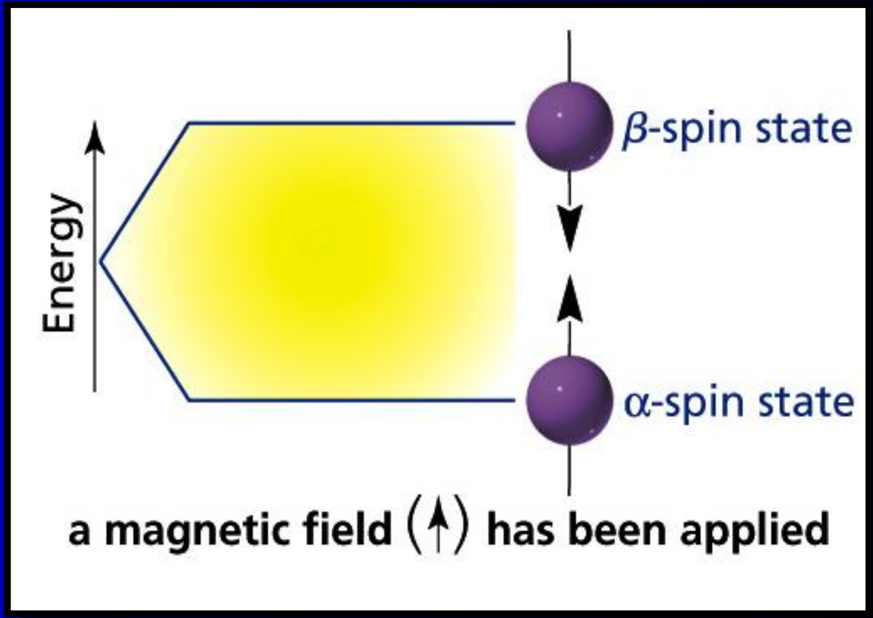
Lecture 3

NMR Spectroscopy



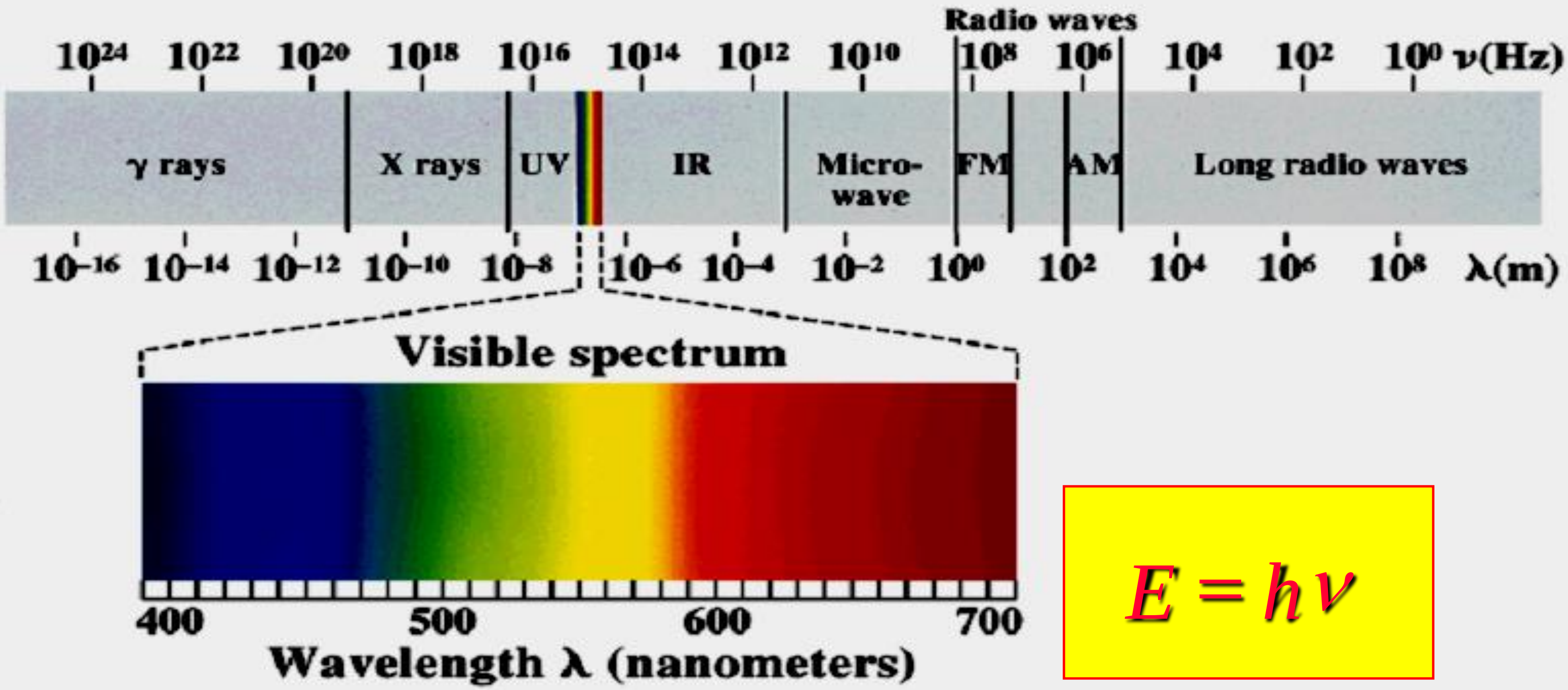
January 26, 2016

Please see me after class

Enrollment issue

- Hugo Nicolas Eichner
- Nurbol Kaliyev

The electromagnetic spectrum



$$E = h\nu$$

Energy per photon

Frequency

Wave Length

Electromagnetic Radiation

Important relationships:

