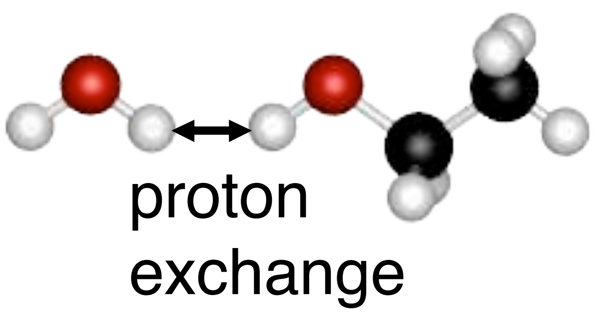
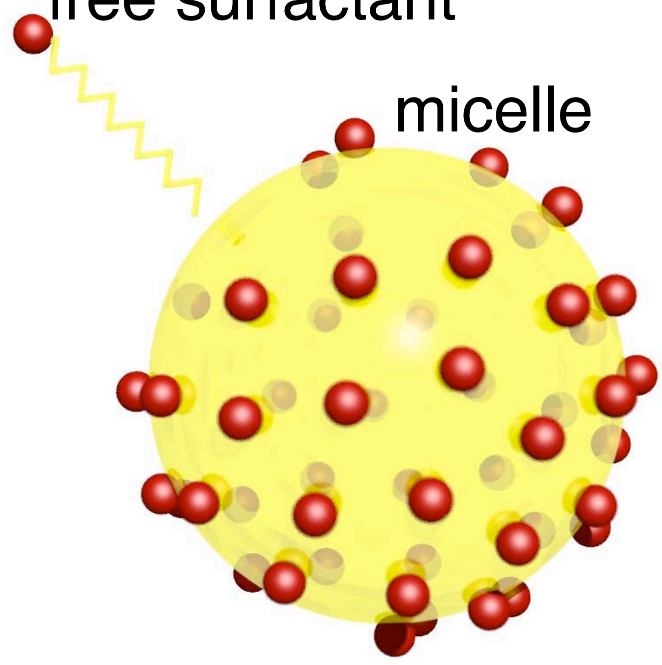
# Exchange

- Time-scales defined by NMR
- NMR spectrum from slow to fast exchange



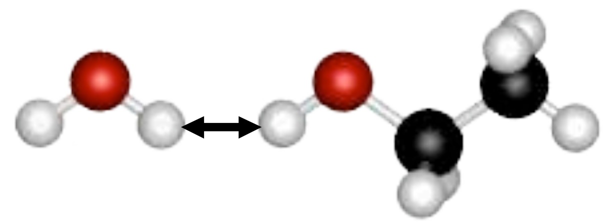



# Relevant time-scales for exchange

- $T_1$-relaxation: s
- $T_2$-relaxation: ms-s
- PGSE: ms-s (under our control!)
- NMR spectrum: ms

