EasySpin: EPR Spectral Analysis, Simulation and Fitting

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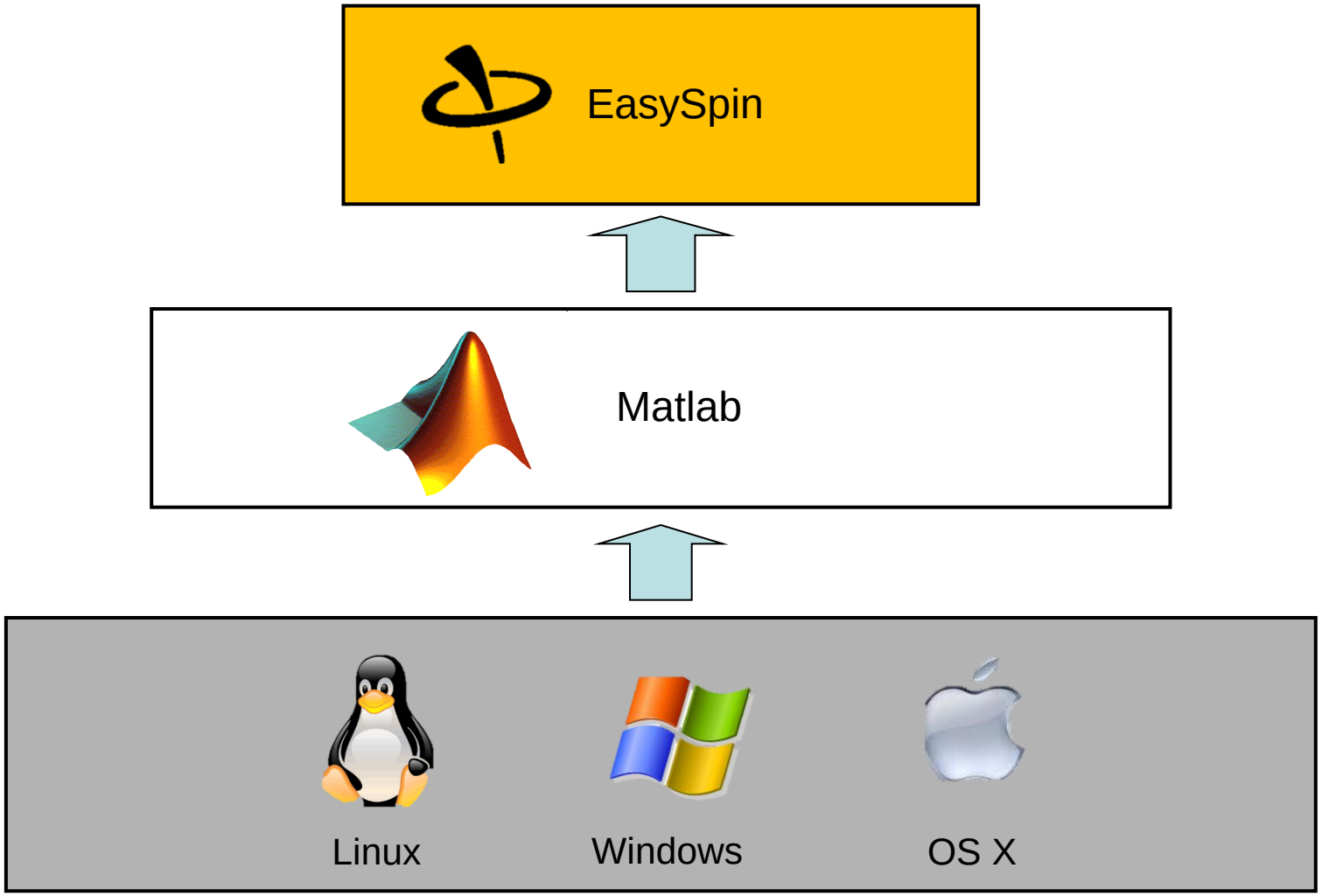
based on EasySpin 5.0 beta
June 2015

EasySpin runs on Matlab, cross-platform



EasySpin development team

Stefan Stoll University of Washington

Jeremy Lehner University of Washington
Stochastic Liouville equation solver

Joscha Nehrkorn Helmholz-Zentrum Berlin
Frequency-domain simulations
General excitation geometries

Matthew Krzyaniak Northwestern University
SpecMan data import

What's new in EasySpin 5

Simulation of frequency-swept EPR spectra
- for all levels of theory and motional regimes

Simulation of magnetization curves
- χ, χT, μ_{eff} for general spin systems

General excitation schemes
- circular and linear polarization, unpolarized mw
- arbitrary angles between $\boldsymbol{B}_0$, $\boldsymbol{B}_1$ and mw beam

New frame definitions, improve single-crystal interface
- simplifies specifications of tensor and crystal orientations

Import of ORCA calculations
- read in calulated g, A, Q, and D tensors

Rapid-scan EPR signals
- time-domain steady-state solutions of Bloch equations

More data formats
- SpecMan, Magnettech, Adani, ActiveSpectrum, JEOL

EasySpin and Matlab: Versions

Matlab

- Two new releases per year (spring and fall)
- Names: R2013a, R2013b, R2014a, R2014b, R2015a, etc.

Always use most recent Matlab version.

EasySpin

- Major new version about once a year, bug fix releases in between
- Supports all Matlab versions starting from 7.5 (R2007b)
- Older Matlab versions cannot supported, since they lack some of the features needed in EasySpin

Regularly check easyspin.org for updates.
Keep EasySpin updated!

EasySpin and Matlab documentation

Web resources

EasySpin documentation http://easyspin.org
EasySpin user forum http://easyspin.org/forum

Matlab documentation
http://www.mathworks.com/access/helpdesk/help/helpdesk.html

Matlab newsgroup
http://www.mathworks.com/matlabcentral/newsreader/
http://groups.google.com/group/comp.soft-sys.matlab/topics

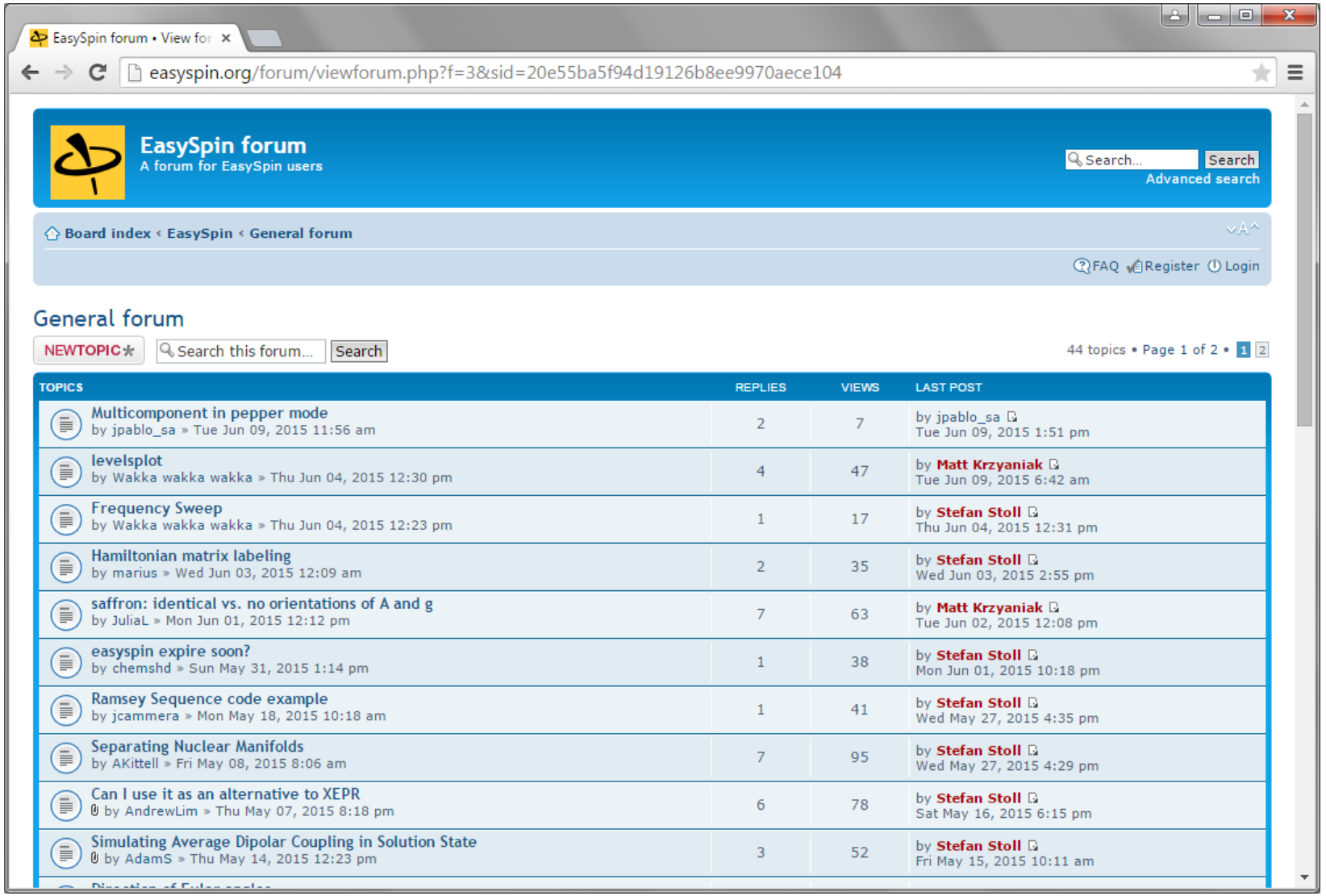
Matlab file exchange
http://www.mathworks.com/matlabcentral/fileexchange

Local Matlab and EasySpin documentation

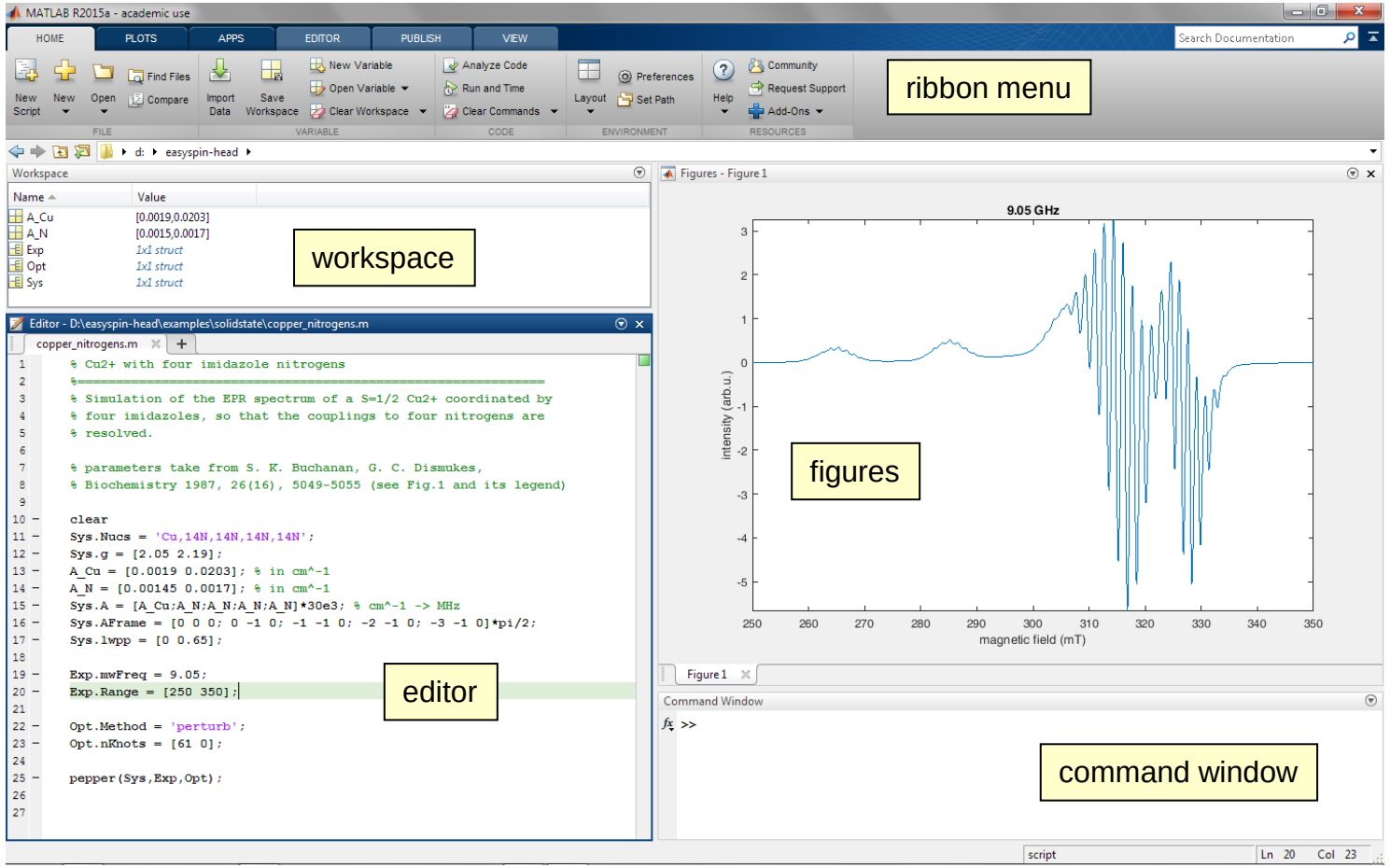
- press **<F1>**
- go to *Start* > *Toolboxes* > *EasySpin* > *Help*
- type **`doc`** in command window
- point browser to <EasySpinDir>/documentation/index.html

- type **`doc plot`** in command window to get help on function **`plot`**

EasySpin user forum at easyspin.org/forum



Matlab: Graphical user interface



Running code from the editor

- press <Ctrl>+<Enter>, or
- select portion of code you want to run and press <F9>, or
- save as a file and press <F5>

Matlab: Vectors and arrays

Row vector (= 1xN array)

```
g = [2.21 2.21 2.03];
```

commas or spaces along rows
semicolons to separate rows

Column vector (= Mx1 array)

```
f = [1; 1; 2; 3; 5; 8];
```

Matrices (= 2D array

```
A = [4 5; 6 7; 8 9];
```

Array functions

`zeros`	array with all 0
`ones`	array with all 1
`rand`	random numbers

Array manipulations

`X(:)`	make column vector
`X.'`	transpose
`X'`	adjoint
`M(3,1) = pi;`	set element
`f(2) = [];`	delete element
`f(1:2) = 1;`	set elements
`f(3:end) = 0;`	set elements
`X(:,3) = 0;`	set column
`X(2,:) = [];`	delete row
`MM = [M; M]`	concatenate

Mathematical operations

`X*Y`	vector/matrix multiply
`X.*Y`	elementwise multiply
`f.^2`	elementwise squared

Matlab is case-sensitive!
So `mwFreq` and `mwfreq` are treated as two separate variables!

