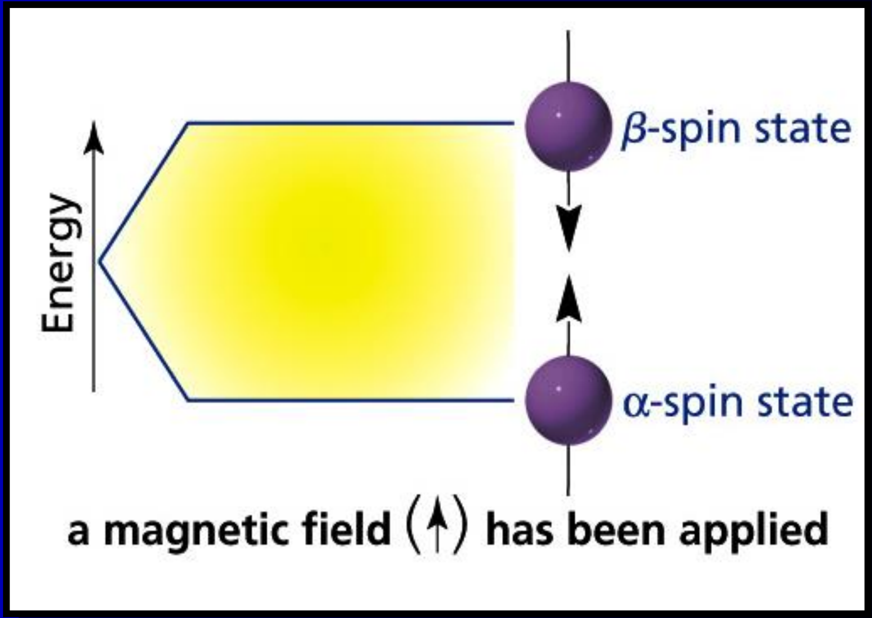
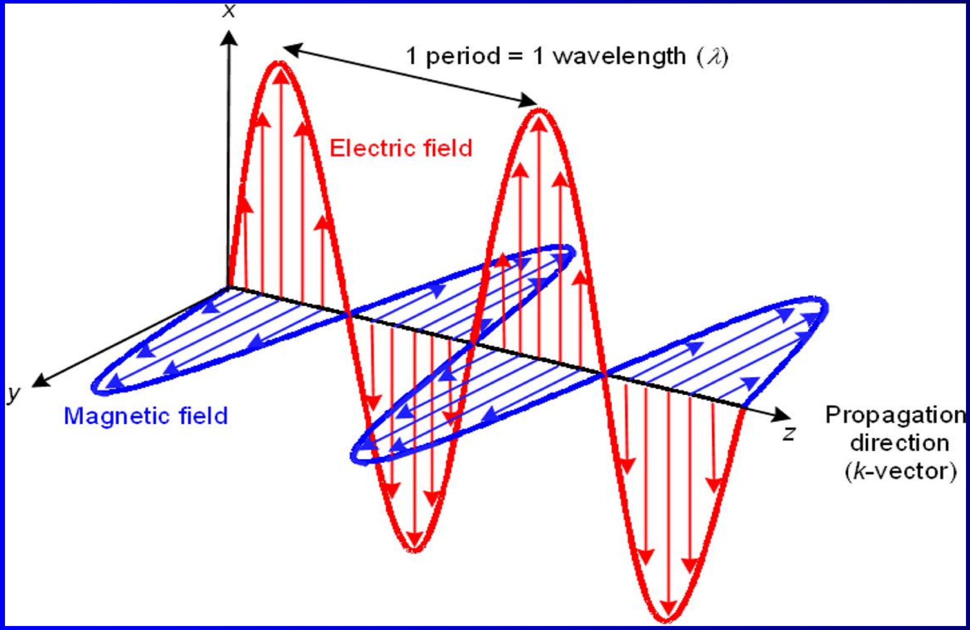
Lecture 3
NMR Spectroscopy



January 29, 2019

Molecular Spectroscopy

- Molecular spectroscopy: the study of the frequencies of electromagnetic radiation that are absorbed or emitted by substances and the correlation between these frequencies and aspects of molecular structure



Max Karl Ernst Ludwig **Planck**
1868 -1947

$$E = h\,C/\lambda$$

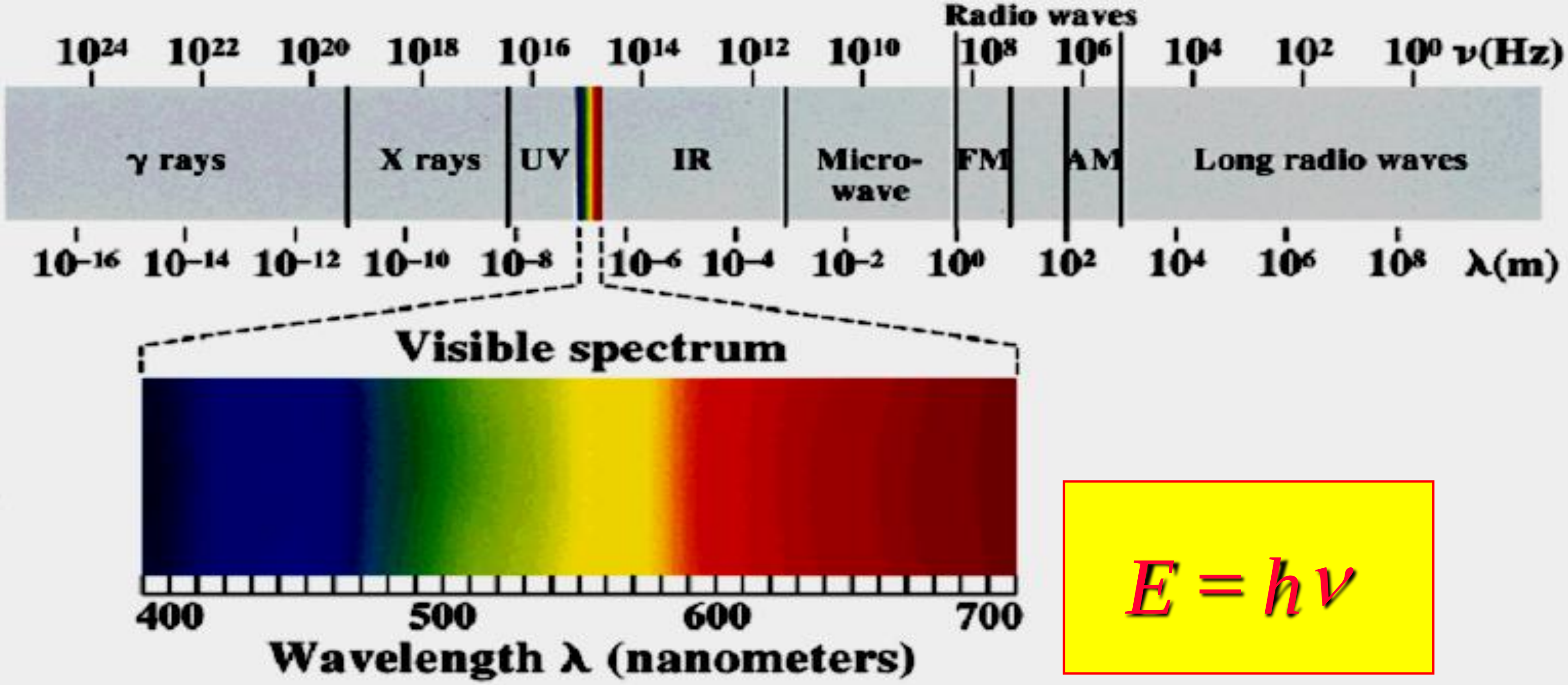
C=299792458
m/s

h=6.62607004 × 10^{-34} Joule-sec

See sections 12.1 and 12.2!

