Quantum Mechanics for NMR (II)

Frank Eisenmenger

Department of Structural Biology
Leibniz-Institut für Molekulare Pharmakologie (FMP)
Robert-Rössle-Str. 10, 13125 Berlin

eisenmenger@fmp-berlin.de

May 25, 2009

Outline

Measurement and Dynamics

Measurement of observable Q in quantum state $|\Psi\rangle = \sum_n c_n |\varphi_n\rangle$ yields one of its eigenvalues ε_n with **probability** $|c_n|^2$.
After the measurement the system remains in eigenstate $|\varphi_n\rangle$.

Postulate

In a **closed** *quantum system the time evolution (dynamics) of states is generated by the Hamiltonian* $\mathbf{H}$

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = \mathbf{H}|\Psi(t)\rangle \qquad \textit{(E. Schrödinger, 1926)}$$

with solution $|\Psi(t)\rangle = e^{-\frac{i}{\hbar}\mathbf{H}t}|\Psi(0)\rangle \quad (\mathbf{H} = \mathbf{H}^\dagger)$

$\mathbf{H}$ time-**in**dependent: $\mathbf{H}|\psi_n\rangle = E_n|\psi_n\rangle$

$|\psi_n(t)\rangle = e^{-\frac{i}{\hbar}E_n t}|\psi_n\rangle$ "stationary states"

Evolution of the Density Operator

$$\boldsymbol{\rho} = \sum_i p_i |\Psi_i\rangle\langle\Psi_i| = \left| |\Psi\rangle = \sum_j c_j |\varphi_j\rangle \right|$$
$$= \sum_i p_i \sum_{j,k} c_j^* c_k |\varphi_j\rangle\langle\varphi_k| = \sum_{j,k} \overline{c_j^* c_k} |\varphi_j\rangle\langle\varphi_k|$$

$$\frac{d\boldsymbol{\rho}}{dt} = \sum_i p_i \left(\frac{d|\Psi_i\rangle}{dt}\langle\Psi_i| + |\Psi_i\rangle\frac{d\langle\Psi_i|}{dt} \right)$$
$$= \frac{1}{\mathrm{i}\hbar} \sum_i p_i \left\{ (\mathbf{H}|\Psi_i\rangle)\langle\Psi_i| - |\Psi_i\rangle(\langle\Psi_i|\mathbf{H}) \right\}$$
$$= \frac{1}{\mathrm{i}\hbar} (\mathbf{H}\boldsymbol{\rho} - \boldsymbol{\rho}\mathbf{H})$$

Conclusion

$i\hbar \frac{d\boldsymbol{\rho}}{dt} = [\mathbf{H}, \boldsymbol{\rho}]$ *(Liouville - von Neumann equation)*

with solution $\boldsymbol{\rho}(t) = e^{-\frac{i}{\hbar}\mathbf{H}t} \boldsymbol{\rho}(0)\, e^{\frac{i}{\hbar}\mathbf{H}t}$

Spin dynamics: General case

Consider observable Q $(= Q^\dagger)$ for states $|\Psi(t)\rangle$ $(\langle\Psi|\,\Psi\rangle = 1,\ \forall t)$:

$$\frac{d\langle Q\rangle}{dt} = \frac{d\langle\Psi(t)|Q|\Psi(t)\rangle}{dt} = \frac{1}{\mathrm{i}\hbar}\langle\Psi(t)|\,Q\mathbf{H} - \mathbf{H}Q\,|\Psi(t)\rangle + \left\langle\Psi(t)\right|\frac{dQ}{dt}\left|\Psi(t)\right\rangle$$

$$\rightarrow \frac{d\langle Q\rangle}{dt} = \frac{1}{\mathrm{i}\hbar}\langle[Q,\mathbf{H}]\rangle + \left\langle\frac{dQ}{dt}\right\rangle$$

Proposition

Spin 1/2 magnetic moment $\boldsymbol{\mu}$ *in field* $\mathbf{B}$*:* $\quad \mathbf{H} = -\mathbf{B}\cdot\boldsymbol{\mu} = -\frac{\hbar\gamma}{2}\mathbf{B}\cdot\boldsymbol{\sigma}$

