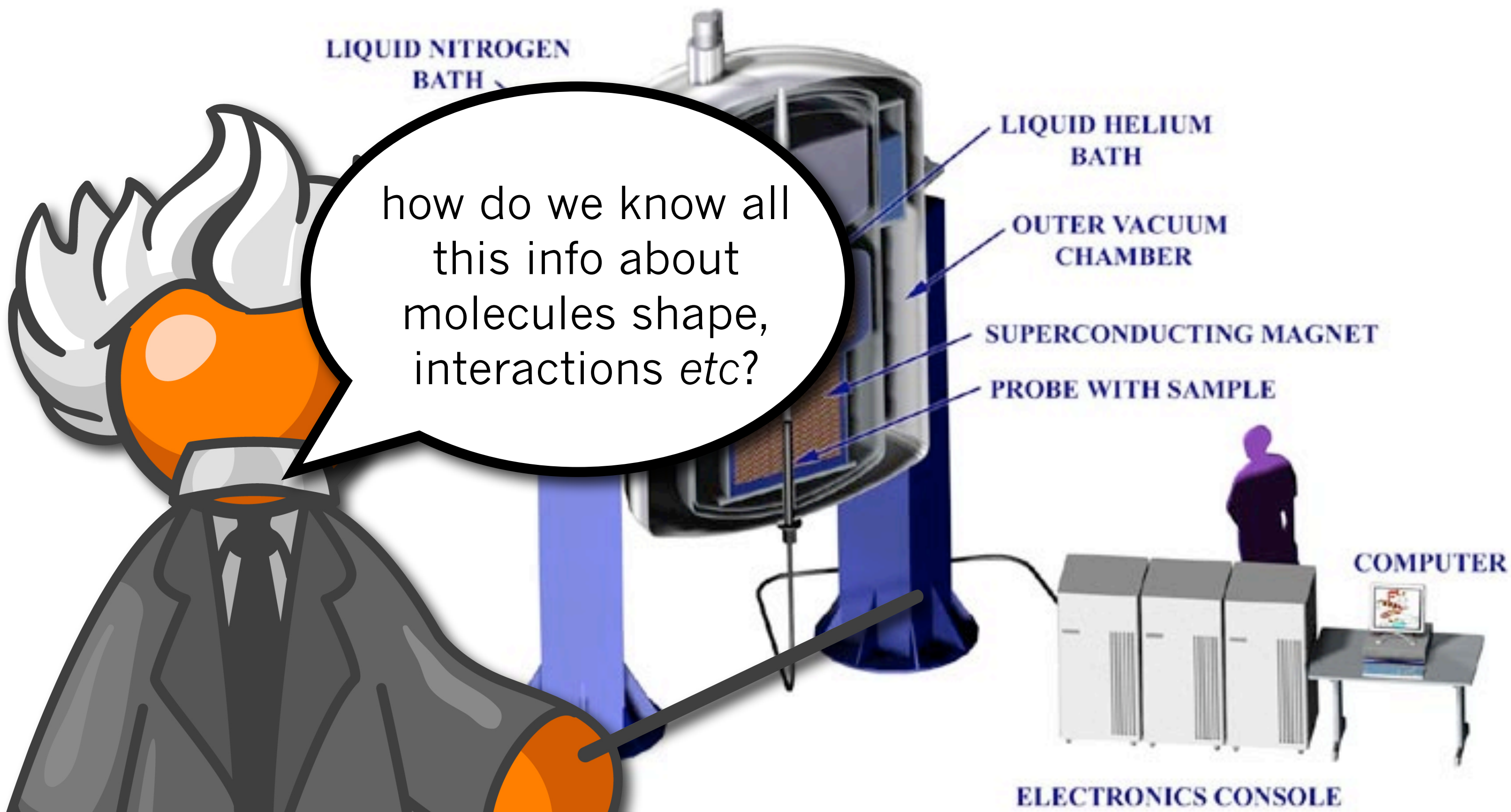
Unit One Part 9:
nuclear magnetic resonance spectroscopy

Unit One Part 9

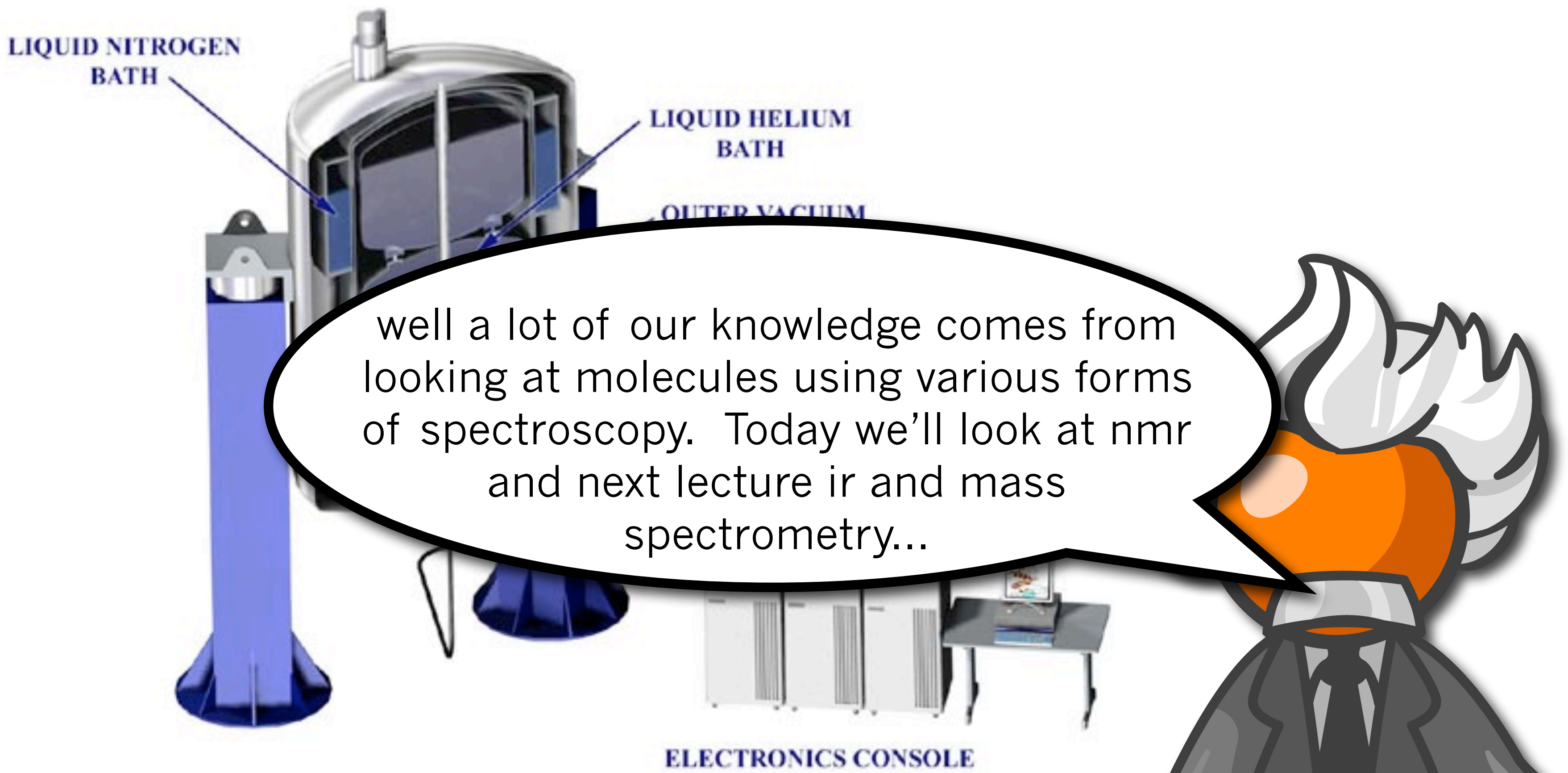
nmr spectroscopy

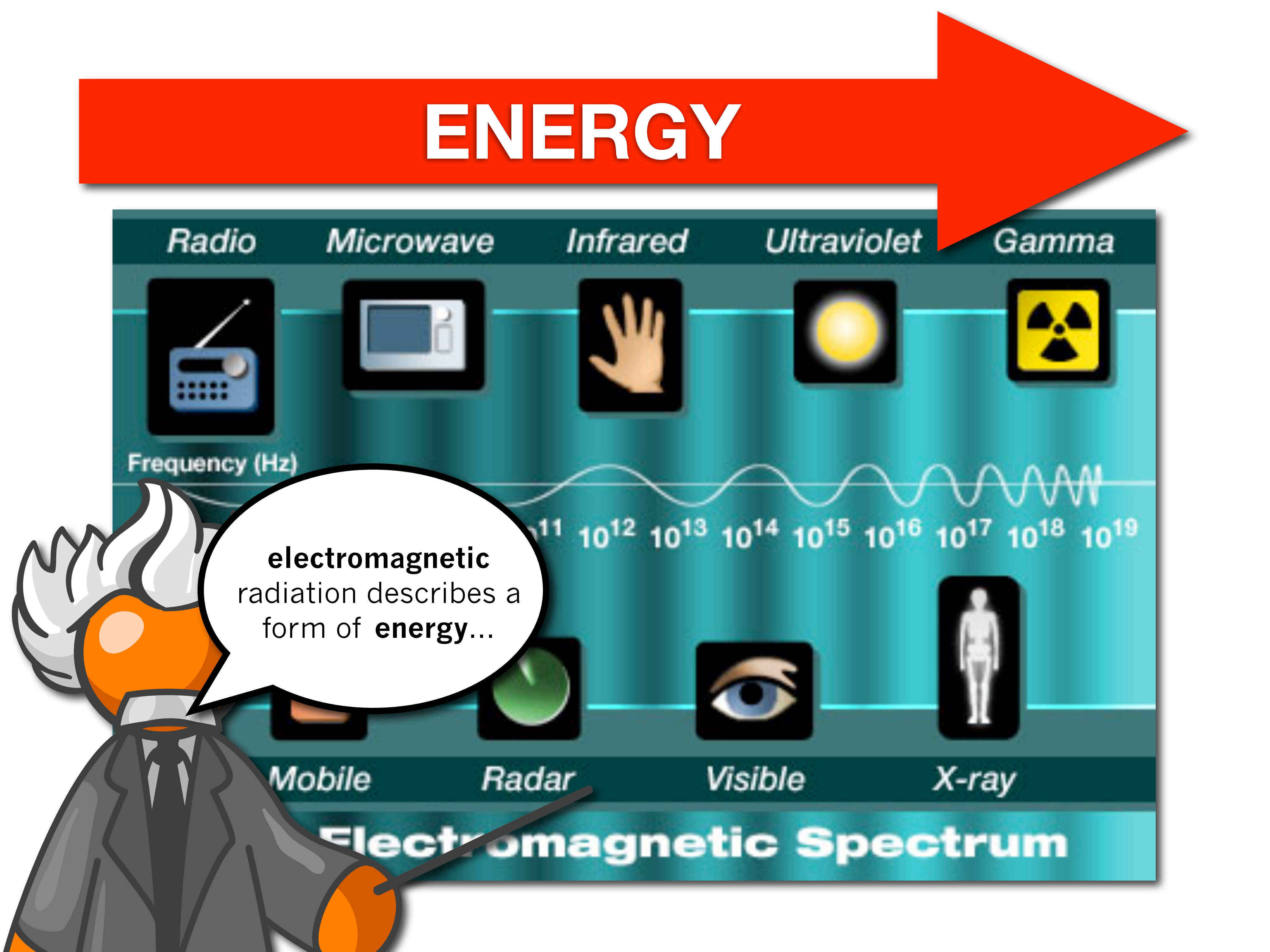
equivalent hydrogens

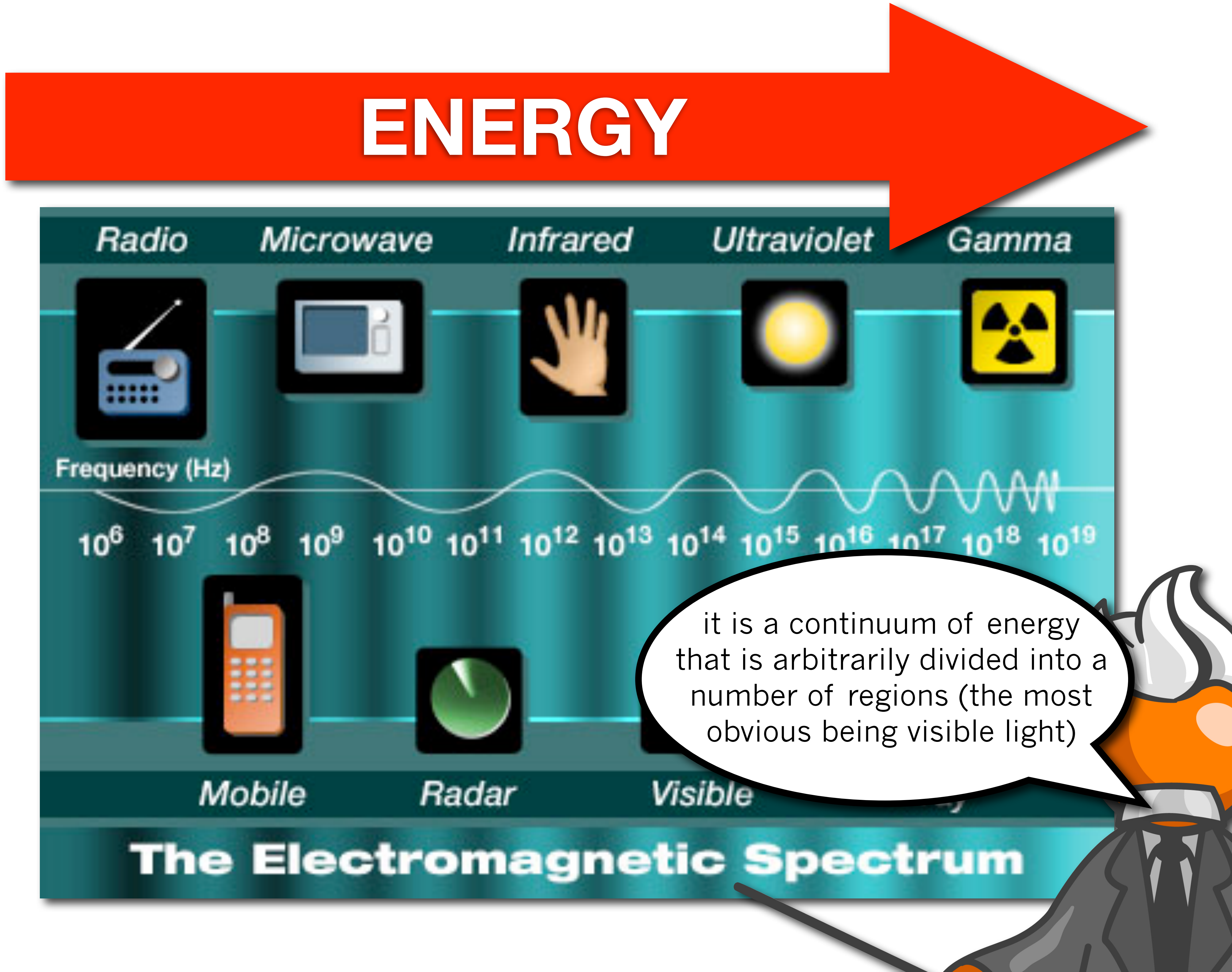
integral vs. number of hydrogens

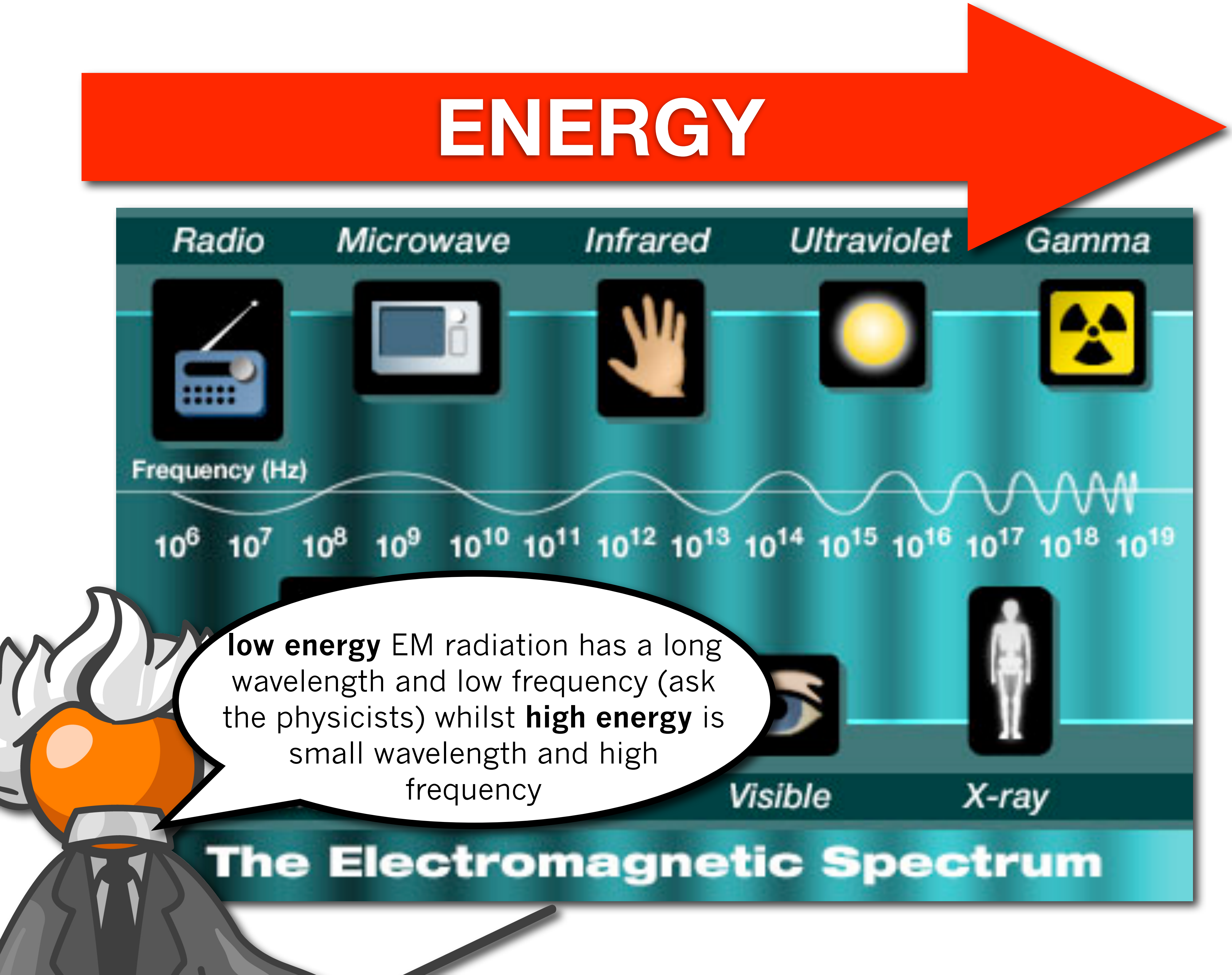


Unit One
Part 9
nmr spectroscopy
equivalent hydrogens
integral vs. number of hydrogens




ENERGY
Radio
Microwave
Infrared
Ultraviolet
Gamma
Frequency (Hz)
10^{12} 10^{13} 10^{14} 10^{15} 10^{16} 10^{17} 10^{18} 10^{19}
Mobile
Radar
Visible
X-ray
omagnetic Spectrum
electromagnetic radiation describes a form of **energy**...


ENERGY
Radio
Microwave
Infrared
Ultraviolet
Gamma
Frequency (Hz)
10^6 10^7 10^8 10^9 10^{10} 10^{11} 10^{12} 10^{13} 10^{14} 10^{15} 10^{16} 10^{17} 10^{18} 10^{19}
Mobile
Radar
Visible
The Electromagnetic Spectrum
it is a continuum of energy that is arbitrarily divided into a number of regions (the most obvious being visible light)

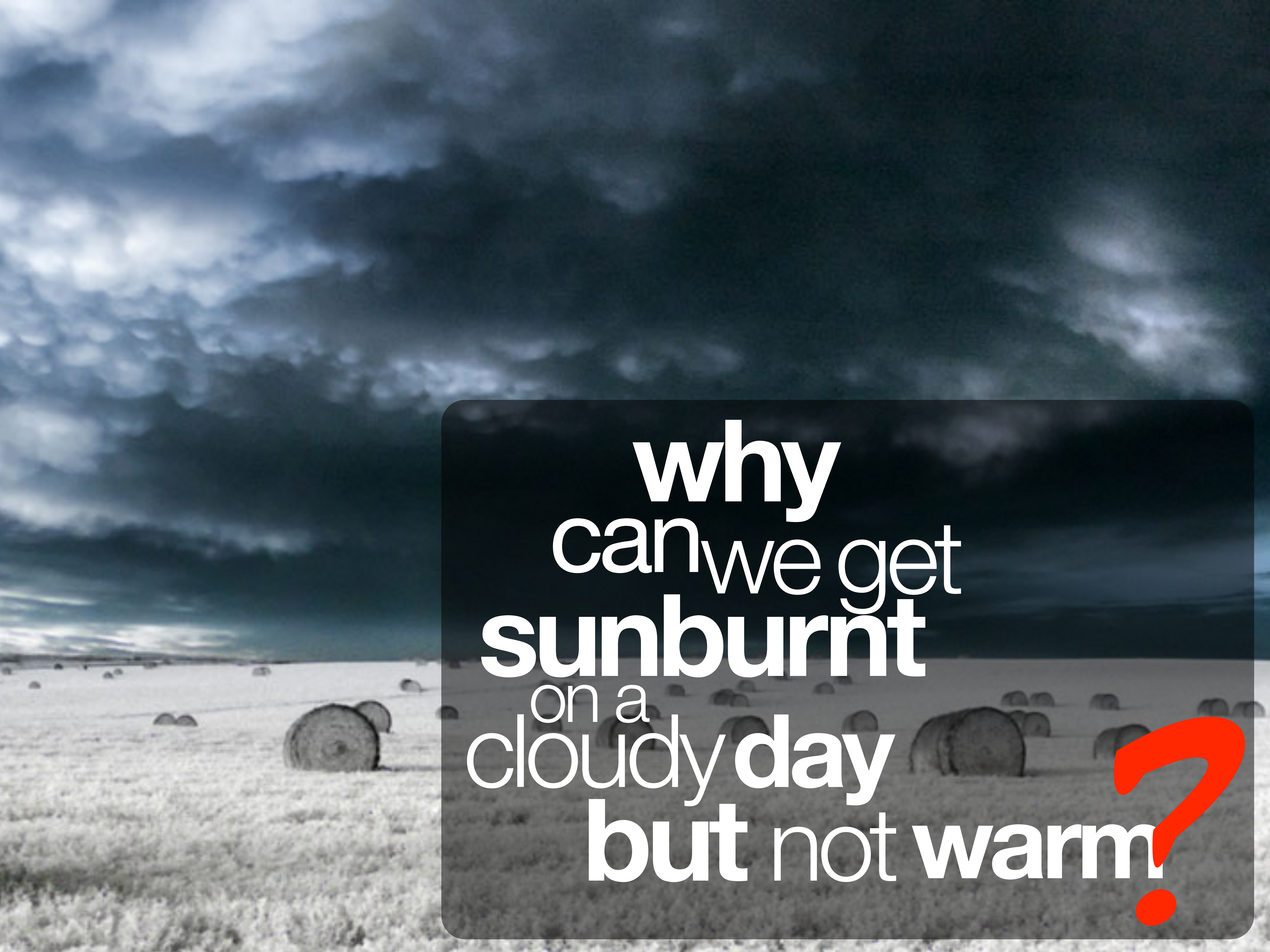

ENERGY
Radio
Microwave
Infrared
Ultraviolet
Gamma
Frequency (Hz)
10^6 10^7 10^8 10^9 10^{10} 10^{11} 10^{12} 10^{13} 10^{14} 10^{15} 10^{16} 10^{17} 10^{18} 10^{19}
low energy EM radiation has a long wavelength and low frequency (ask the physicists) whilst **high energy** is small wavelength and high frequency
Visible
X-ray
The Electromagnetic Spectrum

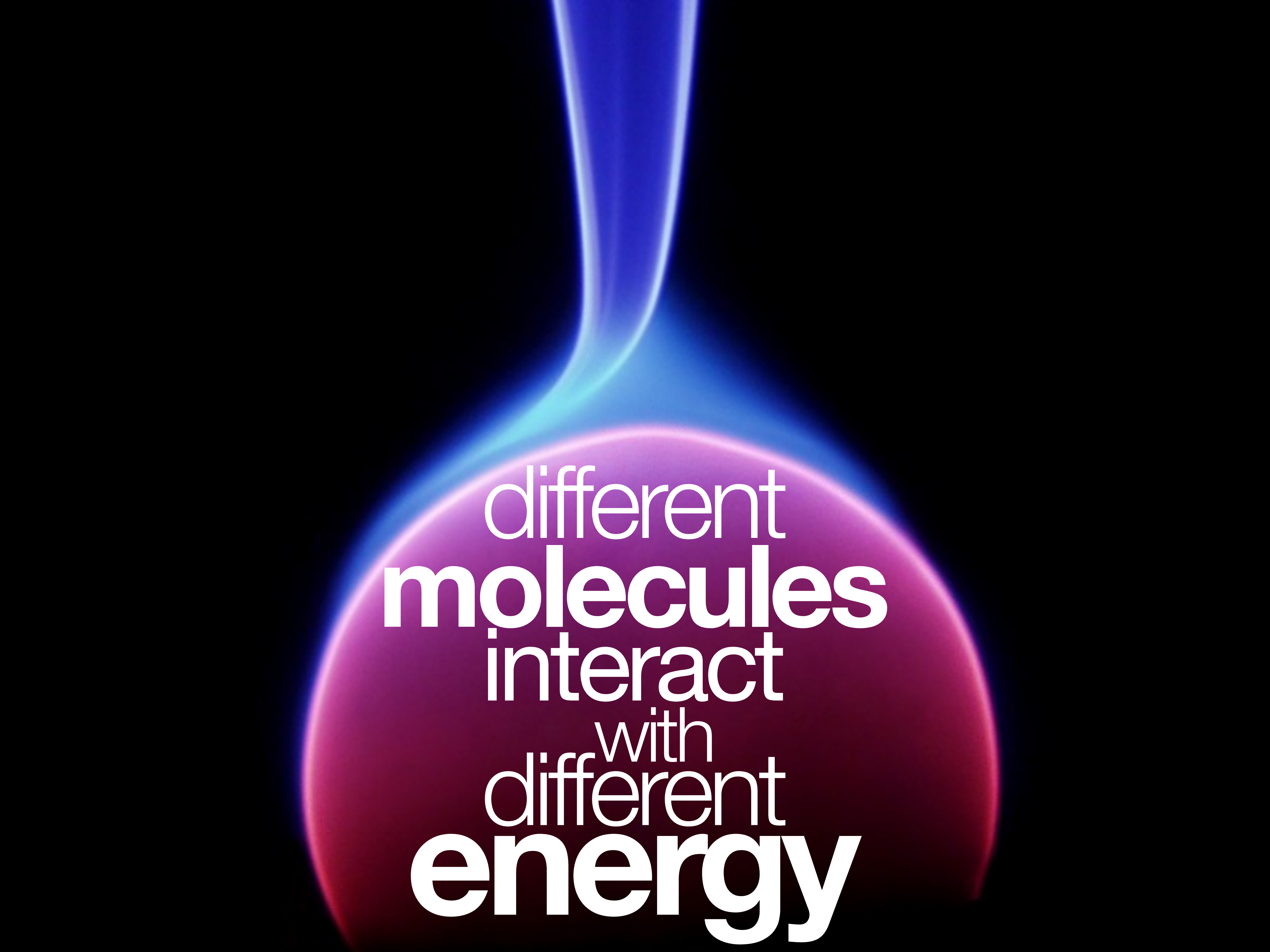
can **electromagnetic radiation** interact with **molecules**?

