The effective field: Phase correction and pseudo-selective pulses

What is this seminar about ?

Phase correction in the indirect dimension

"d0 = (in0 – p2 – 1.28*p3)/2"

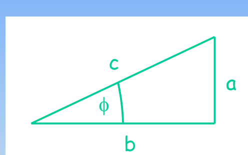
Semi-selective pulses in triple resonance experiments

"p3 = 49 µsec" (90° puls)
"p4 = 44 µsec" (180° puls)

What math do you need ?

Pythagoras

$a^2 + b^2 = c^2$



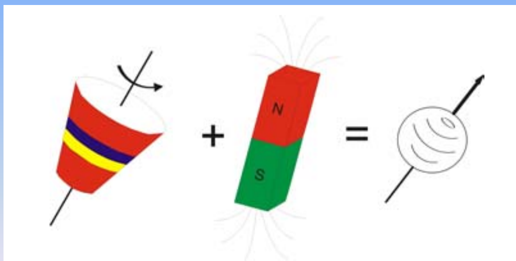
Trigonometrie

$\sin \phi = a/c$

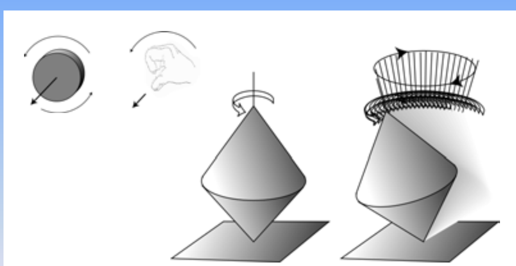
$\cos \phi = b/c$

$\tan \phi = a/b$

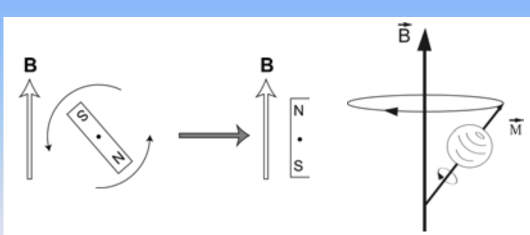
Basis for NMR spectroscopy is the nuclear spin
that can be viewed as a combination
of magnet and spinning top



A spinning top has an angular momentum
the axis of the angular momentum constant in space

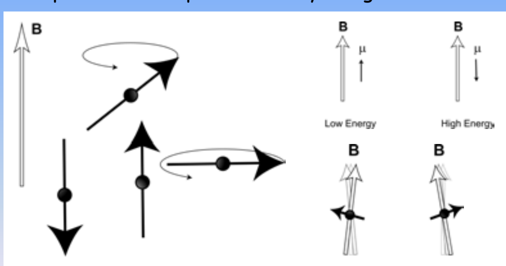


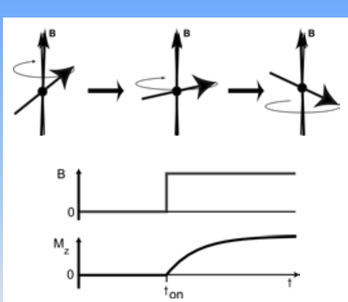
A magnet orients in the direction of the magnetic field,
this is prevented by the fact that its a spinning top
A precession begins



Without an external magnetic field
spins are oriented randomly in all possible directions

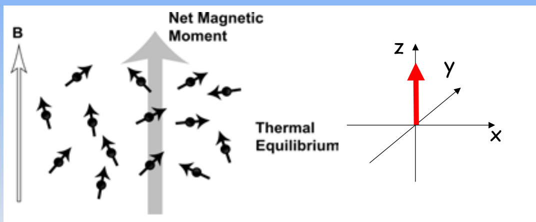
When a magnetic field is switched on, this does not change immediately, but thermal motion drives spins to orient predominantly along the field



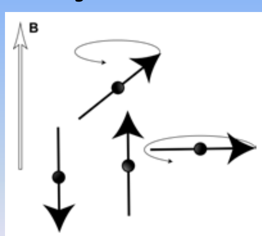


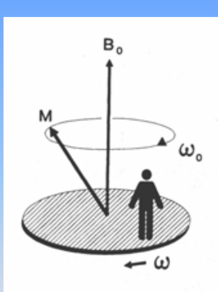
That builds up
a net magnetization...

