Precessão de Larmor

$$\begin{cases} H = H_0 + \left(\dfrac{e}{mc}\right)\vec{S}\cdot\vec{B} \\ l = 0 \\ B = B_0\hat{z} \quad (B_0 > 1\,T) \end{cases} \Longrightarrow H_0 + \frac{e}{mc}\overset{\frac{\hbar}{2}\sigma_z}{S_z}B_0 = i\hbar\frac{\partial\psi}{\partial t}$$

$$\begin{cases} \psi(\vec{r},s,t) = \psi(\vec{r})\,\chi_s(t)\,e^{-i\frac{E}{\hbar}t} \\ H_0\psi = E\psi \\ \chi_s(t) = \begin{pmatrix} \chi_+(t) \\ \chi_-(t) \end{pmatrix} \end{cases}$$

$$\cancel{\chi(H_0\psi)} + \psi\hbar\overbrace{\left(\frac{e}{2mc}\right)B_0}^{\omega_L \text{ (freq. de Larmor)}}\sigma_z\chi = \psi i\hbar\dot{\chi} + \cancel{(E\psi)\chi}$$

$$i\dot{\chi} = \omega_L\sigma_z\chi \Longrightarrow i\begin{pmatrix}\dot{\chi}_+ \\ \dot{\chi}_-\end{pmatrix} = \omega_L\begin{pmatrix}1 & 0 \\ 0 & -1\end{pmatrix}\begin{pmatrix}\chi_+ \\ \chi_-\end{pmatrix}$$

$$\begin{cases} i\dot{\chi}_+ = \omega_L\chi_+ \Rightarrow \chi_+ = c_+e^{-i\omega_L t} \\ i\dot{\chi}_- = -\omega_L\chi_- \Rightarrow \chi_- = c_-e^{i\omega_L t} \end{cases} \Longrightarrow \chi(t) = \begin{pmatrix} c_+e^{-i\omega_L t} \\ c_-e^{i\omega_L t}\end{pmatrix} = c_+e^{-i\omega_L t}\underbrace{\begin{pmatrix}1 \\ 0\end{pmatrix}}_{|+\rangle_z} + c_-e^{i\omega_L t}\underbrace{\begin{pmatrix}0 \\ 1\end{pmatrix}}_{|-\rangle_z}$$

$$\sigma_z = \begin{pmatrix}1 & 0 \\ 0 & -1\end{pmatrix} \begin{cases} |+\rangle_z = \begin{pmatrix}1 \\ 0\end{pmatrix} = \frac{1}{\sqrt{2}}\left(|+\rangle_x - |-\rangle_x\right) = \frac{1}{\sqrt{2}}\left(|+\rangle_y - i|-\rangle_y\right) \\ |-\rangle_z = \begin{pmatrix}0 \\ 1\end{pmatrix} = \frac{1}{\sqrt{2}}\left(|+\rangle_x + |-\rangle_x\right) = \frac{1}{\sqrt{2}}\left(-i|+\rangle_y + |-\rangle_y\right) \end{cases}$$

$$\sigma_x = \begin{pmatrix}0 & 1 \\ 1 & 0\end{pmatrix} \begin{cases} |+\rangle_x = \frac{1}{\sqrt{2}}\begin{pmatrix}1 \\ 1\end{pmatrix} = \frac{1}{\sqrt{2}}\left(|+\rangle_z + |-\rangle_z\right) = \frac{1}{2}\left[(1-i)|+\rangle_y + (1+i)|-\rangle_y\right] \\ |-\rangle_x = \frac{1}{\sqrt{2}}\begin{pmatrix}-1 \\ 1\end{pmatrix} = \frac{1}{\sqrt{2}}\left(-|+\rangle_z + |-\rangle_z\right). \end{cases}$$

$$\sigma_y = \begin{pmatrix}0 & -i \\ i & 0\end{pmatrix} \begin{cases} |+\rangle_y = \frac{1}{\sqrt{2}}\begin{pmatrix}1 \\ i\end{pmatrix} = \frac{1}{\sqrt{2}}\left(|+\rangle_z + i|-\rangle_z\right) \\ |-\rangle_y = \frac{1}{\sqrt{2}}\begin{pmatrix}i \\ 1\end{pmatrix} = \frac{1}{\sqrt{2}}\left(i|+\rangle_z + |-\rangle_z\right) \end{cases}$$

