Density Matrix Description of NMR

BCMB/CHEM 8190

Operators in Matrix Notation

- It will be important, and convenient, to express the commonly used operators in matrix form
- Consider the operator I_z and the single spin functions $|\alpha\rangle$ and $|\beta\rangle$
  - recall

$$\hat{I}_x|\alpha\rangle = 1/2\,\beta \quad \hat{I}_x|\beta\rangle = 1/2\,\alpha \quad \hat{I}_y|\alpha\rangle = 1/2\,\mathrm{i}\beta \quad \hat{I}_y|\beta\rangle = -1/2\,\mathrm{i}\alpha \quad \hat{I}_z|\alpha\rangle = +1/2\,\alpha \quad \hat{I}_z|\beta\rangle = -1/2\,\beta$$

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1 \qquad \langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$$

  - recall the expectation value for an observable

$$\langle Q\rangle = \left\langle \psi\middle|\hat{Q}\middle|\psi\right\rangle = \int \psi^* \hat{Q}\psi \; d\tau \qquad \hat{Q} \text{ - some operator} \quad \psi \text{ - some wavefunction}$$

  - the matrix representation is the possible expectation values for the basis functions

$$\begin{array}{cc} & \begin{array}{cc} \alpha & \beta \end{array} \\ \begin{array}{c} \alpha \\ \beta \end{array} & \begin{bmatrix} \langle\alpha|\hat{I}_z|\alpha\rangle & \langle\alpha|\hat{I}_z|\beta\rangle \\ \langle\beta|\hat{I}_z|\alpha\rangle & \langle\beta|\hat{I}_z|\beta\rangle \end{bmatrix} \end{array}$$

$$\hat{I}_z = \begin{bmatrix} \langle\alpha|\hat{I}_z|\alpha\rangle & \langle\alpha|\hat{I}_z|\beta\rangle \\ \langle\beta|\hat{I}_z|\alpha\rangle & \langle\beta|\hat{I}_z|\beta\rangle \end{bmatrix} = \begin{bmatrix} 1/2\,\langle\alpha|\alpha\rangle & -1/2\,\langle\alpha|\beta\rangle \\ 1/2\,\langle\beta|\alpha\rangle & -1/2\,\langle\beta|\beta\rangle \end{bmatrix} = \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

- This is convenient, as the operator is just expressed as a matrix of numbers – no need to derive it again, just store it in computer

Operators in Matrix Notation

- The matrices for $\boldsymbol{I_x}$, $\boldsymbol{I_y}$, and $\boldsymbol{I_z}$ are called the *Pauli spin matrices*

$$\hat{\boldsymbol{I}}_x = \begin{bmatrix} 0 & 1/2 \\ 1/2 & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \hat{\boldsymbol{I}}_y = \begin{bmatrix} 0 & -1/2\,\mathrm{i} \\ 1/2\,\mathrm{i} & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix} \quad \hat{\boldsymbol{I}}_z = \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

- Express $|\alpha\rangle$,$|\beta\rangle$,$\langle\alpha|$ and $\langle\beta|$ as 1×2 column and 2×1 row vectors

$$|\alpha\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad |\beta\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad \langle\alpha| = [1 \;\; 0] \quad \langle\beta| = [0 \;\; 1]$$

- Using matrices, the operations of $\boldsymbol{I_x}$, $\boldsymbol{I_y}$, and $\boldsymbol{I_z}$ on $|\alpha\rangle$ and $|\beta\rangle$, and the orthonormality relationships, are shown below

$$\hat{I}_x|\alpha\rangle = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{2}|\beta\rangle \qquad \hat{I}_x|\beta\rangle = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}|\alpha\rangle$$

$$\hat{I}_y|\alpha\rangle = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 \\ \mathrm{i} \end{bmatrix} = \mathrm{i}\frac{1}{2}|\beta\rangle \qquad \hat{I}_y|\beta\rangle = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} -\mathrm{i} \\ 0 \end{bmatrix} = -\mathrm{i}\frac{1}{2}|\alpha\rangle$$

$$\hat{I}_Z|\alpha\rangle = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}|\alpha\rangle \qquad \hat{I}_Z|\beta\rangle = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 \\ -1 \end{bmatrix} = -\frac{1}{2}|\beta\rangle$$

$$\langle\alpha|\alpha\rangle = [1 \;\; 0]\begin{bmatrix} 1 \\ 0 \end{bmatrix} = 1 \qquad \langle\beta|\beta\rangle = [0 \;\; 1]\begin{bmatrix} 0 \\ 1 \end{bmatrix} = 1$$

$$\langle\alpha|\beta\rangle = [1 \;\; 0]\begin{bmatrix} 0 \\ 1 \end{bmatrix} = 0 \qquad \langle\beta|\alpha\rangle = [0 \;\; 1]\begin{bmatrix} 1 \\ 0 \end{bmatrix} = 0$$

Operators in Matrix Notation

- Likewise, we can express the two-spin operators in matrix form
  - example: consider the expectation value for the I_x operator on the A spin in an AX system in the two spin basis (recall $\hat{I}_x|\alpha\rangle = 1/2\,\beta \quad \hat{I}_x|\beta\rangle = 1/2\,\alpha \quad \hat{I}_y|\alpha\rangle = 1/2\,\mathrm{i}\beta \quad \hat{I}_y|\beta\rangle = -1/2\,\mathrm{i}\alpha \quad \hat{I}_z|\alpha\rangle = 1/2\,\alpha \quad \hat{I}_z|\beta\rangle = -1/2\,\beta$)

$$
\begin{array}{c}
 & \alpha\alpha \qquad\qquad \alpha\beta \qquad\qquad \beta\alpha \qquad\qquad \beta\beta \\
\begin{array}{c}\alpha\alpha\\ \alpha\beta\\ \beta\alpha\\ \beta\beta\end{array} &
\begin{bmatrix}
\langle\alpha\alpha|\hat{I}_{\mathrm{A}x}|\alpha\alpha\rangle & \langle\alpha\alpha|\hat{I}_{\mathrm{A}x}|\alpha\beta\rangle & \langle\alpha\alpha|\hat{I}_{\mathrm{A}x}|\beta\alpha\rangle & \langle\alpha\alpha|\hat{I}_{\mathrm{A}x}|\beta\beta\rangle \\
\langle\alpha\beta|\hat{I}_{\mathrm{A}x}|\alpha\alpha\rangle & \langle\alpha\beta|\hat{I}_{\mathrm{A}x}|\alpha\beta\rangle & \langle\alpha\beta|\hat{I}_{\mathrm{A}x}|\beta\alpha\rangle & \langle\alpha\beta|\hat{I}_{\mathrm{A}x}|\beta\beta\rangle \\
\langle\beta\alpha|\hat{I}_{\mathrm{A}x}|\alpha\alpha\rangle & \langle\beta\alpha|\hat{I}_{\mathrm{A}x}|\alpha\beta\rangle & \langle\beta\alpha|\hat{I}_{\mathrm{A}x}|\beta\alpha\rangle & \langle\beta\alpha|\hat{I}_{\mathrm{A}x}|\beta\beta\rangle \\
\langle\beta\beta|\hat{I}_{\mathrm{A}x}|\alpha\alpha\rangle & \langle\beta\beta|\hat{I}_{\mathrm{A}x}|\alpha\beta\rangle & \langle\beta\beta|\hat{I}_{\mathrm{A}x}|\beta\alpha\rangle & \langle\beta\beta|\hat{I}_{\mathrm{A}x}|\beta\beta\rangle
\end{bmatrix}
\end{array}
$$

$$
\hat{I}_{\mathrm{A}x} = \begin{bmatrix}
1/2\langle\alpha\alpha|\beta\alpha\rangle & 1/2\langle\alpha\alpha|\beta\beta\rangle & 1/2\langle\alpha\alpha|\alpha\alpha\rangle & 1/2\langle\alpha\alpha|\alpha\beta\rangle \\
1/2\langle\alpha\beta|\beta\alpha\rangle & 1/2\langle\alpha\beta|\beta\beta\rangle & 1/2\langle\alpha\beta|\alpha\alpha\rangle & 1/2\langle\alpha\beta|\alpha\beta\rangle \\
1/2\langle\beta\alpha|\beta\alpha\rangle & 1/2\langle\beta\alpha|\beta\beta\rangle & 1/2\langle\beta\alpha|\alpha\alpha\rangle & 1/2\langle\beta\alpha|\alpha\beta\rangle \\
1/2\langle\beta\beta|\beta\alpha\rangle & 1/2\langle\beta\beta|\beta\beta\rangle & 1/2\langle\beta\beta|\alpha\alpha\rangle & 1/2\langle\beta\beta|\alpha\beta\rangle
\end{bmatrix}
= \begin{bmatrix} 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 \\ 1/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \end{bmatrix}
= \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}
$$

