EPR Interactions

Electron-Nucleus Magnetic Interaction

- contact Fermi mechanism
- dipolar term

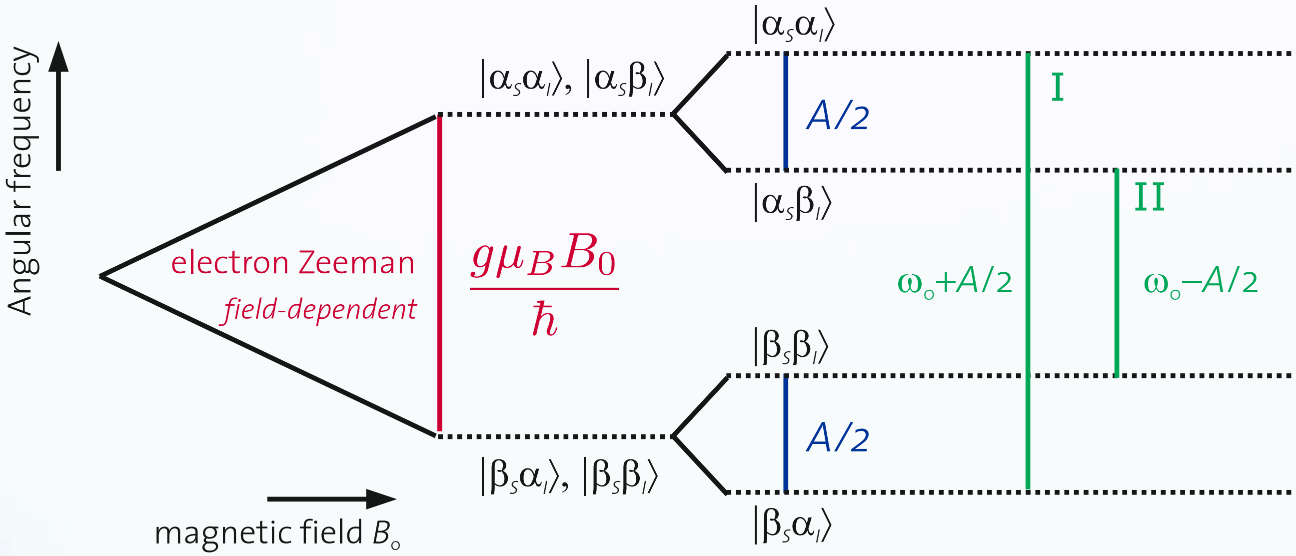
anisotropic (zero trace)

- pseudo contact term

interaction between the nuclear spin and the orbital moment

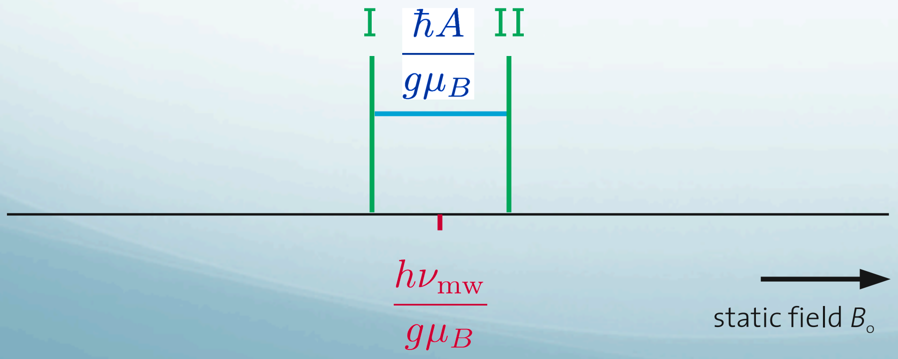
is a function of g anisotropy g (non zero trace: is observed in solution)

Manifestation of hyperfine couplings in EPR spectra



- level shift by hyperfine interaction: $m_S m_I A$
- selection rules: $|\Delta m_S| = 1, \Delta m_I = 0$

