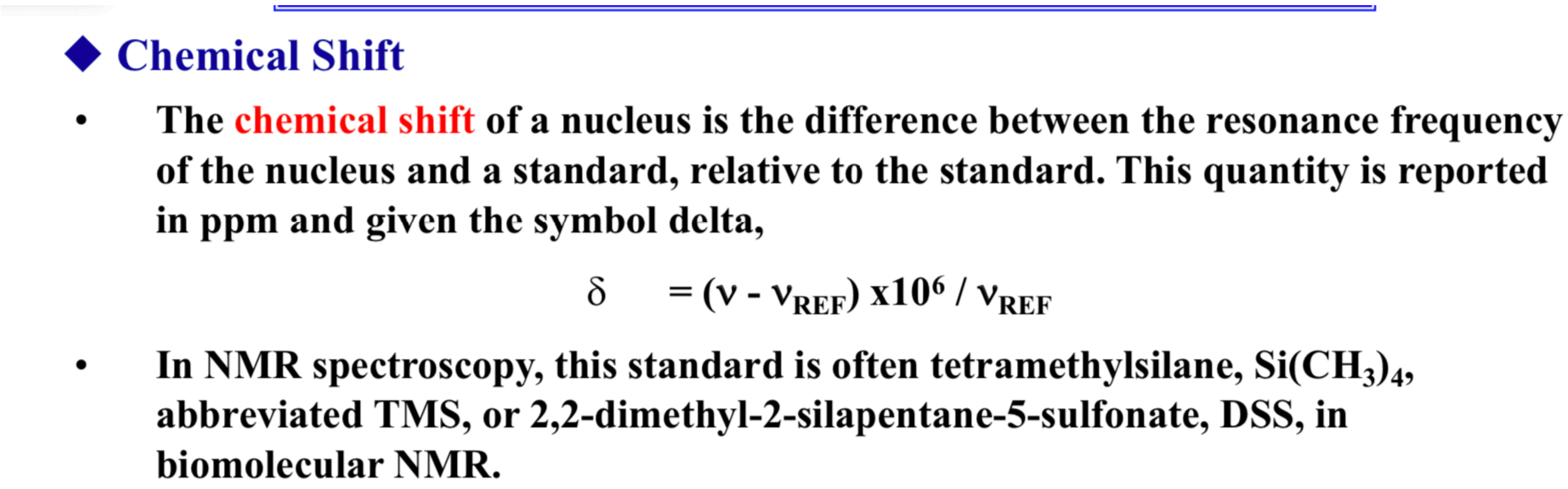
Chemical Shift



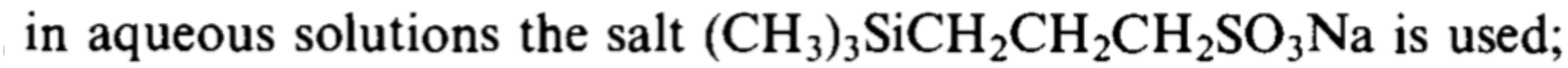
◆ Chemical Shift

- The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard, relative to the standard. This quantity is reported in ppm and given the symbol delta,

$$\delta = (\nu - \nu_{REF})\ \mathrm{x}10^{6} / \nu_{REF}$$

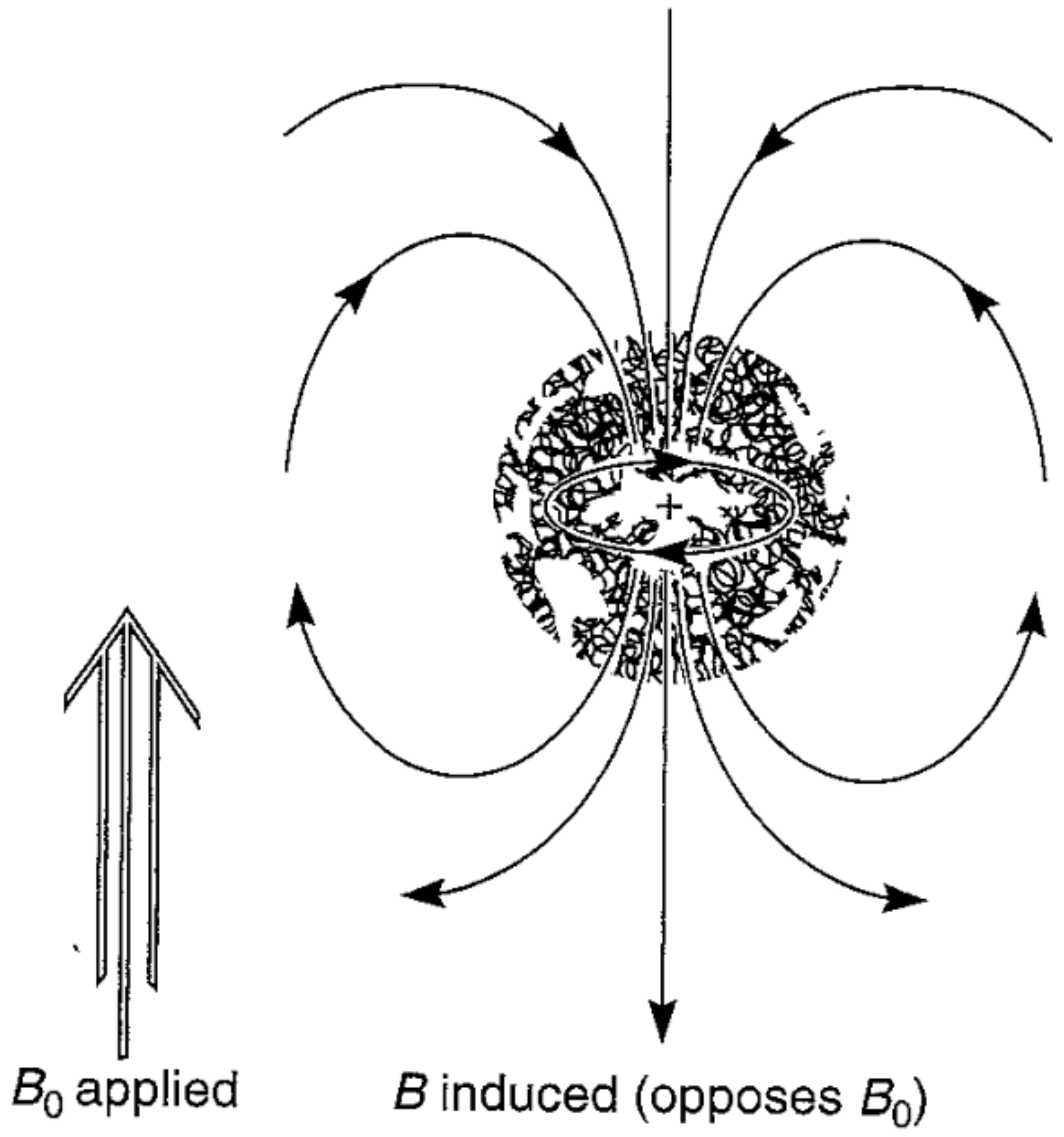
- In NMR spectroscopy, this standard is often tetramethylsilane, $Si(CH_3)_4$, abbreviated TMS, or 2,2-dimethyl-2-silapentane-5-sulfonate, DSS, in biomolecular NMR.

TMS is immiscible in water-



in aqueous solutions the salt $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ is used;

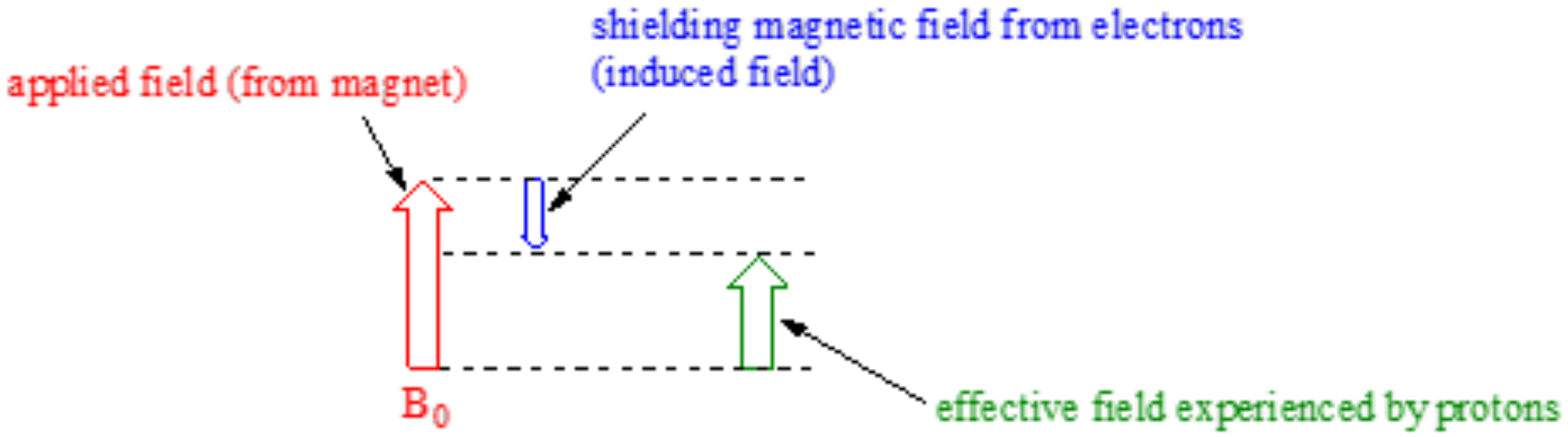
Chemical Shift (What is diamagnetic shielding?)



When a sample placed in a magnetic field the surrounding electron cloud tends to circulate in such a direction as to produce a field *opposing* that applied (so-called diamagnetic circulation)

The greater the electron density around a nucleus, the greater the induced counter field that opposes the applied field.

The Basis for differences in Chemical shifts



$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{induced}}$$

and, since the induced field is directly proportional to the applied field

$$B_{\text{induced}} = \sigma B_{\text{applied}}$$

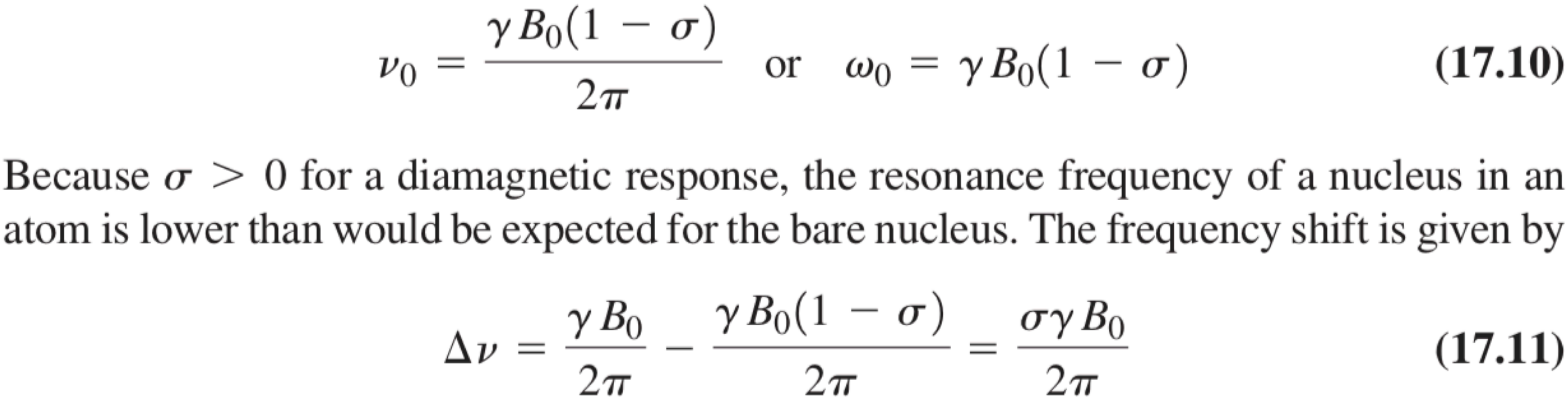
where σ is a constant, we have:

$$B_{\text{effective}} = B_0(1 - \sigma)$$

Due to diamagnetic anisotropy, the nucleus precesses at a lower frequency.

The shielding constant is the sum of a local contribution, a neighbouring group contribution, and a solvent contribution.

Chemical Shift



$$\nu_0 = \frac{\gamma B_0(1 - \sigma)}{2\pi} \quad \text{or} \quad \omega_0 = \gamma B_0(1 - \sigma) \qquad \textbf{(17.10)}$$

Because $\sigma > 0$ for a diamagnetic response, the resonance frequency of a nucleus in an atom is lower than would be expected for the bare nucleus. The frequency shift is given by

$$\Delta\nu = \frac{\gamma B_0}{2\pi} - \frac{\gamma B_0(1 - \sigma)}{2\pi} = \frac{\sigma\gamma B_0}{2\pi} \qquad \textbf{(17.11)}$$

which shows that the electron density around the nucleus reduces the resonance frequency of the nuclear spin.

This effect is the basis for the chemical shift in NMR.

Chemical Shift

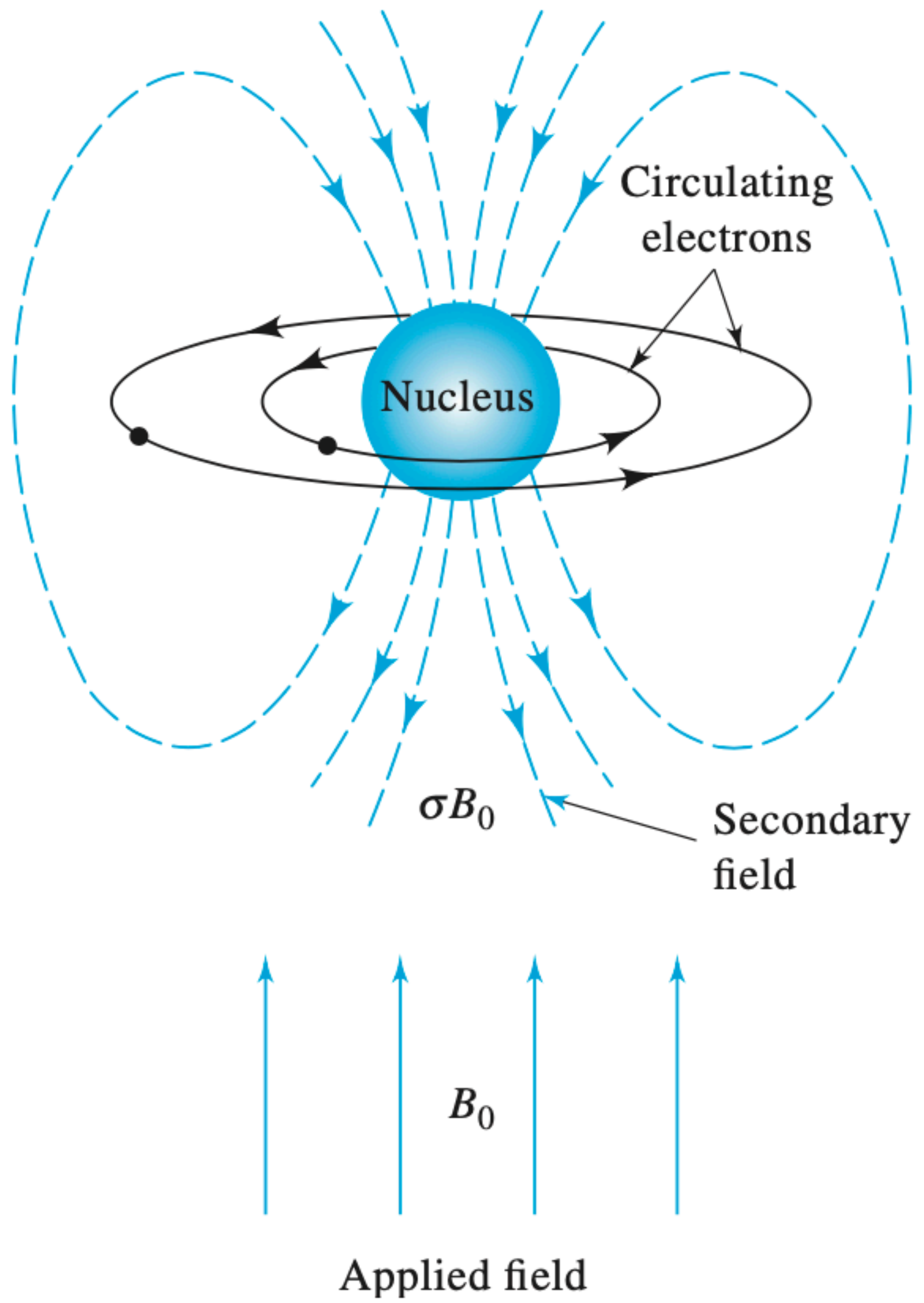


FIGURE 19-14 Diamagnetic shielding of a nucleus.

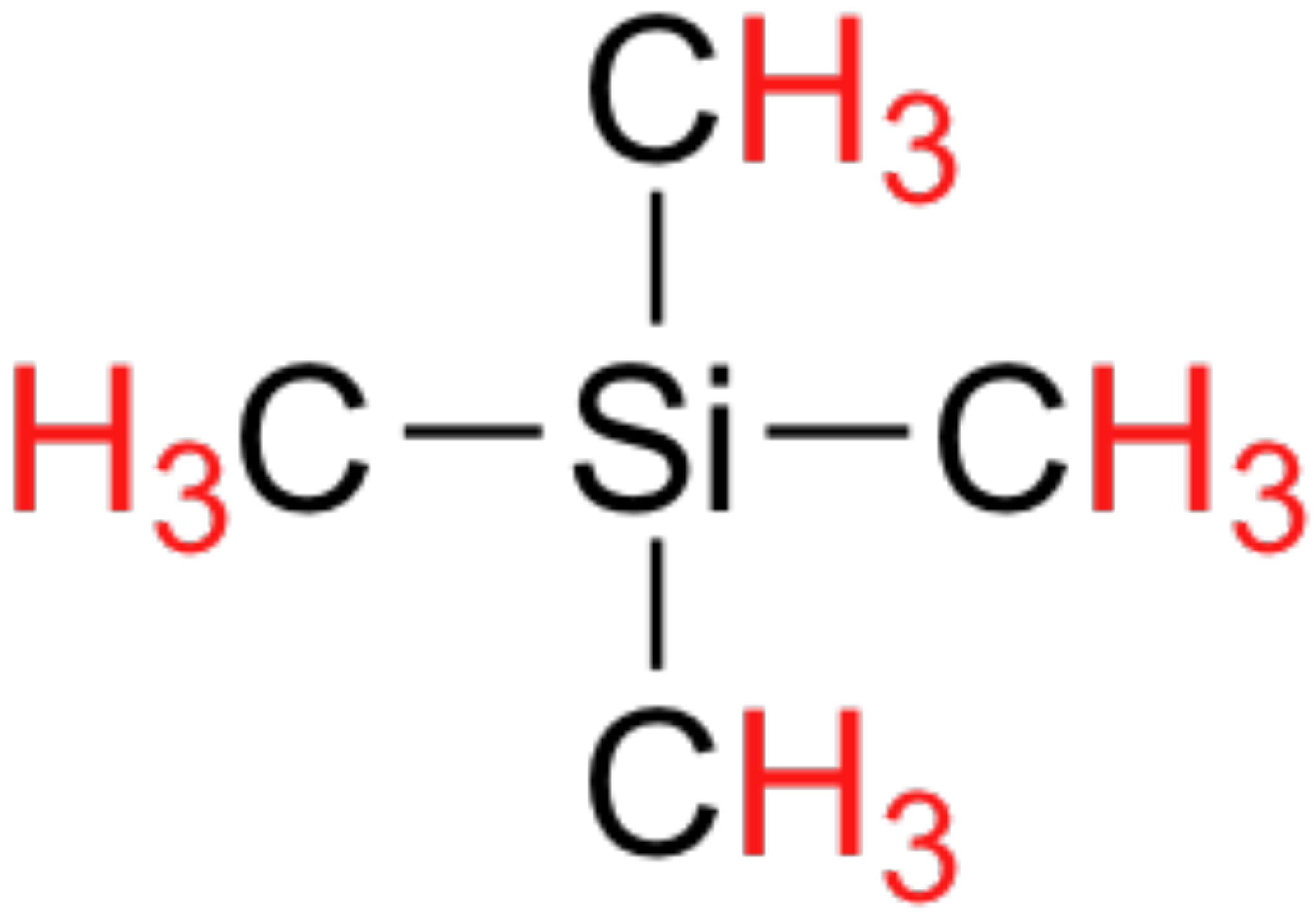
$$\omega_0 = \gamma B_0(1 - \sigma)$$

$$\Delta\nu = \frac{\gamma B_0}{2\pi} - \frac{\gamma B_0(1 - \sigma)}{2\pi} = \frac{\sigma\gamma B_0}{2\pi}$$

The frequency shift for an atom depends linearly on the shielding constants.

This frequency is different for nuclei in different environments Hence, different nuclei, even of the same element, come into resonance at different frequencies if they are in different molecular environments.

Chemical Shift

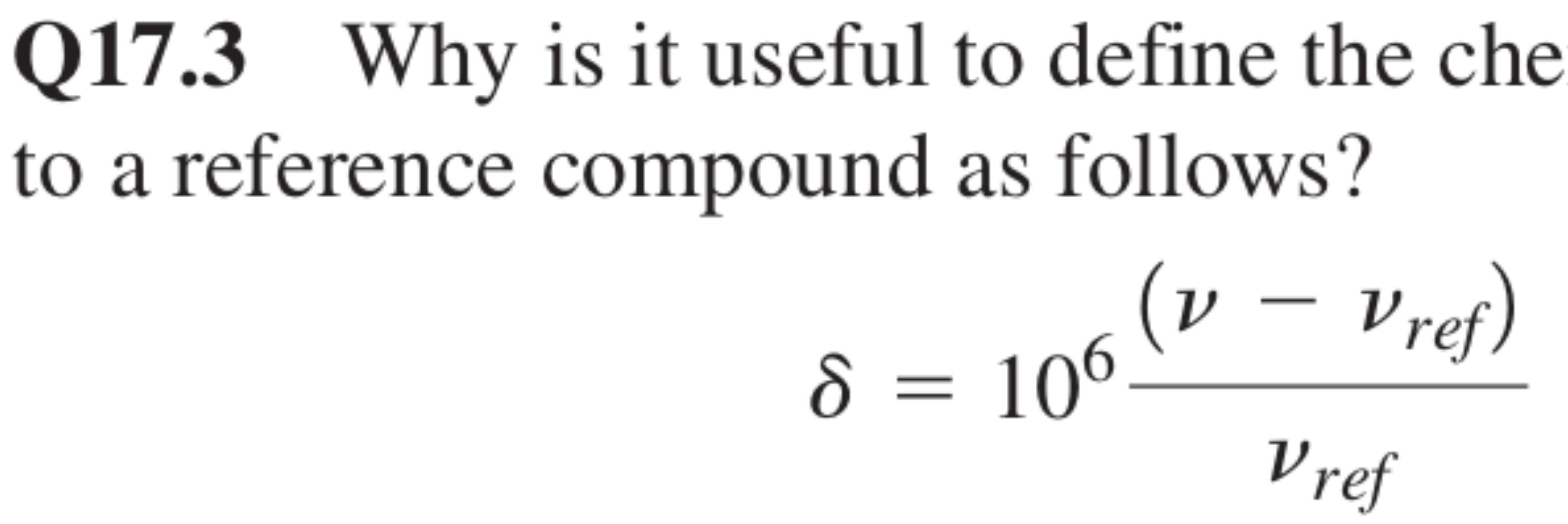


$$Si(CH_3)_4$$

tetramethylsilane (TMS)

$$\frac{100\ \text{MHz}}{60\ \text{MHz}} = \frac{2.35\ \text{Tesla}}{1.41\ \text{Tesla}} = \frac{23{,}500\ \text{Gauss}}{14{,}100\ \text{Gauss}} = \frac{5}{3}$$

Hence, for a given proton, the shift (in Hertz) fromTMS is **5**/3 larger in the100-MHz range **(*B* =2.35 30 Tesla)** than in the 60-MHz range (***B*0 = 1.41 Tesla**) **[Confusing!]**



Q17.3 Why is it useful to define the chemical shift relative to a reference compound as follows?

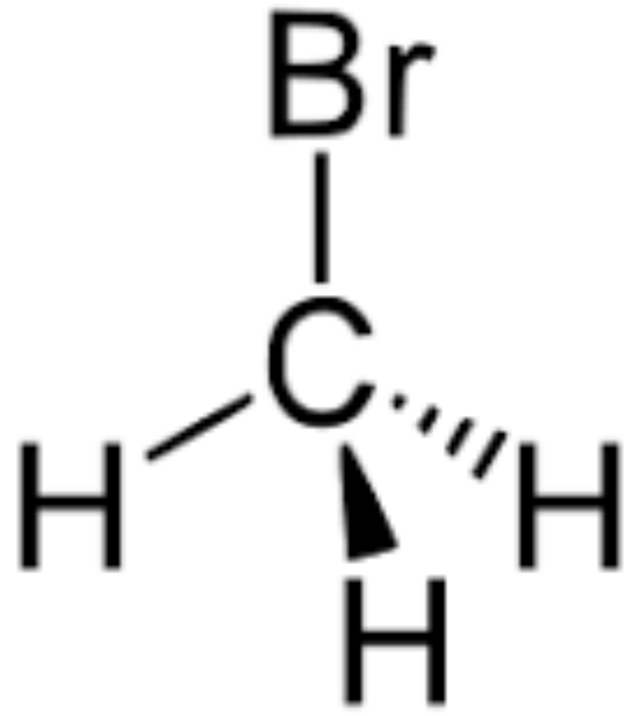
$$\delta = 10^6 \frac{(\nu - \nu_{ref})}{\nu_{ref}}$$

For ^{1}H NMR, tetramethylsilane, (CH3)4Si, is usually used as a reference compound. Defining the chemical shift in this way has the advantage that delta is independent of the frequency, so that all measurements using spectrometers with different magnetic fields will give the same value of delta.

