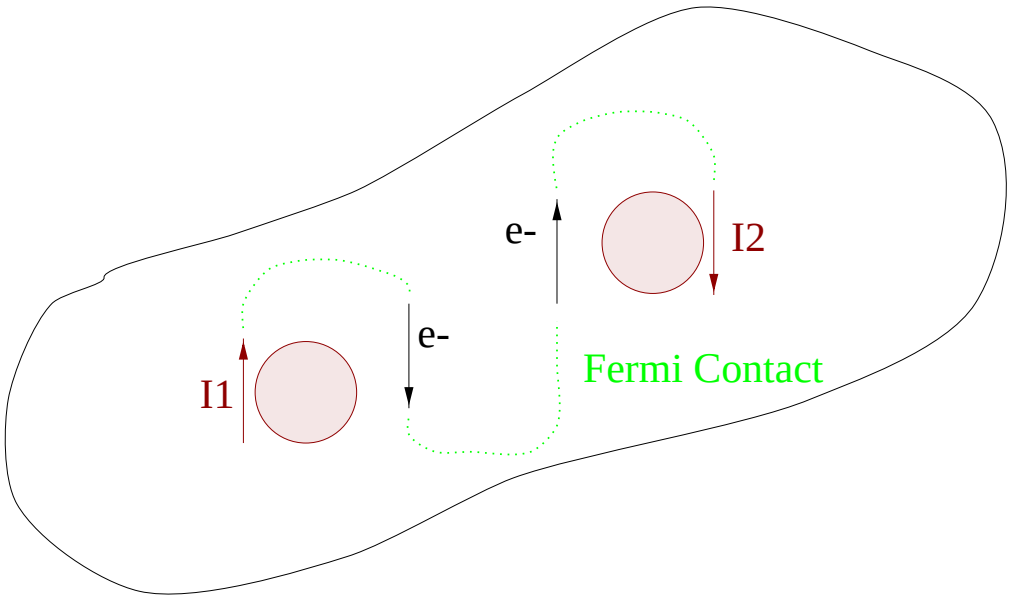
7– NMR Interactions: Scalar Coupling

7.1 Hamiltonian

The scalar interaction arises between two different nuclear spins, I_1 and I_2, and is mediated by the electrons surrounding these two spins. Through the Fermi contact, the electrons are polarised in the opposite direction to the nucleus they are interacting with. This polarisation in turn has an effect on the other electrons in close proximity, which in turn affects the neighbouring nuclei.



Unlike the chemical shift, the scalar interaction does not depend strongly on orientation. In some cases though, for particular compounds, the scalar interaction does exhibit a slight anisotropy. For more details, see R.E. Wasylishen, Encyclopedia of NMR, Grant and Harris (eds).

Written in terms of a Hamiltonian, the scalar interaction is

$$\hat{\mathcal{H}}_J = \sum_k \sum_j 2\pi J_{kj} \hat{\vec{I}}_k \cdot \hat{\vec{I}}_j \tag{7.1}$$

where $k < j$.

As we will see in the next section, this function is analogous to the dipolar Hamiltonian. In fact, the scalar interaction and the dipolar interaction are quite similar in that the interaction occurs between two nuclear spins.

7.2 J-coupling in solution

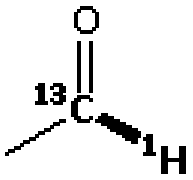
Types of J-coupling

There are two "types" of J-coupling:

1. homonuclear coupling - i.e. between like nuclei (e.g. H-...-H)
2. heteronuclear coupling - i.e. between different types of nuclei (e.g. H-C)

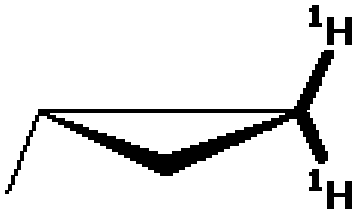
Distance dependence of J-coupling

The number of interceding bonds between coupled nuclei will effect the absolute value of the coupling constant. The order of the strength of coupling is as follows:



