

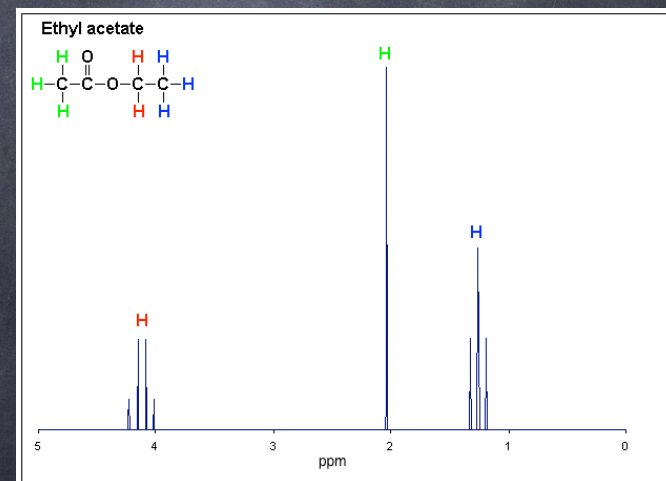
PHY 127 FS2024

Prof. Ben Kilminster

Lecture 12

May 24th, 2024

NMR



NMR: we seek to determine molecular structure, typically by measuring the hydrogen nuclear magnetic moment.

Using Radio frequency (RF) light, we cause energy transitions proportional to magnetic moment + B-field

$$h\nu = \Delta E = 2\mu_z B_z$$

Typically, we use f_{armor} , resonance frequency

$$\omega_{\text{armor}} = 2\pi f_{\text{armor}} = \gamma \cdot B_z$$

m : mass of resonating nucleus

q : charge of nucleus
 g : strength fact

Where γ : gyromagnetic ratio = $\frac{qg}{2m}$

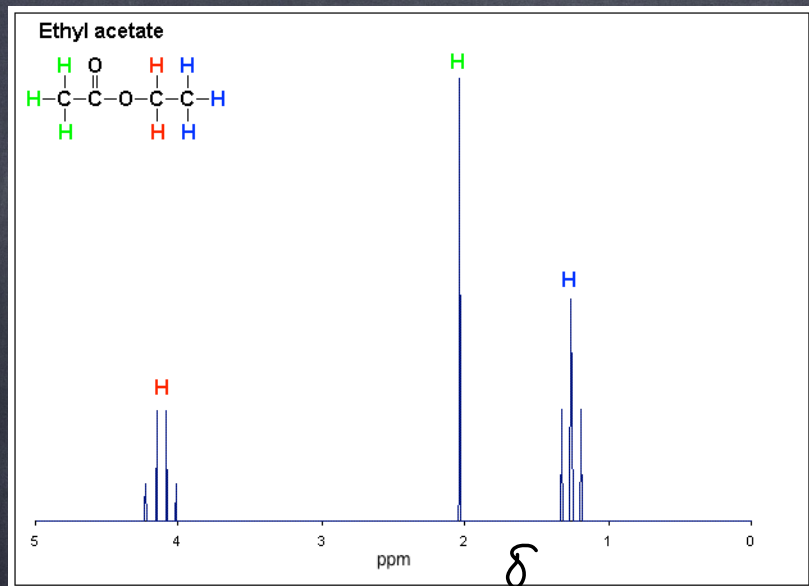
This value for ^1H is:

$$\gamma = \frac{(2\pi)(42.58 \text{ MHz})}{\text{T}}$$

T: the Tesla unit for \vec{B}

e.g. For ^1H in a 1.5T magnetic field

$$f_{\text{armor}} = \frac{\gamma \cdot B_z}{2\pi} = \left(\frac{42.58 \text{ MHz}}{\text{T}} \right) \left(\frac{2\pi}{2\pi} \right) (1.5 \text{ T}) = 63.87 \text{ MHz}$$



← position of peaks measured as a chemical shift, δ .

$$\delta = \frac{f_{\text{sample}} - f_{\text{ref}}}{f_{\text{ext}}} \cdot 10^6$$

$f_{\text{ext}} \Rightarrow$ where $\Delta E = h\nu$
frequency of RF radiation

δ (has units in ppm)

f_{sample} : measured frequency spectrum of the sample

f_{ref} : reference sample, ~~typical~~ typically used TMS "tetramethylsilane"



chemically inert and has a strong signal of 12 protons.

Features : number of peaks
peak multiplicity (singlet, doublet, triplet...)
position of peaks
size (or area) of peaks

area under peaks \rightarrow strength of the peaks is proportional to the relative numbers of hydrogen in the local chemical group.



we expect to see 3 peaks,
areas should be in the ratio
3:2:1

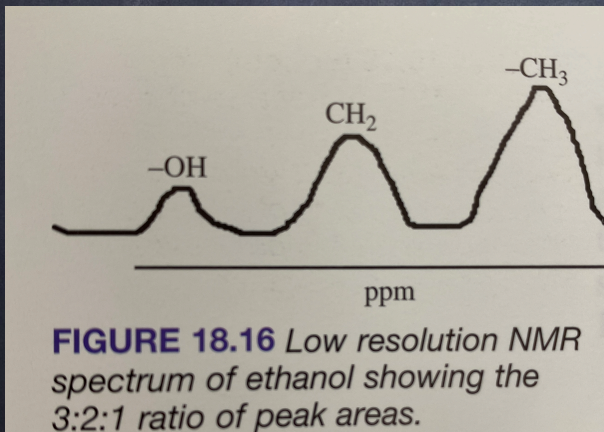
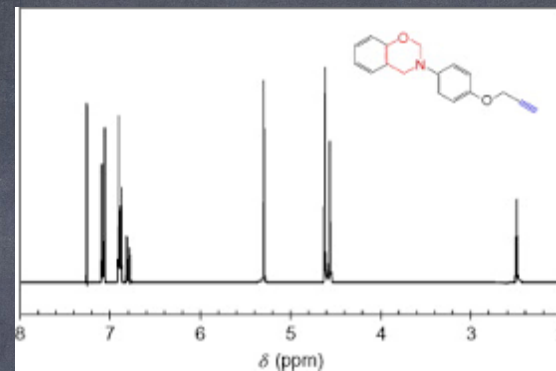
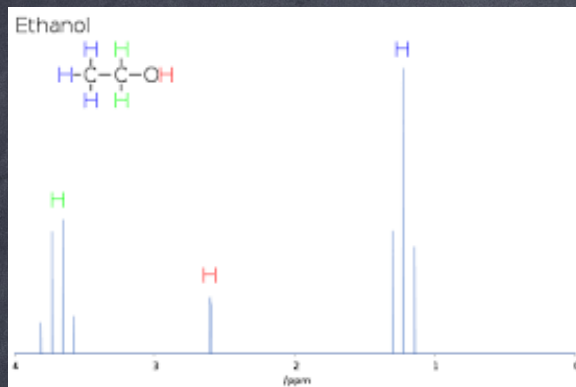


