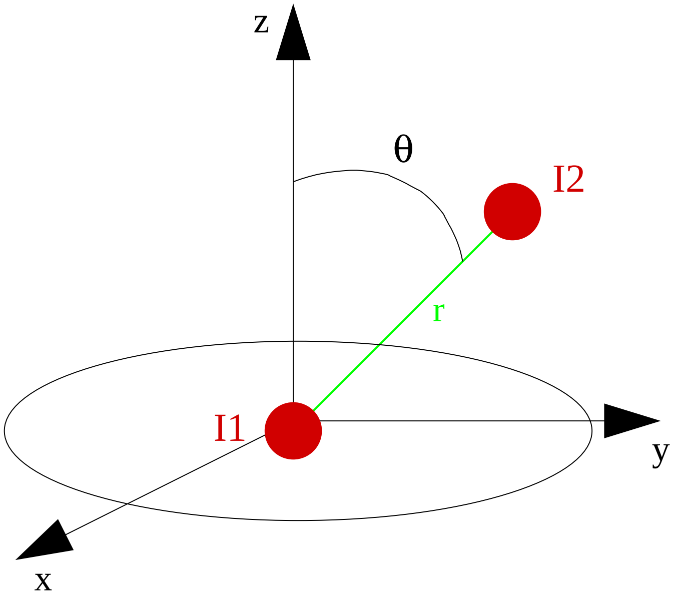
8– NMR Interactions: Dipolar Coupling

8.1 Hamiltonian

As discussed in the first lecture, a nucleus with spin $I \geq 1/2$ has a magnetic moment, μ, associated with it given by

$$\vec{\mu} = \gamma \vec{L}. \tag{8.1}$$

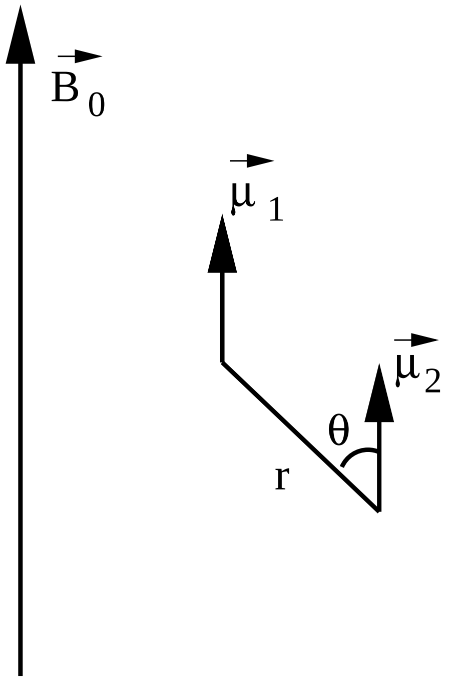
If two different nuclear spins, $\vec{\hat{I}}_1$ and $\vec{\hat{I}}_2$ are separated by a distance r,



then the energy of interaction between the two magnetic dipoles, $\vec{\mu}_1$ and $\vec{\mu}_2$ is given by

$$E = \frac{\mu_0}{4\pi}[(\vec{\mu}_1 \cdot \vec{\mu}_2)r^{-3} - 3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})r^{-5}] \tag{8.2}$$

where μ_0 is the permeability constant and is equal to $4\pi \times 10^{-7} kg.m.s^{-2}.A^{-2}$ (where A is for Amperes). If the two dipoles have the same orientation with respect to $\vec{r}$, then



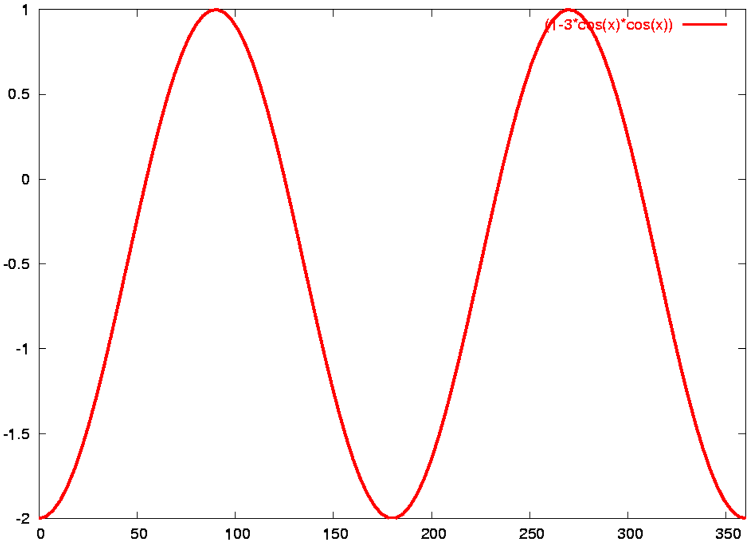
$$(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r}) = (\vec{\mu}_1 \cdot \vec{\mu}_2)r^2 cos^2\theta \tag{8.3}$$