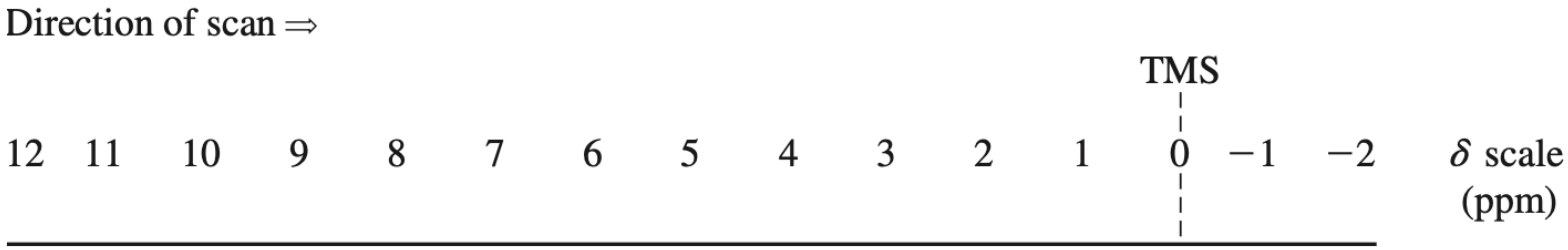
Chemical Shift

[To overcome the Confusion!]

$$\delta = \frac{\text{(shift in Hz)}}{\text{(spectrometer frequency in MHz)}}$$



$$\delta = \frac{162\ \text{Hz}}{60\ \text{MHz}} = \frac{270\ \text{Hz}}{100\ \text{MHz}} = 2.70\ \text{ppm}$$



By convention, NMR spectra are plotted with δ increasing from right to left.

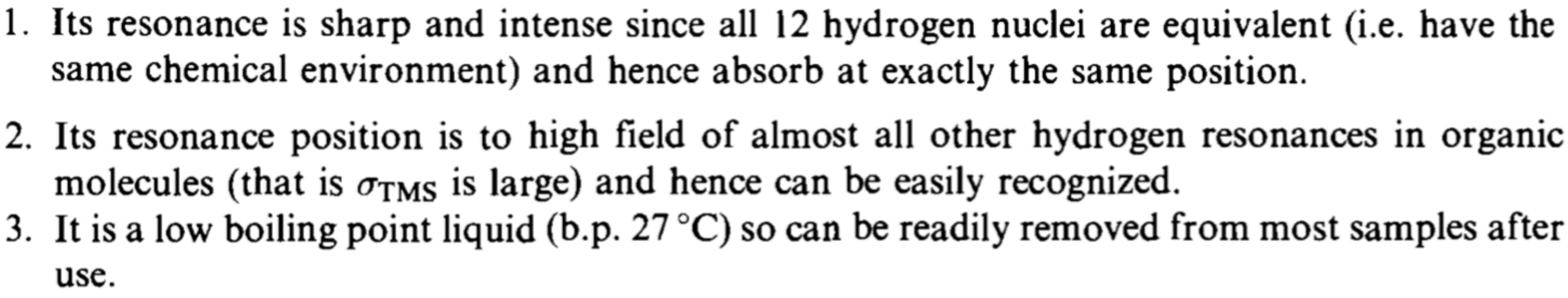
Chemical Shift

$$\delta = (\nu - \nu_{REF})\, x10^6 / \nu_{REF}$$

Proportionality,
it is dimensionless number,
it is independent of field strength

- **The good thing is that since it is a relative scale, the δ for a sample in a 100 MHz magnet (2.35 T) is the same as that obtained in a 600 MHz magnet (14.1 T).**

Advantage



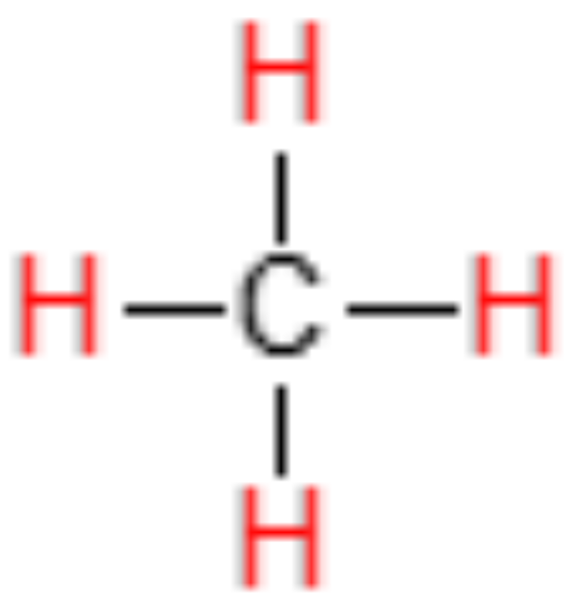
1. Its resonance is sharp and intense since all 12 hydrogen nuclei are equivalent (i.e. have the same chemical environment) and hence absorb at exactly the same position.
2. Its resonance position is to high field of almost all other hydrogen resonances in organic molecules (that is σ_{TMS} is large) and hence can be easily recognized.
3. It is a low boiling point liquid (b.p. 27 °C) so can be readily removed from most samples after use.

The Basis for differences in Chemical shifts

Diamagnetic sheilding and desheilding

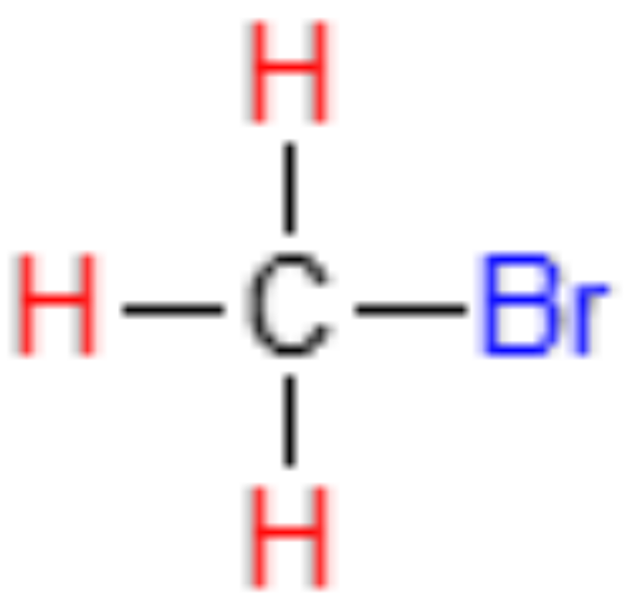
This means that it also **absorbs radio frequency radiation at this lower frequency**.

Each proton in a molecule is in a slightly different c**hemical environment** and consequently has a slightly different amount of electronic shielding, which results in a **slightly different resonance frequency**.



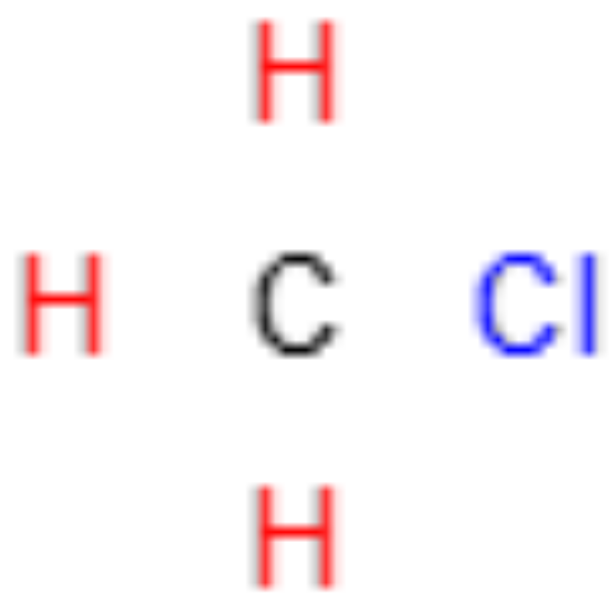
$H-\overset{H}{\underset{H}{C}}-H$

0.23 ppm



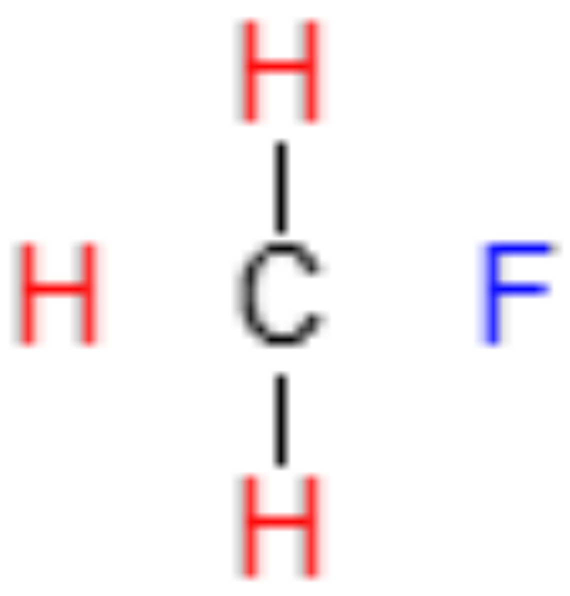
$H-\overset{H}{\underset{H}{C}}-Br$

2.68 ppm



$H\quad\overset{H}{\underset{H}{C}}\quad Cl$

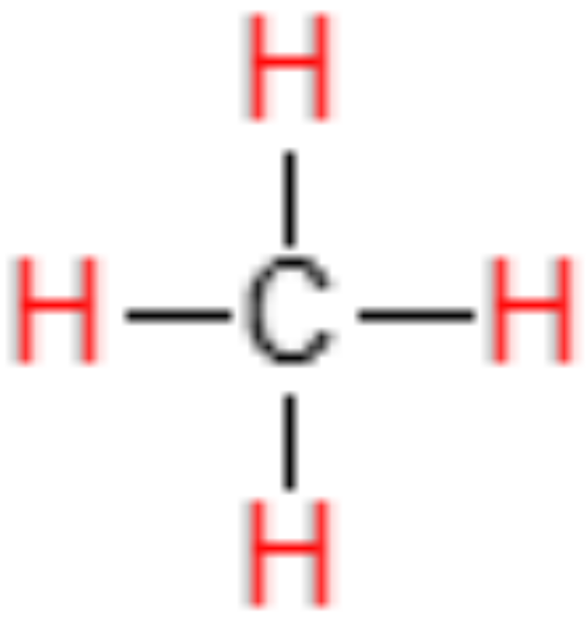
3.05 ppm



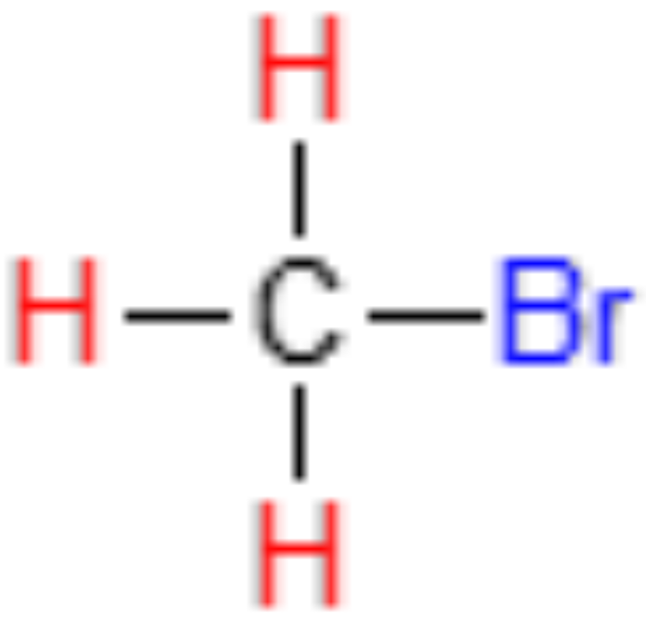
$H\quad\overset{H}{\underset{H}{C}}\quad F$

4.26 ppm

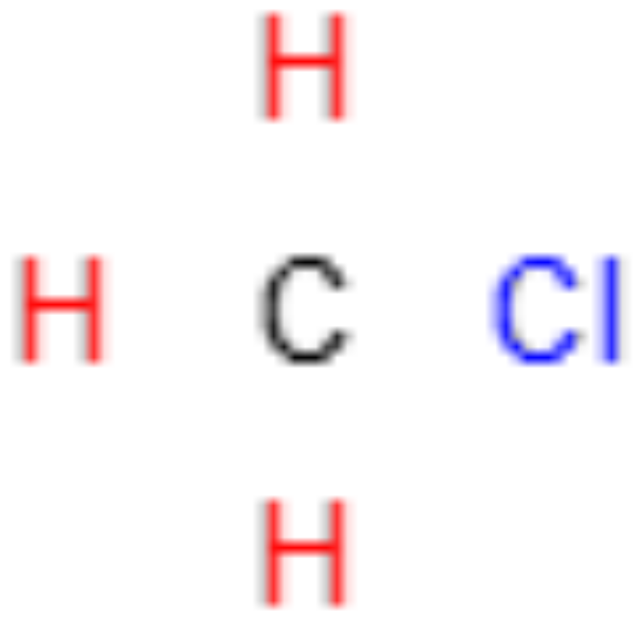
Diamagnetic sheilding and desheilding



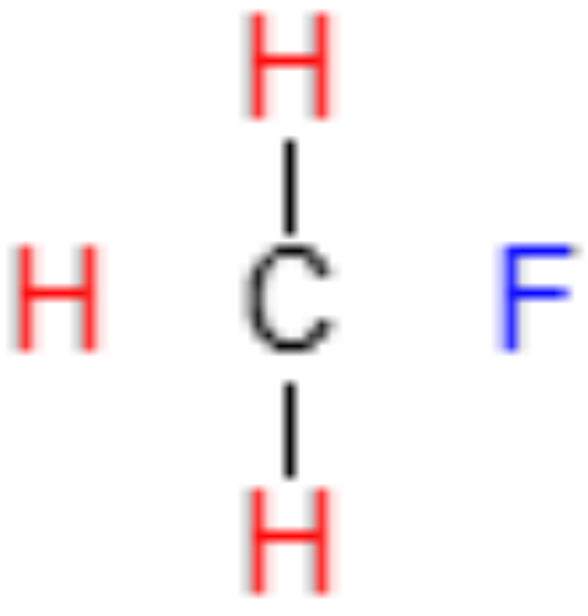
0.23 ppm



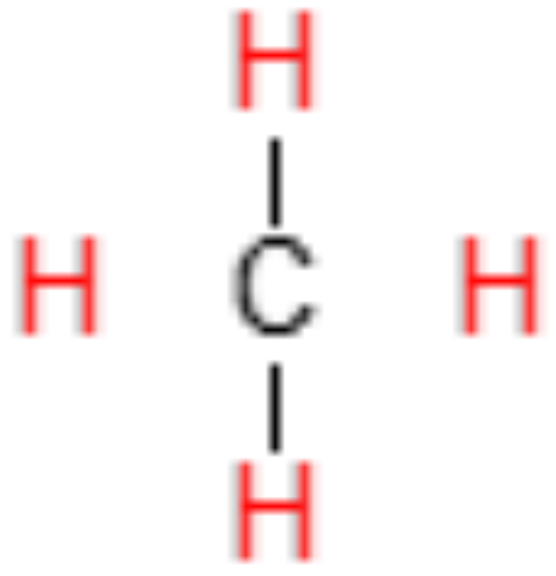
2.68 ppm



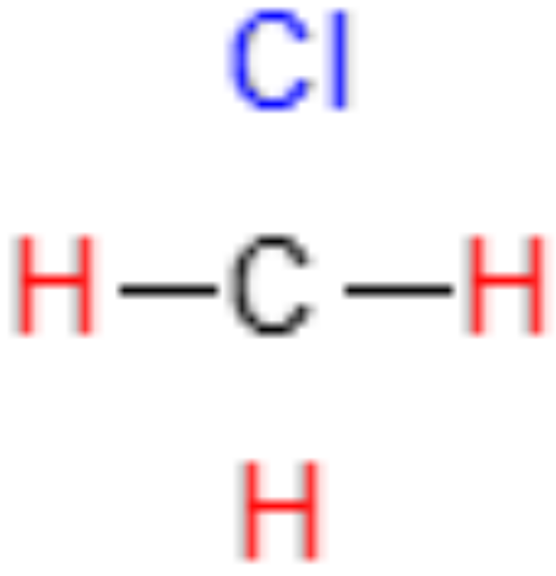
3.05 ppm



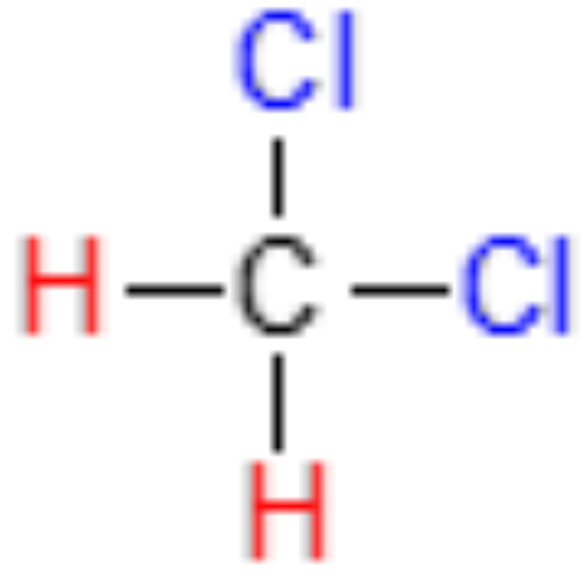
4.26 ppm



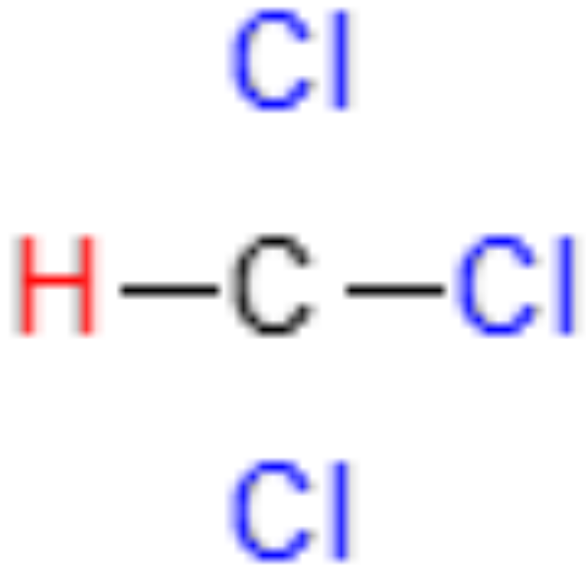
0.23 ppm



3.05 ppm



5.30 ppm



7.27 ppm

As the shielding σ, gets smaller, δ increases. Therefore, we speak of nuclei with large chemical shift as being strongly **deshielded.**

Chemical Shift

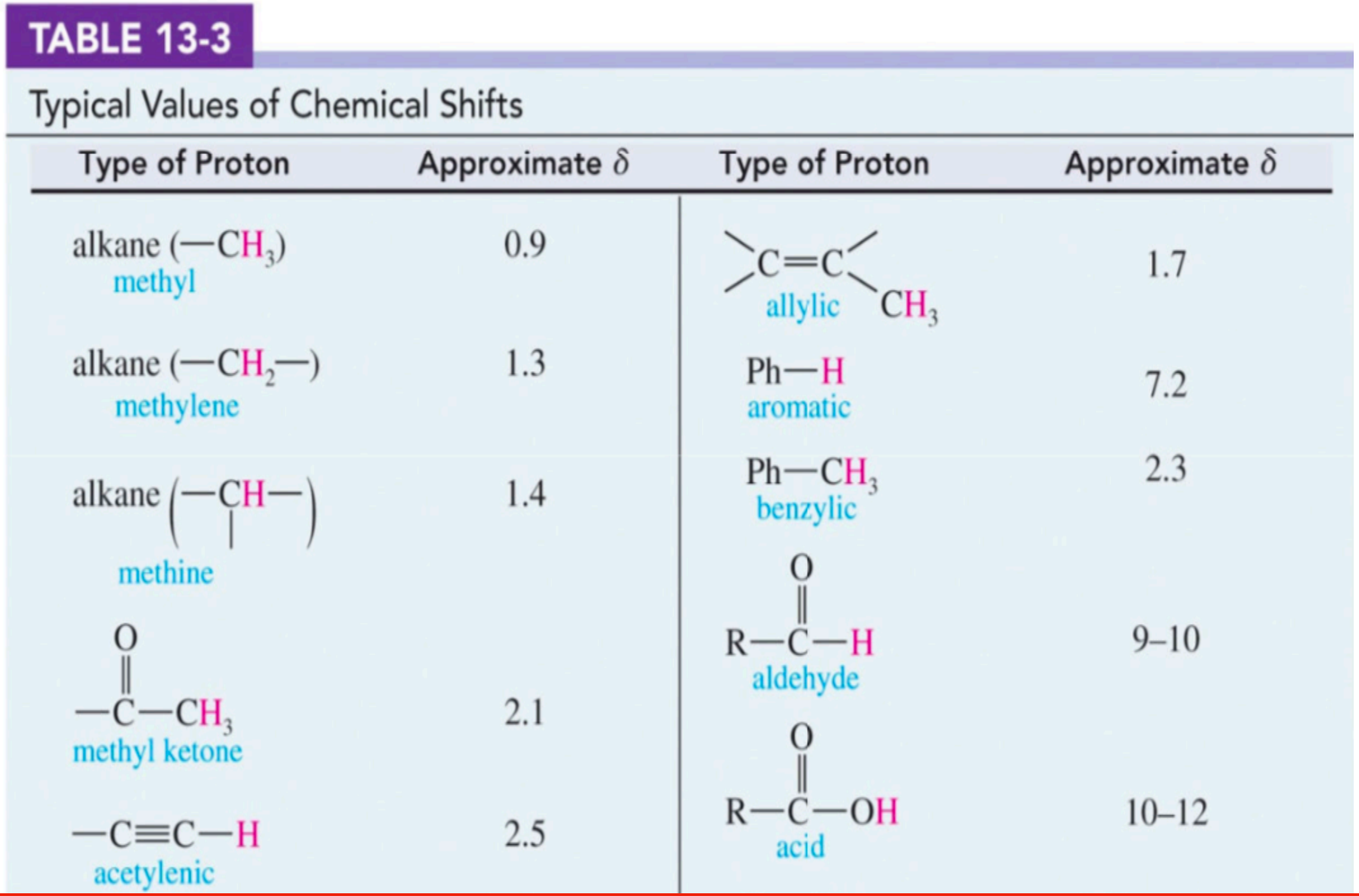
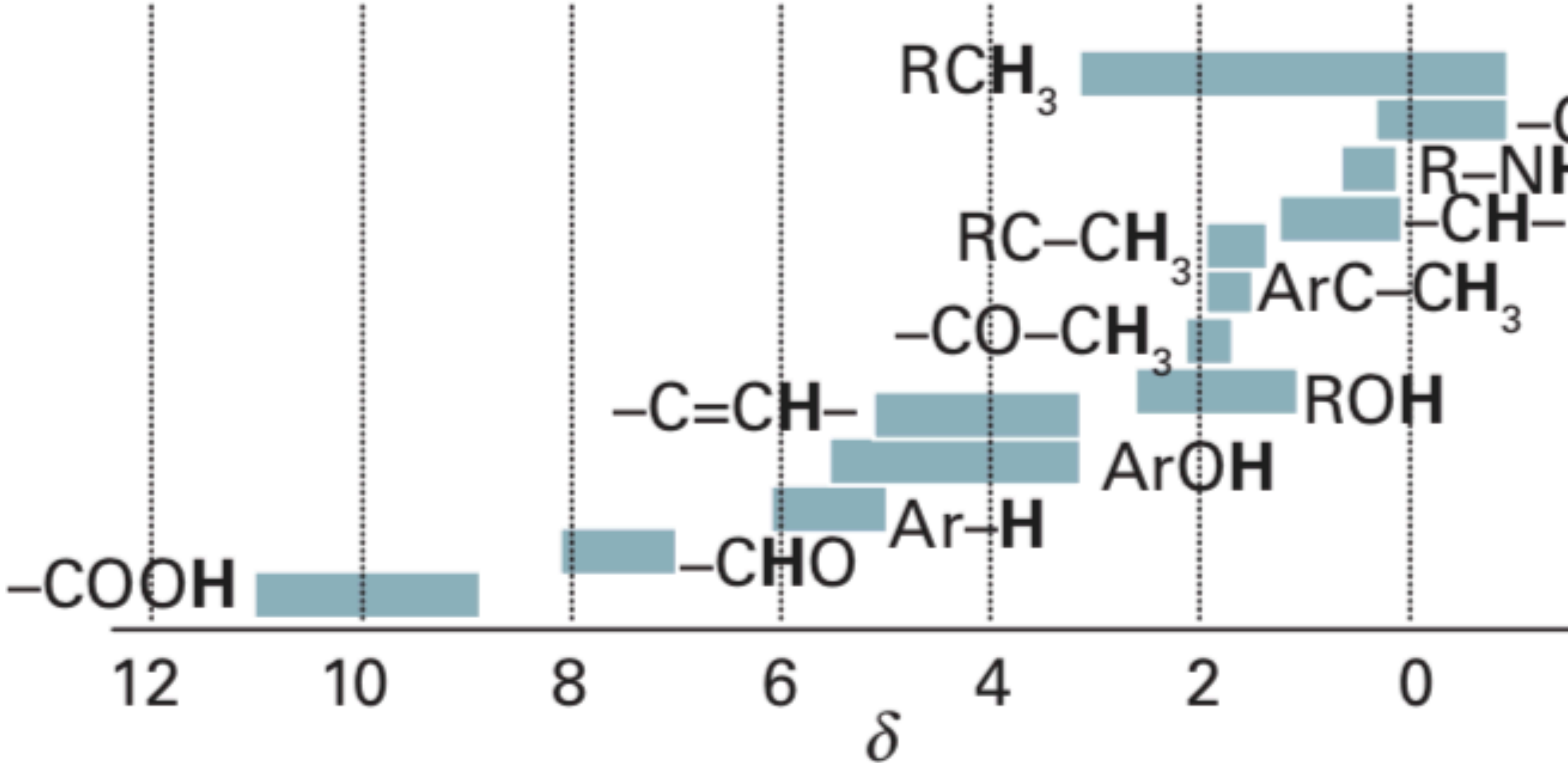