...along the main field,
resulting in a Bolzman distribution

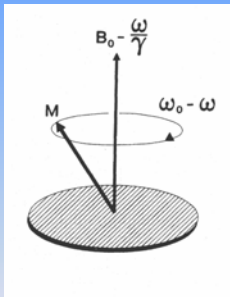


So all spins in the sample carry out their precession at almost the same speed, with small differences due to the chemical shift. To simplify the picture we introduce the "rotating fram of reference"





The concept of a rotating frame of reference should be obvious for us since we live on a spinning object ourself
The observer is moving with the angular velocity ω while the spin is moving with ω_0



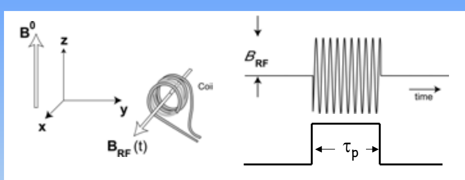
The rotation of a spin is caused by the magnetic field

$\omega_0 = 2\pi\,\nu_0 = \gamma\,B_0$

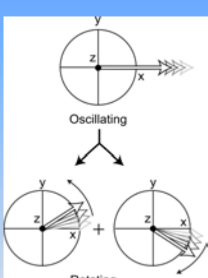
If there is no movement, then there can not be a magnetic field

$\omega_0 - \omega = \Omega = \gamma\,(B_0 - \omega/\gamma)$

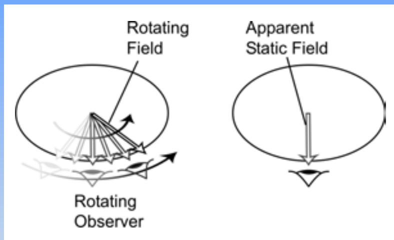
On resonance there is no magnetic field !



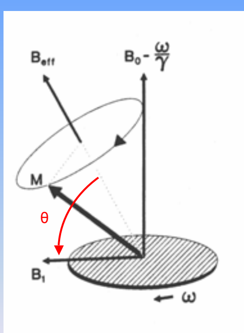
Now we do a pulse, i.e. we irradiate with radio waves and their magnetic component is of relevance here
This is called the RF-field
If the irradiation was not on resonance, it would have to be as strong as the main field to be of significance



We can divide the oszillation of the RF field in two components rotating clockwise and counterclockwise
One component is thus rotating in the opposite direction compared to the spins and can be ignored, the other component, however, is on resonance….



... and does thus appear to be static in the rotating frame of reference



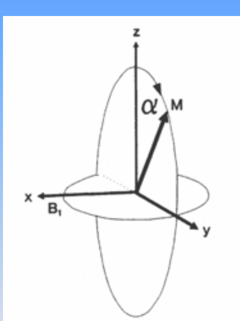
In our rotating frame the remainder of the main field and the RF-field are thus of similar magnitude, resulting in a tilted effective field B_{eff}

$$B_{eff} = \sqrt{(B_1)^2 + (B_0 - \omega/\gamma)^2}$$

$$\gamma B_{eff} = \sqrt{(\gamma B_1)^2 + \Omega^2}$$

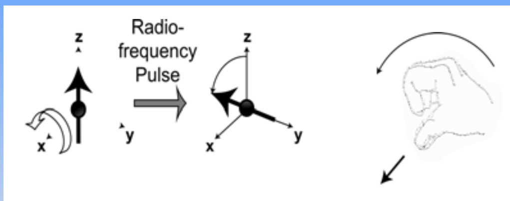
$$\tan\theta = \frac{(B_0 - \omega/\gamma)}{B_1} = \frac{\Omega}{\gamma B_1}$$

$$B_{eff} > B_1$$

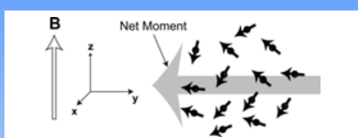


The effective field is the relevant field now and if we are on resonance then the field is identical with the RF-field.
The spins now precess around the effective field.
The angle α is determined by the length of the pulse (τ_p) and the strength of the field (γB_1)