With $\frac{d\boldsymbol{\sigma}_i}{dt} = 0$:

$$\begin{aligned}
\frac{d\langle\boldsymbol{\sigma}_1\rangle}{dt} &= \frac{\mathrm{i}\gamma}{2}\langle[\boldsymbol{\sigma}_1,(\mathrm{B}_1\boldsymbol{\sigma}_1 + \mathrm{B}_2\boldsymbol{\sigma}_2 + \mathrm{B}_3\boldsymbol{\sigma}_3)]\rangle \\
&= \gamma(\mathrm{B}_3\langle\boldsymbol{\sigma}_2\rangle - \mathrm{B}_2\langle\boldsymbol{\sigma}_3\rangle) \\
\frac{d\langle\boldsymbol{\sigma}_2\rangle}{dt} &= \gamma(\mathrm{B}_1\langle\boldsymbol{\sigma}_3\rangle - \mathrm{B}_3\langle\boldsymbol{\sigma}_1\rangle) \\
\frac{d\langle\boldsymbol{\sigma}_3\rangle}{dt} &= \gamma(\mathrm{B}_2\langle\boldsymbol{\sigma}_1\rangle - \mathrm{B}_1\langle\boldsymbol{\sigma}_2\rangle)
\end{aligned}$$

Conclusion

Evolution of average magnetic moment in field $\mathbf{B}$

$$\frac{d\langle\boldsymbol{\mu}\rangle}{dt} = \gamma\langle\boldsymbol{\mu}\rangle\times\mathbf{B}$$

Bloch equations: Relaxation

Relaxation: establish thermodynamic equilibrium of spin system due to its interaction & energy exchange with (1) "lattice" in thermal motion (heat reservior), and (2) neighbouring spins (**direct** dipolar coupling).

Magnetic moment of N spins (bulk magnetization): $\mathbf{M} = \sum_n^N \boldsymbol{\mu}_n$

(1) Spin-lattice ("longitudinal") relaxation: return equilibrium **excess** of spins in "ground state" ($M_0 = n_0 N \mu_z, n_0 \sim 10^{-5}$) at rate $\frac{1}{T_1}$:

$$\frac{dM_z(t)}{dt} = \gamma\left[M_x(t)B_y(t) - M_y(t)B_x(t)\right] + \frac{M_0 - M_z(t)}{T_1}$$

(2) Spin-spin ("transversal") relaxation: x- and y-magnetizations vanish at rate $\frac{1}{T_2}$:

$$\frac{dM_x(t)}{dt} = \gamma\left[M_y(t)B_z(t) - M_z(t)B_y(t)\right] - \frac{M_x(t)}{T_2}$$
$$\frac{dM_y(t)}{dt} = \gamma\left[M_z(t)B_x(t) - M_x(t)B_z(t)\right] - \frac{M_y(t)}{T_2}$$

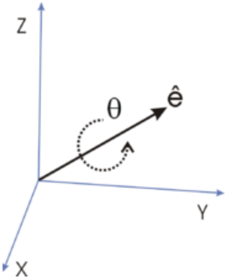
(F. Bloch, 1946)

Rotations in 3D

Rotate vector $\mathbf{r}$ about axis $\hat{\mathbf{e}}$ ($|\hat{\mathbf{e}}| = 1$) by angle θ
(O. Rodrigues, 1840)

$$\mathbf{r}' = \mathrm{c}\ \mathbf{r} + (1 - \mathrm{c})(\hat{\mathbf{e}} \cdot \mathbf{r})\ \hat{\mathbf{e}} + \mathrm{s}\ \hat{\mathbf{e}} \times \mathbf{r} = \mathbf{R}_{\hat{\mathbf{e}}}(\theta)\ \mathbf{r}$$