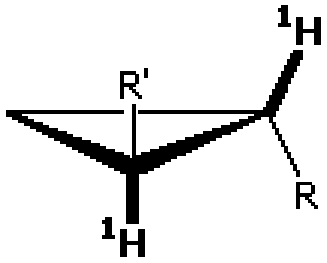
^{1}J

110–270 Hz



^{2}J

9–15 Hz



^{3}J

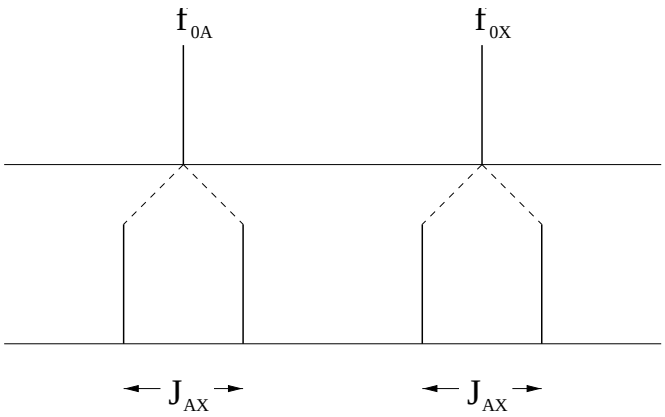
6–8 Hz

Line splitting

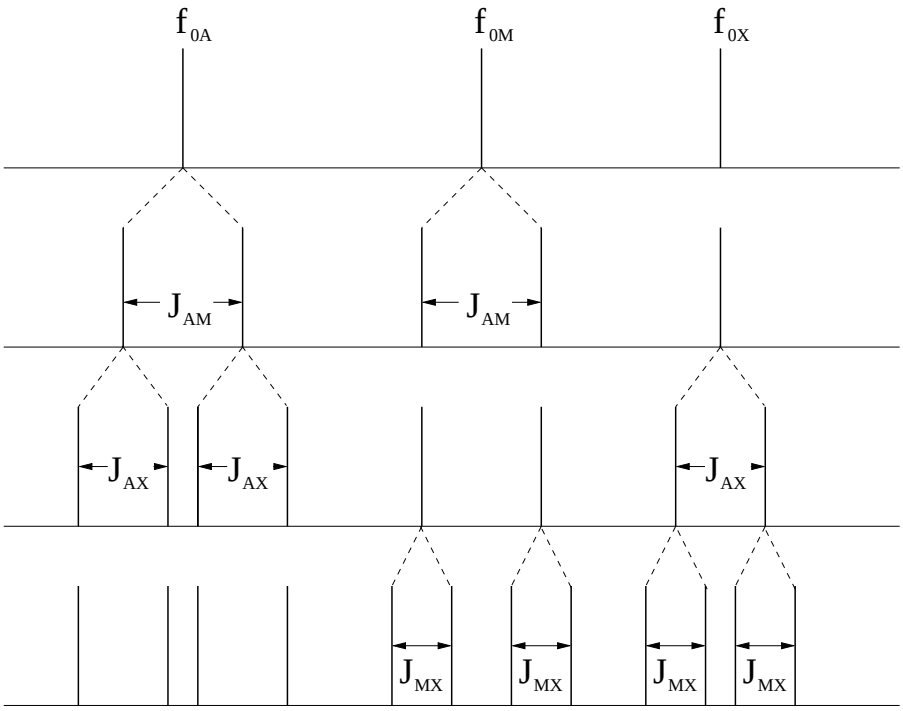
As a result of the scalar interaction between the nuclei, the lines in a non-decoupled spectrum are split. The splitting is independent of $\vec{B}_0$.