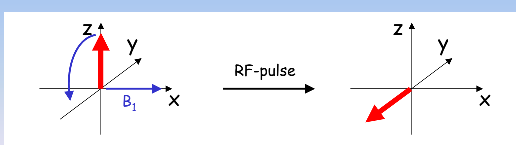
$$\alpha = \tau_p * \gamma B_1$$

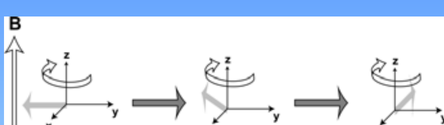


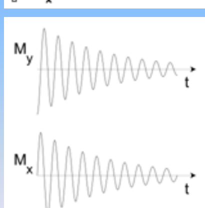
This is true for every spin...



.... and thus also for the net magnetization







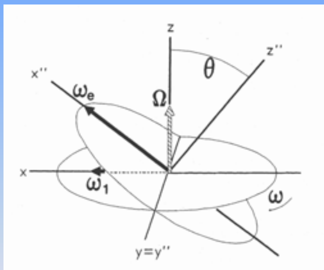
The net magnetization performs a precession

$M_y = \cos \omega t \exp(-t/T_2)$

$M_x = \sin \omega t \exp(-t/T_2)$

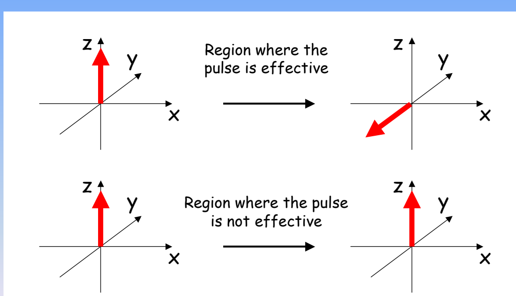
$M = M_y + i M_x$

$M = \exp(i\omega t) \exp(-t/T_2)$

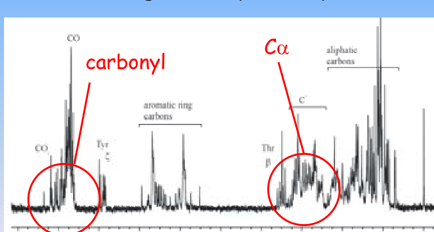


If we are not on-resonance the effective field is tilted in space and the rotation becomes slightly more difficult to describe

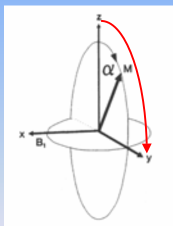
What is a selective pulse ?



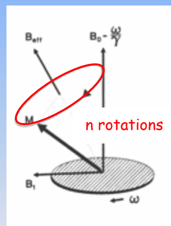
In triple resonance experiments the Cα and carbonyl carbons are treated as separate nuclei and we thus need selective pulses to cover the two regions independently



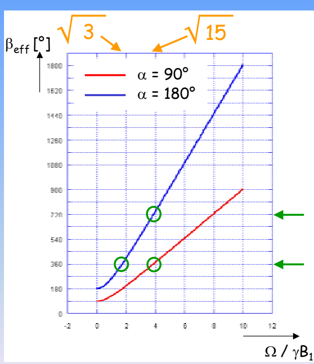
We now want to do a pulse that is a α = 90° pulse for one region (e.g. carbonyl) and a β_{eff} = n * 360° pulse for the other region (e.g. Cα) to achive our selective excitation



on-resonance



off-resonance



β_{eff} = 2π * τ_p * γB_{eff}

$\gamma B_{eff} = \sqrt{(\gamma B_1)^2 + \Omega^2}$

90°

τ_p = 1/(4 * γB_1)

