Mathematics of quantum mechanics

- Linear vector spaces

  vectors: $\psi, \phi, \chi, \ldots$

  scalars: $a, b, c, \ldots$

  \+ addition rule: $\psi + \phi = \gamma$ etc.

  \+ multiplication rule: $a\psi + b\phi = \beta$ etc.

- Hilbert spaces, $\mathcal{H}$

  - Linear space

  - Strictly positive inner product

    $$(\varphi, \psi) = c$$

    $$(\psi, \psi) \geq 0$$

  - $\mathcal{H}$ is separable & complete

- Dirac bra-c-ket notation:

  $$(\varphi, \psi) = \langle \varphi | \psi \rangle$$

Example: Spin-$\frac{1}{2}$ particle (or a qu-bit)

Define two states: $|\uparrow_z\rangle$ & $|\downarrow_z\rangle$

We use the basis $\{|\uparrow_z\rangle, |\downarrow_z\rangle\}$:

$$|\uparrow_z\rangle = 1\,|\uparrow_z\rangle + 0\,|\downarrow_z\rangle$$

$$|\downarrow_z\rangle = 0\,|\uparrow_z\rangle + 1\,|\downarrow_z\rangle$$

thus, in the chosen basis we have (with a slight abuse of notation)

$$|\uparrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \langle\uparrow_z|\uparrow_z\rangle \\ \langle\downarrow_z|\uparrow_z\rangle \end{pmatrix}$$

$$|\downarrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \langle\uparrow_z|\downarrow_z\rangle \\ \langle\downarrow_z|\downarrow_z\rangle \end{pmatrix}$$

Note that if we would reorder the basis to $\{|\downarrow_z\rangle, |\uparrow_z\rangle\}$; the vector representation would change to $|\uparrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ and $|\downarrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, although the actual "kets" would remain the same.

Now we can define e.g.

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle + |\downarrow_z\rangle\right)$$

Is this state normalized?

$$\langle\uparrow_x|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\left(\langle\uparrow_z| + \langle\downarrow_z|\right)\frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle + |\downarrow_z\rangle\right)$$

$$= \frac{1}{2}\Big[\underbrace{\langle\uparrow_z|\uparrow_z\rangle}_{1} + \underbrace{\langle\uparrow_z|\downarrow_z\rangle}_{0} + \underbrace{\langle\downarrow_z|\uparrow_z\rangle}_{0} + \underbrace{\langle\downarrow_z|\downarrow_z\rangle}_{1}\Big]$$

$$= \begin{pmatrix}1\\0\end{pmatrix}\cdot\begin{pmatrix}1\\0\end{pmatrix} = 1 \qquad = \begin{pmatrix}0\\1\end{pmatrix}\cdot\begin{pmatrix}1\\0\end{pmatrix} = 0$$

$$= \frac{1}{2} \times 2 = 1 \checkmark$$

Operators:

Define the operator $\hat{O}_z$ by

$$\hat{O}_z|\uparrow_z\rangle = 1\,|\uparrow_z\rangle$$

$$\hat{O}_z|\downarrow_z\rangle = -1\,|\downarrow_z\rangle$$

What is the matrix representation of $\hat{O}_z$?

$$\underline{\underline{O}}_z\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}? & ?\\ ? & ?\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = 1\begin{pmatrix}1\\0\end{pmatrix} \Rightarrow \underline{\underline{O}}_z = \begin{pmatrix}1 & ?\\ 0 & ?\end{pmatrix}$$

$$\underline{\underline{O}}_z\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}? & ?\\ ? & ?\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = -1\begin{pmatrix}0\\1\end{pmatrix} \Rightarrow \underline{\underline{O}}_z = \begin{pmatrix}? & 0\\ ? & -1\end{pmatrix}$$

Thus, we find $\underline{\underline{O}}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

We also notice that $\underline{\underline{O}}_z = \begin{pmatrix} \langle \uparrow_z | \hat{O}_z | \uparrow_z \rangle & \langle \uparrow_z | O_z | \downarrow_z \rangle \\ \langle \downarrow_z | O_z | \uparrow_z \rangle & \langle \downarrow_z | \hat{O}_z | \downarrow_z \rangle \end{pmatrix}$

↳ matrix elements

Note again that $\underline{\underline{O}}_z = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$ if we change to the basis $\{ |\downarrow_z\rangle, |\uparrow_z\rangle \}$ although $\hat{O}_z$ is unchanged.