Nobel Prize in Physics in 1918

The electromagnetic spectrum



$$E = h\nu$$

← Energy per photon

← Frequency

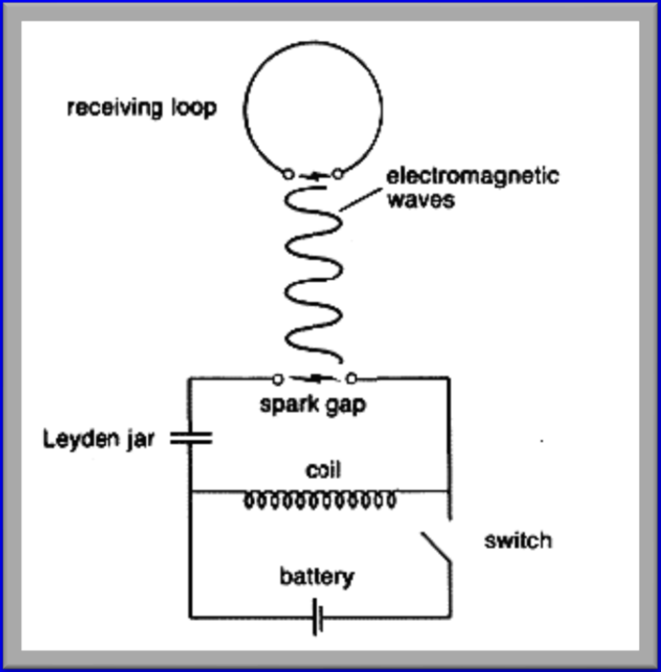
Wave Length →

Heinrich Rudolph Hertz

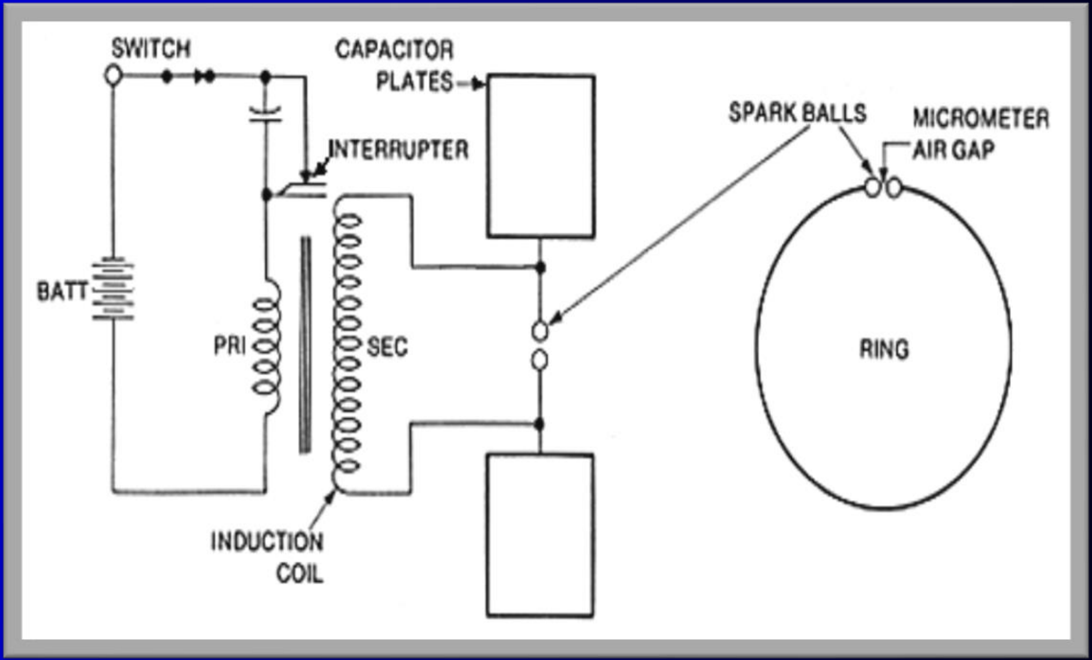
Born: 22 February 1857 in Hamburg
Died: 1 January 1894 in Bonn

- **Hertz (Hz)**
  - the SI unit of frequency, equal to one cycle per second. The frequencies of radio and television waves are measured in kilohertz (kHz), megahertz (MHz), or even gigahertz (GHz), and the frequencies of light waves in terahertz (THz). The unit is named for the German physicist Heinrich Rudolf Hertz (1857-1894), who proved in 1887 that energy is transmitted through a vacuum by electromagnetic waves.