where $\mathrm{s} \equiv \sin\theta$, $\mathrm{c} \equiv \cos\theta$,



with matrix

$$\mathbf{R}_{\hat{\mathbf{e}}}(\theta) = \begin{pmatrix} e_1^2(1-\mathrm{c}) + \mathrm{c} & e_1 e_2(1-\mathrm{c}) - e_3\mathrm{s} & e_1 e_3(1-\mathrm{c}) + e_2\mathrm{s} \\ e_1 e_2(1-\mathrm{c}) + e_3\mathrm{s} & e_2^2(1-\mathrm{c}) + \mathrm{c} & e_2 e_3(1-\mathrm{c}) - e_1\mathrm{s} \\ e_1 e_3(1-\mathrm{c}) - e_2\mathrm{s} & e_2 e_3(1-\mathrm{c}) + e_1\mathrm{s} & e_3^2(1-\mathrm{c}) + \mathrm{c} \end{pmatrix}$$

Example: Rotation about z-axis $\hat{\mathbf{e}} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$: $\quad \mathbf{R}_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Passive rotation =new vector coordinates after **rotation of coordinate system** as $\mathbf{R}(-\theta)\mathbf{r}$, i.e. changing sign of factors "$\sin\theta$".

Symmetry Transformations

Symmetry operator $\mathbf{U}$: $|\Psi'\rangle = \mathbf{U}\,|\Psi\rangle,\ Q' = \mathbf{U}Q\mathbf{U}^\dagger$ conserves:

– *transition probabilities* $p_{\Psi\to\Phi} = |\langle\Phi|\,\Psi\rangle|^2$

$$\curvearrowright\ \mathbf{U}\mathbf{U}^\dagger = \mathbf{I} \to \mathbf{U}^{-1} = \mathbf{U}^\dagger \quad \text{(unitarity)}$$

– *mean & eigenvalues* $\langle Q\rangle = \langle\Psi|\,Q\,|\Psi\rangle,$

$$Q = \sum_n \varepsilon_n\,|\varphi_n\rangle\,\langle\varphi_n|$$

$$\curvearrowright\ [\mathbf{U}, Q] = 0$$

Theorem

$Q = Q^\dagger$: *unitary* $\mathbf{U}(\tau) = e^{i\tau Q} = \sum_n e^{i\varepsilon_n\tau}\,|\varphi_n\rangle\,\langle\varphi_n|\,,\ \tau\in\mathbb{R}$

with $\mathbf{U}(-\tau) = \mathbf{U}^{-1}(\tau)$, $\mathbf{U}(\varsigma)\mathbf{U}(\tau) = \mathbf{U}(\varsigma+\tau)$ *(M.H. Stone, 1930)*

Rotations in $\mathbb{C}^2$

Stones' theorem with $\tau = \frac{\theta}{2}, Q = \boldsymbol{\sigma}_3$:

$$\mathbf{U}_3(\tfrac{\theta}{2}) = e^{\mathrm{i}\frac{\theta}{2}\boldsymbol{\sigma}_3} = e^{\mathrm{i}\frac{\theta}{2}} \left|\alpha\right\rangle \left\langle\alpha\right| + e^{-\mathrm{i}\frac{\theta}{2}} \left|\beta\right\rangle \left\langle\beta\right| = \begin{pmatrix} e^{\mathrm{i}\frac{\theta}{2}} & 0 \\ 0 & e^{-\mathrm{i}\frac{\theta}{2}} \end{pmatrix}$$

Given $\mathbf{r}$ in (X, Y, Z) - rotate **axes** X & Y about Z by θ (**passive** rotation of $\mathbf{r}$) $\rightarrow$ coordinates of $\mathbf{r}$ in (X', Y', Z) :