TABLE 13-3

Typical Values of Chemical Shifts

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$) methyl	0.9	$>C=C<$ CH_3 allylic	1.7
alkane ($-CH_2-$) methylene	1.3	$Ph-H$ aromatic	7.2
alkane ($-\overset{|}{\underset{|}{C}}H-$) methine	1.4	$Ph-CH_3$ benzylic	2.3
$-\overset{O}{\overset{\|}{C}}-CH_3$ methyl ketone	2.1	$R-\overset{O}{\overset{\|}{C}}-H$ aldehyde	9–10
$-C\equiv C-H$ acetylenic	2.5	$R-\overset{O}{\overset{\|}{C}}-OH$ acid	10–12

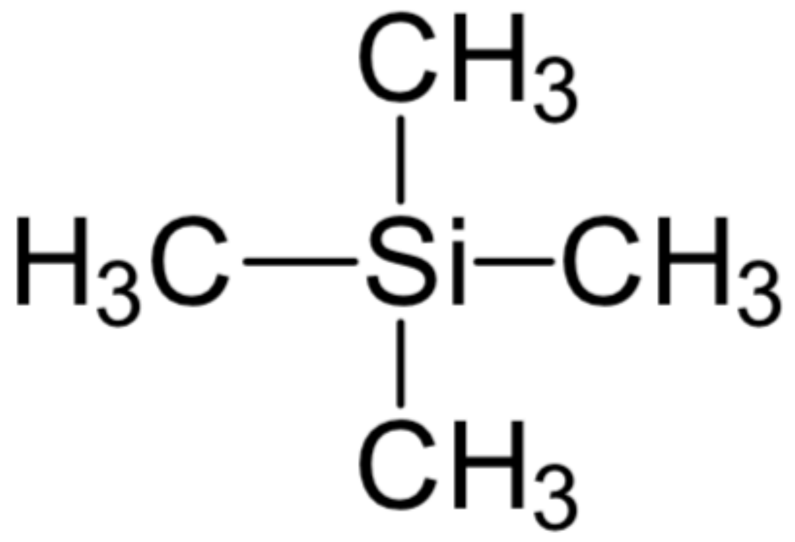


As the shielding σ, gets smaller, δ increases. Therefore, we speak of nuclei with large chemical shift as being strongly **deshielded.**

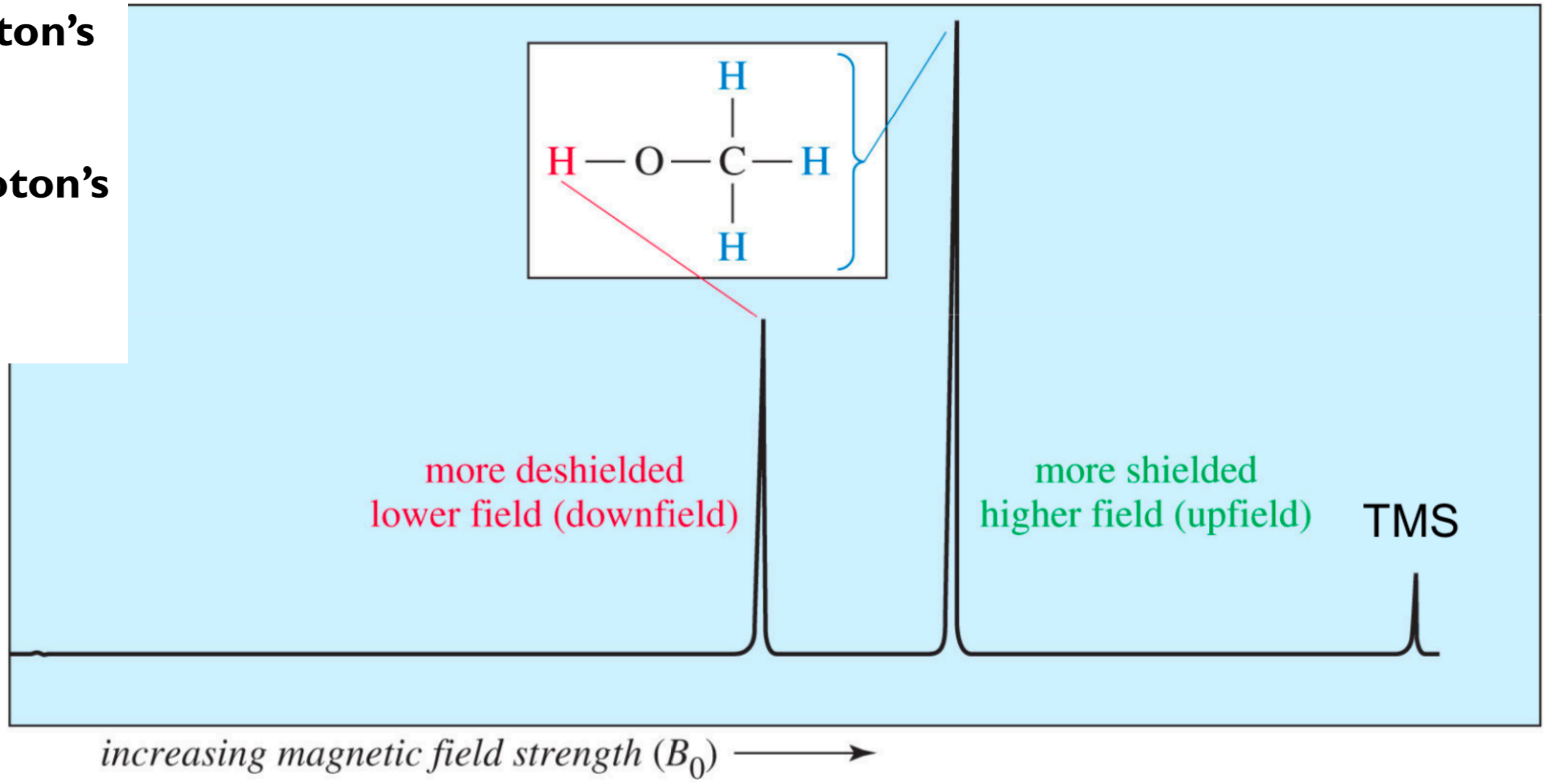
The ranges exhibit the variety of electronic environments of the nuclei in molecules: the higher the atomic number of the element, the greater the number of electrons around the nucleus and hence the greater the range of shieldings.

The origin of Shielding constant

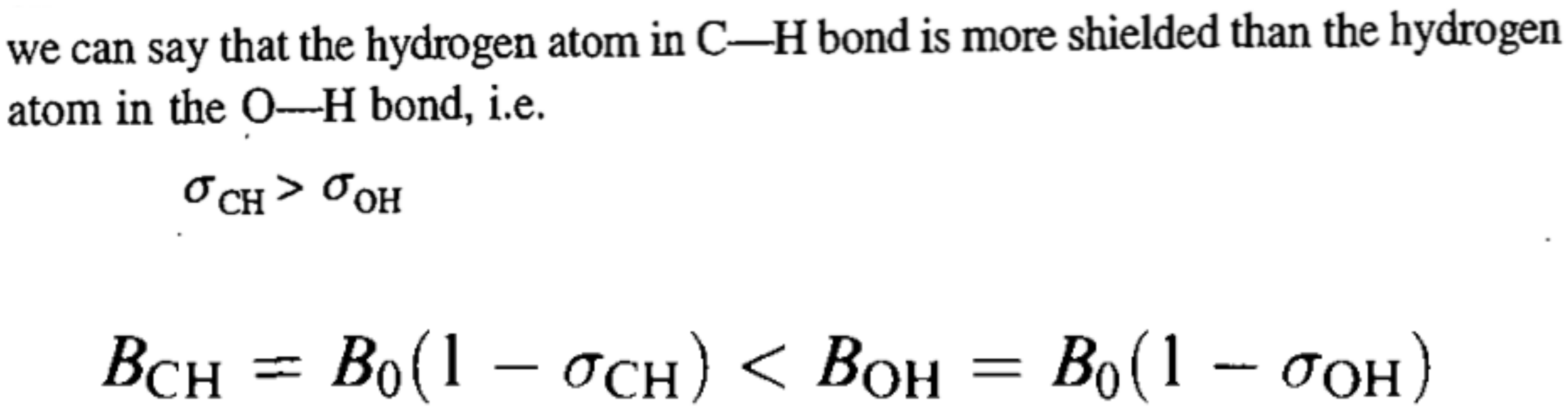
Tetramethylsilane (TMS) is added to a solution and arbitrarily assigned a chemical shift of “0”. All other signals are reported relative to that position.



- **Shielding**: more electron in the proton’s vicinity (dipole effect minimum)
- **Deshielding**: less electron in the proton’s vicinity
  (dipole effect is increased)



The origin of Shielding constant


we can say that the hydrogen atom in C—H bond is more shielded than the hydrogen atom in the O—H bond, i.e.

$$\sigma_{CH} > \sigma_{OH}$$

$$B_{CH} = B_0(1 - \sigma_{CH}) < B_{OH} = B_0(1 - \sigma_{OH})$$

SPIN RESONANCE SPECTROSCOPY 217

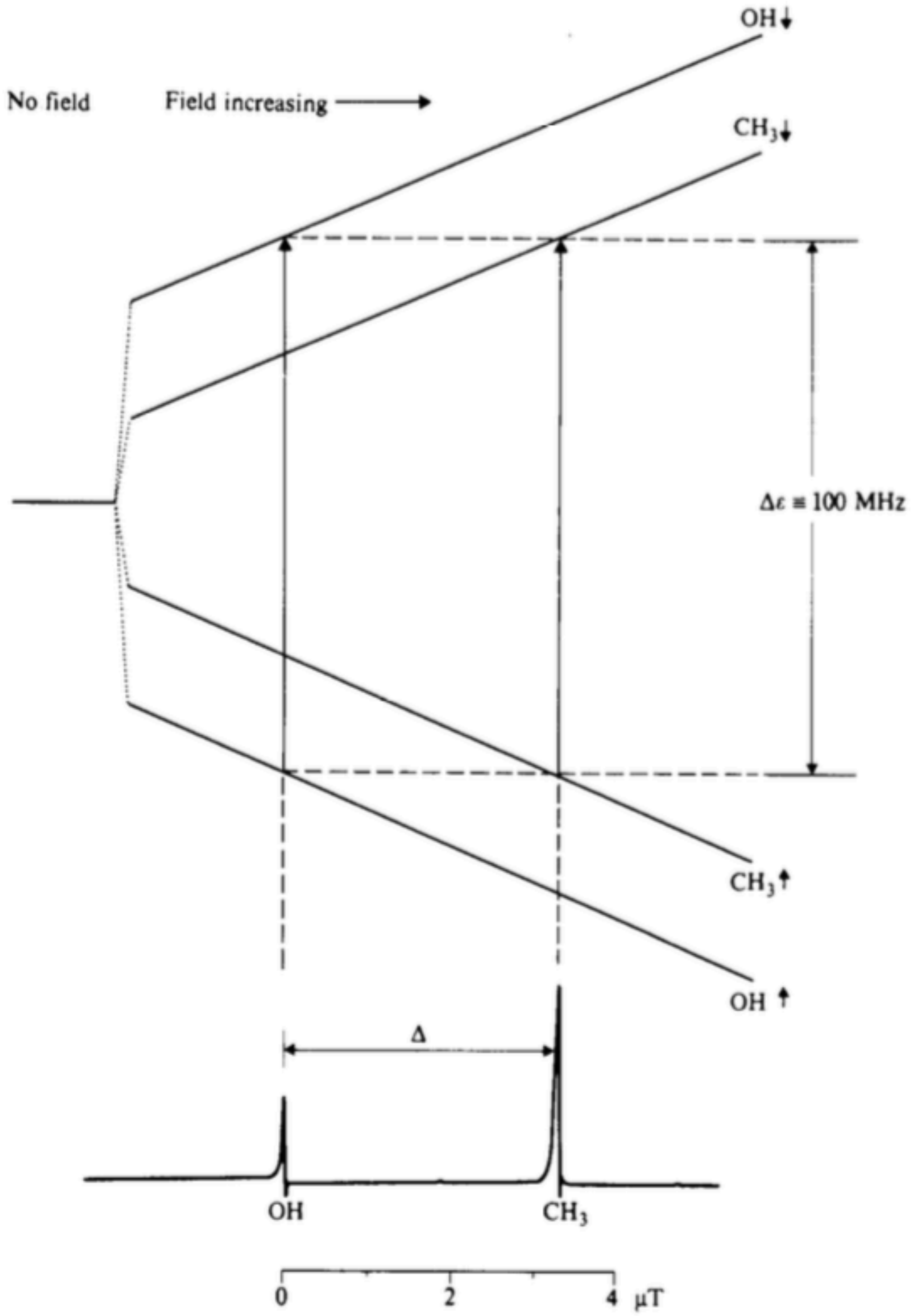


Figure 7.9 The effect of an applied magnetic field on the energy levels of the methyl and hydroxyl nuclei of methanol, CH_3OH. The applied field is increased rapidly initially (dotted portion) until near resonance at 2.3487 T and then the increase is much slower. The n.m.r. spectrum of methanol is shown at the foot of the figure.

The CH hydrogen nuclei will precess with a smaller frequency than that of OH

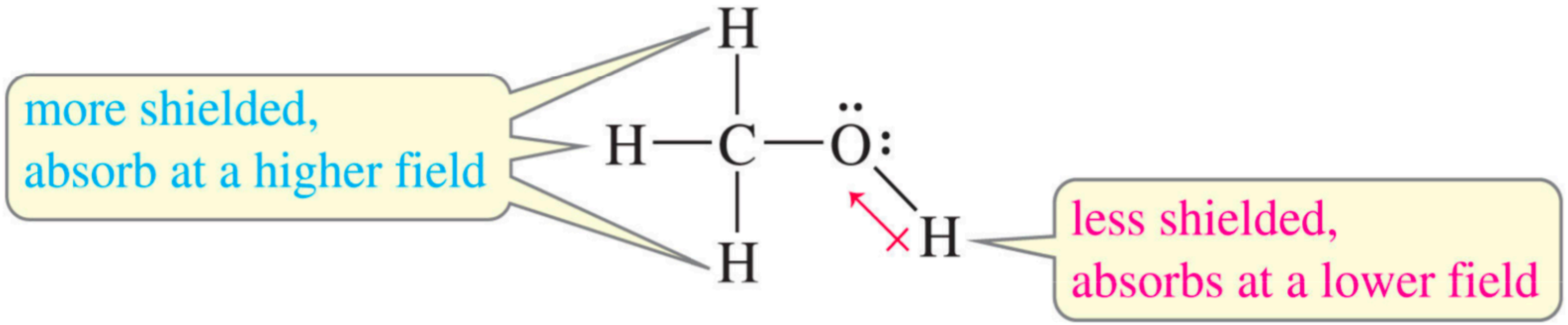
The -OH proton will be thrown into resonance earlier than the methyl protons as the external magnetic field is steadily increased.

This means that the NMR signal of -OH proton will be observed at the low-end field and that of methyl protons at high end field.

The area of methyl proton will be three time larger than the -OH proton

Shielding and Deshielding

No dipole, therefore, maximum electron density near the protons in CH_3 **Shielded**



more shielded, absorb at a higher field

less shielded, absorbs at a lower field

Strong dipole pulling electrons
Away from hydrogen atom,
Therefore, electron density is reduced
Near protons **Deshielded**

The conclusion is that shielded protons absorb radiation at higher fields (frequency) while the deshielded protons will absorb at lower fields (frequency).

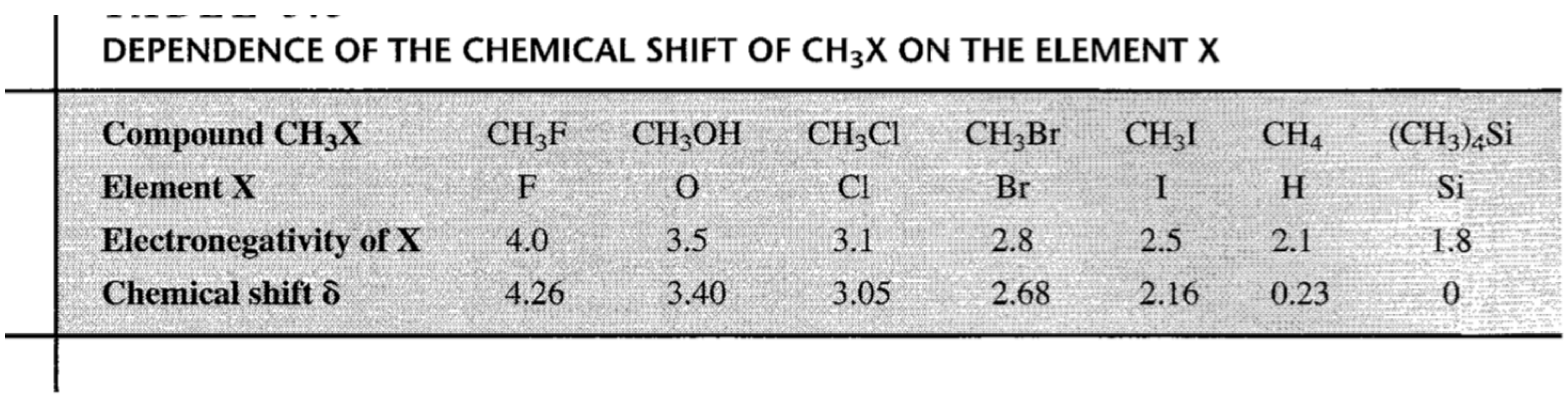
The origin of Shielding constant

Two very important facets of n.m.r. spectroscopy appear:

(i) **Identical nuclei (that is H nuclei) give rise to different absorption positions when in different chemical surroundings** (for this reason the separation between absorption peaks is usually referred to as their chemical shift)

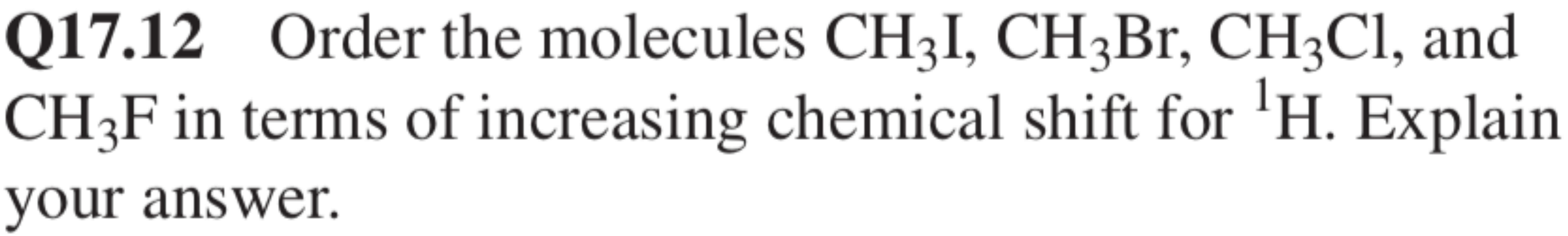
(2) The area of an absorption peak is proportional to the number of equivalent nuclei (i.e. nuclei with the same chemical shift position) giving rise to the absorption.

How can these chemical shifts be understood?



DEPENDENCE OF THE CHEMICAL SHIFT OF CH_3X ON THE ELEMENT X

Compound CH_3X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4Si$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ	4.26	3.40	3.05	2.68	2.16	0.23	0

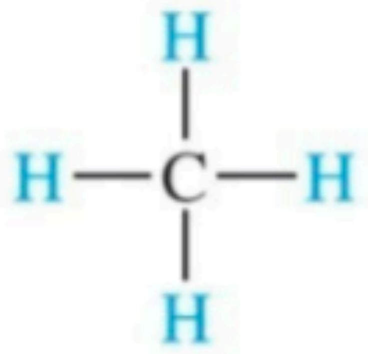
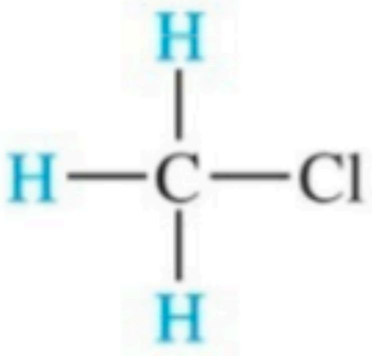
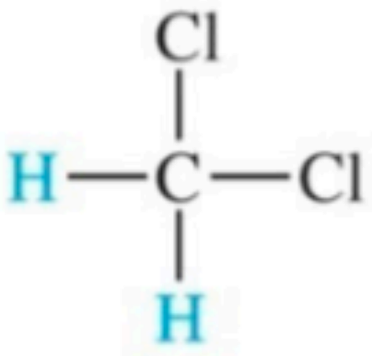
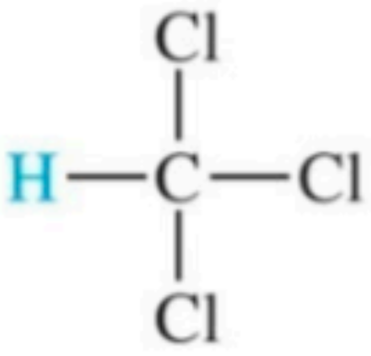


Q17.12 Order the molecules CH_3I, CH_3Br, CH_3Cl, and CH_3F in terms of increasing chemical shift for ^1H. Explain your answer.

- **Shielding: more electron in the proton's vicinity (dipole effect minimum)**
- **Deshielding: less electron in the proton's vicinity (dipole effect is increased)**

TABLE 13-2

Chemical Shifts of the Chloromethanes

Compound	Chemical Shift	Difference
	δ 0.2	
	δ 3.0	2.8 ppm
	δ 5.3	2.3 ppm
	δ 7.2	1.9 ppm

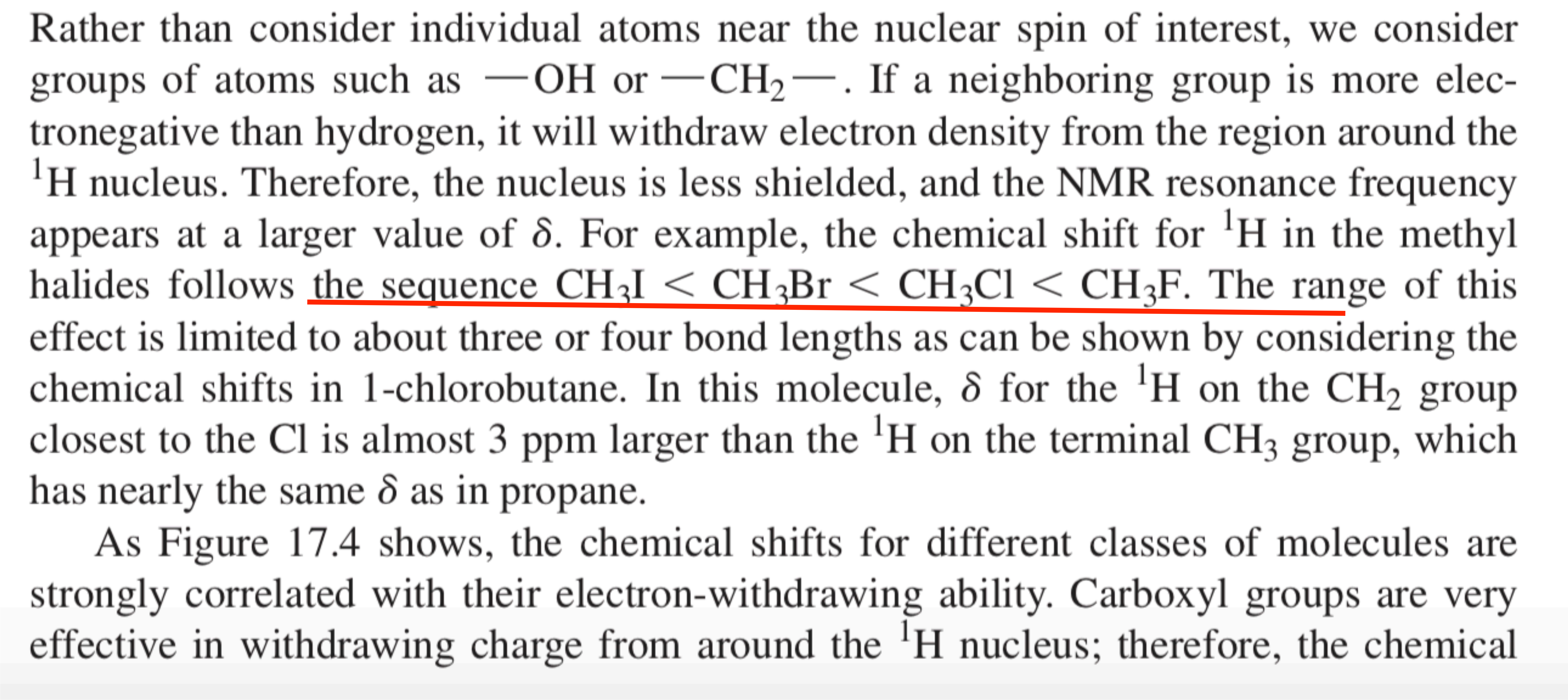
Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by 2 to 3 ppm. These changes are nearly additive.

