EPR with EasySpin

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

This slidedeck is based on EasySpin 6.0.0-dev*.
Some features might change in the final EasySpin 6.0.0.

This slidedeck only shows the basic features of EasySpin.
For a complete overview, see the online documentation.

EasySpin functions are underlined.

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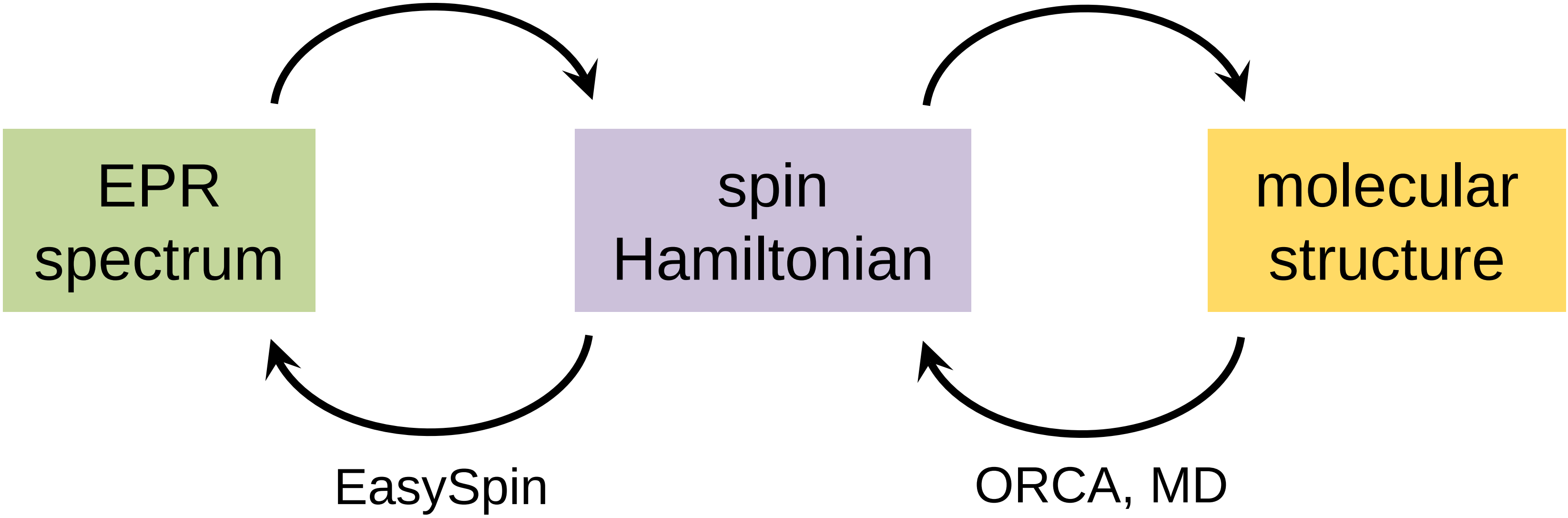
What is EasySpin?

Software for EPR spectroscopy

1. explore fundamentals
2. plan experiments (simulations)
3. analyze data (fitting)