and thus,

$$E = \frac{\mu_0}{4\pi}(\vec{\mu}_1 \cdot \vec{\mu}_2)r^{-3}[1 - 3cos^2\theta]. \tag{8.4}$$

where $\vec{\mu}_1 \cdot \vec{\mu}_2 = \mu_1\mu_2$ since they are parallel.

Therefore the energy has an angular dependence:



NOTE: That the first null in the energy occurs at $\theta = \frac{1}{\sqrt(3)}$ or 54.7 degrees. This angle is known as the *magic angle*.

The Hamiltonian is then given by replacing the vectors $\vec{\mu}_1$ and $\vec{\mu}_2$ by their corresponding operators $\gamma_1\hbar\vec{\hat{I}}_1$ and $\gamma_2\hbar\vec{\hat{I}}_2$ in equation 8.2 above, i.e.

$$\hat{\mathcal{H}}_D = \frac{\mu_0 \gamma_1 \gamma_2 h^2}{16\pi^3}[(\vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2) r^{-3} - 3(\vec{\hat{I}}_1 \cdot \vec{r})(\vec{\hat{I}}_2 \cdot \vec{r}) r^{-5}]. \quad (8.5)$$

This equation represents the full dipolar Hamiltonian. We can write the vector $\vec{r}$ in terms of polar coordinates, i.e.

$$\vec{r} = (r_x, r_y, r_z) = (r sin\theta cos\phi, r sin\theta sin\phi, r cos\theta) \quad (8.6)$$

and therefore rewrite the dipolar Hamiltonian as

$$\hat{\mathcal{H}}_D = \frac{\mu_0 \gamma_1 \gamma_2 h^2}{16\pi^3 r^3}[A + B + C + D + E + F] \quad (8.7)$$

where

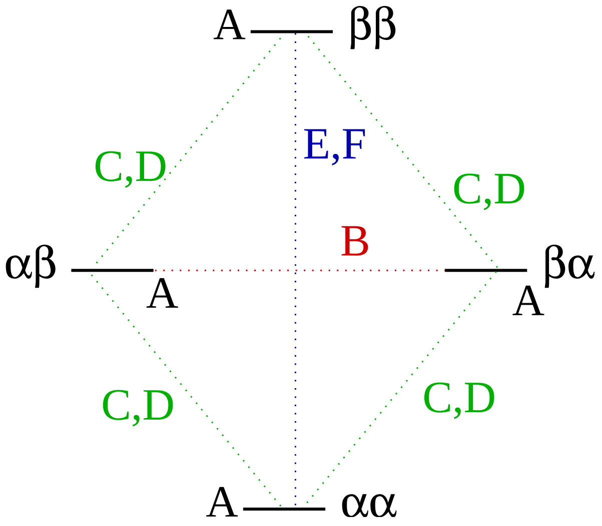
$$\begin{aligned}
A &= \hat{I}_{1z}\hat{I}_{2z}(1 - 3cos^2\theta) \\
B &= -\frac{1}{4}\left[\hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+\right](1 - 3cos^2\theta) \\
C &= -\frac{3}{2}\left[\hat{I}_1^+\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^+\right] sin\theta cos\theta e^{-i\phi} \\
D &= -\frac{3}{2}\left[\hat{I}_1^-\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^-\right] sin\theta cos\theta e^{i\phi} \\
E &= -\frac{3}{4}\hat{I}_1^+\hat{I}_2^+ sin^2\theta e^{-2i\phi} \\
F &= -\frac{3}{4}\hat{I}_1^-\hat{I}_2^- sin^2\theta e^{2i\phi}
\end{aligned}$$

(8.8)

These terms of the Hamiltonian can be represented as a matrix of the form
(A + B + C + D + E + F)

$$= \begin{pmatrix} termsfromA & ...C & ...C & ...E \\ ...D & ...A & ...B & ...C \\ ...D & ...B & ...A & ...C \\ ...F & ...D & ...D & termsfromA \end{pmatrix} \tag{8.9}$$

The eigenvalues of this matrix give the energy levels of the dipolar Hamiltonian in zero magnetic field.