Matlab: Strings

String enclosed between to single quotes

```
Algorithm = 'simplex';
Nucs = '63Cu,14N';
```

Concatenate two strings

```
y = 'Jerry';
X = ['Tom', ' and ', y];
```

Two single quotes to include a quote

```
X = 'Ivar''s Salmon House';
```

String = array of characters

String manipulations

`X(3)`	extract character
`X(1:4)`	extract sub-string
`X(1:4)=[]`	delete sub-string
`findstr(a,X)`	find one string in another
`strcmp(X,Y)`	comparing strings
`strrep(X,a,b);`	search and replace

Converting to/from numbers

`str2num`	string to number
`num2str`	number to string
`mat2str`	matrix to string
`sprintf`	general conversion function (similar to C programming)

Matlab: Structures

Structure = collection of variables (called fields), with a name

An example

```
Software.Name = 'EasySpin';
Software.YOB = 2000;
Software.Version = [4 5 5];
Software.Price = 0;
Software.Users = 'many';
Software.Developers = 1;
Software.Budget = 0;
Software.Functions = 97;
Software.UnitTests = 495;
Software.Citations = 1100;
```

EasySpin spin system

```
Nitroxide.g = [2.0088 2.0061 2.004];
Nitroxide.Nucs = '14N';
Nitroxide.A = [16 16 86];
Nitroxide.lwpp = 1;
```

EasySpin experimental parameters

```
Experiment.mwFreq = 94.9;
Experiment.CenterSweep = [3462 50];
```

Matlab: Cell arrays

Cell arrays = arrays where each element can be **of arbitrary size and type**

```
A{1} = 'EPR';
A{2} = [1 1 2 3 5 7];
A{3} = sin(pi/5);
A{4} = {'x',12};
```

`A(k)` addresses the cell no `k`
`A{k}` addresses the content of cell no `k`

```
A{3} = [];
```
puts an empty array into cell `k`

```
A(3) = [];
```
removes cell `k` altogether

Matlab: Comments

One-line comments: percentage sign

```
a = log(5);          % a sophisticated computation
```

Multi-line comments: `%{` and `%}`

```
a = [5, 3i, 1.4];    % values to be squared
%{
b(1) = a(1)^2;       % element-by-element
b(2) = a(2)^2;
b(3) = a(3)^2;
%}
b = a.^2;            % all in one line
```

Matlab: Scripts and functions

Matlab files `*.m` are either scripts or functions, depending in the keyword `function`.
Each callable function must reside in a separate file.
Functions can have sub-functions, which are not accessible from outside.

mysims.m — Matlab script

```
Nx.Nucs = '14N';
Nx.A = [16 16 86];
Nx.tcorr = 1e-9;
Ex.mwFreq = 9.5;
[B,spc] = chili(Nx,Ex);
save mysims Nx Ex B spc
```

affects variables on the workspace

addnoise.m — Matlab function

```
function ynoisy = addnoise(y,snr)

noise = rand(size(y)) - 0.5;
noiselevel = snr*(max(y)-min(y));
ynoisy = y + noiselevel*noise;
```

has its own workspace

Calling the script

```
>> mysims
```

Calling the function

```
>> spcn = addnoise(sim,0.2)
```

EasySpin: Installation

1. Install auxiliary software
   Win 64bit: download

2. Download zip file from EasySpin website easyspin.org

3. Unpack zip file to a directory *<mydir>*
   e.g. to C:/easyspin-x.y.z or /usr/var/easyspin-x.y.z

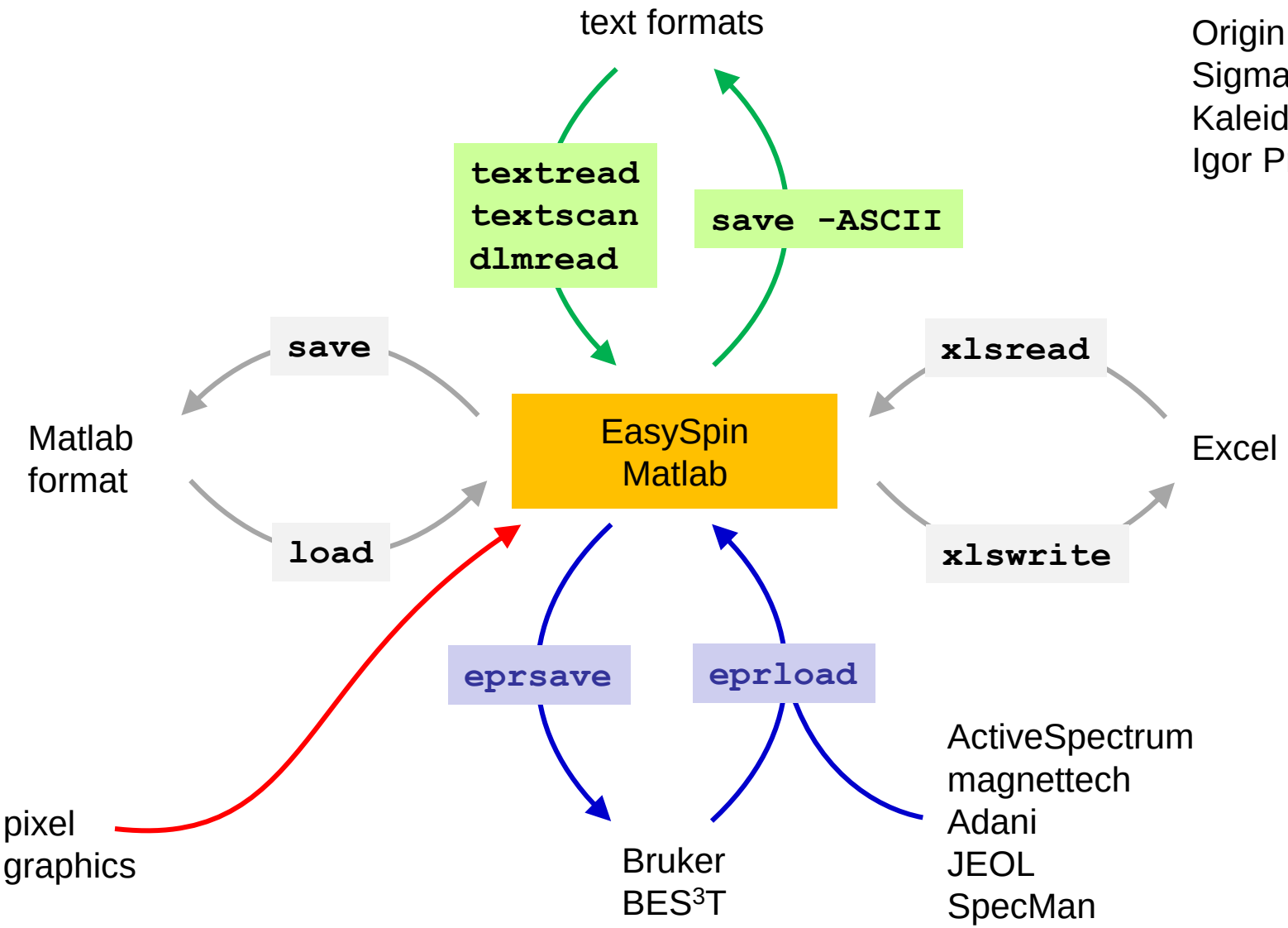
- EasySpin folder structure:

main folder	*<mydir>*/easyspin-x.y.z
toolbox functions	*<mydir>*/easyspin-x.y.z/easyspin
documentation	*<mydir>*/easyspin-x.y.z/documentation
examples	*<mydir>*/easyspin-x.y.z/examples

4. Tell Matlab about EasySpin
- Launch Matlab
- Go to *File* > *Set path* ...
- Remove any old EasySpin entries from Matlab path
- Add the folder *<mydir>*/easyspin-x.y.z/easyspin to Matlab path
- Save and close the Set path window

5. Finish
- Type **easyspincompile** in command window
- Type **easyspininfo** in command window

Data import and export



Data import and export

Loading and importing

`eprload`	reads data from Bruker spectrometers ESP: .spc/.par, BES3T: .DTA/.DSC also loads experimental parameters supports ActiveSpectrum, magnettech and Adani spectrometers
`load`	load data stored in Matlab format (.mat)
`textread`	reads text (ASCII) data
`xlsread`	reads Excel spreadsheets (.xls)

Import wizard: File > Import Data...
or through workspace toolbar

```
[B,spc] = eprload('myoglobin.spc');
[B,spc] = eprload('catalase.DSC');
[B,spc] = textread('data.txt', '%f %f', 'headerlines', 12)
```

Data import and export

Saving and exporting

`save`	saves data in Matlab format (.mat)
`save -ASCII`	saves text (ASCII) data
`xlswrite`	saves as Excel spreadsheet (.xls)

```
data = [B spc];
save -ASCII mysims.txt data
xlswrite('mysims',data,'simul','B34');
```

`eprsave`	saves data in Bruker EPR format (BES3T)

Data work-up

Baseline correction etc

`basecorr`	polynomial baseline correction
`exponfit`	fits exponentials to data
`mean`	computes the mean
`smooth`	data smoothing
`addnoise`	adds noise to data

Fourier transform etc

`fft`	Fast Fourier Transform (complex)
`fdaxis`	frequency-domain axis
`ctafft`	cross-term averaged FFT
`apowin`	apodization window (Hamming etc)

Complex data

`real`	real part
`imag`	imaginary part
`abs`	magnitude

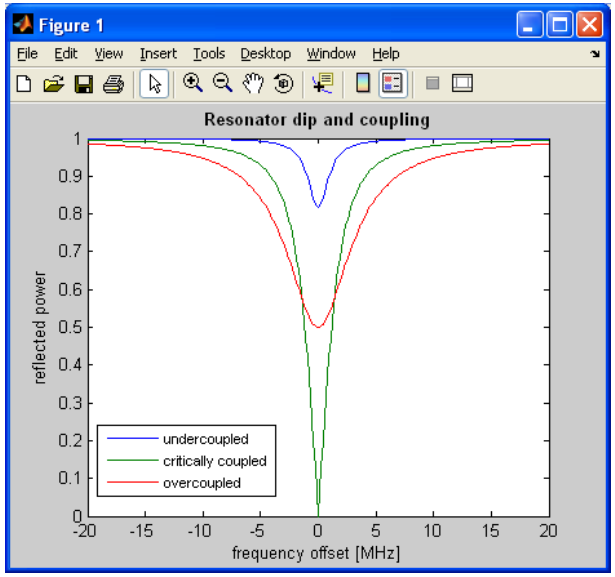
Plotting data

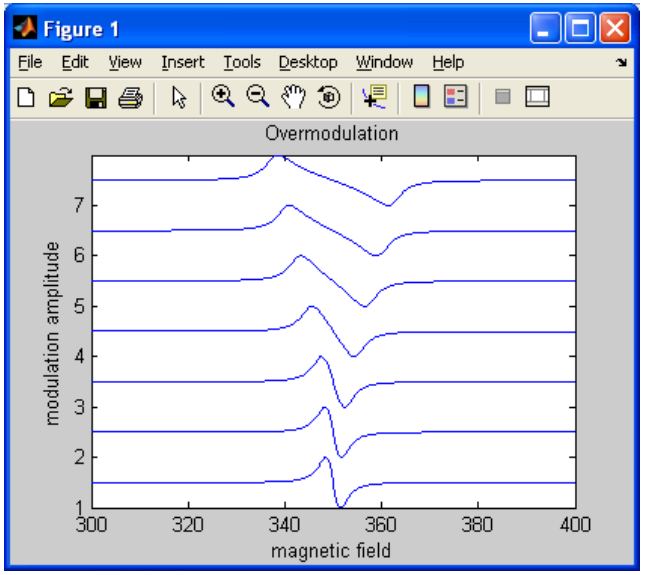
Plotting functions

```
plot(spc)
plot(B,spc)
plot(B,spc,'r')
plot(B1,spc1,'r',B2,spc2,'g')

subplot(2,1,1)
subplot(2,1,2)

semilogx(x,y)
semilogy(x,y)
loglog(x,y)

stackplot(x,y)

xlim([0 30])
ylim([0 2])
```

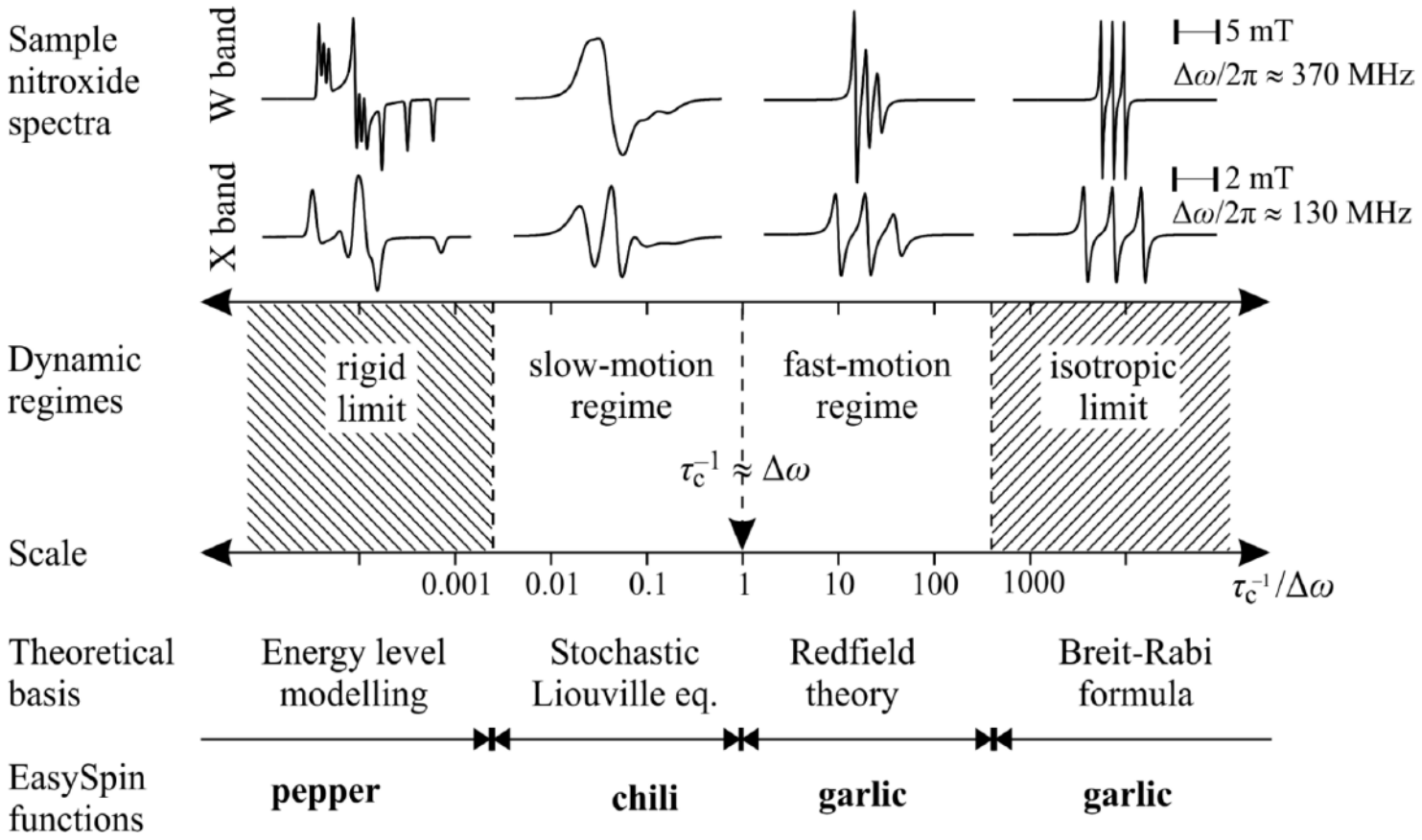
Changing the appearance of plots

```
xlabel('magnetic field [mT]');
ylabel('intensity');
title('EPR spectrum');
legend('first','second','third');

hold on
hold off

axis tight
```





Motional regimes



EasySpin simulation functions

cw EPR:	rigid-limit: `pepper` isotropic-limit and fast-motion: `garlic` slow-motion cw EPR: `chili`
ENDOR:	`salt` (mostly cw)
pulse EPR:	`saffron` (ESEEM and ENDOR)

Calling syntax:

```
pepper(Sys,Exp)
pepper(Sys,Exp,Opt)
```

two input arguments
three input arguments

`Sys`	spin system details (structure)
`Exp`	experimental details (structure)
`Opt`	simulation options (structure)

```
pepper(...)
spc = pepper(...)
[B,spc] = pepper(...)
```

plots the simulated spectrum
returns simulated spectrum
returns spectrum and field axis

Spin system: Electron spins

Input syntax

`Sys.S = 1/2`	one electron spin $S = 1/2$ (default, no need to specify explicitly)
`Sys.S = 5/2`	one electron spin $S = 5/2$
`Sys.S = [1/2, 1/2]`	two electron spins $S_1 = S_2 = 1/2$

Possible values

`pepper`	solid-state cw EPR	arbitrary number, arbitrary spin
`garlic`	isotropic, fast-motion	one spin with S = 1/2
`chili`	slow-motion	one spin with $S = 1/2$
`salt`	ENDOR	arbitrary number, arbitrary spin
`saffron`	pulse EPR	one spin with arbitrary S