- The matrices for I_x, I_y, and I_z are

$$
\hat{I}_{\mathrm{A}x} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}
\quad
\hat{I}_{\mathrm{X}x} = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}
\quad
\hat{I}_{\mathrm{Ay}} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ \mathrm{i} & 0 & 0 & 0 \\ 0 & \mathrm{i} & 0 & 0 \end{bmatrix}
\quad
\hat{I}_{\mathrm{Xy}} = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} & 0 & 0 \\ \mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & \mathrm{i} & 0 \end{bmatrix}
\quad
\hat{I}_{\mathrm{A}z} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}
\quad
\hat{I}_{Xz} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}
$$

Density Matrices and Observables for an Ensemble of Spins

- Expectation values give average results for an observable for a single spin or spin system
  - i.e. for a group of spins that all have the same wavefunction
- The density matrix/operator provides an avenue for average or net behavior of an ensemble of spins
- First, consider a single spin
  - write a wavefunction for a linear combination of the members of the basis set (α and β)

$$\left|\psi\right\rangle = c_1\left|\alpha\right\rangle + c_2\left|\beta\right\rangle = \sum_j c_j\phi_j \qquad \left\langle\psi\right| = c_1^*\left\langle\alpha\right| + c_2^*\left\langle\beta\right| = \sum_j c_j^*\phi_j$$

- We can substitute the vector equivalents for $|\alpha\rangle$, $|\beta\rangle$, $\langle\alpha|$ and $\langle\beta|$ to get vector expressions for $|\psi\rangle$ and $\langle\psi|$

$$\left|\alpha\right\rangle = \begin{bmatrix}1\\0\end{bmatrix} \qquad \left|\beta\right\rangle = \begin{bmatrix}0\\1\end{bmatrix} \qquad \left\langle\alpha\right| = [1 \;\; 0] \qquad \left\langle\beta\right| = [0 \;\; 1]$$

$$\left|\psi\right\rangle = c_1\left|\alpha\right\rangle + c_2\left|\beta\right\rangle = c_1\begin{bmatrix}1\\0\end{bmatrix} + c_2\begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}c_1\\c_2\end{bmatrix} \qquad \left\langle\psi\right| = c_1^*\left\langle\alpha\right| + c_2^*\left\langle\beta\right| = c_1^*[1 \;\; 0] + c_2^*[0 \;\; 1] = [c_1^* \;\; c_2^*]$$

- So, the wavefunction (and its complex conjugate) can be written in terms of vectors of the coefficients only

Density Matrices and Observables for an Ensemble of Spins

- The expectation value for some observable represented by the operator $\boldsymbol{Q}$, operating on a wavefunction ψ can be written as

$$\left|\psi\right\rangle = c_1\left|\alpha\right\rangle + c_2\left|\beta\right\rangle = \sum_j c_j\phi_j \qquad \left\langle\psi\right| = c_1^*\left\langle\alpha\right| + c_2^*\left\langle\beta\right| = \sum_j c_j^*\phi_j$$

$$\begin{aligned}\left\langle\boldsymbol{Q}\right\rangle &= \left\langle\psi\middle|\hat{\boldsymbol{Q}}\middle|\psi\right\rangle \\ &= \left[c_1^*\left\langle\alpha\right| + c_2^*\left\langle\beta\right|\right]\,\hat{\boldsymbol{Q}}\,\left[c_1\left|\alpha\right\rangle + c_2\left|\beta\right\rangle\right] \\ &= c_1^*c_1\left\langle\alpha\middle|\hat{\boldsymbol{Q}}\middle|\alpha\right\rangle + c_1^*c_2\left\langle\alpha\middle|\hat{\boldsymbol{Q}}\middle|\beta\right\rangle + c_2^*c_1\left\langle\beta\middle|\hat{\boldsymbol{Q}}\middle|\alpha\right\rangle + c_2^*c_2\left\langle\beta\middle|\hat{\boldsymbol{Q}}\middle|\beta\right\rangle = \sum_j c_j^*c_k\left\langle\psi_j\right|\hat{\boldsymbol{Q}}\left|\psi_k\right\rangle\end{aligned}$$

- Substitute the matrix/vector equivalents

$$\left|\psi\right\rangle = \begin{bmatrix}c_1\\ c_2\end{bmatrix} \qquad \left\langle\psi\right| = [c_1^* \;\; c_2^*]$$

$$\hat{\boldsymbol{Q}} = \begin{bmatrix}\left\langle\alpha\middle|\hat{\boldsymbol{Q}}_z\middle|\alpha\right\rangle & \left\langle\alpha\middle|\hat{\boldsymbol{Q}}_z\middle|\beta\right\rangle \\ \left\langle\beta\middle|\hat{\boldsymbol{Q}}_z\middle|\alpha\right\rangle & \left\langle\beta\middle|\hat{\boldsymbol{Q}}_z\middle|\beta\right\rangle\end{bmatrix}$$

$$\begin{aligned}\left\langle\boldsymbol{Q}\right\rangle &= \left\langle\psi\middle|\hat{\boldsymbol{Q}}\middle|\psi\right\rangle \\ &= [c_1^* \;\; c_2^*]\begin{bmatrix}\left\langle\alpha\middle|\hat{\boldsymbol{Q}}\middle|\alpha\right\rangle & \left\langle\alpha\middle|\hat{\boldsymbol{Q}}\middle|\beta\right\rangle \\ \left\langle\beta\middle|\hat{\boldsymbol{Q}}\middle|\alpha\right\rangle & \left\langle\beta\middle|\hat{\boldsymbol{Q}}\middle|\beta\right\rangle\end{bmatrix}\begin{bmatrix}c_1\\ c_2\end{bmatrix} = [c_1^* \;\; c_2^*]\begin{bmatrix}c_1\left\langle\alpha\middle|\hat{\boldsymbol{Q}}\middle|\alpha\right\rangle + c_2\left\langle\alpha\middle|\hat{\boldsymbol{Q}}\middle|\beta\right\rangle \\ c_1\left\langle\beta\middle|\hat{\boldsymbol{Q}}\middle|\alpha\right\rangle + c_2\left\langle\beta\middle|\hat{\boldsymbol{Q}}\middle|\beta\right\rangle\end{bmatrix} \\ &= c_1^*c_1\left\langle\alpha\middle|\hat{\boldsymbol{Q}}\middle|\alpha\right\rangle + c_1^*c_2\left\langle\alpha\middle|\hat{\boldsymbol{Q}}\middle|\beta\right\rangle + c_2^*c_1\left\langle\beta\middle|\hat{\boldsymbol{Q}}\middle|\alpha\right\rangle + c_2^*c_2\left\langle\beta\middle|\hat{\boldsymbol{Q}}\middle|\beta\right\rangle = \sum_j c_j^*c_k\left\langle\psi_j\right|\hat{\boldsymbol{Q}}\left|\psi_k\right\rangle\end{aligned}$$

- Note the expression for $\langle\hat{Q}\rangle$ includes products of the coefficients, rather than the coefficients themselves, suggesting a way to represent the spin state (wavefunction) in terms of the products

$$\left|\psi\right\rangle\left\langle\psi\right| = \begin{bmatrix}c_1\\ c_2\end{bmatrix}[c_1^* \;\; c_2^*] = \begin{bmatrix}c_1c_1^* & c_1c_2^* \\ c_2c_1^* & c_2c_2^*\end{bmatrix}$$ - note: *NOT* $\left\langle\psi\middle|\psi\right\rangle = 1$!