How can these chemical shifts be understood?

Two factors are responsible for the major part of the chemical shift:

The electronegativity of the neighboring group and

The induced magnetic field of the neighboring group at the position of the nucleus of interest.

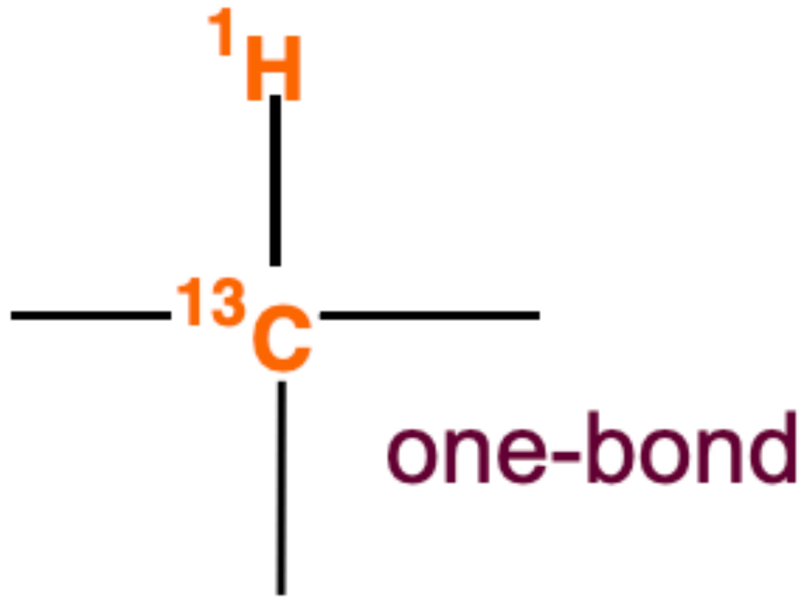


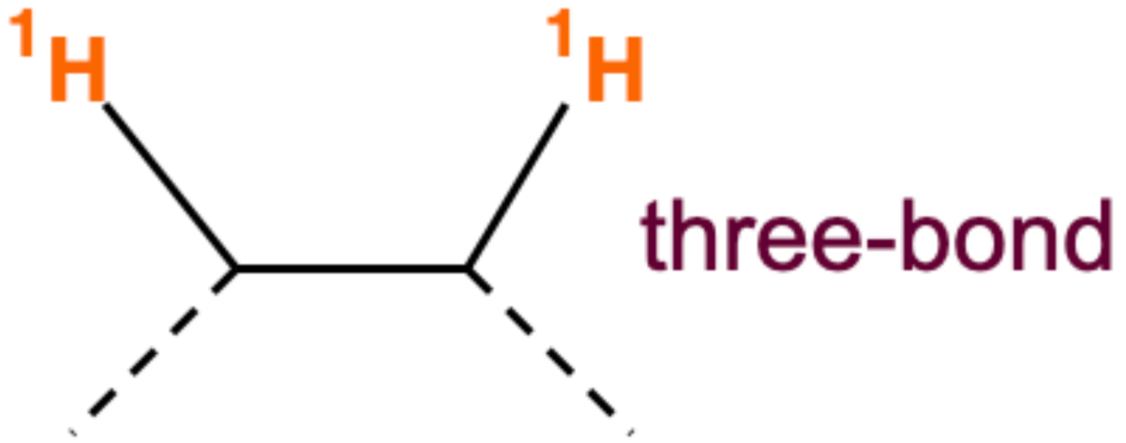
Rather than consider individual atoms near the nuclear spin of interest, we consider groups of atoms such as —OH or $—CH_2—$. If a neighboring group is more electronegative than hydrogen, it will withdraw electron density from the region around the ^1H nucleus. Therefore, the nucleus is less shielded, and the NMR resonance frequency appears at a larger value of δ. For example, the chemical shift for ^1H in the methyl halides follows the sequence $CH_3I < CH_3Br < CH_3Cl < CH_3F$. The range of this effect is limited to about three or four bond lengths as can be shown by considering the chemical shifts in 1-chlorobutane. In this molecule, δ for the ^1H on the CH_2 group closest to the Cl is almost 3 ppm larger than the ^1H on the terminal CH_3 group, which has nearly the same δ as in propane.

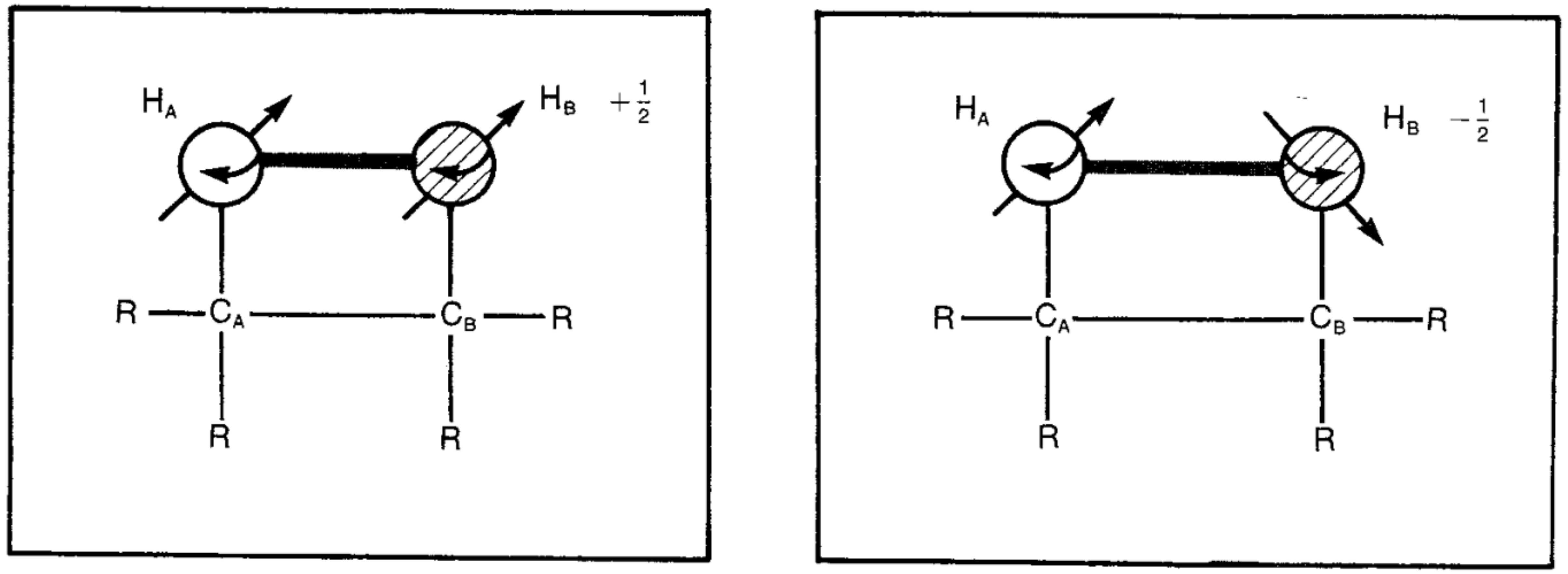
As Figure 17.4 shows, the chemical shifts for different classes of molecules are strongly correlated with their electron-withdrawing ability. Carboxyl groups are very effective in withdrawing charge from around the ^1H nucleus; therefore, the chemical

Concept and origin of spin-spin splitting

- Nuclei which are close to one another could cause an influence on each other's effective magnetic field. If the distance between **non-equivalent nuclei** is less than or equal to three bond lengths, this effect is observable. This is called spin-spin coupling or J coupling.







X-type molecule

Y-type molecule

FIGURE 3.28 Two different molecules in a solution with differing spin relationships between protons

Why the signal for proton A split to a doublet?

Splitting of the spectral line arises because of a coupling interaction between neighbour protons, and related to the number of possible spin orientations that these neighbours can adopt.

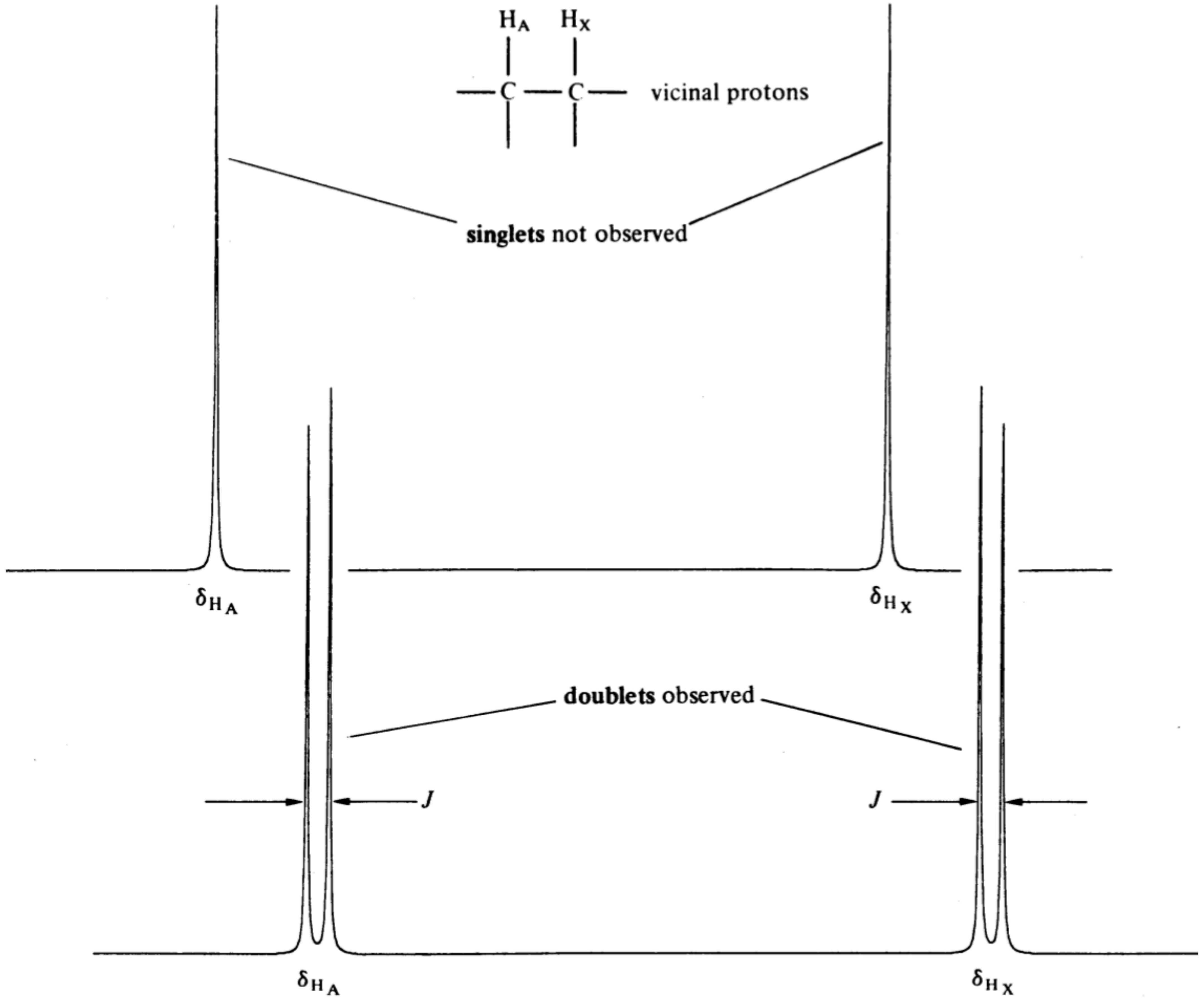


Figure 3.13 *Splitting in the signals of two vicinal protons.*

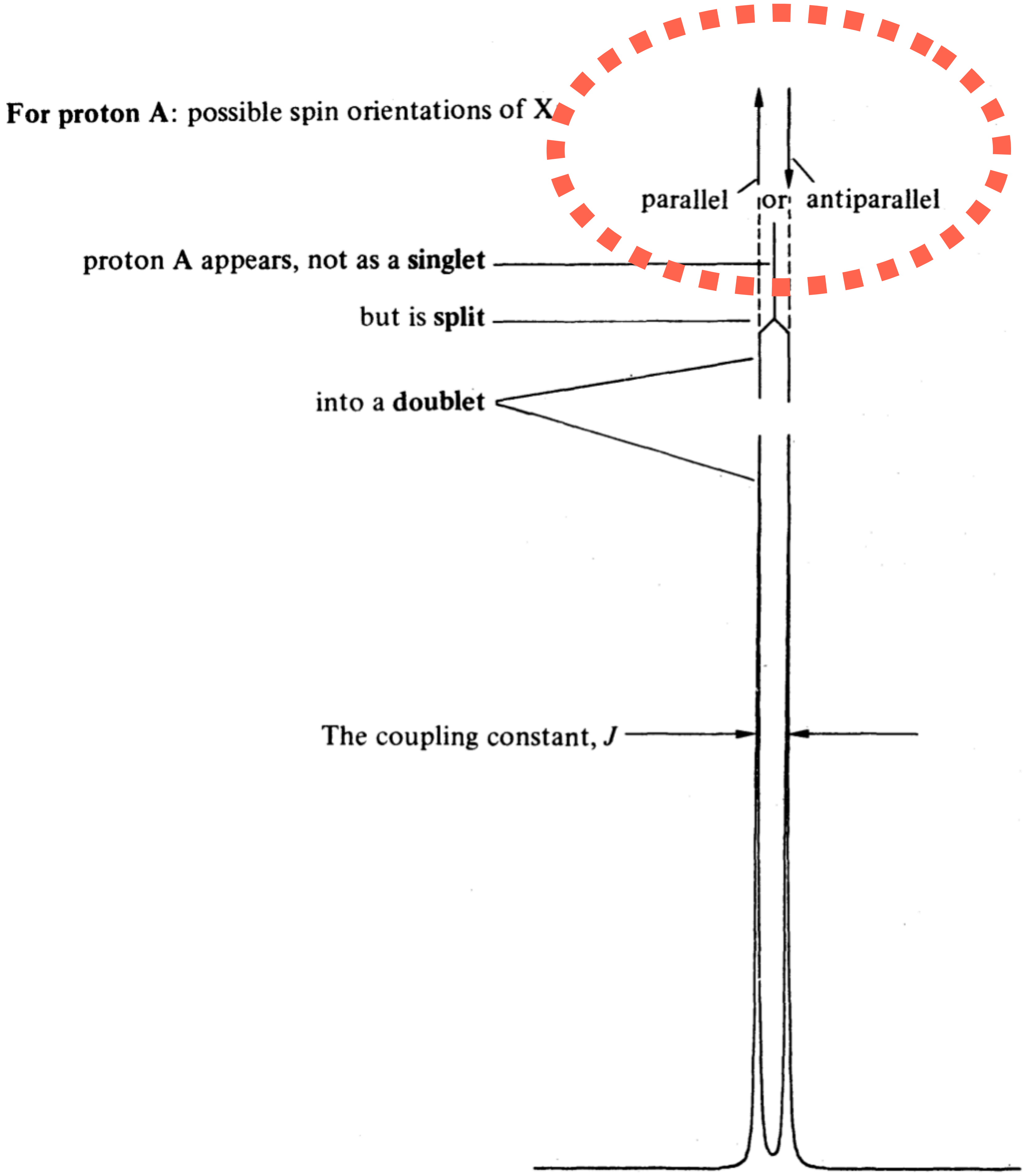


Figure 3.14 *Simulation of spin coupling between a proton A and one neighboring proton X.*

Splitting pattern

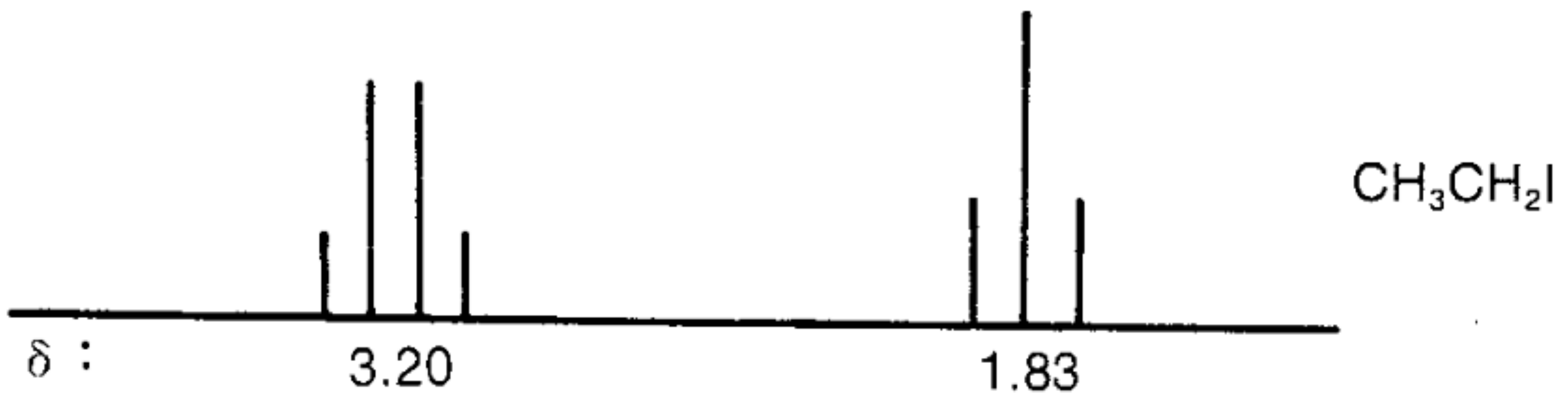


FIGURE 3.30 The ethyl splitting pattern.

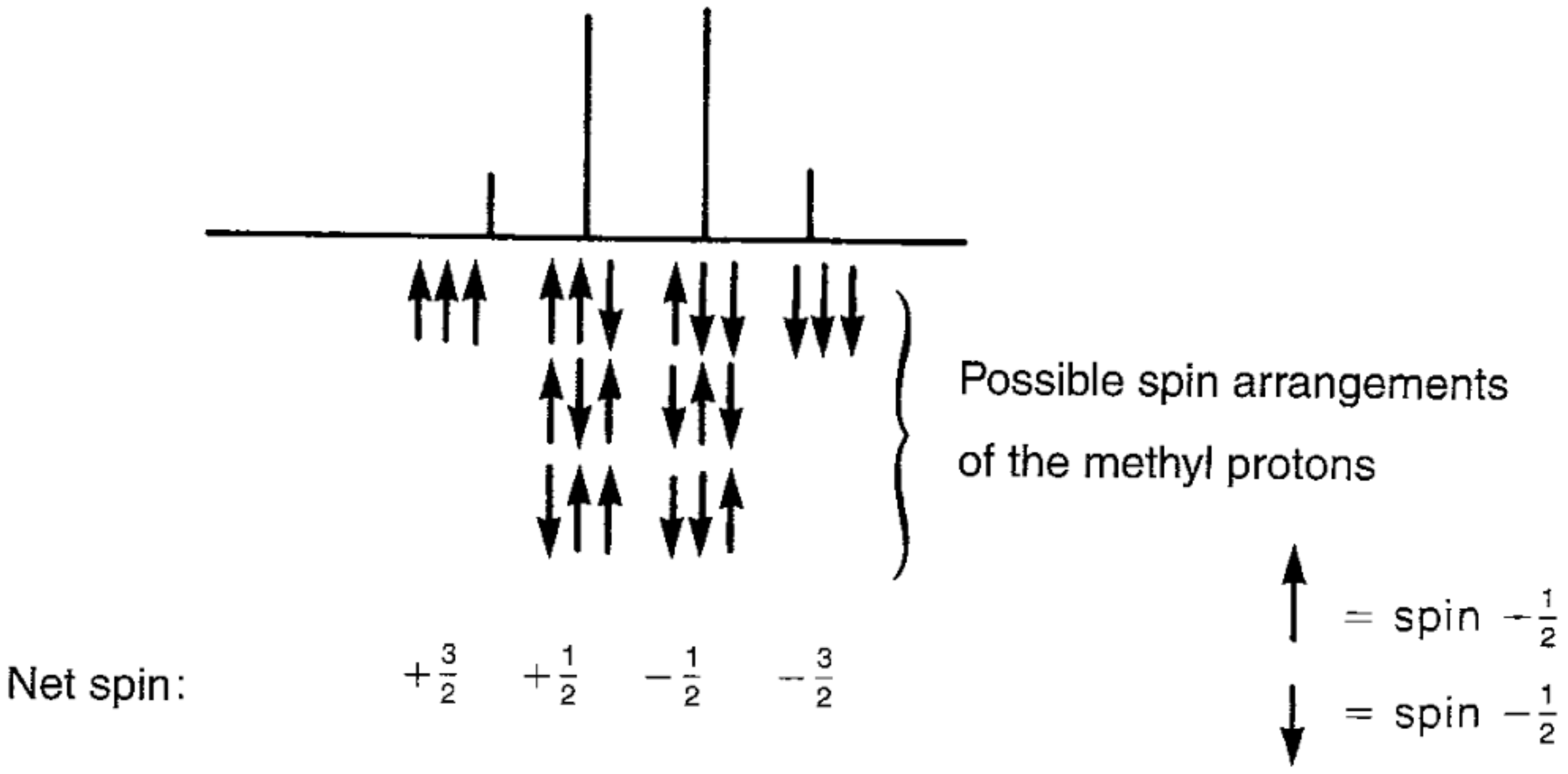


FIGURE 3.31 The splitting pattern of methylene protons due to the presence of an adjacent methyl group.

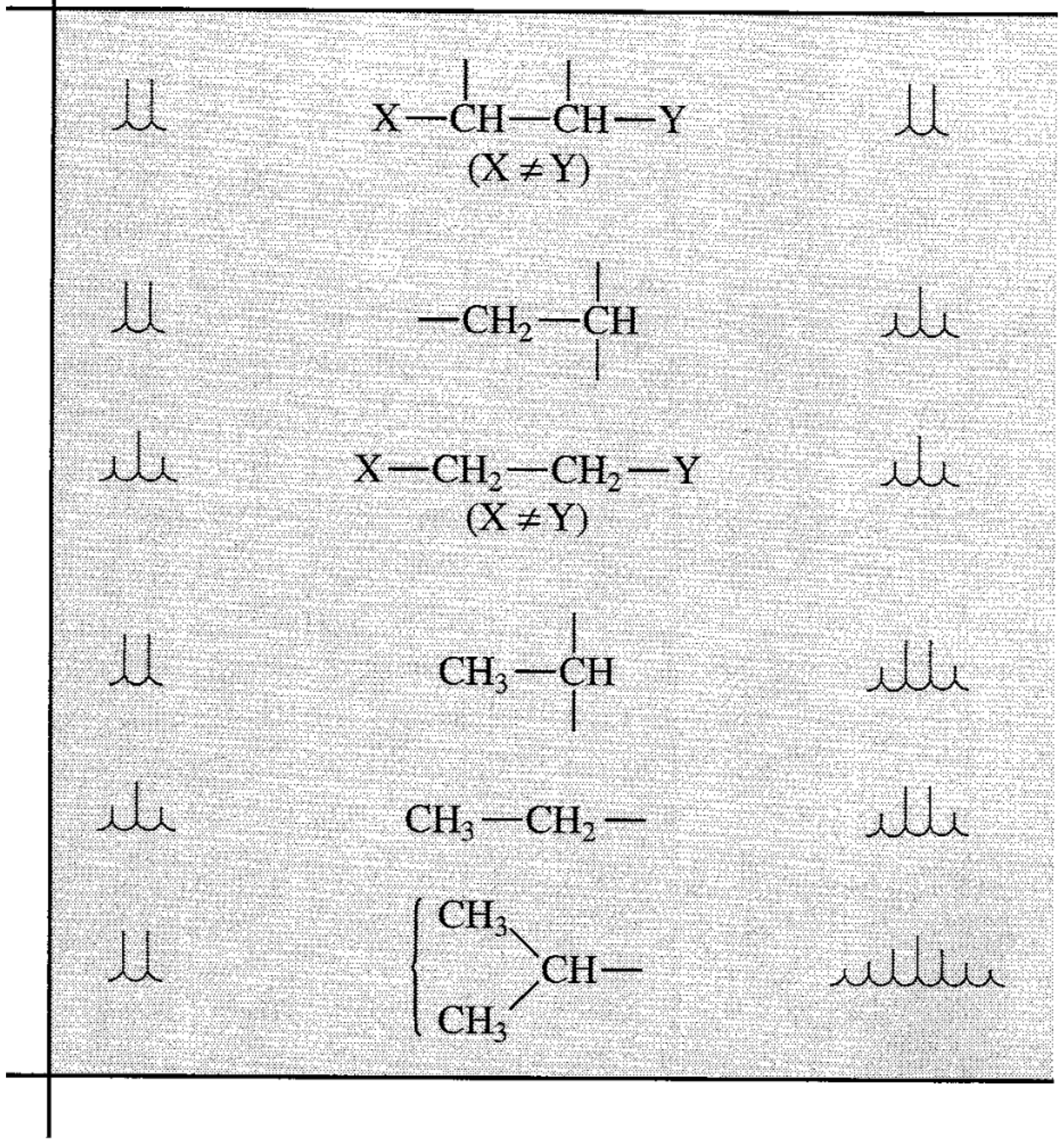
Concept and origin of spin-spin splitting

Splitting reflects the environment of the absorbing protons: not with respect to electrons, but with respect to other nearby proton.

