Description Modulation-excitation Codes

**Preface**

This document describes codes in the MATLAB environment for the treatment and analysis of modulation-excitation codes (developed by Valentijn De Coster – Ghent University).

In what follows, these codes will be mentioned (their name, with input) along with short descriptions of what they do, to what extent they are original or make use of pre-existing codes.

NOTE: If built-in/MATLAB-original codes (e.g. “floor”, “floor”, “repmat”…) are used, these will not be mentioned. THUS it is assumed that the codes mentioned hereafter will be implemented in available MATLAB licenses.

**Functions**

[Xavgd] = avgXASperiods(Xreprod,periods)

This function takes a XAS data matrix "Xreprod", which MUST contain only the reversible/reproducible data part from MEXAS experiments, wherein each row is a data measurement at a given time and each column represents an absorbance value at a certain energy value, and averages this over the total number of periods "periods" that are present within this data matrix. The output “Xavgd” is an averaged time-resolved period of data.

For example, if you have data corresponding to 20 periods (each with 30 time instances measured and 1000 energy points = 600 x 1000 matrix) in a reversible regime, you use Xavgd = avgXASperiods(Xreprod, 20). The output is then 1 period of 30 time instances (30 x 1000 matrix).

PSD(XXnew,delphi,Energy,E1,E2,demodindex)

This function performs and plots results of phase-sensitive detection (PSD) on a pre-averaged XAS spectrum matrix "XXnew", of which an element “XXnew(i,j)” represents a measurement at a certain time “i” in the (averaged, time-resolved) period at energy value “j”. “delphi” represents the sampling step at which phase-resolved spectra will be plotted from phase angle 0° to 359°. So, if 30 is chosen, the plotted values will be 0°, 30°, 60°… 330°. A data matrix "Energy" containing the energy values corresponding with XXnew has to be provided, as well as 2 energy values, "E1" and "E2", which represent the bottom and top limit for which the data will be plotted, respectively. “demodindex” (integer, starting from 0) represents the demodulation index used in PSD.

Numerical integration makes use of the trapezoid rule.

This code is unique in the sense that:

1/ it uses a trapezoid integration scheme, which is more generally applicable than Simpson’s rule, which is commonly used in PSD (see Baurecht and Fringelly, 2001)

2/ users can flexibly decide on the sampling step of phase angles

3/ the use of other demodulation indices is easily done – commonly, only the value 1 is used. Thus, this code easily allows the examination of higher order indices.

4/ it is easily extendable to other non-XAS characterization techniques using the ME approach. This has already been done for infrared data at the LCT.

This code does not use pre-existing PSD codes; it was built from scratch by applying numerical mathematics to the PSD equation.

PSD\_increasingperiods

This function performs PSD of a given XAS data matrix "Xreprod" – which should contain only the periodic changes (and preferably thus also reproducible - though this script can check reversibility if PSDs are of similar shape) of MEXAS data - for incremental averages over the periods, STARTING FROM THE FIRST PERIOD (e.g. PSD of first period, first 2 periods, etc, ...). To do this, the total number of periods in the data "periods" has to be given, as well as "delphi", i.e. the intervals of phase angles for which PSD will be performed, the "Energy" matrix, containing the energy values corresponding to "Xreprod", "E1", and "E2", which are limits for plotting the results. "pngsavename" allows creating unique names, as all the phase-resolved spectra of x periods will be saved in .png AND INTERACTIVE MATLAB .fig files entitled 'Last\_x\_periods\_pngsavename'. “demodindex” is the demodulation index used in PSD and an OPTIONAL input argument. If absent, a standard demodulation index of k = 1 will be used; if it is specified (an integer), then that demod index will be used.

**NOTE: this function requires the PSD.m and avgXASperiods.m functions**

This code is unique in the sense that, apart from containing the unique features of the “PSD” function, it systematically goes through incremental (first 🡪 last) averages of the data and generates and saves the output figures.

PSD\_decreasingperiods

This function performs PSD and plots the results of a given XAS data matrix "Xreprod" – which should contain only the periodic (and preferably also reproducible - though this script can check reversibility if PSDs are similar shape) MEXAS data - for incremental averages over the periods, STARTING FROM THE LAST PERIOD (e.g. PSD of last period, last 2 periods, etc...). So, the results will be plotted for each of these averages. To do this, the total number of periods in the data "periods" has to be given, as well as "delphi", i.e. the intervals of phase angles for which PSD will be performed, the "Energy" matrix, containing the energy values corresponding to "Xreprod", "E1", and "E2", which are limits for plotting the results. "pngsavename" allows creating unique names, as all the phase-resolved spectra of x periods will be saved in .png AND INTERACTIVE MATLAB .fig files entitled 'Last\_x\_periods\_pngsavename'. “demodindex” is the demodulation index used in PSD and an OPTIONAL input argument. If absent, a standard demodulation index of k = 1 will be used; if it is specified (an integer), then that demod index will be used.

**NOTE: this function requires the PSD.m and avgXASperiods.m functions**

This code is unique in the sense that, apart from containing the unique features of the “PSD” function, it systematically goes through incremental (last 🡪 first) averages of the data and generates and saves the output figures.