EPR spectrum

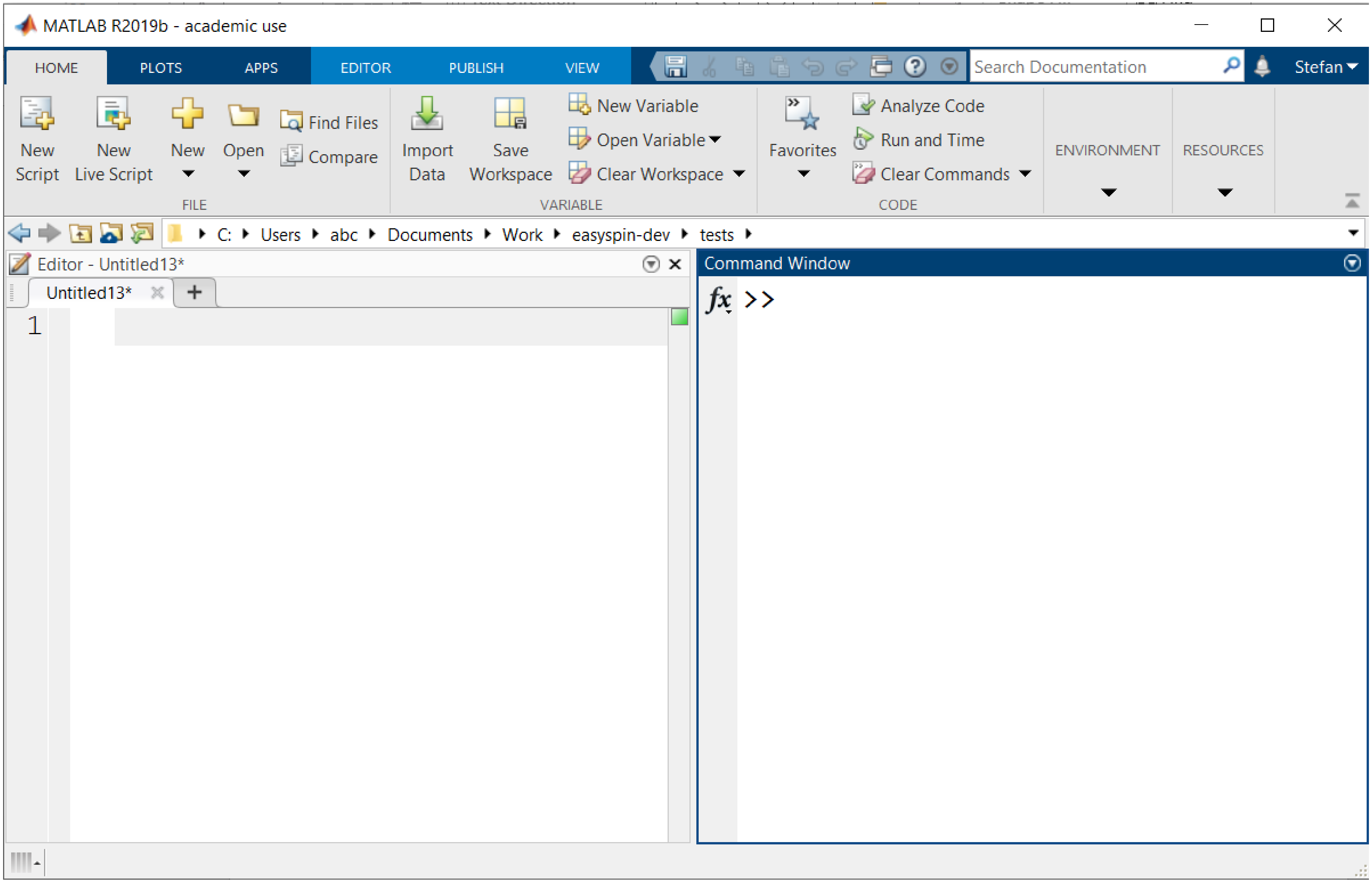
spin Hamiltonian

molecular structure

EasySpin

ORCA, MD

EasySpin runs on MATLAB



Spin operators, spin states

Vectors representing spin states (Zeeman basis)

```
a = [1; 0]                        % α (spin-up) state for spin-1/2
b = [0; 1]                        % β (spin-down) state for spin-1/2
ab = kron([1;0],[0;1])            % αβ state for S1=S2=1/2 system
c = [1;1]/sqrt(2)                 % superposition state for spin-1/2 (+x)
v = [0;1;0]                       % |0> state for S=1
```

Matrices representing spin operators

```
Sx = [0 1/2; 1/2 0]               % Sx operator for spin-1/2
Sx = sop(1/2,'x')                 % same using EasySpin
Sp = sop(1/2,'+')                 % S+ operator for spin-1/2
[Sx,Sy,Sz] = sop(1,'x','y','z')   % Sx,Sy,Sz for spin-1
SxIp = sop([1/2 1],'x+')          % SxI+ for S=1/2 I=1 system
```

Matrices representing spin states (density matrices)

```
sigma = a*a'                     % density matrix corresponding to α state
sigma = [0 1; 0 0]               % density = S+
sigma = sop(1/2,'+')             % same using EasySpin
sigma = c*c'                     % superposition state
```

Spin Hamiltonians

Electron Zeeman term

```
B = [0; 0; 0.35];                                % field vector, T
[Sx,Sy,Sz] = sop([1/2 1/2],'xe','ye','ze');      % spin matrices
Hzee = bmagn*2*(B(1)*Sx+B(2)*Sy+B(3)*Sz);        % Zeeman Hamiltonian, J
Hzee = Hzee/planck/1e6                           % same, MHz
```

Isotropic hyperfine term

```
A = 100;                         % hyperfine coupling constant, MHz
[SxIx,SyIy,SzIz] = sop([1/2 1/2],'xx','yy','zz'); % spin operator matrices
Hhf = A*(SxIx+SyIy+SzIz)         % hyperfine Hamiltonian, MHz
H = Hzee + Hhf                   % sum, MHz
```

Using EasySpin

```
Sys.S = 1/2;                   % define spin quantum number
Sys.g = 2;                     % define g tensor via its principal values
Sys.Nucs = '1H';               % add proton
Sys.A = 100;                   % isotropic hyperfine, MHz
H = sham(Sys,B*1000)           % complete spin Hamiltonian matrix, MHz
```

Eigenvalues, eigenstates, energy level diagram

Eigenvalues and eigenvectors

```
E = eig(H)                       % gives list of eigenvalues
[V,E] = eig(H)                   % eigenvectors and eigenvalues
```

Energy level diagram (by hand)

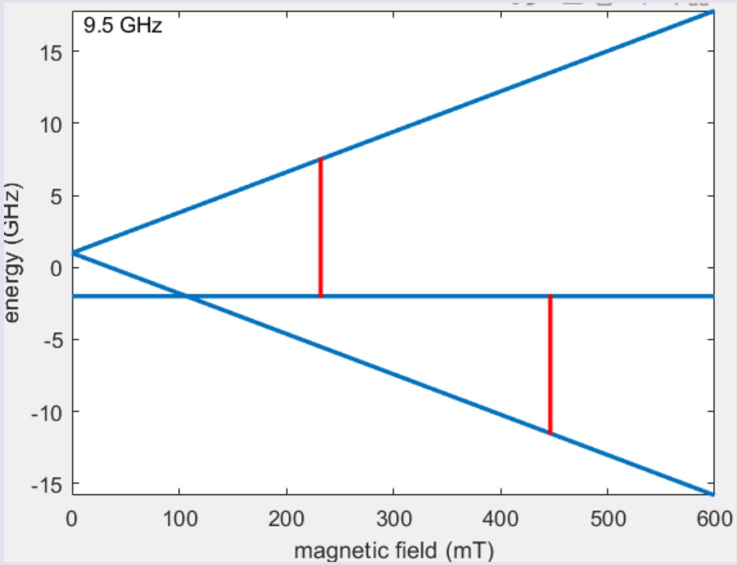
```
Sys.S = 1;
Sys.D = 3000;                    % MHz
[H0,G] = sham(Sys,[0;0;1]);      % H0 in MHz, G in MHz/mT

B = linspace(0,500);             % mT
for k = 1:numel(B)
  H = H0 + B(k)*G;               % assemble Hamiltonian matrix
  E(k,:) = eig(H);               % diagonalize
end
plot(B,E/1e3);                   % plot in GHz
```

Energy level diagram (using EasySpin)

```
levelsplot(Sys,'z',[0 600],9.5);  % range in mT, frequency in GHz
```

Question!

