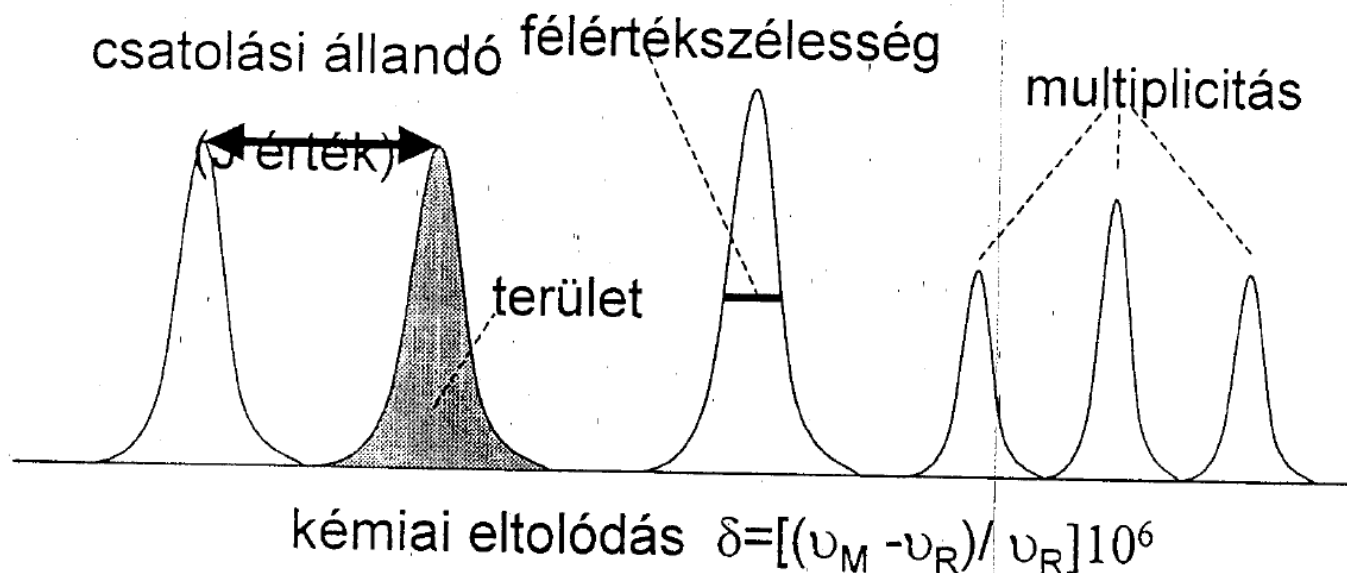


A nagy felbontású NMR-spektrumok öt jellemző paramétere



High-resolution NMR spectra provide a lot of information:

- (1) Shielding (σ), which can be determined from the experimentally measured chemical shifts (δ) (can be computed via QC);
- (2) Spin-spin coupling (J), from the hyperfine structure (can be computed via QC);
- (3) Dynamics, determined by the T_1 and T_2 spin relaxation times.

Chemical shift

The frequency (Larmor frequency) of an NMR transition depends on the local magnetic field, which slightly may differ from the magnetic flux density of the external field, \mathbf{B}_0 . This is basically due to the presence of the moving electrons and the other nuclei (*e.g.*, via the diamagnetic effect). We say that

$$B(\text{nucleus}) = B_0 - \sigma B_0 = B_0(1 - \sigma)$$

The **shielding constant** σ is less than about $10^{-5} = 10 \times 10^{-6}$ for protons and less than about $10^{-3} = 1000 \times 10^{-6}$ for most other nuclei. Since the magnitude of the screening depends on the orientation of the molecule with respect to the applied field, the correct physical picture is that the shielding is actually described by a second-rank tensor (a 3×3 matrix). However, for a liquid or a gas the directional part of the shielding tensor averages out so it may be treated as a scalar (it is more appropriate to talk about **isotropic shielding**).

In summary: identical nuclei in chemically different environments resonate at different values of the applied magnetic field. This is the physical effect responsible for the appearance of high-resolution NMR spectra of tremendous interest to chemists.

Determination of the absolute values of the shielding tensor (even that of the isotropic shielding constant) is a difficult task (even with today's tools offered by quantum chemistry). A practical solution chemists invented: determine relative values with respect to a reference compound containing the nucleus being studied.

^1H NMR: tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, TMS

^{13}C NMR: tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, TMS

Then (S = system investigated, R = reference compound):

$$\nu_S = \frac{\gamma}{2\pi} B_0 (1 - \sigma_S) \quad \text{and} \quad \nu_R = \frac{\gamma}{2\pi} B_0 (1 - \sigma_R).$$

The next important step forward is to define a dimensionless scale as follows:

$$\delta := \frac{\nu_S - \nu_R}{\nu_R} \times 10^6,$$

i.e.,

$$\begin{aligned}\delta &:= \frac{\frac{\gamma}{2\pi} B_0(1-\sigma_S) - \frac{\gamma}{2\pi} B_0(1-\sigma_R)}{\frac{\gamma}{2\pi} B_0(1-\sigma_R)} \times 10^6 = \\ &= \frac{\sigma_R - \sigma_S}{1 - \sigma_R} \times 10^6 = (\sigma_R - \sigma_S) \times 10^6\end{aligned}$$

The **chemical shift** δ is thus independent of the magnetic field strength (magnetic flux density) and is equal to the difference between the shielding constant of the reference and of the sample, expressed in parts per million (ppm). (Although, for example, the ^{13}C frequencies may change by several hundred ppm, this is still substantially less than 1% of the change of the appropriate Larmor frequency.)

For a given nucleus chemical shifts depend on a large number of factors. The most notable ones are as follows: atomic shielding (diamagnetic effect), neighboring atom effect (paramagnetic; double and triple bonds yield especially large effects), ring effect (diamagnetic effect of the π -ring of aromatic systems), ionic effect (*e.g.*, paramagnetic ions (Fe, Mn, Gd) in proteins and biological samples), and H-bond, as well as solvent effect.

Conclusions:

- (1) Chemical shift of the same nucleus in different molecules is different.
- (2) Within the same molecule δ 's are different for the same nucleus, the basis of the chemical application of NMR.

