NMR introduction:
Quantum mechanics meets NMR

Konstantin Ivanov (Novosibirsk, Russia)

Part 1: NMR interactions

Part 2: Basics of spin dynamics

Outline, part 1

- Zeeman interaction

- Chemical shift, chemical shift anisotropy;

- Spin-spin interactions: dipolar coupling and scalar coupling;

- Quadrupolar interaction.

Spin Hamiltonian

- In quantum mechanics, we need to solve the Schrödinger equation for ψ or the Liouville-von Neumann equation for ρ

- Generally, we need to write down and solve the following equation:

$$\frac{\partial}{\partial t}\left|\psi\right\rangle = -i\hat{H}\left|\psi\right\rangle$$
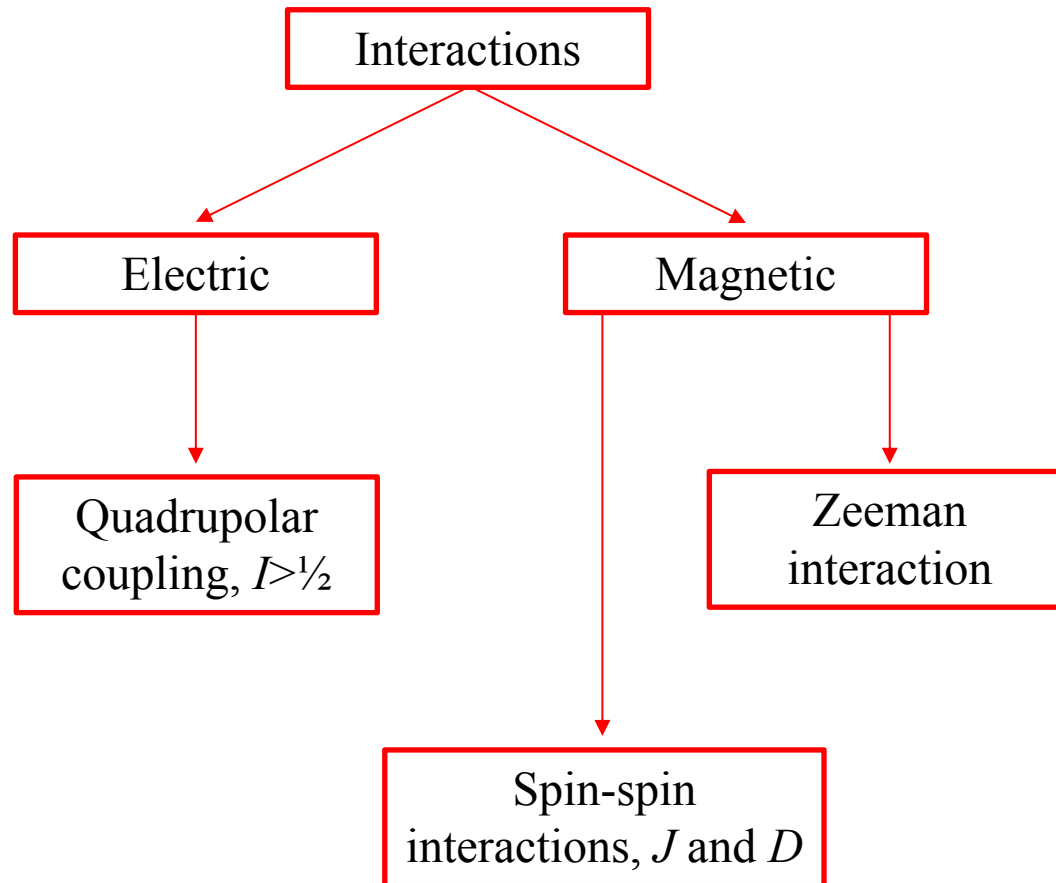
Here ψ is the w.f. of the entire system of electrons and nuclei. This equation is virtually impossible to solve.

- Solution is provided by the spin Hamiltonian hypothesis:

$$\frac{\partial}{\partial t}\left|\psi_{spin}\right\rangle = -i\hat{H}_{spin}\left|\psi_{spin}\right\rangle$$

- We limit ourselves to only nuclear spin degrees of freedom, which are decoupled from other degrees of freedom.

- Key question: how can we write down the spin Hamiltonian?

- In most cases, one can introduce s.H. by separating timescales of electronic and nuclear motions and by keeping in mind that nuclear spin energies are small

Nuclear spin interactions

```
                    ┌──────────────┐
                    │ Interactions │
                    └──────────────┘
                     ╱            ╲
          ┌──────────┐            ┌──────────┐
          │ Electric │            │ Magnetic │
          └──────────┘            └──────────┘
               │                   ╱          ╲
     ┌──────────────────┐  ┌─────────────┐  ┌─────────────┐
     │   Quadrupolar    │  │  Spin-spin  │  │   Zeeman    │
     │ coupling, I>½    │  │ interactions│  │ interaction │
     └──────────────────┘  └─────────────┘  └─────────────┘
```

$$\hat{H}_{spin} = \hat{H}_Z + \hat{H}_J + \hat{H}_D + \hat{H}_Q$$

Angular momentum and magnetic moment

- In NMR we deal with spin magnetism. What is '**spin**'?
- Charged nucleus (or electron) is spinning:

  there is angular momentum (spin) and magnetic moment

  attention: this is a simple view, which is not (entirely) correct
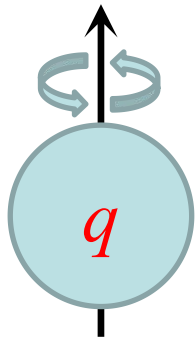
The electric current for a charged particle moving around
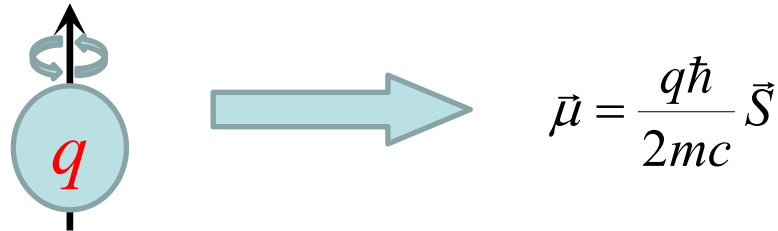
$$I = \frac{qv}{2\pi r}$$

The magnetic moment is

$$\vec{\mu} = \frac{IS}{c}\vec{n} = \frac{qvr}{2c}\vec{n} = \frac{q}{2mc}\vec{J}$$

So, μ is proportional to *a.m.*; when *a.m.* is measured in $\hbar$ units
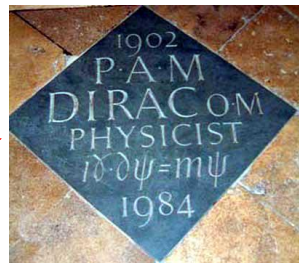
$$\vec{\mu} = \frac{q\hbar}{2mc}\vec{S}$$

Is it entirely correct? The idea of a very small particle turning around is anyway a simplification…

Angular momentum and magnetic moment

$$\vec{\mu} = \frac{q\hbar}{2mc}\vec{S}$$

So, μ is proportional to $a.m.$; when $a.m.$ is measured in $\hbar$ units

Quantum mechanics: this is not entirely correct

We are wrong by the g-factor! g=2 for an elementary spin-½ particle (Dirac)

$$\vec{\mu}_e = g_e\mu_B\vec{S}, \quad \mu_B = -\frac{e\hbar}{2m_ec}, \quad g_e = 2\left(1+\frac{\alpha}{2\pi}+...\right) \approx 2.0023 \quad \text{(QED result)}$$

How about nuclear spins?

$$\vec{\mu}_N = g_N\mu_N\vec{I}, \quad \mu_N = \frac{e\hbar}{2Mc}, \quad g_N \neq 1 \quad (g_p \approx 5.58, \ g_n = -\frac{2}{3}g_p \approx 3.83, \text{QCD result})$$

Proton g-factor is significantly larger than 2, neutron has magnetic moment

Relation between μ and I:

$$\vec{\mu}_e = \gamma_e\vec{S}, \quad \gamma_e = g_e\mu_B$$

$$\vec{\mu}_N = \gamma_N\vec{I}, \quad \gamma_N = g_N\mu_N$$

γ-ratio,
gyromagnetic
ratio

6

Zeeman interaction

- Particles with $I\neq0$ have magnetic moment and interact with external magnetic fields. The energy associated with this interaction is equal to

$$E = -\left(\vec{\mu}\cdot\vec{B}\right) \implies \hat{H} = -\left(\hat{\vec{\mu}}\cdot\vec{B}\right) = -\gamma\left(\hat{\vec{I}}\cdot\vec{B}\right)$$

- The field can be static (along Z) or oscillating (along X/Y)
- Motion in the static field: precession of μ at the frequency $\omega=|\gamma|B$
- Direction of precession depends on the sign of γ.
- Motion in the oscillating transverse field: spin nutation once the resonance condition is fulfilled
- The resonance frequency is determined by γ

Nucleus	Net Spin	(MHz/T)	NMR freq. @ 7 Tesla (MHz)	Natl. abundance (%)
^{1}H	1/2	42.58	300	99.98
^{2}H	1	6.54	46	0.0115
^{13}C	1/2	10.71	75	1.1
^{15}N	1	-4.3	30	0.37
^{19}F	1/2	40.08	282	100
^{31}P	1/2	17.25	121	100

Chemical shift

- The simple expression $\vec{\mu}_N = \gamma_N \hat{\vec{I}}$ is (completely) correct only for a nucleus in vacuum

- In molecules, electrons change the local field experienced by nuclei: Zeeman interaction is modified

- This is a two-stage process:

- the external B_0 field induces currents in the electronic cloud

- when the electrons move, they change the magnetic field at the location of the nucleus: $B_0 \rightarrow B_{loc} = B_0 + B_{ind}$

electrons (shielding)

B_0

B_{ind}

nucleus

- The B_{ind} field is opposite in direction to B_0: the field is "shielded" by the electrons

- There are two contributions to B_{ind} (having similar magnitude but opposite signs)

- circulation of electrons in the ground state (diamagnetic)

- involvement of electrons in the excited state (paramagnetic)

8

Chemical shift

B₀
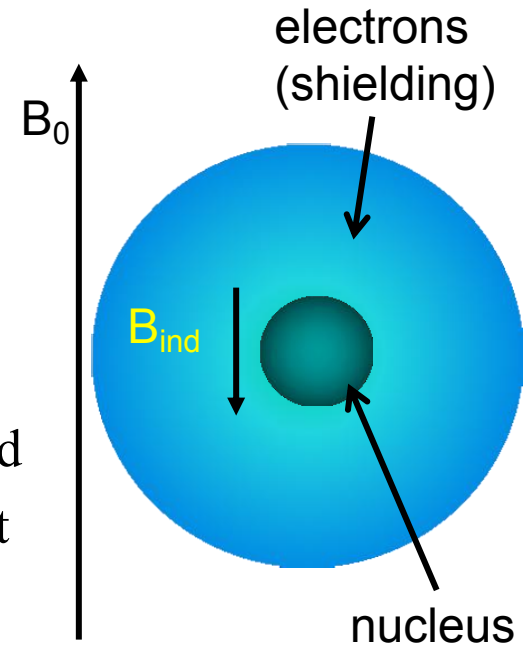
B_ind

- The induced field is always proportional to the B_0 field, therefore

$$\vec{B}_{loc} = \vec{B}_0 + \vec{B}_{ind} = \vec{B}_0 + \delta\vec{B}_0 = \vec{B}_0(1+\delta)$$

- The resonance frequency becomes $\omega = \gamma_N B_0(1+\delta) = \gamma_N B_0(1-\sigma)$

- The new parameter, δ (or σ), is called chemical shift: its precise value depends on the chemical environment of a nucleus (electron density, electronegativity of neighboring atoms, etc.).

- Thus, chemical shift is a **very important** source of information about molecular structure
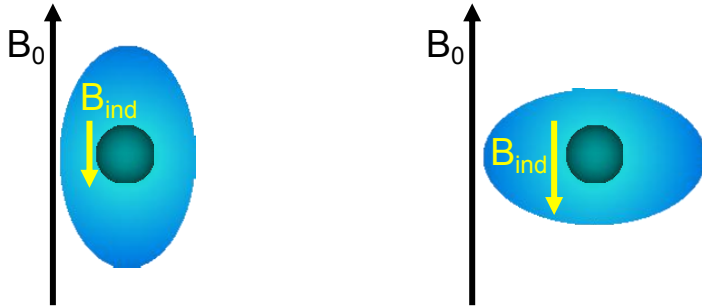
- Chemical shift referencing:

$$\delta = \frac{\omega - \omega_{ref}}{\omega_{ref}}$$

ω_{ref} is the NMR frequency of a standard reference compound (e.g., TMS)

- Chemical shift is usually small, so it is measured in ppm's of ω_{ref}

- Protons have a spread of δ-values of several ppm; other nuclei have a much wide range of δ-values

9
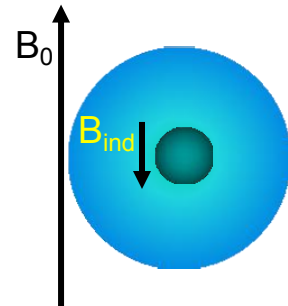
Chemical shift tensor

- For a shape asymmetric molecule, the B_{ind} and B_{loc} fields depend on the orientation

The B_{ind} value is different in these two cases

- The precise value of B_{ind} depends on the orientation. Mathematically, this effect can be described by introducing the chemical shift tensor

$$\vec{B}_{ind} = \hat{\delta}\vec{B}_0 \qquad \hat{\delta} = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix}$$

- Hence, the induced field becomes:

$$\vec{B}_{ind} = B_0 \begin{pmatrix} \delta_{xz} \\ \delta_{yz} \\ \delta_{zz} \end{pmatrix}$$

- At high-fields, only the z-component is of importance

Chemical shift tensor, continued

- The position of the NMR line is given by δ_{zz}, which is different for different orientations of the molecule

- In isotropic liquids, the result is simple: fast reorientation of the molecule gives rise to the symmetric CSA tensor. Hence, the isotropic chem. shift is

$$\delta_{iso} = \frac{1}{3}\left(\delta_{xx} + \delta_{yy} + \delta_{zz}\right) = \frac{1}{3}\text{Tr}\{\hat{\delta}\}$$

- In solids, for different orientations we obtain a different result.