estado inicial

$$|\chi\rangle_0 = |+\rangle_x = \frac{1}{\sqrt{2}}\left(|+\rangle + |-\rangle\right) \Longrightarrow \begin{cases} c_+ = \frac{1}{\sqrt{2}} \\ c_- = 1/\sqrt{2} \end{cases} \Longrightarrow |\chi(t)\rangle = \frac{1}{\sqrt{2}}\left[e^{-i\omega_L t} \underset{\binom{1}{0}}{|+\rangle_z} + e^{i\omega_L t} \underset{\binom{0}{1}}{|-\rangle_z} \right]$$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\omega_0 t} \\ e^{-i\omega_0 t} \end{pmatrix}$$

$$|+\rangle_y = \frac{1}{\sqrt{2}}\, |+\rangle_z + i\,|-\rangle_z$$

$$\begin{cases} P\left(S_x = \hbar/2\right) = \left| {}_x\langle + | \chi(t)\rangle \right|^2 = \left| \underbrace{\frac{1}{2}\left(e^{-i\omega_L t} + e^{i\omega_L t}\right)}_{\cos\omega_L t} \right|^2 = \boxed{\cos^2\omega_L t} \\ P\left(S_x = -\hbar/2\right) = \operatorname{sen}^2 \omega_L t \end{cases}$$

$$P\left(S_y = \hbar/2\right) = \left| {}_y\langle + | \chi(t)\rangle \right|^2 = \left\| \frac{1}{2}\left(e^{-i\omega_L t} - i\, e^{i\omega_L t}\right)\right|^2 = \frac{1}{4}\left| \left(\cos\omega_L t + \operatorname{sen}\omega_L t\right) - i\left(\cos\omega_L t + \operatorname{sen}\omega_L t\right)\right|^2$$

$$= \frac{1}{4}\left|\left(\cos\omega_L t + \operatorname{sen}\omega_L t\right)(1-i)\right|^2 = \frac{1}{2}\left(\cos\omega_L t + \operatorname{sen}\omega_L t\right)^2 = \frac{1}{2}\left(\underbrace{\cos^2\omega_L t + \operatorname{sen}^2\omega_L t}_{1} + \underbrace{2\operatorname{sen}\omega_L t\cos\omega_L t}_{\operatorname{sen} 2\omega_L t} \right)$$

$$= \frac{1 + \operatorname{sen} 2\omega_L t}{2}$$

$$P\left(S_y = -\hbar/2\right) = \frac{1 - \operatorname{sen} 2\omega_L t}{2}$$

$$\begin{cases} P\left(S_z = \hbar/2\right) = \frac{1}{2} \\ P\left(S_z = -\hbar/2\right) = 1/2 \end{cases}$$

$$\langle S_x\rangle = P(S_x=\hbar/2)\frac{\hbar}{2} + P(S_x=-\hbar/2)(-\hbar/2) = \frac{\hbar}{2}\left(\cos^2\omega_0 t - \sin^2\omega_0 t\right) = \frac{\hbar}{2}\cos 2\omega_0 t \qquad \chi(t) = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\omega_0 t} \\ e^{i\omega_0 t}\end{pmatrix}$$

$$\langle S_x\rangle = \langle\chi|S_x|\chi\rangle = \frac{\hbar}{4}\left(e^{i\omega_0 t} \quad e^{-i\omega_0 t}\right)\underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0\end{pmatrix}\begin{pmatrix} e^{-i\omega_0 t} \\ e^{i\omega_0 t}\end{pmatrix}}_{\begin{pmatrix} e^{i\omega_0 t} \\ e^{-i\omega_0 t}\end{pmatrix}} = \frac{\hbar}{4}\left(\underbrace{e^{2i\omega_0 t} + e^{-2i\omega_0 t}}_{2\cos 2\omega_0 t}\right) = \frac{\hbar}{2}\cos 2\omega_0 t$$