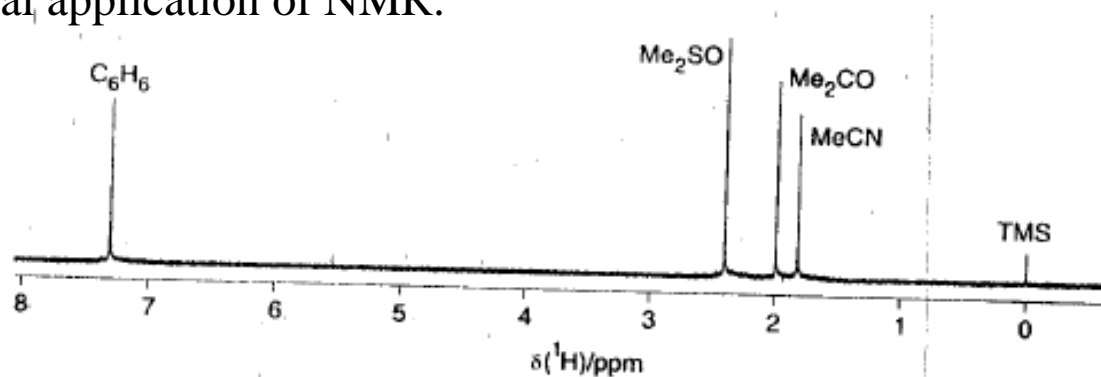
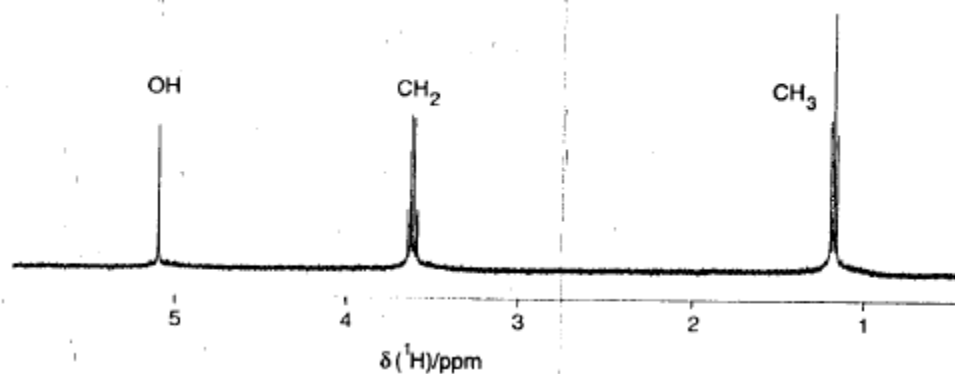
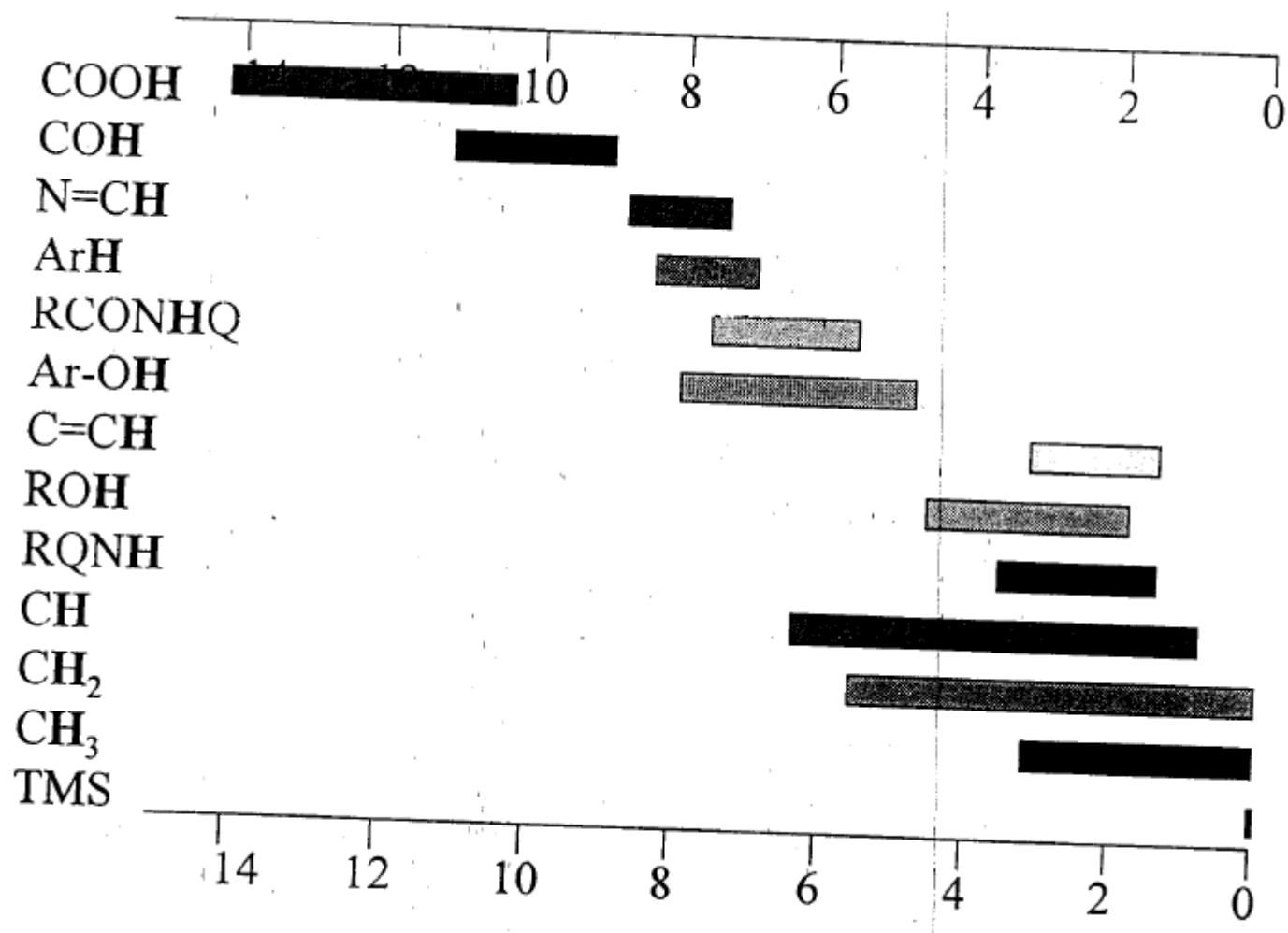


