

Manual

for the visualization toolbox for charge transfer state simulations v2

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Manual

On the Fig. 1a and 1b one can see how toolbox looks like. It has a lot of options and possibilities for more comfortable charge transfer (CT) state simulations.

Here it is explained how one can use this tool. Please, pay attention, that we refer to D_{zz} as D for simplicity.

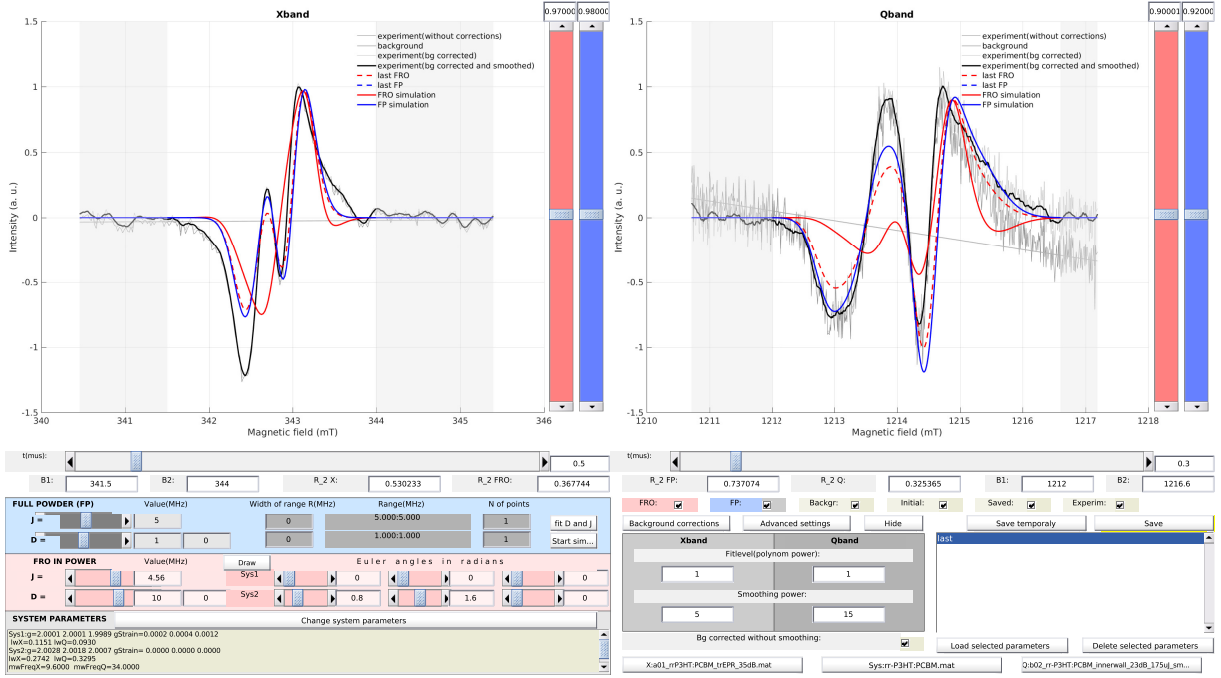
For the theoretical background it is recommended to read theoretical part in Master thesis [1]. More about electron paramagnetic resonance and spectra simulations can be found here [2, 3, 4, 5, 6]. For any further questions feel free to contact the authors.