$$\langle S_y\rangle = P(S_y=\hbar/2)\hbar/2 + P(S_y=-\hbar/2)(-\hbar/2) = \frac{\hbar}{2}\left[\frac{1+\sin 2\omega_0 t}{2} - \frac{(1-\sin 2\omega_0 t)}{2}\right] = \frac{\hbar}{2}\sin 2\omega_0 t$$

$$\langle S_y\rangle = \langle\chi|S_y|\chi\rangle = \frac{\hbar}{4}\left(e^{i\omega_0 t} \quad e^{-i\omega_0 t}\right)\underbrace{\begin{pmatrix} 0 & -i \\ i & 0\end{pmatrix}\begin{pmatrix} e^{-i\omega_0 t} \\ e^{i\omega_0 t}\end{pmatrix}}_{\begin{pmatrix} -i e^{i\omega_0 t} \\ i e^{-i\omega_0 t}\end{pmatrix}} = \frac{\hbar}{4}\left(-i e^{2i\omega_0 t} + i e^{-2i\omega_0 t}\right)$$

$$= \frac{\hbar}{2}\left(\frac{e^{2i\omega_0 t} - e^{-2i\omega_0 t}}{2i}\right) = \frac{\hbar}{2}\sin 2\omega_0 t$$

$$\langle S_z\rangle = P(S_z=\hbar/2)\hbar/2 + P(S_z=-\hbar/2)(-\hbar/2)$$

$$= \frac{\hbar}{2}\left(1/2 - 1/2\right) = 0$$

$$\langle S_z\rangle = \langle\chi|S_z|\chi\rangle = \frac{\hbar}{4}\left(e^{i\omega_0 t} \quad e^{-i\omega_0 t}\right)\underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1\end{pmatrix}\begin{pmatrix} e^{-i\omega_0 t} \\ e^{i\omega_0 t}\end{pmatrix}}_{\begin{pmatrix} e^{-i\omega_0 t} \\ -e^{i\omega_0 t}\end{pmatrix}} = \frac{\hbar}{4}\left(\cancel{e^{0}} - 1\right) = 0$$

$$S_x^2 = \frac{\hbar^2}{4}\overset{1}{\sigma_x^2} = \frac{\hbar^2}{4} \Rightarrow \langle S_x^2\rangle = \langle S_y^2\rangle = \langle S_z^2\rangle = \frac{\hbar^2}{4}$$

$$(\Delta S_x)^2 = \frac{\hbar^2}{4} - \frac{\hbar^2}{4}\cos^2\omega_L t = \frac{\hbar^2}{4}\left(1 - \cos^2 2\omega_L t\right) = \frac{\hbar^2}{4}\sin^2 2\omega_L t \Rightarrow \boxed{\Delta S_x = \frac{\hbar}{2}\sin 2\omega_L t}$$

$$(\Delta S_y)^2 = \frac{\hbar^2}{4} - \frac{\hbar^2}{4}\sin^2\omega_L t = \frac{\hbar^2}{4}\left(1 - \sin^2 2\omega_L t\right) = \frac{\hbar^2}{4}\cos^2 2\omega_L t \Rightarrow \boxed{\Delta S_y = \frac{\hbar}{2}\cos 2\omega_L t}$$

$$(\Delta S_z)^2 = \frac{\hbar^2}{4} \Rightarrow \boxed{\Delta S_z = \frac{\hbar}{2}}$$

Ressonância magnética de spin

$$\begin{cases} H = H_0 + \left(\dfrac{e}{mc}\right)\vec{S}\cdot\vec{B} = H_0 + \dfrac{\hbar}{2}\left(\dfrac{e}{mc}\right)\vec{\sigma}\cdot\vec{B} \quad (l=0) \\ \vec{B} = B_0\hat{z} + B_1(\hat{x}\cos\omega t + \hat{y}\,\mathrm{sen}\,\omega t) \end{cases}$$

(campo girante)