(n + 1) rule. *The simple rule is: to find the multiplicity of the signal from a group of protons, count the number of neighbors* (n) *and add 1.*

TABLE 3.8

SOME COMMONLY OBSERVED SPLITTING PATTERNS



$X-\overset{|}{C}H-\overset{|}{C}H-Y$ $(X \neq Y)$

$-CH_2-\underset{|}{\overset{|}{C}}H$

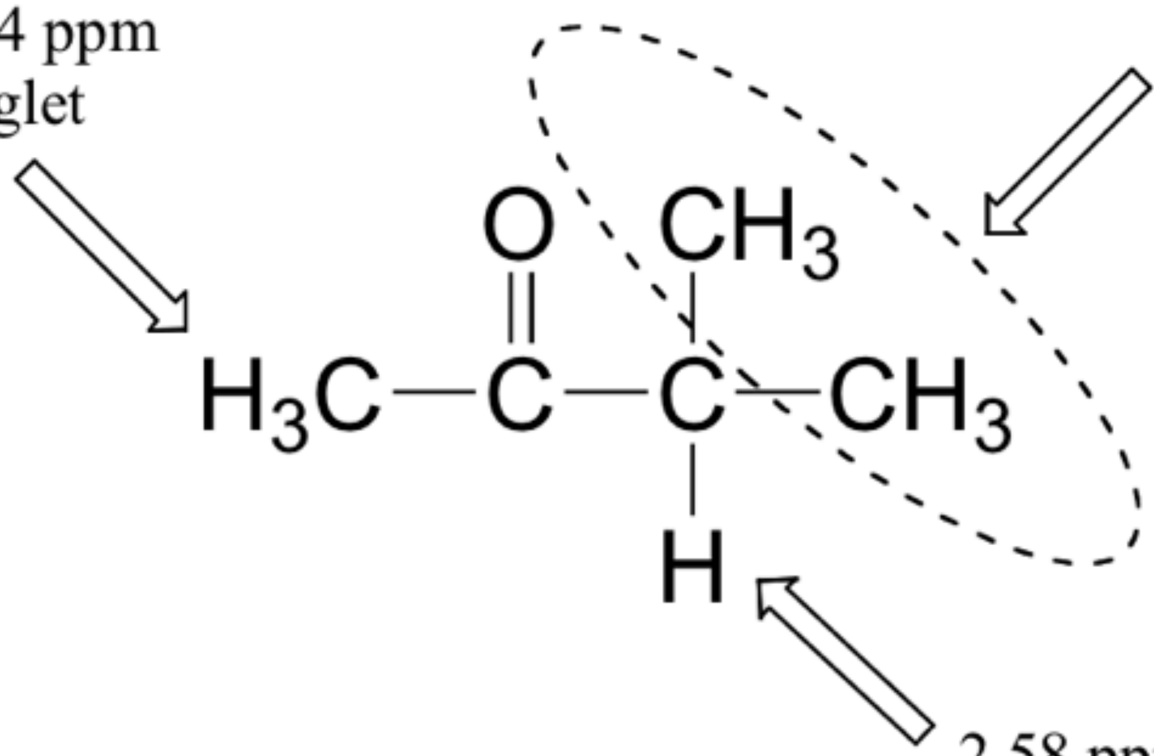
$X-CH_2-CH_2-Y$ $(X \neq Y)$

$CH_3-\underset{|}{\overset{|}{C}}H$

CH_3-CH_2-

$(CH_3)_2CH-$

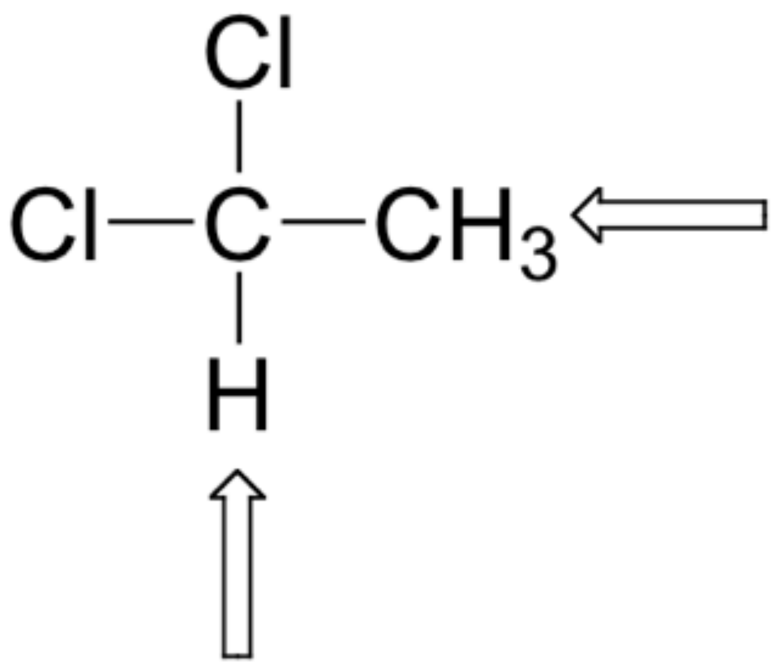
Concept and origin of spin-spin splitting



2.14 ppm
singlet

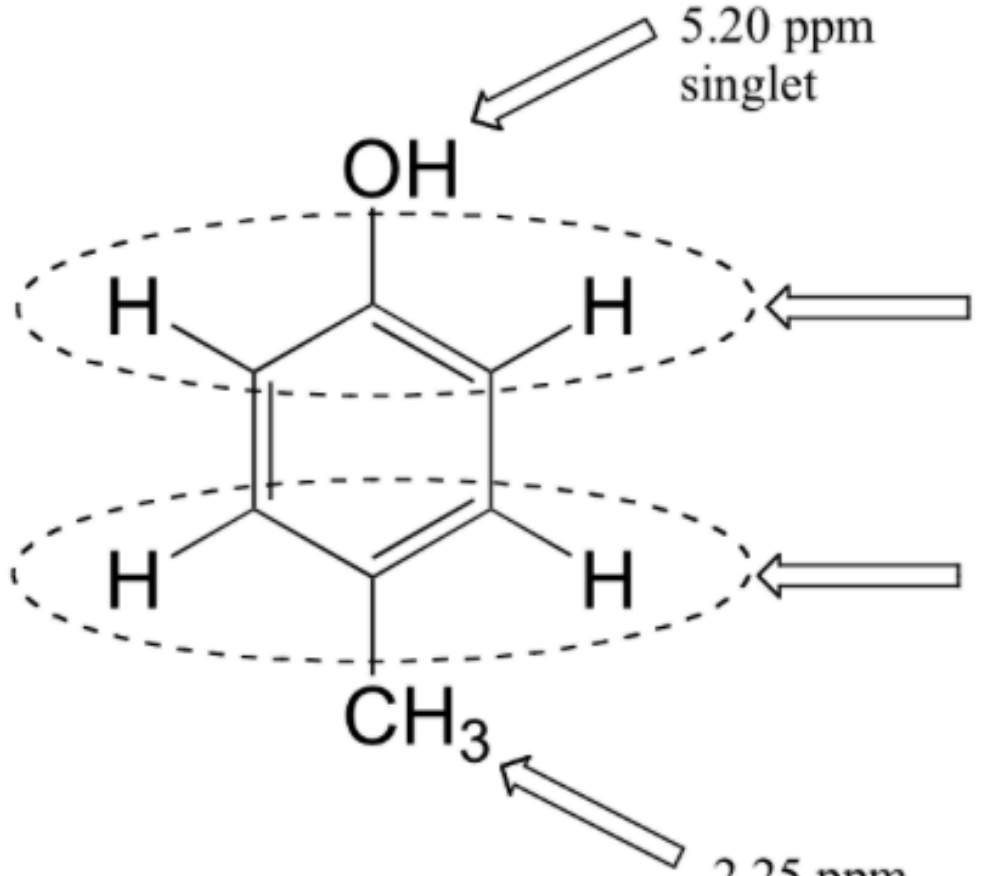
1.11 ppm
doublet

2.58 ppm
septet



2.06 ppm
doublet

5.90 ppm
quartet

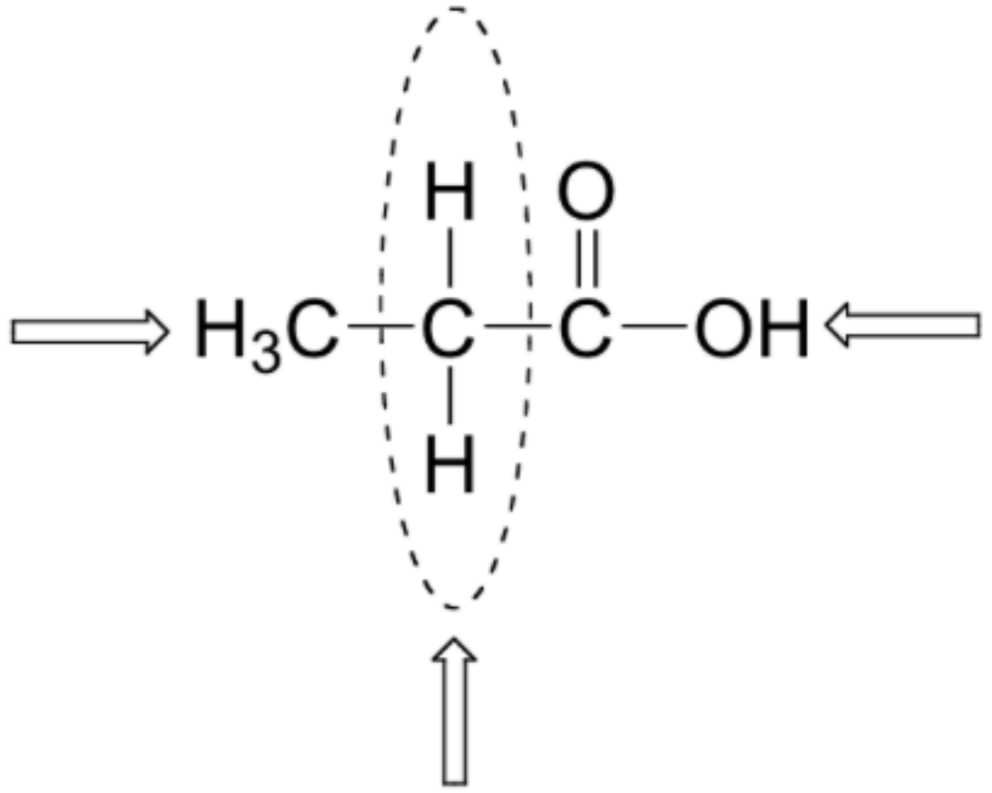


5.20 ppm
singlet

6.72 ppm
doublet

7.00 ppm
doublet

2.25 ppm
singlet



1.16 ppm
triplet

11.73 ppm
singlet

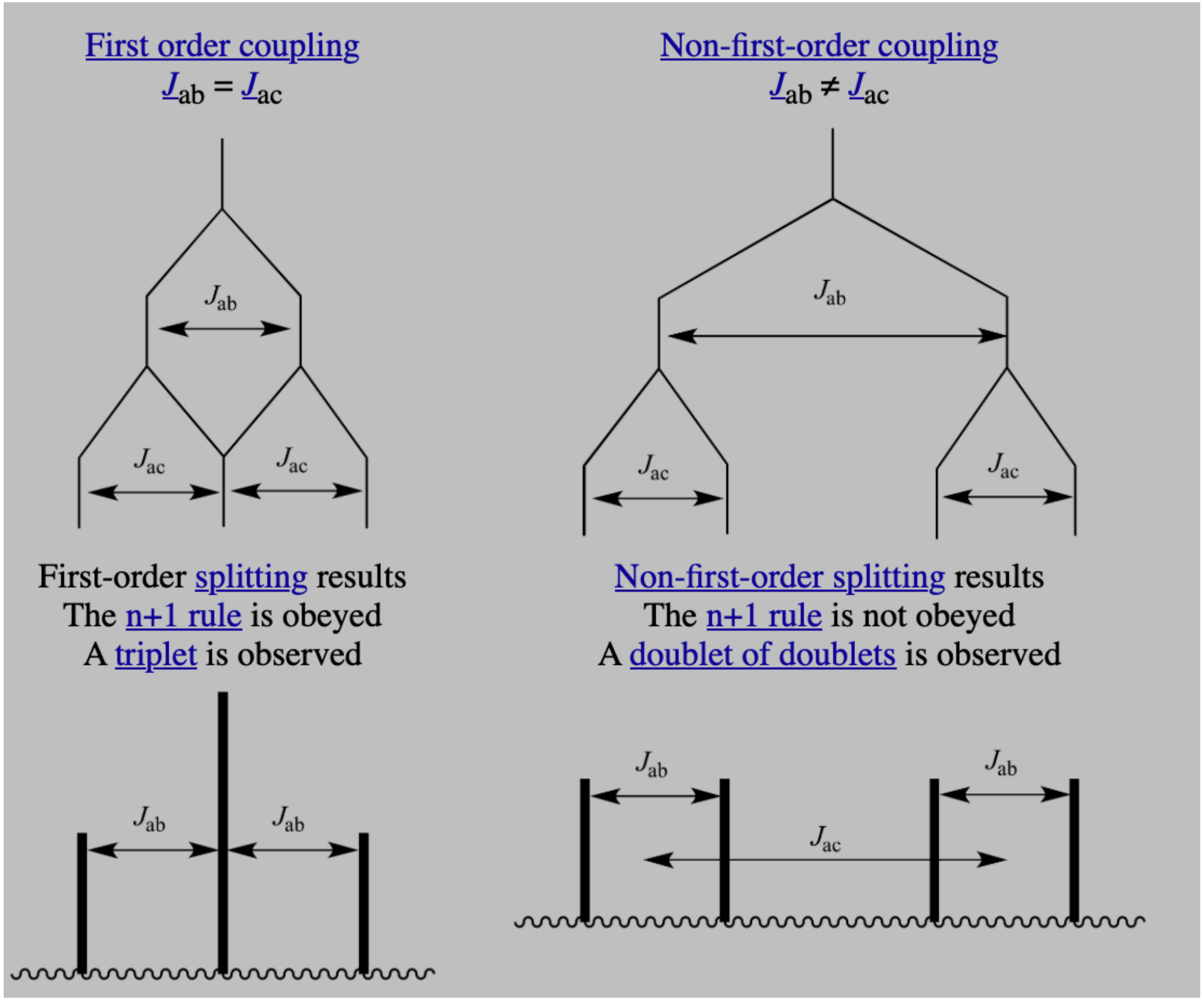
2.38 ppm
quartet

spin-spin splitting

In general, the first order spectra will only arise if the separation between multiplates is much larger than the coupling constant, J.

$$\frac{\Delta \nu}{J} \geq 8$$

Where Δv is the difference of chemical shift.



First order coupling

$J_{ab} = J_{ac}$

Non-first-order coupling

$J_{ab} \neq J_{ac}$

First-order splitting results
The n+1 rule is obeyed
A triplet is observed

Non-first-order splitting results
The n+1 rule is not obeyed
A doublet of doublets is observed

spin-spin splitting

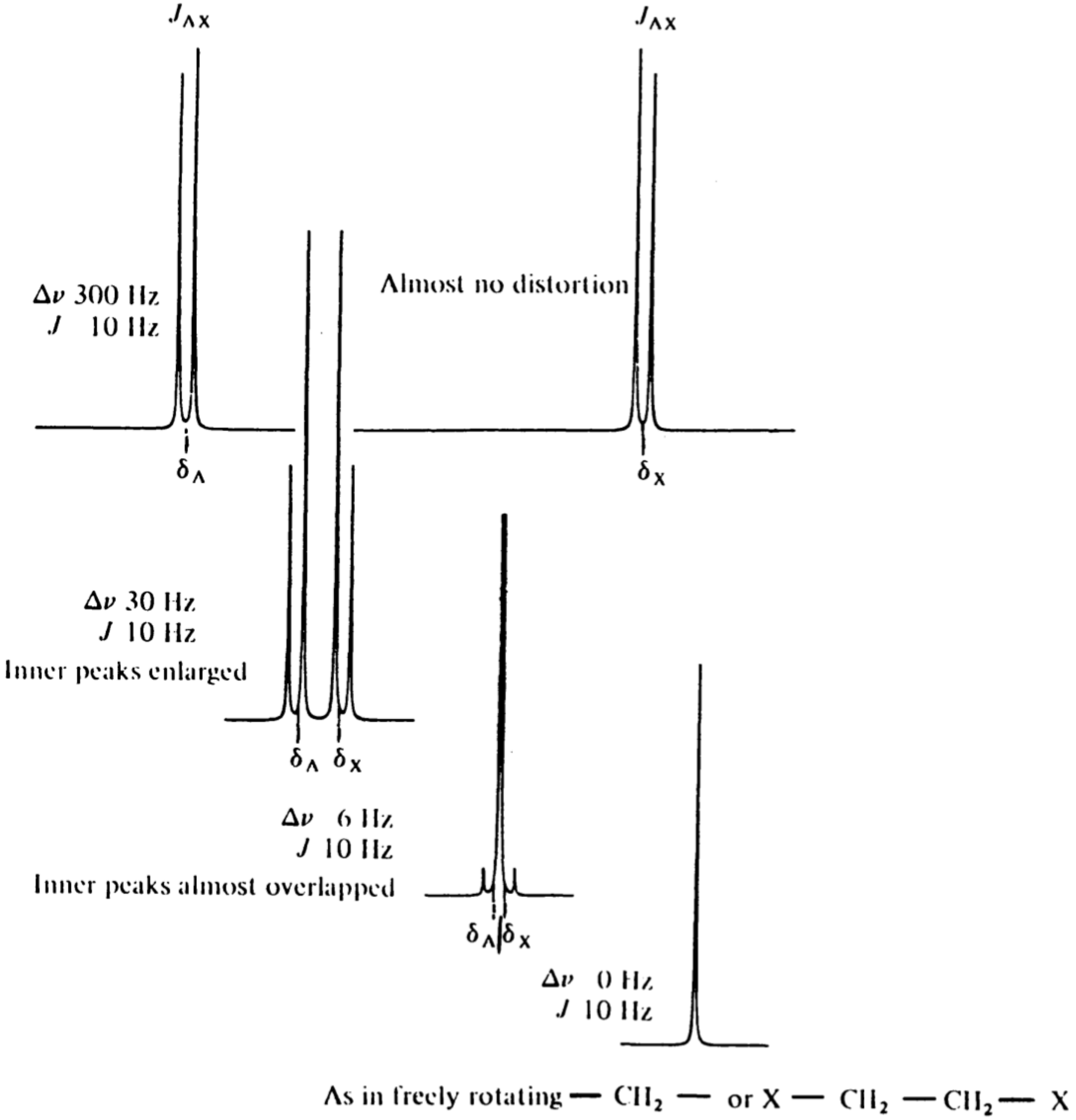


Figure 3.26 *Effect of ratio Δν:J on doublet appearance (computer simulated). For* AB *cases, the origin chemical shift positions can be calculated from* $\nu_A - \nu_B = [(\nu_1 - \nu_4)(\nu_2 - \nu_3)]^{1/2}$.

spin-spin splitting

High-order splitting pattern takes place when chemical shift difference in Hertz is much less or the same that order of magnitude as the j coupling.

$$\frac{\Delta v}{J} \leq 10 \qquad ($$

The second order pattern is observed as leaning of a classical pattern: the inner peaks are taller and the outer peaks are shorter in case of AB system (Figure 4). This is called the **roof effect**.

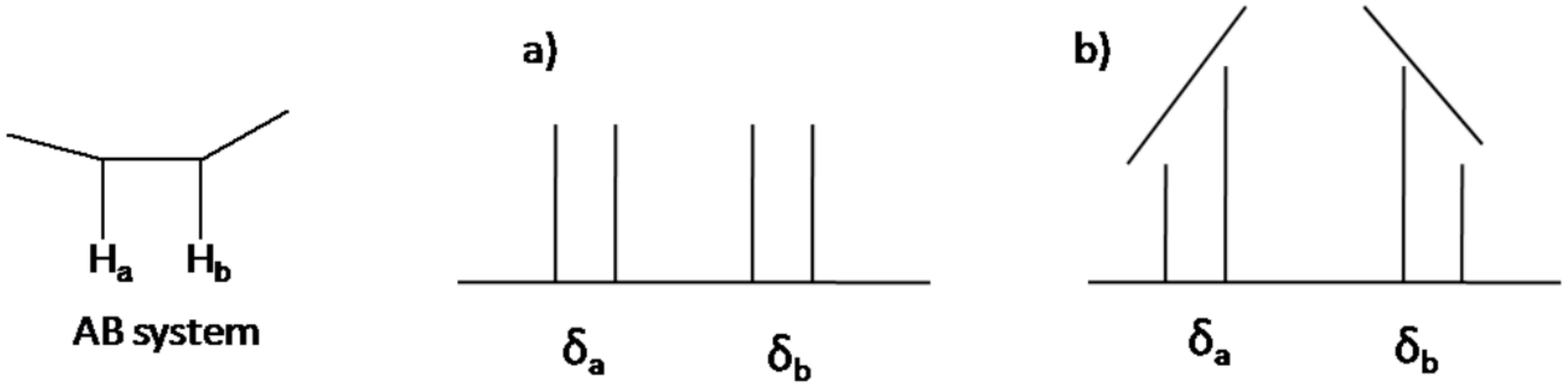


Figure 4: a) first-order pattern and b) second-order pattern of AB system

Here is other system as an example: A_2B_2 (Figure 5). The two triplet incline toward each other. Outer lines of the triplet are less than 1 in relative area and the inner lines are more than 1. The center lines have relative area 2.

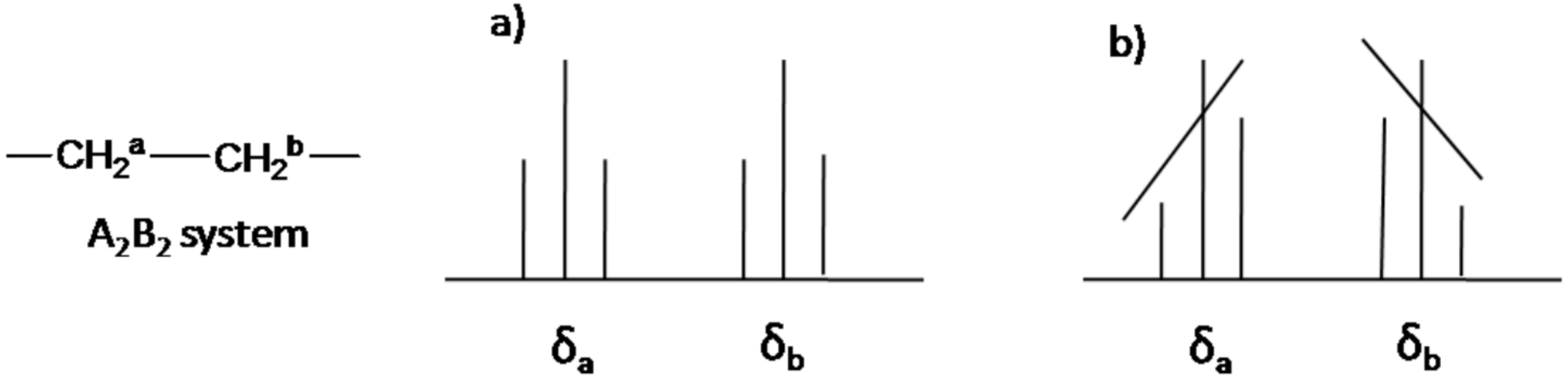
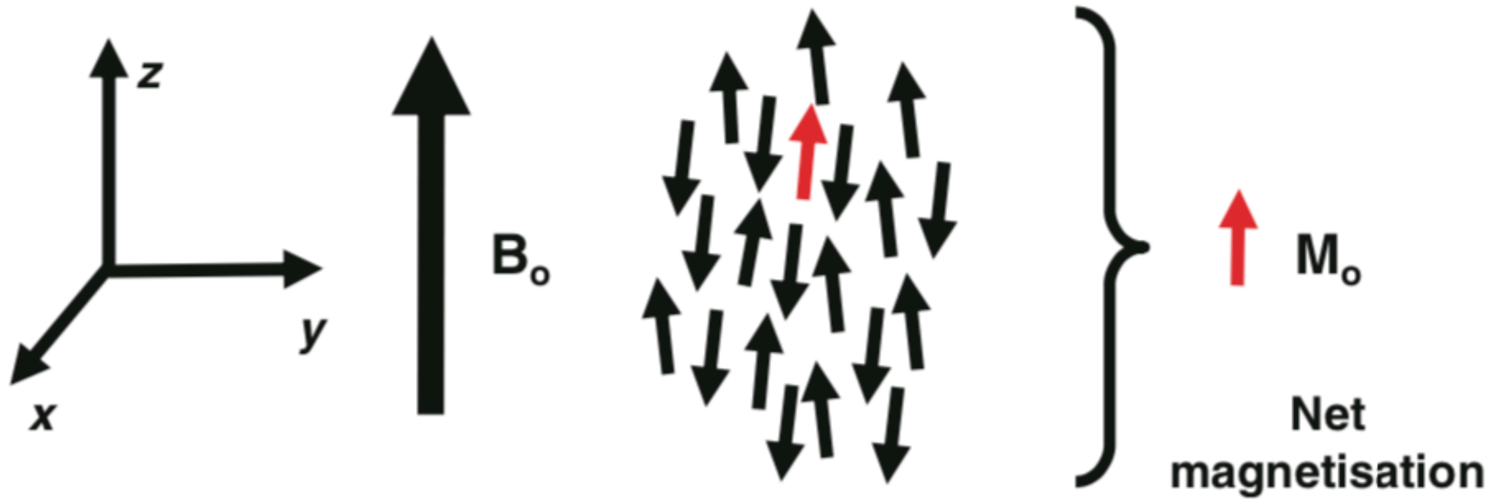
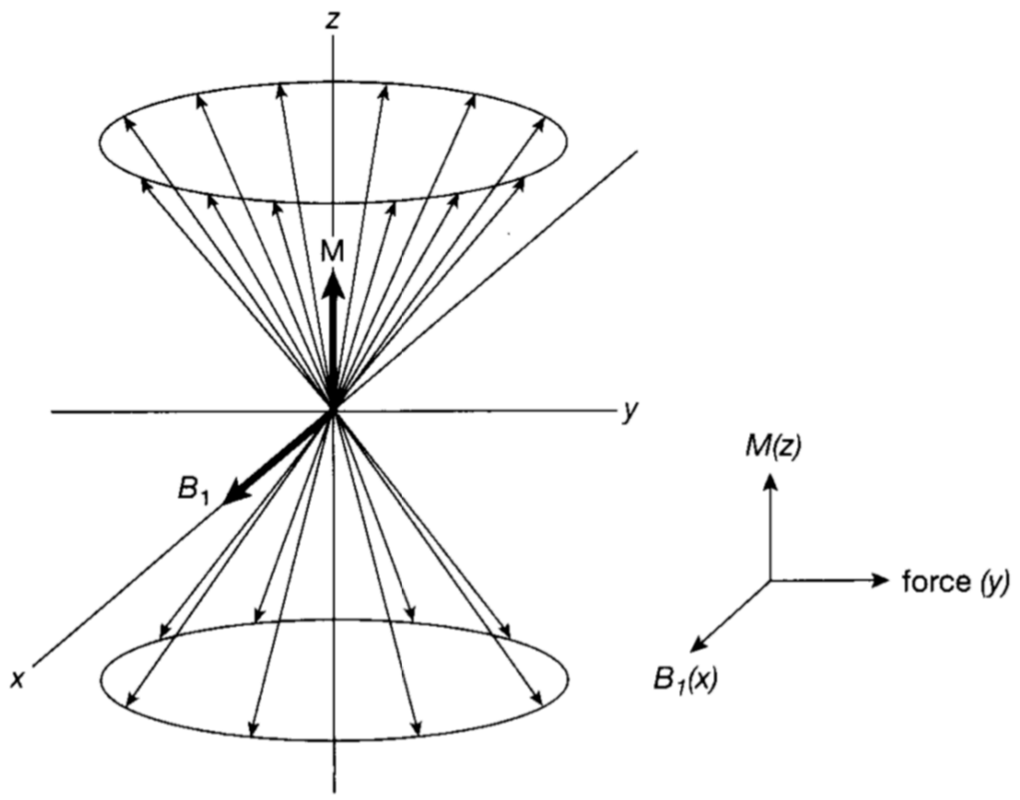


Figure 5: a) first-order pattern and b) second-order pattern of A_2B_2 system

What Determines the Size of the Net Magnetization?