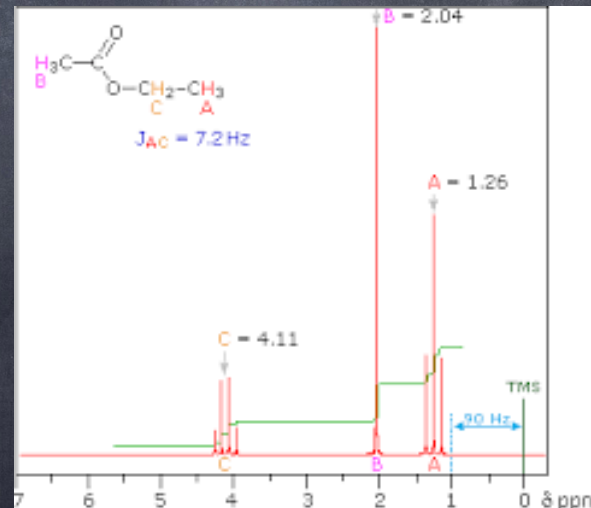
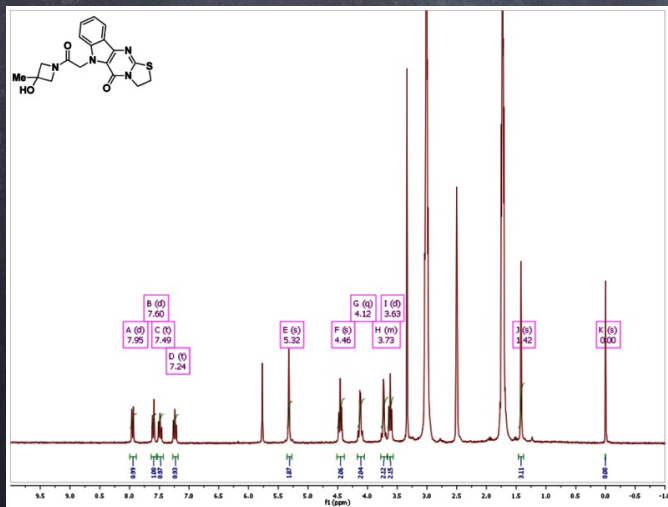
FIGURE 18.16 Low resolution NMR spectrum of ethanol showing the 3:2:1 ratio of peak areas.

widths of the peaks provide structural information on location of nuclei in the larger molecule.

Examples of NMR spectra (τ -axis is δ (ppm))



multiple peaks
from energy splitting
from neighboring protons



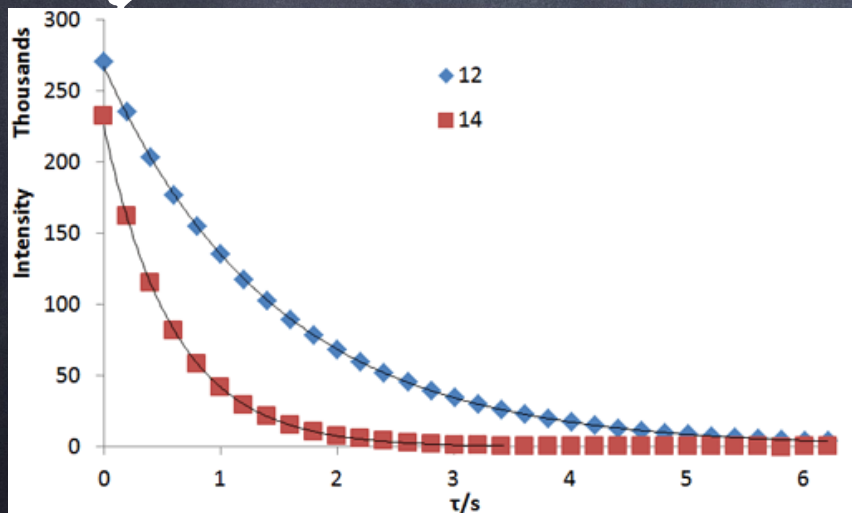
when we put a pulse of RF radiation into our sample, the magnetization of the sample changes, but then the magnetization relaxes to equilibrium.

$$U_{\text{ind}} = U_{\text{ind}}^{\text{max}} e^{-t/T_2}$$

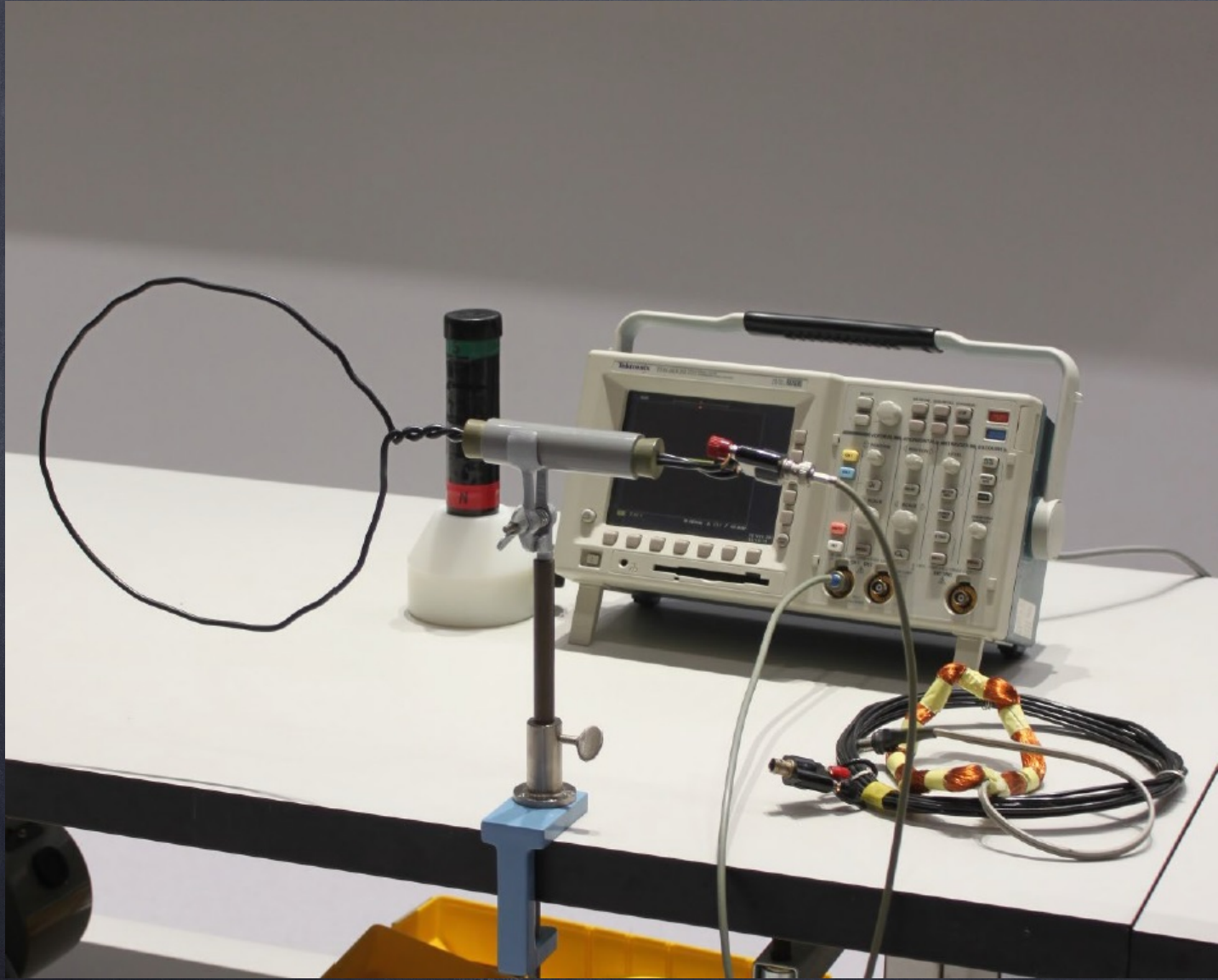
↑
induced energy
in the measuring
solenoidal magnet
coil.