In the presence of an external magnetic field $\vec{B}_0$, however, many of the higher order terms can be neglected, i.e. if the following condition is valid:

$$|\omega_{01} - \omega_{02}| \gg \frac{\mu_0 \gamma_1 \gamma_2 h^2}{16\pi^3 r^3} \tag{8.10}$$

This approximation is called a secular approximation. So let's have a look at which of the terms above (A, B, ..., F) remain and which can be neglected:

A A, written in the basis set of $\alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$, has diagonal elements:

$$< \phi_j|A|\phi_k >= A_{jk}\delta_{jk} \tag{8.11}$$

These terms are always present.

B B has elements between $\alpha\beta$ and $\beta\alpha$

$$< \alpha\beta|B|\beta\alpha >=< \beta\alpha|B|\alpha\beta >= -\frac{1}{4}(1 - 3cos^2\theta) \tag{8.12}$$

When $\omega_{01} = \omega_{02}$, i.e. in the homonuclear case, the approximation above does not hold and the B term must be kept.

C and D These terms connect levels separated by ± 1, i.e. single quantum. For high fields, they can be neglected.

E and F These terms connect levels separated by ± 2, i.e. double quantum. For high fields, they can be neglected.

Thus the Hamiltonian in the case of homonuclear coupling (between like spins) is

$$\hat{\mathcal{H}}_D = \frac{-\mu_0 \gamma_1 \gamma_2 h^2}{16\pi^3 r^3}\frac{1}{2}(3cos^2\theta - 1)[3\hat{I}_{1z}\hat{I}_{2z} - \vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2] \tag{8.13}$$

whereas in the case of heteronuclear coupling, it is given by

$$H_D = \frac{-\mu_0 \gamma_1 \gamma_2 h^2}{16\pi^3 r^3}(3cos^2\theta - 1)\hat{I}_{1z}\hat{I}_{2z}. \tag{8.14}$$

The constant term in front of equations 8.13 and 8.14 are the homonuclear and heteronuclear dipolar coupling constants, respectively. Typical values for ^1H, ^{13}C, and ^{15}N are:

$$d_{IS} = -\frac{\mu_0 \gamma_I \gamma_S \hbar}{8\pi^2 {r_{IS}}^3} (in Hz) \tag{8.15}$$

