Manual: PEPICOBayes

Contents

1 Introduction

PEPICOBayes is a program for reconstructing the probe spectrum from pump-probe and pump-only photoelectron-photoion coincidence (PEPICO) measurements applying Bayesian probability theory. The theory behind the program is described in reference [1]. The PEPICOBayes program is written in C and executed in Matlab. We offer a simple example Matlab-file to demonstrate the usage of the PEPICOBayes program.

2 Abbreviations

The abbreviations in this manual are similar to the abbreviations used in reference [1].

Abbreviation	Description
x	Symbol that refers to $x \in \{1, 2, \alpha, \beta\}$ $1 \cdots$ events due to pump-only laser pulse $2 \cdots$ events due to probe-only laser pulse $\alpha \cdots$ events in the pump-only experiment $\beta \cdots$ events in the pump-probe experiment
$n^{(x)}$	measured count rates $n^{(x)} = \{n^{(x)}_{\mu\nu}\}$, dimension: $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu]$
$q^{(x)}$	Monte Carlo time series of the spectrum $q^{(x)} = \{q^{(x)}_{\mu\nu}\}$, dimension: $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu$ x $N_{\text{sweep}}]$
N_{run}	Number of Monte Carlo steps between Monte Carlo measurements
N_{sweep}	Number of Monte Carlo measurements
$\mathcal{N}_\mu$	Number of elements in dimension μ
$\mathcal{N}_\nu$	Number of elements in dimension ν
$\mathcal{N}_p$	Number of measurements
N_{N_e,N_i}	Number of measurements where N_e electrons *and* N_i ions were detected.
π	Time series of experimental parameters: $\pi = \{\lambda_1, \lambda_2, \xi_i, \xi_e\}$, dimension: [4 x N_{sweep}]
λ_x	Mean number of events in x
ξ_i	Detection probability for ions
ξ_e	Detection probability for electrons

3 PEPICOBayes-Program

3.1 Function definition

The function returns four arguments and can be executed with six or eight arguments as input. Arguments seven and eight ($q_0^{(1)}$ and $q_0^{(2)}$) are start values for the spectra and optional. If no start spectra are passed the algorithm starts with flat spectra.

Input variables:

	Abbreviation	Variable name	Description
1	$n^{(\beta)}$	n_beta	measured pump-probe coincidence spectrum (dimension $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu]$)
2	$n^{(\alpha)}$	n_alpha	measured pump-only coincidence spectrum (dimension $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu]$)
3	N_{run}	Nrun	Number of Monte Carlo steps between measurements
4	N_{sweep}	Nsweep	Number of Monte Carlo measurements
5	parameter	parameter	Parameter vector: parameter $:= \{\sigma_{q^{(1)}}, \sigma_{q^{(\beta)}}, \sigma_{\lambda_1}, \sigma_{\lambda_2}, \sigma_{\xi_i}, \sigma_{\xi_e}, \mathcal{N}_p^{(\beta)}, N_{00}^{(\beta)}, N_{01}^{(\beta)}, N_{02}^{(\beta)}, N_{03}^{(\beta)}, N_{10}^{(\beta)}, N_{11}^{(\beta)}, N_{12}^{(\beta)}, N_{20}^{(\beta)}, N_{21}^{(\beta)}, N_{30}^{(\beta)}, \mathcal{N}_p^{(\alpha)}, N_{00}^{(\alpha)}, N_{01}^{(\alpha)}, N_{02}^{(\alpha)}, N_{03}^{(\alpha)}, N_{10}^{(\alpha)}, N_{11}^{(\alpha)}, N_{12}^{(\alpha)}, N_{20}^{(\alpha)}, N_{21}^{(\alpha)}, N_{30}^{(\alpha)}\}$
6	π_0	Pi0	Start vector of $\pi := \{\lambda_1, \lambda_2, \xi_i, \xi_e\}$
7	$q_0^{(1)}$		(*optional*) start values of $q^{(1)}$ (dimension $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu]$)
8	$q_0^{(2)}$		(*optional*) start values of $q^{(2)}$ (dimension $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu]$)

The size of a Monte Carlo step of variable $T \in \{q^{(1)}, q^{(\beta)}, \lambda_1, \lambda_2, \xi_i, \xi_e\}$ is Gaussian distributed with mean value zero and standard deviation σ_T. σ_T should be adjusted that p_{acc} is at the order of 50% in order to efficiently sample the probability distribution.