Why is there no transition between the lowest and the highest level?



1. photon is destroyed (absorption) or created (emission)
2. photon has one unit of angular momentum
3. overall angular momentum is conserved

$|\Delta m_s| = 1$ intense absorption (allowed)

$|\Delta m_s| = 2$ weak/no absorption (forbidden / disallowed)

g anisotropy

Simulating a spectrum with isotropic g

```
Sys.S = 1/2;
Sys.g = 2;                % equivalent to [2 2 2]
Sys.lwpp = 2;             % Gaussian peak-to-peak, mT

Exp.mwFreq = 9.5;         % GHz
Exp.Range = [280 380]; % mT

pepper(Sys,Exp);
```

Axial g tensor

```
Sys.g = [2 2.3];          % equivalent to [2 2 2.3]
pepper(Sys,Exp);
```

Rhombic g tensor

```
Sys.g = [2 2.04 2.3];
pepper(Sys,Exp);
```

Question!

Why are g values in paramagnetic molecules shifted from 2.0023?

nitroxides	up to 2.009
copper(II)	up to 2.4
manganese(II)	1.98 (ca)
iron(III) low-spin	1.8 – 2.1
titanium(III)	1.9x

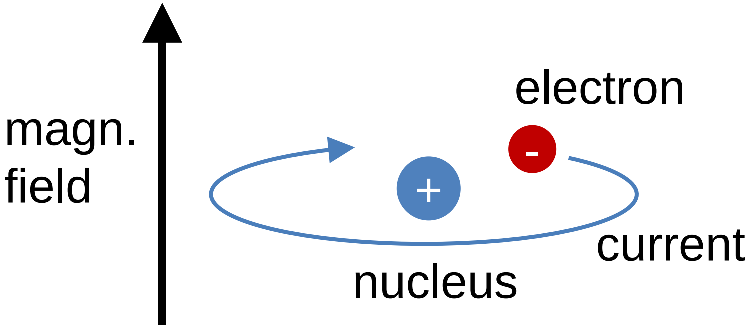
(disregarding effective g values of multiple unpaired electrons)

spin-orbit coupling

1. field induces electron current
2. electron circles around nucleus
3. electron feels field due to nucleus

→ g shift

<50% filled valence shell: g < 2.002
>50% filled valence shell: g > 2.002



Hyperfine coupling

A single isotope: ^{63}Cu

```
Cu.g = [2.05 2.05 2.35];
Cu.Nucs = '63Cu';    % single isotope
Cu.lwpp = 1;         % mT
Cu.A = 130;          % isotropic (unphysical), MHz
Cu.A = [50 300];     % axial, MHz
Cu.A = [50 60 300]; % rhombic, MHz

Exp.mwFreq = 9.5;    % GHz
Exp.Range = [260 350];   % mT
pepper(Cu,Exp);
```

Hyperfine transitions

```
Opt.Output = 'separate';
pepper(Cu,Exp,Opt);
```

Natural abundance: ^{63}Cu and ^{65}Cu

```
Cu.Nucs = 'Cu';            % natural abundance, automatic conversion of hfc
pepper(Cu,Exp);
larmorfrq('63Cu,65Cu',350) % gives Larmor frequency, MHz
```

Line broadenings

Simple anisotropic system

```
Sys.S = 1/2;
Sys.g = [2 2.1 2.2];
Exp.mwFreq = 9.5;         % GHz
Exp.Range = [280 360];    % mT
```

Convolutional broadening

```
Sys.lwpp = 2;           % mT peak-to-peak, Gaussian only
Sys.lwpp = [0 1];       % mT, Lorentzian only
Sys.lwpp = [2 1];       % mT, Gaussian+Lorentzian = Voigtian
pepper(Sys,Exp);
```

Anisotropic broadening (e.g. unresolved hyperfine)

```
Sys.HStrain = [60 120 240];    % MHz, fully rhombic
pepper(Sys,Exp);
```

Question!

What are possible reasons for broadening in EPR spectra?

1. static:
distribution of orientations (powder, frozen solution)
distribution of molecular geometries → distribution of *g*, *A*, etc (strains)
unresolved couplings (hyperfine, electron-electron)

2. dynamic:
librations, rotations, collisions, etc.

3. instrumental:
power broadening, overmodulation, etc.

Line broadenings: g and A strain

g strain

```
Sys.g = [2 2.1 2.2];
Sys.gStrain = [0.03 0.01 0.07]; % Gaussian FWHM

Exp.mwFreq = 95;                % GHz
Exp.CenterSweep = [3250 800];   % mT

pepper(Sys,Exp);
```

g and A strain

```
Cu.g = [2.0 2.25];
Cu.Nucs = '63Cu';
Cu.A = [50 300];         % MHz
Cu.gStrain = 0.01;       % isotropic
Cu.AStrain = 10;         % isotropic, MHz
Cu.gAStrainCorr = +1;    % positive correlation

Exp.Range = [280 350]; % mT
Exp.mwFreq = 9.5;      % GHz
pepper(Cu,Exp);
```

Coupled spins: exchange, Pake patterns

Two coupled spins

```
Two.S = [1/2 1/2];
Two.g = [2; 2.03];
Two.HStrain = 1;                % MHz

Two.J = 0;                      % exchange coupling (+J*S1*S2), MHz

Two.dip = 20;                   % dipolar coupling, MHz
```

