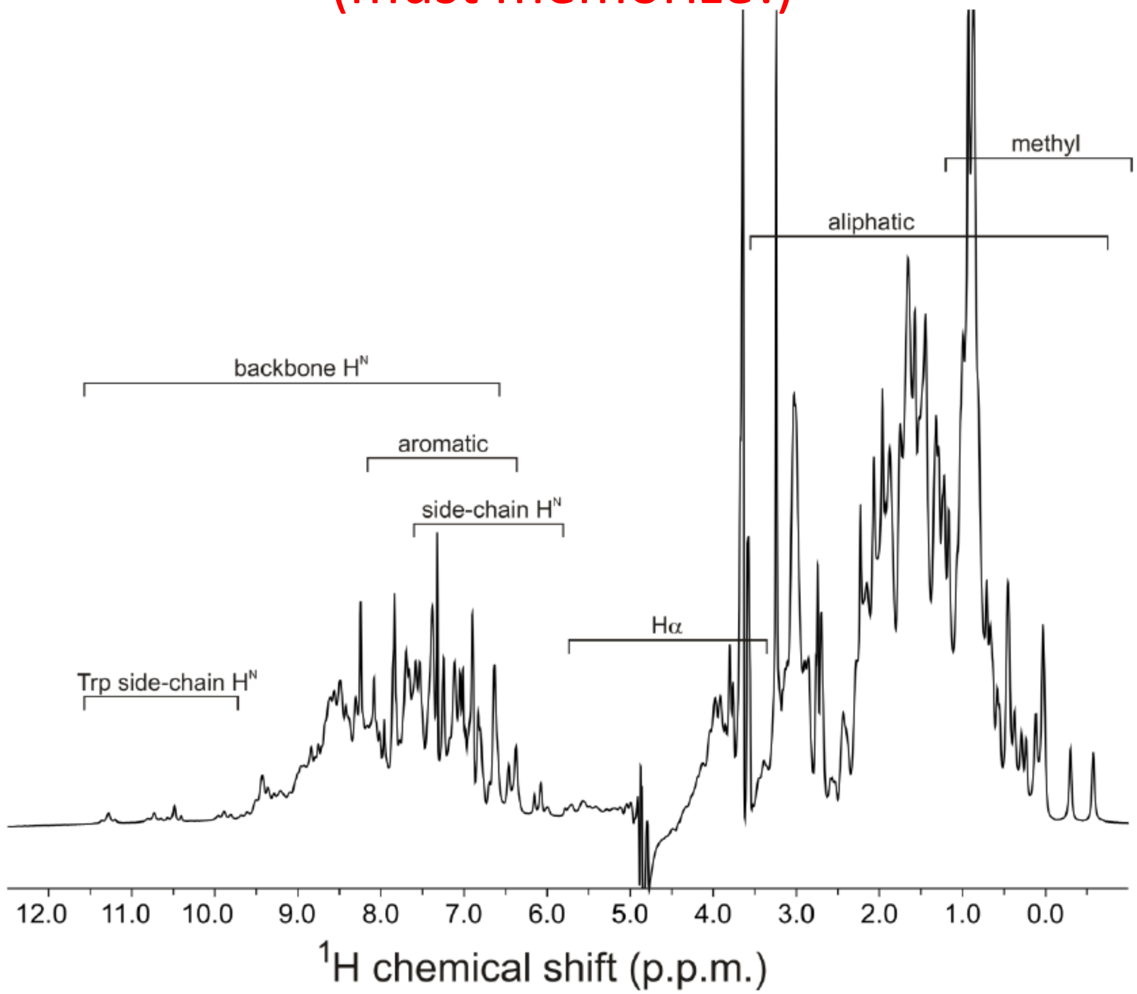
Protein ^{1}H Chemical Shifts

(must memorize!)