Density Matrices and Observables for an Ensemble of Spins

- This leads to a different way to formulate the expectation value
  - i.e. for a group of spins that all have the same wavefunction

$$\left\langle \hat{Q} \right\rangle = \mathrm{Tr}\left\{ |\psi\rangle\langle\psi|\hat{Q} \right\}$$

$$= \mathrm{Tr}\left\{ \begin{bmatrix} c_1c_1^* & c_1c_2^* \\ c_2c_1^* & c_2c_2^* \end{bmatrix} \begin{bmatrix} \langle\alpha|\hat{Q}|\alpha\rangle & \langle\alpha|\hat{Q}|\beta\rangle \\ \langle\beta|\hat{Q}|\alpha\rangle & \langle\beta|\hat{Q}|\beta\rangle \end{bmatrix} \right\} = \mathrm{Tr}\begin{bmatrix} c_1c_1^*\langle\alpha|\hat{Q}|\alpha\rangle + c_1c_2^*\langle\beta|\hat{Q}|\alpha\rangle & c_1c_1^*\langle\alpha|\hat{Q}|\beta\rangle + c_1c_2^*\langle\beta|\hat{Q}|\beta\rangle \\ c_2c_1^*\langle\alpha|\hat{Q}|\alpha\rangle + c_2c_2^*\langle\beta|\hat{Q}|\alpha\rangle & c_2c_1^*\langle\alpha|\hat{Q}|\beta\rangle + c_2c_2^*\langle\beta|\hat{Q}|\beta\rangle \end{bmatrix}$$

$$= c_1c_1^*\langle\alpha|\hat{Q}|\alpha\rangle + c_1c_2^*\langle\beta|\hat{Q}|\alpha\rangle + c_2c_1^*\langle\alpha|\hat{Q}|\beta\rangle + c_2c_2^*\langle\beta|\hat{Q}|\beta\rangle$$

$$= c_1^*c_1\langle\alpha|\hat{Q}|\alpha\rangle + c_1^*c_2\langle\alpha|\hat{Q}|\beta\rangle + c_2^*c_1\langle\beta|\hat{Q}|\alpha\rangle + c_2^*c_2\langle\beta|\hat{Q}|\beta\rangle = \sum_j c_j^*c_k\left\langle\psi_j\right|\hat{Q}\left|\psi_k\right\rangle$$

- Now….for an *ensemble* of spins, the magnitude of an observable is the sum of the expectation values for each spin

$$Q = \left\langle\psi_1\middle|\hat{Q}\middle|\psi_1\right\rangle + \left\langle\psi_2\middle|\hat{Q}\middle|\psi_2\right\rangle + \left\langle\psi_3\middle|\hat{Q}\middle|\psi_3\right\rangle + \ldots\ldots.\left\langle\psi_N\middle|\hat{Q}\middle|\psi_N\right\rangle$$

$$= \mathrm{Tr}\left\{\left(|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + |\psi_3\rangle\langle\psi_3| + \ldots\ldots|\psi_N\rangle\langle\psi_N|\right)\hat{Q}\right\}$$

- The *average* value of an observable for an ensemble is

$$\overline{Q} = (1/N)\sum_{i=1}^{N}\left\langle\psi_i\middle|\hat{Q}\middle|\psi_i\right\rangle$$

$$= \mathrm{Tr}\left\{\left[(1/N)\left(|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + |\psi_3\rangle\langle\psi_3| + \ldots\ldots|\psi_N\rangle\langle\psi_N|\right)\right]\hat{Q}\right\}$$

- the overbar indicating the average over the ensemble

Density Matrices and Observables for an Ensemble of Spins

- To simplify this expression, we'll define the *density operator*

$$\hat{\rho} = (1/N)\left(|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + |\psi_3\rangle\langle\psi_3|\right) + \ldots\ldots|\psi_N\rangle\langle\psi_N| = \overline{|\psi\rangle\langle\psi|}$$

- For an ensemble, the average value of the observable, and the average macroscopic observable, then are

$$\overline{Q} = \mathrm{Tr}\left\{\hat{\rho}\hat{Q}\right\} \qquad \overline{Q}_{\mathrm{macro}} = N\ \mathrm{Tr}\left\{\hat{\rho}\hat{Q}\right\}$$

- What does this mean?
  - any observable can be ascertained from two spin operators
  - one of these represents the observable
  - the other represents the ensemble average of the wavefunctions (not necessary to know the wavefunctions for all *N* members of the ensemble)
- For two non-interacting spins, the matrix representation of the density operator (*density matrix*) is

$$\hat{\rho} = \overline{|\psi\rangle\langle\psi|} = \begin{bmatrix} \overline{c_1 c_1^*} & \overline{c_1 c_2^*} \\ \overline{c_2 c_1^*} & \overline{c_2 c_2^*} \end{bmatrix} = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \qquad \text{recall } \ |\psi\rangle\langle\psi| = \begin{bmatrix} c_1 c_1^* & c_1 c_2^* \\ c_2 c_1^* & c_2 c_2^* \end{bmatrix}$$

  - ρ_{11} and ρ_{22} are the populations of states 1 and 2 (i.e. $|\alpha\rangle$ and $|\beta\rangle$ for spin ½)
  - ρ_{12} and ρ_{21} are the coherences

Solving for the Time Dependence of $\hat{\rho}$

- Our observables are time dependent (for example, bulk magnetization precesses with time) hence requiring Schrodinger's time-dependent equation

$$\mathrm{d}(\psi(t))/\mathrm{d}t = -\mathrm{i}/\hbar\ \hat{\boldsymbol{H}}\psi(t) \qquad \psi = \sum_j c_j \varphi_j$$

- We'll consider a single spin with *two* possible states

$$|\psi(t)\rangle = c_1(t)|\psi_1\rangle + c_2(t)|\psi_2\rangle \qquad \langle\psi_1|\psi_1\rangle = \langle\psi_2|\psi_2\rangle = 1 \quad \langle\psi_1|\psi_2\rangle = \langle\psi_2|\psi_1\rangle = 0$$

$$\mathrm{d}(c_1(t)|\psi_1\rangle + c_2(t)|\psi_2\rangle)/\mathrm{d}t = -\mathrm{i}/\hbar\ \hat{\boldsymbol{H}}\left[c_1(t)|\psi_1\rangle + c_2(t)|\psi_2\rangle\right]$$

$$\mathrm{d}(c_1(t))/\mathrm{d}t\ |\psi_1\rangle + \mathrm{d}(c_2(t))/\mathrm{d}t\ |\psi_2\rangle = -\mathrm{i}/\hbar\, c_1(t)\ \hat{\boldsymbol{H}}|\psi_1\rangle - \mathrm{i}/\hbar\, c_2(t)\ \hat{\boldsymbol{H}}|\psi_2\rangle$$

$$\langle\psi_1|\left[\mathrm{d}(c_1(t))/\mathrm{d}t\right]|\psi_1\rangle + \langle\psi_1|\left[\mathrm{d}(c_2(t))/\mathrm{d}t\right]|\psi_2\rangle = -\mathrm{i}/\hbar\left[c_1(t)\langle\psi_1|\hat{\boldsymbol{H}}|\psi_1\rangle + c_2(t)\langle\psi_1|\hat{\boldsymbol{H}}|\psi_2\rangle\right]$$

$$\left[\mathrm{d}(c_1(t))/\mathrm{d}t\right]\langle\psi_1|\psi_1\rangle + \left[\mathrm{d}(c_2(t))/\mathrm{d}t\right]\langle\psi_1|\psi_2\rangle = -\mathrm{i}/\hbar\left[c_1(t)\langle\psi_1|\hat{\boldsymbol{H}}|\psi_1\rangle + c_2(t)\langle\psi_1|\hat{\boldsymbol{H}}|\psi_2\rangle\right]$$

$$\mathrm{d}(c_1(t))/\mathrm{d}t = -\mathrm{i}/\hbar\left[c_1(t)\langle\psi_1|\hat{\boldsymbol{H}}|\psi_1\rangle + c_2(t)\langle\psi_1|\hat{\boldsymbol{H}}|\psi_2\rangle\right] \quad \text{multipled on left by } \langle\psi_1|$$

$$\mathrm{d}(c_2(t))/\mathrm{d}t = -\mathrm{i}/\hbar\left[c_1(t)\langle\psi_2|\hat{\boldsymbol{H}}|\psi_1\rangle + c_2(t)\langle\psi_2|\hat{\boldsymbol{H}}|\psi_2\rangle\right] \quad \text{multipled on left by } \langle\psi_2|$$

$$\mathrm{d}(c_k(t))/\mathrm{d}t = -\mathrm{i}/\hbar\sum_n c_n(t)\langle\psi_k|\hat{\boldsymbol{H}}|\psi_n\rangle$$

$$\mathrm{d}(c_k^*(t))/\mathrm{d}t = \mathrm{i}/\hbar\sum_n c_n^*(t)\langle\psi_n|\hat{\boldsymbol{H}}|\psi_k\rangle \quad \text{without proof}$$

