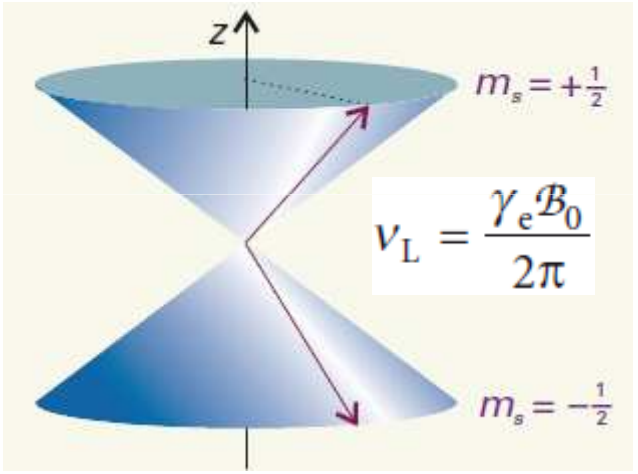
Electron Spin Resonance Spectroscopy (ESR)

Electron spin resonance is a magnetic resonance technique, based on the interaction of **unpaired electron spins** with an external magnetic field.

Only paramagnetic systems show ESR signals:
- ✓molecules containing transition metals as : V, Mn, Fe, Co, Ni, Cu
- ✓molecules in the triplet state: O_2
- ✓organic radicals : NO• , CH_3•
- ✓ metalo-proteins: PS I, PS II

Sample form: solution, powder, crystal, gas phase
< 5µl protein solution with 50µM



(3)

(1) $\hat{\mu}_z = g_e \gamma_e \hat{s}_z \qquad \hat{H} = -g_e \gamma_e \mathcal{B}_0 \hat{s}_z$

g_e = g-value of the free electron: 2.002 319. . . .

Eigenvalues of $\hat{s}_z \qquad m_s \hbar \qquad m_s = +\frac{1}{2}\ (\alpha)\ \ m_s = -\frac{1}{2}\ (\beta)$

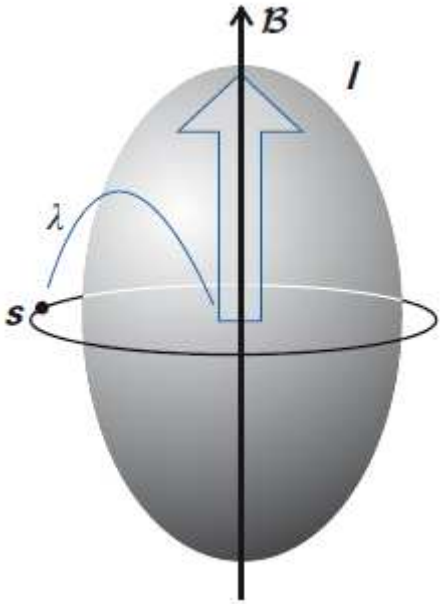
Energies of an electron spin in a magnetic field:

(2) $E_{m_s} = -g_e \gamma_e m_s \hbar \mathcal{B}_0 = g_e \mu_B m_s \mathcal{B}_0$

$\mu_z = g_e \gamma_e m_s \hbar$

The g-factor

The g-factor



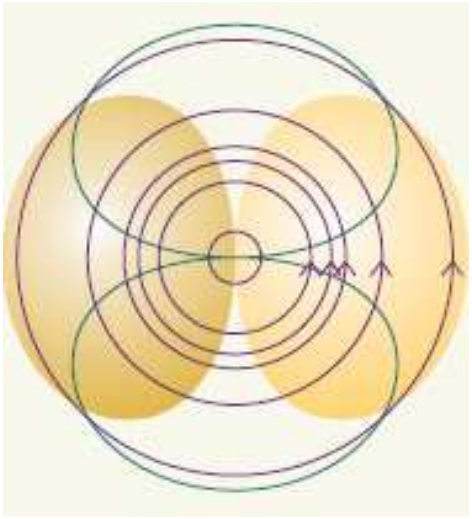
$$\mathbf{B}_{\text{eff}} = \mathbf{B} + \mathbf{B}_{\text{local}} \quad (4)$$

$$\mathbf{B}_{\text{eff}} = (1 - \sigma)\mathbf{B} \qquad (0 \leq \sigma^2 \ll 1) \quad (5)$$

$$= (g/g_e)\mathbf{B}$$

2 .0027 2.0023

differ by a very small amount: s electrons or on a delocalized molecular orbital



$$E^{(2)} = \sum_n{}' \frac{\langle 0|H^{(1)}|n\rangle\langle n|H^{(1)}|0\rangle}{E_0^{(0)} - E_n^{(0)}}$$

paramagnetic d-metal complexes: ΔE small
g-factor: 1-6

Molecules trapped in solids: g-factor is anisotropic.

