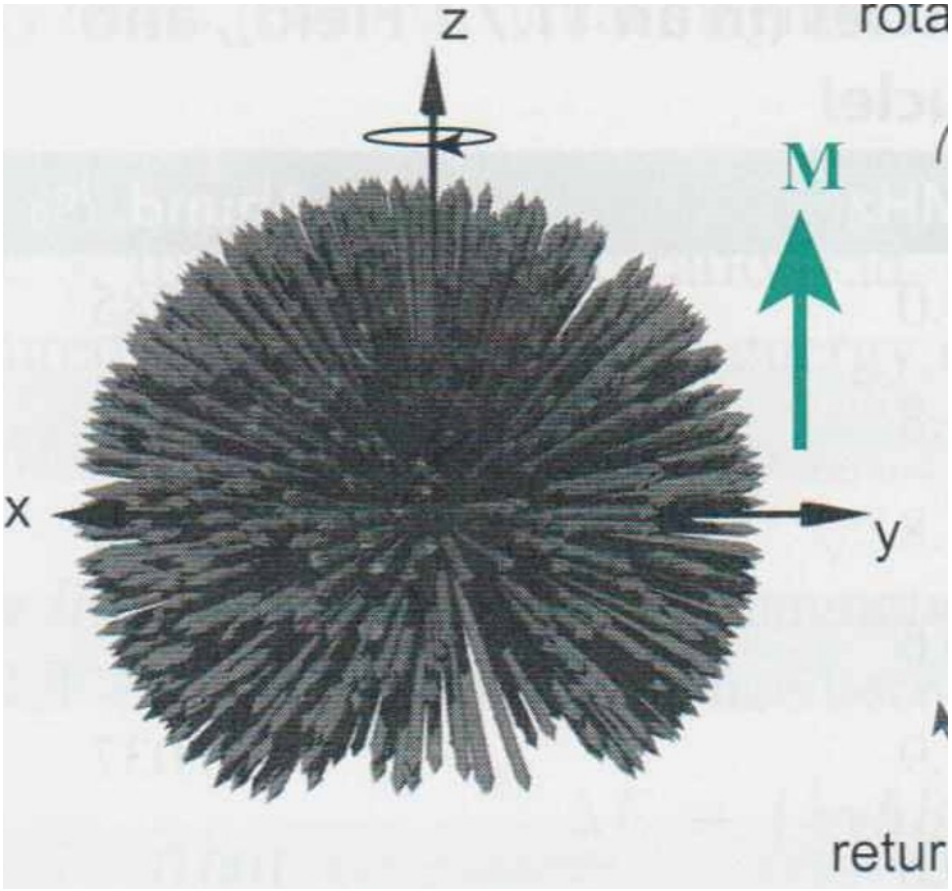
FIGURE 14.3 Visualizing a large number of nuclear magnetic moments of a bulk sample in a bundle. In the absence of any external field (left panel) all nuclear moments μ_i are randomly distributed. In a strong external field along the z-axis (B_0, right panel), the individual moments are very weakly biased 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 $\mathbf{B}_0$. As we discuss shortly, the individual nuclear moments rotate around B_0, a motion termed 'precession.'

Sample is NOT a magnet **Sample IS a magnet**

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

Note that all energies and directions are possible!!


3+
ORIGINAL
ORIGINAL
KOOSH


z
M
x
y

Result of an very short INTENSE pulse of radio frequency light

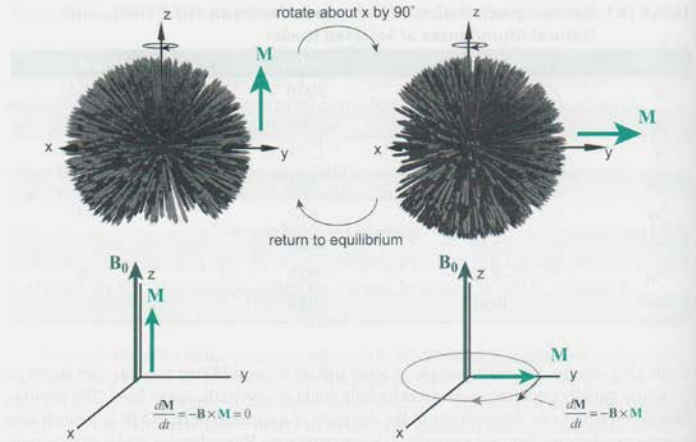


FIGURE 14.4 Schematic of the behavior of both individual and bulk magnetic moments that are parallel (left) or perpendicular (right) to the B_0 field. At equilibrium (left) the individual moments precess but M does not. If the nuclei have been perturbed, then both the individual and bulk moments precess (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 $\mathbf{B_0}$ and $\mathbf{M}$, and so $\mathbf{M}$ must rotate around $\mathbf{B_0}$ 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 $\mathbf{M}$, 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 $\mathbf{M}$

