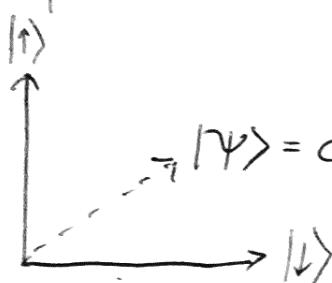


SPIN-1/2 DEGREES OF FREEDOM

Recap - QM wavefunctions (wavevectors) live in 'Hilbert space', a complex vector space.

Spin 1/2 \Rightarrow Two dimensional space

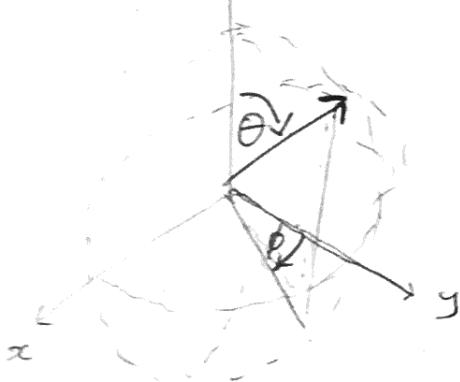
One possible (and useful) basis set is $\{| \uparrow \rangle, | \downarrow \rangle\}$ (also written as $\{|\alpha\rangle, |\beta\rangle\}$ or $\{| +\frac{1}{2}\rangle, | -\frac{1}{2}\rangle\}$)



z — N.B. CARTESIAN COORDINATES!

2 : latitude and longitude !

What about the other 2 d.o.f.?



① Normalisation: $\langle \psi | \psi \rangle = 1$
 $\Rightarrow c_1^* c_1 + c_2^* c_2 = 1$

② Phase: All possible observables are real numbers
 Wavefunctions differing by a complex phase only
 are indistinguishable

$$\text{Rewrite } |\psi\rangle = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} r_1 e^{i\theta_1} \\ r_2 e^{i\theta_2} \end{pmatrix}$$

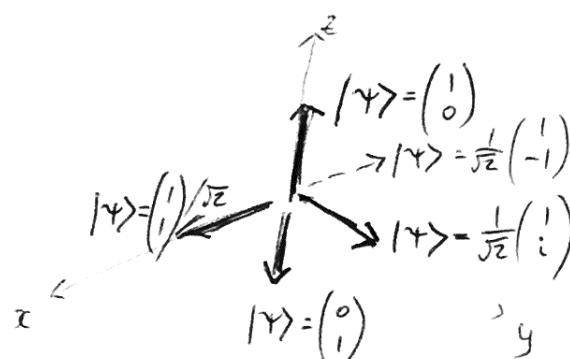
$$= e^{i\theta_1} \left(\begin{matrix} r_1 \\ \sqrt{1-r_1^2} e^{i(\theta_2-\theta_1)} \end{matrix} \right)$$

unobservable

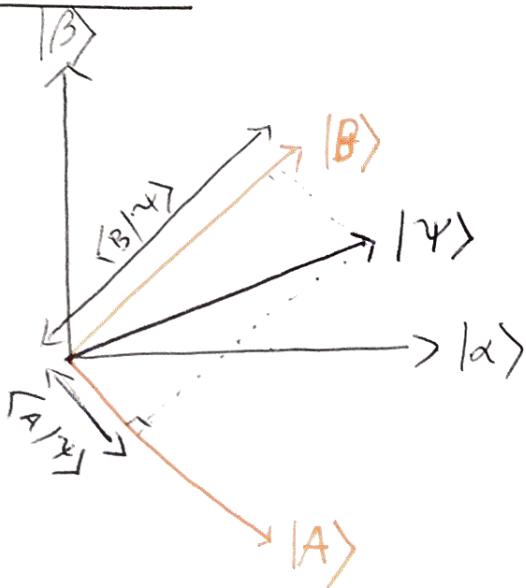
$$r_1^2 + r_2^2 = 1$$

$$\Rightarrow r_2 = \sqrt{1-r_1^2}$$

$|\psi\rangle$ only depends on relative amplitudes
 and phase DIFFERENCE.