Now, consider

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow_z\rangle + |\downarrow_z\rangle \right) \quad \text{and}$$

$$|\downarrow_x\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow_z\rangle - |\downarrow_z\rangle \right)$$

and introduce the operator $\hat{O}_x$ defined by

$$\hat{O}_x |\uparrow_x\rangle = 1 \, |\uparrow_x\rangle \quad \text{and}$$

$$\hat{O}_x |\downarrow_x\rangle = -1 \, |\downarrow_x\rangle$$

What is the matrix representation of $\hat{O}_x$ in the basis $\{ |\uparrow_z\rangle, |\downarrow_z\rangle \}$?

First, note that

$$|\uparrow_z\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle + |\downarrow_x\rangle\right) \quad \text{and}$$

$$|\downarrow_z\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle - |\downarrow_x\rangle\right)$$

Next, we evaluate the matrix elements

$$\langle\uparrow_z|\hat{\sigma}_x|\uparrow_z\rangle = \langle\uparrow_z|\,\hat{\sigma}_x\,\frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle + |\downarrow_x\rangle\right)$$

$$= \langle\uparrow_z|\,\frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle - |\downarrow_x\rangle\right)$$

$$= \langle\uparrow_z|\downarrow_z\rangle = 0$$

$$\langle\downarrow_z|\hat{\sigma}_x|\uparrow_z\rangle = \ \ldots\ = \langle\downarrow_z|\downarrow_z\rangle = 1$$

$$\langle\uparrow_z|\hat{\sigma}_x|\downarrow_z\rangle = \langle\uparrow_z|\,\hat{\sigma}_x\,\frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle - |\downarrow_x\rangle\right)$$

$$= \langle\uparrow_z|\,\frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle + |\downarrow_x\rangle\right)$$

$$= \langle\uparrow_z|\uparrow_z\rangle = 1$$

$$\langle\downarrow_z|\sigma_x|\downarrow_z\rangle = \ \ldots\ = 0$$

and $\underline{\underline{\sigma}}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

Note that the three operators $\hat{1}$, $\hat{\sigma}_z$, and $\hat{\sigma}_x$ are all hermitian, i.e.

$$\mathbb{1}^{+} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}^{+} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbb{1} \quad \checkmark$$

$$\sigma_z^{+} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}^{+} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \sigma_z \quad \checkmark$$

$$\sigma_x^{+} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}^{+} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \sigma_x \quad \checkmark$$

The last linearly independent 2×2 matrix is

$$\sigma_y^{+} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}^{+} = \begin{pmatrix} 0 & -i \\ +i & 0 \end{pmatrix} = \sigma_y \quad \checkmark$$

The eigenvalues and eigenvectors of σ_y are

$$+1: \quad |\uparrow_y\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle + i\,|\downarrow_z\rangle\right)$$

$$-1: \quad |\downarrow_y\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle - i\,|\downarrow_z\rangle\right)$$

The identity matrix $\mathbb{1}$ together with the Pauli matrices, σ_x, σ_y, and σ_z, form a basis for the space of 2×2 hermitian matrices.

Some properties of the Pauli matrices:

Commutation relations:

$$[\hat{\sigma}_a, \hat{\sigma}_b] = \hat{\sigma}_a\hat{\sigma}_b - \hat{\sigma}_b\hat{\sigma}_a = 2i\,\varepsilon_{abc}\,\hat{\sigma}_c,$$

where the Levi-Civita symbol is defined as

$$\varepsilon_{abc} = \varepsilon_{bca} = \varepsilon_{cab} = 1 \quad \text{(even number of permutations)}$$

$$\varepsilon_{bac} = \varepsilon_{cba} = \varepsilon_{acb} = -1 \quad \text{and } 0 \text{ otherwise}$$

For example:

$$[\hat{\sigma}_y, \hat{\sigma}_z] = \underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}}_{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}} - \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}}_{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}$$

$$= 2i\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = 2i\,\hat{\sigma}_x = 2i\,\varepsilon_{yzx}\,\hat{\sigma}_x$$