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

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

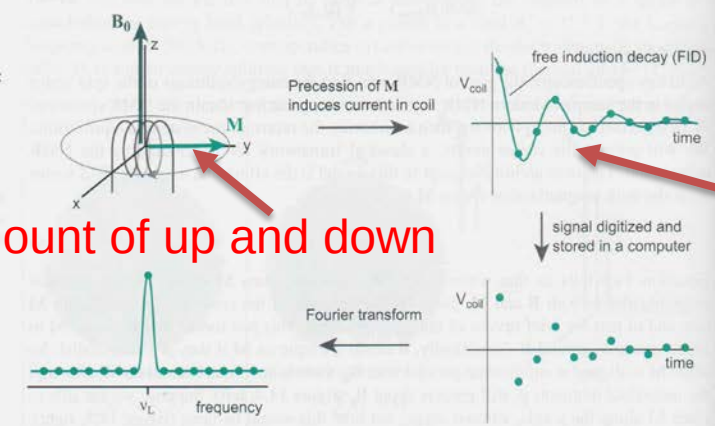


FIGURE 14.5 Signal detection in an NMR experiment. The precessing bulk magnetization **M** induces an oscillating current in the coil which may be detected and digitized using electronic test equipment.

EQUAL amount of up and down

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 EQUILIBRIUM, i.e., Boltzmann energy equilibrium is **T1**

Returning to degeneracy (phase) equilibrium is **T2**.

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

BUT HOW IS EQUILIBRIUM ESTABLISHED???

Vapor Pressure Movie (15th Grade Version)

Much of the "heat" making the 300 K temperature comes from rotating dipoles of water molecules.

This creates oscillating electric and magnetic fields, some of which is in resonance, **$\Delta E = h\nu$.**

So there is constantly excitation and de-exciting.

This thermal excitation is slow.

Modern NMR: Series of very strong , short pulses of radiofrequency

Transitions are not instantaneous!

Quantum mechanics says a single spin in resonance will do the following:

$$\psi_{down} -> \quad \psi_{down} + \psi_{up} \quad -> \quad \psi_{up} \quad -> \quad \psi_{up} - \psi_{down} \quad -> \quad -\psi_{down}$$

When the pulse comes each spin will start in a different place, but will go through the sequence.

