

Indirect Coupling

aka: J -coupling, indirect spin-spin coupling, indirect dipole-dipole coupling, mutual coupling, scalar coupling (liquids only)

First, two comments about *direct coupling*...

Nuclear spins interact directly with one another through space – this is the direct coupling, which is also known as dipole-dipole coupling, or simply the dipolar interaction.

Although the magnitude of the dipolar coupling is quite large, kHz, i.e., as large as chemical shift effects, in solution the direct coupling is usually averaged to zero and does not affect the energy state of the spins – more about how dipolar coupling effects resonances a bit later.

We now turn our focus to a consideration of the fine structure of the NMR resonances, the so called multiplicity patterns of the resonance lines.

The fine structure of the resonances arises from the interaction of the nuclear spins with one another as mediated by the bonding electrons.

J -coupling is the second link between NMR and structural analysis.

J -coupling is a result of the interaction of proximate nuclear spins, usually involving one, two or three bonds, but more remote interactions are possible with some geometries.

J -coupling reveals specific details of the local bonding network.

Since J -coupling is mediated by bonding electrons, it is intrinsically an intramolecular effect.

J -coupling effects are observable between spins linked through a small number of chemical bonds. Observation of the indirect coupling indicates that two spins are nearby in the bonding network.

In NMR, the most substantial energetic effect arises from the interaction of the nuclear spins and magnetic field – this is the Zeeman interaction – MHz frequencies.

Chemical shielding energies are several orders of magnitude less than the Zeeman interaction, but are of fundamental importance to structural analysis – these transitions are in the kHz range..

Indirect coupling effects also affect nuclear spin energy levels, but are even lower in energy – the magnitude of the indirect coupling for $^1\text{H} - ^1\text{H}$ coupling is usually less than 50 Hz, but nevertheless provide key structural information. Heteronuclear couplings can be substantially larger, up to several hundred Hz.

The Zeeman and chemical shift interactions are *external* interactions, i.e., they depend upon the magnitude of the applied magnetic field.

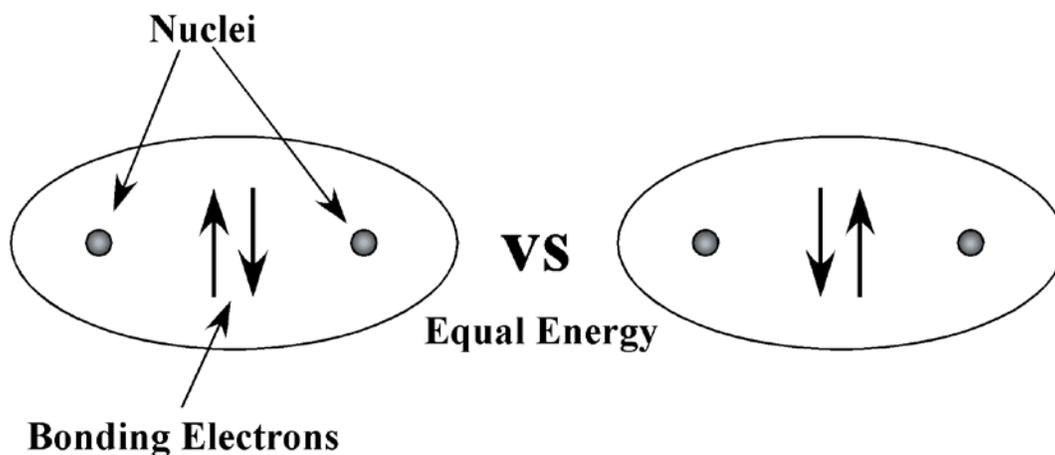
Conversely, *J*-coupling is an entirely *internal* interaction.

Because *J*-coupling is an internal interaction, the magnitude of the effect *does not* depend on the strength of the magnetic applied field.

