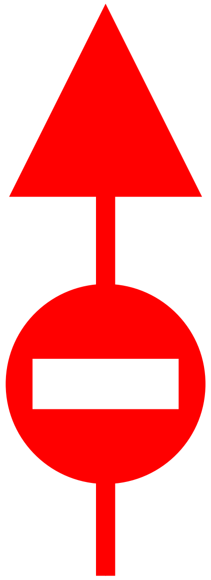
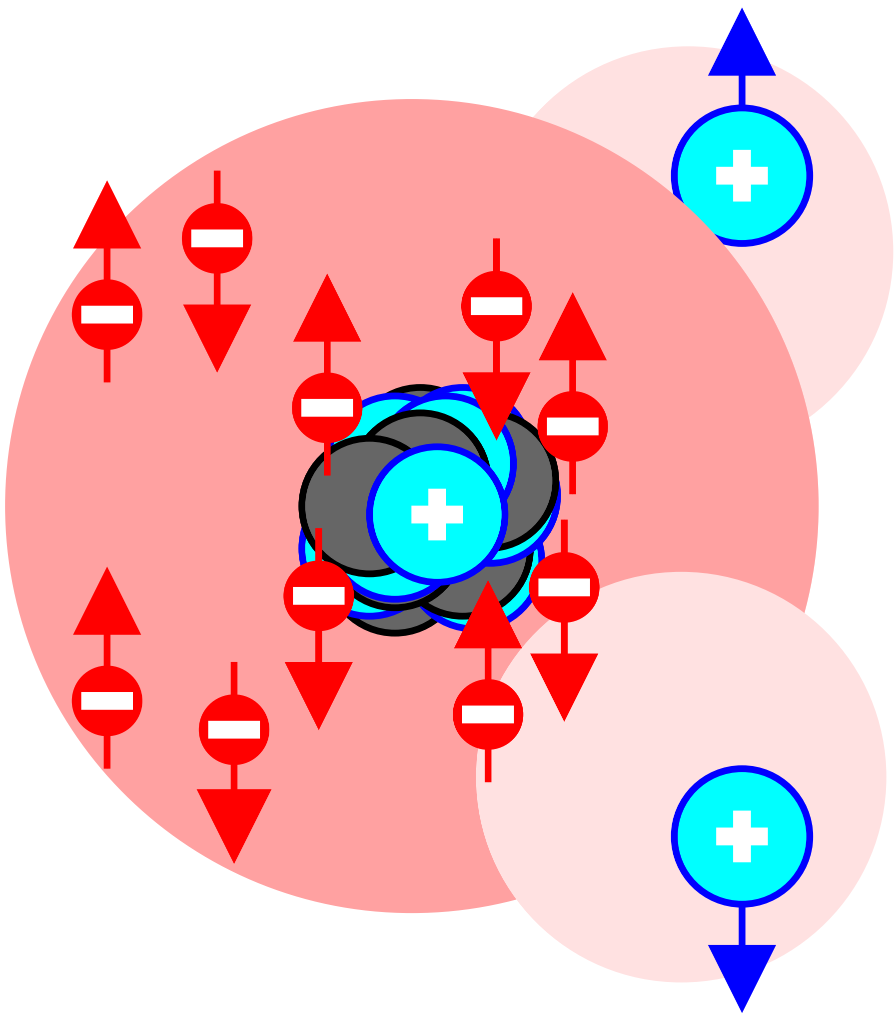
Lecture 6: Ensemble of non-interacting spins

1 particle:



$$\Psi(x, y, z, c_\alpha)$$

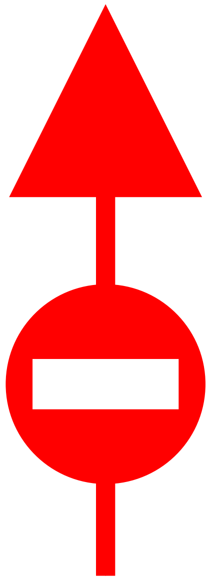
28 particles:



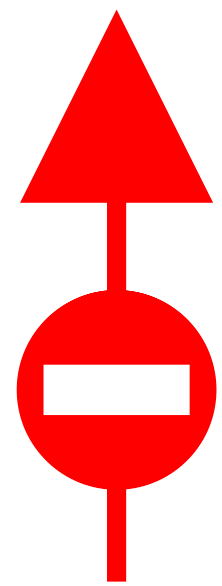
$$\Psi(x(\mathsf{O}), x(\mathsf{H1}), x(\mathsf{H2}), x(\mathsf{e1}), x(\mathsf{e2}), \ldots$$

1 000 000 000 000 000 000 000 000 000 particles:

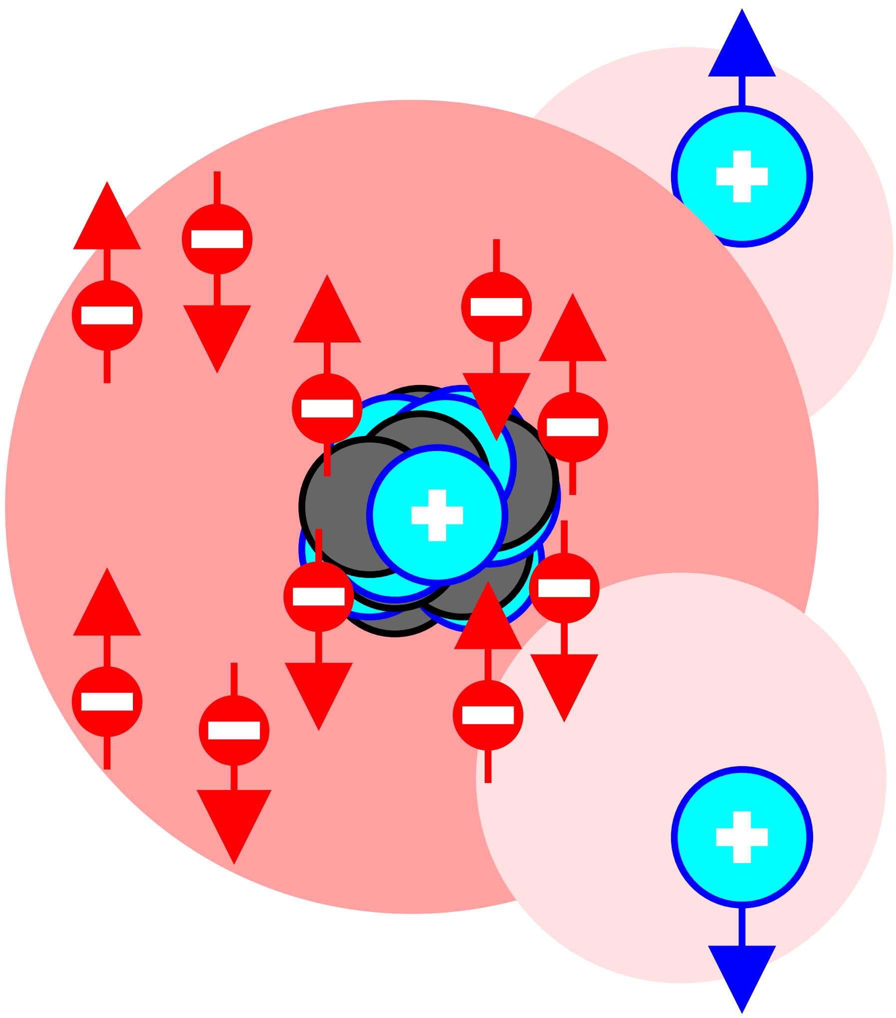
Ψ ???



$$\Psi(x, y, z, c_\alpha)$$



$$\Psi = \sqrt{\frac{1}{h^3}} \cdot \mathrm{e}^{\frac{\mathrm{i}}{\hbar} p_x x} \cdot \mathrm{e}^{\frac{\mathrm{i}}{\hbar} p_y y} \cdot \mathrm{e}^{\frac{\mathrm{i}}{\hbar} p_z z} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$



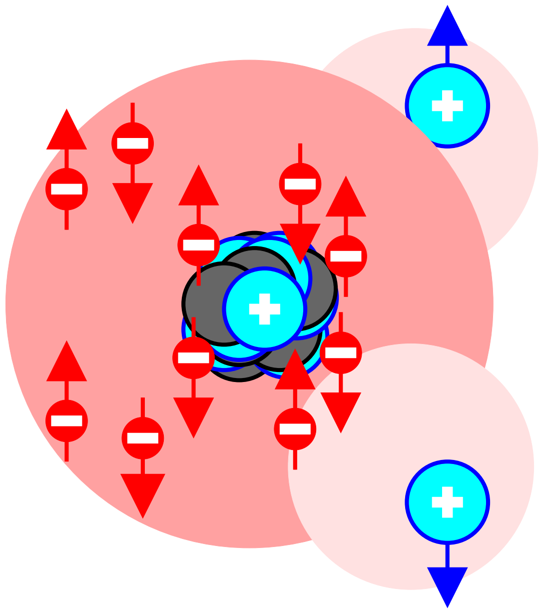
$$\Psi =$$

$$\phi(x(\mathsf{O}), x(\mathsf{H1}), x(\mathsf{e1}), \ldots) \cdot \psi(c_{\alpha,1}, c_{\alpha,2}) \ ?$$

- electron motions: $> 10^{16}\,\mathrm{s}^{-1}$

- molecular rotations: $10^{8}\,\mathrm{s}^{-1}$ (20 kDa protein) to $10^{12}\,\mathrm{s}^{-1}$ (water)

- magnetic moment precession: $\sim 10^{9}\,\mathrm{s}^{-1}$



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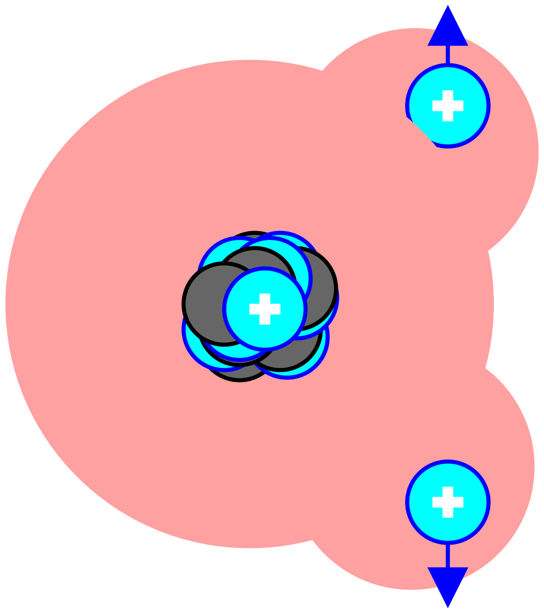
electrons as "blurred cloud of a given shape":