Wavlength is ~ ½ meter, so

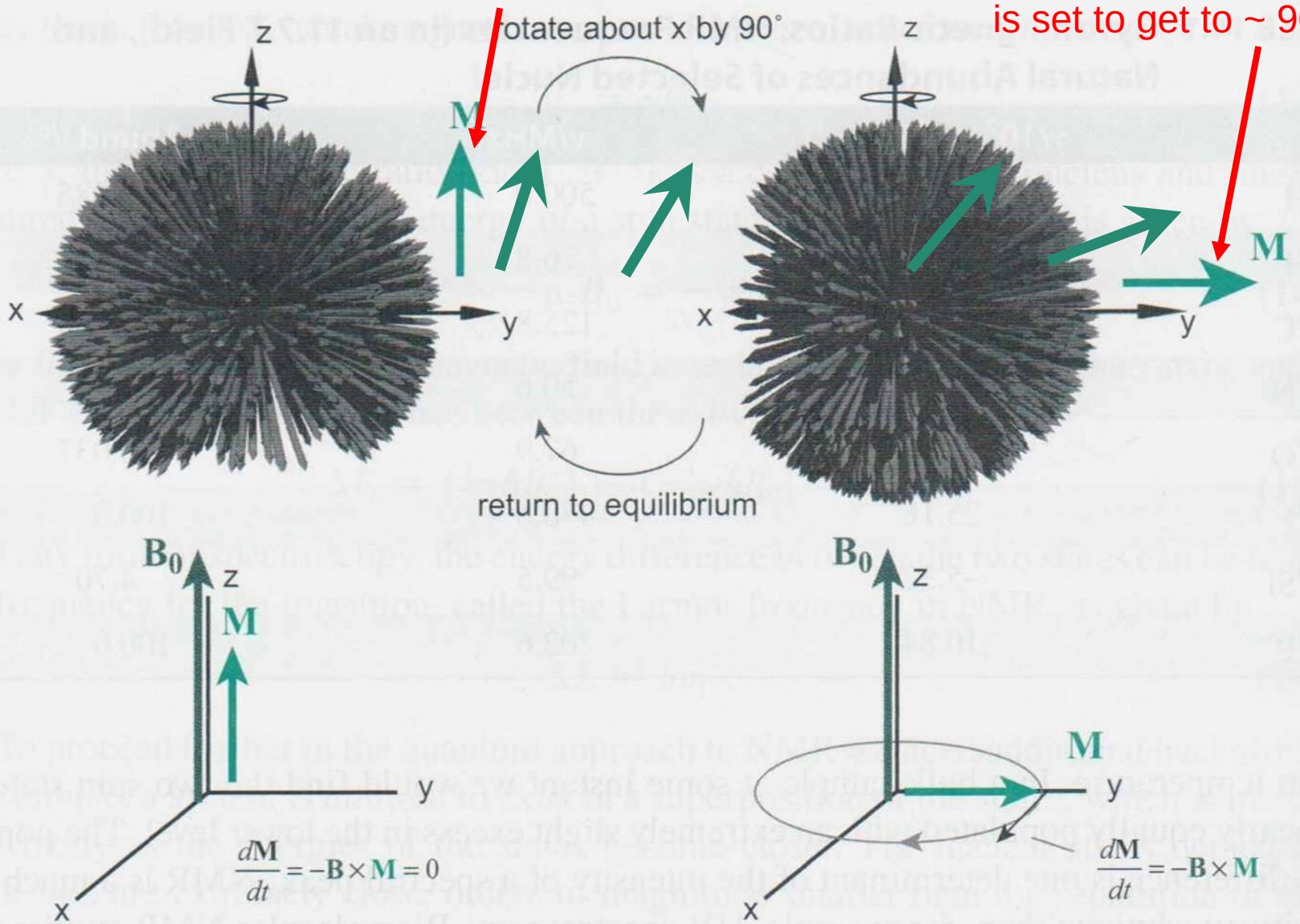
<u>Entire sample literally feels oscillating magnetic field.</u>

ance

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 ~ 90º



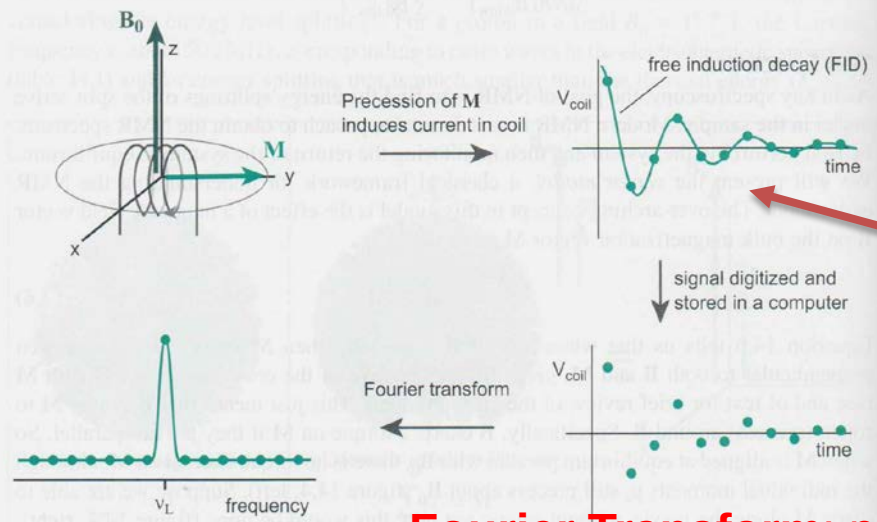


FIGURE 14.5 Signal detection in an NMR experiment. The precessing bulk magnetization **M** induces an oscillating current in the coil which may be detected and digitized using electronic test equipment.

1/e time for returning returning to EQUILIBRIUM, i.e., Boltzmann energy equilibrium is **T1**

Fourier Transform: picking out the frequencies in the signal.

