# CONUSS

***C̲O̲**herent **N̲U̲**clear **S̲**cattering from **S̲**ingle crystals*

## *Software for the evaluation of Synchrotron Mössbauer Spectra*

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# About CONUSS:

- developed 1983-1986 by E. Gerdau and W. Sturhahn at
  the University of Hamburg
  - ✰ coherent elastic nuclear and electronic Bragg scattering
  - ✰ explain first NRS experiments (Gerdau et al. PRL 54, 1985)
  - ✰ FORTRAN code implemented on IBM 360 mainframe (MVS-VM)

- improved 1986-today by W. Sturhahn and supported by
  the University of Hamburg (1986-1993),
  ESRF (1992), APS (1992-2010),
  MPI-Halle (2012-2013)
  - ✰ forward scattering (SMS a.k.a. NFS) added in 1991
  - ✰ ported to Sun UNIX in 1992
  - ✰ extended data handling capability (fitting) added in 1996
  - ✰ ported to Linux in 2004, to OS X in 2011
  - ✰ grazing incidence scattering (GINS) added in 2014

*publications related to CONUSS:*
*W. Sturhahn and E. Gerdau, Phys. Rev. B 49 (1994)*
*W. Sturhahn, Hyperfine Interact 125 (2000)*

# More on CONUSS:

- has been used for data evaluation in numerous publications
- distributed under GPL, source code public, evaluations traceable
- can be obtained at http://www.nrixs.com – no charge
- a major upgrade, CONUSS-2.0.0, was released in 2010
  - ☆ simple installation procedure for Unix and Mac OS X
  - ☆ all previous capabilities of CONUSS
  - ☆ enhanced fit capabilities & run-time graphics
  - ☆ new Monte Carlo approach to find start-values, explore the parameter space, and smart parameter optimization
- CONUSS-2.1.0 was released in 2015
  - ☆ support of grazing incidence geometry
  - ☆ input parameter simplifications
- CONUSS-2.1.1 is the present version
  - ☆ systematic output file naming
  - ☆ dual fit for isomer shift determination from SMS

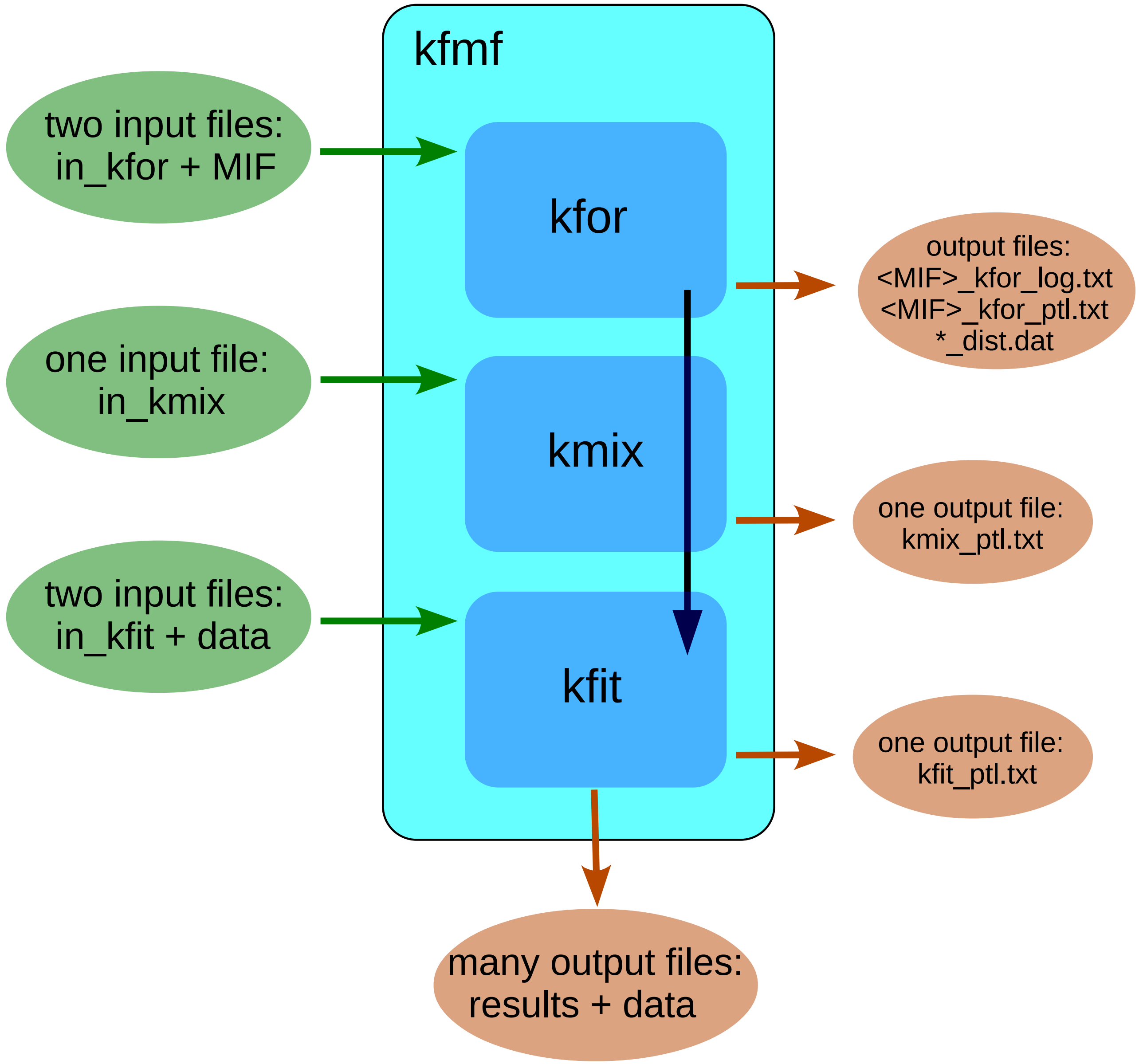
# CONUSS now supports:

- all Mössbauer isotopes
- forward scattering, grazing incidence, and Bragg/Laue reflections
- no limitations by sample structure
- combined hyperfine interactions
- distributions of hyperfine fields
- textures
- relaxation effects
- full polarization and directional dependences
- thickness effects
- time spectra (SMS) and energy spectra (trad. Mössbauer spectr.)
- sample combinations
- time, energy, and angle averaging
- sample thickness distributions
- comparison to experimental data including fitting
- flexible assignment and grouping of fit parameters

# CONUSS provides solutions:

| problem | program | SIF | examples |
|---|---|---|---|
| fitting data | kctl | in_kctl | |
| forward scattering | | in_kfor | kctl-NFS1, kctl-NFS2 |
| dual fit | | in_kfor | kctl-NFS3 |
| Mössbauer spectroscopy | | in_kfor | kctl-MBS1, kctl-MBS2 |
| grazing incidence | | in_kgin | kctl-GINS |
| Bragg/Laue diffraction | | in_kref | kctl-NBS1, kctl-NBS2 |
| explore parameter space | kmco | in_kmco | |
| forward scattering or Mössbauer | | in_kfor | kmco-NFS |
| grazing incidence | | in_kgin | kmco-GINS |
| Bragg/Laue diffraction | | in_kref | kmco-NBS |
| calculate spectra | | | |
| forward scattering or Mössbauer | kfmf | in_kfor | kfmf-NFS, kfor-NFS |
| grazing incidence | kgmf | in_kgin | kgmf-GINS, kgmf-GIS |
| Bragg/Laue diffraction | krmf | in_kref | krmf-NBS |

# Module configuration, theory and simple fit:




energy-dependent
index-of-refraction

polarization,
Fourier transform

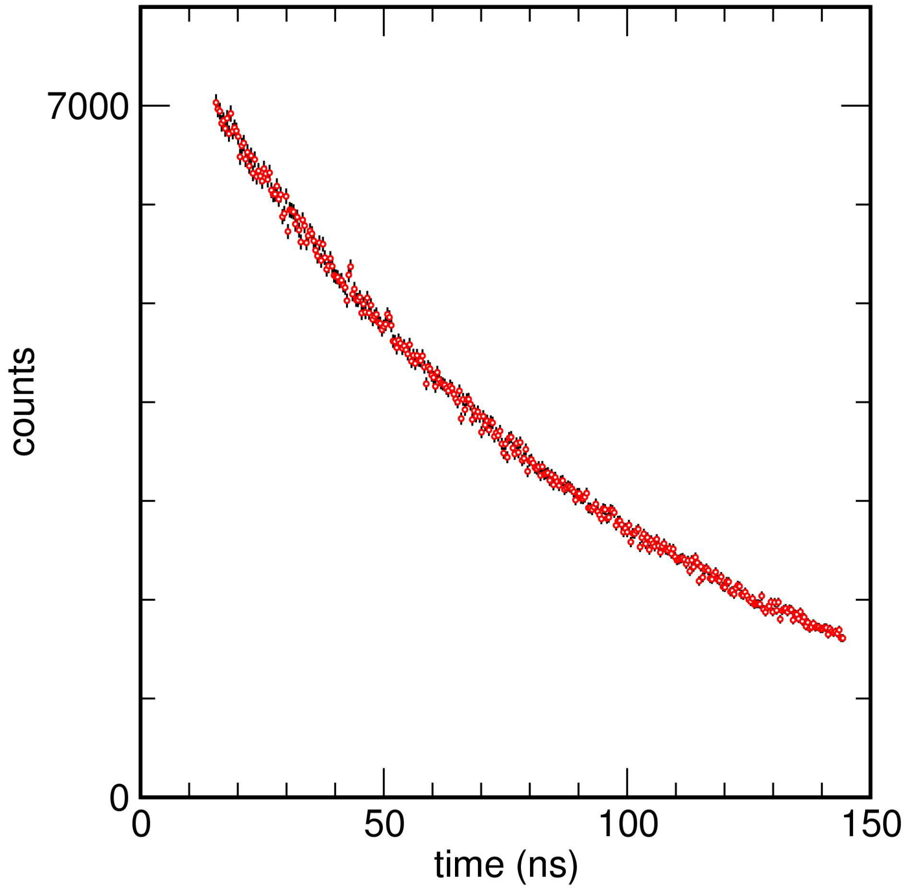
averaging,
comparison to data

Command:

`kfmf`

# SMS example 1.1:

➢ simulate the following SMS spectrum



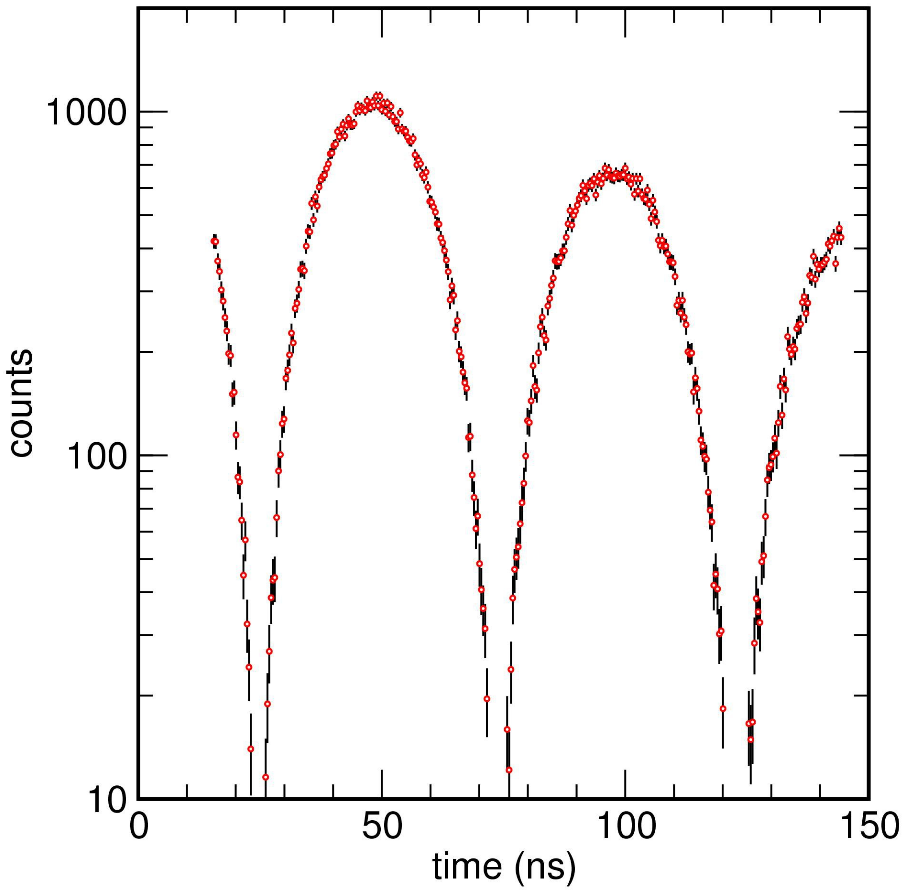

✰ construct the input files
in_kfor, in_kmix, in_kfit, ex1-1.mif

✰ observe the effect of isomer shift,
thickness, quadrupole splitting

✰ Tips: watch correlations

# SMS example 2.1:

➢ simulate the following SMS spectrum

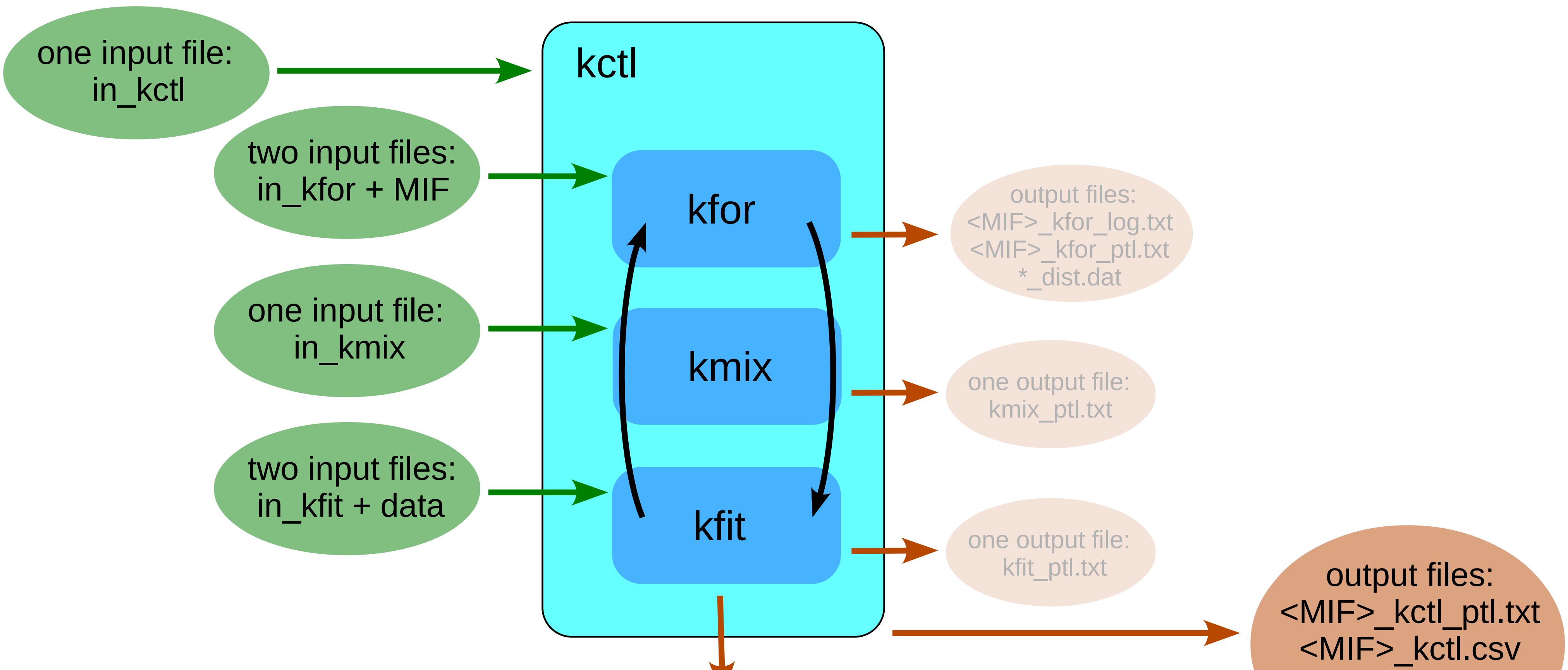



✰ construct the input files
in_kfor, in_kmix, in_kfit, ex2-1.mif

✰ observe the effect of thickness,
quadrupole splitting

✰ Tips: watch correlations

# Module configuration, general fitting:




Command:

`kctl`

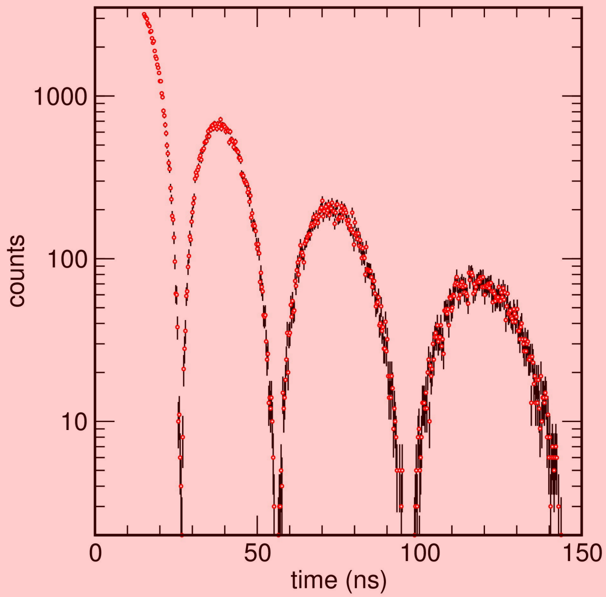
# Fitting of SMS spectra:

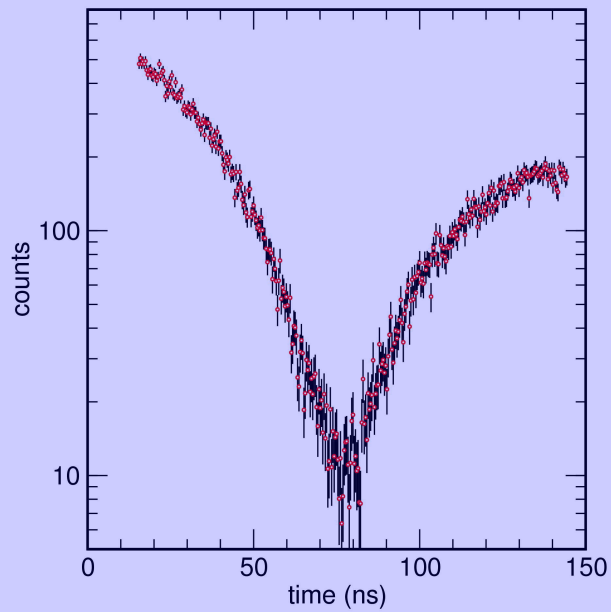
- strategy
  - ✰ identify relevant parameters
  - ✰ find start values using command `kfmf`
  - ✰ optimize parameter values using `kctl`