- There are special directions, for which B_{ind} is parallel to B_0: principal axes of the δ-tensor. In the principal axes system (PAS) the tensor is diagonal:
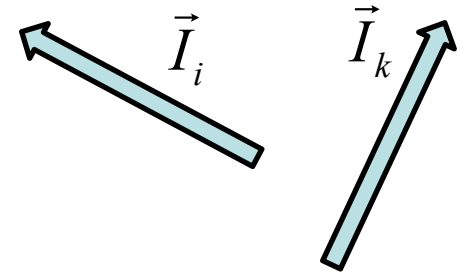
$$\hat{\delta} = \begin{pmatrix} \delta_{xx} & 0 & 0 \\ 0 & \delta_{yy} & 0 \\ 0 & 0 & \delta_{zz} \end{pmatrix}$$
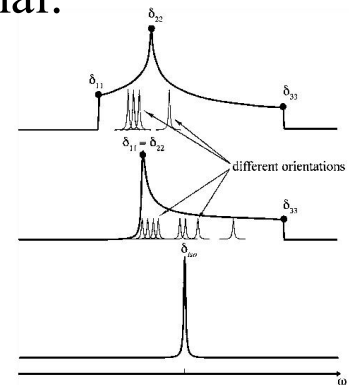
- When the B_0 field is parallel to X,Y,Z of the PAS, the line position is given by δ_{xx}, δ_{yy}, δ_{zz}.

Spin-spin coupling

$\vec{I}_i$ $\vec{I}_k$

- Two nuclei are two magnetic moments, which interact

- There are two contributions:

- dipole-dipole interaction, goes through spaces, complete analogue of the classical DDI

- scalar coupling, bonding electrons are involved quantum effects

- Both contributions can be included in the spin Hamiltonian

$$\hat{H}_D = b_{ik}\left\{ 3\left(\hat{\vec{I}}_i \cdot \vec{e}_{ik} \right)\left(\hat{\vec{I}}_k \cdot \vec{e}_{ik} \right) - \hat{\vec{I}}_i \cdot \hat{\vec{I}}_k \right\} \qquad\qquad \hat{H}_D = J_{ik}\left(\hat{\vec{I}}_i \cdot \hat{\vec{I}}_k \right)$$

- The DDI constant $b_{ik} = -\dfrac{\hbar \gamma_i \gamma_k}{r_{ik}^3}$ depends on the distance between the spins

- DDI depends on molecular orientation, given by the vector connecting the spins, J-coupling is isotropic

Dipole-dipole coupling

- The DDI Hamiltonian can be written by using tensors:

$$\hat{H}_D = b_{ik}\left\{ 3\left(\hat{\vec{I}}_i \cdot \vec{e}_{ik} \right)\left(\hat{\vec{I}}_k \cdot \vec{e}_{ik} \right) - \hat{\vec{I}}_i \cdot \hat{\vec{I}}_k \right\} = \hat{\vec{I}}_i \hat{\mathbf{D}}_{ik} \hat{\vec{I}}_k$$

- The D-tensor is a symmetric traceless tensor

- For this reason, on average DDI is zero: in isotropic liquids DDI does not change the position of NMR lines

- In solids, DDI gives rise to broad lines as it vanishes only at the magic angle.

- In high-field approximation (Zeeman term dominates)

$$\hat{H}_D = d_{ik}\left\{ 3\hat{I}_{iz}\hat{I}_{kz} - \hat{\vec{I}}_i \cdot \hat{\vec{I}}_k \right\}$$

Homonuclear case

$$\hat{H}_J = d_{ik} 2\hat{I}_{iz}\hat{I}_{kz}$$

Heteronuclear case

- The coupling strength is $\quad d_{ik} = \dfrac{1}{3}b_{ik}\left[3\cos\Theta_{ik} - 1 \right]$
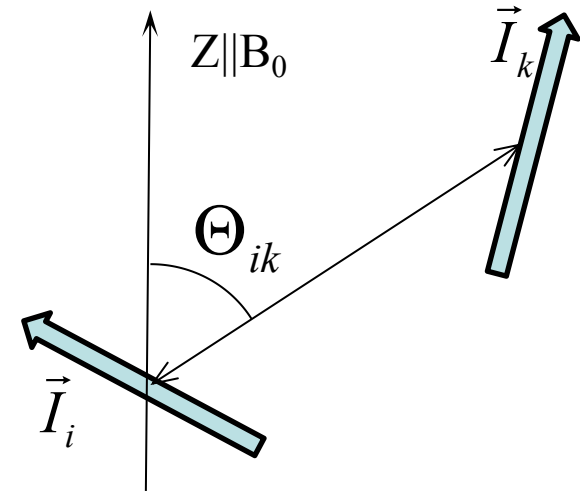
- Some numbers: proton-proton DDI at 1.5 Å is about 35 kHz
- DDI scales with $\gamma_i \times \gamma_k$ and decays as $1/r^3$

13

Dipole-dipole coupling

- Spectral manifestation of DDI:

- In single crystals, DDI gives rise to splitting of the NMR lines. The splitting is given by d_{ik} at a specific Θ_{ik} angle.

- In a powder, the splitting is different for different Θ_{ik} angles (ranging from 0 to π). To calculate the spectrum we need to calculate the splitting for each orientation and weight it with $\sin\Theta$.

$$\text{Splitting} \propto \left(3\cos^2\Theta - 1\right)$$

$$\Theta \in [0, \pi]$$

Such a pattern is termed Pake doublet
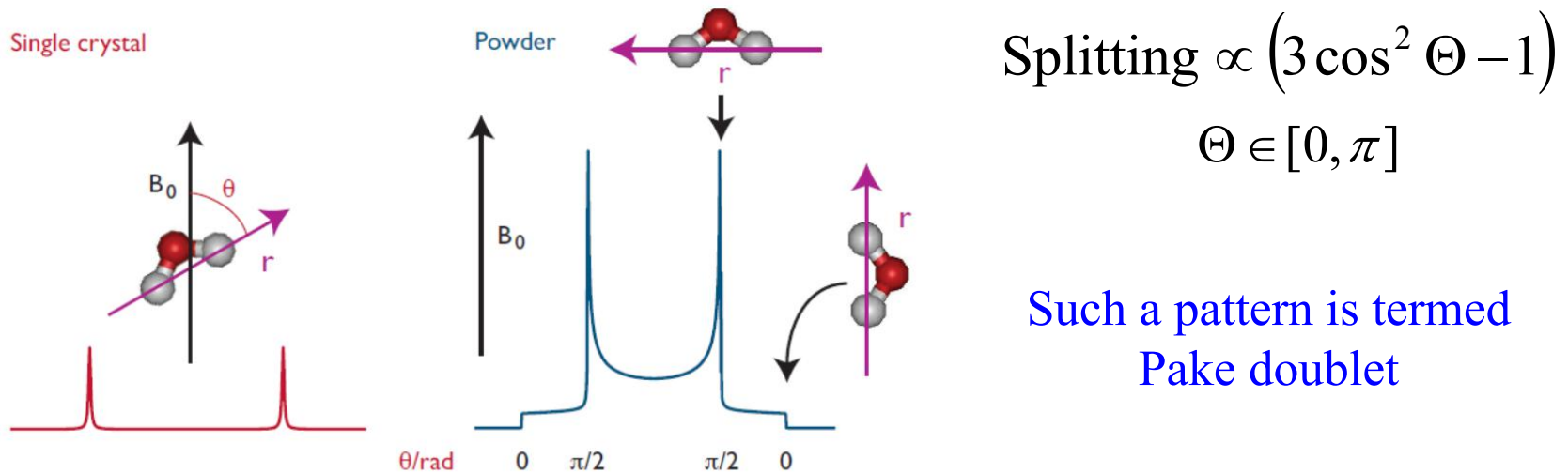
- In some systems, e.g., liquid crystals, partial averaging of DDI takes place. Instead of DDI we deal with RDC (Residual Dipolar Coupling)

$$\text{RDC}_{ik} = \frac{1}{3} b_{ik} \left\langle 3\cos\Theta_{ik} - 1 \right\rangle$$
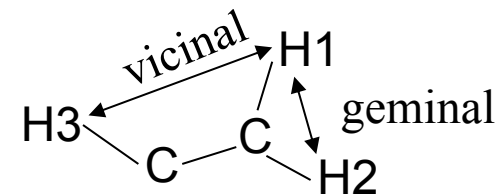
14

Scalar coupling

- Indirect coupling, which goes through bonding electrons

- Physical origin:
- nuclear spins interact with the electrons (hyperfine coupling)
- electrons become partly 'unpaired' and
- start interacting with the other nucleus by creating a small magnetic field
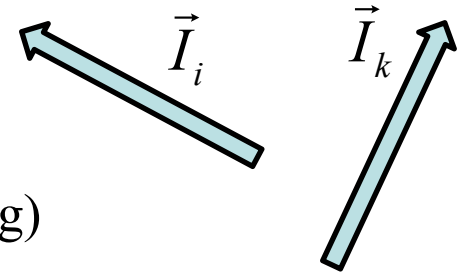
- As a result, a nuclear spin-spin coupling emerges $\hat{H}_J = J_{ik}\left(\hat{\vec{I}}_i \cdot \hat{\vec{I}}_k \right)$

- Typically, J-coupling is much smaller than DDI:
- For protons the largest coupling is usually the geminal coupling ^2J (15-20 Hz, negative), vicinal coupling ^3J is smaller (7 Hz, positive).
- For neighboring atoms in the molecule J-couplings are bigger: about 135 Hz for ^{13}C-H, about 50 Hz for ^{13}C-^{13}C
- J-couplings are not averaged out by motions. In liquid-state NMR they determine splitting of NMR multiplets

15

How can we read NMR spectra?

- For simplicity, here we discuss only liquid-state NMR. We also ignore any details of the spin dynamics and use selection rules $\Delta I_z = \pm 1$ for NMR transitions (single spin flips/flops)

- Hence, we try to construct "stick-spectra". Interactions, which matter, are chemical shifts and J-couplings.

- Algorithm:

(1) Different nuclei give signals at very different frequencies because of the large differences in γ's $\Rightarrow$ in experiment we detect separately NMR signals from protons, or carbons, or nitrogens (etc.);

(2) Different nuclei of the same kind (e.g., protons) give NMR signals not exactly at the same frequency due to chemical shifts;

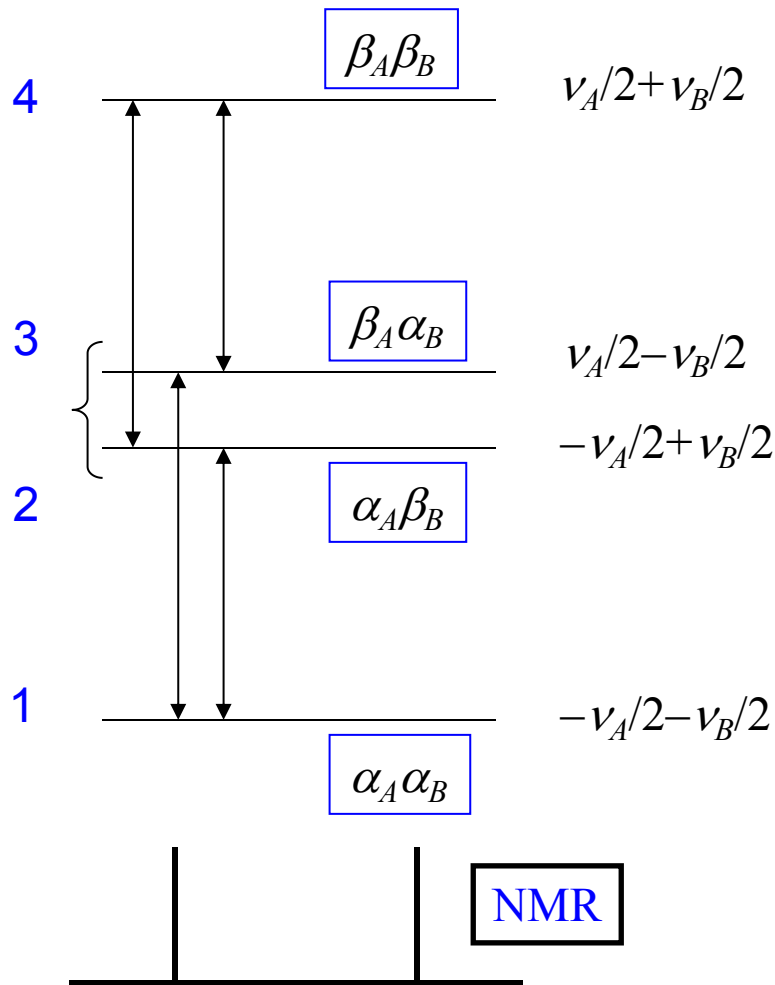(3) Lines corresponding to certain nuclei are split due to the presence of other spins ½.

Having this strategy, we can draw NMR spectra

Simplifications

- (1) Spins will be considered weakly coupled: for each pair of non-equivalents spins difference in Zeeman interactions, $\omega_i - \omega_j$, is much larger than the corresponding coupling J_{ij};

- (2) Quantum mechanics (perturbation theory) tells us that we can leave only $J_{ij}I_{iz}I_{jz}$ terms (secular terms);

- (3) Equivalent spins do not interact with each other (in fact, they do, but these couplings cannot be detected).

- What do we call equivalent spins:

- Same chemical shifts;

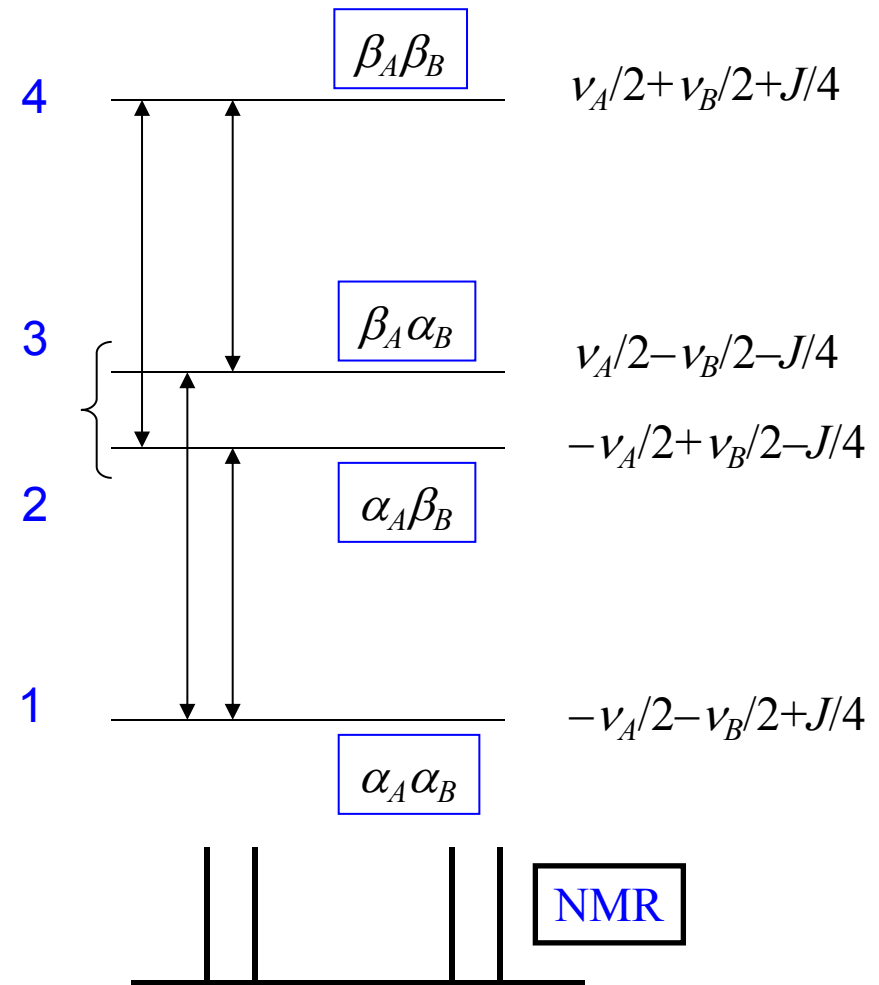- Identical couplings to all other nuclei.