Field-swept EPR spectrum



- be aware: hyperfine couplings are given in
  - field units (G, mT)
  - frequency units (MHz, $A/2\pi$)
  - wave numbers (cm^{-1}, $A/2\pi c$)

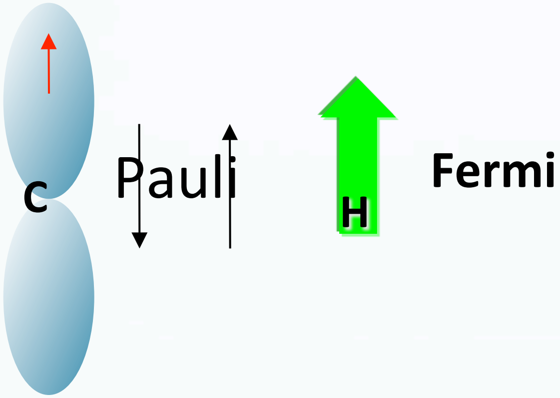
1 G = 0.1 mT ≈ 2.8 MHz ≈ 10^{-4} cm^{-1} (at $g=g_e$)

1) Fermi Contact Term

- ✓ e.g. H atom
- ✓due to a non zero probability to find the e- on the nucleus
- ✓exclusively foe s e-
- ✓in this case it is a scalar. The s orbital is spherically symmetric and therefore it must be isotropic
- ✓ very important for the determination of the structure of organic radicals
- ✓e.g. π radicals (e- in a p orbital) a is proportional to the probability to find e- on the close C

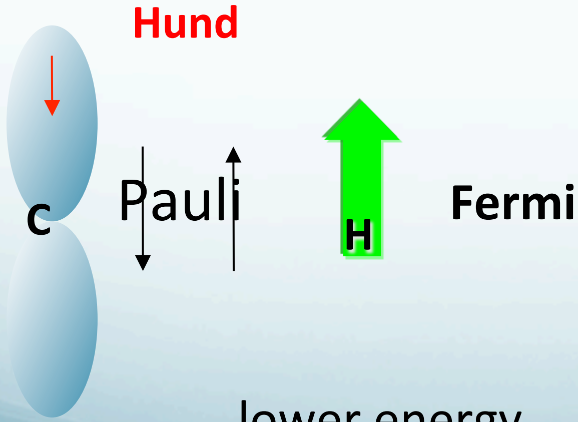
- polarization mechanism for the hyperfine interaction

e.g. for the interaction of the π e- of an aromatic ring with the H nuclei



this hyperfine interaction amounts to

28 G (2.8 mT)



lower energy

for the methyl radical, which is planar

$|a_C| = 3.83$ mT e $|a_H| = 2.30$ mT

2) Dipolar Term A

- Interaction between the magnetic dipoles of the e- and the nucleus
- described according to classical physics
- does not occur with e- with pure s character (spherical symmetry)
- anisotropic with zero trace (averaged out in solution)
- written by capital A maiuscola because it is a tensor

3) Pseudocontact Term

- through space
- it is originated by the nuclear spin and the e- orbital moment
- it is function of the anisotropy g
- non zero trace: it is observed in solution and originates the paramagnetic shift in the NMR spectra

Interaction of Other Electron Spins

- diradicals
- triplet states

depending on the strength of the interaction

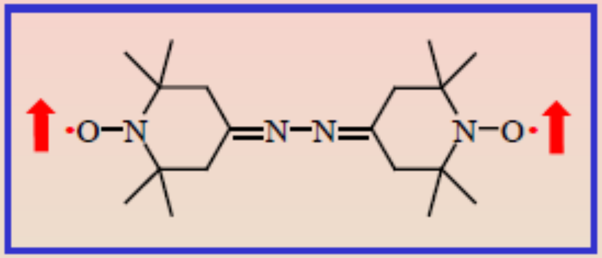
in the former case are separated by a molecular segment

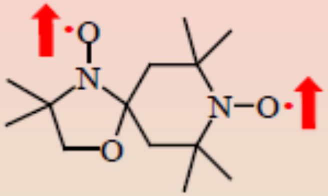
1) exchange interaction ***electric*** (Coulomb) interaction between the two e

