Program ODF3.

Program ODF3 is elaborated for numerical simulation of the EPR spectra and determination of the spectra parameters by fitting procedure. It is aimed first of all at determination of orientation distribution function of paramagnetic particles in partially aligned media. The examples of results obtained using ODF3 are presented in chapter "Simulation of rigid limit and slow motion EPR spectra for extraction of quantitative dynamic and orientational information" (in "Nitroxides - Theory, Experiment and Applications", ISBN 979-953-307-1090-0.). The program can be loaded from the site http://www.chem.msu.ru/eng/lab/chemkin/ODF3/

The program is a working tool used in our laboratory to test different models, approaches and algorithms of spectrum simulation. Thus it is not an accomplished software product and it is not optimized by efficiency. Nevertheless we believe that the program can be useful to reproduce our results or treat similar spectral data.

The program is written using FORTRAN but as the different subprograms have been created by different programmers, in different time, with different aims the project as a whole does not meet any language standard. Of course, this circumstance produces troubles at compilation and debugging of program. The program is presented free for any use with the only conditions that authors are not responsible for any consequences and insist on citation of source, if results obtained using the program are published.

The program allows taking into account the following:

a) Tilt of hfi-tensors relative to g-axes.
b) Forbidden transitions.
c) Convolution of Gaussian and Lorentzian functions for description of the shape of individual spectral line (Voigt profile).
d) Anisotropy of line widths which is described by second-rank tensors of Gaussian and Lorentzian line widths.
e) Tilt of Gaussian and Lorentzian tensors relative to g-axes.
f) Stochastic rotational oscillations of paramagnetic molecules with limited amplitude and high frequency (quasi-librations).
g) Tilt of librations axes relative to g-axes.
h) The orientation distribution functions of paramagnetic probe.
i) Up to 5 magnetic nuclei.
j) Up to 5 different paramagnetic centers
h) Dependence of line width from projection of nuclear spin $\boldsymbol{m}$.

EPR spectra are computed in accordance with explicit formulas presented in [A1]. Two types of spectrum calculation can be performed. Both types of calculation use the Hamiltonian within perturbation theory of second order. First type of calculation assumes the coincidence of g-tensor frame with hfi-tensor frame. Second type of calculation takes into account any tilt of hfi-tensors relative to g-axes and forbidden transitions.

[A1] G.M. Zhidomirov, Ia.S.Lebedev, C.A.Dobriakov, N.Ia.Shtenshneider, A.K.Chirkov, V.A.Gubanov "Interpretation of complex EPR spectra", Moscow, Nauka, 1975, 216 p. (Russ).

To do fitting the following files are used:

File NameODF3.nam contains:

names of files describing set of initial parameters of paramagnetic center and initial orientation distribution function,

names of files for storing the set of final parameters f paramagnetic center and initial orientation distribution function,

file names of experimental EPR spectra,

file name for storing of resulting spectra.

All filenames should be no longer than 8 characters before point.

File 'nameODF3.nam' can contain the instruction for some consecutive fitting procedures. Format of the file is following:

	String	Description
1	1	number of simulation
2	RtestF1.par,In_F1_4.par, no, 10	RtestF1.par - input file of parameters radical, In_F1_4.par - input file of ODF parameters no - input file of point factors; unused in the simulation; 10 - number of experimental spectra/
3	OutR_1_6.par,Out_F1_4.par	OutR_1_6.par - output file of parameters radical, Out_F1_4.par - outpput file of ODF parameters
4	96-0i.esr, 1_4_10.dat,0,1	96-0i.esr - input file of experimental spectrum, 1_4_10.dat - output file for spectra, 0 - experimental angle between sample director and magnetic field, 1 - factor for multyplying of calculated spectrum
5-13	……..	strings in the same format for every experimental spectrum
14	2	next simulation
	…….	
	end	

Files of EPR spectra are ASCII files. They consist of two columns of real numbers. The first column presents the magnetic field strength, the right one - the spectrum amplitude.
For the correct opening of the spectrum file should contain:
- free number of lines with numeral or literal remarks,
- the line containing the single word: "Spectr:"
After this line the two columns of numbers follow.

