Quantum mechanics for NMR

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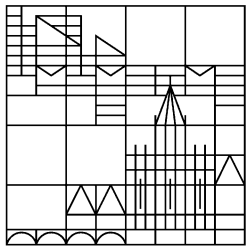


Two-level system

for example, a ^{1}H spin in a magnetic field, I = ½

- An arbitrary state is specified by a ket

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle$$

- or a column vector

$$\boldsymbol{\psi} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

- The corresponding bra is given by

$$\langle\psi| = c_1^*\langle 1| + c_2^*\langle 2|$$

- or a row vector

$$\boldsymbol{\psi} = \begin{pmatrix} c_1^* & c_2^* \end{pmatrix}$$

- States span a reduced Hilbert space with dimension

$$n_{\mathrm{H}} = \prod_{k=1}^{n}(2I_k + 1)$$

- Suppose that $|1\rangle$ and $|2\rangle$ are eigenstates of operator $\hat{A}$

$$\hat{A}|1\rangle = a_1|1\rangle \qquad \hat{A}|2\rangle = a_2|2\rangle$$

- If we measure $\hat{A}$, we are certain to get one of its eigenvalues with probabilities

$$|\langle 1|\psi\rangle|^2 = |c_1|^2 \qquad |\langle 2|\psi\rangle|^2 = |c_2|^2$$

- Note that

$$|c_1|^2 + |c_2|^2 = 1$$

- Results of measurements follow statistics, but cannot be predicted with certainty in an individual case.

Expectation value

mean or weighted average

- The average outcome of repeated measurements on an ensemble of identically prepared systems *can* be predicted.

$$\left\langle \hat{A} \right\rangle = \left\langle \psi \left| \hat{A} \right| \psi \right\rangle = \left[c_1^* \left\langle 1 \right| + c_2^* \left\langle 2 \right| \right] \left[a_1 c_1 \left| 1 \right\rangle + a_2 c_2 \left| 2 \right\rangle \right] = a_1 \left| c_1 \right|^2 + a_2 \left| c_2 \right|^2$$

- Generally ($\left|1\right\rangle$ and $\left|2\right\rangle$ don't have to be eigenstates of $\hat{A}$)

$$\left\langle \hat{A} \right\rangle = \left[c_1^* \left\langle 1 \right| + c_2^* \left\langle 2 \right| \right] \left[a_1 c_1 \left| 1 \right\rangle + a_2 c_2 \left| 2 \right\rangle \right]$$

$$= c_1^* c_1 \left\langle 1 \left| \hat{A} \right| 1 \right\rangle + c_1^* c_2 \left\langle 1 \left| \hat{A} \right| 2 \right\rangle + c_2^* c_1 \left\langle 2 \left| \hat{A} \right| 1 \right\rangle + c_2^* c_2 \left\langle 2 \left| \hat{A} \right| 2 \right\rangle$$

$$= c_1^* c_1 A_{11} + c_1^* c_2 A_{12} + c_2^* c_1 A_{21} + c_2^* c_2 A_{22}$$

- or using the vector notation

$$\left\langle \hat{A} \right\rangle = \begin{pmatrix} c_1^* & c_2^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \boldsymbol{\psi}^\dagger \mathbf{A} \boldsymbol{\psi}$$

Larmor precession

- Energy of a classical magnetic dipole in a magnetic field along z

$$E = -\boldsymbol{\mu} \cdot \mathbf{B}_0 = -\mu_z B_0$$

- For elementary particles with a (spin) angular momentum $\mu_z = \gamma I_z$, this gives the familiar Hamiltonian for a nucleus in a magnetic field

$$\hat{H} = -\gamma B_0 \hbar \hat{I}_z = \hbar \omega_0 \hat{I}_z \quad \text{or, in frequency units,} \quad \hat{H} = \omega_0 \hat{I}_z$$

- Time evolution of state $\boldsymbol{\psi} = \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}$ is determined by the Schrödinger equation

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle = -i\hat{H}|\psi\rangle \quad \text{or, in vector notation,} \quad \dot{\boldsymbol{\psi}} = -i\hat{\mathbf{H}}\boldsymbol{\psi}$$