Spin system: g matrices

$$(\mu_B/h)\boldsymbol{B}\boldsymbol{g}\hat{\boldsymbol{S}} = (\mu_B/h)(B_x g_x \hat{S}_x + B_y g_y \hat{S}_y + B_z g_z \hat{S}_z)$$

g eigenframe

g values, one electron spin

```
Sys.g = [1.9, 2.1, 2.2]
Sys.g = [1.9, 2.2]
Sys.g = 2
```

rhombic *g*
axial *g*, `=[1.9, 1.9, 2.2]`
isotropic *g*, `=[2, 2, 2]`

g values, two electron spins

```
Sys.g = [2,2,2; 2.1,2.1,2]
Sys.g = [2 2.1; 2.05 1.98]
Sys.g = [2.03; 2.01]
```

one row per electron spin
rhombic *g*
axial *g*
isotropic *g*

Tensor orientation

```
Sys.gFrame = [0,pi/4,0]
```

one row per electron spin
orientation of *g* tensor frame in molecular frame

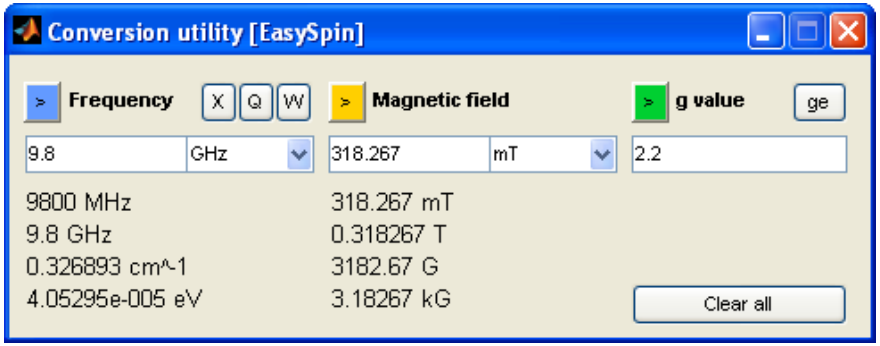
Units: radians

Frequency/field/g conversions

(ν/GHz) = 13.9962 *g* (B_0/T)

71.4477 (ν/GHz) = *g* (B_0/mT)

or use **`eprconvert`**



Spin system: Zero-field splitting tensors

Hamiltonian (in frequency units)

$$\boldsymbol{S}\,\boldsymbol{D}\,\boldsymbol{S} = D_x S_x^2 + D_y S_y^2 + D_z S_z^2 = D(S_z^2 - \boldsymbol{S}^2/3) + E(S_x^2 - S_y^2)$$

$$\boldsymbol{D} = \begin{pmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_z \end{pmatrix} = \begin{pmatrix} -\frac{1}{3}D + E & 0 & 0 \\ 0 & -\frac{1}{3}D - E & 0 \\ 0 & 0 & \frac{2}{3}D \end{pmatrix}$$

EasySpin input

Units: MHz

1 cm^{-1} = 30 GHz

```
Sys.D = 100
Sys.D = [100 10]
Sys.D = [-40 -40 80]
```

D = 100 MHz, E = 0
D = 100 MHz, E = 10 MHz
[D_x, D_y, D_z] in MHz

Tensor orientation

Units: radians

```
Sys.DFrame = [0 40 32]*pi/180;
```

EasySpin also supports higher-order zero field terms. See documentation.

Spin system: Magnetic nuclei

Specifying nuclear spins comma-separated list of isotopes

```
Sys.Nucs = '1H';
Sys.Nucs = '63Cu,14N';
Sys.Nucs = '13C';
Sys.Nucs = '1H,1H,1H,1H';
```

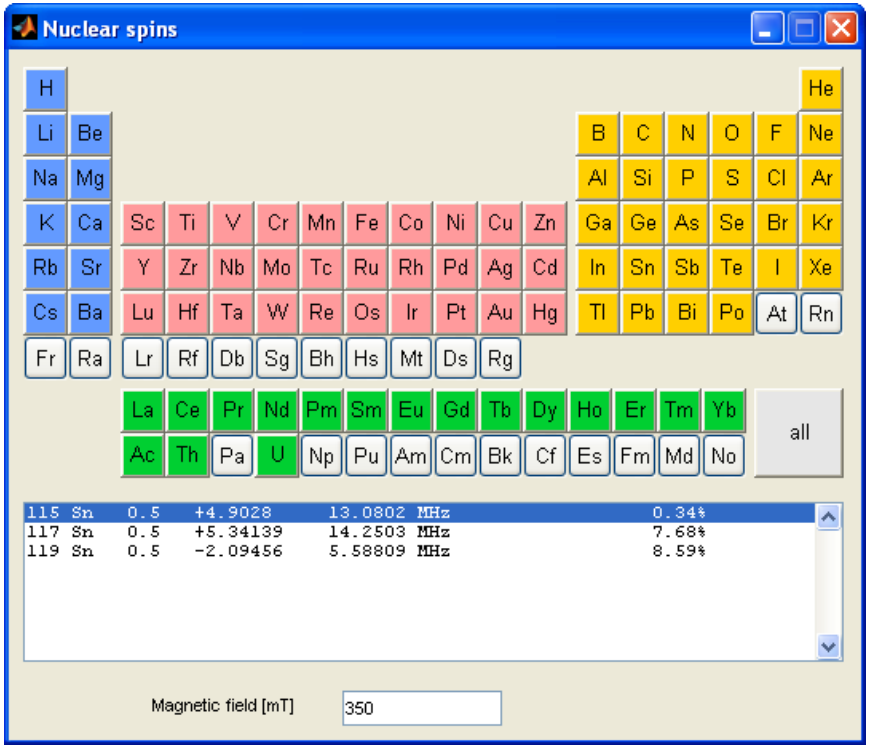
Helper functions to add or remove nuclear spins from the spin system

```
Sys = nucspinadd(Sys,'1H',[2 8]);
Sys = nucspinrmv(Sys,2);
```

Spin system: Magnetic nuclei

Nuclear constants

`isotopes`	interactive periodic table with nuclear isotope database
`nucabund`	natural abundance
`nucgval`	nuclear g factors
`nucqmom`	nuclear electric quadrupole moments
`nucspin`	nuclear spin quantum numbers
`larmorfrq`	Larmor frequency



Spin system: Isotope mixtures

Natural-abundance mixtures: omit mass number

```
Sys.Nucs = 'Cu';
Sys.Nucs = 'Cu,14N';
Sys.Nucs = 'Cu,Cl';
Sys.Nucs = 'C';
```

69% ^{63}Cu, 31% ^{65}Cu

53% ^{63}Cu/^{35}Cl, 23% ^{65}Cu/^{35}Cl, 17% ^{63}Cu/^{37}Cl, etc

98.9% ^{12}C, 1.1% ^{13}C

"natural abundance" can vary!

Mixtures with custom abundances: separate field

```
Sys.Nucs = '(14,15)N';
Sys.Abund = [50 50];

Sys.Nucs = 'Cu,(32,33)S';
Sys.Abund = [0.1 0.9];
```

Spin system: Multiple components

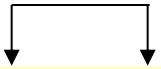
One component

one spin system


```
... = pepper(SysA,Exp,...)
```

Two components

two spin systems



```
... = pepper({SysA,SysB},Exp,...)
```

Weights in SysA.weight, SysB.weight.

Arbitrary number of components possible.

Spin system: Hyperfine matrices

Hamiltonian (in frequeny units)

$$\hat{\boldsymbol{S}}\boldsymbol{A}\hat{\boldsymbol{I}} = \hat{S}_x A_x \hat{I}_x + \hat{S}_y A_y \hat{I}_y + \hat{S}_y A_y \hat{I}_y$$

Units: MHz

1 mT = 28 MHz
10^{-4} cm^{-1} = 3 MHz

Principal values one row per nucleus

```
Sys.Nucs = '1H'
Sys.A = 10
Sys.A = [4, 12]
Sys.A = [3, 5, 12]
```

one nuclear spin
isotropic *A*, = [10 10 10]
axial *A* (A_{xx}=A_{yy}), = [4, 4, 12]
rhombic *A*

```
Sys.Nucs = '1H,14N'
Sys.A = [3 5 12; 1 2 3]
```

two nuclear spins
two rhombic *A*

Isotropic, axial, rhombic components one row per nucleus

```
Sys.A_ = [4 2 0];
```

[a_{iso}, T, ρ]

$$A = a_{iso} + \begin{pmatrix} -T-\rho & 0 & 0 \\ 0 & -T+\rho & 0 \\ 0 & 0 & 2T \end{pmatrix}$$

Orientation one row per nucleus

Units: radians

```
Sys.AFrame = [0,pi/4,0]
```

Euler angles of A eigenframe in molecular frame

Spin system: Nuclear quadrupole tensors

Hamiltonian (in frequeny units)

$$\hat{\boldsymbol{I}}\boldsymbol{P}\hat{\boldsymbol{I}} = P_x\hat{I}_x^2 + P_y\hat{I}_y^2 + P_z\hat{I}_z^2$$

(in eigenframe of $\boldsymbol{P}$)

$$\boldsymbol{P} = \frac{e^2qQ}{4I(2I-1)h}\begin{pmatrix} -(1-\eta) & 0 & 0 \\ 0 & -(1+\eta) & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

$$e^2qQ/h = 2I(I-1)P_{zz}$$

$$\eta = \frac{P_{xx} - P_{yy}}{P_{zz}}$$

Tensor principal values one row per nucleus Units: MHz

`Sys.Q = 0.7;` e^2qQ/h = 0.7 MHz

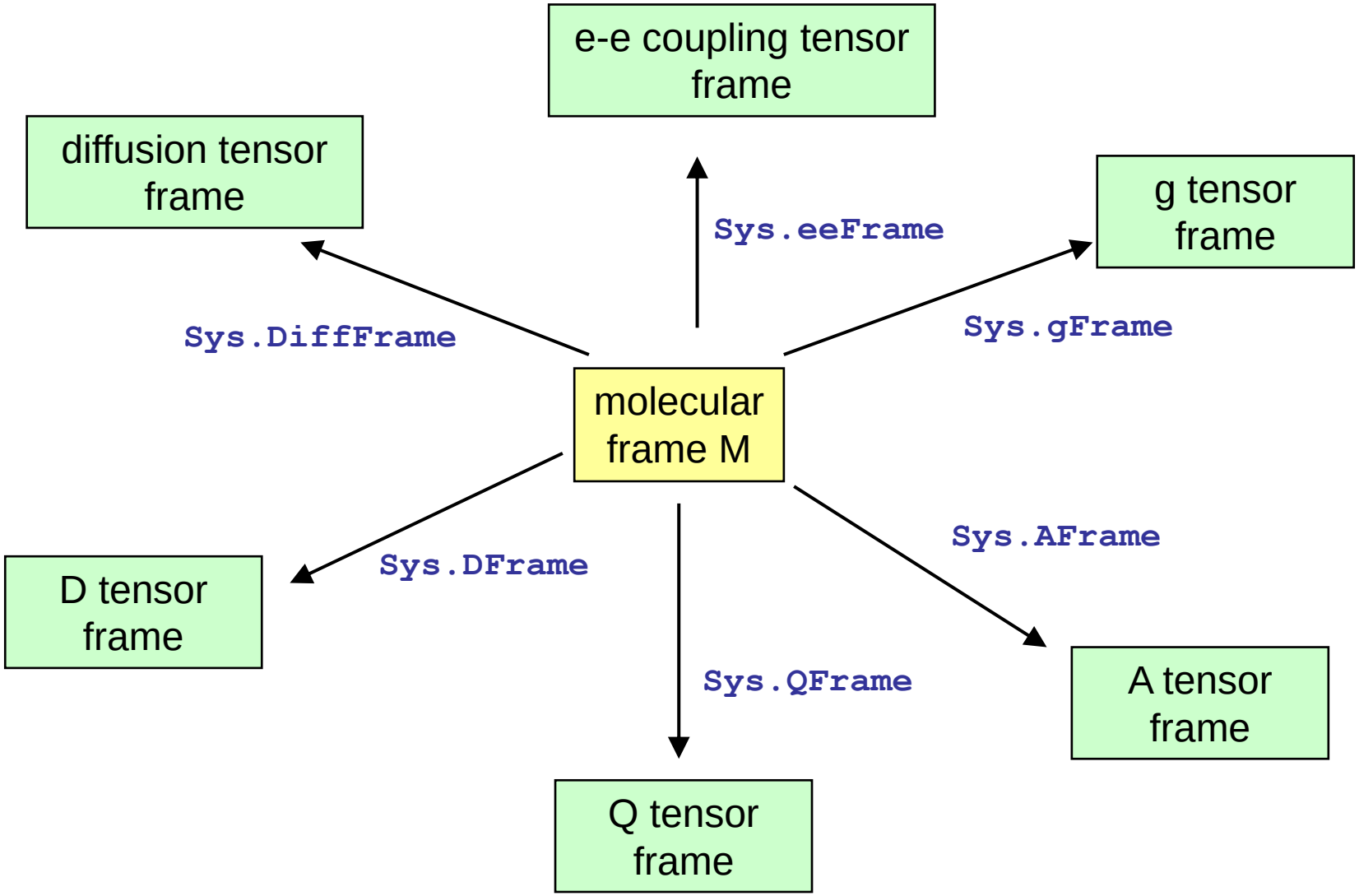
`Sys.Q = [0.7, 0.1]` e^2qQ/h = 0.7 MHz, and η = 0.1 (between 0 and 1)

`Sys.Q = [-1.2,-0.8,2]` 3 principal values (in MHz)

Tensor orientation one row per nucleus Units: radians

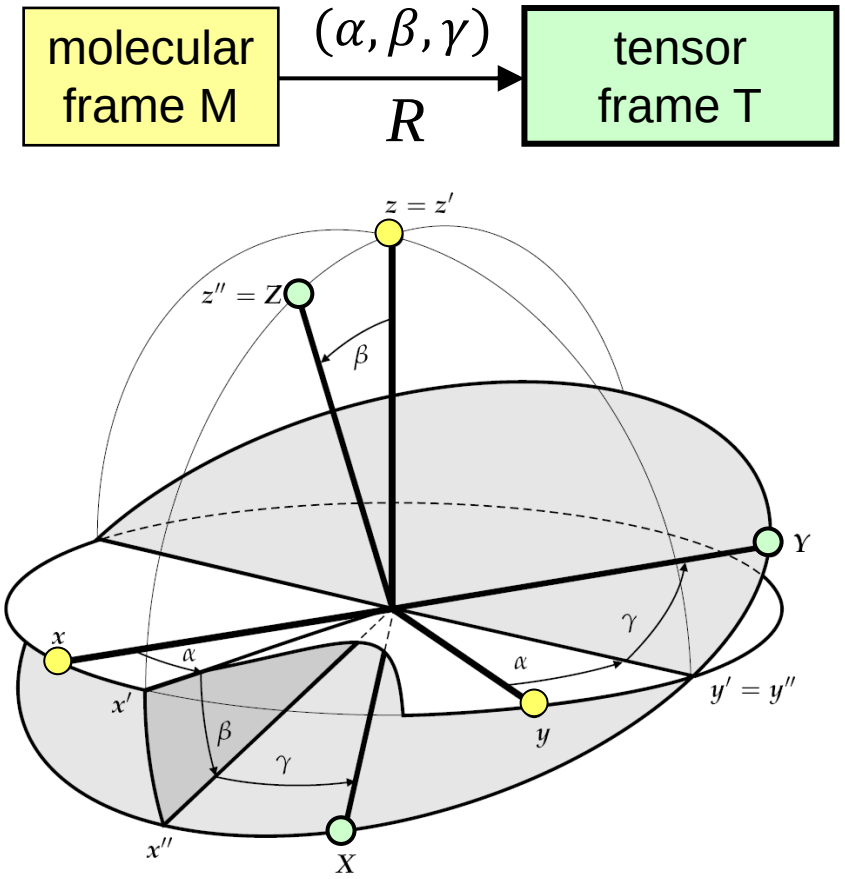
`Sys.QFrame = [0,pi/4,0]` Euler angles of *Q* eigenframe in molecular frame

Frames and tensor orientations



For each frame orientation: 3 Euler angles (α, β, γ) that transform M frame to tensor frame.