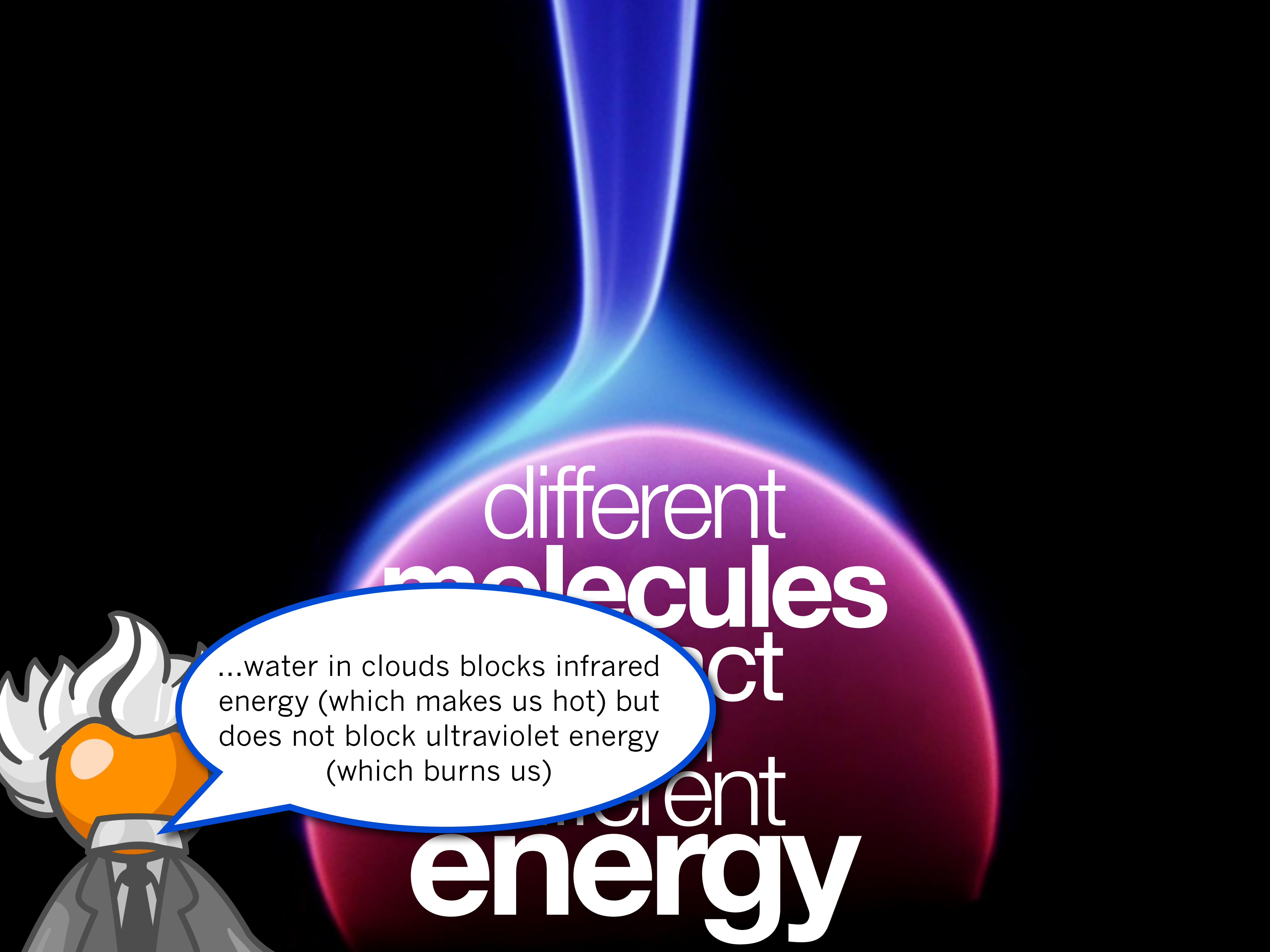

yes!


sunburn...simple interaction of energy and molecules...
yes!


the fact you can see this slide means EM (visible light) must be able to interact with our eyes

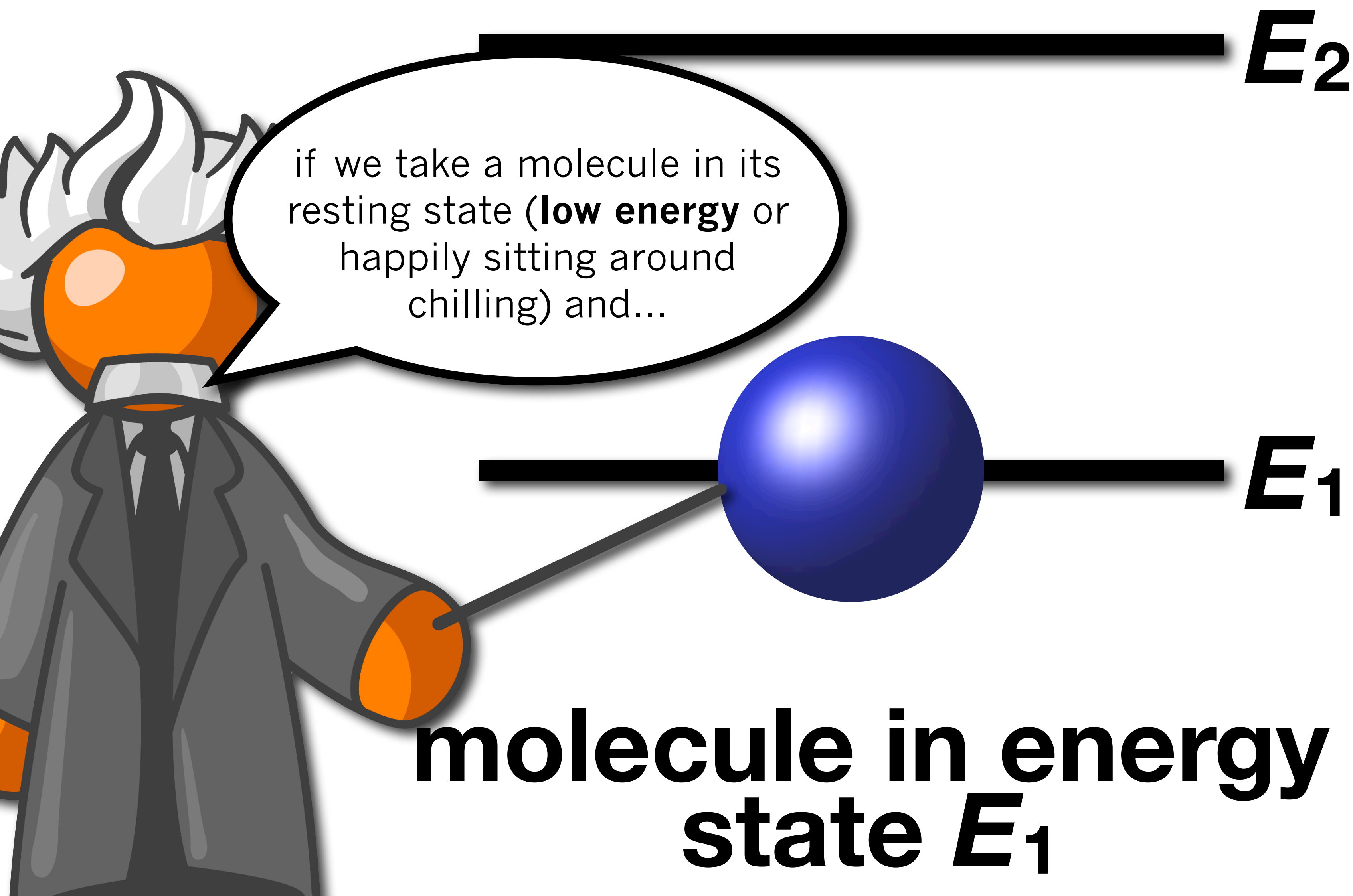

why
can we get
sunburnt
on a
cloudy day
but not warm
?

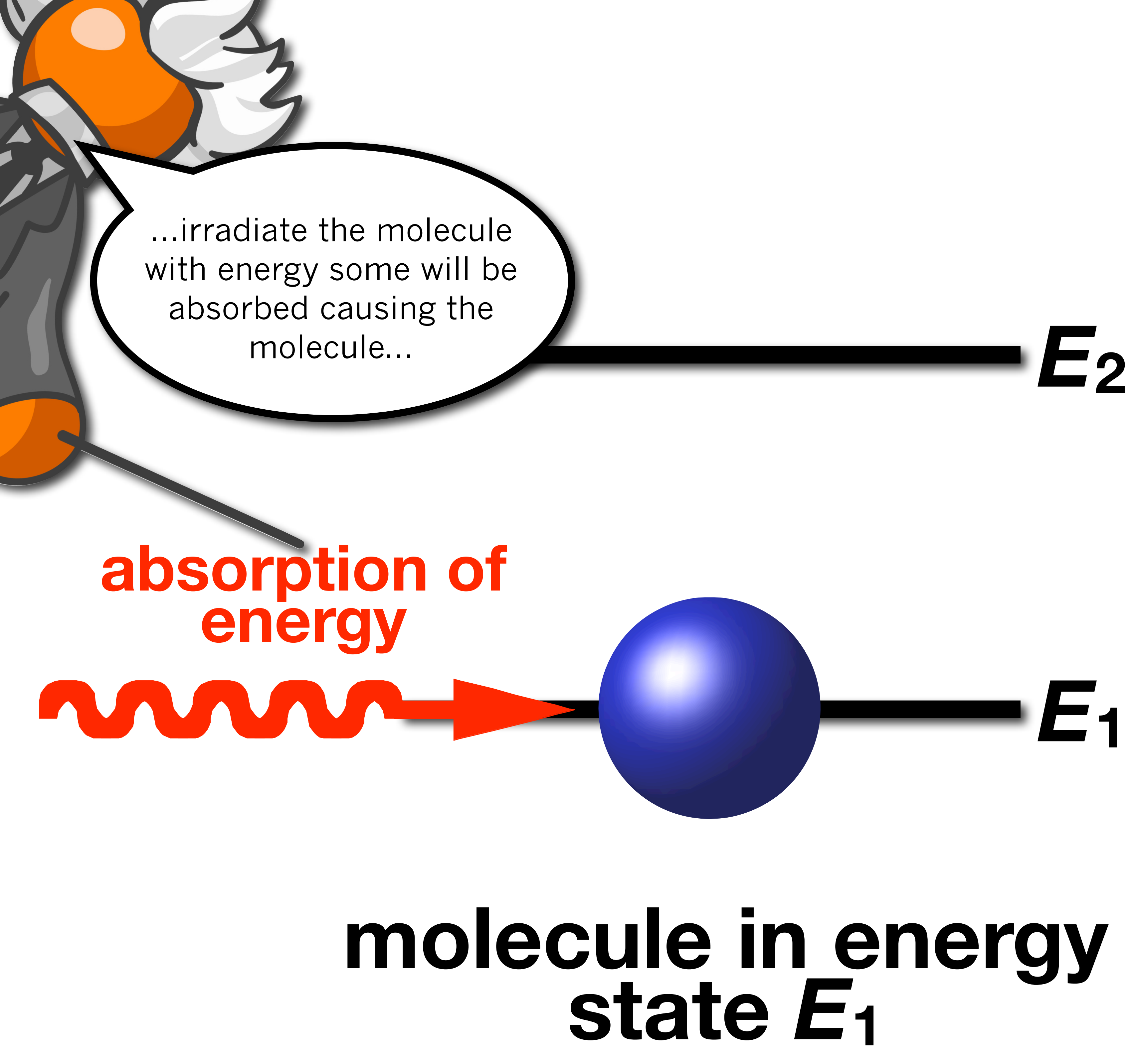

different
molecules
interact
with
different
energy

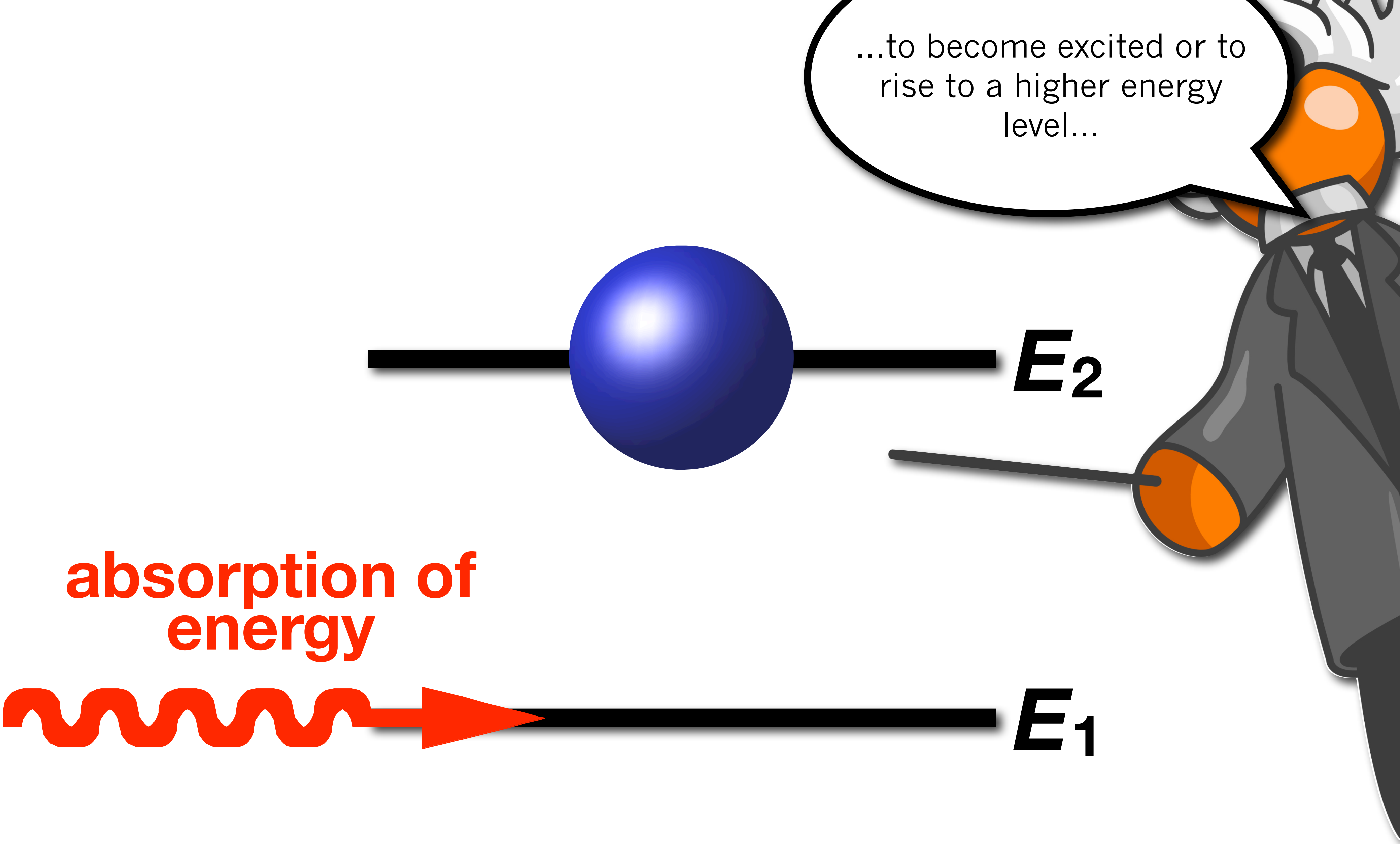


different
...water in clouds blocks infrared energy (which makes us hot) but does not block ultraviolet energy (which burns us)
energy

so how do
we **use** this?

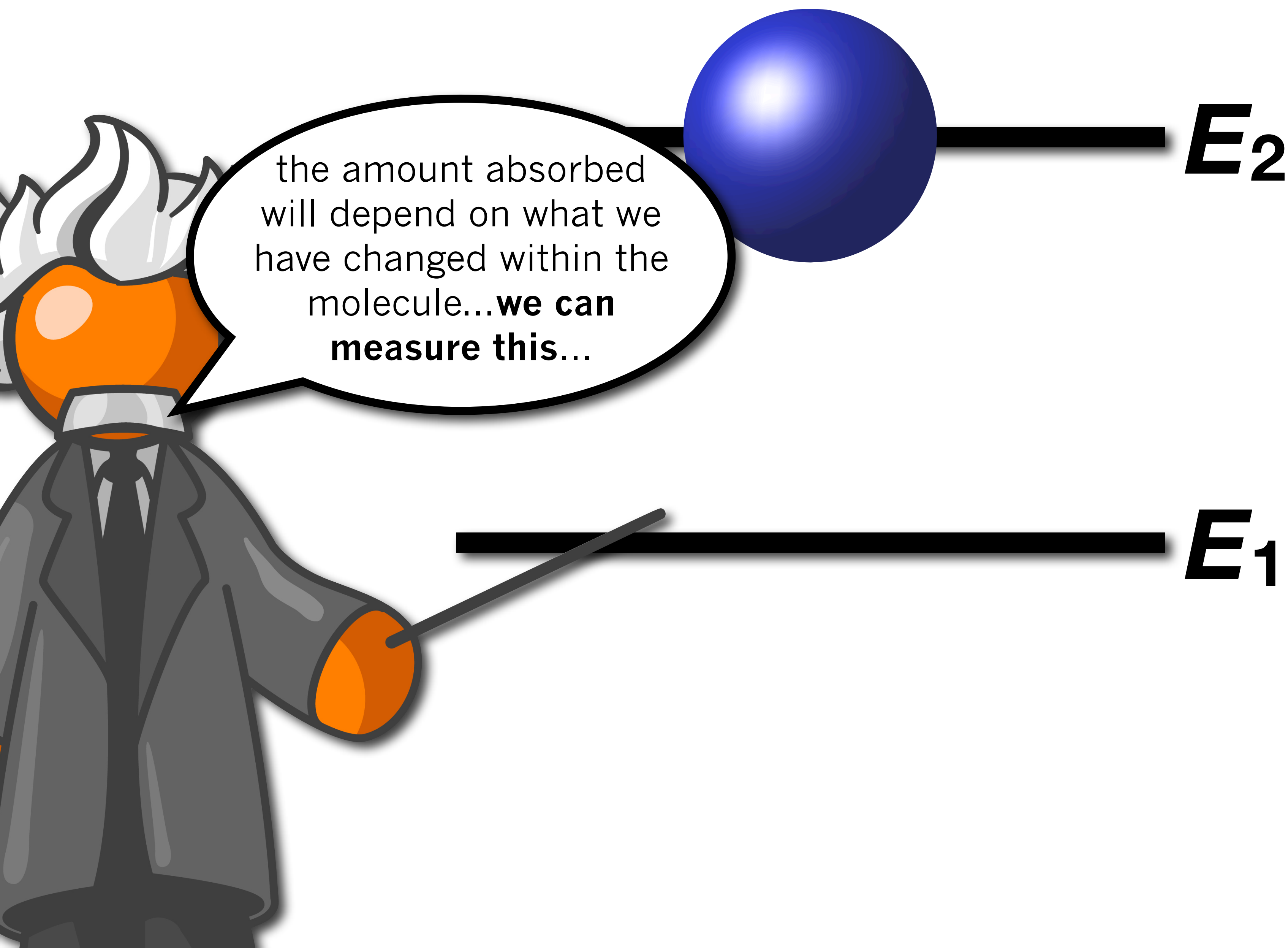

if we take a molecule in its resting state (**low energy** or happily sitting around chilling) and...
E_2
E_1
molecule in energy state E_1


...irradiate the molecule with energy some will be absorbed causing the molecule...
E_2
absorption of energy
E_1
molecule in energy state E_1

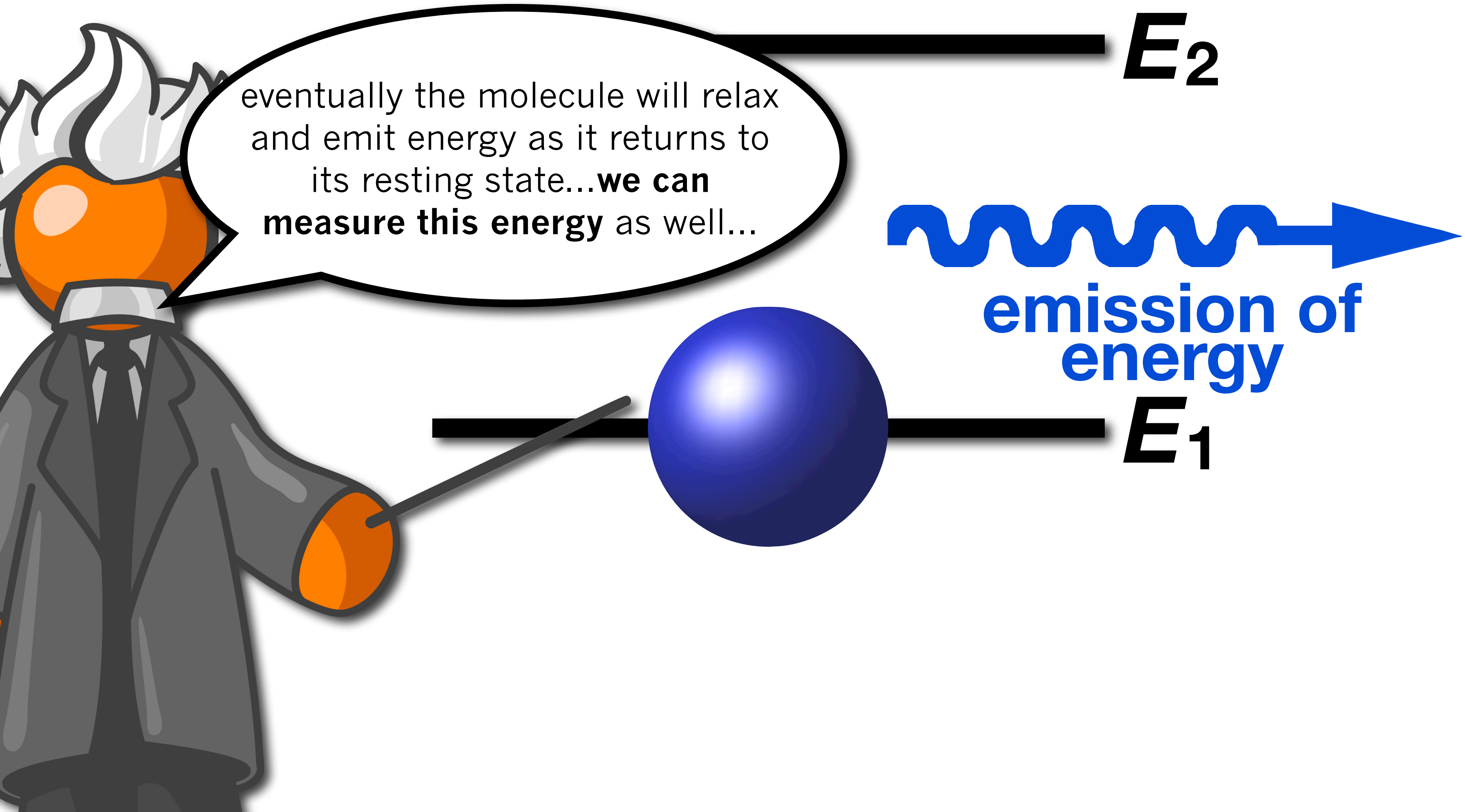


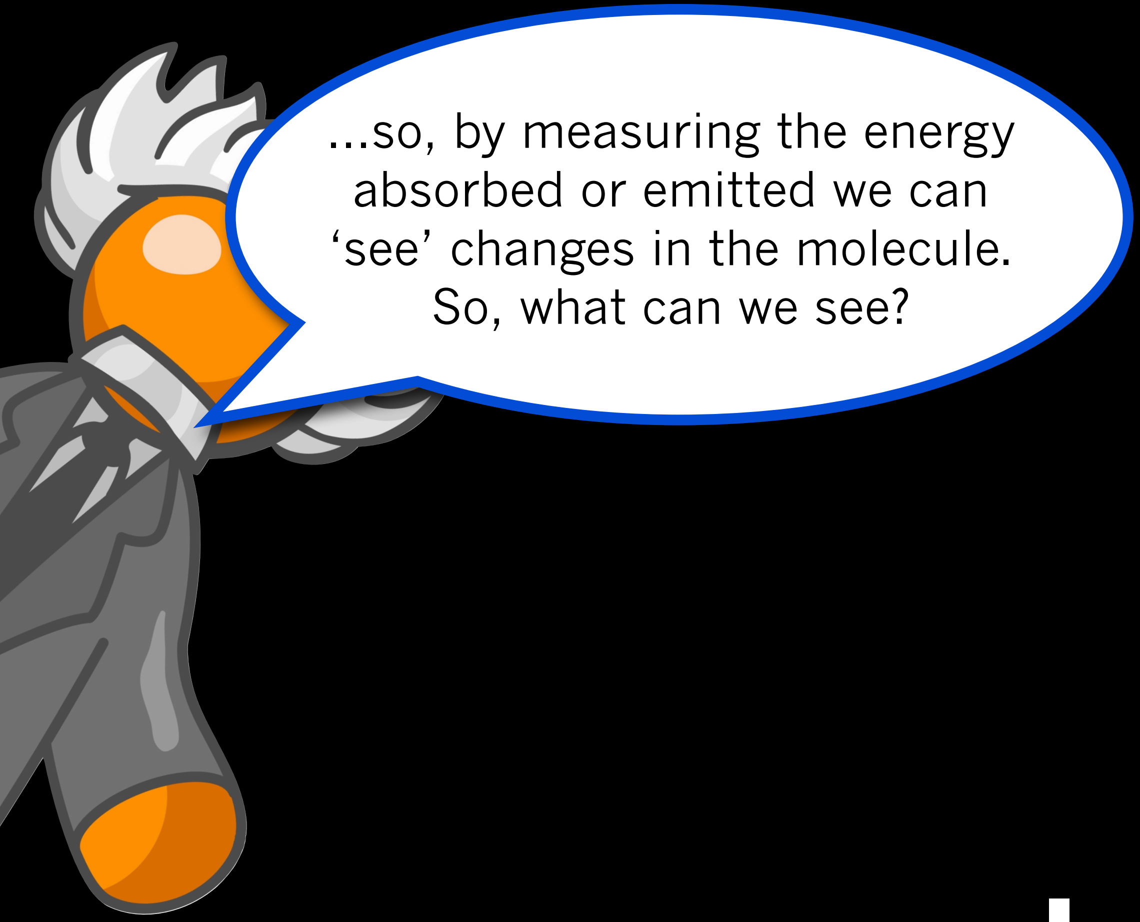
molecule in energy state E_1

molecule in energy state E_2 or 'excited'



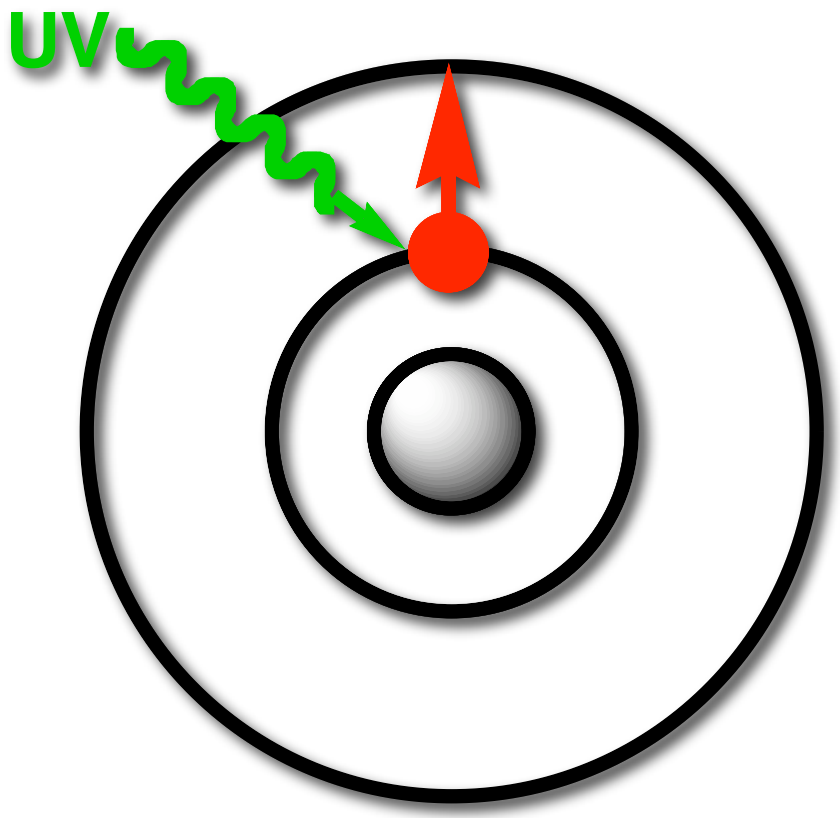
molecule in energy state E_2 or 'excited'



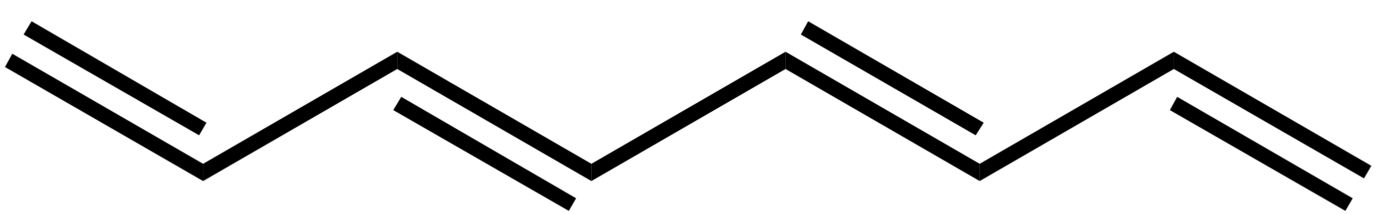


what part of the **molecule** is effected?

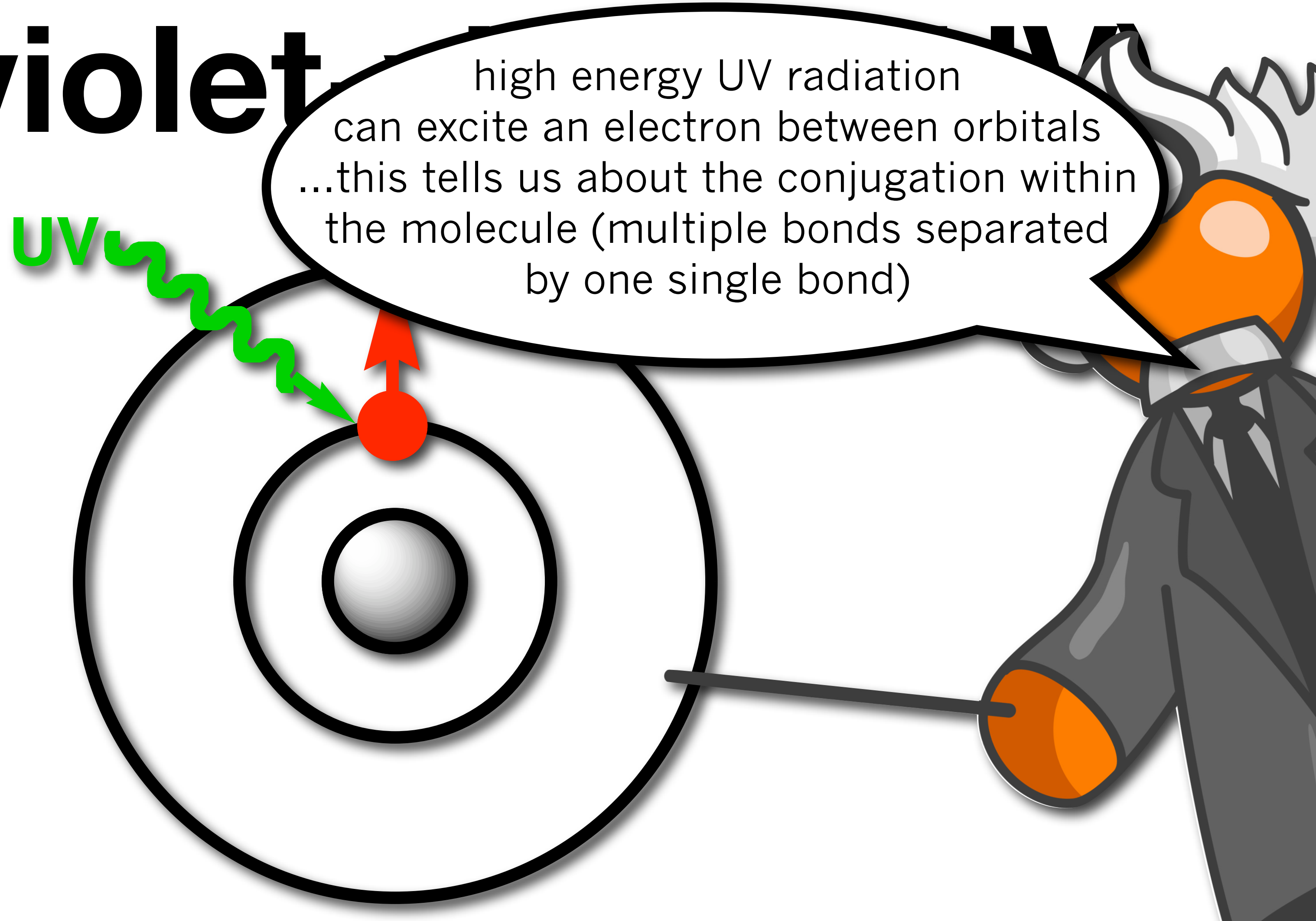
ultraviolet-visible (UV)