Solving for the Time Dependence of $\hat{\rho}$

- These equations tell us how the wavefunctions (coefficients) change with time

$$\mathrm{d}(c_k(t))/\mathrm{d}t = -\mathrm{i}/\hbar \sum_n c_n(t)\langle\psi_k|\hat{\boldsymbol{H}}|\psi_n\rangle \qquad \mathrm{d}(c_k^*(t))/\mathrm{d}t = \mathrm{i}/\hbar \sum_n c_n^*(t)\langle\psi_n|\hat{\boldsymbol{H}}|\psi_k\rangle$$

- Thus, we can write a general expression for the change with time of the density matrix

$$\begin{aligned}
\frac{\mathrm{d}\langle\psi_k|\hat{\boldsymbol{\rho}}|\psi_m\rangle}{\mathrm{d}t} &= \overline{\frac{\mathrm{d}(c_k c_m^*)}{\mathrm{d}t}} = \overline{c_k\frac{\mathrm{d}(c_m^*)}{\mathrm{d}t}} + \overline{\frac{\mathrm{d}(c_k)}{\mathrm{d}t}c_m^*} \\
&= \mathrm{i}/\hbar \sum_n c_k c_n^* \langle\psi_n|\hat{\boldsymbol{H}}|\psi_m\rangle - \mathrm{i}/\hbar \sum_n \langle\psi_k|\hat{\boldsymbol{H}}|\psi_n\rangle\, c_n c_m^* \\
&= \mathrm{i}/\hbar \sum_n \langle\psi_k|\hat{\boldsymbol{\rho}}|\psi_n\rangle\langle\psi_n|\hat{\boldsymbol{H}}|\psi_m\rangle - \mathrm{i}/\hbar \sum_n \langle\psi_k|\hat{\boldsymbol{H}}|\psi_n\rangle\langle\psi_n|\hat{\boldsymbol{\rho}}|\psi_m\rangle \\
&= \mathrm{i}/\hbar\left[\langle\psi_k|\hat{\boldsymbol{\rho}}\hat{\boldsymbol{H}}|\psi_m\rangle - \langle\psi_k|\hat{\boldsymbol{H}}\hat{\boldsymbol{\rho}}|\psi_m\rangle\right]
\end{aligned}$$

$$\frac{\mathrm{d}\hat{\boldsymbol{\rho}}(t)}{\mathrm{d}t} = \mathrm{i}/\hbar\left\{[\hat{\boldsymbol{\rho}}][\hat{\boldsymbol{H}}] - [\hat{\boldsymbol{H}}][\hat{\boldsymbol{\rho}}]\right\} \equiv \mathrm{i}/\hbar\left[\hat{\boldsymbol{\rho}}(t), \hat{\boldsymbol{H}}\right] \quad \text{(commutator)}$$

- The last expression is called the Lioville - von Neuman equation
  - knowing $\hat{\rho}$ at some given time (i.e. at equilibrium, t = 0), can solve for the time dependence of $\hat{\rho}$ (i.e. $\hat{\rho}$ at any other time), so can calculate observables

$$\overline{\boldsymbol{Q}} = \mathrm{Tr}\left\{[\hat{\boldsymbol{\rho}}][\hat{\boldsymbol{Q}}]\right\} \qquad \overline{\boldsymbol{Q}}_{\mathrm{macro}} = N\ \mathrm{Tr}\left\{[\hat{\boldsymbol{\rho}}][\hat{\boldsymbol{Q}}]\right\}$$

Example: Precession of x Magnetization in B_0

- The Bloch equation analysis demonstrated how x magnetization (M_x) precesses with time about the B_0 axis

$$M_x(t) = M_{x,0}\cos(\omega_0 t) - M_{y,0}\sin(\omega_0 t)$$

- Here, we'll see if we can predict this behavior (roughly) using the QM methods we've outlined
  - recall $\overline{Q} = \mathrm{Tr}\left\{\left[\hat{\rho}\right]\left[\hat{Q}\right]\right\}$ $\quad \overline{Q}_{\mathrm{macro}} = N\ \mathrm{Tr}\left\{\left[\hat{\rho}\right]\left[\hat{Q}\right]\right\}$ $\quad \hat{I}_x = \begin{bmatrix} 0 & 1/2 \\ 1/2 & 0 \end{bmatrix}$
  - ask, "What elements of the density matrix are important for Ix?"
  - determine $\overline{I}_x$ (spin ½)

$$\overline{I}_x = \mathrm{Tr}\left\{\left[\hat{\rho}\right]\left[\hat{I}_x\right]\right\} = \mathrm{Tr}\left\{\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}\begin{bmatrix} 0 & 1/2 \\ 1/2 & 0 \end{bmatrix}\right\} = \mathrm{Tr}\begin{bmatrix} \rho_{11}\times 0 + \rho_{12}\times 1/2 & \rho_{11}\times 1/2 + \rho_{12}\times 0 \\ \rho_{21}\times 0 + \rho_{22}\times 1/2 & \rho_{21}\times 1/2 + \rho_{22}\times 0 \end{bmatrix} = 1/2(\rho_{12} + \rho_{21})$$

- This says x-magnetization is proportional to ρ_{12} and ρ_{21} (only those density matrix elements are relevant for x-magnetization
- If we like, we can write a density matrix/operator with only elements ρ_{12} and ρ_{21} to analyze x-magnetization

$$\hat{\rho}_x = \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix}$$

Example: Precession of *x* Magnetization in B_0

- How do the elements of $\hat{\rho}$ and $\hat{\rho}_x$ vary with time?

$$\frac{\mathrm{d}\left[\hat{\boldsymbol{\rho}}_x\right]}{\mathrm{d}t} = \mathrm{i}/\hbar\left[\hat{\boldsymbol{\rho}}_x, \hat{\boldsymbol{H}}\right] = \mathrm{i}/\hbar\left\{\left[\hat{\boldsymbol{\rho}}_x\right]\left[\hat{\boldsymbol{H}}\right] - \left[\hat{\boldsymbol{H}}\right]\left[\hat{\boldsymbol{\rho}}_x\right]\right\} \qquad \hat{\boldsymbol{H}} = -\gamma\hbar B_0 \hat{\boldsymbol{I}}_z = -\gamma\hbar B_0 \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}$$

$$= \mathrm{i}/\hbar(-\gamma\hbar B_0)\left\{\begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix}\begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} - \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}\begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix}\right\}$$

$$= -\mathrm{i}\gamma B_0\left\{\begin{bmatrix} 0 & -1/2\,\rho_{12} \\ 1/2\,\rho_{21} & 0 \end{bmatrix} - \begin{bmatrix} 0 & 1/2\,\rho_{12} \\ -1/2\,\rho_{21} & 0 \end{bmatrix}\right\} = -\mathrm{i}\gamma B_0\begin{bmatrix} 0 & -\rho_{12} \\ \rho_{21} & 0 \end{bmatrix}$$

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

$$= \mathrm{i}/\hbar(-\gamma\hbar B_0)\left\{\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}\begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} - \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}\right\}$$

$$= -\mathrm{i}\gamma B_0\left\{\begin{bmatrix} 1/2\,\rho_{11} & -1/2\,\rho_{12} \\ 1/2\,\rho_{21} & -1/2\,\rho_{22} \end{bmatrix} - \begin{bmatrix} 1/2\,\rho_{11} & 1/2\,\rho_{12} \\ -1/2\,\rho_{21} & -1/2\,\rho_{22} \end{bmatrix}\right\} = -\mathrm{i}\gamma B_0\begin{bmatrix} 0 & -\rho_{12} \\ \rho_{21} & 0 \end{bmatrix}$$