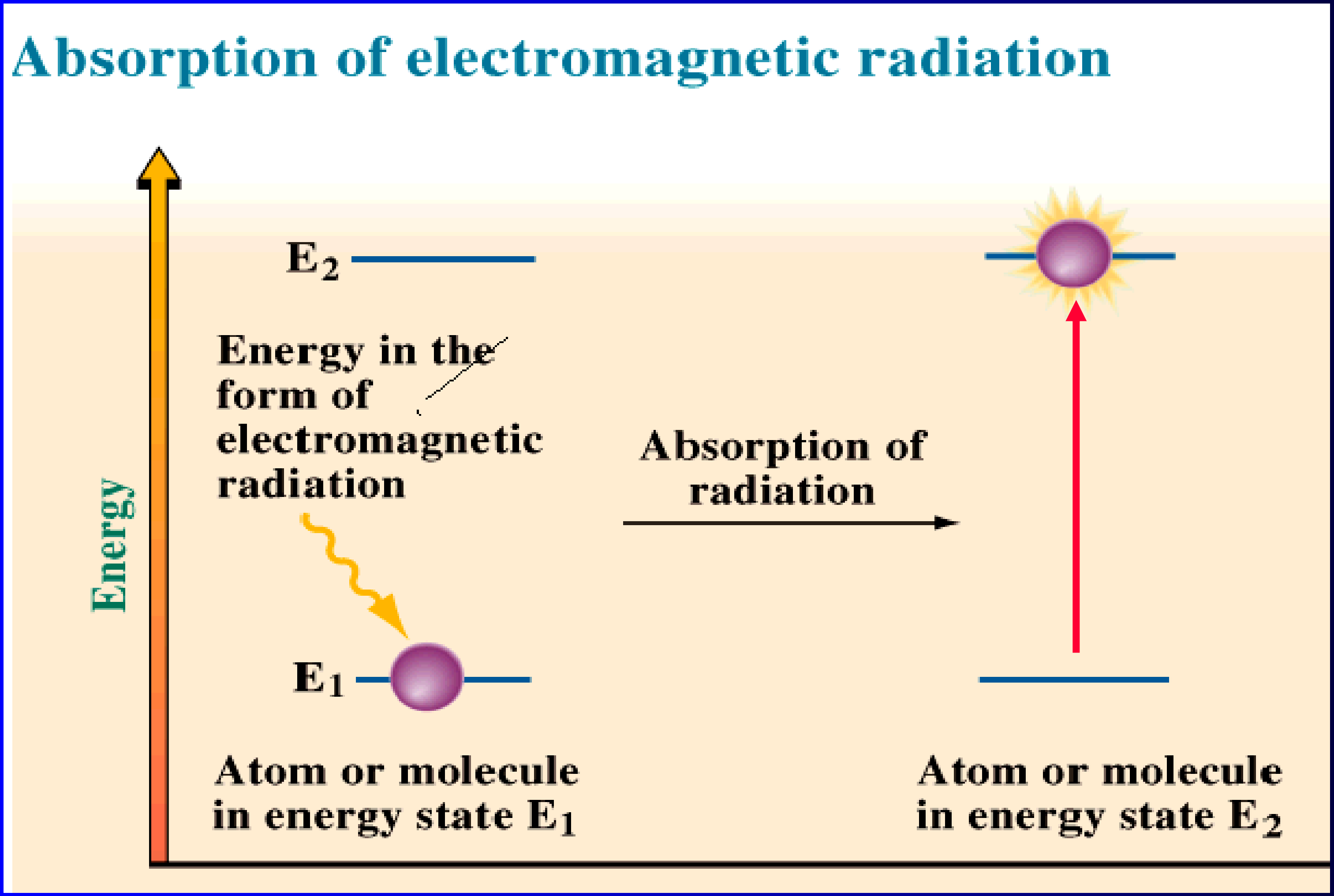
$$\nu\lambda = c$$

Where **C** = 3.00 x 10^8 m/s

$$E = h\nu = \frac{hc}{\lambda}$$

Where h = 9.537 x 10^{-14} kcal sec/mol

See examples of calculations in sections 12.1 &12.2



Absorbance promotes atom or molecule to higher energy state

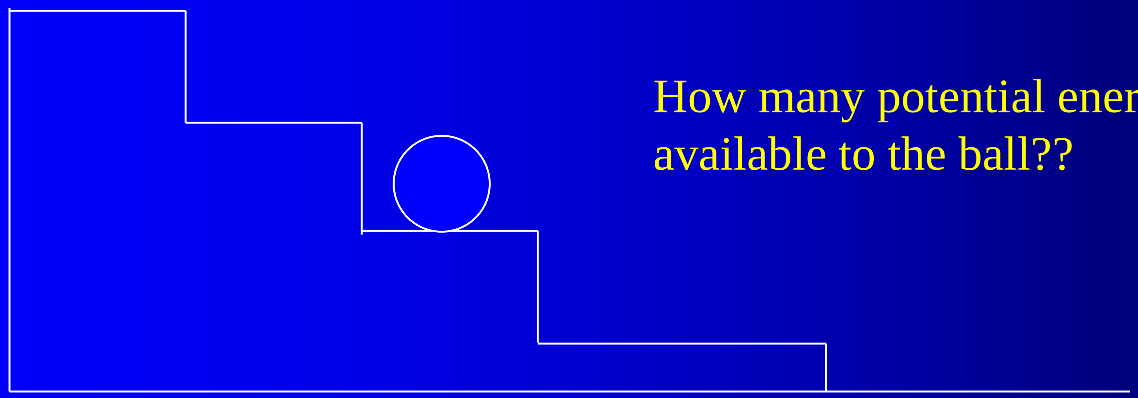
Molecular Spectroscopy

- We study three types of molecular spectroscopy

Region of the Spectrum	***Absorption of Radiation Results in Transition Between:***
radio frequency →	**nuclear spin energy levels**
infrared →	**vibrational energy levels**
ultraviolet-visible →	**electronic energy levels**

Absorption of electromagnetic radiation

- Described by quantum mechanical theories
- Only discrete (unique) energy states are allowed (accessible)
- Therefore only discrete (unique) amounts of radiation can be absorbed (or emitted)

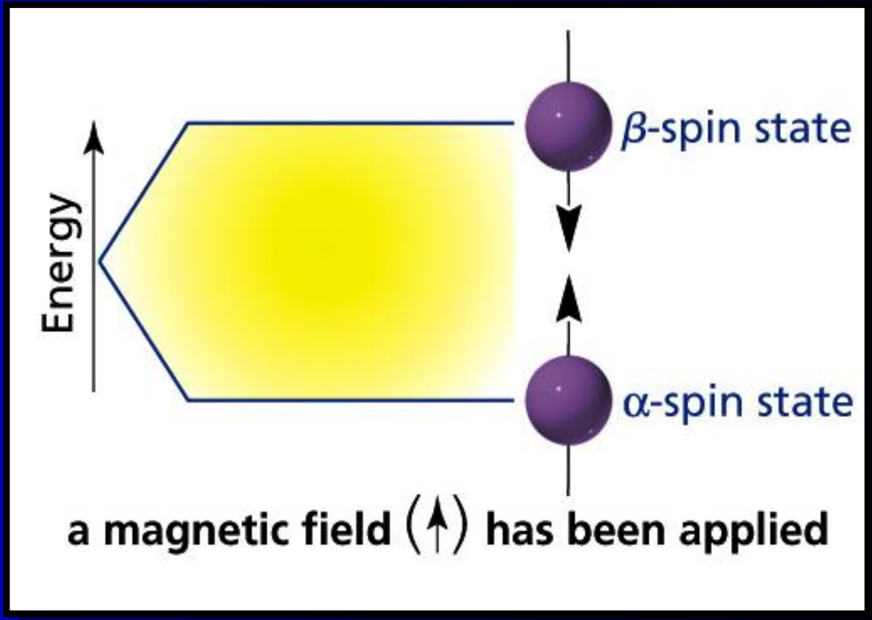


How many potential energy states are available to the ball??

Summary

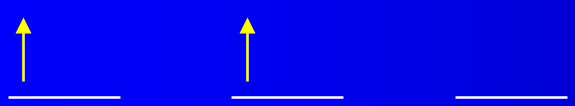
- Molecular Spectroscopy Concept...
  - Discrete transitions in energy levels
  - Transitions with varying energy (areas of spectrum)
    - Nmr : nuclear spin, radio frequency region
    - IR : vibration, infrared region
    - UV-Vis : electronic transitions, UV to visible
- Please know relationships between frequency, wave length and energy.
    - Know length scale conversions…micron, millimeter, nanometer, angstrom...

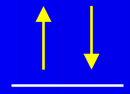
NMR Spectroscopy



Spin States

- Electrons have a spin quantum number of 1/2 with allowed values of +1/2 and -1/2
  - One can consider this as spinning charge that creates an associated magnetic field
  - Electrons therefore behave like tiny bar magnets
  - Remember the Pauli exclusion principle?

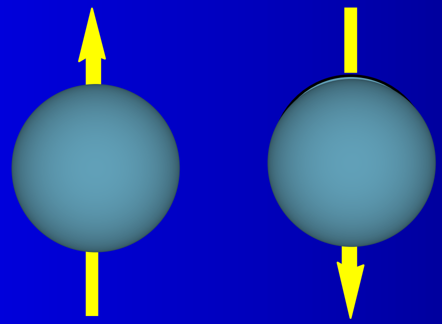




Spin “up” and spin “down”

Nuclear Spin States

- Nuclei with an odd mass, an odd atomic number, or both also have a net spin and a resulting nuclear magnetic moment.
- The allowed nuclear spin states are determined by the spin quantum number, *I* , of the nucleus.
- For each *I* there are 2*I* + 1 spin states
- If *I* = 1/2, there are two allowed spin states



Nuclear Spins

- The shell model for the nucleus tells us that nucleons, just like electrons, fill orbitals. When the number of protons or neutrons equals 2, 8, 20, 28, 50, 82, and 126, orbitals are filled. Because nucleons have spin, just like electrons do, their spin can pair up when the orbitals are being filled and cancel out.