Powder spectrum

```
Exp.Field = 350;                % mT
Exp.mwRange = [9.7 10];         % GHz
pepper(Two,Exp);                % frequency sweep
```

Rigid limit, slow-motion regime, fast limit

Nitroxide

```
Nx.g = [2.008 2.006 2.002];
Nx.Nucs = '14N';
Nx.A = [20 20 85];              % MHz
Nx.lwpp = 0.2;                  % mT
```

Different functions for different motional regimes

```
Exp.mwFreq = 9.5;               % GHz
Exp.Range = [334 344];          % mT
pepper(Nx,Exp);                 % rigid limit (matrix diagonalization)

Nx.tcorr = 2e-9;                % rotational correlation time, seconds
chili(Nx,Exp);                  % slow motion (Stoch. Liouville equation)

Nx.tcorr = 0.1e-9;
[B,spcc] = chili(Nx,Exp);         % fast motion (stoch. Liouville eq.)
[B,spcg] = garlic(Nx,Exp);        % fast motion (Redfield theory)
plot(B,spcc,B,spcg);
```

The spices of EasySpin

CW EPR

solid state	`pepper`
liquid state	`chili` (slow-motion, simple Brownian diffusion model) `garlic` (fast-motion) `cardamom` (using molecular dynamics trajectories)

OTHER EXPERIMENTS

ENDOR	`salt`
pulse EPR	`saffron`
magnetometry	`curry`

Nitroxide spectrum, multi-frequency

X-band

```
Nx.g = [2.008 2.006 2.002];
Nx.Nucs = '14N';
Nx.A = [20 20 85];           % MHz
Nx.lwpp = 0.02;              % mT

Exp.mwFreq = 9.5;            % GHz
Exp.CenterSweep = [340 12]; % mT
Exp.Harmonic = 0;
Opt.Output = 'separate';
pepper(Nx,Exp,Opt);
```

Q-band

```
Exp.mwFreq = 35;              % GHz
Exp.CenterSweep = [1248 12]; % mT
pepper(Nx,Exp,Opt);
```

W-band

```
Exp.mwFreq = 95;              % GHz
Exp.CenterSweep = [3385 22]; % mT
pepper(Nx,Exp,Opt);
```

Resonator mode

Basic parameters

```
nu0 = 9.5;       % resonator frequency, GHz
Qu = 1000;       % resonator Q-factor (unloaded)

beta = 1;        % coupling coefficient (critical coupling, matched)
beta = 0.1;      % (undercoupled)
beta = 3;        % (overcoupled)
```

Calculating the dip

```
nu = linspace(9,10,1001);            % GHz
G = resonatorfunc(nu,nu0,Qu,beta);   % voltage reflection coefficient
```

Plotting the tuning picture

```
plot(nu,abs(G));                     % voltage refl. coeff., linear scale
ylim([0 1]);                         %   full range

P_refl = abs(G).^2;                  % power refl. coeff.
plot(nu,P_refl);                     %   linear scale
plot(nu,10*log10(P_refl));           %   logarithmic dB scale
```

Question!

What are the benefits and drawbacks of using resonators?

Benefits
1. keep E1 microwave field away from sample (no losses)
2. increase B1 microwave field at sample (high conversion efficiency)

Drawback
1. limited bandwidth

Required bandwidth
- pulse EPR: large (at least 100 MHz)
- CW EPR: not much (100 kHz modulation)
- rapid-scan EPR: in between

Field modulation, harmonics, overmodulation

Spin system and experiment

```
Nx.g = [2.008 2.006 2.002];
Nx.Nucs = '14N';
Nx.A = [20 20 85];      % MHz
Nx.lwpp = 0.3;          % mT

Exp.mwFreq = 9.5;           % GHz
Exp.Range = [333 345];      % mT
```

Harmonic and modulation amplitude

```
Exp.Harmonic = 0;           % no field modulation
pepper(Nx,Exp);

Exp.Harmonic = 1;           % first harmonic
pepper(Nx,Exp);

Exp.ModAmp = 0.5;           % peak-to-peak modulation amplitude, mT
pepper(Nx,Exp);
```

Absorption and dispersion

Spin system and experiment

```
Sys.g = 2;
Sys.lwpp = 0.3;            % MHz

Exp.mwFreq = 9.5;          % GHz
Exp.Range = [337 342];     % mT
Exp.Harmonic = 0;          % no field modulation
```

Different microwave phasing

```
Exp.mwPhase = 0;                  % pure absorption
[B,spc1] = pepper(Sys,Exp);
Exp.mwPhase = pi/2;               % pure dispersion
[B,spc2] = pepper(Sys,Exp);
Exp.mwPhase = 15*pi/180;          % absorption + small dispersion admixture
[B,spc3] = pepper(Sys,Exp);

plot(B,spc1,B,spc2,B,spc3);
```

Field vs. frequency sweep

Nitroxide radical

```
Nx.g = [2.008 2.006 2.002];
Nx.Nucs = '14N';
Nx.A = [20 20 85];          % MHz
```

Field and frequency sweep at X-band

```
Nx.lwpp = 0.4;                  % mT
Exp1.mwFreq = 9.7;              % GHz
Exp1.Range = [340 350];         % mT
Exp1.Harmonic = 0;
[B,spc1] = pepper(Nx,Exp1);     % field sweep

Nx.lwpp = 0.4*28;               % MHz
Exp2.Field = 340;               % mT
Exp2.mwRange = [9.4 9.7];       % GHz
[nu,spc2] = pepper(Nx,Exp2);    % frequency sweep
```