# Dynamic equilibrium

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B$$



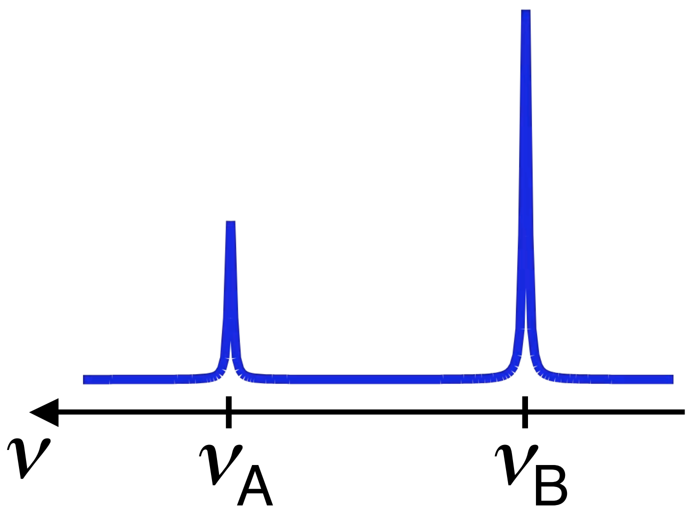
Fractional populations: $p_A$ and $p_B$

Resonance frequencies: $\nu_A$ and $\nu_B$

Exchange rate: $k = p_A k_A = p_B k_B$

# Slow exchange

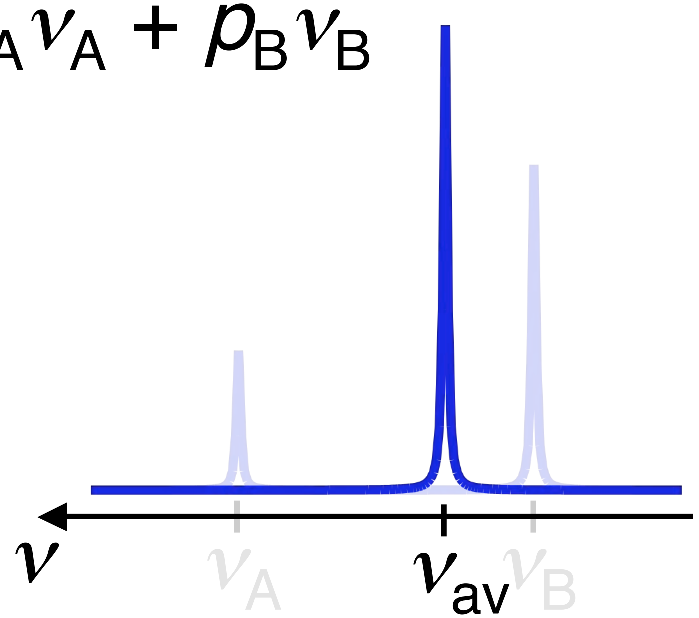
- $k << |\nu_A - \nu_B|$
- Superposition of sub-spectra



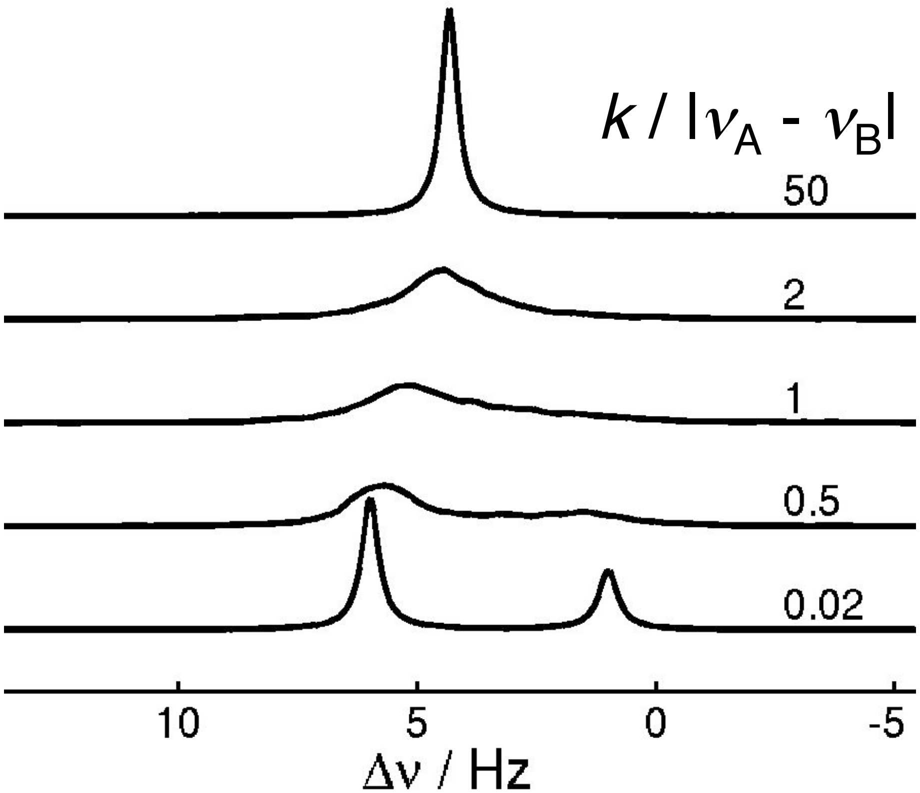
# Fast exchange

- $k >> |\nu_A - \nu_B|$
- One peak at weighted average frequency:

$$\nu_{av} = p_A \nu_A + p_B \nu_B$$



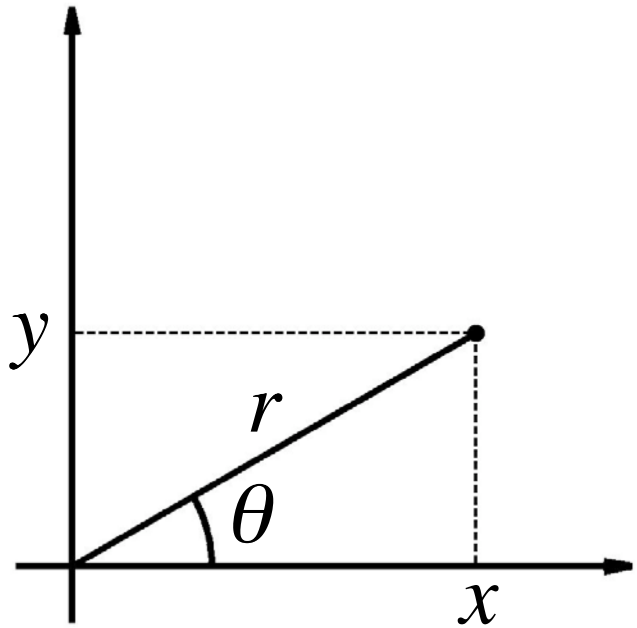
# From slow to fast exchange




$\Delta\nu_A$ = 6 Hz
$\Delta\nu_B$ = 1 Hz
$p_A/p_B$ = 2
$\Delta\nu_{av}$?

How to explain transition from slow to fast?
Why is $|\nu_A - \nu_B|$ important?