Anti-commutation relations:

$$\{\hat{\sigma}_a; \hat{\sigma}_b\} \equiv \hat{\sigma}_a\hat{\sigma}_b + \hat{\sigma}_b\hat{\sigma}_a = 2\,\underbrace{\delta_{ab}}_{\begin{cases} 0, & a \neq b \\ 1, & a = b \end{cases}}\,\mathbb{1}$$

For example:

$$\{\hat{\sigma}_x, \hat{\sigma}_x\} = \hat{\sigma}_x^2 + \hat{\sigma}_x^2 = 2 \cdot \mathbb{1}$$

Note that $\hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = \mathbb{1}$

$\Rightarrow \hat{\sigma}_x^{-1} = \hat{\sigma}_x = \hat{\sigma}_x^{+}$, etc. $\Rightarrow$ the Pauli operators are unitary.

Bloch sphere:

In general, the state of the spin (qubit) is

$$|\psi\rangle = \alpha|\uparrow_z\rangle + \beta|\downarrow_z\rangle$$

with $|\alpha|^2 + |\beta|^2 = 1$

We can write this as

$$|\psi\rangle = e^{i\varphi_\alpha}\cos\frac{\theta}{2}|\uparrow_z\rangle + e^{i\varphi_\beta}\sin\frac{\theta}{2}|\downarrow_z\rangle$$

$$= e^{i\gamma}\left[\cos\frac{\theta}{2}|\uparrow_z\rangle + e^{i\varphi}\sin\frac{\theta}{2}|\downarrow_z\rangle\right]$$

this prefactor has no observable effects and can be ignored.

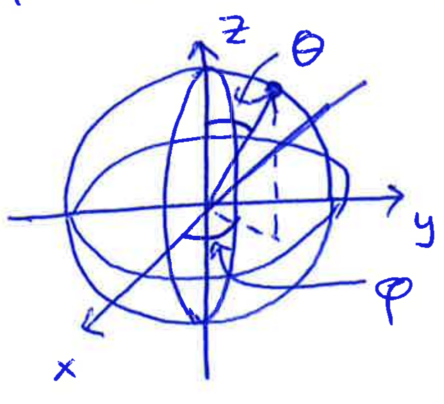
Notice that

$\theta = 0$: $|\psi\rangle = |\uparrow_z\rangle$

$\theta = \pi$: $|\psi\rangle = |\downarrow_z\rangle$

$\theta = \frac{\pi}{2}$, $\varphi = 0, \pi$: $|\psi\rangle = \frac{1}{\sqrt{2}}\left[|\uparrow_z\rangle \pm |\downarrow_z\rangle\right] = |\uparrow_x, \downarrow_x\rangle$

$\theta = \frac{\pi}{2}$; $\varphi = \pm\frac{\pi}{2}$: $|\psi\rangle = \frac{1}{\sqrt{2}}\left[|\uparrow_z\rangle \pm i|\downarrow_z\rangle\right] = |\uparrow_y, \downarrow_y\rangle$



Bloch sphere

Time-evolution:

The time evolution of a quantum state is determined by the Schrödinger equation

$$i\hbar \partial_t |\psi(t)\rangle = \hat{H} |\psi(t)\rangle ,$$

where the Hamiltonian $\hat{H}$ is the operator for the ~~total~~ energy of the system.

If $\hat{H}$ is time-independent, the formal solution reads

$$|\psi(t)\rangle = e^{-i\hat{H}(t-t_0)/\hbar} |\psi(t_0)\rangle ,$$

where $|\psi(t_0)\rangle$ is the initial state at time t_0.

We can easily check that

$$i\hbar \partial_t |\psi(t)\rangle = i\hbar \left(-\frac{i}{\hbar} \hat{H}\right) |\psi(t)\rangle$$

$$= \hat{H} |\psi(t)\rangle \quad \checkmark$$

We can also express this as

$$|\psi(t)\rangle = \hat{U}(t,t_0) |\psi(t_0)\rangle ,$$

where

$$\hat{U}(t,t_0) = e^{-i\hat{H}(t-t_0)/\hbar}$$

is the time-evolution operator. We note that it is unitary, since

$$\hat{U}(t,t_0)\,\hat{U}^{+}(t,t_0) = e^{-iH(t-t_0)/\hbar}\,e^{iH(t-t_0)/\hbar} = 1$$