Time to randomize the "phase" of the selected spin vectors (dephasing) equilibrium is **T2**.

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

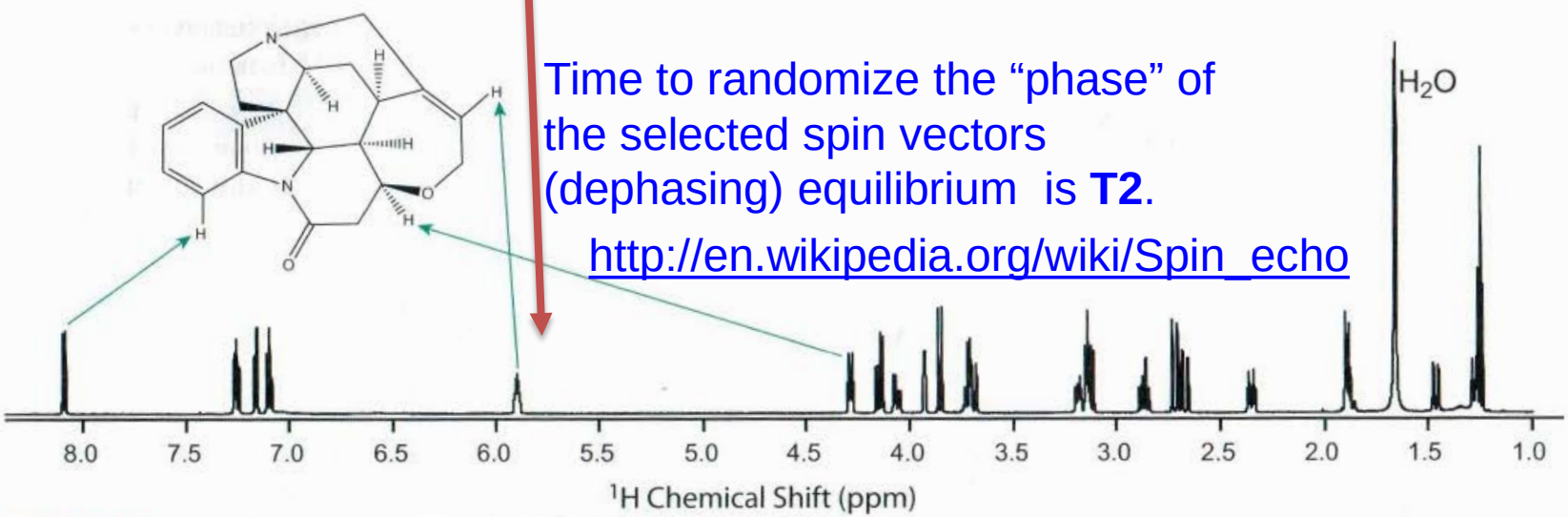


FIGURE 14.1 The ^{1}H NMR spectrum of strychnine (5 mM, 600 MHz) in deuterocholoroform ($CDCl_3$) illustrates the ability of NMR to obtain richly detailed information on complex molecules with atomic resolution. Each H atom gives a distinct signal with a characteristic position, splittings and relative 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 ($CHCl_3$) has been digitally removed, while dissolved H_2O 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

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_2s ~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_2s in the 1-10 ms range,

crystals have T_2s around the 0.05 ms range.

What is the pattern?????

very short pulse contains many frequencies

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

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

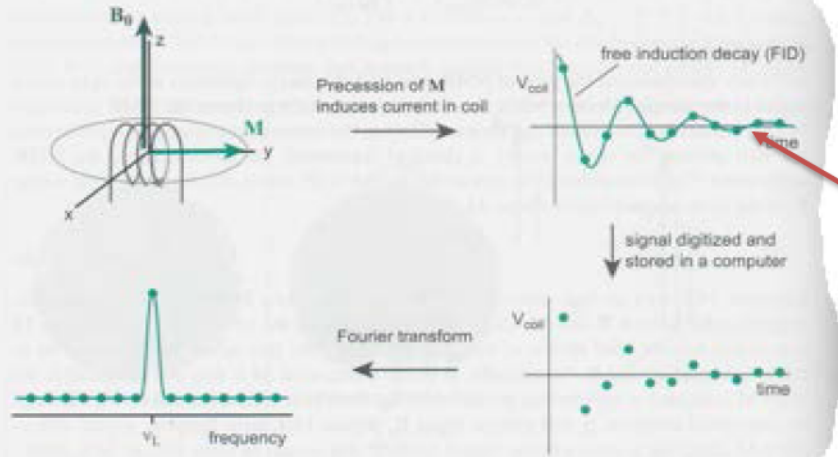


FIGURE 14.5 Signal detection in an NMR experiment. The precessing bulk magnetization **M** induces an oscillating current in the coil which may be detected and digitized using electronic test equipment.