↑
max.
value

T_2 : spin-relaxation time



← shows T_2 for 2 different t -butyl protons from 12,14-di t -butyl benzo[*g*]chrysene



In our class experiment, we change magnetic field, and measure induced current with Solenoid.

In NMR, we instead use a radio frequency pulse tuned to the resonance frequency f_{Larmor} to change the magnetic moment of our sample, and measure induced current with a solenoid.

Now, we talk about MRI (magnetic resonance imaging)
Our goal is to do a 3-D scan of a human body.



we use NMR to map out the location of hydrogen (protons) in the human body.

If the magnetic field were constant over the body, there would be no way to tell where the NMR signal is coming from.

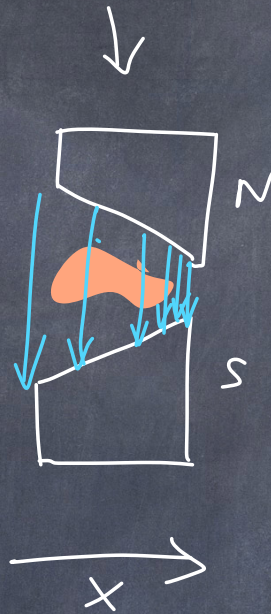
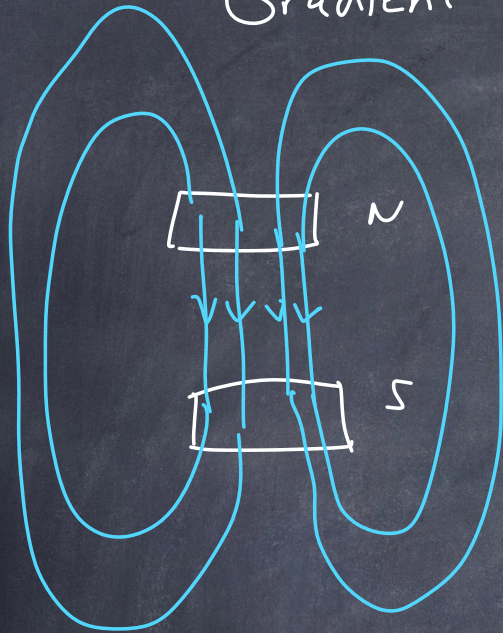
so we apply a magnetic field gradient to our body in 3 dimensions. So the magnetic field is different as a function of x, y, z

Gradients are typically 10^{-2} T/m are used so that the resonance condition $\Delta E = 2\mu B = h\nu$ will vary along some direction according to the value of B .

If an RF pulse matches the resonance condition of a particular slice (or plane), then only these protons will be detected.

The x, y, z positions of the body are encoded in the RF frequency.

Gradient magnetic field



$$\bar{B}_x = \bar{B} + \bar{B}_{gr}(x)$$

↑
nominal
value

$$\omega_{Larmor} = \gamma \cdot (B + B_{gr}(x))$$

ω_{Larmor} frequency varies
with x .

The level of the NMR signal at a frequency ω_i is a measure of the density of hydrogen nuclei at the location x .