Moreover, it fulfills the Schrödinger equation

$$i\hbar\,\partial_t\,\hat{U}(t,t_0) = \hat{H}\,\hat{U}(t,t_0)$$

Example: Spin-½ in a magnetic field:

Energy of magnetic dipole in magnetic field $\underline{B}$:

$$\hat{H} = -\hat{\underline{\mu}}\cdot\underline{B}$$
$$= -\frac{\hbar}{2}\gamma\,\underline{B}\cdot\underline{\sigma}$$

Take for example a magnetic field pointing in the z direction and the initial state $|\psi(t_0)\rangle = |\uparrow_z\rangle$

Now, the state evolves as

$$|\psi(t)\rangle = e^{-i\hat{H}(t-t_0)/\hbar}\,|\psi(t_0)\rangle$$

$$= e^{i\frac{\gamma}{2}B_z\hat{\sigma}_z(t-t_0)}\,|\uparrow_z\rangle$$

$$= \sum_{n=0}^{\infty}\frac{(i\frac{\gamma}{2}B_z(t-t_0))^n}{n!}\underbrace{\hat{\sigma}_z^n\,|\uparrow_z\rangle}_{=|\uparrow_z\rangle}$$

$$= \underbrace{e^{i\frac{\gamma}{2}B_z(t-t_0)}}_{\text{overall phase with no observable effects.}}|\uparrow_z\rangle$$

Thus, the system remains in the state $|\uparrow_z\rangle$

Now consider instead a magnetic field pointing in the ~~z~~ x-direction:

$$|\psi(t)\rangle = e^{i\frac{\gamma}{2}\cdot B_x\hat{\sigma}_x(t-t_0)}\,|\uparrow_z\rangle$$

$$= e^{i\frac{\gamma}{2}B_x\hat{\sigma}_x(t-t_0)}\,\frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle+|\downarrow_x\rangle\right)$$

$$= \frac{1}{\sqrt{2}}\left[e^{i\frac{\gamma}{2}B_x\sigma_x(t-t_0)}|\uparrow_x\rangle + e^{i\frac{\gamma}{2}B_x\sigma_x(t-t_0)}|\downarrow_x\rangle\right]$$

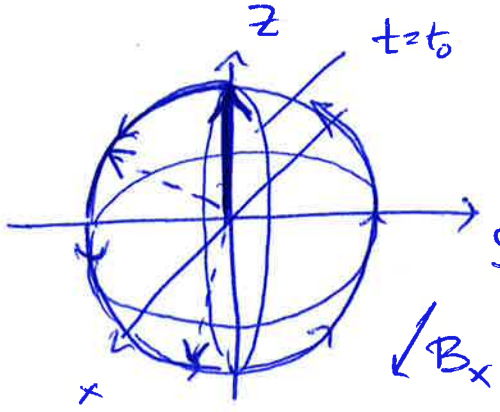
$$= \frac{1}{\sqrt{2}}\left[e^{i\frac{\gamma}{2}B_x(t-t_0)}|\uparrow_x\rangle + e^{-i\frac{\gamma}{2}B_x(t-t_0)}|\downarrow_x\rangle\right]$$

$$= e^{i\frac{\gamma}{2}B_x(t-t_0)}\frac{1}{\sqrt{2}}\left[|\uparrow_x\rangle + e^{-i\gamma B_x(t-t_0)}|\downarrow_x\rangle\right]$$

Thus, the state evolves as

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle + e^{-i\omega_x(t-t_0)}|\downarrow_x\rangle\right)$$

where $\omega_x \equiv \gamma B_x$



Spin precession on the Bloch sphere

Measurements in quantum mechanics:

If the system is in the state

$$|\psi\rangle = \alpha|\uparrow_z\rangle + \beta|\downarrow_z\rangle$$

and we measure the z-component of the spin, we find +1 with probability $|\alpha|^2$ and −1 with probability $|\beta|^2$, remembering that $|\alpha|^2 + |\beta|^2 = 1$

If we measure +1, the state "collapses" to the state $|\uparrow_z\rangle$, and if we find −1, it collapses to $|\downarrow_z\rangle$