Input file of parameters of radical is an ASCII file. The example of the file is ODF3R.par. Format of the file is the following:

	String	Description
1	0	control value: 0 - continue, 1 - stop iterations
2	0, 1	Number of varied parameters, number of paramagnetic centers (max=5)
3	500, 1500	Number points in calculated spectrum (max -2048), number of points in integration net.
4	1, 0	NUMAVE - number point of experimental spectrum that averaged in course preparation spectrum to fitting; every fitted value of spectrum amplitude is obtained by linear interpolation between NUMAVE experimental points at less magnetic field and NUMAVE experimental points at larger magnetic field; Libration model: 0 - no librations,

		1 - small libration amplitides (see, for example, S. V. Paschenko et al. J. Chem. Phys. 1999, 110, N. 16, p.8150), 2 - uniform angular displacements around g-tensor axes from -α to +α (O. H. Griffith et al. in: L.J. Berliner (Ed.) Spin Labeling: Theory and applications, Academic Press, New York, 1976, p. 53) 3 - uniform angular displacements around arbitrary axes from -α to +α (V. Timofeev et al, J. Chem. Soc. Perkin Trans. 1995, 2, p. 2175)
5	1, 1	phase of experimental and calculated EPR spectra
6	1, 0	Type of spectrum simulation 1 - coinciding axes of A- and g-tensors 2 - tilted A-tensor, nuclear Zeeman, forbidden transitions, 3 - similar to type 2, but restricted by the number of transitions according to level probability, 4 - similar to 2, probability of transitions is taken from precalculated file *.trn; the second value is not used
7	1, 1	Line shape, (1,0) - Gaussian, (0,1) - Lotentzian, (1,1) - convolution (Voigt),
8	2, 0	Numbers of anisotropic nuclei; second value is not used
9	2, 0	2 - use FFT for convolution; 0 - key for use of weighted points of spectra, the weights are taken from a separate file.
10	1.0, 1.0	Nuclear spins, number of values should correspond to numbers of anisotropic nuclei.
11	60.0, 3315.0, 1.00000	Field range for calculated spectra, field of center for calculated spectra, coefficient for scaling of experimental spectra
12	1.0D-8, 1.0D-6, 1.0D-6, 1.0D-5, 0.0	Step for calculation of gradients, RFCTOL - function convergence level, XCTOL - arguments convergence level, probability level for transitions, last value is not used
13	Flag Flag Flag	Header of the section where varied parameters are described. The integer value "flag" should be placed after every parameter value.
14	66.0 0 0.31 0 1.0 0	Shift of the spectrum, hw, content factor of paramagnetic center.
15	6.6 0 4.7 0 4.4 0	Components of Gaussian line width tensor
16	0.0 0 0.0 0 0.0 0	Euler angles that transform Gaussian width-frame to g-frame, in degrees
17	0.001 0 0.001 0 5.4 0	Components of Lorentzian line width tensor
18	0.0 0 0.0 0 0.0 0	Euler angles that transform Lorentzian width-frame to g-frame, in degrees
19	2.00834 0 2.00662 0 2.00214 0	Components of g-tensor
20	0.0 0 0.0 0 0.0 0	Amplitudes of librations around gx, gy, gz axes
21	0.0 0 0.0 0 0.0 0	Euler angles that transform libration frame to g-frame, in degrees

22	0.0 0 0.0 0 0.0 0	??? betta coefficients (before m) for Gaussian line width
23	0.0 0 0.0 0 0.0 0	gamma coefficients (before m2) for Gaussian line
24	0.0 0 0.0 0 0.0 0	betta coefficients (before m) for Lorentzian line
25	0.0 0 0.0 0 0.0 0	gamma coefficients (before m2) for Lorentzian line
26	1.0 0 4.4 0 31.4 0 0.0 0 0.0 0 0.0 0 0.403562 0	Three components of A-tensor, three Euler angles that transform A-frame to g-frame and nuclear g-value. Last integer value shows the equivalence of the nuclei.
27	1.0 0 4.4 0 31.4 0 0.0 0 0.0 0 0.0 0 0.403562 1	The second nucleus. The last value 1 means that this nucleus is equivalent to the nucleus number 1. Magnetic parameters of this nucleus should not be marked as varied ones. The parameters for this nucleus will be equal to parameters of the first nucleus.
28	0, 2000	Desciption of the additional paramagnetic center containing lines 3-10 and 13-27. The values that are common for all centers are used as specified for the first one.
	…….	

Description of keys "flag":

0 - keep constant

1 - vary,

2 - vary in transformed form, can be used for parameter "hw" and "Components of g-tensor". The option is used for convergence of these values.

3 - calculate from varied parameter. The options should be used for "Components of g-tensor" and " Three components of A-tensor" The marked value will calculated so that tensor trace is constant.