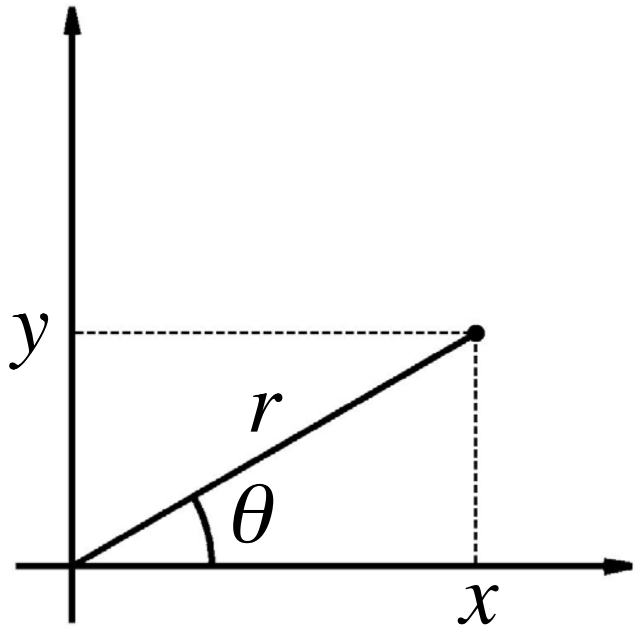
# Complex numbers




$$z = x + iy = re^{i\theta}$$

real part, $x$
imaginary part, $y$
magnitude, $r$
phase, $\theta$

# Useful relations



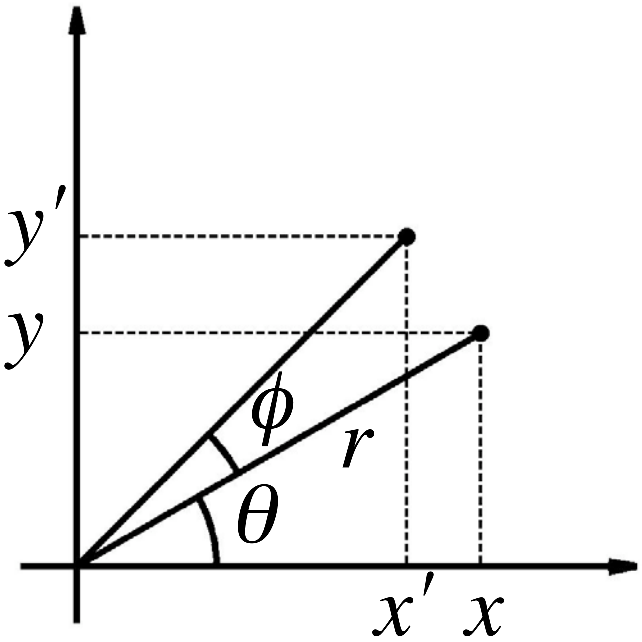

$$x = r\cos\theta$$

$$y = r\sin\theta$$

$$r = \sqrt{x^2 + y^2}$$

$$\theta = \tan^{-1}\left(y/x\right)$$

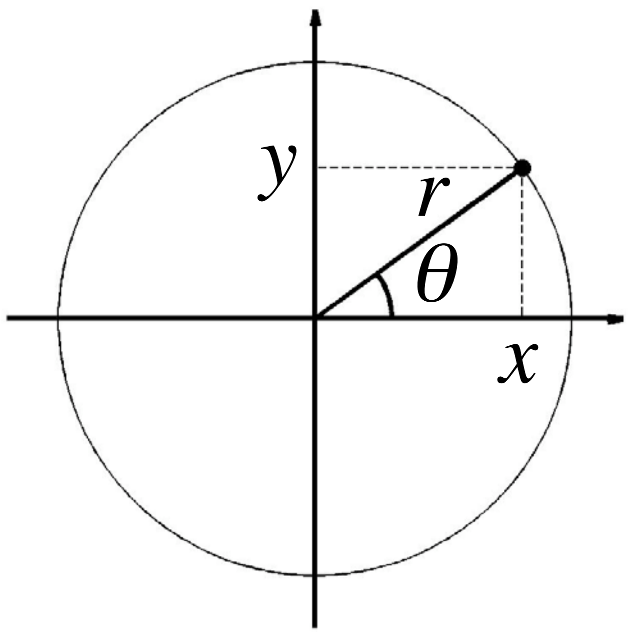
# Rotation in 2D




$$z = x + iy = re^{i\theta}$$

$$z' = x' + iy' = re^{i(\theta+\phi)} = ze^{i\phi}$$

# Circular motion




$$\theta = \omega t$$

angular frequency, $\omega$

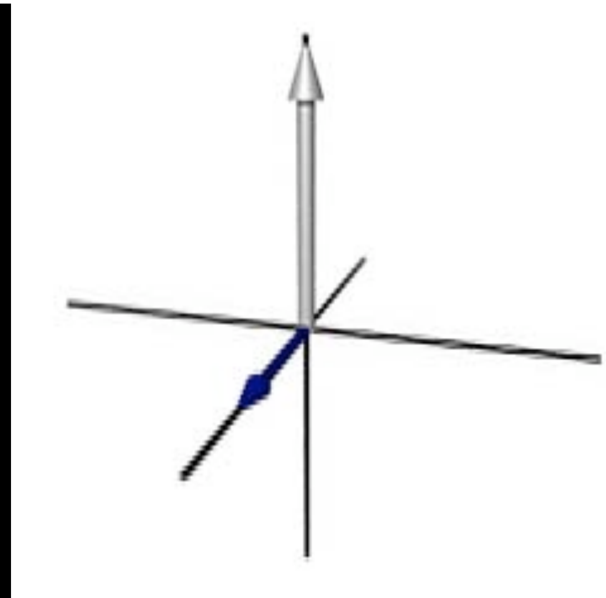