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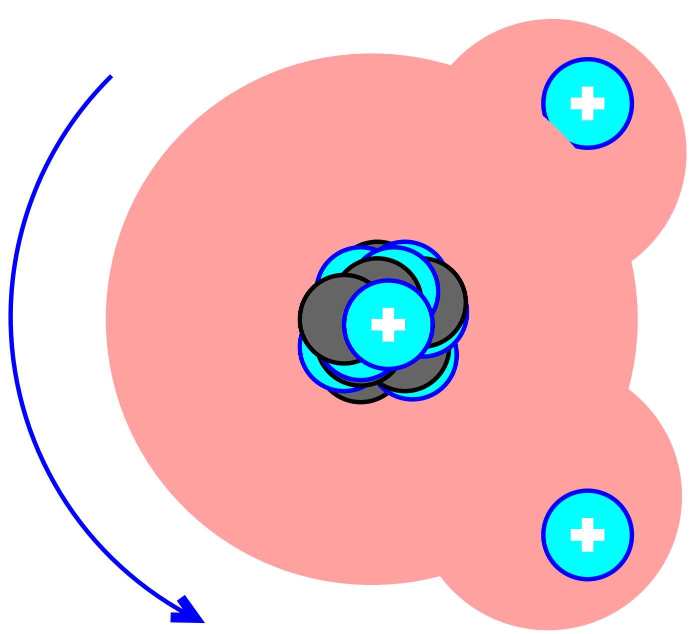
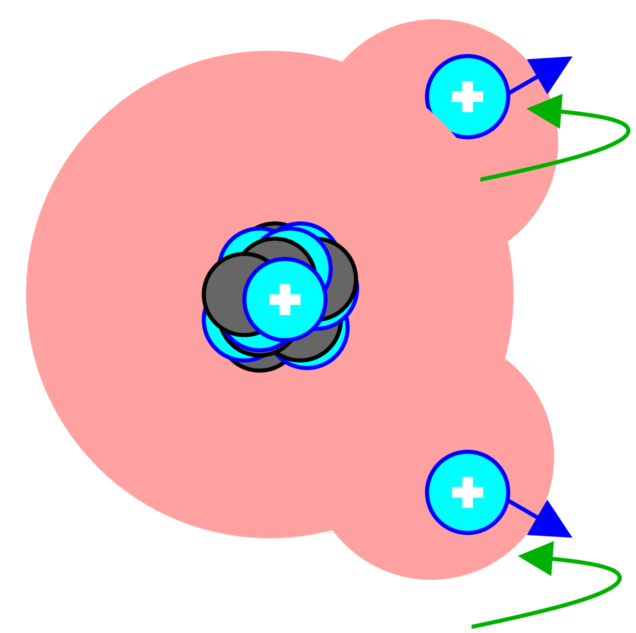
molecular motions $\leftarrow$ almost independent $\rightarrow$ magnetic moment precession



$\leftarrow$ almost independent $\rightarrow$



$$\Psi = \phi(x_1, x_2, x_3, \ldots) \cdot \psi(c_1, c_2, c_3, \ldots)$$

$$\psi(c_1, c_2, c_3, \ldots) = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \\ \vdots \\ \vdots \\ \vdots \\ c_{99999999999999999999999998} \\ c_{99999999999999999999999999} \\ c_{100000000000000000000000000} \end{pmatrix}$$

$$\psi(c_1, c_2, c_3, \ldots) = \psi_1(c_1) \cdot \psi_2(c_2) \cdot \psi_3(c_3) \ldots \ ?$$

Is it possible to separate ψ of individual magnetic moments?

Yes, if interactions of magnetic moments

- depend only on external fields

  $\Rightarrow$ interactions change energy eigenvalues, not eigenfunctions

- the external fields are homogeneous (same in the whole sample)

  not true in MRI.

Then, $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ form basis for all ψ's

$\Rightarrow$ operators are represented by 2×2 matrices.

Pure state:

Expected value $\langle A \rangle$ of a quantity A for *single nucleus*:

$$\langle A \rangle = \mathrm{Tr}\left\{ \begin{pmatrix} c_\alpha c_\alpha^* & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \right\}$$

Mixed state:

Expected value $\langle A \rangle$ for *multiple nuclei with the same basis*:

$$\begin{aligned}
\langle A \rangle &= \mathrm{Tr}\left\{\begin{pmatrix} c_{\alpha,1}c^*_{\alpha,1} & c_{\alpha,1}c^*_{\beta,1} \\ c_{\beta,1}c^*_{\alpha,1} & c_{\beta,1}c^*_{\beta,1} \end{pmatrix}\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} + \begin{pmatrix} c_{\alpha,2}c^*_{\alpha,2} & c_{\alpha,2}c^*_{\beta,2} \\ c_{\beta,2}c^*_{\alpha,2} & c_{\beta,2}c^*_{\beta,2} \end{pmatrix}\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} + \cdots \right. \\
&= \mathrm{Tr}\left\{\left(\begin{pmatrix} c_{\alpha,1}c^*_{\alpha,1} & c_{\alpha,1}c^*_{\beta,1} \\ c_{\beta,1}c^*_{\alpha,1} & c_{\beta,1}c^*_{\beta,1} \end{pmatrix} + \begin{pmatrix} c_{\alpha,2}c^*_{\alpha,2} & c_{\alpha,2}c^*_{\beta,2} \\ c_{\beta,2}c^*_{\alpha,2} & c_{\beta,2}c^*_{\beta,2} \end{pmatrix} + \cdots \right)\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\right\} \\
&= \mathcal{N}\,\mathrm{Tr}\left\{\underbrace{\begin{pmatrix} \overline{c_\alpha c^*_\alpha} & \overline{c_\alpha c^*_\beta} \\ \overline{c_\beta c^*_\alpha} & \overline{c_\beta c^*_\beta} \end{pmatrix}}_{\hat{\rho}} \underbrace{\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}}_{\hat{A}}\right\} = \mathcal{N}\,\mathrm{Tr}\left\{\hat{\rho}\hat{A}\right\}.
\end{aligned}$$

$\hat{\rho}$ is the *(probability) density matrix*

- Two-dimensional basis for $\mathcal{N}$ uncoupled nuclei.
- Statistical approach: *macroscopic* result – *mixed state* no insight into *microscopic* states.
- Choice of the basis of ψ is encoded in definition of $\widehat{\rho}$ (eigenfunctions of $\widehat{I}_z$)
- The state is described not by a vector, but by a matrix $\widehat{\rho}$ is a matrix like matrices representing the operators.