Plotting

```
subplot(2,1,1); plot(B,spc1);
subplot(2,1,2); plot(nu,spc2);
```

Break

Filters: RC filter, Savitzky-Golay

Spectral line with noise

```
B = linspace(300,400,1001);         % mT
B0 = 340;                           % mT, line center
FWHM = 10;                          % mT, full width at half maximum
spc = gaussian(B,B0,FWHM,1);        % first derivative Gaussian
spc = addnoise(spc,50,'n');         % SNR = 50
```

RC filter (don't use it!)

```
spcRC = rcfilt(spc,1,20);           % conversion time, time constant
```

Savitzky-Golay filter (much better!)

```
spcSG = datasmooth(spc,20);         % length of smoothing window
```

Comparative plot

```
plot(B,spc,B,spcRC,B,spcSG);
legend('data','RC','S-G');
```

Crystals: frames and space groups

Simple spin system and powder spectrum

```
P1.g = 2.0024;               % substitutional nitrogen center in diamond
P1.Nucs = '14N';
P1.A = [81 114];             % MHz
P1.lwpp = 0.05;              % mT

Exp.mwFreq = 9.5;            % GHz
Exp.CenterSweep = [339 10];  % mT

pepper(P1,Exp);
```

Single-crystal spectrum

```
ma = 54.736;                                % magic angle (deg)
Exp.MolFrame = [45 ma 0]*pi/180;            % mol. frame ori. in crystal
Exp.CrystalOrientation = [0 ma 0]*pi/180;   % crystal ori. in spectrometer
Exp.CrystalSymmetry = 'Fd-3m';              % space group of diamond (#227)

pepper(P1,Exp);

Exp.SampleRotation = 10*pi/180;             % rotate sample
pepper(P1,Exp);
```

Small zero-field splitting

Organic triplet

```
Triplet.S = 1;
Triplet.D = 1000;     % MHz
Triplet.lwpp =  2;    % mT

Exp.mwFreq = 9.5;     % GHz
Exp.Range = [0 600]; % mT

pepper(Triplet,Exp);
```

Energy level diagram

```
levelsplot(Triplet,'z',[0 600],9.5);

theta = 30*pi/180;    % radians
phi = 20*pi/180;      % radians
levelsplot(Triplet,[phi theta],[0 600],9.5);
```

Large zero-field splitting

High-spin Fe^{3+}

```
Fe.S = 5/2;
Fe.g = 2;
Fe.D = 300e3;          % MHz
Fe.lwpp =  2;          % mT

Exp.mwFreq = 9.5;      % GHz
Exp.Range = [0 600]; % mT
Exp.Harmonic = 0;

pepper(Fe,Exp);
```

Energy level diagram

```
levelsplot(Fe,'xz',Exp.Range,Exp.mwFreq);
```

Question!

What are the physical origins of zero-field splitting?

1. Dipolar coupling between electron spins
2. Spin-orbit interactions

Organic radicals: spin-spin coupling dominates
Transition metals: both terms are important

D strain; temperature dependence

Gadolinium(III)

```
Gd.S = 7/2;
Gd.D = 1000;     % MHz
Gd.lwpp = 10;    % mT
```

D strain

```
Gd.DStrain = 0;      % no D strain
Gd.DStrain = 300;    % some D strain

Wband.mwFreq = 95;             % GHz
Wband.Range = [3100 3700];   % mT
pepper(Gd,Wband);
```

High field, low temperature

```
Wband.Temperature = 4;     % temperature, in K

pepper(Gd,Wband);          % reveals sign of D
```

Interfacing with ORCA

ORCA input file: OH.oif

```
! UKS B3LYP 6-31G
*xyz 0 2
O 0 0 0
H 0 0 0.98
*
%eprnmr
  gtensor 1
  Nuclei = all H {aiso, adip, aorb}
end
```

Running the ORCA calculation

```
user@linux:~$  orca OH.oif > OH.oof
```

gives OH.oof, OH.xyz, OH.prop

EasySpin simulation

```
OH = orca2easyspin('OH.prop');
OH.lwpp = 1;                   % mT
Wband.mwFreq = 95;             % GHz
pepper(OH,Wband);
```

ENDOR

Weak coupling regime

```
Sys.S = 1/2;
Sys.Nucs = '1H';
Sys.A = [5 10];       % MHz
Sys.lwEndor = 0.2;    % MHz

Exp.Field = 1200;     % mT
Exp.Range = [40 60]; % MHz

salt(Sys,Exp);
```