with

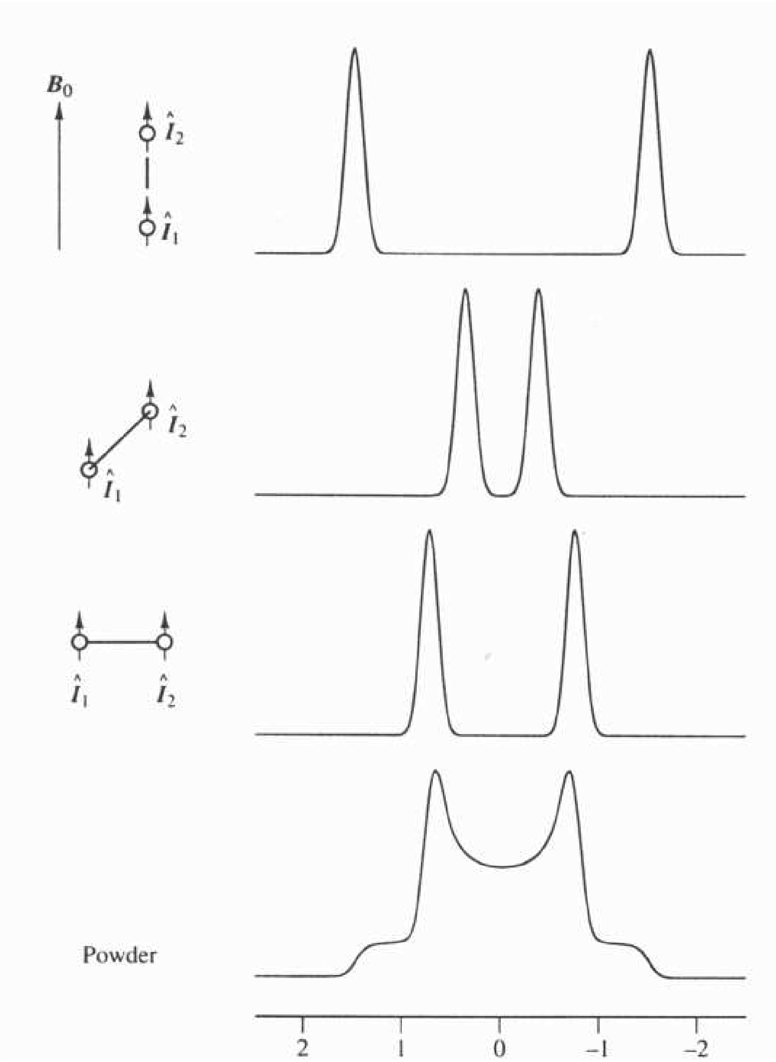
$$\begin{aligned}
\gamma_{1H} &= 42.5759 * 10^6 Hz.T^{-1} \\
\gamma_{13C} &= 10.7054 * 10^6 Hz.T^{-1} \\
\gamma_{15N} &= 4.3142 * 10^6 Hz.T^{-1} \\
\mu_0 &= 4\pi * 10^{-7} N.A^{-2} \\
h &= 1.0546 * 2\pi * 10^{-34} J.s
\end{aligned} \tag{8.16}$$

Thus

$$\begin{aligned}
d_{HH}.r^3 &= 120000 \quad Hz.\AA^3 \\
d_{CC}.r^3 &= 7500 \quad Hz.\AA^3 \\
d_{NN}.r^3 &= 1200 \quad Hz.\AA^3 \\
d_{HC}.r^3 &= 30000 \quad Hz.\AA^3 \\
d_{HN}.r^3 &= 12000 \quad Hz.\AA^3 \\
d_{CN}.r^3 &= 3000 \quad Hz.\AA^3
\end{aligned} \tag{8.17}$$

Note that since the static magnetic field lies along the z-axis in the figure on page 1, the dipolar interaction has an orientational dependence with respect to $\vec{B}_0$ given by the expression $3cos^2\theta - 1$. This manifests itself by a dependence of the observed dipolar splitting on the orientation of the crystallite in a single crystal in the probe (recall the orientation dependence of the CSA for single crystals). For a powder sample, a Pake pattern, which is the sum of the spectra of individual crystallites which are randomly distributed in the sample, is observed.

The maximum splitting which can be observed is $3 * d_{II}$ for the homonuclear case and $2 * d_{IS}$ for the heteronuclear case.



ref: R.E. Wasylishen, Encyclopedia of NMR, Grant and Harris (eds.)

8.2 Spherical Tensor Notation

As mentioned previously, many of the terms in the spin spherical tensors are the same for the scalar coupling as for the dipolar interaction:

$$T_{10} = 0$$

$$
\begin{aligned}
T_{1\pm 1} &= 0 \\
T_{20} &= \frac{1}{\sqrt{6}}(3I_zS_z - \mathbf{I}\cdot\mathbf{S}) \\
T_{2\pm 1} &= \mp\frac{1}{2}(I_zS_\pm + I_\pm S_z) \\
T_{2\pm 2} &= \frac{1}{2}I_\pm S_\pm
\end{aligned}
\tag{8.18}
$$

Note, that here I chose to write the two spins as I and S instead of I_1 and I_2, as above. Both notations are equivalent. The choice depends on you.