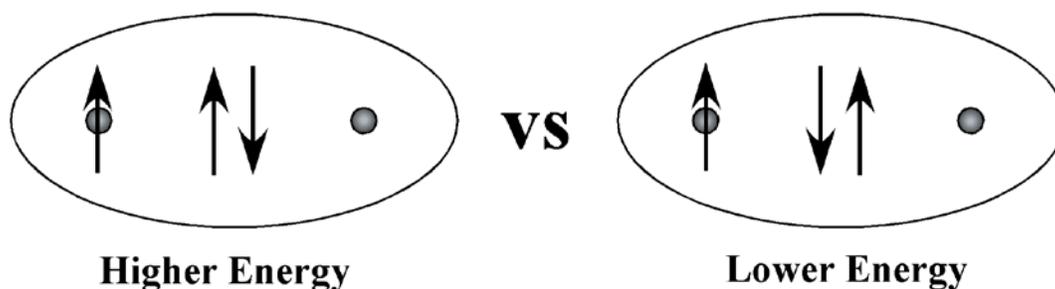
Since the value of the indirect-coupling is independent of field strength it is often referred to as the *coupling constant*.

For directly bonded nuclei the sign of the indirect coupling depends upon the gyromagnetic ratios, γ , of the nuclei involved, nuclei with the same γ give rise to 1-bond couplings with positive values. Things get complicated fast...

One Nuclear Spin

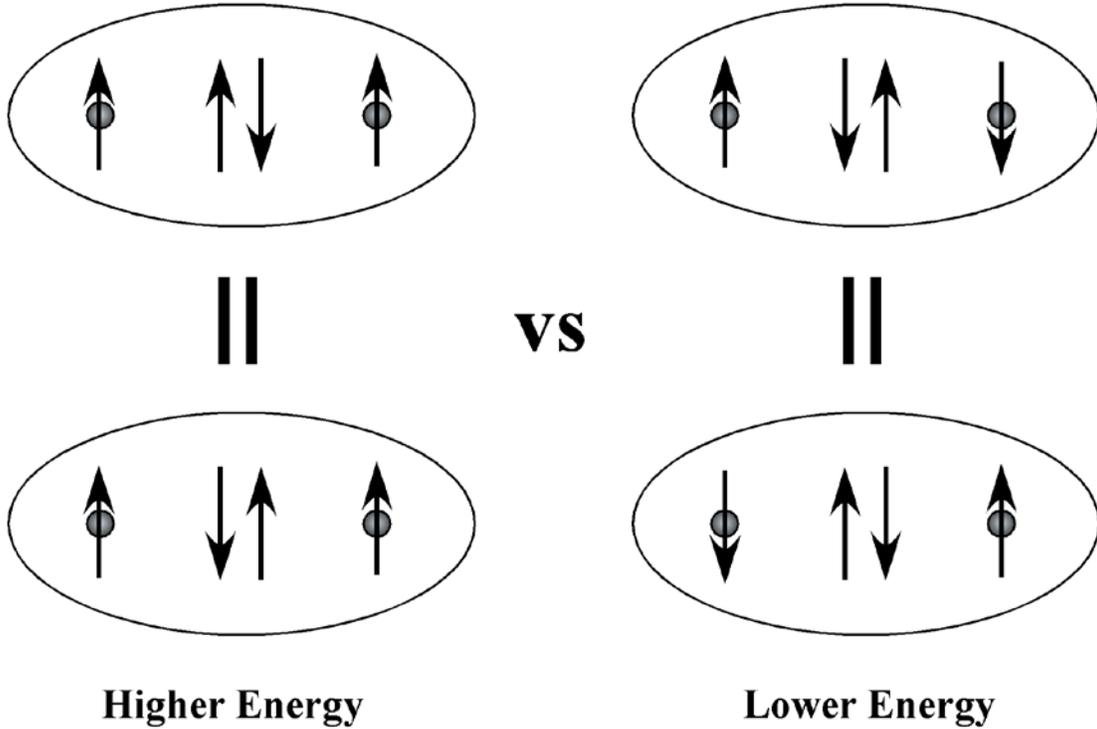


In the absence of nuclear spins, electron spins are paired according to the Pauli principle. The 'up-down' and 'down-up' states have the same energy.