The average of many repeated measurements on the same state is

$$\langle \Psi | \hat{\sigma}_z | \Psi \rangle = \left(\langle \uparrow_z | \alpha^* + \langle \downarrow_z | \beta^* \right) \hat{\sigma}_z \times$$

$$\left(\alpha | \uparrow_z \rangle + \beta | \downarrow_z \rangle \right)$$

$$= |\alpha|^2 \langle \uparrow_z | \hat{\sigma}_z | \uparrow_z \rangle + |\beta|^2 \langle \downarrow_z | \hat{\sigma}_z | \downarrow_z \rangle$$

$$+ \alpha^* \beta \langle \uparrow_z | \sigma_z | \downarrow_z \rangle + \alpha \beta^* \langle \downarrow_z | \sigma_z | \uparrow_z \rangle$$

$$= |\alpha|^2 \langle \uparrow_z | \hat{\sigma}_z | \uparrow_z \rangle + |\beta|^2 \langle \downarrow_z | \hat{\sigma}_z | \downarrow_z \rangle$$

$$+ \underbrace{2 \,\mathrm{Re} \{ \alpha^* \beta \langle \uparrow_z | \hat{\sigma}_z | \downarrow_z \rangle \}}_{\substack{\text{interference term} \\ \text{(no-classical)}}}$$

$$= |\alpha|^2 \times 1 + |\beta|^2 \times -1 + 0 = |\alpha|^2 - |\beta|^2$$

Notice how

$$\langle \Psi | \hat{\sigma}_x | \Psi \rangle = |\alpha|^2 \langle \uparrow_z | \hat{\sigma}_x | \uparrow_z \rangle + |\beta|^2 \langle \downarrow_z | \sigma_x | \downarrow_z \rangle$$

$$+ 2 \,\mathrm{Re} \{ \alpha^* \beta \langle \uparrow_z | \hat{\sigma}_x | \downarrow_z \rangle \}$$

$$= |\alpha|^2 \cdot 0 + |\beta|^2 \cdot 0 + 2 \,\mathrm{Re} \{ \alpha^* \beta \} = 2 \,\mathrm{Re} \{ \alpha^* \beta \}$$

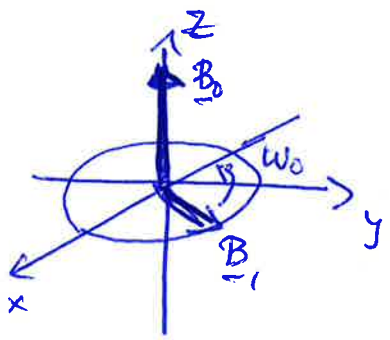
So if $|\Psi\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow_z\rangle + |\downarrow_z\rangle \right)$, $\langle \Psi | \sigma_x | \Psi \rangle = 1$

Electron spin resonance (ESR):

Let us now consider a magnetic field of the form

$$\underline{B}(t) = B_0 \underline{z} + B_1 \left[\cos(\omega_0 t)\, \underline{x} + \sin(\omega_0 t)\, \underline{y} \right],$$

which has a constant component along the z-axis of strength B_0 and a time-dependent component of strength B_1 that rotates in the x-y plane at frequency ω_0



The Hamiltonian reads

$$\hat{H}(t) = -\frac{\hbar}{2}\gamma\, \underline{B}(t)\cdot \hat{\underline{\sigma}}$$

$$= -\frac{\hbar}{2}\gamma B_0 \hat{\sigma}_z$$

$$-\frac{\hbar}{2}\gamma B_1 \left[\cos(\omega_0 t)\, \hat{\sigma}_x + \sin(\omega_0 t)\, \hat{\sigma}_y \right]$$

$$\equiv -\frac{\hbar}{2}\gamma B_0 \hat{\sigma}_z - \frac{\hbar}{2}\gamma B_1\, \hat{\sigma}_u(t),$$

where $\hat{\sigma}_u(t)$ is the spin-component pointing in the direction of $\underline{B}_1$. This direction can be obtained by rotating the x-axis by the angle $\omega_0 t$. Such a rotation can be implemented with the operator $\hat{R}_z(\omega_0 t) \equiv e^{i\omega_0 t \hat{\sigma}_z/2}$.