we would have gradients in $x, y, \& z$

$$\bar{B}_y = \bar{B} + \bar{B}_{gr}(y)$$

↑
static
value

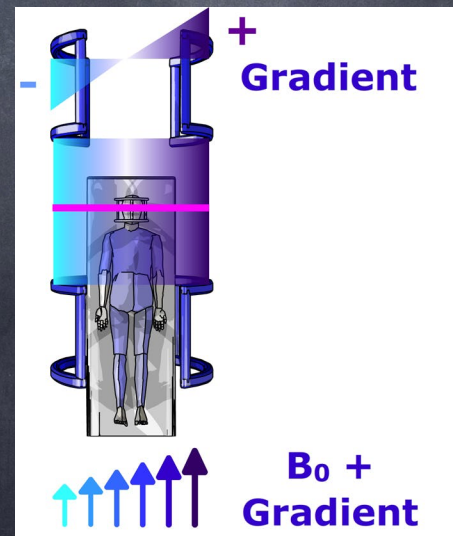
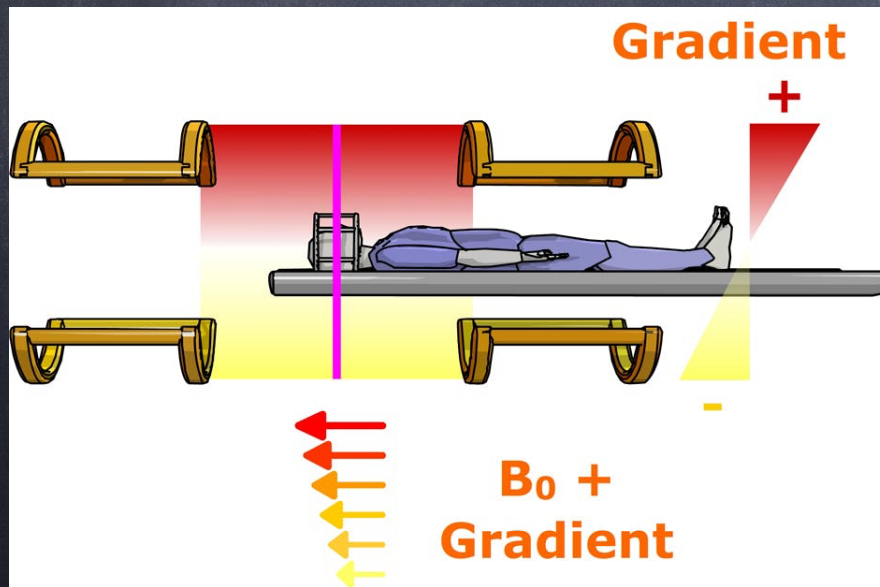
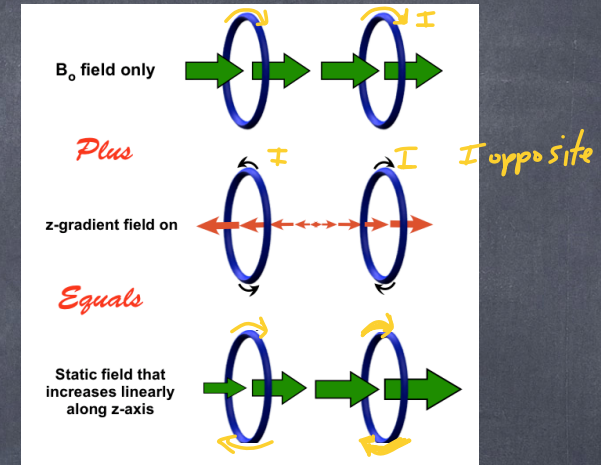
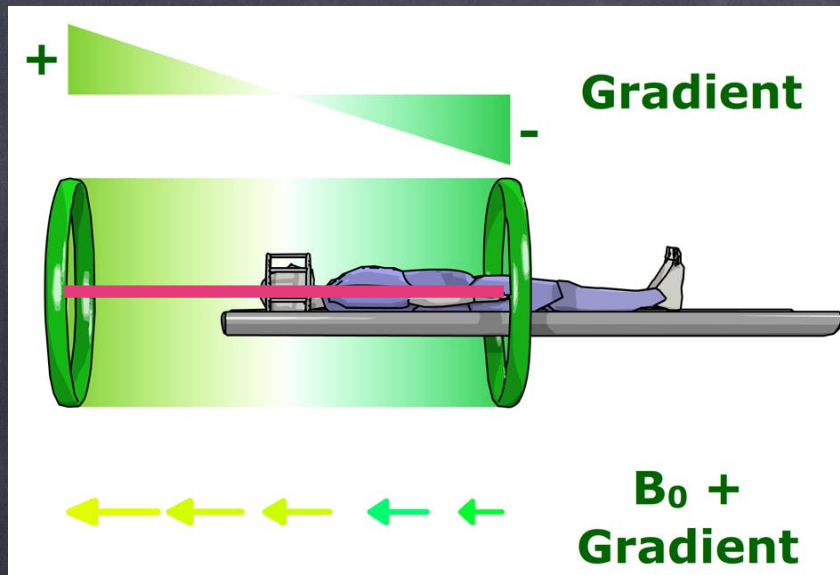
$$B_z = \bar{B} + \bar{B}_{gr}(z)$$

Applying the gradients sequentially in 3 directions. Transmit our RF pulses, then we measure the induced current (in our solenoid), determines the magnetization at a specific location \rightarrow density of hydrogen at that location.

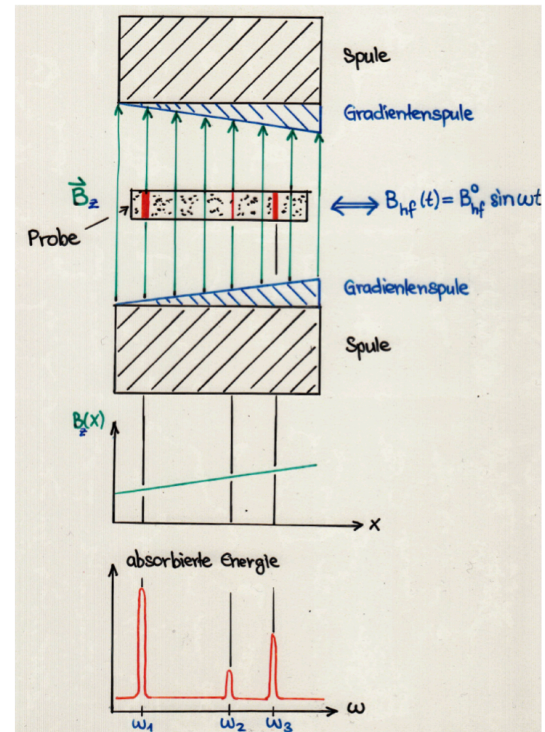
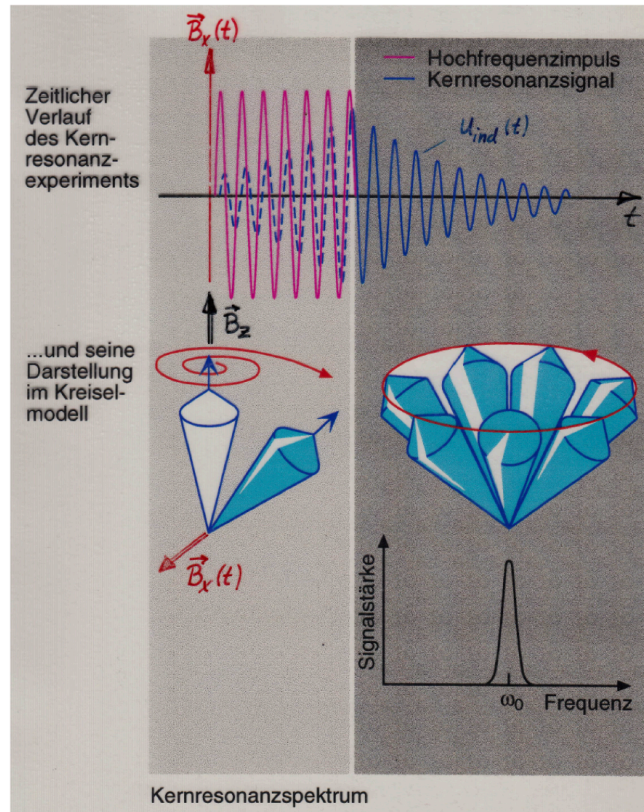
(This measured signal is proportional to the # hydrogen nuclei at a specific x, y, z)

Then a computer reconstructs this 3D image.

