ELECTRON PARAMAGNETIC RESONANCE

= MAGNETIC RESONANCE TECHNIQUE

FOR STUDYING PARAMAGNETIC SYSTEMS

i.e. SYSTEMS WITH AT LEAST ONE UNPAIRED ELECTRON

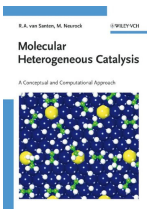
Examples of paramagnetic systems

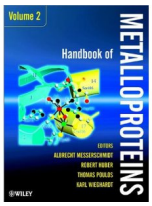
Transition-metal complexes

Paramagnetic states:

Mn(II), Cu(II), Fe(III), Co(II), Co(IV), Cr(III), Cr(V), V(IV), Ni(I), Ni(III), ...

Extremely important role in biochemistry (metalloproteins, metals in biology) and in synthetic catalysis (inorganic chemistry)

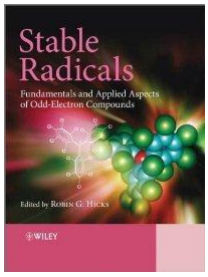


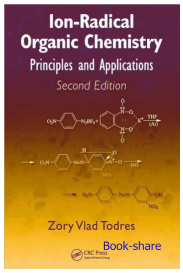


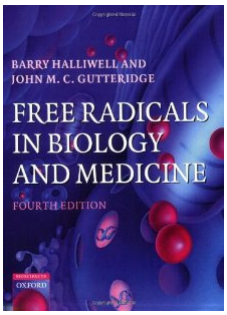
Examples of paramagnetic systems

Organic radicals

In biology: tyrosyl radicals, cysteinyl radicals,
ROS (reactive oxygen species:
O_2^{-}, $^{\cdot}OH$, ...), etc.
In organic and polymer chemistry
In catalysis



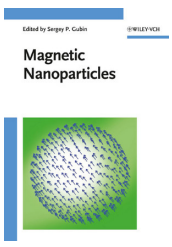


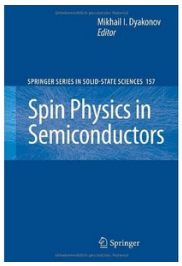


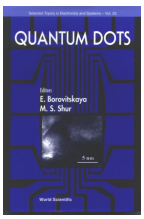
Examples of paramagnetic systems

Paramagnetic states in solid-state physics

In semi-conductors: electron-hole creation,
polaron states, dangling bonds
In nanoparticles: ferromagnetic states of
metaloxide nanoparticles
Quantum dots
Rare-earth centers in refractive crystals





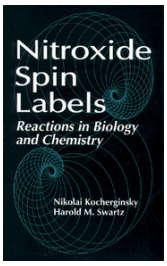


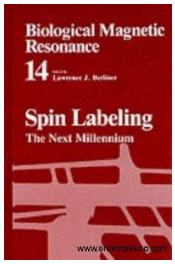
Examples of paramagnetic systems

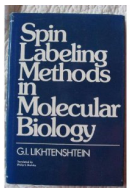
Rendering diamagnetic systems paramagnetic