- examples 1.2-4, 2.1-3, and 3.1-3
  - ✰ construct the input files in_kfor, in_kmix, in_kfit, ex.mif, in_kctl
  - ✰ focus on isomer shift, thickness, quadrupole splitting

# SMS examples:

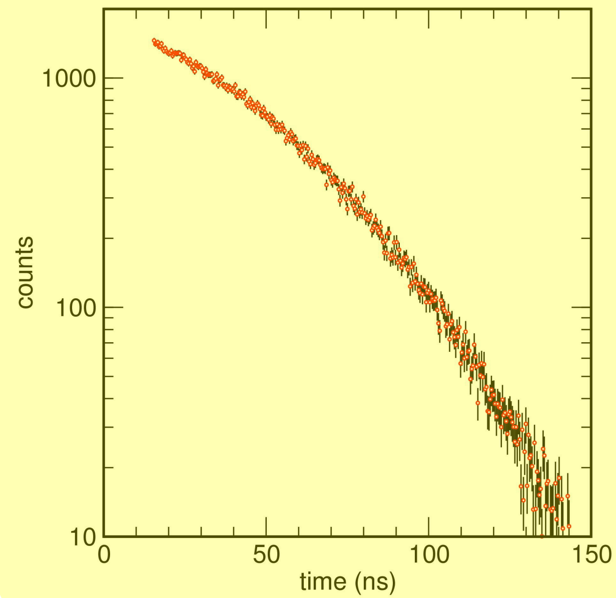
➢ example 1.2
focus on thickness



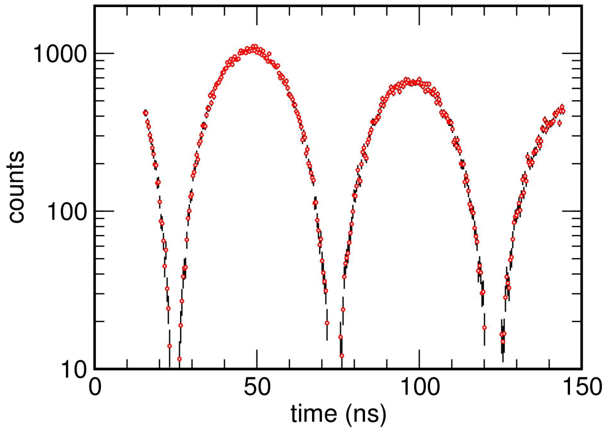

➢ example 1.3
two sites; isomer shift;
thickness 0.1μm

➢ example 1.4
IS distribution;
thickness 0.1μm

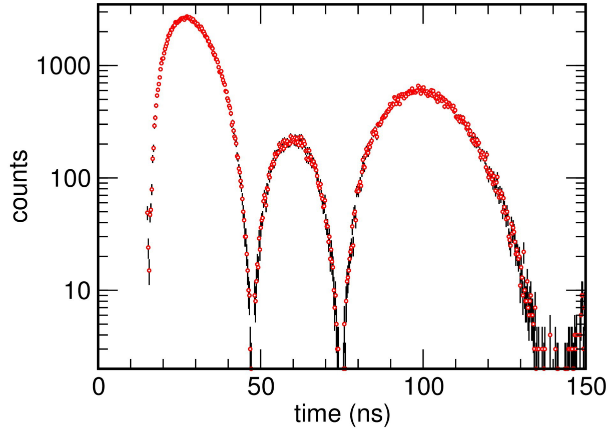


# SMS examples, quadrupole splitting, isomer shift:

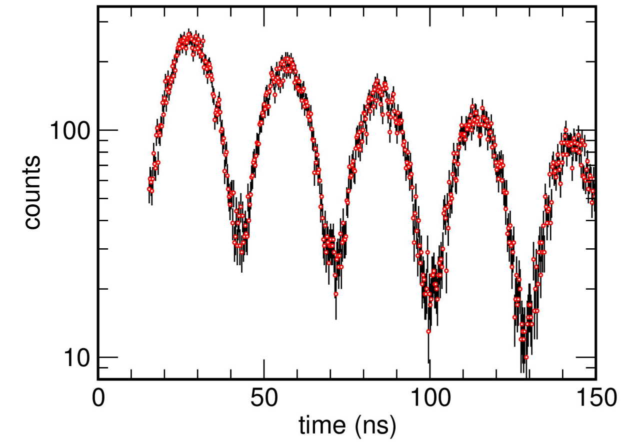
- example 2.1
  thickness 0.1µm



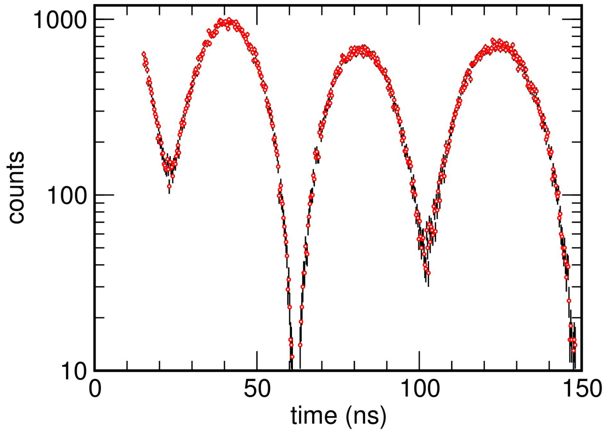

- example 2.2



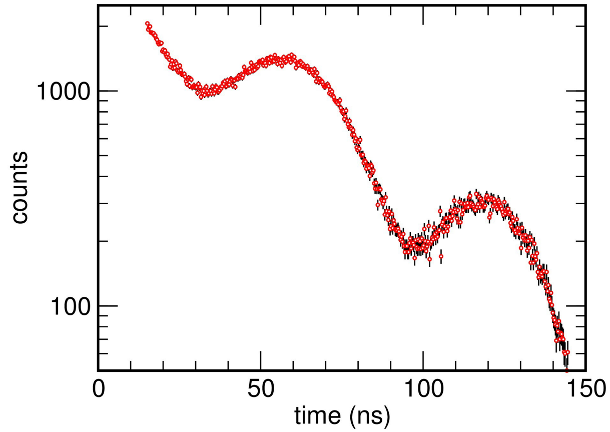

- example 2.3
  thickness 0.1µm; texture



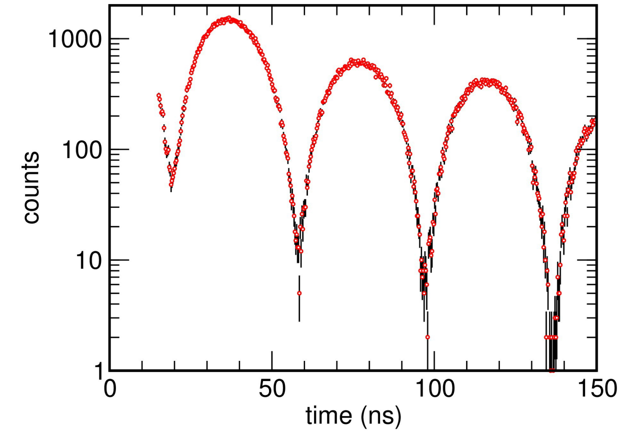

- example 3.1
  0.1µm; two sites




- example 3.2
  0.1µm; two sites

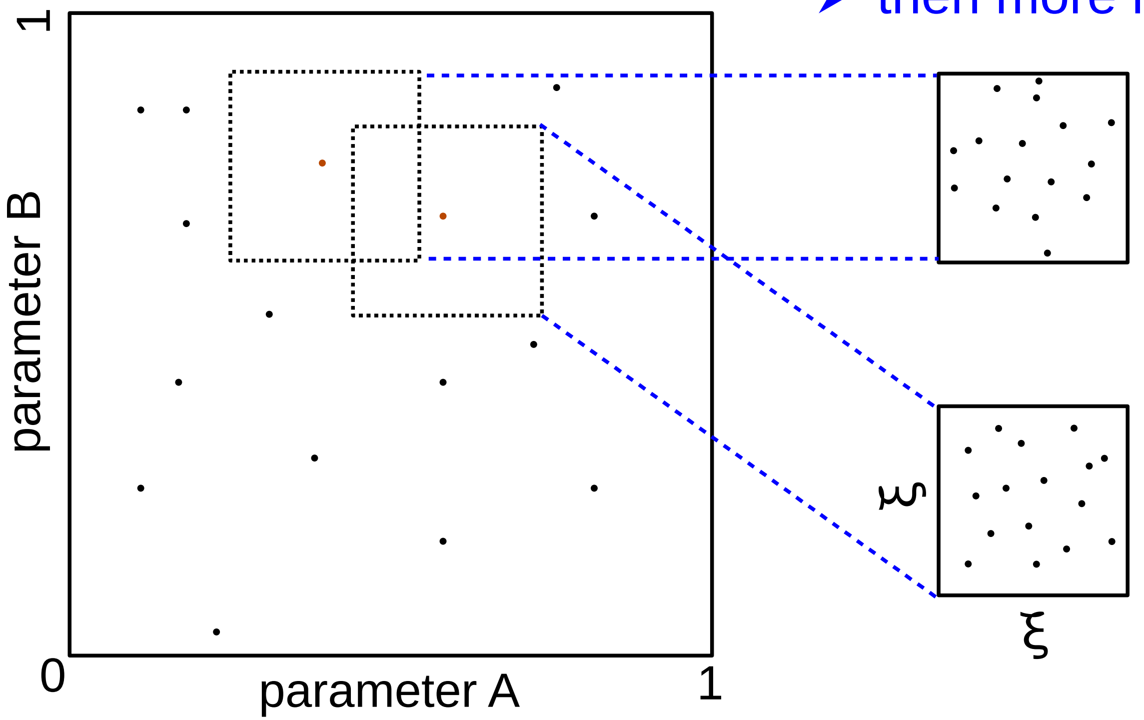



- example 3.3
  0.05µm; two sites; distr.