time, $t$

$$z = re^{i\omega t}$$

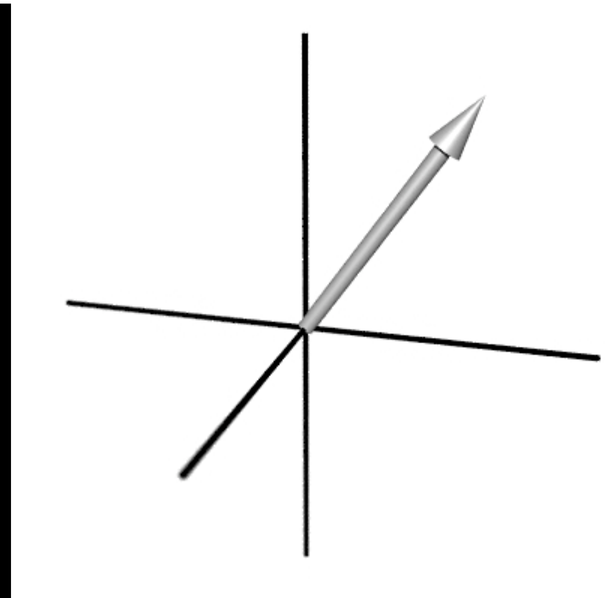
$$x = r\cos(\omega t)$$

$$y = r\sin(\omega t)$$

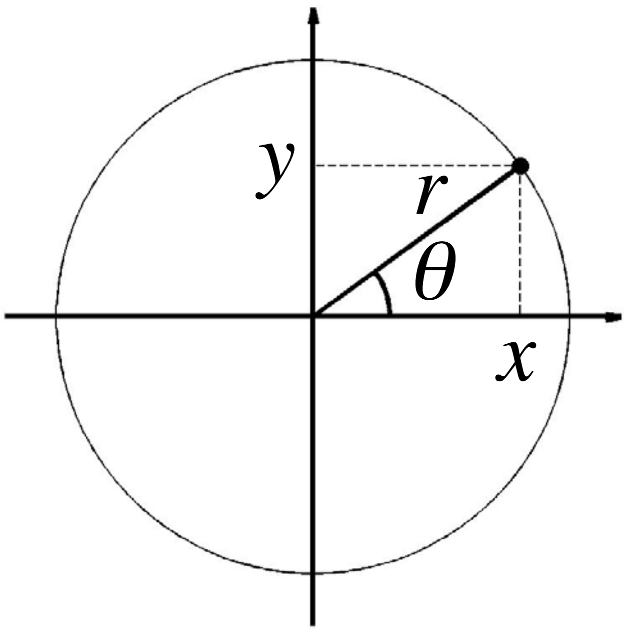
Sketch $m_x(t)$, $m_y(t)$, and $m_z(t)$ for the magnetization vector below.



Sketch $m_z(t)$, $m_x(t)$, $m_y(t)$, and $\theta(t)$ for the magnetization vector below.



# Time-dependent frequency

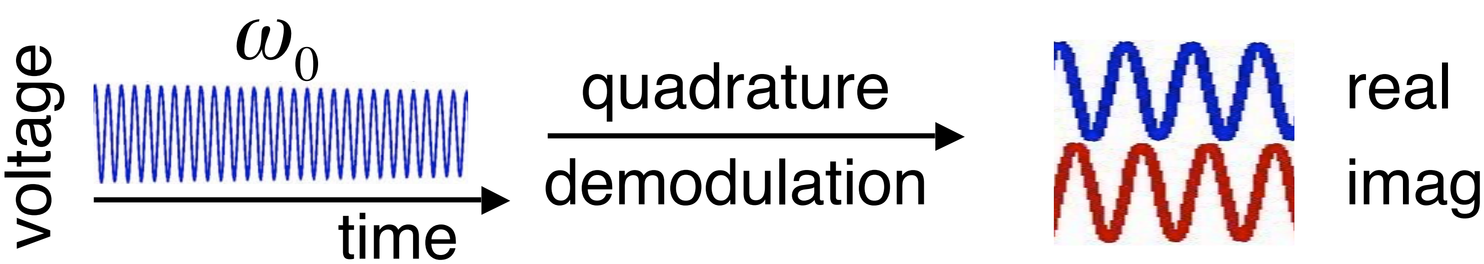



$$\theta(t) = \int_0^t \omega(t')dt'$$

$\omega$ fluctuates with time

(chemical exchange, decoupling, magic-angle spinning, diffusion, imaging ...)