The Hertz Experiment 1887

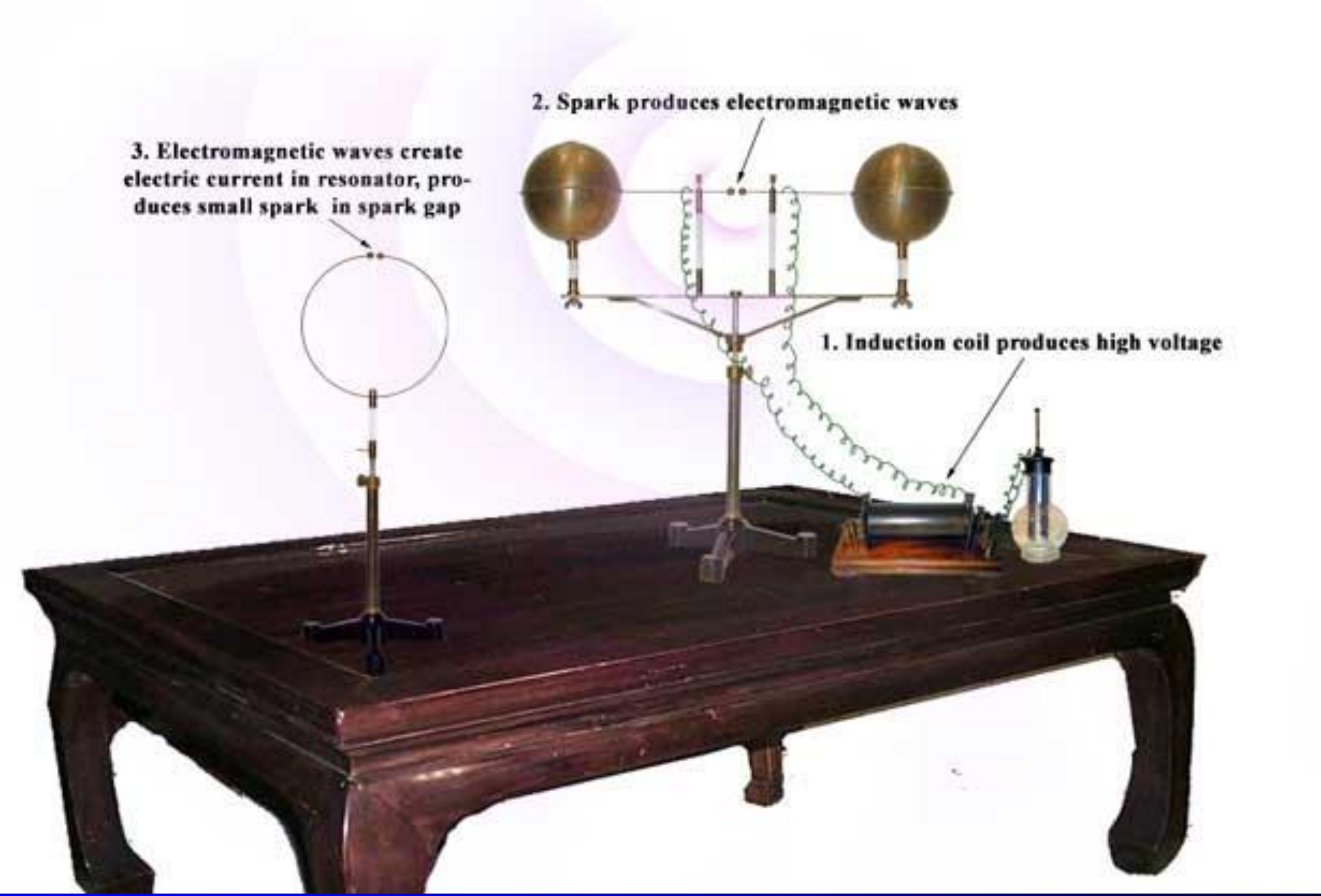


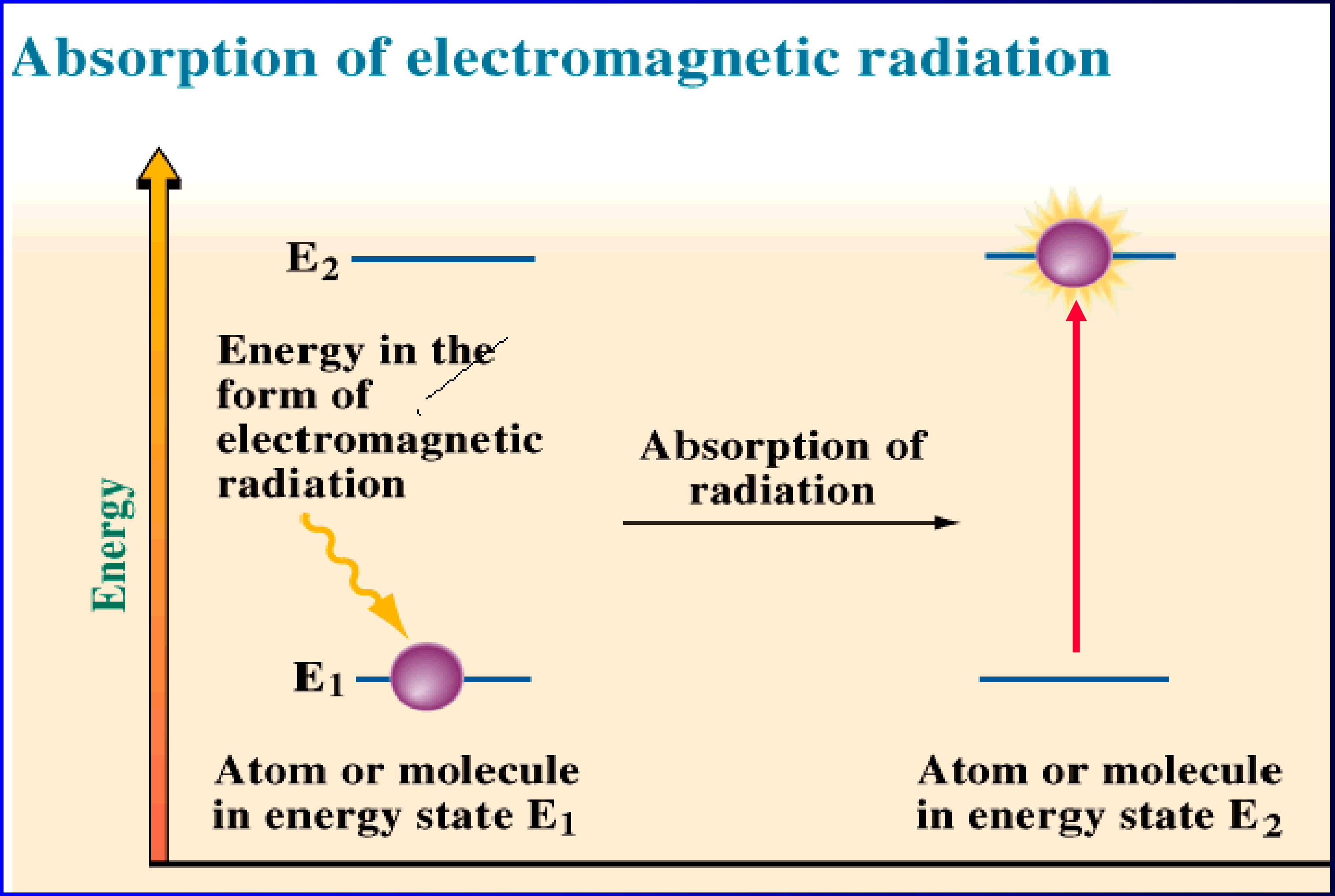
CONCEPTUAL DESIGN



MORE DETAIL

The Hertz Experiment

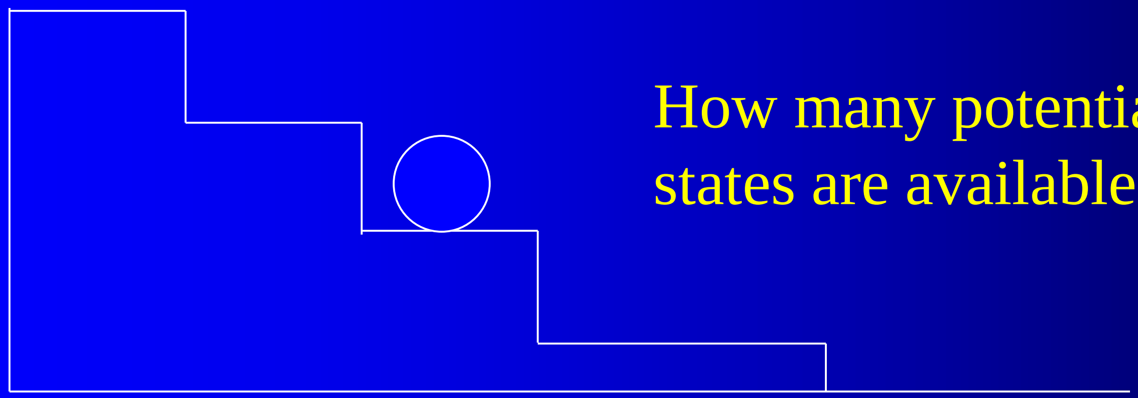




Absorbance promotes atom or molecule to higher energy state

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??

Molecular Spectroscopy

- We study three types of molecular spectroscopy

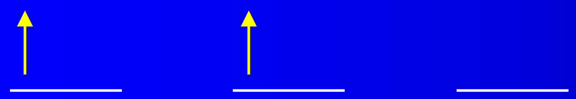
Region of the Spectrum	***Absorption of Radiation Results in Transition Between:***
radio frequency →	**nuclear spin energy levels**
infrared →	**vibrational energy levels**
ultraviolet-visible →	**electronic energy levels**

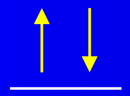
Summary

- 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...

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?

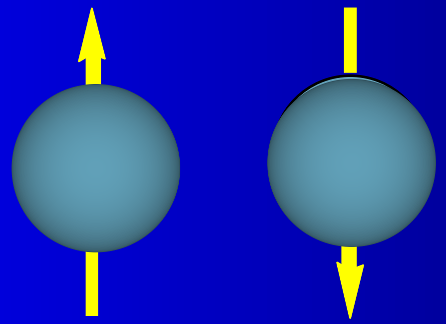




Spin “up” and spin “down”

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 $2I + 1$ spin states
- If $I = 1/2$, there are two allowed spin states



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 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

Nuclear Spins in a Magnetic Field

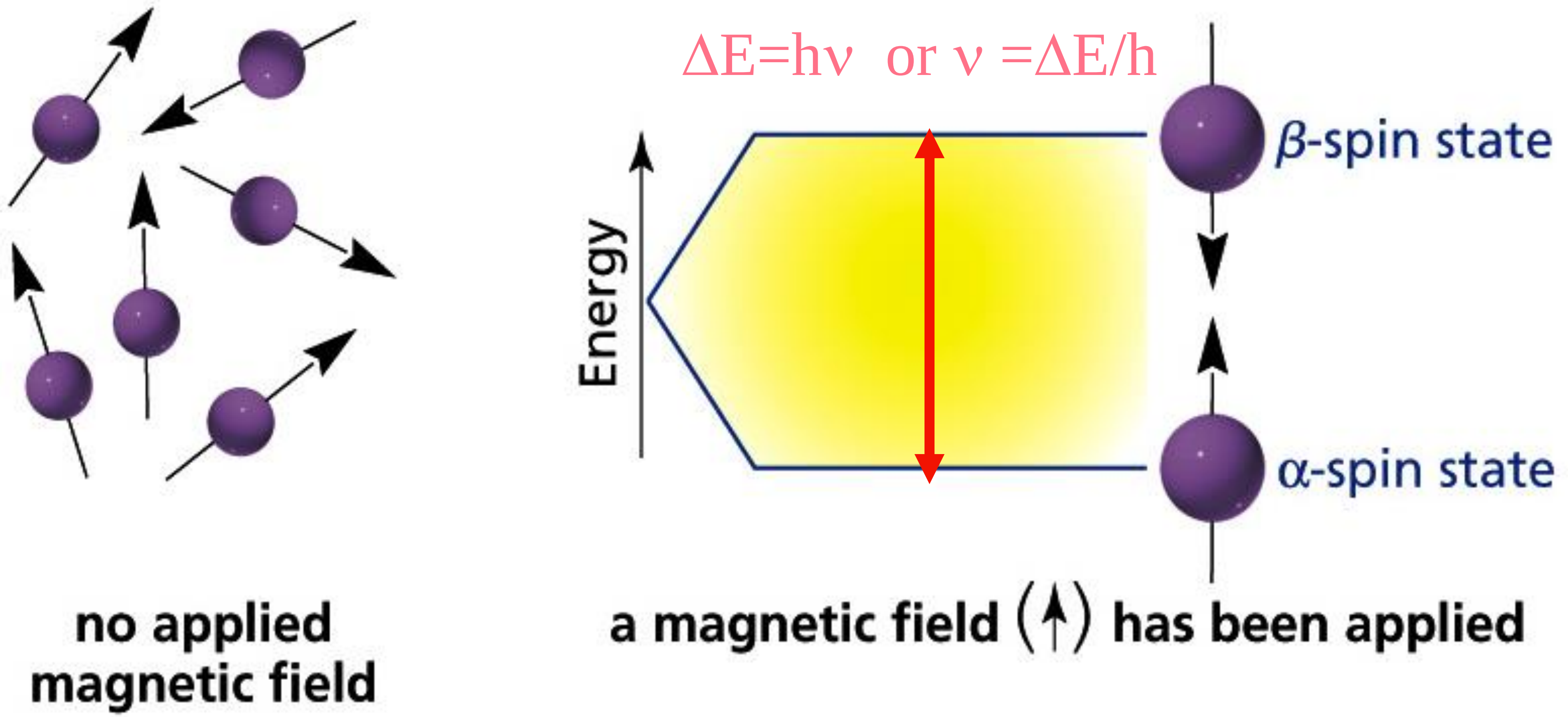
- Within a collection of ^{1}H or ^{13}C atoms, nuclear spins are random in orientation