How to make gradient field:



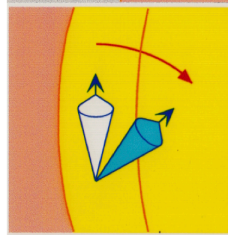
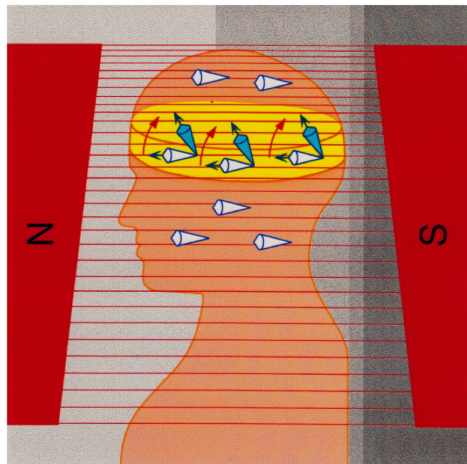
Magnetische Resonanz-Spektroskopie



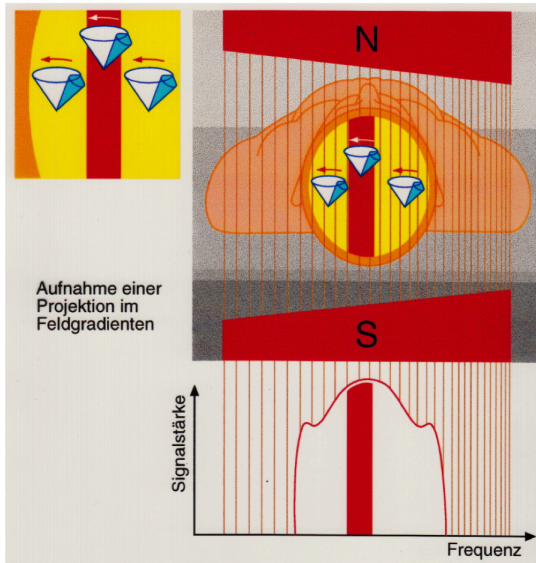
Die Ortsinformation, von woher ein Signal stammt, wird über die bekannte Ortsabhängigkeit des B-Feldes kodiert, welche in die Resonanzfrequenz eingeht.

von Hugo Keller

Magnetische Resonanz-Tomographie



Selektive
Anregung
einer Schicht

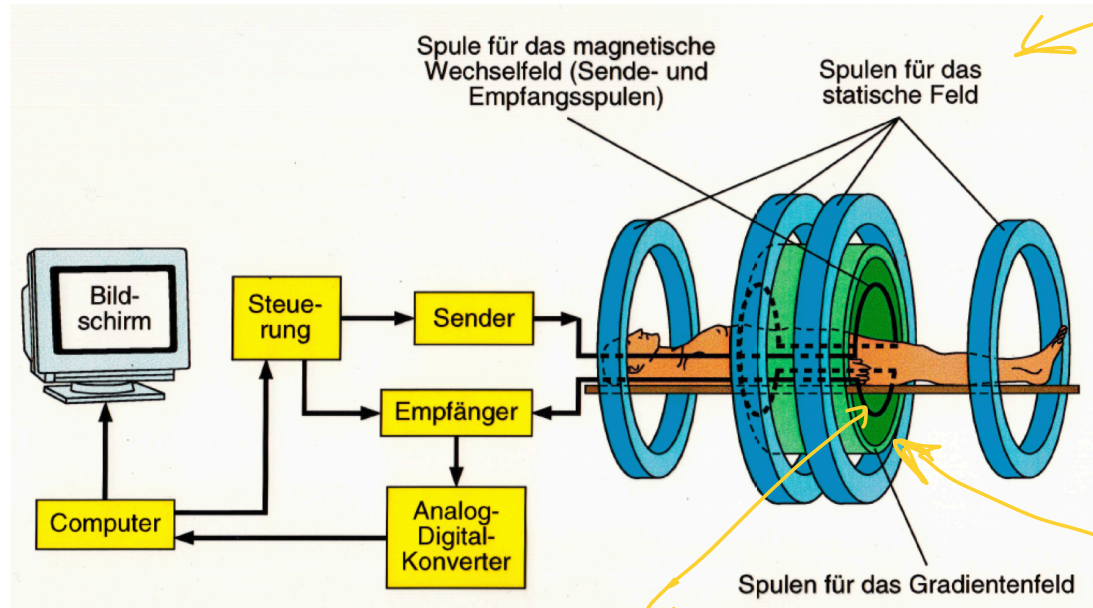


Aufnahme einer
Projektion im
Feldgradienten

Die verschiedenen Schnitte und Projektionen werden im Computer zu einem drei-dimensionalen Bild zusammengesetzt, woraus man dann Schnitte in beliebigen Richtungen generieren kann. (altgriechisch 'tome' bedeutet Schnitt)

