Density Matrix – Interpretation and Transformations

BCMB/CHEM 8190

Density Matrix at Equilibrium

- Have a route to an observable:

  $\overline{\langle\psi|\ \mathbf{Ix}(t)|\psi\rangle} = \mathrm{Tr}\ |\ \rho(t)\ |\ |\ \mathbf{Ix}|$

- Have a route to $\rho(t)$:

  $d/dt\ |\rho(t)| = i\ /(h/2\pi)\ [\ |\rho\mathbf{(t)|,}\ |\mathbf{H}|\ ]$

- Need a place to start: $\rho(0)$
- Diagonal elements; work from $c_n c_n^*$ as a probabliity
- $\overline{c_n c_n^*} = \exp(-E_n/(kT))/Z \cong 1/Z - E_n/(kT)/Z$; (small E_n)
- $\rho_{nn} = 1/Z - \sigma_{nn}$; $Z \cong$ # of states
- Note: text uses σ for density matrix
  - really deviation matrix

Off-diagonal elements at equilibrium

- ψ must satisfy time dependent Schrodinger Eq.

  $\mathbf{H}\psi = (i2\pi/h)\partial\psi/\partial t = E\psi$; in limit of $\mathbf{H} = \mathbf{H_0}$
- Solution is: $\psi_n = \phi_n \exp(i2\pi/h)E_n t$
- But, the members of the ensemble have not common origin in time.
- Hence add a random phase factor:

  $\psi_{nm} = \phi_n \exp(i((2\pi/h)E_n t + \alpha_m) = \phi_n c_{mn}(t)$
- $c_{mn}(t) = \cos\theta(n,m,t) + i \sin\theta(n,m,t)$
- Density matrix element = $\overline{c_i c_j^*(t)} = \overline{\cos\theta_i \cos\theta_j} +$

  $\overline{\sin\theta_i \cos\theta_j} + \overline{\cos\theta_l \sin\theta_j} + \overline{\sin\theta_l \sin\theta_j}$
- if $i = j$, $\int_\alpha P(\theta)(\cos\theta_i^2 + \sin\theta_i^2) \cong P(\theta)$
- If $l \neq j$, $\overline{\cos\theta_i \cos\theta_j}$ etc = 0, and all off diagonals = 0

Examples for a spin ½ nucleus

- **H** = $-\gamma h/(2\pi)B_0\mathbf{I_z}$, E = $(+/-)\gamma\, h/(4\pi)B_0$

$$\rho_{\mathbf{eq}} = 1/2\begin{bmatrix} \exp(\gamma\hbar\mathbf{B}_0/2\mathbf{kT}) & 0 \\ 0 & \exp(-\gamma\hbar\mathbf{B}_0/2\mathbf{kT}) \end{bmatrix}$$

$$\boldsymbol{\sigma}_{\mathbf{eq}} = 1/2\begin{bmatrix} \gamma\hbar\mathbf{B}_0/2\mathbf{kT}) & 0 \\ 0 & -\gamma\hbar\mathbf{B}_0/2\mathbf{kT}) \end{bmatrix}$$

- No time variation as expected:
- $(d/dt)\sigma = (i2\pi/h)[\,\sigma, \mathbf{H}\,] = [\sigma\,\mathbf{H}] - [\mathbf{H}\,\sigma] = 0$ (product of diagonal matrices)

What about M_Z and M_X?

- Curies law for susceptibility

$$\overline{\mathbf{M_Z}} = \mathbf{Tr}([\boldsymbol{\sigma}][\boldsymbol{\mu}_\mathbf{Z}])$$

$$= \mathbf{Tr}(\begin{bmatrix} {}^{\gamma\hbar\mathbf{B}_0}\!/\!_{\mathbf{4kT}} & 0 \\ 0 & -{}^{\gamma\hbar\mathbf{B}_0}\!/\!_{\mathbf{4kT}} \end{bmatrix}(\gamma\hbar/2)\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}) = {}^{\gamma^2\hbar^2\mathbf{B}_0}\!/\!_{\mathbf{4kT}}$$

- Expect no X magnetization at equilibrium

$$\overline{\mathbf{M_X}} = \mathbf{Tr}([\boldsymbol{\sigma}][\boldsymbol{\mu}_\mathrm{X}]); [\boldsymbol{\mu}_\mathrm{X}] = {}^1\!/\!_2\,\gamma\hbar\mathbf{I}_\mathrm{X} = {}^1\!/\!_2\,\gamma\hbar\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\overline{\mathbf{M_X}} \propto \mathbf{Tr}(\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}) = 0$$

What elements do give M_X?