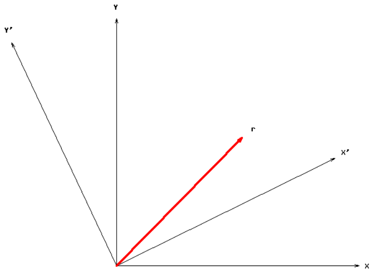
$$\mathbf{r}' = \mathbf{R}_z(-\theta)\mathbf{r} = \begin{pmatrix} r_1 \cos\theta + r_2 \sin\theta \\ -r_1 \sin\theta + r_2 \cos\theta \\ r_3 \end{pmatrix}$$

equivalent to

$$\mathbf{U}_3(\tfrac{\theta}{2}) \begin{pmatrix} r_3 & r_1 - \mathrm{i}r_2 \\ r_1 + \mathrm{i}r_2 & -r_3 \end{pmatrix} \mathbf{U}_3^{-1}(\tfrac{\theta}{2}) =$$

$$\begin{pmatrix} r_3 & (r_1 - \mathrm{i}r_2)e^{\mathrm{i}\theta} \\ (r_1 + \mathrm{i}r_2)e^{-\mathrm{i}\theta} & -r_3 \end{pmatrix}$$

Rotating frame



Note: $\mathbf{R}_z(-\theta) \in \mathbb{R}^3 \longleftrightarrow \mathbf{U}_3(\frac{\theta}{2}) \in \mathbb{C}^2$

Rotations in $\mathbb{C}^2$ (2)

$$\mathbf{R}_1(\phi) = e^{-\mathrm{i}\frac{\phi}{2}\boldsymbol{\sigma}_1}$$
$$= \frac{1}{2}\left[e^{-\mathrm{i}\frac{\phi}{2}}\left(|\alpha\rangle + |\beta\rangle\right)\left(\langle\alpha| + \langle\beta|\right) + e^{\mathrm{i}\frac{\phi}{2}}\left(|\alpha\rangle - |\beta\rangle\right)\left(\langle\alpha| - \langle\beta|\right)\right]$$
$$= \begin{pmatrix} \cos\frac{\phi}{2} & -\mathrm{i}\sin\frac{\phi}{2} \\ -\mathrm{i}\sin\frac{\phi}{2} & \cos\frac{\phi}{2} \end{pmatrix} \quad \curvearrowright \quad \mathbf{R}_1^{-1}(\phi) = \begin{pmatrix} \cos\frac{\phi}{2} & \mathrm{i}\sin\frac{\phi}{2} \\ \mathrm{i}\sin\frac{\phi}{2} & \cos\frac{\phi}{2} \end{pmatrix}$$

$$\mathbf{R}_2(\chi) = e^{-\mathrm{i}\frac{\chi}{2}\boldsymbol{\sigma}_2}$$
$$= \frac{1}{2}\left[e^{-\mathrm{i}\frac{\chi}{2}}\left(|\alpha\rangle + \mathrm{i}\,|\beta\rangle\right)\left(\langle\alpha| - \mathrm{i}\,\langle\beta|\right) + e^{\mathrm{i}\frac{\chi}{2}}\left(\mathrm{i}\,|\alpha\rangle + |\beta\rangle\right)\left(-\mathrm{i}\,\langle\alpha| + \langle\beta|\right)\right]$$
$$= \begin{pmatrix} \cos\frac{\chi}{2} & -\sin\frac{\chi}{2} \\ \sin\frac{\chi}{2} & \cos\frac{\chi}{2} \end{pmatrix} \quad \curvearrowright \quad \mathbf{R}_2^{-1}(\chi) = \begin{pmatrix} \cos\frac{\chi}{2} & \sin\frac{\chi}{2} \\ -\sin\frac{\chi}{2} & \cos\frac{\chi}{2} \end{pmatrix}$$

$$\mathbf{R}_3(\theta) = e^{-\mathrm{i}\frac{\theta}{2}\boldsymbol{\sigma}_3} = e^{-\mathrm{i}\frac{\theta}{2}}\,|\alpha\rangle\,\langle\alpha| + e^{\mathrm{i}\frac{\theta}{2}}\,|\beta\rangle\,\langle\beta|$$
$$= e^{-\mathrm{i}\frac{\theta}{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix}(1\ \ 0) + e^{\mathrm{i}\frac{\theta}{2}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}(0\ \ 1) = \begin{pmatrix} e^{-\mathrm{i}\frac{\theta}{2}} & 0 \\ 0 & e^{\mathrm{i}\frac{\theta}{2}} \end{pmatrix}$$
$$= \begin{pmatrix} \cos\frac{\theta}{2} - \mathrm{i}\sin\frac{\theta}{2} & 0 \\ 0 & \cos\frac{\theta}{2} + \mathrm{i}\sin\frac{\theta}{2} \end{pmatrix} \quad \curvearrowright \quad \mathbf{R}_3^{-1}(\theta) = \begin{pmatrix} e^{\mathrm{i}\frac{\theta}{2}} & 0 \\ 0 & e^{-\mathrm{i}\frac{\theta}{2}} \end{pmatrix}$$

