⇒ an coherent electronically excited state is a dynamic state that oscillates between the ground & excited state.

pump-probe

1> Pump → excite the sys. into a coherent superposition. 2> probe measure how sys elvoves 3> the detected sign oscillates in time.

1-5. spin precession. ($|\alpha, t_0; t\rangle$)

$\hat{H}$ for spin ½ sys.

$\downarrow$

(Energy)

magnetic energy $E = -\vec{\mu}\cdot\vec{B}$

$\vec{\mu}$: magnetic dipole moment.

$\vec{\mu} = \gamma \cdot \vec{S}$

$\vec{S}$: $+\frac{\hbar}{2}$: Angular momentum of particle.

γ: gyromagnetic ratio

classic: related to particle's charge & mass.

by $\gamma = \frac{q}{2mc}$

more quantum: for e- $\gamma = -\frac{e}{2m_e c} \cdot g_e$

g_e: g-factor (~2) (Landé)

$\Rightarrow E = -\vec{\mu}\cdot\vec{B} = -\gamma \cdot \vec{S} \cdot \vec{B}$

$\Rightarrow \hat{H} = -\gamma \cdot \hat{S} \cdot \vec{B} \longrightarrow (B_x, B_y, B_z)$

$\hat{S}$: $(\hat{S}_x, \hat{S}_y, \hat{S}_z)$

since $\hat{S}_x = \frac{\hbar}{2}\hat{\sigma}_x$, $\hat{S}_y = \frac{\hbar}{2}\hat{\sigma}_y$. $\hat{S}_z = \frac{\hbar}{2}\hat{\sigma}_z$

$$\Rightarrow \hat{H} = -\frac{\hbar}{2}\gamma\cdot \underbrace{\hat{\sigma}}_{(\hat{\sigma}_x,\, \hat{\sigma}_y,\, \hat{\sigma}_z)}\cdot \vec{B}$$

$$\Rightarrow \hat{H} = -\frac{\hbar}{2}\cdot\gamma\cdot(\hat{\sigma}_x B_x + \hat{\sigma}_y B_y + \hat{\sigma}_z B_z)$$

$$= -\frac{\hbar}{2}\cdot\gamma\cdot\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} B_x + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} B_y + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} B_z\right]$$

$$= -\frac{\hbar}{2}\cdot\gamma\cdot\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}$$

Now. if $\vec{B}$ is static $\left(\frac{\partial \vec{B}}{\partial t} = 0\right)$

$\vec{B}$ is only along $z \Rightarrow B_z$.

$$\Rightarrow \hat{H} = -\frac{\hbar}{2}\cdot\gamma\,\hat{\sigma}_z\cdot B_z$$

$$\Rightarrow [\hat{H}, \hat{\sigma}_z] = 0$$

$\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ & $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

also, $\hat{\sigma}_z$ ($\hat{S}_z$) has eigen base kets. $|z;\pm\rangle$

Here, $\hat{\sigma}_z$ or $\hat{S}_z$ is $\hat{A}$. $|z;\pm\rangle$ is $\{|a'\rangle\}$

suppose $|\alpha; t_0\rangle = C_+|z;+\rangle + C_-|z;-\rangle$

what is $|\alpha, t_0; t\rangle = ?$ $(= \hat{u}\,|\alpha; t_0\rangle)$

$$\Rightarrow \hat{u}(t, \overset{0}{\overset{\|}{t_0}}) = e^{-\frac{i}{\hbar}\hat{H}t}$$

$$= e^{-\frac{i}{\hbar}\left(-\frac{\hbar}{2}\cdot\gamma\,\hat{\sigma}_z\cdot B_z\right)t}$$

$$= e^{\frac{i}{2}\gamma\cdot\hat{\sigma}_z B_z t} = e^{\frac{i}{\hbar}\gamma\cdot\hat{S}_z\cdot B_z\cdot t}$$

$$\hat{H}\cdot|z;+\rangle = E_{z+}|z;+\rangle \qquad \hat{H}\cdot|z;-\rangle = E_{z-}|z;-\rangle$$