Populations

- *Diagonal elements* of $\hat{\rho}$ or matrices with diagonal elements only.
- describe *longitudinal polarization* of $\vec{\mu}$ (distribution along $\vec{B}_0$)
- real numbers, $\overline{c_\alpha c_\alpha^*} + \overline{c_\beta c_\beta^*} = 1$
- $\overline{c_\alpha c_\alpha^*} = 1/2$: no net polarization along $\vec{B}_0$

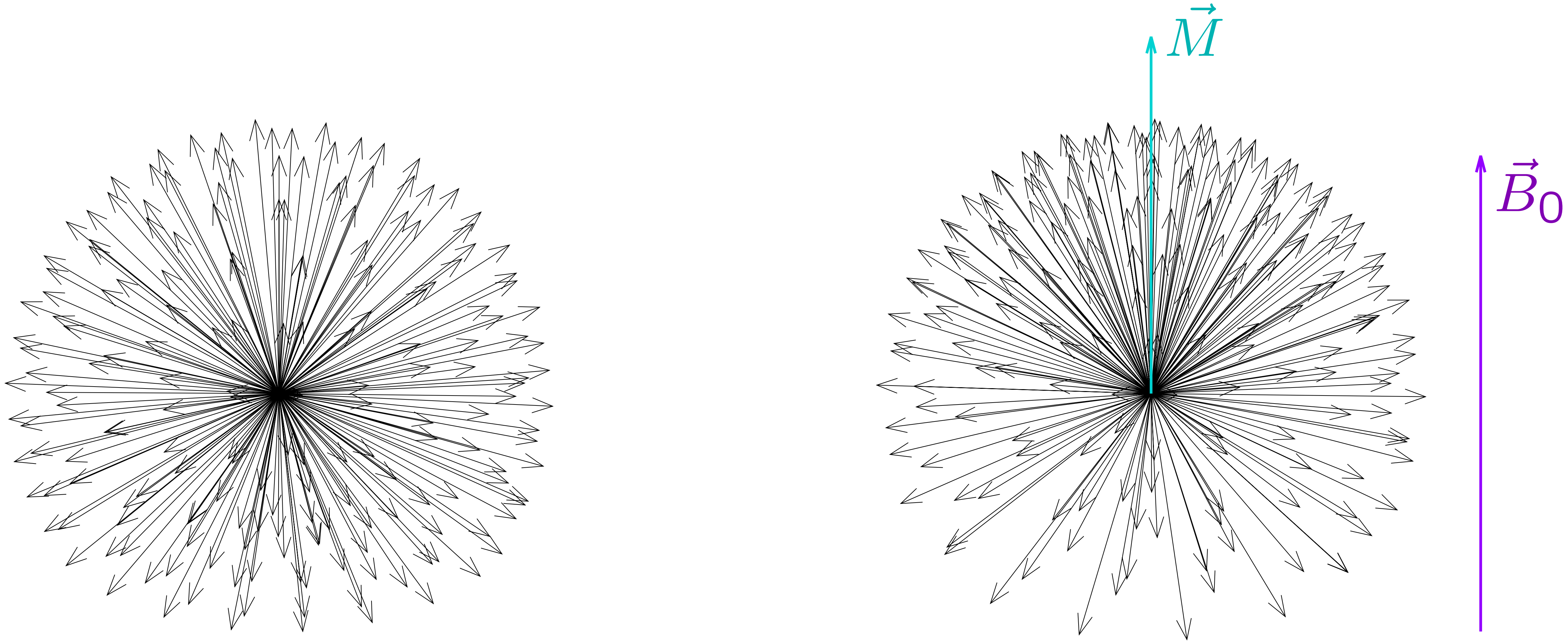
  equal populations of the α and β states

  It does not indicate that all spins must be either in α or β state!

  Any combination of superposition states,

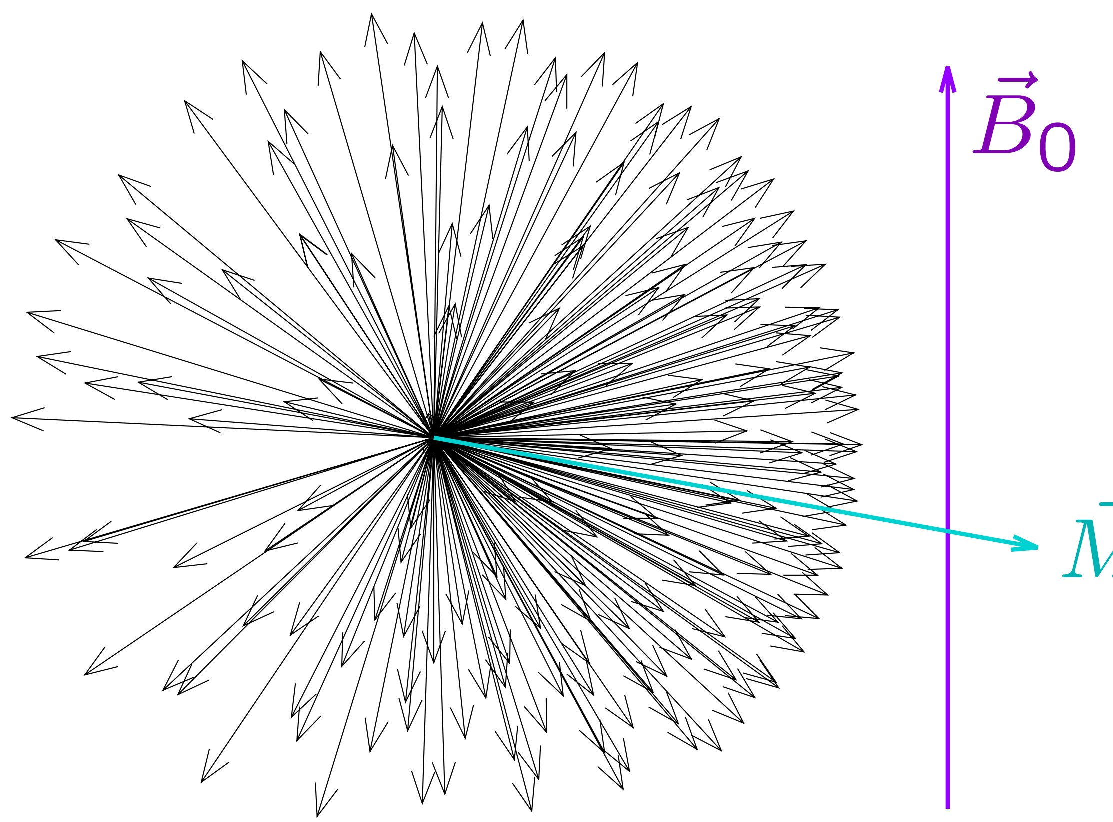
  $\vec{\mu}$ pointing in all possible directions as long as $M_z = 0$