EXPECTATIONS



$|\alpha\rangle, |\beta\rangle$ are eigenstates of $\hat{H} = \omega \hat{I}_z$ (2)

$|\alpha\rangle, |\beta\rangle$ are eigenstates of \hat{Q}

Recap: What is outcome of measuring \hat{Q} on state $|\gamma\rangle$?

Write $|\gamma\rangle$ in terms of \hat{Q} eigenstates:

$$|\gamma\rangle = (|A\rangle\langle A| + |B\rangle\langle B|)|\gamma\rangle$$

$$= \underbrace{\langle A|\gamma\rangle |A\rangle}_{\text{get state } A \text{ and } \lambda_A} + \underbrace{\langle B|\gamma\rangle |B\rangle}_{\text{get state } B \text{ and } \lambda_B} = c_A |A\rangle + c_B |B\rangle$$

with probability $|\langle A|\gamma\rangle|^2$

with probability $|\langle B|\gamma\rangle|^2$

Result is always purely random - but what if we had many identical copies of $|\gamma\rangle$? Then we could calculate average or EXPECTATION:

$$\langle \hat{Q} \rangle = \langle \gamma | \hat{Q} | \gamma \rangle$$

$|A\rangle$ and $|B\rangle$ are eigenstates of \hat{Q} :

$$\hat{Q}|A\rangle = \lambda_A |A\rangle$$

$$\hat{Q}|B\rangle = \lambda_B |B\rangle$$

$$= (c_A^* \langle A | + c_B^* \langle B |) \hat{Q} (c_A |A\rangle + c_B |B\rangle)$$

$$= (c_A^* \langle A | + c_B^* \langle B |) (c_A \lambda_A |A\rangle + c_B \lambda_B |B\rangle)$$

$$= \underbrace{c_A^* c_A \cdot \lambda_A}_{\text{This is } P(A) \text{ for}} + \underbrace{c_B^* c_B \cdot \lambda_B}_{P(B)} \quad \text{because } \langle A | A \rangle = 1, \langle A | B \rangle = 0, \text{ etc (orthonormality)}$$

a single measurement!

Can also write in matrix notation (in $\{|A\rangle, |B\rangle\}$ basis)

$$\langle Q \rangle = \langle \gamma | \hat{Q} | \gamma \rangle = (c_A^* \ c_B^*) \underbrace{\begin{pmatrix} \cdot & ? & \cdot \\ \cdot & ? & \cdot \end{pmatrix}}_{\hat{Q}} \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

Operators are DIAGONAL when written in their own eigenbasis.

$$\hat{Q} = \begin{pmatrix} \lambda_A & 0 \\ 0 & \lambda_B \end{pmatrix}$$

What happens if we only know $|\gamma\rangle$ in the \hat{H} eigenbasis? (Just more algebra!)
 Nothing! Geometric picture is exactly the same!

$$|\gamma\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle = (|A\rangle\langle A| + |B\rangle\langle B|)(c_\alpha |\alpha\rangle + c_\beta |\beta\rangle)$$

$$= c_\alpha \langle A|\alpha\rangle |A\rangle + c_\beta \langle A|\beta\rangle |A\rangle + c_\alpha \langle B|\alpha\rangle |B\rangle + c_\beta \langle B|\beta\rangle |B\rangle$$

$$= c_A |A\rangle + c_B |B\rangle, \quad c_A = c_\alpha \langle A|\alpha\rangle + c_\beta \langle A|\beta\rangle$$

$$c_B = c_\alpha \langle B|\alpha\rangle + c_\beta \langle B|\beta\rangle$$

i.e. rewrite in \hat{Q} eigenbasis.