From “Peptide Resonance Assignments.”
Girvin, M, AECOM, Course 1022

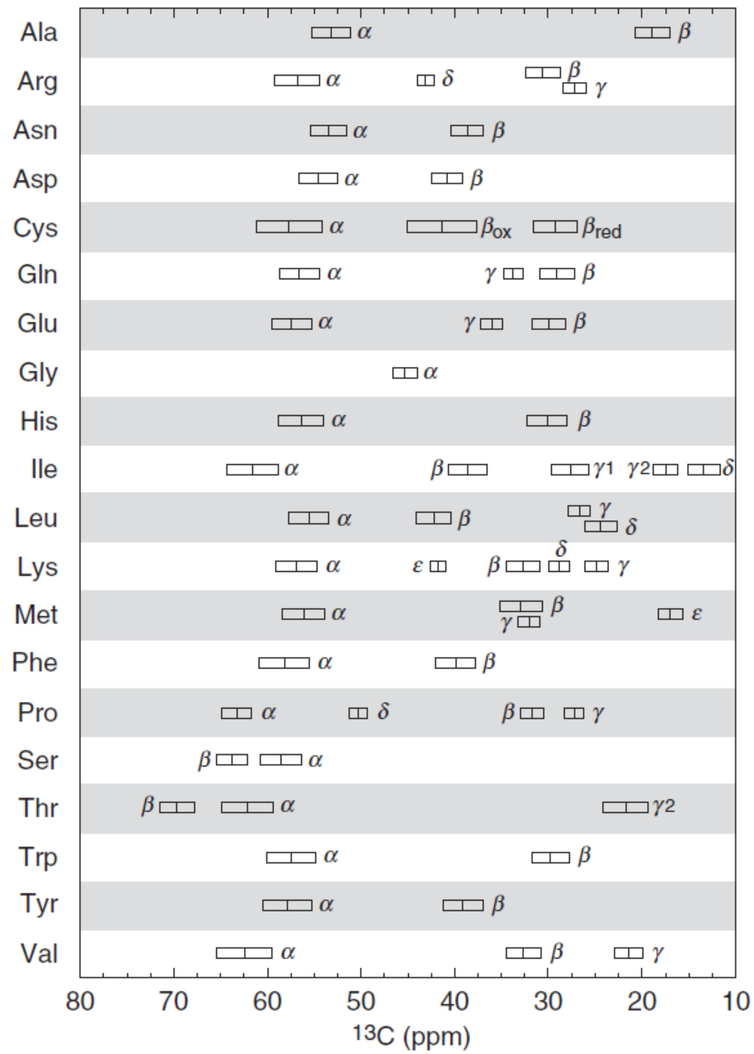
Protein ^{1}H Chemical Shifts

Typical proton chemical shifts for amino acids within a protein.

type	HN	HA	HB	other
gly	8.0	4.2,3.8		
ala	8.0	4.4	1.4β	
val	8.0	4.4	2.0β	1.0,0.9γ
ser	8.0	4.5	3.7,3.6β	
thr	8.0	4.5	4.4β	1.2γ
cys	8.0	4.5	3.3,3.1β	
asp	8.0	4.6	2.5,2.3β	

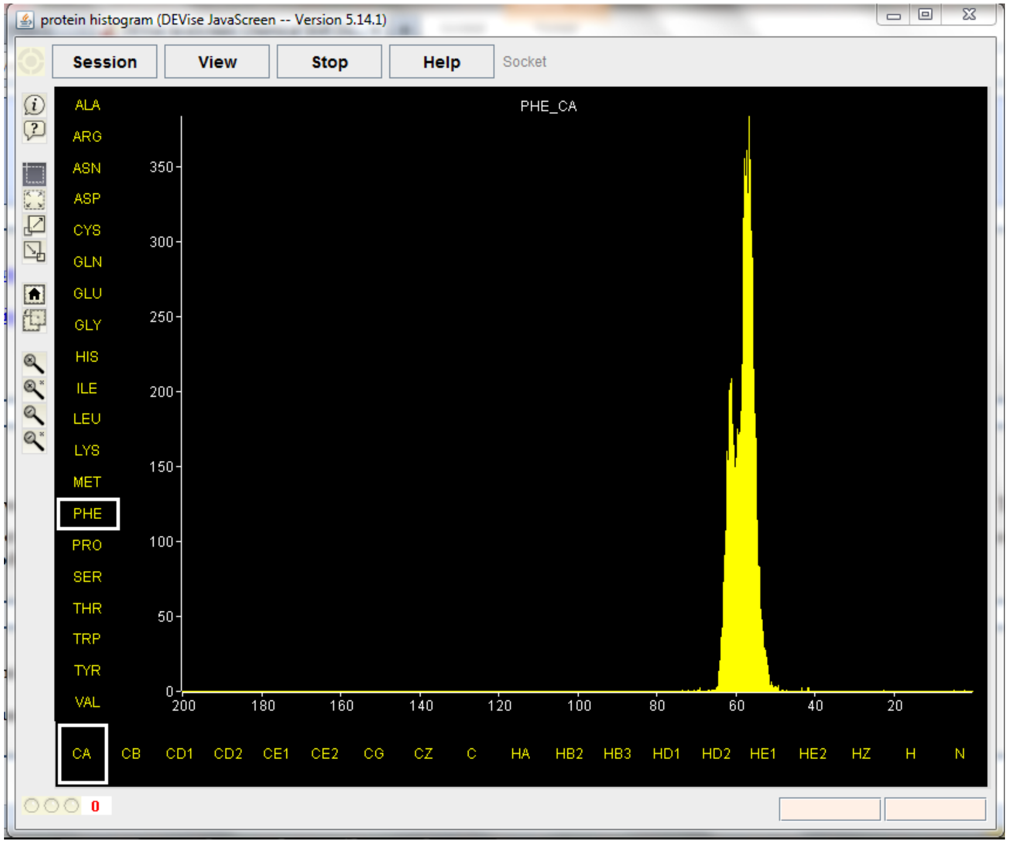
- Excerpt from: http://hoffman.cm.utexas.edu/research/h_cs.pdf