- So, both ρ_{12} and ρ_{21} change with time, and we can solve for their time dependence

$$\frac{\mathrm{d}\left[\rho_{12}(t)\right]}{\mathrm{d}t} = -\mathrm{i}\gamma B_0(-\rho_{12}(t)) = \mathrm{i}\omega_0\rho_{12}(t) \qquad \rho_{12}(t) = \rho_{12}(0)e^{(\mathrm{i}\omega_0 t)} = \rho_{12}(0)(\cos(\omega_0 t) + \mathrm{i}\,\sin(\omega_0 t))$$

$$\frac{\mathrm{d}\left[\rho_{21}(t)\right]}{\mathrm{d}t} = -\mathrm{i}\gamma B_0(\rho_{21}(t)) = -\mathrm{i}\omega_0\rho_{21}(t) \qquad \rho_{21}(t) = \rho_{21}(0)e^{(-\mathrm{i}\omega_0 t)} = \rho_{21}(0)(\cos(\omega_0 t) - \mathrm{i}\,\sin(\omega_0 t))$$

Example: Precession of *x* Magnetization in B_0

- So, both ρ_{12} and ρ_{21} change with time, and we can solve for their time dependence

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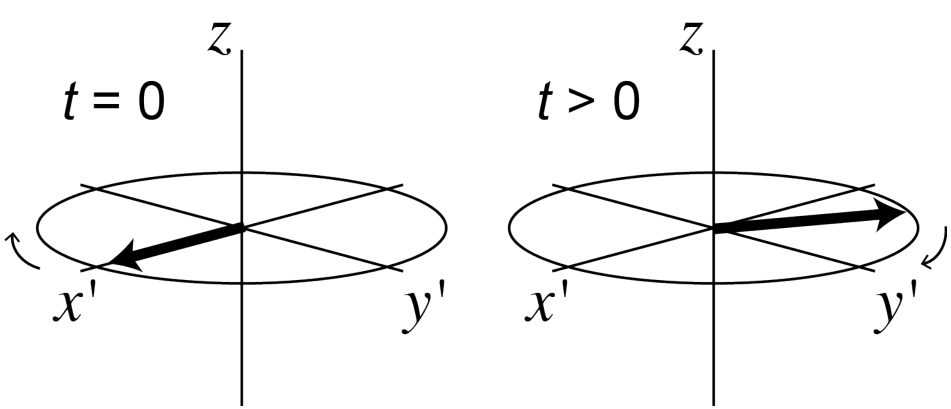
$$\frac{\mathrm{d}[\rho_{21}(t)]}{\mathrm{d}t} = -\mathrm{i}\gamma B_0(\rho_{21}(t)) = -\mathrm{i}\omega_0\rho_{21}(t) \qquad \rho_{21}(t) = \rho_{21}(0)e^{(-\mathrm{i}\omega_0 t)} = \rho_{21}(0)(\cos(\omega_0 t) - \mathrm{i}\,\sin(\omega_0 t))$$

- Results echo Bloch equation results

- Elements that represent *x*-magnetization precess



Density Matrix at Equilibrium

- So…..what do we have?
  - we have a route to an observable:

$$\overline{\boldsymbol{Q}} = \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\rho}}\right]\left[\hat{\boldsymbol{Q}}\right]\right\} \quad \text{for instance} \quad \overline{\boldsymbol{I}_x} = \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\rho}}\right]\left[\hat{\boldsymbol{I}}_x\right]\right\}$$

  - we have a route to the time dependence of the density matrix

$$\frac{\mathrm{d}\hat{\boldsymbol{\rho}}(t)}{\mathrm{d}t} = \mathrm{i}/\hbar\left\{\left[\hat{\boldsymbol{\rho}}\right]\left[\hat{\boldsymbol{H}}\right] - \left[\hat{\boldsymbol{H}}\right]\left[\hat{\boldsymbol{\rho}}\right]\right\} \equiv \mathrm{i}/\hbar\left[\hat{\boldsymbol{\rho}}(t), \hat{\boldsymbol{H}}\right]$$

- So…..what *don't* we have
  - a place to start, for instance, at equilibrium (ρ at equilibrium, ρ_{eq})
  - values for density matrix elements
- Assume ρ at equilibrium, ρ_{eq}
  - presumably, we can decide what all elements of ρ are at some time, so choose t = 0 (equilibrium)
- What are the diagonal elements (ρ_{nn})?
  - $\rho_{nn} = c_n c_n^*$ = a probability of being in a particular state (*i.e.* α or β)
  - these we can get from Boltzman factors/statistics

$$\rho_{nn} = c_n c_n^* = e^{(-E_n/(k_B T))}/Z \cong 1/Z - E_n/(Z k_\mathrm{B} T) \qquad Z = \sum_n e^{(-E_n/(k_\mathrm{B} T))} = 1 + 1 = 2 \text{ for } |\alpha\rangle, |\beta\rangle \text{ basis and small } E_n$$

  - so, $Z \cong$ number of states

- For convenience, we define a *deviation matrix*, σ, with elements

$$\rho_{nn} \cong 1/Z - E_n/(Z k_\mathrm{B} T) = 1/Z - \sigma_{nn}$$

Density Matrix at Equilibrium

- What are off-diagonal elements (ρ_{nm}) at equilibrium?

  - off-diagonal elements represent *coherences*

  - these are only finite when there are spins that have transverse polarization vectors (wavefunction is linear combination of basis set elements) *AND* there is a net alignment of these in the *x*-*y* plane

  - *at equilibrium, there is no net bulk magnetic moment in the x-y plane, so these elements are zero*

Examples for a spin ½ nucleus

$$\rho_{nn} = c_n c_n^* = e^{(-E_n/(k_B T))}/Z \cong 1/Z - E_n/(Zk_\mathrm{B}T) = 1/Z - \sigma_{nn} \qquad \hat{\boldsymbol{H}} = -\gamma\hbar B_0 \hat{\boldsymbol{I}}_z \qquad E = -m\gamma\hbar B_0$$

$$Z = \sum_n e^{(-E_n/(k_\mathrm{B}T))} = 2 \text{ for spin } 1/2 \qquad \hat{\boldsymbol{H}} = -\gamma\hbar B_0 \hat{\boldsymbol{I}}_z = -\gamma\hbar B_0 \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}$$

- The density matrix, and deviation matrix, at equilibrium are:

$$\hat{\boldsymbol{\rho}}_{eq} = \begin{bmatrix} e^{(-E_n/(k_B T))}/Z & 0 \\ 0 & e^{(-E_n/(k_B T))}/Z \end{bmatrix} = \frac{1}{2}\begin{bmatrix} e^{(-E_n/(k_B T))} & 0 \\ 0 & e^{(-E_n/(k_B T))} \end{bmatrix} = \frac{1}{2}\begin{bmatrix} e^{(\gamma\hbar B_0/(2k_B T))} & 0 \\ 0 & e^{(-\gamma\hbar B_0/(2k_B T))} \end{bmatrix}$$

$$\hat{\boldsymbol{\sigma}}_{eq} = \begin{bmatrix} -E_n/Zk_B T & 0 \\ 0 & -E_n/Zk_B T \end{bmatrix} = \frac{1}{2}\begin{bmatrix} -E_n/k_B T & 0 \\ 0 & -E_n/k_B T \end{bmatrix} = \frac{1}{2}\begin{bmatrix} \gamma\hbar B_0/2k_B T & 0 \\ 0 & -\gamma\hbar B_0/2k_B T \end{bmatrix}$$

- There should be no time dependence of these at equilibrium:

$$\frac{\mathrm{d}\left[\hat{\boldsymbol{\sigma}}_{eq}\right]}{\mathrm{d}t} = \mathrm{i}/\hbar\left[\hat{\boldsymbol{\sigma}}_{eq}, \hat{\boldsymbol{H}}\right] = \mathrm{i}/\hbar\left\{\left[\hat{\boldsymbol{\sigma}}_{eq}\right]\left[\hat{\boldsymbol{H}}\right] - \left[\hat{\boldsymbol{H}}\right]\left[\hat{\boldsymbol{\sigma}}_{eq}\right]\right\}$$

$$= \mathrm{i}/\hbar(-\gamma\hbar B_0)\left\{\frac{1}{2}\begin{bmatrix} \gamma\hbar B_0/2k_B T & 0 \\ 0 & -\gamma\hbar B_0/2k_B T \end{bmatrix}\begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} - \frac{1}{2}\begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}\begin{bmatrix} \gamma\hbar B_0/2k_B T & 0 \\ 0 & -\gamma\hbar B_0/2k_B T \end{bmatrix}\right\}$$

$$= -\mathrm{i}\gamma B_0\left\{\frac{1}{2}\begin{bmatrix} 1/2\,\gamma\hbar B_0/2k_B T & 0 \\ 0 & 1/2\,\gamma\hbar B_0/2k_B T \end{bmatrix} - \frac{1}{2}\begin{bmatrix} 1/2\,\gamma\hbar B_0/2k_B T & 0 \\ 0 & 1/2\,\gamma\hbar B_0/2k_B T \end{bmatrix}\right\} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} = 0$$