Frames and tensor orientations



$$R = R_{z''}(\gamma) \cdot R_{y'}(\beta) \cdot R_z(\alpha)$$

$$= \begin{pmatrix} c\gamma & s\gamma & 0 \\ -s\gamma & c\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} c\beta & 0 & -s\beta \\ 0 & 1 & 0 \\ s\beta & 0 & c\beta \end{pmatrix} \cdot \begin{pmatrix} c\alpha & s\alpha & 0 \\ -s\alpha & c\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} c\gamma c\beta c\alpha - s\gamma s\alpha & c\gamma c\beta s\alpha + s\gamma c\alpha & -c\gamma s\beta \\ -s\gamma c\beta c\alpha - c\gamma s\alpha & -s\gamma c\beta s\alpha + c\gamma c\alpha & s\gamma s\beta \\ s\beta c\alpha & s\beta s\alpha & c\beta \end{pmatrix}$$

```
% g tensor in eigenframe
g_eig = diag([1.9, 2.0, 2.1])
    1.9000         0         0
         0    2.0000         0
         0         0    2.1000

% Euler angles α, β, γ (in radians)
abc = [10 45 30]*pi/180
    0.1745    0.7854    0.5236

% Rotation matrix
R = erot(abc)
    0.5162    0.5987   -0.6124
   -0.4986    0.7915    0.3536
    0.6964    0.1228    0.7071
```

rows of R: g axes in molecular frame
columns of R: molecular axes in g frame

```
% g tensor in molecular frame
g_mol = R.'*g_eig*R
    2.0218   -0.0224    0.0809
   -0.0224    1.9657    0.0453
    0.0809    0.0453    2.0125

% get Euler angles from R
eulang(R)*180/pi
   10.0000   45.0000   30.0000
```

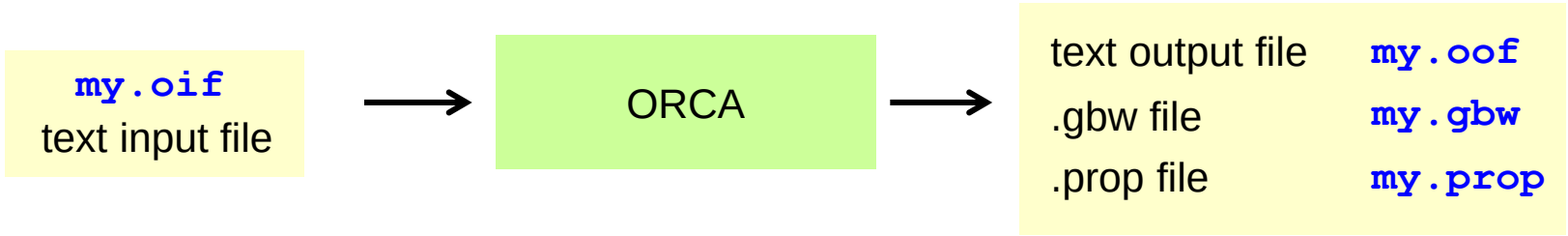
Spin system: Import from ORCA calculation

Requesting EPR parameters in ORCA

Include `%eprnmr` section:

```
%eprnmr
  gtensor 1
  Nuclei = all H {aiso, adip, aorb, fgrad, rho}
end
```

ORCA calculation



Import into EasySpin

Thanks to Frank Neese

Obtain EPR parameters from .prop file:

```
Sys = orca2easyspin('my.prop')
```

reads the .prop file

Visualization

`orcaview`

Spin system: Static broadenings

Convolutional broadenings isotropic only

Units: mT

phenomenologically account for line broadening

```
Sys.lwpp = [0.2 0.3];
Sys.lwpp = 0.3;
Sys.lw = [0 0.1];
```

1st element	Gaussian
2nd element	Lorentzian (optional)
`lwpp`	peak-to-peak linewidth
`lw`	full width at half maximum (FWHM)

```
Sys.lwEndor = 0.3;
```

(only `salt` and `saffron`), in MHz

Strain broadenings (only `pepper`) isotropic or anisotropic

Units: MHz

line broadening due to unresolved hf splittings and site-to-site disorder

`Sys.HStrain`	unresolved hyperfine splittings (MHz)
`Sys.gStrain`	distribution of g values
`Sys.AStrain`	distribution of A values (correlated with g) (MHz)
`Sys.DStrain`	distribution of D and E (MHz)

Spin system: Rotational diffusion

Rotational correlation time (`garlic` and `chili`) Units: s

```
Sys.tcorr = 1e-9;
Sys.logtcorr = -9;
```

$$\tau_c = \frac{1}{6R}$$

Diffusion tensor (`chili` only) Units: 1/s

```
Sys.Diff = 1e9;
Sys.logDiff = 9;
```
isotropic

```
Sys.Diff = [1 2]*1e8;
Sys.logDiff = [8 8.3];
```
axial

```
Sys.Diff = [2,2.5,3]*1e8;
Sys.logDiff = [8.3,8.4,8.5];
```
rhombic

```
Sys.DiffFrame = [0 20 0]*pi/180;
```
tilt angles for tensor orientation

Spin system: Ordering potential

Ordering potential coefficients (`chili`)

Expansion coefficients for potential

$$U(\boldsymbol{\Omega}) = -k_{\mathrm{B}}T \sum_{L,M} c_{L,M} D^{L}_{M0}(\boldsymbol{\Omega})$$

```
Sys.lambda = [1 0 0 0 0];
```

First 5 terms: $(L,M) = (2,0),\ (2,2),\ (4,0),\ (4,2),\ (4,4)$

Frame aligns with diffusion tensor frame

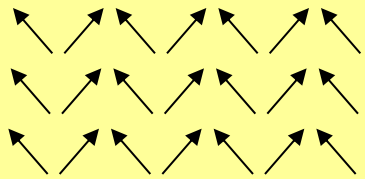
Static orientational distributions

Orientation of a spin center in the sample: $\boldsymbol{\Omega} = (\phi, \theta, \chi)$

Distribution of orientations of the spin center: $P(\boldsymbol{\Omega})$

Crystals

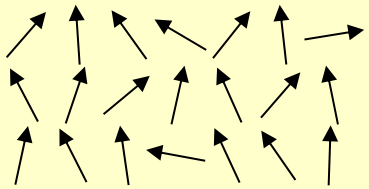
one or several distinct orientations with equal probabilities



`Exp.Orientations`
`Exp.CrystalSymmetry`

Partially oriented systems

probability is varying function of orientation

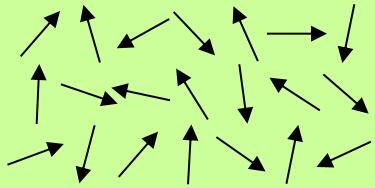


`Exp.Ordering`

Slow motion: "partial MOMD"

Powders

all orientations with equal probability



default

Slow motion: "MOMD"

Single crystals

Specify site splittings via the space or point group of the crystal

space group → number and orientation of sites in unit cell → site splitting

```
Exp.CrystalSymmetry = 'P21/m';
```
space group symbol, Hermann-Mauguin

```
Exp.CrystalSymmetry = 11;
```
space group number (between 1 and 230)

Not all space group settings are supported.
EasySpin requires the third axis of the crystal abc frame to be the unique axis.

```
Exp.CrystalSymmetry = 'C2h';
```
point group, Schönflies notation

```
Exp.CrystalSymmetry = '2/m';
```
point group, Hermann-Mauguin notation

Use the point subgroup of the space group, not the local point group of the paramagnetic center.

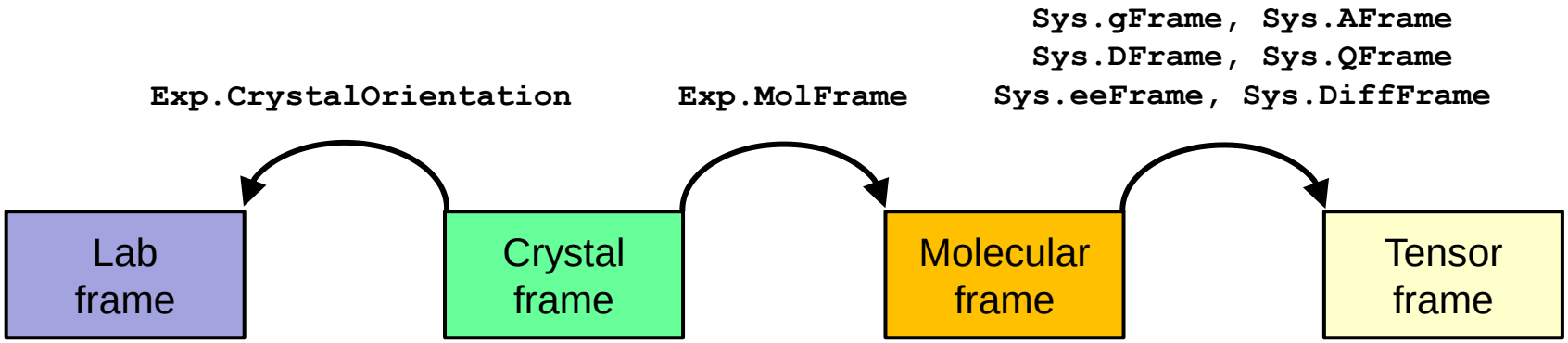
Crystal orientation in the spectrometer

three Euler angles

```
Exp.CrystalOrientation = [0 0 0];
```
orientation of a crystal

```
Exp.CrystalOrientation = [0 0 0; 0 pi/2 0];
```
twin crystal

Frames



zL along static field ($\boldsymbol{B}_0$)
xL along mw field ($\boldsymbol{B}_1$)

zC along highest crystal symmetry axis
xC along another symmetry axis perpendicular to zC

local symmetry frame of spin center

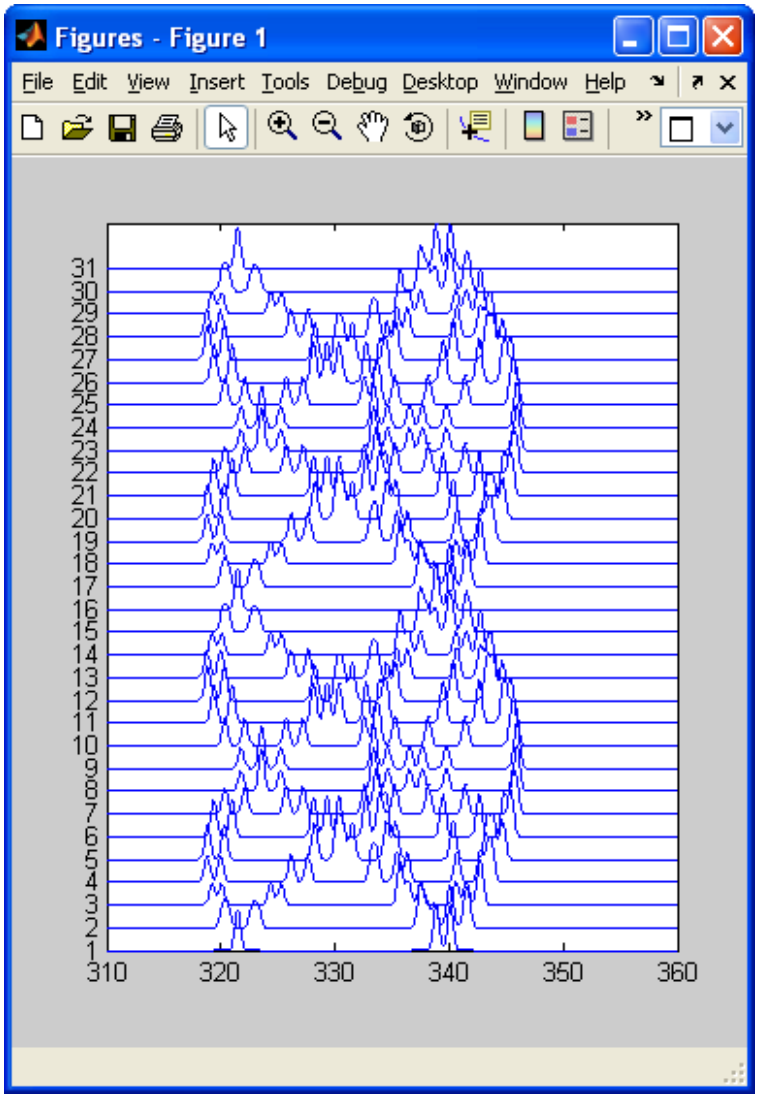
aligned with tensor principal axes

Single crystals

Crystal rotations

- specify rotation axis
- generate rotated orientations
- specify crystal symmetry

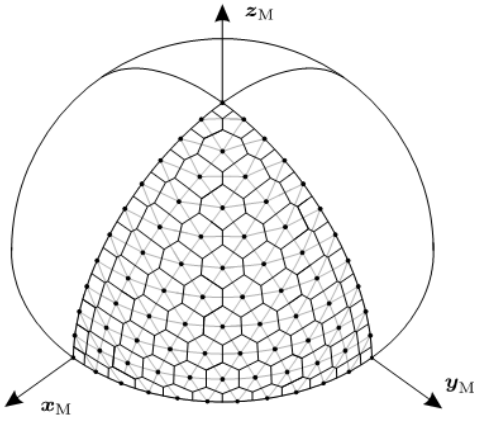
```
n = [1 0 0];
[phi,theta] = rotplane(n,[0 pi],31);
Exp.Orientations = [phi;theta];
Exp.CrystalSymmetry = 'P21212';

Opt.Output = 'separate';

[B,spc] = pepper(Sys,Exp,Opt);

stackplot(B,spc);
```



Powder spectra: Orientational averaging

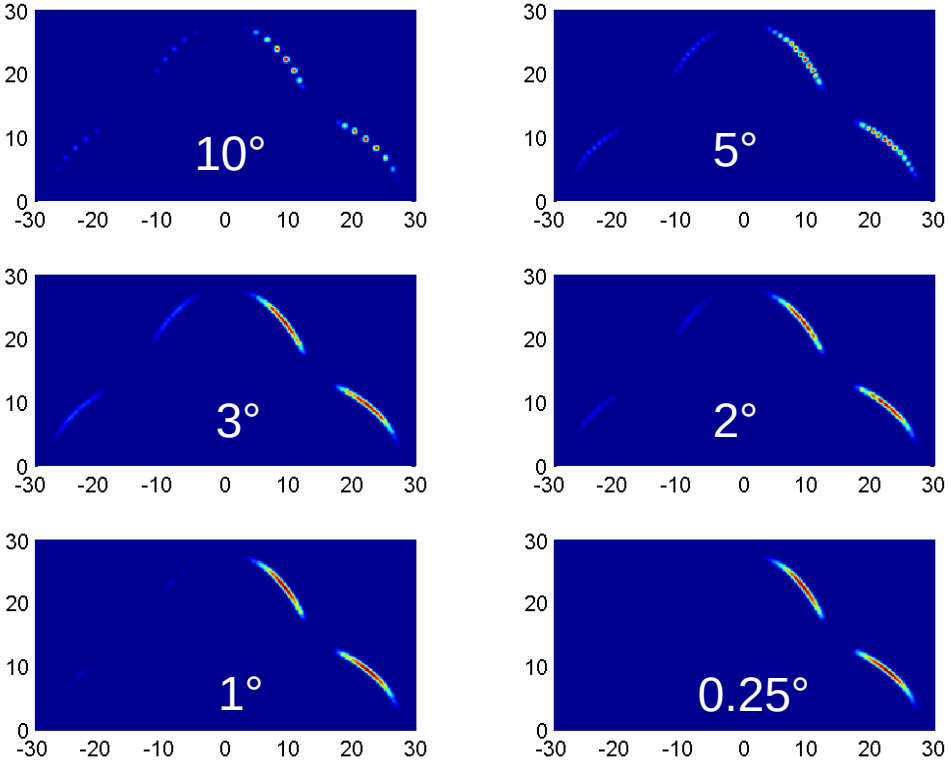
EasySpin computes powder spectra by default.