- 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

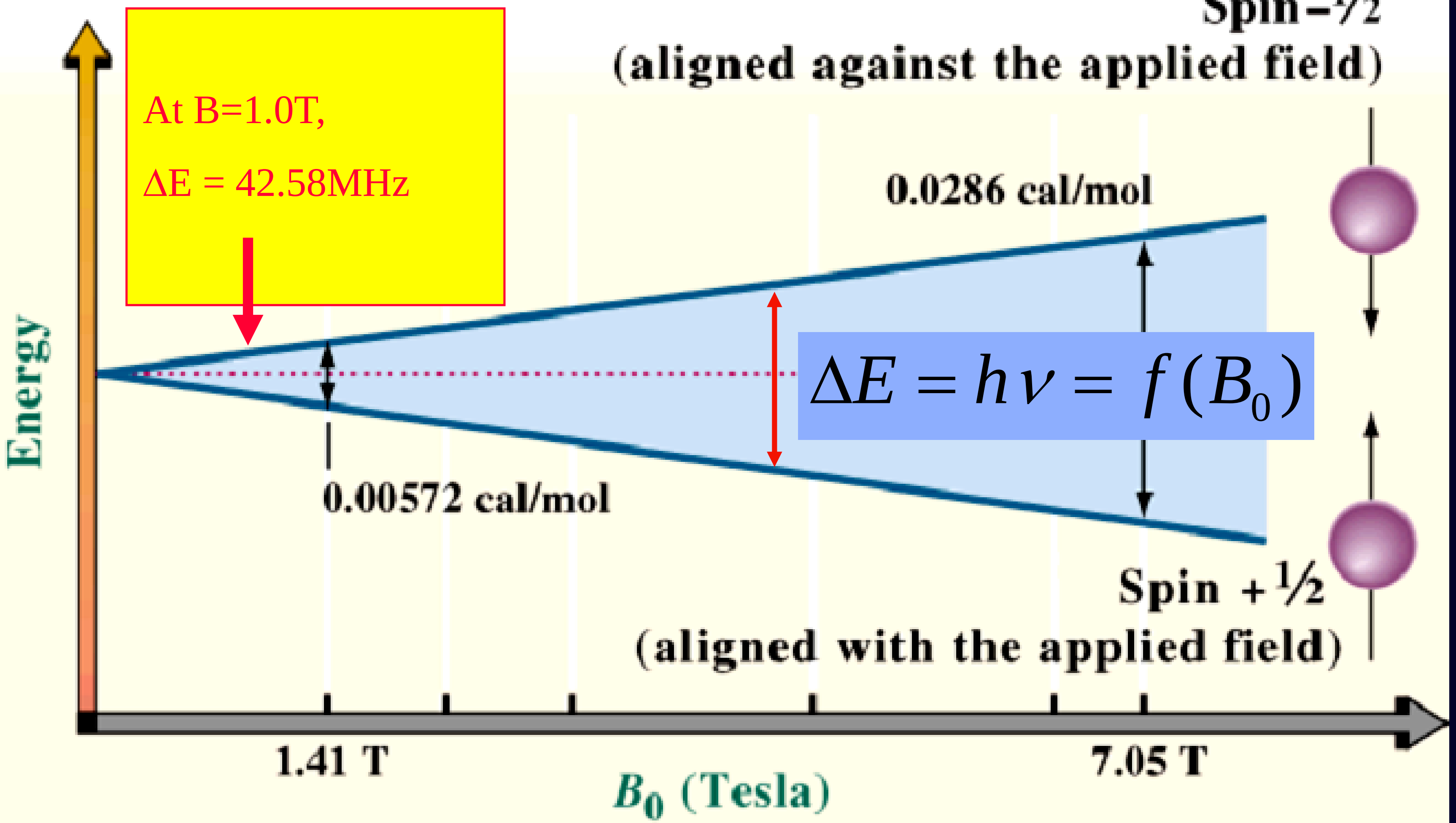
Nuclear Magnetic Resonance

- If the nucleus is irradiated with radiation having energy ($E=h\upsilon$) <u>that is exactly</u> the same as the difference in energy 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)