The spatial parts are:

$$
\begin{aligned}
A_{20}^{PAS} &= \sqrt{6}d_{IS} \\
A_{2\pm 1} &= 0 \\
A_{2\pm 2} &= 0
\end{aligned}
\tag{8.19}
$$

where

$$d_{IS} = -\frac{\mu_0}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3} \tag{8.20}$$

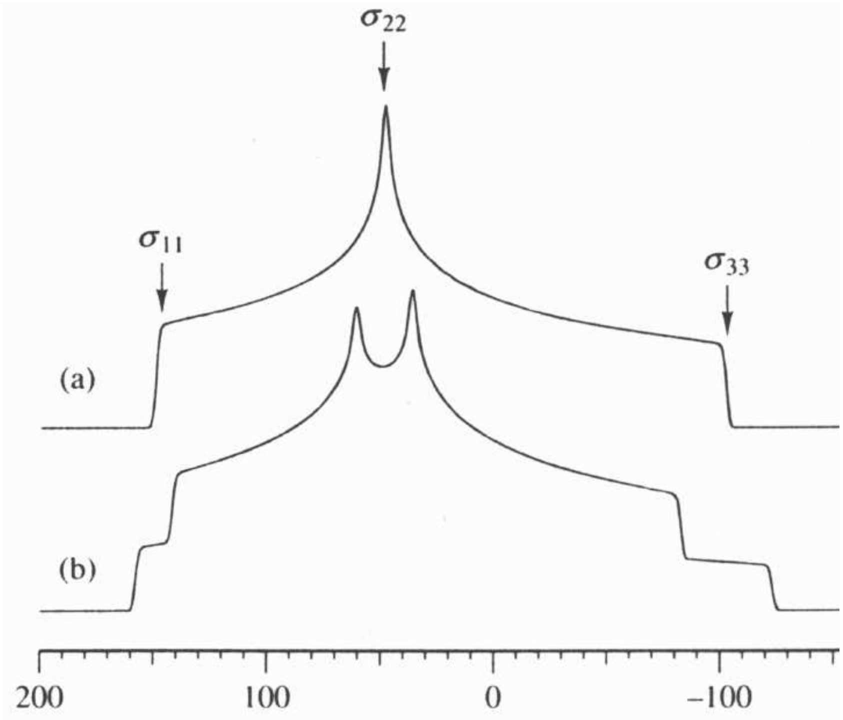
is the dipolar coupling constant.

As before, we can transform the spatial part into any arbitrary frame:

$$\begin{aligned} A_{20} &= \sqrt{\frac{3}{2}} d_{IS}(3cos^2\beta - 1) \\ A_{2\pm1} &= \pm\frac{3}{2} d_{IS} sin(2\beta) e^{\mp i\gamma} \\ A_{2\pm2} &= \frac{3}{2} d_{IS}(sin^2\beta) e^{\mp i\gamma}. \end{aligned} \tag{8.21}$$

8.3 Measuring the Dipolar Splitting

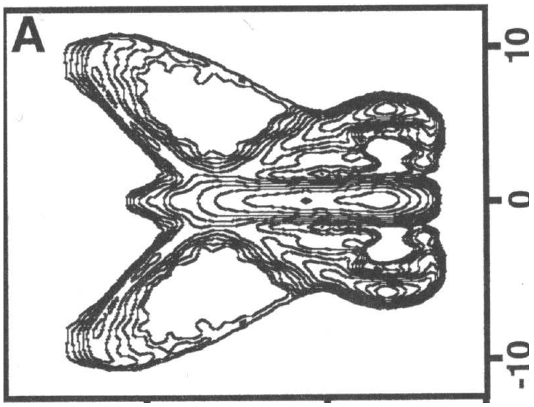
The dipolar interaction can be measured in a number of ways. As with the CSA, the methods used depend on the state of the sample. For a powder, for instance, one can obtain dipolar information from the powder pattern directly, as shown in b):



ref: R.E. Wasylishen, Encyclopedia of NMR, Grant and Harris (eds.)