Number of orientations



`Opt.nKnots` gives the orientational resolution in terms of number of orientations between $\theta = 0°$ (north pole) and $\theta = 90°$ (equator)

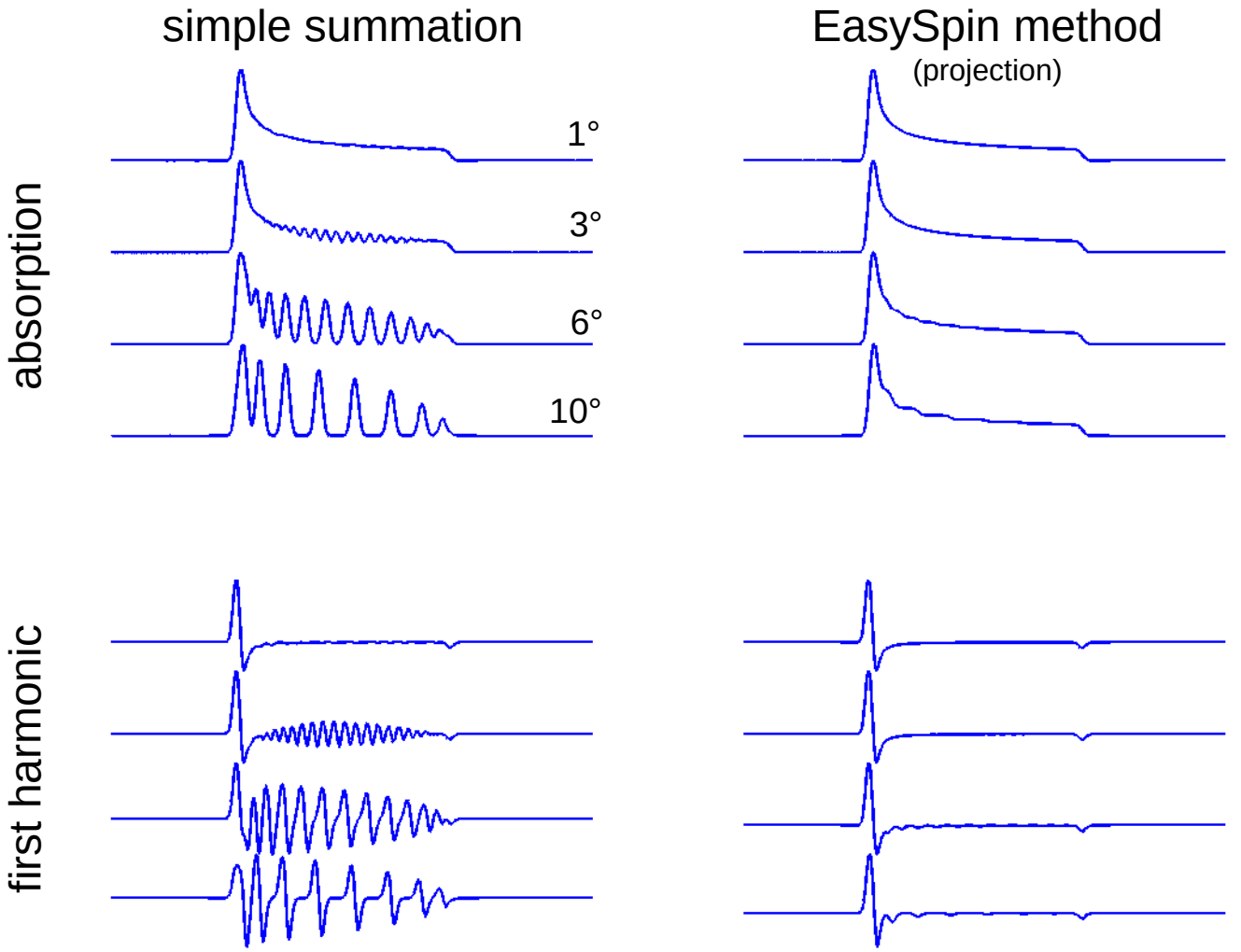
```
Opt.nKnots = 10;   10°
Opt.nKnots = 31;    3°
Opt.nKnots = 91;    1°
Opt.nKnots = 361;   0.25°
Opt.nKnots = 901;   0.1°
```



The more orientations, the
- smoother the spectrum
- longer the computation time

Powder spectra: orientational averaging

"Simulation grass"



`pepper, salt, saffron: Opt.nKnots`

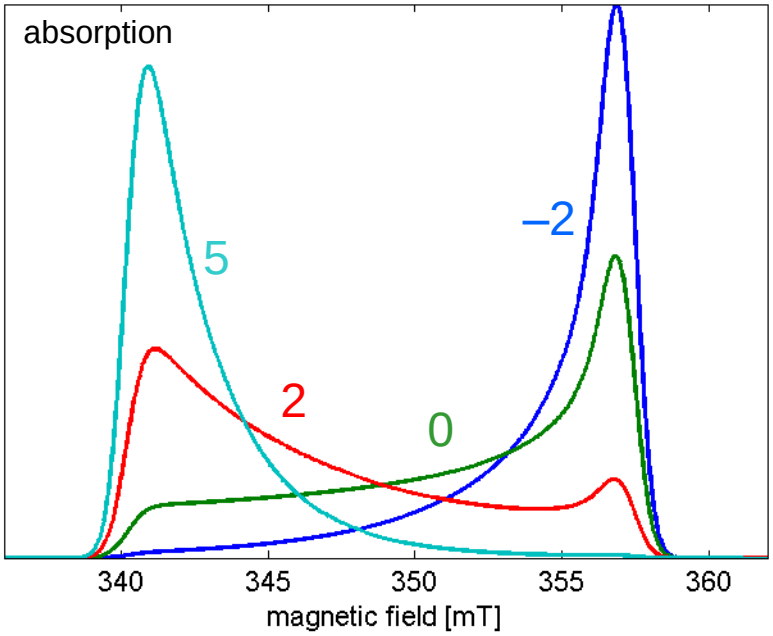
Partially oriented systems

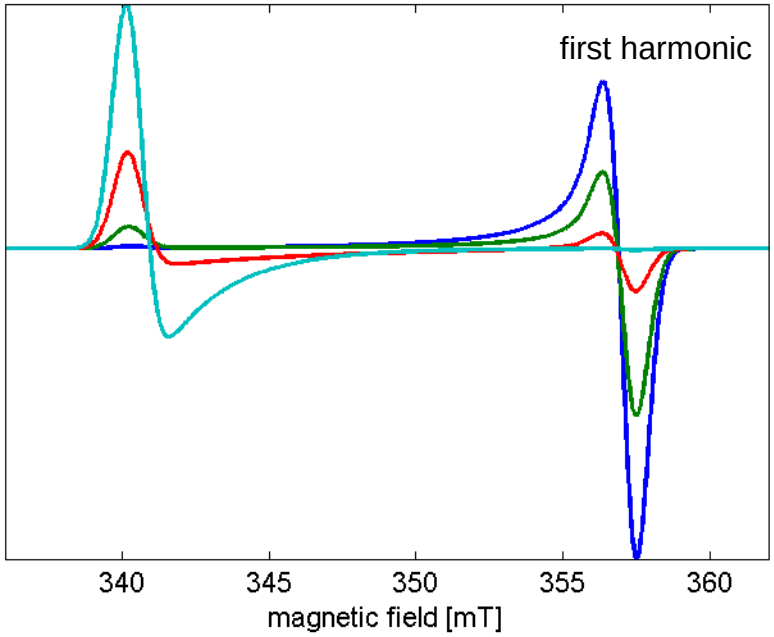
Orientational distribution	Orientational potential
$P(\boldsymbol{\Omega}) \propto \exp[-U(\boldsymbol{\Omega})/k_\mathrm{B}T]$	$U(\boldsymbol{\Omega}) = -k_B T \sum_{L,K} \lambda_K^L \, Y_K^L(\boldsymbol{\Omega})$

Predefined potential in EasySpin: `Exp.Ordering = 2;`

$$U(\boldsymbol{\Omega}) = -k_\mathrm{B}T\,\lambda' \frac{3\cos^2\theta - 1}{2}$$

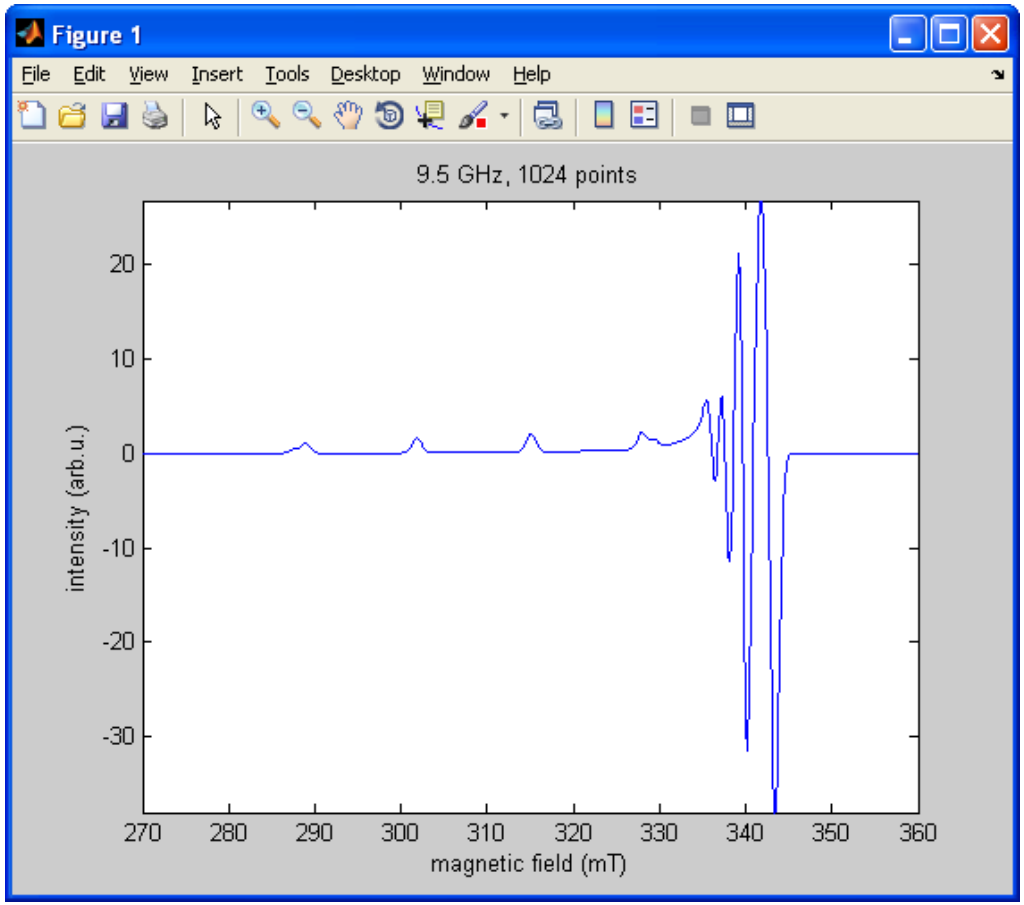
Custom potential in EasySpin: `Exp.Ordering = @(ph,th) cos(3*th).^2;`





cw EPR: a simple example

```
SysCu.g = [2 2.2];
SysCu.lwpp = 1;
SysCu.Nucs = 'Cu';
SysCu.A = [50 400];

ExpX.mwFreq = 9.5;
ExpX.Range = [270 360];

pepper(SysCu,ExpX);
```



Field sweeps and frequency sweeps

Field sweep

```
Sys.g = [2.05 2.3];
Sys.Nucs = '63Cu';
Sys.A = [40 300];

Sys.lwpp = 1;   % mT

Exp1.mwFreq = 9.5;          % GHz
Exp1.Range = [250 360];     % mT

pepper(Sys,Exp1);
```

Frequency sweep

```
Sys.g = [2.05 2.3];
Sys.Nucs = '63Cu';
Sys.A = [40 300];

Sys.lwpp = 1;   % MHz

Exp2.Field = 350;       % mT
Exp2.mwRange = [7 10];% GHz

pepper(Sys,Exp2);
```

- Field sweep: use **`Exp.mwFreq`** and **`Exp.Range`**
- Frequency sweep: use **`Exp.Field`** and **`Exp.mwRange`**
- If **`Exp.Range`** is omitted, EasySpin automatically determines range
- Units for **`Sys.lw`** and **`Sys.lwpp`** different for field and frequency sweeps
- Works equally for pepper, chili, garlic and all theory levels
- Field sweep gives first-harmonic, frequency sweep absorption spectrum

Matrix diagonalization vs. perturbation theory

Matrix diagonalization

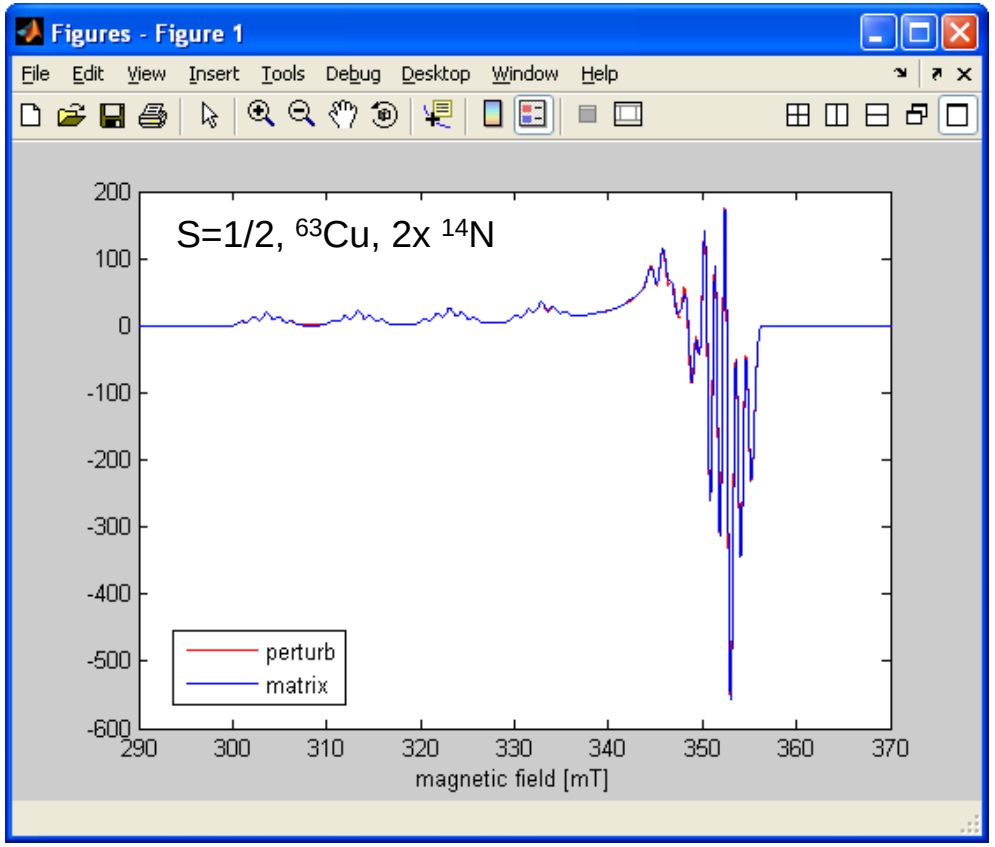
+ arbitrary number of electron and nuclear spins
+ general spin Hamiltonian
+ all transitions
+ always exact
- slow

always ok!

2nd-order perturbation theory

- for one electron spin only (S=1/2 and S>1/2)
- neglects some Hamiltonian terms
- only allowed transitions
- accurate only for small A and D
+ many nuclei possible
+ fast

use with care!