von Hugo Keller

Aufbau einer MRT-Anlage



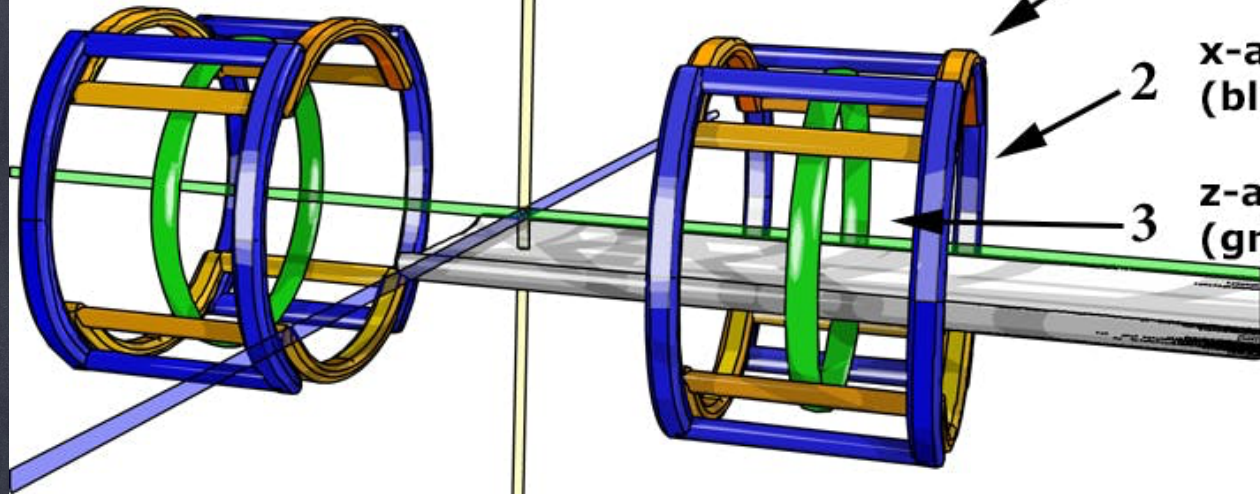
\vec{B} is static

coil for measuring the changes

green : $\vec{B}(x)$ gradient field

von Hugo Keller

Gradients X, Y, Z

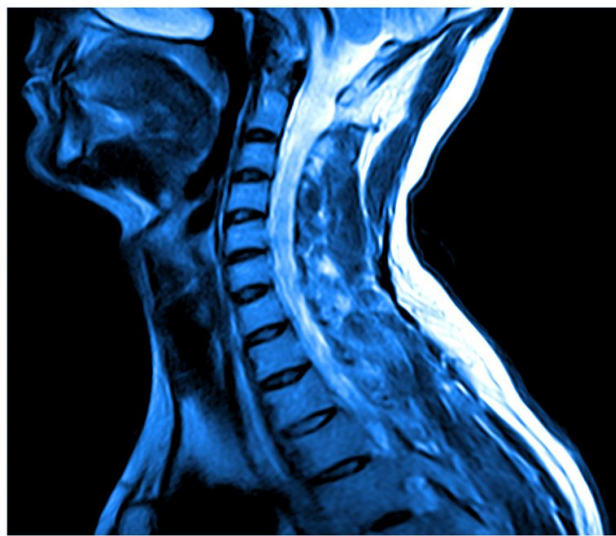
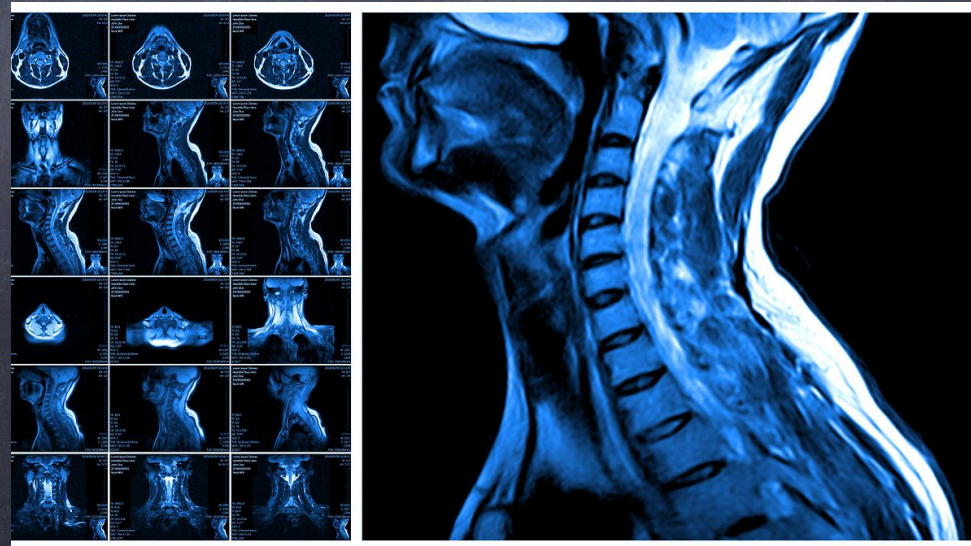


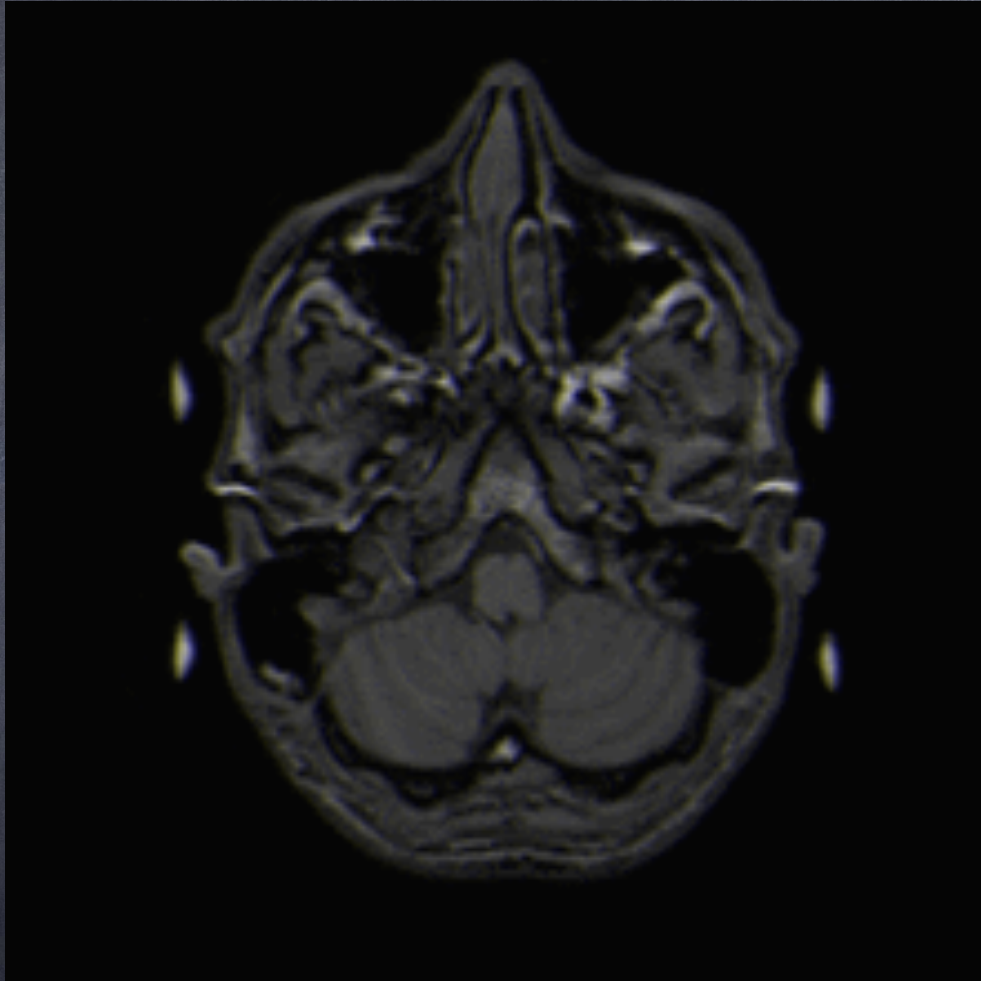
1 y-axis gradient
(yellow coils)