0.1 Running the tool

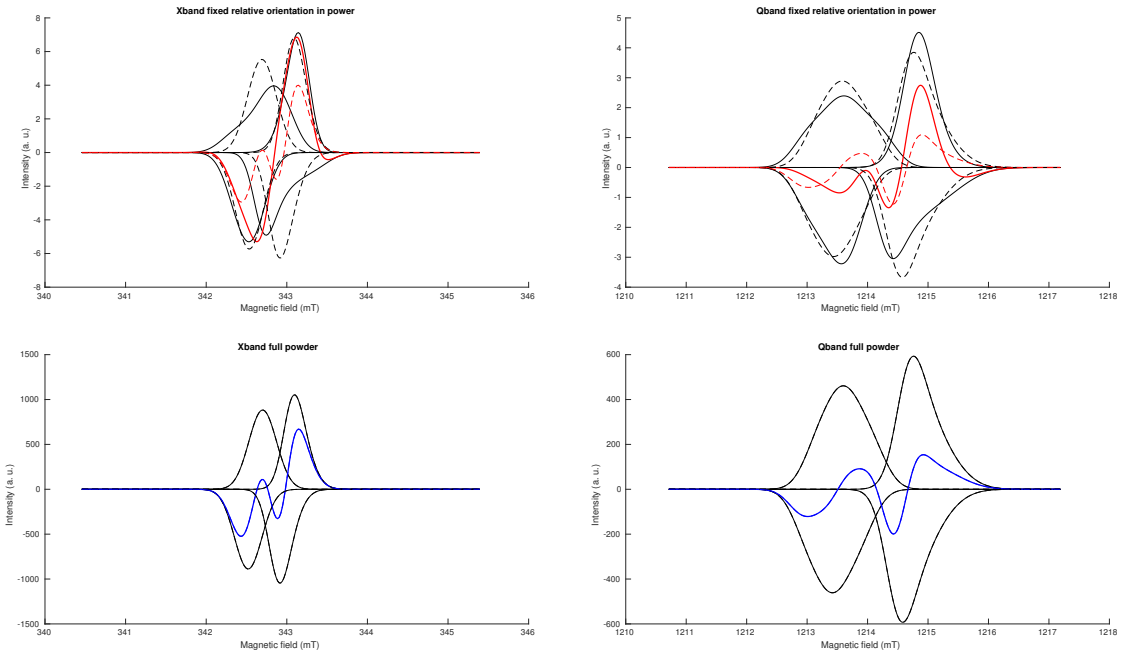
1. Run the program.
2. The dialog is automatically open: "Choose file for system data". If one runs the program for the first time or wants to create or change file with data about the system, then chose "Create/change file":
 - The new dialog is open.
 - Here one enters main information about the system (that is extracted from cwEPR spectrum). One can enter different line widths for X- and Q-band. This is useful if one does not distinguish between g-strains and line widths.
 - If such file already exists for the system and one wants to change it, press "Open" and chose corresponding file.
 - For saving the data press "Save" button. You can save it in the new file or replace existing one. If you do not save changes, they will be lost. If you rewrite file, previous data will be lost (saved simulations stay, but they will give another result with new system parameters).
 - After saving close the window.
 - If dialog "Choose file for system data" appears again, something wrong was done. Repeat previous steps.

If special file with information about the system (g-factors, line widths, ...) already exists, then chose "Open file". And chose the file.

3. The dialog is automatically open: "Select the MATLAB code file for X-band". One needs to select '*.mat' file that contains 1x1 'file' structure, where all needed information about experiment and spectra are stored: mw_freq_set (frequency of mw in GHz or Hz), B0 (magnetic field in mT), t (time in μ s), s_trcorr (spectra - recorded intensities).
4. The same for Q-band.
5. Additional window can appear. There you can chose saved simulations.
6. It can take several minutes for initial calculations. Afterwards the spectra are opened and the tool is ready for usage.



(a) Different parameters can be changed. In black - background corrected and smoothed experimental spectrum, red - fixed relative orientation simulations, blue - arandom relative orientations simulations. Dashed line shows temporary saved simulations for easier comparison of a different parameter set. In dark-gray - initial spectrum, in light-gray - background corrected spectrum.



(b) Here, four simulated transitions are shown separately in black. The sum of them is shown in blue or in red, depending on the relative orientations (random or fixed). Dashed lines show spectra for temporary saved simulations for another parameter set.

Figure 1: Screen shot of the visualization tool. It consist of two windows. In one window parameters can be changed and all spectra and simulations can be observed. In the other one, four separate transitions are simulated.

0.2 Background corrections and initial parameters

In visualization toolbox color plays a role: black - experimental spectrum, red - simulations for fixed relative orientation in powder model, blue - simulations for random relative orientations in powder model.

To better see the made changes, one can hide or show different spectra: simulations for fixed relative orientation in powder model ('FRO'), simulations for all relative orientation in powder model or full powder ('FP'), initial spectrum without any corrections ('Initial'), background corrections ('Backgr'), temporary saved spectra ('Saved'), experimental spectrum ('Experim'). Check-boxes are located below Q-band plot.