Nuclear Spins

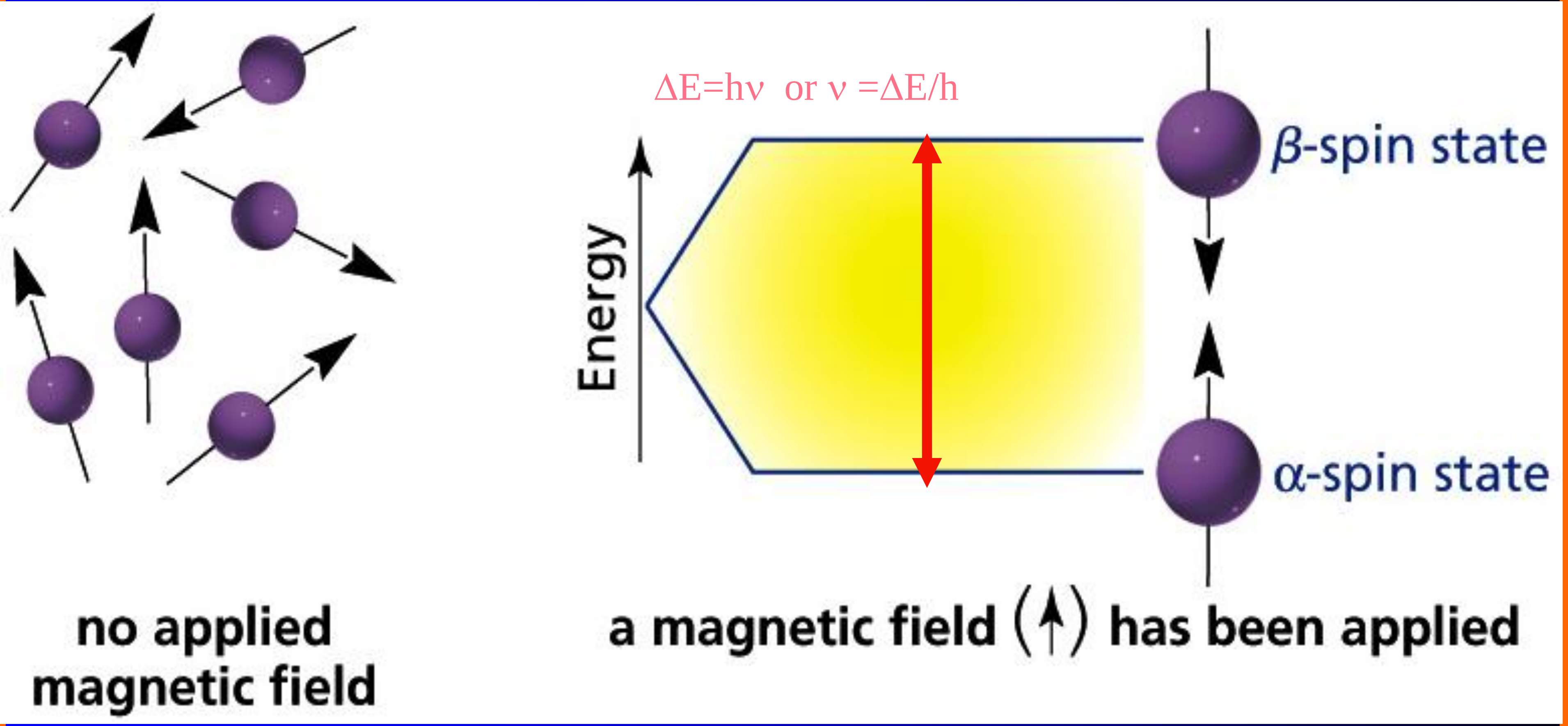
1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin. He, for example has no spin
2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2) (H and ^{13}C for example are both 1/2)
3. If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3) (Deuterium or N for example)

Nuclear Spins in a Magnetic Field

- Within a collection of ^{1}H or ^{13}C atoms, nuclear spins are random in orientation

- When placed in a strong external magnetic field the interaction between nuclear spins and the applied magnetic field is quantized, with the result that only certain orientations of the nuclear magnetic moments are allowed

Nuclear Spins in a Magnetic Field



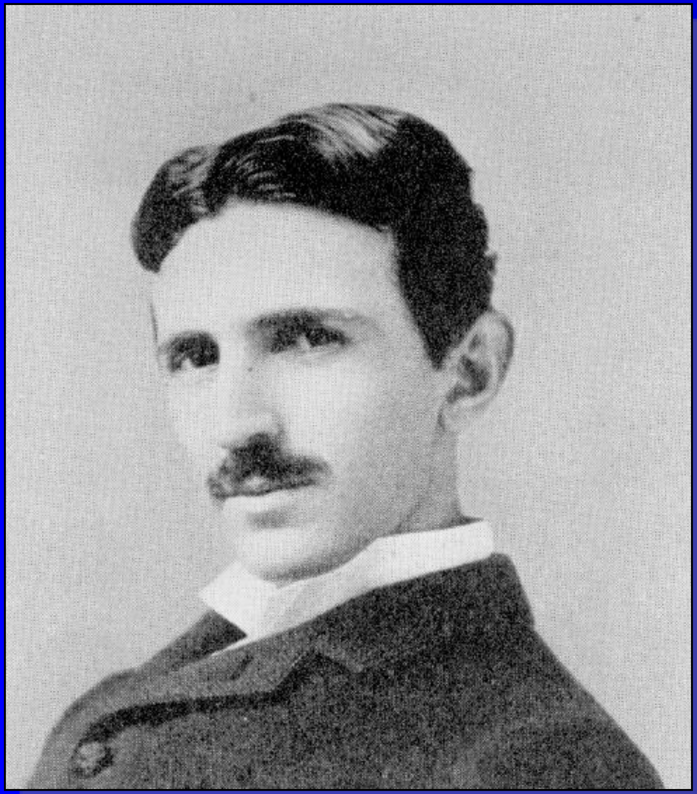
Nuclear Magnetic Resonance

- If the nucleus is irradiated with radiation having energy ($E=h\upsilon$) that is exactly the same as the difference between the nuclear spin states,
  - energy is absorbed, and
  - the nuclear spin is flipped from spin state +1/2 (with the applied field) to -1/2 (against the applied field)

Nuclear Spin States

- Spin quantum numbers and allowed nuclear spin states for selected isotopes of elements common to organic compounds

Element	^{1}H	^{2}H	^{12}C	^{13}C	^{14}N	^{16}O	^{31}P	^{32}S
nuclear spin quantum number (*I*)	1/2	1	0	1/2	1	0	1/2	0
number of spin states	2	3	1	2	3	1	2	1



$$\mathbf{T}\ \text{(Tesla)} = \frac{\mathbf{W}\ \text{(Weber)}}{\text{m}^2}$$

Nikola Tesla

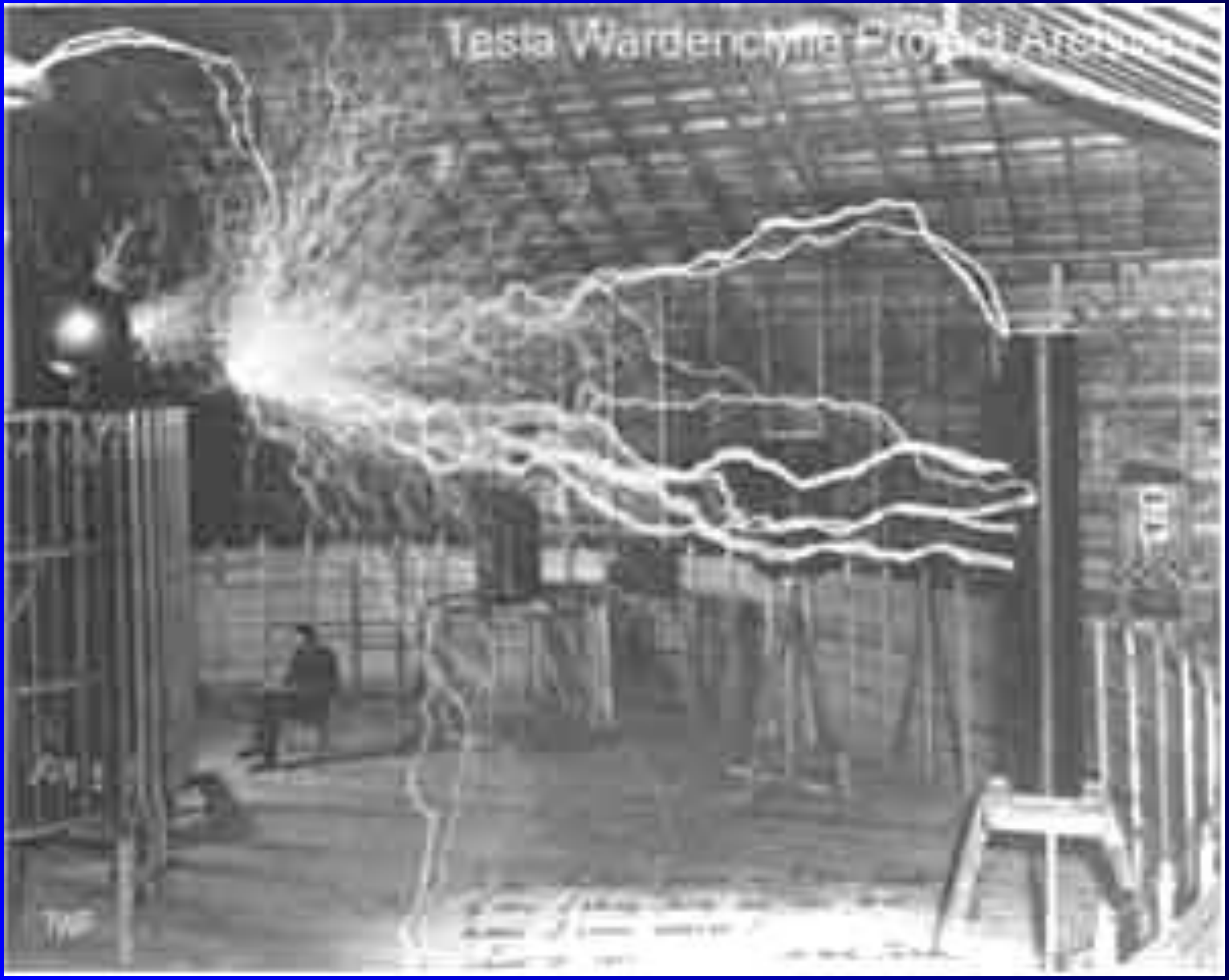
Serbian-American inventor, electrical engineer and scientist