If one nuclear spin is present, the two electron spins states no longer have exactly the same energy. The interaction between nuclear and electron spins is named the *hyperfine interaction* and acts to lower the energy of the electron spin that is paired with the nuclear spin.

Two Nuclear Spins



When a second nuclear spin is present, the state in which the two nuclear spins are antiparallel is lower in energy since in this state the electron spins may align themselves to lie antiparallel to both nuclear spins.

The diagrams shown above correspond to nuclear spin interactions (J -coupling) for directly bonded nuclei, i.e., most commonly the interaction between ^1H and ^{13}C nuclei, but it might also include $^1\text{H} - ^{15}\text{N}$ interactions, or even $^{13}\text{C} - ^{15}\text{N}$ interactions. Although the extent of the indirect spin interaction is limited, it does generally extend across several bonds.

The Weak-Coupling Limit: First-Order Spectra

For many molecular systems, the weak-coupling condition applies:

$$\nu_j - \nu_k \ll J_{jk}$$

The weak coupling conditions implies that the difference in chemical shifts between two resonances is much greater (10 \times) than the magnitude of the J -coupling – if this is not true, then the energy level transitions no longer can be considered to correspond to resonances of individual nuclei.

Such strong-coupling effects were more common on spectrometers operating at lower fields, modern high field magnet systems tend to minimize these effects:

$$\begin{aligned} 60 \text{ MHz } ^1\text{H} &\rightarrow 60 \text{ Hz/ppm} \\ 500 \text{ MHz } ^1\text{H} &\rightarrow 500 \text{ Hz/ppm} \end{aligned}$$

First-order spectra possess relative simplicity and exhibit the following characteristics:

n equivalent spins alter the fine structure (multiplicities) of a neighboring spin, producing $n+1$ lines.

The relative intensities of individual components of multiplicity may be evaluated using Pascale's triangle.

Nuclei with the exact same chemical shift do not produce fine structure in one another.

The frequency displacements of each component of a multiplicity reflects the coupling constant.

J -couplings are symmetrical about the uncoupled frequency.

The Pople Notation

A convenient shorthand for describing NMR spectral features is named the *Pople notation*. The relative position of nuclei are given alphabetical equivalents, thus an AX spin system represents nuclei that are far apart relative to their mutual coupling, i.e., ($\Delta\delta \gg J$).

A weak convention assigns letters from higher chemical shift to lower chemical shift beginning with the letter A, i.e. a spectrum with an aromatic resonance and an aliphatic proton resonance might be designated AX.

Nuclei that have the exact same chemical shift share the same letter. This condition indicates that the nuclei have the same chemical environment and they are said to be *chemically equivalent*.

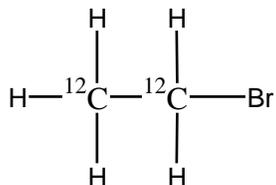
Nuclei that have similar but not identical chemical shifts acquire letters that are close together in the alphabet, i.e., AB.

The number of such chemically equivalent nuclei is designated with a number subscript, i.e., the protons in a methyl group are represented as A_3 .

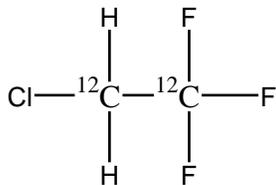
Note that chemical equivalence may arise from symmetry, or may be due to rapid rotation about a bond or it even may be coincidental.