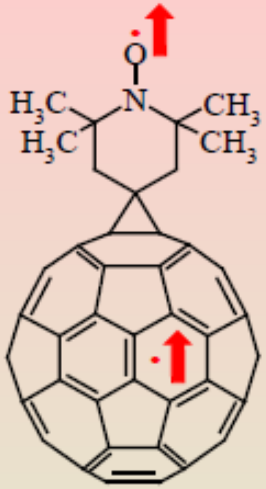
2) dipolar interaction magnetic interaction

Spettri EPR di molecole con due elettroni spaiati

- Biradicali



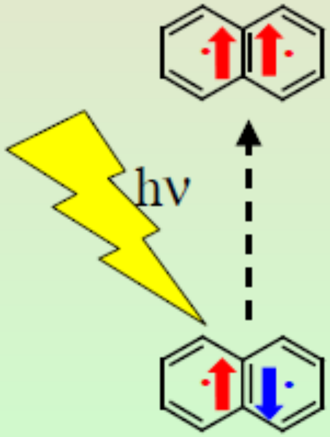




si osserva lo spettro EPR
nello stato elettronico fondamentale

- Tripletti

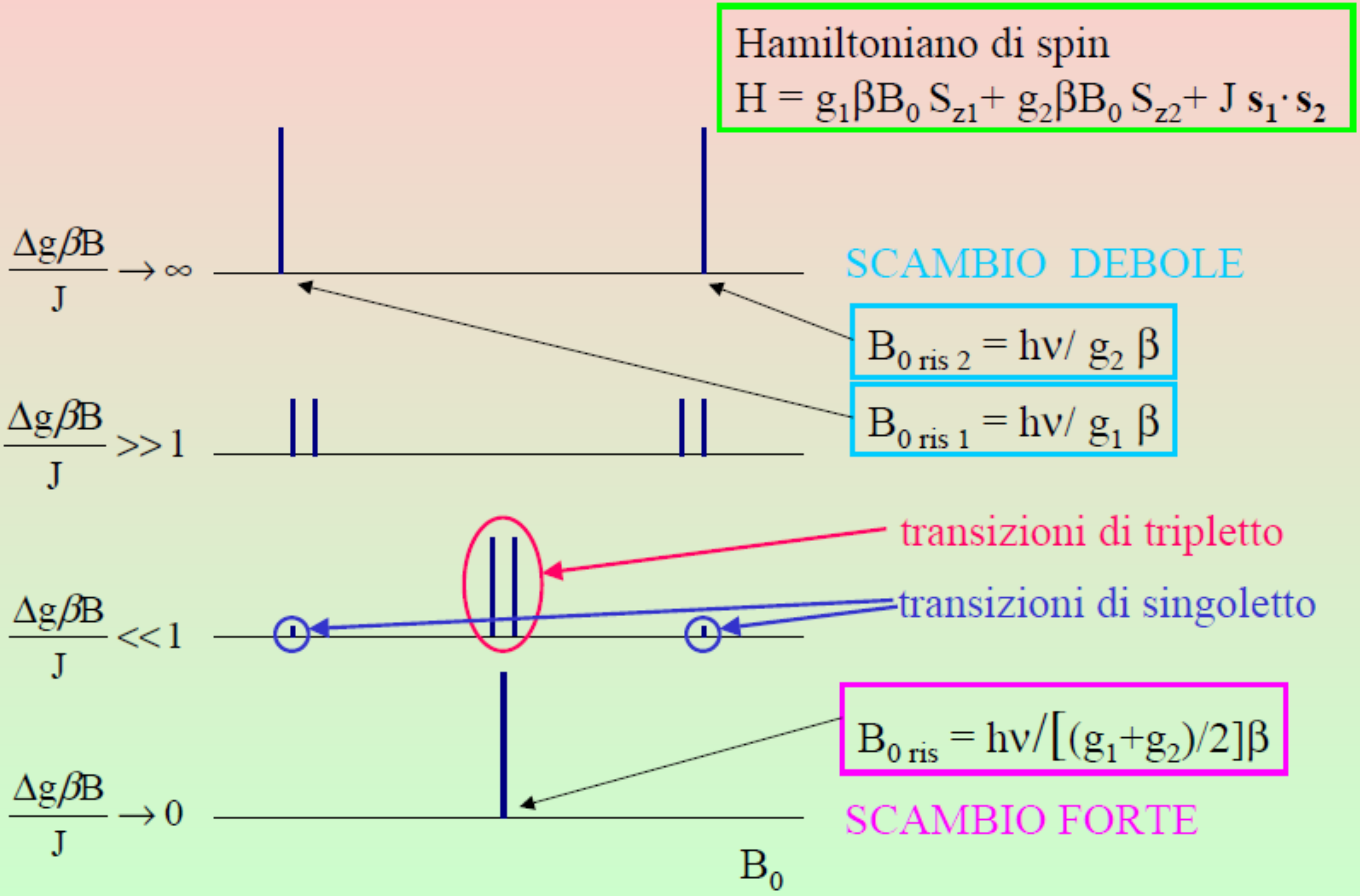
Per molte molecole organiche lo stato di tripletto è uno stato elettronico eccitato