# Randomized search:

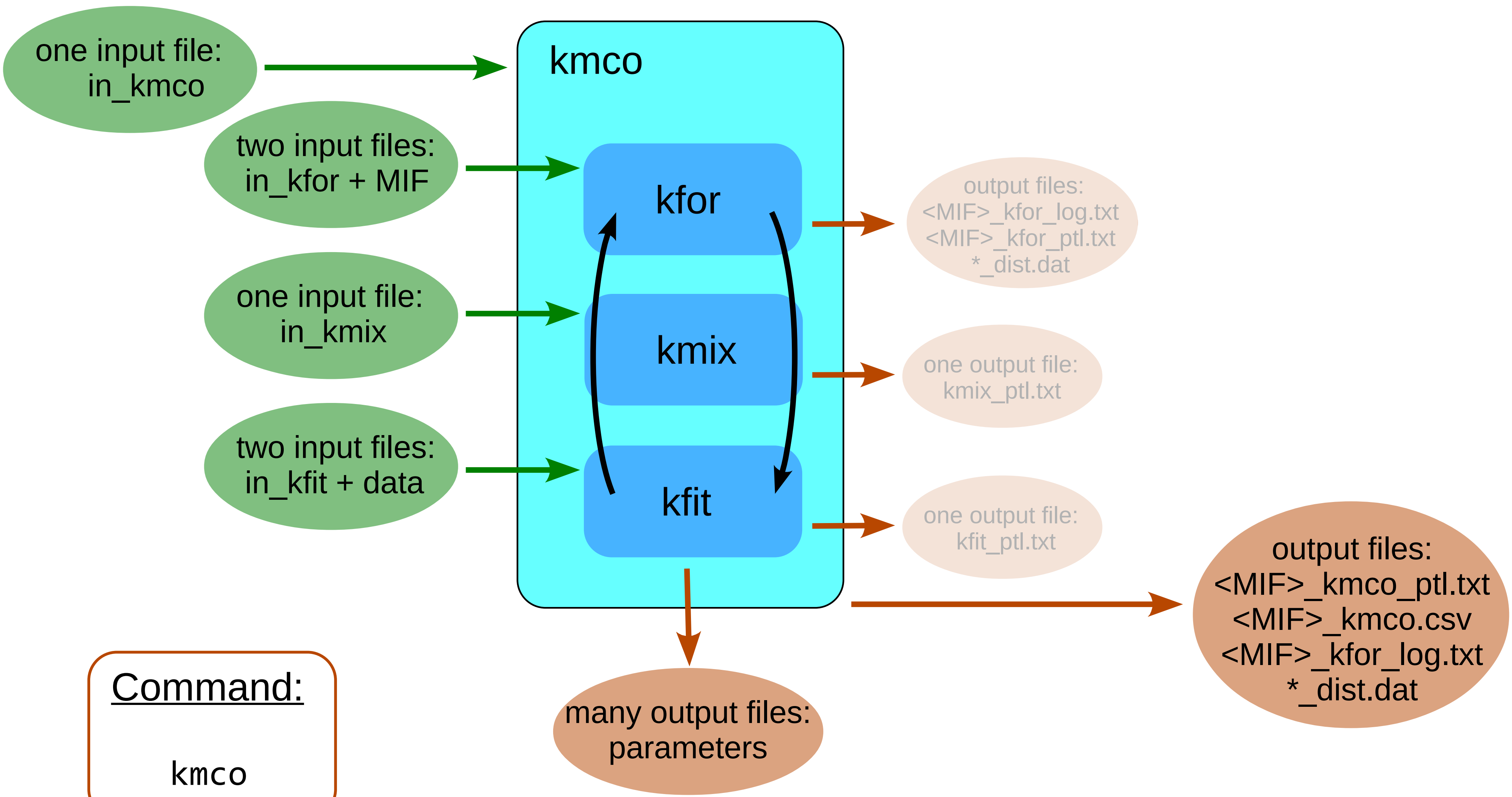
- random picks
- new search boxes
- then more random picks




- repeat

☆ in each step the N-dimensional search space shrinks by $\xi^N$

# Module configuration, Monte Carlo gamble:




Command:

`kmco`

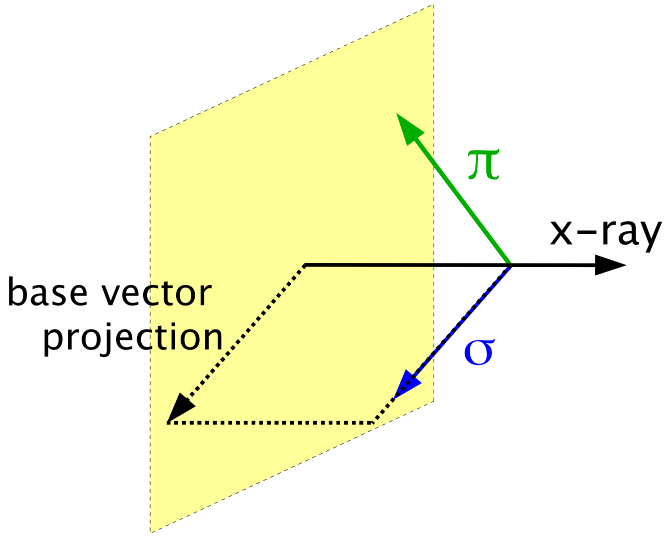
# Shot gun approach to fitting of SMS spectra:

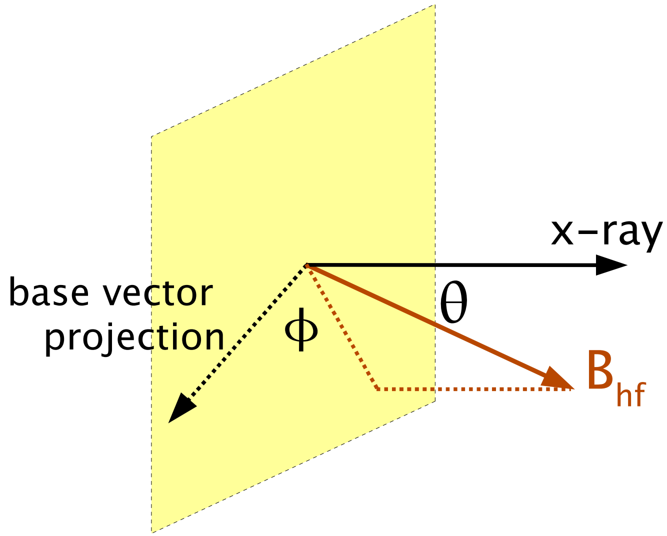
- strategy
  - identify relevant parameters
  - explore parameter space using command `kmco`
  - optimize parameter values using `kctl`
- re-do examples that you thought most difficult to fit
  - construct the input files in_kfor, in_kmix, in_kfit, exp.mif, in_kctl
  - focus on isomer shift, thickness, quadrupole splitting

# Polarization and magnetic field directions:

- defined by a chosen base vector projection
  and the direction of the x-rays

- base vector *(1,0,0)* is used for the projection
  unless the x-rays are collinear with (1,0,0);
  then base vector *(0,1,0)* is used for the projection.



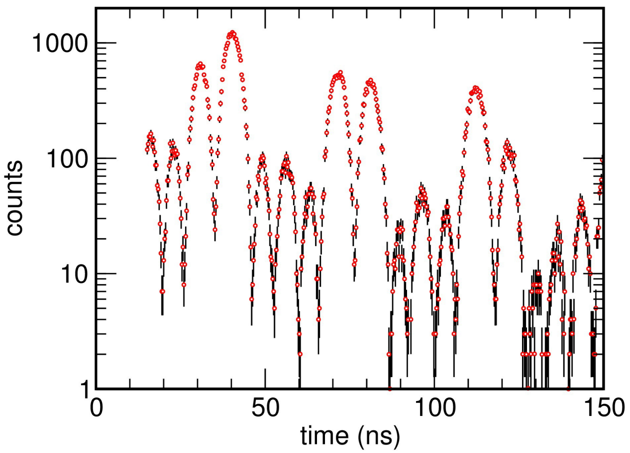
# Magnetic SMS spectra:

- strategy
  - identify relevant parameters
  - use your choice approach...