$$\overline{\mathbf{M_X}} = \mathbf{Tr}\left\{\begin{bmatrix} \boldsymbol{\sigma}_{11} & \boldsymbol{\sigma}_{12} \\ \boldsymbol{\sigma}_{21} & \boldsymbol{\sigma}_{22} \end{bmatrix} {}^{1}\!/_{2}\,\gamma\hbar \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\right\} = {}^{1}\!/_{2}\,\gamma\hbar(\boldsymbol{\sigma}_{12} + \boldsymbol{\sigma}_{21})$$

- We have argued that these are related to transition probabilities
- We have shown that these precess in a magnetic field

Rotation operators – a more general description of rotation

- $(d/dt)\sigma(t) = i/(h/2\pi)\,[\boldsymbol{\sigma}\mathbf{(t), H}]$
- General solution:

$$\sigma(t) = \exp(-(i2\pi/h)\mathbf{H}t)\sigma(0)\exp((i2\pi/h)\mathbf{H}t) = \mathbf{R}(t)\sigma(0)\mathbf{R}^{-1}(t)$$

- If basis set elements are eigen functions of **H, R** is diagonal and easy to evaluate
- Chemical shift evolution: $\mathbf{R_Z =} \exp(-i\overbrace{\gamma B_0\sigma_{cs}}^{\Delta\omega}t\,\mathbf{I_Z})$

$$\mathbf{R}_Z = \begin{bmatrix} \exp(\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) & 0 \\ 0 & \exp(-\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) \end{bmatrix}; \boldsymbol{\sigma}(0) = \begin{bmatrix} 0 & \delta \\ \delta & 0 \end{bmatrix}$$

M_X and M_X Precess at $\Delta\omega$

$$\boldsymbol{\sigma}(\mathbf{t}) = \begin{bmatrix} \exp(\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) & 0 \\ 0 & \exp(-\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) \end{bmatrix} \begin{bmatrix} 0 & \delta \\ \delta & 0 \end{bmatrix} \begin{bmatrix} \exp(-\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) & 0 \\ 0 & \exp(\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) \end{bmatrix}$$

$$\boldsymbol{\sigma}(\mathbf{t}) = \begin{bmatrix} \exp(\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) & 0 \\ 0 & \exp(-\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) \end{bmatrix} \begin{bmatrix} 0 & \delta\exp(\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) \\ \delta\exp(-\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}/2) & 0 \end{bmatrix}$$

$$\boldsymbol{\sigma}(\mathbf{t}) = \begin{bmatrix} 0 & \delta\exp(\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}) \\ \delta\exp(-\mathbf{i}\Delta\boldsymbol{\omega}\mathbf{t}) & 0 \end{bmatrix}$$

$$\boldsymbol{\sigma}(\mathbf{t}) = \delta\begin{bmatrix} 0 & \cos(\Delta\boldsymbol{\omega}\mathbf{t}) \\ \cos(\Delta\boldsymbol{\omega}\mathbf{t}) & 0 \end{bmatrix} + \delta\begin{bmatrix} 0 & \mathbf{i}\sin(\Delta\boldsymbol{\omega}\mathbf{t}) \\ -\mathbf{i}\sin(\Delta\boldsymbol{\omega}\mathbf{t}) & 0 \end{bmatrix} \propto \delta(\mathbf{M}_\mathbf{X} + \mathbf{M}_\mathbf{Y})$$

Rotation operators for an X pulse

- Hamiltonian in the rotating frame: $\mathbf{H'} = -(\gamma 2\pi B_1/h)\mathbf{I'_X}$
- Formal solution at end of pulse (time t) is given as:

  $\boldsymbol{\sigma}(t) = \exp(-(i2\pi/h)\mathbf{H'}t)\boldsymbol{\sigma}(0)\exp((i2\pi/h)\mathbf{H'}t) = \mathbf{R_X}\boldsymbol{\sigma}(0)\mathbf{R_X}^{\mathbf{-1}}$
- Cannot simply insert $\mathbf{I'_X}$ in exponential operator to evaluate matrix elements; $\mathbf{I'_X}$ mixes spin states
- Solution: $\exp(i\gamma B_1\mathbf{I'_X}t) \cong 1 + \gamma B_1\mathbf{I'_X}t - (\gamma B_1\mathbf{I'_X}t)^2/2! + ..$
- an even number of $\mathbf{I'_X}|\alpha>$ gives $\alpha/2^n$, odd gives $\beta/2^n$
- Even series is cos $(\omega_1 t/2)$; odd is I $\sin(\omega_1 t/2)$