- This gives

$$\begin{pmatrix} \dot{c}_\alpha \\ \dot{c}_\beta \end{pmatrix} = -i\omega_0 \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} \quad \text{or} \quad \begin{aligned} \dot{c}_\alpha &= -\tfrac{1}{2} i\omega_0 c_\alpha \\ \dot{c}_\beta &= \tfrac{1}{2} i\omega_0 c_\beta \end{aligned}$$

- Integrate to find

$$c_\alpha = c_\alpha(0)e^{-i\omega_0 t} \quad \text{and} \quad c_\beta = c_\beta(0)e^{i\omega_0 t}$$

Larmor precession

- The state of the system with initial conditions $c_\alpha(0) = c_\beta(0) = 1/\sqrt{2}$

$$\boldsymbol{\psi}_{t=0} = \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2}\, e^{-i\omega_0 t} \\ 1/\sqrt{2}\, e^{i\omega_0 t} \end{pmatrix}$$

- Let's calculate the expectation value $\langle \hat{I}_x \rangle$.

$$\langle \hat{I}_x \rangle = \boldsymbol{\psi}^\dagger \mathbf{I}_z \boldsymbol{\psi} = \begin{pmatrix} c_\alpha^* & c_\beta^* \end{pmatrix} \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = 1/2\, c_\alpha^* c_\beta + 1/2\, c_\alpha c_\beta^* = \mathrm{Re}\{c_\alpha c_\beta^*\} = \mathrm{Re}\{1/2\, e^{-i\omega_0 t/2} e^{-i\omega_0 t/2}\} = 1/2 \cos\omega_0 t$$

- Likewise for $\langle \hat{I}_y \rangle$ and $\langle \hat{I}_z \rangle$.

$$\langle \hat{I}_y \rangle = \begin{pmatrix} c_\alpha^* & c_\beta^* \end{pmatrix} \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = -\mathrm{Im}\{c_\alpha c_\beta^*\} = 1/2 \sin\omega_0 t$$

$$\langle \hat{I}_z \rangle = \begin{pmatrix} c_\alpha^* & c_\beta^* \end{pmatrix} \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = 1/2 |c_\alpha|^2 - 1/2 |c_\beta|^2 = 0$$

- In a uniform magnetic field, the expectation value $\langle \hat{\mathbf{I}} \rangle$ precesses at the Larmor frequency.

Density operator

statistical operator

- Expectation values depend on products of coefficients

$$\left\langle \hat{A} \right\rangle = c_\alpha^* c_\alpha A_{\alpha\alpha} + c_\alpha^* c_\beta A_{\alpha\beta} + c_\beta^* c_\alpha A_{\beta\alpha} + c_\beta^* c_\beta A_{\beta\beta}$$

- Useful to define an operator with a matrix representation that has these products of coefficients as its elements.

$$\rho_{rs} = \left\langle r \left| \hat{\rho} \right| s \right\rangle = c_r c_s^*$$

- This is the density operator.

$$\boldsymbol{\rho} = \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} \begin{pmatrix} c_\alpha^* & c_\beta^* \end{pmatrix} = \begin{pmatrix} c_\alpha c_\alpha^* & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{pmatrix}$$

- In general, it is the outer product of the states

$$\boldsymbol{\rho} = \boldsymbol{\psi}\boldsymbol{\psi}^\dagger \quad \text{or} \quad \hat{\rho} = \left| \psi \right\rangle \left\langle \psi \right|$$