# Detection in the rotating frame



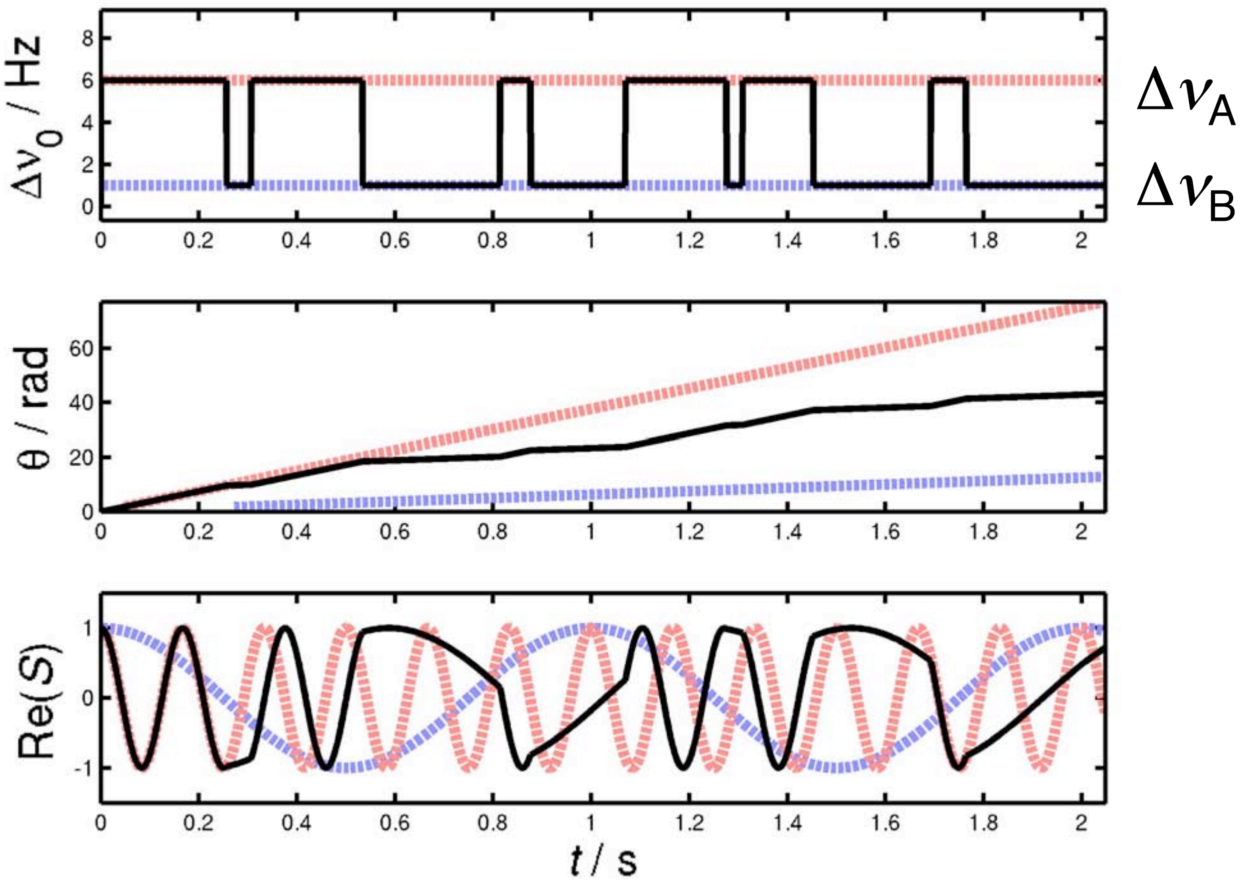

$$\Delta\omega_0 = \omega_0 - \omega_{\mathrm{RF}}$$

offset frequency, $\Delta\omega_0$

- Real and imaginary parts of the signal $S$ correspond to $M_x$ and $M_y$ in the rotating frame

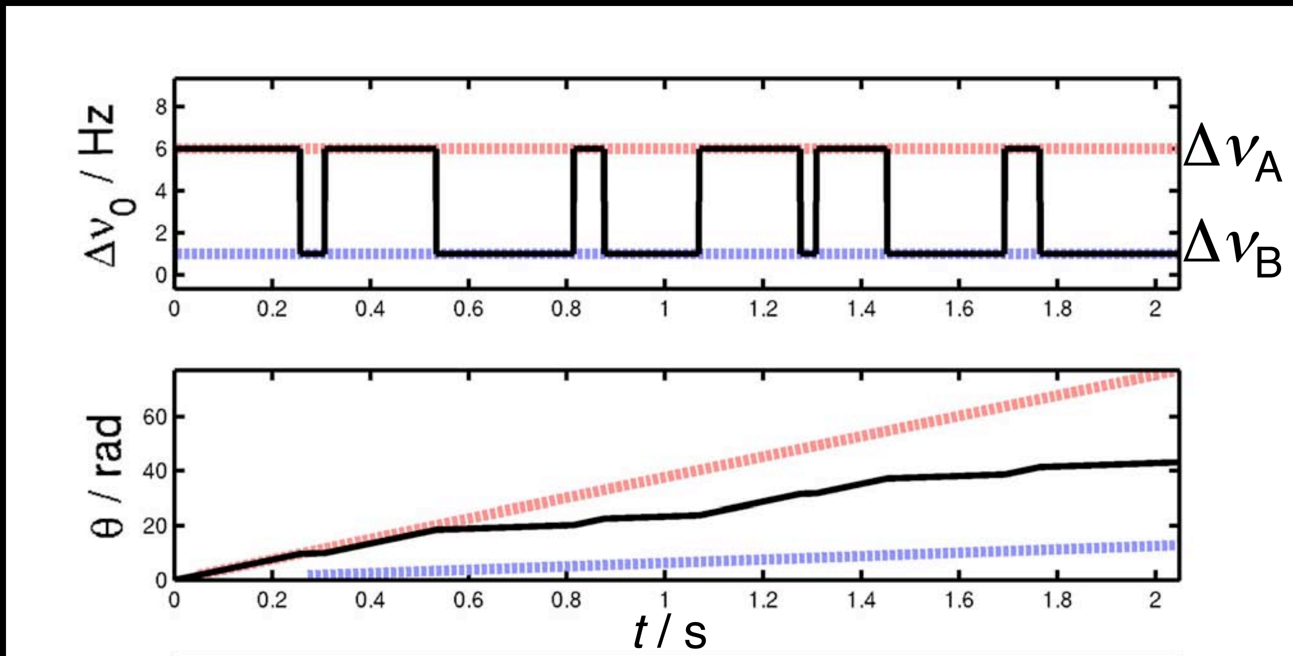
$$S(t) \propto M_x(t) + iM_y(t) = M_{xy}\exp(i\theta)$$