si può osservare lo spettro EPR

~~spettro EPR~~

Spettri EPR di biradicali



Hamiltoniano di spin

$H = g_1\beta B_0 S_{z1} + g_2\beta B_0 S_{z2} + J\,\mathbf{s_1}\cdot\mathbf{s_2}$

$\frac{\Delta g\beta B}{J} \rightarrow \infty$

SCAMBIO DEBOLE

$B_{0\ ris\ 2} = h\nu/\ g_2\ \beta$

$B_{0\ ris\ 1} = h\nu/\ g_1\ \beta$

$\frac{\Delta g\beta B}{J} >> 1$

transizioni di tripletto

transizioni di singoletto

$\frac{\Delta g\beta B}{J} << 1$

$B_{0\ ris} = h\nu/[(g_1+g_2)/2]\beta$

$\frac{\Delta g\beta B}{J} \rightarrow 0$

SCAMBIO FORTE

Dipole Interaction (solid state)

Originates the largest splitiing of the EPR spectrum, therefore it is called **fine splitting**. It is the magnetic interaction through space between two close electronic magnetic moments

The D matrix of the dipolar coupling has zero trace: no splitting in isotropic solution

- In the case of ESR it is known as **Z**ero **F**ield **S**plitting matrix, because the energy levels are no longer degenerate in the absence of magnetic field (i.e. at zero magnetic field).
- It is indipendent of the static magnetic field
- Not only the through space interaction between the two unpaired e-, but also the spin-orbit interaction originates a term of the same kind

For the dipolar interaction tensor the elements on the diagonal of the matrix in the Principal Axes System
are expressed by two quantities (D and E) since it has zero trace (at variance with the tensor g where they are 3)

$$\boxed{D = \frac{3}{2} D_{33}} \qquad \boxed{E = \frac{1}{2}\left(D_{11} - D_{22}\right)}$$

Usually they are reported in cm^{-1}.
Since the usual spectrum scale is either G orT, D’ are E’ the D and E values in T:

$$D' = \frac{D}{g_e \mu_B} \qquad E' = \frac{E}{g_e \mu_B}$$

1 T corresponds to 0.93 cm^{-1} (0.011kJ·mol^{-1}) for $g_e \approx 2$
Usually the D values range between 0.001 a 2 cm^{-1}, thus D’ lies in the range 1 mT - 2 T.

The distance r between the two e- in pm, using D’ in mT is obtained by the formula.