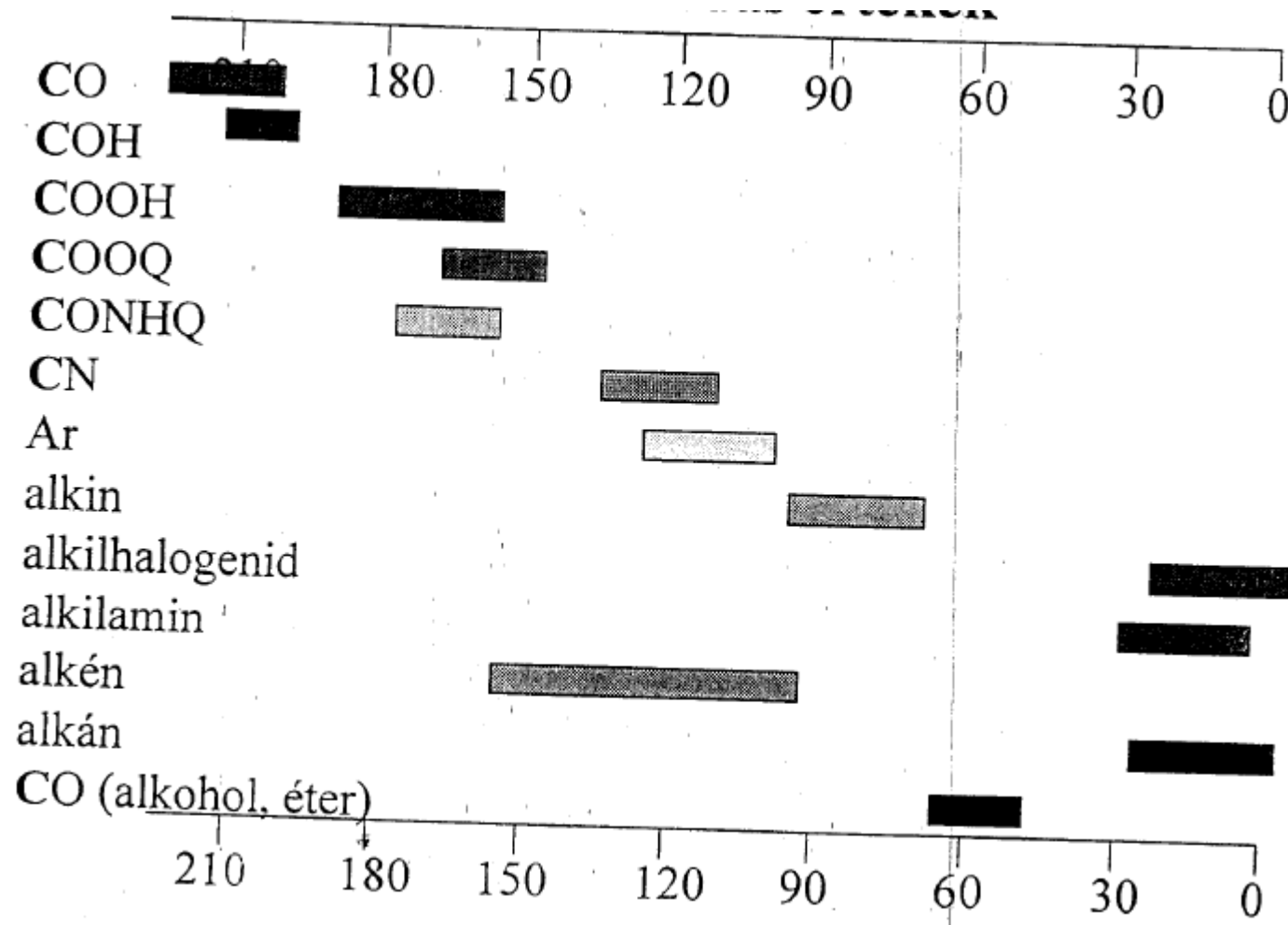
Fig. 2.5 400 MHz ^1H NMR spectrum of a mixture of benzene, dimethylsulphoxide, acetone, acetonitrile and tetramethylsilane.

Fig. 3.1 400 MHz ^1H NMR spectrum of liquid ethanol showing the splittings produced by spin-spin coupling. Compare this spectrum with Fig. 1.2, in which the fine structure is obscured by instrumental linebroadening.



Characteristic proton chemical shifts

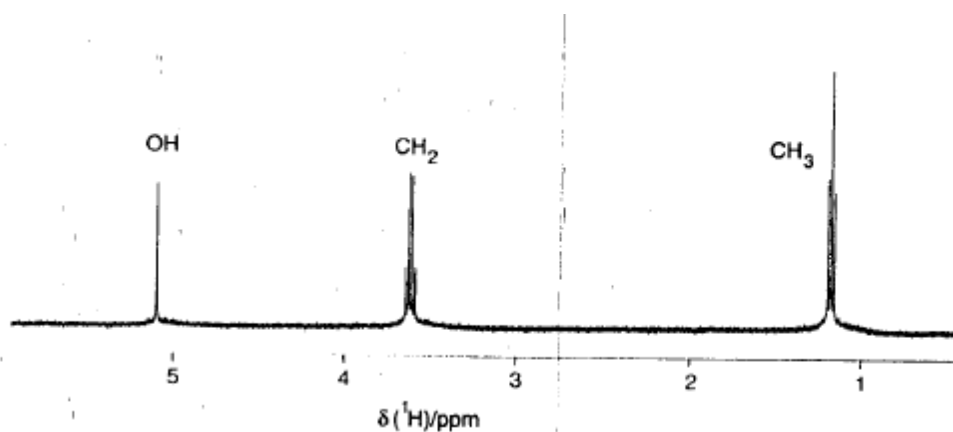


Characteristic ^{13}C chemical shifts

Spin-spin coupling

So far we have not talked about the interaction of the nuclear spins in different chemical environments. Nevertheless, based on the coupling of angular momentum vectors we expect that the energy of a system consisting of two (or more) nuclear spins will depend on the relative orientation of the spins. The interaction between nuclei which in NMR gives rise to the fine structure of the spectrum is called **spin-spin coupling**.

Fig. 3.1 400 MHz ^1H NMR spectrum of liquid ethanol showing the splittings produced by spin-spin coupling. Compare this spectrum with Fig. 1.2, in which the fine structure is obscured by instrumental linebroadening.



The strength of the interaction of two nuclei A and B is denoted by J_{AB} , unit: Hz. If $J > 0$, the two nuclei have a lower energy when their spins are antiparallel, while if $J < 0$, the opposite is true. J s are independent of the strength of the applied field..

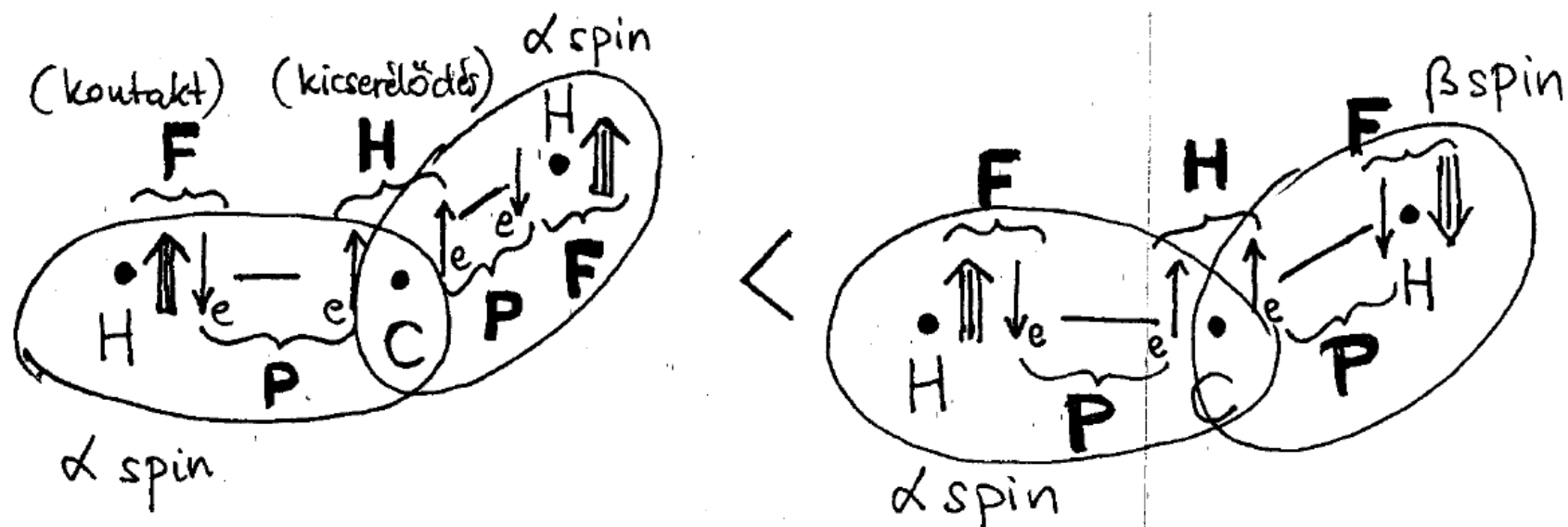
Two mechanisms could be responsible for the coupling: direct dipole-dipole interaction or a polarization mechanism.