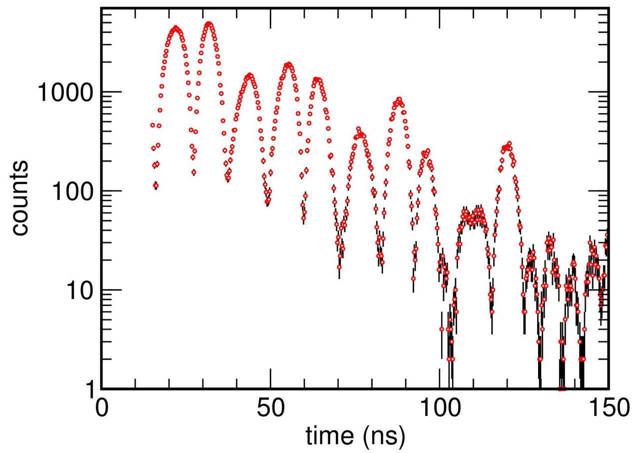
- examples 4.1-3 and 5.1-3
  - construct the input files in_kfor, in_kmix, in_kfit, exp.mif, in_kctl
  - focus on magnetic fields: magnitude, direction, and distribution

# SMS examples, magnetic fields:

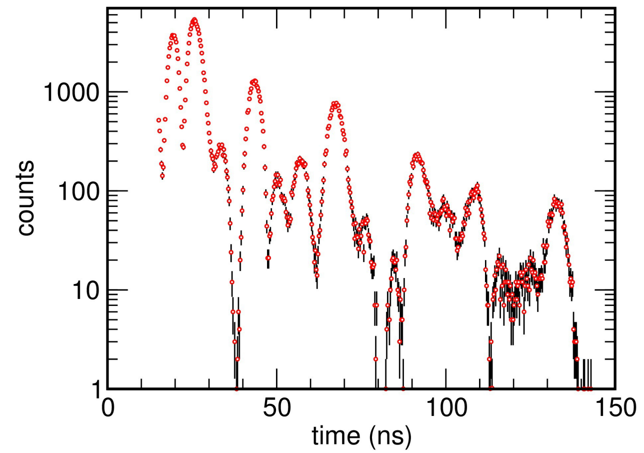
- example 4.1
  no texture



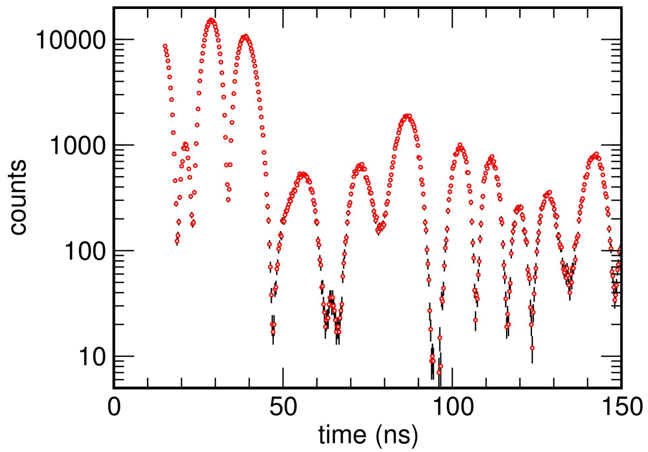

- example 4.2
  texture



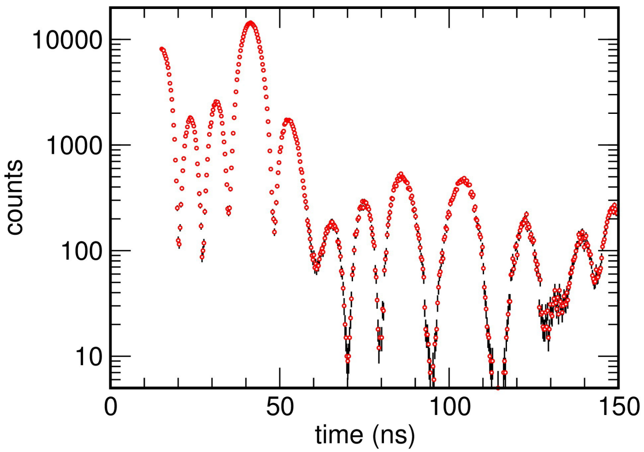

- example 4.3
  no texture; distribution



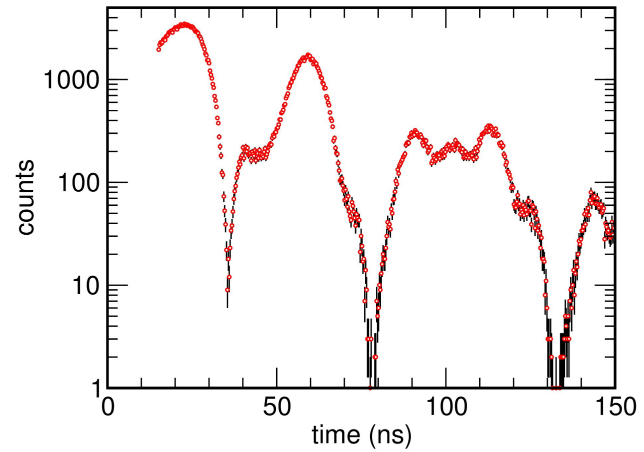

- example 5.1
  no texture



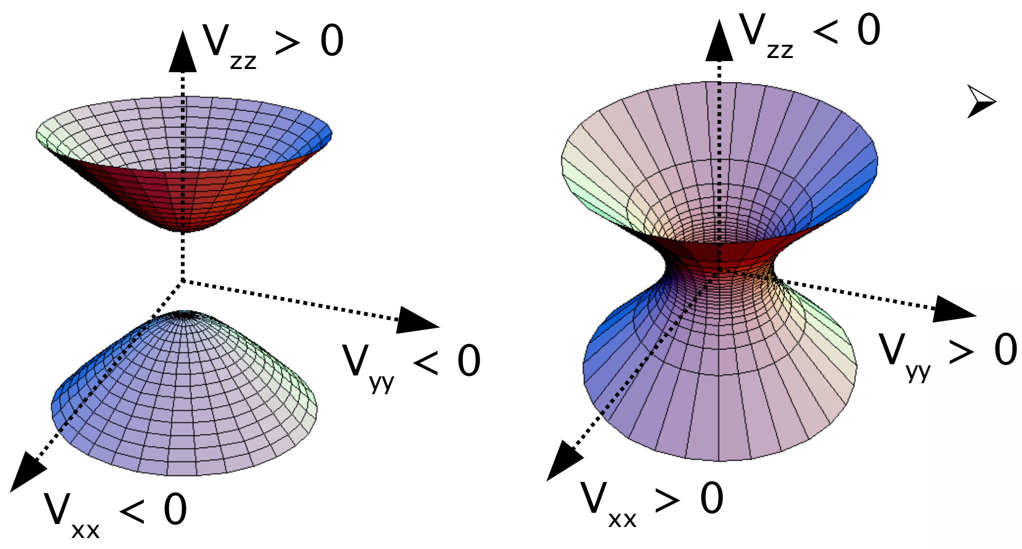

- example 5.2



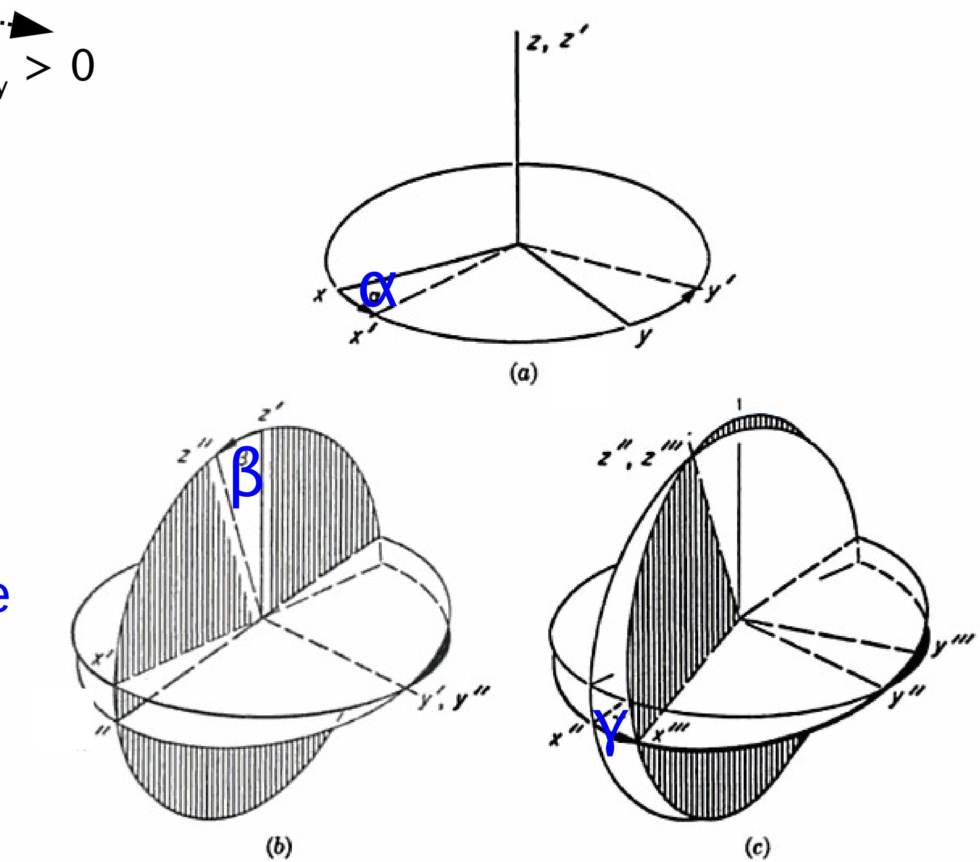

- example 5.3



# Electric field gradient as hyperboloid:




- axes: $|V_{zz}| > |V_{yy}| > |V_{xx}|$
  $V_{zz} + V_{yy} + V_{xx} = 0$
- asymmetry parameter: $|V_{yy} - V_{xx}| / |V_{zz}|$

