

# Electron-Nucleus Magnetic Interaction

- contact Fermi mechanism
- dipolar term

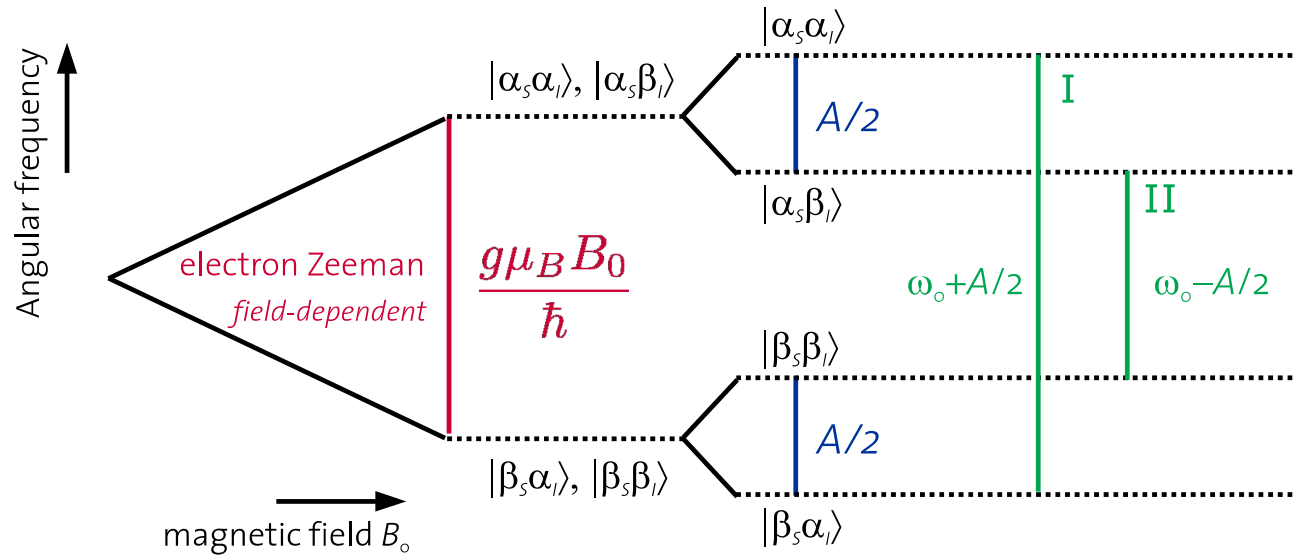
anisotropic (zero trace)

- 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)

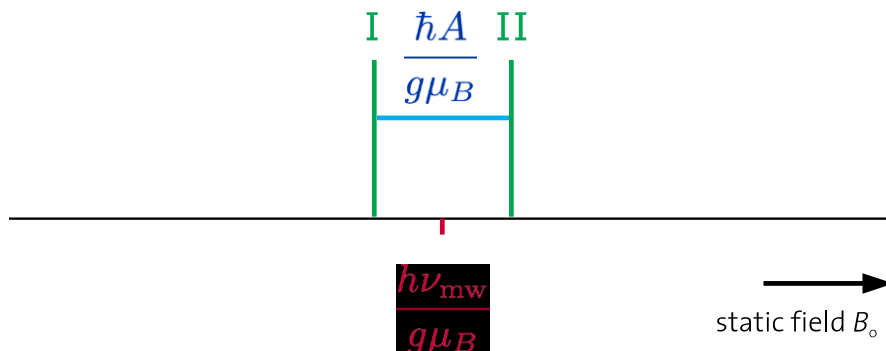
# Manifestation of hyperfine couplings in EPR spectra



- 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 ( $\text{cm}^{-1}$ ,  $A/2\pi c$ )

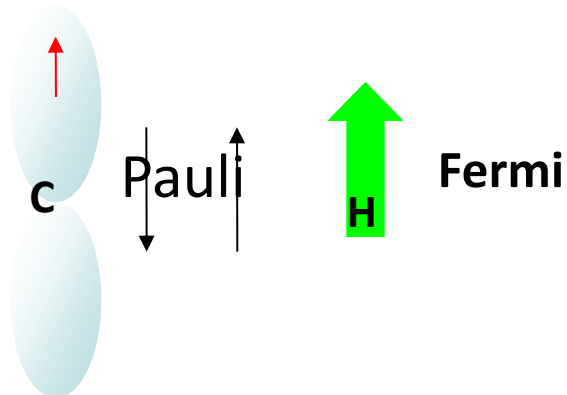
$$1 \text{ G} = 0.1 \text{ mT} \approx 2.8 \text{ MHz} \approx 10^{-4} \text{ cm}^{-1} \text{ (at } g=g_e\text{)}$$

# 1) Fermi Contact Term

- ✓ e.g. H atom
- ✓ due to a non zero probability to find the e- on the nucleus
- ✓ exclusively for 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.  $\pi$  radicals (e- in a p orbital) a is proportional to the probability to find e- on the close C