Bloch vector

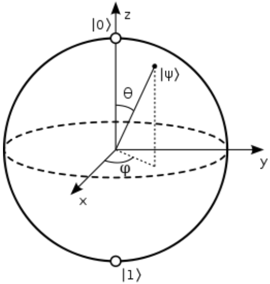
1) $\rho = \sum_j p_j \left|\Psi_j\right\rangle \left\langle\Psi_j\right|$

$$\langle \boldsymbol{\sigma}_i \rangle = \mathrm{Tr}(\rho \boldsymbol{\sigma}_i) = \sum_j p_j \left\langle\Psi_j\right| \boldsymbol{\sigma}_i \left|\Psi_j\right\rangle = \sum_j p_j \sigma_{ij} \equiv b_i$$

2) $\rho = \frac{1}{2}\left(\mathbf{I} + b_1 \boldsymbol{\sigma}_1 + b_2 \boldsymbol{\sigma}_2 + b_3 \boldsymbol{\sigma}_3\right):\quad \langle \boldsymbol{\sigma}_i \rangle = \mathrm{Tr}(\rho \boldsymbol{\sigma}_i) \equiv b_i$

$\rightarrow$ **Bloch vector** $\mathbf{b} \equiv \langle \boldsymbol{\sigma} \rangle = \frac{2}{\hbar\gamma} \langle \boldsymbol{\mu} \rangle$ $=$ **average magnetization**

Bloch sphere (Qubit)



$$\mathbf{b} = \begin{pmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{pmatrix}$$

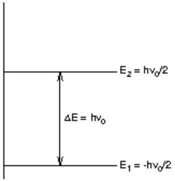
$$\mathbf{b}\cdot\boldsymbol{\sigma} = \begin{pmatrix} \cos\theta & e^{-i\varphi}\sin\theta \\ e^{i\varphi}\sin\theta & -\cos\theta \end{pmatrix}$$

eigenvector $=$ **any** spin-1/2 state:

$$|\Psi\rangle = \cos\frac{\theta}{2}|\alpha\rangle + e^{i\varphi}\sin\frac{\theta}{2}|\beta\rangle$$

Larmor precession

$$\mathbf{H}_0 = -\mathrm{B}_0 \boldsymbol{\mu}_3 = -\frac{\hbar\gamma}{2}\mathrm{B}_0\boldsymbol{\sigma}_3 \quad \text{(Zeeman Hamiltonian)}$$
$$= |\gamma > 0: \ \omega_0 \equiv \gamma \mathrm{B}_0| = -\frac{\hbar}{2}\begin{pmatrix}\omega_0 & 0 \\ 0 & -\omega_0\end{pmatrix}$$



$\curvearrowright$ 2 eigenstates $|\alpha\rangle: \ E_1 = -\frac{\hbar\omega_0}{2}$
$|\beta\rangle: \ E_2 = \frac{\hbar\omega_0}{2}$

Spin-1/2 evolution $\quad |\Psi(t)\rangle = e^{-\frac{\mathrm{i}}{\hbar}\mathbf{H}_0 t}\,|\Psi(0)\rangle$

Stone's theorem: $\quad e^{-\frac{\mathrm{i}}{\hbar}\mathbf{H}_0 t} = \begin{pmatrix} e^{\mathrm{i}\frac{\omega_0}{2}t} & 0 \\ 0 & e^{-\mathrm{i}\frac{\omega_0}{2}t}\end{pmatrix} \equiv \mathbf{U}(t)$