Protein ^{13}C Chemical Shifts



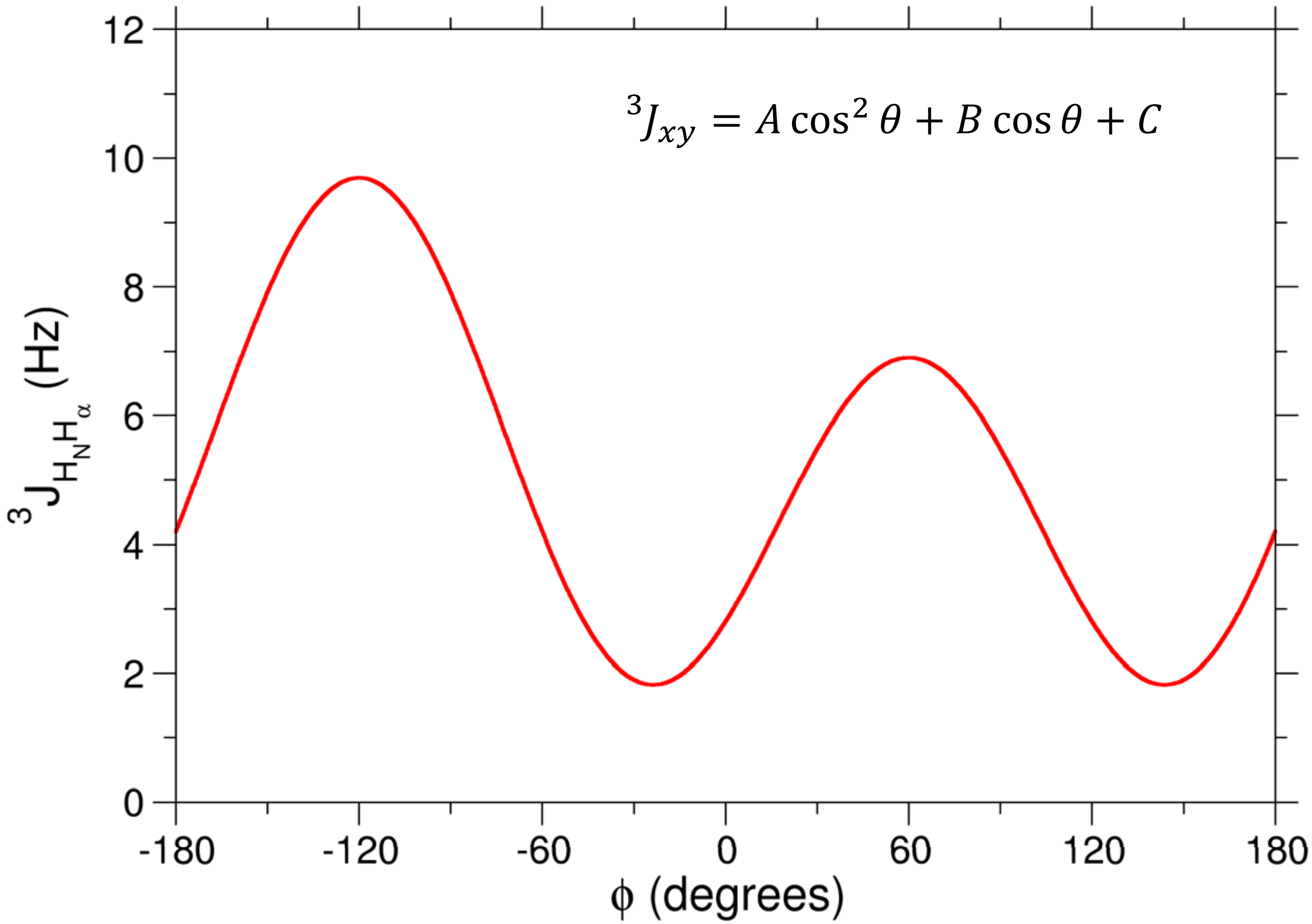
From *Protein NMR Spectroscopy*
Cavanagh, *et al.*, Chapt. 10, p. 795