NMR spectrum of two weakly coupled spins

Without interaction

4    $\boxed{\beta_A\beta_B}$ $\nu_A/2+\nu_B/2$

3    $\boxed{\beta_A\alpha_B}$ $\nu_A/2-\nu_B/2$

         $-\nu_A/2+\nu_B/2$

2    $\boxed{\alpha_A\beta_B}$

1    $-\nu_A/2-\nu_B/2$

$\boxed{\alpha_A\alpha_B}$

$\boxed{\text{NMR}}$

4 transitions from rules $\Delta I_z=\pm1$; 2 lines
because transitions overlap

With interaction

4    $\boxed{\beta_A\beta_B}$ $\nu_A/2+\nu_B/2+J/4$

3    $\boxed{\beta_A\alpha_B}$ $\nu_A/2-\nu_B/2-J/4$

         $-\nu_A/2+\nu_B/2-J/4$

2    $\boxed{\alpha_A\beta_B}$

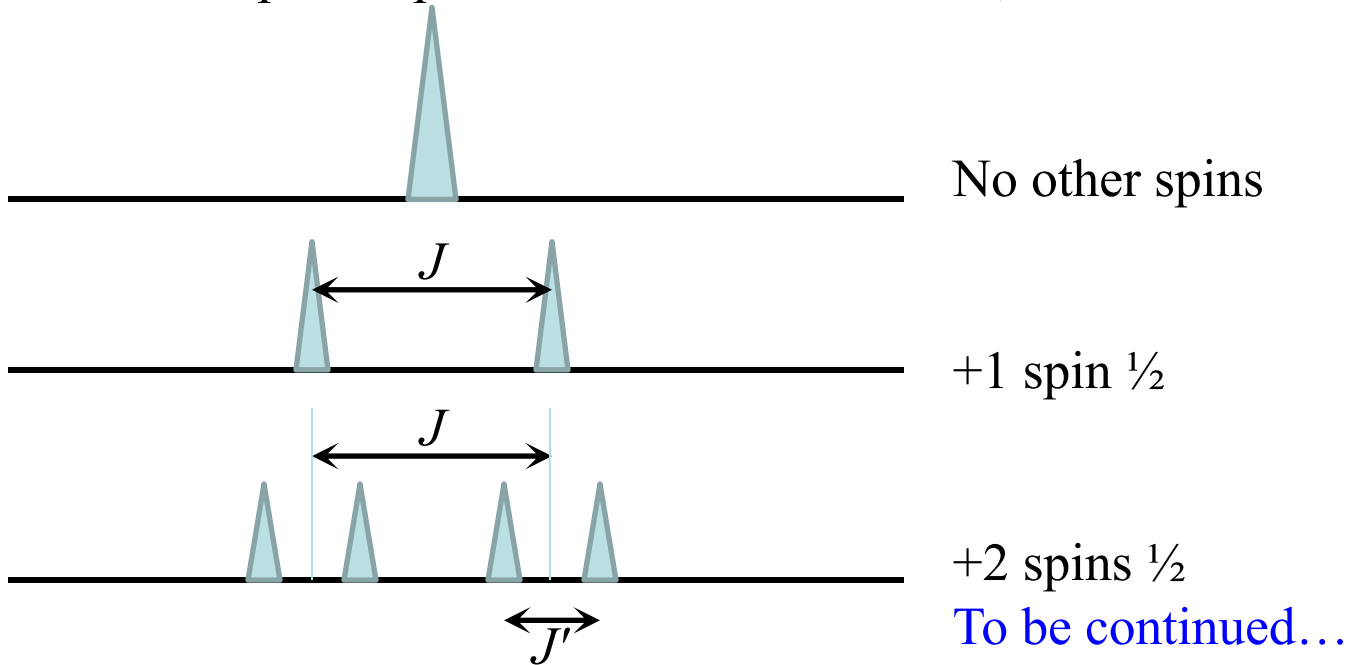1 $-\nu_A/2-\nu_B/2+J/4$
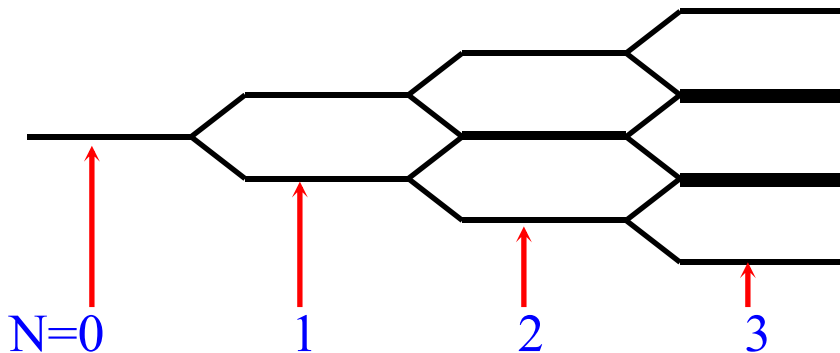
$\boxed{\alpha_A\alpha_B}$

$\boxed{\text{NMR}}$

4 transitions from rules $\Delta I_z=\pm1$; 4 lines
because transitions do not overlap

18

What to do for a large number of spins?

- Each spin ½ splits NMR line in two lines; their intensities are 2 times lower

No other spins

J

+1 spin ½

J

+2 spins ½
To be continued…

J'

- Coupling to a group of equivalent spins

N=0   1   2   3

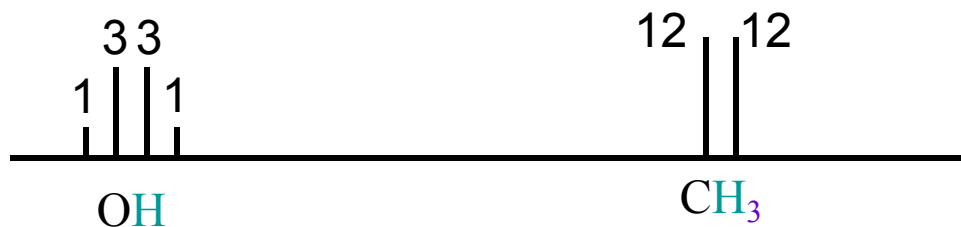Relative line intensities
in the multiplet

```
        1
      1   1
    1   2   1
  1   3   3   1
```
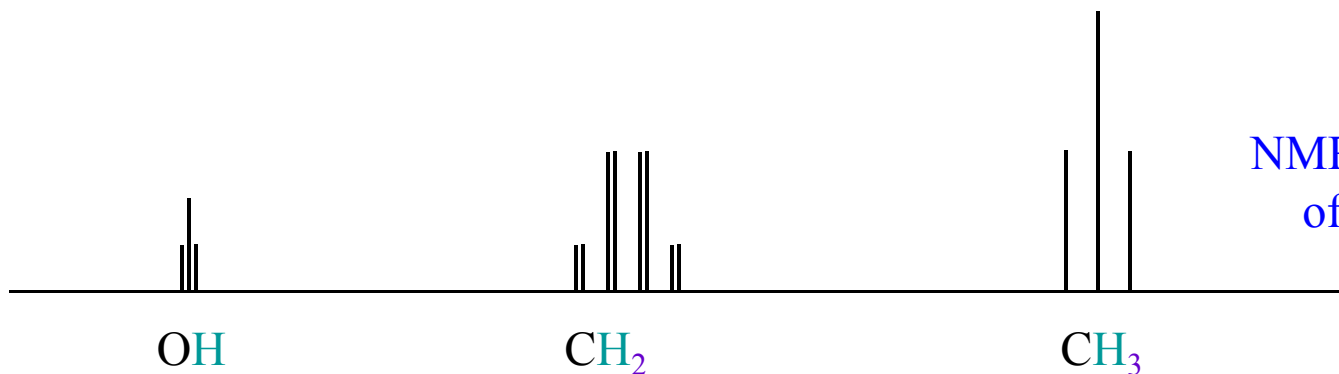
Pascal's triangle

Examples: CH_3OH and CH_3CH_2OH

NMR spectrum of methanol

NMR spectrum of ethanol

Intensity of all lines in the multiplet is proportional to the number of spins in the group
Splitting is the same for both spins (same J is operative)
Distribution of the intensities is given by Pascal's triangle rules

Quadrupolar coupling

- Q.C. is an <u>electric</u> interaction, which is nonetheless included in the nuclear spin Hamiltonian

- Origin of Q.C.

- A nucleus has electric charges, which interact with external E-fields

- Positive electric charge can be distributed non-uniformly

- The charge distribution can be decomposed into multipole components (charge q, dipole moment d, quadrupolar moment Q, etc.); the same is true for the field: the potential is given by the potential V_0 at the nucleus, its gradient V_1, gradient of the gradient V_2, etc.

- The energy of interaction is the sum of the following components:

   E_0, energy of q in potential V_0

   E_1, energy of d in potential V_1

   E_2, energy of Q in potential V_2

   continued...

- Important: nuclei have $d=0$! Shape of the nucleus, i.e. charge distribution, is related to the value of its spin I: $Q=0$ for $I=0,\frac{1}{2}$. Spin comes into play!

Quadrupolar coupling

- Q.C. is of importance for nuclei with $I > \frac{1}{2}$

- It comes from interaction of Q with the electric field gradient at the nucleus

- E-field gradient is a tensor, V-tensor:
$$V_{ij} = \frac{\partial^2 V}{\partial r_i \partial r_j}$$

- As any other tensor, it has a PAS, in this frame, simply
$$\hat{V} = \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix}$$

- The interaction of the E-field gradient with Q can be expressed via I
$$\hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \hat{\vec{I}} \mathbf{\hat{V}} \hat{\vec{I}}$$

- If H_Q is much smaller than the Zeeman terms, we can use perturbation theory. First-order Q.C. is
$$\hat{H}_Q^{(1)} = \frac{1}{6} \omega_Q^{(1)} \left(3\hat{I}_z^2 - I(I+1) \right), \quad \omega_Q^{(1)} = \frac{3eQV_{zz}}{2I(2I-1)\hbar}$$

- Second-order Q.C. is about $\omega_Q^{(2)} \sim \left(\omega_Q^{(1)} \right)^2 / \omega_0$

22

Quadrupolar coupling

- From the expression

$$\hat{H}_Q^{(1)} = \frac{1}{6}\omega_Q^{(1)}\left(3\hat{I}_z^2 - I(I+1)\right), \quad \omega_Q^{(1)} = \frac{3eQV_{zz}}{2I(2I-1)\hbar}$$

we can see that

- Q.C. vanishes for $I=0$ and $I=\frac{1}{2}$

- Orientation dependence is given by V_{zz}, which is the zz-component of the V-tensor.

- The result is different for a single crystal and for a powder sample

- The result is also different for half-integer and for integer I

- If we include the second-order terms into consideration the result becomes even more complex.

- In some cases, when Q is very large, we have to consider this contribution as well.
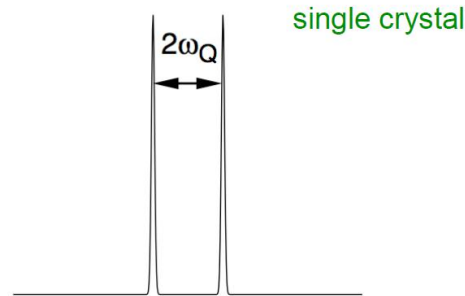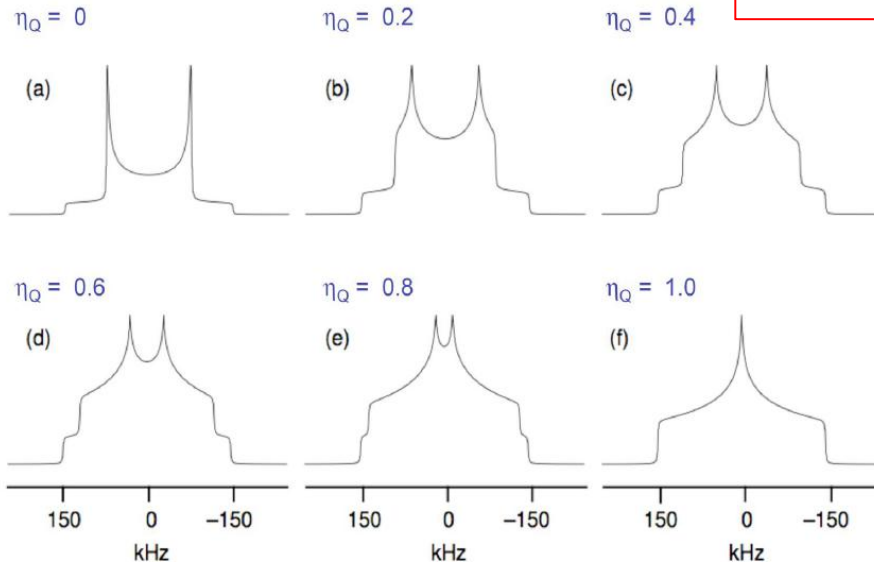
Quadrupolar coupling, integer spin