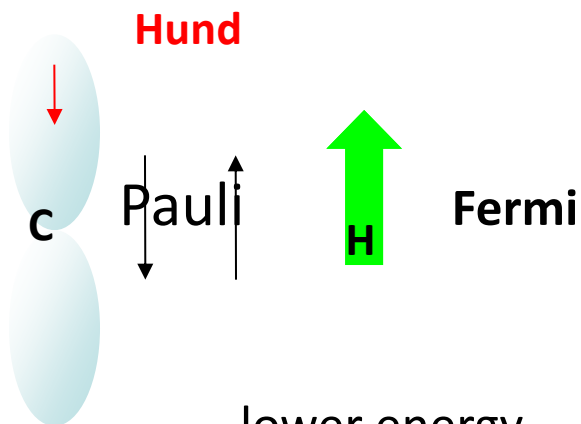
- polarization mechanism for the hyperfine interaction

e.g. for the interaction of the  $\pi$  e<sup>-</sup> 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

$|a_C| = 3.83 \text{ mT}$  e  $|a_H| = 2.30 \text{ mT}$

## 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 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

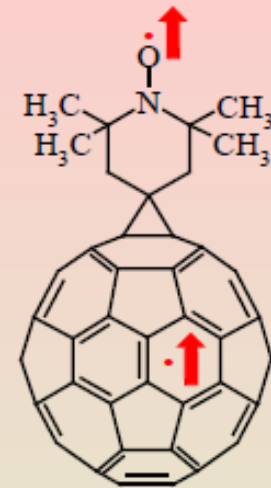
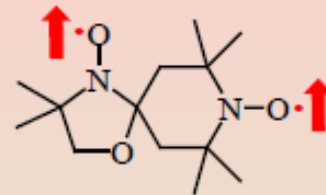
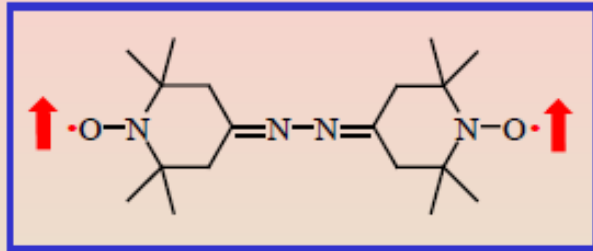
in the former case are separated by a molecular segment

**1) exchange interaction**

**2) dipolar interaction**

Spettri EPR di molecole con due elettroni spaiati

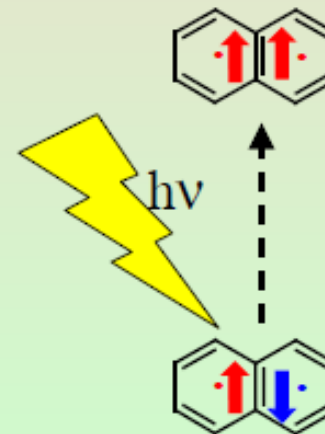
•Biradicali



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~~



## Interazioni tra $s_1$ , $s_2$ , il campo $B_0$ e gli spin nucleari $I_i$

- Zeeman ( $g_i \beta B_0 s_{zi}$ )      proporzionale al campo statico  $B_0$
  - di scambio ( $J s_1 \cdot s_2$ )
  - dipolare ( $s_1 \cdot \mathbf{D} \cdot s_2$ )
  - iperfine ( $a_i s_i \cdot \mathbf{I}_i$ )
- } sono sempre presenti anche se  $B_0 = 0$
- 
- Zeeman      il fattore  $g$  determina la posizione del centro dello spettro EPR
  - di scambio      - fenomeno quantistico dovuto alla necessità della antisimmetria delle funzioni che descrivono più elettroni  
                          - permette di distinguere tra biradicali e tripletti

# 1) Exchange Interaction

- when two e- have a certain probability to be in the same orbital
- it is due to the *electric* (Coulomb) interaction between the two e-, at variance to the dipolar interaction, which is magnetic
- it has a scalar part,  $J_0$ , which at a first approximation corresponds to the exchange integral
- the  $J_0$  sign states if the lower energy is that of the singlet or triplet state
- it contributes with a term of equal energy for all the three triplet states

There are two kinds of exchange interactions:

### 1) Kinetic exchange

- there is the mixing of an ionic state, with one e<sup>-</sup> in the orbital of the latter, with the fundamental state
- antiferromagnetic coupling (↑↓)
- J is negative

### 2) Potential exchange

- Depends on the Coulomb interaction, expressed by the exchange integral
- It destabilizes the singlet states
- ferromagnetic coupling (↑↑)
- J is positive