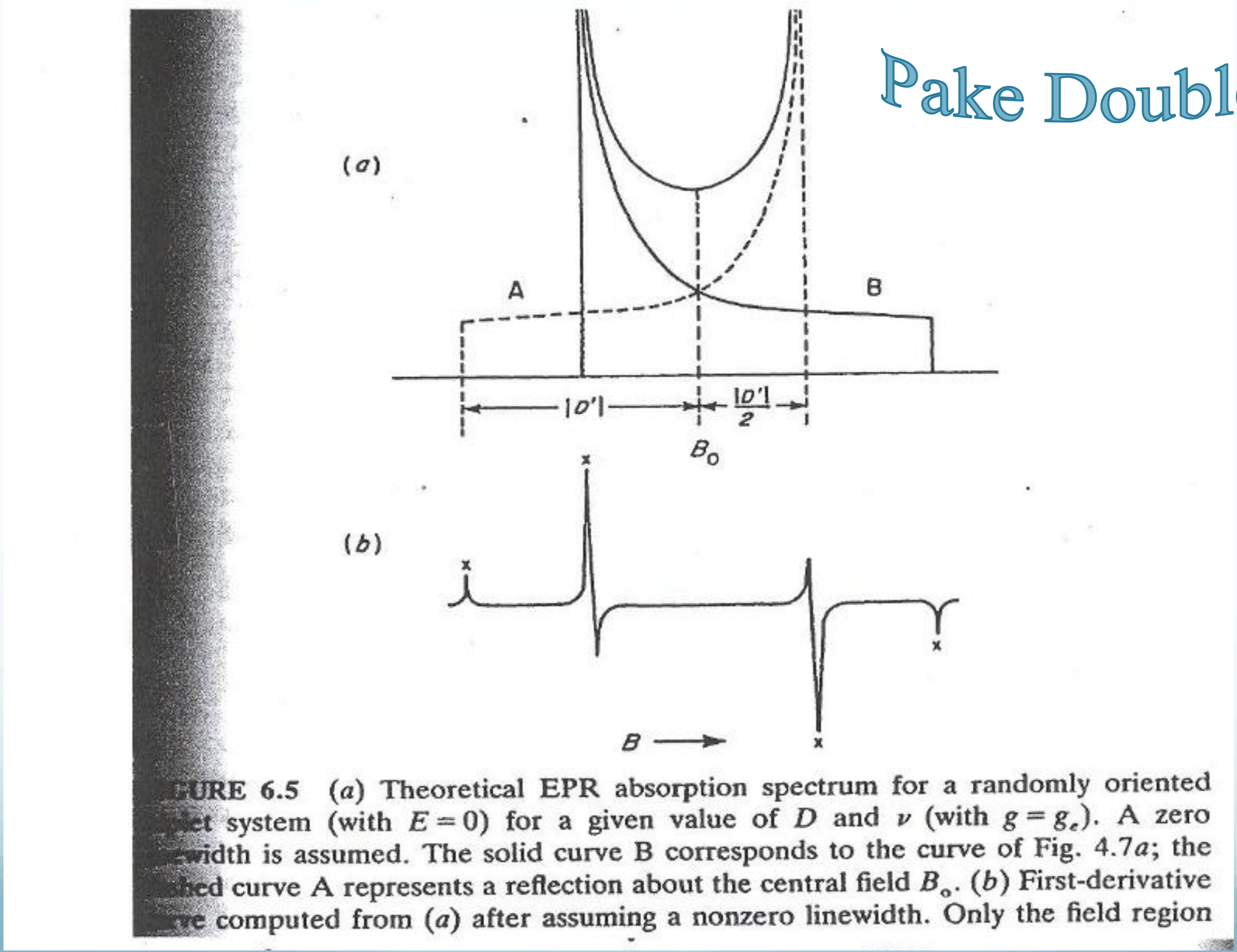
$$r = \sqrt[3]{\frac{2.78 \cdot 10^{9}}{|D'|}}$$

Due to the large D value for two e- in a triplet state, the Brownian motion in solution usually does not succeed in averaging it to zero . The signals are very broad, hampering the obtainment of the spectrum in solution, except for quite far apart e-pairs.

Usually, the spectra are recorded from powders or frozen solutions.