$$\langle \gamma | = c_A^* \langle A | + c_B^* \langle B |$$

$$\therefore \langle Q \rangle = \langle \gamma | Q | \gamma \rangle = (c_A^* \ c_B^*) \begin{pmatrix} \lambda_A & 0 \\ 0 & \lambda_B \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

$$= c_A^* c_A \lambda_A + c_B^* c_B \lambda_B$$

$$= (c_\alpha^* \langle A|\alpha\rangle^* + c_\beta^* \langle A|\beta\rangle^*)(c_\alpha \langle A|\alpha\rangle + c_\beta \langle A|\beta\rangle) \lambda_A + \dots \lambda_B$$

$$= c_\alpha^* c_\alpha (\langle A|\alpha\rangle^* \langle A|\alpha\rangle \lambda_A + \langle B|\alpha\rangle^* \langle B|\alpha\rangle \lambda_B)$$

$$+ c_\alpha^* c_\beta (\langle A|\alpha\rangle^* \langle B|\alpha\rangle \lambda_A + \langle B|\alpha\rangle^* \langle B|\beta\rangle \lambda_B)$$

$$= (c_\alpha^* \ c_\beta^*) \underbrace{\begin{pmatrix} \langle A|\alpha\rangle^* \langle A|\alpha\rangle \lambda_A & \dots \\ \dots & \dots \end{pmatrix}}_{\text{matrix representation of } \hat{Q} \text{ in } \hat{H} \text{ eigenbasis.}} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}$$

N.B. not diagonal!

TIME EVOLUTION: THE SCHRÖDINGER EQUATION

(4)

Fundamental postulate: $i\hbar \frac{d}{dt} |\psi\rangle = \hat{H} |\psi\rangle$

Looks like an eigenvalue equation, but $|\psi\rangle$ does not need to be eigenstate of \hat{H} .

Eigenvalues of \hat{H} do however form complete orthonormal basis set (because it's an observable operator) so we can write $|\psi\rangle$ in terms of \hat{H} eigenstates $\{|n\rangle\}$: $\hat{H}|n\rangle = E_n |n\rangle$

$$|\psi\rangle = \sum_n c_n |n\rangle \quad c_n = \langle n | \psi \rangle \quad (\text{recall: } \sum_n |n\rangle \langle n| = 1)$$

~~WAVEFUNCTION~~

Suppose $|\psi\rangle$ is an eigenstate of \hat{H} , $|\psi\rangle = |n\rangle$:

$$\text{then } i\hbar \frac{d}{dt} |\psi\rangle = i\hbar \frac{d}{dt} |n\rangle = \hat{H} |n\rangle = E_n |n\rangle$$

$$\Rightarrow \frac{d}{dt} |n\rangle = \frac{E_n}{i\hbar} |n\rangle = -\frac{i}{\hbar} E_n |n\rangle$$

All you need to know about differential equations:

General solution of $\frac{d}{dt} y(t) = A y(t)$

$$\text{is } y(t) = e^{At} y(0)$$

$$\text{so } |n(t)\rangle = \underbrace{e^{-iE_n t/\hbar}}_{\text{phase factor}} |n(0)\rangle$$

i.e. eigenstates of \hat{H} just change complex phase at a rate proportional to their energy

If $|\psi\rangle = |n\rangle$, this phase change is undetectable.

But what if $|\psi\rangle$ is not an eigenstate of \hat{H} ?