Consider $|\Psi(t)\rangle = \mathbf{U}(t)\,|\Psi(0)\rangle$ with "any" $|\Psi(0)\rangle = \cos\frac{\theta}{2}\,|\alpha\rangle + e^{\mathrm{i}\varphi}\sin\frac{\theta}{2}\,|\beta\rangle$:

$$\mathbf{b}(t) = \begin{pmatrix}\langle\Psi(t)|\,\boldsymbol{\sigma}_1\,|\Psi(t)\rangle \\ \langle\Psi(t)|\,\boldsymbol{\sigma}_2\,|\Psi(t)\rangle \\ \langle\Psi(t)|\,\boldsymbol{\sigma}_3\,|\Psi(t)\rangle\end{pmatrix} = \begin{pmatrix}\cos\omega_0 t & \sin\omega_0 t & 0 \\ -\sin\omega_0 t & \cos\omega_0 t & 0 \\ 0 & 0 & 1\end{pmatrix}\mathbf{b}(0) = \mathbf{R}_z(-\omega_0 t)\ \mathbf{b}(0)$$

Conclusion

The Bloch vector of nuclear 1/2-spins precesses **clockwise** *with* **Larmor** *frequency ω_0 about the direction of a static homogenous magnetic field (if $b_1(0) \neq 0$ or $b_2(0) \neq 0$).*

Nuclear Magnetic Resonance

Apply static & perpendicular to it magnetic field rotating clockwise

$$\mathbf{H} = -\frac{\hbar\gamma}{2}\begin{pmatrix} \mathrm{B}_1 \cos\omega t \\ -\mathrm{B}_1 \sin\omega t \\ \mathrm{B}_0 \end{pmatrix} \cdot \boldsymbol{\sigma} = \begin{vmatrix} \omega_0 \equiv \gamma \mathrm{B}_0 \\ \omega_1 \equiv \gamma \mathrm{B}_1 \end{vmatrix} = -\frac{\hbar}{2}\begin{pmatrix} \omega_0 & \omega_1 e^{\mathrm{i}\omega t} \\ \omega_1 e^{-\mathrm{i}\omega t} & -\omega_0 \end{pmatrix}$$

Transformation **into** clockwise rotating frame by $\mathbf{U} = \begin{pmatrix} e^{-\mathrm{i}\frac{\omega t}{2}} & 0 \\ 0 & e^{\mathrm{i}\frac{\omega t}{2}} \end{pmatrix}$:

$$|\Upsilon\rangle \equiv \mathbf{U}\,|\Psi\rangle \quad \curvearrowright \quad |\Psi\rangle = \mathbf{U}^{-1}\,|\Upsilon\rangle$$

$$\mathrm{i}\hbar\frac{d|\Psi\rangle}{dt} = \mathbf{H}\,|\Psi\rangle \quad \rightarrow \quad \mathrm{i}\hbar\mathbf{U}^{-1}\frac{d|\Upsilon\rangle}{dt} = \left(\mathbf{H}\mathbf{U}^{-1} - \mathrm{i}\hbar\frac{d\mathbf{U}^{-1}}{dt}\right)|\Upsilon\rangle \quad \| \ \mathbf{U}\cdot$$

$$\mathrm{i}\hbar\frac{d|\Upsilon\rangle}{dt} = \left(\mathbf{U}\mathbf{H}\mathbf{U}^{-1} - \mathrm{i}\hbar\mathbf{U}\frac{d\mathbf{U}^{-1}}{dt}\right)|\Upsilon\rangle$$