Interazione di **scambio** caratterizzata dalla costante di scambio  $J$

$$H_{\text{ex}} = J \mathbf{s}_1 \cdot \mathbf{s}_2$$

Autofunzioni:

tripletto

$$\tau_1 = \alpha\alpha$$

$$\tau_0 = 1/\sqrt{2} \{ \alpha\beta + \beta\alpha \}$$

$$\tau_{-1} = \beta\beta$$

singoletto

$$\sigma_0 = 1/\sqrt{2} \{ \alpha\beta - \beta\alpha \}$$

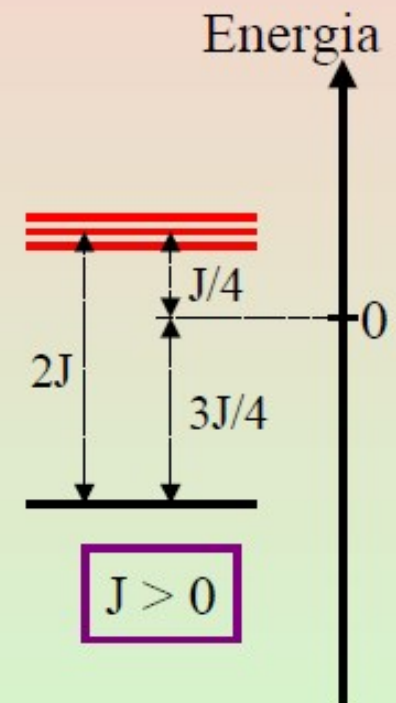
Energie:

$$E_1 = + J/4$$

$$E_0 = + J/4$$

$$E_{-1} = + J/4$$

$$E_0 = - 3J/4$$



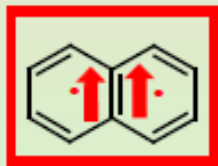
## Distinzione tra biradicali e tripletti

tripletto

se l'energia associata al termine  $H_{\text{ex}} = J \mathbf{s}_1 \cdot \mathbf{s}_2$  è molto maggiore dell'energia associata a tutti gli altri termini di interazione che coinvolgono  $\mathbf{s}_1$  ed  $\mathbf{s}_2$  allora si ha un **tripletto**

biradicale

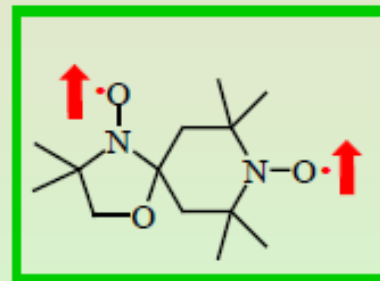
se invece l'energia di scambio è minore o dello stesso ordine di grandezza di tutte le altre interazioni allora si ha un **biradicale**



Zeeman (banda X)  $\approx 0.3 \text{ cm}^{-1}$

$J \approx 15000 \text{ cm}^{-1}$

$D \approx 0.1 \text{ cm}^{-1}$



Zeeman (banda X)  $\approx 0.3 \text{ cm}^{-1}$

$J \approx 0.03 \text{ cm}^{-1}$

( $D \approx 0.03 \text{ cm}^{-1}$ )

## Spettri EPR di biradicali

Interazione **Zeeman** caratterizzata dai fattori  $g$  ( numeri )

$$H_{\text{Zeeman}} = g_1 \beta B_0 s_{z1} + g_2 \beta B_0 s_{z2} \quad \text{per radicali organici } g \approx 2$$

Interazione di **scambio** caratterizzata dalla costante  $J$  ( un numero )

$$H_{\text{ex}} = J \mathbf{s}_1 \cdot \mathbf{s}_2$$

Interazione **dipolare** tra i due elettroni spaiati caratterizzata dal tensore  $\mathbf{D}$  ( una matrice )