Spin I = 1

$m_I = -1$

$m_I = 0$

$m_I = +1$

ω_0

ω_0

$\omega_0 + \omega_Q$

$\omega_0 - \omega_Q$
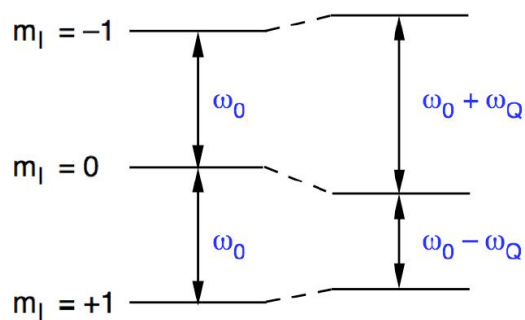
Zeeman   Quadrupolar

single crystal

$2\omega_Q$

Single crystal:
Just two lines

Powder spectra

$\eta_Q = 0$ (a)

$\eta_Q = 0.2$ (b)

$\eta_Q = 0.4$ (c)

$\eta_Q = 0.6$ (d)

$\eta_Q = 0.8$ (e)

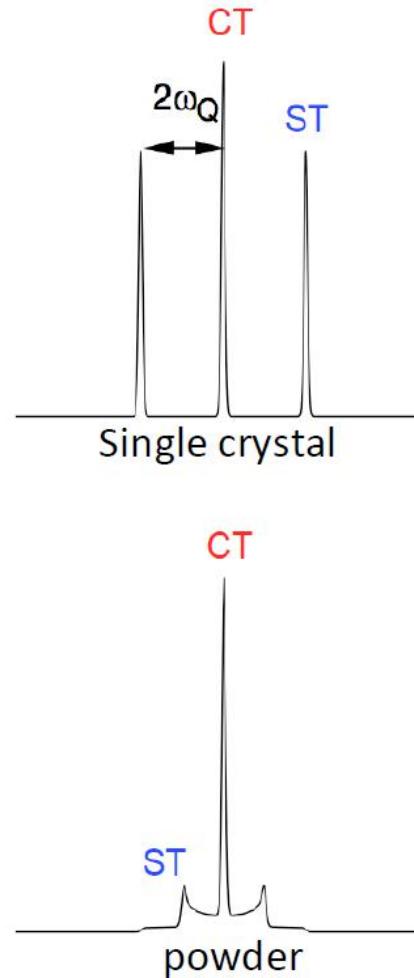$\eta_Q = 1.0$ (f)

150   0   −150
kHz

150   0   −150
kHz

150   0   −150
kHz
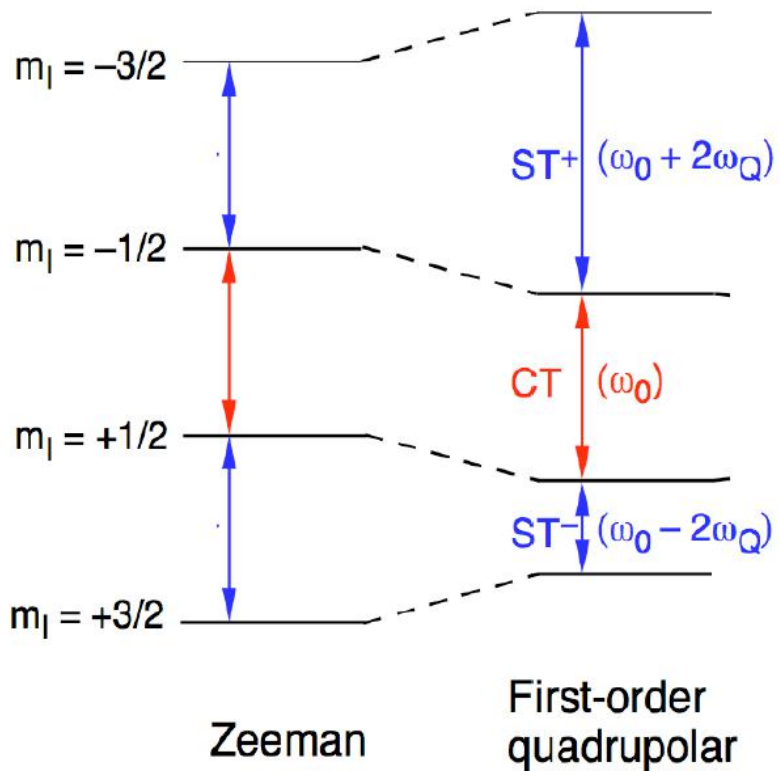
- Each component is broadened, since the splitting is different for different orientations

- For axially-symmetric V-tensor Pake pattern is obtained

- Otherwise, the pattern is more complex

24

Quadrupolar coupling, half-integer spin

Spin 3/2

$m_I = -3/2$

$m_I = -1/2$

$m_I = +1/2$

$m_I = +3/2$

$ST^+ \ (\omega_0 + 2\omega_Q)$

$CT \ (\omega_0)$

$ST^- \ (\omega_0 - 2\omega_Q)$

Zeeman

First-order quadrupolar

CT

$2\omega_Q$

ST

Single crystal

CT

ST

powder

Single crystal: Just two lines

- In a powder, the central line remain narrow
- Other lines get broadened, like in the previous example

25

Summary, part 1

- Key NMR interactions are introduced;

- We may also need to mention spin-rotation interaction, which is usually (not always) not that important for NMR;

- Spectral manifestations of the interactions are discussed.

Outline, part 2

- Notion of spin;

- Spin ensembles: density matrix;

- Density matrix description of NMR experiments;

- Some examples.

Spin: some history

- **Zeeman effect**: lines split in the presence of magnetic field
- Normal Zeeman effect (theory by **Lorentz**): splitting into three components

In the presence

of $\boldsymbol{B}_0 \| Z$

$\boldsymbol{k} \| Z$

$\sigma^+ \quad \sigma^-$

$\boldsymbol{k} \perp Z$

$\sigma \quad \pi \quad \sigma$
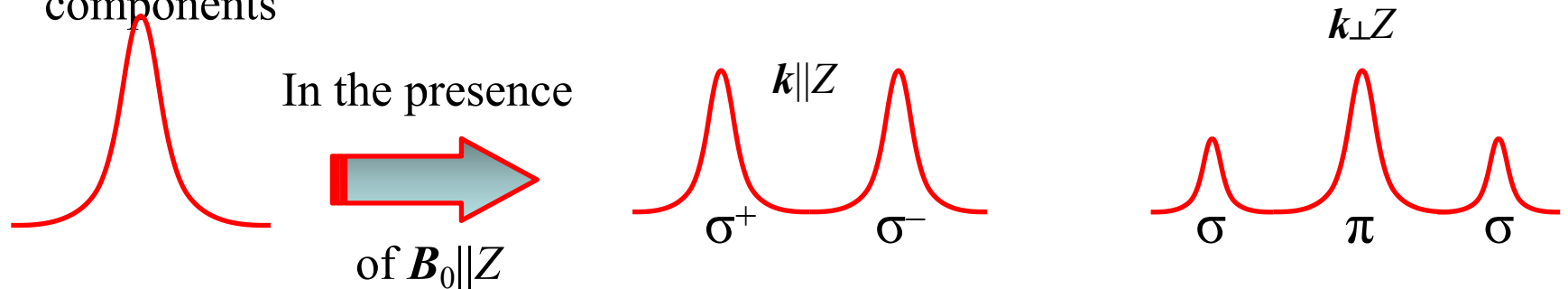
$$\omega_0; \ \omega_0 \pm \Omega \qquad \Omega = \frac{eB_0}{2m_e}$$

- Atom is a harmonic oscillator, its frequency is

- Problem: anomalous Zeeman effect also exists (met even more often)!

- A colleague who met me [Pauli] strolling rather aimlessly in the beautiful streets of Copenhagen said to me in a friendly manner, "You look very unhappy"; whereupon I answered fiercely, "**How can one look happy when he is thinking about the anomalous Zeeman effect?**"
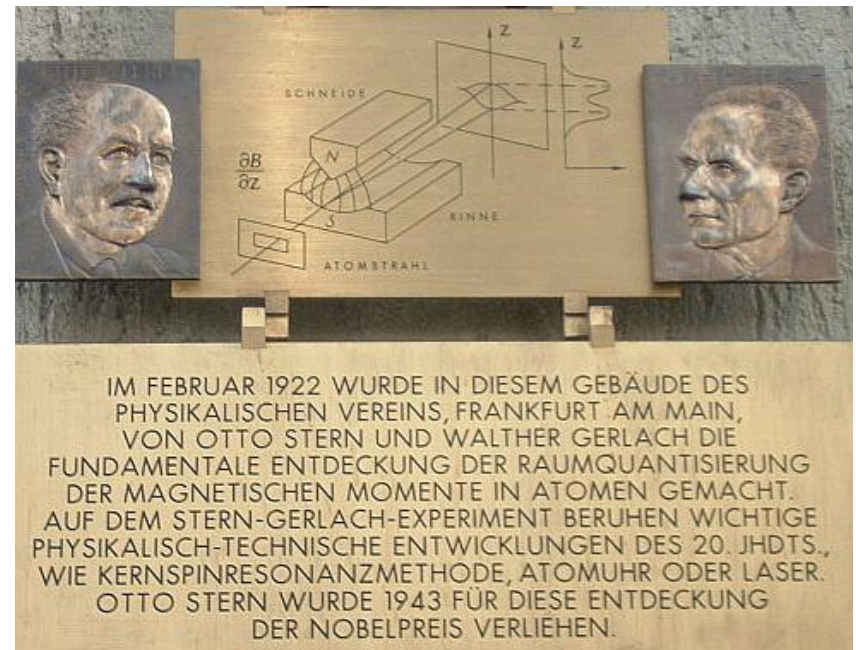
Spin: some history

- Pauli also tried to solve the problem concerning the number of electrons in each electron shell

- For a given n we have l from 0 to $(n-1)$, l_z from $-l$ to l ⟹ n^2 states

- In reality there are $2n^2$ electrons in each shell. Why 2 electrons for $n=1$, 8 electrons for $n=2$, 18 electrons for $n=3$?

- **Pauli's answer**:

  (1) there is one more quantum number, which

  can take only two possible values (*Zweideutigkeit*)

  (2) there cannot be two electrons in the same state, i.e., with

  all q. numbers being the same – exclusion principle

- **Problem**: nice answer, which leads to even harder questions: Why is it so? What is the last quantum number? To what degree of freedom does it correspond?

Spin: some history

- **Uhlenbeck and Goudsmit**: particles have "spin", corresponding to rotation of a particle spinning around its own axis

- Spin of the electron is ½: two states +½="spin-up" and −½="spin-down"

- This is not fully consistent from what people knew before. However, this is appropriate because spin is a quantum notion (we do not know why!)

- (S + L) can to explain the anomalous Zeeman effect (Pauli can be happy ☺)

- Stern-Gerlach experiment

✓ The beam of atoms is deflected by inhomogeneous field

✓ Reason: intrinsic magnetic moment (spin) of particles

✓ The distribution of the μ-vector is not continuous!

✓ Spin is quantized!!!

IM FEBRUAR 1922 WURDE IN DIESEM GEBÄUDE DES PHYSIKALISCHEN VEREINS, FRANKFURT AM MAIN, VON OTTO STERN UND WALTHER GERLACH DIE FUNDAMENTALE ENTDECKUNG DER RAUMQUANTISIERUNG DER MAGNETISCHEN MOMENTE IN ATOMEN GEMACHT. AUF DEM STERN-GERLACH-EXPERIMENT BERUHEN WICHTIGE PHYSIKALISCH-TECHNISCHE ENTWICKLUNGEN DES 20. JHDTS., WIE KERNSPINRESONANZMETHODE, ATOMUHR ODER LASER. OTTO STERN WURDE 1943 FÜR DIESE ENTDECKUNG DER NOBELPREIS VERLIEHEN.

Spin

- Spin of a particle is its intrinsic angular momentum (as if the particle rotates). Honestly, nobody knows where spin comes from.

- Spin is a very fundamental concept, which also affects the symmetry of the w.f. of a system of identical particles. Example: Pauli principle.

- Spin is a quantum notion: it vanishes if we tend $\hbar \to 0$!

- Spin operators are introduced in the same way as those for the angular momentum:

eigen-states are $\left| S, S_z \right\rangle$; $S^2 = S(S+1)$, S_z varies from $-S$ to S. commutation rules are

$$[\hat{S}_y, \hat{S}_z] = i\hat{S}_x, \ [\hat{S}_z, \hat{S}_x] = i\hat{S}_y, \ [\hat{S}_x, \hat{S}_y] = i\hat{S}_z$$

- An important difference from angular momentum: spin can be half-integer
- Spin operators are $(2S+1)*(2S+1)$ matrices
- For $S=1/2$ such matrices are related to the Pauli matrices

Spin ½

- Spin operator can be written as

$$\hat{\vec{S}} = \frac{1}{2}\hat{\vec{\sigma}}, \quad \hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$|\alpha\rangle = |\uparrow\rangle$$
$$|\beta\rangle = |\downarrow\rangle$$

- Useful relations of the Pauli matrices:

$$\hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = \hat{e}, \quad \hat{\sigma}_y\hat{\sigma}_z = i\hat{\sigma}_x, \quad \hat{\sigma}_z\hat{\sigma}_x = i\hat{\sigma}_y, \quad \hat{\sigma}_x\hat{\sigma}_y = i\hat{\sigma}_z$$

$$\hat{\sigma}_i\hat{\sigma}_k + \hat{\sigma}_k\hat{\sigma}_i = 2\delta_{ik}, \quad \left[\hat{\sigma}_i, \hat{\sigma}_j\right] = 2i\varepsilon_{ijk}\hat{\sigma}_k, \quad \mathrm{Tr}\{\hat{\sigma}_i\} = 0$$

- Every 2*2 hermitian matrix is a linear combination of the unity matrix and the Pauli matrices

- Rotations (same results as for *L*):
for an infinitely small rotation
$$\hat{U}(\vec{n}, \delta\varphi) = 1 - i\delta\varphi\left(\vec{n}\cdot\hat{\vec{S}}\right)$$

for a rotation by an arbitrary angle (rotation by 2π changes the sign of ψ!)

$$\hat{U}(\vec{n}, \varphi) = \exp\left[-i\varphi(\vec{n}\cdot\hat{\vec{\sigma}})/2\right] = \cos\frac{\varphi}{2} - i(\vec{n}\cdot\hat{\vec{\sigma}})\sin\frac{\varphi}{2}$$

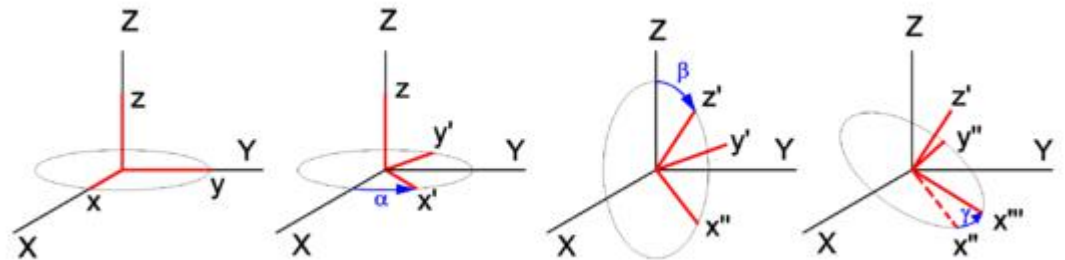# Spin ½: rotations

- Generally, the rotation operator is

$$\hat{U}(\vec{n}, \varphi) = \exp\left[-i\varphi(\vec{n} \cdot \hat{\sigma})/2\right] = \cos\frac{\varphi}{2} - i(\vec{n} \cdot \hat{\sigma})\sin\frac{\varphi}{2}$$

- Explicitly, rotations about X, Y, Z

$$\hat{U}_x(\varphi) = \begin{pmatrix} \cos\dfrac{\varphi}{2} & \sin\dfrac{\varphi}{2} \\ \sin\dfrac{\varphi}{2} & \cos\dfrac{\varphi}{2} \end{pmatrix}, \quad \hat{U}_y(\varphi) = \begin{pmatrix} \cos\dfrac{\varphi}{2} & i\sin\dfrac{\varphi}{2} \\ -i\sin\dfrac{\varphi}{2} & \cos\dfrac{\varphi}{2} \end{pmatrix}, \quad \hat{U}_z(\varphi) = \begin{pmatrix} e^{i\varphi/2} & 0 \\ 0 & e^{-i\varphi/2} \end{pmatrix},$$

- Euler rotations transition from any reference frame to a new frame can be achieved by three elemental rotations

- We go from an old x,y,z to new x,y,z : zyz-rotation by α, β, γ
- The rotation operator is

$$\hat{R} = \hat{R}(\alpha, \beta, \gamma) = \hat{R}_{z''}(\gamma)\hat{R}_y(\beta)\hat{R}_z(\alpha)$$

33

Spin evolution

- We can write the **Schrödinger equation** for the spin w.f.