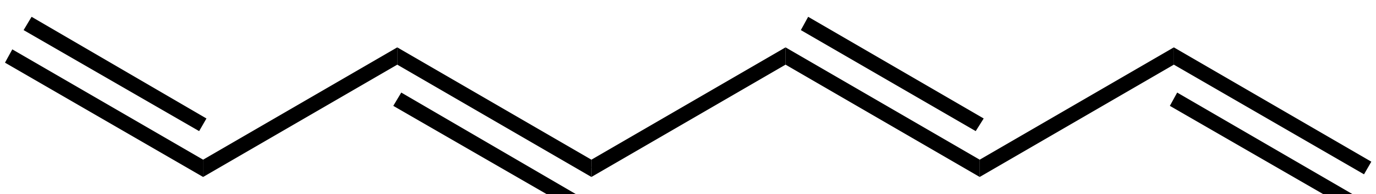
excites an electron



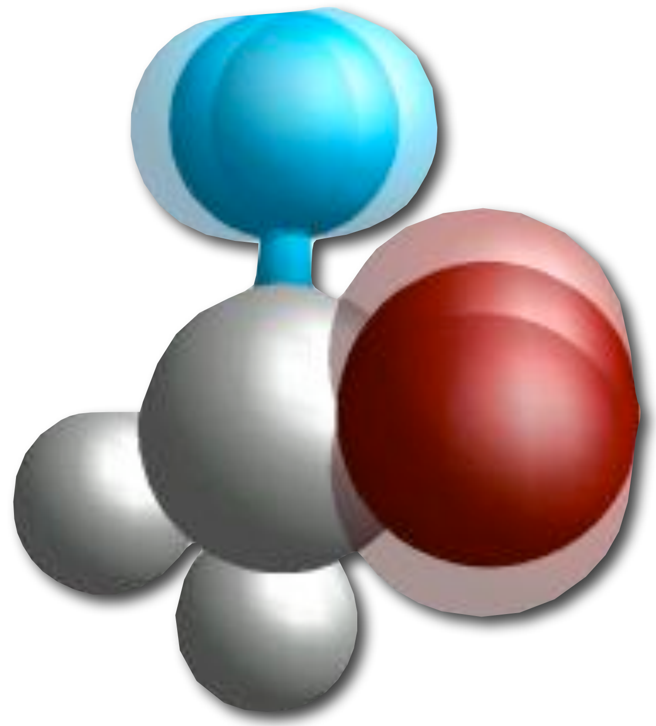
ultraviolet



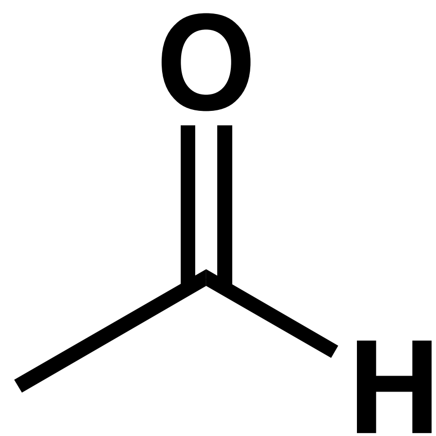
excites an electron



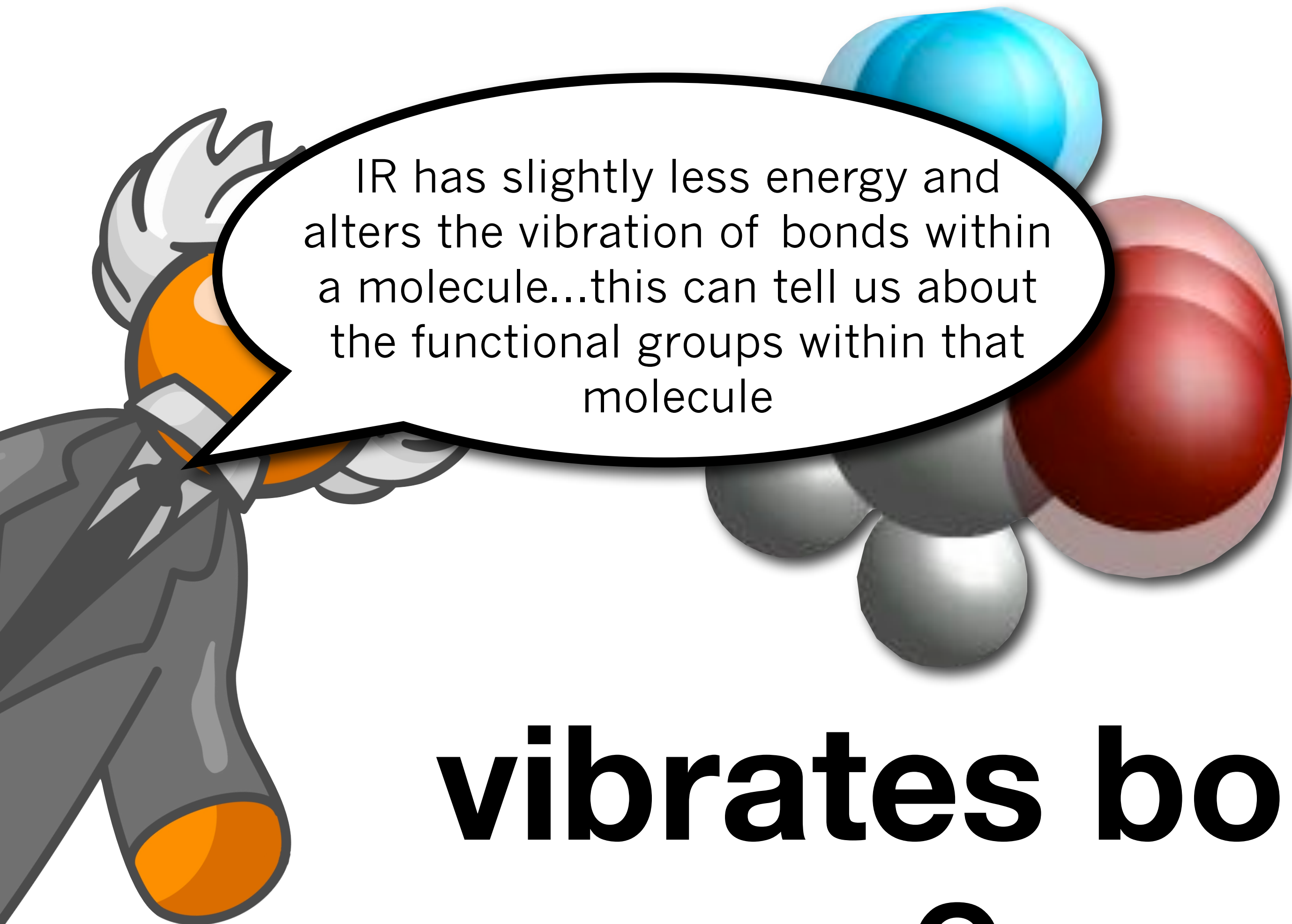
infrared (IR)



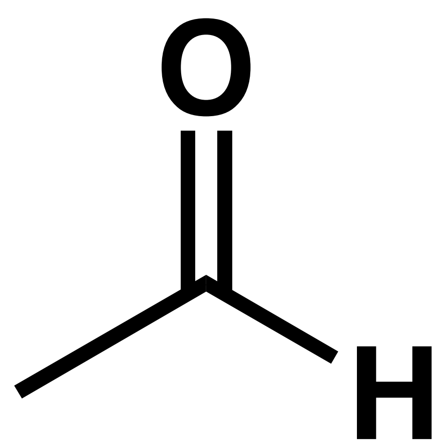
vibrates bonds



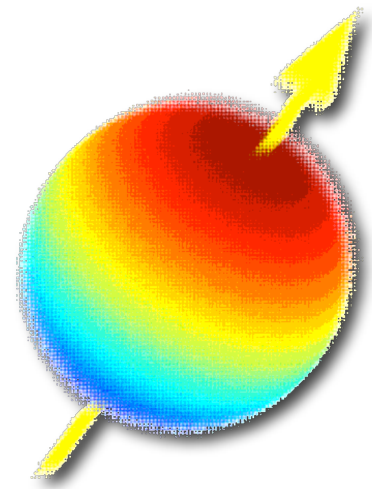
infrared (IR)



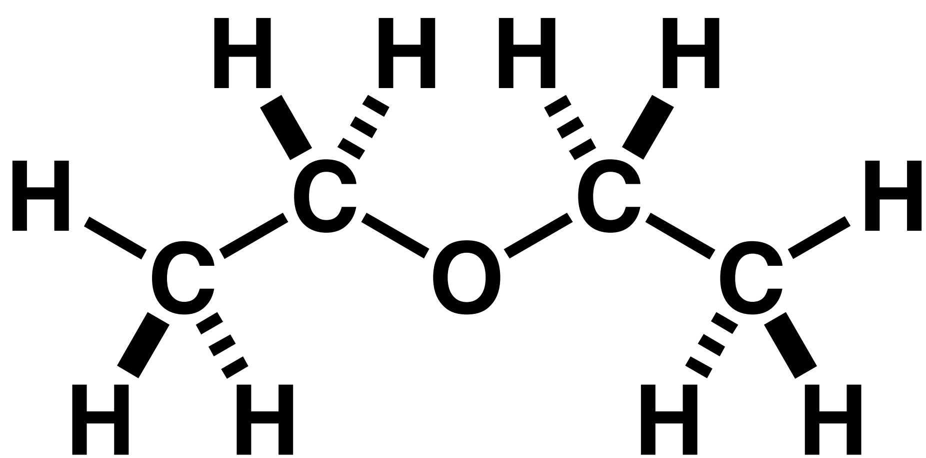
vibrates bonds



nuclear magnetic resonance (NMR)

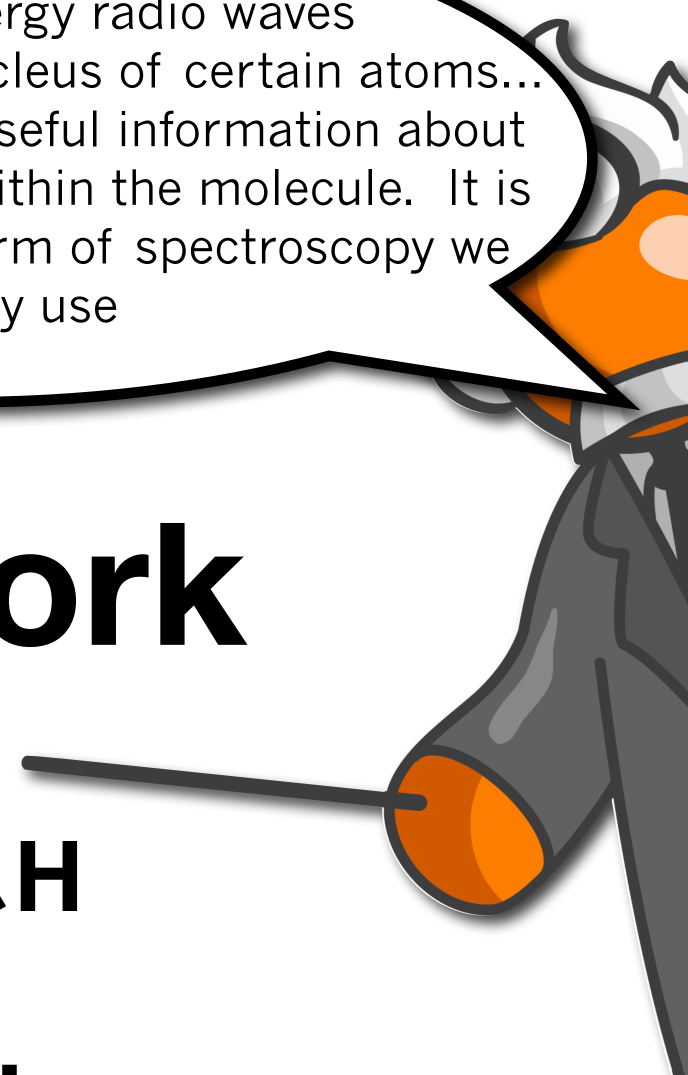


C-H framework

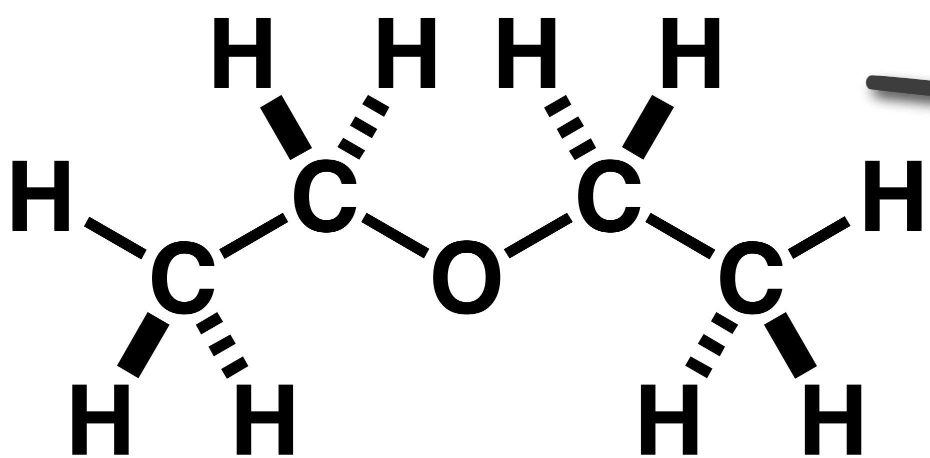


nuclear magnetic resonance (NMR)

NMR uses low energy radio waves
to alter the spin of the nucleus of certain atoms...
this can give us a lot of useful information about
the position of C and H within the molecule. It is
by far the most useful form of spectroscopy we
routinely use

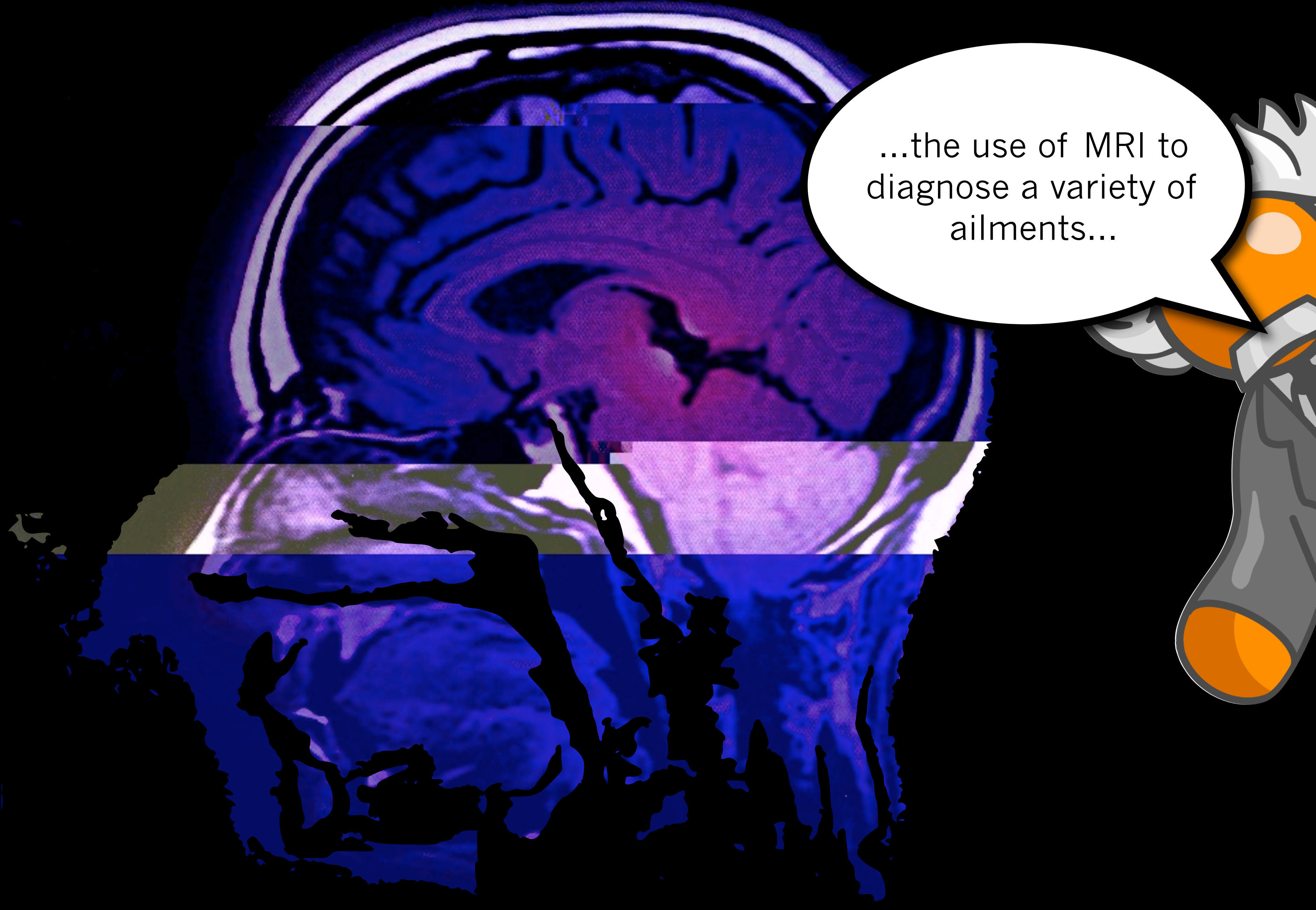


C-H framework



what is **nmr**?


I guess most of you know the character House? and for those of you that have watched it you might recognise...
©Fox TV

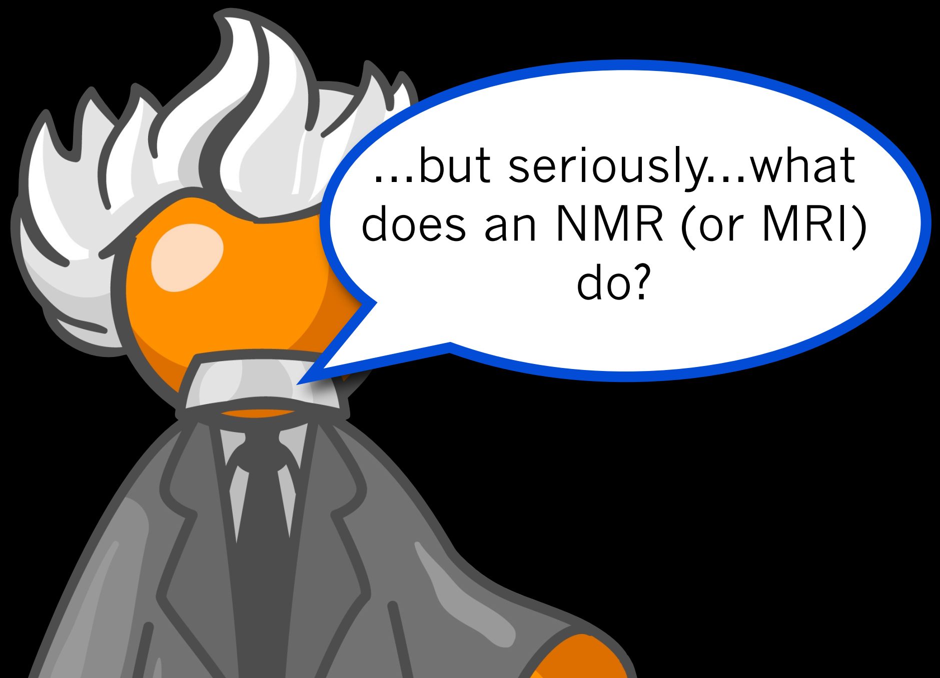


magnetic resonance imaging

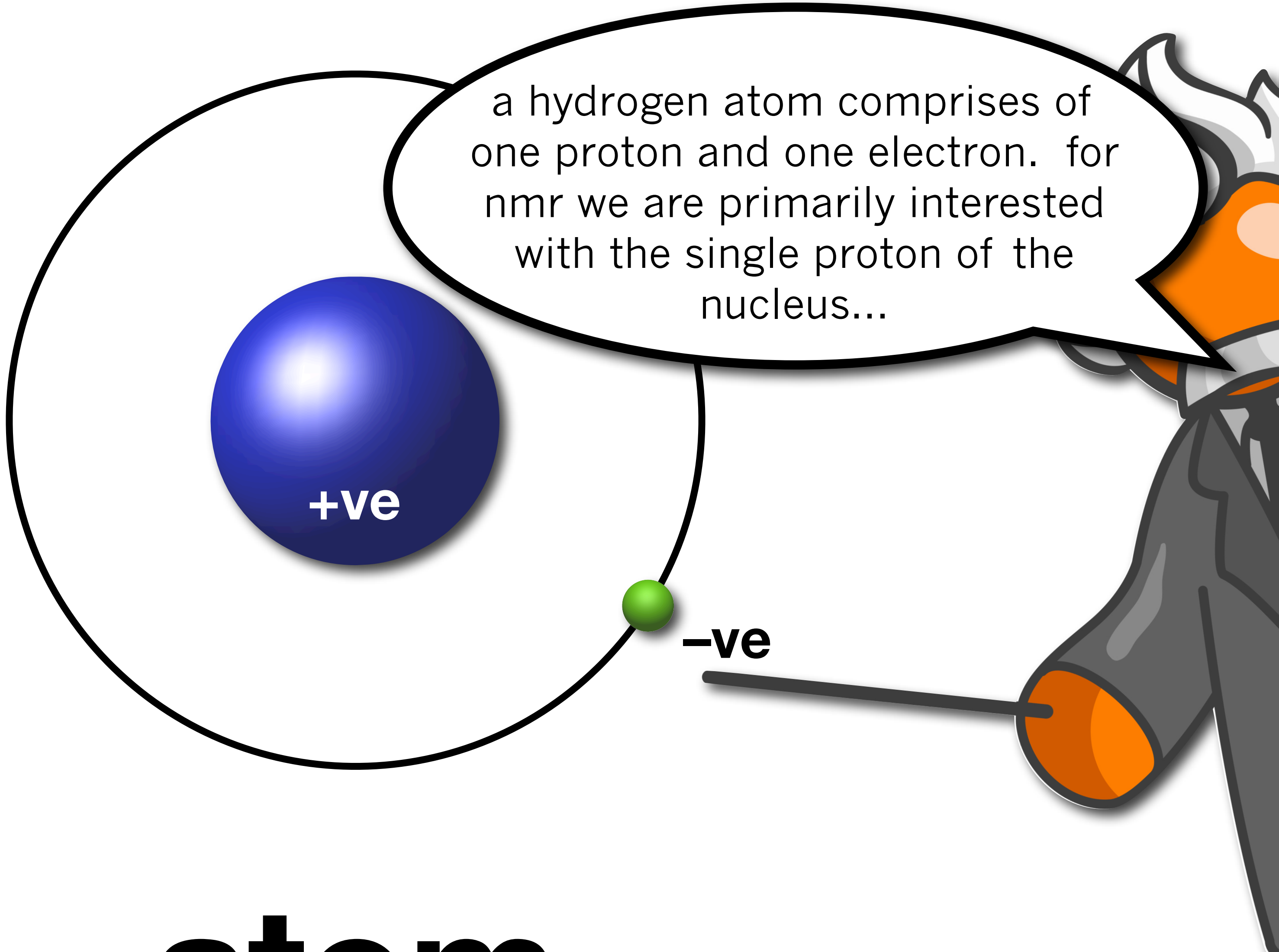

this beast is an MRI...it is identical to an NMR machine except it spins a magnet around a patient and an NMR spins the sample...


I guess it's called MRI and not NMR as no patient would allow a doctor to insert them in a machine with the word "nuclear" in the title
Photo: Industrial Light and Magic

so what **is** nmr?