- so, no variation with time, as expected (diagonal matrices commute: AB=BA, so AB-BA=0 for diagonal matrices A and B)

What about M_z?

$$\overline{Q} = \mathrm{Tr}\left\{\hat{\rho}\hat{Q}\right\} \qquad \overline{Q}_{\text{macro}} = N\ \mathrm{Tr}\left\{\hat{\rho}\hat{Q}\right\} \qquad \hat{\boldsymbol{\mu}}_z = \gamma\hbar\hat{\boldsymbol{I}}_z = \frac{\gamma\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$$

- At thermal equilibrium, the equilibrium bulk magnetization along the *z*-axis, M_z, is equal to what we have defined as M_0

$$M_0 \approx \frac{N\gamma^2\hbar^2 B_0}{k_B T(2I+1)}\sum_{m=-I}^{I} m^2 \approx \frac{N\gamma^2\hbar^2 B_0 I(I+1)}{3k_B T} \qquad \text{for spin } 1/2,\ M_0 \approx \frac{N\gamma^2\hbar^2 B_0}{4k_B T}$$

- We can calculate this observable

$$M_{z,eq} = M_0 = N\ \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\sigma}}_{eq}\right]\left[\hat{\boldsymbol{\mu}}_z\right]\right\} = N\ \mathrm{Tr}\left\{\frac{1}{2}\begin{bmatrix}\gamma\hbar B_0/2k_BT & 0\\ 0 & -\gamma\hbar B_0/2k_BT\end{bmatrix}\frac{\gamma\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\right\}$$

$$= N\ \mathrm{Tr}\left\{\frac{\gamma\hbar}{4}\begin{bmatrix}\gamma\hbar B_0/2k_BT & 0\\ 0 & \gamma\hbar B_0/2k_BT\end{bmatrix}\right\} = \frac{N\gamma^2\hbar^2 B_0}{(4k_BT)}$$

- Curie's law (Curie-Weiss law) for magnetic susceptibility in paramagnetic compounds

$$\chi_m = \frac{N_A\mu_0}{3k_BT}\mu^2$$

- the dimensionless quantity χ_m is the molar magnetic susceptibility, μ_0 is the permeability of free space (proportional to B_0), μ is the Bohr magneton (J/T)

What about M_x?

$$\overline{\boldsymbol{Q}} = \mathrm{Tr}\left\{\hat{\rho}\hat{\boldsymbol{Q}}\right\} \qquad \overline{\boldsymbol{Q}}_{\mathrm{macro}} = N\ \mathrm{Tr}\left\{\hat{\rho}\hat{\boldsymbol{Q}}\right\} \qquad \hat{\boldsymbol{\mu}}_x = \gamma\hbar\hat{\boldsymbol{I}}_x = \frac{\gamma\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

- At thermal equilibrium, no net, bulk magnetization is expected in the transverse plane (M_x or M_y)
  - this is confirmed by the following calculation

$$M_{x,eq} = N\ \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\sigma}}_{eq}\right]\left[\hat{\boldsymbol{\mu}}_{\boldsymbol{x}}\right]\right\} = N\ \mathrm{Tr}\left\{\frac{1}{2}\begin{bmatrix} \gamma\hbar B_0/2k_BT & 0 \\ 0 & -\gamma\hbar B_0/2k_BT \end{bmatrix}\frac{\gamma\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\right\}$$

$$= N\ \mathrm{Tr}\left\{\frac{\gamma\hbar}{4}\begin{bmatrix} 0 & \gamma\hbar B_0/2k_BT \\ -\gamma\hbar B_0/2k_BT & 0 \end{bmatrix}\right\} = 0$$

- Same result for M_y at equilibrium (zero)

- So, these methods reproduce our expectations based on what we know already about bulk equilibrium magnetization

What elements give M_x?

- The *equilibrium* density matrix (or deviation density matrix) indicates no *x*-magnetization at equilibrium
- How about not at equilibrium?
- The elements of the density matrix can be associated with particular properties (especially for first order systems)

  - previously, we asked, "What elements of the density matrix are important for Ix?"

$$\overline{\boldsymbol{I}_x} = \mathrm{Tr}\left\{[\hat{\rho}][\hat{\boldsymbol{I}}_x]\right\} = \mathrm{Tr}\left\{\begin{bmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{bmatrix}\begin{bmatrix}0 & 1/2\\ 1/2 & 0\end{bmatrix}\right\} = \mathrm{Tr}\begin{bmatrix}\rho_{11}\times 0+\rho_{12}\times 1/2 & \rho_{11}\times 1/2+\rho_{12}\times 0\\ \rho_{21}\times 0+\rho_{22}\times 1/2 & \rho_{21}\times 1/2+\rho_{22}\times 0\end{bmatrix} = 1/2(\rho_{12}+\rho_{21})$$

  - ask again, for M_x

$$M_x = \mathrm{Tr}\left\{[\hat{\boldsymbol{\sigma}}][\hat{\boldsymbol{\mu}}_x]\right\} = \mathrm{Tr}\left\{\begin{bmatrix}\boldsymbol{\sigma}_{11} & \boldsymbol{\sigma}_{12}\\ \boldsymbol{\sigma}_{21} & \boldsymbol{\sigma}_{22}\end{bmatrix}\frac{\gamma\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\right\} = \mathrm{Tr}\left\{\frac{\gamma\hbar}{2}\begin{bmatrix}\boldsymbol{\sigma}_{12} & \boldsymbol{\sigma}_{11}\\ \boldsymbol{\sigma}_{22} & \boldsymbol{\sigma}_{21}\end{bmatrix}\right\} = \gamma\hbar/2(\boldsymbol{\sigma}_{12}+\boldsymbol{\sigma}_{21})$$

  - so, σ_{12} and σ_{21} (ρ_{12}, ρ_{21}) are associated with *x*-magnetization
  - and, as we've demonstrated previously, these precess in a magnetic field
  - these are also associated with transition probabilities: connect $|\alpha\rangle$ and $|\beta\rangle$ for single spin cases

Rotation operators – a more general description of rotation (precession)

- We previously wrote an expression for the time dependence of the density matrix (same for deviation matrix)

$$\frac{\mathrm{d}\hat{\boldsymbol{\rho}}(t)}{\mathrm{d}t} = \mathrm{i}/\hbar\left\{\left[\hat{\boldsymbol{\rho}}\right]\left[\hat{\boldsymbol{H}}\right]-\left[\hat{\boldsymbol{H}}\right]\left[\hat{\boldsymbol{\rho}}\right]\right\} \equiv \mathrm{i}/\hbar\left[\hat{\boldsymbol{\rho}}(t),\hat{\boldsymbol{H}}\right] \quad \text{(commutator)}$$

$$\frac{\mathrm{d}\hat{\boldsymbol{\sigma}}(t)}{\mathrm{d}t} = \mathrm{i}/\hbar\left\{\left[\hat{\boldsymbol{\sigma}}\right]\left[\hat{\boldsymbol{H}}\right]-\left[\hat{\boldsymbol{H}}\right]\left[\hat{\boldsymbol{\sigma}}\right]\right\} \equiv \mathrm{i}/\hbar\left[\hat{\boldsymbol{\sigma}}(t),\hat{\boldsymbol{H}}\right] \quad \text{(commutator)}$$

- The general solution to this latter equation (without proof) is:

$$\hat{\boldsymbol{\sigma}}(t) = e^{(-(\mathrm{i}/\hbar)\hat{\boldsymbol{H}}t)}\hat{\boldsymbol{\sigma}}(0)\; e^{((\mathrm{i}/\hbar)\hat{\boldsymbol{H}}t)} = \hat{\mathbf{R}}(t)\hat{\boldsymbol{\sigma}}(0)\hat{\mathbf{R}}^{-1}(t)$$

 - can write in terms of rotation operators ($\hat{\mathbf{R}}$, $\hat{\mathbf{R}}^{-1}$) that include the Hamiltonian