Spin labeling -> attaching a paramagnetic label to a diamagnetic molecule

Spin probing -> using a paramagnetic molecule as spy in diamagnetic surrounding



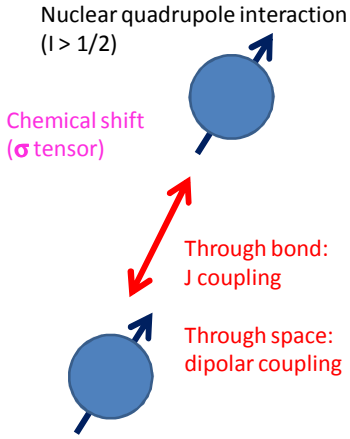


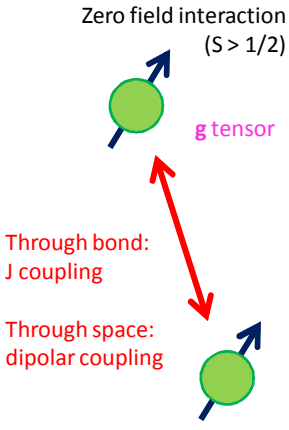


TYPES OF INTERACTIONS

Nuclear Zeeman effect (I>0)
-> $\nu_L \propto B_0$

Electron Zeeman effect (S>0)
-> $\nu_L \propto B_0$





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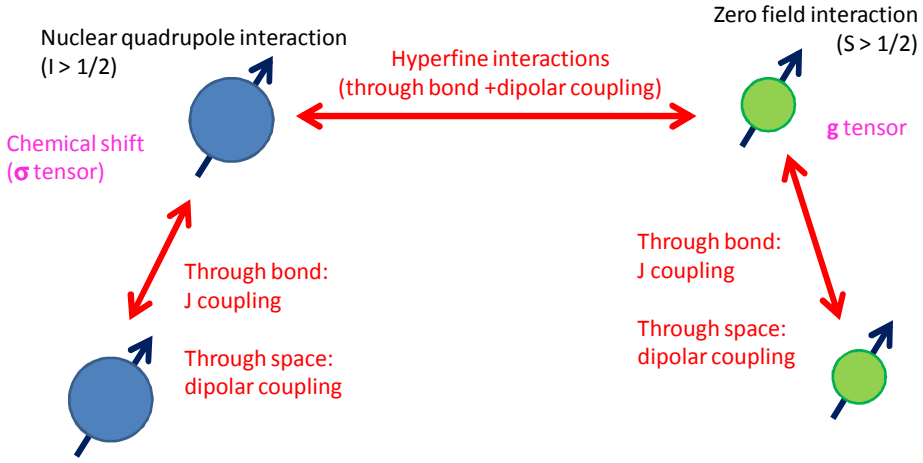
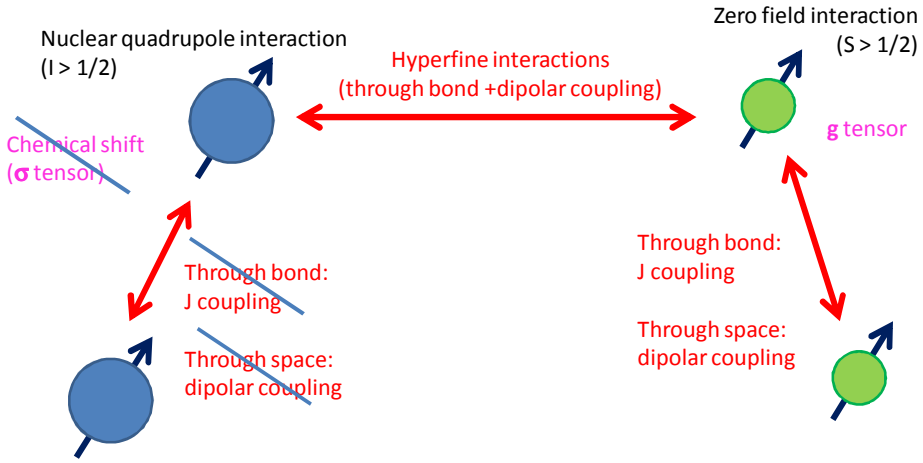


OBSERVABLE TYPES OF INTERACTIONS IN EPR

Nuclear Zeeman effect (I>0)
-> $\nu_L \propto B_0$

Electron Zeeman effect (S>0)
-> $\nu_L \propto B_0$ (1- 100's GHz)



INFORMATION FROM EPR

1. Quantification of paramagnetic molecules
   => Signal intensity

2. Local geometric and electronic structure

g tensor
Hyperfine tensors
Zero field splitting
Nuclear quadrupole interactions

Quantum Chemistry (DFT)