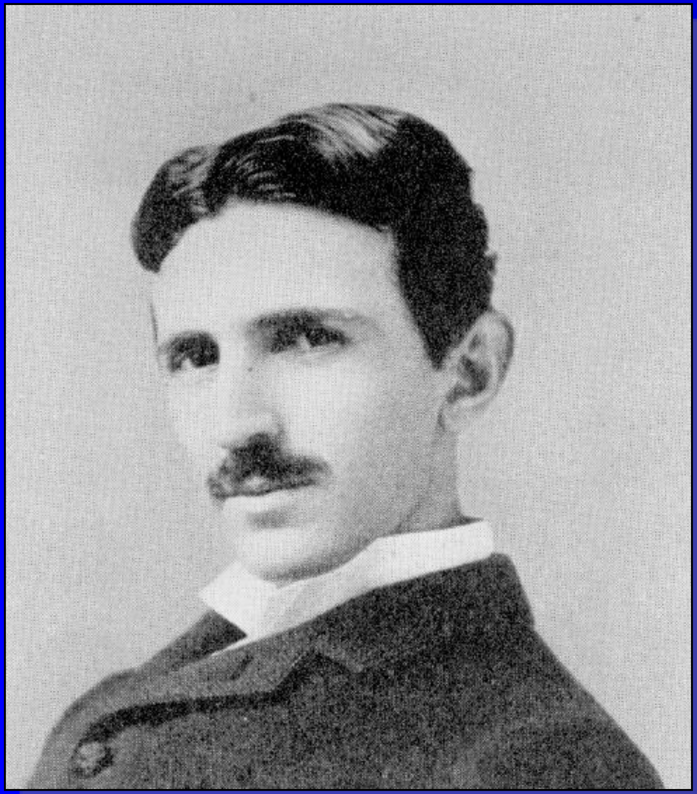
Nuclear Spins in a Magnetic Field



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



$$\Delta E = h\nu = f(B_0)$$



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

Nikola Tesla

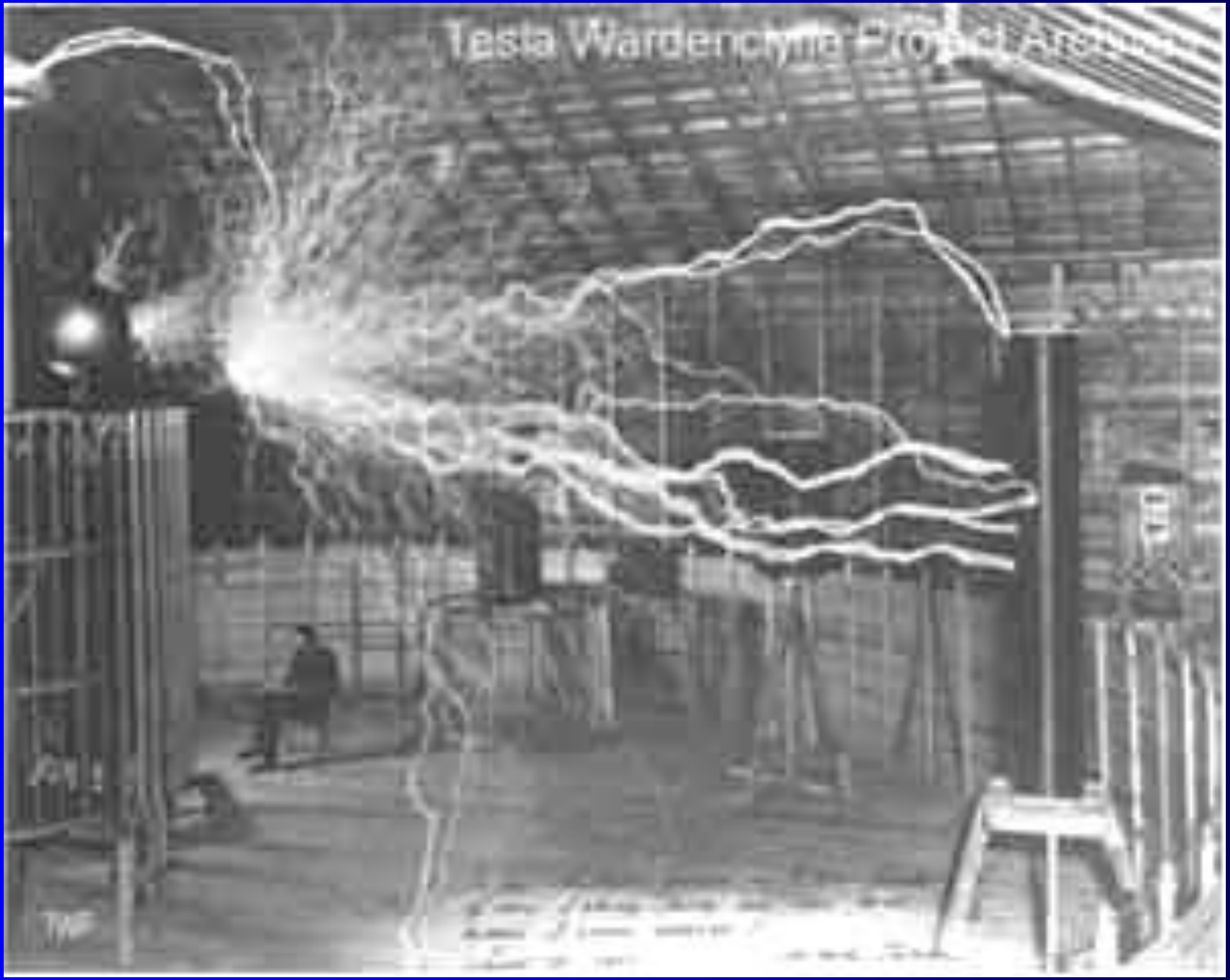
Serbian-American inventor, electrical engineer and scientist

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

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

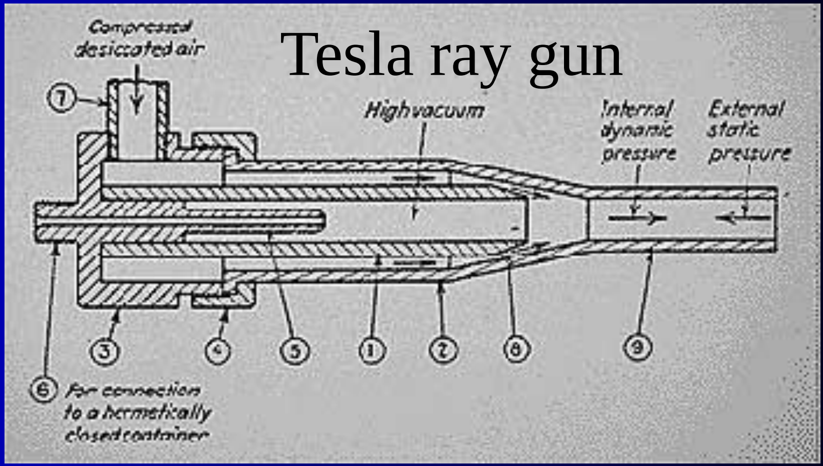
Inventions: a telephone repeater, rotating magnetic field principle, polyphase alternating-current system, induction motor, alternating-current power transmission, Tesla coil transformer, wireless communication, radio, fluorescent lights, and more than 700 other patents.

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

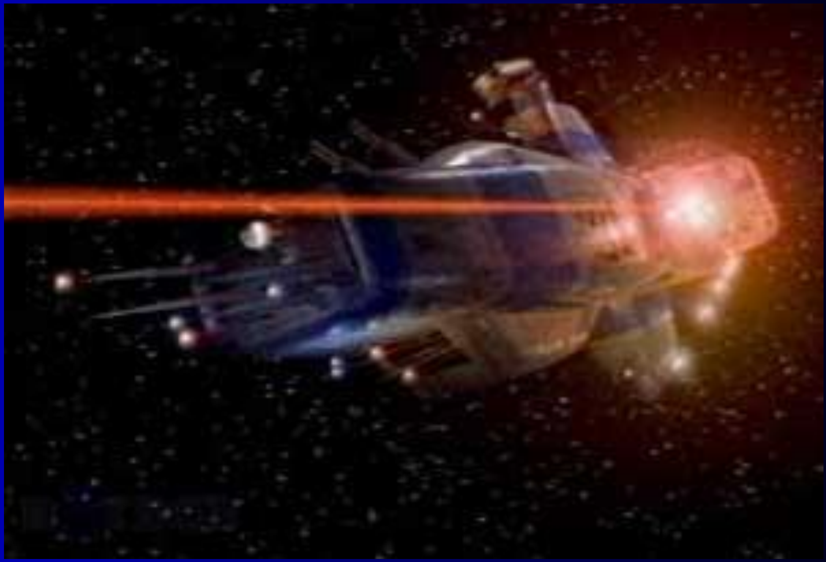


Famous and Controversial picture of Tesla

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."



Tesla ray gun



"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.

Induction Motor

Nuclear Spins in B_0

- In an applied field strength of 7.05T (BIG!) ΔE between nuclear spin states for
  - ^1H 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…so low frequency radiation induces "flip" (resonance)

"Resonance in nmr"

- 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.