- Expectation values are readily calculated by taking the trace of the product of $\boldsymbol{\rho}$ and $\mathbf{A}$

$$\boldsymbol{\rho}\mathbf{A} = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix} \begin{pmatrix} A_{\alpha\alpha} & A_{\alpha\beta} \\ A_{\beta\alpha} & A_{\beta\beta} \end{pmatrix}$$

$$= \begin{pmatrix} \rho_{\alpha\alpha} A_{\alpha\alpha} + \rho_{\alpha\beta} A_{\beta\alpha} & \rho_{\alpha\alpha} A_{\alpha\beta} + \rho_{\alpha\beta} A_{\beta\beta} \\ \rho_{\beta\alpha} A_{\alpha\alpha} + \rho_{\beta\beta} A_{\beta\alpha} & \rho_{\beta\alpha} A_{\alpha\beta} + \rho_{\beta\beta} A_{\beta\beta} \end{pmatrix}$$

$$\left\langle \hat{A} \right\rangle = Tr\left\{ \boldsymbol{\rho}\mathbf{A} \right\} = \rho_{\alpha\alpha} A_{\alpha\alpha} + \rho_{\alpha\beta} A_{\beta\alpha} + \rho_{\beta\alpha} A_{\alpha\beta} + \rho_{\beta\beta} A_{\beta\beta}$$

Time evolution

- Since

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle = -i\hat{H}|\psi\rangle$$

- also

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi| = i\langle\psi|\hat{H}$$

- Hence (using the product rule)

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho} = \frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle\langle\psi|$$

$$= \left\{\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle\right\}\langle\psi| + |\psi\rangle\left\{\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi|\right\}$$

$$= -i\hat{H}|\psi\rangle\langle\psi| + i|\psi\rangle\langle\psi|\hat{H}$$

$$= -i\hat{H}\hat{\rho} + i\hat{H}\hat{\rho} = -i\left[\hat{H}, \hat{\rho}\right]$$

- The Liouville-von Neumann equation describes the time evolution of the density operator.

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho} = -i\left[\hat{H}, \hat{\rho}\right]$$

- If the Hamiltonian is time-independent, its solution is simple.

$$\hat{\rho}(t) = e^{-i\hat{H}t}\hat{\rho}(0)e^{i\hat{H}t}$$

- A unitary transformation propagates the density operator forward in time.

$$\hat{U} = e^{-i\hat{H}t}$$

Describing macroscopic systems

with the density operator

- Consider a macroscopic system made up of a large number of independent microscopic systems with identical spin Hamiltonians - a typical NMR sample.
- It is possible to add density operators before evaluating expectation values.

$$\left\langle \hat{A} \right\rangle_1 + \left\langle \hat{A} \right\rangle_2 = Tr\{\boldsymbol{\rho}_1 \mathbf{A}\} + Tr\{\boldsymbol{\rho}_2 \mathbf{A}\} = Tr\{[\boldsymbol{\rho}_1 + \boldsymbol{\rho}_2]\mathbf{A}\}$$

- The same applies for time evolution.

$$\hat{\rho}_1(t) + \hat{\rho}_2(t) = e^{-i\hat{H}t}\hat{\rho}_1(0)e^{i\hat{H}t} + e^{-i\hat{H}t}\hat{\rho}_2(0)e^{i\hat{H}t}$$
$$= e^{-i\hat{H}t}[\hat{\rho}_1(0) + \hat{\rho}_2(0)]e^{i\hat{H}t}$$

- Thus, a summed density operator can describe this macroscopic system.
- We can even consider weighted contributions from all microscopic systems.

$$\hat{\rho} = \sum_i p_i \hat{\rho}_i$$

with p_i the probability of a microscopic system being in state $\hat{\rho}_i$.

- The elements of $\hat{\rho}$ are given by

$$\hat{\rho}_{rs} = \overline{c_r c_s^*}$$

- The bar indicates the ensemble average.

Pure state vs mixed state

- The microscopic states are described by

$$|\psi\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle = a_\alpha e^{i\phi_\alpha} |\alpha\rangle + a_\beta e^{i\phi_\beta} |\beta\rangle$$

  with the amplitudes and phases of the complex coefficients written out explicitly.

- The corresponding density operator is

$$\rho = \begin{pmatrix} a_\alpha^2 & a_\alpha a_\beta e^{i(\phi_\alpha - \phi_\beta)} \\ a_\alpha a_\beta e^{-i(\phi_\alpha - \phi_\beta)} & a_\beta^2 \end{pmatrix}$$

- In a pure state, all microscopic systems are in the same state.

$$\hat{\rho}_{micro} = \hat{\rho}_{ensemble}$$

- In a mixed state, the phases of the microscopic systems may vary randomly.

$$\rho = \begin{pmatrix} \overline{a_\alpha^2} & 0 \\ 0 & \overline{a_\beta^2} \end{pmatrix}$$

- Ensemble averaged density matrices describe mixed states.

