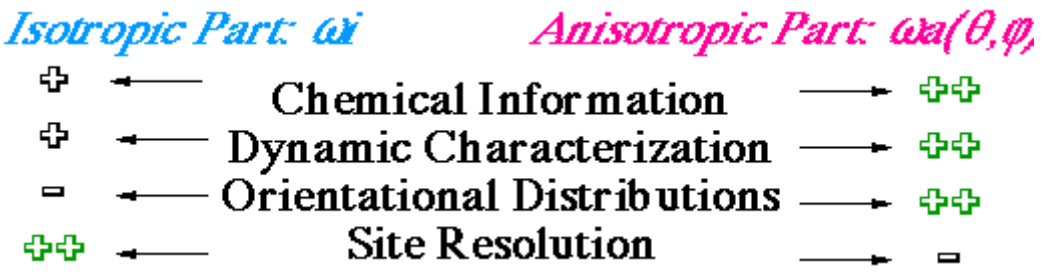
2. MULTIDIMENSIONAL SOLIDS NMR: CORRELATING ISOTROPIC AND ANISOTROPIC INTERACTIONS

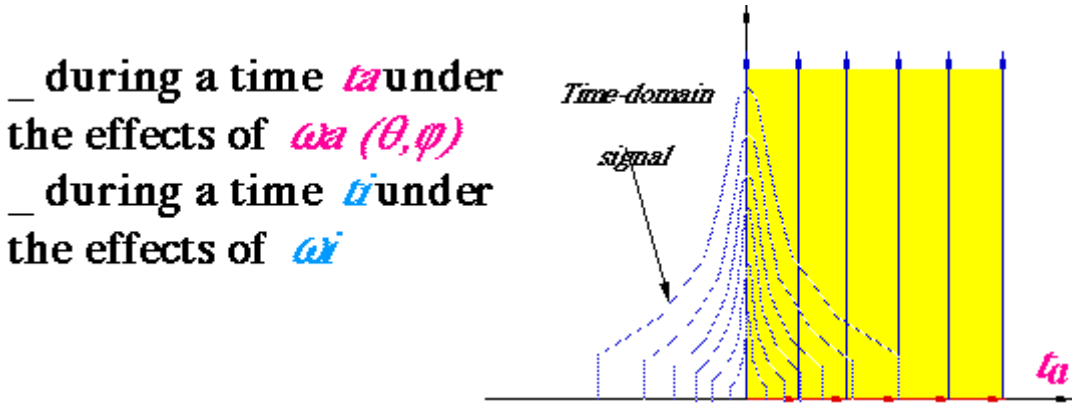
Non-cartesian sampling schemes can also play an important role in separating the orientation-dependent components of spin interactions from their isotropic counterparts. These separations are highly important in the study of solids, as the former can provide valuable information about a system but only the latter can endow spectra with a high enough resolution.

For instance the chemical shift interaction can be described as the sum of two terms:



To obtain all the information encoded by the chemical shift interaction one needs to separate these two components employing 2D NMR.

Using standard 2D NMR techniques this would imply allowing spins to evolve



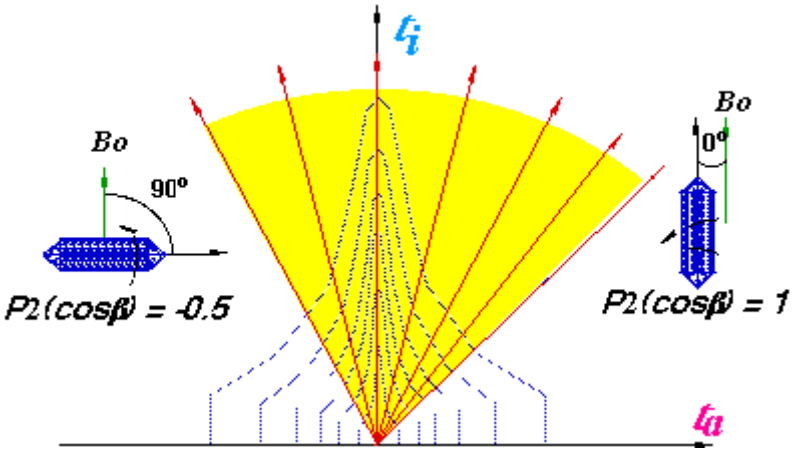
A much simpler way to sample this space is by acquiring signals as a function of variable spinning angles ß