4 - uniaxial tensor (mark valY, means valY=valX)

5 - isotropic tensor (mark valY and valZ, means valY=valX and valZ=valX)

11 - value is determined by constant ratio with the same value for 1st center

12 - value is determined by constant ratio with the same value for 2nd center

13 - value is determined by constant ratio with the same value for 3rd center

14 - value is determined by constant ratio with the same value for 4th center

15 - value is determined by constant ratio with the same value for 5th center

Input file of orientation distribution function is an ASCII file. The example of the file is ODF3F.par. Format of the file id following:

	string	description
1	4	Rank of expansion
2	0 1.000000000000000	Penalty flag: 0 - penalty off, ≠ 0 penalty on; Penalty coefficient
3	3	Type of axial ODF: keyODF=1 - general form is described by expression (1), keyODF=2 - hidden uniaxiality of R is described by expressions (2), keyODF=3 - ordered uniaxiality is described by expressions (3)
4	2 0.001	method for calculations of errors in the final point of fitting,

		1 - using Hessian and Jacobian, 2 - using Hessian only, 3 - using Jacobian only. The second value is not used.
5	Parameters:	Header of the section where varied parameters are described. The integer value "flag" should be placed after every parameter value.
6	0.0 0	hi0 - angular error at the initial setting of the sample. This value will be added to every angle between the sample director and magnetic field that is specified in file NameODF3.nam.
7	Uniaxial:	Header of the section where uniaxial ODF is specified. These parameters are used when keyODF=2 or keyODF=3 are chosen in string No 3.
8	10.0 0 20.0 0 30.0 0	Angles θ = 10.0, φ = 20.0, ψ = 30.0 that are used in expressions(2a) and (3a)
9	An0 Fl An2 Fl An4 Fl…	Header of ODF coefficients. When keyODF=2 in the string No 3 is indicated only first value in following strings are used as $(a_{j0})_t$ When keyODF=3 in the string No 3 is indicated values in following strings are used as $(a_{jk})_u$
10	1.0 0	Coefficient $(a_{00})_t = 1.0$ or $(a_{00})_u = 1.0$. Variation of this coefficient is equivalent to variation of content factor in the Input file of parameters of radical.
11	2.0 0 0.1 0	Coefficient $(a_{20})_t = 2.0$ (keyODF=2) is used or $(a_{20})_u = 2.0$ and $(a_{22})_u = 0.1$ (keyODF=3).
12	4.0 0 0.2 0 0.3 0	Coefficient $(a_{40})_t = 4.0$ (keyODF=2) is used or $(a_{40})_u = 4.0$, $(a_{42})_u = 0.2$ and $(a_{44})_u = 0.3$ (keyODF=3).
	6.0 0 0.4 0 0.5 0 0.600000 0	Number of similar strings is determined by rank of expansion used.
	General:	Header of ODF coefficients a_{jm} and b_{jm} (expression (1)
	0 2.0 0	Rank = 0, $a_{00} = 2.0$, variation of this coefficient is equivalent to variation of content factor in the Input file of parameters of radical.
	2 -2.15726 0 0.0 0 0.0 0 0.613718 0 0.0 0	Rank=0, $a_{20} = -2.15726$, $a_{21} = 0.0$, $b_{21} = 0.0$, $a_{22} = 0.613718$, $b_{22} = 0.0$
	4 0.857624 0 0.0 0 0.0	Number of similar strings is determined by the rank of expansion used.

Description of keys "fl":

0 - keep constant

1 - vary,

$$r(b,g) = \frac{1}{2p}\sum_{j=0}^{\infty}\left(\frac{1}{2}a_{j0}P_j(\cos b) + \sum_{m=1}^{j}P_{jm}(\cos b)\left[a_{jm}\cos mg + b_{jm}\sin mg\right]\right) \qquad \textbf{(1)}$$

$$r(b_t) = \frac{1}{4p} \sum_{j=0}^{\infty} (a_{j0})_t P_j(\cos b_t) \qquad \textbf{(2)}$$

where j is even and coefficients of expansion (1) can be obtained by expressions:

$$a_{jm} = (a_{j0})_t \frac{(-1)^m (j-m)!}{(j+m)!} \cos mj \; P_{jm}(\cos q)$$
$$b_{jm} = -(a_{j0})_t \frac{(-1)^m (j-m)!}{(j+m)!} \sin mj \; P_{jm}(\cos q) \qquad \textbf{(2a)}$$

$$r(b_u, g_u) = \frac{1}{2p} \sum_{j=0}^{\infty} \left(\frac{1}{2} (a_{j0})_u P_j(\cos b_u) + \sum_{m=1}^{j} (a_{jm})_u P_{jm}(\cos b_u) \cos m g_u \right) \qquad \textbf{(3)}$$