With $\mathbf{UHU}^{-1} = -\frac{\hbar}{2}\begin{pmatrix} \omega_0 & \omega_1 \\ \omega_1 & -\omega_0 \end{pmatrix}$ and $\mathbf{U}\frac{d\mathbf{U}^{-1}}{dt} = \frac{\mathrm{i}}{2}\begin{pmatrix} \omega & 0 \\ 0 & -\omega \end{pmatrix}$:

$$\mathrm{i}\hbar\frac{d|\Upsilon\rangle}{dt} = \tilde{\mathbf{H}}\,|\Upsilon\rangle \quad \text{with } \tilde{\mathbf{H}} = -\frac{\hbar}{2}\begin{pmatrix} \Omega & \omega_1 \\ \omega_1 & -\Omega \end{pmatrix} = -\frac{\hbar}{2}\left(\Omega\boldsymbol{\sigma}_3 + \omega_1\boldsymbol{\sigma}_1\right)$$

and $\Omega \equiv \omega_0 - \omega$

Conclusion

*In the coordinate frame rotating with the applied perpendicular magnetic field the Hamiltonian of the spin-1/2 system becomes time-**in**dependent:* $\tilde{\mathbf{H}} \simeq -\frac{\hbar\Omega}{2}\boldsymbol{\sigma}_3 \ \ (B_1 \ll B_0)$

Nuclear Magnetic Resonance (2)

Time-dependent perturbation $\mathbf{V}(t)$: $\mathrm{i}\hbar \frac{d|\Psi(t)\rangle}{dt} = (\mathbf{H}_0 + \mathbf{V}(t))\,|\Psi(t)\rangle$

Set $|\psi(t)\rangle = \sum_n c_n(t)\,|\varphi_n(t)\rangle = \sum_n c_n(t) e^{-\frac{\mathrm{i}}{\hbar}\varepsilon_n t}\,|\varphi_n\rangle \;\;\|\;\; \mathbf{H}_0\,|\varphi_n\rangle = \varepsilon_n\,|\varphi_n\rangle$

Spin-1/2 **two-state system** $|\psi(t)\rangle = c_1(t)e^{\mathrm{i}\frac{\omega_0}{2}t}\,|\alpha\rangle + c_2(t)e^{-\mathrm{i}\frac{\omega_0}{2}t}\,|\beta\rangle$
with $V_{12} = -\frac{\hbar\omega_1}{2}e^{\mathrm{i}\omega t}$, $V_{21} = V_{12}^*$, $V_{11} = V_{22} = 0$, $\boldsymbol{\omega_1 \ll \omega_0}$,
and $\Omega \equiv \omega_0 - \omega$:

$$\begin{cases} \frac{dc_1(t)}{dt} = \frac{\mathrm{i}\omega_1}{2}e^{-\mathrm{i}\Omega t}c_2(t) \\ \frac{dc_2(t)}{dt} = \frac{\mathrm{i}\omega_1}{2}e^{\mathrm{i}\Omega t}c_1(t) \end{cases} \implies \begin{cases} \frac{d^2c_1(t)}{dt^2} + \mathrm{i}\Omega\frac{dc_1(t)}{dt} + \frac{\omega_1^2}{4}c_1(t) = 0 \\ \frac{d^2c_2(t)}{dt^2} - \mathrm{i}\Omega\frac{dc_2(t)}{dt} + \frac{\omega_1^2}{4}c_2(t) = 0 \end{cases}$$

Initial conditions ($c_1 = 1$, $c_2 = 0$ at $t = 0$), i.e. start in state $|\alpha\rangle$:

$$\begin{cases} c_1(t) = e^{-\mathrm{i}\frac{\Omega}{2}t}\left[\cos(\Lambda t) + \frac{\mathrm{i}\Omega}{2\Lambda}\sin(\Lambda t)\right] \\ c_2(t) = \frac{\mathrm{i}\omega_1}{2\Lambda}e^{\mathrm{i}\frac{\Omega}{2}t}\sin(\Lambda t) \end{cases} \quad \text{with } \Lambda \equiv \frac{1}{2}\sqrt{\Omega^2 + \omega_1^2}$$

Conclusion

$P_{|\beta\rangle}(t) = |c_2(t)|^2 = \frac{\omega_1^2}{\Omega^2+\omega_1^2} sin^2\left(\frac{t}{2}\sqrt{\Omega^2+\omega_1^2}\right)$ *(I.I. Rabi, 1937)*