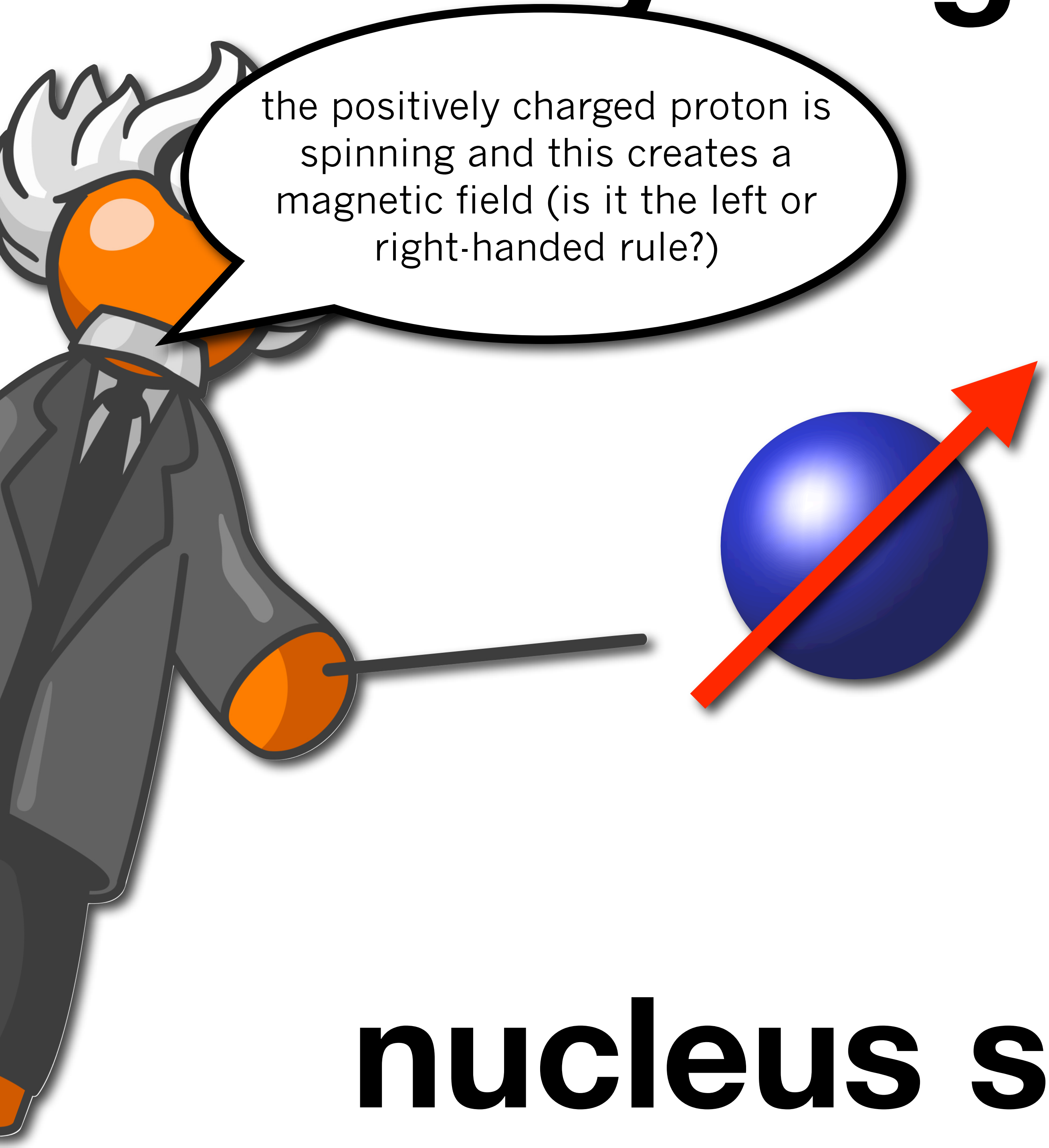


hydrogen

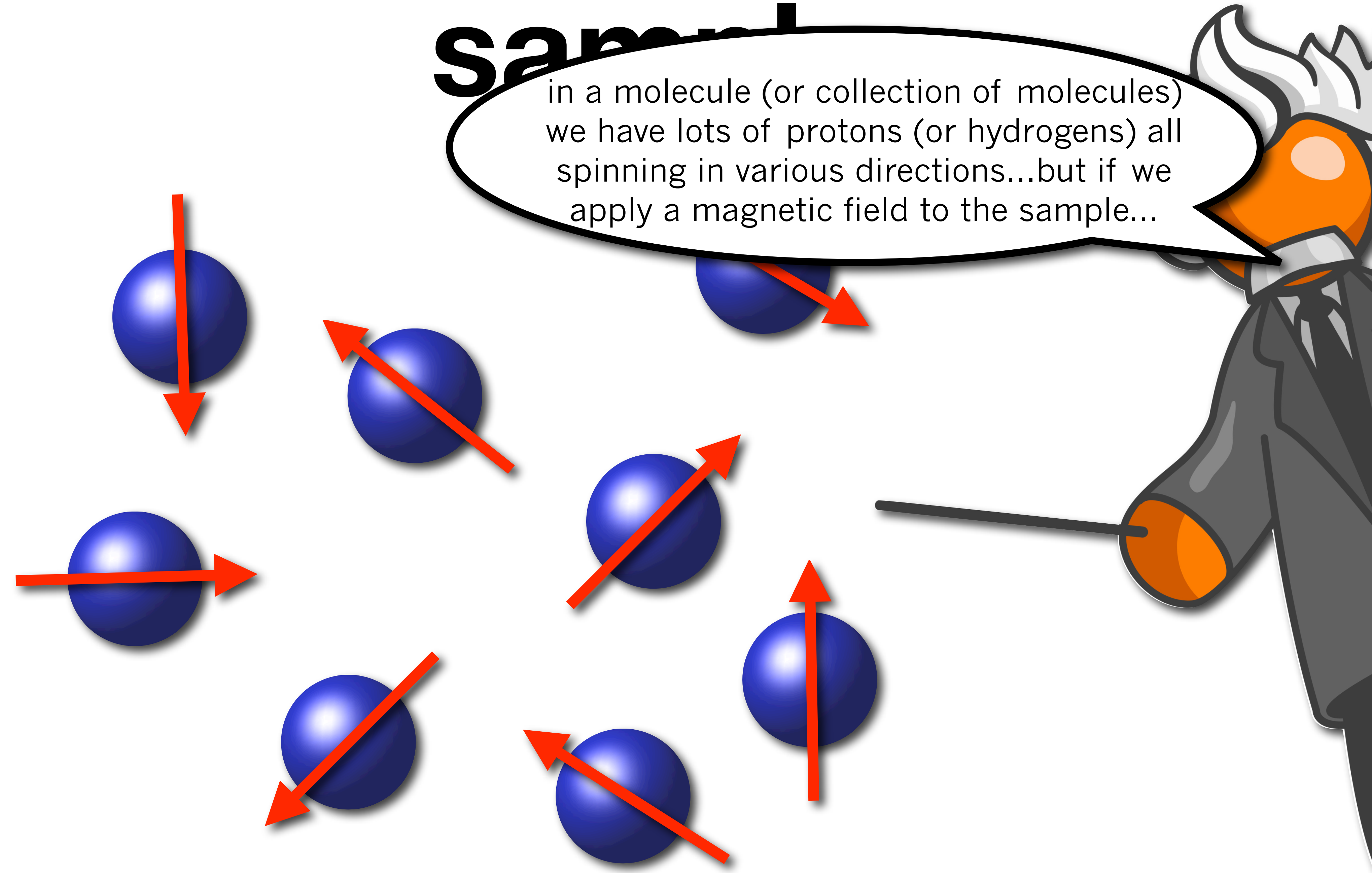


atom

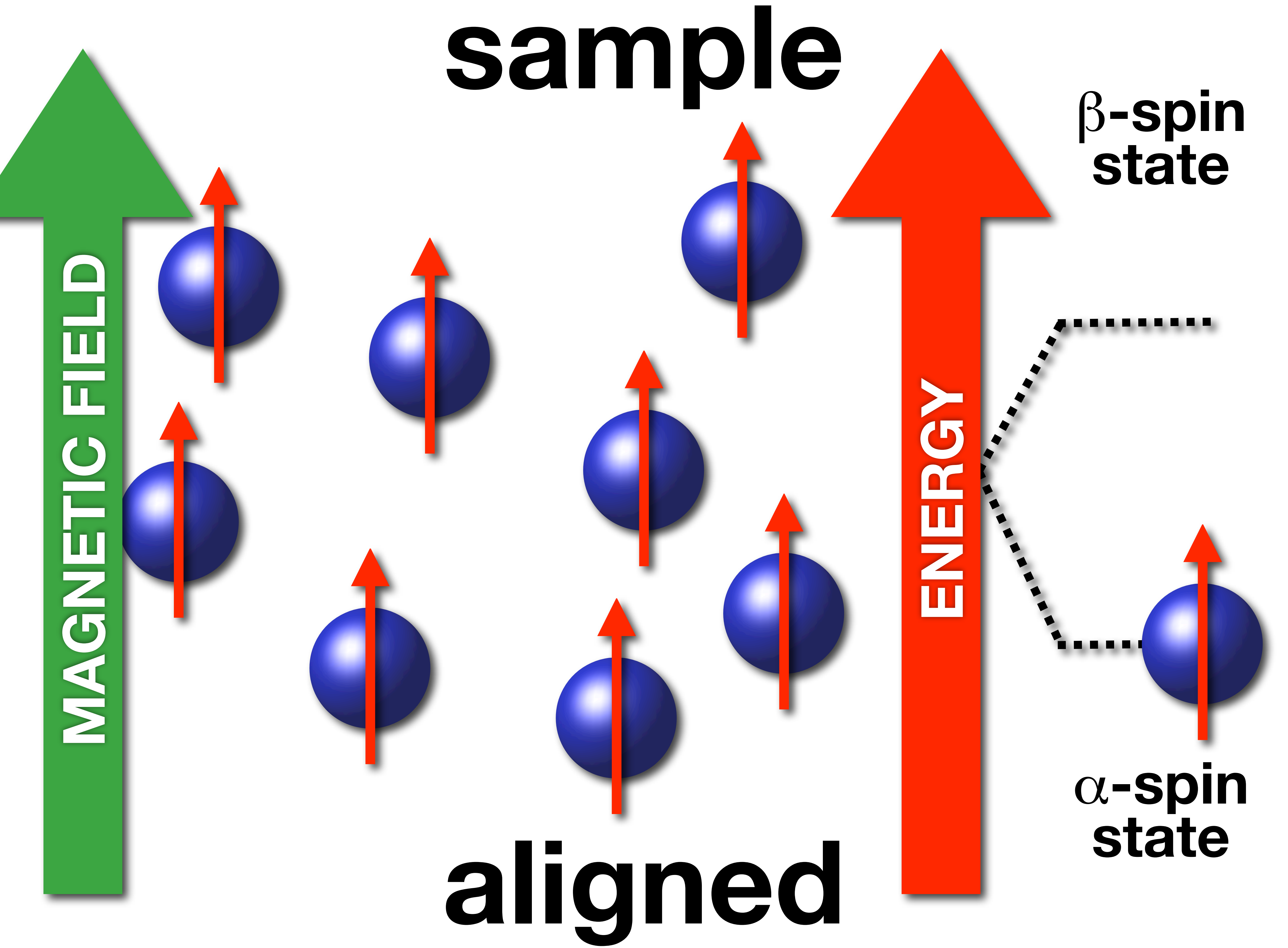
hydrogen

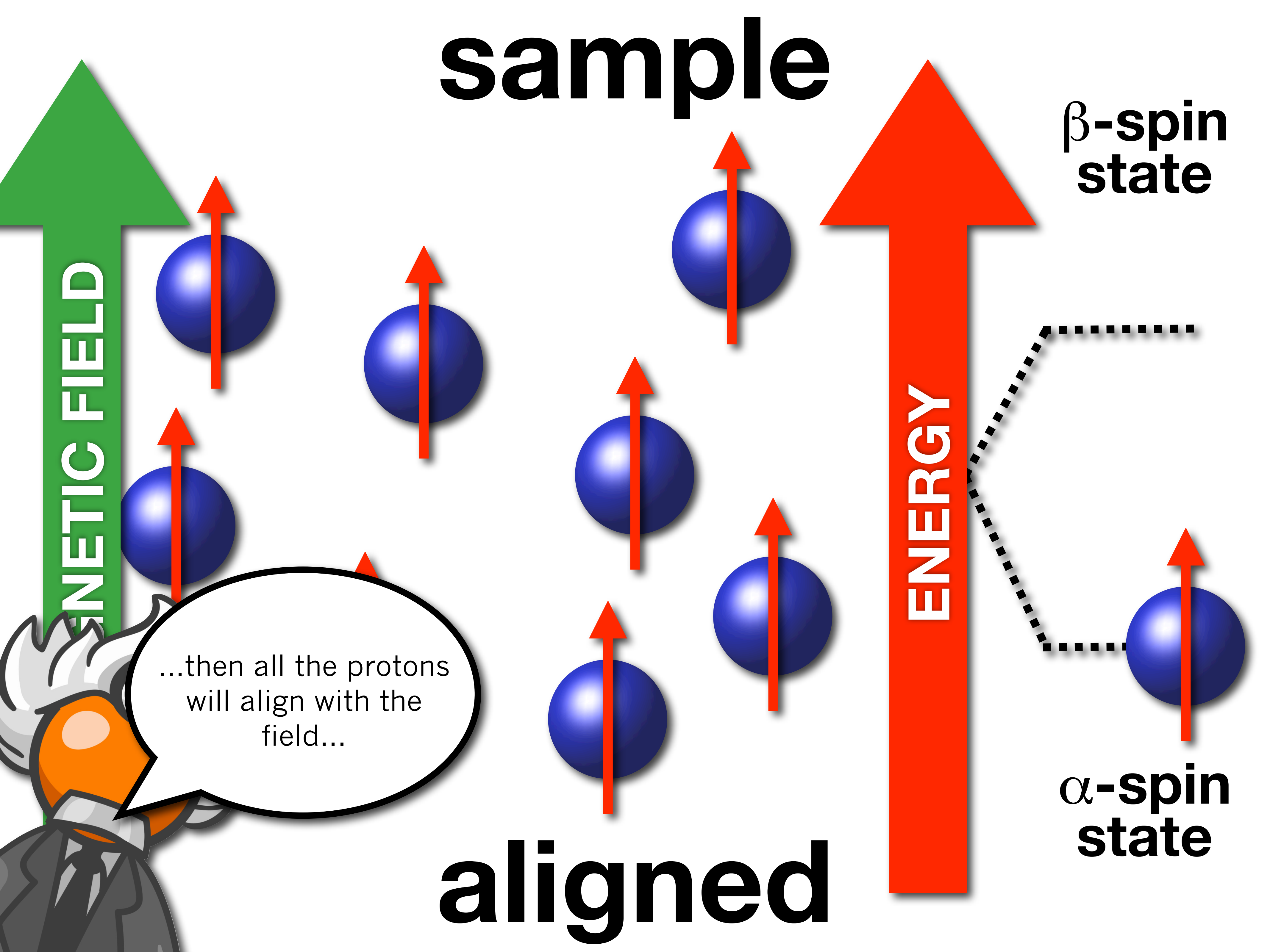


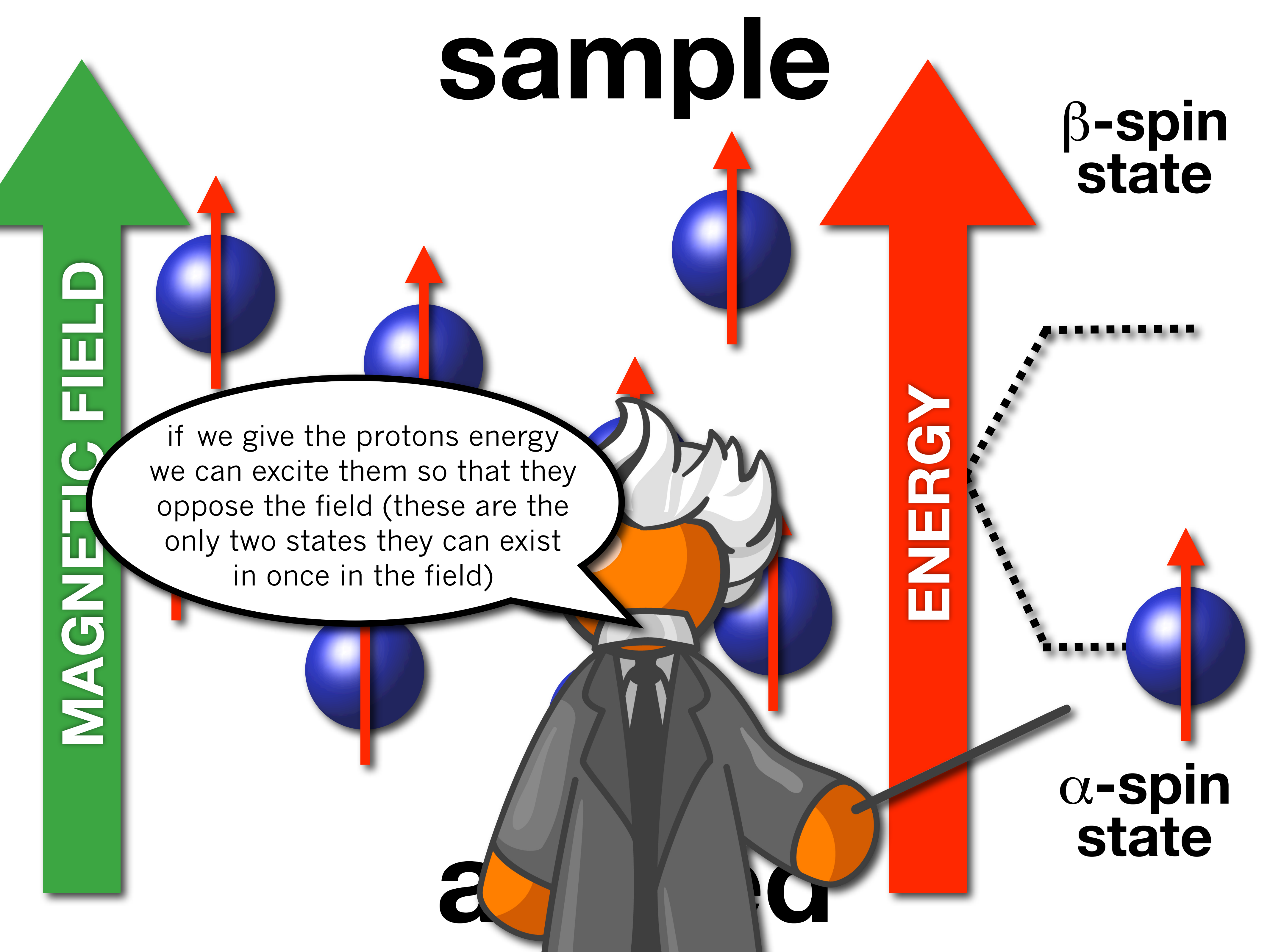
nucleus spins

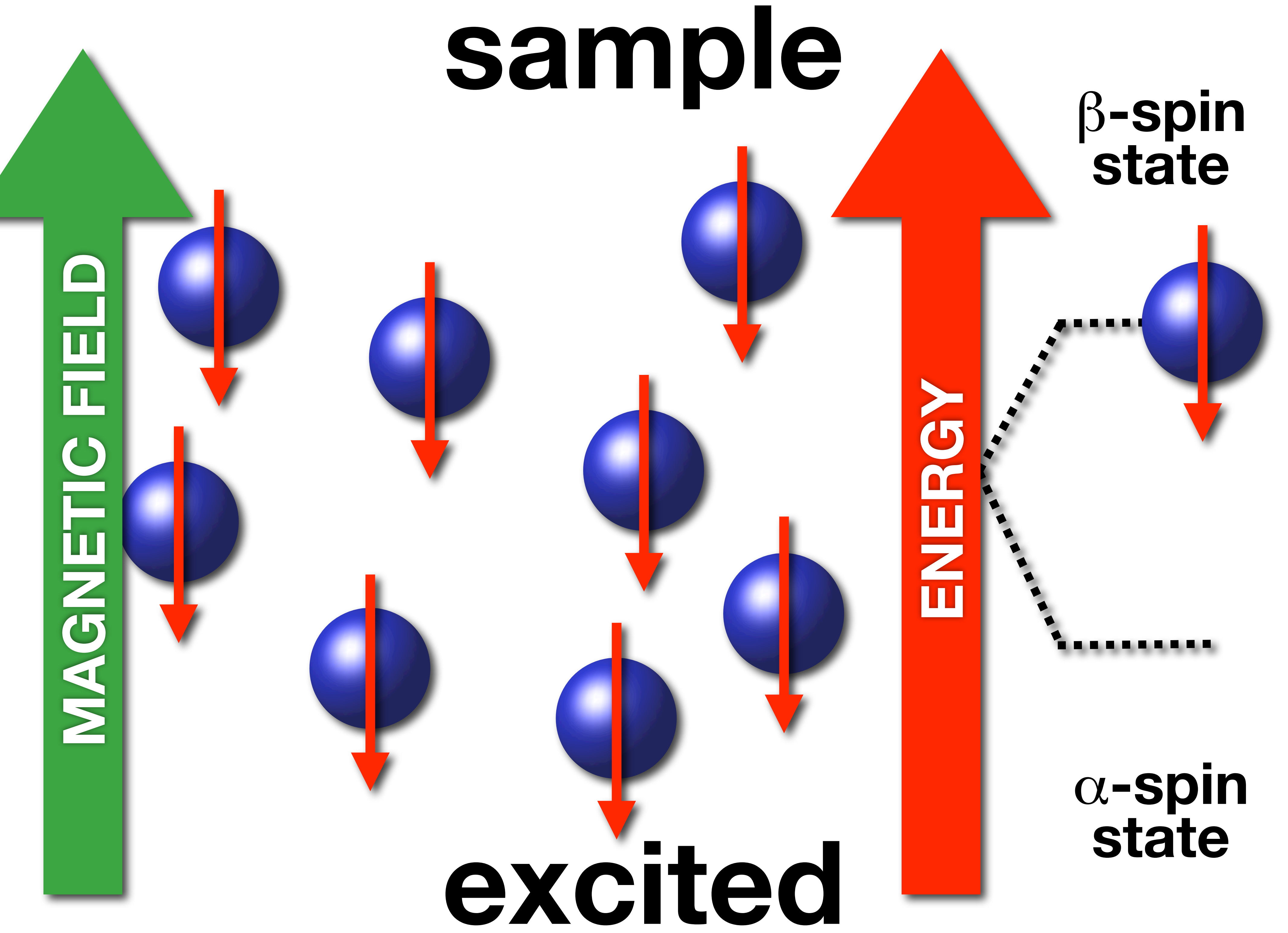


random orientation

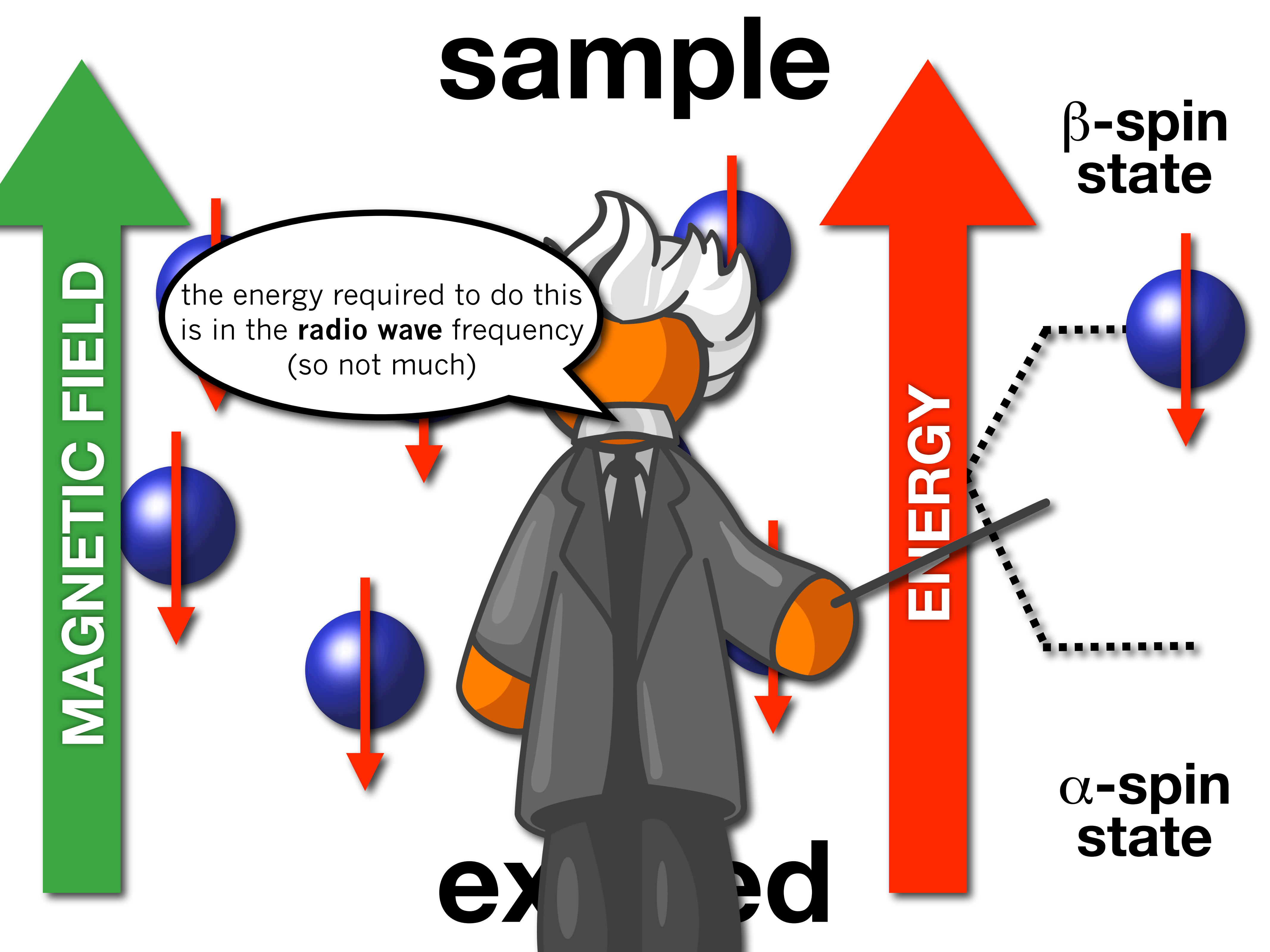

sample
MAGNETIC FIELD
ENERGY
β-spin state
α-spin state
aligned


sample
aligned
NETIC FIELD
ENERGY
β-spin state
α-spin state
...then all the protons will align with the field...

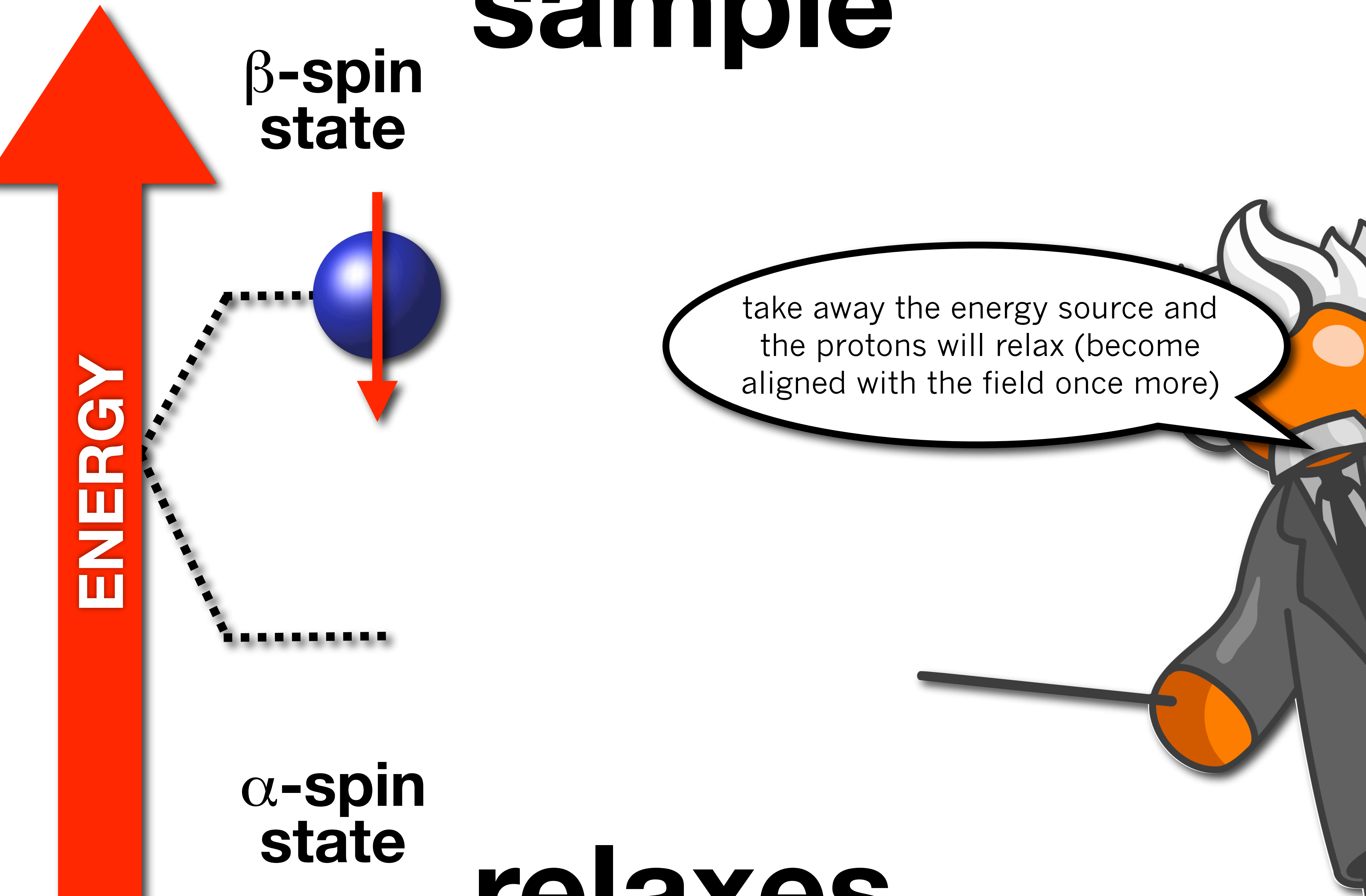

sample
MAGNETIC FIELD
if we give the protons energy we can excite them so that they oppose the field (these are the only two states they can exist in once in the field)
ENERGY
β-spin state
α-spin state



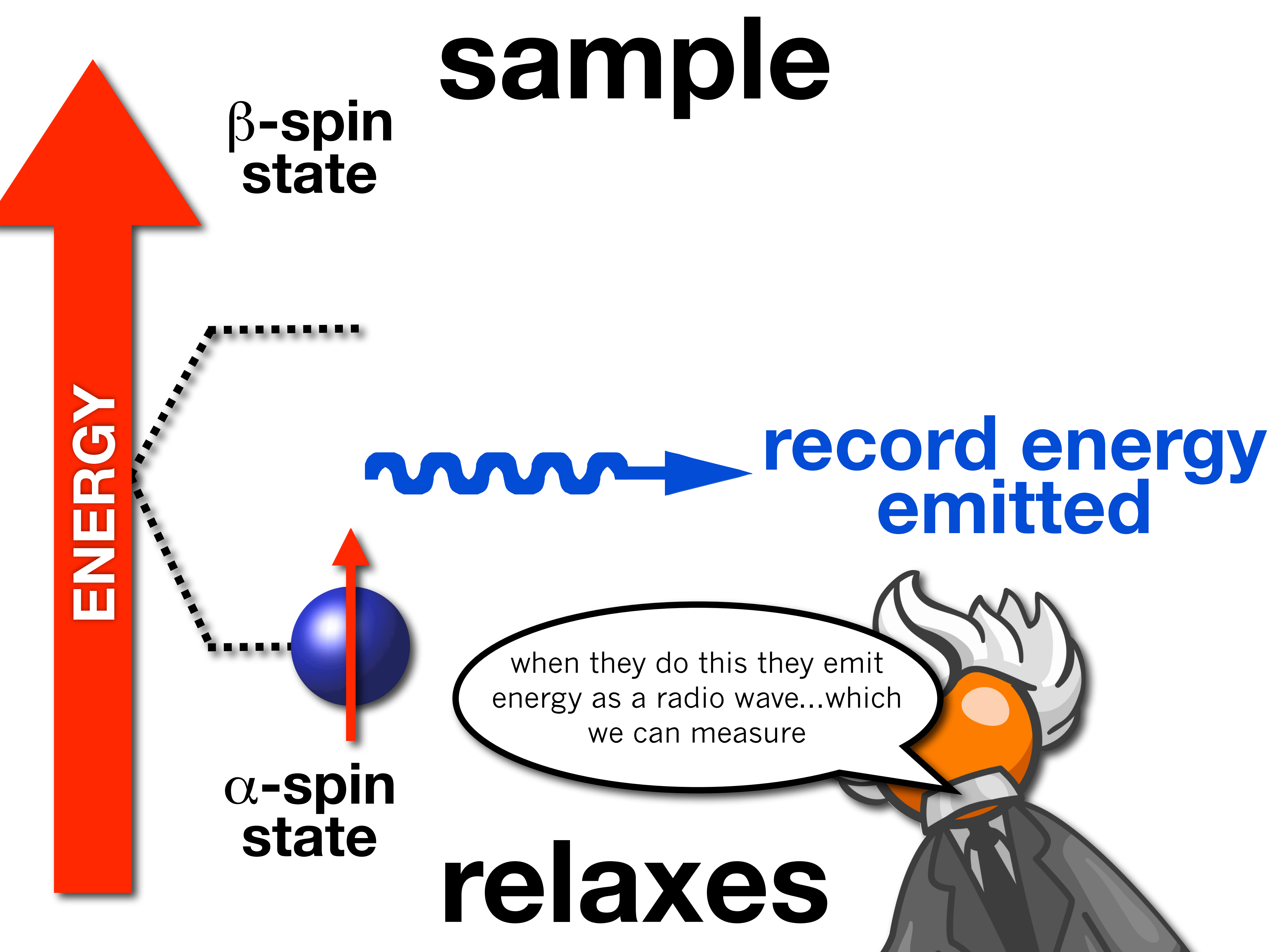
sample
MAGNETIC FIELD
ENERGY
β-spin state
α-spin state
excited

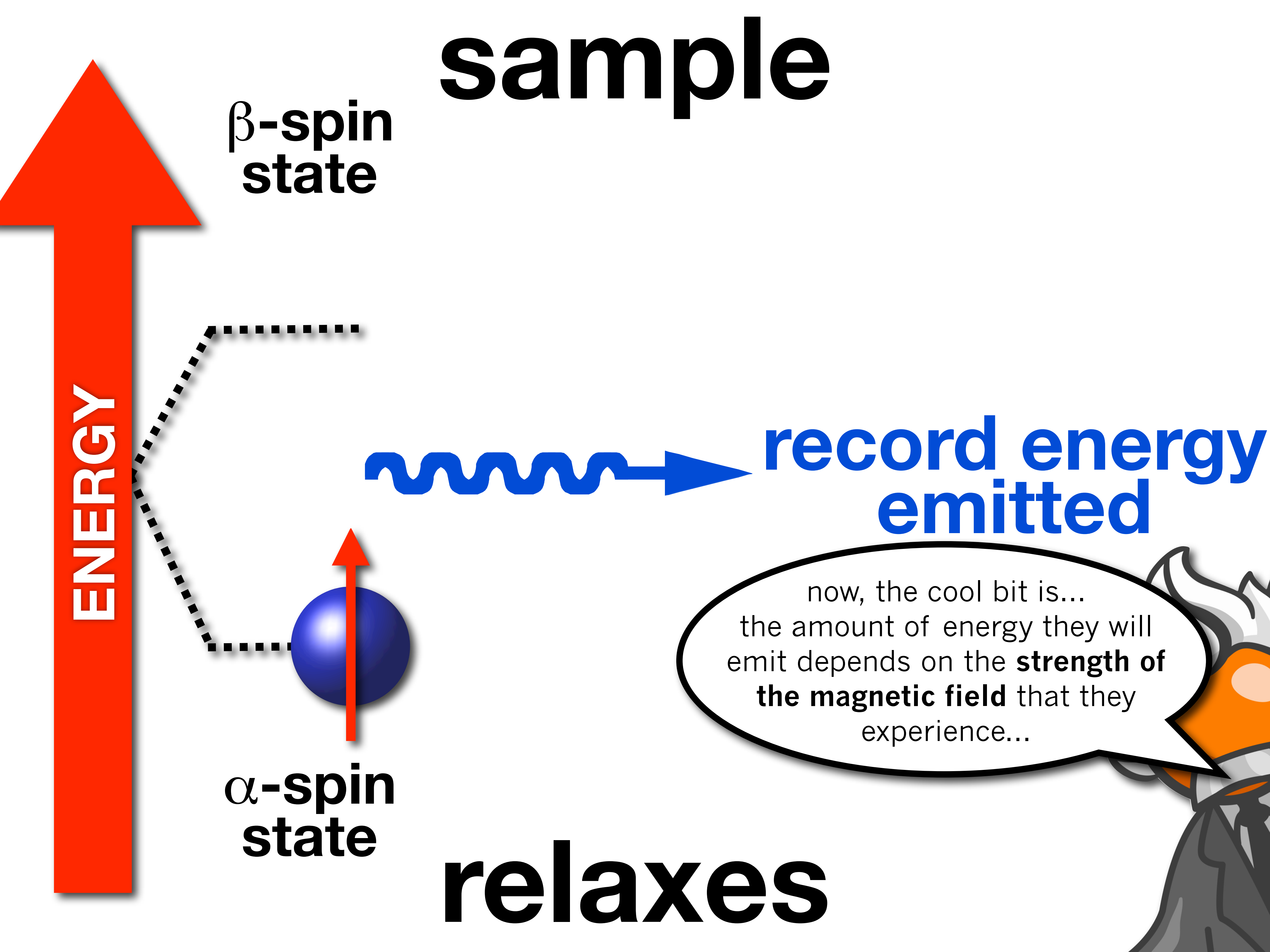

sample
MAGNETIC FIELD
the energy required to do this is in the **radio wave** frequency (so not much)
ENERGY
β-spin state
α-spin state
ex
ed