Born, 1856 in Smiljan, Lika (Austria-Hungary)

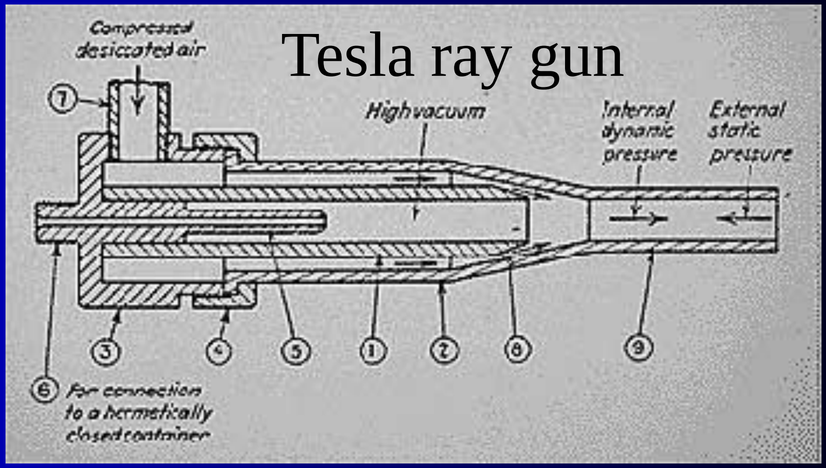
Died 1943 in New York City, New York (USA)

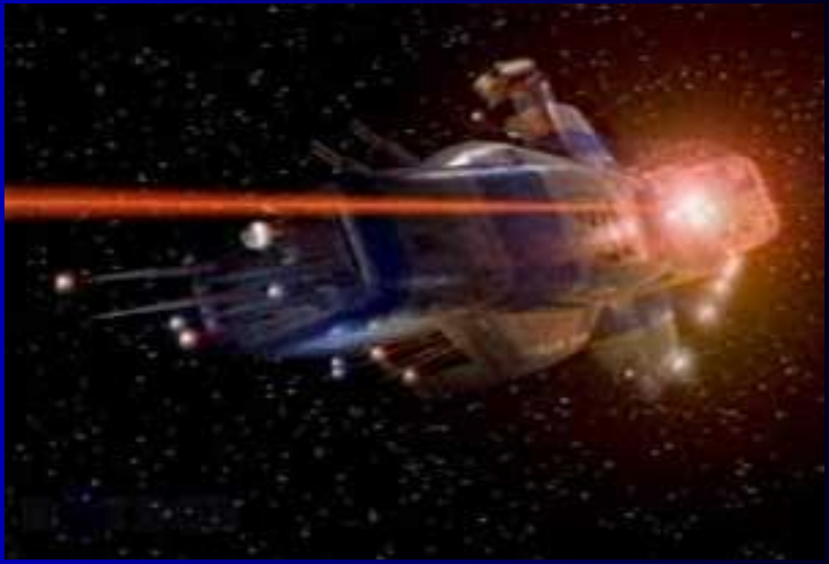
Inventions: a telephone repeater, rotating magnetic field principle, polyphase alternating-current system, induction motor, alternating-current power transmission, Tesla coil transformer, wireless communication, radio, fluorescent lights, and more than 700 other patents.

http://www.teslasociety.com/index.html



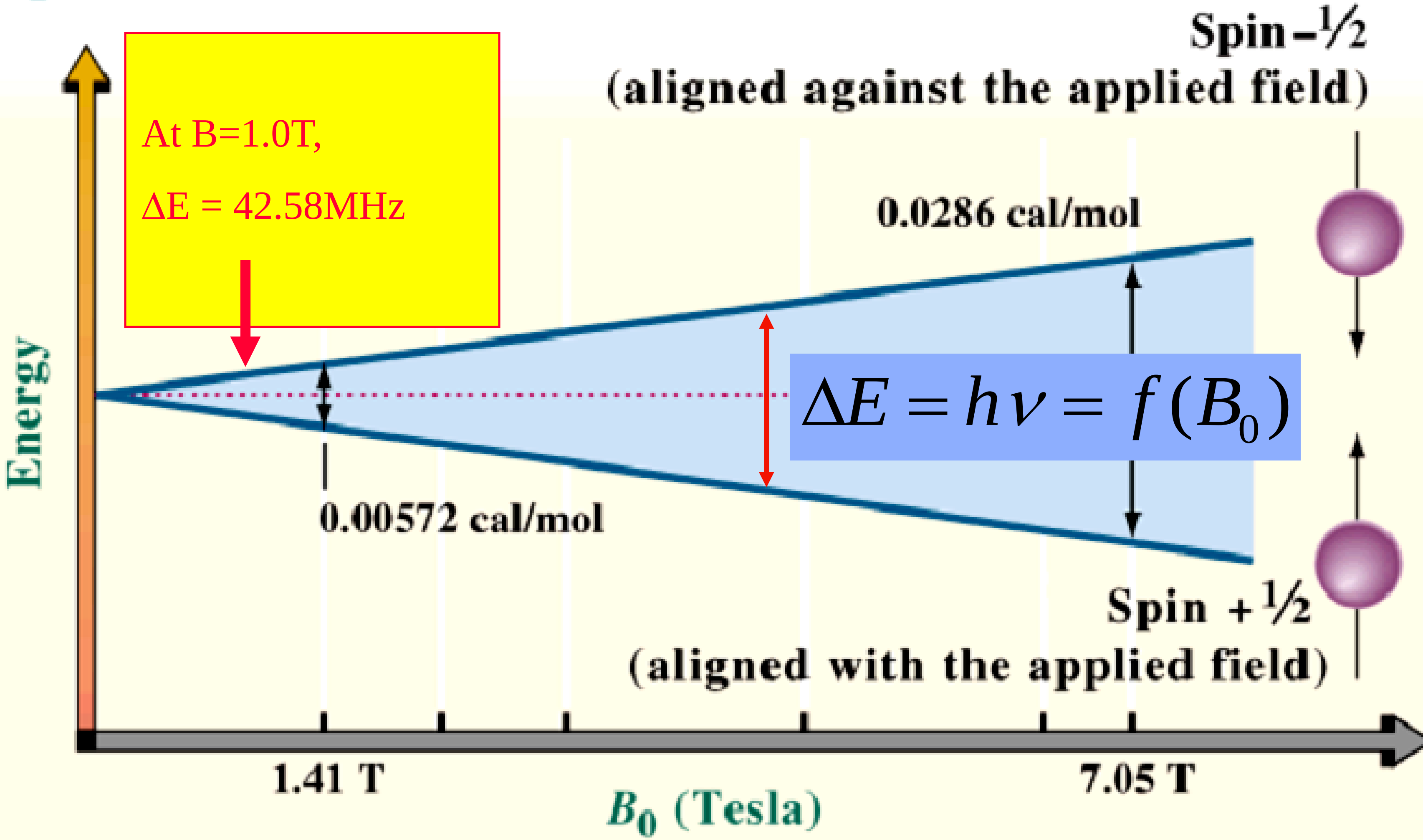
Famous and Controversial picture of Tesla if constructed, would result in: "An inexpensive instrument, not bigger than a watch, will enable its bearer to hear anywhere, on sea or land, music or song, the speech of a political leader, the address of an eminent man of science, or the sermon of an eloquent clergyman, delivered in some other place, however distant. In the same manner any picture, character, drawing, or print can be transferred from one to another place."