1.) *Direct dipole-dipole interaction*

Occurs between the two nuclear spin magnetic moments (or electron–nucleus dipolar hyperfine interaction). The spherical average of such an interaction is zero \Rightarrow cannot account for the fine structure of nuclei in a molecule that is freely rotating in a fluid medium.

2.) *Polarization mechanism*

Utilizes the electron in the bonds as intermediaries in transmitting the interaction between the nuclei.



F: Fermi-contact interaction (a magnetic hyperfine interaction between a nucleus and an electron that approach each other so closely that they are effectively in contact; since only s electrons have a non-zero probability of being found at their own nucleus, only they have FCI) \rightarrow favors opposite spins

P: Pauli exclusion principle \rightarrow favors opposite spins

H: Hund's rule of maximum multiplicity \rightarrow favors same spin

Therefore, by the collaboration that we can represent as Fermi | Pauli | Hund | Pauli | Fermi, it is energetically favorable for the two nuclear spins to be antiparallel. If the orientation of either proton is changed, the energy rises slightly. Hence, the energy of the nuclei depends on their relative orientation, and we conclude that there is a spin–spin interaction (coupling).

If N bonds separate two nuclear spins, we may talk about a spin-spin coupling constant $^N J$ (an example is $^2 J_{\text{CH}} \rightarrow ^{13}\text{C}-\text{C}-\text{H}$). Characteristic spin-spin coupling values:

	sp	sp ²	sp ³
$^1 J_{\text{CH}}/\text{Hz}$	250	160	125

There are different energy levels, “waiting for” a resonance interaction with the incoming radiofrequency irradiation, due to spin-spin coupling. The resulting spectrum is explained by relying on the ΣI_z values of the interacting spin systems (groups).

Example 1: Splitting of the CH₃ signal due to CH₂

	ΣI_z	stat. weight
$\alpha\alpha$	1	1
$\alpha\beta$	0 \}	2
$\beta\alpha$	0 \}	
$\beta\beta$	-1	1

Example 2: Splitting of the CH₂ signal due to CH₃

	ΣI_z	stat. weight
$\alpha\alpha\alpha$	3/2	1
$\beta\alpha\alpha$	1/2 \}	3
$\alpha\beta\alpha$	1/2 \}	
$\alpha\alpha\beta$	1/2 \}	
$\alpha\beta\beta$	-1/2 \}	3
$\beta\alpha\beta$	-1/2 \}	
$\beta\beta\alpha$	-1/2 \}	
$\beta\beta\beta$	-1	1

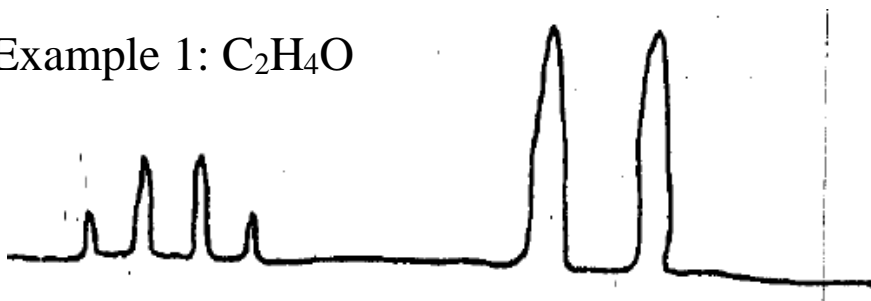
Intensity distribution in general: Pascal's triangle \rightarrow expand $(1+x)^N$ and select the coeffs

N

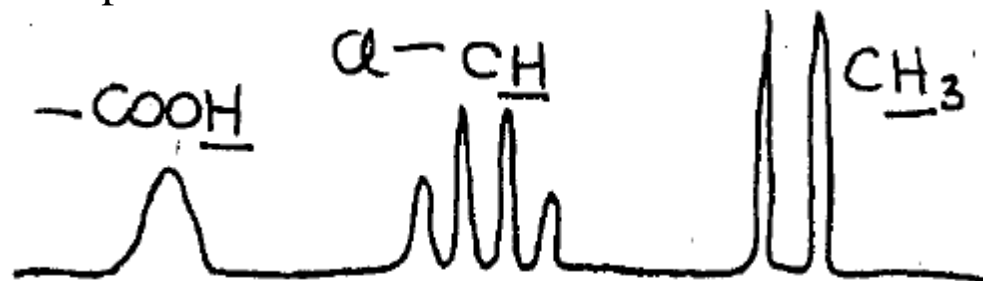
0				1				
1			1		1			
2		1		2		1		
3	1		3		3		1	
4	1	4		6		4		1

Structure determination:

Example 1: C_2H_4O



Example 2: $C_3H_5O_2Cl$



Mathematics of spin-spin coupling

Consider a molecule containing two identical spin-1/2 nuclei and no other nuclei with nonzero spin:

$$E = -\mathbf{B}_2 \cdot \hat{\boldsymbol{\mu}}_1 = -g_N \mu_N \hbar^{-1} \mathbf{B}_2 \cdot \hat{\mathbf{I}}_1,$$

where μ_N is the nuclear magneton, and \mathbf{B}_2 is the magnetic field generated by $\boldsymbol{\mu}_2$ at nucleus 1, having a magnetic dipole moment of $\hat{\boldsymbol{\mu}}_1$.

Since $\mathbf{B}_2 \propto \boldsymbol{\mu}_2 \propto \mathbf{I}_2$,

$$-g_N \mu_N \hbar^{-1} \mathbf{B}_2 \cdot \hat{\mathbf{I}}_1 \cong \left(\frac{h}{\hbar^2} \right) J_{12} (\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2),$$

and the proportionality constant J_{12} is what we call spin–spin coupling constant (unit: Hz).