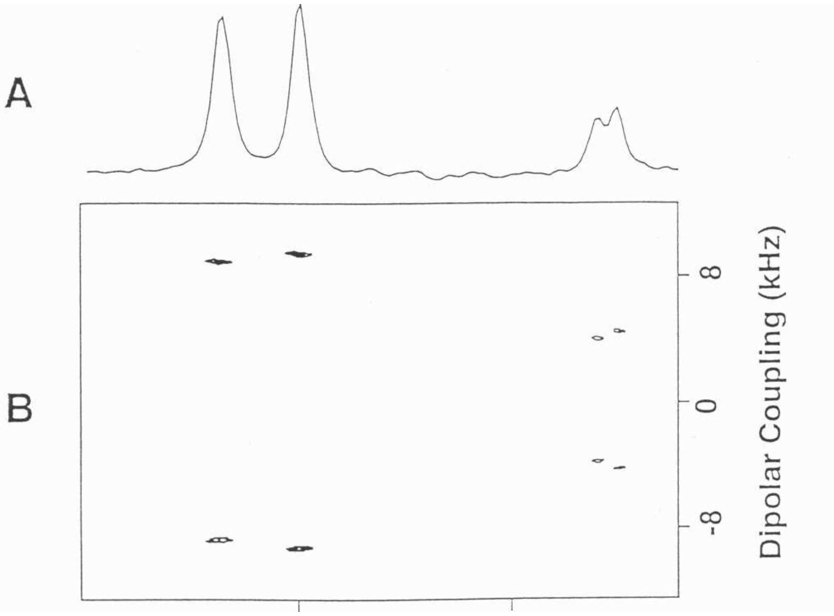
The dipolar information can be extracted by fitting the spectra to extract the dipolar splitting. Again, as with the methods to determine the CSA, this method of fitting spectra is limited to the cases where the lines are not overlapped.

Otherwise, two-dimensional methods such as the “separated local field” experiment (SLF) or the “polarization inversion spin exchange at the magic angle” experiment (PISEMA) can be used. Both of these experiments work well on powders as well as single crystals.



chemical shift (ppm)

ref: A. Ramamoorthy, S.J. Opella, *Solid State NMR*, **4**, 387-392 (1995).



chemical shift (ppm)

ref: A. Ramamoorthy, C.H. Wu, S.J. Opella, *J. Magn. Reson.*, **140**, 131-40 (1999).

For more details on dipolar spectroscopy see also:

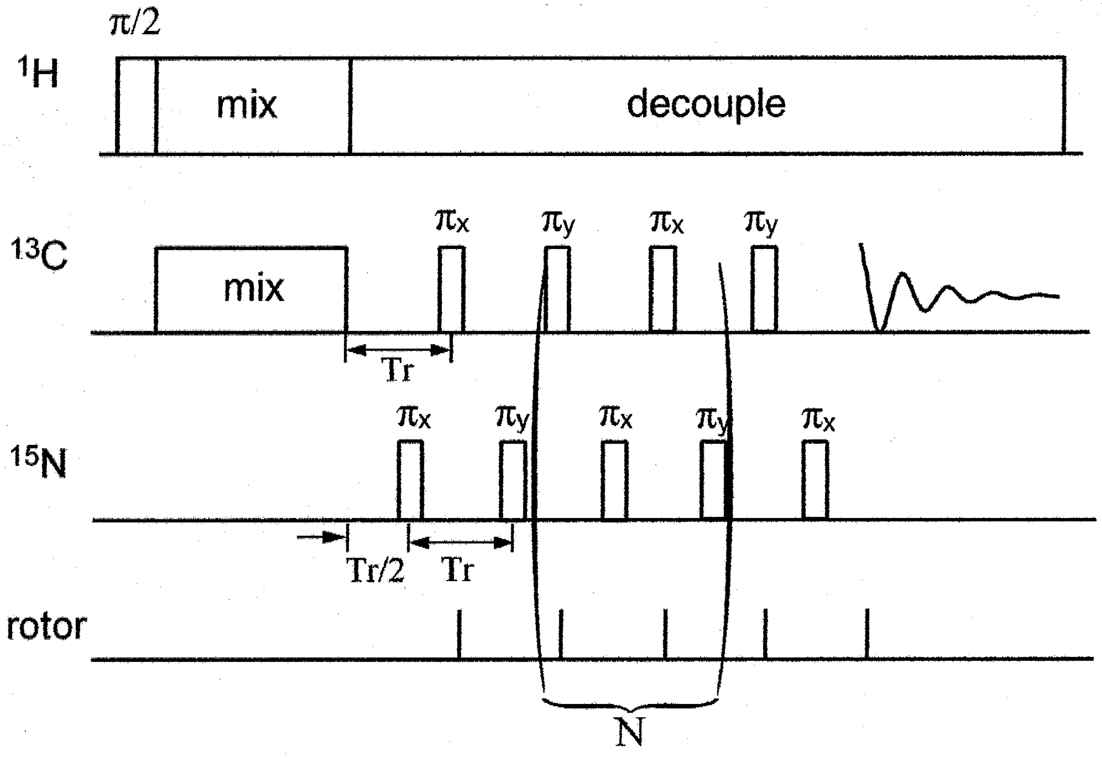
1. M. Engelsberg, Encyclopedia of NMR, Grant and Harris (eds.).
2. K. Schmidt-Rohr, H.W. Spiess, Mutlidimensional Solid-State NMR and Polymers, Academic Press, San Diego, CA, 1994.