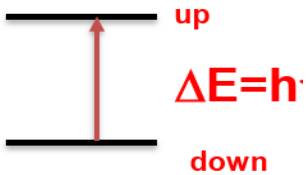
Intense pulse of radio freq. in coil perpendicular changes ratio of up/down from .9999 to 1.0 Causes ***coherent motion*** of the 0.0001 excess spin up.

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

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 <u>electrons</u>

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

Light emitted by all objects not at 0 Kelviin.

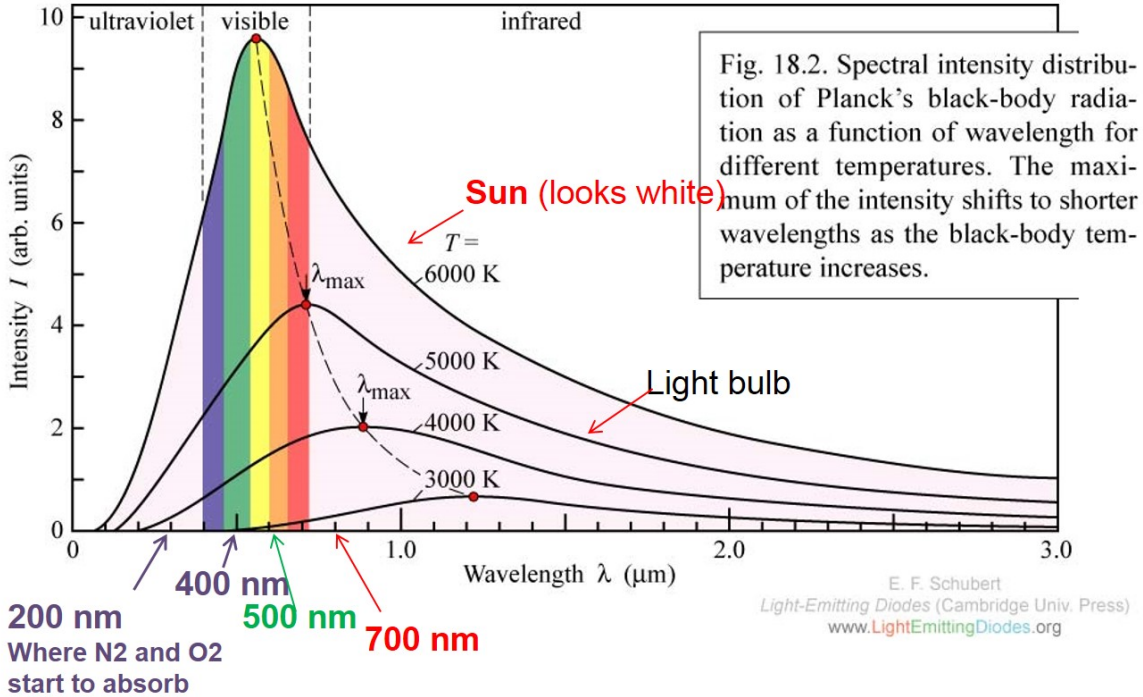


Fig. 18.2. Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The maximum of the intensity shifts to shorter wavelengths as the black-body temperature increases.

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 $\Delta E = h\nu = hc/\lambda$
then classical mechanics predicted the curves perfectly!!!!

Planck **<u>varied</u>** ***h*** and found that ***6.62 x 10^{-34} gave a perfect match to experiment.***

In other words, **h** is an ***<u>experimentally derived</u>*** constant.
No theory predicts h

Light emitted by all objects not at 0 Kelviin.