  Probability of 50 % spins in α state, 50 % spins in β state negligible


$\vec{M}$
$\vec{B}_0$

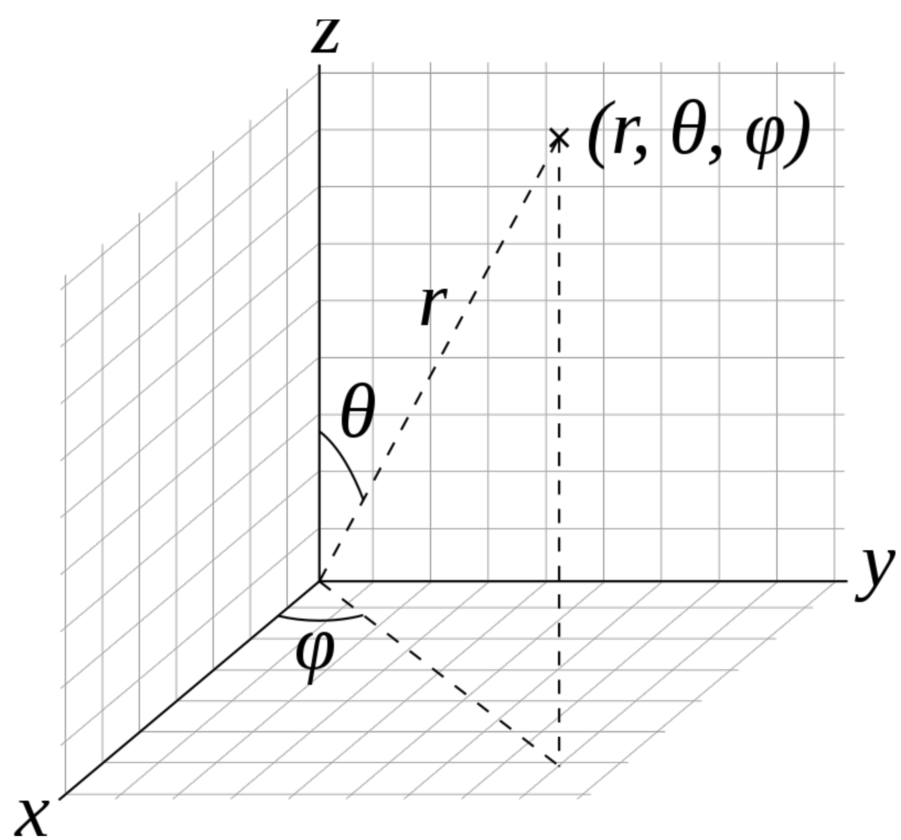
Coherences

- *Off-diagonal elements* or matrices with diagonal elements only
- *Pure state*: $c_\beta c_\alpha^* = |c_\alpha||c_\beta|\mathrm{e}^{-\mathrm{i}(\phi_\alpha - \phi_\beta)}$
- *Mixed state*: $\overline{c_\beta c_\alpha^*}$ is complex number $\overline{|c_\alpha||c_\beta|} \cdot \overline{\mathrm{e}^{-\mathrm{i}(\phi_\alpha - \phi_\beta)}}$ amplitude $\overline{|c_\alpha||c_\beta|}$, phase given by $\overline{\mathrm{e}^{-\mathrm{i}(\phi_\alpha - \phi_\beta)}}$
- $\overline{c_\beta c_\alpha^*} \cdot \overline{c_\alpha c_\beta^*} = 1$
- Describe *transverse polarization* of $\vec{\mu}$ in the plane $\perp \vec{B}_0$ with magnitude $\overline{|c_\alpha||c_\beta|}$ and in direction given by the phase.
- *Incoherent superposition of states* α, β: $\overline{\mathrm{e}^{-\mathrm{i}(\phi_\alpha - \phi_\beta)}} = 0 \Rightarrow \overline{c_\beta c_\alpha^*} = 0$
- *Coherent superposition of states* α, β: $\overline{c_\beta c_\alpha^*} \neq 0$
- *Coherent evolution*: $\phi_{\alpha,j}$ and $\phi_{\beta,j}$ vary, but with identical frequency ω_0 for all j: $\overline{\mathrm{e}^{-\mathrm{i}(\phi_\alpha - \phi_\beta)}} = \overline{\mathrm{e}^{-\mathrm{i}(\phi_\alpha(0) - \phi_\beta(0))}} \cdot \mathrm{e}^{\mathrm{i}\omega_0 t}$



$\vec{B}_0$
$\vec{M}$

Phases and coherences



$$|\vartheta_j, \varphi_j\rangle = \begin{pmatrix} \cos\frac{\vartheta_j}{2} \mathrm{e}^{-\mathrm{i}\frac{\varphi_j}{2}} \\ \sin\frac{\vartheta_j}{2} \mathrm{e}^{+\mathrm{i}\frac{\varphi_j}{2}} \end{pmatrix} = \begin{pmatrix} c_{\alpha,j} \\ c_{\beta,j} \end{pmatrix} = c_{\alpha,j}|\alpha\rangle + c_{\beta,j}|\beta\rangle$$

$$\overline{c_\beta c_\alpha^*} = \overline{\cos\frac{\vartheta}{2}\sin\frac{\vartheta}{2}\mathrm{e}^{+\mathrm{i}\varphi}} = \frac{1}{2}\overline{\sin\vartheta\mathrm{e}^{+\mathrm{i}\varphi}} \qquad 2\sin a\cos a = \sin(2a)$$

Phases and coherences

Independent distribution of ϑ and φ:

$$\overline{c_\beta c_\alpha^*} = \overline{\cos\frac{\vartheta}{2}\sin\frac{\vartheta}{2}\mathrm{e}^{+\mathrm{i}\varphi}} = \frac{1}{2}\overline{\sin\vartheta\mathrm{e}^{+\mathrm{i}\varphi}} = \frac{1}{2}\overline{\sin\vartheta}\cdot\overline{\mathrm{e}^{+\mathrm{i}\varphi}}$$

Evolution in $\vec{B}_0$: Hamiltonian $\hat{H} = -\gamma B_0\hat{I}_z = \omega_0\hat{I}_z$