- The $\hat{\mathbf{R}}_z$ operator describes precession (B_0 interacting with $\hat{\boldsymbol{I}}_z$)

 - the matrix elements of $\hat{\mathbf{R}}_z$ are

$$\hat{\boldsymbol{H}} = -\gamma\hbar B_0\hat{\boldsymbol{I}}_z = -\gamma\hbar B_0\begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} \quad \hat{\boldsymbol{I}}_z = \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}$$

$$\hat{\mathbf{R}}_z(t) = e^{(-(\mathrm{i}/\hbar)\hat{\boldsymbol{H}}(t))} = e^{(-(\mathrm{i}/\hbar)(-\gamma\hbar B_0\hat{\boldsymbol{I}}_z)t)} = e^{(\mathrm{i}\gamma B_0 t\hat{\boldsymbol{I}}_z)} = e^{(\mathrm{i}\omega t\hat{\boldsymbol{I}}_z)}$$

 - the matrix representation of $\hat{\mathbf{R}}_z$ is then

$$\hat{\mathbf{R}}_z = \begin{bmatrix} e^{(\mathrm{i}\Delta\omega t/2)} & 0 \\ 0 & e^{(-\mathrm{i}\Delta\omega t/2)} \end{bmatrix}$$

M_X and M_y Precess at $\Delta\omega$

- For convenience, we'll write the deviation matrix for M_x as chemical shift offsets (δ) in σ_{12} and σ_{21} (elements involved in precession)

$$\hat{\boldsymbol{\sigma}}(0) = \begin{bmatrix} 0 & \delta \\ \delta & 0 \end{bmatrix}$$

- We can then calculate $\hat{\boldsymbol{\sigma}}(t)$ from $\hat{\boldsymbol{\sigma}}(0)$ under the $\hat{\mathbf{R}}_z$ operator

$$\hat{\boldsymbol{\sigma}}(t) = \hat{\mathbf{R}}_z(t)\hat{\boldsymbol{\sigma}}(0)\hat{\mathbf{R}}_z^{-1}(t) = \begin{bmatrix} e^{(\mathrm{i}\Delta\omega t/2)} & 0 \\ 0 & e^{(-\mathrm{i}\Delta\omega t/2)} \end{bmatrix}\begin{bmatrix} 0 & \delta \\ \delta & 0 \end{bmatrix}\begin{bmatrix} e^{(-\mathrm{i}\Delta\omega t/2)} & 0 \\ 0 & e^{(\mathrm{i}\Delta\omega t/2)} \end{bmatrix}$$

$$= \begin{bmatrix} e^{(\mathrm{i}\Delta\omega t/2)} & 0 \\ 0 & e^{(-\mathrm{i}\Delta\omega t/2)} \end{bmatrix}\begin{bmatrix} 0 & \delta e^{(\mathrm{i}\Delta\omega t/2)} \\ \delta e^{(-\mathrm{i}\Delta\omega t/2)} & 0 \end{bmatrix} = \begin{bmatrix} 0 & \delta e^{(\mathrm{i}\Delta\omega t)} \\ \delta e^{(-\mathrm{i}\Delta\omega t)} & 0 \end{bmatrix}$$

- We can write the complex exponentials as cosines and sines (Euler's formula) $e^{\mathrm{i}x} = \cos x + \mathrm{i}\sin x \qquad e^{\mathrm{i}\omega t} = \cos\omega t + \mathrm{i}\sin\omega t$

$$\hat{\boldsymbol{\sigma}}(t) = \begin{bmatrix} 0 & \delta e^{(\mathrm{i}\Delta\omega t)} \\ \delta e^{(-\mathrm{i}\Delta\omega t)} & 0 \end{bmatrix} = \delta\begin{bmatrix} 0 & \cos(\Delta\omega t) \\ \cos(\Delta\omega t) & 0 \end{bmatrix} + \delta\begin{bmatrix} 0 & \mathrm{i}\sin(\Delta\omega t) \\ -\mathrm{i}\sin(\Delta\omega t) & 0 \end{bmatrix}$$

- Results are expected (same as predicted by Bloch equations)

$$\hat{\boldsymbol{\sigma}}_{12}(t) = \cos(\Delta\omega t) + \mathrm{i}\sin(\Delta\omega t) \qquad M_x(t) = M_{x,0}\cos(\omega_0 t) - M_{y,0}\sin(\omega_0 t)$$

$$\hat{\boldsymbol{\sigma}}_{21}(t) = \cos(\Delta\omega t) - \mathrm{i}\sin(\Delta\omega t) \qquad M_y(t) = M_{y,0}\cos(\omega_0 t) + M_{x,0}\sin(\omega_0 t)$$

Rotation operators for an RF pulse along *x*-axis in the rotating frame

- In the rotating frame, an RF pulse, say along the x-axis, produces a magnetic field (B_1) in the *x*-direction
- In the rotating frame, the Hamiltonian is

$$\hat{\boldsymbol{H}}' = -(\gamma B_1/\hbar)\hat{\boldsymbol{I}}'_x$$

- The $\hat{\mathbf{R}}_x$ operator describes rotation around the *x*-axis (RF pulse along the *x*-axis)

$$\hat{\boldsymbol{\sigma}}(t) = e^{(-(\mathrm{i}/\hbar)\hat{\boldsymbol{H}}'t)}\hat{\boldsymbol{\sigma}}(0)\ e^{((\mathrm{i}/\hbar)\hat{\boldsymbol{H}}'t)} = \hat{\mathbf{R}}_x\hat{\boldsymbol{\sigma}}(0)\hat{\mathbf{R}}_x^{-1}$$

- Problem: the $\boldsymbol{I}_x$ operator doesn't commute with the Hamiltonian that gave rise to our basis set functions

  -can't simply insert $\boldsymbol{I}_x$ in the exponential operator to evaluate matrix elements ($\boldsymbol{I}_x$ mixes spin states, creates transverse magnetization, coherences)

- Operations of $\hat{\mathbf{R}}_x$ operators don't simply cause elements of $\sigma(t)$ to oscillate, but convert diagonal elements (*z*-magnetization, σ_{11}, σ_{22}) to off-diagonal elements (*x*- and *y*-magnetization, coherences) in a $\sin(B_1\gamma t)$ dependent manner

Rotation operators for an RF pulse along *x*-axis in the rotating frame

- The $\mathbf{R}_x$ operator in the rotating frame is (for spin ½)

$$\hat{\mathbf{R}}_x = \begin{bmatrix} \cos(\omega_1 t/2) & -\mathrm{i}\sin(\omega_1 t/2) \\ -\mathrm{i}\sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix} \quad \hat{\mathbf{R}}_x^{-1} = \begin{bmatrix} \cos(\omega_1 t/2) & \mathrm{i}\sin(\omega_1 t/2) \\ \mathrm{i}\sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix}$$

- here ω_1 is the frequency (radians/sec) of rotation due to the B_1 field
- $\omega_1 t$ is the pulse angle (radians): $\omega_1 t = \pi/2$ (90° pulse), $\omega_1 t = \pi$ (180° pulse)

- The most common pulses in NMR are 90° and 180° pulses, so and we can easily write R_x operators for these

$$\cos(\omega_1 t/2) = \cos((\pi/2)/2) = \pm\sqrt{(1+\cos(\pi/2))/2} = \pm\sqrt{1/2} = \pm\sqrt{2}/2$$

$$\sin(\omega_1 t/2) = \sin((\pi/2)/2) = \pm\sqrt{(1-\cos(\pi/2))/2} = \pm\sqrt{1/2} = \pm\sqrt{2}/2$$

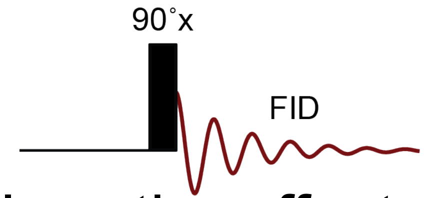
$$\cos(\omega_1 t/2) = \cos(\pi/2) = 0 \qquad \sin(\omega_1 t/2) = \sin(\pi/2) = 1$$