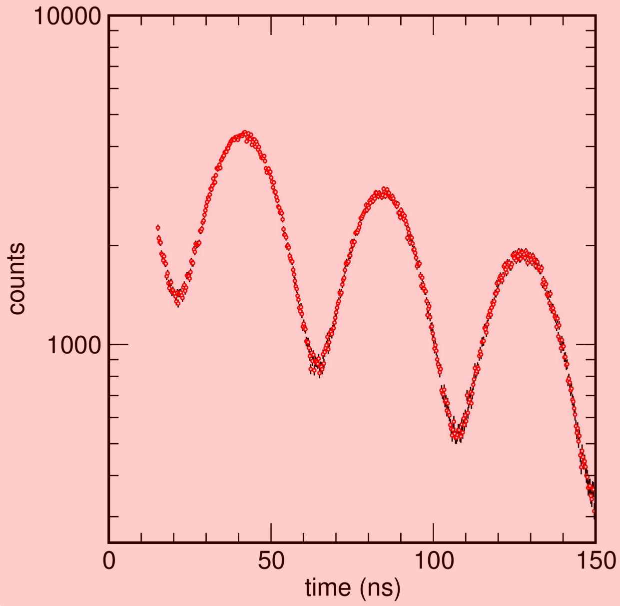


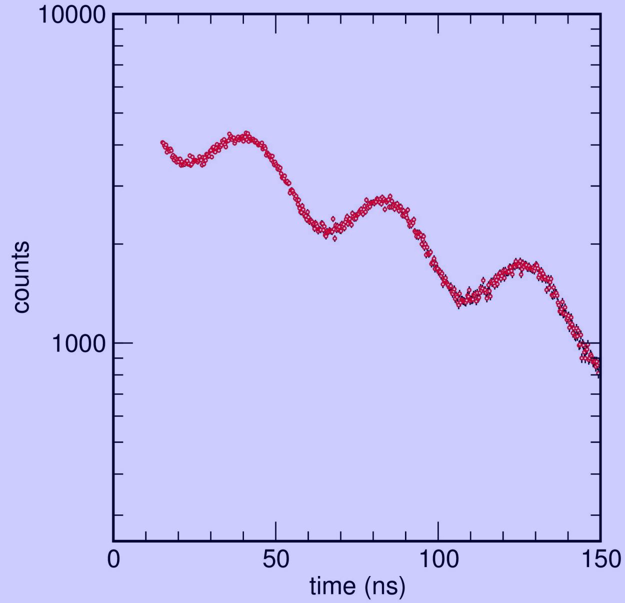

- the orientation is defined by the Euler angles (α,β,γ) that rotate the ellipsoid out of the reference frame given by the unit cell.

# SMS examples:

- $V_{zz}$ is perpendicular to the x-ray direction, thickness 0.1 µm

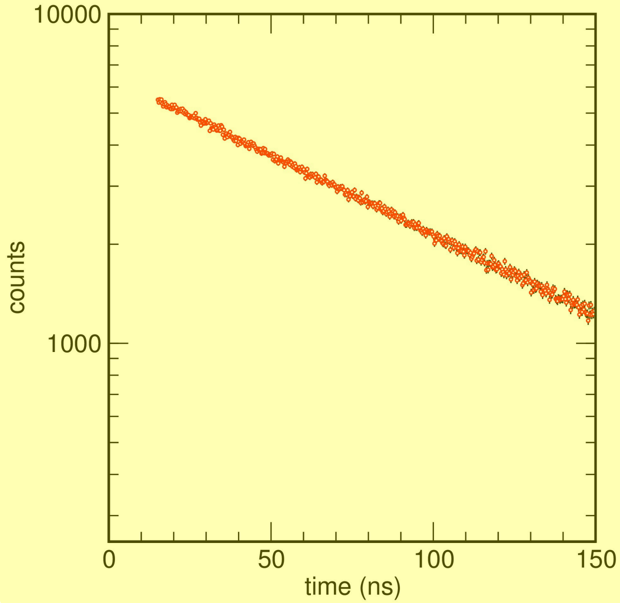
- example 7.1




- example 7.2

- example 7.3



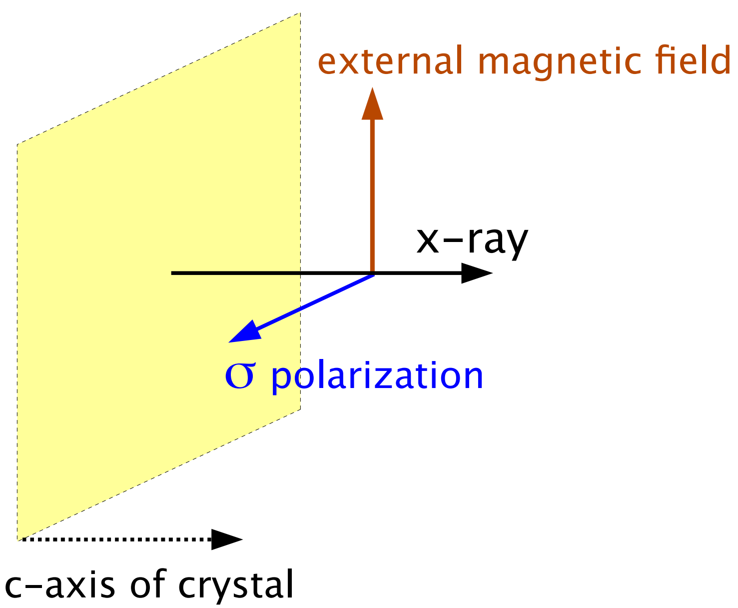
End of regular Class.

Continue with advanced Studies...

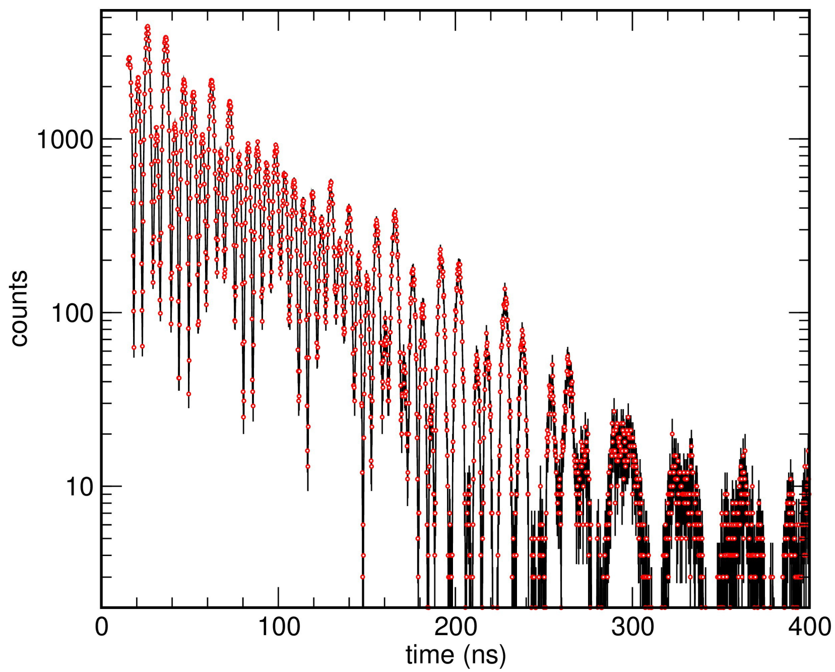
# SMS example Y.1:

- ✫ SMS data were taken on a hematite single crystal, natural enrichment
- ✫ magnetic susceptibility studies indicate a weak antiferromagnetic state
- ✫ x-ray diffraction studies show two crystallographically distinguishable sites
- ✫ other info: hybrid mode, $Fe_2O_3$, = 5.254 g/cm$^3$, $F_{LM}$ = 0.79

➢ experimental geometry



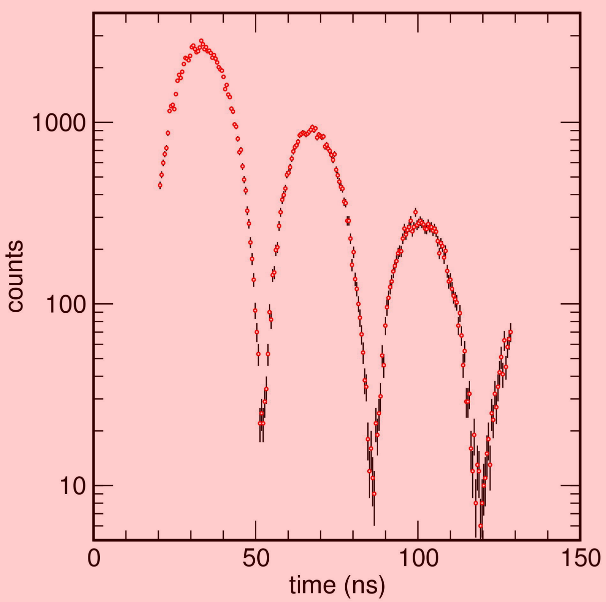

➢ data: expY-1.dat

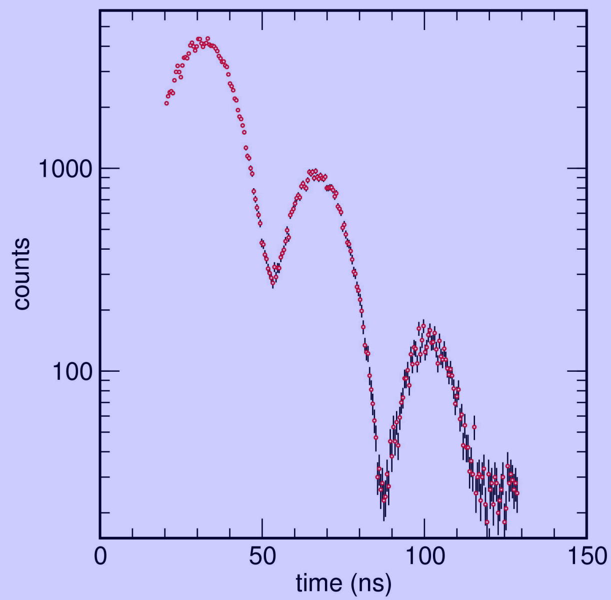


# SMS dual fit example Y.2:

- ✰ construct the input files in_kfor, in_kmix, in_kfit, exp.mif, in_kctl
- ✰ prepare input files in_kctl and in_kfit for dual fit
- ✰ two sites, no magnetic field, isomer shift distributions,
  bunch separation 153 ns, $Mg_{0.87}Fe_{0.13}SiO_3$, = 3.31 g/cm$^3$, $F_{LM}$ = 0.8

