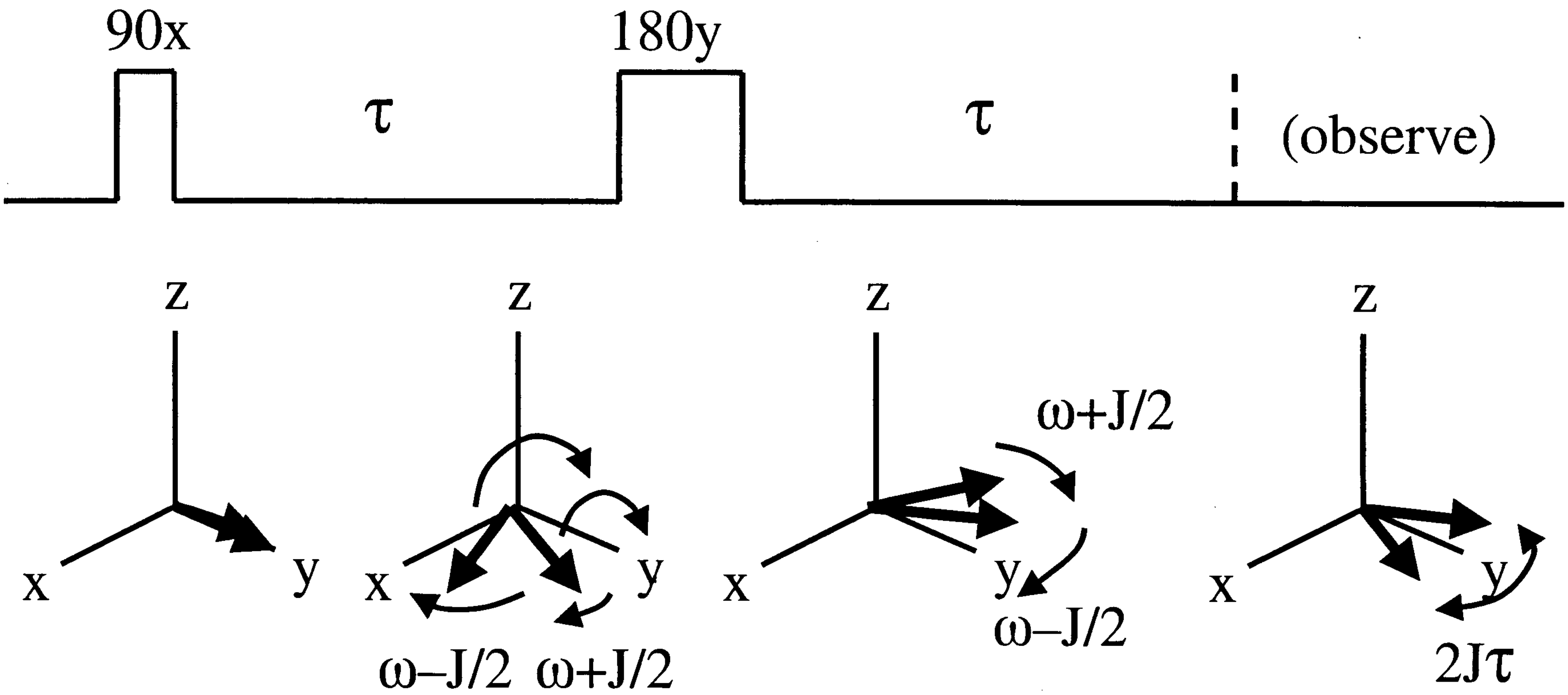
Quantum Description of NMR Experiments

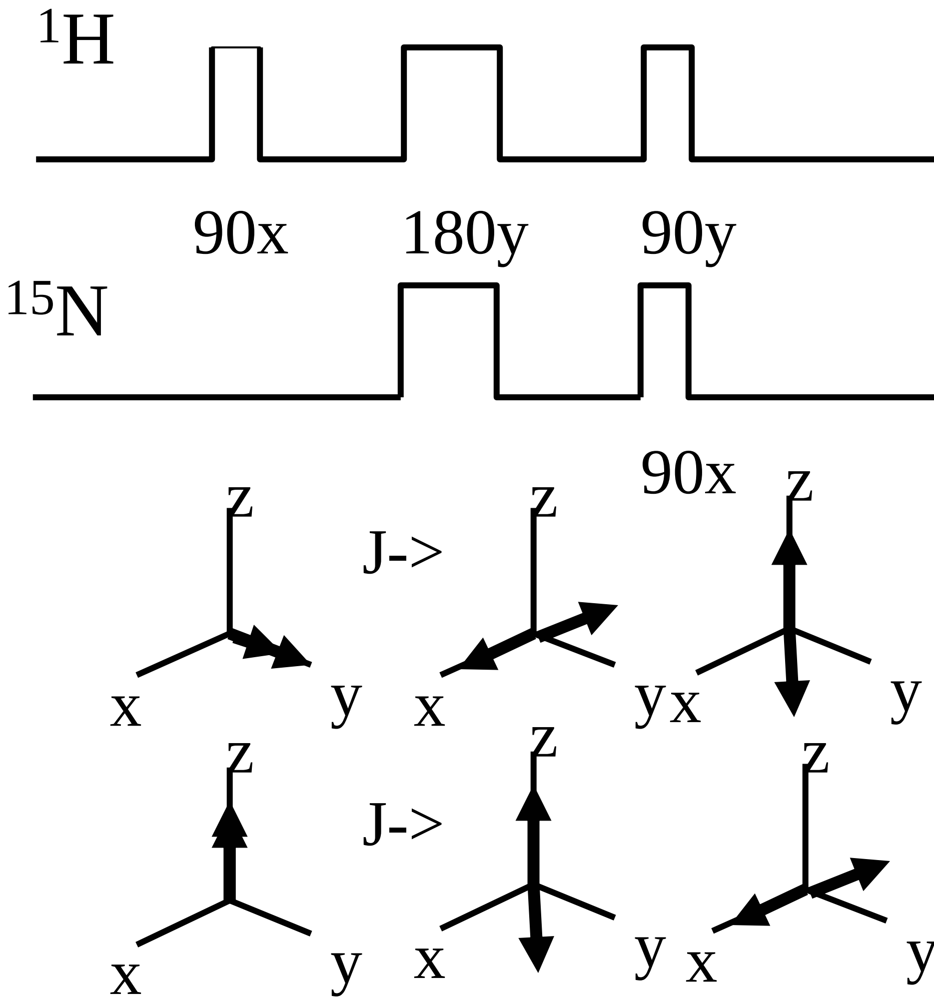
- Not all experiments can be described by Bloch equations – a scalar coupling example
- Hamiltonians and Schrodinger's equation
- Density matrix and Lioville-VonNeuman eq
- Product operators and transformation rules
- INEPT and HSQC examples

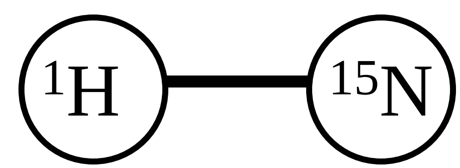
Evolution of Coupled Spins Under a 180° Pulse



This is in contrast to two independent spins which totally refocus.
The effects of J are better understood as a QM phenomenon.

Mixing by Scalar Coupling of Directly Bonded Nuclei: the INEPT and HSQC Experiments (Z polarization of ^{15}N Needs Quantum Explanation)





Quantum Mechanics Fundamentals (Spin Operations)

Expectation values correspond to observables:

$$\mu = \langle\psi|\ \mu\ |\psi\rangle = \int \psi^*\ \mu\ \psi\ d\tau$$

μ - an operator, ψ - a wave function (spin function)

Examples:

$\psi = \alpha, \beta$ (one spin ½) $\psi = \alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$ (two spins ½)

solutions to Schrodinger's equation: $\mathbf{H}\ \psi = E\ \psi$

$\mu = \gamma\ \mathbf{I}\ (h/2\pi)$ $\mu\mathbf{z} = \gamma\ \mathbf{Iz}\ (h/2\pi)$ (magnetic moments)

(in terms of spin operators)

Operations:

$\mathbf{Iz}\ (h/2\pi)\ |\alpha\rangle = (h/2\pi)\ ½\ \alpha$, , $\mathbf{Iz}\ (h/2\pi)\ |\beta\rangle = -(h/2\pi)\ ½\ \beta$

$\mathbf{H_z} = -\ \mu \bullet B$, $E_z = \langle\ \alpha|-\ \mu \bullet B_0\ |\alpha\rangle = -½\ \gamma(h/2\pi)\ B_0\langle\alpha^*|\alpha\rangle$