Thus, the NMR Hamiltonian of our model system has a simple form with a single added interaction term:

$$\hat{H} = -\frac{g_N \mu_N B_0}{\hbar} (1 - \sigma_1) \hat{I}_{z1} - \frac{g_N \mu_N B_0}{\hbar} (1 - \sigma_2) \hat{I}_{z2} + \frac{h J_{12}}{\hbar^2} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2.$$

Unfortunately, this Hamiltonian is not separable into a sum of operators for the individual nuclei. Solution: expand the unknown wave functions in terms of a *complete* set of basis functions.

Let α and β denote nuclear spin wave functions with $M_I = +1/2$ and $-1/2$, respectively. If the spin–spin coupling term is omitted from \hat{H} , we get

$$\hat{H}_{\text{red}} = -g_N \mu_N B_0 \hbar^{-1} (1 - \sigma_1) \hat{I}_{z1} - g_N \mu_N B_0 \hbar^{-1} (1 - \sigma_2) \hat{I}_{z2} = -c_1 \hbar^{-1} \hat{I}_{z1} - c_2 \hbar^{-1} \hat{I}_{z2},$$

the eigenfunctions of the reduced problem become proportional to $|M_{I1}(1)\rangle |M_{I2}(2)\rangle$, while the eigenvalues will be $M_{I1} = \pm 1/2$ and $M_{I2} = \pm 1/2$.

Thus, the complete set of basis functions is

$$\begin{aligned} \phi_1 &= \alpha(1)\alpha(2) & \phi_2 &= \alpha(1)\beta(2) \\ \phi_3 &= \beta(1)\alpha(2) & \phi_4 &= \beta(1)\beta(2) \end{aligned}$$

To set up the corresponding 4×4 matrix representation of the Hamiltonian and the secular determinant, take advantage of the following known relations:

$$\hat{I}_z \alpha = \frac{1}{2} \hbar \alpha \quad \text{and} \quad \hat{I}_z \beta = -\frac{1}{2} \hbar \beta.$$

Furthermore, angular momentum algebra yields the following relations –also applicable for electron spins–

$$\begin{aligned} \hat{I}_x \alpha &= \frac{1}{2} \hbar \beta, & \hat{I}_x \beta &= \frac{1}{2} \hbar \alpha, \\ \hat{I}_y \alpha &= \frac{1}{2} i \hbar \beta, & \hat{I}_y \beta &= -\frac{1}{2} i \hbar \alpha. \end{aligned}$$

Then, with the help of the last four equations we can write, for example, that

$$\begin{aligned} hJ_{12} \hbar^{-2} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \phi_1 &= hJ_{12} \hbar^{-2} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 [\alpha(1)\alpha(2)] = \\ &= \frac{1}{4} hJ_{12} [\beta(1)\beta(2) - \beta(1)\alpha(2) + \alpha(1)\alpha(2)] = \frac{1}{4} hJ_{12} \phi_1 \end{aligned}$$

Similarly,

$$\begin{aligned} hJ_{12} \hbar^{-2} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \phi_2 &= \frac{1}{4} hJ_{12} (2\phi_3 - \phi_2) \\ hJ_{12} \hbar^{-2} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \phi_3 &= \frac{1}{4} hJ_{12} (2\phi_2 - \phi_3) \\ hJ_{12} \hbar^{-2} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \phi_4 &= \frac{1}{4} hJ_{12} \phi_4. \end{aligned}$$

To move forward toward building the 4×4 matrix representation of the Hamiltonian, we can summarize the results as

$$\begin{aligned}\hat{H}\phi_1 &= \left(-\frac{1}{2}c_1 - \frac{1}{2}c_2 + \frac{1}{4}hJ_{12}\right)\phi_1 \\ \hat{H}\phi_2 &= \left(-\frac{1}{2}c_1 + \frac{1}{2}c_2 - \frac{1}{4}hJ_{12}\right)\phi_2 + \frac{1}{2}hJ_{12}\phi_3 \\ \hat{H}\phi_3 &= \left(\frac{1}{2}c_1 - \frac{1}{2}c_2 - \frac{1}{4}hJ_{12}\right)\phi_3 + \frac{1}{2}hJ_{12}\phi_2 \\ \hat{H}\phi_4 &= \left(\frac{1}{2}c_1 + \frac{1}{2}c_2 + \frac{1}{4}hJ_{12}\right)\phi_4.\end{aligned}$$

Note that ϕ_1 and ϕ_4 are eigenfunctions of the Hamiltonian, so that we already have two of the solutions of our time-independent Schrödinger equation, those corresponding to the two one-dimensional blocks of the representation.

The next step is the determination of the matrix elements of the Hamiltonian (but only for the remaining two-dimensional block involving ϕ_2 and ϕ_3). For example,

$$\langle \phi_2 | \hat{H} | \phi_2 \rangle = \left(-\frac{1}{2}c_1 + \frac{1}{2}c_2 - \frac{1}{4}hJ_{12}\right)\langle \phi_2 | \phi_2 \rangle + \frac{1}{2}hJ_{12}\langle \phi_2 | \phi_3 \rangle = -\frac{1}{2}c_1 + \frac{1}{2}c_2 - \frac{1}{4}hJ_{12}.$$

After evaluating all the required matrix elements, one can set up the following secular determinant:

$$\begin{vmatrix} -\frac{1}{2}(c_1 + c_2) + \frac{1}{4}hJ_{12} - E_i & 0 & 0 & 0 \\ 0 & -\frac{1}{2}(c_2 - c_1) - \frac{1}{4}hJ_{12} - E_i & \frac{1}{2}hJ_{12} & 0 \\ 0 & \frac{1}{2}hJ_{12} & -\frac{1}{2}(c_1 - c_2) - \frac{1}{4}hJ_{12} - E_i & 0 \\ 0 & 0 & 0 & \frac{1}{2}(c_1 + c_2) + \frac{1}{4}hJ_{12} - E_i \end{vmatrix} = 0$$

Thus, we arrived at the following eigenfunctions and eigenvalues for our model two spin-1/2 nuclei problem:

$$\begin{aligned}
 E_1 &= -\frac{1}{2}(c_1 + c_2) + \frac{1}{4}hJ_{12} & \psi_1 &= \alpha(1)\alpha(2) \\
 E_2 &= -\frac{1}{4}hJ_{12} - \frac{1}{2}\left[(c_1 - c_2)^2 + h^2J_{12}^2\right]^{1/2} & \psi_2 &= a\alpha(1)\beta(2) - b\beta(1)\alpha(2) \\
 E_3 &= -\frac{1}{4}hJ_{12} + \frac{1}{2}\left[(c_1 - c_2)^2 + h^2J_{12}^2\right]^{1/2} & \psi_3 &= b\alpha(1)\beta(2) + a\beta(1)\alpha(2) \\
 E_4 &= \frac{1}{2}(c_1 + c_2) + \frac{1}{4}hJ_{12} & \psi_4 &= \beta(1)\beta(2)
 \end{aligned}$$