➢ data: expY-1.dat
enstatite at 30GPa
two sites iso=0




➢ data: expY-1r.dat
enstatite +
55 m SS reference

➢ how to create
the reference file:

- ✰ construct the input files
  in_kfor_ss and ss.mif
- ✰ run the command

```
kfor --infile=in_kfor_ss
```

# Thickness effects:

- Distortions of time or energy spectra by thickness effects are often unwanted and complicate data evaluation and interpretation

- Time spectrum expanded

$$\frac{\mathrm{d}I}{\mathrm{d}t} = \left| \sum_{n=1}^{\infty} D_{\mathrm{eff}}^{n} \int \mathbf{g}^{n}(E)\, \mathsf{e}^{-\mathsf{i}Et/h} \frac{dE}{2h} \right|^2$$

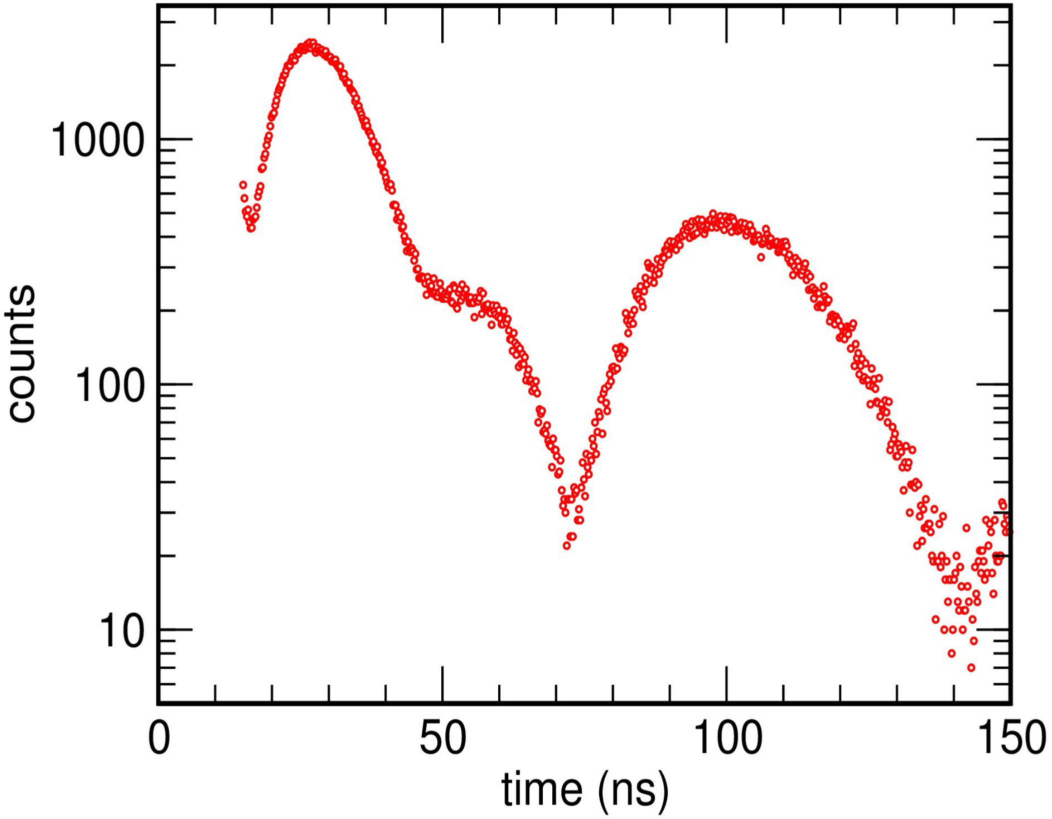
with $$\mathbf{g}(E) = \mathsf{i}\,\frac{\Gamma}{4} \sum_{mm'} \frac{\mathbf{W}_{mm'}}{E_{mm'} - E - \mathsf{i}\Gamma/2}$$

- Higher order terms (n>1) become important if

$$D_{\mathrm{eff}} \max_{E} |\mathbf{g}| \approx 1 \quad \Rightarrow \quad D_{\mathrm{eff}} \approx \frac{2}{\max_{mm'} |\mathbf{W}|}$$

# SMS example Y.3:

☆ one site, thickness distribution

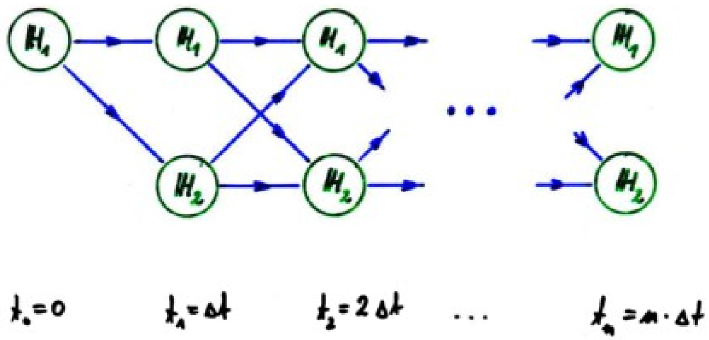



☆ adapt the input files
in_kfor, in_kfit

☆ observe the effect of the
thickness distribution

The hyperfine interaction is described by

$\mathbb{H}_1$ or $\mathbb{H}_2$ dependent on time




paths : $\{\mathbb{H}\}^n$

probability for path j : $P(\{\mathbb{H}\}_j^n)$ ; $\sum_{\{j\}^n} P(\{\mathbb{H}\}_j^n) = 1$

path integral : $\mathbb{I}_j^n = \sum_{\ell=0}^{n} \mathbb{H}_j(t_\ell) \cdot \Delta t$

stochastical average :

$$\langle F(t) \rangle_{av} = \lim_{\substack{n \to \infty \\ (t = n \cdot \Delta t)}} \sum_{\{j\}^n} P(\{\mathbb{H}\}_j^n) \cdot F(\mathbb{I}_j^n)$$

$$= \sum_{\alpha\beta} \underbrace{\lim_{n \to \infty} \sum_{\{j\}^{n-2}} P(\{\mathbb{H}\}_{\alpha j \beta}^n)\, F(\mathbb{I}_{\alpha j \beta}^n)}_{G_{\alpha\beta}(t)}$$



consider a stationary Markoff process ...

$$P(\{\mathbb{H}\}_j^n) = P(\mathbb{H}_{j_0}(t_0), t_0) \cdot W(\mathbb{H}_{j_0}(t_0) \,|\, \mathbb{H}_{j_1}(t_1), \Delta t) \ldots$$
$$W(\mathbb{H}_{j_{n-1}}(t_{n-1}) \,|\, \mathbb{H}_{j_n}(t_n), \Delta t)$$

introduce :

$$W_{\beta\gamma}(\Delta t) = W(\mathbb{H}_\beta \,|\, \mathbb{H}_\gamma, \Delta t) = \delta_{\beta\gamma} + \lambda_{\beta\gamma} \cdot \Delta t$$

with $\sum_\gamma W_{\beta\gamma} = 1$ , $\sum_\gamma \lambda_{\beta\gamma} = 0$

transition probabilities

and ...

$$F(\mathbb{I}_{\alpha j \beta\gamma}^{n+1}) = F(\mathbb{I}_{\alpha j \beta}^n + \mathbb{H}_\gamma \Delta t)$$

$$= F(\mathbb{I}_{\alpha j \beta}^n) + D_{\alpha j \beta\gamma}^n \cdot \Delta t$$

derivation of $F(t)$

„equation of motion“ :

$$\frac{d}{dt} G_{\alpha\beta}(t) = \sum_{\gamma} G_{\alpha\gamma}(t)\, \lambda_{\gamma\beta} + \sum_{\{j\}^{n-2}} P(\{H\}^{n}_{\alpha j\beta})\, D^{n}_{\alpha j\beta\beta}(t)$$

in our case we have

$$D^{n}_{\alpha j\beta\beta}(t) = i\, H_\beta\, F(\mathbb{I}^{n}_{\alpha j\beta}) - i\, F(\mathbb{I}^{n}_{\alpha j\beta})\, H_\beta$$

and we get

$$\frac{d}{dt} G_{\alpha\beta}(t) = \sum_{\gamma} G_{\alpha\gamma}(t)\, \lambda_{\gamma\beta} + i\, H_\beta\, G_{\alpha\beta}(t) - i\, G_{\alpha\beta}(t)\, H_\beta$$

with the starting condition

$$G_{\alpha\beta}(0) = p_\alpha\, \delta_{\alpha\beta}\, J_\mu(-\vec{k})$$



solution of the „equation of motion“ :

introduce matrix elements

$$\langle I m |\, H_\beta\, | I' m' \rangle = \delta_{II'}\, H_\beta^{Imm'}$$

$$\langle I m |\, G_{\alpha\beta}\, | I' m' \rangle = G_{\alpha\beta}^{II'mm'}$$

$$\langle I m |\, J_\mu(-\vec{k})\, | I' m' \rangle = \sqrt{\frac{4\pi c \Lambda}{k}} \times \sum_{L\lambda} \Delta_{L\lambda} \cdot C(I L I'; m\, m'-m) \cdot \left[\vec{Y}^{(\lambda)}_{L,m'-m}(\hat{k})\right]_\mu$$

for a pure $(L\lambda)$ multipole transition
(e.g. $M1 \hat{=} L=1, \lambda=0$ for $^{57}Fe$, $^{169}Tm$, $^{119}Sn$)
the last term simplifies to