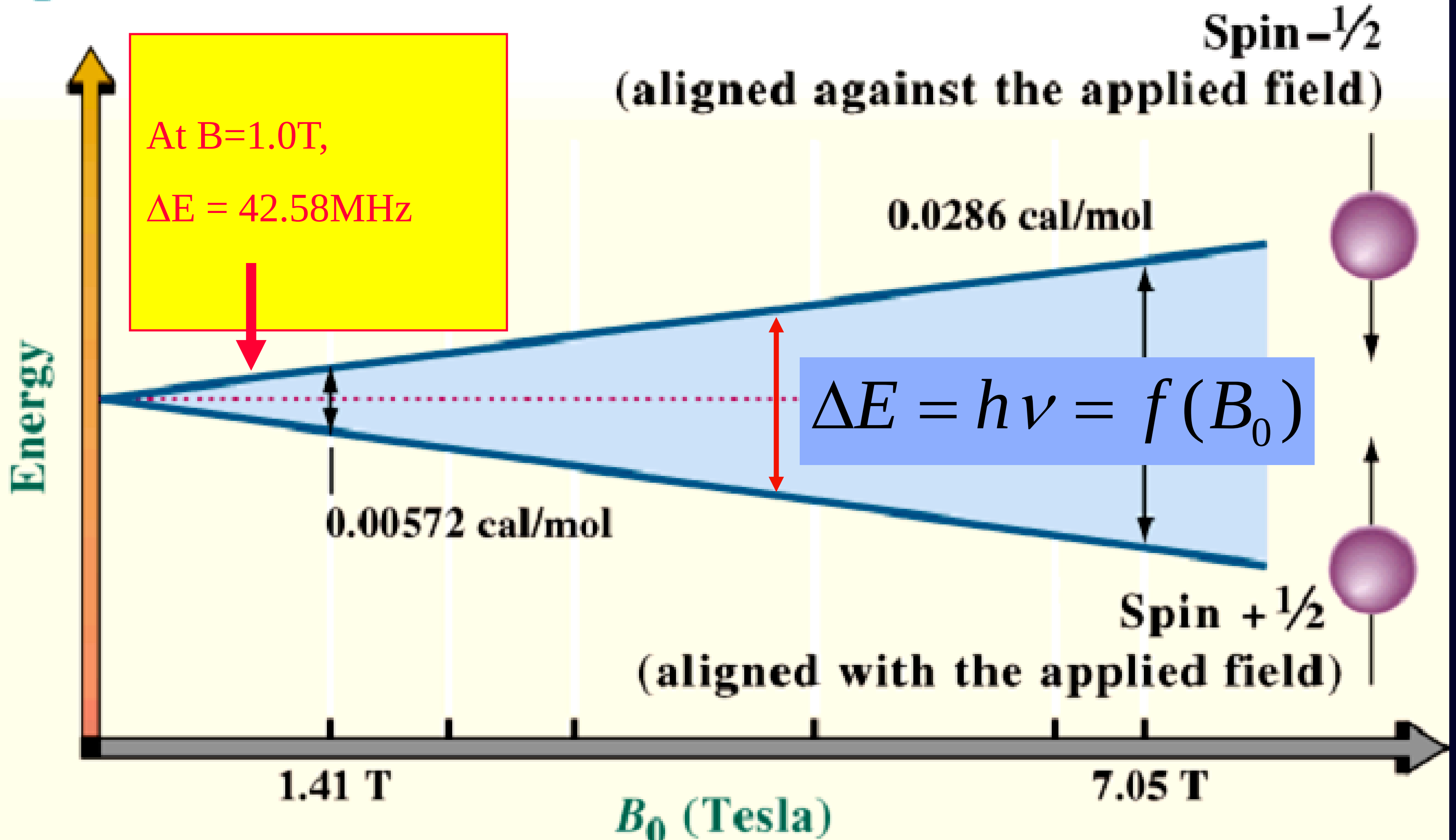
$$\nu = \gamma B$$

For hydrogen, γ = 42.58 MHz / Tesla

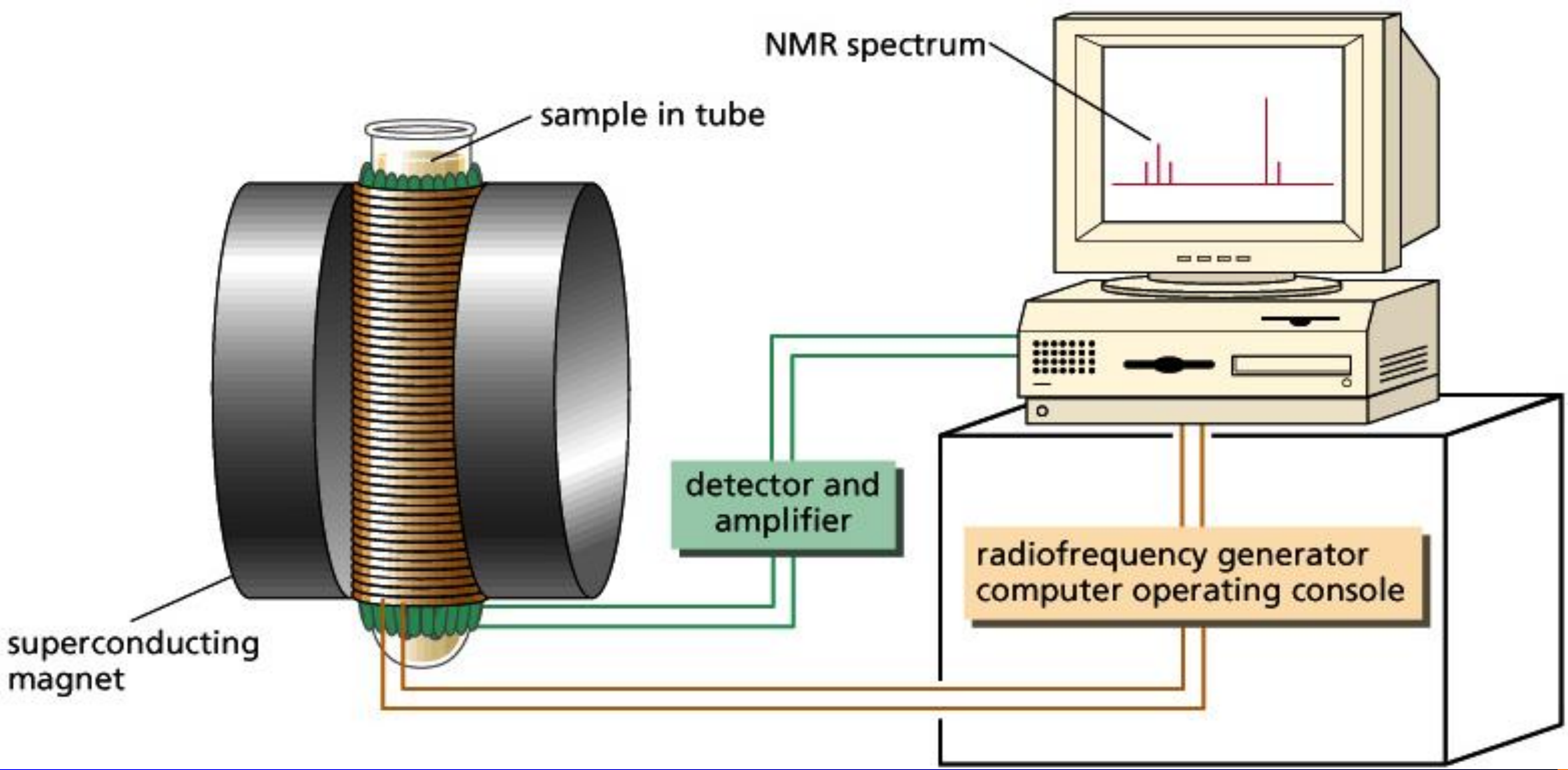
Allows you to calculate "spectrometer frequency" for ^{1}H !!

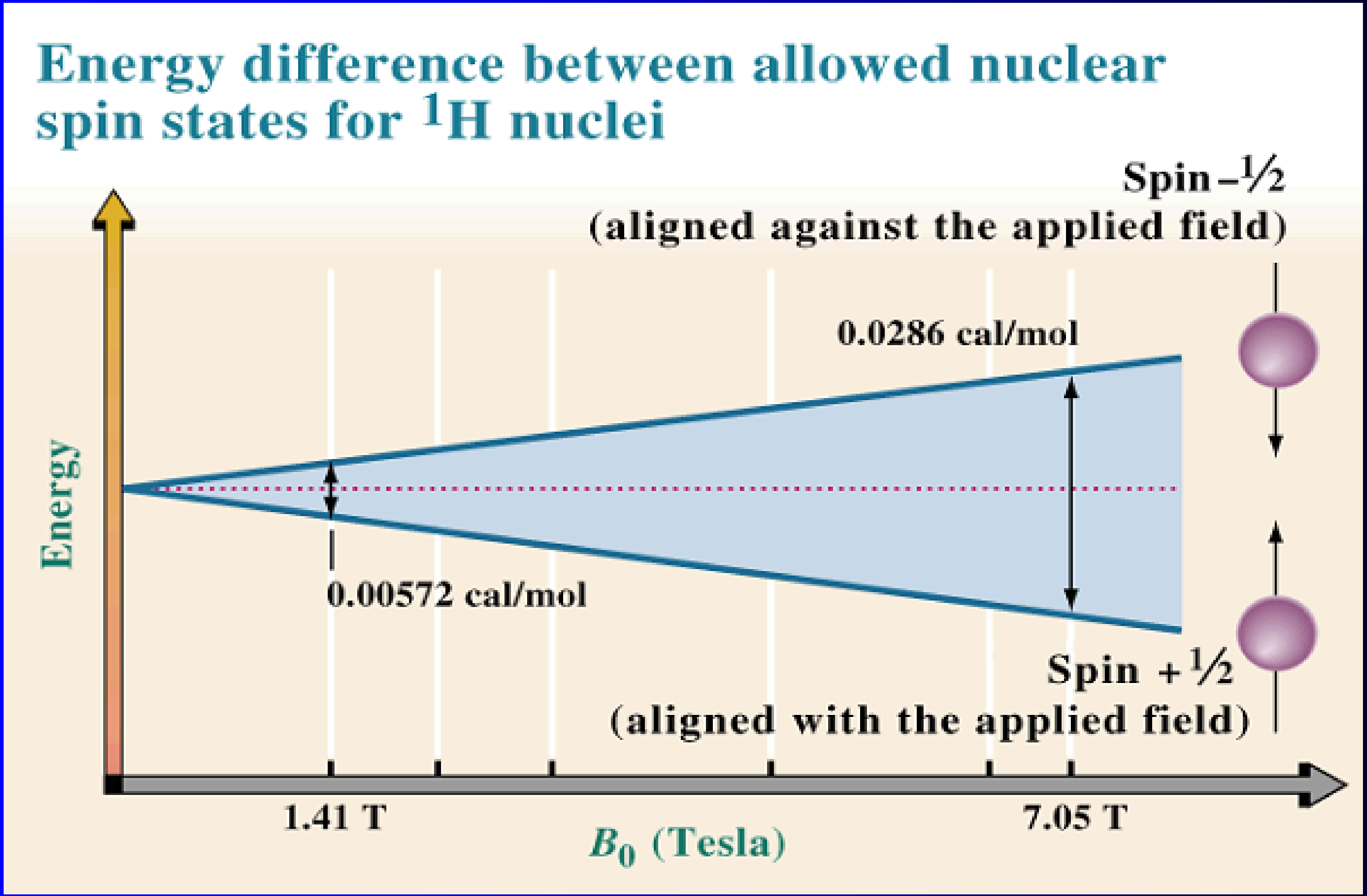
This is the frequency at which "naked" ^{1}H resonates in that machine