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H}\Psi, \qquad \Psi(t=0) = \Psi_0$$

- Here the **Hamiltonian** (operator, which stands for the energy) is a matrix, which acts on the spin w.f.; it includes magnetic interactions

- For instance, interaction with external field, spin-spin interactions, etc.

$$\hat{H} = -\omega_0 \sum_i (1+\delta_i)\hat{S}_{iz} + \sum_{j<i} J_{ij}\left(\hat{\vec{S}}_i \cdot \hat{\vec{S}}_j\right)$$

- To solve the time-dependent solution we first solve the eigen-problem

$$\hat{H}\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle, \qquad \left|\Psi_0\right\rangle = \sum_n c_n\left|\Psi_n\right\rangle$$

- Then the solution is $\left|\Psi(t)\right\rangle = \sum_n c_n e^{-iE_n t/\hbar}\left|\Psi_n\right\rangle$

- Physical observables are:

$$\left\langle f\right\rangle = \left\langle\Psi(t)\left|\hat{f}\right|\Psi(t)\right\rangle = \sum_{mn} \exp(i\omega_{mn}t)c_m^* c_n f_{mn}, \quad \omega_{mn} = (E_m - E_n)/\hbar$$

Spin Hamiltonian

- To calculate what happens to the spin system we need to know the Hamiltonian
- Spins are little magnets, μ is proportional to S $\qquad \vec{\mu} = g\, \dfrac{q\hbar}{2mc}\, \vec{S}$

- Spin interactions coming from μ
- ✓ Zeeman interaction

$$E = -\left(\vec{\mu} \cdot \vec{B}\right) = -g\beta B_0 \hat{S}_z = -\hbar \omega_0 \hat{S}_z$$

in molecules this interaction is modified due to shielding of the external field (chemical shift). Generally, C.S. is a tensor
- ✓ Interaction with time-dependent RF-fields can be treated in the same way
- ✓ Spin-spin interaction

scalar   dipolar

$$E = J(\vec{S}_1 \cdot \vec{S}_2) \qquad\qquad E = -\frac{1}{r^3}\left[3(\vec{\mu}_1 \cdot \vec{n})(\vec{\mu}_2 \cdot \vec{n}) - (\vec{\mu}_1 \cdot \vec{\mu}_2)\right]$$

- ✓ Quadrupolar interaction

Simple example: spin ½ particle in an external field

- The Hamiltonian $\hat{H} = -\hbar \omega_0 \hat{S}_z, \quad E_{\alpha,\beta} = \mp \hbar \omega_0 / 2$

- Let us calculate the "spin polarization" vector: $\vec{P} = \left\langle \hat{\vec{\sigma}} \right\rangle \propto \vec{J} \propto \vec{M}$

- General expression for the w.f.: $\left| \Psi \right\rangle = \cos \dfrac{\theta}{2} \left| \alpha \right\rangle + e^{i\delta} \sin \dfrac{\theta}{2} \left| \beta \right\rangle$

- Calculation result:

$$P_x = \sin \theta \cos \delta, \quad P_y = \sin \theta \sin \delta, \quad P_z = \cos \theta \Rightarrow |\vec{P}| = 1$$

- What happens to the P-vector? Example:

$$\left| \Psi_0 \right\rangle = \frac{1}{\sqrt{2}} \left(\left| \alpha \right\rangle + \left| \beta \right\rangle \right) \Rightarrow \theta = \frac{\pi}{2}, \delta = 0 \Rightarrow \vec{P} \parallel x$$

- The time-dependent S.e. gives the following result (Larmor precession):

$$P_x(t) = \cos(\omega_0 t), \quad P_y(t) = -\sin(\omega_0 t), \quad P_z(t) = 0$$

Ensemble of spins

- This is not the end of the story: the w.f. description is often not sufficient

- Example: N_1 spins in the α-state and N_2 spins in the β-state

- What is the P-vector in this case?

$$P_x = P_y = 0, \quad P_z = (+1)\frac{N_1}{N_1 + N_2} + (-1)\frac{N_2}{N_1 + N_2} \quad \Rightarrow \quad |P| \le 1$$

- When spin ½ has a w.f. $|P|$=1: the spin ensemble does not have a w.f.!

- Similar problems arise when a system contains two subsystems: there might be a total w.f. existing, but (sometimes) no w.f. of a subsystem

- What should we do if the w.f. does not exist? Can we still evaluate expectation values of interest and describe experiments?

Density matrix

- If we have two sub-ensembles, we calculate expectation values for each realization and then perform averaging

$$\langle f \rangle = w_1 \langle \Psi_1 | \hat{f} | \Psi_1 \rangle + w_2 \langle \Psi_2 | \hat{f} | \Psi_2 \rangle, \quad w_i = \frac{N_i}{N}$$

- From the mathematical point of view:

$$\langle f \rangle = \mathrm{Tr}\{\hat{f}\hat{\rho}\}, \quad \hat{\rho} = \sum_i w_i | \Psi_i \rangle \langle \Psi_i | = \overline{| \Psi \rangle \langle \Psi |}$$

- The new operator is called "density operator" or "density matrix"
- The problem is solved: we can calculate expectation values!

$$\langle f \rangle = \mathrm{Tr}\{\hat{f}\hat{\rho}\} = \sum_{mn} \overline{c_m^* c_n} f_{mn} = \sum_{mn} \rho_{nm} f_{mn}$$

$$\hat{\rho} = \sum_{m,n} \rho_{mn} | m \rangle \langle n |, \quad \rho_{mn} = \overline{c_m c_n^*}$$

- **Questions**:
  Properties of the d.m.? Time-dependence of d.m.?

Properties of the density matrix

- Physical meaning of the elements:

  Diagonal elements are populations $p_n = \rho_{nn} = \overline{\left| c_n \right|^2}$

  Off-diagonal elements are coherences ρ_{mn} (explained later)

- The trace of d.m. is equal to 1

- The d.m. is a hermitian matrix: $(N^2 - 1)$ independent parameters

- When can we still use the w.f. description?

- When the w.f. is existing (pure state), we obtain

$$\hat{\rho} = \left| \Psi \right\rangle \left\langle \Psi \right| \;\Rightarrow\; \hat{\rho}^2 = \left| \Psi \right\rangle \left\langle \Psi \mid \Psi \right\rangle \left\langle \Psi \right| = \left| \Psi \right\rangle \left\langle \Psi \right| = \hat{\rho}$$

- When this relation does not hold (mixed state), we must not (!) use the w.f. description. Example: ensemble of spins-1/2 at equilibrium

$$\hat{\rho}_{eq} = \frac{1}{Z} \exp\left[-\frac{\hat{H}}{kT} \right] \;\Rightarrow\; w_\alpha \Big/ w_\beta = \exp\left[-\frac{\Delta E}{kT} \right] = 1 + \delta p \Big/ 2 \,, \quad \delta p \ll 1$$

In this case $\rho^2 = \rho$ does not hold

Density matrix of a spin-½ particle

- D.m. of a spin ½ particle $\quad \hat{\rho} = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix}$

- The polarization vector components are

$$P_x = 2\,\text{Re}\{\rho_{\alpha\beta}\}, \quad P_y = -2\,\text{Im}\{\rho_{\alpha\beta}\}, \quad P_z = \rho_{\alpha\alpha} - \rho_{\beta\beta}$$

- Rewriting the d.m.: $\quad \hat{\rho} = \dfrac{1}{2}\begin{pmatrix} 1+P_z & P_x - iP_y \\ P_x + iP_y & 1 - P_z \end{pmatrix} = \dfrac{1}{2}\left[\hat{E} + \left(\vec{P}\cdot\hat{\vec{\sigma}}\right)\right]$

- The d.m. is expressed via the P-vector and the Pauli matrices

$$\rho_{\alpha\alpha} \qquad\qquad \rho_{\beta\beta} \qquad\qquad \rho_- = \rho_{\alpha\beta} \qquad\qquad \rho_+ = \rho_{\beta\alpha}$$
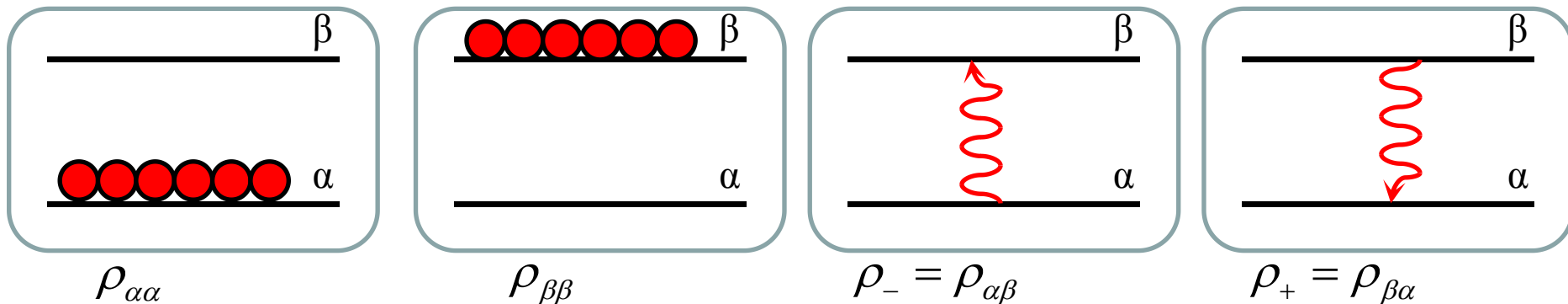
- Longitudinal $M = \Delta$(population); transverse M = coherence
- Phase of the coherence: direction in the $\{x,y\}$-plane

40

Density matrix of a spin-½ particle

- D.m. of a spin ½ particle $\hat{\rho} = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix}$

- The polarization vector components are

$$P_x = 2\,\mathrm{Re}\{\rho_{\alpha\beta}\}, \quad P_y = -2\,\mathrm{Im}\{\rho_{\alpha\beta}\}, \quad P_z = \rho_{\alpha\alpha} - \rho_{\beta\beta}$$

- Rewriting the d.m.: $\hat{\rho} = \frac{1}{2}\begin{pmatrix} 1+P_z & P_x - iP_y \\ P_x + iP_y & 1-P_z \end{pmatrix} = \frac{1}{2}\left[\hat{E} + \left(\vec{P}\cdot\hat{\sigma}\right)\right]$

- We can use the operator basis (each matrix is like a basis ket)

$$\{\hat{E}, \hat{S}_x, \hat{S}_y, \hat{S}_z\}$$

- The d.m. is a vector in this basis:

$$\hat{\rho} = \frac{1}{2}\hat{E} + P_x\,\hat{S}_x + P_y\,\hat{S}_y + P_z\,\hat{S}_z = \sum c_i\hat{Q}_i$$

- It is easy to obtain the equation of motion (comes later)

Two or more spins ½

- The d.m. for two spins can be expressed in terms of product operators

$$\{\hat{E}, \hat{S}_x, \hat{S}_y, \hat{S}_z\} \otimes \{\hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z\} = \begin{Bmatrix} \hat{E}; \hat{S}_x, \hat{S}_y, \hat{S}_z; \hat{I}_x, \hat{I}_y, \hat{I}_z; \hat{S}_x\hat{I}_x, \hat{S}_y\hat{I}_x, \hat{S}_z\hat{I}_x, \\ \hat{S}_x\hat{I}_y, \hat{S}_y\hat{I}_y, \hat{S}_z\hat{I}_y, \hat{S}_x\hat{I}_z, \hat{S}_y\hat{I}_z, \hat{S}_z\hat{I}_z \end{Bmatrix}$$

- Each product operator is now a 4*4 matrix; likewise, the Hamiltonian is a 4*4 matrix and it is expressed via the product operators

- What is the direct product (Kronecker product)?

$$\hat{A} \otimes \hat{B} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \otimes \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_{11}\hat{B} & a_{12}\hat{B} \\ a_{21}\hat{B} & a_{22}\hat{B} \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{pmatrix}$$

- Example with 2 spins:

$$\hat{S}_x = \hat{S}_x \otimes \hat{E} = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

- Other operators can be constructed in the same way. More spins: use direct products of spin operators

42

Two spins ½

- Relation between populations/coherences and d.m. elements

Energy level diagram
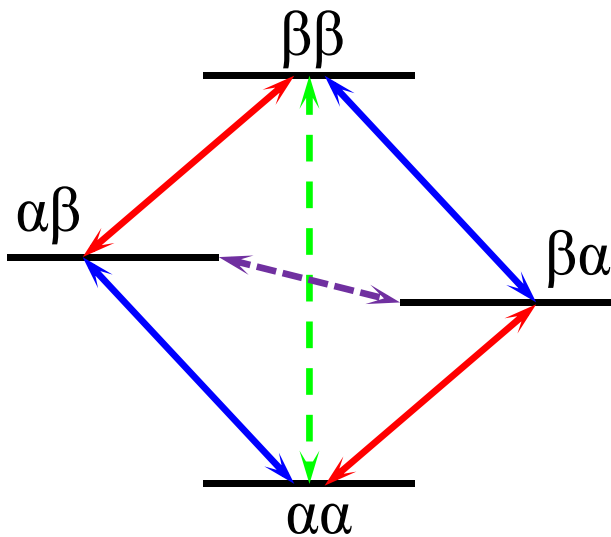
Density matrix

	αα	αβ	βα	ββ
αα	$p_{\alpha\alpha}$	SQC	SQC	DQC
αβ	SQC	$p_{\alpha\beta}$	ZQC	SQC
βα	SQC	ZQC	$p_{\beta\alpha}$	SQC
ββ	DQC	SQC	SQC	$p_{\beta\beta}$

- SQCs are given by S_x, S_y, S_xI_z, S_yI_z, I_x, I_y, S_zI_x, S_zI_y
- DQCs and ZQCs are given by combinations of S_xI_x, S_yI_y, S_xI_y, S_yI_x
- We can directly measure only transverse magnetization S_x, S_y, I_x, I_y
- Other operators cannot be observed directly, but they affect the signal
- Coherence order for ρ_{mn}: $p_{mn} = M(|m\rangle) - M(|n\rangle)$

How does the d.m. evolve?