The phase Φ evolved by the spins in this experiment:

$$\Phi = \omega_i t + \omega_a P2(\cos\beta) t,$$

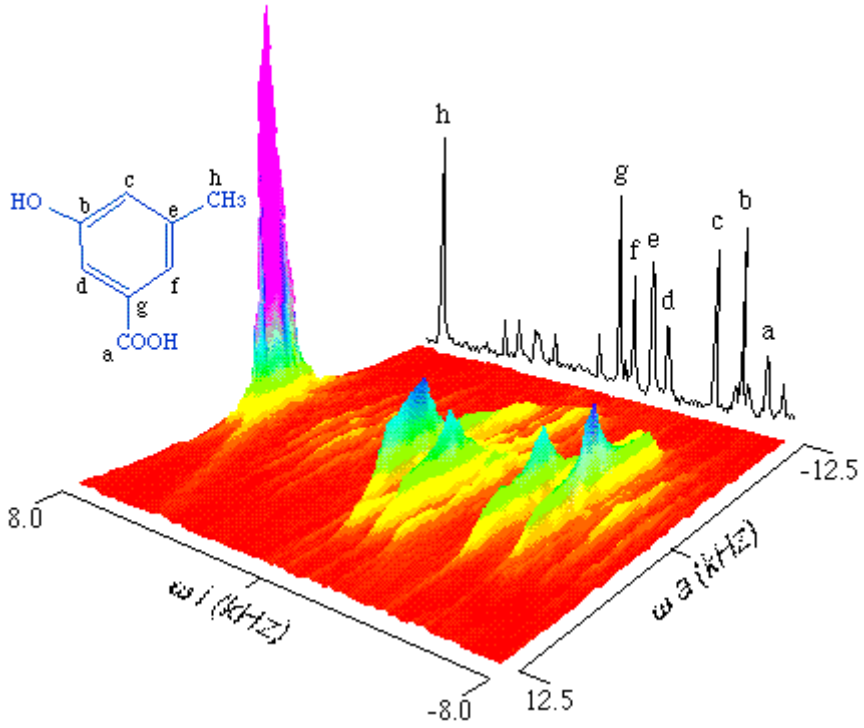
$$P2(\cos\beta) = (3\cos^2\beta - 1)/2.$$

This time evolution can then be represented by the following non-cartesian sampling



We employ these principles as basis for the Variable Angle Correlation Spectroscopy (VACSY) experiment. Fourier transformation of its data yields in a simple manner isotropic-anisotropic 2D NMR spectra.

A ^{13}C NMR example on 3-methylsalycilic acid:



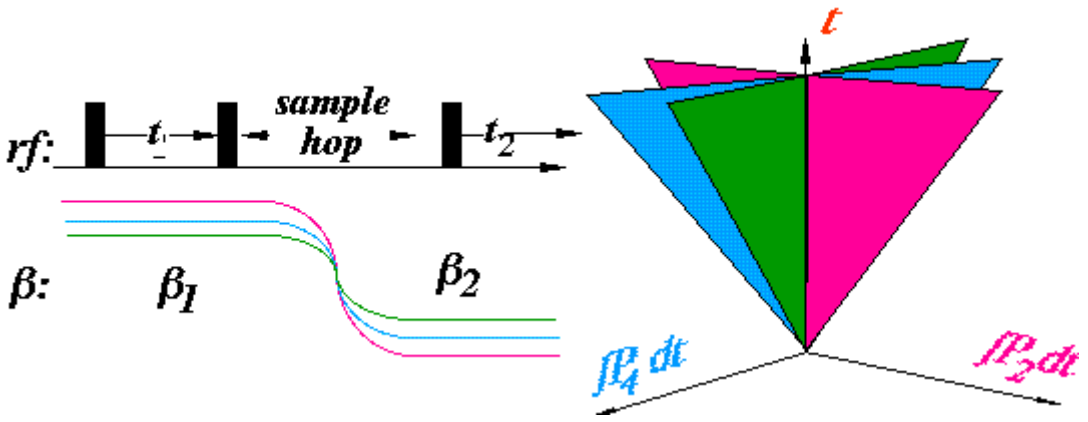
We have employed this technique extensively on studies of order and dynamics in polymers.

This type of analysis can be extended to the case of nuclei possessing spin>1/2. The treatment, however, becomes more complex, as it becomes then necessary to deal with the quadrupolar interaction.