sample

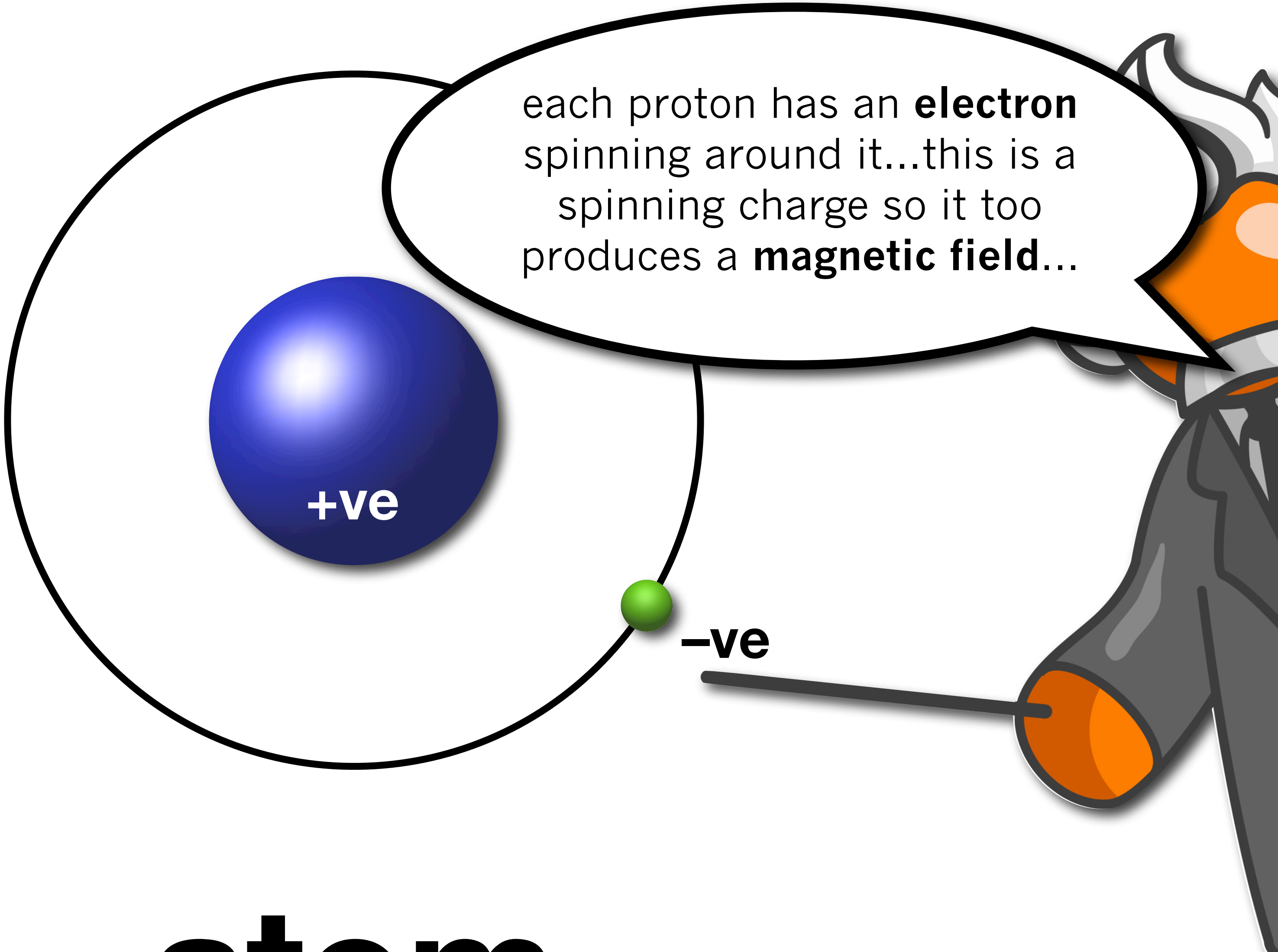


relaxes

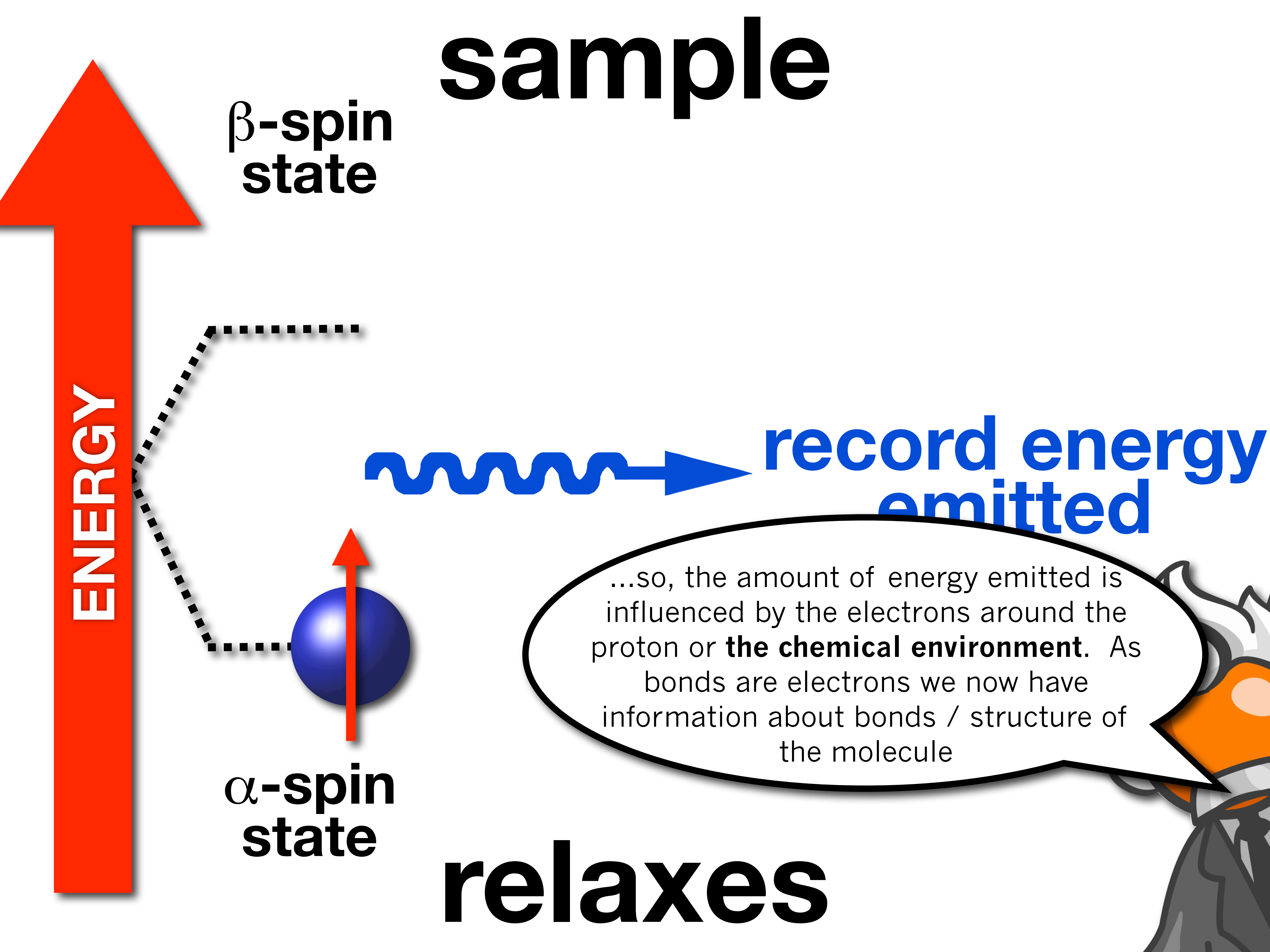

sample
β-spin state
ENERGY
record energy emitted
when they do this they emit energy as a radio wave...which we can measure
α-spin state
relaxes


sample
β-spin state
ENERGY
record energy emitted
now, the cool bit is... the amount of energy they will emit depends on the **strength of the magnetic field** that they experience...
α-spin state
relaxes

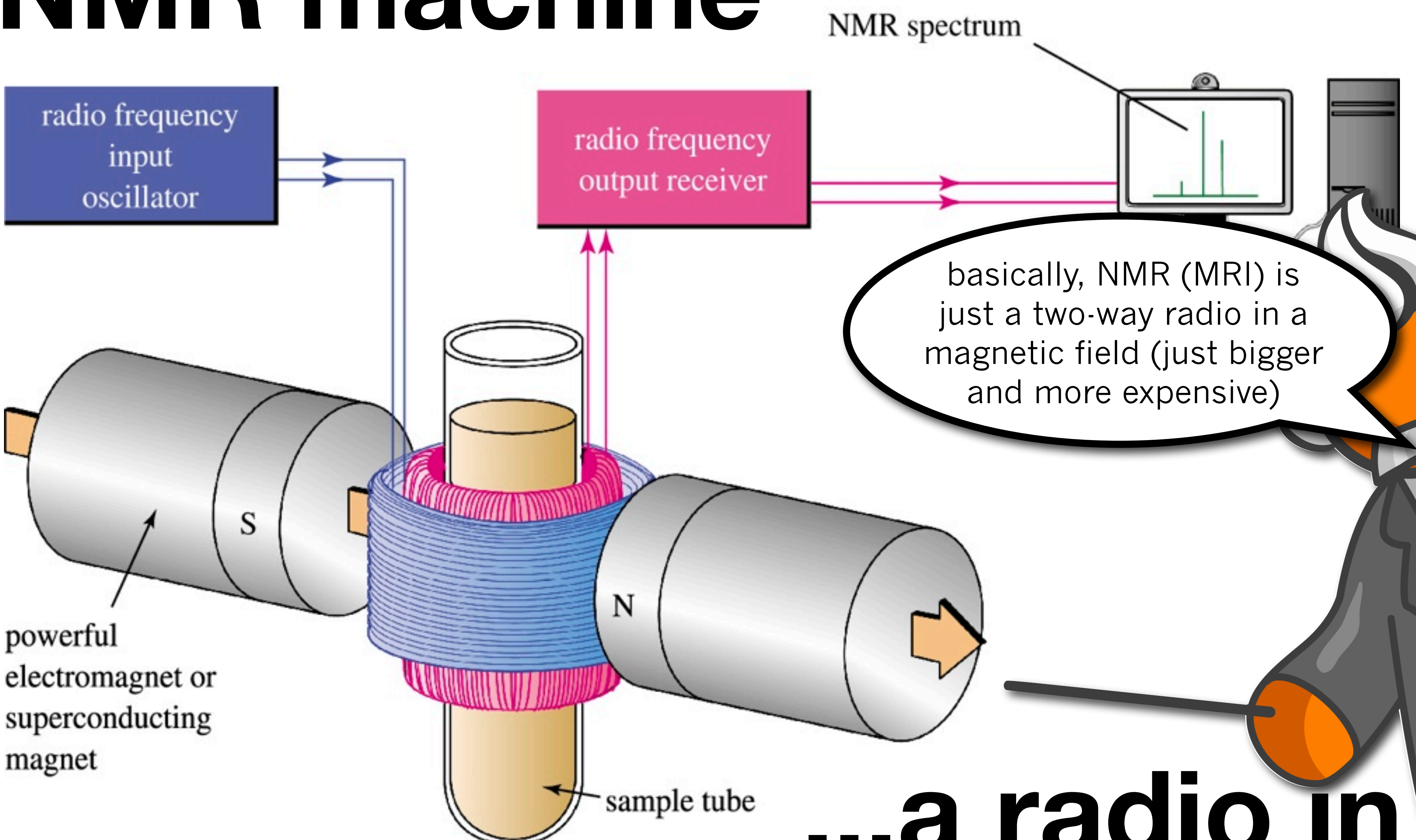
hydrogen



atom


sample
β-spin state
ENERGY
record energy emitted
...so, the amount of energy emitted is influenced by the electrons around the proton or **the chemical environment**. As bonds are electrons we now have information about bonds / structure of the molecule
α-spin state
relaxes

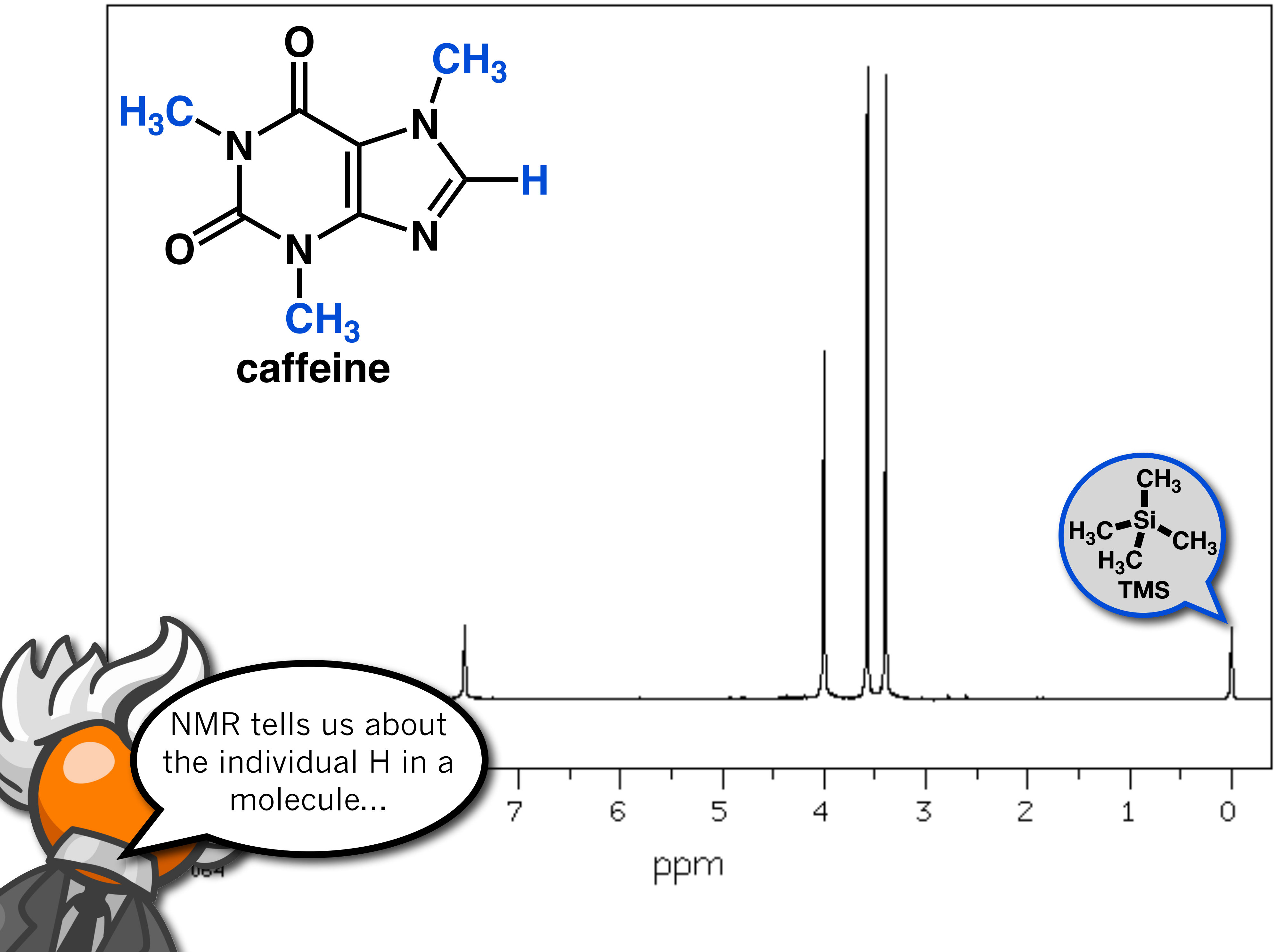
NMR machine

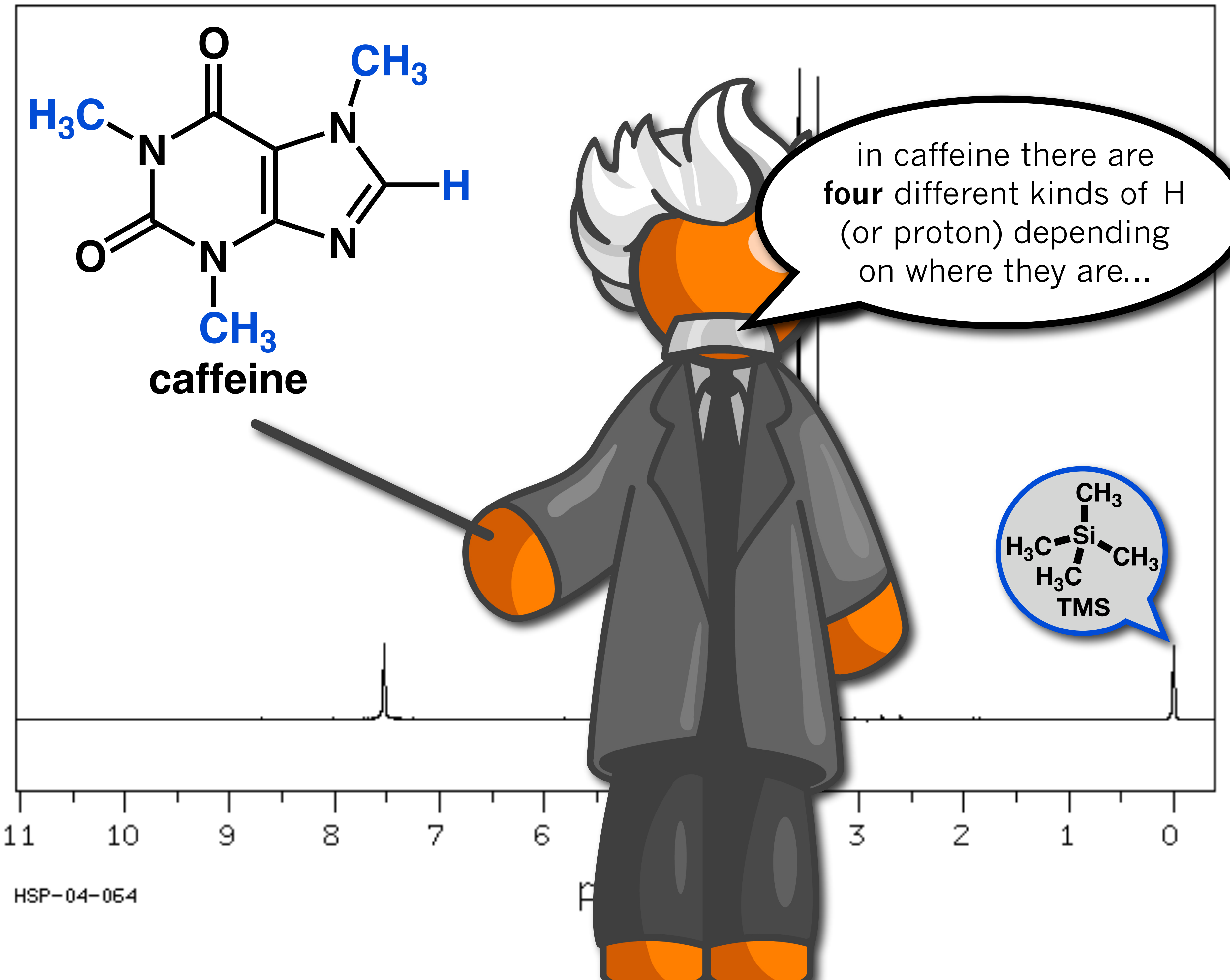


...a radio in a magnet...

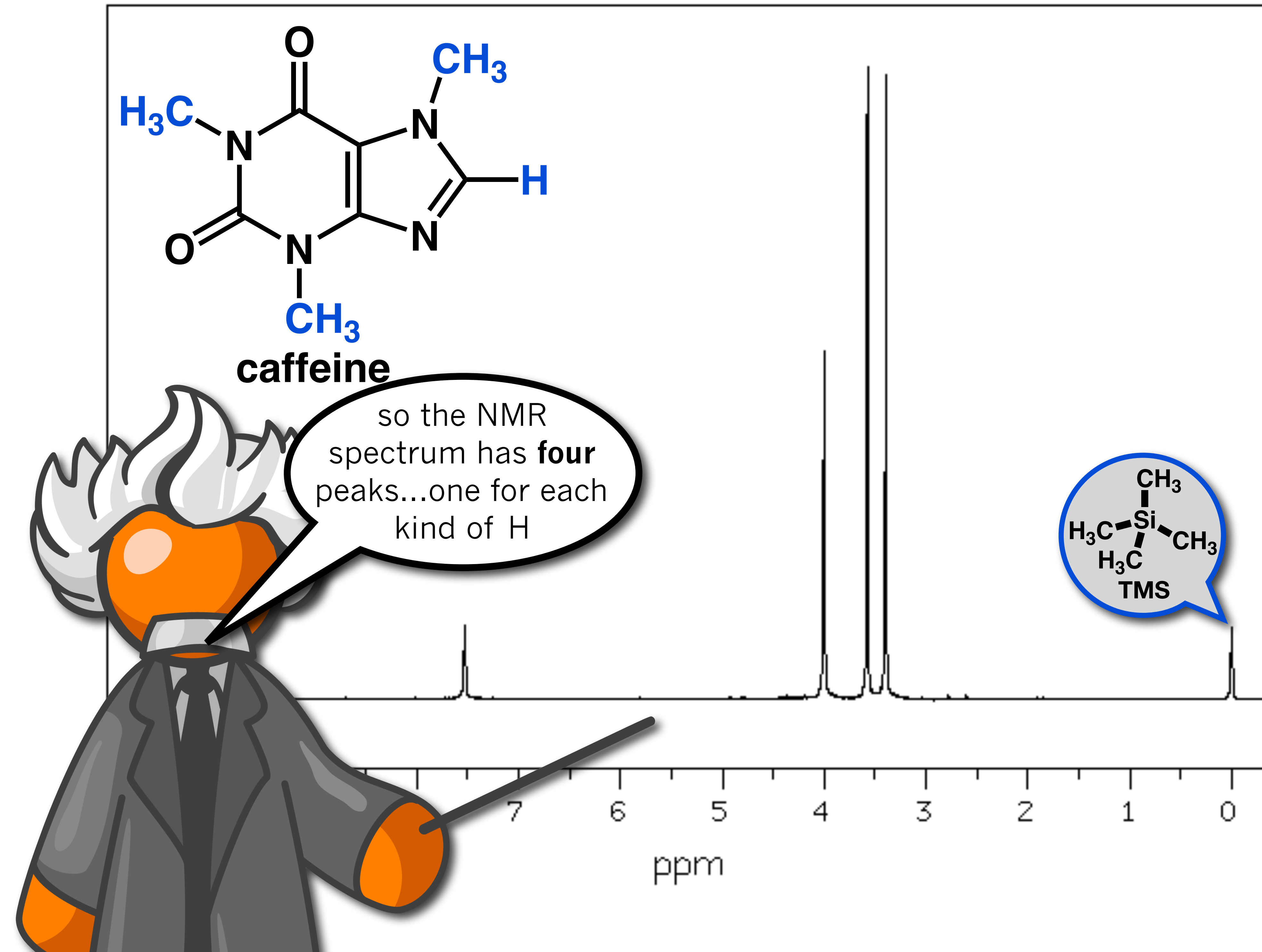
picture: ©Blackman *et al.* Wiley

so what does the
nmr tell us?

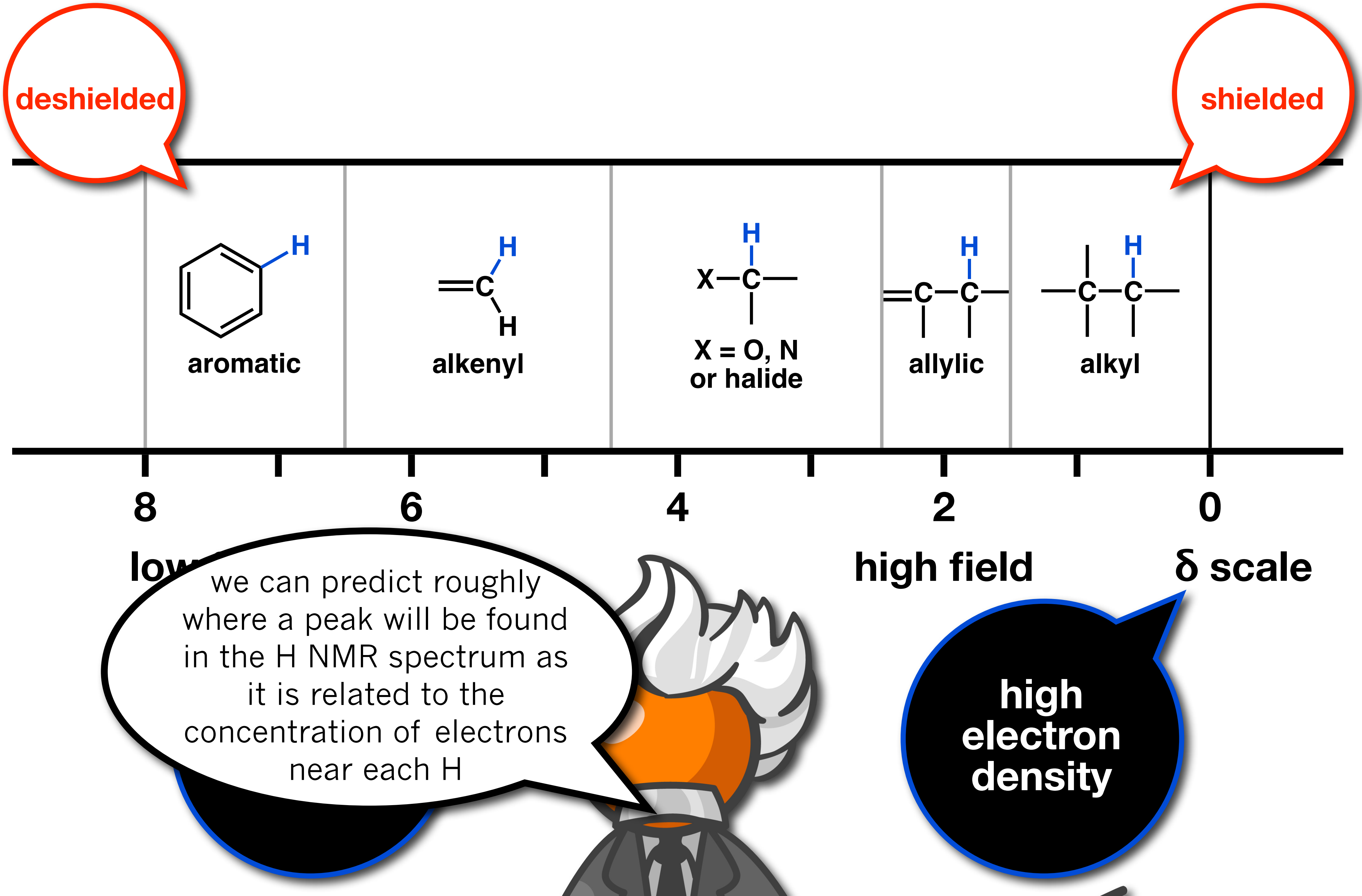

O
H_3C
N
CH_3
N
H
O
N
N
CH_3
caffeine
CH_3
H_3C
Si
CH_3
H_3C
TMS
NMR tells us about the individual H in a molecule...
7
6
5
4
3
2
1
0
ppm



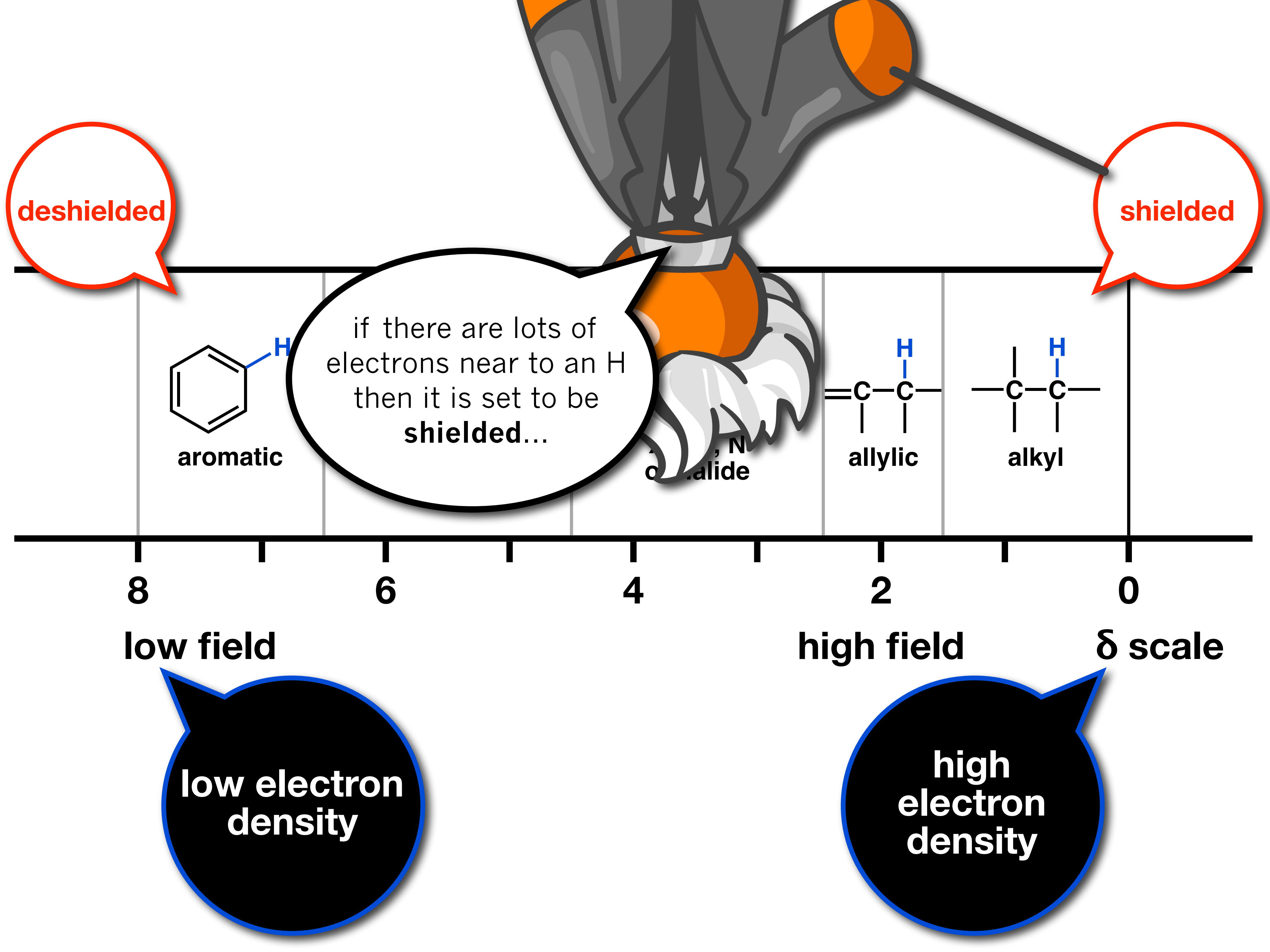
caffeine
in caffeine there are **four** different kinds of H (or proton) depending on where they are...
TMS
11 10 9 8 7 6 3 2 1 0
HSP-04-064



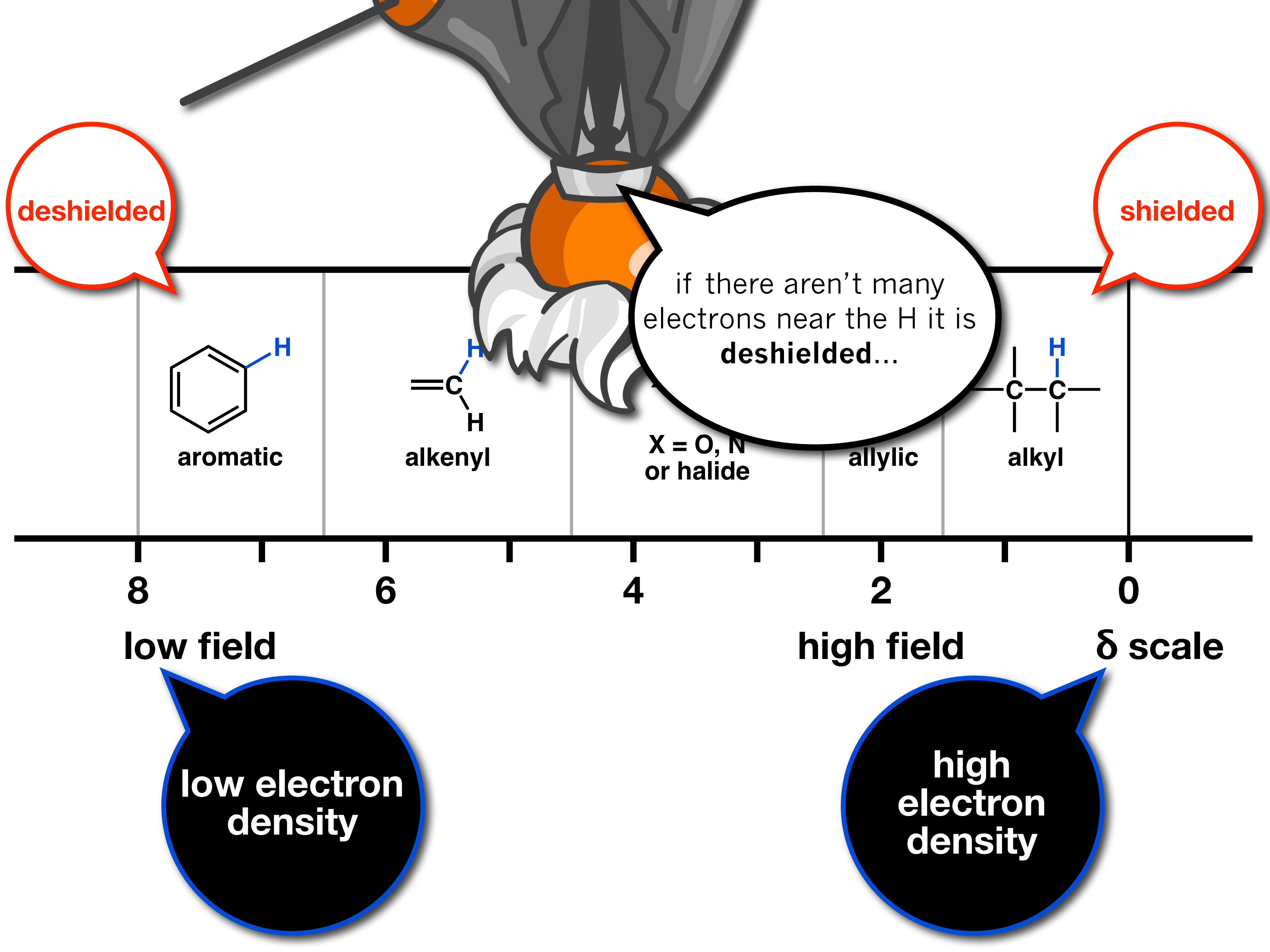
O
CH3
H3C
N
N
H
O
N
N
CH3
caffeine
so the NMR spectrum has **four** peaks...one for each kind of H
CH3
H3C
Si
CH3
H3C
TMS
7
6
5
4
3
2
1
0
ppm