- The S.e. in the bra and ket representations is

$$\frac{\partial}{\partial t}|\Psi\rangle = -\frac{i}{\hbar}\hat{H}|\Psi\rangle, \qquad \frac{\partial}{\partial t}\langle\Psi| = \frac{i}{\hbar}\langle\Psi|\hat{H}$$

- The equation for the d.m. is as follows:

$$\frac{\partial}{\partial t}\hat{\rho} = \frac{\partial}{\partial t}\left\{|\Psi\rangle\langle\Psi|\right\} = \left\{\frac{\partial}{\partial t}|\Psi\rangle\right\}\langle\Psi| + |\Psi\rangle\left\{\frac{\partial}{\partial t}\langle\Psi|\right\} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right]$$

Liouville-von Neumann equation

- The solution is simple for a time-independent Hamiltonian:

$$\hat{\rho}(t) = \exp\left[-\frac{i}{\hbar}\hat{H}t\right]\hat{\rho}_0 \exp\left[\frac{i}{\hbar}\hat{H}t\right]$$

- For a time-dependent Hamiltonian we solve the equation numerically in small time steps or use some tricks

- The LvN equation is similar to that for the time-derivative of an operator in the Heisenberg representation. However, the sign is "–" and the meaning is different: in the Heisenberg representation the d.m. and w.f are constant

Time-dependence of the d.m.

- The LvN equation is simple in the eigen-basis of the Hamiltonian

$$\frac{\partial}{\partial t}\rho_{mm} = 0, \quad \frac{\partial}{\partial t}\rho_{mn} = -\frac{i}{\hbar}\left(E_m - E_n\right)\rho_{mn} = -i\omega_{mn}\rho_{mn}$$

- The solution is also simple:

$$\rho_{mm} = \text{const}, \quad \rho_{mn} = e^{-i\omega_{mn}t}\rho_{mn}^0$$

- Eigen-state populations do not evolve (a quantum system stays forever in an eigen-state); off-diagonal elements oscillate at the ω_{mn} frequency (coherence).

- Oscillatory evolution comes about when the initial state is a coherent superposition of eigen-states.

- Expectation value of an operator evolves as follows:

$$\langle f \rangle = \sum_{mn} f_{mn}\rho_{nm}(t) = \sum_{mn} f_{mn}\rho_{nm}\exp\{i\omega_{mn}t\}$$

coherences result in "quantum beats"

Precession of spins ½

- The d.m. is $\hat{\rho} = \frac{1}{2}\left[\hat{E} + \left(\vec{P}\cdot\hat{\sigma}\right)\right]$

- Likewise, the Hamiltonian is: $\hat{H} = \frac{1}{2}\left[\hat{E}\cdot\mathrm{Tr}\{\hat{H}\} + \left(\vec{H}\cdot\hat{\sigma}\right)\right]$

- So, we can define the *P*-vector and the field-vector

- Substitution to the LvN equation:

$$2\frac{\partial}{\partial t}\hat{\rho} = \frac{\partial}{\partial t}\left\{\left(\vec{P}\cdot\hat{\sigma}\right)\right\} = -\frac{i}{2\hbar}\left[\left(\vec{H}\cdot\hat{\sigma}\right),\left(\vec{P}\cdot\hat{\sigma}\right)\right]$$

- The commutator term is:

$$\left[\left(\vec{H}\cdot\hat{\sigma}\right),\left(\vec{P}\cdot\hat{\sigma}\right)\right] = \sum_{i,j}H_i P_j\left[\sigma_i,\sigma_j\right] = 2i\sum_{i,j}H_i P_j \varepsilon_{ijk}\hat{\sigma}_k = 2i\left(\left[\vec{H}\times\vec{P}\right]\cdot\hat{\sigma}\right)$$

- Finally we obtain **precession** of the *P*-vector: $\dfrac{d\vec{P}}{dt} = \dfrac{1}{\hbar}\left[\vec{H}\times\vec{P}\right]$

- Furthermore, all 2-level systems behave this way: precession of the effective spin in an external field in 3D. The prec. frequency is $\omega_{pr}=|H|/\hbar$

46

Magnetic resonance

- Let us consider also the B_1-field (circular polarization)

$$\vec{B} = \vec{i} B_1 \cos(\omega t) - \vec{j} B_1 \sin(\omega t) + \vec{k} B_0$$

- The Hamiltonian is

$$\hat{H} = -\hbar\gamma\left(B_0 \hat{S}_z + B_1 e^{i\omega t \hat{S}_z} \hat{S}_x e^{-i\omega t \hat{S}_z}\right)$$

- The LvN equation reads

$$\frac{\partial \hat{\rho}}{\partial t} = i\omega_0\left(\hat{S}_z \hat{\rho} - \hat{\rho}\hat{S}_z\right) - i\omega_1\left\{e^{i\omega t \hat{S}_z} \hat{S}_x e^{-i\omega t \hat{S}_z} \hat{\rho} - \hat{\rho} e^{i\omega t \hat{S}_z} \hat{S}_x e^{-i\omega t \hat{S}_z}\right\}$$

- We can define the d.m. in the **rotating frame** (interaction representation)

$$\hat{\rho} = e^{i\omega t \hat{S}_z} \tilde{\hat{\rho}} e^{-i\omega t \hat{S}_z}$$

- Equation for the new d.m.

$$\frac{\partial \tilde{\hat{\rho}}}{\partial t} = i\omega_0\left(\hat{S}_z \tilde{\hat{\rho}} - \tilde{\hat{\rho}}\hat{S}_z\right) + i\omega_1\left(\hat{S}_x \tilde{\hat{\rho}} - \tilde{\hat{\rho}}\hat{S}_x\right) = -\frac{i}{\hbar}\left[\hat{H}_{eff}, \tilde{\hat{\rho}}\right]$$

- The result is (still) precession in an **effective field**

$$\hat{H}_{eff} = -\hbar(\omega_0 - \omega)\hat{S}_z - \hbar\omega_1\hat{S}_x \implies \vec{H}_{eff}, \Omega_{pr} = \sqrt{\Delta\omega^2 + \omega_1^2}$$

47

QM description of NMR experiments

- We (usually) start with thermally polarized spins:

$$\hat{\rho}_{eq} = \frac{1}{Z}\exp\left[-\frac{\hat{H}_0}{kT}\right] \approx \frac{1}{Z}\left(\hat{E} + \frac{\hbar\omega_0}{kT}\hat{S}_z\right)$$

- The same is true in the rotating frame because the d.m. commutes with the rotation operator; the unity operator can be dropped off.

- The d.m. evolves under the action of a time-dependent Hamiltonian (pulses, free evolution, MAS)

- Solution methods: split the time-axis into small intervals δt, where $H \approx$ const

$$\hat{\rho}(t) = e^{-i\hat{H}(t_n)\delta t} \cdot e^{-i\hat{H}(t_{n-1})\delta t} \cdot \ldots \cdot e^{-i\hat{H}(t_2)\delta t} \cdot e^{-i\hat{H}(t_1)\delta t} \times$$

$$\times \hat{\rho}_0 e^{i\hat{H}(t_1)\delta t} \cdot e^{i\hat{H}(t_2)\delta t} \cdot \ldots \cdot e^{i\hat{H}(t_{n-1})\delta t} \cdot e^{i\hat{H}(t_n)\delta t}$$

- Looks complex, but the idea is simple: each evolution period leads to two multiplications (at the left and at the right)

- In many cases the solution can only be done numerically

- When the Hamiltonian is changed in a periodic way, there are some tricks available (AHT, Floquet theory)

RF-pulses

- What happens to the d.m. (magnetization) when we apply a pulse?
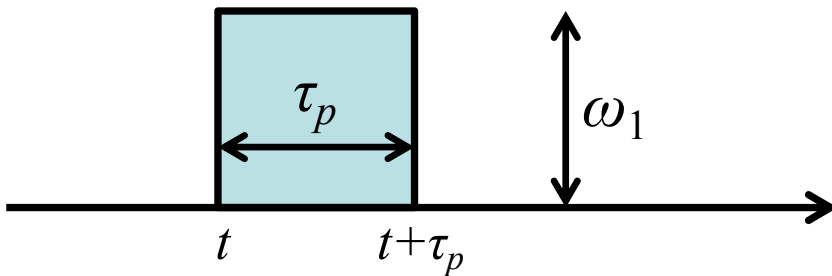
the phase is ϕ_p
the flip angle is $\varphi = \omega_1 \tau_p$

- The w.f. and d.m. after the pulse

$$\left| \Psi_{after} \right\rangle = \hat{R}_{\phi_p}(\varphi) \left| \Psi_{before} \right\rangle, \qquad \left\langle \Psi_{after} \right| = \left\langle \Psi_{before} \right| \hat{R}_{\phi_p}(-\varphi)$$

$$\hat{\rho}_{after} = \hat{R}_{\phi_p}(\varphi) \hat{\rho}_{before} \hat{R}_{\phi_p}(-\varphi)$$

- The action of a strong pulse is equivalent to a rotation (we assume that only the B_1-term is relevant)

$$\hat{R}_{\phi_p}(\varphi) = \exp\left[-i\omega_1 \tau_p \left(\cos\phi_p \hat{S}_x + \sin\phi_p \hat{S}_y\right)\right] = \exp\left[-i\varphi\left(\cos\phi_p \hat{S}_x + \sin\phi_p \hat{S}_y\right)\right]$$

- A $\pi/2$-pulse generates a coherence, a π-pulse inverts the populations

$$\hat{R}_{\phi_p}(\pi/2)\hat{S}_z \hat{R}_{\phi_p}(-\pi/2) = -\hat{S}_y, \qquad \hat{R}_{\phi_p}(\pi)\hat{S}_z \hat{R}_{\phi_p}(-\pi) = -\hat{S}_z$$

49

"Sandwich relationships"

- Is there a simple way to calculate the effect of pulses?

- Three cyclically commuting operators:

$$[\hat{A}, \hat{B}] = i\hat{C}, \quad [\hat{C}, \hat{A}] = i\hat{B}, \quad [\hat{B}, \hat{C}] = i\hat{A}$$

- Example:

$$[\hat{S}_y, \hat{S}_z] = i\hat{S}_x, \quad [\hat{S}_z, \hat{S}_x] = i\hat{S}_y, \quad [\hat{S}_x, \hat{S}_y] = i\hat{S}_z$$

- The following relation is then true:

$$\exp[-i\theta\hat{A}]\hat{B}\exp[i\theta\hat{A}] = \cos\theta\,\hat{B} + \sin\theta\,\hat{C}$$

- A, B, C are like the axis of our 3D-space; we "rotate" *B* "around" A by the angle θ. Cyclic permutations provide two more relations

$$\exp[-i\theta\hat{B}]\hat{C}\exp[i\theta\hat{B}] = \cos\theta\,\hat{C} + \sin\theta\,\hat{A}$$
$$\exp[-i\theta\hat{C}]\hat{A}\exp[i\theta\hat{C}] = \cos\theta\,\hat{A} + \sin\theta\,\hat{B}$$

- Of course, these rules apply to the spin operators

- RF-pulses give *x* and *y*-rotations. Free precession gives a *z*-rotation by a time-dependent angle ωt

See M. H. Levitt, "Spin Dynamics", cyclic commutation

50

Phase of the pulse

- Different phases

  x-pulse, $_p$=0
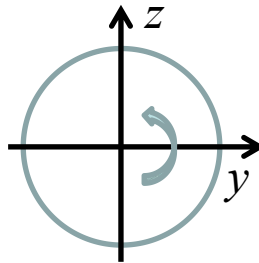
  y-pulse, $_p$=$\pi/2$
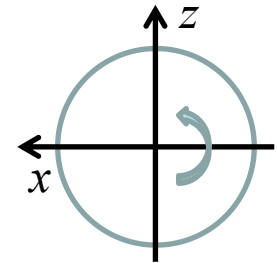
  $-x$-pulse, $_p$=π
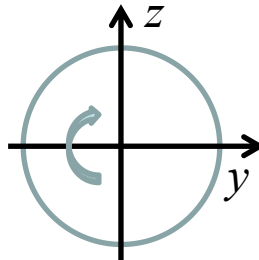
  $-y$-pulse, $_p$=$2\pi/2$
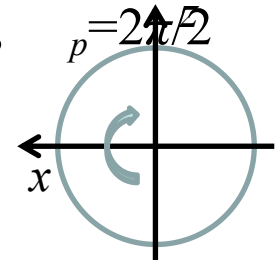
- Pulse of a general phase is a combination of three rotations

$$\hat{R}_{\phi_p}(\varphi) = \exp\left[-i\varphi\left(\cos\phi_p\hat{S}_x + \sin\phi_p\hat{S}_y\right)\right] = \hat{R}_z(\phi_p)\hat{R}_x(\varphi)\hat{R}_z(-\phi_p)$$

- Rotation about z turns the {x,y} axes; then a pulse is turning the spins around the new x; finally, we return to the original frame.