- A macroscopic system at thermal equilibrium is in a mixed state.

Coherences and populations

- The off-diagonal elements of the density matrix are only non-zero if there is phase coherence between the states of the microscopic systems.

$$\rho = \begin{pmatrix} \overline{a_\alpha^2} & \overline{a_\alpha a_\beta e^{i(\phi_\alpha - \phi_\beta)}} \\ \overline{a_\alpha a_\beta e^{-i(\phi_\alpha - \phi_\beta)}} & \overline{a_\beta^2} \end{pmatrix}$$

- Recall slide 5: macroscopic transverse magnetization is associated with the off-diagonal elements of the density matrix.

$$\left\langle \hat{I}_x \right\rangle = \overline{\left\langle \hat{I}_x \right\rangle} = \mathrm{Re}\left\{ \overline{a_\alpha a_\beta e^{i(\phi_\alpha - \phi_\beta)}} \right\} = \overline{a_\alpha a_\beta \cos\left(\phi_\alpha - \phi_\beta\right)}; \quad M_x = \hbar\gamma N \overline{\left\langle \hat{I}_x \right\rangle}$$

$$\left\langle \hat{I}_y \right\rangle = \overline{\left\langle \hat{I}_y \right\rangle} = -\mathrm{Im}\left\{ \overline{a_\alpha a_\beta e^{i(\phi_\alpha - \phi_\beta)}} \right\} = \overline{a_\alpha a_\beta \sin\left(\phi_\beta - \phi_\alpha\right)}; \quad M_y = \hbar\gamma N \overline{\left\langle \hat{I}_y \right\rangle}$$

- In NMR, phase coherence/transverse magnetization is created by applying one or more (near-)resonant radiowave pulses.

- The diagonal elements give the probabilities of finding a random microscopic system in state $|\alpha\rangle$ or $|\beta\rangle$. Hence, they represent level populations.

- Their difference is associated with longitudinal magnetization.

$$\left\langle \hat{I}_z \right\rangle = \overline{\left\langle \hat{I}_z \right\rangle} = \overline{\tfrac{1}{2} a_\alpha^2 - \tfrac{1}{2} a_\beta^2}; \quad M_z = \hbar\gamma N \overline{\left\langle \hat{I}_z \right\rangle}$$

- In thermal equilibrium, populations follow the Boltzmann distribution.

$$\rho_{\mathrm{eq}} = \begin{pmatrix} \tfrac{1}{2} e^{-E_\alpha / k_B T} & 0 \\ 0 & \tfrac{1}{2} e^{-E_\beta / k_B T} \end{pmatrix}$$

Decompose into basis operators

- The density operator can be decomposed into a linear combination of orthogonal basis operators.

- This is analogous to expressing a vector as a linear combination of unit vectors.

$$\mathbf{v} = a_x\mathbf{e}_x + a_y\mathbf{e}_y + a_z\mathbf{e}_z \quad \text{or} \quad \mathbf{v} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$$

with unit vectors $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

- Two matrices are orthogonal if their trace is zero.

$$Tr\{\mathbf{AB}\} = 0$$

- The Cartesian basis is a good choice.

$$\hat{I}_x = \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \hat{I}_y = \tfrac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},$$

$$\hat{I}_z = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

- The density operator now takes the general form.

$$\hat{\rho} = a_1\mathbf{1} + a_x\hat{I}_x + a_y\hat{I}_y + a_z\hat{I}_z$$

- The orthogonal basis operators span a new space, Liouville space, with dimension

$$n_{\mathrm{L}} = n_{\mathrm{H}}^2$$

Pulse NMR experiments

- Recall slide 7: if the Hamiltonian is time independent, the solution to the Liouville-von Neumann equation takes a simple form.