Suppose $|\psi\rangle$ is a combination (superposition) of \hat{H} eigenstates $|\alpha\rangle$ and $|\beta\rangle$

$$|\psi\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle$$

$$\text{it } \frac{d}{dt} |\psi\rangle = i\hbar \cancel{\frac{d}{dt}} (c_\alpha |\alpha\rangle + c_\beta |\beta\rangle) = \hat{H} (c_\alpha |\alpha\rangle + c_\beta |\beta\rangle) \\ = c_\alpha E_\alpha |\alpha\rangle + c_\beta E_\beta |\beta\rangle$$

Multiply from left by $\langle \alpha |$ and use orthonormality:

$$\text{it } \frac{dc_\alpha}{dt} = c_\alpha E_\alpha \implies c_\alpha(t) = e^{-iE_\alpha t/\hbar} c_\alpha(0)$$

$$\text{and } \langle \beta |: \text{it } \frac{dc_\beta}{dt} = c_\beta E_\beta \implies c_\beta(t) = e^{-iE_\beta t/\hbar} c_\beta(0)$$

~~∴~~ ∴ $|\psi(t)\rangle = \begin{pmatrix} e^{-iE_\alpha t/\hbar} c_\alpha(0) \\ e^{-iE_\beta t/\hbar} c_\beta(0) \end{pmatrix}$ ie. each component picks up phase according to its energy.

Are these phase factors observable?

Yes! DIFFERENCES are observable!

$$|\psi(t)\rangle = e^{-iE_\alpha t/\hbar} \cdot \begin{pmatrix} c_\alpha(0) \\ e^{-i(E_\alpha - E_\beta)t/\hbar} c_\beta(0) \end{pmatrix}$$

Example: $\hat{H} = -\omega \hbar \hat{I}_z = \begin{pmatrix} -\omega t/2 & 0 \\ 0 & +\omega t/2 \end{pmatrix}$

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad (\text{spin along } z\text{-axis})$$

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{i\omega t} \end{pmatrix} \quad (\text{ignoring phase factor})$$

$$\text{so } \begin{pmatrix} 1 \\ 1 \end{pmatrix} \xrightarrow{x} \begin{pmatrix} 1 \\ i \end{pmatrix} \xrightarrow{y} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \xrightarrow{-x} \begin{pmatrix} 1 \\ -i \end{pmatrix} \xrightarrow{-y} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \xrightarrow{x}$$

Larmor precession!

Other operators have representations in the Zeeman basis (another name for ~~the other~~ basis $\{\alpha\}, \langle\beta\}$): (6)

$$I_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad I_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ +i & 0 \end{pmatrix}$$

could use to calculate precession during pulses like earlier

also: $I_\alpha = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad I_\beta = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad I_+ = I_x + iI_y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad I_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

PURE AND MIXED STATES

We now know how to write pure states,

e.g. $| \uparrow \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad | \downarrow \rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad | \rightarrow \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

superposition of $| \uparrow \rangle$ and $| \downarrow \rangle$ leads to quantum uncertainty when measuring I_z

But how do we represent statistical uncertainty?

e.g. $| 50\% \text{ chance of } \uparrow, 50\% \text{ chance of } \downarrow \rangle = ?$

$\frac{1}{\sqrt{2}} (| \uparrow \rangle + | \downarrow \rangle)$? but that is just $| \rightarrow \rangle$

This is a mixed state – cannot be written as any combination of basis vectors.
– can be represented using a DENSITY MATRIX

DENSITY MATRICES/OPERATORS

(not restricted to eigenstates)

If we have a mixture $\{p_i, |\psi_i\rangle\}$ we can write the density operator:

$$\rho = \sum_i p_i |\psi_i\rangle \langle \psi_i|$$

For above example, 50% $| \uparrow \rangle$ and 50% $| \downarrow \rangle$:

$$\rho = \frac{1}{2} | \uparrow \rangle \langle \uparrow | + \frac{1}{2} | \downarrow \rangle \langle \downarrow |$$

$$= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

off-diagonals don't need to
be zero, eg:
pure $| \rightarrow \rangle$: $\rho = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$
 $= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$

diagonal ALWAYS
adds up to 1: $\text{Tr } \rho = 1$

~~Measurement: Probability of system in state $|x\rangle$:~~

$$P(|\psi\rangle) = \sum_j p_j |\langle \psi_j | \psi \rangle|^2 = \sum_j p_j \langle \psi | \psi_j \rangle \langle \psi_j | \psi \rangle$$