B can induce circulation of excited electrons.

Theoretical aspects of ESR

Two - spin system (S = 1/2, I = 1/2) in an external applied field **B**

$$H = H_{EZ} - H_{NZ} - H_{HFS}$$

$$= g\mu_B B S_Z - g_N \mu_N B I_Z + hSaI \tag{6}$$

The energy:

$$E(M_S, M_I) = g\mu_B B M_S - g_N \mu_N B M_I + haM_S M_I \tag{7}$$

$$E(M_S, M_I)/h = \nu_e M_S - \nu_N M_I + aM_S M_I \tag{8}$$

$$\nu_e = g\mu_B B/h \qquad \nu_N = g_N \mu_N B/h$$

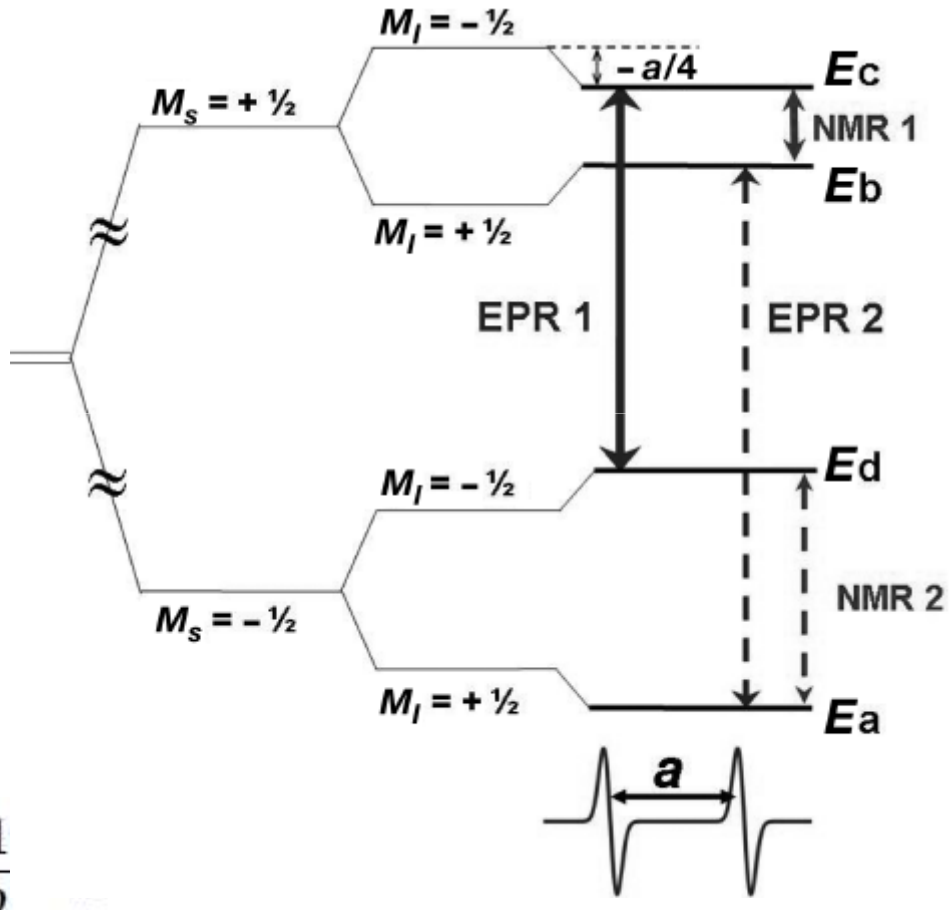
4 energy levels:

$$\begin{array}{lcllll} & & & & M_S & M_I \\ E_a & = & -\frac{1}{2}g\mu_B B_o & +\frac{1}{2}g_N\mu_N B_o & -\frac{1}{2} & +\frac{1}{2} \\ E_b & = & +\frac{1}{2}g\mu_B B_o & +\frac{1}{2}g_N\mu_N B_o & +\frac{1}{2} & +\frac{1}{2} \\ E_c & = & +\frac{1}{2}g\mu_B B_o & -\frac{1}{2}g_N\mu_N B_o & +\frac{1}{2} & -\frac{1}{2} \\ E_d & = & -\frac{1}{2}g\mu_B B_o & -\frac{1}{2}g_N\mu_N B_o & -\frac{1}{2} & -\frac{1}{2} \end{array} \tag{9}$$