2 x-axis gradient
(blue coils)

3 z-axis gradient
(green coils)

non-destructive
slices





Contrast between tissues in MRI comes from two processes. One is that different tissues have different water content (H_2O)

The second differentiation is from the relaxation time, T_2

TABLE 23.5

Relaxation time of hydrogen nuclear spins in an external magnetic field as a function of tissue with and without tumours

Tissue	Relaxation time T_{relax} (s)	
	Healthy	With tumour
Breast	0.37	1.08
Skin	0.62	1.05
Muscle	1.02	1.41
Liver	0.57	0.83
Stomach	0.77	1.24
Lung	0.79	1.10
Bone	0.55	1.03
Water	3.6	—

Table 18.2 Water Content of Normal Human Tissue

Tissue	% water
Brain (white matter)	84
Kidney	81
Myocardium	80
Skeletal muscle	79
Brain (gray matter)	72
Liver	71
Nerve	56
Bone (cortex)	12
Teeth	10

Nuclear physics

Atomic sizes $\sim 0.1 \text{ nm}$ (10^{-10} m)

Nuclear sizes $\sim 10^{-15} \text{ m}$

IF an atom was the size of a football field,
the nucleus would be the size of a
pin head (1mm)

proton mass $\sim 1800 \times$ electron mass

Elements: $A = Z + N$

↑ ↑ ↑
atomic number of number
number of protons of neutrons

Notation for element, E: ${}^A_Z E \rightarrow {}^A E$

units $1 \text{ u} \equiv \frac{1}{12} \text{ C}^{12} \text{ atom}$

example ${}^{13}_6 \text{C} \equiv {}^{13}\text{C}$

Nuclide refers to a particular Z and N combination.
Nuclides with the same Z but different N
are called isotopes.

Some isotopes are stable, and some are radioactive.

Structure of isotopes has been determined by
scattering electrons on the isotope.

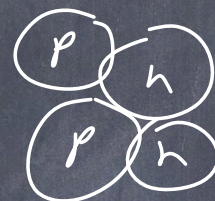
$$\lambda = \frac{h}{p}$$

For electron with $p = 200 \frac{\text{MeV}}{c}$ $c = 3 \times 10^8 \frac{\text{m}}{\text{s}}$

$$\lambda = \frac{h}{p} = \frac{4.1357 \times 10^{-15} \text{ eV} \cdot \text{s}}{200 \frac{\text{MeV}}{c}} = \frac{4.1357 \times 10^{-15} \text{ eV} \cdot \text{s}}{200 \times 10^6 \text{ eV}} \cdot 3 \times 10^8 \frac{\text{m}}{\text{s}}$$

$$\lambda = 6 \times 10^{-15} \text{ m} = 6 \text{ fm}$$

This is small enough to probe nuclear sizes.



Note: formula for energy relates momentum
and mass $E^2 = (cp)^2 + \underbrace{(mc^2)^2}$

can be neglected
if $p \gg m$

Then $p = \frac{E}{c}$

Example: for electron with $p = 200 \text{ MeV}/c$
 $E^2 = (200 \text{ MeV})^2 + (0.511 \text{ MeV})^2$
 $E = 200.0007 \text{ MeV}$

units: E [eV]
 p [$\frac{\text{eV}}{c}$]
 m [$\frac{\text{eV}}{c^2}$]

Nuclei are mostly spherical, but some are
elipsoidal

size $R \cong R_0 A^{1/3}$ $R_0 \sim 1.2 \text{ fm}$

density is almost the same for all nuclei;

density of a proton: $\rho = \frac{m_p}{\frac{4}{3}\pi r^3} = \frac{1.67 \times 10^{-27} \text{ kg}}{\frac{4}{3}\pi (1.2 \times 10^{-15} \text{ m})^3}$

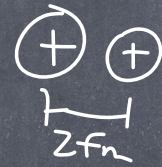
$$\rho = 2 \times 10^{17} \text{ kg/m}^3$$

ρ is 10^{14} times larger than the density
of an atom.

Why is the nucleus ever stable?

Densely packed with protons that repel each other.

Coulomb force: $F = \frac{e^2}{4\pi\epsilon_0 r^2}$



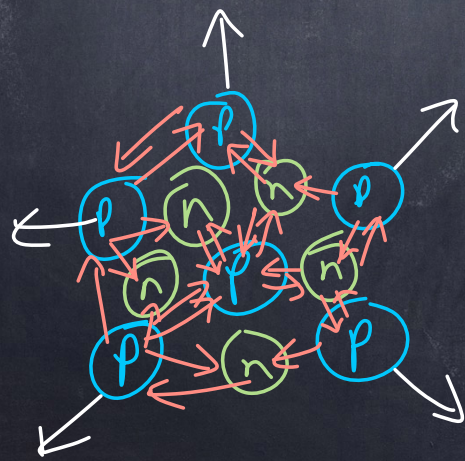
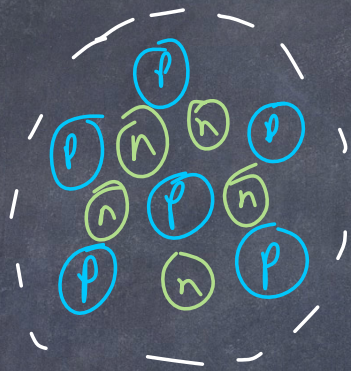
For $r = 2 \text{ fm}$, 2 protons repel each other with a force of $F = 60 \text{ N}$.
(equivalent to a 6 kg weight)

Answer: the nucleus is held together by the strong nuclear force. This is an attractive force more than 100 times stronger than the Coulomb force repulsion.

↓
only when the protons are close to each other (as in a nucleus)

nucleon = proton or a neutron
Nucleons are all attracted by the strong nuclear force.