"The ray was described as the most important of all Tesla's inventions so far. It was said that IT COULD SEND CONSECRATED BEAMS OF PARTICLES THROUGH FREE AIR, and could cause armies of millions to drop dead in their tracks.

Energy difference between allowed nuclear spin states for ^{1}H nuclei



Nuclear Spins in B_0

- In an applied field strength of 7.05T (BIG!) ΔE between nuclear spin states for
  - ^{1}H is approximately 0.0286 cal/mol, which corresponds to electromagnetic radiation of 300 MHz (300,000,000 Hz)
  - ^{13}C is approximately 0.00715 cal/mol, which corresponds to electromagnetic radiation of 75MHz (75,000,000 Hz)
  - This ΔE is quite small…low frequency radiation induces "flip" (resonance)

"Resonance"

- The transition from the lower state to the higher occurs at unique combinations of magnetic field and frequency of electromagnetic radiation.

- When placed in a magnetic field of strength B, a particle with a net spin can absorb a photon, of frequency ν. The frequency, ν depends on the gyromagnetic ratio γ , of the particle.

$$\nu = \gamma B$$

For hydrogen, γ = 42.58 MHz / Tesla

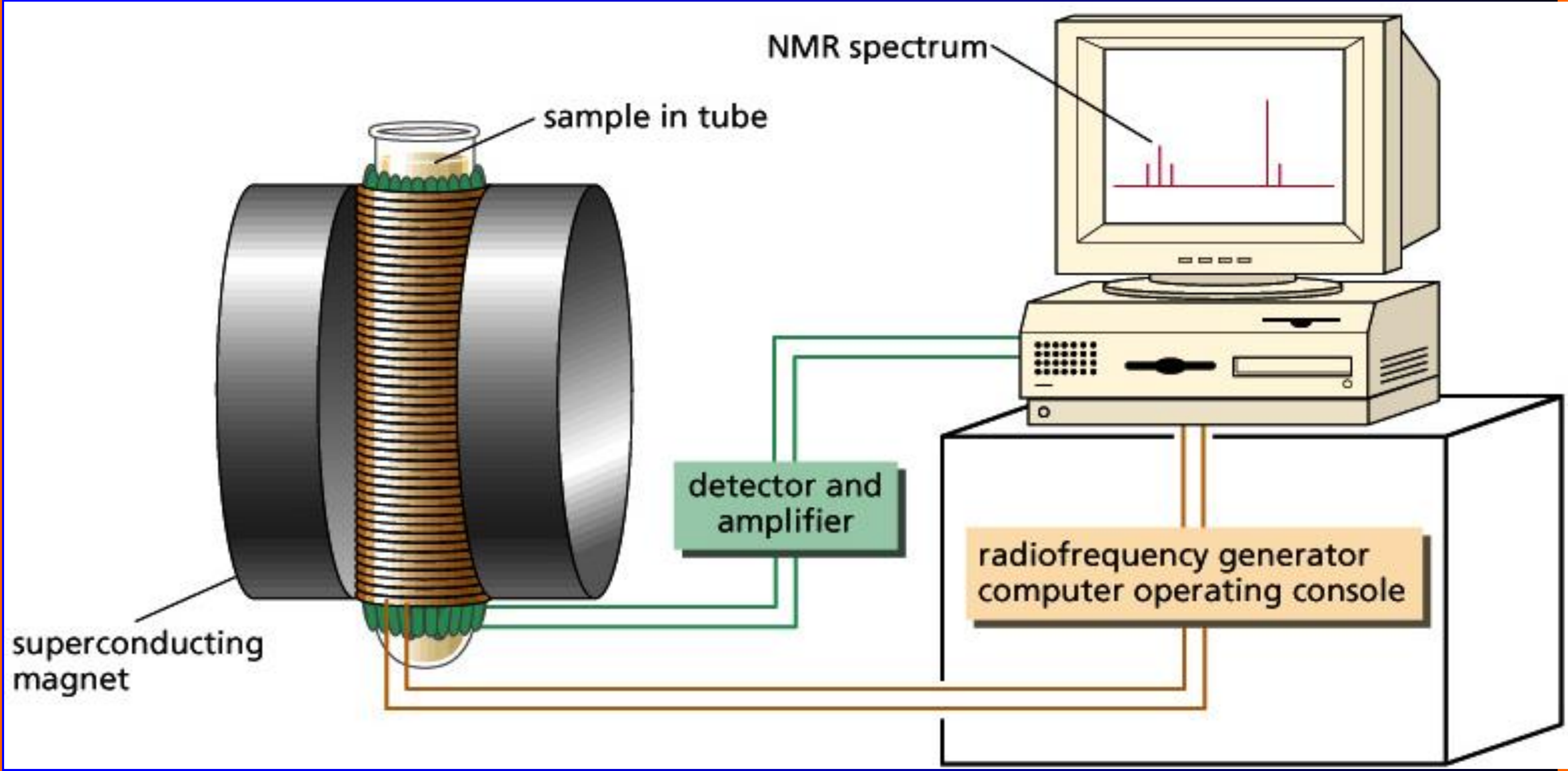
Allows you to calculate "spectrometer frequency" for ^{1}H !!