$$-\gamma\cdot\hat{S}_z\cdot B_z|z;+\rangle = \boxed{-\gamma\cdot B_z\cdot\frac{\hbar}{2}}\cdot|z;+\rangle$$

$$E_{z+} = -\left(\frac{-e}{2m_e c}\cdot \overset{2}{g_e}\right)\cdot B_z\cdot\frac{\hbar}{2}$$

$$= \frac{B_z e}{2m_e c}\cdot\hbar$$

likewise $E_{z-} = -\frac{B_z e}{2m_e c}\cdot\hbar$

$$\Rightarrow |\alpha, t_0; t\rangle = \sum_{a'} C_{a'}\, e^{-\frac{i}{\hbar}E_{a'}t}\,|a'\rangle$$

$$\Rightarrow \left(e^{-\frac{i}{\hbar}\frac{B_z e}{2m_e c}\cdot\hbar\cdot t}\cdot C_+\cdot|z;+\rangle\right) + \left(e^{-\frac{i}{\hbar}\frac{-B_z e}{2m_e c}\cdot\hbar\cdot t}\cdot C_-\cdot|z;-\rangle\right)$$

$$= C_+ e^{-\frac{i\omega t}{2}}\cdot \overset{\begin{pmatrix}1\\0\end{pmatrix}}{|z;+\rangle} + C_- e^{\frac{i\omega t}{2}}\cdot \overset{\begin{pmatrix}0\\1\end{pmatrix}}{|z;-\rangle}$$

$$\left(\omega = \frac{B_z e}{m_e c}\right)$$

$$= \begin{pmatrix} C_+ e^{-i\omega t/2} \\ C_- e^{i\omega t/2}\end{pmatrix}$$

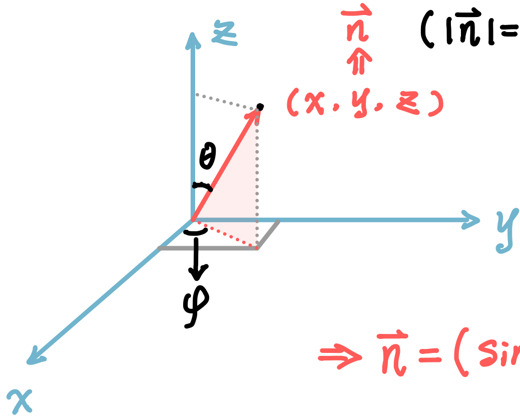
if $t=0 \Rightarrow |\alpha; t_0\rangle = \begin{pmatrix} C_+ \\ C_- \end{pmatrix}$

if $C_-=0 \Rightarrow |\alpha; t_0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |z;+\rangle$

⊛ NOTE: This is a very general case. Because $|x;\pm\rangle$ & $|y;\pm\rangle$ and other arbitrary forms can all be constructed by $|z;\pm\rangle$ based on C_+ & C_-.

Now, assuming we have an initial spin.

$$C_+|z;+\rangle + C_-|z;-\rangle \quad \text{or} \quad \begin{pmatrix} C_+ \\ C_- \end{pmatrix}$$



$\vec{n}$ $(|\vec{n}|=1)$
⇑
(x, y, z)

$$\Rightarrow \begin{cases} x = \sin\theta\cdot\cos\varphi \\ y = \sin\theta\cdot\sin\varphi \\ z = \cos\theta \end{cases}$$

$$\Rightarrow \vec{n} = (\sin\theta\cdot\cos\varphi,\ \sin\theta\cdot\sin\varphi,\ \cos\theta)$$

This initial state $\begin{pmatrix} C_+ \\ C_- \end{pmatrix}$ must be the eigen state of $\hat{\sigma}\cdot\vec{n}$ $= (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)(x, y, z)$ w/ eigenvalue of unit.