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

$$\Psi(\vec{r},s,t) = \psi(\vec{r})\,\chi(t)\,e^{-i\frac{E}{\hbar}t}$$

$$H_0\psi = E\psi$$

$$\chi(t) = \begin{pmatrix} \chi_+(t) \\ \chi_-(t) \end{pmatrix}$$

$$H = H_0 + \frac{\hbar}{2}\Big(\overbrace{\frac{e}{mc}B_0}^{\omega_0}\Big)\sigma_z + \frac{\hbar}{2}\Big(\overbrace{\frac{e}{mc}B_1}^{\omega_1}\Big)\sigma_x\cos\omega t + \frac{\hbar}{2}\Big(\overbrace{\frac{e}{mc}B_1}^{\omega_1}\Big)\sigma_y\,\mathrm{sen}\,\omega t$$

$$= H_0 + \frac{\hbar\omega_0}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} + \frac{\hbar\omega_1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\cos\omega t + \frac{\hbar\omega_1}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\mathrm{sen}\,\omega t$$

$$H = H_0 + \underbrace{\begin{pmatrix}\hbar\omega_0/2 & \hbar\omega_1/2\, e^{-i\omega t}\\ \hbar\omega_1/2\, e^{i\omega t} & -\hbar\omega_0/2\end{pmatrix}}_{V(t)} = H_0 + V(t)$$

$$\boxed{i\hbar\dot{\chi} = V(t)\,\chi(t)}$$

$$\begin{cases} B_1 = 0 \\ \chi \sim \begin{pmatrix} c_+\, e^{-i\frac{\omega_0}{2}t} \\ c_-\, e^{i\omega_0\frac{t}{2}} \end{pmatrix} \end{cases} \qquad c_+, c_- \ (\text{cte})$$

$$\begin{cases} B_1 \neq 0 \\ \chi_+ = c_+(t)\, e^{-i\omega\frac{t}{2}} \\ \chi_- = c_-(t)\, e^{i\omega\frac{t}{2}} \end{cases} \Rightarrow i\hbar\begin{pmatrix}\dot{\chi}_+\\ \dot{\chi}_-\end{pmatrix} = \begin{pmatrix}\hbar\omega_0/2 & \hbar\omega_1/2\, e^{-i\omega t}\\ \hbar\omega_1/2\, e^{i\omega t} & -\hbar\omega_0/2\end{pmatrix}\begin{pmatrix} c_+(t)\, e^{-i\omega t/2} \\ c_-(t)\, e^{i\omega t/2}\end{pmatrix}$$

$$i\hbar \dot{x}_+ = \frac{\hbar\omega}{2} c_+(t) \cancel{e^{-i\omega t/2}} + i\hbar \dot{c}_+(t) \cancel{e^{-i\omega t/2}} = \frac{\hbar\omega_0}{2} c_+(t) \cancel{e^{-i\omega t/2}} + \frac{\hbar\omega_1}{2} e^{-i\omega t} \underbrace{c_-(t) e^{i\omega t/2}}_{\cancel{e^{-i\omega t/2}}}$$

$$\boxed{i \dot{c}_+ = \left(\frac{\omega_0 - \omega}{2}\right) c_+ + \frac{\omega_1}{2} c_-}$$

$$i\hbar \dot{x}_- = -\frac{\hbar\omega}{2} c_-(t) \cancel{e^{i\omega t/2}} + i\hbar \dot{c}_-(t) \cancel{e^{i\omega t/2}} = \frac{\hbar\omega_1}{2} e^{i\omega t} \underbrace{c_+(t) e^{-i\omega t/2}}_{\cancel{e^{i\omega t/2}}} - \frac{\hbar\omega_0}{2} c_- \cancel{e^{i\omega t/2}}$$

$$\boxed{i \dot{c}_- = \frac{\omega_1}{2} c_+ - \left(\frac{\omega_0 - \omega}{2}\right) c_+}$$

$$i \frac{d}{dt} \underbrace{\begin{pmatrix} c_+ \\ c_- \end{pmatrix}}_{c} = \frac{1}{2} \underbrace{\begin{pmatrix} \Delta\omega & \omega_1 \\ \omega_1 & -\Delta\omega \end{pmatrix}}_{A(\omega)} \underbrace{\begin{pmatrix} c_+ \\ c_- \end{pmatrix}}_{c} \qquad (\Delta\omega = \omega_0 - \omega)$$