$$\hat{\rho}(t) = \hat{U}\hat{\rho}(0)\hat{U}^{\dagger} \quad \text{with} \quad \hat{U} = e^{-i\hat{H}t}$$

- Often a pulse NMR experiment can be described as a sequence of time intervals governed by different, time-independent Hamiltonians.

$$\hat{\rho}(t) = \hat{U}_n \ldots \hat{U}_2 \hat{U}_1 \hat{\rho}(0) \hat{U}_1^{-1} \hat{U}_2^{-1} \ldots \hat{U}_n^{-1}$$

- The expectation value of an observable of interest can be read out any time.

$$\left\langle \hat{A} \right\rangle (t) = Tr\left\{ \hat{\rho}(t)\hat{A} \right\}$$

- The starting state is usually thermal equilibrium.

Equilibrium density operator

- In the high-temperature limit

$$\rho_{eq} = \begin{pmatrix} \tfrac{1}{2} e^{-E_\alpha / k_B T} & 0 \\ 0 & \tfrac{1}{2} e^{-E_\beta / k_B T} \end{pmatrix} \approx \tfrac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \tfrac{1}{2} \begin{pmatrix} \hbar\omega_0 / 2k_B T & 0 \\ 0 & -\hbar\omega_0 / 2k_B T \end{pmatrix}$$

  where we have inserted $E_\alpha = -\tfrac{1}{2}\hbar\omega_0$ and $E_\beta = \tfrac{1}{2}\hbar\omega_0$ used that $e^x \approx 1 + x$ for small x .

- The identity operator is invariant throughout the experiment and can be dropped.

- The prefactor gives the size of the magnetization and hence the signal strength. Unless the absolute number of spins is of interest, it can be conveniently ignored.

- Hence, for the purpose of analytical calculations, we write $\hat{\rho}(0) = \hat{\rho}_{eq} = \hat{I}_z$

- In the subsequent calculation of the evolution of the system with time, we will get

$$M_x(t) = a_x(t) \qquad M_y(t) = a_y(t) \qquad M_z(t) = a_z(t)$$

Rotations

Towards the product operator formalism

- To propagate the density operator we will have to evaluate expressions of the form

$$\hat{\rho}(t_2) = e^{-i\hat{H}\Delta t}\hat{\rho}(t_1)e^{i\hat{H}\Delta t} \quad \text{or generally} \quad e^{-i\phi\hat{B}}\hat{A}e^{i\phi\hat{B}} = ?$$

- Use the Baker-Hausdorff formula

$$e^{-i\phi\hat{B}}\hat{A}e^{i\phi\hat{B}} = \hat{A} - i\phi\left[\hat{B},\hat{A}\right] - \frac{\phi^2}{2!}\left[\hat{B},\left[\hat{B},\hat{A}\right]\right] + \frac{i\phi^3}{3!}\left[\hat{B},\left[\hat{B},\left[\hat{B},\hat{A}\right]\right]\right] + \ldots$$

  together with the canonical commutation relations,

$$\left[\hat{I}_x,\hat{I}_y\right] = i\hat{I}_z, \left[\hat{I}_y,\hat{I}_z\right] = i\hat{I}_x, \left[\hat{I}_z,\hat{I}_x\right] = i\hat{I}_y \quad \text{which imply that} \quad \left[\hat{B},\left[\hat{B},\hat{A}\right]\right] = \hat{A}$$

- For $\hat{B} \neq \hat{A}$:

$$e^{-i\phi\hat{B}}\hat{A}e^{i\phi\hat{B}} = \hat{A}\left(1 - \frac{\phi^2}{2!} + \frac{\phi^4}{4!} - \ldots\right) - i\phi\left[\hat{B},\hat{A}\right]\left(1 - \frac{\phi^3}{3!} + \frac{\phi^5}{5!} - \ldots\right)$$

shorthand notation

$$= \hat{A}\cos\phi - \mathrm{i}\left[\hat{B},\hat{A}\right]\sin\phi \longrightarrow \boxed{\hat{A} \xrightarrow{\phi\hat{B}} \hat{A}\cos\phi - \mathrm{i}\left[\hat{B},\hat{A}\right]\sin\phi}$$

- and for $\hat{B} = \hat{A}$:

$$e^{-i\phi\hat{B}}\hat{A}e^{i\phi\hat{B}} = \hat{A} \longrightarrow \boxed{\hat{A} \xrightarrow{\phi\hat{B}} \hat{A}}$$

Simple Hamiltonian

- Transform to a reference frame rotating around the z-axis at the frequency of the radiowaves.