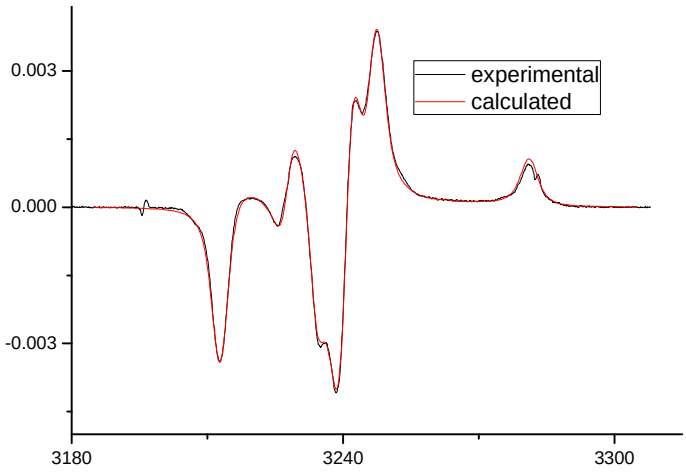
where j, m - even and coefficients of expansion (1) can be obtained by expressions:

$$a_{jm} = (-1)^m \left(\frac{(j-m)!}{(j+m)!} \right)^{1/2} \mathrm{Re} \left[\sum_k \left(\frac{(j-k)!}{(j+k)!} \right)^{1/2} (a_{jk})_u D^j_{mk}(j, q, y) \right]$$
$$b_{jm} = (-1)^m \left(\frac{(j-m)!}{(j+m)!} \right)^{1/2} \mathrm{Im} \left[\sum_k \left(\frac{(j-k)!}{(j+k)!} \right)^{1/2} (a_{jk})_u D^j_{mk}(j, q, y) \right] \qquad \textbf{(3a)}$$

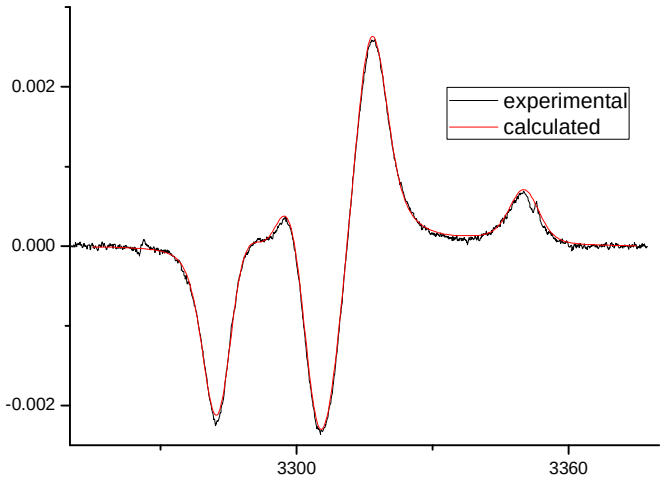
List of tests:
testR1 - rigid limit spectrum of nitroxide without minimization;
testR2 - rigid limit spectrum of nitroxide without minimization;
testR3 - rigid limit spectrum of nitroxide, determination of parameters by minimization;
testR4 - rigid limit spectrum of radical-anion Cl_2^- , two nuclei with spin 3/2, two paramagmetic centers ($^{35}Cl^{35}Cl$, $^{35}Cl^{37}Cl$), dependence of line width on nuclear spin projection.
testR5 - spectrum of nitroxide, libration around gX axis, determination of parameters by minimization

testF1 - rigid limit spectra of nitroxide, simulation of angular dependence (10 spectra), determination of ODF in approximation of hidden axiality of probe (expressions (2)).
testF2 - rigid limit spectra of nitroxide, simulation of angular dependence (10 spectra), determination of orthorhombic ODF (expressions (1)).
testF3 - rigid limit spectra of nitroxide, simulation of angular dependence (10 spectra), determination of ODF in approximation of orthorhombic symmetry of the probe (expressions (3)).
testF4 - spectra of nitroxide, librations around three axes, libration frame is tilted relative to g-frame, simulation of angular dependence (10 spectra), determination of ODF in approximation of hidden axiality of the probe (expressions (2)).