The effect of the static field



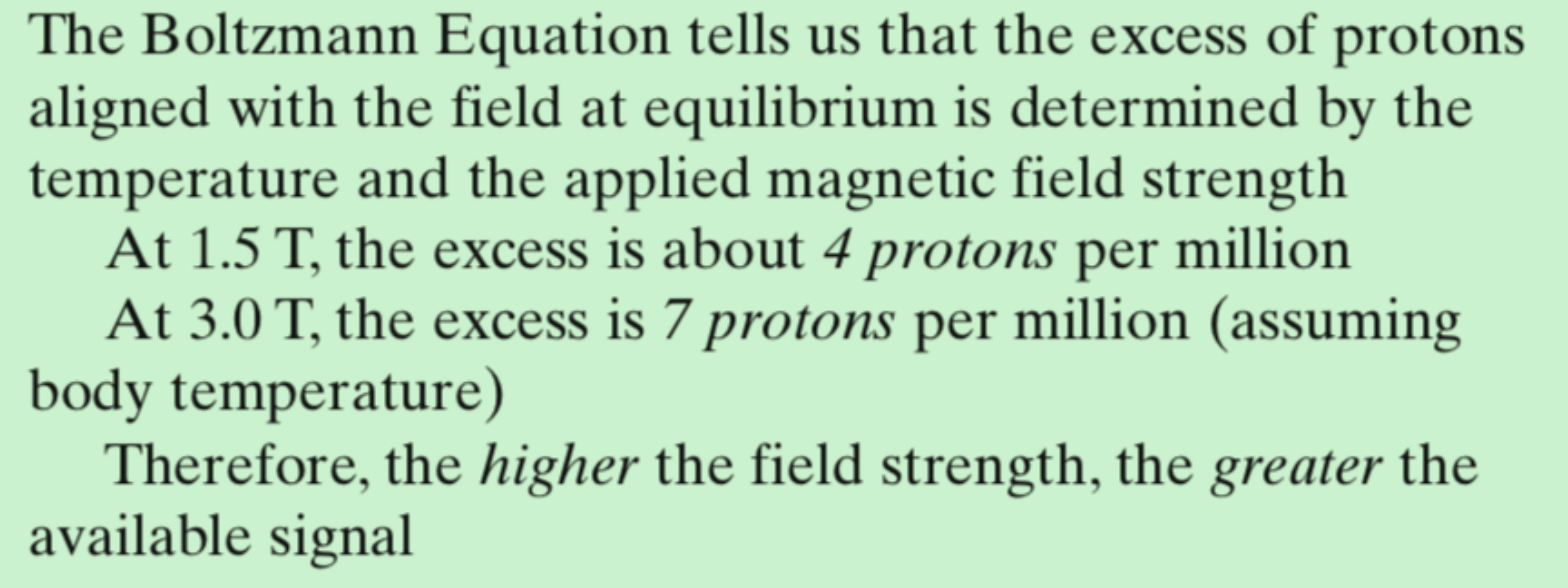


As the field is increased, the Larmor frequency increases and the precession becomes faster.

Secondly, the populations of the two spin states (the numbers of α and β spins) at thermal equilibrium change, and there will be more α spins than β states

What Determines the Size of the Net Magnetization?

The value of the Net Magnetization determines the maximum available NMR signal.



The Boltzmann Equation tells us that the excess of protons aligned with the field at equilibrium is determined by the temperature and the applied magnetic field strength

At 1.5 T, the excess is about *4 protons* per million

At 3.0 T, the excess is *7 protons* per million (assuming body temperature)

Therefore, the *higher* the field strength, the *greater* the available signal

The greater the field strength, the greater is the size of the Net Magnetisation

How Do We Generate a Signal?

In order to generate a signal from the net magnetization that is detectable, t**he radiofrequency (rf) magnetic field is generated by the rf transmitter coil** (the integral body coil) and used to deliver energy into the population of protons.

This field must be applied at a particular frequency, known as the *Larmor frequency*, that is determined by the strength of the magnetic field such that:

$$\text{Larmor frequency} = \text{constant} \times B_o$$

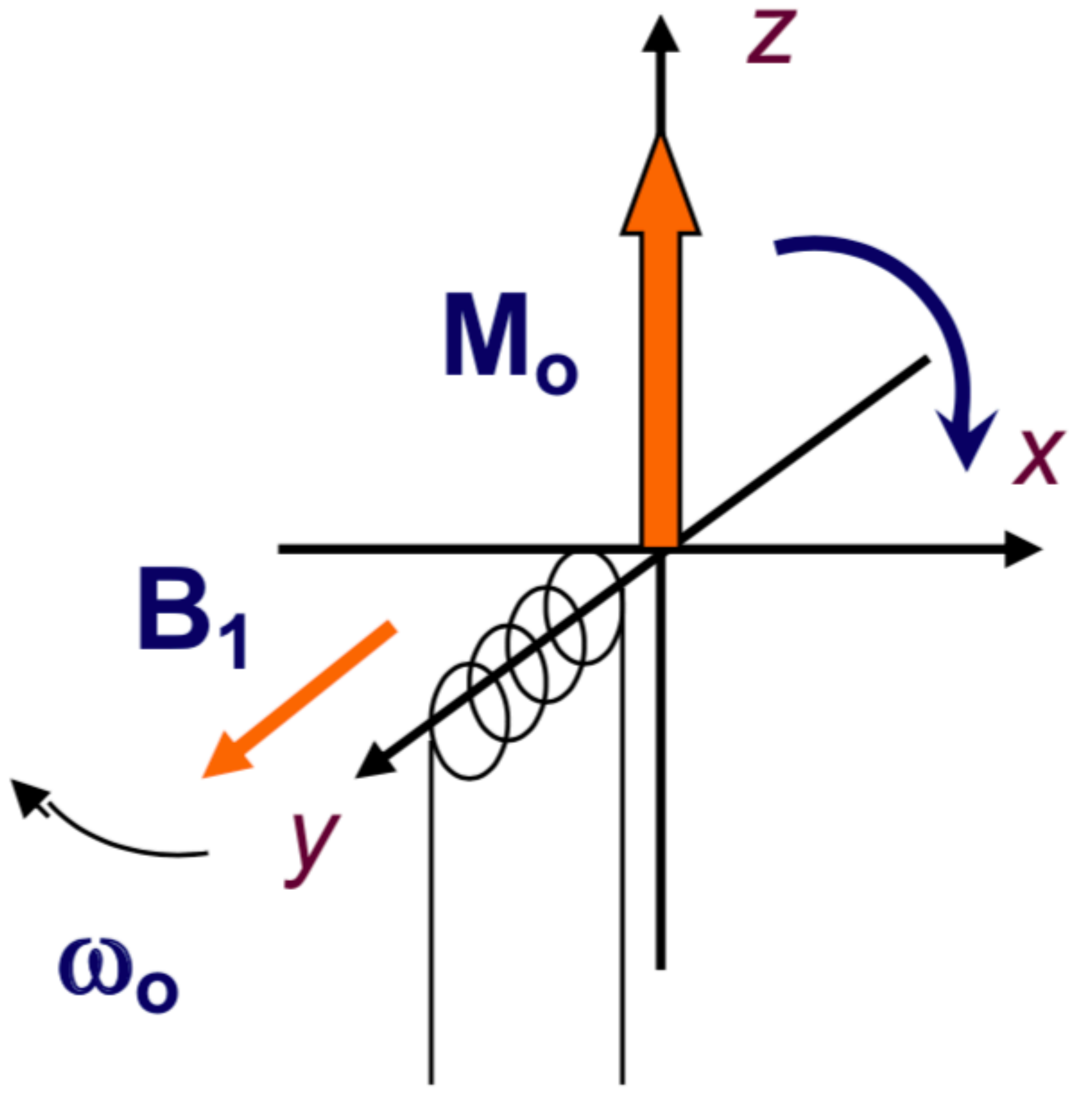
***Larmor equation*.**

The Larmor frequency is proportional to the strength of the magnetic field and is typically in the Megahertz range, for example, for 1.5 T, the Larmor frequency is 63 MHz. This is also known as ***the resonant frequency*,** as the protons absorb energy (or resonate) only at this characteristic frequency. The constant in the Larmor equation is known as the ***gyromagnetic ratio*** and has a value that is characteristic for a particular nucleus (42.6 MHz/T for the proton).

The rf field is normally applied as a short pulse, known as an *rf pulse*.

How Do We Generate a Signal?

Why are two separate magnetic fields needed for the experiment?



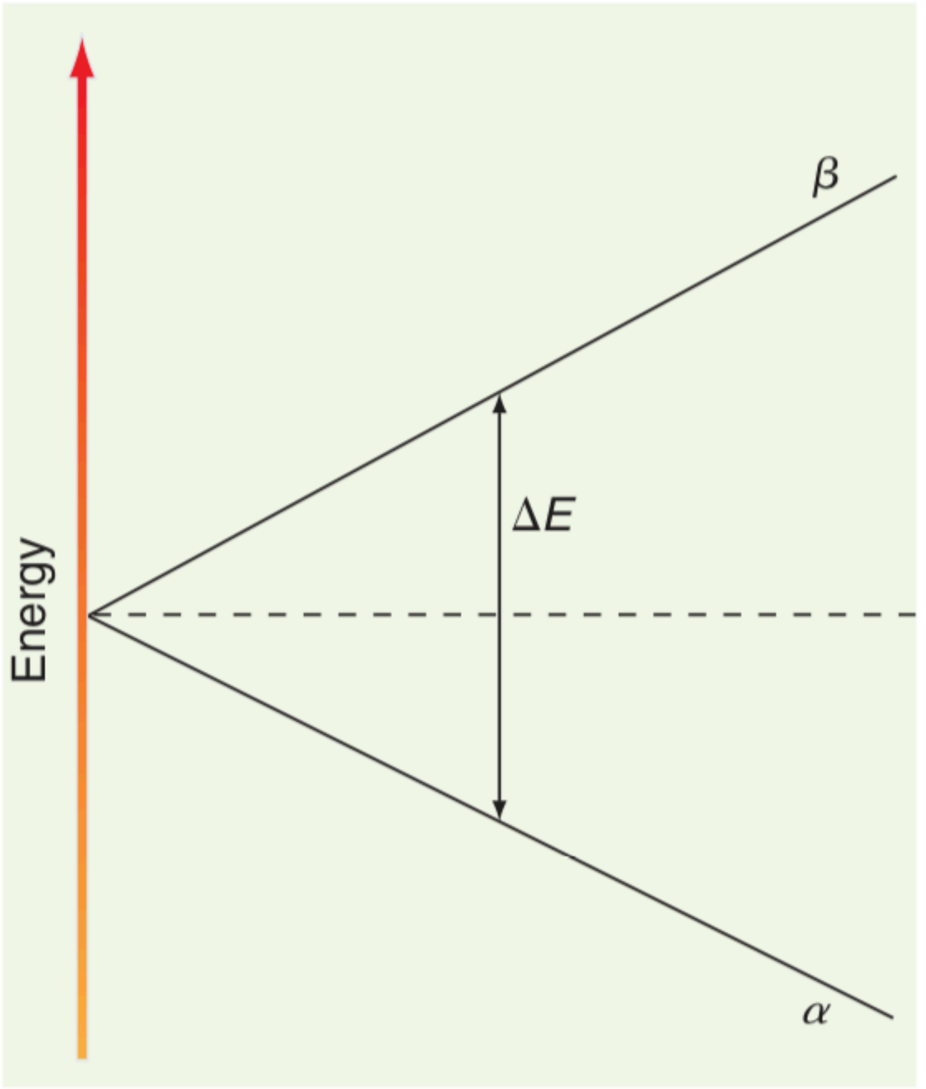
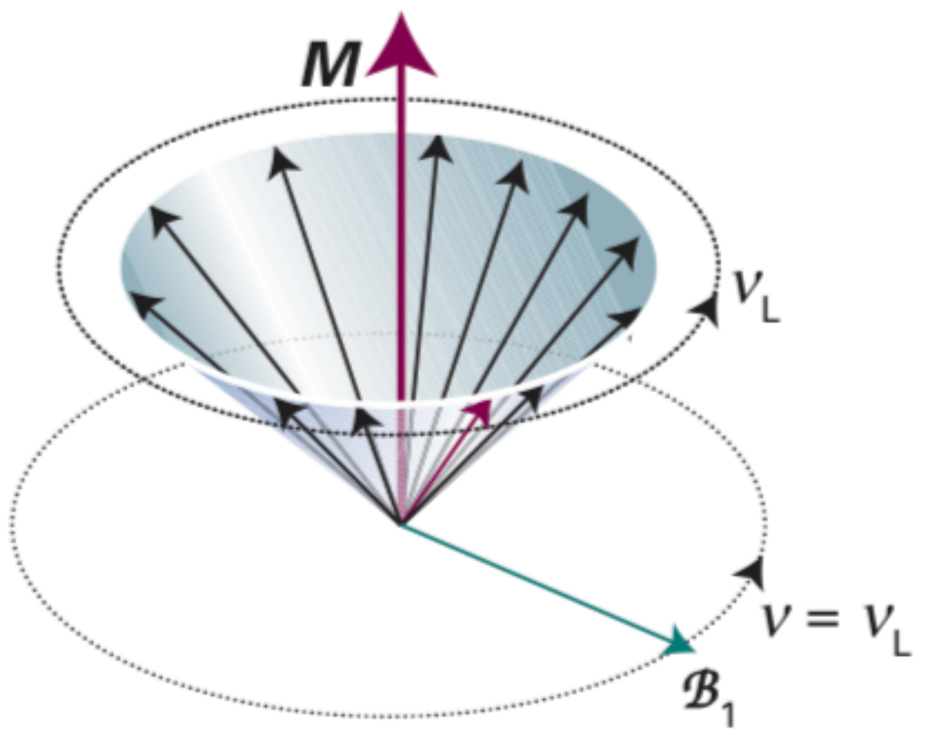


FIGURE 17.1
Energy of a nuclear spin of quantum number 1/2 as a function of the magnetic field.

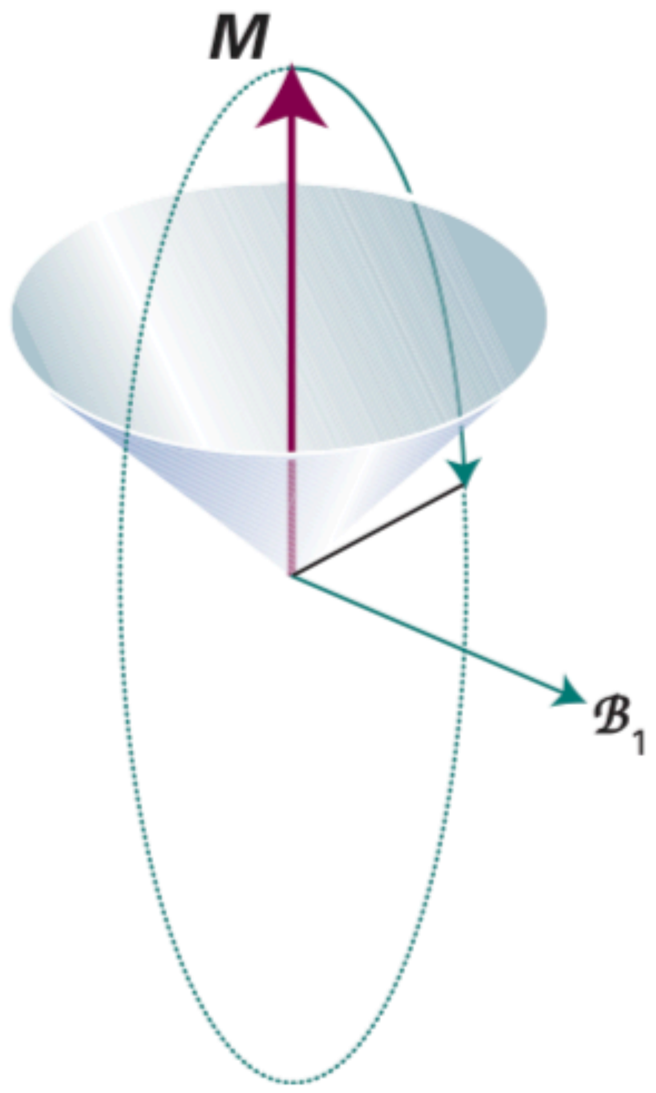
The static magnetic field **B0** gives rise to the two energy levels shown as a function of the magnetic field strength. It does not induce transitions between the two states. However, the rf field **B1** induces transitions between the two levels if the resonance condition is met.

How Do We Generate a Signal?



(a)

In a resonance experiment, a circularly polarized radiofrequency magnetic field B1 is applied in the *xy*-plane (the magnetization vector lies along the *z*-axis).



(b)

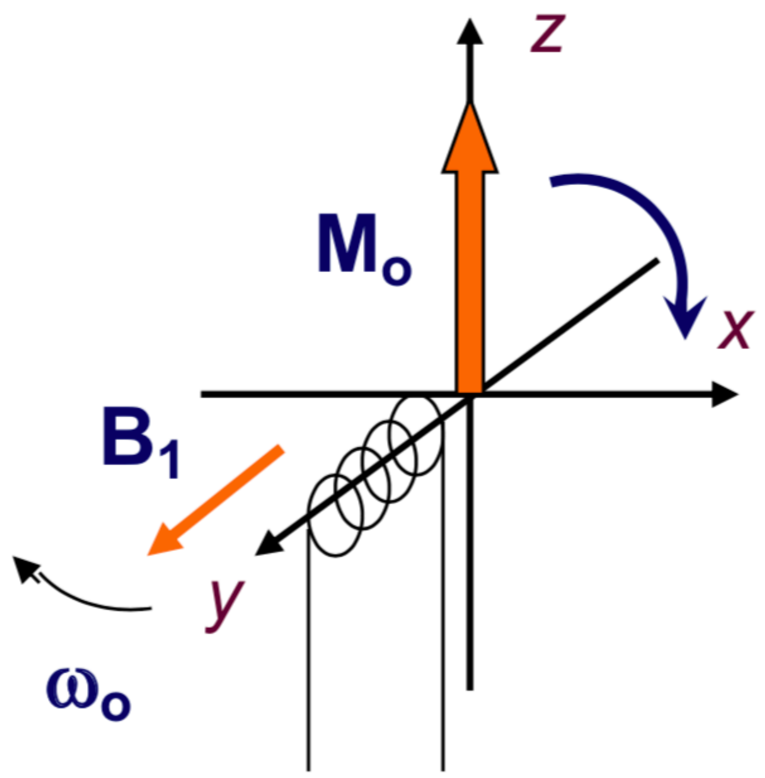
If we step into a frame rotating at the radiofrequency, B1 appears to be stationary, as does the magnetization *M* if the Larmor frequency is equal to the radiofrequency. When the two frequencies coincide, the magnetization vector of the sample rotates around the direction of the B1 field.

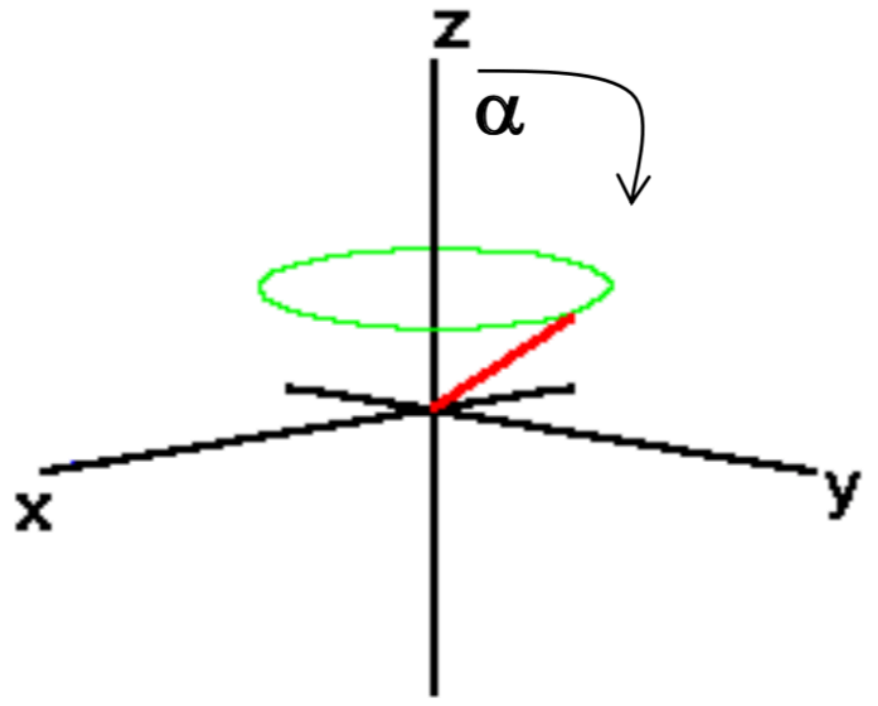
How Do We Generate a Signal?

The B1 interacts with the magnetisation M to produce a torque which moves the magnetisation toward the xy plane.