This interaction gives origin to two different kind of anisotropies that scale in different manners upon sample spinning. The evolution of the spins needs to be described now in a three-dimensional time-domain space:

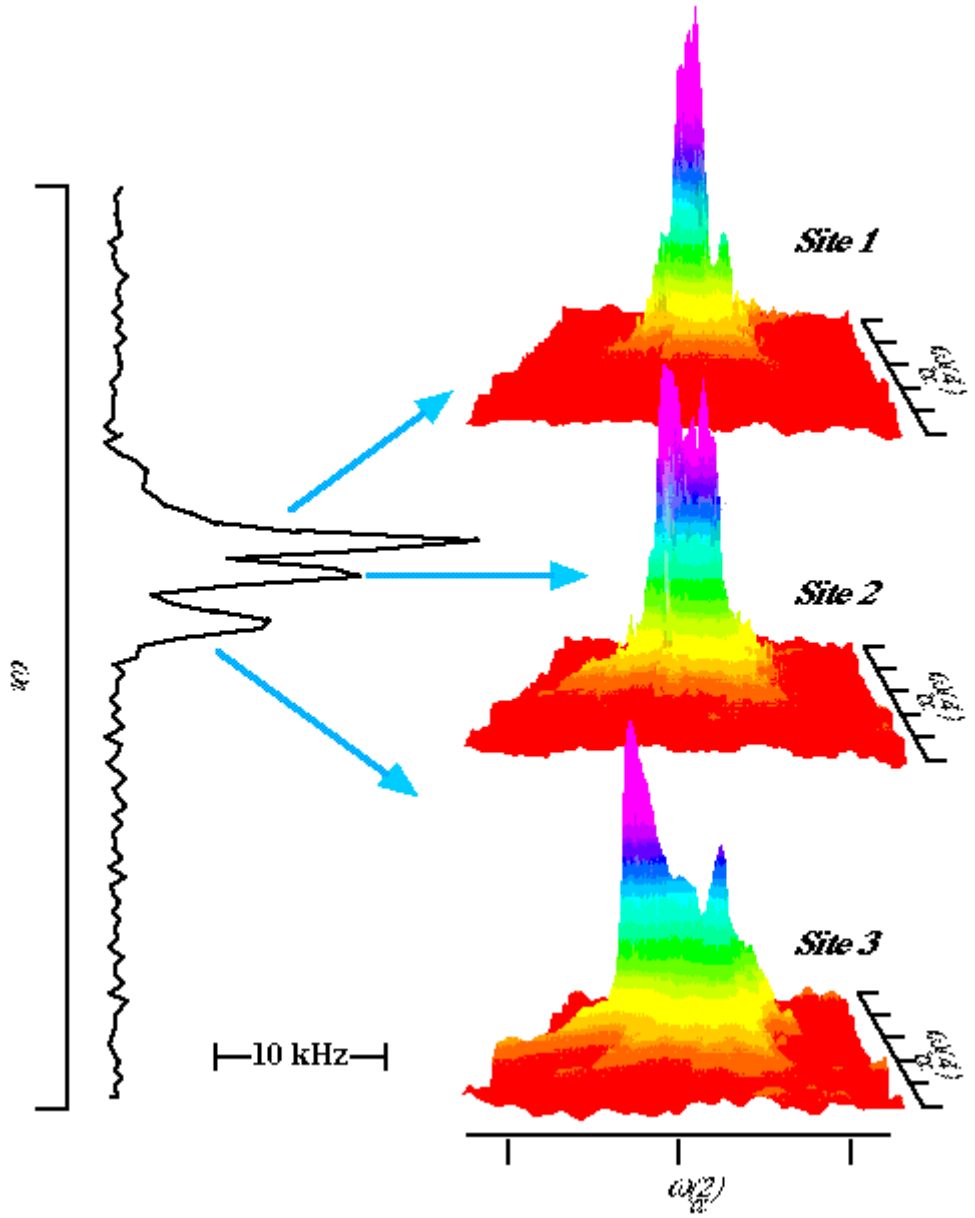
$$\Phi(\beta,t) = \omega i \cdot t + \omega(2) \cdot P2(\cos\beta)t + \omega(4) \cdot P4(\cos\beta)t$$
$$P4(\cos\beta) = (35\cos 4\beta - 30\cos 2\beta + 3)/8.$$

The non-cartesian sampling of the relevant 3D space can be carried out using a dynamic-angle strategy, whereby the spinning angle is changed throughout the course of the experiment.



Fourier transformation of these Dynamic Angle Correlation Spectroscopy (DACSY) data yields the desired isotropic-anisotropic-anisotropic 3D NMR spectra.

Example: ^{87}Rb 3D DACSY NMR of RbNO$_3$ (3 inequivalent sites in the crystal)



This patterns provide a highly detailed description of the electronic environments surrounding each site.