$= -½\ \gamma(h/2\pi)\ B_0$

Hamiltonian Operator Containing Primary Observables for High Resolution NMR

$$\mathbf{H} = -\gamma B_0 \sum_i (1-\sigma_i)\mathbf{I_{Zi}} + \sum_{j>i} 2\pi\, J\, \mathbf{I_i} \cdot \mathbf{I_j} + \sum_{j>i} 2\pi\, \mathbf{I_i} \cdot D \cdot \mathbf{I_j}$$

chemical shift scalar coupling dipolar coupling

$$\mathbf{I_i} = \mathbf{I_{ix}} + \mathbf{I_{iy}} + \mathbf{I_{iz}}$$

In "first order" spectra scalar coupling term can be approximated as:

$$\sum_{j>i} 2\pi\, J\, \mathbf{I_{iz}} \cdot \mathbf{I_{jz}}$$

Spin functions ($\psi = \alpha, \beta, \alpha\beta, \beta\alpha \ldots$) are solutions to Schrodinger's Equation: $\mathbf{H}\psi = E\psi$

Properties of Eigenfunctions

$\alpha\beta$ is an eigenfunction of $\hat{\mathcal{H}}$:

$\hat{\mathcal{H}}\psi_i = E_i\psi_i$ where E_i is a number.

$\alpha\alpha$, $\beta\alpha$, $\beta\beta$ are as well as long as $\hat{\mathcal{H}}$ is 1st order.

members are orthonormal:

$$\langle\alpha\alpha|\alpha\alpha\rangle = \int \alpha^*\alpha^*\alpha\alpha\, d\tau = 1$$

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

They are not eigenfunctions of every Hamiltonian. ie 2nd order. contains

$$J_{12}\hat{I}_1\cdot\hat{I}_2 = J_{12}(\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z})$$

Some other spin operators:

$\mathbf{Ix}\,|\alpha> \;=\; \frac{1}{2}\,\beta$

$\mathbf{Iy}\,|\alpha> \;=\; \frac{1}{2}\,i\beta$

$\mathbf{I1y}\,|\alpha\,\beta> \;=\; \frac{1}{2}\,i\beta\beta$

$\mathbf{I1yI2y}\,|\alpha\,\beta> \;=\; \frac{1}{4}\,\beta\alpha$

$\mathbf{Ix}\,|\,\beta> \;=\; \frac{1}{2}\,\alpha$

$\mathbf{Iy}\,|\,\beta> \;=\; -\frac{1}{2}\,i\alpha$

$\mathbf{I2y}\,|\alpha\,\beta> \;=\; -\frac{1}{2}\,i\alpha\alpha$

$\mathbf{I1zI2y}\,|\alpha\,\beta> \;=\; -\frac{1}{4}\,i\alpha\alpha$

Note: α, β, are not eigenfunctions of Hamiltonians (**H**) that contain these operators.

Solution: Sets such as $\alpha\alpha$, $\beta\alpha$, $\alpha\beta$, $\alpha\alpha$ are complete orthonormal sets.

Any spin function can be written in terms of these

$\psi = c1\ \alpha\alpha + c2\ \alpha\beta + c3\ \beta\alpha + c4\ \beta\beta \;=\; \sum_j c_j\, \phi_j$

Effects of Some Other Operators on Simple product spin functions

$I_x|\alpha\rangle = \frac{1}{2}\beta$ $\qquad$ $I_y|\alpha\rangle = \frac{1}{2}i\beta$

$I_x|\beta\rangle = \frac{1}{2}\alpha$ $\qquad$ $I_y|\beta\rangle = -\frac{1}{2}i\alpha$

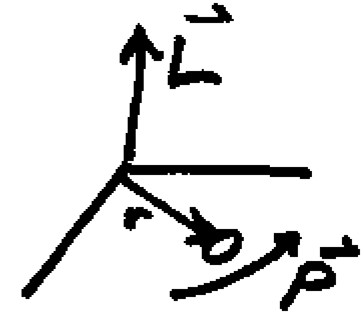
If $\vec{\mathcal{H}}$ contains I_x, $\vec{\mathcal{H}}|\alpha\alpha\rangle \neq E_i\alpha\alpha$

How do we know above set of operations?

- spin operators are postulated to have the same set of "commutation" properties as angular momentum operators in space.