DEVise Chemical Shift Viewer



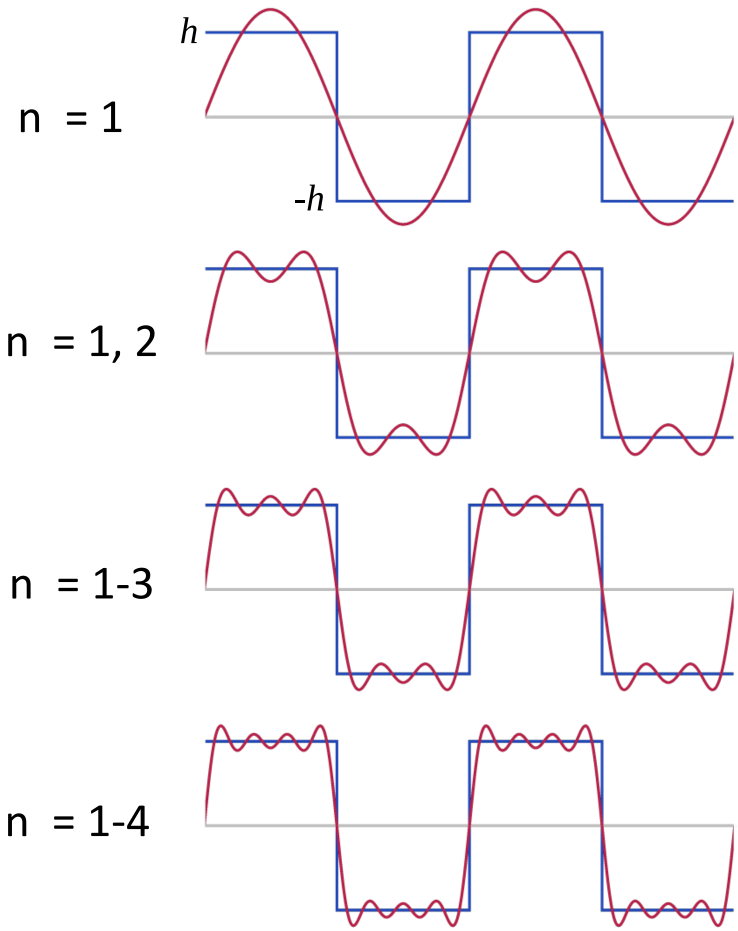
- Available at the BMRB: http://www.bmrb.wisc.edu/ref_info/

Karplus Equation



Fourier Transforms: Periodic Functions

(with period 2π)



$$f(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} [a_n \cos(nt) + b_n \sin(nt)]$$