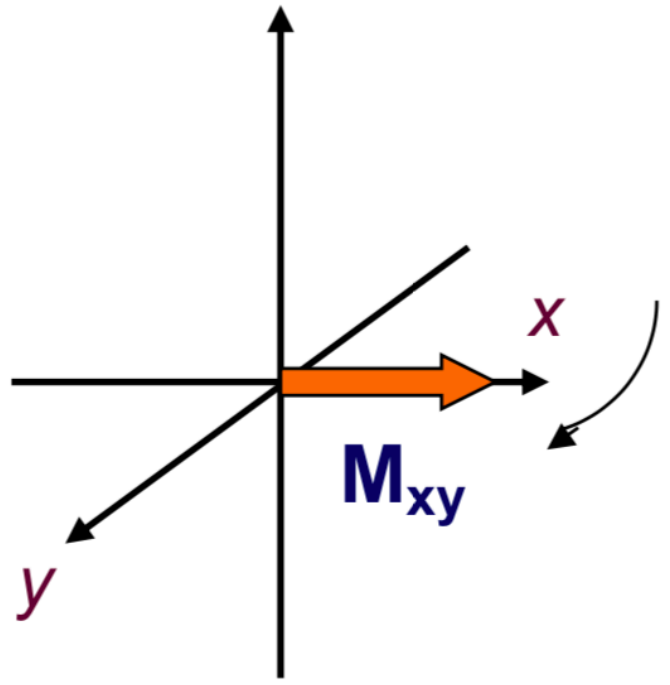
To interpret the effects of radiofrequency pulses on the magnetization, it is useful to imagine stepping on to a platform, a so-called **rotating frame.**

$$\alpha = \gamma B_1 t_p = \omega t_p$$

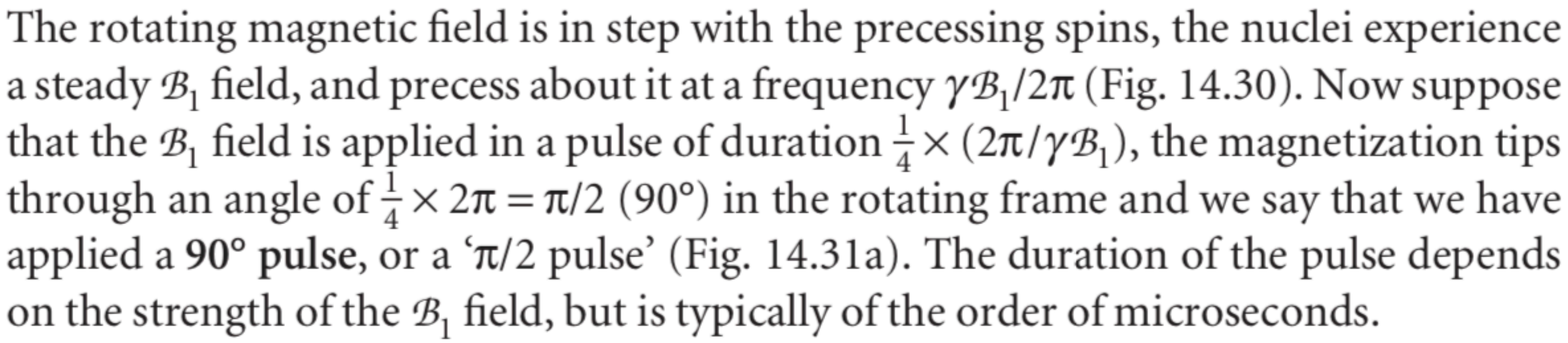




α deg pulse



90 deg pulse



The rotating magnetic field is in step with the precessing spins, the nuclei experience a steady $\mathcal{B}_1$ field, and precess about it at a frequency $\gamma\mathcal{B}_1/2\pi$ (Fig. 14.30). Now suppose that the $\mathcal{B}_1$ field is applied in a pulse of duration $\frac{1}{4}\times(2\pi/\gamma\mathcal{B}_1)$, the magnetization tips through an angle of $\frac{1}{4}\times 2\pi = \pi/2$ (90°) in the rotating frame and we say that we have applied a **90° pulse**, or a 'π/2 pulse' (Fig. 14.31a). The duration of the pulse depends on the strength of the $\mathcal{B}_1$ field, but is typically of the order of microseconds.

What Does the RF Pulse Do to the Magnetization?

When the rf pulse is switched on, the proton magnetic moments start to rotate together about the main magnetic field. This causes the *net magnetization* to move away from its alignment with the *z*-axis and to rotate around it.

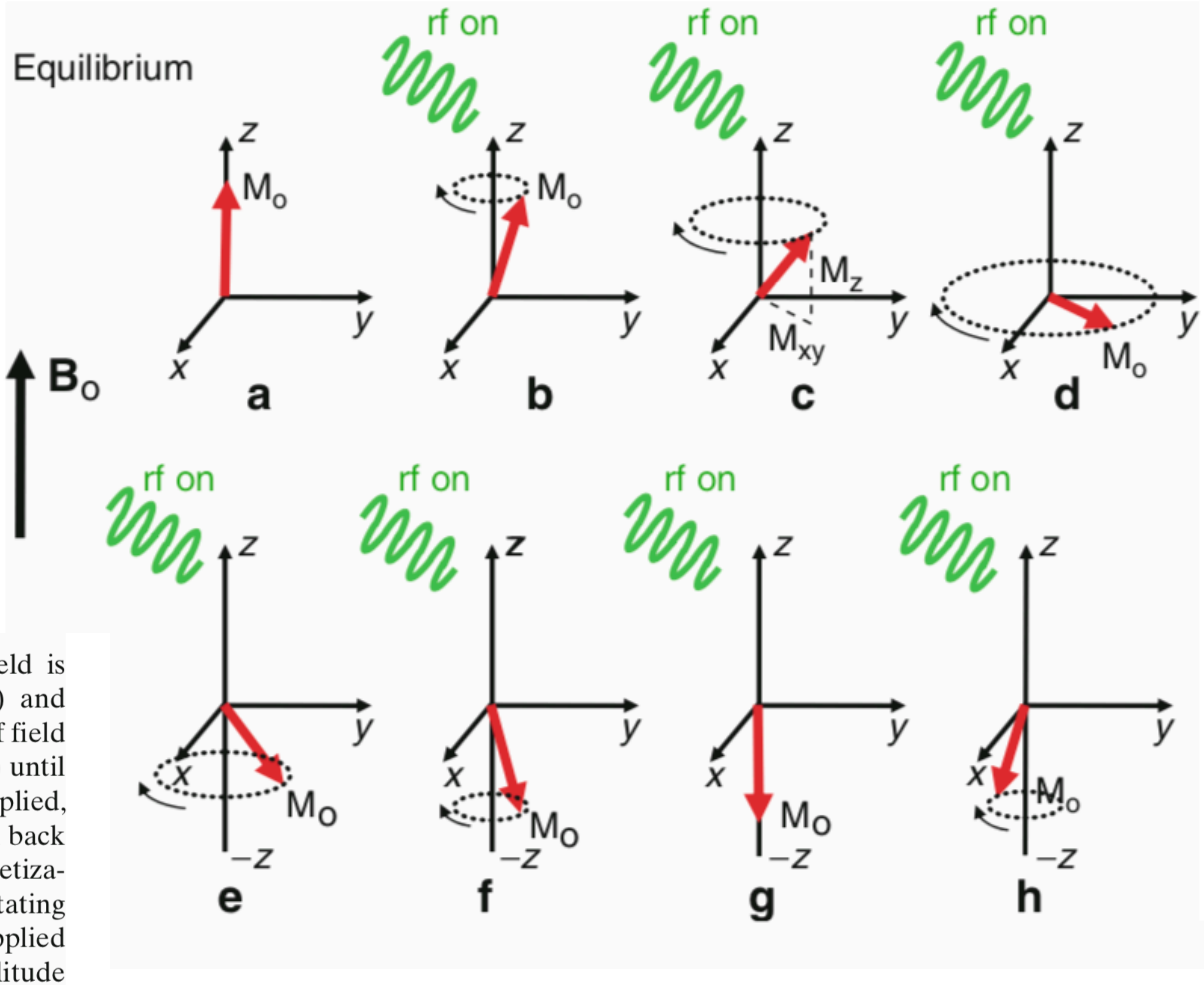


FIGURE 4.1. Initially, M_o is at equilibrium (**a**). As the rf field is applied, M_o makes an increasing angle with the *z*-axis (**b**) and rotates in the direction of the curved arrow. For as long as the rf field is applied, the angle with the *z* axis continues to increase (**b–f**) until M_o lies along the –ve *z*-axis (**g**). If the rf field continues to be applied, the angle will increase beyond 180°, driving the magnetization back toward the +ve *z* axis once more (**h**). At any instant, the magnetization can be split into two components, M_z and M_{xy}, (**c**). The rotating M_{xy} component generates the detectable MR signal once the applied rf field is switched off. The maximum detectable signal amplitude occurs when M_o lies entirely in the plane of the *x* and *y* axes (**d**) as this gives the largest M_{xy} component.

This angle that the net magnetization is rotated through by the rf pulse is known as *the flip angle*.

What is the effects of a 90° pulse and of a 180° pulse on a system of spin1/2 nuclei in a static magnetic field?

Before the application of a pulse the magnetization vector, $\boldsymbol{M}$, points along the direction of the static external magnetic field $\mathcal{B}_0$. There are more α spins than β spins. When we apply a rotating magnetic field $\mathcal{B}_1$ at right angles to the static field, the magnetization vector as seen in the rotating frame begins to precess about the $\mathcal{B}_1$ field with angular frequency $\omega_1 = \gamma\mathcal{B}_1$. The angle through which $\boldsymbol{M}$ rotates is $\theta = \gamma\mathcal{B}_1 t$, where t is the time for which the $\mathcal{B}_1$ pulse is applied. When $t = \pi/2\gamma\mathcal{B}_1$, $\theta = \pi/2 =$ 90°, and $\boldsymbol{M}$ has rotated into the xy plane. Now there are equal numbers of α and β spins. A 180° pulse applied for a time $\pi/\gamma\mathcal{B}_1$, rotates $\boldsymbol{M}$ antiparallel to the static field. Now there are more β spins than α spins. A population inversion has occurred.

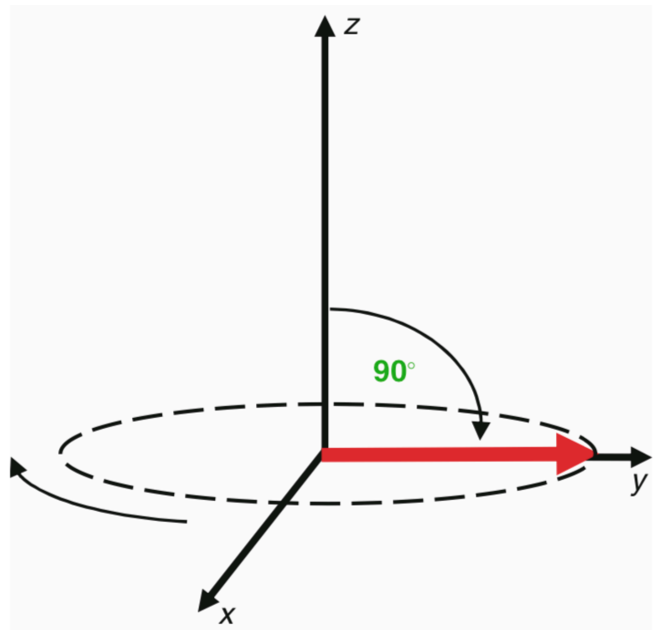


FIGURE 4.3. 90° rf pulse.

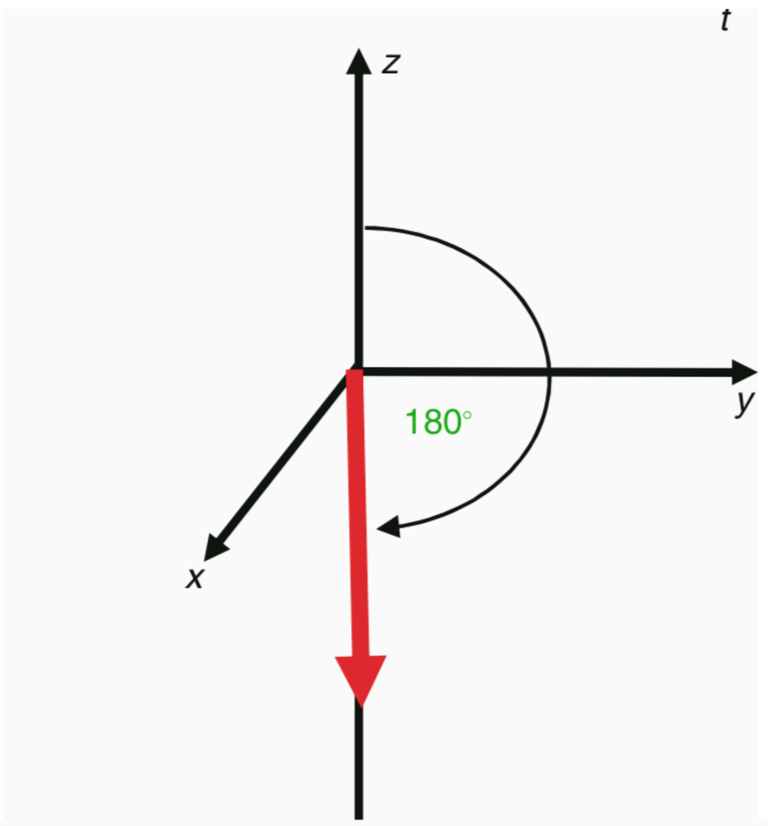
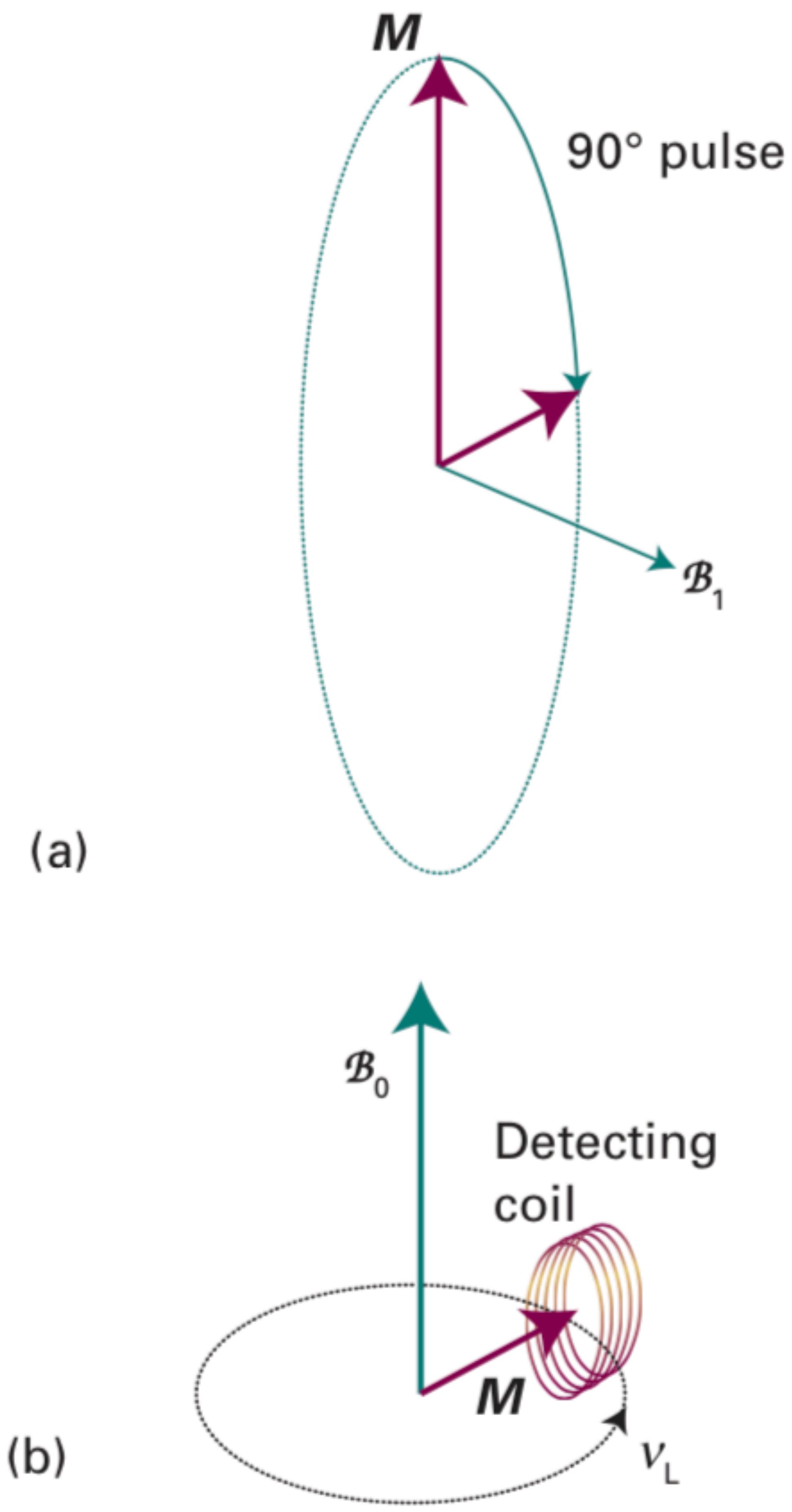


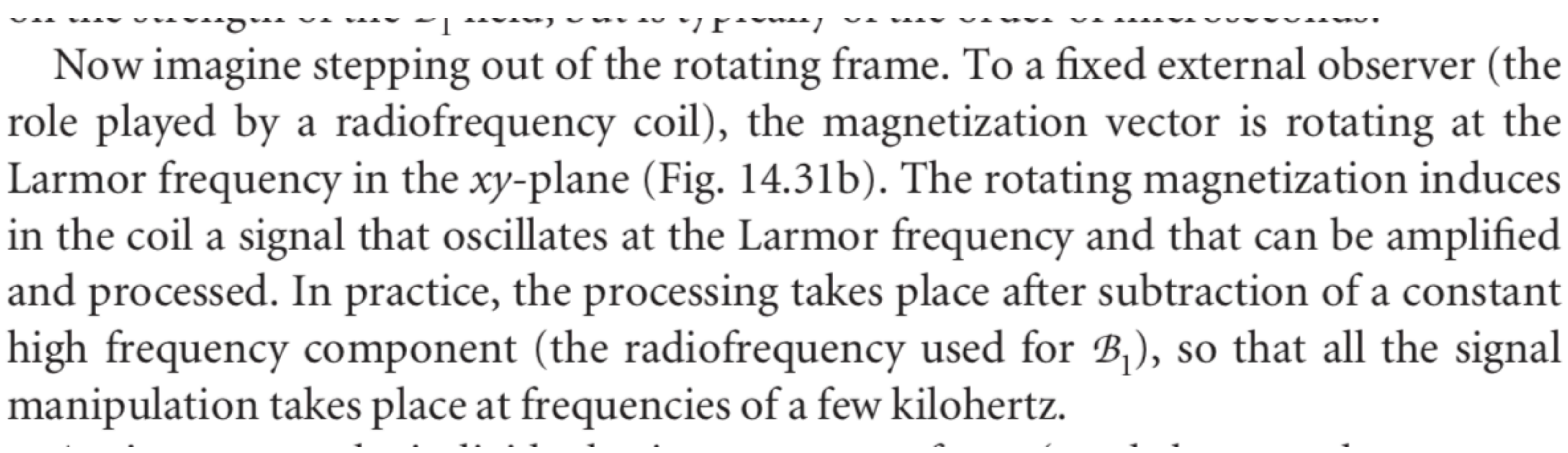
FIGURE 4.5. 180° rf inversion pulse.

How Do We Generate a Signal?



(a)If the radio-frequency field is applied for a certain time, the magnetization vector is rotated into the *xy*-plane.

(b) To an external stationary observer (the coil), the magnetization vector is rotating at the Larmor frequency, and can induce a signal in the coil.



Now imagine stepping out of the rotating frame. To a fixed external observer (the role played by a radiofrequency coil), the magnetization vector is rotating at the Larmor frequency in the *xy*-plane (Fig. 14.31b). The rotating magnetization induces in the coil a signal that oscillates at the Larmor frequency and that can be amplified and processed. In practice, the processing takes place after subtraction of a constant high frequency component (the radiofrequency used for $\mathcal{B}_1$), so that all the signal manipulation takes place at frequencies of a few kilohertz.

Free-induction decay (FID)

Free- free of the influence of Rf

Induction- induced in the coil

Decay- decaying back to equilibrium

As time passes, the individual spins move out of step (partly because they are precessing at slightly different rates, as we shall explain later), so the magnetization vector shrinks exponentially with a time and induces an ever weaker signal in the detector coil. The form of the signal that we can expect is therefore the oscillating- decaying **free-induction decay** (FID)

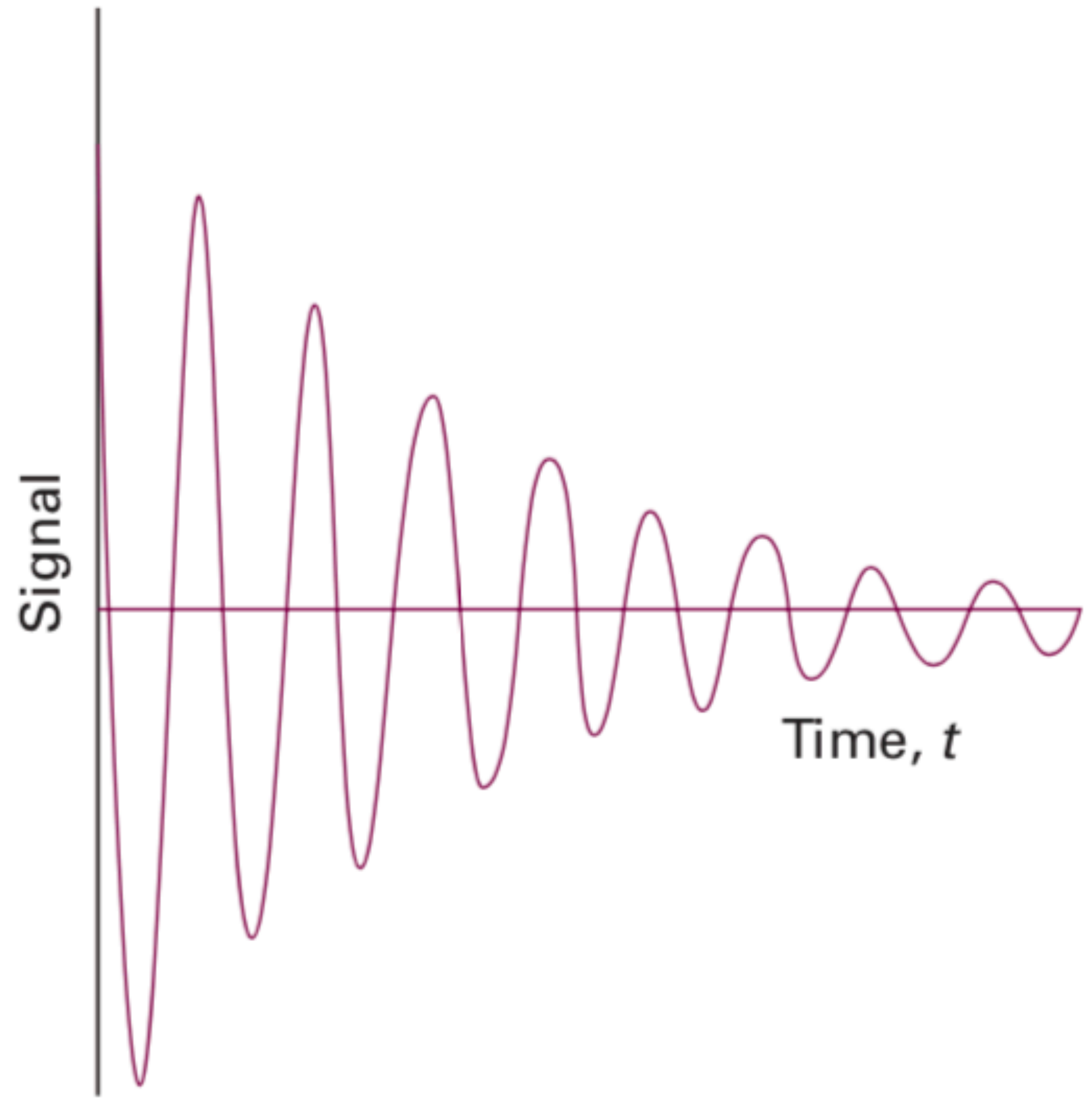
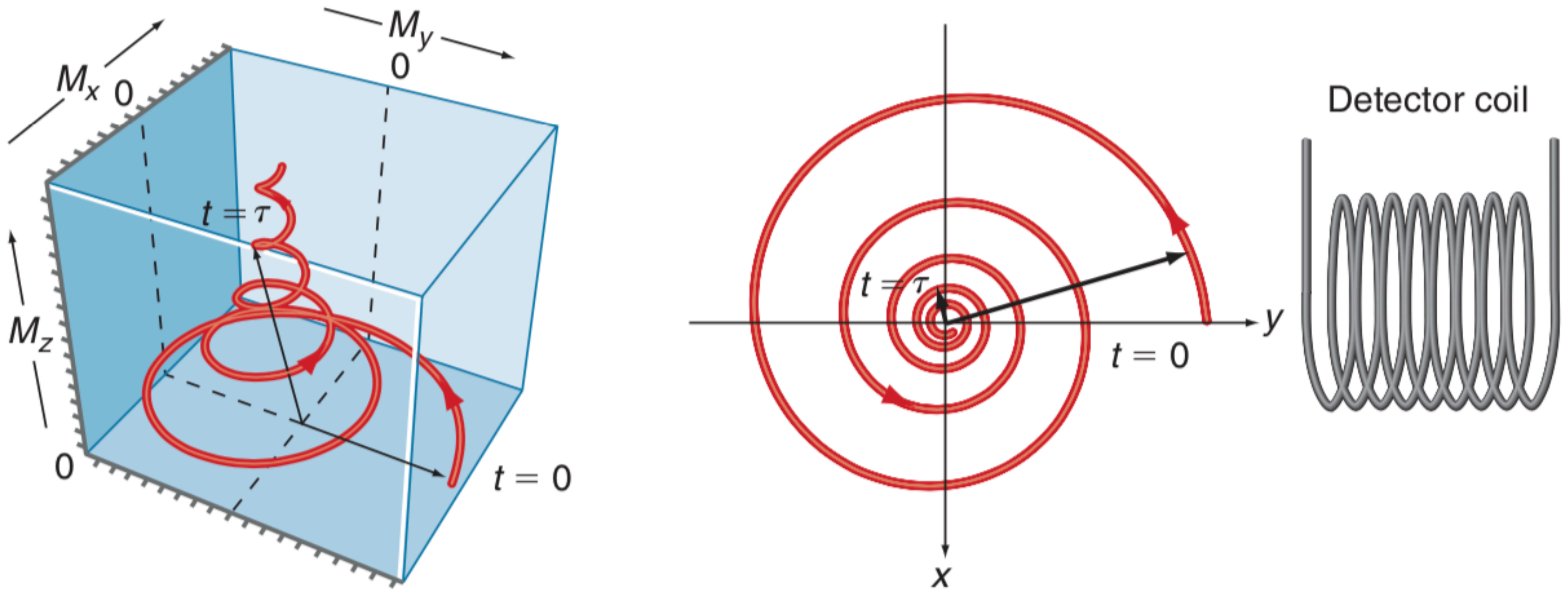


Fig. 14.32 A simple free-induction decay of a sample of spins with a single resonance frequency.