[Xphi] = PSD\_data\_noplot(XXnew,delphi,Energy,E1,E2,demodindex)

The same function as the abovementioned “PSD”, i.e. does PSD of pre-averaged data, yet does not plot the results AND gives the demodulated data as output “Xphi”, where each row represents a demodulated spectrum at a certain phase angle and each column represents (demodulated) absorbance values at a certain energy value (corresponding to “Energy” matrix) for the generated phase angles.

**NOTE: Though no plots are made, E1 and E2 have to be provided.**

**NOTE: Does not require custom codes to run.**

[Xphi] = PSD\_data(XXnew,delphi,Energy,E1,E2,demodindex)

Similar function as “PSD\_data\_noplot”, yet this one DOES PLOT the results.

[Xphidata] = getPSDdata\_increaspingperiods\_noplot(Xreprod,periods,delphi,Energy,E1,E2,demodindex)

This function generates phase-resolved data without plotting the data. Similar to the “PSD\_increasingperiods” function, "Xreprod" is given – which should contain only the periodic MEXAS data – and PSD is performed for incremental averages over the number periods in this data matrix, i.e. “periods”, STARTING FROM THE FIRST PERIOD (e.g. PSD of first period, first 2 periods, etc...). To do this, the total number of periods in the data "periods" has to be given, as well as "delphi", i.e. the intervals of phase angles for which PSD will be performed, the "Energy" matrix, containing the energy values corresponding to "Xreprod". "E1" and "E2", ‘old’ energy ranges for plots, have to be provided even though no plots are made by this function. (The latter in view of the function “PSD\_data\_noplot”, being called back in this function).

The output matrix “Xphidata” thus contains phase-resolved data for each of the incremental averages, concatenated under each other. That is, 1st period’s PSD results are on top, subsequently the PSD results for the average of the first 2 periods PSD, followed by PSD results for the average of the first 3 periods PSD, …. NOTE: corresponding phase angles for which phase-resolved spectra are generated are put as a column in front of this matrix.

For example, if “nperiods”=20, “delphi”=30 and “Energy” contains 1000 points, then “Xphidata” is a 400 x 1001 matrix. 400 rows, because steps of 30° are being used for PSD 🡪 20 phase-resolved spectra per averaged dataset. 1001 columns because 1000 energy points are sampled and +1 column is added, containing the phase angles.

**NOTE: This function uses the “avgXASperiods” and “PSD\_data\_noplot” custom codes.**

[Xphidata] = getPSDdata\_increaspingperiods(Xreprod,periods,delphi,Energy,E1,E2,demodindex)

Similar function as “getPSDdata\_increaspingperiods\_noplot”, yet this one DOES PLOT the results for each periodic average. So, “periods” is the total number of figures generated.

[diffspectra,combonames] = makerefcombos\_withnames(srefs,refnames,Energy,E1,E2)

Makes all possible binary combos of difference reference spectra (in “srefs”), used for fingerprinting purposes to identify phase-resolved spectra, and PLOTS them. The output consists of the resulting difference spectra “diffspectra” and the names of these differences in the string matrix “combonames”.

E.g.: You have 4 references (A, B, C, D) and you want to plot all possible combinations of difference spectra (one – other). This leads to combinations of 2 out of 4, hence 6 possible combinations. Resulting combos are: A-B, B-C, C-D, A-C, A-D and B-C.

NOTE: opposite differences (e.g. B-A) differ from calculated ones by their sign. In the above code, these opposite differences were chosen to not be included since their information content is redundant with respect to their ‘original’ difference, as well as to avoid visual overload of the plots. (For instance, inputting 9 references gives 36 difference spectra (without opposite differnces) within the plot, which are already difficult to distinguish from one another.)

Requires as input:

“srefs”: a matrix, of which each row contains a reference spectrum

“refnames”: a string matrix (all names in between “…”), containing the names contained within “srefs”, mentioned in the same order of appearance as in this latter matrix.

“Energy”: matrix, containing the energy values corresponding to the spectra

“E1” and “E2”: the lower and upper energy value limits, for which difference spectra will be plotted.

[inphaseangles\_MAX] = KineticDiffMEXAS(Xperiodic,periods,deltaphi,Energy,E1,E2,kindex)

Performs PSD and kinetic differentiation of given data. Plots the in-phase angle map plot and gives as output the in-phase angles.

Calculates the time-resolved average of the “Xperiodic” dataset, containing reversible data, over “periods”, i.e. the number of periods; “Energy” is the matrix with corresponding energy values of the collected spectra. PSD is performed over this averaged dataset with demodulation index “kindex” and using “deltaphi” as sampling interval to generate phase-resolved spectra from 0° till (360-deltaphi)°. For each value in “Energy”, the phase angle which gives maximum amplitude in the phase-resolved spectra, is calculated, i.e. the in-phase angle. These are collected in the output “inphaseangles\_MAX”. Additionally, the function yields a plot of these in-phase angles as a function of the Energy for the energy range [“E1”, “E2”].