To see this, we first rewrite the rotation operator as

$$\hat{R}_z(\varphi) = e^{i\varphi\hat{\sigma}_z/2}$$

$$= \sum_{n=0}^{\infty} \frac{(i\varphi/2)^n}{n!} \hat{\sigma}_z^n$$

$$= \sum_{n=0}^{\infty} \frac{(i\varphi/2)^{2n}}{2n!} \underbrace{(\hat{\sigma}_z)^{2n}}_{=1} + \sum_{n=0}^{\infty} \frac{(i\varphi/2)^{2n+1}}{(2n+1)!} \underbrace{\hat{\sigma}_z^{2n}\hat{\sigma}_z}_{\hat{\sigma}_z}$$

$$= \left[\sum_{n=0}^{\infty} (-1)^n \frac{(\varphi/2)^{2n}}{(2n)!}\right] \mathbb{1} + i\left[\sum_{n=0}^{\infty} (-1)^n \frac{(\varphi/2)^{2n+1}}{(2n+1)!}\right] \hat{\sigma}_z$$

$$= \cos(\varphi/2)\,\hat{1} + i\sin(\varphi/2)\,\hat{\sigma}_z$$

We then have

$$\hat{R}_z^{+}(\varphi)\hat{\sigma}_x\hat{R}_z(\varphi) = \left[\cos(\varphi/2) - i\sin(\varphi/2)\hat{\sigma}_z\right]\hat{\sigma}_x\left[\cos(\varphi/2) + i\sin(\varphi/2)\hat{\sigma}_z\right]$$

$$= \cos^2(\varphi/2)\hat{\sigma}_x + i\cos(\varphi/2)\sin(\varphi/2)\underbrace{(\hat{\sigma}_x\hat{\sigma}_z - \hat{\sigma}_z\hat{\sigma}_x)}_{=-2i\hat{\sigma}_y}$$
$$+ \sin^2(\varphi/2)\underbrace{\hat{\sigma}_z\hat{\sigma}_x\hat{\sigma}_z}_{=-\hat{\sigma}_x}$$

$$= \left[\cos^2(\varphi/2) - \sin^2(\varphi/2)\right]\hat{\sigma}_x + 2\cos(\varphi/2)\sin(\varphi/2)\,\hat{\sigma}_y$$

$$= \cos\varphi\,\hat{\sigma}_x + \sin\varphi\,\hat{\sigma}_y$$

Thus, we can write

$$\hat{\sigma}_x(t) = \hat{R}_z^{+}(\omega_0 t)\,\hat{\sigma}_x\,\hat{R}_z(\omega_0 t)$$

Now, our Hamiltonian reads

$$\hat{H}(t) = -\frac{\hbar}{2}\gamma B_0 \hat{\sigma}_z - \frac{\hbar}{2}\gamma B_1 \hat{R}_z^{\dagger}(\omega_0 t)\,\hat{\sigma}_x\,\hat{R}_z(\omega_0 t)$$

with $\hat{R}_z(\omega_0 t) = e^{i\omega_0 t \hat{\sigma}_z/2}$

To solve the Schrödinger equation, we introduce the rotated spin state

$$|\Phi(t)\rangle \equiv \hat{R}_z(\omega_0 t)\,|\Psi(t)\rangle$$

with the equation of motion

$$i\hbar\partial_t|\Phi(t)\rangle = \left(i\hbar\partial_t \hat{R}_z(\omega_0 t)\right)|\Psi(t)\rangle + \hat{R}_z(\omega_0 t)\, i\hbar\partial_t|\Psi(t)\rangle$$

$$= \left(i\hbar\frac{i\omega_0}{2}\hat{\sigma}_z\right)\hat{R}_z(\omega_0 t)|\Psi(t)\rangle + \hat{R}_z(\omega_0 t)\,\hat{H}(t)|\Psi(t)\rangle$$

$$= -\frac{\hbar\omega_0}{2}\hat{\sigma}_z|\Phi(t)\rangle + \hat{R}_z(\omega_0 t)\,\hat{H}(t)\underbrace{\hat{R}_z^{\dagger}(\omega_0 t)\,\hat{R}_z(\omega_0 t)}_{1}|\Psi(t)\rangle$$

$$= -\frac{\hbar\omega_0}{2}\hat{\sigma}_z|\Phi(t)\rangle + \underbrace{\hat{R}_z(\omega_0 t)\,\hat{H}(t)\,\hat{R}_z^{\dagger}(\omega_0 t)}_{= -\frac{\hbar}{2}\gamma B_0\hat{\sigma}_z - \frac{\hbar}{2}\gamma B_1\hat{\sigma}_x}|\Phi(t)\rangle$$