8.4 Importance of the Dipolar Interaction

1. In solution, though the dipolar interaction is averaged (because all θ's are sampled), it still plays a role in cross-relaxation and is used in NOESY spectroscopy - more on this later. Relaxation.
2. In solids, the dipolar interaction is used to get distance and orientational information:

   e.g. REDOR

   Rotational-Echo Double Resonance is a MAS experiment for measuring distance between two selectively labelled site (e.g. ^{13}C and ^{15}N). MAS averages the dipolar interaction between these two, so the pulse sequence works to reintroduce this interaction by breaking the averaging:



Data is collected for an increasing number of rotor cycles N.

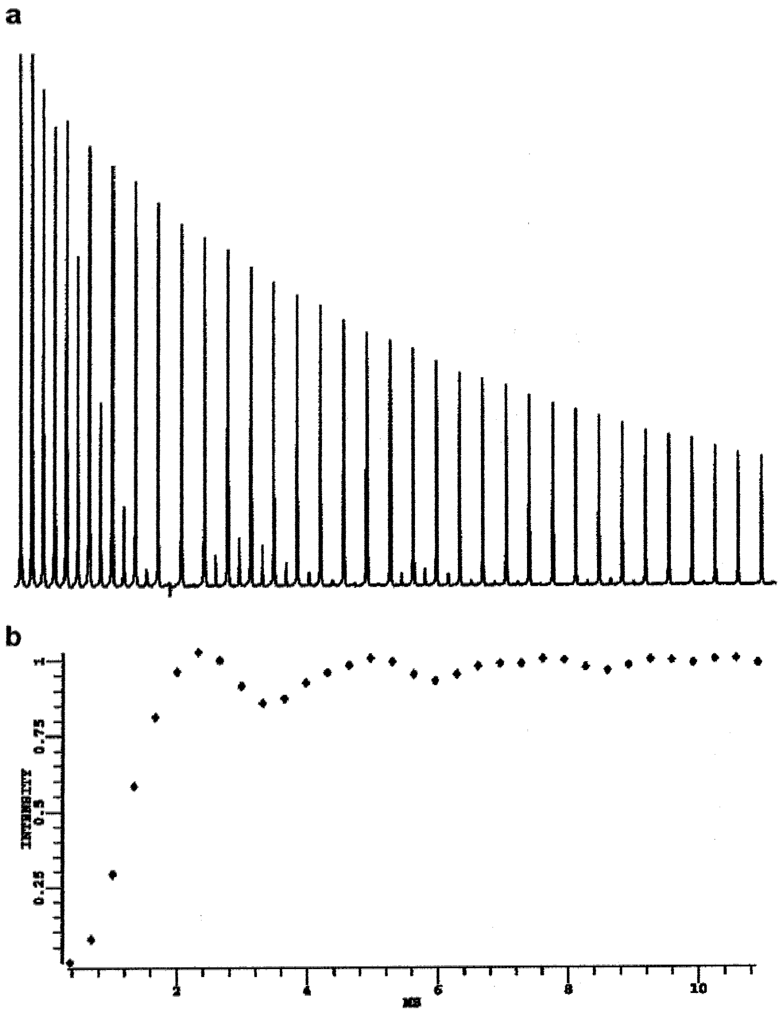


Figure 3 *a) REDOR Spectra. REDOR data obtained for 2-^{13}C, ^{15}N glycine, acquired using a 3.2-mm Chemagnetics T3 Balun probe* ***(Varian)****. MAS speed = 6 kHz; sample volume = 20 μL. CP was performed at 62.5 kHz B_1; ^{1}H decoupling during acquisition = 70 kHz TPPM; ^{1}H decoupling during REDOR mixing = 110 kHz TPPM. b) REDOR curve obtained from the data shown for the REDOR Spectra. REDOR transform of this data gives a coupling of 820 Hz. (Courtesy of* ***Varian Inc.****)*

e.g. PISEMA

Using both the orientational dependence of the chemical shift and that of the dipolar interaction, it is possible to determine the three-dimensional structure of an aligned protein using the PISEMA pulse sequence.