0.2.1 Initial settings

1. Set the suitable **time slice** directly or by using a slider. Remember that for simulations relaxation effects are not taken into account and approximation, that only states $|2\rangle$ and $|3\rangle$ are occupied, is made. Hence, try to choose as early times as possible but not too early because of spectrometer time resolution and signal to noise ratio.
2. Next step is **background corrections**. Initially program is automatically in "Background corrections" regime. If not, press the button 'Background corrections'.
 - Choose ranges [minimum B0, B1] and [B2, maximum B0] by entering **B1** and **B2** for both X- and Q- band. These ranges are used for background fitting.
 - On the gray background (black color corresponds to experimental spectrum) one can see parameters that can be changed: **fitting polynomial power** and **smoothing power**. Below there is an additional check-box, that allows to show/hide experimental spectrum with background corrections without smoothing. This is useful for finding appropriate smoothing power.

On the figures ranges (areas) that are used for background corrections are gray rectangles; polynomial background is shown as a gray curve (line); initial spectrum is dark-gray; background corrected experimental spectra without smoothing - light-gray; with smoothing - black.

3. When background corrections are done you can hide corresponding spectra and parameters by anticking the box 'Backgr corrections'.
4. Now one can start with simulations. First step is **number of points** that should be used for the model: an amount of different angles θ that should be considered. The total number of points is then recalculated automatically in Easyspin 'sphgrid' function (for more details see [7]). For changing number of points press 'Advanced settings' button.
 - To easily see the difference between different amounts of points tick 'Saved spectrum' box. In the list below 'last' spectrum should be selected.
 - Check that the simulated spectrum of the chosen model(s) is on.
 - Now, when one changes the number of points there will be a solid line for new amount of points and a dashed line for previous one. If they are identical it does not matter which amount of points to use - current one or previous one. In

oder to have faster calculations it is better to chose as small amount of points N as possible but such that for N+1 points result is the same.

- **Attention!** Calculation takes time, be patient. If you press the same amount of points twice (if after entering the number of points, 'Enter' button was pressed twice), then previous and current spectra are the same! This can lead to the selection of the wrong N. It is important to remember, that different line widths, coupling and other parameters can require different amount of points. It is usefull to check if the right number of points is used, when parameters are changed.

5. There is '**Additional broadening**'. The line widths are taken from cwEPR spectrum. In trEPR line widths are slightly different, because of Heisenberg uncertainty principle and probably different delocalization, hence different HFI. It was calculated from Heisenberg uncertainty principle that for X-band it is about $0.2 \mu\text{s}$ and for Q-band is about 0.4 mT for early times.

0.3 Simulations

The spectra are chosen, background corrections are made and optimal number of points is found. The simulations can be started. Here we describe which parameters can be changed.

0.3.1 Random relative orientations or full powder (FP) model (blue)

1. **Couplings J and D.** They can be changed by entering a number or by using a slider. It is also possible to enter E (the second field near D). But then calculations will take more time, as then more points should be considered.
2. Additionally **strains of J and D** can be chosen. $J \propto \exp(-R)$ and $D \propto \frac{1}{R^3}$. They are recalculated from the fact that distances R between radicals can be various. Approximation is made that R have Gaussian distributions around some average value. Because proportional coefficients between J(D) and R are usually not known by user, one enters the average value and a range in terms of J(D).

As average entered J_0 value is taken. In '**Width of range**' the $2\Delta J = 2 \cdot (|J|_{\text{max}} - J_0)$ should be put in. Then this values are recalculated to distance Gaussian distribution and back in order to find second limit of J. The resulting J(D) range is written in the '**Range**' field. Also one needs to enter total **number of points for the range** - number of different J-values from range that should be considered. It should be odd. If it is even it is automatically changed to bigger odd number.

The calculating time for J(D) strains is very long. So calculation does not start automatically. One should press 'Start simulation button'. Appeared dialog after parameter change reminds about this.

After calculations additional window is appearing. It shows distribution of the considered J and D values.