- Hamiltonian during free precession

$$\hat{H}_{\text{free}} = \Omega \hat{I}_z \quad \text{with} \quad \Omega = \omega_0 - \omega_{\text{RF}} \quad \text{the resonance offset.}$$

- Hamiltonian during a radiowave pulse along the x-axis

$$\hat{H}_{\text{p}} = \Omega \hat{I}_z + \omega_1 \hat{I}_x$$

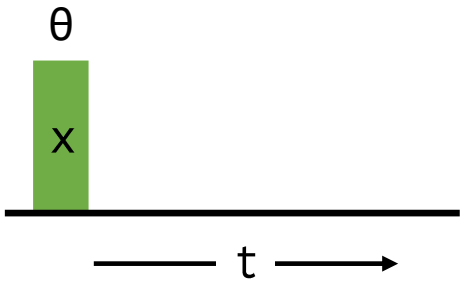
- Assuming hard pulses

$$\omega_1 = |\gamma| B_1 \gg |\Omega|$$

simplifies the Hamiltonian during the pulse to

$$\hat{H}_{\text{p}} = \omega_1 \hat{I}_x$$

Example 1: Pulse-acquire



- Start in thermal equilibrium and apply H_{p} for duration of the pulse t_{p} .

$$\hat{\rho}(t_{\mathrm{p}}) = e^{-i\hat{H}_{\mathrm{p}}t_{\mathrm{p}}}\hat{\rho}(0)e^{i\hat{H}_{p}t_{p}} = e^{-i\omega_1\hat{I}_x t_{\mathrm{p}}}\hat{I}_z e^{i\omega_1\hat{I}_x t_{p}} = e^{-i\theta\hat{I}_x}\hat{I}_z e^{i\theta\hat{I}_x}$$

- Use the shorthand notation to calculate the rotation.

$$\hat{A} \xrightarrow{\phi B} \hat{A}\cos\phi - i\left[\hat{B},\hat{A}\right]\sin\phi$$

$$\hat{I}_z \xrightarrow{\theta\hat{I}_x} \hat{I}_z\cos\theta - i\left[\hat{I}_x,\hat{I}_z\right]\sin\theta = \hat{I}_z\cos\theta - i\cdot -i\hat{I}_y\sin\theta = \hat{I}_z\cos\theta - \hat{I}_y\sin\theta$$

- Next, the free evolution

$$\hat{\rho}(t) = e^{-i\hat{H}_{\mathrm{free}}t}\hat{\rho}(t_{\mathrm{p}})e^{i\hat{H}_{\mathrm{free}}t} = {}^{-i\Omega\hat{I}_z t}\ (\hat{I}_z\cos\theta - \hat{I}_y\sin\theta)e^{i\Omega\hat{I}_z t}$$

- Calculate the rotation for $\hat{I}_y$ ($\hat{I}_z$ is not affected).

$$\hat{I}_y \xrightarrow{\Omega\hat{I}_z t} \hat{I}_y\cos\Omega t - i\left[\hat{I}_z,\hat{I}_y\right]\sin\Omega t = \hat{I}_y\cos\Omega t - i\cdot -i\hat{I}_x\sin\Omega t = \hat{I}_y\cos\Omega t - \hat{I}_x\sin\Omega t$$