This is the frequency at which "naked" ^{1}H resonates in that machine

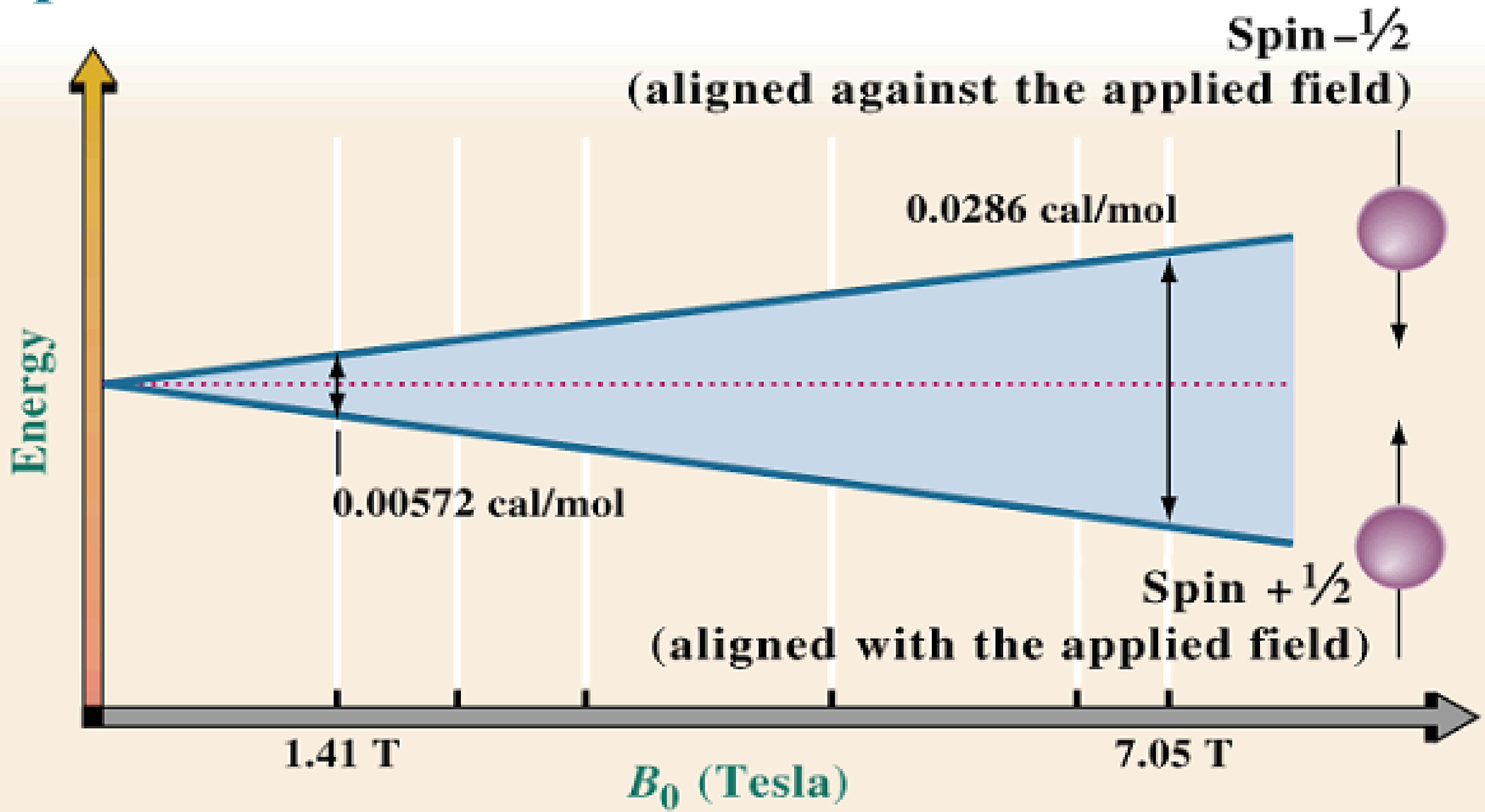
Some Proportionality Constants

- Gyromagnetic Ratio $\nu = \gamma B$
  - For ^{1}H $\gamma = 42.58$ MHz/T
- Planck's Constant $E = h\,\nu$
- Speed of light $\nu = c / \lambda$ or $c = \nu\,\lambda$
- Chemical Shift $d(ppm) = \dfrac{\Delta\nu}{Spectrometer\ frequency}$

NMR Spectrometer

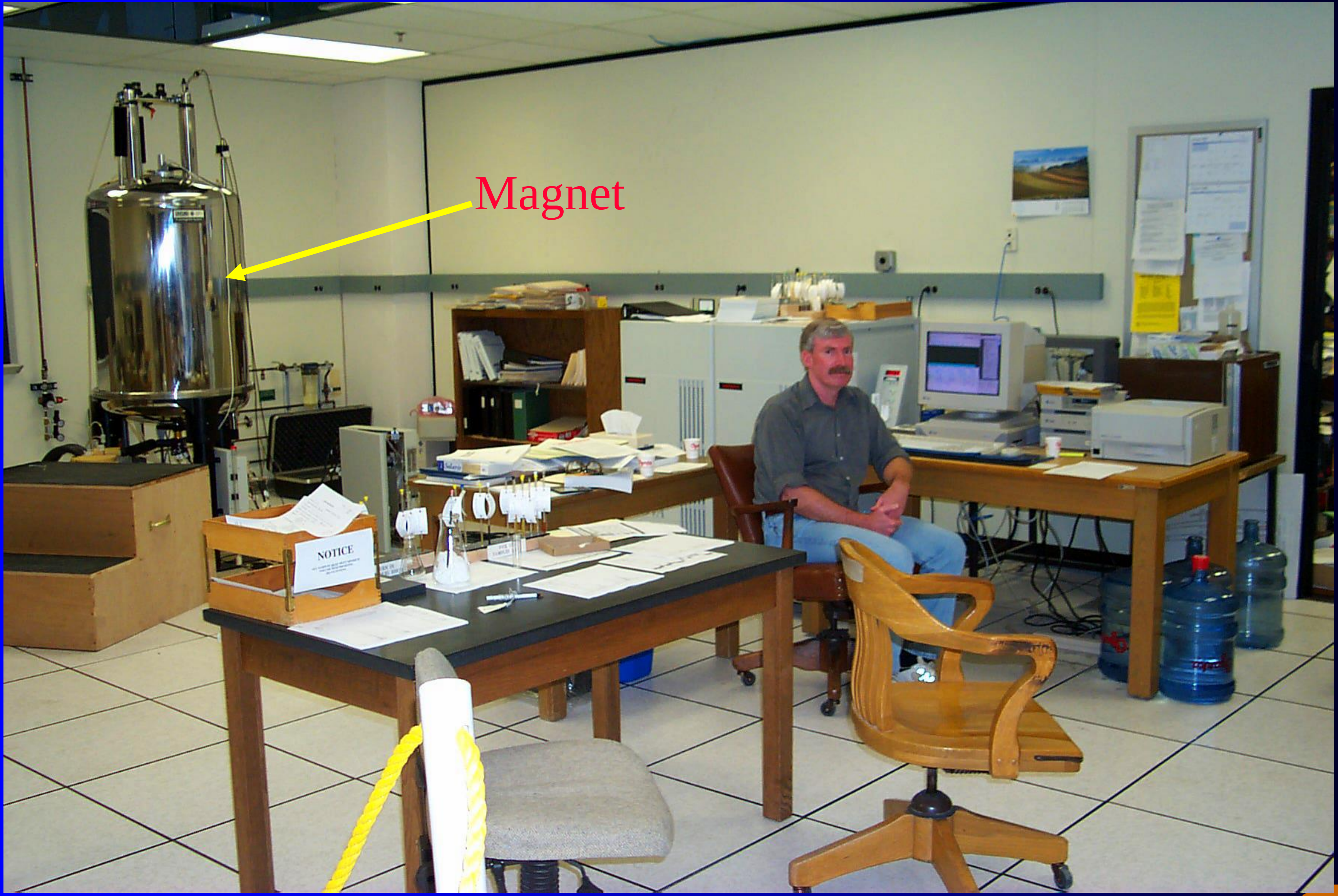


Energy difference between allowed nuclear spin states for ^1H nuclei



In principle, we could hold field constant and scan frequency looking for resonance, but it is equally effective to scan field strength and hold frequency constant

500MHz ^{1}H-nmr Spectrometer



http://www.jeolusa.com/RESOURCES/AnalyticalInstruments/NMRMagnetDestruction/tabid/390/Default.aspx