# One spin packet

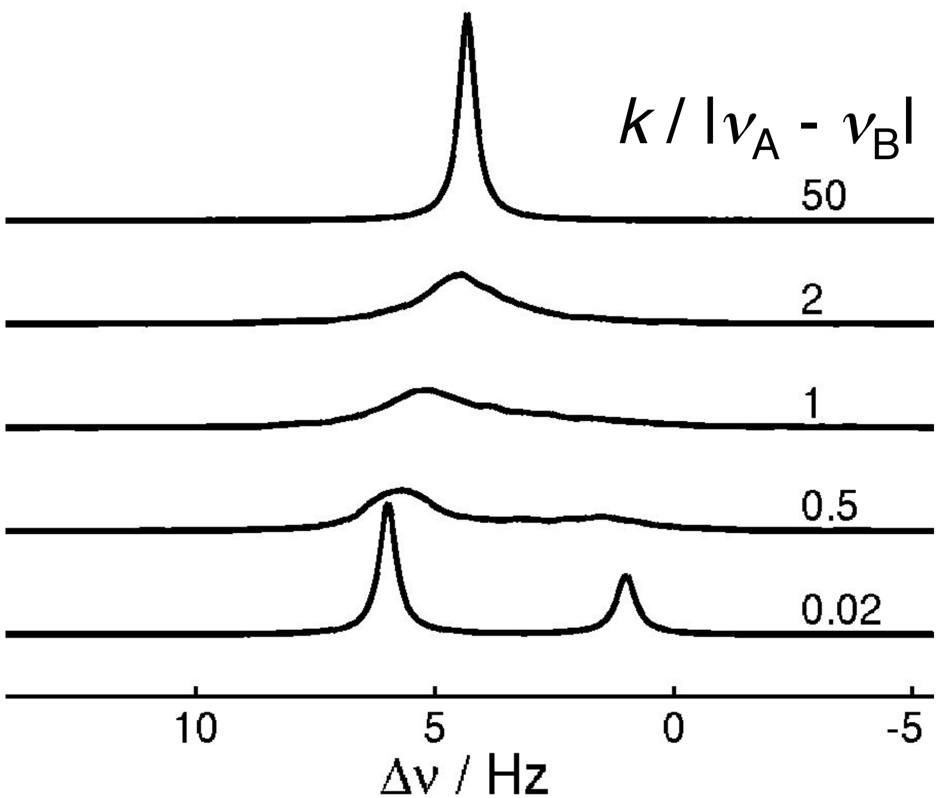



random jumps between site A and site B

What would the figure below look like in the case of a) fast and b) slow exchange? Make sketches in the figure. $p_A/p_B = 2$



# Intermediate exchange




$\Delta\nu_A$ = 6 Hz
$\Delta\nu_B$ = 1 Hz
$p_A/p_B$ = 2

simulation with
1000 spin packets