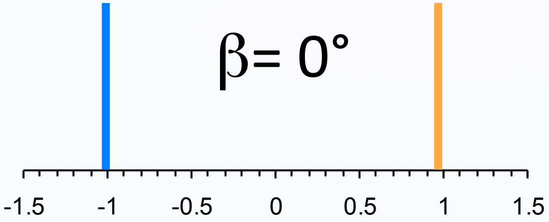
The distribution of orientations must be considered

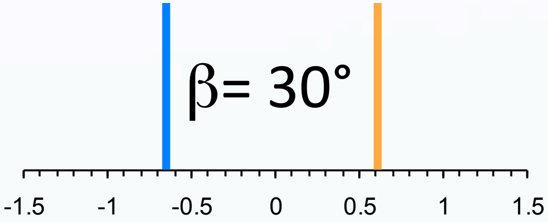
Pake Doublet

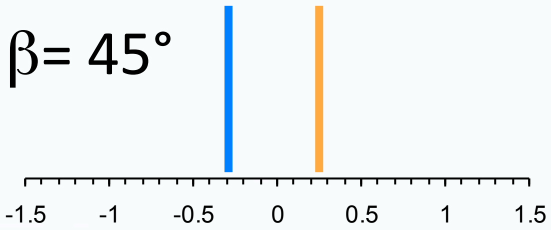


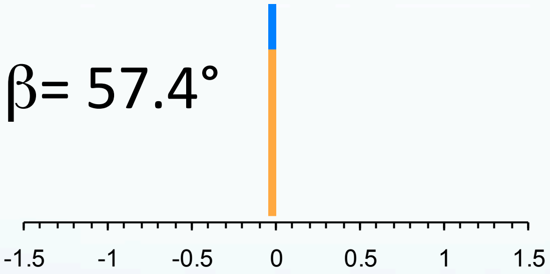
URE 6.5 (*a*) Theoretical EPR absorption spectrum for a randomly oriented
plet system (with $E = 0$) for a given value of D and ν (with $g = g_e$). A zero
width is assumed. The solid curve B corresponds to the curve of Fig. 4.7*a*; the
hed curve A represents a reflection about the central field B_0. (*b*) First-derivative
ve computed from (*a*) after assuming a nonzero linewidth. Only the field region

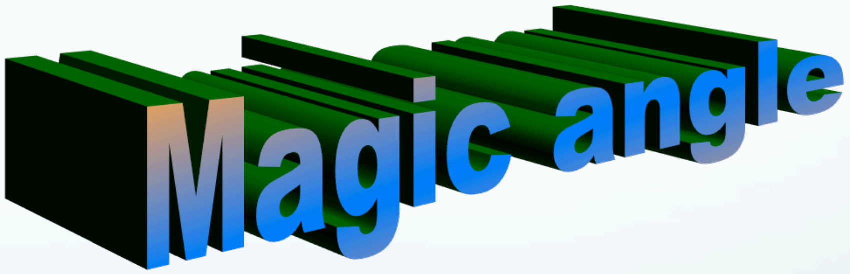
The positions of the resonances depends on the orientation respect to B_0 (β angle) of the **r** vector joining the two magnetic dipoles, according to the ($3\cos^2\beta-1$) factor