$$H_{\text{dip}} = \mathbf{s}_1 \cdot \mathbf{D} \cdot \mathbf{s}_2$$

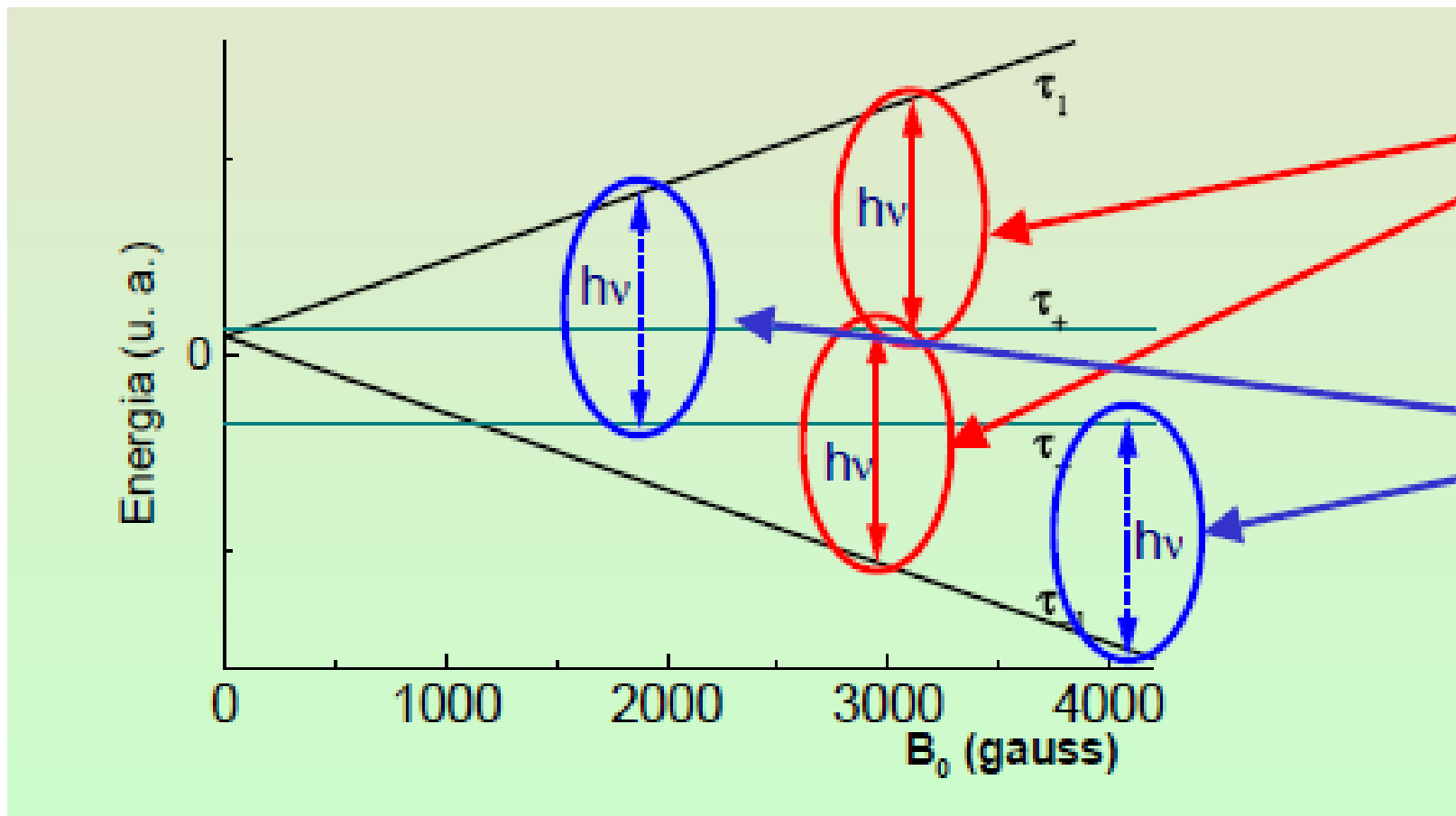
Interazione iperfine dei i due elettroni spaiati caratterizzata dalle costanti di accoppiamento iperfini  $a_1$  e  $a_2$  ( numeri )

$$H_{\text{hyp}} = a_1 \mathbf{s}_1 \cdot \mathbf{I}_1 + a_2 \mathbf{s}_2 \cdot \mathbf{I}_2$$