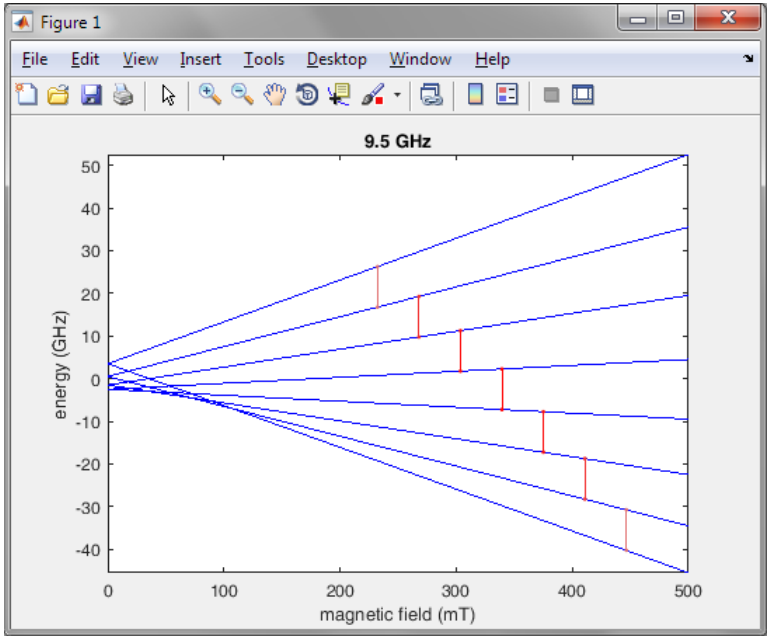

```
Opt.Method = 'matrix'     8.4 s
Opt.Method = 'perturb'    0.08 s
```

Energy level diagrams

Plotting of energy level diagrams:

```
levelsplot(Sys,Ori,Range,mwFreq)
```

`Sys`	spin system
`Ori`	orientation `'x'`, `'y'`, `'z'`, or angles $[\phi, \theta]$
`Range`	field range (mT) [minB0 maxB0]
`mwFreq`	microwave frequency (GHz) optional



(color indicated allowed/forbidden)

Calculation of energy level diagrams without plotting:

```
E = levels(Sys,Ori,Range,mwFreq)
```

Slow-motion regime simulations

EasySpin implements Freed's SLE solver

Rotational dynamics

Rotational correlation time

```
Sys.tcorr = 1e-9;
```
isotropic

```
Sys.tcorr = [1 2 10]*1e-9;
```
anisotropic (axial or rhombic)

Rotational diffusion tensor

```
Sys.Diff = 1e-9;
```
isotropic

```
Sys.Diff = [1 2 2]*1e-9;
```
anisotropic (axial or rhombic)

Partial ordering

Ordering potential

```
Sys.lambda = [3 1 0 0 0];
```
potential coefficients

Powders vs. single orientation

Powder spectrum (MOMD) by default
Single-orientation spectrum: use `Exp.CrystalOrientation`

Slow-motion regime simulations

Orientational basis set Wigner functions $D^{L}_{K,M}(\phi,\theta,\chi)$

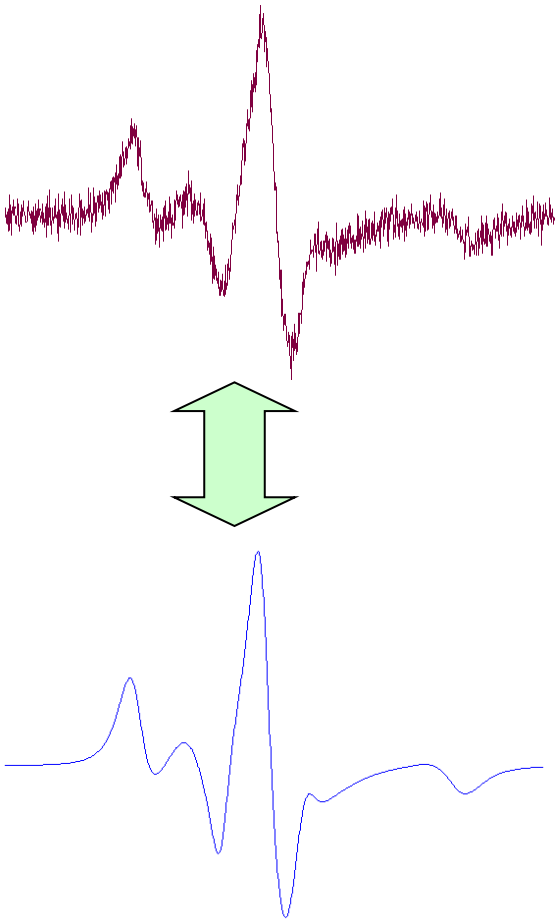
Maximum values for even L, odd L, K and M:

```
Opt.LLKM = [12 0 6 6];
```

The slower the motion and the more anisotropic the spectrum, the larger these values have to be to produce artifact-free spectra.

Least-squares fitting: Overview

experimental spectrum y_{exp}



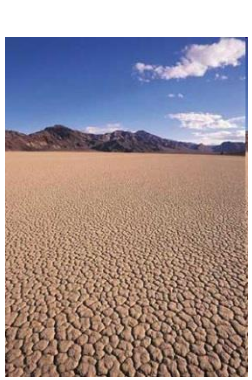
model simulation, y_{sim}

Residuals	$r_i = f(y_{i,\mathrm{exp}}) - f(y_{i,\mathrm{sim}}(\boldsymbol{p}))$
Sum of squares	$\chi^2 \propto \sum_{i=1}^{n} r_i^2$
rmsd	$\varepsilon = \sqrt{\chi^2 / N}$

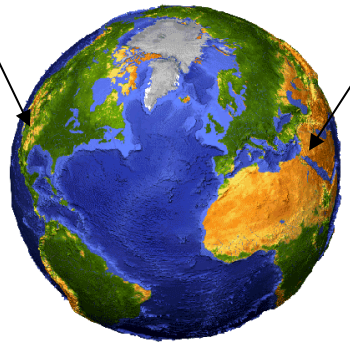
The global minimum is very difficult to locate!

a local minimum

the global minimum



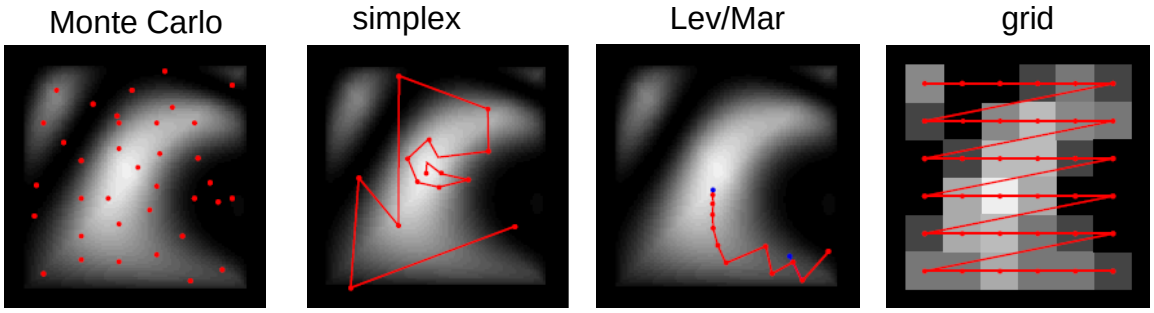
Death Valley



Dead Sea shore

Least-squares fitting: Methods

EasySpin does not use analytical derivatives



Global methods
(search all over the place)
- Monte Carlo
- genetic algorithms
- simulated annealing
- tree and grid searches

Local methods
(downhill into valley from a starting point)
- Nelder-Mead simplex
- Levenberg-Marquardt
- NL2SOL, NL2SNO
- Powell

Hybrid methods
1) global method to locate promising region(s)
2) local method to zero in on minimum

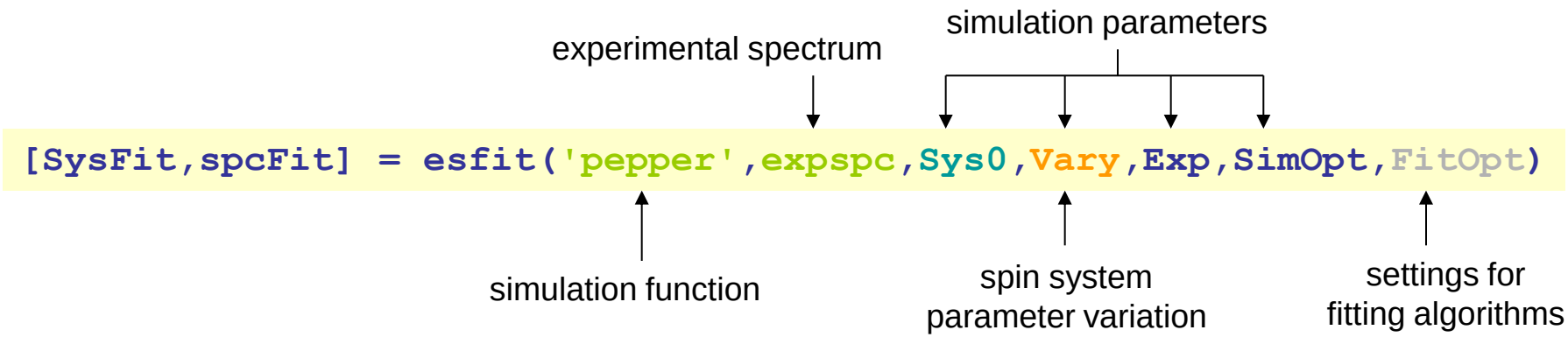
Available in EasySpin:
global methods:
- grid search
- genetic algiorithm
- Monte Carlo

local methods:
- Levenberg-Marquardt
- Nelder-Mead simplex

hybrid methods

Least-squares fitting: esfit

One interface for all simulation functions.



(1) Central values of parameters

```
Sys0.g = [2.008 2.006 2.003];
Sys0.Nucs = '14N';
Sys0.A = [16 16 86];
Sys0.logtcorr = -8.5;
```

(2) Allowed variation of parameters

one parameter, for 1D search

```
Vary.logtcorr = 1;
```

two parameters, for 2D search

```
Vary.logtcorr = 0.2;
Vary.g = [0, 0, 0.0005];
```

No limit on number of parameters, but the more parameters the slower the fitting.

Least-squares fitting: Multiple components

One component

one spin system

```
... = esfit('pepper',expspc,SysA,VaryA,,Exp,...)
```

one spin system
parameter variation

Two components

two spin systems

```
... = esfit('pepper',expspc,{SysA,SysB},{VaryA,VaryB},Exp,...)
```

two spin system
parameter variations

Weights in SysA.weight, SysB.weight, VaryA.weight, VaryB.weight.

Least-squares fitting: Settings

Choosing the algorithm:

`FitOpt.Method`

`'simplex'` = Nelder/Mead simplex (default)
`'levmar'` = Levenberg/Marquardt
`'montecarlo'` = Monte Carlo
`'genetic'` = genetic algorithm + simplex
`'grid'` = grid search + simplex

`'fcn'` = use spectrum
`'int'` = use integral

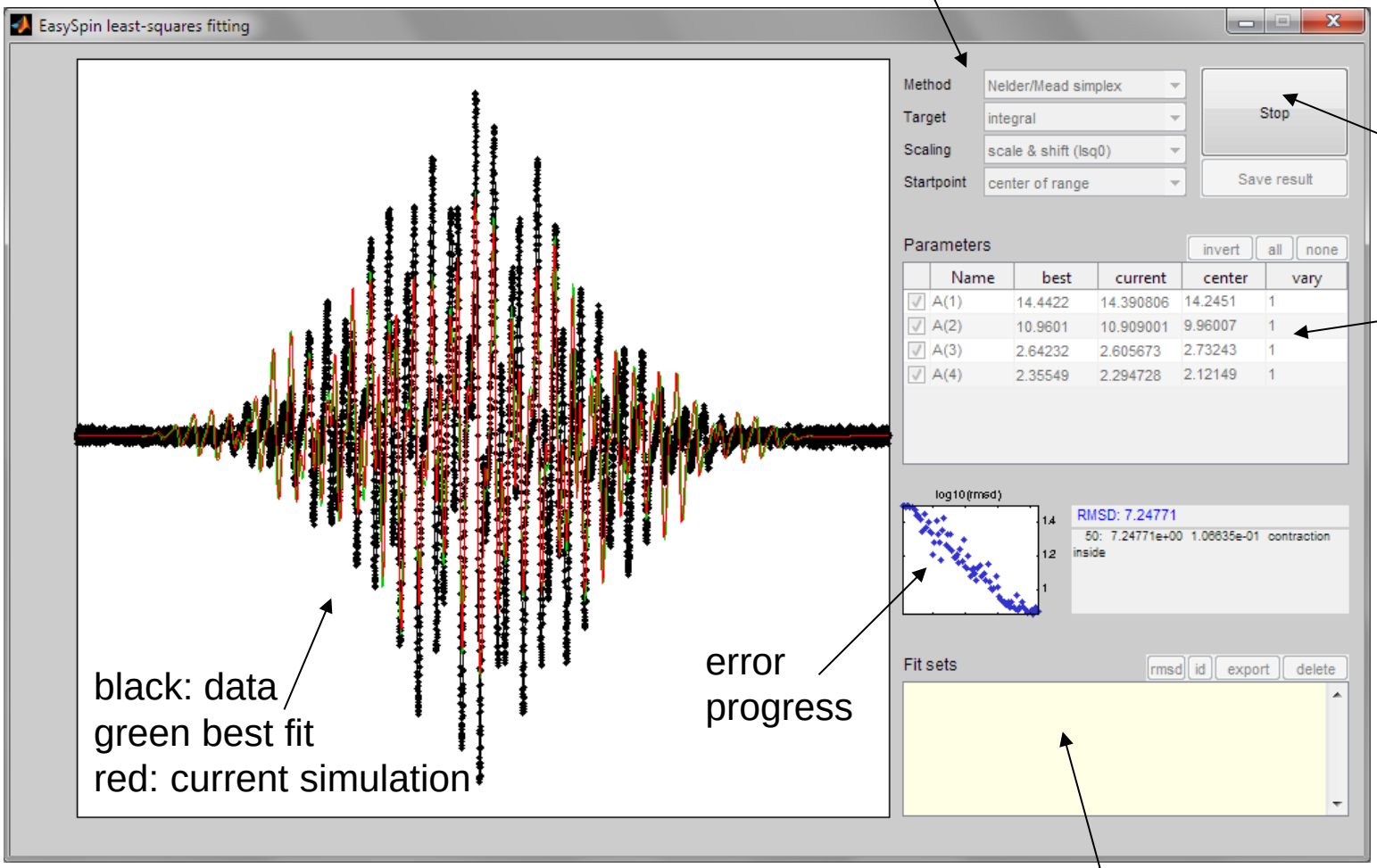
Example: `FitOpt.Method = 'simplex int'`

Knowing when to stop:

`FitOpt.TolFun`	termination tolerance for chi-squared
`FitOpt.TolX`	termination tolerance for parameter step
`FitOpt.maxTime`	maximum runtime

each algorithm has different additional parameters

Least-squares fitting: GUI



Least-squares fitting: Quality of fit

Quality of fit: How deep is the minimum?

indicators:
- maximum/mean/standard deviation of residuals
- residual index *R*
- correlation coefficient of experimental and simulated spectrum
- eye + expertise

compare to noise level σ:
- max/mean residual < σ
  accurate fit, only random errors in experimental data
- max/mean residual >> σ
  inaccurate fit, systematic errors in simulated spectrum
  no convergence or wrong model

Error of parameters: How steep are the the walls?

sensitivity of chi-square to change of parameter values

Least-squares fitting: Best practices

Before you start fitting

- Baseline correct the spectrum; smooth the spectrum if too noisy.
- Choose a physically reasonable model (number of spins, tensors, etc).
- Keep the number of fitting parameters as small as possible.
- Find good starting parameters by (1) analyzing your spectrum thoroughly, (2) studying literature of similar systems, and (3) using theoretical estimates.
- Narrow down the parameter ranges as much as possible.

EasySpin (or any other program) cannot find the minimum

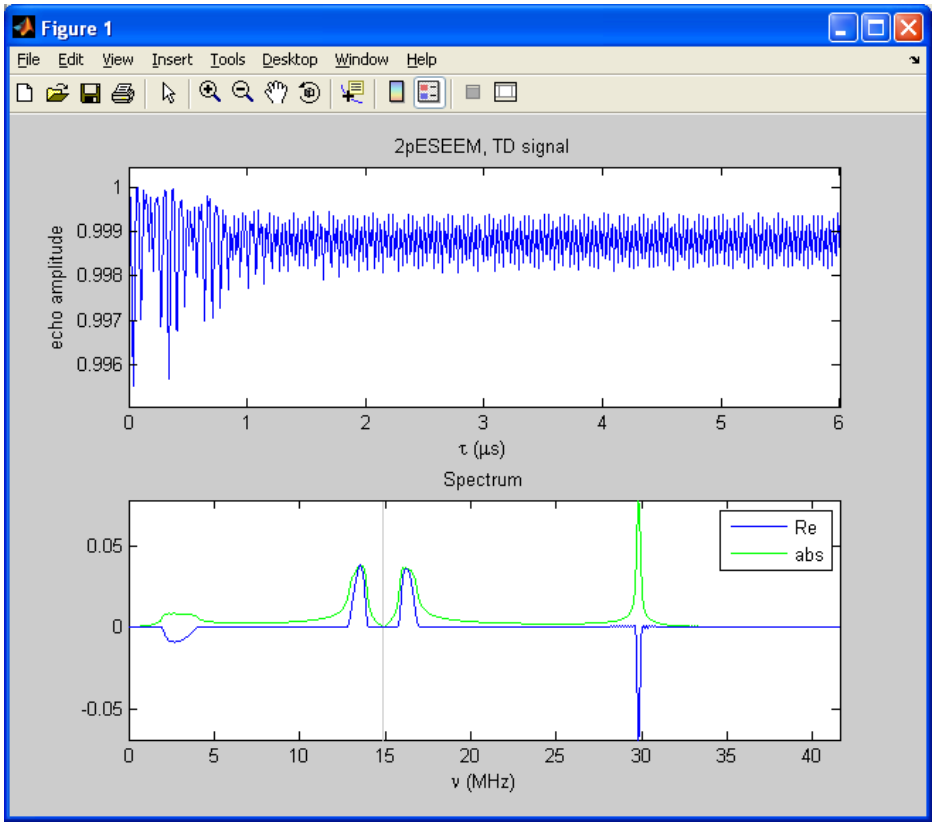
- if you are too far off initially.
- if the parameter ranges are too large or too small.
- if there are too many parameters.
- if the model is wrong.
- if there is too much noise or a non-flat baseline in the spectrum.