$P_{|\alpha\rangle}(t) = 1 - P_{|\beta\rangle}(t)$

Radio-frequency pulses

Rotate z-magnetization ($\sim \boldsymbol{\sigma}_3$) by $R(\phi) = e^{-\mathrm{i}\frac{\phi}{2}\boldsymbol{\sigma}_1}$ in $\mathbb{C}^2$ ($\phi = \omega t = 2\pi\nu t$):

$$\begin{pmatrix} \cos\frac{\phi}{2} & -\mathrm{i}\sin\frac{\phi}{2} \\ -\mathrm{i}\sin\frac{\phi}{2} & \cos\frac{\phi}{2} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \cos\frac{\phi}{2} & \mathrm{i}\sin\frac{\phi}{2} \\ \mathrm{i}\sin\frac{\phi}{2} & \cos\frac{\phi}{2} \end{pmatrix}$$
$$= \left(\cos^2\frac{\phi}{2} - \sin^2\frac{\phi}{2}\right)\boldsymbol{\sigma}_3 - 2\sin\frac{\phi}{2}\cos\frac{\phi}{2}\ \boldsymbol{\sigma}_2 = \cos\phi\ \boldsymbol{\sigma}_3 - \sin\phi\ \boldsymbol{\sigma}_2$$

From $\boldsymbol{\mu} = \frac{\hbar\gamma}{2}\boldsymbol{\sigma} \equiv \hbar\gamma\mathbf{I} \quad \longmapsto \quad \mathbf{I}_x = \frac{1}{2}\boldsymbol{\sigma}_1, \mathbf{I}_y = \frac{1}{2}\boldsymbol{\sigma}_2, \mathbf{I}_z = \frac{1}{2}\boldsymbol{\sigma}_3$:

$$\mathbf{I}_x \xrightarrow{\phi\mathbf{I}_{\pm x}} \mathbf{I}_x \qquad\qquad \mathbf{I}_x \xrightarrow{\theta\mathbf{I}_{\pm y}} \mathbf{I}_x\cos\theta \mp \mathbf{I}_z\sin\theta$$
$$\mathbf{I}_y \xrightarrow{\phi\mathbf{I}_{\pm x}} \mathbf{I}_y\cos\phi \pm \mathbf{I}_z\sin\phi \qquad\qquad \mathbf{I}_y \xrightarrow{\theta\mathbf{I}_{\pm y}} \mathbf{I}_y$$
$$\mathbf{I}_z \xrightarrow{\phi\mathbf{I}_{\pm x}} \mathbf{I}_z\cos\phi \mp \mathbf{I}_y\sin\phi \qquad\qquad \mathbf{I}_z \xrightarrow{\theta\mathbf{I}_{\pm y}} \mathbf{I}_z\cos\theta \pm \mathbf{I}_x\sin\theta$$

Coupled spin systems

System of N 1/2 spins

$$\mathbf{H} = \hbar \left(\sum_{k}^{N} \omega_{0_k} \mathbf{I}_{z_k} + 2\pi \sum_{k<l}^{N} \mathbf{J}_{kl} \mathbf{I}_k \mathbf{I}_l \right)$$

with $\omega_{0_k} = -(1-\sigma_k)\gamma B_0$, σ_k - isotropic chemical shielding

$\mathbf{J}_{kl}$ - indirect spin-spin coupling tensor

$\mathbf{I}_k \mathbf{I}_l = \mathbf{I}_{z_k} \mathbf{I}_{z_l} + (\mathbf{I}_{x_k} \mathbf{I}_{x_l} + \mathbf{I}_{y_k} \mathbf{I}_{y_l})$

For $2\pi |\mathbf{J}_{kl}| \ll |\omega_{0_k} - \omega_{0_l}|$ and without $\hbar$

$$\mathbf{H} = \sum_{k}^{N} \omega_{0_k} \mathbf{I}_{z_k} + 2\pi \sum_{k<l}^{N} J_{kl} \mathbf{I}_{z_k} \mathbf{I}_{z_l}$$

During acquisition single spin magnetization is propagated **in the rotating frame** by $U = e^{-\frac{i}{\hbar}\tilde{\mathbf{H}}t}$, but evolution of coupled spin systems follows direct product algebra.