- allo stato solido
- in soluzione

- **normalmente allo stato solido**
- in soluzione solo in casi particolari

singlet transitions

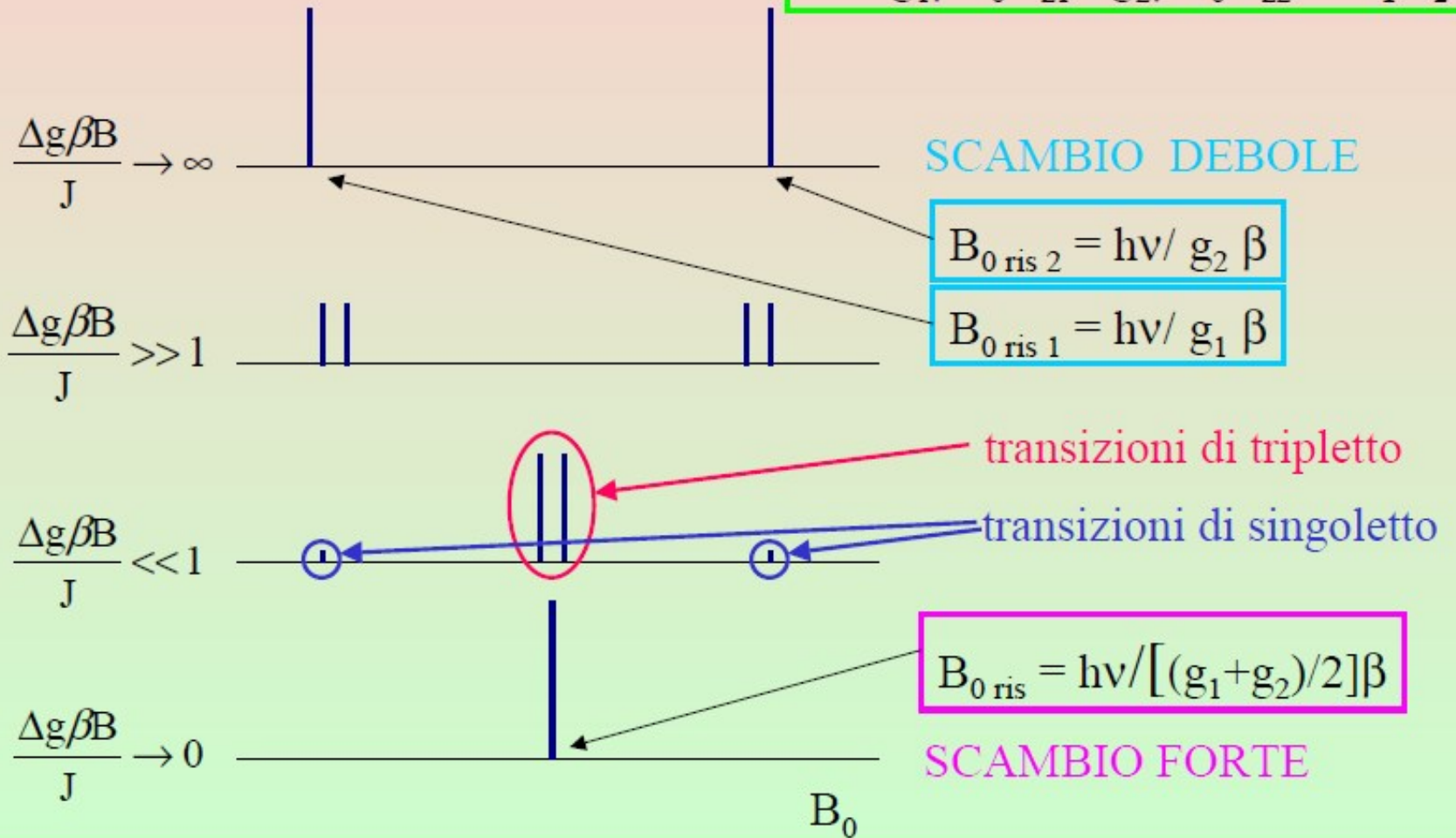


triplet transitions

# Spettri EPR di biradicali

Hamiltoniano di spin  

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





## 2) Dipole Interaction (solid state)

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

$$\mathbf{B}_{ij} = \frac{\mu_0}{4\pi} \left( -\frac{\boldsymbol{\mu}_j}{r_{ij}^3} + 3 \frac{(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij}) \mathbf{r}_{ij}}{r_{ij}^5} \right)$$

Magnetic field at i due to the magnetic dipole  $\mu_j$ .

in polar coordinate, the component along z:

$$B_{zij} = \frac{\mu_0 \mu_j (3 \cos^2 \theta - 1)}{4\pi r^3}$$

- The splitting due to the dipolar interaction is averaged to zero in isotropic solution by of the molecular motion.
- The D matrix of the dipolar coupling has zero trace
- In the case of ESR it is known as **Zero Field Splitting** matrix, because the energy levels are no longer degenerate in the absence of magnetic field (i.e. at zero magnetic field).
- It is independent 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)

$$D = \frac{3}{2} D_{33}$$

$$E = \frac{1}{2} (D_{11} - D_{22})$$

Usually they are reported in  $\text{cm}^{-1}$ .

Since the usual spectrum scale is either G or T,  $D'$  are  $E'$  the D and E values in T:

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

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

1 T corresponds to  $0.93 \text{ cm}^{-1}$  ( $0.011 \text{ kJ} \cdot \text{mol}^{-1}$ ) for  $g_e \approx 2$

Usually the D values range between  $0.001$  a  $2 \text{ cm}^{-1}$ , 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