After convergence

- Estimate the goodness-of-fit at the global minimum. It might still be bad.
- Look how sensitive the goodness-of-fit is to changes in parameters.
- Even the best minimum you find might be physically incorrect.
- The global minimum might not be the real minimum due to noise effects.

Pulse EPR: A first example

```
clear

Sys.Nucs = '1H';
Sys.A = [2 4];

Exp.Field = 350;

Exp.Sequence = '2pESEEM';
Exp.tau = 0.0001;
Exp.dt = 0.012;
Exp.nPoints = 501;

saffron(Sys,Exp);
```



Pulse EPR: Overview

Simulation function: `saffron`

Pre-defined pulse sequence

```
Exp.Sequence = '2pESEEM';
Exp.Sequence = '3pESEEM';
Exp.Sequence = '4pESEEM';
Exp.Sequence = 'HYSCORE';
Exp.Sequence = 'MimsENDOR';
```

Timings

```
Exp.tau = 0.120;
Exp.dt = 0.008;
```

Units: μs

Echo-detected field sweep?
Simulate cw EPR spectrum with `pepper`, using `Exp.Harmonic = 0`.

What it supports

- hard and soft pulses
- several nuclear spins
- high electron spin
- user-defined pulse sequences
- orientation selection built-in
- data processing built-in

Pulse EPR: Basic experimental settings

Magnetic field (in mT)

```
Exp.Field = 350;
```

Number of points

```
Exp.nPoints = 201;          1D and 2D
Exp.nPoints = [64 201];     2D
```

If not given, EasySpin uses default values.

Dwell time (in µs)

```
Exp.dt = 0.008;             1D and 2D
Exp.dt = [0.008 0.012];     2D
```

This has to be given for ESEEM experiments.

Frequency range (in MHz)

```
Exp.Range = [0 30];
```

This has to be given for ENDOR experiments.

Spectrometer frequency (in GHz)

```
Exp.mwFreq = 9.5;
```

Only needed for orientation selection.

Excitation bandwidth (in MHz)

```
Exp.ExciteWidth = 100;
```

Only needed for orientation selection.

Pulse experiment

```
Exp.Sequence
```

for pre-defined pulse experiments

```
Exp.Flip, Exp.Inc, Exp.t, Exp.tp
```

for user-defined pulse experiments

Pulse EPR: Pre-defined sequences

Two-pulse ESEEM

```
Exp.Sequence = '2pESEEM';
Exp.tau = 0.080;
```

Three-pulse ESEEM

```
Exp.Sequence = '3pESEEM';
Exp.tau = 0.100;
Exp.T = 0.080;
```

HYSCORE

```
Exp.Sequence = 'HYSCORE';
Exp.tau = 0.172;
Exp.t1 = 0.08;
Exp.t2 = 0.08;
```

Mims ENDOR

```
Exp.Sequence = 'MimsENDOR';
Exp.tau = 0.100;
Exp.Range = [0 30];
```

all times and delays in microseconds

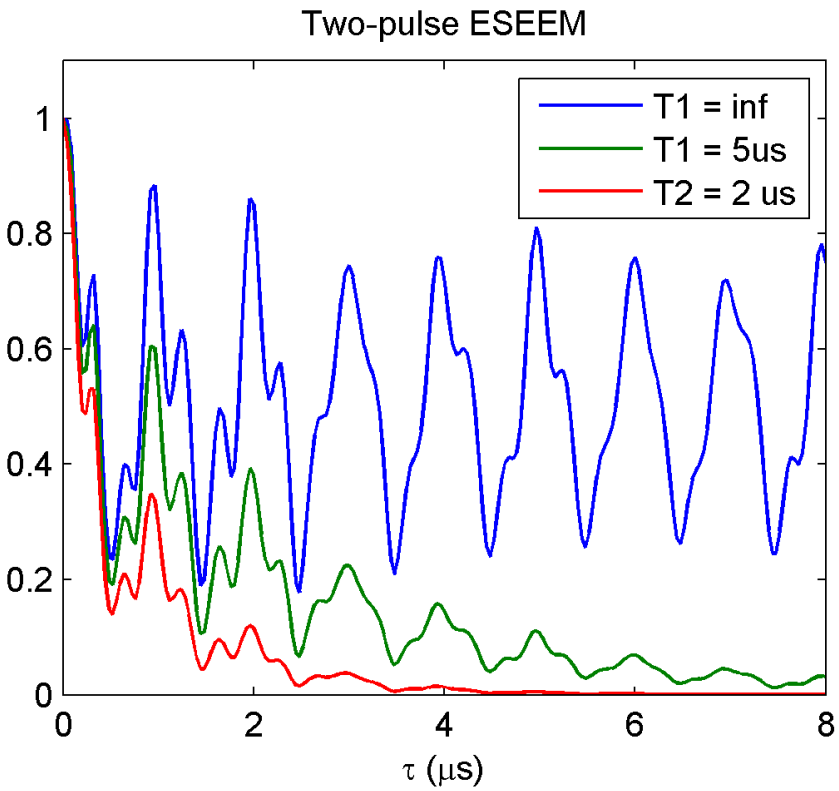
Pulse EPR: T_1 and T_2 relaxation

Relaxation time constants (time for fall-off to 36.8%)

```
Sys.T1T2 = [10 2];
```

first element: T_1

second element: T_2



Pulse EPR, ENDOR: Orientation selection

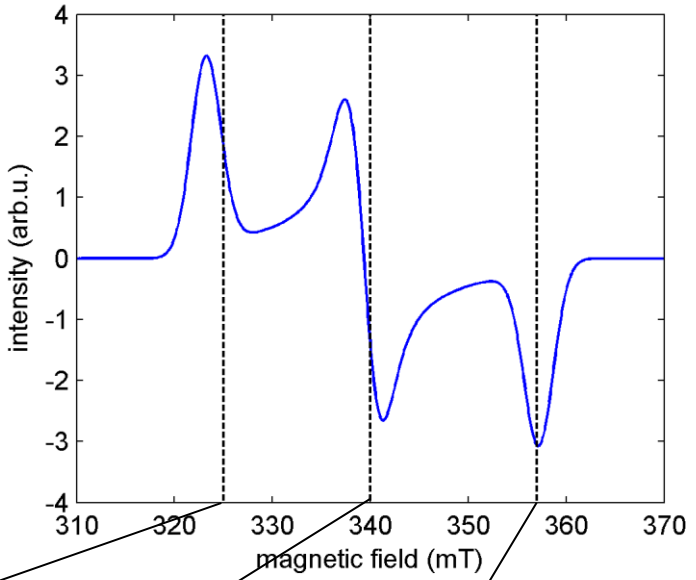
Orientation/transition selection

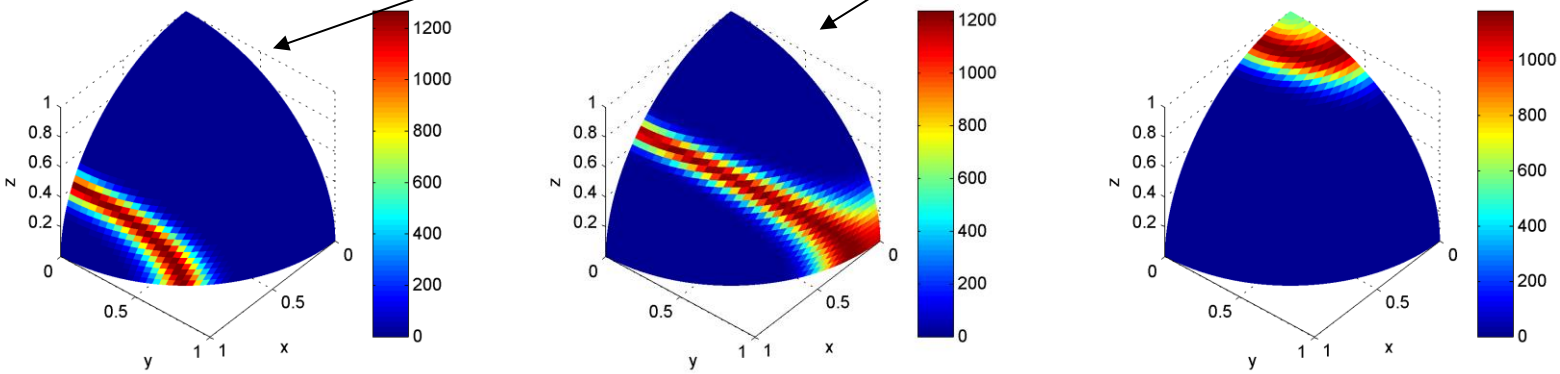
1. large anisotropies, wide EPR spectrum
2. limited excitation bandwidth of mw pulses

Parameters necessary

```
Exp.ExciteWidth = 100;
```
(Gaussian FWHM, in MHz)

```
Exp.mwFreq = 9.5;
```
(has to be given, in GHz)





Pulse EPR: S > 1/2

Set electron spin

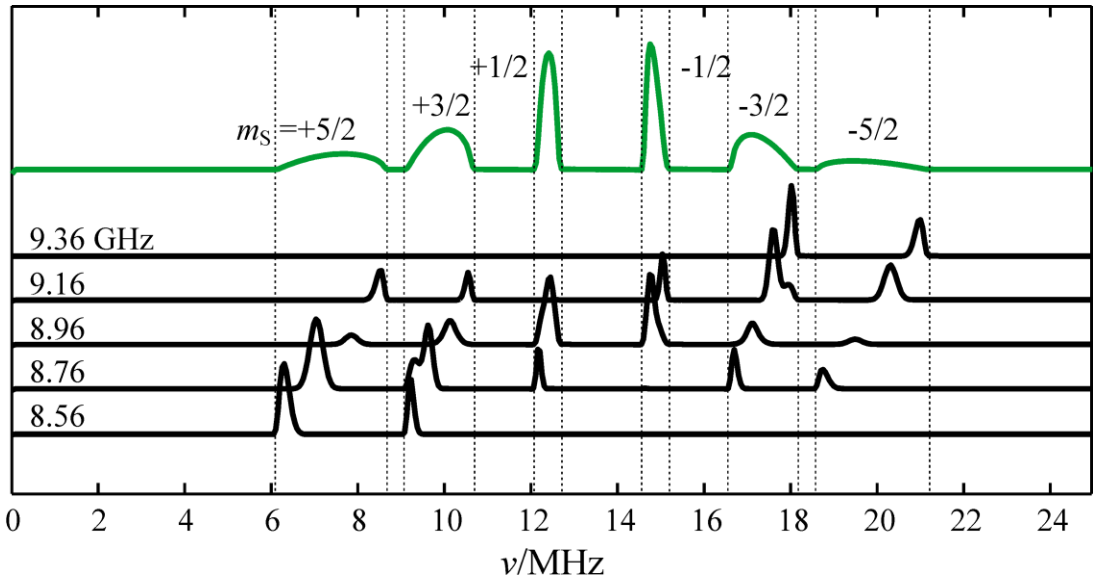
```
Sys.S = 1;
Sys.S = 5/2;
Sys.S = 7/2;
```

Set zero-field interaction

```
Sys.D = -200;
Sys.D = [-130 -80 210];
```

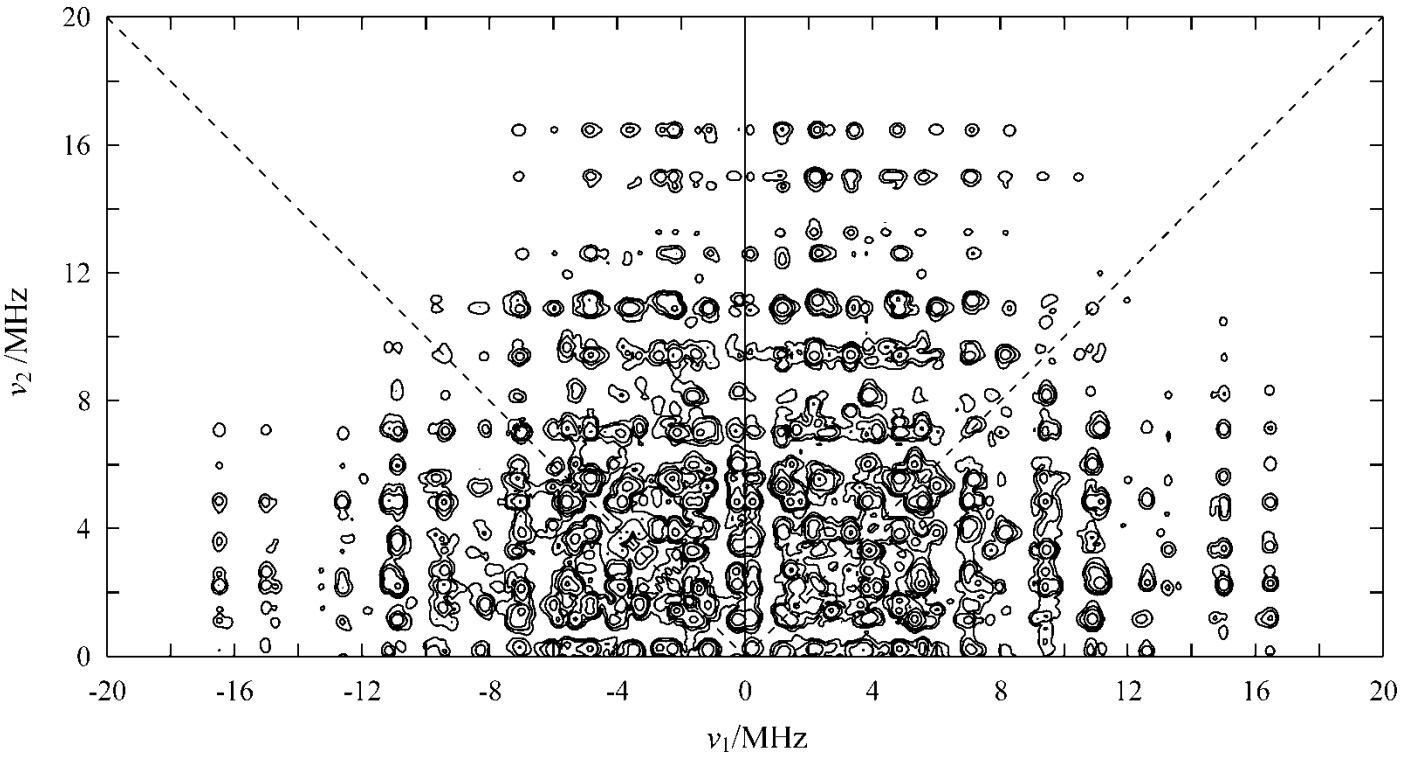
What to remember

- flip angles are different for different transitions
- optimized echo amplitude might not correspond to 90° flips for any transition
- often strong orientation selection
- nuclear frequencies strongly depend on m_S



Pulse EPR: S > 1/2, many nuclei

$Mn(II)(Im)_6$ S = 5/2, I = 5/2, and six I = 1 (26244 spin states)



simulated single-crystal HYSCORE, ideal pulses (6 seconds)

Pulse EPR: User-defined pulse experiments

Fields needed for a user-defined experiment

`Exp.Flip`	pulse flip angle in multiples of 90°
`Exp.Inc`	incrementation scheme (0 = const., 1 = first dim., 2 = second dim.)
`Exp.t`	initial delays, in microseconds

Example: Two-pulse ESEEM

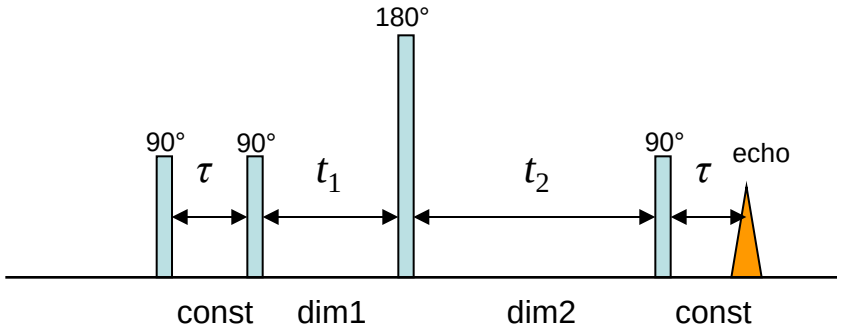
```
Exp.Flip = [1 2];
Exp.Inc  = [1 1];
Exp.t    = [0 0];
```