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



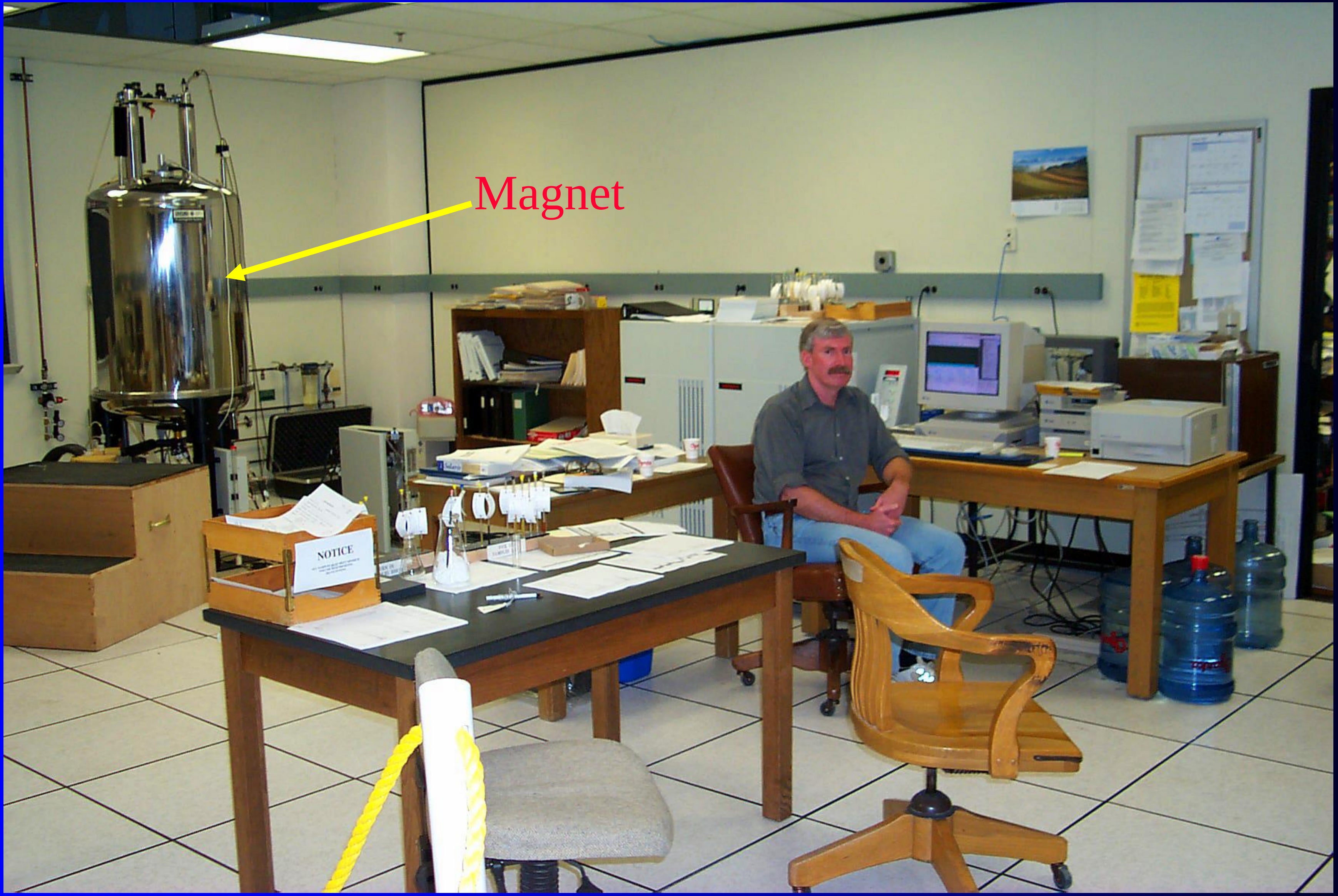
NMR Spectrometer





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

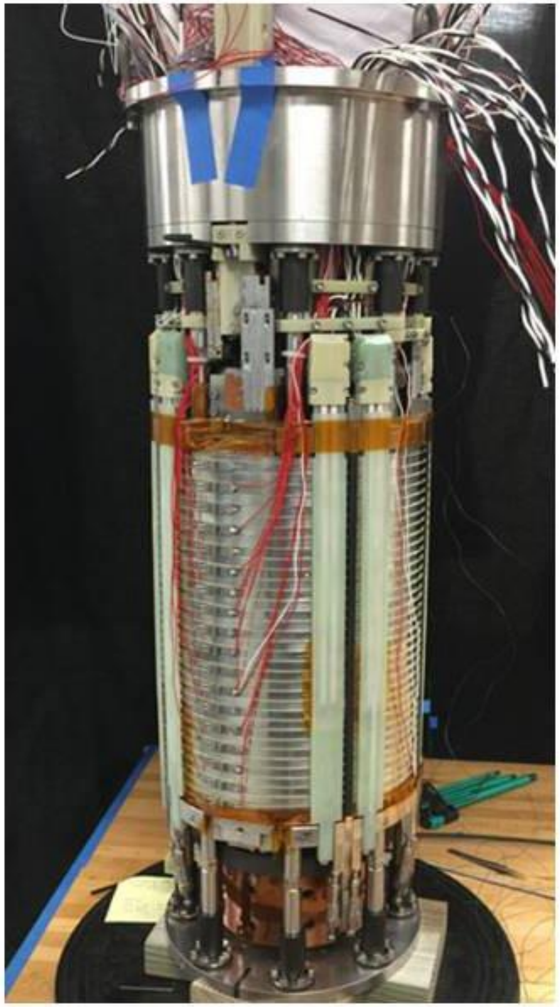


http://www.jeolusa.com/RESOURCES/AnalyticalInstruments/NMRMagnetDestruction/tabid/390/Default.aspx

The
deli
Trè


1020 MHz nmr
June 2015
Weight 15 tons

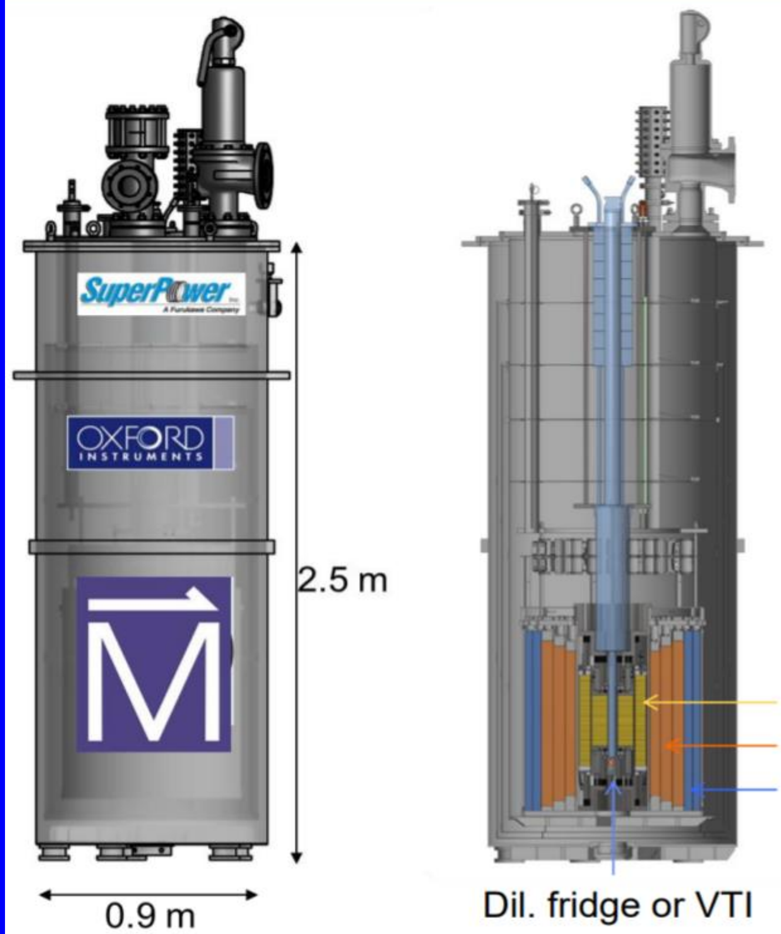
32T in Florida - 12/5/2017



The 32 T's two YBCO coils before
being integrated with the
low-temperature outer magnet.