Hyperfine interaction

Hyperfine interaction: due to the interaction of the unpaired electron and nuclei

Selection rule: $\Delta M_I = 0$ *and* $\Delta M_S = \pm 1$



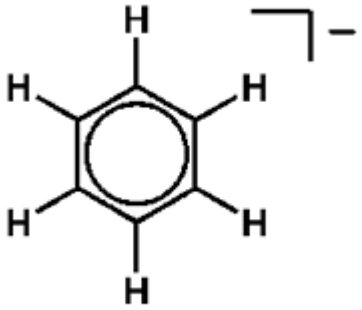
$$\Delta E_{cd} = E_c - E_d = g\mu_B B + \frac{1}{2}$$

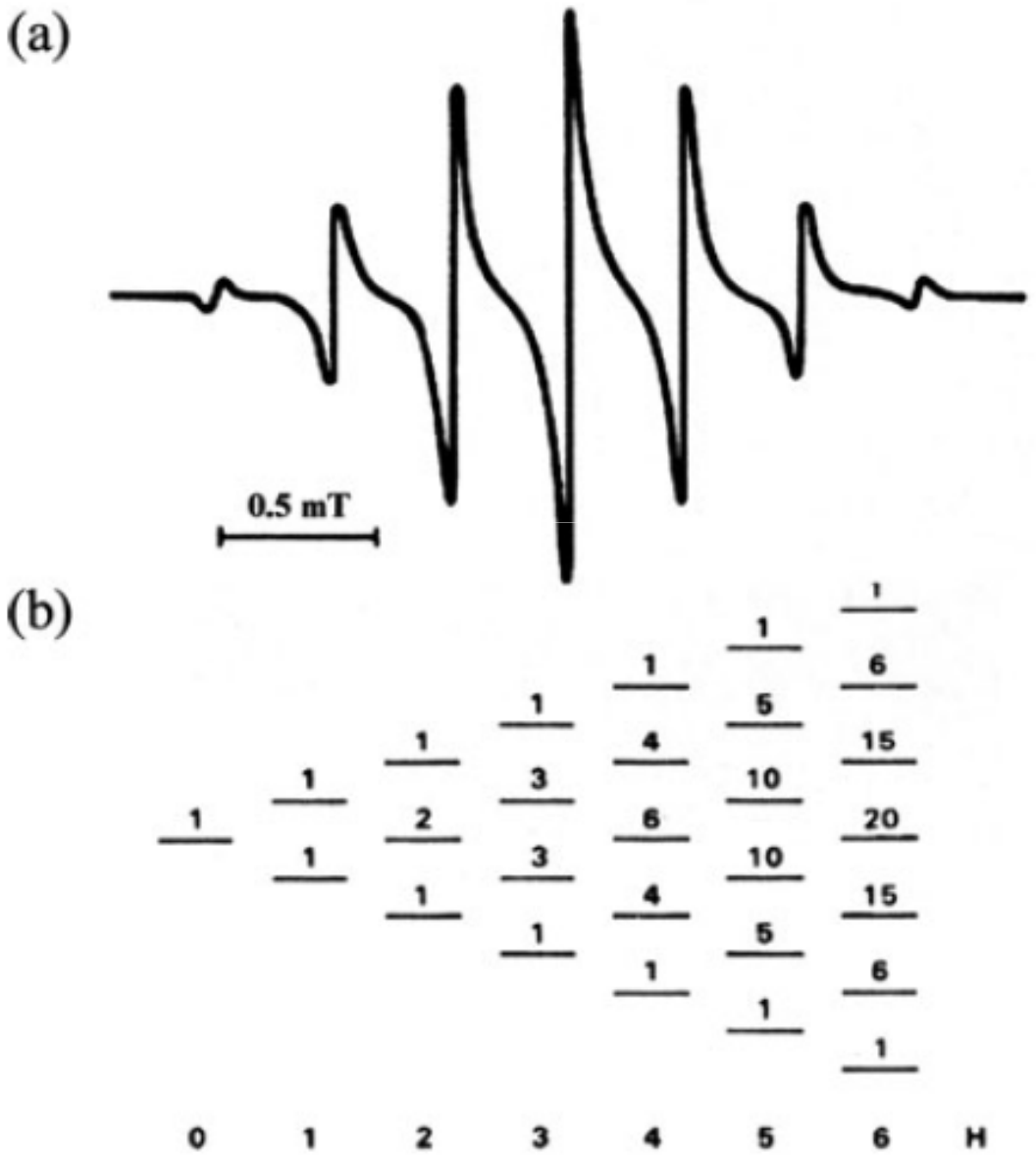
Transitions:

$$\Delta E_{ab} = E_b - E_a = g\mu_B B - \frac{1}{2}ha_{iso}$$

2n I +1 lines

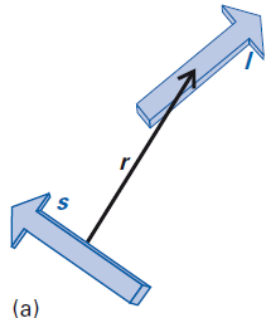
Hyperfine interaction





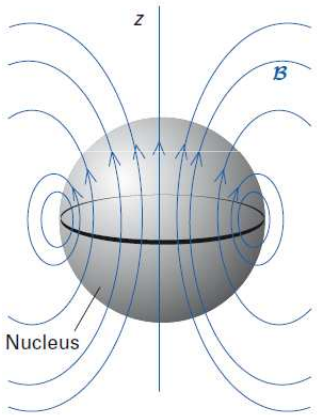
The origin of the hyperfine interaction

• dipole– dipole interaction (p electrons):
radicals trapped in solids
2p electron: 3.4 mT from the ^{14}N nucleus



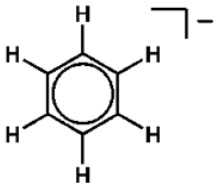
$$\Delta\omega = \frac{\hbar\gamma_I\gamma_S}{r^3}[3cos^2\theta - 1]$$

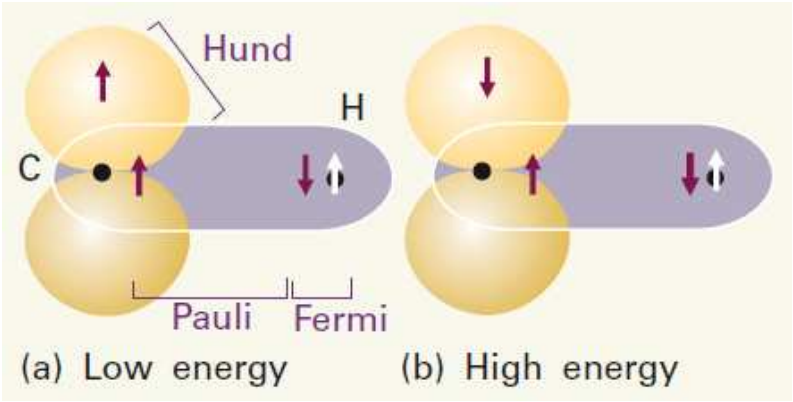
•Fermi contact interaction (s electron):
in liquids
1s electron: 50 mT from the ^{1}H nucleus