Example: 2D three-pulse ESEEM

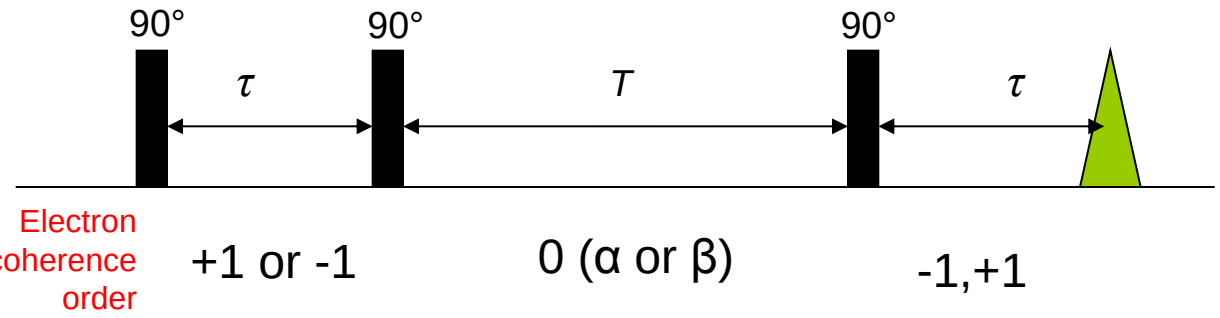
```
Exp.Flip = [1 1 1];
Exp.Inc  = [1 2 1];
Exp.t    = [0.112 0 0.112];
```

Example: HYSCORE

```
Exp.Flip = [1 1 2 1];
Exp.Inc  = [0 1 2 0];
Exp.t    = [0.1 0 0 0.1];
```



Pulse EPR: Transfer pathways and filters



Echo pathways:

(+α-), (+β-)
(-α+), (-β+)

Pathways with detectable echo
- equal times in + and in –
- ending in –

Examples:

two-pulse ESEEM	(+-)
three-pulse ESEEM	(+α-), (+β-)
HYSCORE	(+αβ-), (+βα-)
DONUT-HYSCORE	(+αβα-), (+βαβ-)
refocused primary	(-+-)

Pathway filter in EasySpin:
three-pulse ESEEM:Exp.Filter = '.a.'
five-pulse ESEEM: Exp.Filter = '+....';

Pathway filter in EasySpin:

`Exp.Filter` one character per delay

`'+'`	+1
`'-'`	-1
`'a'`	0 (α)
`'b'`	0 (β)
`'.'`	anything
`'0'`	0 (α or β)
`'1'`	+ or -

```
Exp.Filter = '.a.'
Exp.Filter = '+....';
```

Pulse EPR: Soft (real, non-ideal) pulses

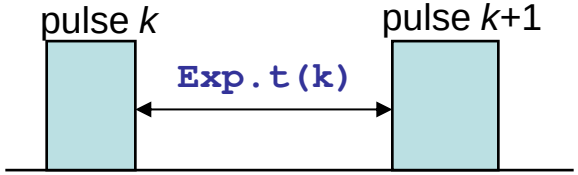
Soft pulses in user-defined sequences

`Exp.tp` length of pulses

Units: µs

Example: HYSCORE

```
Exp.Flip = [1 1 2 1];
Exp.Inc = [0 1 2 0];
Exp.t = [100 0 0 100]*1e-3;
Exp.tp = [10 10 20 10]*1e-3;
```



Delay values in `Exp.t`: between end of one pulse and beginning of next

Soft pulses: Offset integration needed

`Opt.lwOffset` width of offset distribution, in MHz
(about 1/tp of first pulse; typically 100 MHz)

`Opt.nOffsets` number of integration points (typically 10-30)

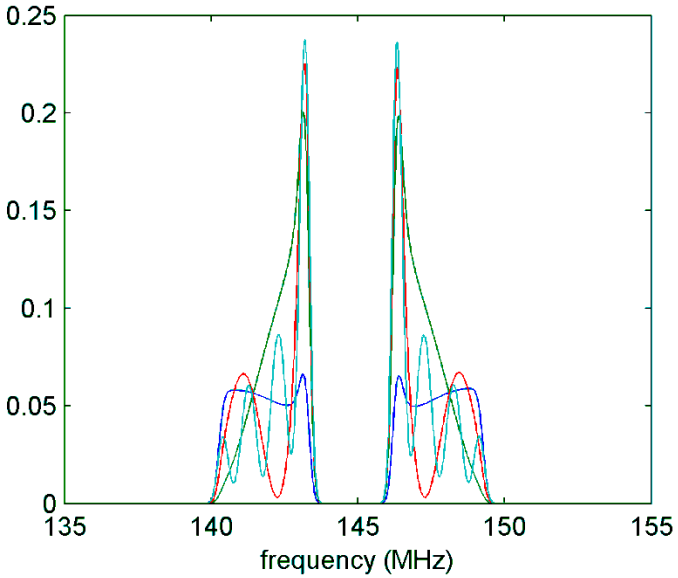
Soft pulses are not possible with pre-defined sequences!

Pulse EPR: ENDOR

Specifying ENDOR

```
Exp.Sequence = 'MimsENDOR';
Exp.Range = [135 155];
Exp.tau = 0.100;
```

frequency range (in MHz)



What to think about

- `saffron` does not (yet) take hyperfine enhancement into account (in contrast to `salt`)
- ENDOR spectrum is simulated as sum over nuclei

ENDOR linewidth (in MHz) stick spectrum is convoluted with lineshape

```
Sys.lwEndor = 0.1;
```
Gaussian FWHM

```
Sys.lwEndor = [0.1 0.2];
```
[Gaussian FWHM, Lorentzian FWHM]

Pulse EPR: Some options

Product rule

```
Opt.ProductRule = 0;
```
product rule off (default)

```
Opt.ProductRule = 1;
```
product rule on, faster for 3+ nuclei

HYSCORE log plot

```
Opt.logplot = 0;
```
linear coloring of intensities (default)

```
Opt.logplot = 1;
```
logarithmic coloring of intensities, gives more detail

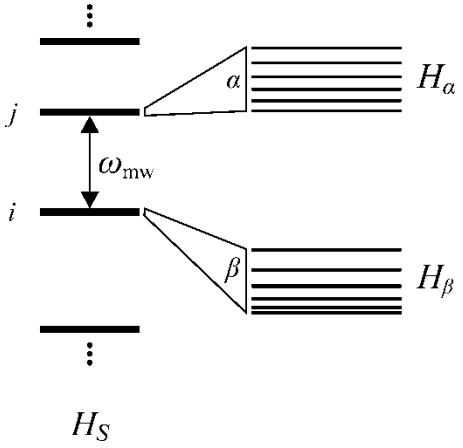
Processing options

```
Opt.Window = 'ham';
```
apodization window, applied before FFT

```
Opt.ZeroFillFactor = 2;
```
factor for zero filling before FFT

Pulse EPR: Theoretical background

1. Hamiltonians
- Set up Hamiltonian H_S for spins other than the ESEEM/ENDOR nuclei
- Compute energy levels and finds EPR transitons resonant with microwave frequency
- For each transition, compute nuclear sub-Hamiltonians for upper (α) and lower (β) manifold
- Compute energies and eigenstates for each nuclear sub-Hamiltonian



2. Pulse sequence
- Analyze the pulse sequence to determine pathways contributing to the echo

3. Peaks
- Use a submatrix formalism to compute the peak amplitudes and frequencies from the nuclear sub-Hamiltonians for each EPR transition and pathway
- Can use product rule to speed up calculations with many nuclei

4. Spectrum
- Construct a high-resolution stick spectrum
- Compute the time domain signal by inverse Fourier transform

For a powder, run this for a set of orientations.

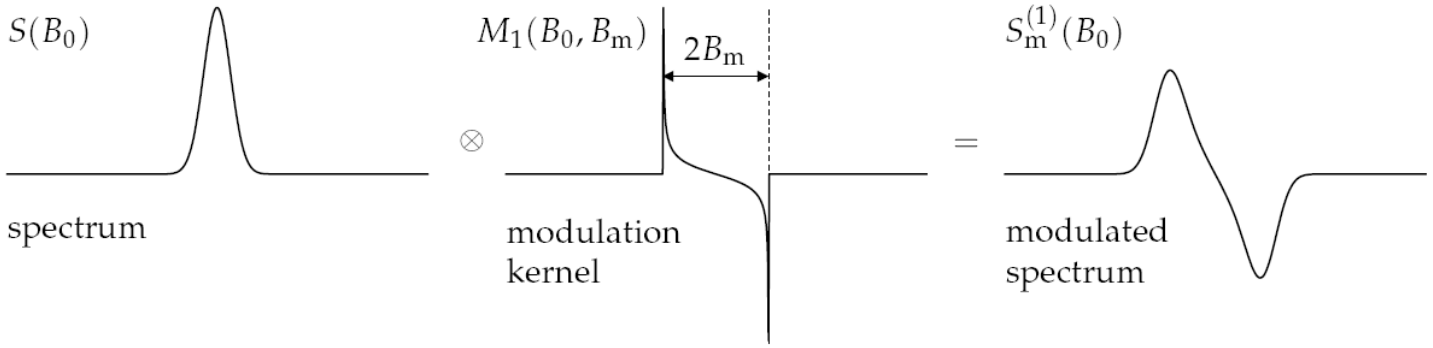
Rotations, orientations and vectors

EasySpin functions for dealing with angles, orientations and rotations

`degree`	for angle unit conversion, `pi = 180*degree`
`vec2ang`	convert vector(s) to polar angles
`ang2vec`	convert polar angles to vector(s)
`erot`	computer rotation matrix from Euler angles
`eulang`	computer Euler angles from rotation matrix
`rotaxi2mat`	convert rotation axis plus angle to rotation matrix
`rotmat2axi`	convert rotation matrix to rotation axis plus angle
`rotplane`	generate vectors in a plane
`sphgrid`	generate uniformly distributed orientations
`sphrand`	generate randomly distributed orientations

Field modulation

Convolution of absorption spectrum with modulation kernel



Built into simulation functions

```
Exp.ModAmp = 0.5;     % 5 G pp modulation amplitude
[B,spc] = pepper(Sys,Exp);
```

Separate modulation function

```
spcmod = fieldmod(B,spc,ppAmpl);
```

Fundamental constants

2010 CODATA recommended values in S.I. units

gfree	g value of the free electron *latest value (2010):* 2.00231930436153(53)
bmagn	Bohr magneton
nmagn	Nuclear magneton
planck	Planck constant
hbar	Reduced Planck constant
amu	Atomic unit of mass
avogadro	Avogadro constant
bohrrad	Bohr radius
boltzm	Boltzmann constant
clight	Vacuum speed of light
echarge	Elementary electric charge
emass	Mass of electron
eps0	Electric constant
faraday	Faraday constant
hartree	Atomic unit of energy
molgas	Molar gas constant
mu0	Magnetic constant
nmass	Mass of neutron
pmass	Mass of proton
rydberg	Rydberg constant
angstrom	Molecular-scale length unit
barn	Conventional unit of nuclear quadupole moments
evolt	Electron volt

Units and conversions

Units used in EasySpin:

mT	for all magnetic fields
mT	for convolutional line widths
GHz	for EPR spectrometer frequencies (microwave)
MHz	for all other frequencies (ENDOR)
MHz	for energy levels, nuclear frequencies, etc
MHz	for hyperfine and quadrupole tensors
MHz	for zero-field tensors etc
s	for correlation times
1/s	for diffusion tensors
Hz	for Heisenberg exchange frequency
rad	for angles (a full turn is 2π)

1 mT → 10 G

1 mT → 28.0 MHz (g = 2)
1 mT → 14.0 MHz x g

1 mT → 42.6 MHz (^{1}H)
1 mT → 6.54 MHz (^{2}H)
1 mT → 10.7 MHz (^{13}C)
1 mT → 3.08 MHz (^{14}N)
1 mT → 4.32 MHz (^{15}N)

10^{-4} cm^{-1} → 3.00 MHz

Conversion functions: **`mt2mhz`**, **`mhz2mt`**, **`larmorfrq`**, **`degree`**

Spin operators

all spin operators are in units of $\hbar$

`sop`	cartesian and ladder operators
`stev`	higher-order operators

```
sop(1/2,'x')
```

```
    0    0.5
  0.5      0
```

```
sop([1/2 1/2],'z+')
```

```
  0  0.5    0      0
  0    0    0      0
  0    0    0   -0.5
  0    0    0      0
```

```
[Sx,Sy,Sz] = sop(1,'x','y','z')
```

```
Sx =
       0  0.7071         0
  0.7071         0  0.7071
       0  0.7071         0
Sy =
  0             0 - 0.7071i   0
  0 + 0.7071i   0             0 - 0.7071i
  0             0 + 0.7071i   0
Sz =
  1     0     0
  0     0     0
  0     0    -1
```

Angular momentum

EasySpin includes basic support for general angular momenta computations

`clebschgordan`	Clebsch-Gordan coefficients	$\langle j_1 j_2 m_1 m_2 \vert j_1 j_2 j m\rangle$
`wigner3j`	Wigner 3-*j* symbols	$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$
`wigner6j`	Wigner 6-*j* symbols	$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix}$
`cgmatrix`	Matrix for transformation between coupled and uncoupled representations	

`plegendre`	Associated Legendre polynomials	$P_l^m(x)$
`spherharm`	Spherical harmonics	$Y_l^m(\theta,\phi)$

Line shapes

Gaussian

```
y = gaussian(B,B0,FWHM,Derivative)
```

Lorentzian

```
y = lorentzian(B,B0,FWHM,Derivative)
```

Voigtian (= convolution of Gaussian and Lorentzian)

```
y = voigtian(B,B0,[FWHM_Gau FWHM_Lor],Derivative)
```

Pseudo-Voigtian (= weighted sum of Gaussian and Lorentzian)

```
y = lshape(B,B0,FWHM,Derivative,weightGau)
```

Common EasySpin mistakes

1. **Left-over fields in spin system or experiment structure**

```
Sys = nucspinadd(Sys,'14N',...);
```

➡ Start every simulation with **`clear`**.

2. **Wrong capitalization**

```
Sys.g = [2.3 2]; pepper(sys,Exp);
```

➡ Make sure capitalization is what Matlab and EasySpin expect.

3. **Options not included in simulation function call**

```
Opt.Method = 'perturb';
pepper(Sys,Exp);
```

➡ Whenever you add options, immediately add **`Opt`** to the function call.

4. **Using incorrect units**
5. **Using the wrong simulation function**
6. **Frames**
7. **Fitting: Parameter values and ranges**

EasySpin references

S. Stoll, A. Schweiger
EasySpin, a comprehensive software package for spectral simulation and analysis in EPR
J. Magn. Reson. 178, 42-55 (**2006**), http://dx.doi.org/10.1016/j.jmr.2005.08.013
The principal publication. Please cite if you publish results obtained with the help of EasySpin.
A PDF version is included in every EasySpin installation.

S. Stoll
CW-EPR Spectral Simulations: Solid State
Methods Enzymol., in press, **2015**
An overview of the key decision and choices to be made by a practicioner when simulating EPR spectra.

S. Stoll
Computational Modeling and Least-Squares Fitting of EPR Spectra
in S. Misra, ed.
Handbook of Multifrequency Electron Paramagnetic Resonance, Wiley-VCH, **2014**
A comprehensive review of the underlying theory with over 500 references.

S. Stoll, R. D. Britt
General and efficient simulation of pulse EPR spectra
Phys. Chem. Chem. Phys.11, 6614-6635 (**2009**), http://dx.doi.org/10.1039/b907277b
Contains background to EasySpin's pulse EPR capabilities.

S. Stoll, A. Schweiger
Easyspin: simulating cw ESR spectra,
Biol. Magn. Reson. 27, 299-321 (**2007**)
An overview of EasySpin with special focus on the simulation of nitroxide spectra.

S. Stoll, A. Schweiger
An adaptive method for computing resonance fields for continuous-wave EPR spectra
Chem. Phys. Lett. 380, 464-470 (**2003**), http://dx.doi.org/10.1016/j.cplett.2003.09.043

S. Stoll
Spectral Simulations in Solid-State Electron Paramagnetic Resonance
PhD thesis, ETH Zurich, **2003,** http://e-collection.ethbib.ethz.ch/show?type=diss&nr=15059

S. Stoll
EasySpin: a Software Package for the Computation of EPR and ENDOR spectra
EPR Newsletter 13(1-2), 24-26 (**2003**)