$\beta_{eff} = \pi/2 * \sqrt{1 + (\Omega/\gamma B_1)^2}$

180°

τ_p = 1/(4 * γB_1)

$\beta_{eff} = \pi * \sqrt{1 + (\Omega/\gamma B_1)^2}$

on-resonance

90°

$\pi/2 = 2\pi\,(\tau_p\,\gamma\,B_1) \longrightarrow 1/(4\,\gamma\,B_1) = \tau_p$

180°

$\pi = 2\pi\,(\tau_p\,\gamma\,B_1) \longrightarrow 1/(2\,\gamma\,B_1) = \tau_p$

off-resonance

$2n\pi = 2\pi\,(\tau_p\,\gamma\,B_{eff}) \longrightarrow n/(\gamma\,B_{eff}) = \tau_p$

$$n/(\gamma B_{eff}) = 1/(4\,\gamma B_1)$$

$$\gamma B_{eff} = 4n\,\gamma B_1$$

$$\sqrt{(\gamma B_1)^2 + \Omega^2} = 4n\,\gamma B_1$$

$$(\gamma B_1)^2 + \Omega^2 = (4n)^2 (\gamma B_1)^2$$

$$\Omega = \sqrt{((4n)^2-1)}\,(\gamma B_1)$$

$$(\gamma B_1) = \Omega / \sqrt{((4n)^2-1)}$$

180° pulse $(\gamma B_1) = \Omega / \sqrt{((2n)^2-1)}$

The offset Ω between the Cα and the carbonyl regions is 120 ppm, on a 600 MHz spectrometer this is 18000 Hz

Lets assume the pulse on resonance should be a 90° pulse the pulse off-resonance should be a 360° pulse, thus n = 1

$$(\gamma B_1) = \Omega / \sqrt{15}$$

$$(\gamma B_1) = 18000 / \sqrt{15} = 4.65 \text{ kHz}$$

$$\tau_p = 1/(4\,\gamma B_1) = 54\ \mu\text{sec}$$

Lets assume the pulse on resonance should be a 180° pulse, the pulse off-resonance should be a

360° pulse, thus n = 1

$$(\gamma B_1) = \Omega / \sqrt{3}$$

$$(\gamma B_1) = 18000 / \sqrt{3} = 10.4 \text{ kHz}$$

$$\tau_p = 1/(2\,\gamma B_1) = 49\ \mu\text{sec}$$

720° pulse, thus n = 2

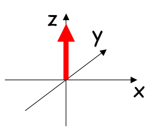
$$(\gamma B_1) = \Omega / \sqrt{15}$$

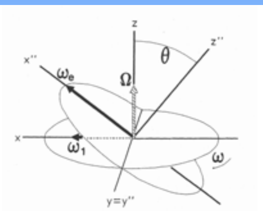
$$(\gamma B_1) = 18000 / \sqrt{15} = 4.65 \text{ kHz}$$

$$\tau_p = 1/(2\,\gamma B_1) = 108\ \mu\text{sec}$$

		400 MHz		600 MHz		750 MHz		900 MHz	
$\Delta(C^{\alpha},CO)$ 120 ppm		12000 Hz		18000 Hz		22500 Hz		27000 Hz	
$\Delta(C^{\alpha,\beta},CO)$ 130 ppm		13000 Hz		19500 Hz		24375 Hz		29250 Hz	
		γB_1	τ_p	γB_1	τ_p	γB_1	τ_p	γB_1	τ_p
90°, 120 ppm	n=1	3.1	81	4.7	54	5.8	43	7.0	36
90°, 130 ppm	n=1	3.3	75	5.0	49	6.3	40	7.6	33
180°, 120 ppm	n=1	6.9	72	10.4	48	13.0	38	15.6	32
	n=2	3.1	161	4.7	108	5.8	86	7.0	72
180°, 130 ppm	n=1	7.5	67	11.3	44	14.0	35	16.9	30
	n=2	3.3	149	5.0	99	6.3	79	7.6	66

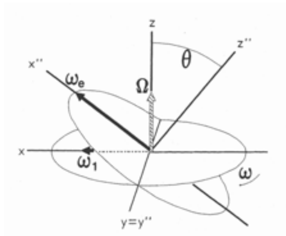
What happens if we are not not on-resonance and apply an RF-field along the x-axis ?