For a two spin 1/2 system (AX), with J-coupling

J_{AX}, the resulting spectrum is:



For a three spin 1/2 system (AMX), with J-coupling J_{AX}, J_{AM}, and J_{MX}, the resulting spectrum is:

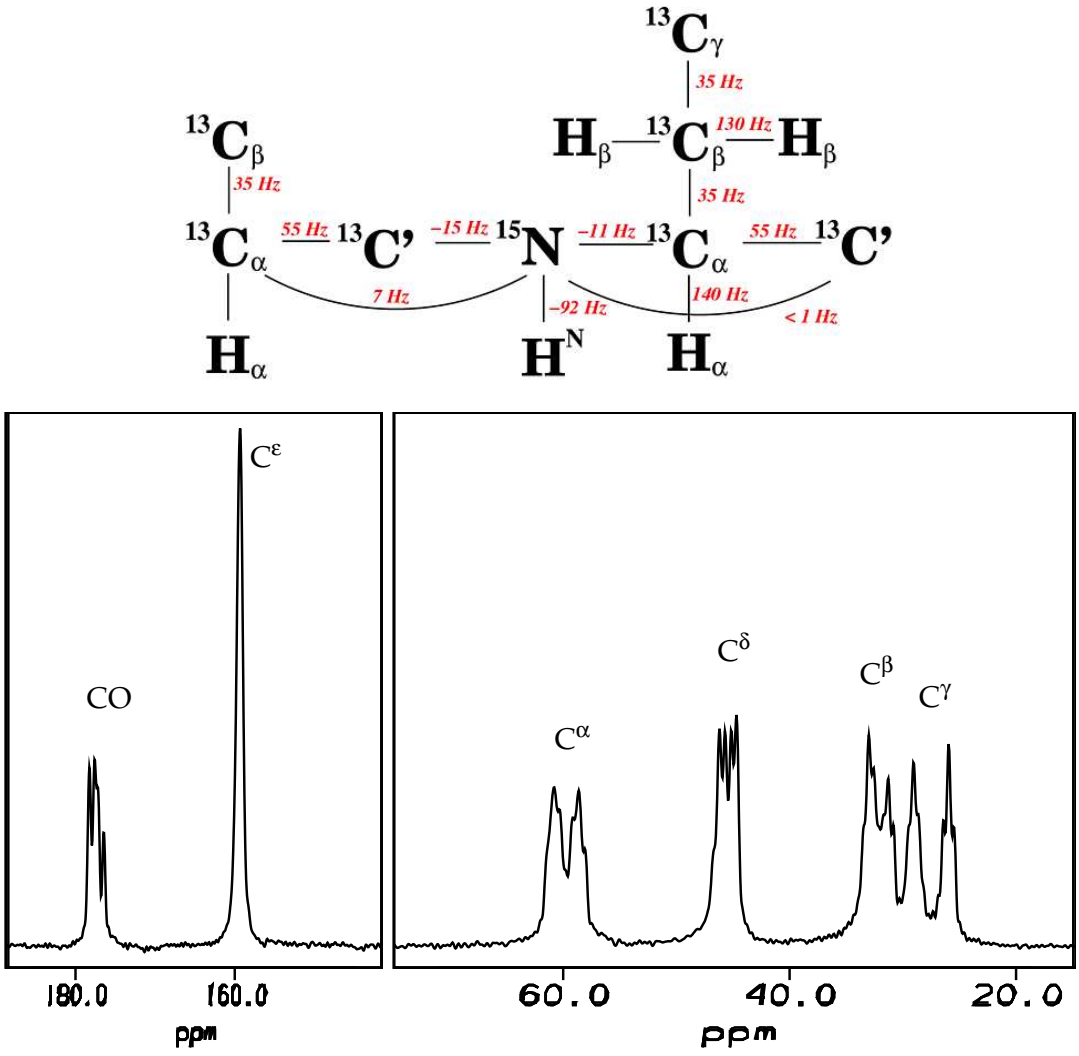


7.3 J-coupling in the solid state

In the solid state, J-coupling typically does not result

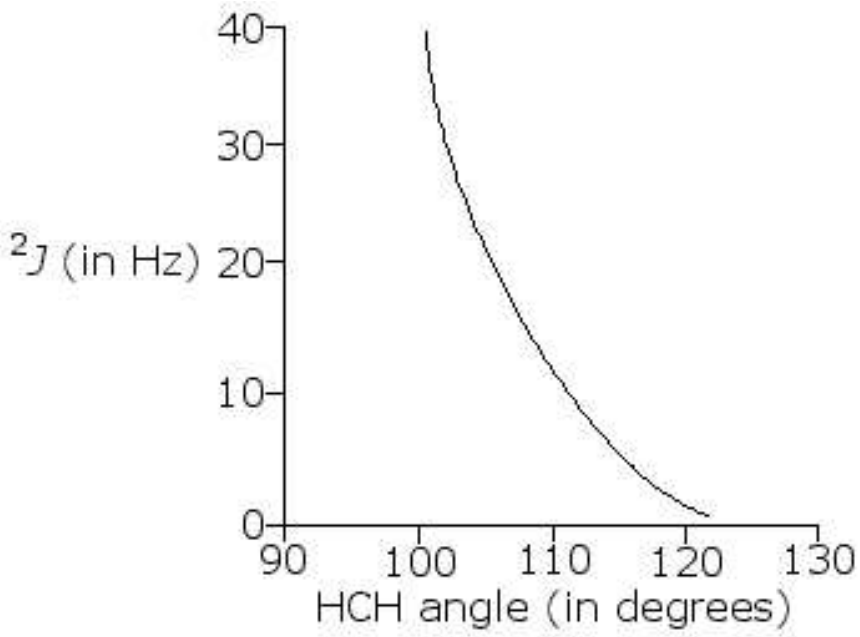
in a clear separation of a line into two, as illustrated above. The reason for this is that typical linewidths obtained in the solid state (100 Hz - 10's of kHz) are often greater than the J-splitting.

Nonetheless, there are a few cases, where some splitting can be observed, as shown for the spectrum of fully $^{13}C/^{15}N$- labelled arginine below.

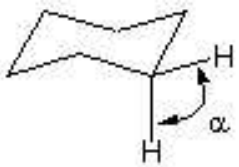


7.4 Importance of the Scalar Interaction

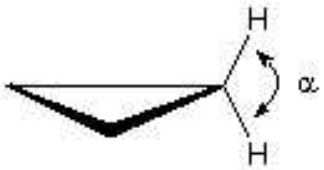
1. Determination of angles between nuclei via geminal and vicinal J coupling:
   - Geminal coupling: Geminal coupling or ^2J coupling is dependent upon the bond angle between the nuclei. Generally, the smaller the angle the bigger the coupling constant.



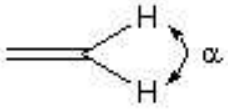
Example:



α = 109°
^2J = 12 - 18 Hz



α = 118°
^2J = 3 - 7 Hz



α = 120°
^2J = 0 - 3 Hz

- Vicinal coupling: dihedral angle via the Karplus equation

$$^3J = A + Bcos\varphi + Ccos2\varphi \qquad (7.2)$$

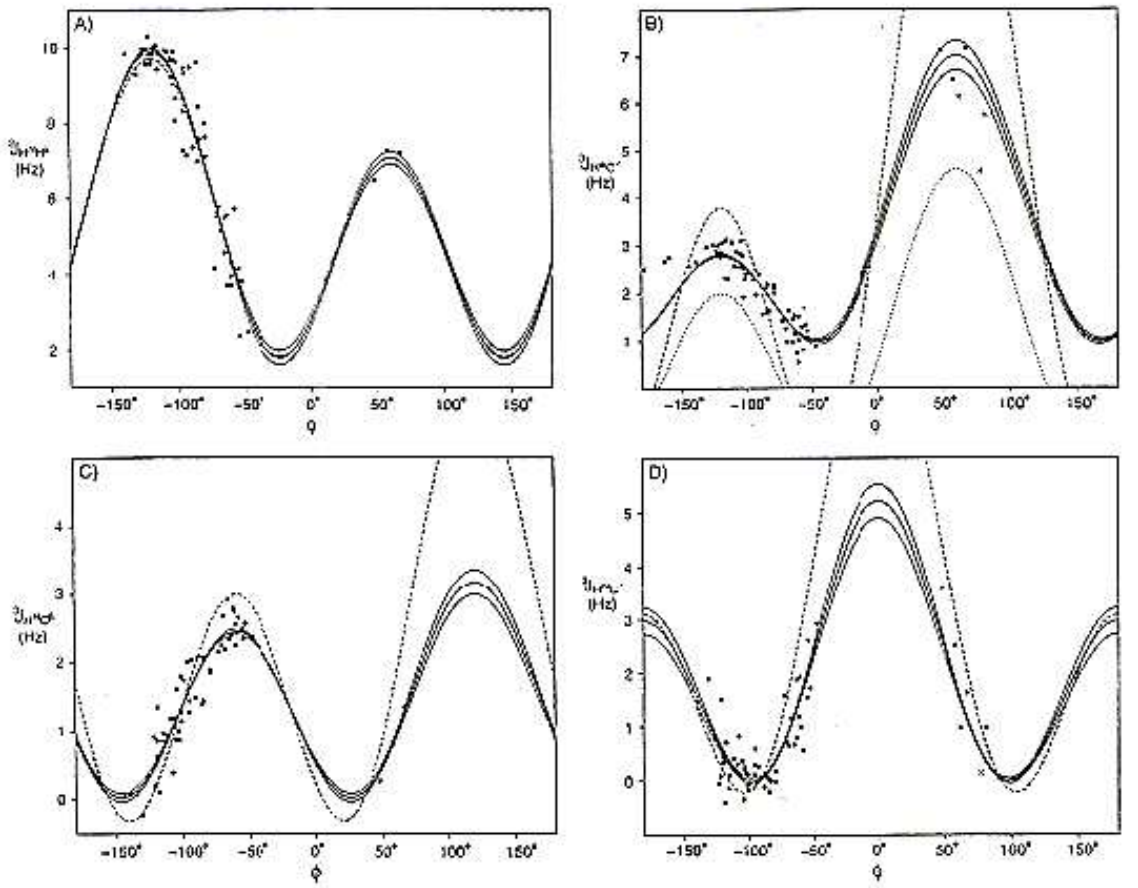


Figure 4. Reparametrized Karplus curves for (A) $^3J_{H^N H^\alpha}$, (B) $^3J_{H^N C'}$, (C) $^3J_{H^N H^\beta}$, and (D) $^3J_{H^N C'}$, calculated using singular value decomposition on the measured couplings and corresponding ϕ angles derived from the X-ray structure. The best fit to the data is shown as a thick solid line, and the thin solid lines are plotted at ±2 standard deviations, calculated from repeating the fit 1000 times with 10% of the points, chosen randomly, omitted for each fit. Dashed lines represent previous parametrizations from (A) Pardi et al.,[3] (B) Bystrov,[2] based on experimental data (longer dashes) and on FPT-INDO theoretical calculations (shorter dashes), and (C and D) FPT-INDO theoretical calculations by Bystrov.[4] In all four plots, the ● symbols mark J values for those residues which have at least three measured J couplings and were the only ones later subjected to ϕ angle refinement. In part B, the + symbols mark residues for which only the $^3J_{H^N C'}$ coupling could be measured, including three Pro residues. The × symbols mark the J values measured for Gly residues. Glycine couplings were included for reparametrizing the $^3J_{H^N C'}$ curve only and were never subjected to ϕ angle refinement.

2. Correlation between nuclei (e.g. COSY, TOCSY and analogous experiments in the solid state)