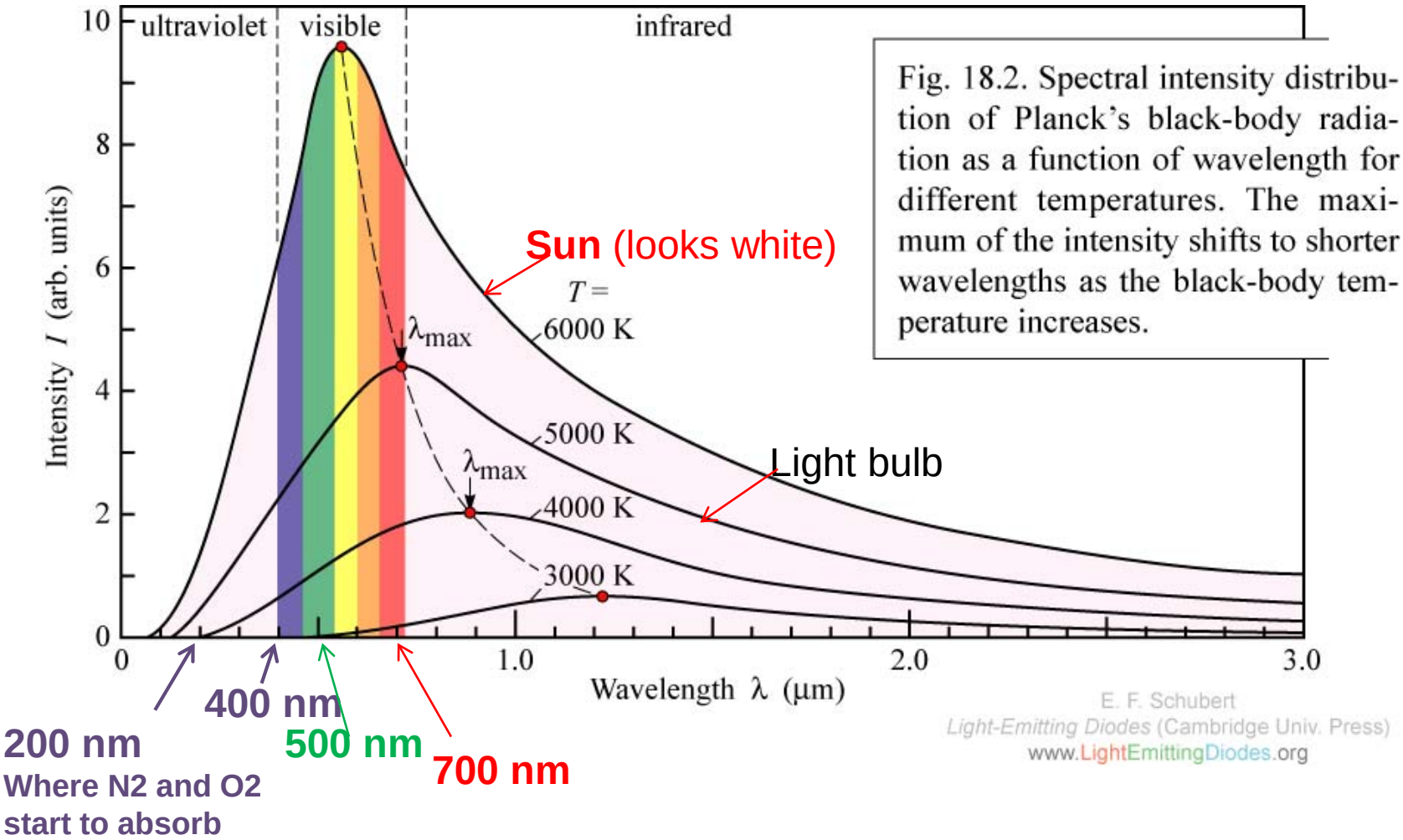


Fig. 18.2. Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The maximum of the intensity shifts to shorter wavelengths as the black-body temperature increases.

Temperature dependence is from the Boltzmann ratio for probability for the hot matter to be in an excited state:

$\mathbf{N_{excited}/N_{ground}=exp(\Delta E/k_BT)}$, where $\mathbf{\Delta E= hc/\lambda}$