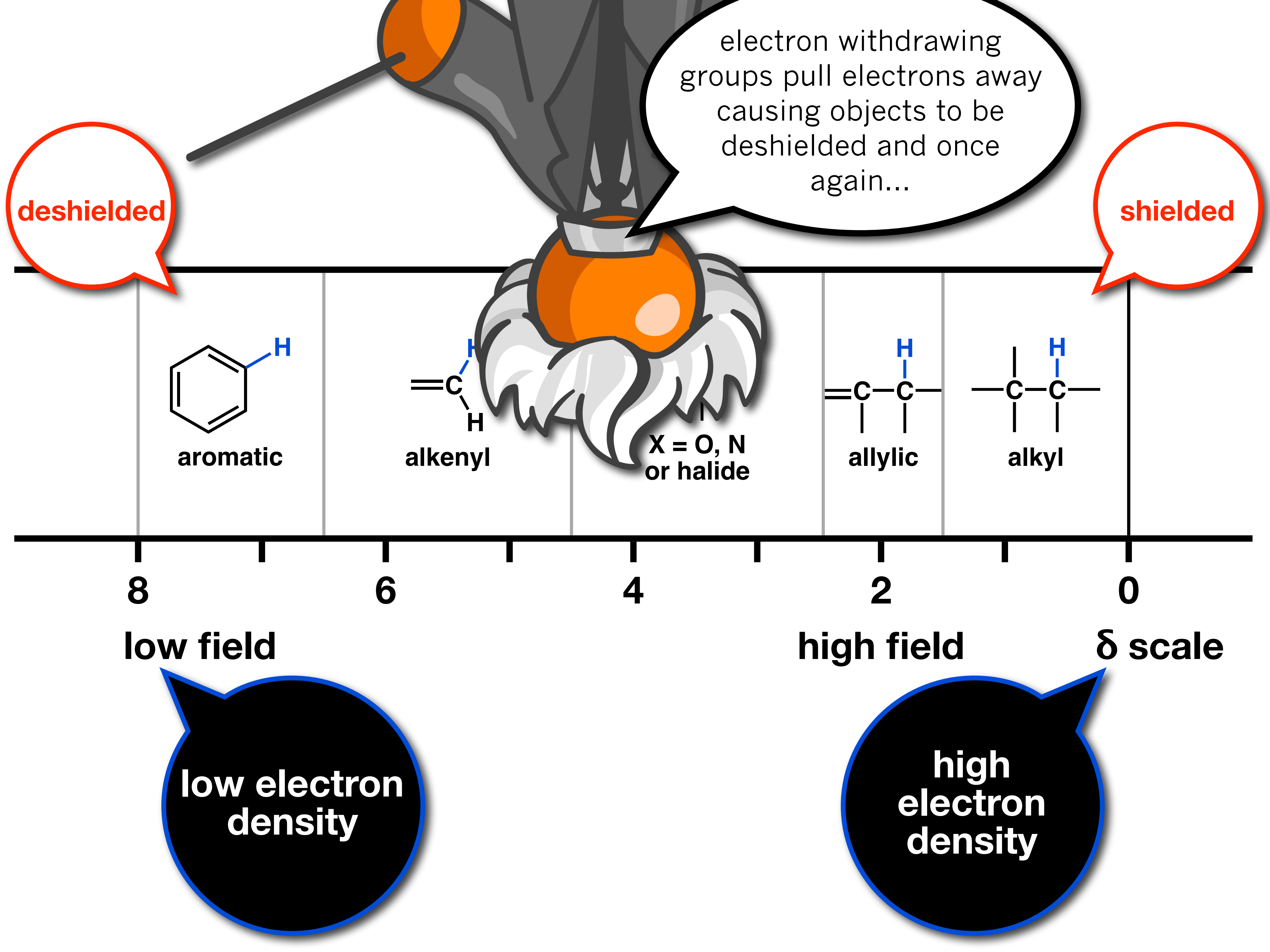


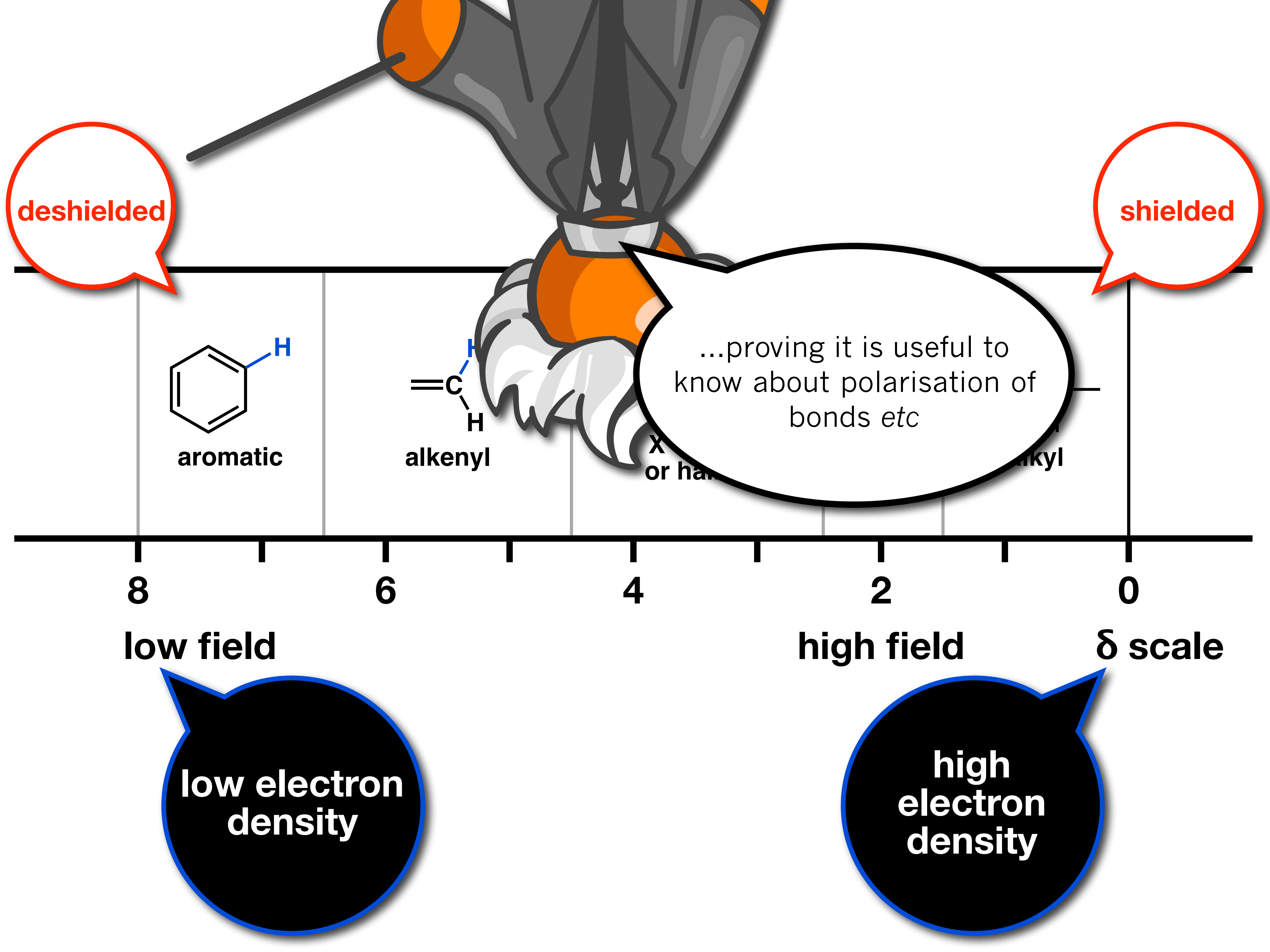
deshielded
shielded
H
aromatic
H
C
H
alkenyl
H
X
C
X = O, N
or halide
H
C
C
allylic
H
C
C
alkyl
8
6
4
2
0
high field
δ scale
we can predict roughly where a peak will be found in the H NMR spectrum as it is related to the concentration of electrons near each H
high electron density



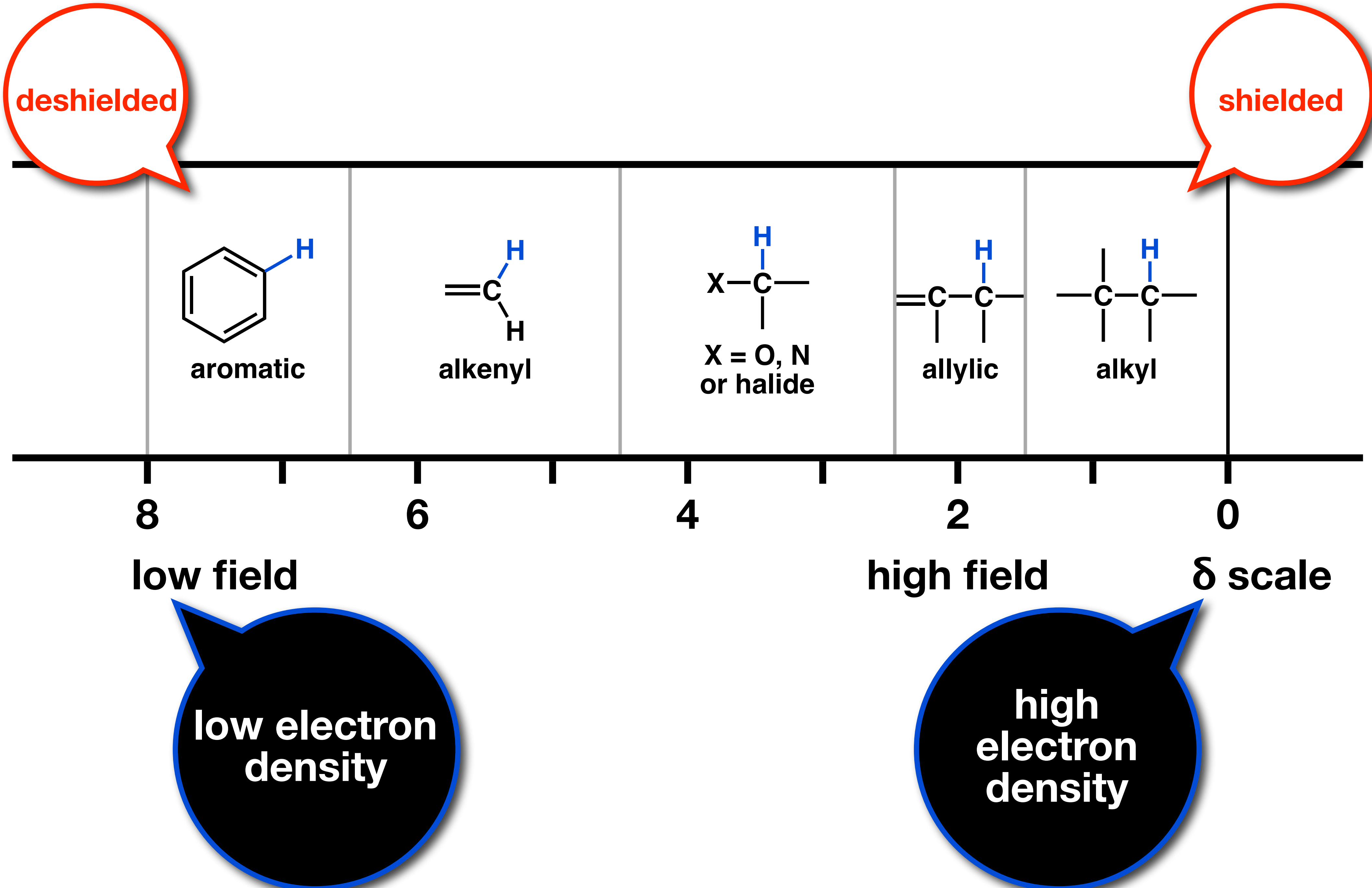
deshielded
shielded
if there are lots of electrons near to an H then it is set to be **shielded...**
H
aromatic
H
allylic
H
alkyl
8
6
4
2
0
low field
high field
δ scale
low electron density
high electron density


deshielded
shielded
if there aren't many electrons near the H it is deshielded...
H
aromatic
H
C
H
alkenyl
X = O, N
or halide
allylic
H
C
C
alkyl
8
6
4
2
0
low field
high field
δ scale
low electron density
high electron density


electron withdrawing groups pull electrons away causing objects to be deshielded and once again...
deshielded
shielded
H
aromatic
H
C
H
alkenyl
X = O, N or halide
H
C–C
allylic
H
C–C
alkyl
8
6
4
2
0
low field
high field
δ scale
low electron density
high electron density



deshielded
shielded
aromatic
alkenyl
...proving it is useful to know about polarisation of bonds *etc*
8
6
4
2
0
low field
high field
δ scale
low electron density
high electron density

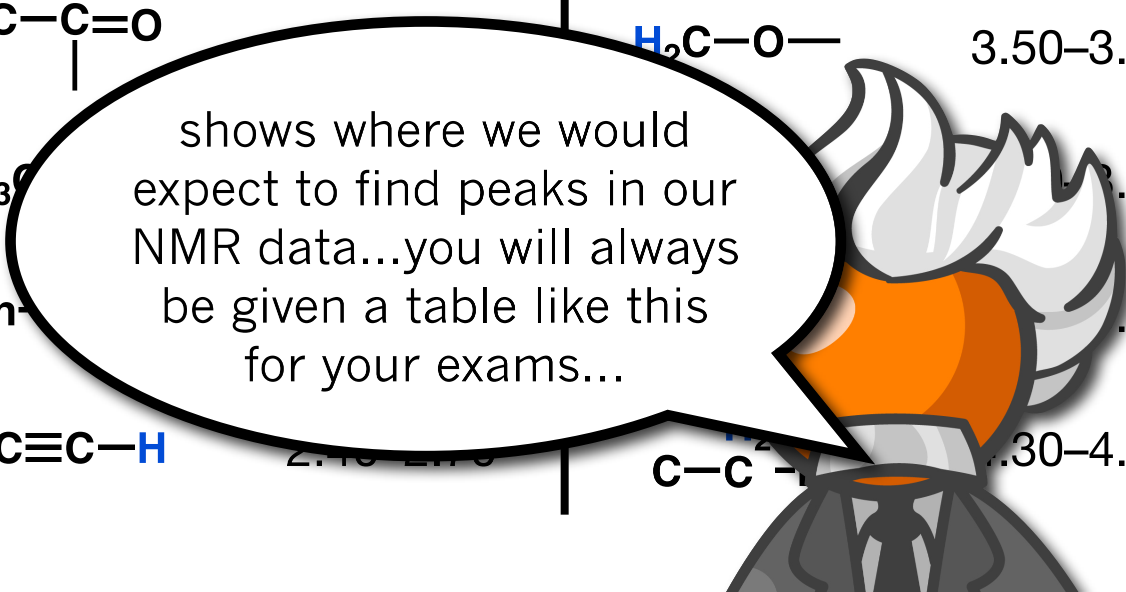

deshielded
shielded
H
aromatic
H
H
alkenyl
H
X—C—
X = O, N
or halide
H
=C—C—
allylic
H
—C—C—
alkyl
8
6
4
2
0
low field
high field
δ scale
low electron density
high electron density

correlation table

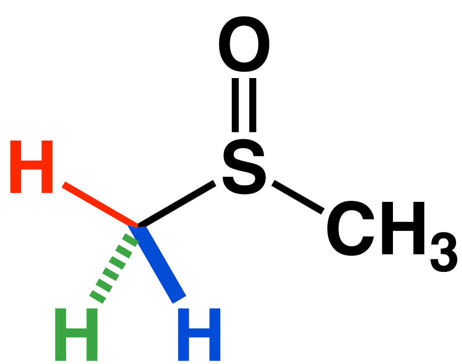
Type of hydrogen	δ (ppm)	Type of hydrogen	δ (ppm)	Type of hydrogen	δ (ppm)
$C{-}CH_3$	0.70–1.30	$C{-}CH_2{-}Ph$	2.60	$C{=}CH_2$	4.60–5.00
$C{-}CH_2{-}C$	1.20–1.35	$C{-}CH_2{-}I$	3.10–3.30	$C{-}CH{=}C$	5.20–5.70
$C{-}CH(C){-}C$	1.40–1.65	$C{-}CH_2{-}Br$	3.40	$—CHCl_2$	5.80–5.90
$H_3C{-}C{=}C$	1.60–1.90	$C{-}CH_2{-}Cl$	3.50	$Ph{-}H$	6.60–8.00
$H_3C{-}C({=}O){-}$	2.10–2.60	$H_2C{-}O{-}$	3.50–3.80	$C{-}C({=}O){-}H$	9.50–9.70
$H_3C{-}N\langle$	2.10–3.00	$H_3C{-}O{-}$	3.50–3.80	$C{-}C({=}O){-}OH$	10.00–13.00
$Ph{-}CH_3$	2.20–2.50	$Ar{-}OH$	4.00–8.00	$R{-}OH$	0.50–5.50
$—C{\equiv}C{-}H$	2.40–2.70	$C{-}CH_2{-}F$	4.30–4.40		

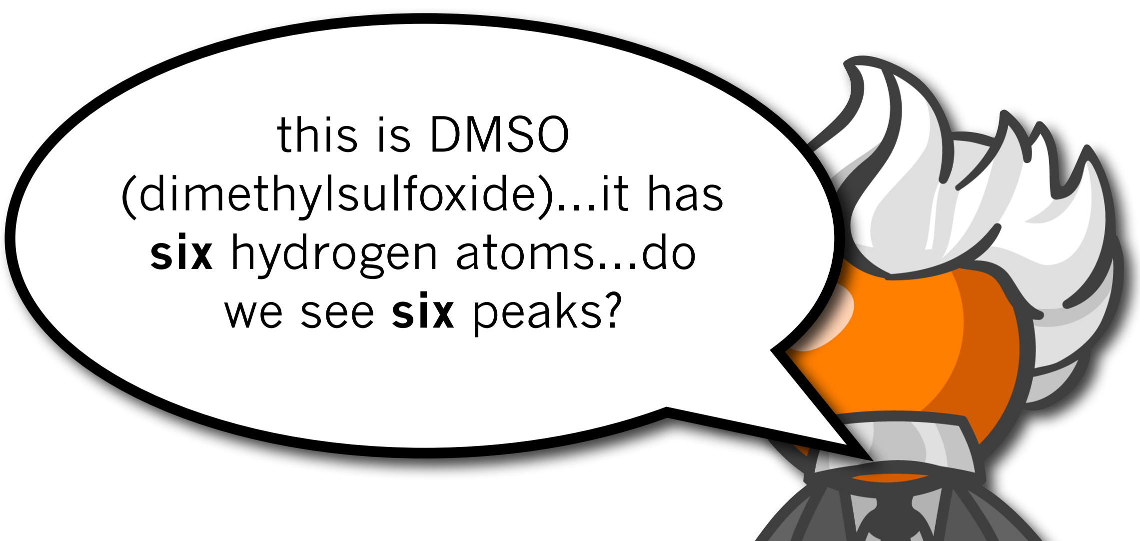
correlation table

Type of hydrogen	δ (ppm)	Type of hydrogen	δ (ppm)	Type of hydrogen	δ (ppm)
C—CH_3	0.70–1.30	C—CH_2–Ph	2.60	C=CH_2	4.60–5.00
C—CH_2–C	1.20–1.35	C—CH_2–I	3.10–3.30	C—CH=C	5.20–5.70
C—CH(C)—C	1.40–1.65	C—CH_2–Br	3.40	—$CHCl_2$	5.80–5.90
H_3C—C=C	1.60–1.90	C—CH_2–Cl	3.50	Ph—H	6.60–8.00
H_3C—C(=O)—	[illegible]	H?C—O—	3.50–3.80	C—C(=O)—H	9.50–9.70
[illegible]	[illegible]	[illegible]	.80	C—C(=O)—OH	10.00–13.00
Ph–	[illegible]	[illegible]	.00	R—OH	0.50–5.50
—C≡C—H	[illegible]	[illegible]	.30–4.40		