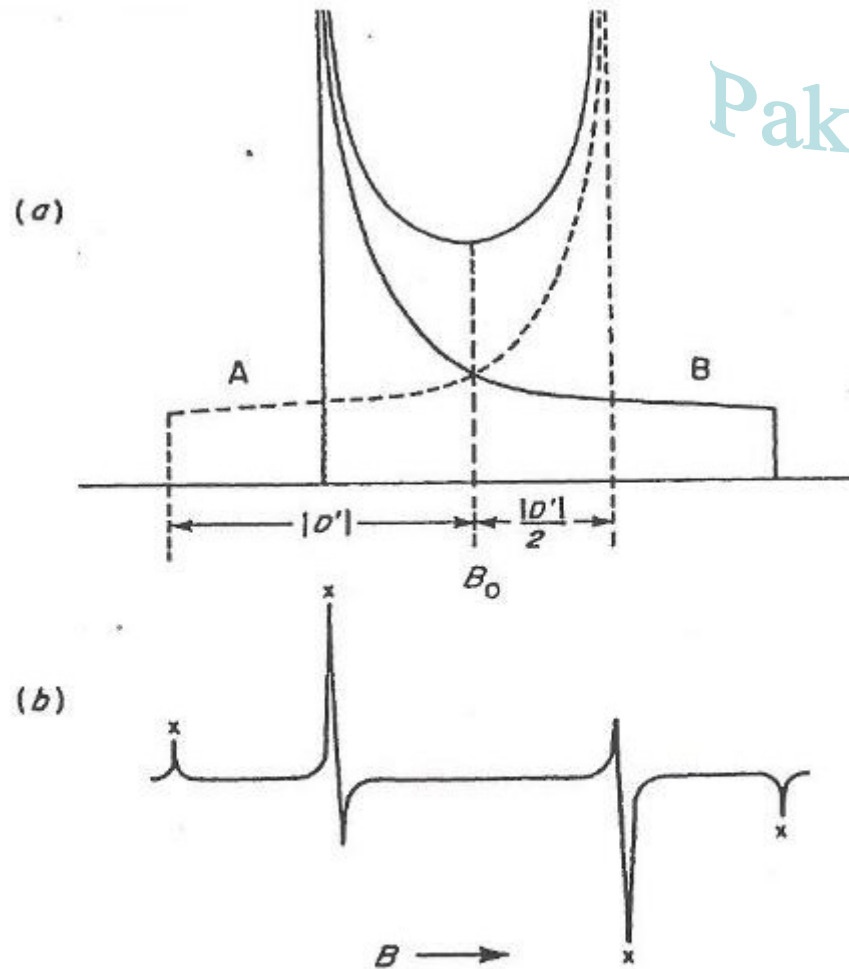


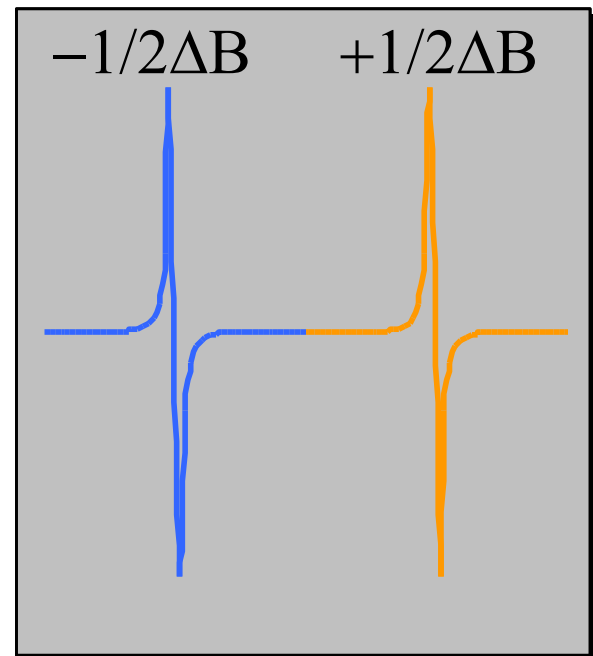
FIGURE 6.5 (a) Theoretical EPR absorption spectrum for a randomly oriented doublet system (with  $E = 0$ ) for a given value of  $D$  and  $\nu$  (with  $g = g_e$ ). A zero linewidth is assumed. The solid curve B corresponds to the curve of Fig. 4.7a; the dashed curve A represents a reflection about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

- the spectrum depends on the orientation, respect to  $B_0$ , of the vector joining the two magnetic moments
- The splitting between the two triplet transitions,  $\Delta M_S = \pm 1$ , is:

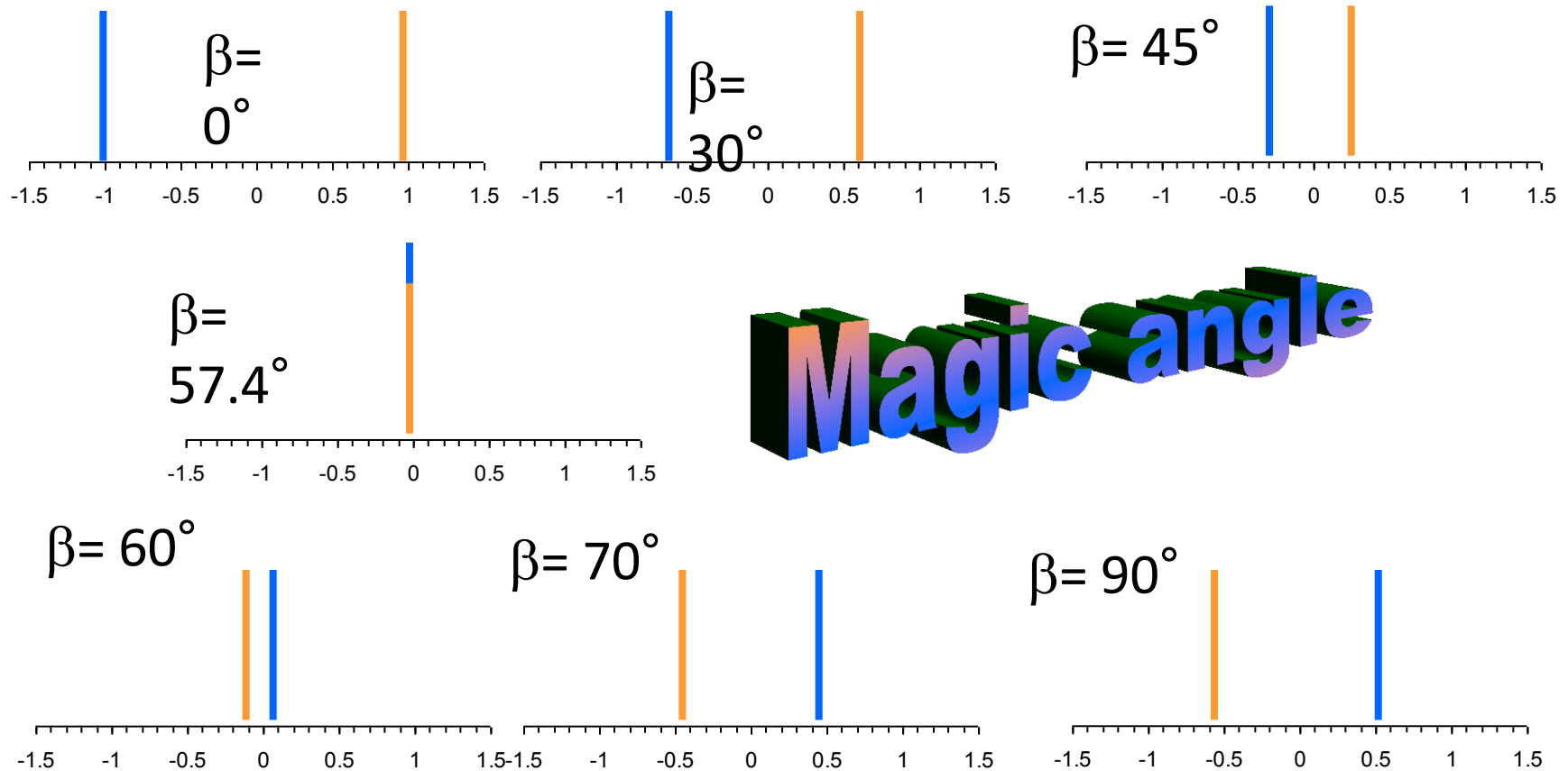
$$\Delta B = \frac{1}{g\mu_B} 3d(3 \cos^2 \beta - 1)$$

The spectrum affords only the absolute value of the splitting

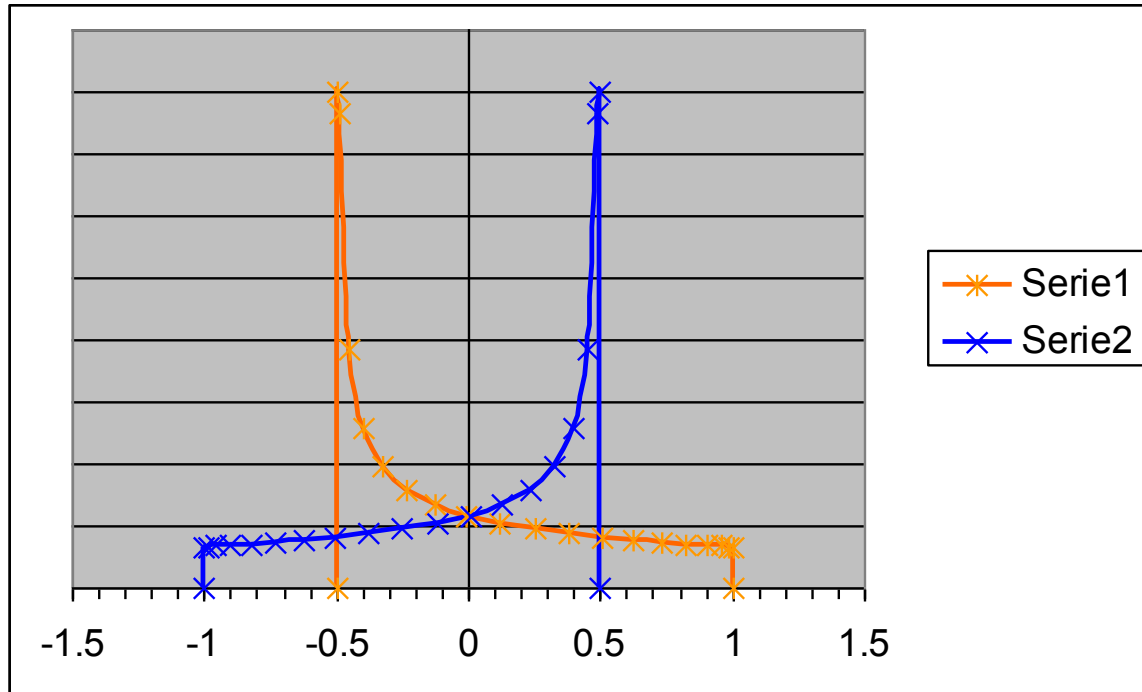
NB is solutions it is averaged to zero (zero trace) by isotropic molecular motion