$$\langle I m |\, J_\mu\, | I' m' \rangle = \sqrt{\frac{4\pi c \Lambda}{k}} \cdot \Delta_{L\lambda} \times C(I L I'; m\, m'-m) \cdot \left[\vec{Y}^{(\lambda)}_{L,m'-m}(\hat{k})\right]_\mu$$

$$\leadsto \quad \dot{G}_{\alpha\beta}^{II'mm'}(t) = -i \sum_{\gamma M M'} A_{\gamma\beta}^{II'mm'MM'}\, G_{\alpha\gamma}^{II'MM'}(t)$$

with

$$A_{\gamma\beta}^{II'mm'MM'} = i\, \lambda_{\gamma\beta}\, \delta_{mM}\, \delta_{m'M'} - H_\beta^{ImM}\, \delta_{\beta\gamma}\, \delta_{m'M'} + H_\beta^{I'M'm'}\, \delta_{\beta\gamma}\, \delta_{mM}$$

this differential equation solves immediately

$$G_{\alpha\beta}^{II'mm'}(t) = \sum_{\gamma MM'} \left( e^{-i\underline{\underline{A}}^{II'} \cdot t} \right)_{\gamma\beta}^{mm'MM'} \cdot G_{\alpha\gamma}^{II'MM'}(0)$$

$$= \rho_\alpha \cdot \sqrt{\frac{4\pi c \Lambda}{k}} \, \Delta_{L\lambda} \times$$

$$\sum_{MM'} \left( e^{-i\underline{\underline{A}}^{II'} \cdot t} \right)_{\alpha\beta}^{mm'MM'} \cdot C(I L I'; M\, M'-M) \cdot \left[ \bar{Y}^{(\lambda)}_{L, M'-M} \right]_\mu$$

and we get for the stochastical average

$$\left\langle \langle Im | \mathcal{U}^+(t)\, \mathcal{J}_\mu\, \mathcal{U}(t) | I'm' \rangle \right\rangle_{av} = \sum_{\alpha\beta} G_{\alpha\beta}^{II'mm'}(t)$$

$$= \sqrt{\frac{4\pi c \Lambda}{k}} \cdot \Delta_{L\lambda} \times$$

$$\sum_{\alpha\beta MM'} \rho_\alpha \left( e^{-i\underline{\underline{A}}^{II'} \cdot t} \right)_{\alpha\beta}^{mm'MM'} C(I L I'; M\, M'-M) \times \left[ \bar{Y}^{(\lambda)}_{L, M'-M} \right]_\mu$$



the numerical treatment focusses on the solution of the eigenwert problem:

$$\sum_{\substack{jj'll' \\ \gamma\varepsilon}} L_{\alpha\gamma}^{mm'jj'} \; A_{\gamma\varepsilon}^{jj'll'} \; R_{\varepsilon\beta}^{ll'MM'} = \Omega_\alpha^{mm'} \cdot \delta_{\alpha\beta}\, \delta_{mM}\, \delta_{m'M'}$$

- $L$: left eigenvectors
- $R$: right eigenvectors
- $\Omega$: eigenvalues

the dimension of the matrices is

$$(2I+1) \times (2I'+1) \times N$$

- $(2I+1)$: spin of nuclear ground state
- $(2I'+1)$: spin of nuclear excited state
- $N$: number of external states

e.g.: $^{57}Fe_{5/2}$

$$2I+1 = 2$$
$$2I'+1 = 4$$
$$N = 6$$

$$\rightsquigarrow (2I+1)(2I'+1)\,N = 48$$

After the EV problem has been solved numerically we write

$$A_{\alpha\beta}^{mm'MM'} = \sum_{jj'\gamma} R_{\alpha\gamma}^{mm'jj'}\, \Omega_{\gamma}^{jj'}\, L_{\gamma\beta}^{jj'MM'}$$

and

$$\left(e^{-i\underline{\underline{A}}^{II'}\cdot t}\right)_{\alpha\beta}^{mm'MM'} = \sum_{jj'\gamma} R_{\alpha\gamma}^{mm'jj'}\, e^{-i\Omega_{\gamma}^{jj'}t}\, L_{\gamma\beta}^{jj'MM'}$$

<u>note</u>: $\Omega_{\gamma}^{jj'}$ values are not real since $\underline{\underline{A}}$ is not hermitian

in detail ..

$$A_{\alpha\beta}^{mm'MM'} - \left(A_{\beta\alpha}^{m'mM'M}\right)^{*} = i\,(\lambda_{\alpha\beta} + \lambda_{\beta\alpha})\,\delta_{mM}\,\delta_{m'M'}$$

this reflects the speed up of nuclear decay due to relaxation.



the nuclear scattering matrix is then given by

$$\tilde{M}_{\mu\nu}^{(elastic)} = \frac{k}{2}\,\sigma_0\, F_{ML} \cdot \sum_{\gamma jj'} \frac{\left[\vec{\mathcal{L}}_{L\gamma}^{(\lambda)jj'}(\hat{k})\right]_{\mu} \left[\vec{\mathcal{R}}_{L\gamma}^{(\lambda)jj'}(\hat{k}')\right]_{\nu}}{z_{\gamma}^{jj'}(\omega) - i}$$

with $z_{\gamma}^{jj'}(\omega) = \frac{1}{\Gamma}\left(\Omega_{\gamma}^{jj'} - \omega\right)$

$$\vec{\mathcal{L}}_{L\gamma}^{(\lambda)jj'}(\hat{k}) = \sqrt{\frac{8\pi}{2I'+1}} \sum_{\beta MM'} L_{\gamma\beta}^{jj'MM'}\, C(ILI';M\,M'-M)\, \vec{Y}_{L,M'-M}^{(\lambda)}(\hat{k})$$

$$\vec{\mathcal{R}}_{L\gamma}^{(\lambda)jj'}(\hat{k}') = \sqrt{\frac{8\pi}{2I'+1}} \cdot \sum_{\beta MM'} p_{\beta}\, R_{\beta\gamma}^{MM'jj'}\, C(ILI';M\,M'-M)\, \vec{Y}_{L,M'-M}^{(\lambda)*}(\hat{k}')$$

the effects of multiple scattering are obtained by the usual procedure starting at the scattering matrix of the MB atom.



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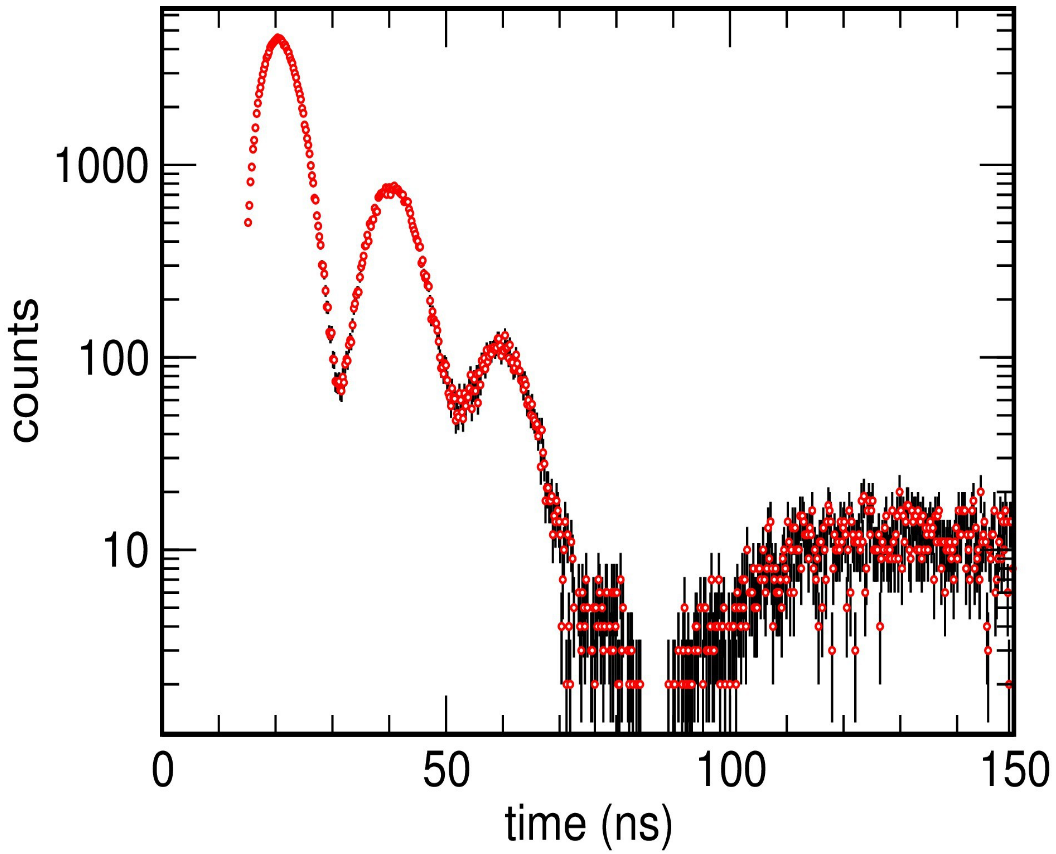
# SMS relaxation example Y.4:

- ✰ one site, 0.1 micron thickness
- ✰ magnetic up/down random fluctuations along σ polarization




- ✰ relaxation matrix (flips/lifetime)

$$\mathcal{R} = \begin{pmatrix} -R_{12} & R_{12} \\ R_{21} & -R_{21} \end{pmatrix}$$

- ✰ equilibrium population

$$\vec{p} = \frac{1}{R_{12} + R_{21}} \begin{pmatrix} R_{21} \\ R_{12} \end{pmatrix}$$