$[I_x, I_y]|\alpha\rangle = I_x I_y|\alpha\rangle - I_y I_x|\alpha\rangle = i I_z|\alpha\rangle$

$$\vec{L} = \vec{r} \times \vec{p}$$



in QM, $p_x = -i\hbar \frac{\partial}{\partial x}$ etc.

$$r \times p = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

can prove: $[\hat{L}_x, \hat{L}_y] = i \hat{L}_z$

More Operators!

$$\hat{I}^2|\psi\rangle = I(I+1)\psi = \tfrac{3}{4}\psi \quad \text{for } I=\tfrac{1}{2}$$

$$\hat{I}^2 = \hat{I}_x\hat{I}_x + \hat{I}_y\hat{I}_y + \hat{I}_z\hat{I}_z\ .$$

$$\hat{I}^2|\alpha\rangle = \hat{I}_x\tfrac{1}{2}\beta + \hat{I}_y\tfrac{1}{2}i\beta + \hat{I}_z\tfrac{1}{2}\alpha$$

$$= \tfrac{1}{4}\alpha + \tfrac{1}{4}\alpha + \tfrac{1}{4}\alpha = \tfrac{3}{4}\alpha$$

Raising + Lowering Operators.

$$I_x = \frac{I_+ + I_-}{2}, \quad I_y = \frac{I_+ - I_-}{2i}$$

$$I_+|\beta\rangle = I_x|\beta\rangle + i\,I_y|\beta\rangle = \tfrac{1}{2}\alpha + \tfrac{1}{2}\alpha = \alpha$$

$$I_+|\alpha\rangle = 0, \quad I_-|\alpha\rangle = \beta, \quad I_-|\beta\rangle = 0$$

Using Operators: Energy Levels.

$$E_i = \langle \psi_i | \hat{\mathcal{H}} | \psi_i \rangle$$

$$\hat{\mathcal{H}} = -h\nu_1 \hat{I}_{1z} - h\nu_2 \hat{I}_{2z} + hJ_{12} I_{1z} I_{2z}$$

$$\nu_i = \frac{\gamma B_0 (1 - \sigma_i)}{2\pi}$$

$$\hat{\mathcal{H}} | \alpha\alpha \rangle = -h\nu_1 \tfrac{1}{2} \alpha\alpha - h\nu_2 \tfrac{1}{2} \alpha\alpha + h J_{12} (\tfrac{1}{2})(\tfrac{1}{2}) \alpha\alpha$$

$$\langle \alpha\alpha | \hat{\mathcal{H}} | \alpha\alpha \rangle = -h\nu_1 \tfrac{1}{2} - h\nu_2 \tfrac{1}{2} + hJ_{12} \tfrac{1}{4}$$

$$\langle \alpha\beta | \hat{\mathcal{H}} | \alpha\beta \rangle = -h\nu_1 \tfrac{1}{2} + h\nu_2 \tfrac{1}{2} - hJ_{12} \tfrac{1}{4}$$

etc.

One Quantum Transitions

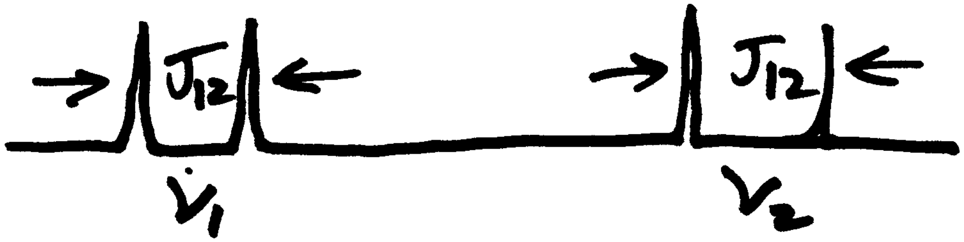
$\Delta m = \pm 1$ $\qquad \alpha\beta \rightarrow \beta\beta$

$\alpha\alpha \rightarrow \alpha\beta$

etc

$$\Delta E_{\alpha\beta \rightarrow \beta\beta} = -\frac{h}{2}(-\nu_1 - \nu_2) + \tfrac{1}{4} h J_{12}$$
$$- \left(-\frac{h}{2}(\nu_1 - \nu_2) - \tfrac{1}{4} h J_{12}\right)$$
$$= h\nu_1 + \tfrac{1}{2} J_{12} h$$

$$\Delta E_{\alpha\alpha \rightarrow \beta\alpha} = -h/2(\nu_2 - \nu_1) - \tfrac{1}{4} h J_{12}$$
$$- (-h/2(\nu_1 + \nu_2) + \tfrac{1}{4} h J_{12}$$
$$= h\nu_1 - \tfrac{1}{2} J_{12} h$$