Output variables:

	Abbreviation	Variable name	Description
1	$q^{(1)}$	q1_timeseries	Time series of $q^{(1)}$ (dimension $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu$ x $N_{\text{sweep}}]$)
2	$q^{(2)}$	q2_timeseries	Time series of $q^{(2)}$ (dimension $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu$ x $N_{\text{sweep}}]$)
3	π	Pi	Time series of π (dimension $[4$ x $N_{\text{sweep}}]$)
4	p_{acc}	p_acc	Vector of acceptance rates with 6 entries: $p_{\text{acc}}(1)$: Acceptance rate of λ_1 $p_{\text{acc}}(2)$: Acceptance rate of λ_2 $p_{\text{acc}}(3)$: Acceptance rate of ξ_i $p_{\text{acc}}(4)$: Acceptance rate of ξ_e $p_{\text{acc}}(5)$: Acceptance rate of $q^{(1)}$ $p_{\text{acc}}(6)$: Acceptance rate of $q^{(\beta)}$

Note that the first entry in the time series is the start value of the corresponding variable.

3.2 Pseudocode of the algorithm

A Metropolis Hastings Monte Carlo algorithm is used to sample the probability distribution for $q^{(1)}$, $q^{(2)}$ and π. The algorithm samples λ_β and $q^{(\beta)}$ instead of λ_2 and $q^{(2)}$ because it is computationally less expensive.

PEPICOBayes($n^{(\beta)}$, $n^{(\alpha)}$, N_{run}, N_{sweep}, parameter, π_0, $q_0^{(1)}$, $q_0^{(2)}$)

```
PEPICOBayes(n^(β), n^(α), N_run, N_sweep, parameter, π_0, q_0^(1), q_0^(2) )
    read all input variables
    compute q^(β) and λ_β = λ_1 + λ_2
    for k < N_sweep
        for i < N_run
            suggest Monte Carlo step in λ_1, λ_β, ξ_e, ξ_i, q^(1) or q^(β)
            compute Monte Carlo step probability
            if update is accepted
                overwrite corresponding variable with the new value
            else
                do nothing
            end
        end
        compute q^(2) and λ_2
        copy λ_1, λ_2, ξ_e, ξ_i, q^(1) and q^(2) into output variables at Monte Carlo time k
    end
end
```

3.3 Start value for π

The start values of π can for example be approximated by the formula given by Stert et. al. [2]. In summary this means solving the following equation for λ

$$\frac{N_e N_i}{\lambda \mathcal{N}_p}\left(1+\lambda\left(1-\frac{N_e}{\lambda \mathcal{N}_p}\right)\left(1-\frac{N_i}{\lambda \mathcal{N}_p}\right)\right) e^{-\lambda\left(1-\left(1-\frac{N_e}{\lambda \mathcal{N}_p}\right)\left(1-\frac{N_i}{\lambda \mathcal{N}_p}\right)\right)} \approx N_{11} \tag{1}$$

and insert the resulting λ into

$$\xi_e \approx \frac{N_e}{\lambda \mathcal{N}_p} \tag{2}$$

$$\xi_i \approx \frac{N_i}{\lambda \mathcal{N}_p} \tag{3}$$

N_{11} is the total number of measured coincidencies and N_e and N_i are the total number of detected electrons and ions, respectively.

4 Results of example.m

In the example two ion types ($\mathcal{N}_\mu = 2$) and seven different electron flight times ($\mathcal{N}_\nu = 2$) were detected.
The result of the converged Monte Carlo computation for the example data should look like figure 3. Converged time series are shown in figure 1 and 2 for demonstration purposes. Check for correlations by evaluating the autocorrelation function or with techniques like jackknife or binning.