Planck ALSO determined the NUMERICAL value of Boltzmann's constant, k_B

So was born the **FIRST QUANTUM CONCEPT:** **Energy is quantized!**

Classical thinking does not work for electrons nor for light. $\Delta E = h\nu$

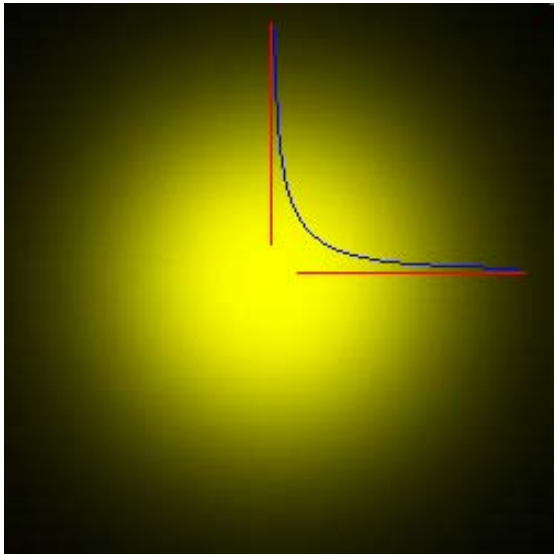
If the structure of the atom were known in 1905 this would have been much more evident.

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 electron



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

Coulomb's Law Force $\oplus \leftarrow 1\text{Å} \rightarrow \ominus$

$$\frac{(9\times10^{9})(1.6\times10^{-19})^{2}}{(1\times10^{-10}\,m)^{2}} = 2.3\times10^{-8}\ N$$

For 2 elementary charges 1Å apart.

at 0.01 Å 2.3×10^{-4} N

FOR ONE proton & ONE e^-

Equivalent to Gravitational force of EARTH ON 0.025 gram

But, Experimentally $\bar{e}$ is in the 1s orbital, even at 0 Kelvin!

Striking Example of Zero point Energy

KINETIC E = 1.3×10^{6} J/mol $u_{rms} = 2\times10^{6}\ ms^{-1}$

YET, IS ABSOLUTELY COLD (& DARK)

Quantum Behavior & Quantum Mechanics

Applies to EVERYTHING

But most evident for particles with mass equal or less than proton

Absolutely NECESSARY for electrons and light (photons),

which are neither particles or waves;
there is nothing like them in the macroscopic world !

Thus, Quantum Mechanics cannot be "understood" in the usual sense***—not even by the world's greatest minds.***

Quantum Mechanics was ***discovered***—NOT derived

Newton's Laws, however, **CAN** be derived from quantum mechanics

Quantum Mechanics has ***never failed*** to agree with experiment—yet.

Quantum Concepts

Who	When	What	Equation
1. Planck	1905	Quantization of Energy	$\Delta E = h\nu$
2. Einstein	1905	Particle Nature of Light	$p = h/\lambda$
3. DeBroglie	~1920	Wave Nature of Particles	$\lambda = h/p$
4. Bohr	~1920	Quantization of Angular Momentum	$L^2 = l(l+1)\,(h/2\pi)^2$; $L_z = m\,(h/2\pi)$ 2L+1 m values from –L to +L
5. Heisenberg	~1925	Uncertainty Principle	$\Delta p_x\,\Delta x \cong h$ or: "why the electron does not fall into the nucleus" i.e., the concept of **ZERO POINT ENERGY**

More on **zero point energy** and uncertainty principle

Zero point kinetic energy is $\cong$ **$h^2/(m\,\Delta x^2)$,** where h = Planck's constant, m = mass, and Δx is the length of the region to which the particle is confined. For example, as a nucleus pulls an electron close, the zero-point energy increases and ***the electron will not fall to the nucleus***. (It is as if the small things like electrons "refuse" to be localized.)

Note: $h^2 = J^2\,s^2 = kg^2\,m^4 s^{-4}\,s^2$, so $h^2/(m\,\Delta x^2) = kg^2\,m^4 s^{-2}/(kg m^2) = kg\,m^2 s^{-2} = J$

<u>Heisenberg Uncertainty</u>: $\Delta x\,\Delta p \cong h$, i.e., product of uncertainty in x and uncertainty in momentum is about = h.

ΔH of chemical reactions is equal to the **change in quantum zero point energy** at 0 Kelvin, and is only slightly different at room temperature due to heat capacity differences.

The mysterious **"DARK ENERGY"** that is apparently causing the acceleration of expansion of the Universe is most discussed as **quantum zero point energy** (of gravity, for which there is no quantum theory yet.)

THEN CAME THE Schrödinger Equation (1926)

which says all of the above

This equation was **DISCOVERED**, not derived

Schrodinger did not know what to make of Ψ when he published his equation. Everyone knew it was important because the equation gave all the correct energies for the "well behaved" solutions.

Also was immediately shown that Newton's Laws could be derived from the Schrodinger Eq.
(but not the other way around)