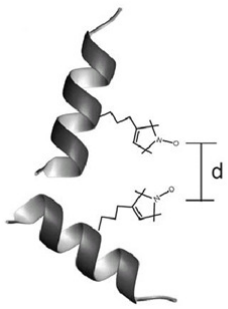
electronic and geometric structure of local paramagnetic site

INFORMATION FROM EPR

3. Molecular structures

Dipolar interactions between electron spins (often spin labels)
(distance constraints: 1-8 nm)

MD



Overall structure determination

INFORMATION FROM EPR

4. Dynamics

Spectral features depend on movement of paramagnetic center

Which dynamics in biomolecules do we probe in this way ?

Side-chain reorientation
Helix dynamics
Protein rotational diffusion

Time frame that is partially overlapping with what is theoretically studied by molecular dynamics

RELAXATION TIMES

Electron spin-spin relaxations: T_2

Order of ns to a few µs

Electron spin-lattice relaxations: T_1

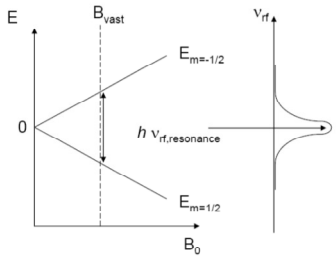
Order of a few µs to ms (often more in the order of nuclear T_2)

Often need to lower the temperature in order to see a signal (especially for transition-metals)

Pulses need to be short: microwave pulses (GHz frequencies!), a few ns in length

DIFFERENT EPR TECHNIQUES

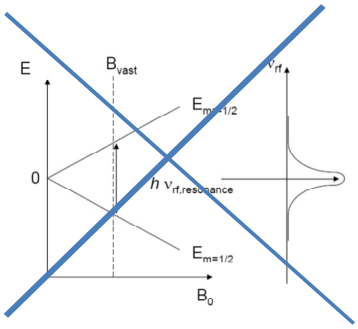
CW-NMR



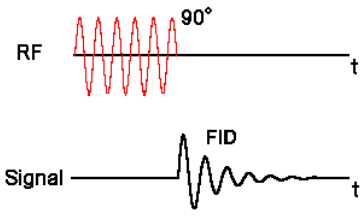
Continuous irradiation of rf
Fixed magnetic field
Vary rf
Detection of absorption of rf

DIFFERENT EPR TECHNIQUES

CW-NMR



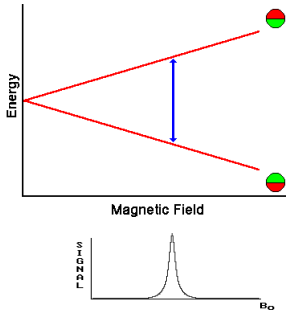
FT-NMR



Continuous irradiation of mw
Fixed magnetic field
Vary rf
Detection of absorption of rf

DIFFERENT EPR TECHNIQUES

CW-EPR



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Fixed microwave frequency
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DIFFERENT EPR TECHNIQUES

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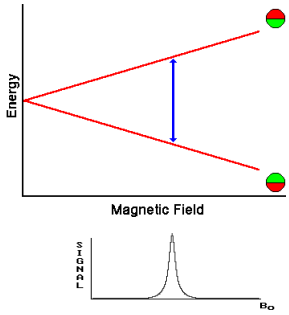


Continuous irradiation of mw
Fixed microwave frequency
Vary magnetic field
Detection of absorption of mw

FT-EPR

Did not replace CW-EPR !!!