- Free precession is just a z-rotation

51

Single-pulse NMR experiment

- Initial spin order is S_z

$$\hat{\rho} = \frac{1}{2}\hat{E} + \frac{1}{2}P\hat{S}_z$$

- A pulse generates transverse magnetization

$$\hat{\rho} = \frac{1}{2}\hat{E} - \frac{1}{2}P\hat{S}_y$$

- Free precession changes the d.m.

$$\hat{\rho} = \frac{1}{2}\hat{E} - \frac{1}{2}P\left(\hat{S}_y \cos \omega t - \hat{S}_x \sin \omega t\right)$$

- We can detect the FID and obtain the spectrum by doing the Fourier transform

- Generally, the FID is

$$\text{FID}(t) \propto 2i\rho_- \exp(-i\phi_{rec}), \qquad \rho_- = \rho_{\beta\alpha} = P_x + iP_y$$

- If the receiver phase is 0 we obtain a positive Lorentzian (after adding T_2)

  when $\phi_{rec}=\pi$ we obtain a negative line

  when $\phi_{rec}=\pm\pi/2$ we obtain a dispersive line

More complex NMR experiments

- The S_x, S_y, S_z are not the only operators, which satisfy the cyclic commutation relation

- Other operators of this kind:

$$\left\{ \hat{S}_x, \hat{S}_y \hat{I}_z, \hat{S}_z \hat{I}_z \right\} \qquad\qquad \left\{ \hat{S}_y, \hat{S}_x \hat{I}_z, \hat{S}_z \hat{I}_z \right\}$$

- The operator $S_z I_z$ is often present in the Hamiltonian (secular interaction)
- We can immediately obtain what different interactions do

Effect of the chemical shift:
$S_x \Rightarrow S_x \cos(\omega_a t) + S_y \sin(\omega_a t)$

Effect of J-coupling with spin I:
$S_x \Rightarrow S_x \cos(J_{ab} t) + S_y I_z \sin(J_{ab} t)$
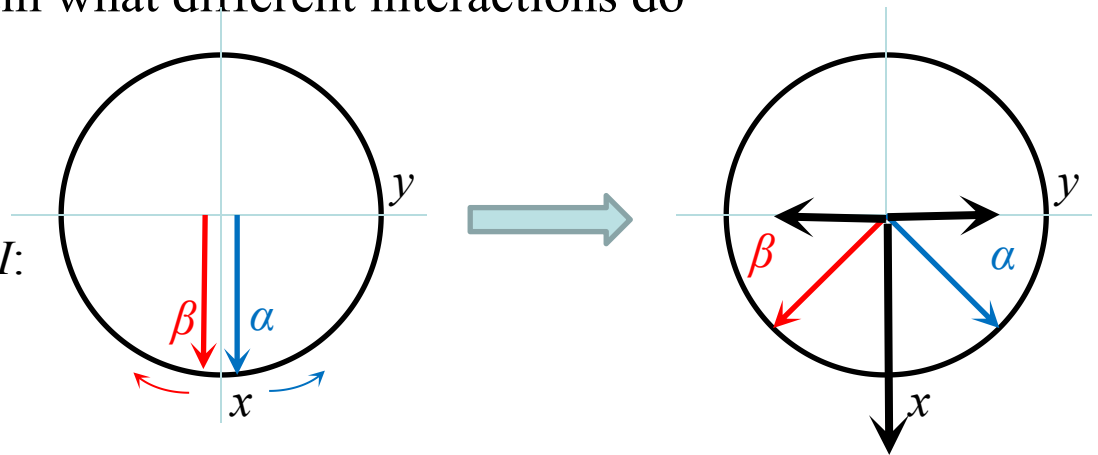
x-component changes in the usual way; y-component is given by the population difference of the α- and β-states of spin I, which is I_z

53

Key to simple experiments (from Shimon Vega)
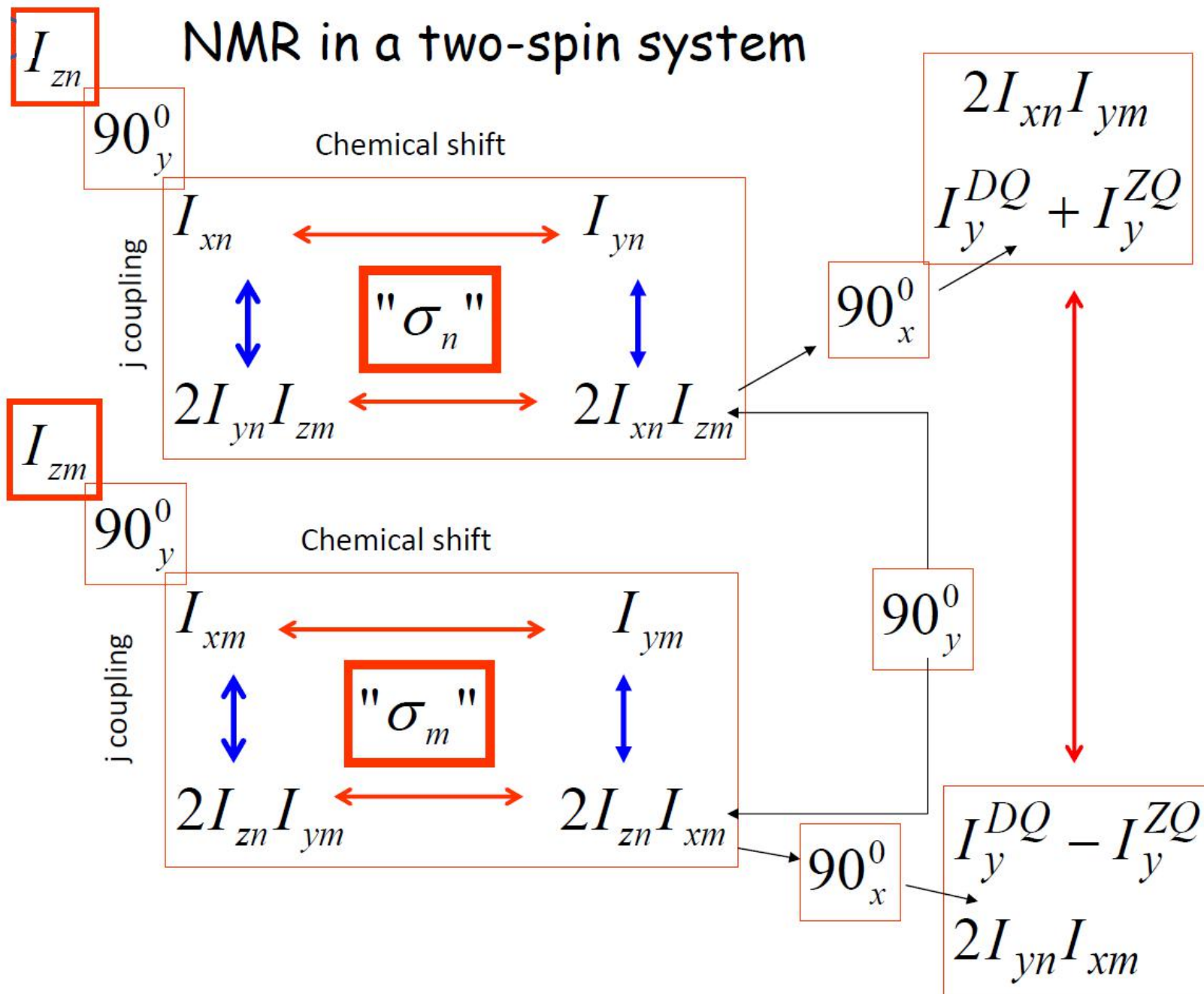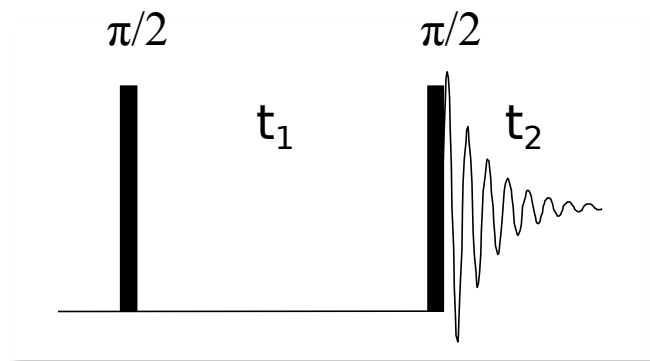
NMR in a two-spin system

I_{zn}

90^0_y

Chemical shift

j coupling

I_{xn} ⟷ I_{yn}

$"\sigma_n"$

$2I_{yn}I_{zm}$ ⟷ $2I_{xn}I_{zm}$

I_{zm}

90^0_y

Chemical shift

j coupling

I_{xm} ⟷ I_{ym}

$"\sigma_m"$

$2I_{zn}I_{ym}$ ⟷ $2I_{zn}I_{xm}$

90^0_x

90^0_y

90^0_x

$2I_{xn}I_{ym}$

$I_y^{DQ} + I_y^{ZQ}$

$I_y^{DQ} - I_y^{ZQ}$

$2I_{yn}I_{xm}$

Example: COSY experiment

π/2   π/2

t_1 t_2

COSY: J-coupling (through bond connectivities of neigh-boring atoms, max. ~3 bonds)

How does it work?

$$S_z \overset{\pi/2_x}{\Longrightarrow} -S_x \overset{t_1}{\Longrightarrow} S_x \overset{\pi/2_x}{\Longrightarrow} S_x \overset{t_2}{\Longrightarrow} -S_y$$

x-magnetization stays on spin a
The efficiency of this pathway is
$\sin(\omega_a t_1)\cos(J_{ab}t_1)\sin(\omega_a t_2)\cos(J_{ab}t_2)$

A diagonal peak will appear in the COSY-spectrum

Gain is two-fold:
(1) Spectral resolution is increased because peaks become resolved in 2D;
(2) Knowledge on additional coherence pathways can be obtained.

Example: COSY experiment

$\pi/2$ $\pi/2$

t_1 t_2
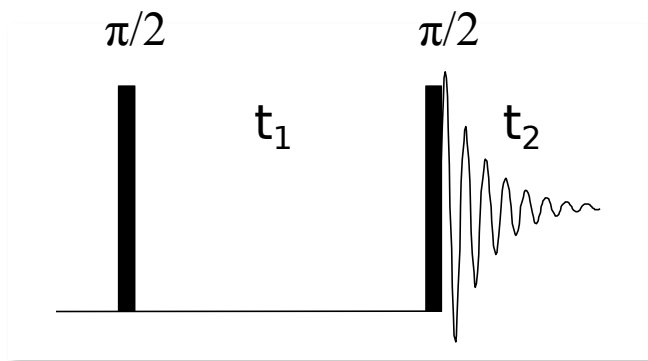
COSY: J-coupling (through bond connectivities of neigh-boring atoms, max. ~3 bonds)

How does it work?

$$S_z \overset{\pi/2_x}{\Rightarrow} -S_y \overset{J_{ab}}{\Rightarrow} 2S_yI_z \overset{\pi/2_x}{\Rightarrow} 2S_zI_x \overset{J_{ab}}{\Rightarrow} -I_y$$

x-magnetization has gone from spin a to spin b

The efficiency of transfer is

$$\sin(\omega_a t_1)\sin(J_{ab}t_1) \; \sin(\omega_b t_2)\sin(J_{ab}t_2)$$

A cross-peak will appear in the COSY-spectrum

The cross-peak is the direct evidence for J-coupling

Gain is two-fold:
(1) Spectral resolution is increased because peaks become resolved in 2D;
(2) Knowledge on additional coherence pathways can be obtained.

Example: COSY experiment

$\pi/2$ $\pi/2$

t_1 t_2
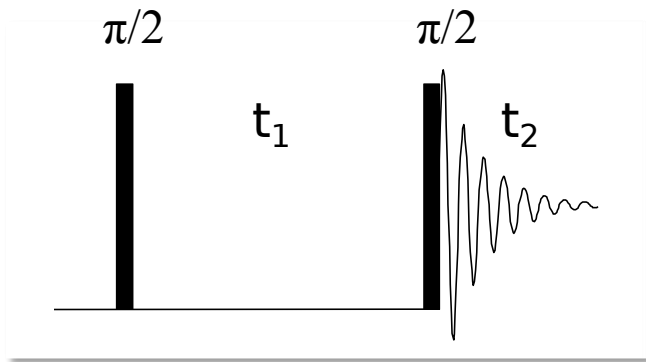
COSY: J-coupling (through bond connectivities of neighboring atoms, max. ~3 bonds)

Result for more than 2 spins

$\omega_2 \rightarrow$

Ω_1 Ω_2 Ω_3 Ω_4

$\omega_1 \rightarrow$
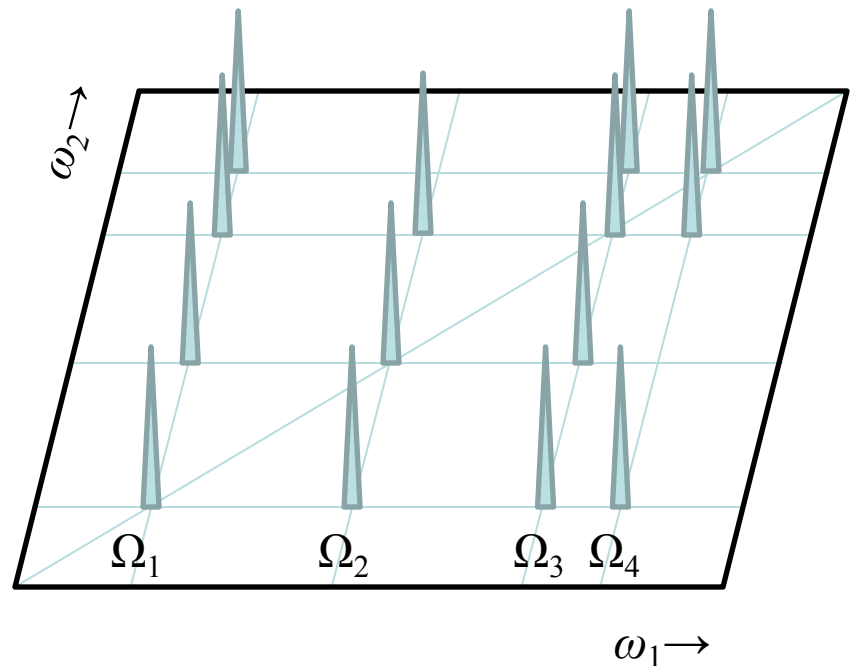
When the spins are scalar coupled cross-peak will appear
In 2D peaks, which overlap in 1D-spectrum, become resolved