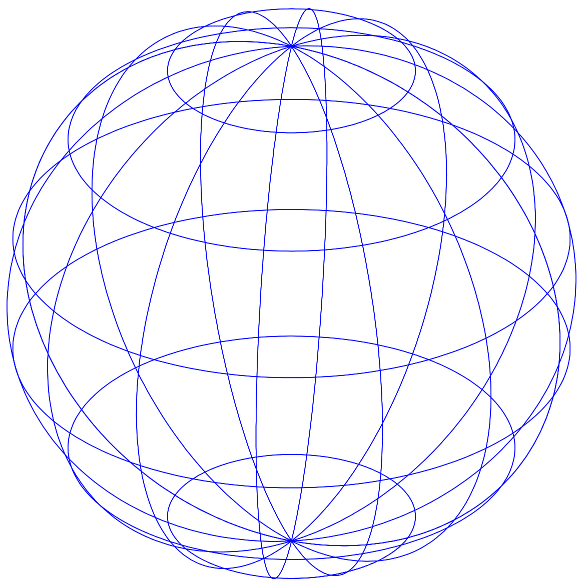
$$\begin{aligned} c_\alpha(t) &= c_\alpha(t=0)\mathrm{e}^{+\mathrm{i}\frac{\gamma B_0}{2}t} = \cos\frac{\vartheta}{2}\mathrm{e}^{-\mathrm{i}\frac{\varphi(t=0)}{2}}\mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t} \\ c_\beta(t) &= c_\beta(t=0)\mathrm{e}^{-\mathrm{i}\frac{\gamma B_0}{2}t} = \sin\frac{\vartheta}{2}\mathrm{e}^{+\mathrm{i}\frac{\varphi(t=0)}{2}}\mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t} \end{aligned}$$

$$\overline{c_\beta c_\alpha^*}(t) = \frac{1}{2}\overline{\sin\vartheta}\ \overline{\mathrm{e}^{\mathrm{i}\varphi(t=0)}}\ \mathrm{e}^{\mathrm{i}\omega_0 t}$$

Coherent *evolution* if $\omega_0 = \gamma B_0$ is the same for all j

Phases and coherences

Random distribution of $\varphi(t=0)$ $\Rightarrow$ ϑ distributed on the whole sphere

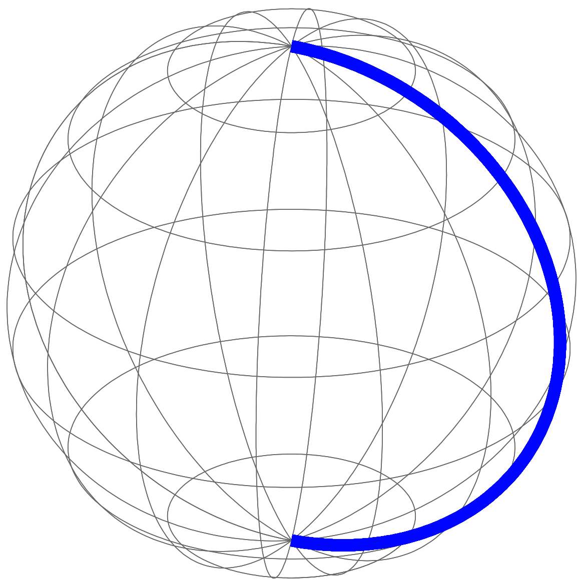


$$\overline{\mathrm{e}^{\mathrm{i}\varphi(t=0)}} = 0 \quad \Rightarrow \quad \overline{\cos\vartheta} = 0 \quad \overline{\sin\vartheta} = 0$$

Incoherent *superposition* of $|\alpha\rangle$ and $|\beta\rangle$

Phases and coherences

Random distribution of $\varphi(t=0)$ $\Rightarrow$ ϑ distributed on a meridian



$$\overline{\mathrm{e}^{\mathrm{i}\varphi(t=0)}} = 1 \quad \Rightarrow \quad \overline{\cos\vartheta} = 0 \quad \overline{\sin\vartheta} = \frac{1}{2}$$

Coherent *superposition* of $|\alpha\rangle$ and $|\beta\rangle$

Basis:

- Any 2×2 matrix can be written as a linear combination of four 2×2 matrices. Such four matrices can be used as a *basis*

Example:

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} = a \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + b \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + c \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + d \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

Basis:

- A good basis is a set of *orthonormal* matrices:

$$\mathrm{Tr}\{\hat{A}_j^\dagger \hat{A}_k\} = \delta_{jk}$$

$j, k \in \{1, 2, 3, 4\}$,

$\delta_{jk} = 1$ for $j = k$, $\delta_{jk} = 0$ for $j \neq k$,

$\hat{A}_j^\dagger$ is an *adjoint* matrix of $\hat{A}_j$

(*adjoint matrix*: matrix obtained from $\hat{A}_j$ by exchanging rows and columns and replacing all numbers with their complex conjugates.)

E.g., for $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ and $\begin{pmatrix} e & f \\ g & h \end{pmatrix}$:

calculate $\begin{pmatrix} a^* & c^* \\ b^* & d^* \end{pmatrix} \begin{pmatrix} e & f \\ g & h \end{pmatrix} = \begin{pmatrix} a^*e + c^*g & a^*f + c^*h \\ b^*e + d^*g & b^*f + d^*h \end{pmatrix}$

Trace: $a^*e + c^*g + b^*f + d^*h$

Example:

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} = a\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + b\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + c\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + d\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

The basis is orthonormal, e.g.:

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} {\color{red}0} & 1 \\ 0 & {\color{red}0} \end{pmatrix}, \text{ trace: } {\color{red}0} + {\color{red}0} = {\color{red}0}$$

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} {\color{blue}1} & 0 \\ 0 & {\color{red}0} \end{pmatrix}, \text{ trace: } {\color{blue}0} + {\color{red}0} = {\color{blue}1}$$