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

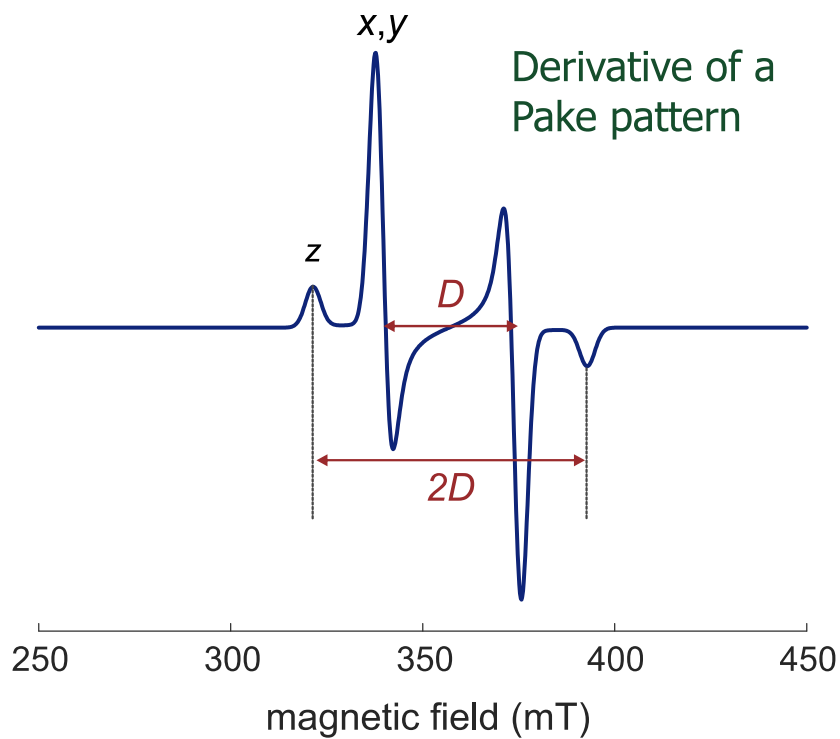


# Powder Distribution of Orientations



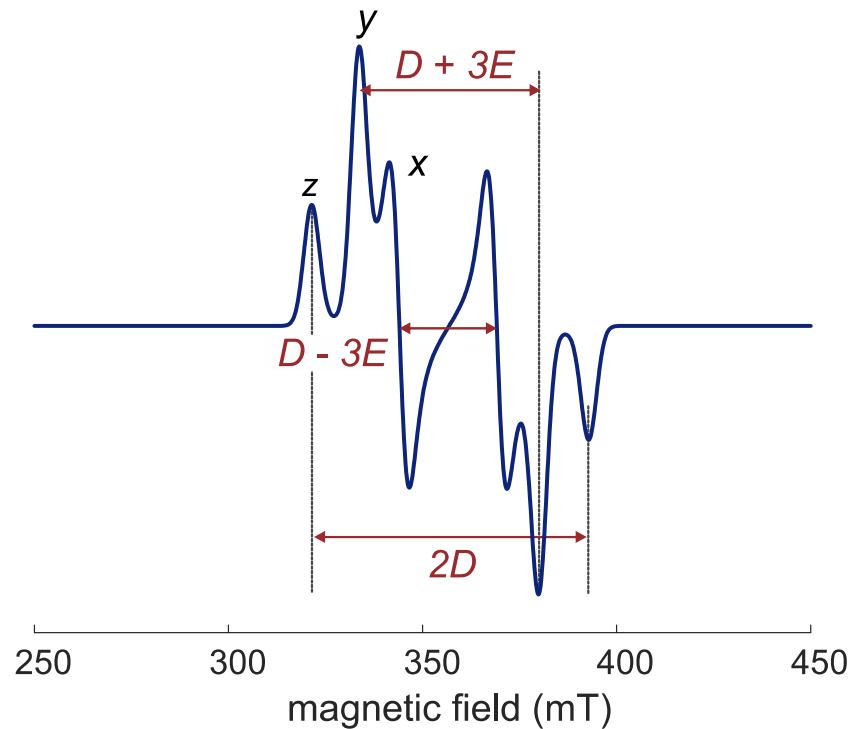


## Spectra for triplet species ( $S = 1$ )



$$D = 1000 \text{ MHz}$$

$$E = 0 \text{ MHz}$$



$$D = 1000 \text{ MHz}$$

$$E = 100 \text{ MHz}$$

Gunnar Jeschke, HCI F227, gjeschke@ethz.ch