Some other examples are given below:

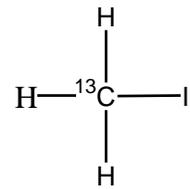
$\text{CH}_3\text{CH}_2\text{Br}$ is an A_3B_2 spin system (yeah, Br does have spin, as does Cl, but they are not practically observable):



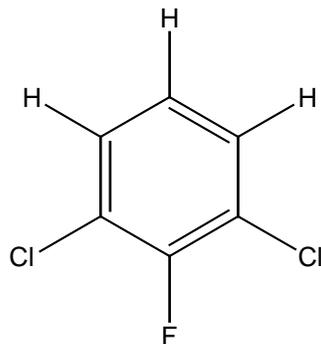
ClCH_2CF_3 is an A_2X_3 spin system:



$^{13}\text{CH}_3\text{I}$ is an A_3X spin system:

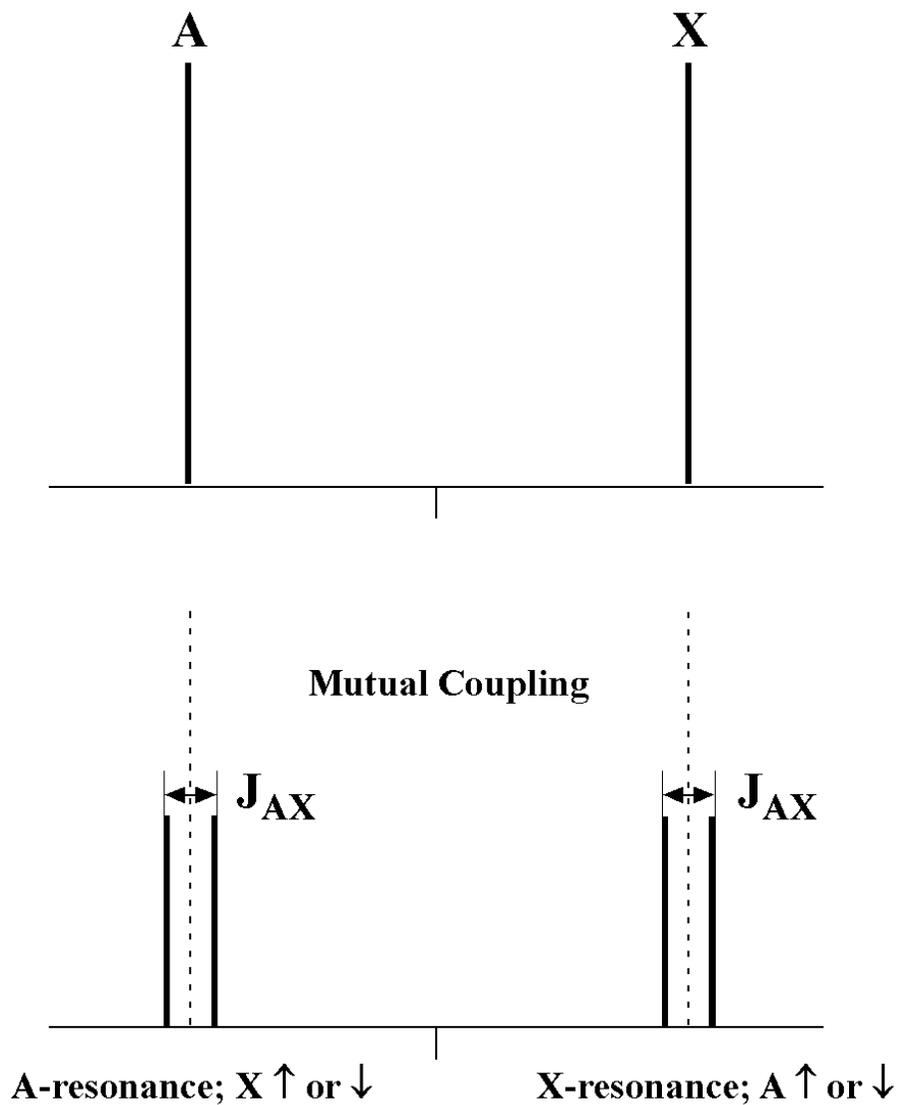


$\text{C}_6\text{H}_3\text{Cl}_2\text{F}$ is an A_2BX spin system:



The NMR spectrum corresponding to an AX system might appear as shown below:

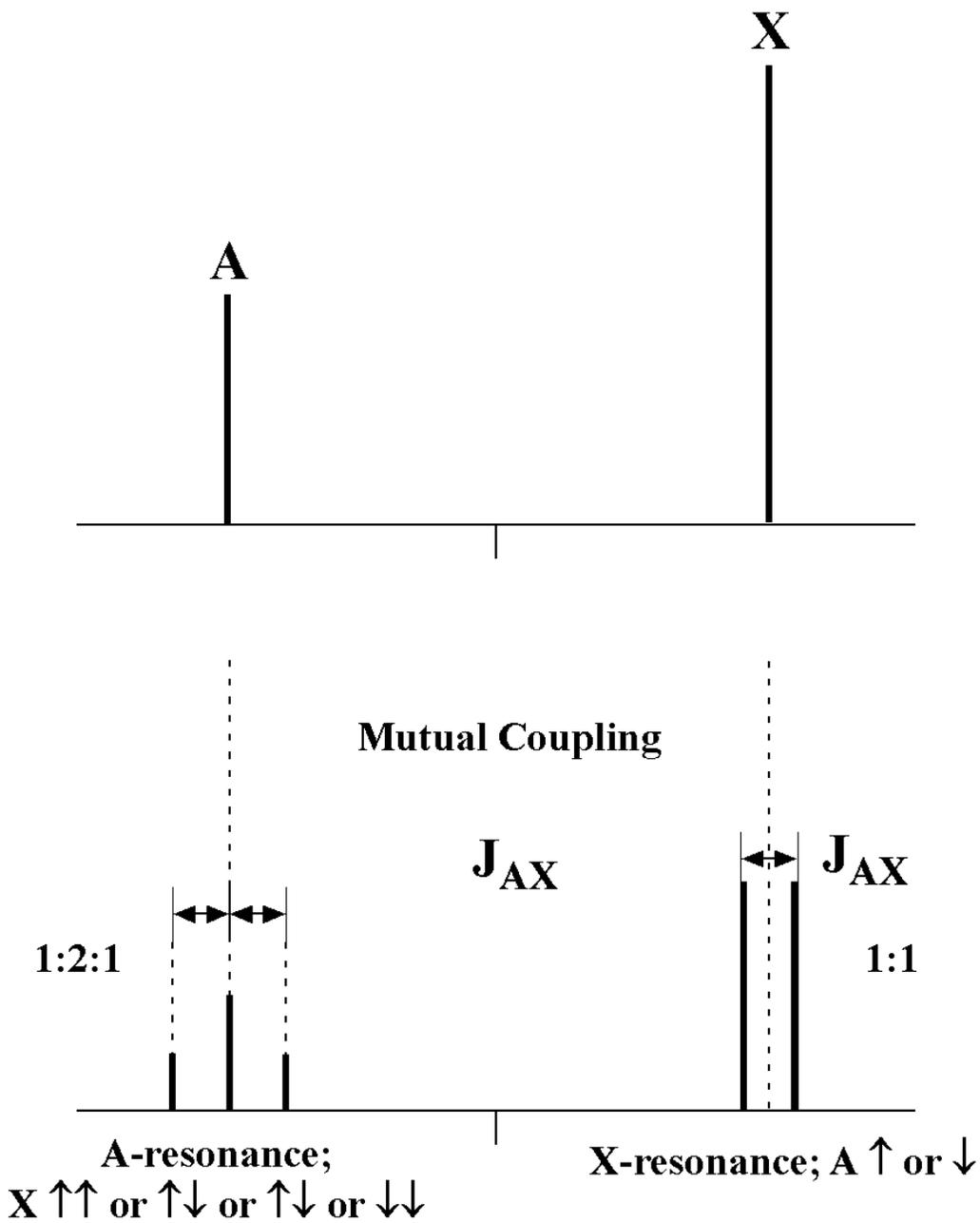
AX Spin System



Note that this same pattern could also represent two spins separated by two or three bonds.