To calculate that we will have to switch coordinate systems back and forth

The RF-field that is now relevant is B_{eff}

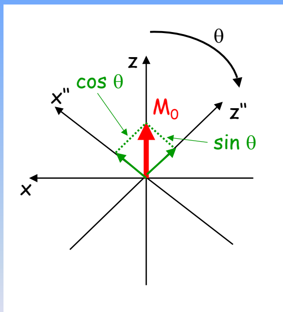


$$\gamma B_{eff} = \sqrt{(\omega_1)^2 + \Omega^2}$$

$$\gamma B_{eff} = \omega_{eff}$$

the pulse angle is

$$\beta_{eff} = \tau_p\, \omega_{eff}$$



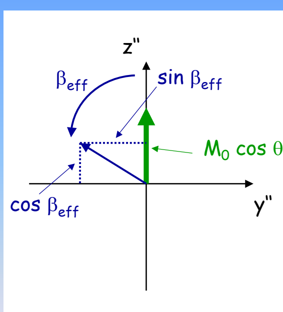
In the beginning we have

$$\begin{matrix} x \\ y \\ z \end{matrix} \quad \begin{pmatrix} 0 \\ 0 \\ M_0 \end{pmatrix} \quad \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix}$$

and we get

$$\begin{matrix} x'' \\ y'' \\ z'' \end{matrix} \quad \begin{pmatrix} M_0 \sin\theta \\ 0 \\ M_0 \cos\theta \end{pmatrix}$$

in the new coordinate system



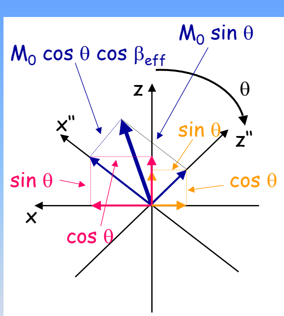
Now we start from

$$\begin{pmatrix} M_0 \sin\theta \\ 0 \\ M_0 \cos\theta \end{pmatrix}$$

and obtain

$$\begin{pmatrix} M_0 \sin\theta \\ M_0 \cos\theta\,(-\sin\beta_{eff}) \\ M_0 \cos\theta \cos\beta_{eff} \end{pmatrix}$$

after the puls



Now we go back from

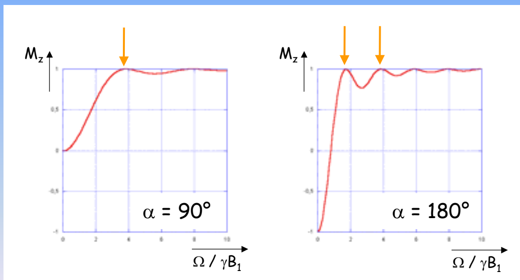
$$\begin{pmatrix} M_0 \sin\theta \\ -\,M_0 \cos\theta \sin\beta_{eff} \\ M_0 \cos\theta \cos\beta_{eff} \end{pmatrix}$$

y to y" does not change

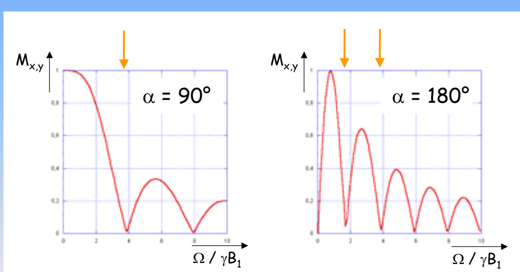
$$\begin{pmatrix} M_0 \sin\theta \cos\theta\,(1-\cos\beta_{eff}) \\ -\,M_0 \cos\theta \sin\beta_{eff} \\ M_0\,[(\cos\theta)^2 \cos\beta_{eff} + (\sin\theta)^2] \end{pmatrix}$$