$$c = \begin{pmatrix} a \\ b \end{pmatrix} e^{\frac{\lambda}{2} t} \implies i \frac{\lambda}{\cancel{2}} \begin{pmatrix} a \\ b \end{pmatrix} = \frac{1}{\cancel{2}} \begin{pmatrix} \Delta\omega & \omega_1 \\ \omega_1 & -\Delta\omega \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} \implies \underbrace{\begin{pmatrix} \Delta\omega - i\lambda & \omega_1 \\ \omega_1 & -\Delta\omega - i\lambda \end{pmatrix}}_{B} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

$$\det B = 0 \implies -\Delta\omega^2 - \lambda^2 - \omega_1^2 = 0 \implies \lambda = \pm i \underbrace{\sqrt{\omega_1^2 + \Delta\omega^2}}_{\Omega} = \pm i\Omega \qquad (\Omega^2 = \omega_1^2 + \Delta\omega^2)$$

$$\underline{\lambda_1 = i\Omega} \qquad \begin{pmatrix} \Delta\omega & \omega_1 \\ \omega_1 & -\Delta\omega \end{pmatrix} \begin{pmatrix} a_1 \\ b_1 \end{pmatrix} = -\Omega \begin{pmatrix} a_1 \\ b_1 \end{pmatrix} \Rightarrow (\Delta\omega + \Omega)\, a_1 = -\omega_1 b_1 \Rightarrow a_1 = \frac{-\omega_1}{(\Delta\omega + \Omega)}\, b_1$$

$$\underline{\lambda_2 = -i\Omega} \qquad \begin{pmatrix} \Delta\omega & \omega_1 \\ \omega_1 & -\Delta\omega \end{pmatrix} \begin{pmatrix} a_2 \\ b_2 \end{pmatrix} = \Omega \begin{pmatrix} a_2 \\ b_2 \end{pmatrix} \Rightarrow (\Delta\omega - \Omega)\, a_2 = -\omega_1 b_2 \Rightarrow a_2 = \frac{-\omega_1}{(\Delta\omega - \Omega)}\, b_2$$

solução geral

$$\begin{cases} c_+(t) = \dfrac{-\omega_1}{(\Delta\omega + \Omega)}\, b_1\, e^{i\frac{\Omega}{2}t} - \dfrac{\omega_1}{(\Delta\omega - \Omega)}\, b_2\, e^{-i\frac{\Omega}{2}t} \\[2ex] c_-(t) = b_1\, e^{i\frac{\Omega}{2}t} + b_2\, e^{-i\frac{\Omega}{2}t} \end{cases}$$

condições iniciais

$$\begin{cases} P(S_z = \hbar/2) = |c_+(0)|^2 = 1 \\[1ex] |c_-(0)|^2 = 0 \Rightarrow c_-(0) = 0 \Rightarrow b_2 = -b_1 \Rightarrow \boxed{c_- = 2i\, b_1 \sin\frac{\Omega}{2} t} \end{cases}$$

$$\begin{cases} c_+(t) = \omega_1 b_1 \left[\dfrac{-1}{\Delta\omega + \Omega}\, e^{i\frac{\Omega}{2}t} + \dfrac{1}{\Delta\omega - \Omega}\, e^{-i\frac{\Omega}{2}t} \right] \\[2ex] c_+^*(t) = \omega_1 b_1 \left[\dfrac{-1}{\Delta\omega + \Omega}\, e^{-i\frac{\Omega}{2}t} + \dfrac{1}{\Delta\omega - \Omega}\, e^{i\frac{\Omega}{2}t} \right] \end{cases}$$

$$|c_+(t)|^2 = \omega_1^2 b_1^2 \left[\underbrace{\frac{1}{(\Delta\omega + \Omega)^2} + \frac{1}{(\Delta\omega - \Omega)^2}}_{\frac{2(\Delta\omega^2 + \Omega^2)}{\omega_1^4}} \underbrace{- \frac{1}{\Delta\omega^2 - \Omega^2}\, e^{-i\Omega t} - \frac{1}{\Delta\omega^2 - \Omega^2}\, e^{i\Omega t}}_{-\frac{2}{\Delta\omega^2 - \Omega^2} \cos\Omega t} \right] = 2 b_1^2 \left[\frac{\Delta\omega^2 + \Omega^2}{\omega_1^2} + \cos\Omega t \right]$$