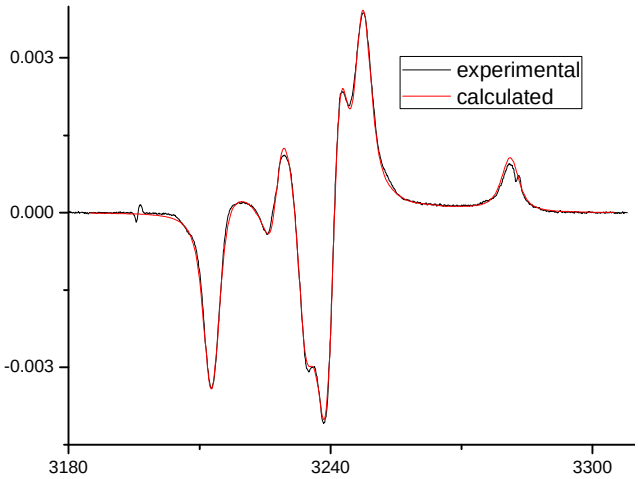
Result of tests:



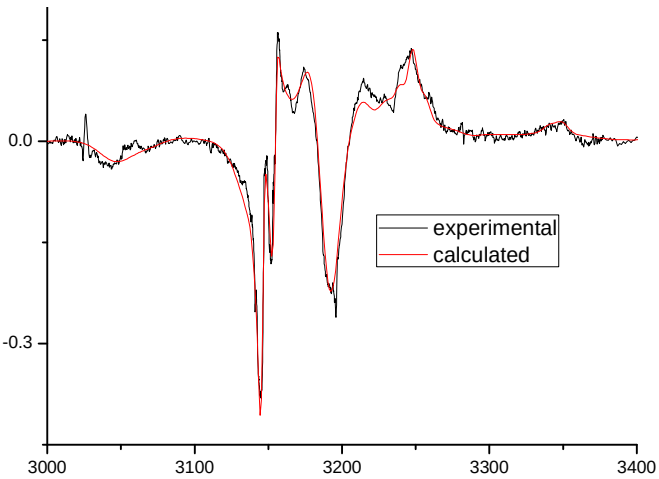
testR1



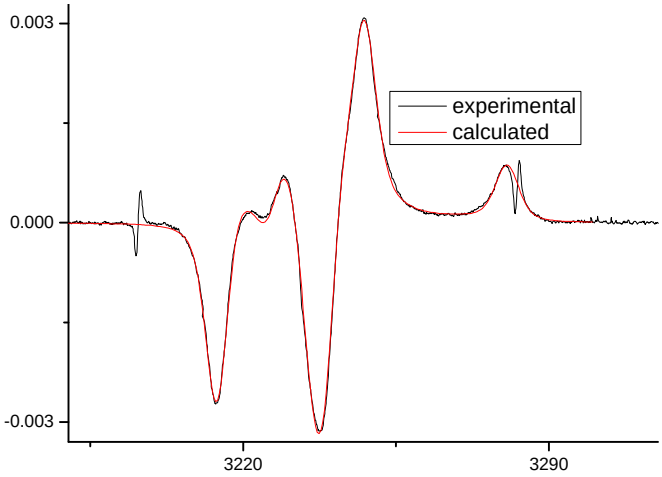
testR2



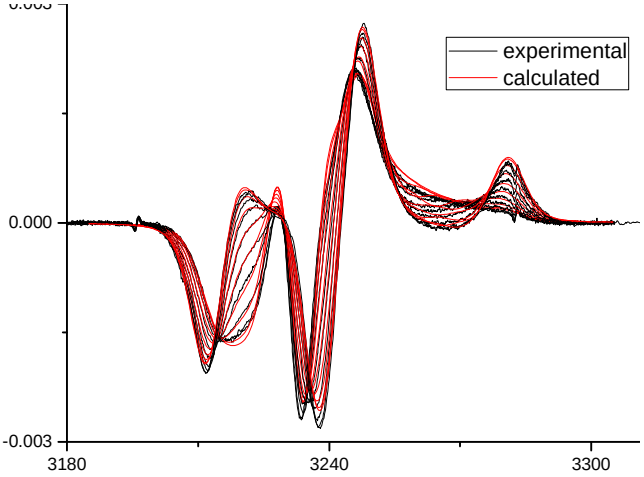
testR3



testR4



testR5



testF1