Substituting back the c_i values, our relatively simple final energy expressions are:

$$\begin{aligned}
 E_1 &= -g_N\mu_N B_0\left(1 - \frac{1}{2}\sigma_1 - \frac{1}{2}\sigma_2\right) + \frac{1}{4}hJ_{12} \\
 E_2 &= -\frac{1}{4}hJ_{12} - \frac{1}{2}h\left[J_{12}^2 + g_N^2\mu_N^2 B_0^2 h^{-2}(\sigma_2 - \sigma_1)^2\right]^{1/2} \\
 E_3 &= -\frac{1}{4}hJ_{12} + \frac{1}{2}h\left[J_{12}^2 + g_N^2\mu_N^2 B_0^2 h^{-2}(\sigma_2 - \sigma_1)^2\right]^{1/2} \\
 E_4 &= g_N\mu_N B_0\left(1 - \frac{1}{2}\sigma_1 - \frac{1}{2}\sigma_2\right) + \frac{1}{4}hJ_{12}
 \end{aligned}$$

Comments:

- (1) As during the variational solution we employed no approximations (our basis set was complete), the obtained energies (and the wave functions) are “exact”.
- (2) In the limit of $J_{12} \rightarrow 0$, the energy levels (and necessarily the wave functions) go over the energy levels characterizing the systems of (two) independent nuclear spins ($E = -\mu_N B_0 \sum_i g_i (1 - \sigma_i) M_{I,i}$).
- (3) Once again, the step required to move from energy levels to spectra is to determine the selection rules. One could prove that the NMR selection rules of two coupled protons are

$$\begin{array}{cccc} \psi_1 \leftrightarrow \psi_2 & \psi_1 \leftrightarrow \psi_3 & \psi_2 \leftrightarrow \psi_4 & \psi_3 \leftrightarrow \psi_4 \\ \psi_1 \leftrightarrow \psi_4 & \psi_2 \leftrightarrow \psi_3 & & \end{array}$$

Therefore, there are altogether four allowed transitions.

Transition	Frequency	Rel. intensity
$\psi_1 \rightarrow \psi_2$	$\nu_0(1 - \frac{1}{2}\sigma_1 - \frac{1}{2}\sigma_2) - \frac{1}{2}J_{12} - \frac{1}{2}[J_{12}^2 + \nu_0^2\delta_{12}^2]^{1/2}$	$(a - b)^2$
$\psi_3 \rightarrow \psi_4$	$\nu_0(1 - \frac{1}{2}\sigma_1 - \frac{1}{2}\sigma_2) + \frac{1}{2}J_{12} - \frac{1}{2}[J_{12}^2 + \nu_0^2\delta_{12}^2]^{1/2}$	$(a + b)^2$
$\psi_1 \rightarrow \psi_3$	$\nu_0(1 - \frac{1}{2}\sigma_1 - \frac{1}{2}\sigma_2) - \frac{1}{2}J_{12} + \frac{1}{2}[J_{12}^2 + \nu_0^2\delta_{12}^2]^{1/2}$	$(a + b)^2$
$\psi_2 \rightarrow \psi_4$	$\nu_0(1 - \frac{1}{2}\sigma_1 - \frac{1}{2}\sigma_2) + \frac{1}{2}J_{12} + \frac{1}{2}[J_{12}^2 + \nu_0^2\delta_{12}^2]^{1/2}$	$(a - b)^2$

$$\delta_{12} \equiv \sigma_2 - \sigma_1 \quad \nu_0 = g_N \mu_N B_0 h^{-1}$$

- (4) The appearance of the spectrum is independent of the sign of J_{12} . The appearance of the spectrum will depend on the relative magnitude of $\nu_0\delta_{12}$ and J_{12} .
- (5) For two chemically equivalent protons ($\sigma_1 = \sigma_2 = \sigma$) $a = b$; thus, the two outer lines disappear, while the inner lines become degenerate. It often happens (but not always!) that chemically equivalent nuclei give no spin-spin splitting.

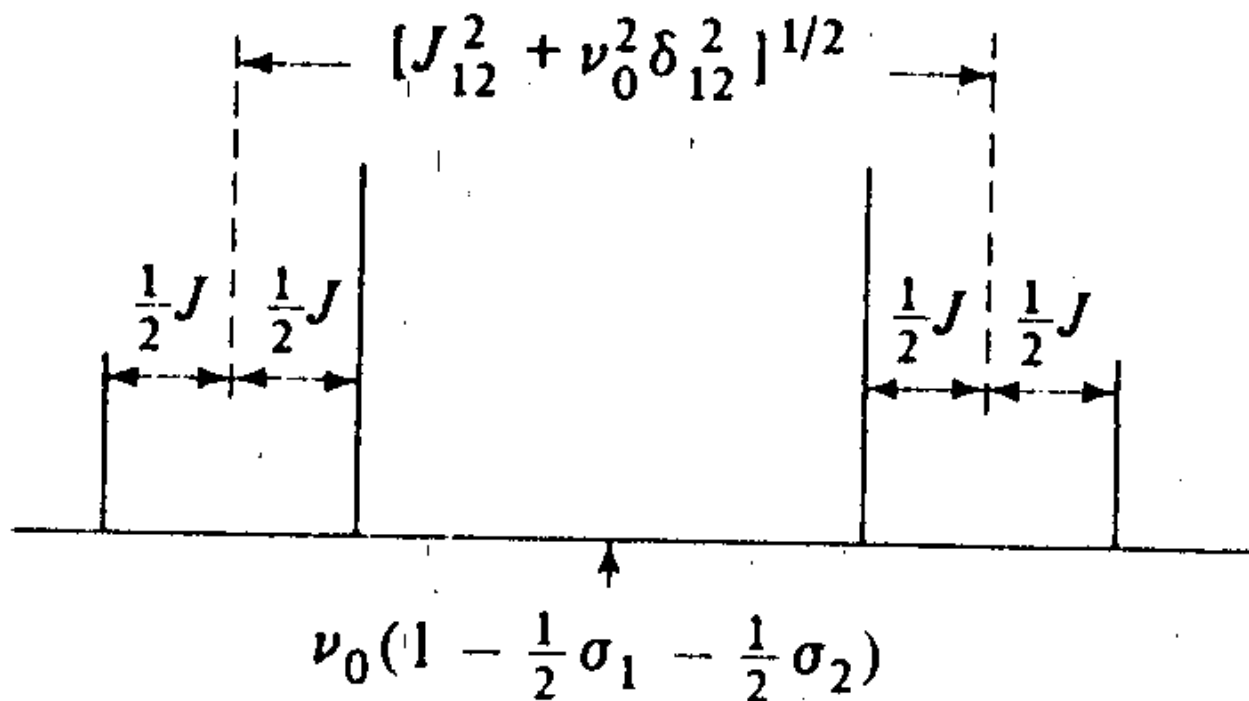


Fig. 8.5 Pattern of the NMR spectrum of two coupled nuclei of spin $\frac{1}{2}$.

Conclusion: the nature of the NMR spectrum depends on the relative magnitudes of $\nu_0 \delta_{12}$ and J_{12} .