$$= -\frac{\hbar}{2}\left[\omega_0\hat{\sigma}_z + \gamma B_0\hat{\sigma}_z + \gamma B_1\hat{\sigma}_x\right]|\Phi(t)\rangle$$

$$= \hat{H}_{eff}|\Phi(t)\rangle$$

with $\hat{H}_{eff} = -\frac{\hbar}{2}\left[\omega_0\hat{\sigma}_z + \gamma B_0\hat{\sigma}_z + \gamma B_1\hat{\sigma}_x\right]$,

which is time-independent!

To rotate a spin that initially ($t=0$) points up, we need to cancel the effective field in the z-direction. To this end, we choose the resonance condition $\omega_0 = -\gamma B$, with the sign (+/-) determining the direction in which the magnetic field rotates. We then have

$$\hat{H}_{eff} = -\frac{\hbar}{2}\gamma B_1 \hat{\sigma}_x$$

and the time evolution becomes

$$|\Phi(t)\rangle = e^{-i\hat{H}_{eff}t/\hbar}|\Phi(0)\rangle$$

$$= e^{-i\hat{H}_{eff}t/\hbar}\underbrace{\hat{R}_z(0)}_{1}|\uparrow\rangle$$

$$= e^{i\gamma B_1 t\hat{\sigma}_x/2}|\uparrow\rangle$$

$$= \cos(\gamma B_1 t/2)|\uparrow\rangle + i\sin(\gamma B_1 t/2)\hat{\sigma}_x|\uparrow\rangle$$

$$= \cos(\gamma B_1 t/2)|\uparrow\rangle + i\sin(\gamma B_1 t/2)|\downarrow\rangle$$

Thus, at the time $\gamma B_1 t^* = \pi \rightarrow t^* = \frac{\pi}{\gamma B_1}$, we have

$|\Phi(t^*)\rangle = 0|\uparrow\rangle + i|\downarrow\rangle$ and

overall phase

$$|\Psi(\tfrac{\pi}{\gamma B_1})\rangle = \hat{R}_z^{\dagger}\left(\frac{\omega_0\pi}{\gamma B_1}\right)i|\downarrow\rangle = ie^{-i\frac{\omega_0\pi}{2\gamma B_1}\hat{\sigma}_z}|\downarrow\rangle = ie^{i\frac{\omega_0\pi}{2\gamma B_1}}|\downarrow\rangle$$

$\longrightarrow$ the spin has been flipped!

In the case, where the spin precessed around a constant magnetic field in the x-direction, we found

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle + e^{-i\omega_x t}|\downarrow_x\rangle\right),$$

where $\omega_x \equiv \gamma B_x/\hbar$ and $\hat{H} = -\frac{\gamma}{2} B_x \hat{\sigma}_x$.

For the average energy, we the get

$$\langle \hat{H}\rangle = \langle \psi(t)|\hat{H}|\psi(t)\rangle$$

$$= \frac{1}{2}\left(-\frac{\gamma B_x}{2}\right)\left(\langle\uparrow_x| + \langle\downarrow_x|e^{i\omega_x t}\right)\hat{\sigma}_x \left(|\uparrow_x\rangle + e^{-i\omega_x t}|\downarrow_x\rangle\right)$$

$$= -\frac{\gamma B_x}{4}\Big(e^{-i\omega_x t}\langle\uparrow_x|\hat{\sigma}_x|\downarrow_x\rangle + e^{i\omega_x t}\langle\downarrow_x|\hat{\sigma}_x|\uparrow_x\rangle + \langle\uparrow_x|\hat{\sigma}_x|\uparrow_x\rangle + \langle\downarrow_x|\hat{\sigma}_x|\downarrow\rangle\Big)$$

$$= -\frac{\gamma B_x}{4}\left(0 + 0 + 1 - 1\right) = 0$$

Thus, the average is constant / time-independent.