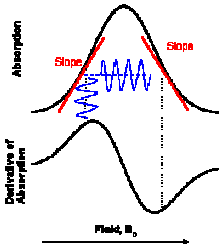
For most cases:
Excitation width of current pulses
is too small to excite the full spectrum

(spectrum width determined by
g anisotropy and zero field splitting)

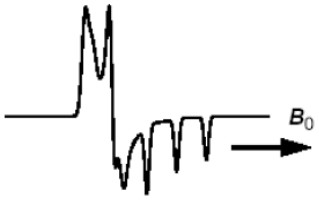
DIFFERENT EPR TECHNIQUES

CW-EPR → Method of choice to determine largest interactions
- g tensor
- zero field splitting
- large hyperfine values

Spectrum is first derivative because of technical reasons



Spectrum can be complex, especially for solid state cases



DIFFERENT EPR TECHNIQUES

Magnetic fields depend on microwave frequency

X-band – 9.5 GHz
Water-cooled electromagnet
Sweep from 0 to 1.4 Tesla

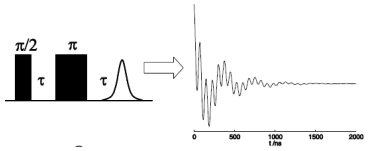
W-band – 95 GHz
Cryo magnet
Sweep from 0 to 6 Tesla

DIFFERENT EPR TECHNIQUES

Pulsed EPR techniques => monitor smaller interactions

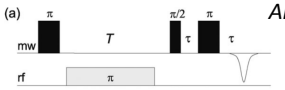
ESEEM techniques

(electron spin echo modulation techniques)
Only microwave pulses, one microwave frequency



ENDOR techniques

(electron nuclear double resonance techniques)
Microwave and rf pulses



Also exists in CW version

(think of heteronuclear NMR)

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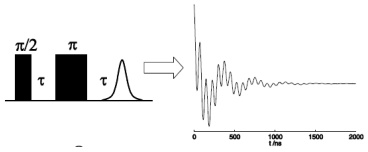
ESEEM techniques

(electron spin echo modulation techniques)
Only microwave pulses



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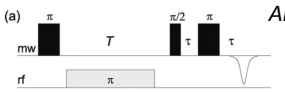


Also exists in CW version

(think of heteronuclear NMR)

Nuclear frequencies

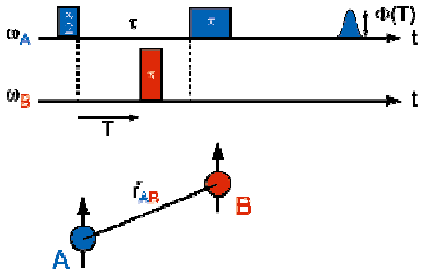
-Hyperfine couplings
- Nuclear Zeeman interaction
- nuclear quadrupole coupling

DIFFERENT EPR TECHNIQUES

Pulsed EPR techniques => monitor smaller interactions

(P)ELDOR techniques

(pulsed electron double resonance techniques)
Only microwave pulses, two microwave frequencies



(think of heteronuclear NMR)

Dipolar interactions

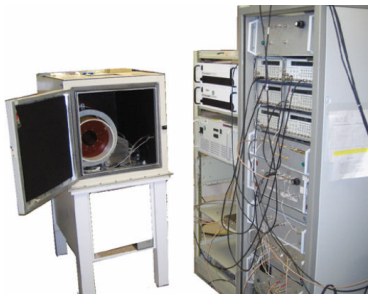
Inter electron spin distances
Up till 8 nm

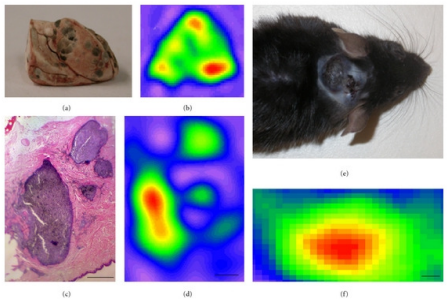
Often used method of this class:
DEER method

DIFFERENT EPR TECHNIQUES

EPR imaging techniques also exist!!

Limited in size
(no whole-body scan for humans)





(e.g. Imaging of melanoma)