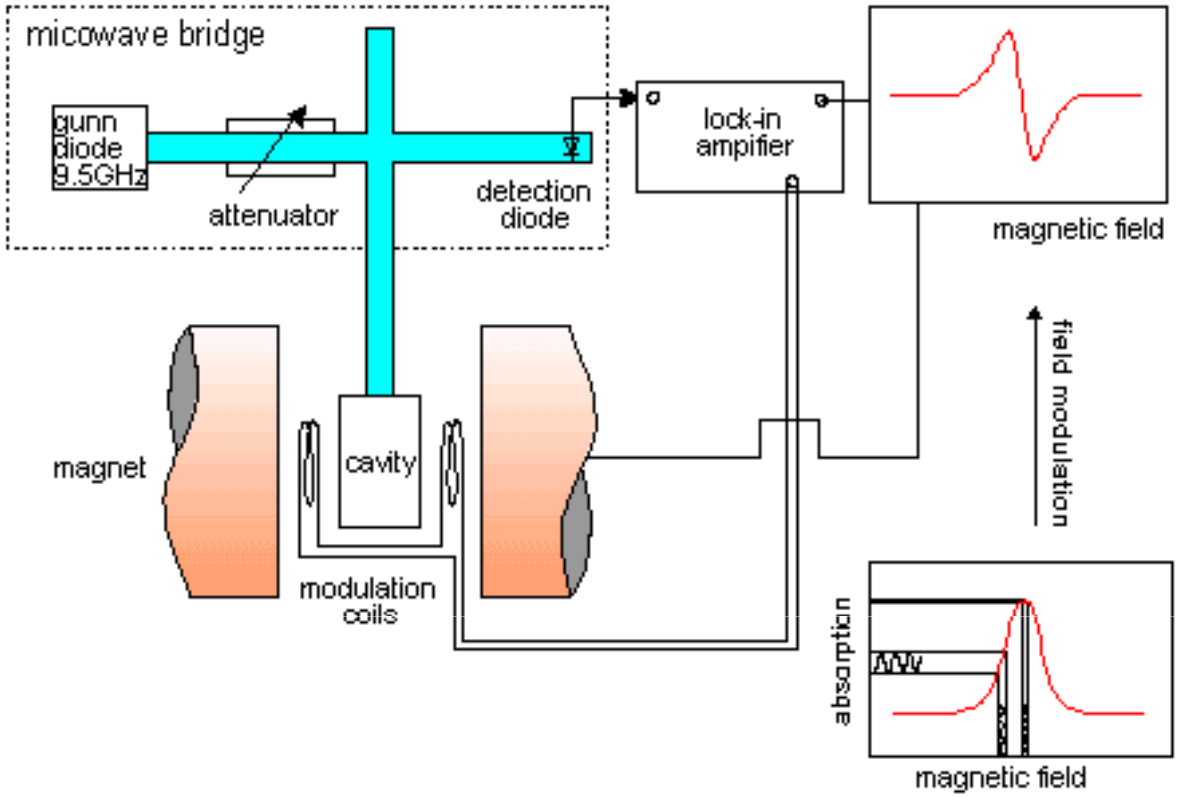
The analysis of hyperfine structure in radicals gives information about the composition of the orbital (hybridization of the atomic orbitals).