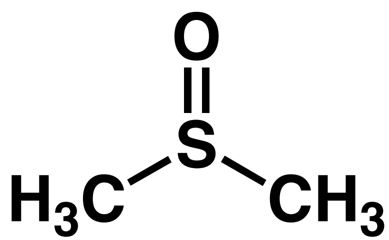


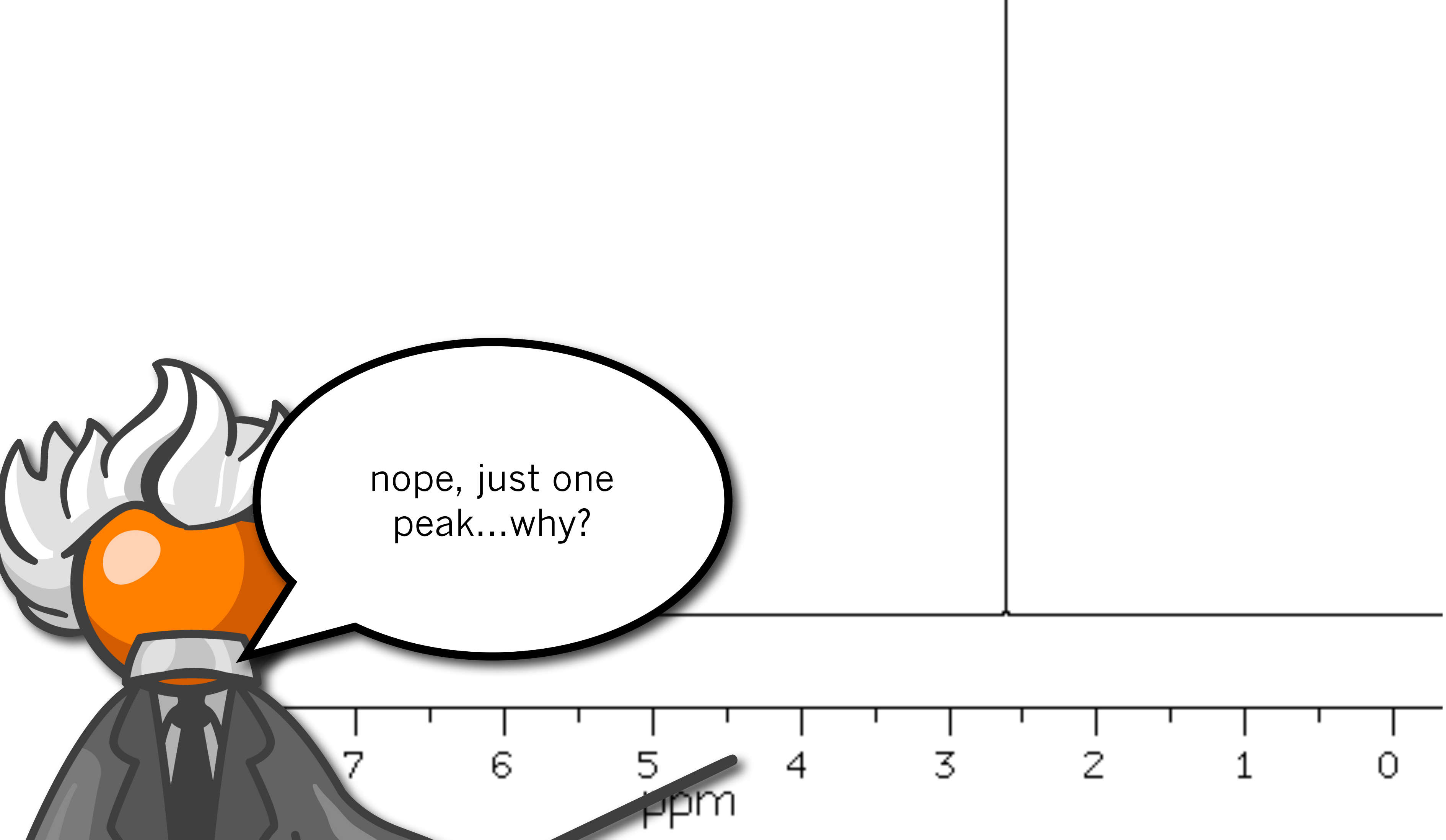
chemically equivalent hydrogen



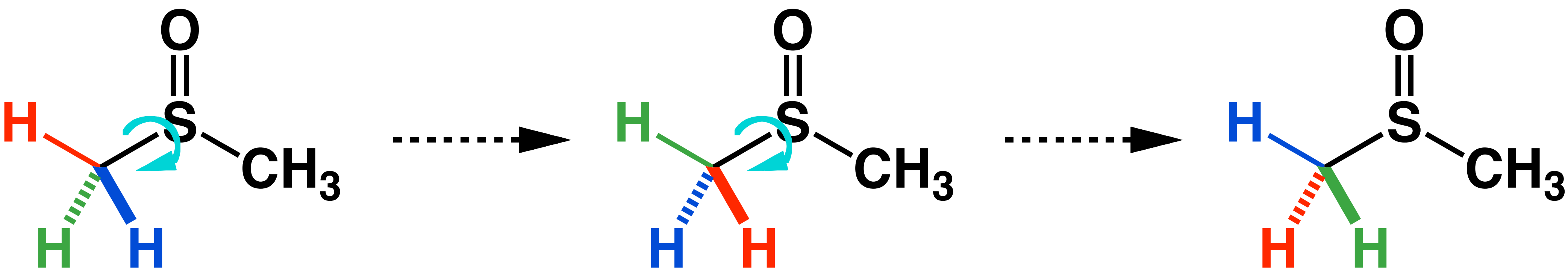


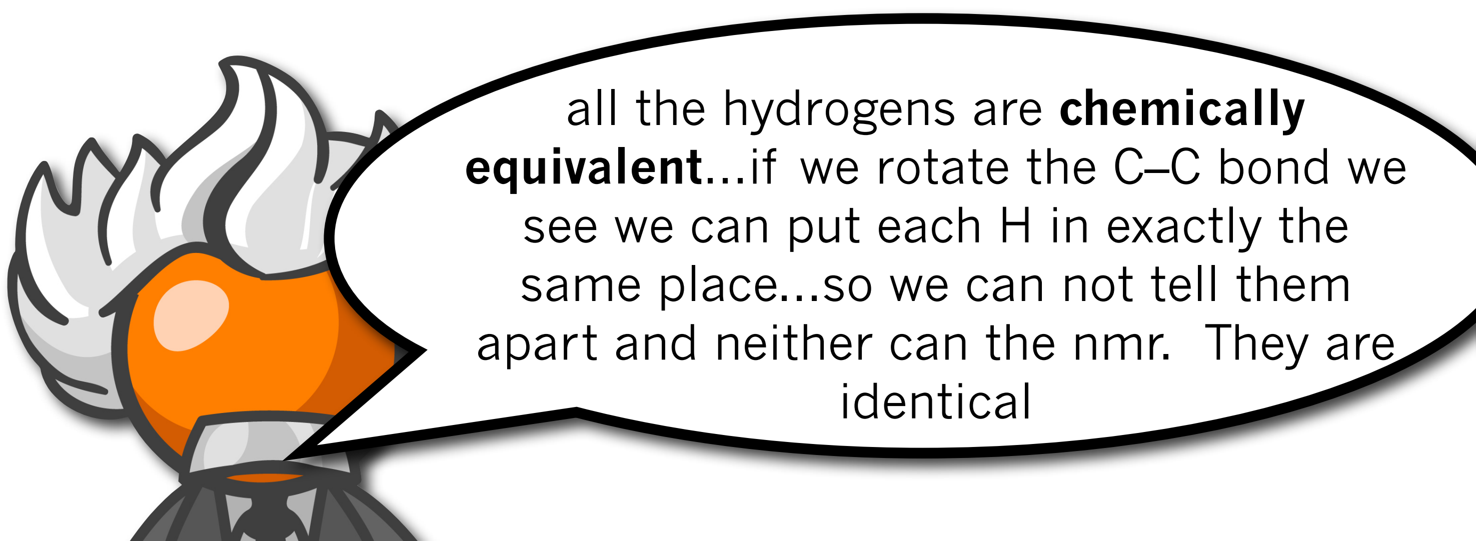
chemically equivalent hydrogen



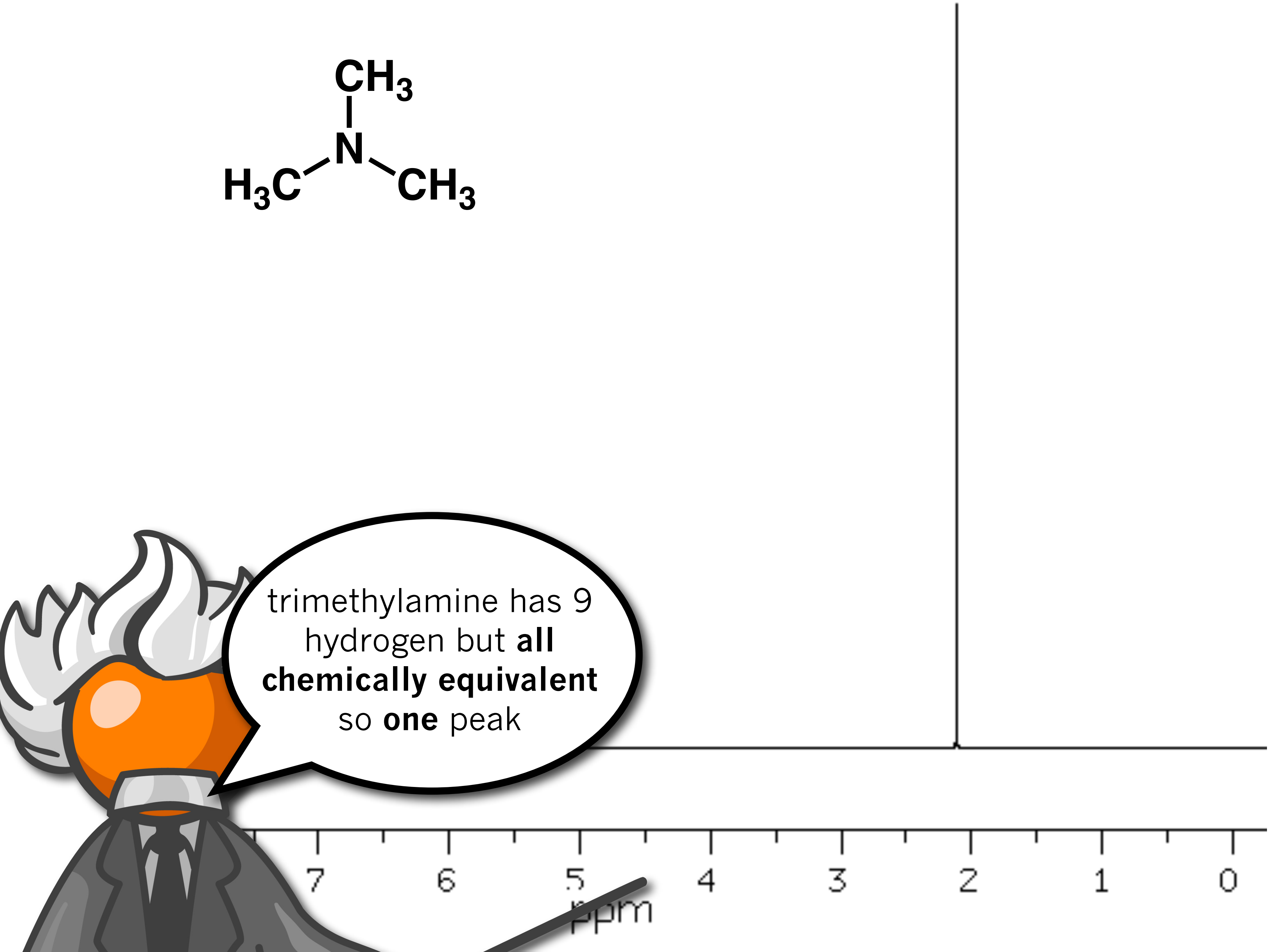


chemically equivalent hydrogen

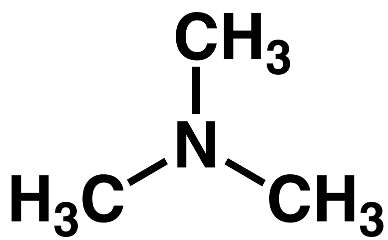


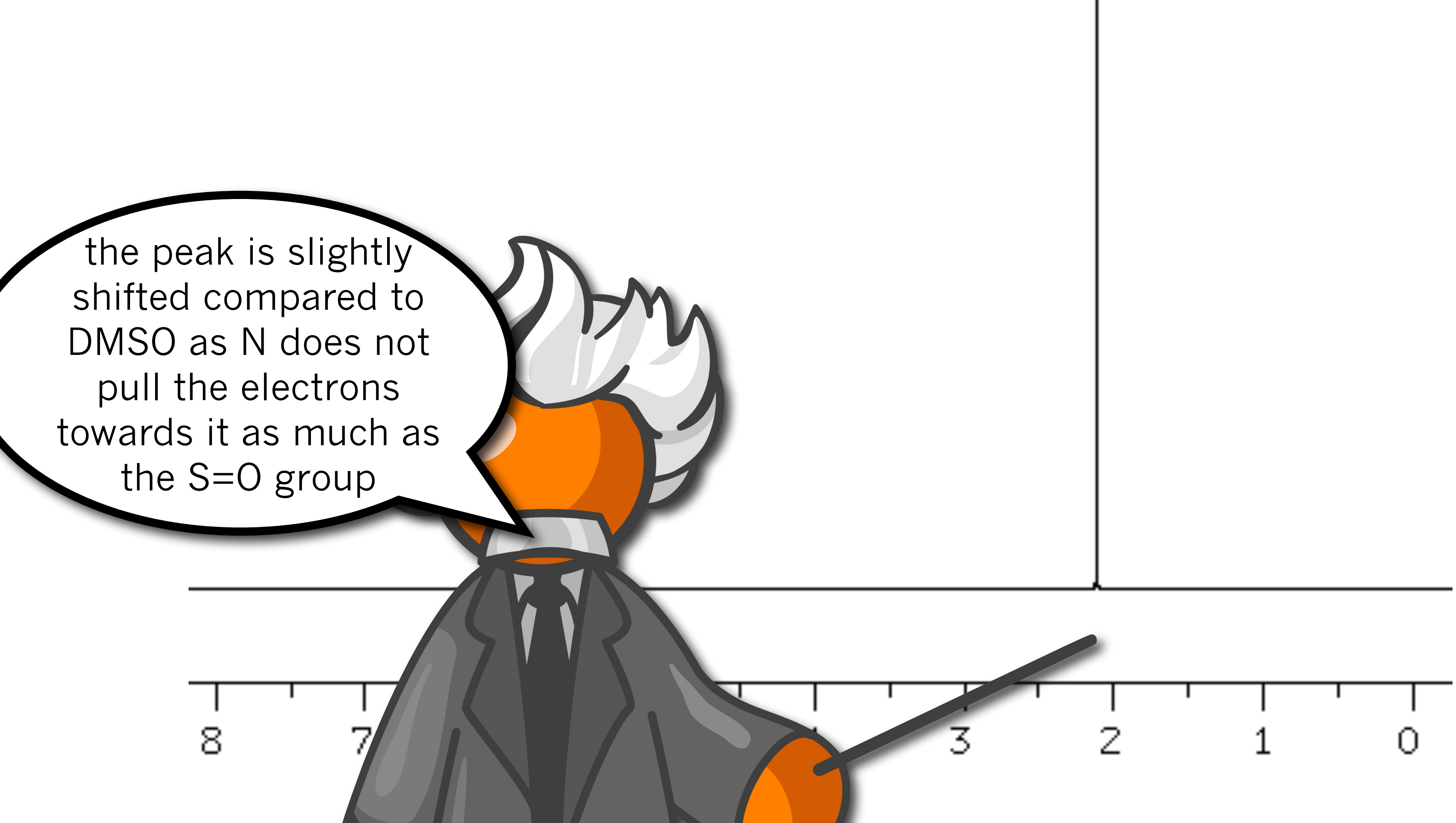


chemically equivalent hydrogen

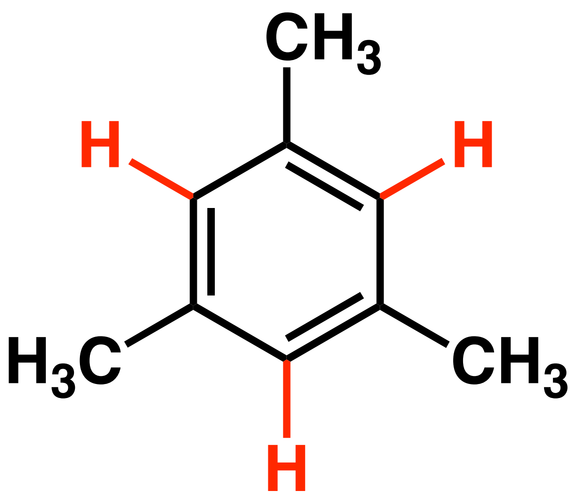


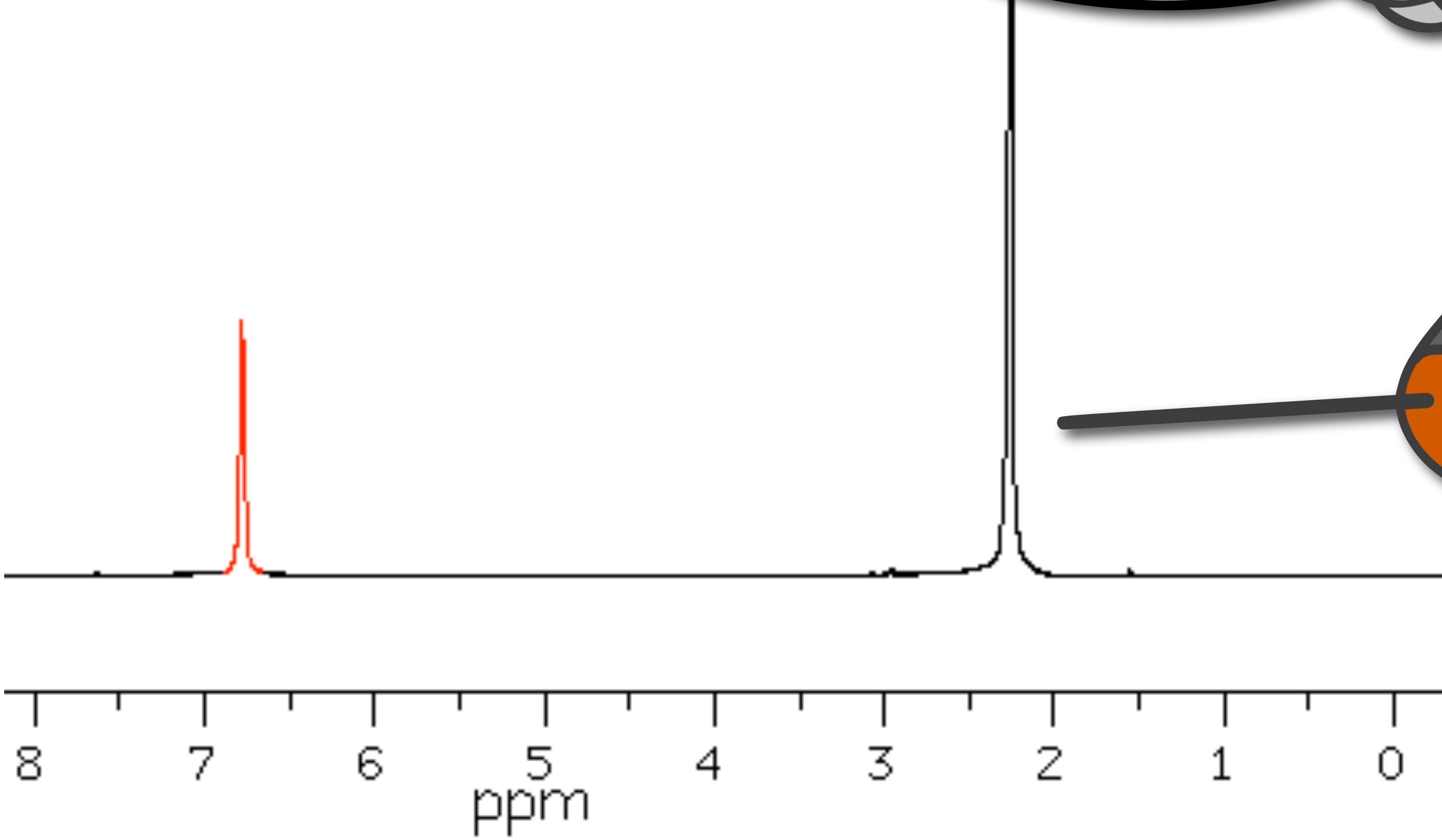
chemically equivalent hydrogen

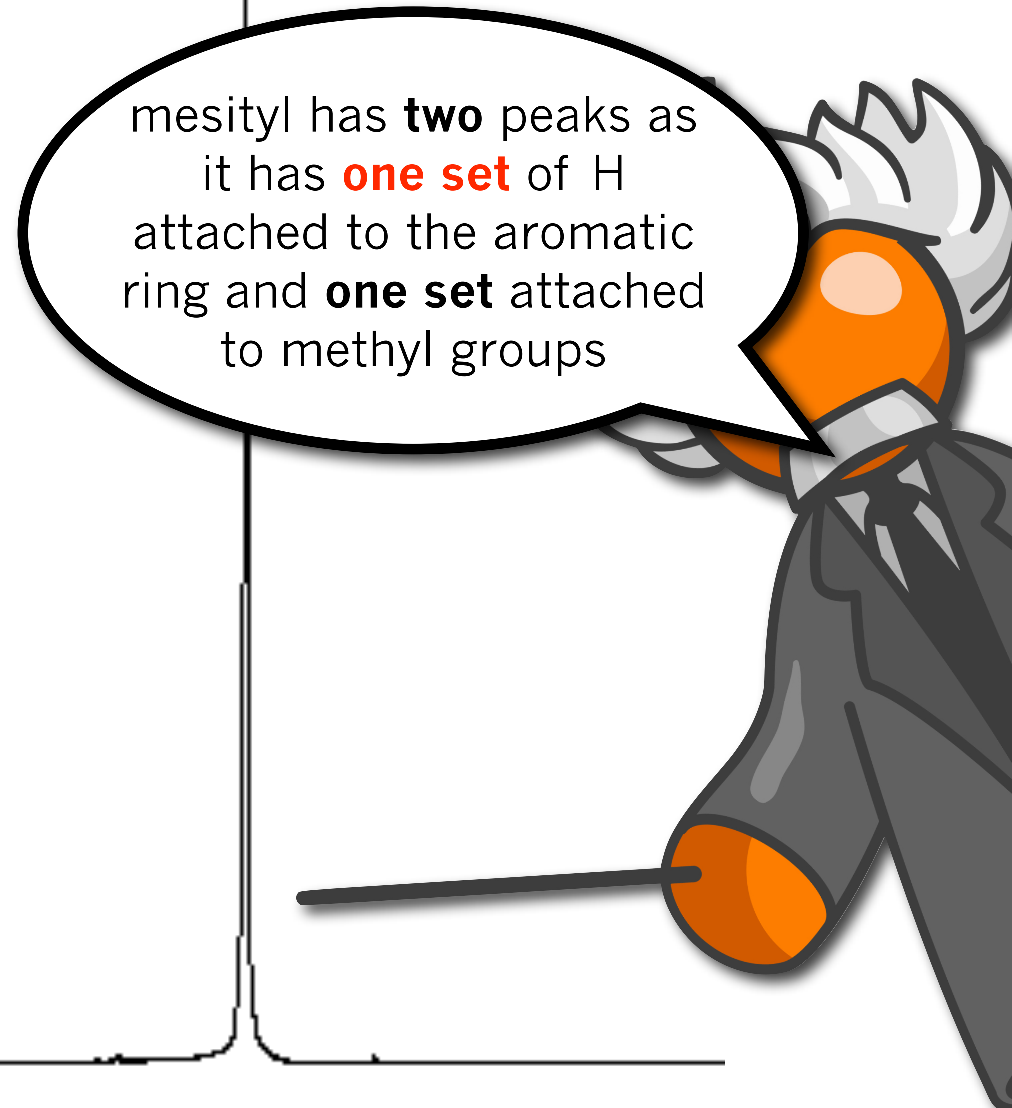




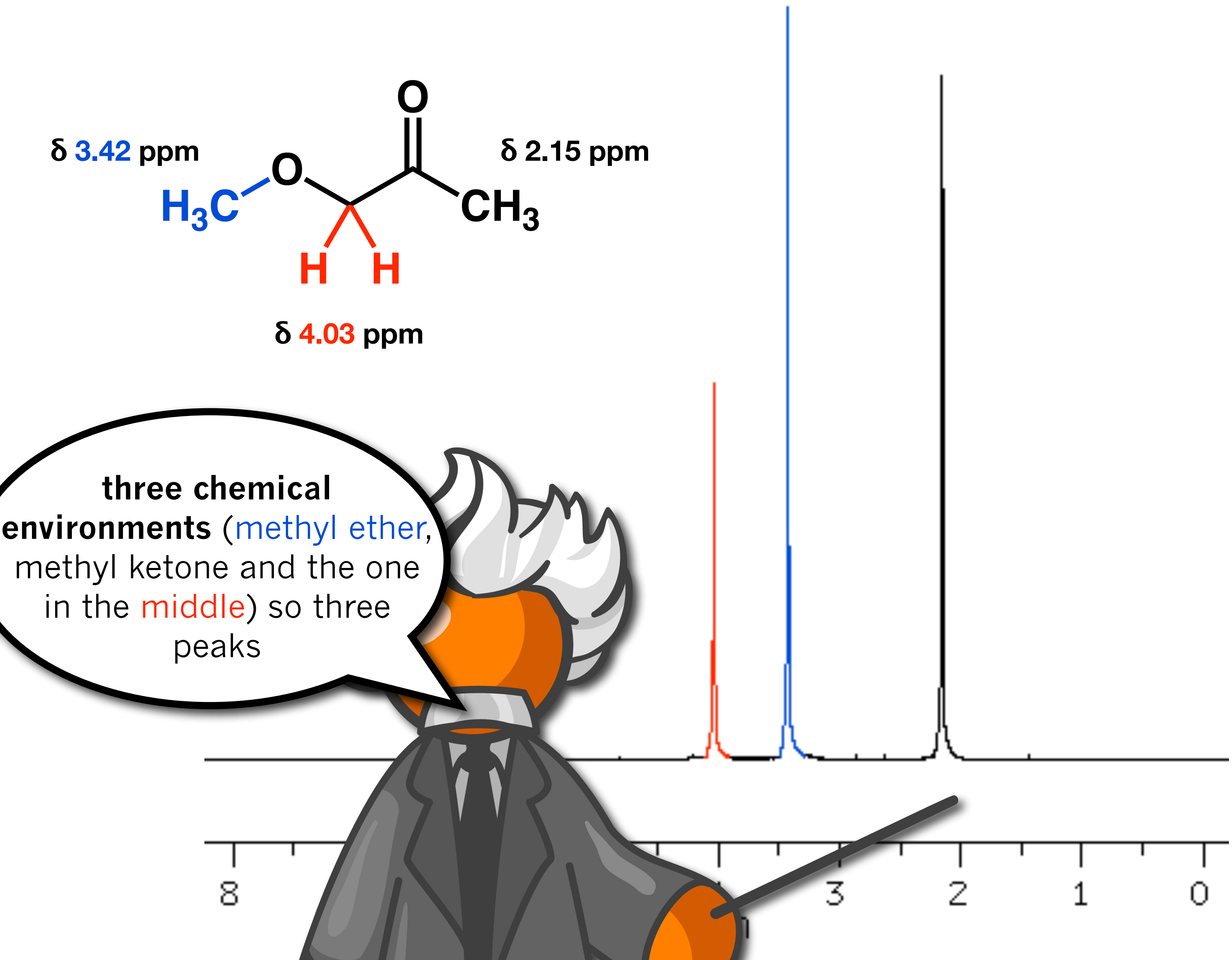
two chemical environments



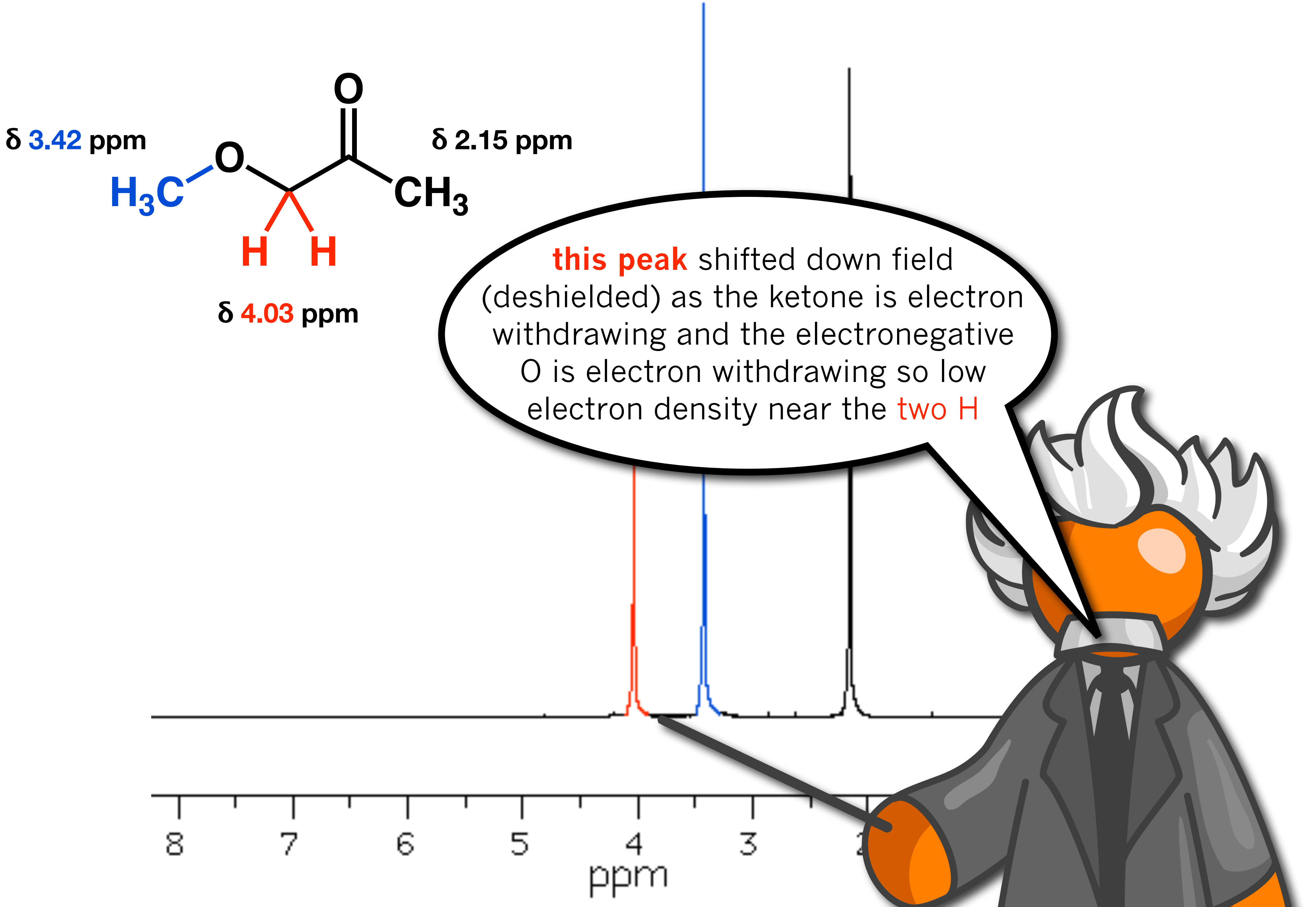




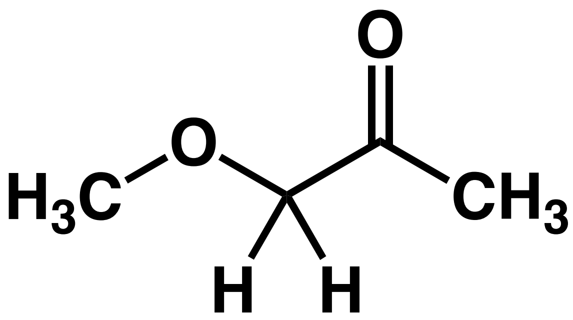
three chemical environments

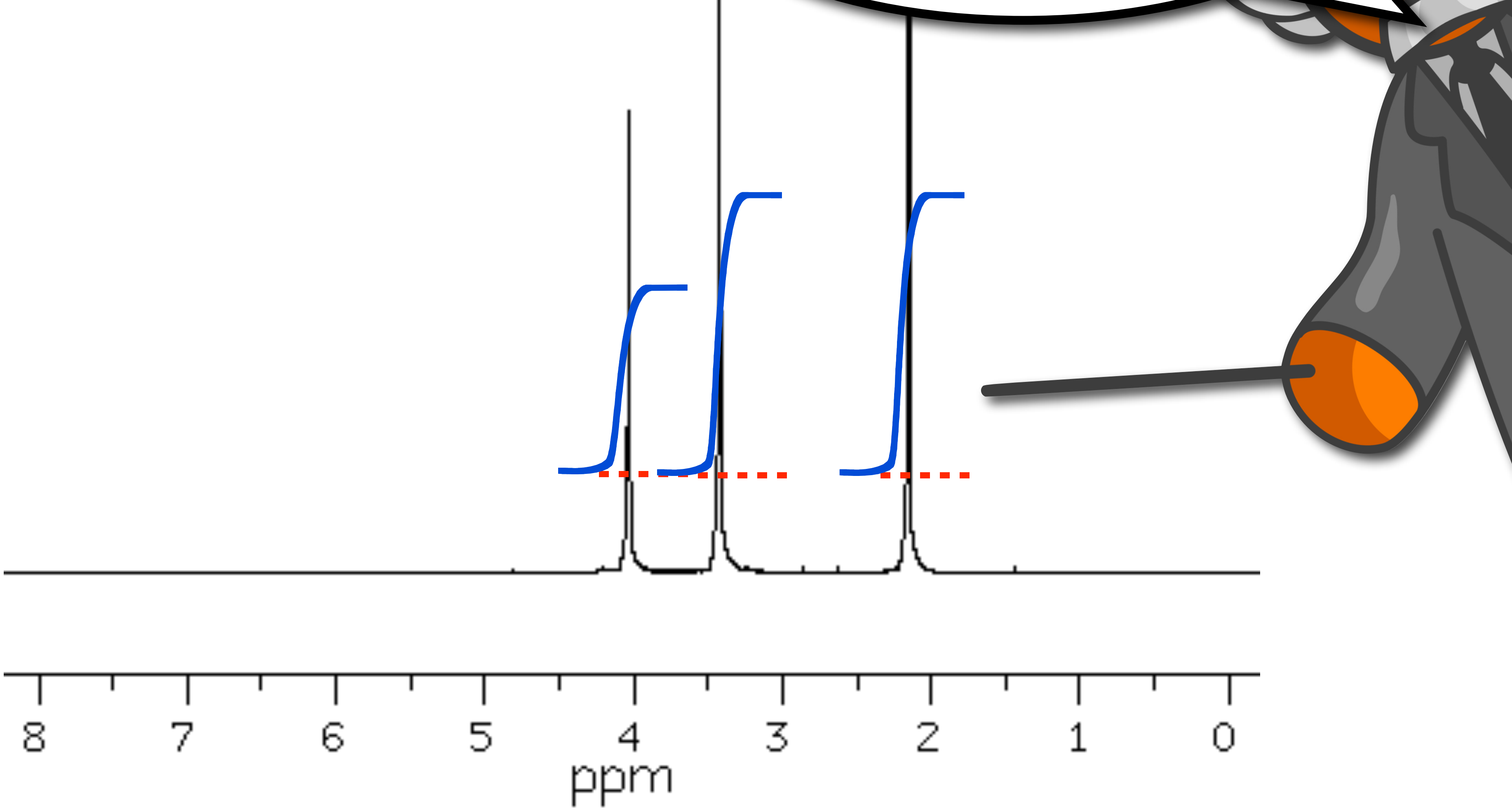


three chemical environments

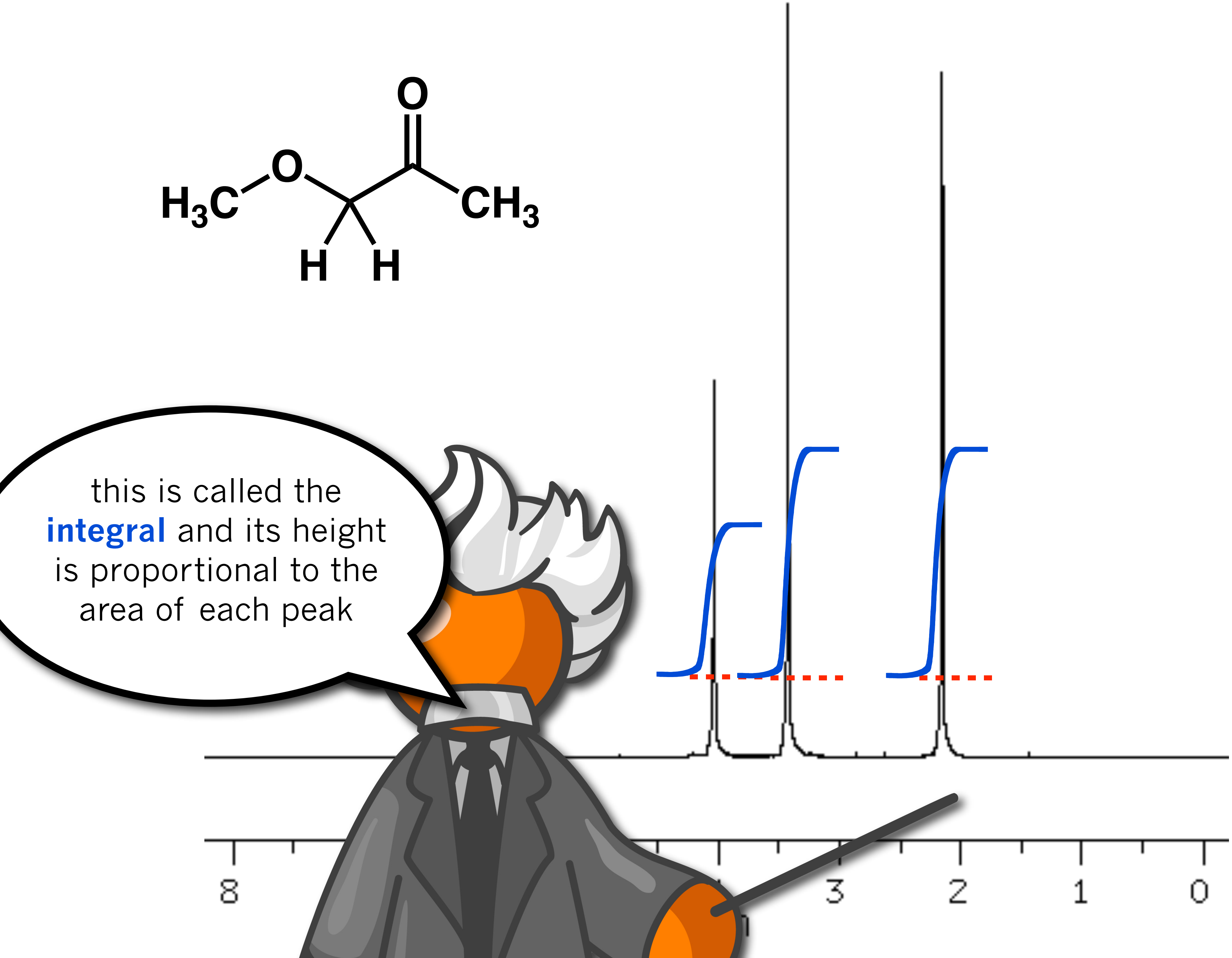


integration (hydrogen counting)