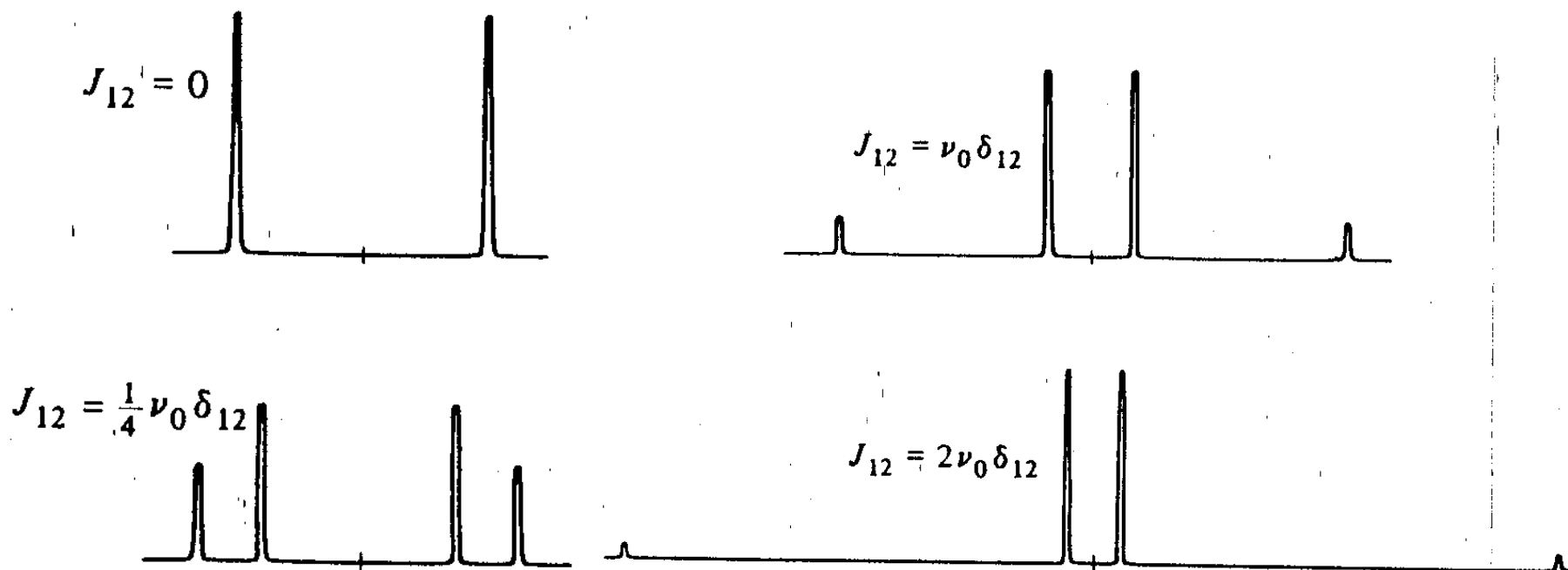


Fig. 8.6 The NMR spectrum of two nuclei of spin $\frac{1}{2}$, as a function of $J_{12}/\nu_0\delta_{12}$. In this figure, $\nu_0\delta_{12}$ is held fixed while J_{12} varies.

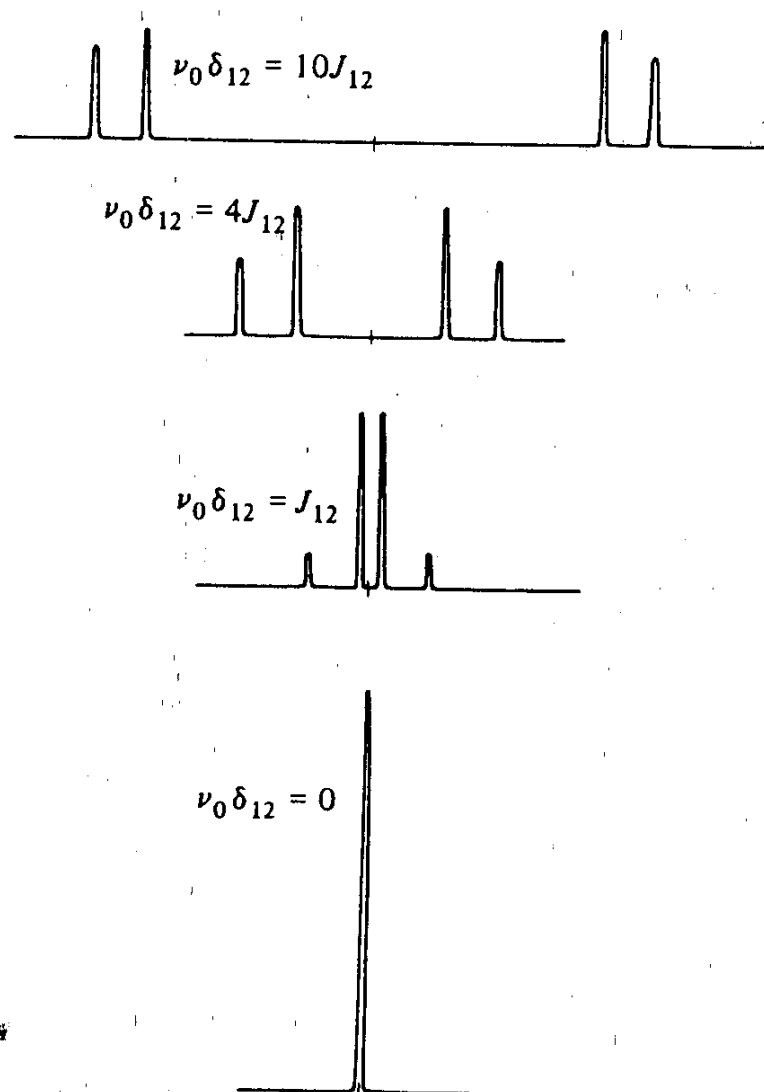


Fig. 8.7 The NMR spectrum of two nuclei of spin $\frac{1}{2}$, as a function of $J_{12}/\nu_0\delta_{12}$. In this figure, J_{12} is held fixed while $\nu_0\delta_{12}$ varies.

NMR spectroscopists employ a standard terminology to refer to the relative importance of the $\nu_0\delta_{12}$ and J_{12} terms. The essence of this notation:

- letters from the same part of the alphabet label nuclei for which J_{12} is comparable in magnitude to $\nu_0\delta_{12}$,
- letters from the two ends of the alphabet label nuclei for which $J_{12} \ll \nu_0\delta_{12}$.

In the latter case the usual designation of the spectrum is AX. It contains two doublets, separated from each other by $\nu_0\delta_{12}$. All lines have essentially the same intensity. AB: no equal intensities, four lines. Quite frequently in organic compounds the spin-spin splittings are much smaller than the chemical shifts.

For a molecule with three spin-1/2 nuclei, the secular determinant is of size 8×8 , detailed analysis is omitted. A couple of possible spectrum designations: A_3 , AB_2 , AX_2 , ABC, and ABX. For four coupled nuclear spins the mathematical analysis will become complicated if performed on paper but remains simple if computer algebra is used.