Free-induction decay (FID)



Evolution of **M** in three dimensions

Evolution of **M** in *xy* plane

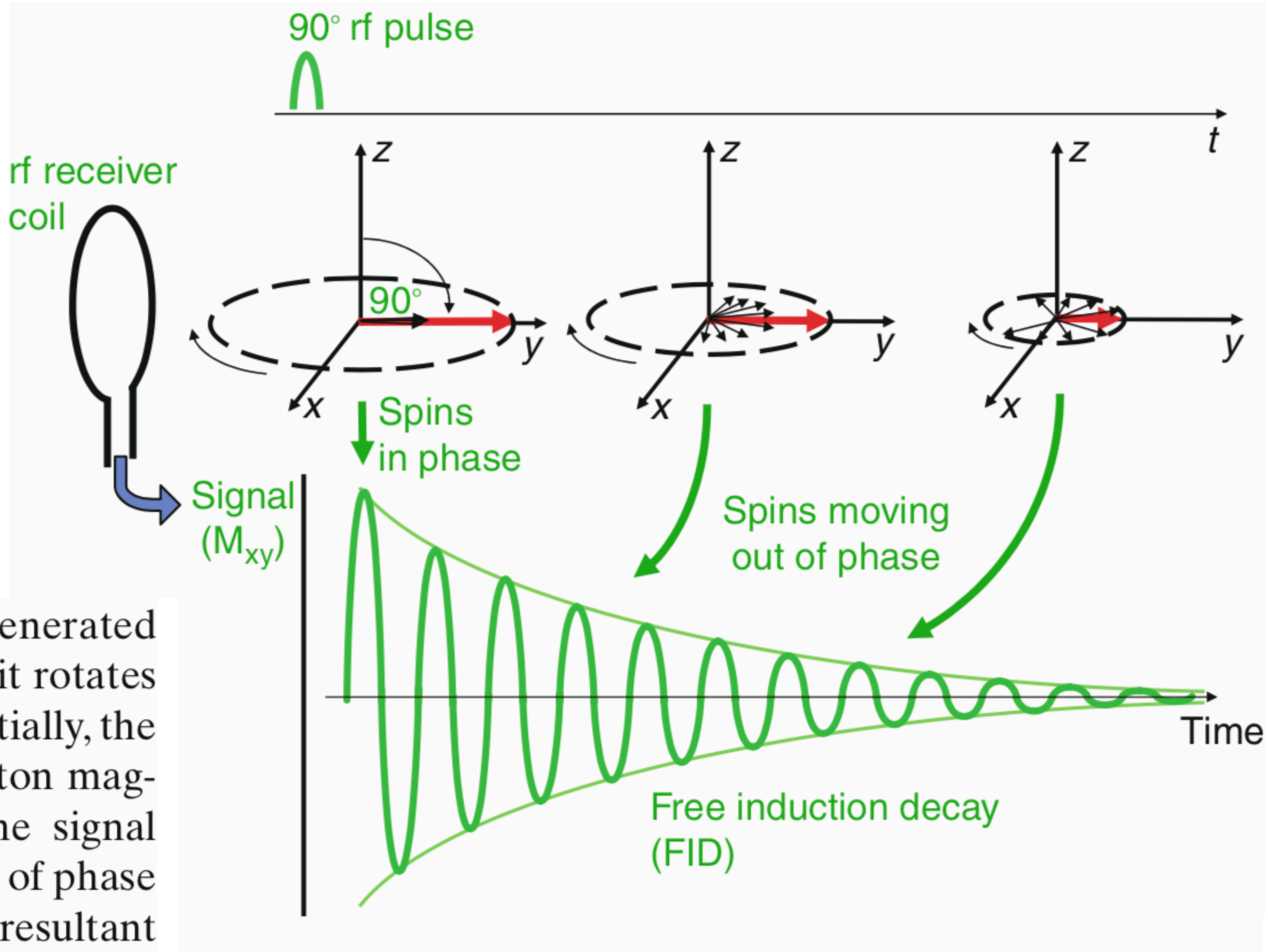


FIGURE 4.6. The net transverse magnetization (*red arrow*) generated by a 90° rf pulse generates an oscillating magnetic field as it rotates in the *xy* plane that can be detected by a rf receiver coil. Initially, the signal has a maximum amplitude as the population of proton magnetic moments (spins) is in phase. The amplitude of the signal detected decays as the proton magnetic moments move out of phase with one another (shown by the small *black arrows*). The resultant decaying signal is known as the free induction decay (FID).

Relaxation:What Happens After the RF Excitation Pulse?

Immediately after the rf pulse, the spin system starts to return back to its original state, that is, equilibrium. This process is known as ***relaxation.***

*T*here are two distinct relaxation processes that relate to the two components of the net magnetization, the longitudinal (*z*) and transverse (*xy*) components.

The first ***longitudinal relaxation*** process, commonly referred to as *T1 relaxation*, is responsible for the regrowth of the z component along the longitudinal (z) axis to its original value at equilibrium.

NMR Relaxation

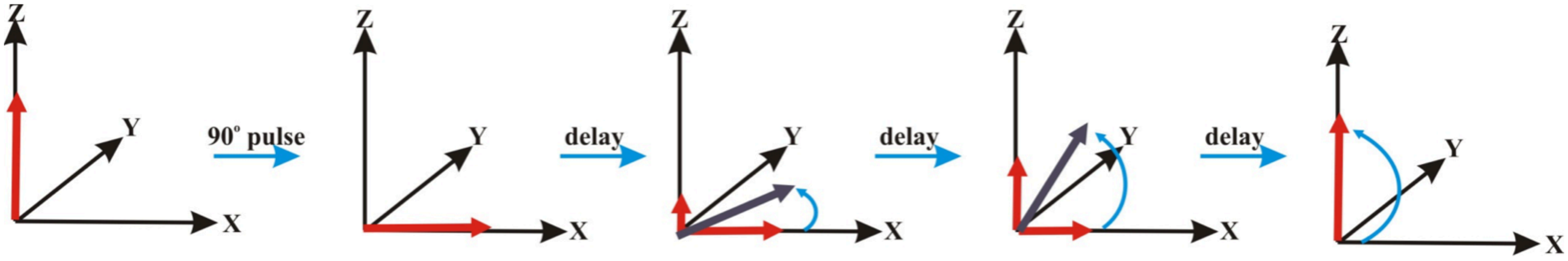
T1 relaxation describes the recovery of the *z*-component (M_z) of the magnetization following an rf pulse as the population of protons returns to its equilibrium state.

Spin-Lattice or Longitudinal Relaxation (T_1)

i. transfer of energy to the lattice or solvent material

ii. coupling of nuclei magnetic field with magnetic fields created by the ensemble of vibrational and rotational motion of the lattice or solvent.

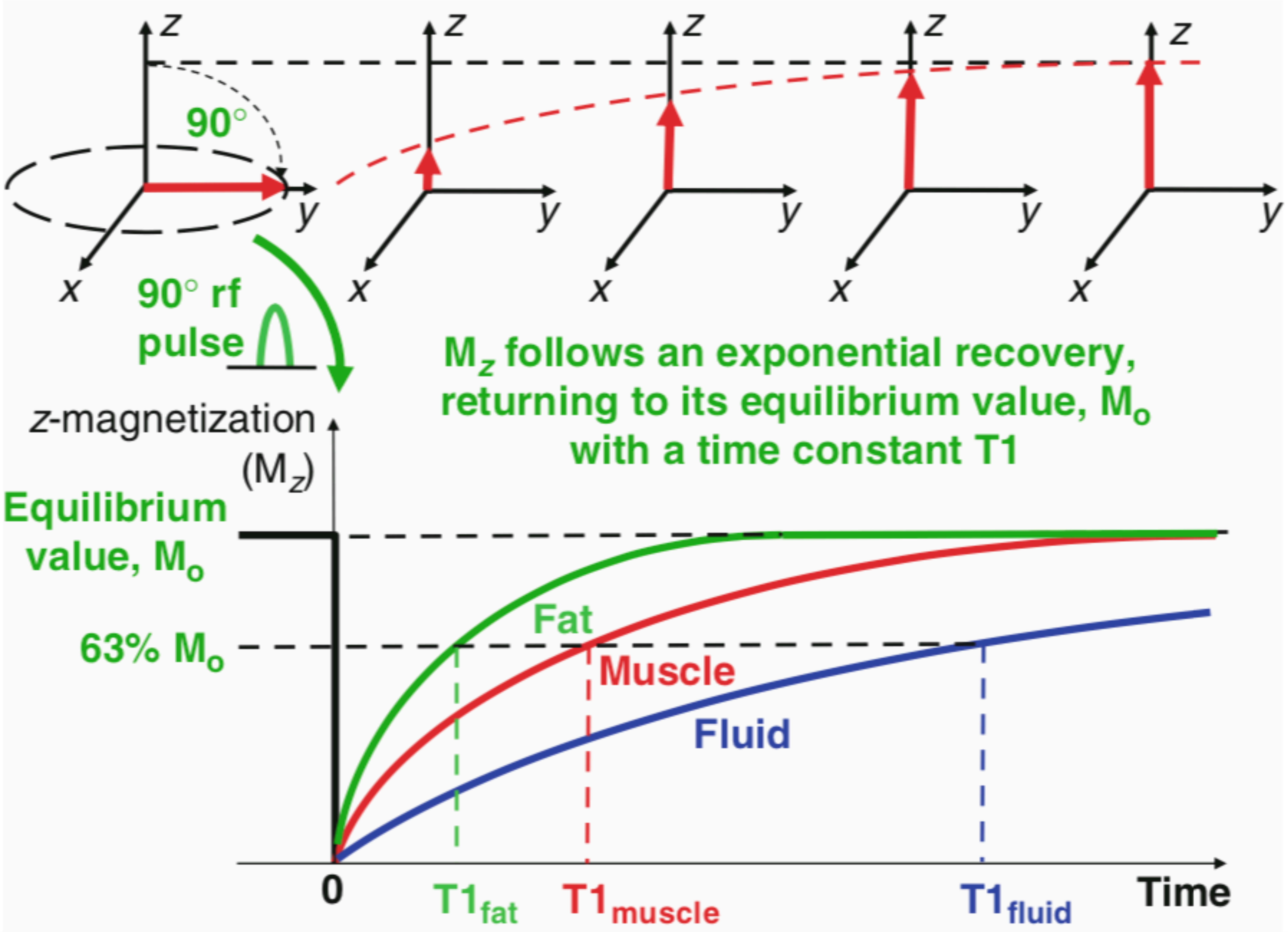
iii. results in a minimal temperature increase in sample



$$M_z = M_0(1-\exp(-t/T_1))$$

Recycle Delay: General practice is to wait 5xT_1 for the system to have fully relaxed.

What is T1 Relaxation?



What is T2 Relaxation?

The rate of precession for an individual proton depends on the applied magnetic field. It is however possible for the **magnetic moment of one proton to slightly modify the magnetic field of a neighboring proton constituents of atoms within molecules**, they are moving rapidly and randomly, and so, such effects are **transient and random**. The net effect is for the Larmor frequency of the individual protons to fluctuate in a random fashion, **leading to a loss of coherence across the population of protons**. That is, the spins gradually acquire different phase angles, pointing in different directions to one another and are said to move out of phase with one another (this is often referred to as ***dephasing***).

The resultant decay of the transverse component of the magnetization (M_{xy}) has an exponential form with a time constant, T2, hence this contribution to transverse relaxation is known as *T2 relaxation*.

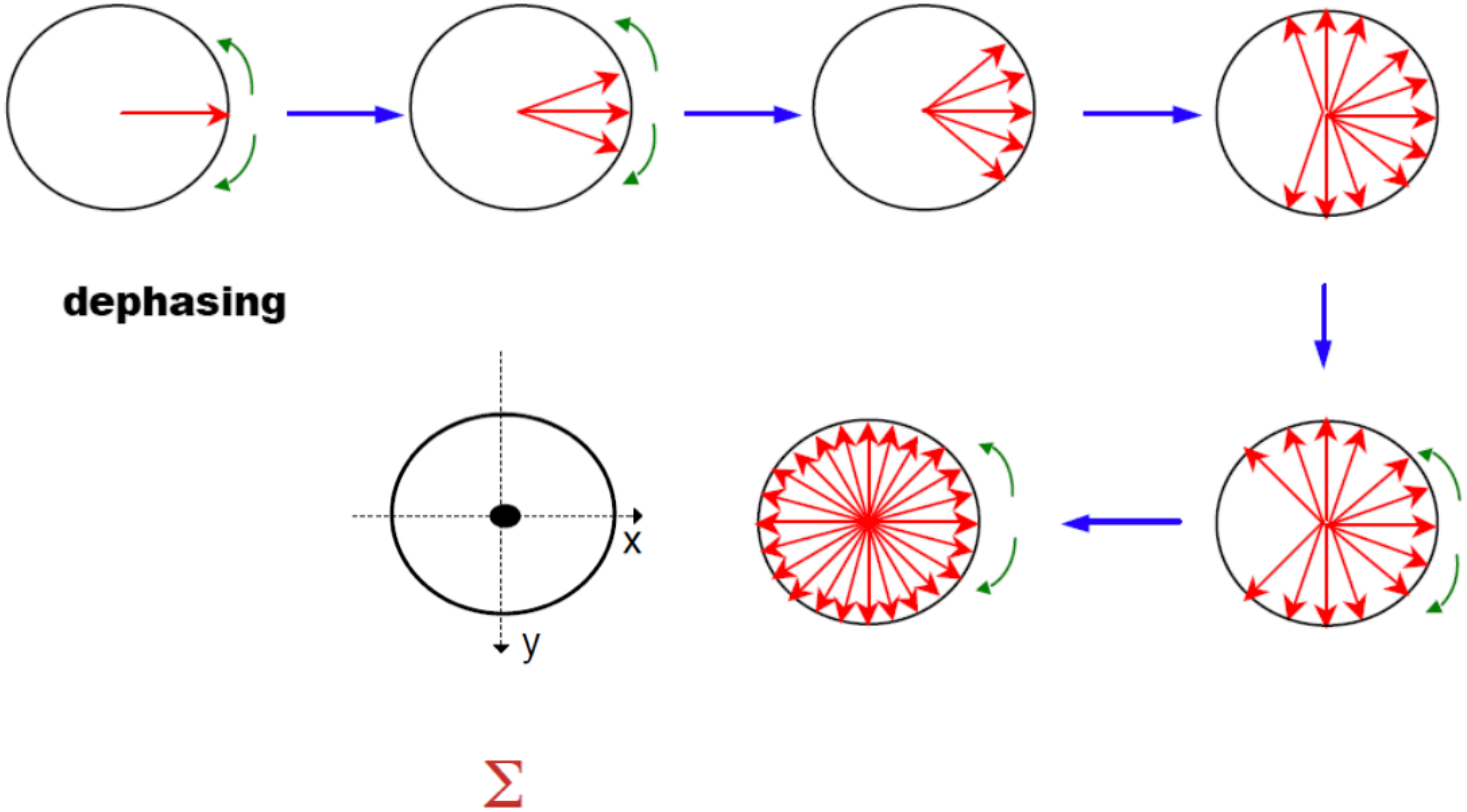
NMR Relaxation

spin-spin or transverse relaxation (T_2)

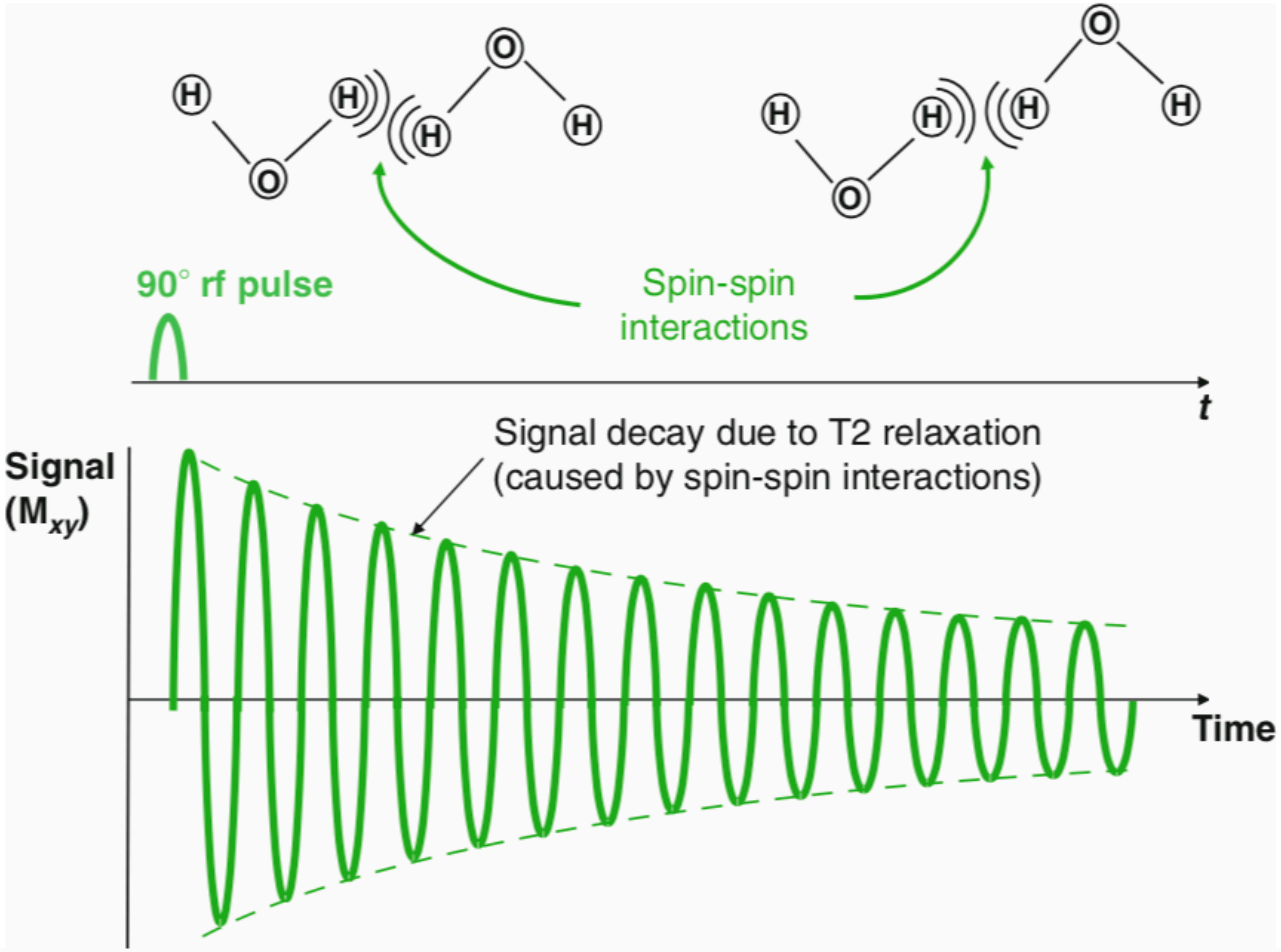
i. exchange of energy between excited nucleus and low energy state nucleus

ii. randomization of spins or magnetic moment in x,y-plane

$$M_x = M_y = M_0 \exp(-t/T_2)$$



What is T2 Relaxation?



How to determine spin-lattice relaxation time?

The longitudinal relaxation time T_1 can be measured by the **inversion recovery technique**. The first step is to apply a 180° pulse to the sample. A 180° pulse is achieved by applying the $\mathcal{B}_1$ field for twice as long as for a 90° pulse, so the magnetization vector precesses through 180° and points in the *z*-direction (Fig. 14.39). No signal can be seen at this stage because there is no component of magnetization in the *xy*-plane (where the coil can detect it). The β spins begin to relax back into α spins, and the magnetization vector first shrinks exponentially, falling through zero to its thermal equilibrium value, M_0. After an interval τ, a 90° pulse is applied that rotates the remaining magnetization into the *xy*-plane, where it generates an FID signal. The frequency-domain spectrum is then obtained by Fourier transformation.

The intensity of the spectrum obtained in this way depends on the length of the magnetization vector that is rotated into the *xy*-plane. The length of that vector changes exponentially as the interval between the two pulses is increased, so the intensity of the spectrum also changes exponentially with increasing τ. We can therefore measure T_1 by fitting an exponential curve to the series of spectra obtained with different values of τ.

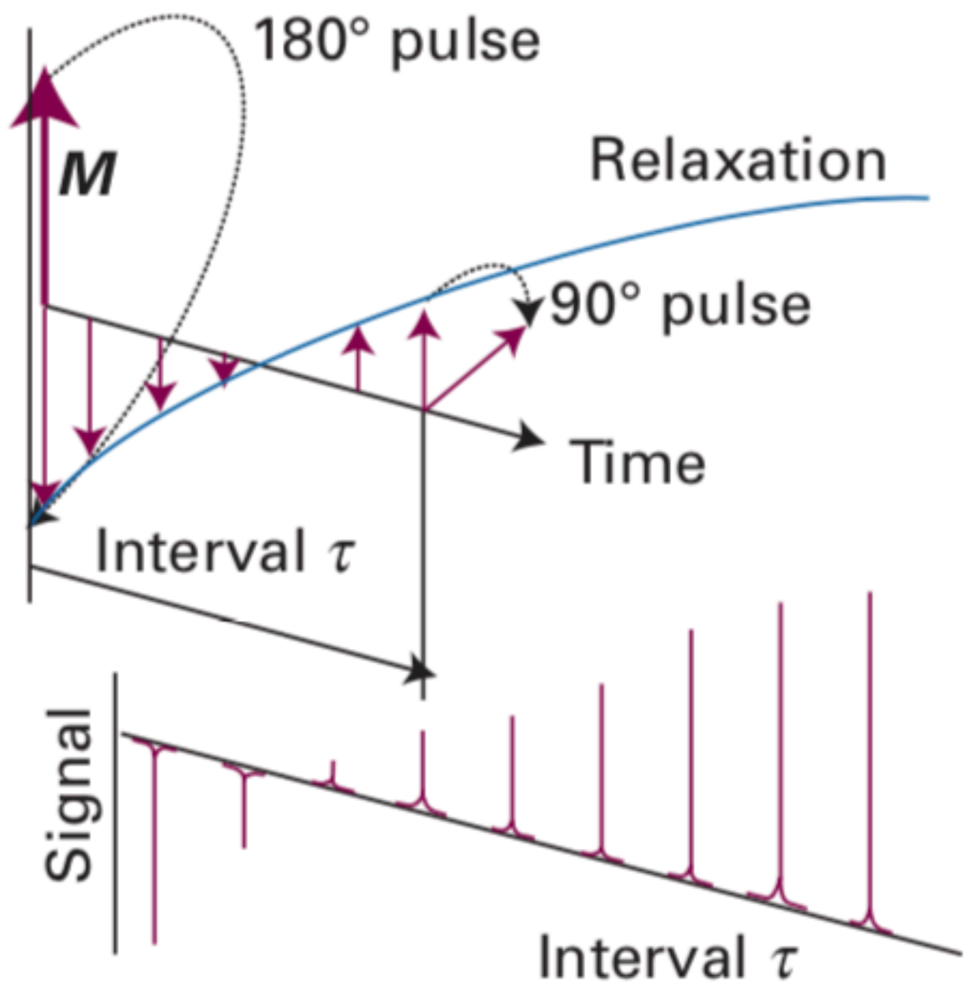


Fig. 14.39 The result of applying a 180° pulse to the magnetization in the rotating frame and the effect of a subsequent 90° pulse. The amplitude of the frequency-domain spectrum varies with the interval between the two pulses because spin–lattice relaxation has time to occur.

Bloch Equations

Net Magnetization (M) placed in a magnetic Field (B) will precess:

$$\frac{d\mathbf{M}(t)}{dt} = \mathbf{M}(t) \times \gamma \mathbf{B}(t)$$

and relax (R)

$$\frac{d\mathbf{M}(t)}{dt} = \mathbf{M}(t) \times \gamma \mathbf{B}(t) - \mathbf{R}(\mathbf{M}(t) - M_0)$$


Felix Bloch
(1905-1983)

and relax individual components:

$$\frac{dM_z(t)}{dt} = \gamma[M_x(t)B_y(t) - M_y(t)B_x(t)] - \frac{M_z(t) - M_0}{\mathrm{T}_1}$$

$$\frac{dM_x(t)}{dt} = \gamma[M_y(t)B_z(t) - M_z(t)B_y(t)] - \frac{M(t)_x}{\mathrm{T}_2}$$

$$\frac{dM_y(t)}{dt} = \gamma[M_z(t)B_x(t) - M_x(t)B_z(t)] - \frac{M(t)_y}{\mathrm{T}_2}$$