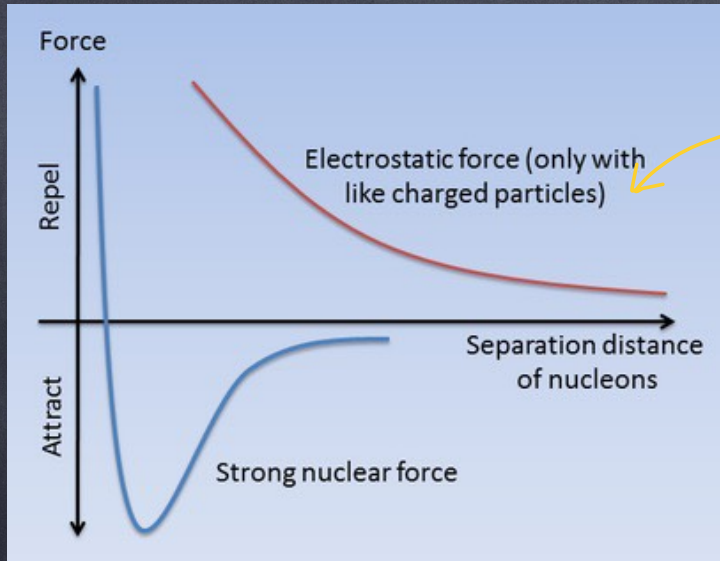
Nucleus



strong force
electrostatic repulsion

force between protons

← Two separate forces



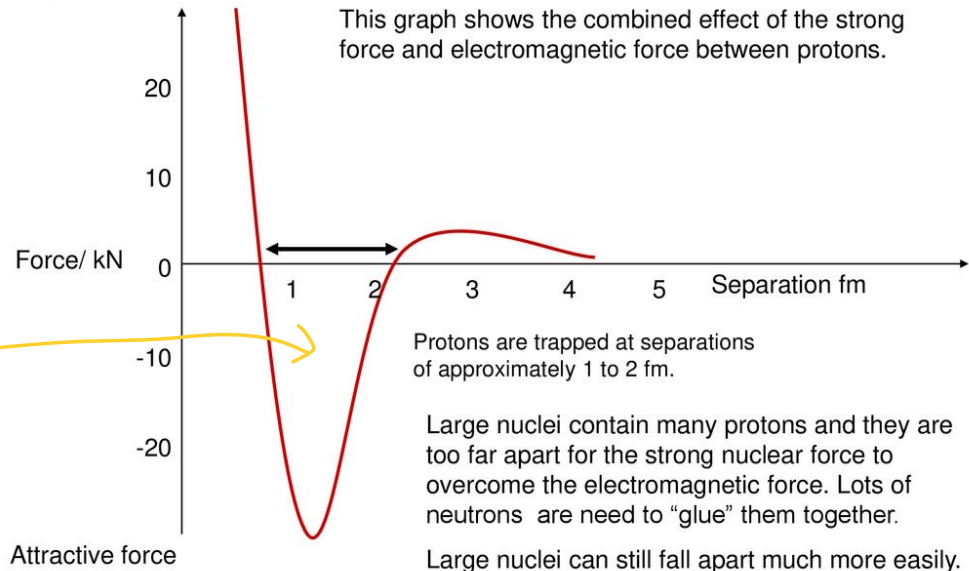
Coulomb force

the combined effect of the two forces is here ↓

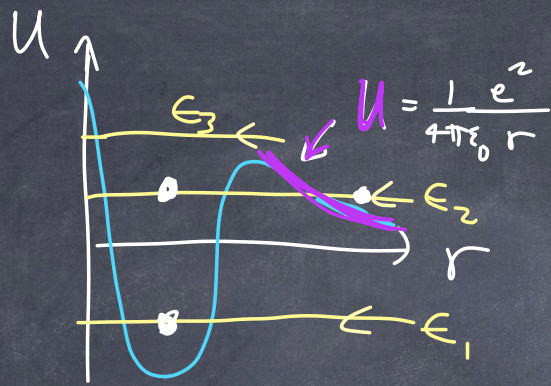
where protons would be trapped in the potential

The force between protons

Repulsive force



Attractive force



U : potential energy of a proton at a given radius.

So, imagine a proton approaching a nucleus, it needs enough energy to overcome the barrier, then it can be trapped in the potential well.

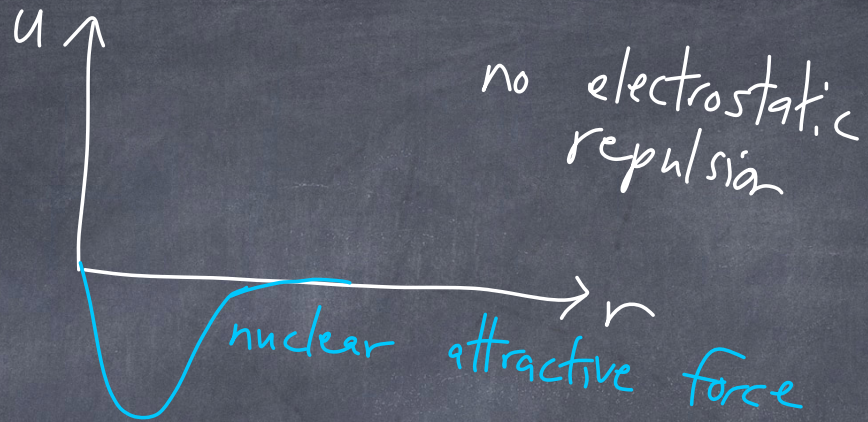
total energy of proton in well

E_1 : stuck in the potential, not enough energy to escape (stable nuclei)

E_2 : meta-stable, quantum mechanics lets the proton tunnel out of the well, since it has enough energy to exist outside the nucleus.

E_3 : unstable, immediately escapes the nucleus.

For a neutron



Easier for a neutron to get captured by a nucleus (than a proton)

The nucleus is often thought of as a liquid drop.

nucleus

drop

both are incompressible and have uniform density

held together by the nuclear force

held together by surface tension

drop can break into smaller drops

The total energy of a nucleus is the sum of the kinetic energy & potential energy of the constituents (nucleons). The potential energy is negative and larger than the kinetic energy, so the total energy is negative.

The total energy of the individual constituents (nucleons) is larger than the energy of the assembled nucleus. The difference is due to the binding energy of the nucleus.

$$\text{Nuclear binding energy} = Z(m_p c^2) + N(m_n c^2) - mc^2$$

m_p : mass of proton
 m_n : mass of neutron
 m : mass of the assembled nucleus.

The binding energy is about 1% of the mass

$$\frac{\downarrow 8 \text{ MeV}}{1 \text{ u}} = \frac{8 \text{ MeV}}{930 \text{ MeV}} \sim 1\%$$