Generally, the appearance of NMR spectra is complicated enough so that all cases should be treated individually.

Factors determining the appearance of NMR spectra

Chemically equivalent nuclei: nuclei are related by a symmetry operation of the molecule and have the same chemical shift.

Magnetically equivalent nuclei: nuclei are chemically equivalent AND they also have identical spin-spin interactions.

Examples:

CH_2F_2 Chemically equivalent protons, both H are equally distant from F's, so there is no distinction between them \Rightarrow magnetically equivalent protons

$\text{CH}_3\text{CH}_2\text{OH}$ Strictly speaking the CH_3 protons in ethanol are magnetically inequivalent on account of their different interactions with the neighboring $-\text{CH}_2$ protons. However, they are in practice made magnetically equivalent by the rapid rotation of the CH_3 group, which averages out any differences.

Dilute-spin species: ^{13}C (as well as ^{15}N) is a dilute-spin species in the sense that it is unlikely that more than one ^{13}C nucleus will be found in any given molecule. It is normally not necessary to take into account ^{13}C – ^{13}C spin-spin coupling (however, isotopic enrichment).

Abundant-spin species: a molecule is likely to contain many of them (*e.g.*, ^1H). If we were observing a ^{13}C NMR spectrum, we would obtain a very complex spectrum on account of the coupling of the ^{13}C nucleus with all the protons that are present.

Proton decoupling (an example): If the CH_3 protons of ethanol are irradiated with a second, strong, resonant *rf* source, they undergo rapid spin reorientations and the ^{13}C nucleus senses an average orientation. Thus, its resonance is a single line and not a 1 : 3 : 3 : 1 quartet. Additional advantage: sensitivity enhancement. Disadvantage: signal strength is no longer proportional to the number of nuclei.

Chemical exchange: loss of structure in solvents able to exchange protons with the sample. For example, ROH_α rapidly converts to ROH_β and then to ROH_α again, because the protons provided by the solvent molecules in successive exchanges have random spin orientations. This effect is observed when the lifetime of a molecule due to chemical exchange is so short that the lifetime broadening is greater than the doublet splitting. In very dry alcohol the exchange rate may be slow enough to detect the $\text{ROH}_\alpha - \text{ROH}_\beta$ splitting.

Conformational exchange: the appearance of an NMR spectrum is changed if magnetic nuclei can jump rapidly between different environments (conformations). For example, when the axial–equatorial inversion rate is slow, two sets of lines is observed, when the inversion is fast, single line at the mean of the two chemical shifts.

Temperature dependence: example: cyclohexane, from the temperature-dependence of the NMR spectrum the height of the hindering barrier can be determined.

Deuterium substitution: simplifies NMR spectra. $g_{\text{D}}/g_{\text{H}} \approx 1/6$, hence H–D spin-spin coupling is about one-sixth of the corresponding H–H coupling. Moreover, the D resonances do not appear in the ^1H portion of the spectrum.

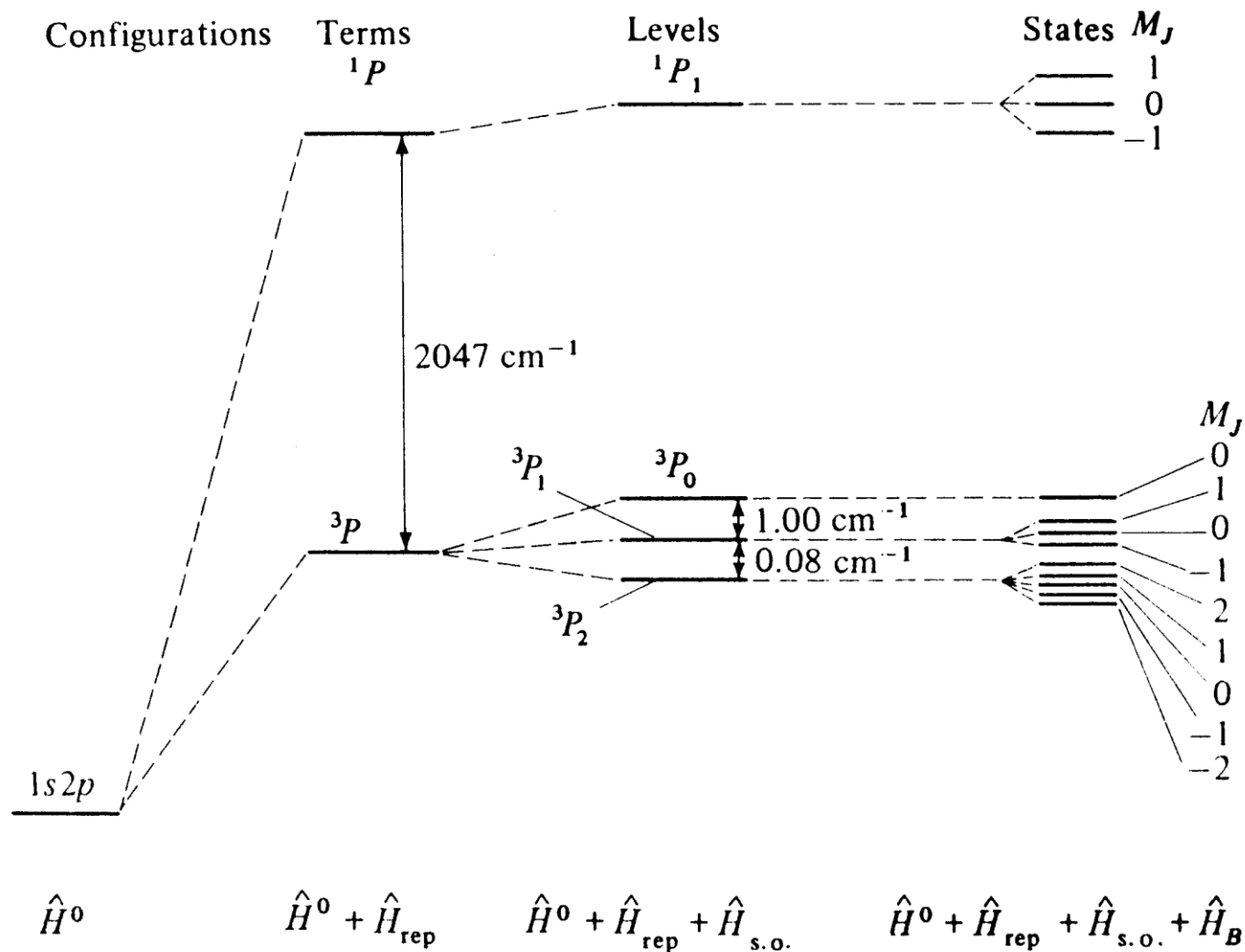


Figure 11.6 Effect of inclusion of successive terms in the atomic Hamiltonian for the $1s2p$ helium configuration. \hat{H}_B is not part of the atomic Hamiltonian but is due to an applied magnetic field.