When $|\psi\rangle$ given in terms of basis $|A\rangle, |B\rangle$:

$$\rho = \begin{pmatrix} \overline{c_A^* c_A} & \overline{c_A^* c_B} \\ \overline{c_B^* c_A} & \overline{c_B^* c_B} \end{pmatrix} \quad \text{where } \overline{c_\alpha^* c_\alpha} \text{ indicates ensemble average}$$

diagonals \rightarrow "populations"] but these labels only
 off-diagonals \rightarrow "coherences"] make sense when
 written in $\hat{\mathcal{H}}$ eigenbasis.

Expectation values of density matrices:

$$\langle Q \rangle = \sum_j p_j \langle j | Q | j \rangle \quad (\text{definition of ensemble averaged expectation})$$

Insert two complete basis sets:

$$\Rightarrow \langle Q \rangle = \sum_j p_j \sum_{\mu, \nu} \underbrace{\langle j | \mu \times \mu | Q | \nu \rangle}_{=1} \langle \nu | j \rangle$$

$$= \sum_{\mu, \nu} \left(\sum_j p_j \langle \nu | j \rangle \langle j | \mu \rangle \right) \langle \mu | Q | \nu \rangle$$

$$= \sum_{\mu, \nu} \langle \nu | \underbrace{\rho}_{=1} | \mu \rangle \langle \mu | Q | \nu \rangle$$

$$= \sum_{\nu} \langle \nu | \rho Q | \nu \rangle = \text{Tr}(\rho Q)$$

Time evolution of density matrix:

TDSE: $i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H} |\psi\rangle$ and h.c. $-i\hbar \frac{\partial}{\partial t} \langle \psi | = \langle \psi | \hat{H}$

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \rho &= i\hbar \frac{\partial}{\partial t} \sum_j p_j |j\rangle \langle j| = i\hbar \sum_j p_j \left(\frac{\partial |j\rangle}{\partial t} \langle j| + |j\rangle \frac{\partial \langle j|}{\partial t} \right) \\ &= i\hbar \sum_j p_j \left(-\frac{i}{\hbar} \hat{H} |j\rangle \langle j| + \frac{i}{\hbar} |j\rangle \langle j| \hat{H} \right) \\ &= \hat{H} \rho - \rho \hat{H} = [\hat{H}, \hat{\rho}] \end{aligned}$$

This is solved by $\hat{\rho}(t) = e^{-i\hat{H}t} \hat{\rho}(0) e^{+i\hat{H}t}$

{ Liouville-von
Neumann
equation }

Commutators and matrix exponentials

The commutator $[A, B] = AB - BA$

If $[A, B] = 0$, A and B are said to commute and their order can be interchanged.

Nothing odd about this! Rotations do not commute.

Important to simplify calculations,

e.g. if $[\hat{H}, \hat{\rho}] = 0$, $\frac{d\rho}{dt} = 0$! No time evolution!

Commutation important when calculating matrix exponentials:

$e^{AB} \neq e^A e^B$ unless A and B commute

e.g. if Hamiltonian has two parts, $\hat{H} = \hat{H}_A + \hat{H}_B$, can only calculate time evolution for A and B separately if \hat{H}_A and \hat{H}_B commute:

$$\hat{\rho}(t) = e^{-i(H_A+H_B)t} \hat{\rho}(0) e^{+i(H_A+H_B)t} \neq e^{-iH_A t} e^{-iH_B t} \hat{\rho}(0) e^{+iH_A t} e^{+iH_B t}$$

(in general)