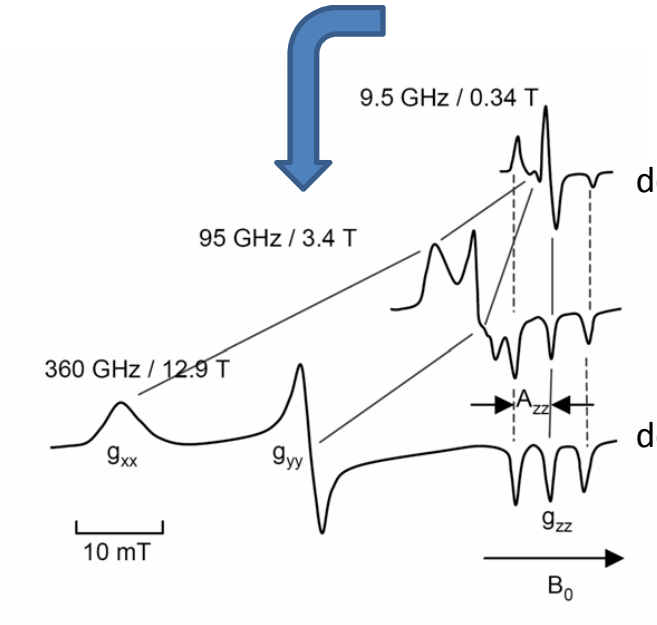
•polarization mechanism





EPR Spectrometer

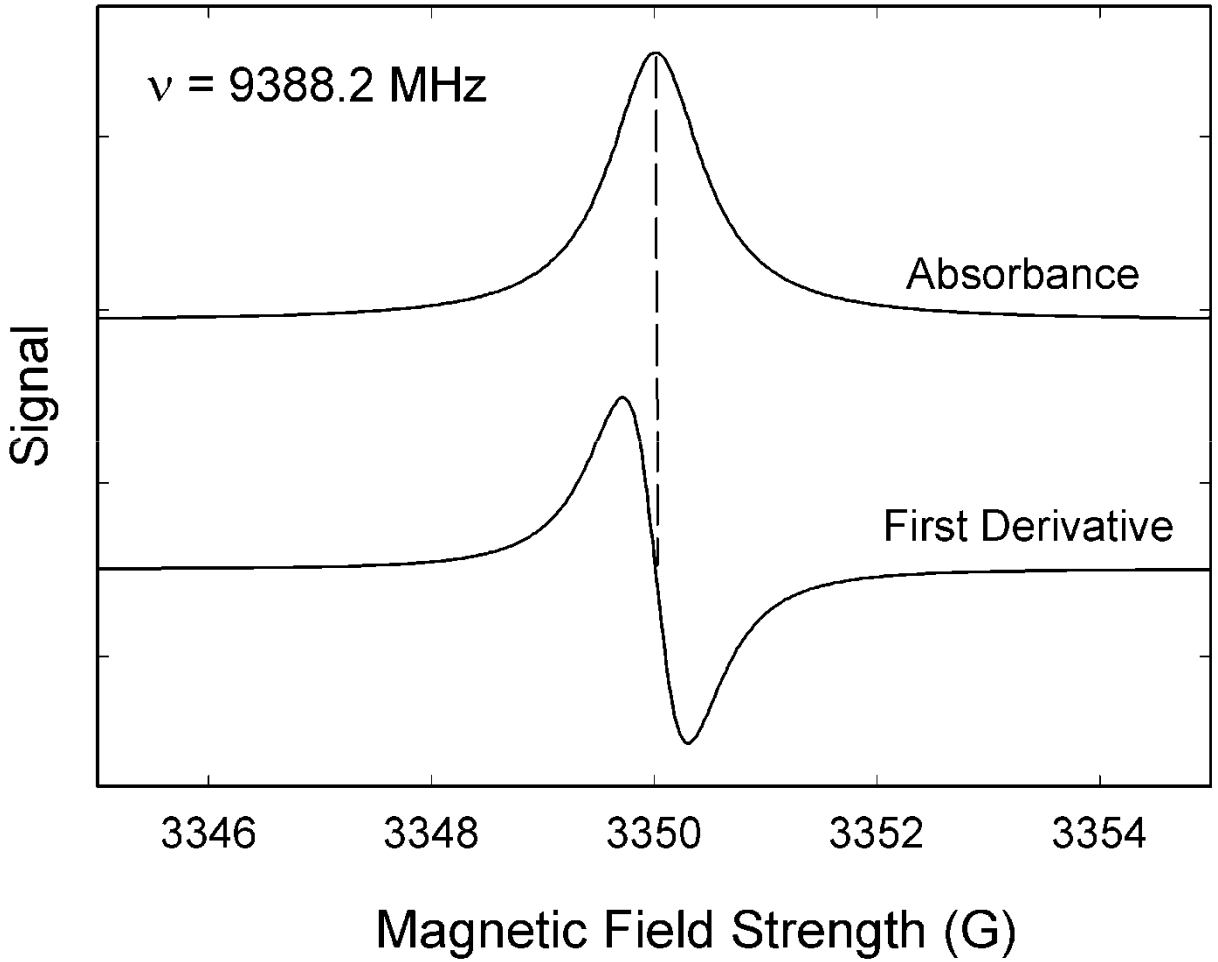




dominated by hyperfine interaction tensor

dominated by g-factor

ESR Spectra


ν = 9388.2 MHz
Absorbance
First Derivative
Signal
3346
3348
3350
3352
3354
Magnetic Field Strength (G)

ESR vs. NMR

Resonance Frequency: 1000 times larger (GHz vs. MHz)

Coupling constants: 1. 000. 000 times larger (MHz vs. Hz)

Relaxation times: **10^6 times shorter (µs vs s)**

Sensitivity: **1000 times larger (µM vs. mM**)

EPR techniques: Electron Nuclear Double Resonance (ENDOR)

1. **cw technique** : sweep magnetic field B_0, microwave frequency is constant

2. **pulsed-FT technique**: short, intense MW pulse --- signal f(t) --- spectrum s (υ)

Electron Nuclear Double Resonance (ENDOR):

- increase of hyperfine resolution
-information about the nuclear environment
- spin-spin distance (proteins: structure information)