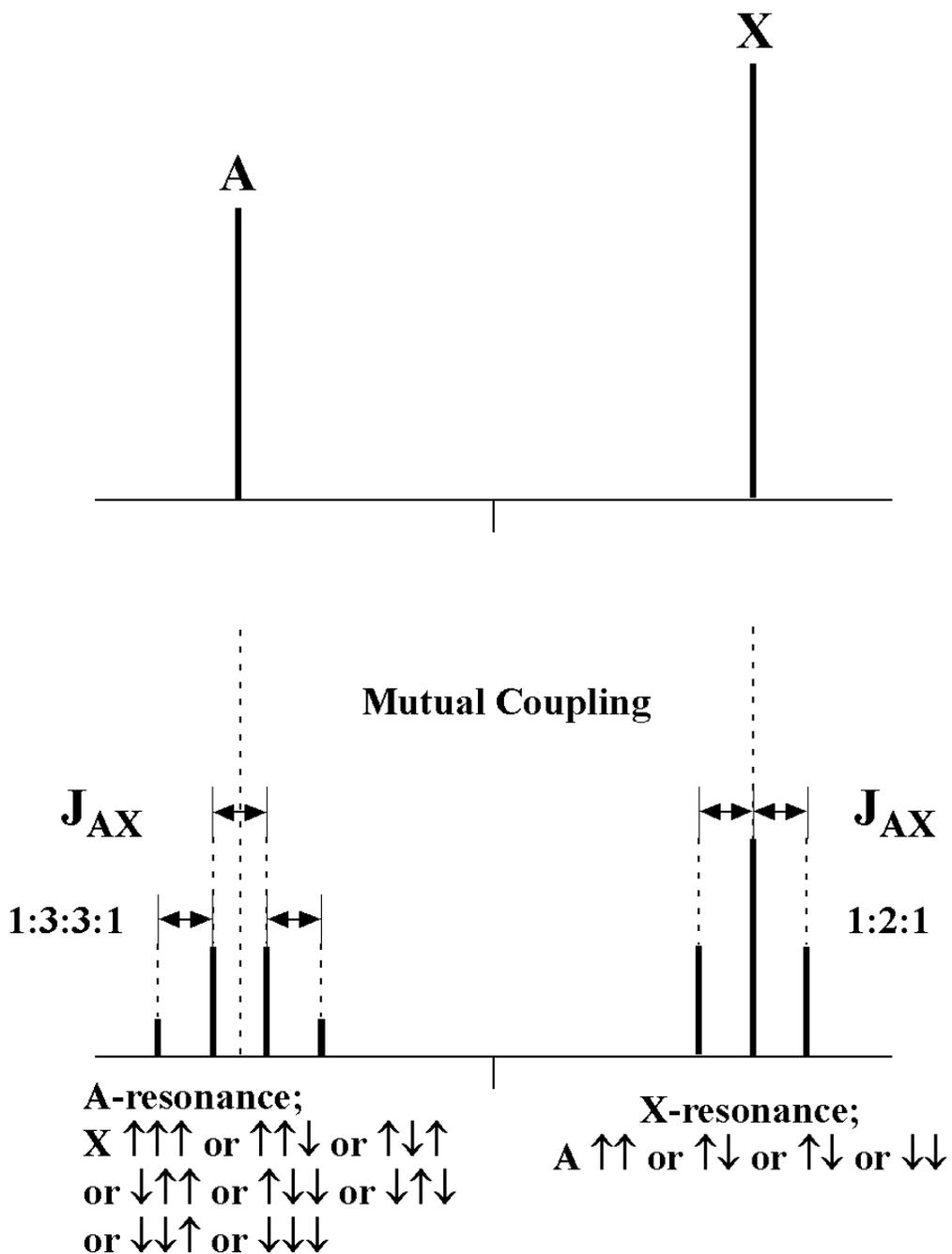
The following spectrum represents one A-type nucleus coupled to two identical X-type nuclei:

AX₂ Spin System



In the following spectrum, one two identical A-type nuclei are coupled to three X-type nuclei:

A_2X_3 Spin System



A Useful Pyramid Scheme Pascal's Triangle

				1																				
				1		1																		
				1		2		1																
				1		3		3		1														
				1		4		6		4		1												
				1		5		10		10		5		1										
				1		6		15		20		15		6		1								
				1		7		21		35		35		21		7		1						
				1		8		28		56		70		56		28		8		1				
				1		9		36		84		126		126		84		36		9		1		
				1		10		45		120		210		252		210		120		45		10		1

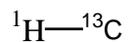
Intensity ratios of the resonance multiplicity may be predicted using Pascale's triangle. For example, a doublet has an intensity ration of 1:1, while a triplet has an intensity ratio of 1:2:1, a quartet has 1:3:3:1, and so forth.

The intensity coefficients derive directly from the ways spins in which the multispin states with equal energies may be arranged.

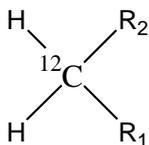
Coupling Order

A nomenclature to indicate the number of bonds between the interacting nuclei may be defined as follows:

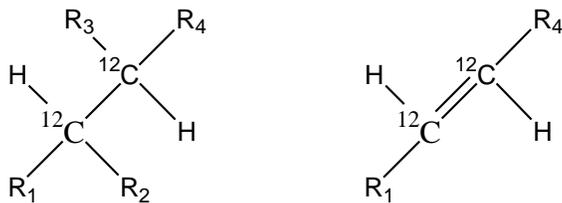
1 Bond between nuclei α and β : ${}^1J_{\alpha\beta}$, i.e., ${}^1J_{\text{HC}}$, a *direct coupling*



2 Bonds between nuclei α and β : ${}^2J_{\alpha\beta}$, i.e., ${}^2J_{\text{HH}}$, a *geminal coupling*



3 Bonds between nuclei α and β : ${}^3J_{\alpha\beta}$, i.e., ${}^3J_{\text{HH}}$, a *vicinal coupling*



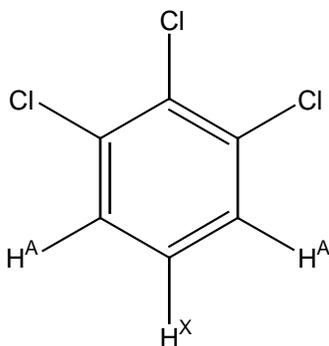
Magnetic Equivalence

A more subtle consideration in the characterization of spin systems involves the notion of magnetic equivalence.

Magnetic equivalence extends the idea of chemical equivalence, i.e., identical chemical shifts, to include indirect coupling effects.

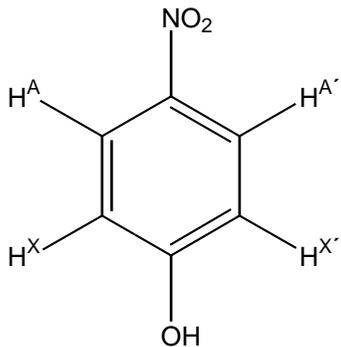
Two chemically equivalent nuclei are magnetically equivalent if and only if all of their indirect couplings to other nuclei in the molecule are identical.