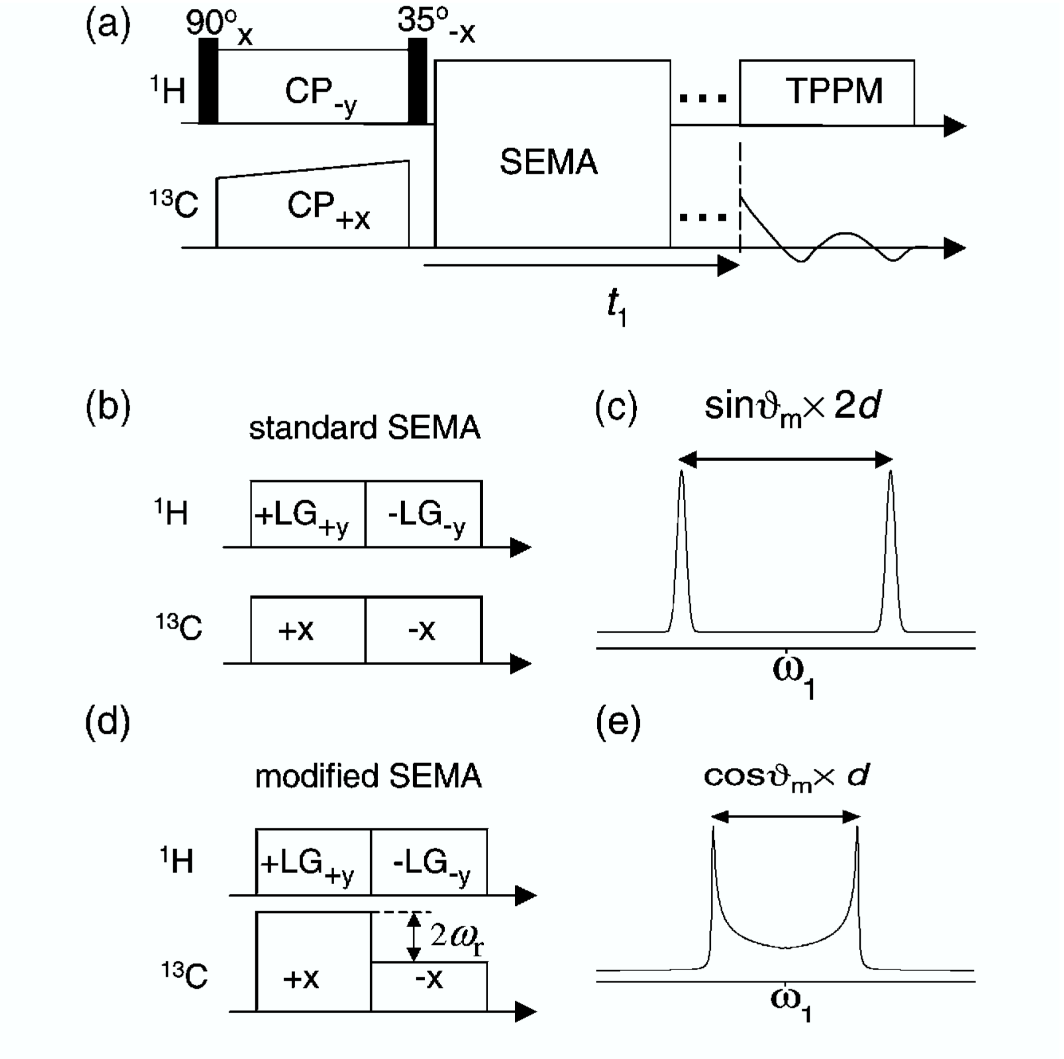


Fig. 1. (a) Pulse sequence for 2D PISEMA spectroscopy. (b) Standard SEMA multiple-pulse cycle. (c) Dipolar spectrum of an oriented system obtained using the standard SEMA sequence on a stationary sample. (d) Modified SEMA multiple-pulse cycle for MAS experiments. (e) Dipolar spectrum of an unoriented system using the modified SEMA sequence under MAS condition.