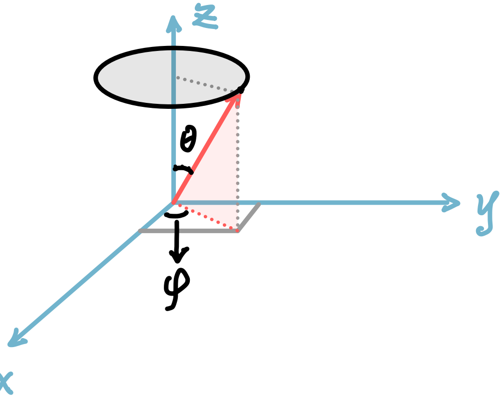
$$\Rightarrow \hat{\sigma}\cdot\vec{n}\begin{pmatrix} C_+ \\ C_- \end{pmatrix} = 1\cdot\begin{pmatrix} C_+ \\ C_- \end{pmatrix}$$

$\Rightarrow$ solve $\begin{pmatrix} c_+ \\ c_- \end{pmatrix} = \begin{pmatrix} e^{-i\varphi/2} \cos(\theta/2) \\ e^{i\varphi/2} \sin(\theta/2) \end{pmatrix} \begin{matrix} \rightarrow c_+ \\ \rightarrow c_- \end{matrix}$

Now $\Rightarrow |\alpha, t_0; t\rangle$

$$= \begin{pmatrix} c_+ e^{-i\omega t/2} \\ c_- e^{+i\omega t/2} \end{pmatrix}$$

$$= \begin{pmatrix} e^{\frac{-i(\omega t+\varphi)}{2}} \cos(\theta/2) \\ e^{\frac{i(\omega t+\varphi)}{2}} \sin(\theta/2) \end{pmatrix}$$



along z $\langle \hat{S}_z \rangle$

$$= \frac{\hbar}{2} |\langle z;+|\alpha, t_0; t\rangle|^2 + \left(-\frac{\hbar}{2}\right) |\langle z;-|\alpha, t_0; t\rangle|^2$$

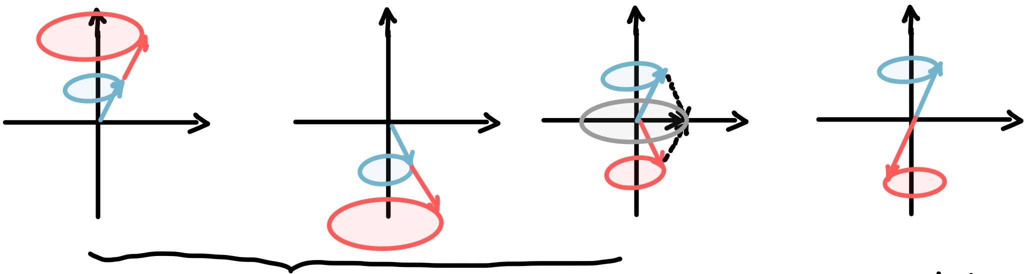
$$= \frac{\hbar}{2} \cdot \cos\theta$$

*. However along x & y

$\langle \hat{S}_x \rangle$ & $\langle \hat{S}_y \rangle$ will be related to cos or sin $(\omega t + \varphi)$

Triplet & Singlet

$(\uparrow\uparrow)$ $(\uparrow\downarrow)$



Triplet. Singlet

1.6 Correlation Amplitude.

$|\alpha; t_0\rangle$

Definition: $C(t) \equiv \langle \underline{\alpha} | \alpha, t_0; t\rangle$

$= \langle \alpha | \hat{u}(t,0) | \alpha\rangle$

How much $|\alpha, t_0; t\rangle$ resemble the initial state $|\alpha\rangle$

$\underline{|C(t)|}$ quantifies the similarity.

1) if $|\alpha\rangle = |a'\rangle$

$$\Rightarrow C(t) = \langle a' | \underline{a', t_0; t\rangle} = \langle a' | \underline{e^{-\frac{i}{\hbar}E_{a'}t} | a'\rangle}$$

$$= e^{-\frac{i}{\hbar}E_{a'}t}$$

$\Rightarrow |C(t)| = 1 \Rightarrow$ stationary state.