Special cases of X pulses: $\omega_1 t = \pi, \pi/2$

For one spin 1/2 $\quad \mathbf{R}_X = \begin{bmatrix} \cos(\boldsymbol{\omega}_1 \mathbf{t}/2) & \mathbf{i}\sin(\boldsymbol{\omega}_1 \mathbf{t}/2) \\ \mathbf{i}\sin(\boldsymbol{\omega}_1 \mathbf{t}/2) & \cos(\boldsymbol{\omega}_1 \mathbf{t}/2) \end{bmatrix}$

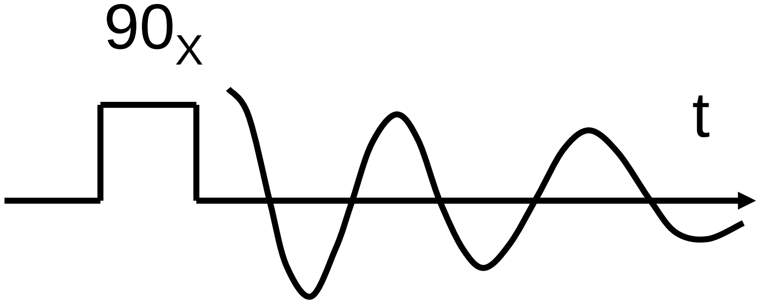
$$\mathbf{R}_{X,\pi} = \begin{bmatrix} 0 & \mathbf{i} \\ \mathbf{i} & 0 \end{bmatrix}; \mathbf{R}_{X,\pi}^{-1} = \begin{bmatrix} 0 & -\mathbf{i} \\ -\mathbf{i} & 0 \end{bmatrix};$$

$$\mathbf{R}_{X,\pi/2} = \sqrt{2}\big/2 \begin{bmatrix} 1 & \mathbf{i} \\ \mathbf{i} & 1 \end{bmatrix}; \mathbf{R}_{X,\pi/2}^{-1} = \sqrt{2}\big/2 \begin{bmatrix} 1 & -\mathbf{i} \\ -\mathbf{i} & 1 \end{bmatrix};$$

Similar arguments lead to Y pulse operations

The One Pulse FID

- $\sigma(t) = \mathbf{R_Z(t)\ R_{X,\pi/2}}\ \sigma(0)\ \mathbf{R_{X,\pi/2}\ R_Z^{-1}(t)}$



$$\boldsymbol{\sigma}(0) = \begin{bmatrix} \delta & 0 \\ 0 & -\delta \end{bmatrix} \propto \mathbf{M_Z(eq)}$$

$$\boldsymbol{\sigma}(\mathbf{t_p}) = (2/\sqrt{2})\begin{bmatrix} 1 & \mathbf{i} \\ \mathbf{i} & 1 \end{bmatrix}\begin{bmatrix} \delta & 0 \\ 0 & -\delta \end{bmatrix}(2/\sqrt{2})\begin{bmatrix} 1 & -\mathbf{i} \\ -\mathbf{i} & 1 \end{bmatrix}$$

$$\boldsymbol{\sigma}(\mathbf{t_p}) = (1/2)\begin{bmatrix} 1 & \mathbf{i} \\ \mathbf{i} & 1 \end{bmatrix}\begin{bmatrix} \delta & -\mathbf{i}\delta \\ \mathbf{i}\delta & -\delta \end{bmatrix} = (1/2)\begin{bmatrix} 0 & -\mathbf{i}\delta \\ \mathbf{i}\delta & -0 \end{bmatrix}$$

Evolution of the FID

- First point in the FID:
- $\sigma(t_1) = \mathbf{R_Z}(d_w)\sigma(t_p)\mathbf{R_Z}^{\mathbf{-1}}(d_w)$; ($d_w$ = dwell time); $\sigma(t_1)$ =

$$\begin{bmatrix} \exp(\frac{\mathbf{i\Delta\omega d_w}}{2}) & 0 \\ 0 & \exp(\frac{-\mathbf{i\Delta\omega d_w}}{2}) \end{bmatrix} (1/2) \begin{bmatrix} 0 & -\mathbf{i\delta} \\ \mathbf{i\delta} & 0 \end{bmatrix} \begin{bmatrix} \exp(\frac{-\mathbf{i\Delta\omega d_w}}{2}) & 0 \\ 0 & \exp(\frac{\mathbf{i\Delta\omega d_w}}{2}) \end{bmatrix}$$

- $\sigma(t_2) = \mathbf{R_Z}(dw)\sigma(t_1)\mathbf{R_Z}^{\mathbf{-1}}(dw)$; (second point in FID)
- .
- .
- Calculating the FID: FID = $\mathrm{Tr}\{[\sigma(t_i)]\ [\mathbf{M_X + M_Y}]\}$
- Program like GAMMA work this way