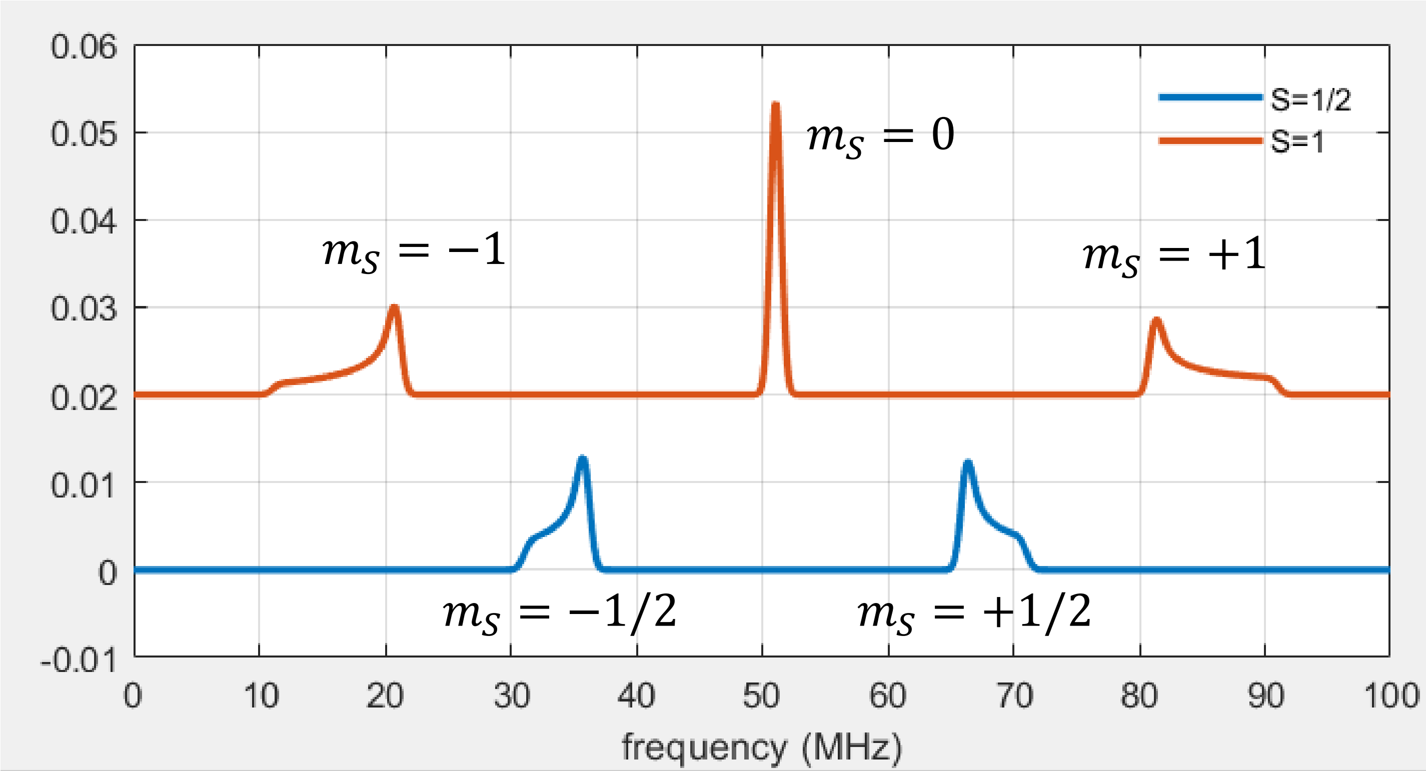
Strong coupling regime

```
Sys.Nucs = '15N';
Sys.A = [30 40];      % MHz

Exp.Range = [0 50];  % MHz

salt(Sys,Exp);
```

one peak for each electron m_S manifold

Question!

How many ENDOR peaks to you expect for a ^{1}H coupled to S = 1



Orientation selection

Anisotropic spectrum

```
Sys.g = [2 2.06 2.2];
Sys.HStrain = 20;       % MHz

Exp.Field = 320;        % fixed field, mT

subplot(1,2,1);
pepper(Sys,Exp);

mw = 9.4;               % GHz
xline(mw,'r');
```

Orientation selection

```
Exp.mwFreq = mw;
Exp.ExciteWidth = 100;  % MHz, FWHM

subplot(1,2,2);
orisel(Sys,Exp);
```

Pulse shapes and excitation profiles

Pulse shapes

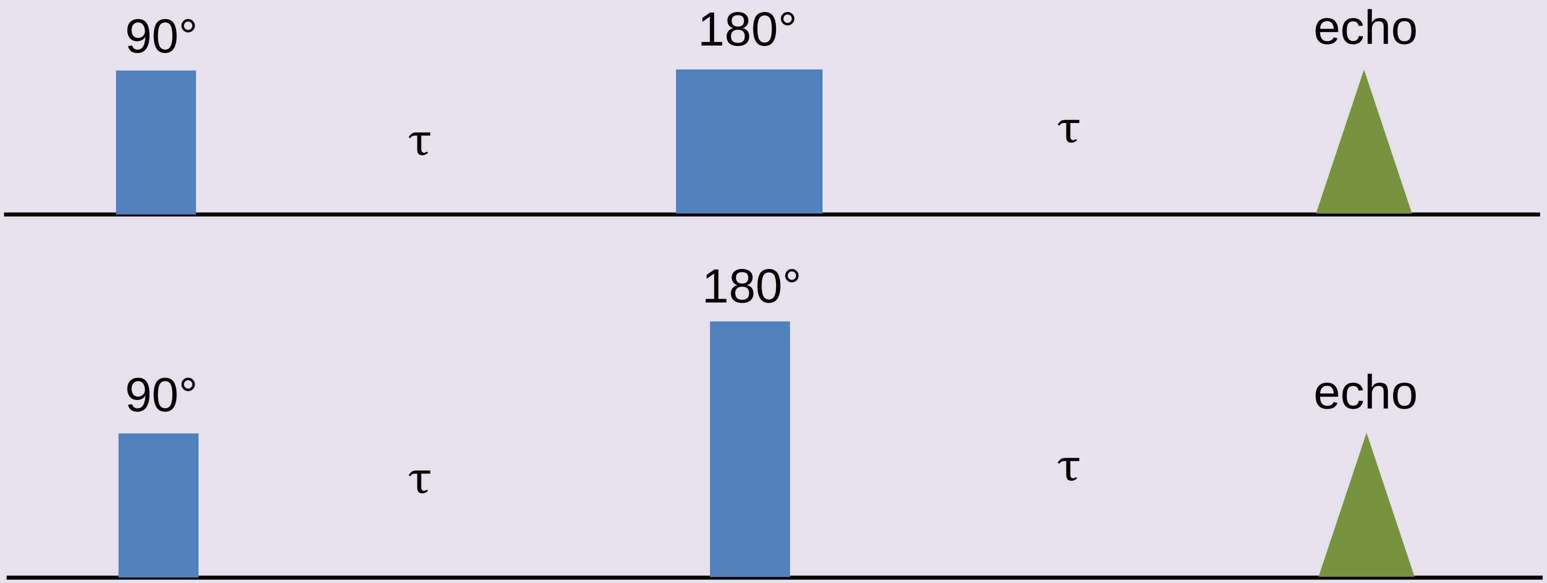
```
par.Type = 'rectangular/none';      % shape: rectangular AM, no FM
par.tp = 0.2;                       % pulse length, microseconds
par.Flip = pi;                      % flip angle, radians

pulse(par);


par.Type = 'sech/tanh';             % shape: hyperbolic secant/tangent
par.Frequency = [-30 30];           % frequency range (up-sweep), MHz
par.beta = 5;                       % truncation parameter

[t,IQshape] = pulse(par);
plot(t,real(IQshape),t,imag(IQshape));
```