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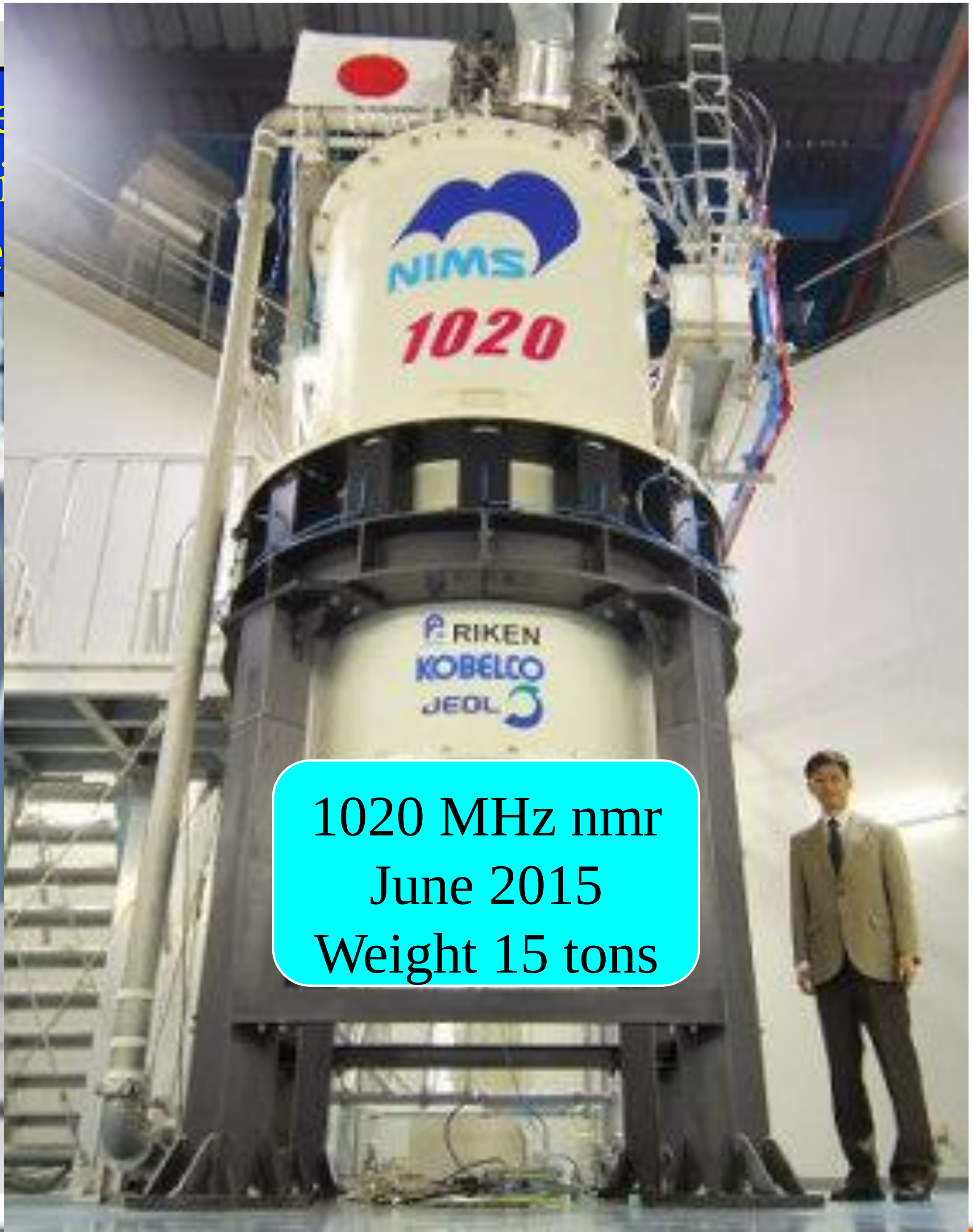
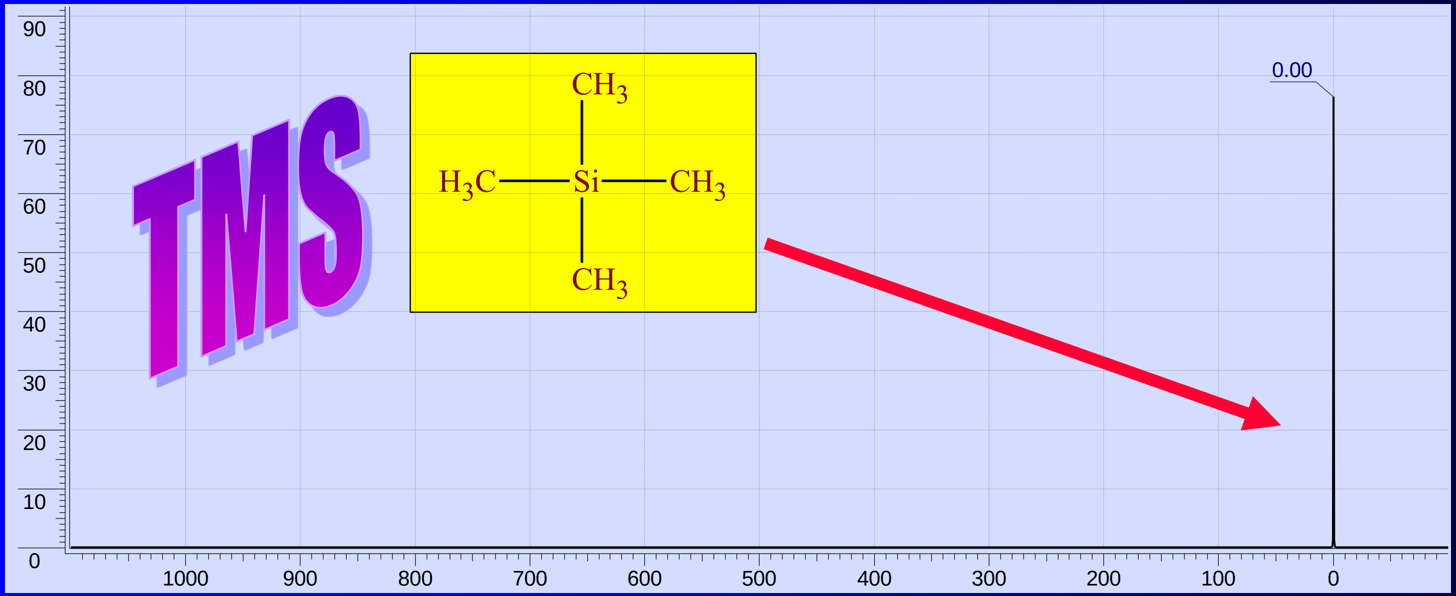