3. There is additional possibility that allows automatically find J- and D-couplings (without strains). It can be ran by pressing '**fit D and J**' button. After fitting

the old results are open in new window. It is not clear why, but it finds opposite result almost all the time. Even if it finds some fitting, one should keep in mind that found minimum can be just local one and it can be possible to find a better fitting.

0.3.2 Fixed relative orientation (FRO) in a powder model (red)

1. **Couplings J and D.** They can be changed by entering a number or by using a slider. It is also possible to enter E (the second field near D).
2. **Euler angles.** There are three Euler angles for first system and three for the second one. They can have values from 0 to π .
3. In order to visualize relative orientation of radicals, press '**Draw**' button.

0.3.3 Temporaly saving

If one finds parameters or the simulations one want to remember for some time, one can temporary save this data. Data is saved only while program is working. For temporary saving press 'Save temporary' button. In opened window one can enter desired name of saving. After 'Ok' pressing, new line appears in the list box below with the entered name. By selecting saved data in the list one can:

- **Plot saved result.** For this 'Saved spectrum' check-box should be ticked. Saved spectra will be plotted as a dashed line.
- **Load saved parameters** by pressing 'Load selected parameters' button.
- **Delete saved parameters** by pressing 'Delete selected parameters' button.

0.3.4 Additional possibilities

1. One can change **normalizations** of simulations separately. This can be done by entering the values or by using sliders. See on the left side of the plots. Red one correspond to the fixed relative orientation and gray one to the all relative orientation model.
2. **Coefficient of determination R^2** is calculated. There are four of them (below plots). **R^2 FRO** is for fixed relative orientation model calculated for X- and Q-band simultaneous. **R^2 FP** is for random relative orientations model (full powder) calculated together for both bands. **R^2 X** is one for X-band and **R^2 Q** is one for Q-band, which calculated for the current model. If both models are considered, then the R^2 parameters show the result for FRO model.
3. In the lower left corner data about system are written. If one presses '**Change system parameters**' button, they can be changed. Here one can open another file with system data or change parameters manually. One can see changes in spectra without saving by pressing 'Update without saving'. If one wants to save changes, one should press 'Save'. If saving was done, then one needs to reopen file with system data (see next point).

4. In the lower right corner there is three buttons. 1st one with opened X-band spectrum path and file name, 2nd one with system data file path and 3rd one for Q-band. This files can be changed by pressing corresponding data.

0.3.5 Saving the result

After right parameters are found and a good fitting occurs, one can save the result by pressing **yellow 'Save' button** in different ways. The different variants are indicated in new dialog:

1. **'System data file'**. It is useful to save parameters that was used for simulations in the file with system data. When this visualization tool will be run again there will be opportunity to open saved parameters and continue simulations. Only in this type of saving it is possible to resume fitting from saved parameters (all temporary saved data will be lost).
2. **'mat-file'**. It saves the parameters in a file with extention '.mat'. This type of file is used in the Matlab. There the simulated spectra as well as experimental spectrum are saved for both X- and Q-band. All the used parameters are saved in the parameter 'info'. This is useful if one wants to replot simulations.
3. **'Picture'**. It is nice feature if one wants to save plots only like a picture. The plots can be saved in two formats: '.bmp' and '.eps'. There will be two plots and below them all parameters that were used for simulations.
4. **'ASCII'**. Needed if one wants to save result external. In the beginning of the file all parameters that were used for simulations are stored. Afterwards there are columns of data:
 - Magnetic fields for X- and Q-band: 'XbandB0 (mT)' and 'QbandB0 (mT)'
 - Initial spectra for X- and Q-band without any changes: 'initialX' and 'initialQ'
 - Background corrected spectrum without smoothing: 'bgcorrX' and 'bgcorrQ'
 - Background corrected spectrum with smoothing: 'bgcorrsmoothX' and 'bgcorrsmoothQ'
 - All relative orientation in powder (full powder) model simulations and separated four peaks: 'FullPowderSimX< _,1,2,3,4>' and 'FullPowderSimQ< _,1,2,3,4>'
 - Fixed relative orientation in powder model simulations and separated four peaks: 'FixedOrSimX< _,1,2,3,4>' and 'FixedOrSimQ< _,1,2,3,4>'

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