Excitation profile

```
exciteprofile(t,IQshape)
```

Question!

How do these two pulse sequences differ?



Second one has more uniform bandwidth than first.

2-pulse and 3-pulse ESEEM

Proton ESEEM

```
Sys.Nucs = '1H';
Sys.A = [-4 8];       % MHz
Sys.T1 = 50;          % µs
Sys.T2 = 4;           % µs

Exp.Field = 350;      % mT
Exp.Sequence = '2pESEEM';   % '2pESEEM', '3pESEEM'
Exp.tau = 0.010;      % µs; blindspots for 3pESEEM
Exp.dt = 0.010;       % µs

Opt.nKnots = 181;     % number of orientations between z axis and xy plane

saffron(Sys,Exp,Opt);
```

Nitrogen ESEEM

```
Sys.Nucs = '14N';
Sys.A = 2.2;          % MHz
Sys.Q = 2;            % e^2Qq/h, MHz
Exp.dt = 0.040;       % µs
saffron(Sys,Exp,Opt);
```

HYSCORE

Weak coupling regime

```
Sys.Nucs = '1H';
Sys.A = [-5 -5 10];          % MHz

Exp.Field = 350;             % mT
Exp.Sequence = 'HYSCORE';
Exp.tau = 0.0010;            % tau, µs; blindspots!
Exp.dt = 0.020;              % time increment, µs
saffron(Sys,Exp);
```

Strong coupling regime

```
Sys.Nucs = '14N';
Sys.A = [8 10];           % MHz
Exp.dt = 0.040;           % µs
saffron(Sys,Exp);
```

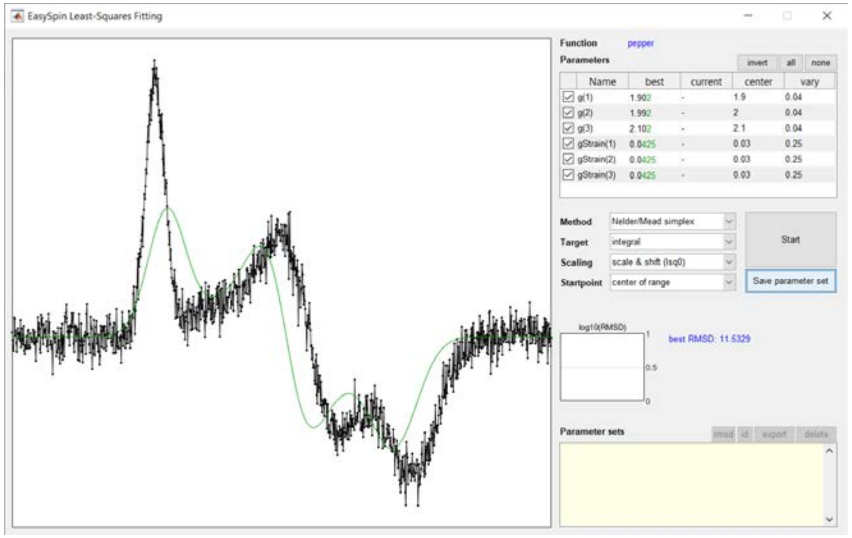
Quadrupole coupling

```
Sys.Q = 0.2;              % e2Qq/h, MHz
saffron(Sys,Exp);
```

Fitting

Interactive fitting

```
[B,spc] = eprload('FeS_1.DTA');
plot(B,spc);

Exp.mwFreq = 9.5; % GHz
Exp.Range = [300 380]; % mT

Fe.g = [1.9 2.0 2.1];
Fe.gStrain = [1 1 1]*0.03;

Vary.g = [1 1 1]*0.04;
Vary.gStrain = [1 1 1]*0.25;

esfit(@pepper,spc,Fe,Vary,Exp);
```



Function pepper

Parameters

	Name	best	current	center	vary
☑	g(1)	1.902	-	1.9	0.04
☑	g(2)	1.992	-	2	0.04
☑	g(3)	2.102	-	2.1	0.04
☑	gStrain(1)	0.0425	-	0.03	0.25
☑	gStrain(2)	0.0425	-	0.03	0.25
☑	gStrain(3)	0.0425	-	0.03	0.25