$$|c_+(0)|^2 = \frac{2b_1^2}{\omega_1^2}\left(\Delta\omega^2 + \overbrace{\Omega^2 + \omega_1^2}^{\Omega^2}\right) = 1 = \left(\frac{2\,b_1\Omega}{\omega_1}\right)^2 \Rightarrow \boxed{b_1 = \frac{\omega_1}{2\Omega}}$$

$$|c_-(t)|^2 = P(S_z = -\hbar/2) = \underbrace{\left(\frac{\omega_1}{\Omega}\right)^2}_{A(\omega)} \operatorname{sen}^2\frac{\Omega t}{2}$$

(fórmula de Rabi)

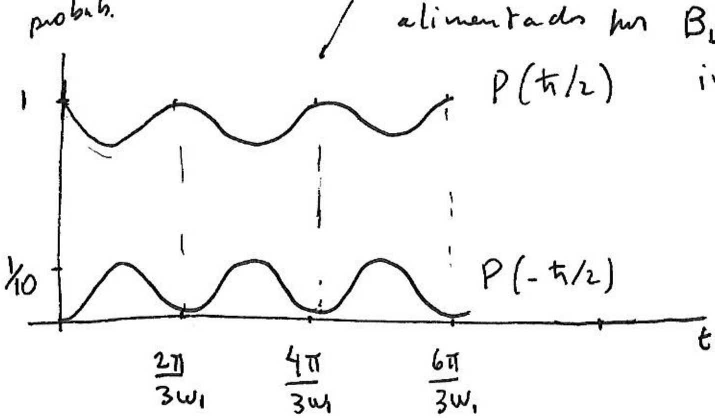
$$\Omega(\omega) = \sqrt{\omega_1^2 + (\omega_0-\omega)^2}$$

$$A(\omega) = \frac{\omega_1^2}{\omega_1^2 + (\omega_0-\omega)^2}$$

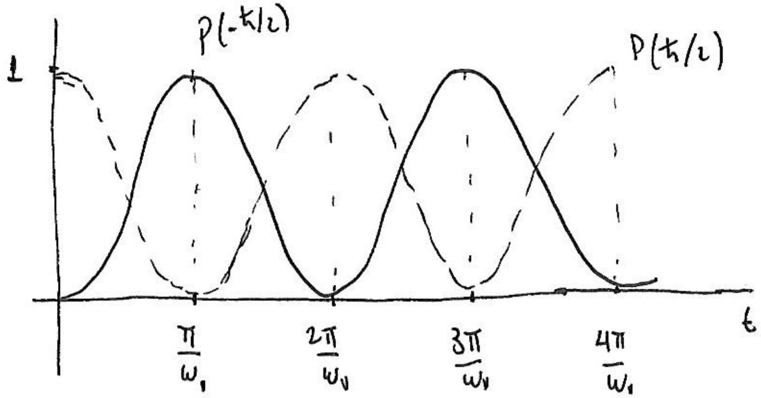
$B_1 \ll B_0\ (\sim 1\,T)$

- $\nu_0 \sim 10\,GHz$ (microondas) $\Rightarrow \omega_0 \sim 10^{11}s^{-1}$ (ESR)
- $\nu_0 \sim 5\,MHz$ (r. f.) $\Rightarrow \omega_0 \sim 10^{8}s^{-1}$ (NMR)

$\Delta\omega \sim 3\omega_1 \Rightarrow \begin{cases} A \sim 1/10 \\ \Omega \sim 3\omega_1 \end{cases}$



ressonância $(\omega = \omega_0)$ $\begin{cases} A(\omega_0) = 1 \\ \Omega = \omega_1 \end{cases}$



- mesmo um campo fraco ($B_1 \ll B_0$) é capaz de reverter o sentido do spin