Basis sets: Cartesian

$$\sqrt{2}\mathscr{I}_t = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \sqrt{2}\mathscr{I}_z = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sqrt{2}\mathscr{I}_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sqrt{2}\mathscr{I}_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \tag{1}$$

$$\mathscr{I}_t = \frac{1}{2}\ \hat{1} \qquad \mathscr{I}_x = \frac{1}{\hbar}\ \hat{I}_x \qquad \mathscr{I}_y = \frac{1}{\hbar}\ \hat{I}_y \qquad \mathscr{I}_z = \frac{1}{\hbar}\ \hat{I}_z \tag{2}$$

Basis sets: Single-element

$$\mathscr{I}_\alpha = \mathscr{I}_t + \mathscr{I}_z = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \qquad \mathscr{I}_\beta = \mathscr{I}_t - \mathscr{I}_z = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\mathscr{I}_+ = \mathscr{I}_x + \mathrm{i}\mathscr{I}_y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \mathscr{I}_- = \mathscr{I}_x - \mathrm{i}\mathscr{I}_y = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{3}$$

Basis sets: Mixed

$$\sqrt{2}\mathscr{I}_t = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \sqrt{2}\mathscr{I}_z = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\mathscr{I}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \mathscr{I}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{4}$$

Liouville - von Neumann equation

evolution in time

$$\frac{\mathrm{d}\widehat{\rho}}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}(\widehat{\rho}\widehat{H} - \widehat{H}\widehat{\rho}) = \frac{\mathrm{i}}{\hbar}[\widehat{\rho}, \widehat{H}] = -\frac{\mathrm{i}}{\hbar}[\widehat{H}, \widehat{\rho}] \tag{5}$$

or in the units of (angular) frequency

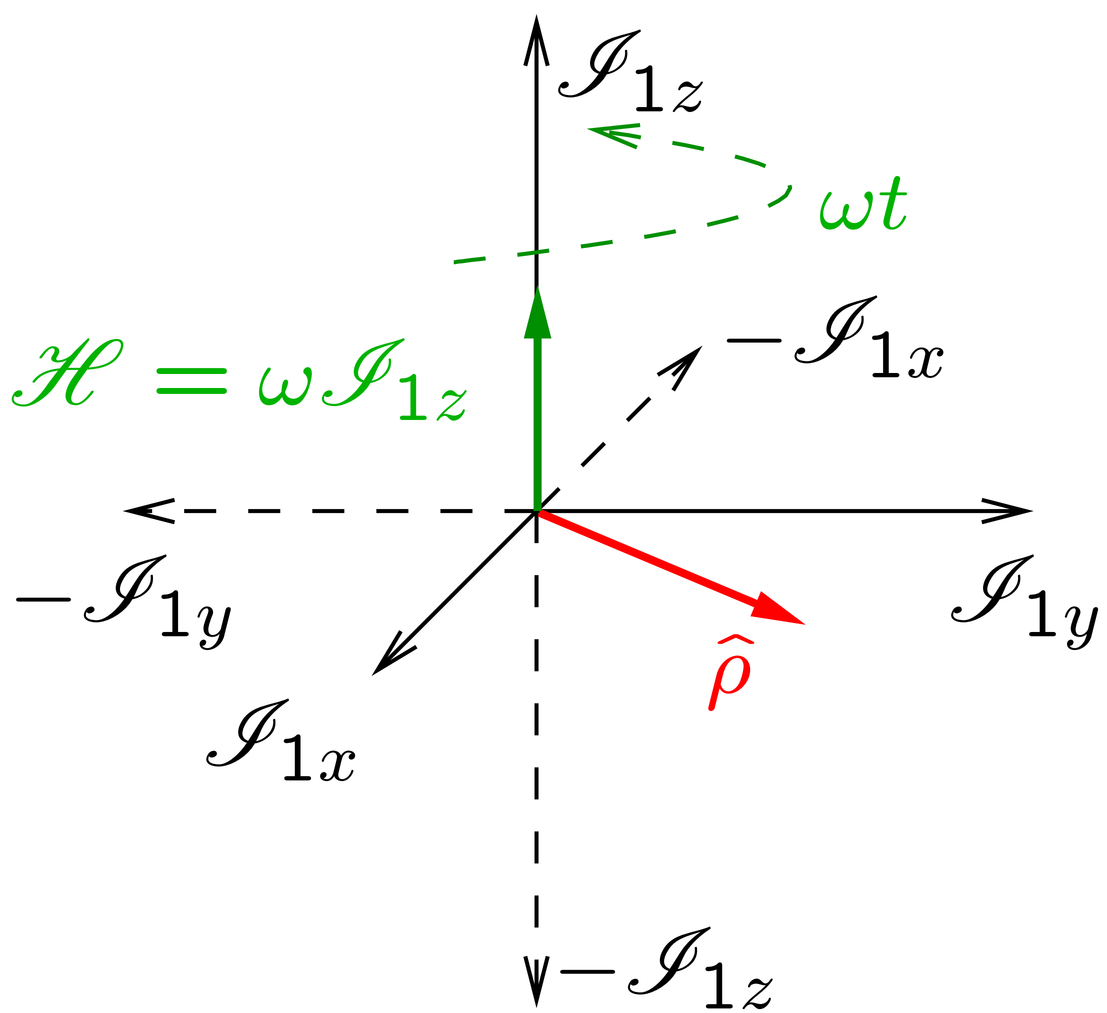
$$\frac{\mathrm{d}\widehat{\rho}}{\mathrm{d}t} = \mathrm{i}(\widehat{\rho}\mathscr{H} - \mathscr{H}\widehat{\rho}) = \mathrm{i}[\widehat{\rho}, \mathscr{H}] = -\mathrm{i}[\mathscr{H}, \widehat{\rho}]. \tag{6}$$

$$\mathscr{H} = \frac{1}{\hbar}\ \widehat{H} \tag{7}$$

If $\hat{\rho} = c\mathscr{I}_j$, $\mathscr{H} = \omega\mathscr{I}_l$, and $[\mathscr{I}_j, \mathscr{I}_k] = \mathrm{i}\mathscr{I}_l$,
then the density matrix evolves as

$$\hat{\rho} = c\mathscr{I}_j \quad \longrightarrow \quad c\mathscr{I}_j \cos(\omega t) + c\mathscr{I}_l \sin(\omega t)$$

rotation about $\mathscr{I}_k$ in abstract 3D space defined by the basis $\mathscr{I}_j, \mathscr{I}_k, \mathscr{I}_l$.