Recap: Matrix representation

All operators can be written in a matrix representation (for a specific basis set) such that

$$\begin{aligned}\langle \hat{Q} \rangle &= \langle \psi | \hat{Q} | \psi \rangle = (\langle \alpha | \langle \beta |) \cdot \hat{Q} \cdot \begin{pmatrix} |\alpha\rangle \\ |\beta\rangle \end{pmatrix} \\ &= \begin{pmatrix} \langle \alpha | Q | \alpha \rangle & \langle \beta | Q | \alpha \rangle \\ \langle \alpha | Q | \beta \rangle & \langle \beta | Q | \beta \rangle \end{pmatrix} = \begin{pmatrix} c_\alpha^* c_\alpha & c_\beta^* c_\alpha \\ c_\alpha^* c_\beta & c_\beta^* c_\beta \end{pmatrix}\end{aligned}$$

Important examples:

$$\hat{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad I_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad I_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

One-pulse experiment

Density matrix at equilibrium: $\hat{\rho}_0 = \frac{e^{-\hat{H}/kT}}{Z}$ ← normalization

$$\begin{aligned}\hat{\rho}_0 &= \frac{1}{Z} \begin{pmatrix} \langle \alpha | e^{-\hat{H}/kT} | \alpha \rangle & \langle \alpha | e^{-\hat{H}/kT} | \beta \rangle \\ \langle \beta | e^{-\hat{H}/kT} | \alpha \rangle & \langle \beta | e^{-\hat{H}/kT} | \beta \rangle \end{pmatrix} \quad e^{-\hat{H}/kT} | \alpha \rangle = e^{-E_\alpha/kT} | \alpha \rangle \\ &= \frac{1}{Z} \begin{pmatrix} e^{-E_\alpha/kT} & 0 \\ 0 & e^{-E_\beta/kT} \end{pmatrix} \quad e^\alpha \approx 1 + \alpha + O(\alpha^2) \\ &= \frac{1}{Z} \begin{pmatrix} 1 + \frac{1}{2} \hbar \omega_0 / kT & 0 \\ 0 & 1 - \frac{1}{2} \hbar \omega_0 / kT \end{pmatrix} \quad E_\alpha = -\frac{1}{2} \hbar \omega_0 \\ &= \frac{1}{Z} \left(\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{Z} \cdot \frac{\hbar \omega_0}{2kT} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right) \quad E_\beta = +\frac{1}{2} \hbar \omega_0 \\ &= \frac{1}{Z} \left(E + \frac{\hbar \omega_0}{2kT} I_z \right) \rightarrow \text{ignoring constant and identity } E\end{aligned}$$

Now consider rotation about x -axis (ω -pulse)

$$H_1 = \omega_1, I_x = \frac{\omega_1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\frac{\pi}{2} \text{ pulse} \Rightarrow T_p = \frac{\pi}{2} \cdot \frac{1}{\omega_1}$$

$$e^{-iH_1 t_p} = e^{-i\frac{\pi}{2} I_x} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix} \quad e^{+iH_1 t_p} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix}$$

$$\rho_0 \rightarrow \rho_1 = e^{-iH_1 t_p} \rho_0 e^{iH_1 t_p}$$

$$= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix} \cdot \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \cdot \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix}$$

$$= \frac{1}{2} \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} = -I_y$$

$$\overline{\langle I_y \rangle} = \text{Tr} (\rho I_y) = \text{Tr} (-I_y \cdot I_y) = \text{Tr} \left[-\frac{1}{2} \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \cdot \frac{1}{2} \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} \right] = -\frac{1}{2}$$

Product operator expansion:

$$\hat{\rho} = a_1 \hat{I}_x + a_2 \hat{I}_y + a_3 \hat{I}_z$$

write $\hat{\rho}$ in terms of 'component' matrices, can simplify calculations:

$$\hat{\rho} \rightarrow e^{-iHt} \hat{\rho} e^{+iHt} = e^{-iHt} (\rho_1 + \rho_2 + \dots) e^{+iHt}$$

$$= e^{-iHt} \rho_1 e^{+iHt} + e^{-iHt} \rho_2 e^{+iHt} + \dots \text{etc}$$

} can calculate evolution of component separately.