1020 MHz nmr
June 2015
Weight 15 tons

The 100MHz nmr Chart

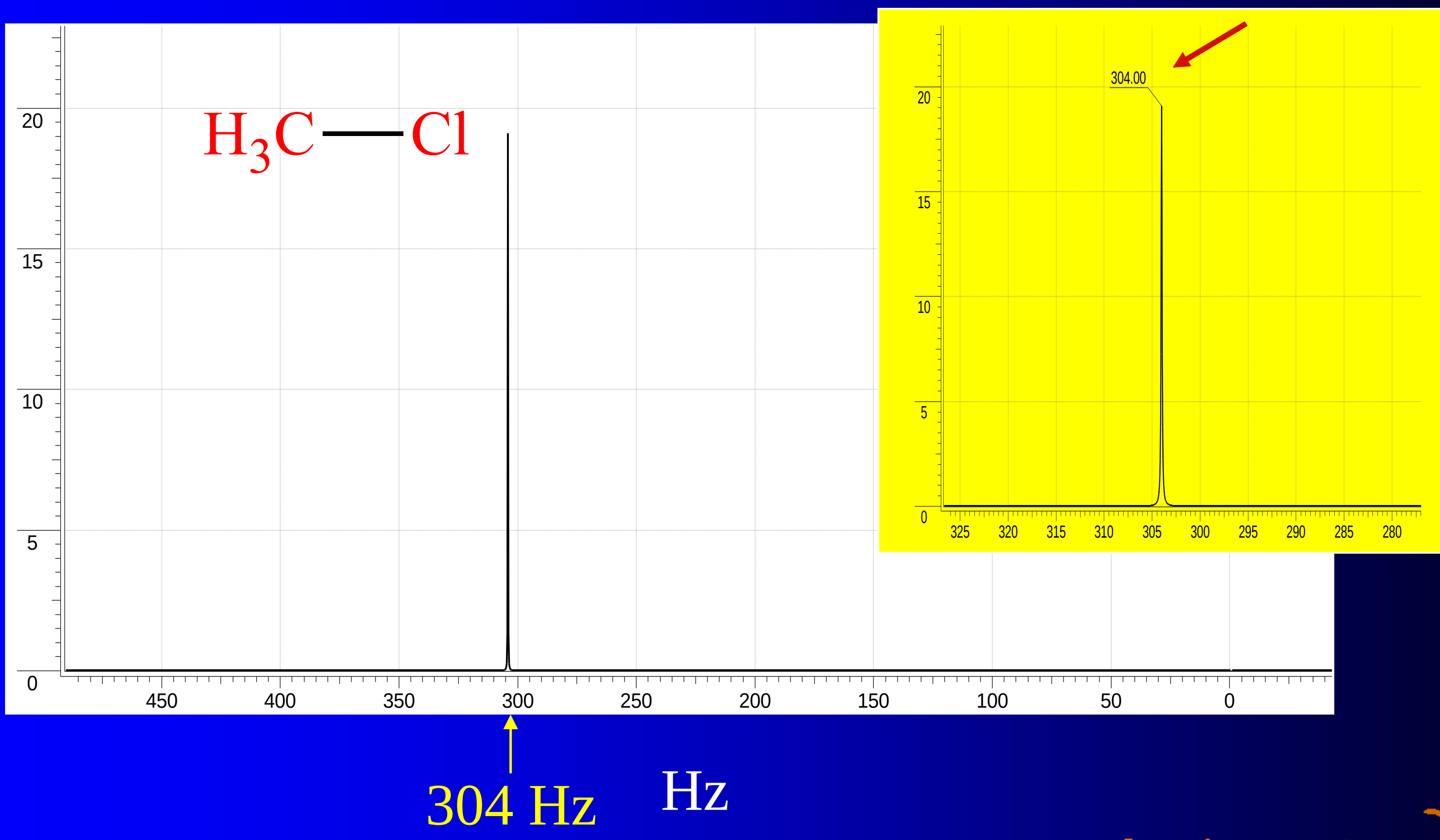


Frequency

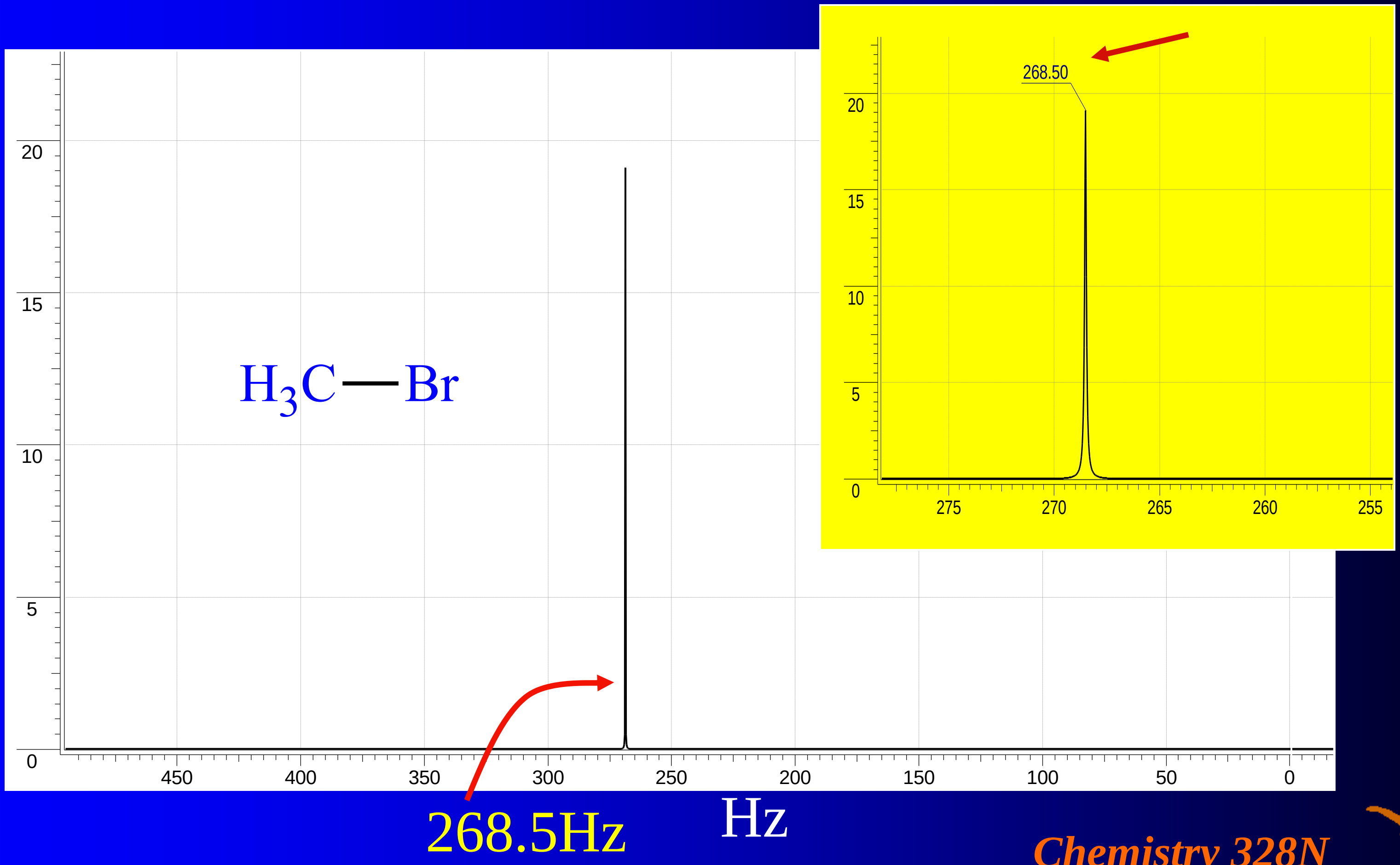
field

The TMS resonance is defined as having "0" frequency

100MHz Spectrum



100MHz nmr Spectrum



Nuclear Magnetic Resonance

- If we were dealing with ^{1}H nuclei isolated from all other atoms and electrons, any combination of applied field and radiation that produces a signal for one ^{1}H would produce a signal for all ^{1}H. The same for ^{13}C nuclei

- But ….hydrogens in organic molecules are <u>not</u> isolated from all other atoms; they are surrounded by electrons, which are caused to circulate by the presence of the applied field

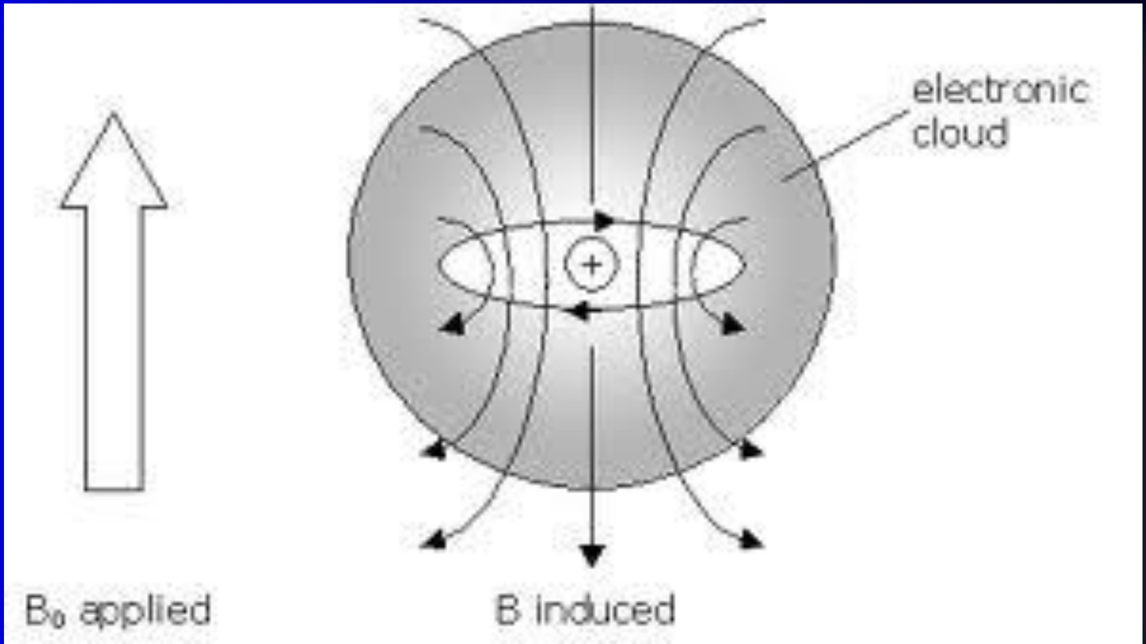
Nuclear Magnetic Resonance

- The circulation of electrons around a nucleus in an applied field is called diamagnetic current.
- This current generates a field that opposes the applied field ...diamagnetic nuclear shielding results. Lenz's Law??
- The difference in resonance frequencies between the various hydrogen nuclei within a molecule is due to shielding/deshielding is very small but very important

Lenz's Law

Heinrich Lenz

1804-1865



Conditions for Resonance

- It is the frequency of the radiation and the **NET** field at the nucleus that matters.
- The NET field is the sum of all incident magnetic fields including those from:
  - The Giant Magnet (applied field)
  - Diamagnetic Shielding field (electrons)
  - Coupling (spin fields of adjacent nuclei)
  - credit card strips, earth's field, etc…..