Operators in Matrix Notation

If we stay with one basis set, properties vary only because of changes in the coefficients weighting each basis set function

$\mu_x = \gamma(h/2\pi)\langle\psi|\, \mathbf{Ix}\, |\psi\rangle$

$\psi = c1\ \alpha\alpha + c2\ \alpha\beta + c3\ \beta\alpha + c4\ \beta\beta\ =\ \sum_j c_j\ \phi_j$

$\langle\psi|\, \mathbf{Ix}\, |\psi\rangle\ =\ \sum_{j,k} c_j^*\ c_k\ \langle\phi_j|\, \mathbf{Ix}\, |\phi_k\rangle$

We need calculate $\langle\phi_j|\, \mathbf{Ix}\, |\phi_k\rangle$ only once if we stay with this basis set – these can be put in a n x n matrix.

Matrix equivalent: $\langle\psi|\, \mathbf{Ix}\, |\psi\rangle\ = (c1, c2, \ldots)^* \begin{bmatrix} & \\ \mathbf{Ix} & \\ & \end{bmatrix} \begin{pmatrix} c1 \\ c2 \\ \bullet \end{pmatrix}$

Special Case: Pauli Spin Matrices

$$|\mathbf{Ix}| = \begin{vmatrix} 0 & ½ \\ ½ & 0 \end{vmatrix}$$

Note: $< \alpha \mid \mathbf{Ix} \mid \alpha > = ½ < \alpha \mid \beta > = 0$

$< \alpha \mid \mathbf{Ix} \mid \beta > = ½ < \alpha \mid \alpha > = ½$

$$|\mathbf{Iy}| = \begin{vmatrix} 0 & -i½ \\ i½ & 0 \end{vmatrix} \qquad |\mathbf{Iz}| = \begin{vmatrix} ½ & 0 \\ 0 & ½ \end{vmatrix}$$

How do they work? Try something we know: $\mathbf{Ix} \mid \alpha > = ½\, \beta$

$$\begin{vmatrix} 0 & ½ \\ ½ & 0 \end{vmatrix} \begin{vmatrix} 1 \\ 0 \end{vmatrix} = \begin{vmatrix} 0 \\ ½ \end{vmatrix} = ½ \begin{vmatrix} 1 \\ 0 \end{vmatrix} = ½\ \beta$$

Operators are a matrix of numbers, Spin functions a vector of numbers

Larger Collections of Spin ½ Nuclei

$$\tilde{I}_{x1} = \begin{array}{c} \alpha\alpha \\ \beta\alpha \\ \alpha\beta \\ \beta\beta \end{array}\left[\begin{array}{c|c|c|c} \; & \; & \; & \; \\ \hline \; & \; & \; & \; \\ \hline \; & \; & \; & \; \\ \hline \; & \; & \; & \; \end{array}\right]$$

$$\quad\quad\quad \alpha\alpha \;\; \beta\alpha \;\; \alpha\beta \;\; \beta\beta$$

$\langle \alpha\alpha | \hat{I}_{x1} | \beta\alpha \rangle =$

$\langle \alpha\alpha | \tfrac{1}{2} \alpha\alpha \rangle = \tfrac{1}{2}$

$$= \begin{bmatrix} 0 & \tfrac{1}{2} & 0 & 0 \\ \tfrac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \tfrac{1}{2} \\ 0 & 0 & \tfrac{1}{2} & 0 \end{bmatrix} \; ; \; \tilde{I}_{x2} = \begin{bmatrix} 0 & 0 & \tfrac{1}{2} & 0 \\ 0 & 0 & 0 & \tfrac{1}{2} \\ \tfrac{1}{2} & 0 & 0 & 0 \\ 0 & \tfrac{1}{2} & 0 & 0 \end{bmatrix}$$

an easier way: $\tilde{E} \otimes \hat{I}_{x1}$ - direct products

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 0 & \tfrac{1}{2} \\ \tfrac{1}{2} & 0 \end{bmatrix} \quad , \quad \tilde{I}_{x_{total}} = \tilde{I}_{x1} + \tilde{I}_{x2}$$