- substituting

$$\hat{\mathbf{R}}_{x,\pi/2} = \frac{\sqrt{2}}{2}\begin{bmatrix} 1 & -\mathrm{i} \\ -\mathrm{i} & 1 \end{bmatrix} \quad \hat{\mathbf{R}}_{x,\pi/2}^{-1} = \frac{\sqrt{2}}{2}\begin{bmatrix} 1 & \mathrm{i} \\ \mathrm{i} & 1 \end{bmatrix} \quad \hat{\mathbf{R}}_{x,\pi} = \begin{bmatrix} 0 & -\mathrm{i} \\ -\mathrm{i} & 0 \end{bmatrix} \quad \hat{\mathbf{R}}_{x,\pi}^{-1} = \begin{bmatrix} 0 & \mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}$$

- The $\mathbf{R}_y$ operators are derived in the same manner

One Pulse and FID



- Example: using the $\mathbf{R}_x$ and $\mathbf{R}_z$ operators, analyze the effect of a 90° pulse along the *x*-axis on equilibrium magnetization, and then monitoring precession of the transverse magnetization

$$\hat{\boldsymbol{\sigma}}(t) = \hat{\boldsymbol{R}}_z(t)\hat{\mathbf{R}}_x\hat{\boldsymbol{\sigma}}(0)\hat{\mathbf{R}}_x^{-1}\hat{\boldsymbol{R}}_z^{-1}(t)$$

- First, using the $\mathbf{R}_x$ operators, apply a 90° pulse along the *x*-axis to equilibrium magnetization

$$\hat{\boldsymbol{\sigma}}(t) = e^{(-(\mathrm{i}/\hbar)\hat{\boldsymbol{H}}'t)}\hat{\boldsymbol{\sigma}}(0)\ e^{((\mathrm{i}/\hbar)\hat{\boldsymbol{H}}'t)} = \hat{\mathbf{R}}_x\hat{\boldsymbol{\sigma}}(0)\hat{\mathbf{R}}_x^{-1}$$

- Here, at t = 0 (equilibrium), the equilibrium deviation density matrix ($\sigma(0)=\sigma_{eq}$) can be written as

$$\hat{\boldsymbol{\sigma}}_{eq} = \frac{1}{2}\begin{bmatrix} \gamma\hbar B_0/2k_BT & 0 \\ 0 & -\gamma\hbar B_0/2k_BT \end{bmatrix} \equiv \frac{1}{2}\begin{bmatrix} \delta & 0 \\ 0 & -\delta \end{bmatrix} \propto M_z(\mathrm{eq})$$

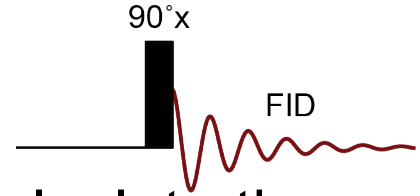
- So, $\boldsymbol{\sigma}(t)$ (time just after the pulse) is

$$\hat{\boldsymbol{\sigma}}(t) = \hat{\mathbf{R}}_{x,\pi/2}\hat{\boldsymbol{\sigma}}_{eq}\hat{\mathbf{R}}_{x,\pi/2}^{-1} = \frac{\sqrt{2}}{2}\begin{bmatrix} 1 & -\mathrm{i} \\ -\mathrm{i} & 1 \end{bmatrix}\frac{1}{2}\begin{bmatrix} \delta & 0 \\ 0 & -\delta \end{bmatrix}\frac{\sqrt{2}}{2}\begin{bmatrix} 1 & \mathrm{i} \\ \mathrm{i} & 1 \end{bmatrix} = \frac{1}{4}\begin{bmatrix} 1 & -\mathrm{i} \\ -\mathrm{i} & 1 \end{bmatrix}\begin{bmatrix} \delta & \mathrm{i}\delta \\ -\mathrm{i}\delta & -\delta \end{bmatrix} = \frac{1}{4}\begin{bmatrix} 0 & 2\mathrm{i}\delta \\ -2\mathrm{i}\delta & 0 \end{bmatrix} = \delta\frac{1}{2}\begin{bmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{bmatrix}$$

- Recall $\hat{\boldsymbol{I}}_y = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}$ and $-\hat{\boldsymbol{I}}_y = \frac{1}{2}\begin{bmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{bmatrix}$

  - so, the result gives -*y* magnetization ($-\boldsymbol{I}_y$)

Evolution of the FID



- Starting just after the pulse (call this t_0) we can calculate the density matrix at each point in the FID (t_1, t_2, t_3, etc., where the time between points, Δt, is the dwell time) using $\mathbf{R}_z$ operators

$$\hat{\boldsymbol{\sigma}}(t_1) = \hat{\boldsymbol{R}}_z(t_1)\hat{\boldsymbol{\sigma}}(t_0)\hat{\boldsymbol{R}}_z^{-1}(t_1) \qquad \hat{\boldsymbol{\sigma}}(t_2) = \hat{\boldsymbol{R}}_z(t_2)\hat{\boldsymbol{\sigma}}(t_1)\hat{\boldsymbol{R}}_z^{-1}(t_2) \qquad \hat{\boldsymbol{\sigma}}(t_3) = \hat{\boldsymbol{R}}_z(t_3)\hat{\boldsymbol{\sigma}}(t_2)\hat{\boldsymbol{R}}_z^{-1}(t_3)$$

$$\hat{\boldsymbol{\sigma}}(t_1) = \hat{\mathbf{R}}_z(t_1)\hat{\boldsymbol{\sigma}}(t_0)\hat{\mathbf{R}}_z^{-1}(t_1) = \begin{bmatrix} e^{(\mathrm{i}\Delta\omega t_1/2)} & 0 \\ 0 & e^{(-\mathrm{i}\Delta\omega t_1/2)} \end{bmatrix} \begin{bmatrix} 0 & \mathrm{i}\delta \\ -\mathrm{i}\delta & 0 \end{bmatrix} \begin{bmatrix} e^{(-\mathrm{i}\Delta\omega t_1/2)} & 0 \\ 0 & e^{(\mathrm{i}\Delta\omega t_1/2)} \end{bmatrix}$$

- Once the density matrix for each point in the FID is known, the expectation value for the amplitude of the magnetization can be calculated at each point (thus, we have calculated the FID)

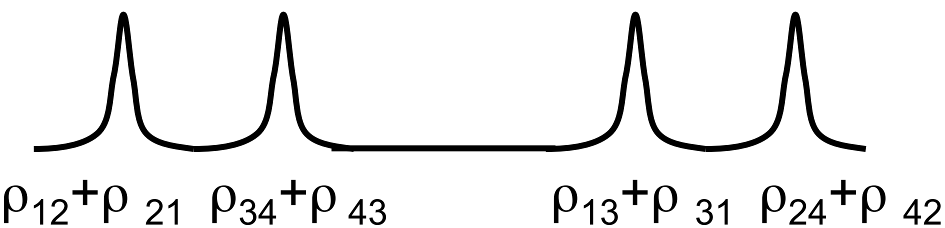
$$M_x(t) = N\ \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\sigma}}(t)\right]\left[\hat{\boldsymbol{\mu}}_x\right]\right\} \qquad M_y(t) = N\ \mathrm{Tr}\left\{\left[\hat{\boldsymbol{\sigma}}(t)\right]\left[\hat{\boldsymbol{\mu}}_y\right]\right\}$$

- Programs like GAMMA, SPINEVOLUTION work this way
  - Smith, S. A., Levante, T. O., Meier, B. H., and Ernst, R. R. (1994) *J. Magn. Reson. A* **106**, 75-105
  - Veshtort, M., and Griffin, R. G. (2006) *J. Magn. Reson*. **178**, 248-282

Density Matrix Simulation of 2nd Order Spectra

- For two spin basis set is: $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, $\beta\beta$

$$\boldsymbol{\rho} = \begin{bmatrix} \boldsymbol{\rho}11 & \boldsymbol{\rho}12 & \boldsymbol{\rho}13 & . \\ \boldsymbol{\rho}21 & \boldsymbol{\rho}22 & . & . \\ \boldsymbol{\rho}31 & . & . & . \\ . & . & . & . \end{bmatrix}$$



- ρ_{12}, ρ_{21}, … are associated with lines in an AX spectrum. 1:1 for first order spectrum
- Don't have to have a 1:1 association if ψ is not an eigen function of **H.**
- $c_i\phi_l$ + $c_i\phi_l$ may evolve coherently as one line – ie ρ_{12}, ρ_{13}, are mixed
- Calculation of Mx still works for a second order system