Consider 1,2,3-trichlorobenzene:



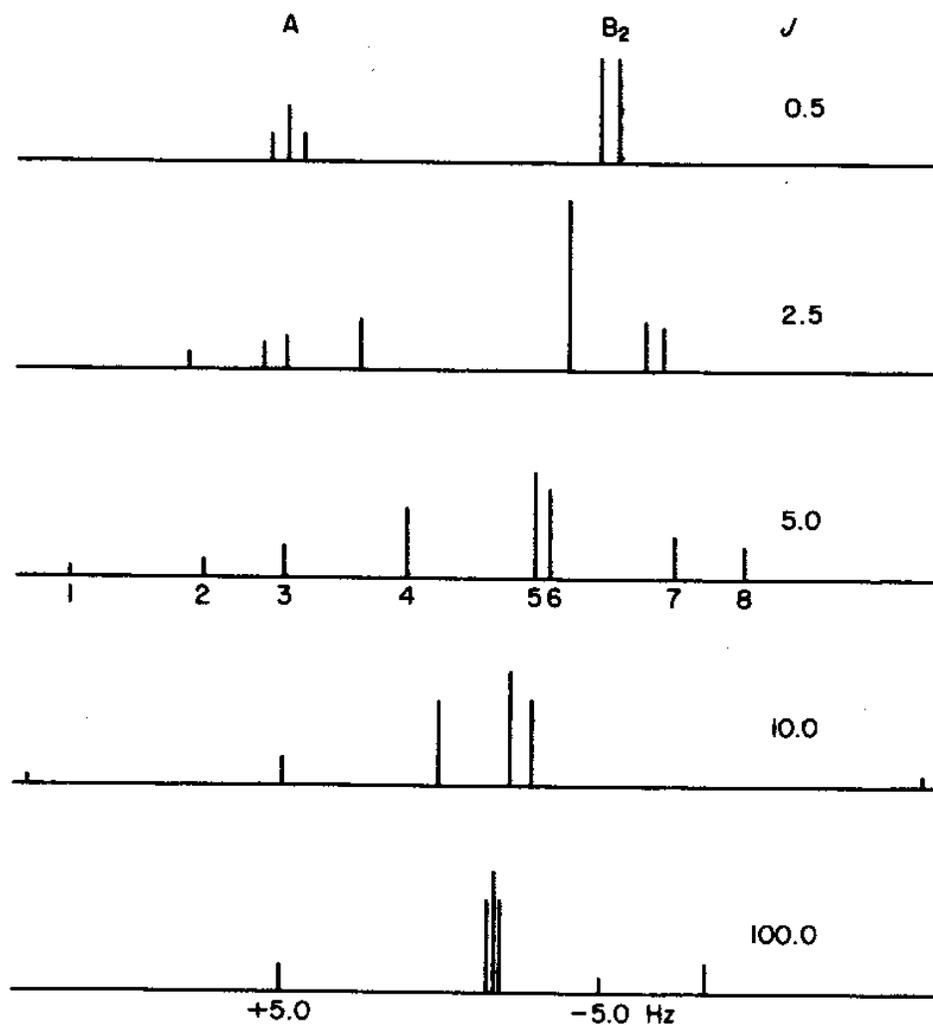
In this molecule, we can predict that the two H^A protons will have the same chemical shift since they exist in the same chemical environment. Furthermore, the coupling between H^X and either H^A is identical, thus the H^A are also magnetically equivalent and the spin system is named A₂X.

By contrast consider 1,4- nitrophenol:



The H^A and H^{A'} spins appear to be in chemically identical environments, as do the H^X and H^{X'} spins. However, H^A and H^X are coupled *ortho* with respect to one another but the spins H^A and H^{X'} are coupled *para* with respect to one another. Such ortho and para coupling will not be identical and the spins are therefore magnetically inequivalent. The designation of this spin system will be AA'XX'.

Strong Coupling Effects



Calculated AB₂ spectra for different values of J_{AB} with ν_A 5.0 Hz and ν_B -5.0 Hz.

Figure 4.5 from Abraham, R.J. and Loftus, P. (1978) *Proton and Carbon-13 NMR Spectroscopy*. Heyden, Philadelphia, PA.