General strategy

1. Define $\widehat{\rho}$ at $t = 0$

2. Describe evolution of $\widehat{\rho}$ using the relevant Hamiltonians
   usually several steps

3. Calculate the expectation value of the measured quantity
   (magnetization components in the x, y plane) according to Eq. 1
   $\langle M_+ \rangle = \langle M_x + \mathrm{i} M_y \rangle = \mathcal{N} \mathrm{Tr}\left\{\widehat{\rho}\ \widehat{M}_+\right\}$

The procedure requires knowledge of

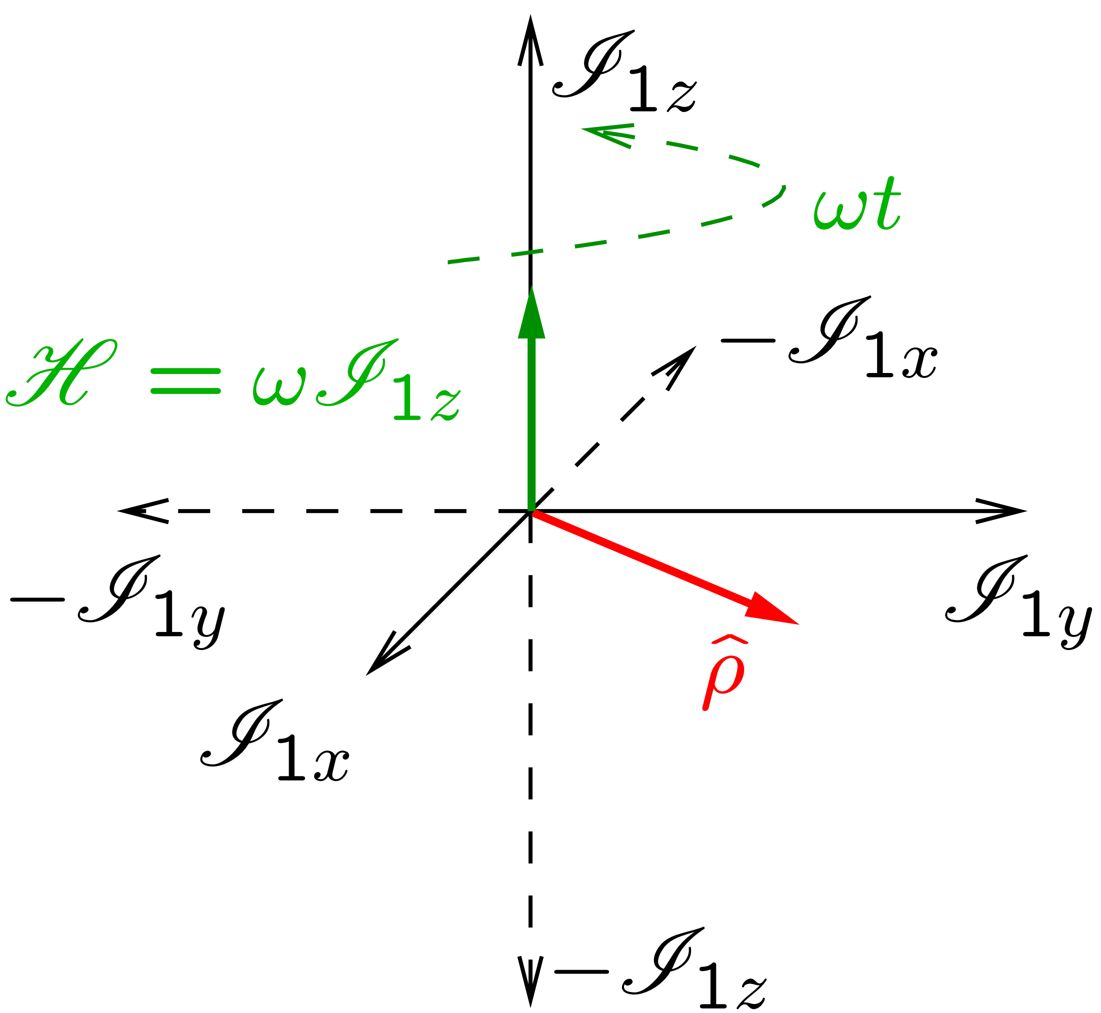
1. relation(s) describing the initial state of the system ($\widehat{\rho}(0)$)

2. all Hamiltonians ($\mathscr{H}$)

3. the operator representing the measurable quantity ($\widehat{M}_+$)

HOMEWORK:

$$\begin{aligned}
\hat{\rho}(0) &= \mathscr{I}_y \\
\mathscr{H} &= \omega \mathscr{I}_z \\
\omega &= \pi \times 10^5\,\mathrm{rad/s} \\
t &= 2.5 \times 10^{-5}\,\mathrm{s}
\end{aligned}$$



SOLUTION:

$$\begin{aligned} \widehat{\rho}(0) &= \mathscr{I}_y \\ \mathscr{H} &= \omega \mathscr{I}_z \\ \omega &= \pi \times 10^5 \, \text{rad/s} \\ t &= 2.5 \times 10^{-5} \, \text{s} \end{aligned}$$

$$\widehat{\rho}(0) = \mathscr{I}_y \rightarrow \ \mathscr{I}_y \cos(\omega t) - \mathscr{I}_x \sin(\omega t)$$

$$\omega t = 2.5\pi = 2\pi + \tfrac{\pi}{2}$$

$$\cos(\omega t) = \cos\left(2\pi + \tfrac{\pi}{2}\right) = \cos\left(\tfrac{\pi}{2}\right) = 0$$

$$\sin(\omega t) = \sin\left(2\pi + \tfrac{\pi}{2}\right) = \sin\left(\tfrac{\pi}{2}\right) = 1$$

$$\widehat{\rho}(0) = \mathscr{I}_y \rightarrow \ -\mathscr{I}_x$$