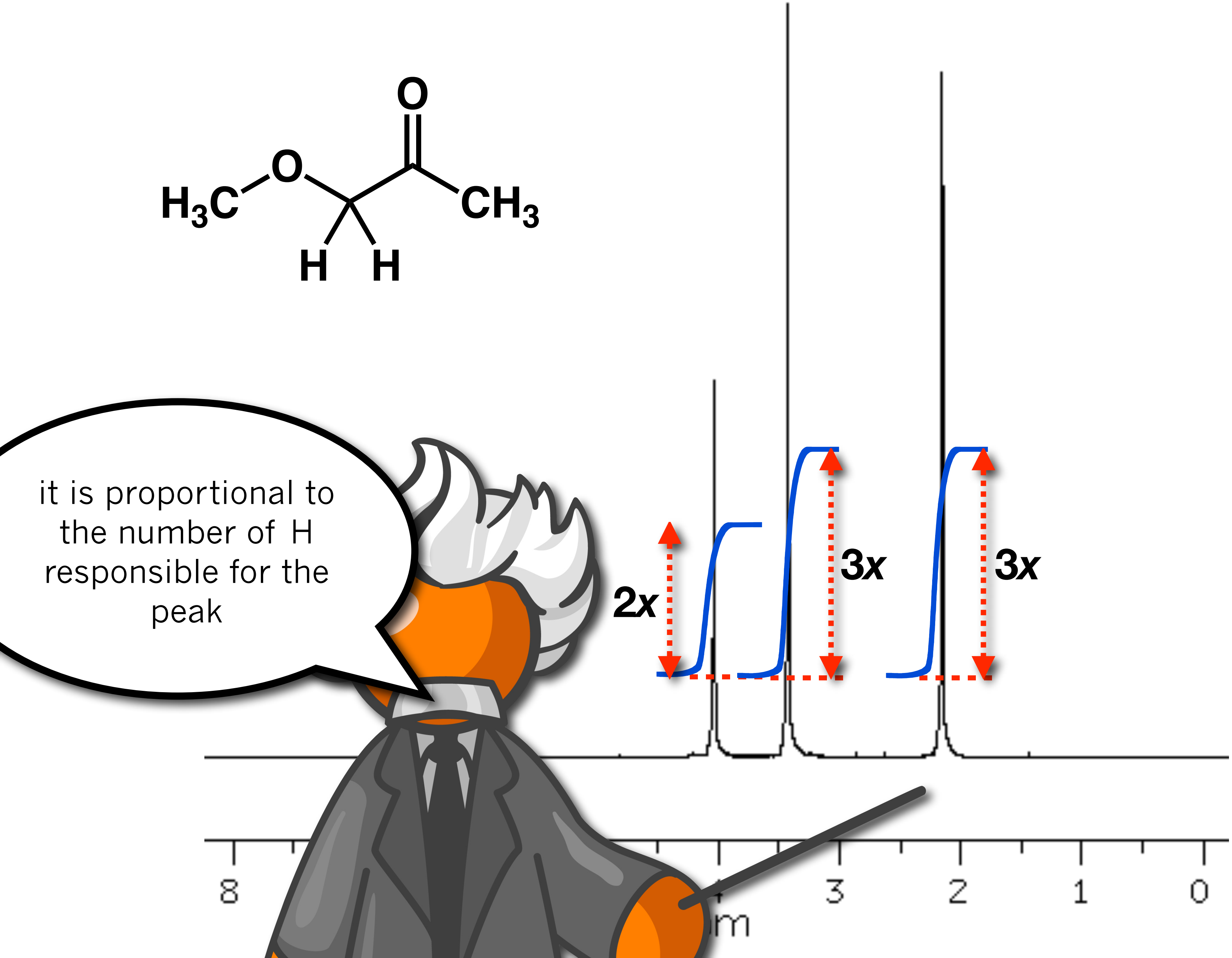




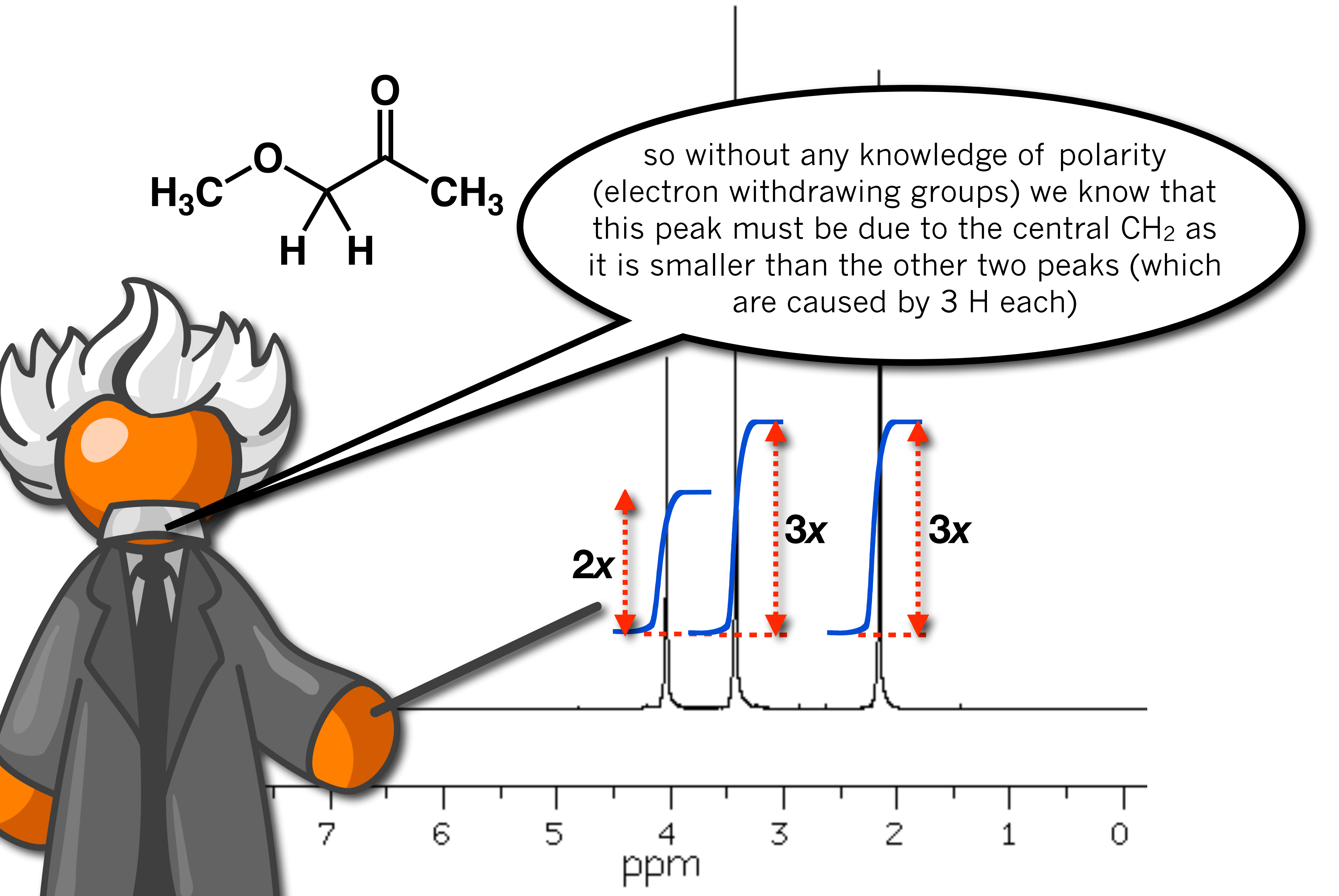
integration (hydrogen counting)



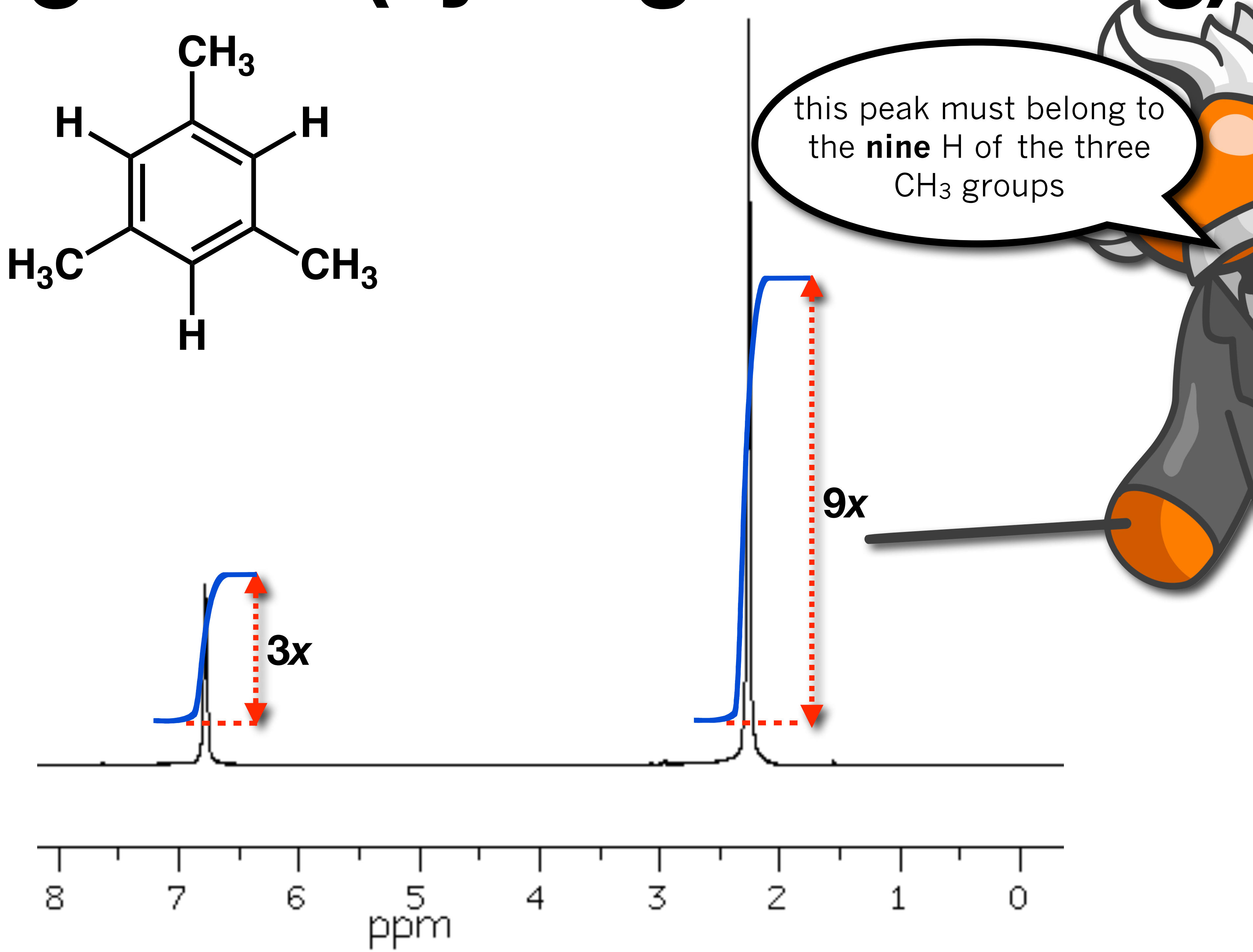
integration (hydrogen counting)



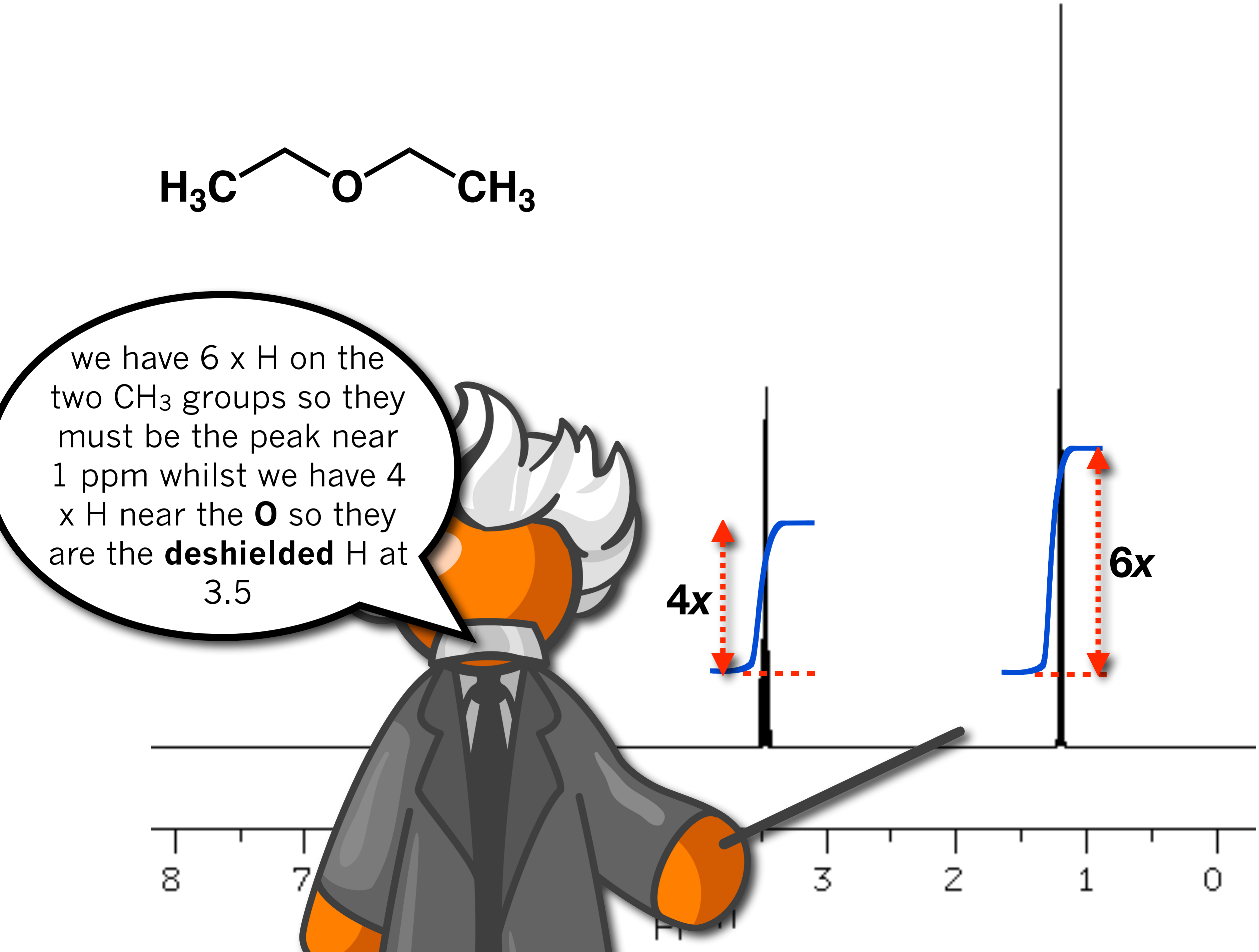
integration (hydrogen counting)



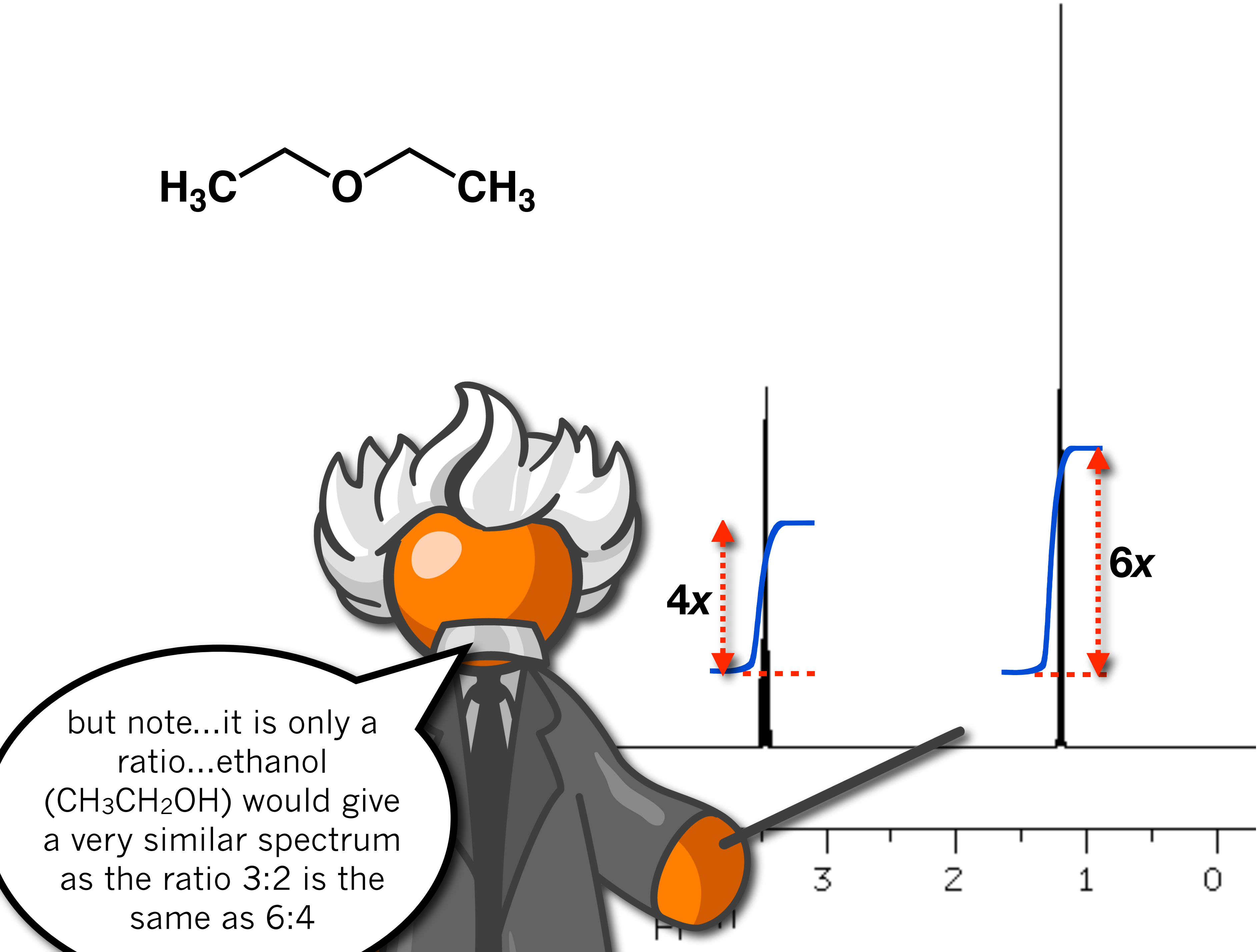
integration (hydrogen counting)



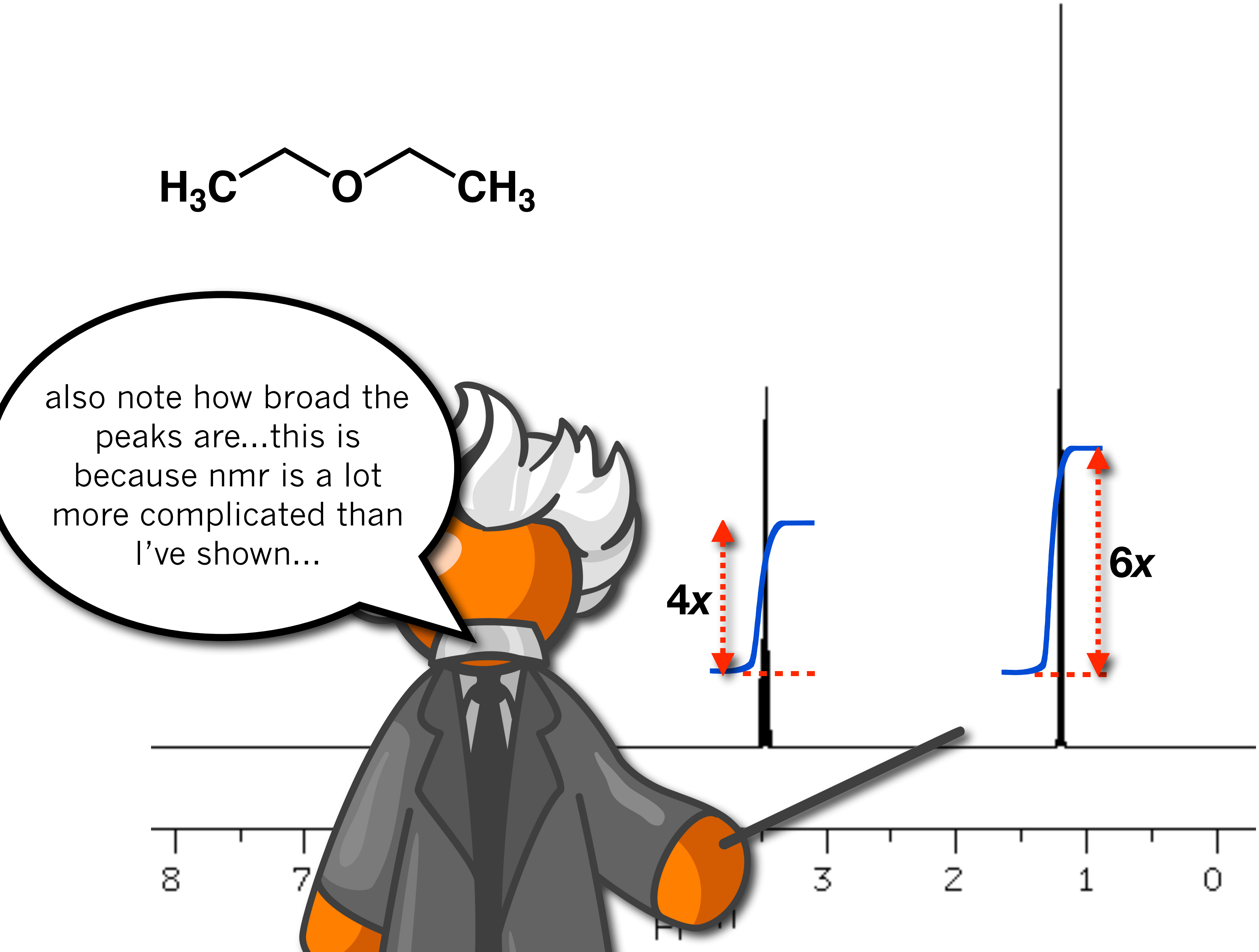
integration (hydrogen counting)



integration (hydrogen counting)



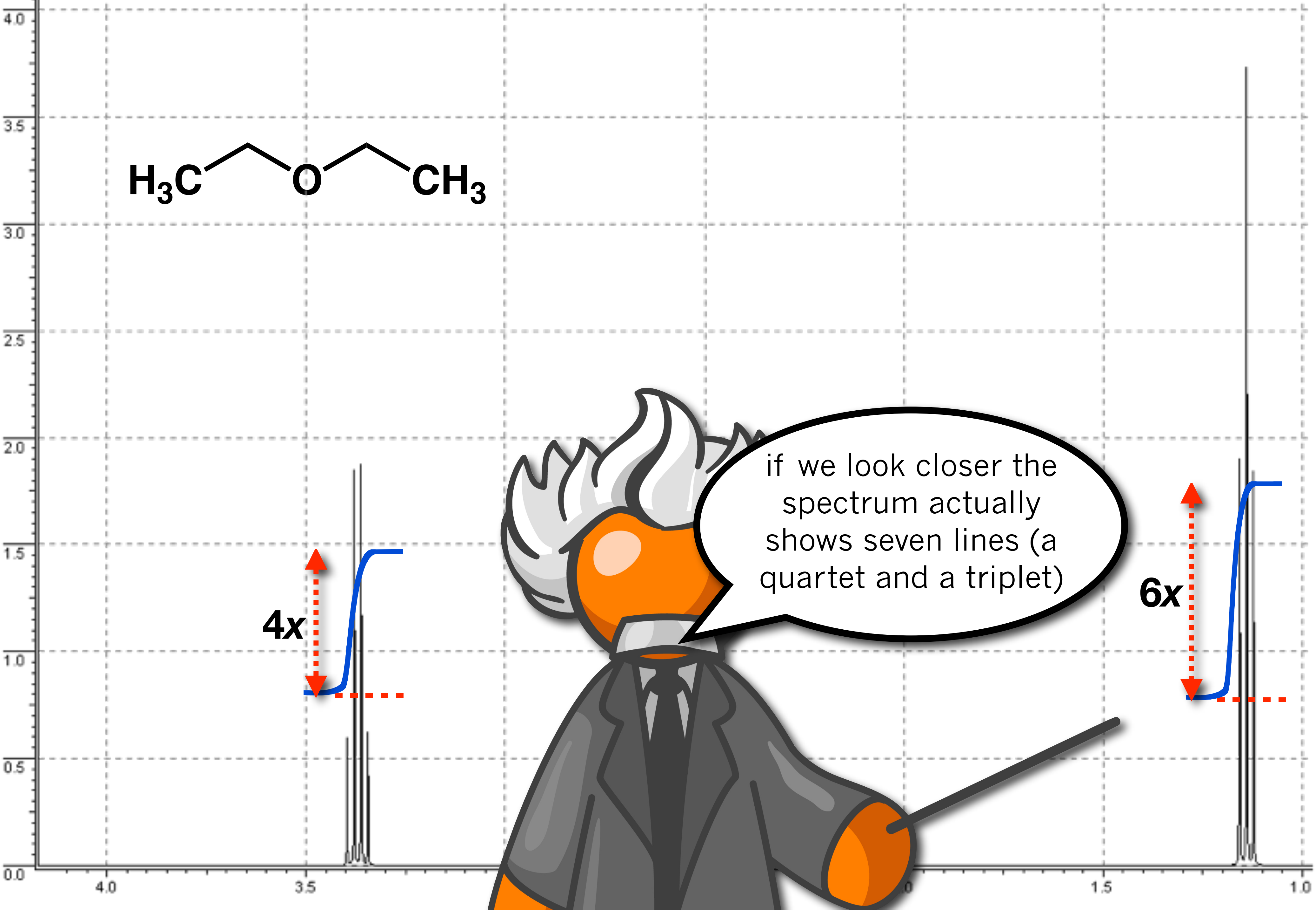
integration (hydrogen counting)



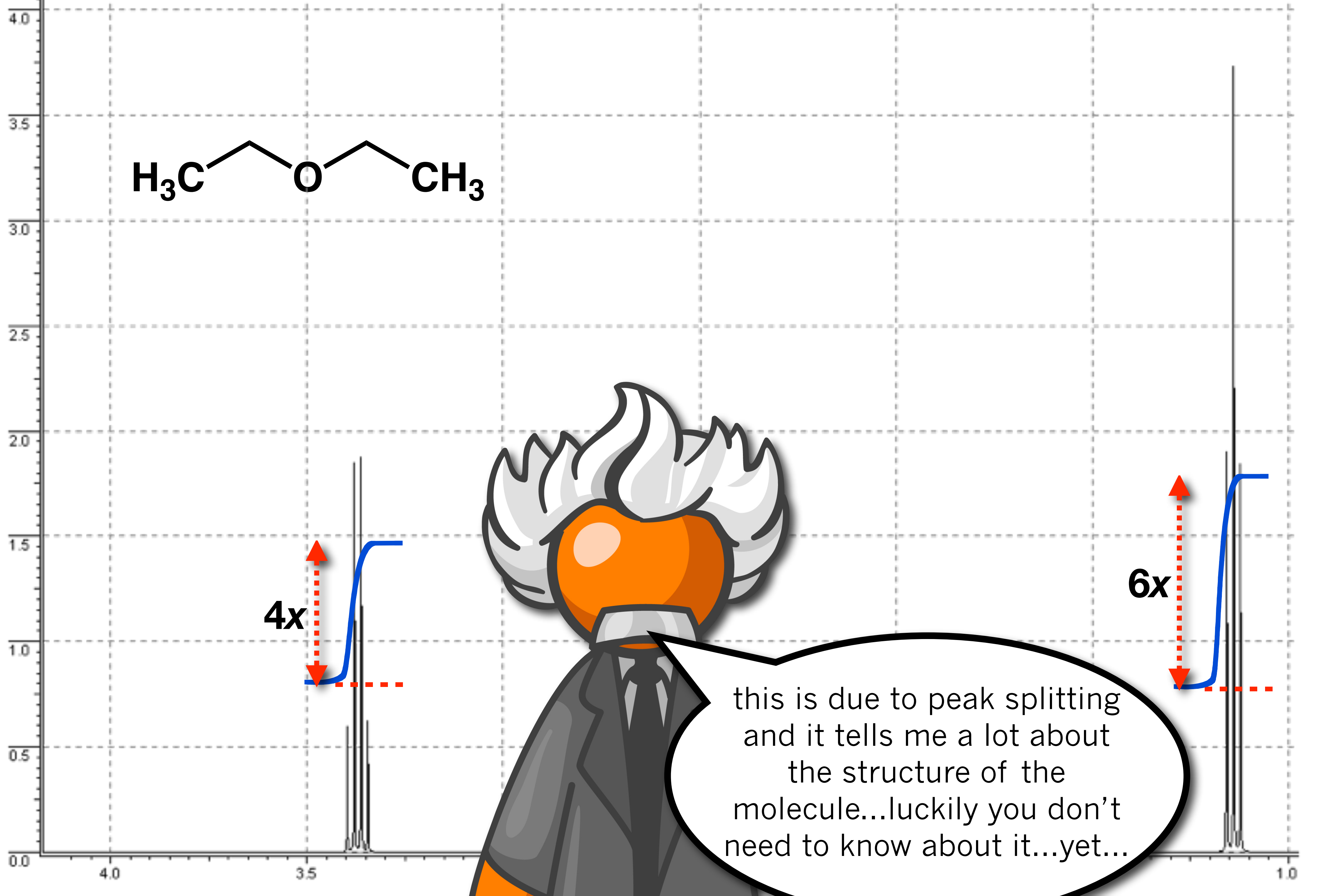
this is chemistry...

...it gets more complicated...

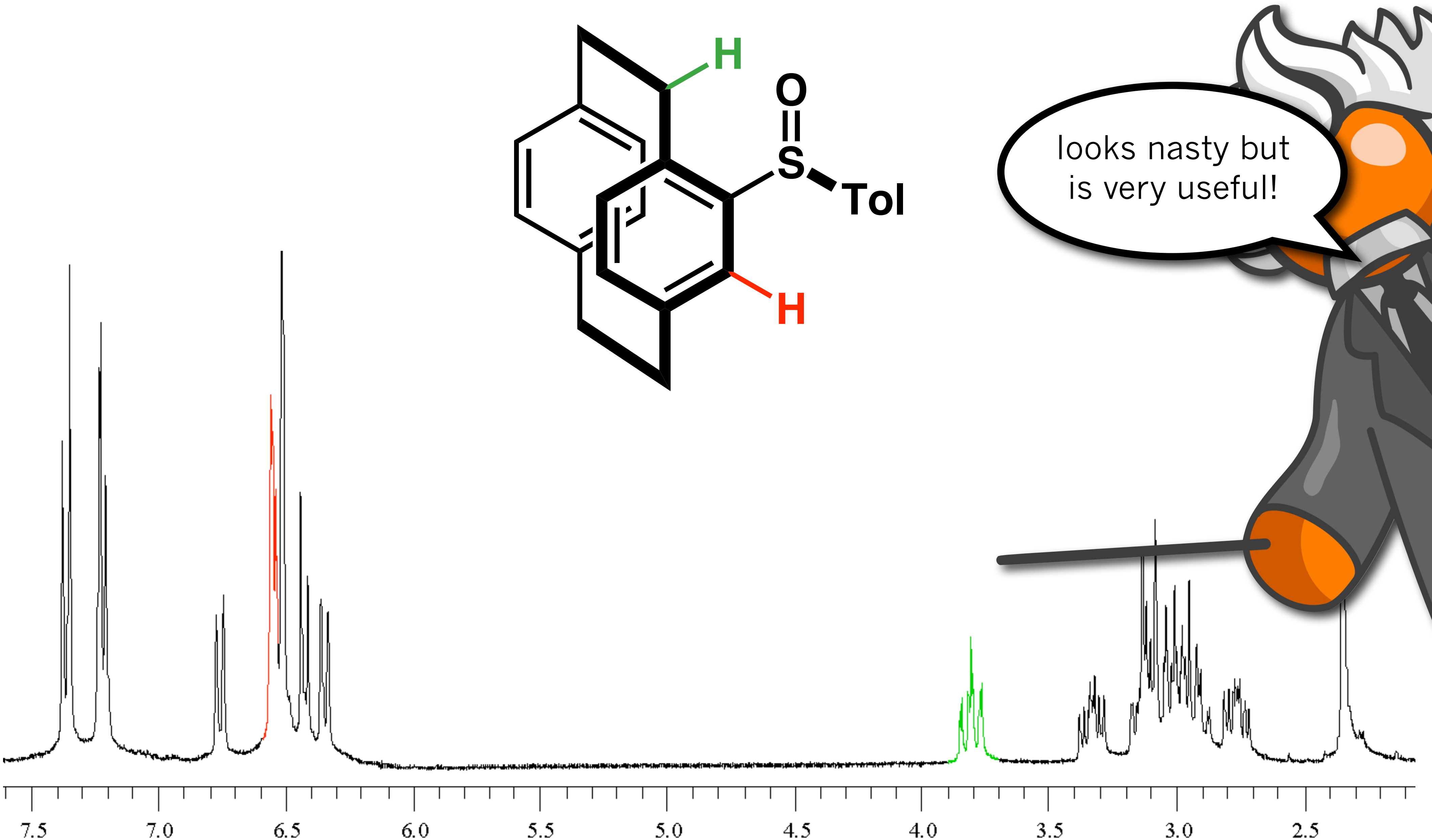
signal splitting



signal splitting



a real ^{1}H NMR spectrum



what have we **learnt**?

all about **NMR**