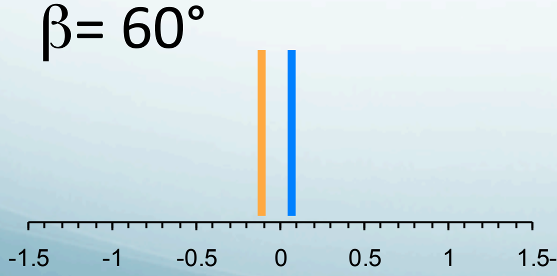

β= 0°

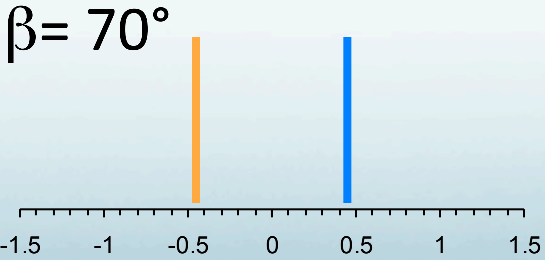

β= 30°

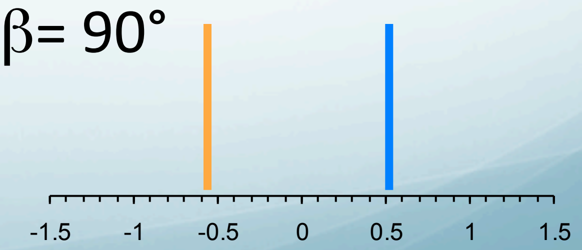

β= 45°


β= 57.4°

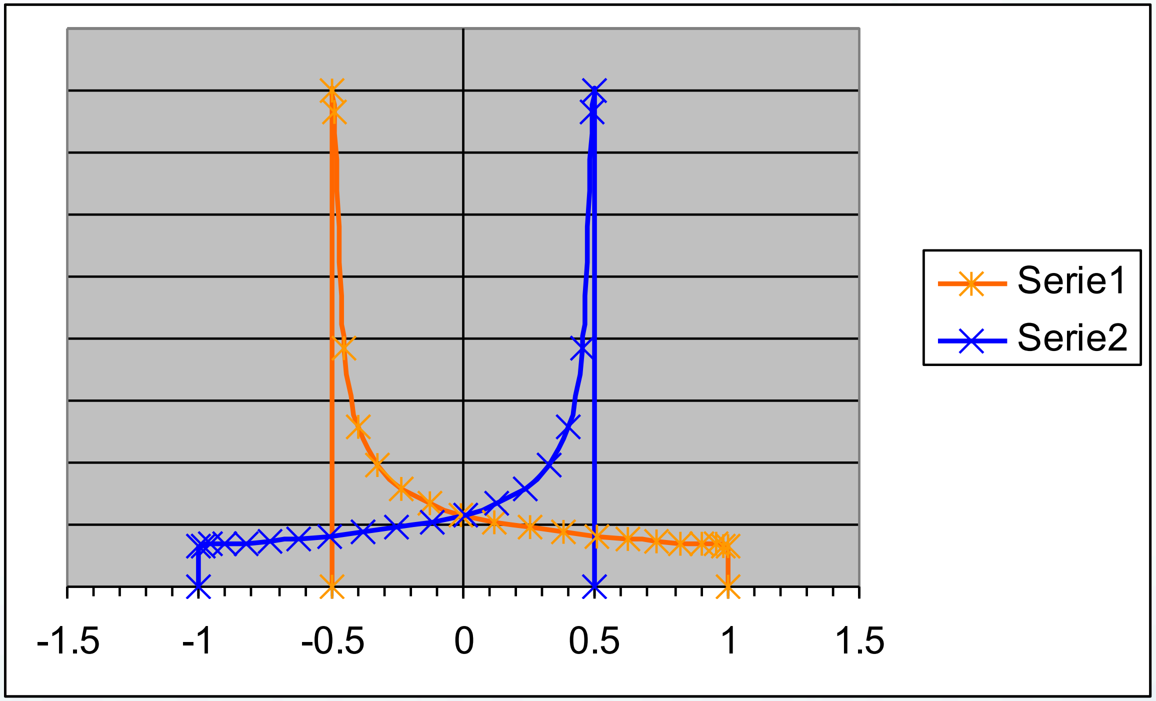



β= 60°

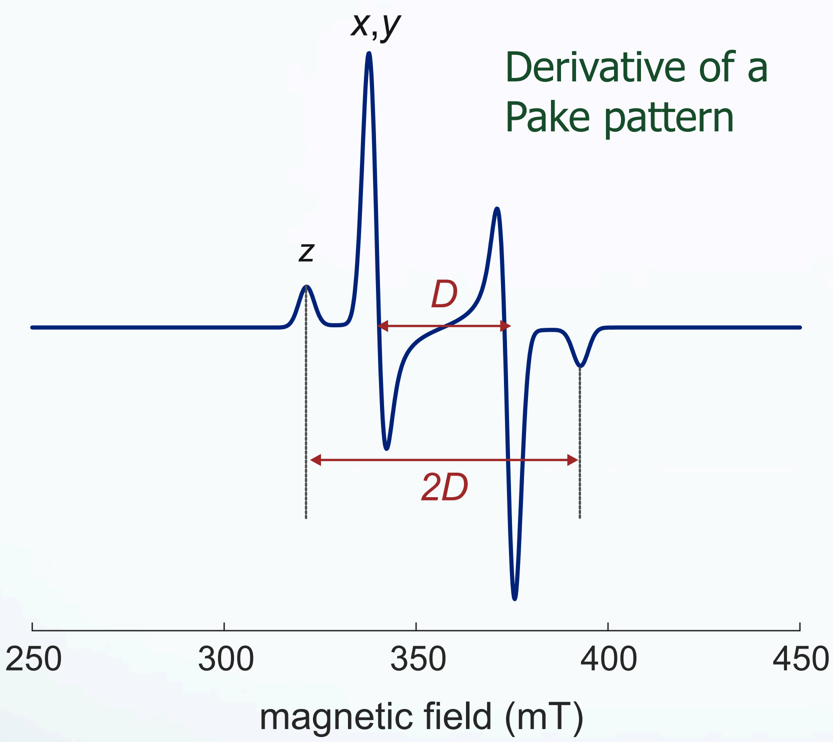

β= 70°