The 32 T is lowered into its cryostat,
which keeps the instrument at
a very cold operating temperature.

32 Tesla Magnet - 2017



Key parameters:

Center field	32 T
Clear bore	34 mm
Ramp time	1 hour
Uniformity 1 cm DSV	5×10^{-4}
Operating temperature	4.2 K
Stored energy	8.3 MJ
Expected cycles/20 years	50,000
System weight	2.6 ton

15 T / 250 mm bore LTS magnet
17 T / 34 mm bore REBCO coils
Separately powered, simultaneously ramped

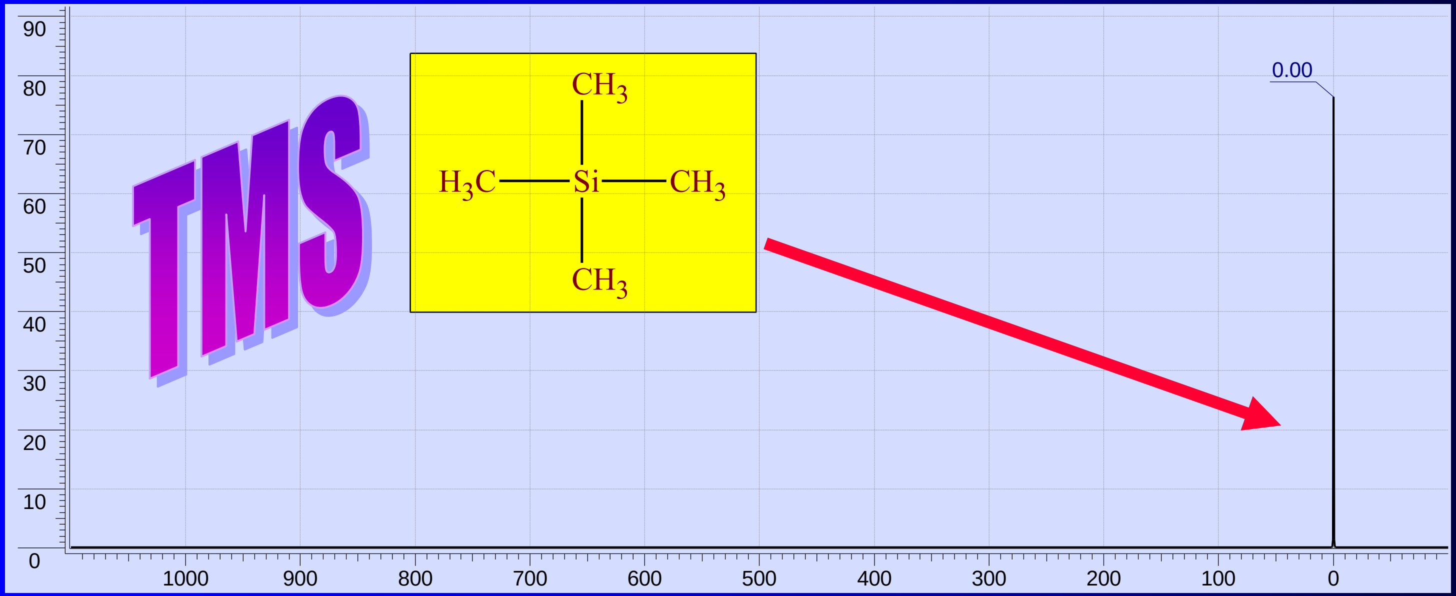
REBCO: 2 double pancake coils
Nb_3Sn coils
NbTi coils

https://indico.cern.ch/event/659554/contributions/2708372/attachments/1525993/2386079/3P1-01_Huub_Weijers_Room_1.pdf

Bonus…$$$$

Calculate the resonance frequency of ^{1}H at 32 T

The 100MHz nmr Chart

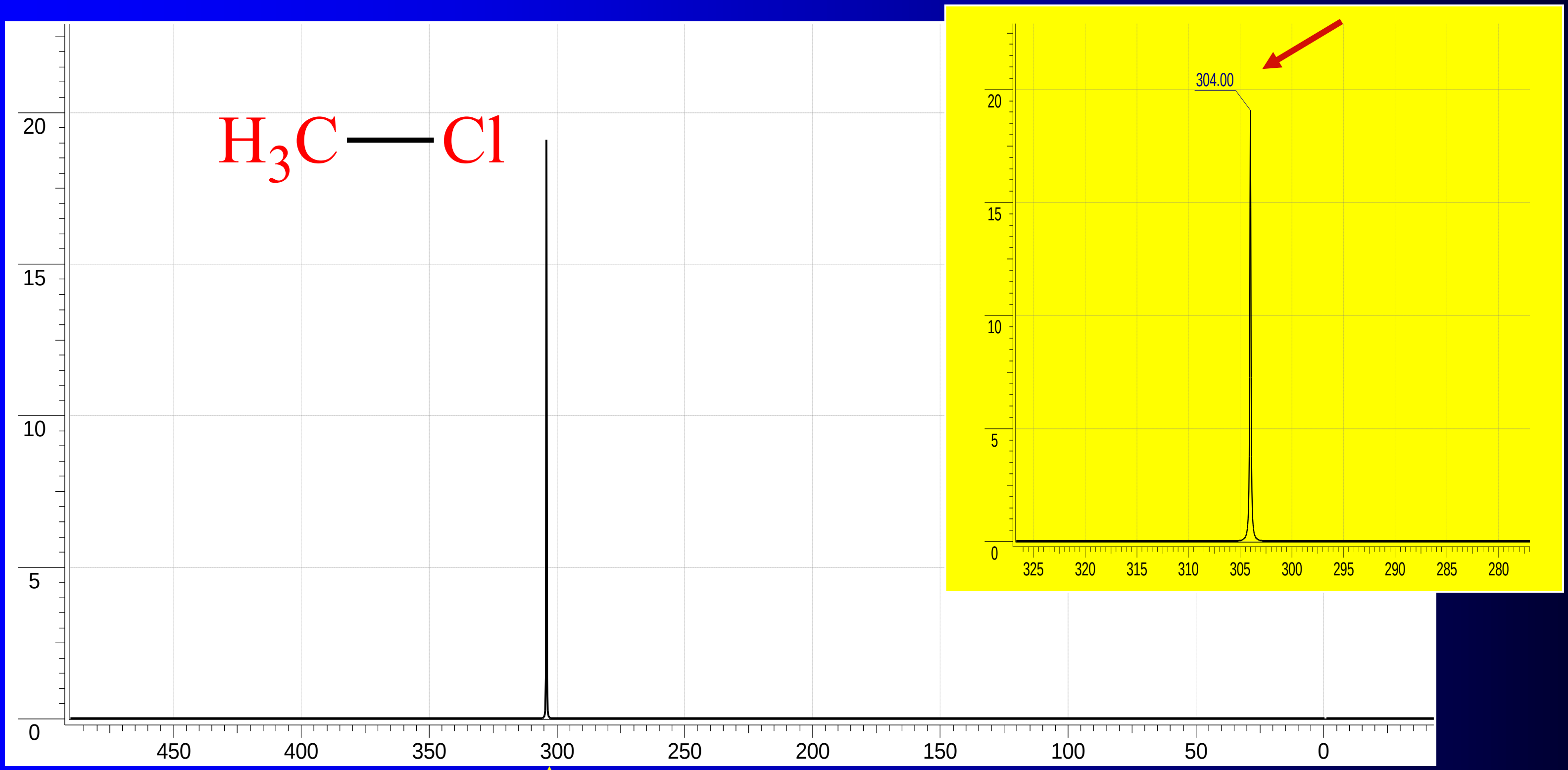


Frequency

field

The TMS resonance is defined as having “0” frequency

100MHz Spectrum



304 Hz

Hz

100MHz nmr Spectrum