We can also see this by calculating

$$i\hbar\frac{d}{dt}\langle\hat{H}\rangle = \left(i\hbar\frac{d}{dt}\langle\psi(t)|\right)\hat{H}|\psi(t)\rangle + \langle\psi(t)|\hat{H}\left(i\hbar\frac{d}{dt}|\psi(t)\rangle\right)$$

$$= -\langle\psi(t)|\hat{H}\hat{H}|\psi(t)\rangle + \langle\psi(t)|\hat{H}\hat{H}|\psi(t)\rangle$$

$$= 0$$

With electron spin resonance, we found

$$|\psi(t)\rangle = \hat{R}_z^{+}(\omega_0 t)\left[\cos(\gamma B_1 t/2)|\uparrow\rangle + i\sin(\gamma B_1 t/2)|\downarrow\rangle\right]$$

and

$$\hat{H}(t) = -\frac{\hbar}{2}\gamma B_0\hat{\sigma}_z - \frac{\hbar}{2}\gamma B_1 \hat{R}_z^{+}(\omega_0 t)\hat{\sigma}_x\hat{R}_z(\omega_0 t),$$

where

$$\hat{R}_z(\omega_0 t) \equiv e^{i\omega_0 t\hat{\sigma}_z/2}.$$

For the average energy, we then find

$$\langle\hat{H}(t)\rangle = \langle\psi(t)|\hat{H}(t)|\psi(t)\rangle$$

$$= \left[\langle\uparrow|\cos(\gamma B_1 t/2) - i\sin(\gamma B_1 t/2)\langle\downarrow|\right]\hat{R}_z(\omega_0 t)\times$$
$$\left[-\frac{\hbar}{2}\gamma B_0\hat{\sigma}_z - \frac{\hbar}{2}\gamma B_1\hat{R}_z^{+}(\omega_0 t)\hat{\sigma}_x\hat{R}_z(\omega_0 t)\right]\times$$
$$\hat{R}_z^{+}(\omega_0 t)\left[\cos(\gamma B_1 t/2)|\uparrow\rangle + i\sin(\gamma B_1 t/2)|\downarrow\rangle\right]$$

$$= \left[\langle\uparrow|\cos(\gamma B_1 t/2) - i\sin(\gamma B_1 t/2)\langle\downarrow|\right]\times$$
$$\left[-\frac{\hbar}{2}\gamma B_0\hat{\sigma}_z - \frac{\hbar}{2}\gamma B_1\hat{\sigma}_x\right]\times$$
$$\left[\cos(\gamma B_1 t/2)|\uparrow\rangle + i\sin(\gamma B_1 t/2)|\downarrow\rangle\right]$$

$$= \cos^2(\gamma B_1 t/2)\, \langle \uparrow | \left(-\frac{\hbar}{2}\gamma B_0 \hat{\sigma}_z - \frac{\hbar}{2}\gamma B_1 \hat{\sigma}_x \right) | \uparrow \rangle$$

$$+ \sin^2(\gamma B_1 t/2)\, \langle \downarrow | \left(\text{———} \;\;''\;\; \text{———} \right) | \downarrow \rangle$$

$$+ i \cos(\gamma B_1 t/2) \sin(\gamma B_1 t/2)\, \langle \uparrow | \left(\text{——} \;''\; \text{——} \right) | \downarrow \rangle$$

$$- i \cos(\gamma B_1 t/2) \sin(\gamma B_1 t/2)\, \langle \downarrow | \left(\text{——} \;''\; \text{——} \right) | \uparrow \rangle$$

$$= -\frac{\hbar}{2}\gamma B_0 \left(\cos^2(\gamma B_1 t/2) - \sin^2(\gamma B_1 t/2) \right)$$

$$+ i \cos(\gamma B_1 t/2) \sin(\gamma B_1 t/2) \underbrace{\left(-\frac{\hbar}{2}\gamma B_1 + \frac{\hbar}{2}\gamma B_1 \right)}_{0}$$

$$= -\frac{\hbar}{2}\gamma B_0 \cos(\gamma B_1 t)$$

Thus, in this case, the average energy changes with time! Initially, we have $\langle \hat{H}(0) \rangle = -\frac{\hbar}{2}\gamma B_0$, while at $t^* = \frac{\pi}{\gamma B_1}$, when the spin has flipped, we have $\langle \hat{H}(t^*) \rangle = -\frac{\hbar}{2}\gamma B_0 (-1) = \underline{+\frac{\hbar}{2}\gamma B_0}$

In other words, we have done work on the system, and changed its energy by $\Delta E = \hbar \gamma B_0$ //