Method: Nelder/Mead simplex
Target: integral
Scaling: scale & shift (lsq0)
Startpoint: center of range

best RMSD: 11.5329

User-defined pulse sequences

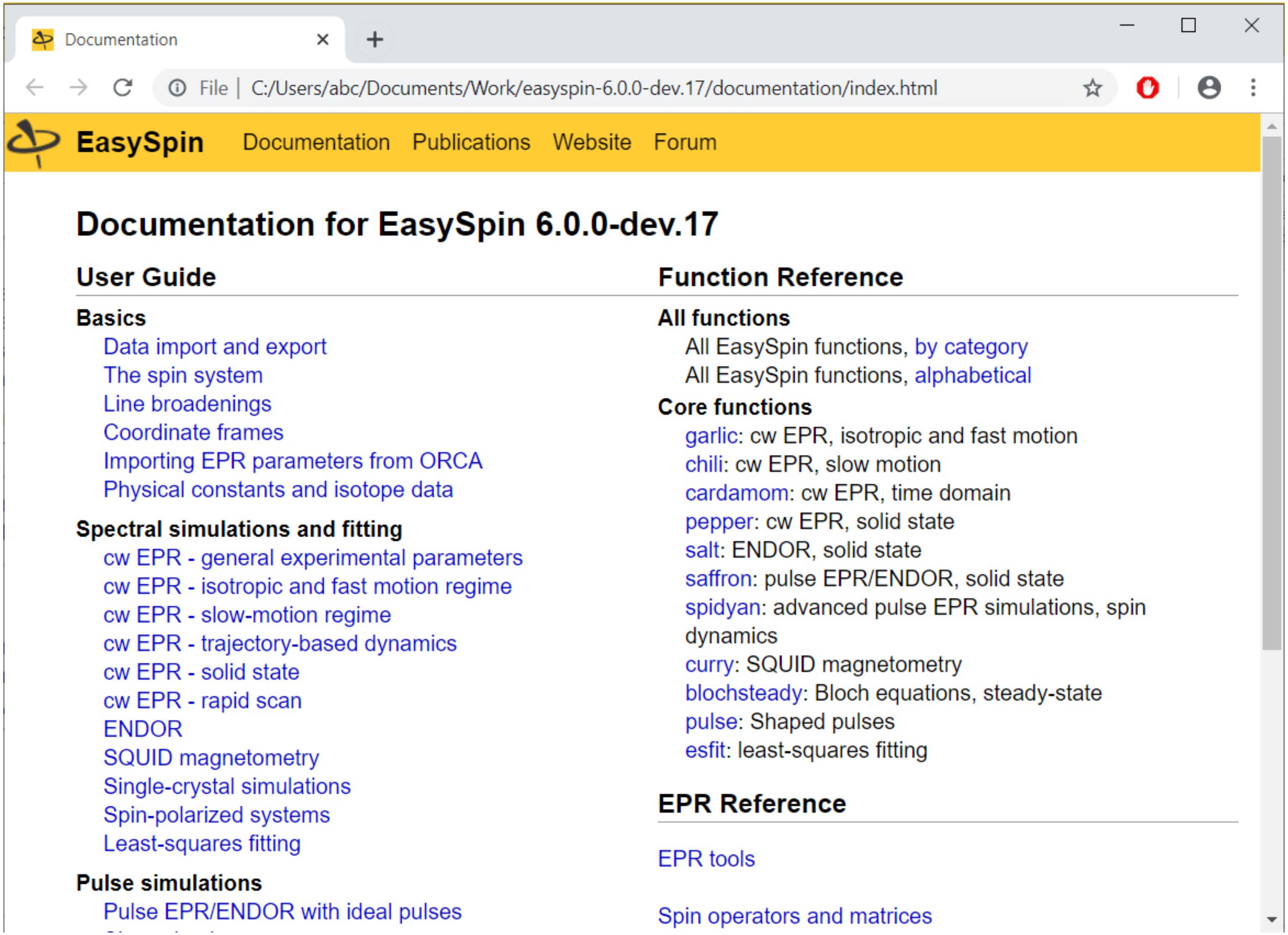
Four-pulse ESEEM

```
Sys.Nucs = '1H';
Sys.A = [2 8];                % MHz
Sys.Q = 0.2;                  % e^2Qq/h, MHz

Exp.Field = 350;              % mT
Exp.Flip = [1 1 2 1];         % multiples of 90deg: 90-90-180-90
Exp.Inc = [0 1 1 0];          % incrementation scheme (0 = fixed)
Exp.dt = 0.010;               % µs
Exp.t = [1 0 0 1]*0.080;      % µs

saffron(Sys,Exp);
```

Simulation noise: incomplete averaging

```
Opt.nKnots = 271;             % number of orientations between z axis and xy plane
saffron(Sys,Exp,Opt);
```

Final slide



Documentation for EasySpin 6.0.0-dev.17

User Guide

Basics

- Data import and export
- The spin system
- Line broadenings
- Coordinate frames
- Importing EPR parameters from ORCA
- Physical constants and isotope data

Spectral simulations and fitting

- cw EPR - general experimental parameters
- cw EPR - isotropic and fast motion regime
- cw EPR - slow-motion regime
- cw EPR - trajectory-based dynamics
- cw EPR - solid state
- cw EPR - rapid scan
- ENDOR
- SQUID magnetometry
- Single-crystal simulations
- Spin-polarized systems
- Least-squares fitting

Pulse simulations

- Pulse EPR/ENDOR with ideal pulses

Function Reference

All functions

- All EasySpin functions, by category
- All EasySpin functions, alphabetical

Core functions

- garlic: cw EPR, isotropic and fast motion
- chili: cw EPR, slow motion
- cardamom: cw EPR, time domain
- pepper: cw EPR, solid state
- salt: ENDOR, solid state
- saffron: pulse EPR/ENDOR, solid state
- spidyan: advanced pulse EPR simulations, spin dynamics
- curry: SQUID magnetometry
- blochsteady: Bloch equations, steady-state
- pulse: Shaped pulses
- esfit: least-squares fitting

EPR Reference

EPR tools

Spin operators and matrices