is our result

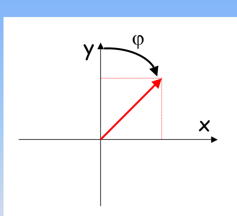
$$M_z \sim [(\cos\theta)^2 \cos\beta_{eff} + (\sin\theta)^2]$$



$$M_{x,y} \sim \sqrt{(\sin\theta\cos\theta\,(1-\cos\beta_{eff}))^2 + (\cos\theta\sin\beta_{eff})^2}$$



From this general result we want to derive a special case regarding the phaseshift caused by a short 90° pulse of finite length



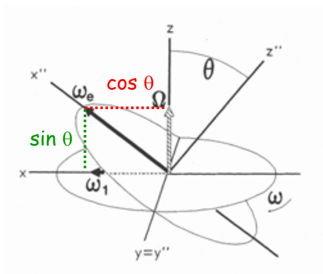
$$\tan\varphi = \frac{M_x}{M_y}$$

from above we get

$$\tan\varphi = \frac{\sin\theta\cos\theta\,(1-\cos\beta_{eff})}{\cos\theta\sin\beta_{eff}}$$

this phase shift corresponds to

$$\varphi = \Delta * \Omega$$



$$\sin\theta = \frac{\Omega}{\omega_{eff}}$$

$$\cos\theta = \frac{\omega_1}{\omega_{eff}}$$

From

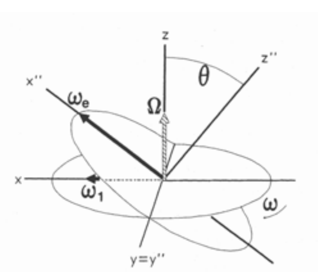
$$\tan\varphi = \frac{\sin\theta\cos\theta\,(1-\cos\beta_{eff})}{\cos\theta\sin\beta_{eff}}$$

we obtain

$$\tan\varphi = \frac{(\Omega/\omega_{eff})\cos\theta\,(1-\cos\beta_{eff})}{(\omega_1/\omega_{eff})\sin\beta_{eff}}$$

$$\tan\varphi = \frac{\cos\theta\,(1-\cos\beta_{eff})}{\sin\beta_{eff}} \quad \frac{\Omega}{\omega_1}$$

Now we start with the simplifications assuming that we have a strong 90° pulse



$\theta \sim 0$

$\beta_{eff} \sim 90°$

$\omega_{eff} \sim \omega_1$

$\tan\varphi \sim \varphi$

$\pi/2 = \omega_1 * \tau_p$

$\omega_1 = \pi/(2 * \tau_p)$

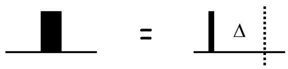
From

$$\tan \varphi = \frac{\cos \theta\,(1 - \cos \beta_{eff})}{\sin \beta_{eff}} \quad \frac{\Omega}{\omega_1}$$

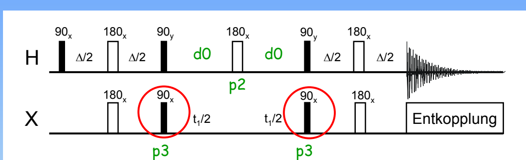
we obtain

$$\varphi = \frac{\Omega}{\omega_1} = \Delta * \Omega$$

$$\Delta = 1/\omega_1 = (2/\pi) * \tau_p = 0.64 * \tau_p$$



In an HSQC this appears twice



and thats where the formula comes from

"d0 = (in0 – p2 – 1.28*p3)/2"

$2 * (2/\pi)$!

That's it