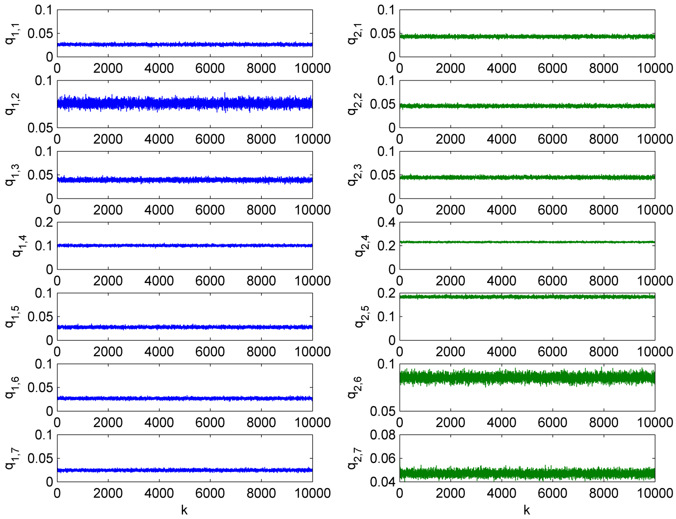

Figure 1: Time series of $q^{(2)}$.

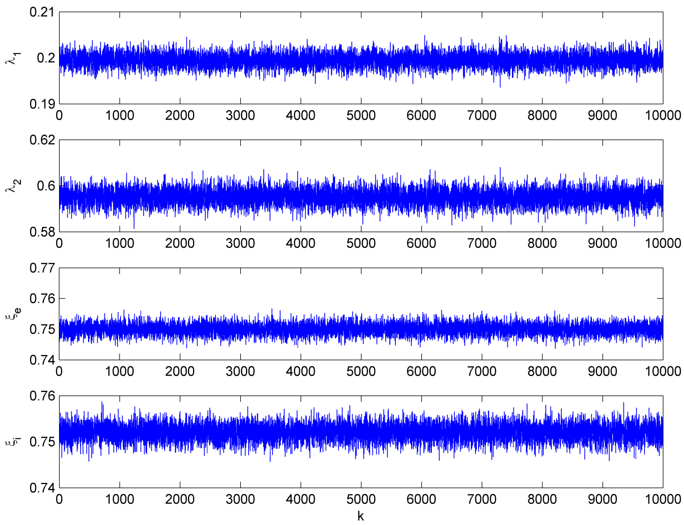

Figure 2: Time series of π. The real values are $\lambda_1 = 0.2$, $\lambda_2 = 0.6$, $\xi_i = 0.75$, $\xi_e = 0.75$.

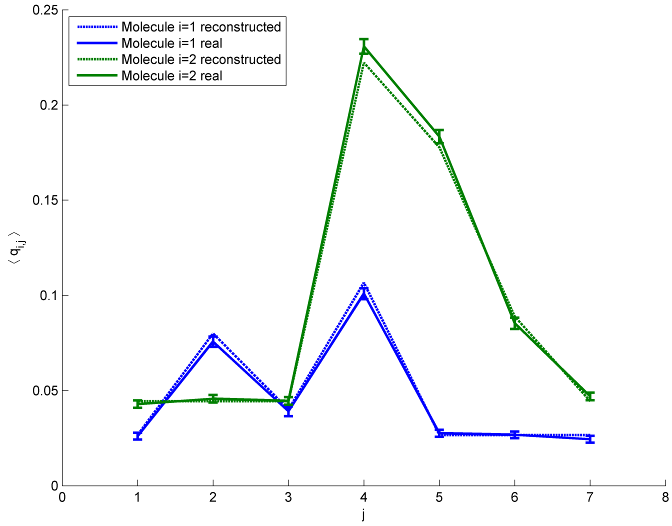

Figure 3: Reconstructed spectrum $q^{(2)}$.

5 Troubleshooting

5.1 Reconstruction is not converged

If the result is not converged the last entry of the time series of $q^{(1)}$, $q^{(2)}$ and π can be used as start parameter for a new calculation. Extend the Monte Carlo chain until the desired results are converged.

5.2 C file in MATLAB

In the downloaded folder are pre-compiled c files (tested with *Windows7*, *Windows10* and *Debian 8.9* - MATLAB version 2013a, 2016b). If the pre-compiled files dont work see `https://de.mathworks.com/help/matlab/matlab_external/what-you-need-to-build-mex-files.html`, follow the instructions and compile the c file on your computer.

References

[1] M. Rumetshofer, P. Heim, B. Thaler, W.E. Ernst, M Koch, and W. von der Linden. Analysis of femtosecond time-resolved photoelectron-photoion coincidence measurements applying bayesian probability theory.

[2] V. Stert, W. Radloff, C.P. Schulz, and I.V. Hertel. Ultrafast photoelectron spectroscopy: Femtosecond pump-probe coincidence detection of ammonia cluster ions and electrons. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics*, 5(1):97–106, 1999.