Summary, part 2

- ✓ Density matrix description of spin ensembles

- ✓ QM description of NMR experiments

- ✓ QM in action: some NMR examples

Example: INEPT experiment

Populations at equilibrium
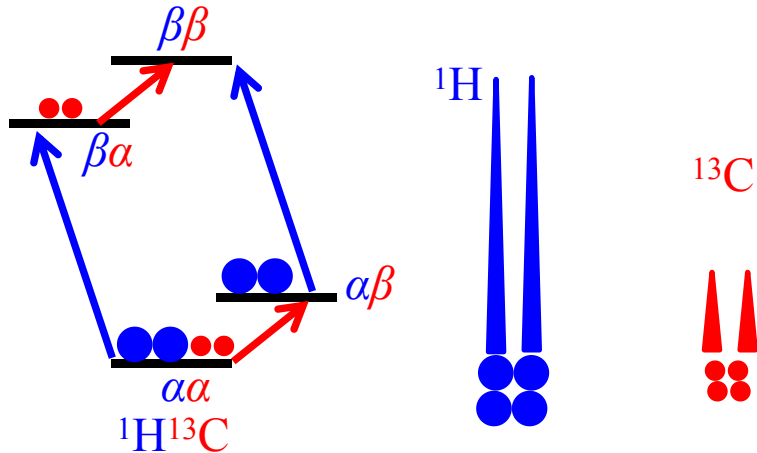
NMR signal is proportional to the γ-ratio

4 times higher signals for protons than for ^{13}C; even 10 higher than for ^{15}N

Possible improvement is polarization transfer $^{1}H \rightarrow X$-spin

NOE is not (always) the best solution: coherent mechanism and proper pulsing work better

INEPT=**I**nsensitive **N**uclei **E**nhanced by **P**olarization **T**ransfer
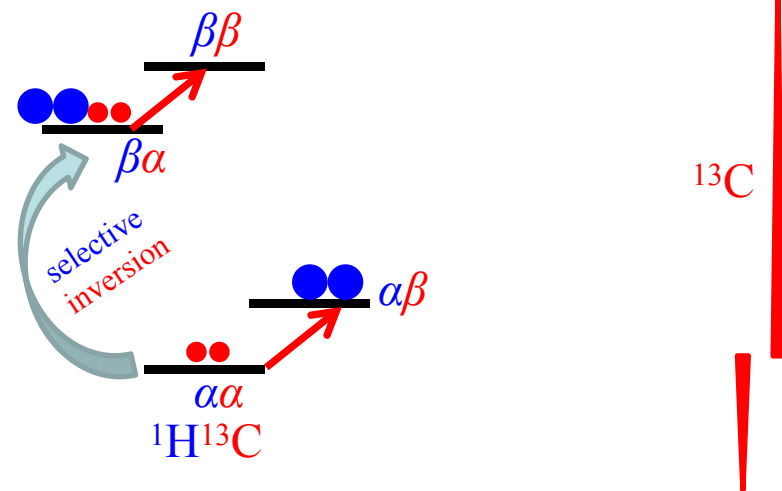
INEPT experiment: explanation
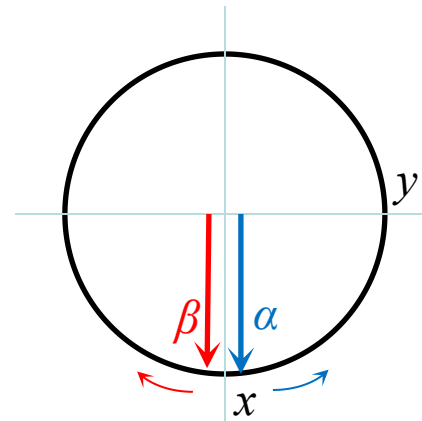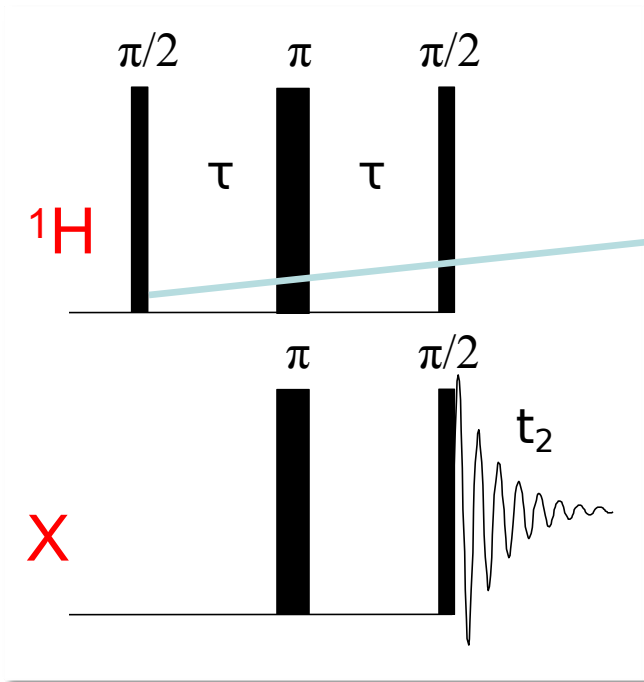
All spins are along x

INEPT: transferring polarization
from proton to X-nucleus

INEPT experiment: explanation

$\pi/2$ π $\pi/2$

τ τ

^1H

π $\pi/2$

t_2

X

y

β α

x
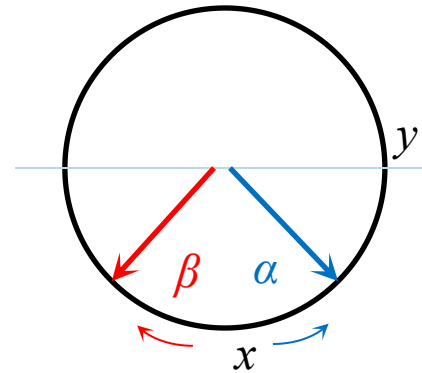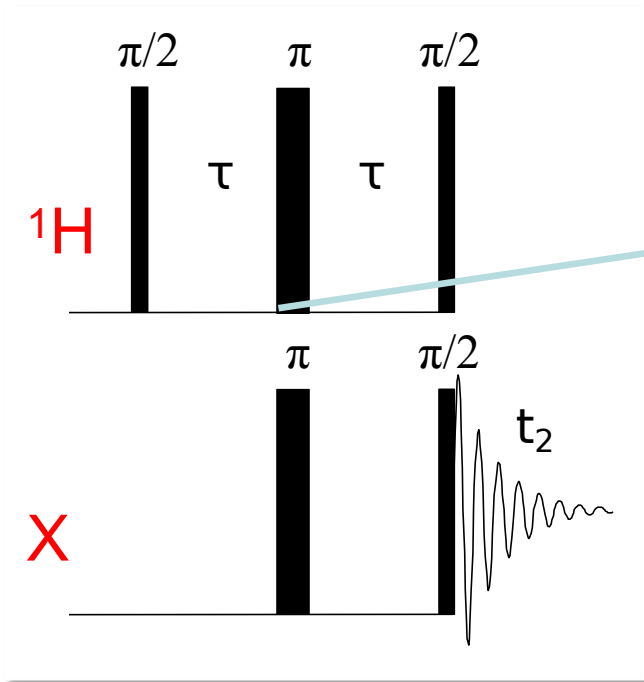
For $\tau = 1/4J$ the angle between spins is 90 degrees

INEPT: transferring polarization from proton to X-nucleus

INEPT experiment: explanation
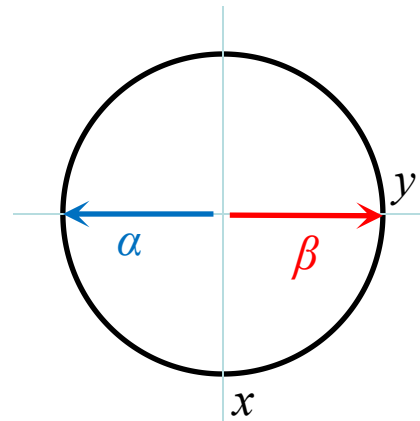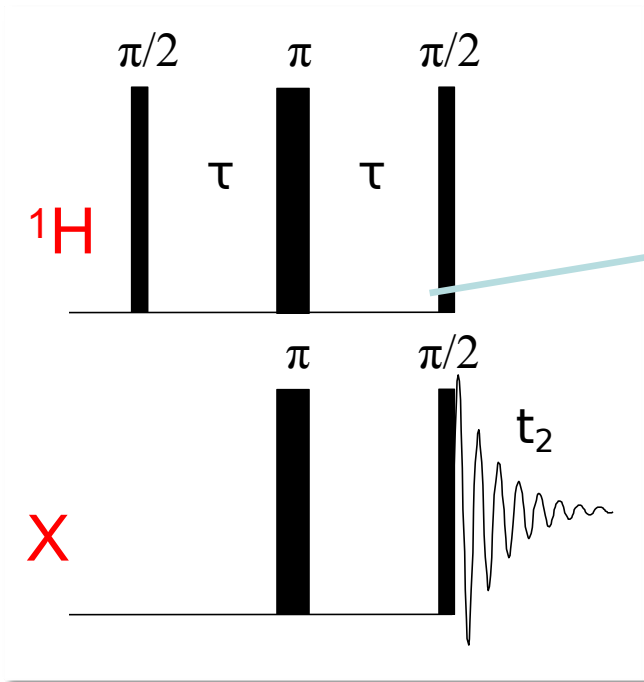

π/2   π   π/2

¹H

τ   τ

π   π/2

X

t₂

INEPT: transferring polarization
from proton to X-nucleus

α   β

y

x
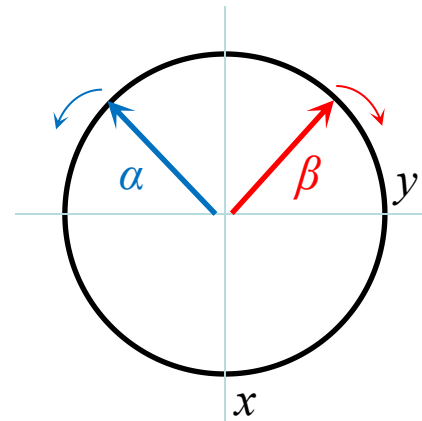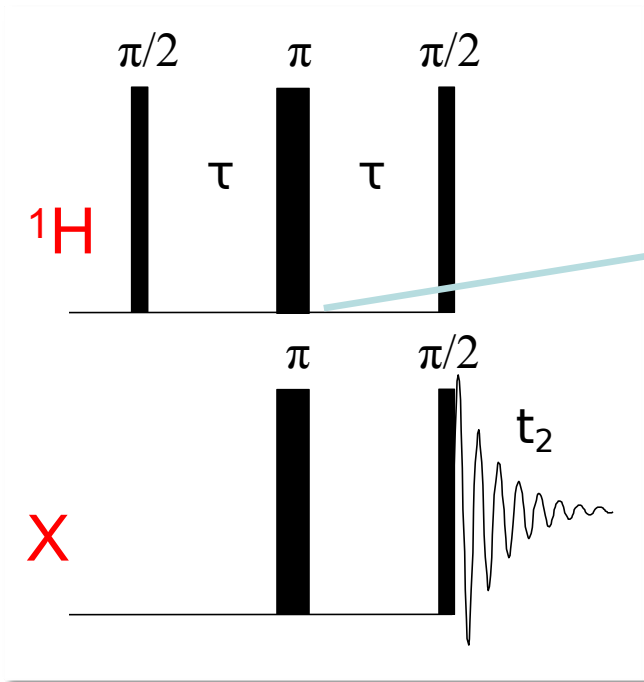
Components are flip by
protons pulse
Their colors are exchanged by
X-nucleus pulse

INEPT experiment: explanation

INEPT: transferring polarization from proton to X-nucleus

Spins are along y for $\tau = 1/4J$

The last proton pulse results in one component positive and one negative
Reminder: first both were positive

INEPT experiment: explanation

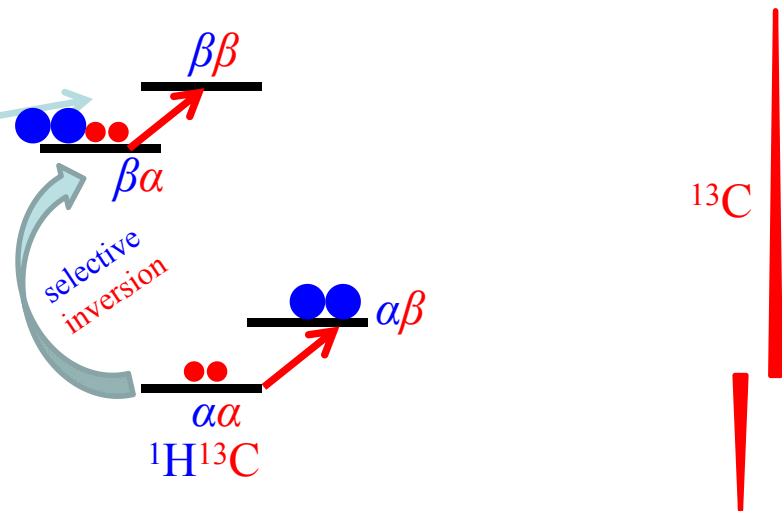Resulting populations
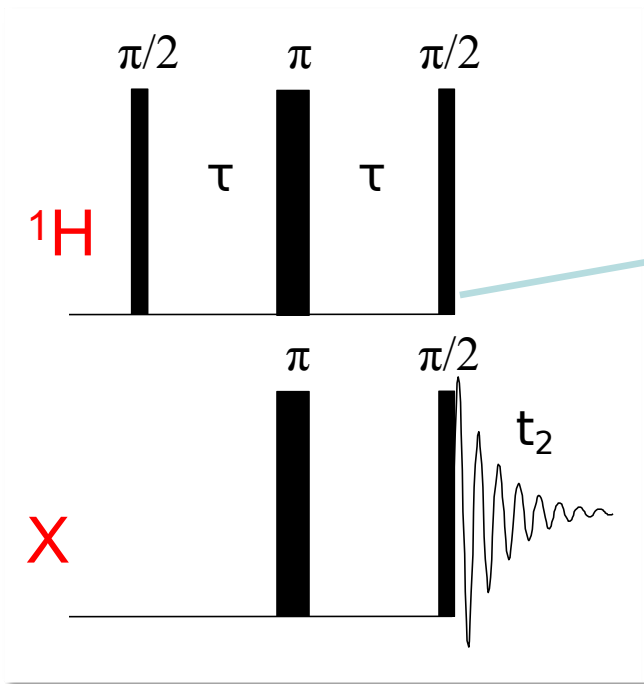
INEPT: transferring polarization from proton to X-nucleus

Pulses really make possible many nice tricks with spins ☺

Now the final pulse for X-nucleus does the detection
The gain is given by the ratio of gammas
The gain can be further increased when NMR of X is detected via protons