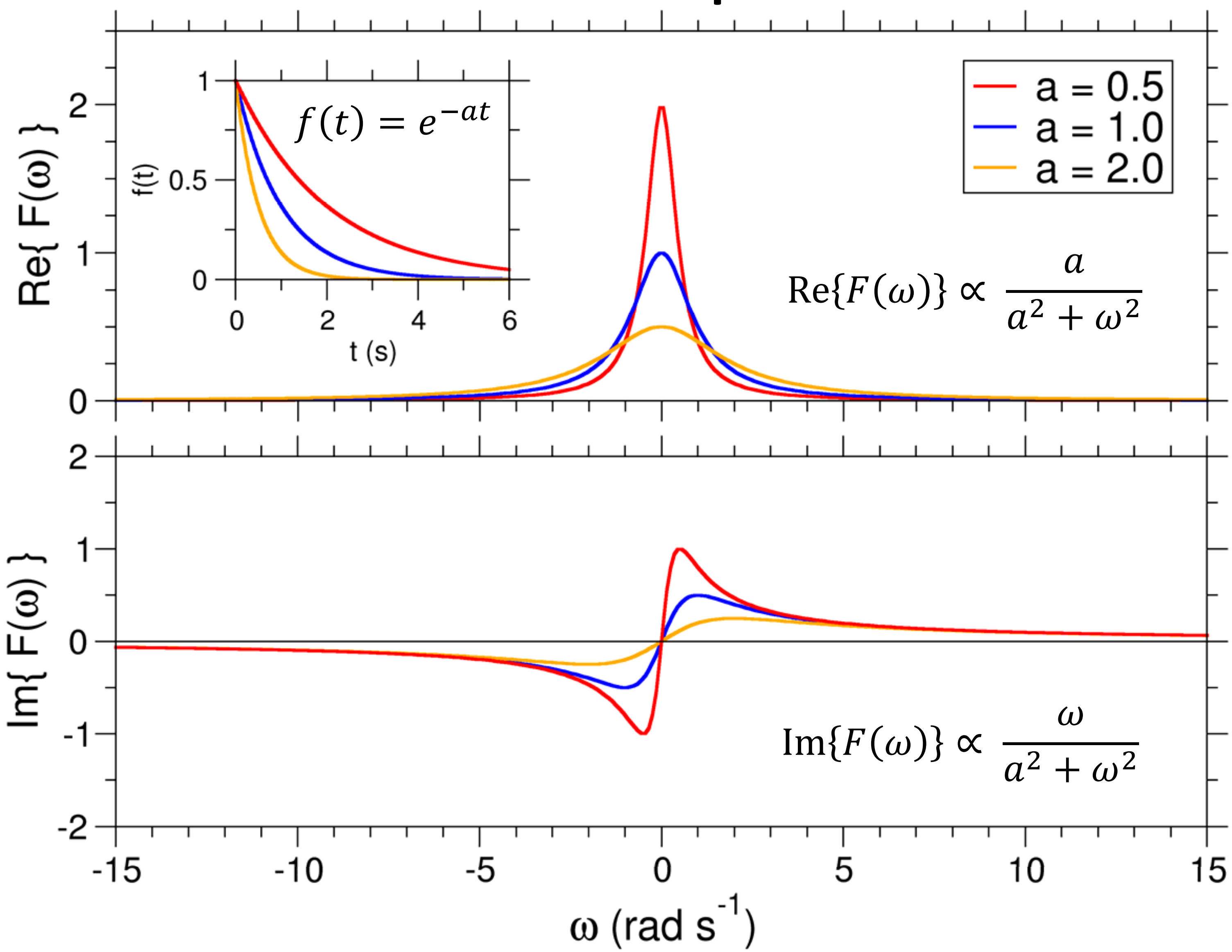
$$a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(t) \cos(nt)\, dt$$

$$b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(t) \sin(nt)\, dt$$

$$f(t) = \frac{4h}{\pi} \left(\frac{\sin t}{1} + \frac{\sin 3t}{3} + \ \dots \right)$$

Image from "Fourier Series"
http://en.wikipedia.org/wiki/Fourier_series

Fourier Transform: Exponential Decay



Summary

Chemical Shifts and J-Coupling

- Chemical shifts allow comparison of NMR frequencies at different fields
- Chemical shifts are different depending on environment and nucleus type
- Scalar coupling gives rise to multiple signals for nuclei that are electronically coupled (independent of B_0)

Summary

Fourier Transforms

- Any function can be represented by a sum of periodic functions with different frequencies
- Fourier transforms tell you the contribution of each frequency to the sum above
- NMR signals can be built up from sines, cosines, and decays. These all have characteristic transforms; Faster decay → broader peak.
- The *product* of two time domain functions ($e^{-at}\sin(\omega t)$) results in a *convolution* of their Fourier transforms. The signals are "mixed."