β= 90°

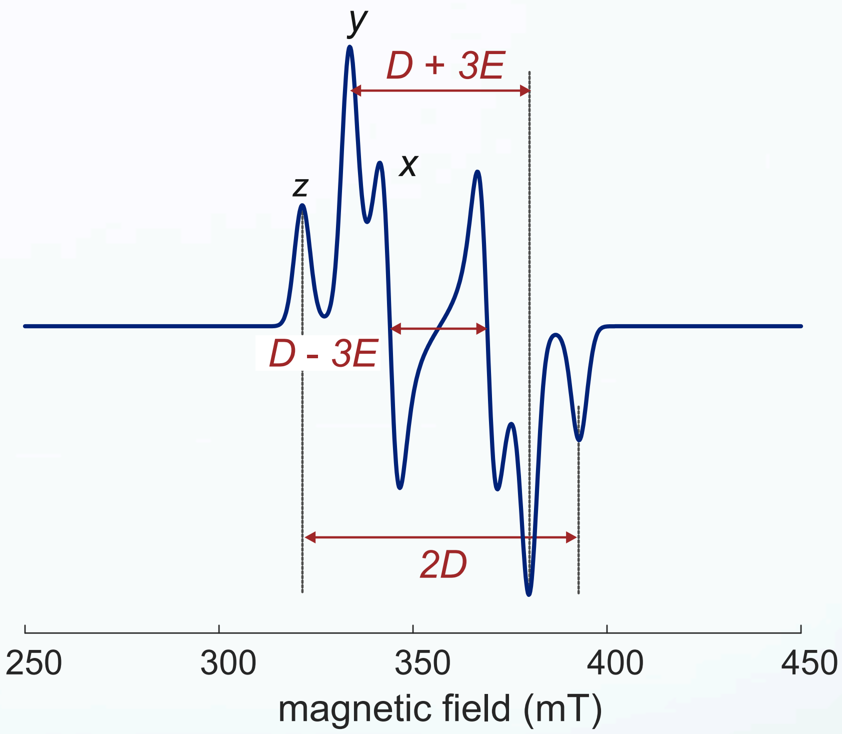
Powder Distribution of Orientations



Spectra for triplet species ($S = 1$)


Derivative of a Pake pattern

D = 1000 MHz
E = 0 MHz



D = 1000 MHz
E = 100 MHz

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