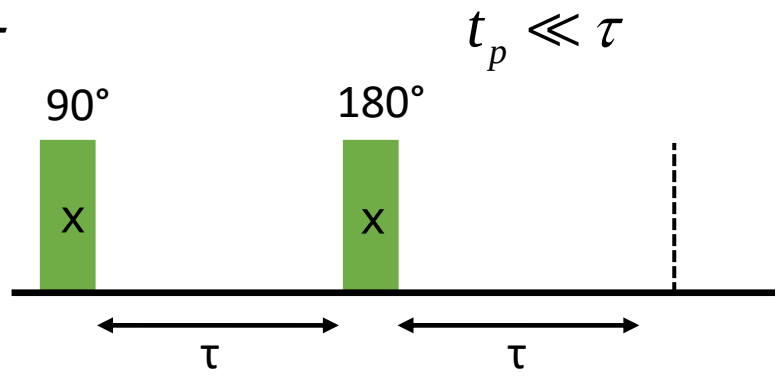
- The magnetization precesses clockwise at frequency Ω .

$$\hat{\rho}(t) = \hat{I}_z\cos\theta - \hat{I}_y\cos\Omega t\sin\theta + \hat{I}_x\sin\Omega t\sin\theta$$

Example 2: Spin echo

- Start with the result of the previous slide for $\theta = \pi / 2$ and $t = \tau$

$$\hat{\rho}(\tau) = -\hat{I}_y \cos\Omega\tau + \hat{I}_x \sin\Omega\tau$$



- Calculate the effect of the π-pulse.

$$\hat{I}_y \xrightarrow{\pi\hat{I}_x} \hat{I}_y \cos\pi - i\left[\hat{I}_x, \hat{I}_y\right]\sin\pi = -\hat{I}_y$$

$$\hat{\rho}(t_\pi) = \hat{I}_y \cos\Omega\tau + \hat{I}_x \sin\Omega\tau$$

- And of the 2nd delay

$$\hat{I}_y \xrightarrow{\Omega\hat{I}_z\tau} \hat{I}_y \cos\Omega\tau - i\left[\hat{I}_z, \hat{I}_y\right]\sin\Omega\tau = \hat{I}_y \cos\Omega\tau - \hat{I}_x \sin\Omega\tau$$

$$\hat{I}_x \xrightarrow{\Omega\hat{I}_z\tau} \hat{I}_x \cos\Omega\tau - i\left[\hat{I}_z, \hat{I}_x\right]\sin\Omega\tau = \hat{I}_x \cos\Omega\tau + \hat{I}_y \sin\Omega\tau$$

- Regardless of offset and delay length, the magnetization ends up along y.

$$\hat{\rho}(2\tau) = \hat{I}_y \cos\Omega\tau\cos\Omega\tau - \hat{I}_x \cos\Omega\tau\sin\Omega\tau + \hat{I}_x \sin\Omega\tau\cos\Omega\tau + \hat{I}_y \sin\Omega\tau\sin\Omega\tau = \hat{I}_y$$

Summary

- Pulse NMR experiments can be described using quantum mechanics.
- The density operator describes the state of an ensemble, without referring to the individual states. This is extremely useful in magnetic resonance.
- The product operator formalism is a cunning way of doing analytical density matrix calculations.

Note: Perhaps you have been wondering where the name *product* operator formalism comes from? The formalism comes into its own when dealing with two or more coupled spins – it then requires product operators like

$$2\hat{I}_x\hat{S}_x, 2\hat{I}_x\hat{S}_y, 2\hat{I}_x\hat{S}_z, 2\hat{I}_y\hat{S}_x, 2\hat{I}_y\hat{S}_y, \ldots$$

You are now ready to tackle those cases on your own. Have fun!

Literature

1) Hore, Jones, and Wimperis, *NMR: The Toolkit* (2nd edition, 2014)

   For this lecture, I largely followed their derivation of the density operator. They write "The density operator can be derived in many ways, with varying degrees of mathematical formality. Here we mostly use simple analogies."

   Other textbooks I consulted:

2) Griffiths, *Introduction to Quantum Mechanics* (2nd edition, 2005)

3) Keeler, *Understanding NMR Spectroscopy* (2nd edition, 2010)

4) Levitt, *Spin Dynamics* (2nd edition, 2008)

5) Schweiger and Jeschke, *Principles of Pulse Electron Paramagnetic Resonance* (2001)