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 Refs. [1, 2]. 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.

Ref. [2] extends the algorithm developed in Ref. [1] by including fluctuating laser intensities. We offer the input data for the mock data analysis and experimental data presented in Ref. [2] in the download folder. These data can be analysed using the PEPICOBayes program.

2 Abbreviations

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

Abbreviation	Description
j	Symbol that refers to $j \in \{1, 2\}$ $1 \cdots$ events due to pump-only laser pulse $2 \cdots$ events due to probe-only laser pulse
ρ	Symbol that refers to $\rho \in \{\alpha, \beta\}$ $\alpha \cdots$ events in the pump-only experiment $\beta \cdots$ events in the pump-probe experiment
$n^{(\rho)}$	measured count rates $n^{(\rho)} = \{n^{(\rho)}_{\mu\nu}\}$, dimension: $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu]$
$q^{(j)}$	Monte Carlo time series of the spectrum $q^{(j)} = \{q^{(j)}_{\mu\nu}\}$, 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: $\pi = \{\underline{\lambda}_1, \underline{\lambda}_2, \sigma_1, \sigma_2, \xi_i, \xi_e\}$, dimension: $[6$ x $N_{\text{sweep}}]$
$\underline{\lambda}_j$	Mean number of events in channel j
σ_j	Fluctuations of mean number of events in channel j
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 := $\{\underline{\lambda}_1, \underline{\lambda}_2, \sigma_1, \sigma_2, \xi_i, \xi_e,$ $\sigma_{q^{(1)}}, \sigma_{q^{(2)}}, \sigma_{\underline{\lambda}_1}, \sigma_{\underline{\lambda}_2}, \sigma_{\sigma_1}, \sigma_{\sigma_2}, \sigma_{\xi_i}, \sigma_{\xi_e},$ $\mathcal{N}_p^{(\beta)}, N_{00}^{(\beta)}, N_{01}^{(\beta)}, N_{02}^{(\beta)}, N_{03}^{(\beta)}, N_{10}^{(\beta)}, N_{11}^{(\beta)}, N_{12}^{(\beta)}, N_{20}^{(\beta)}, N_{21}^{(\beta)}, N_{30}^{(\beta)},$ $\mathcal{N}_p^{(\alpha)}, N_{00}^{(\alpha)}, N_{01}^{(\alpha)}, N_{02}^{(\alpha)}, N_{03}^{(\alpha)}, N_{10}^{(\alpha)}, N_{11}^{(\alpha)}, N_{12}^{(\alpha)}, N_{20}^{(\alpha)}, N_{21}^{(\alpha)}, N_{30}^{(\alpha)}\}$
6	$q_0^{(1)}$		(*optional*) start values of $q^{(1)}$ (dimension $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu]$)
7	$q_0^{(2)}$		(*optional*) start values of $q^{(2)}$ (dimension $[\mathcal{N}_\mu$ x $\mathcal{N}_\nu]$)

The size of a Monte Carlo step of variable $T \in \{q^{(1)}, q^{(2)}, \underline{\lambda}_1, \underline{\lambda}_2, \sigma_1, \sigma_2, \xi_i, \xi_e\}$ 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. Note that the standard deviation of the step distribution for σ_j is $\min\{\sigma_{\sigma_j}, \sigma_j\}$. This means that the maximum value of the standard deviation of the step distribution is σ_{σ_j} but if σ_j gets near zero it ensures that the value zero is always one standard deviation away in the step size probability distribution. If the fluctuations are very small this gets important because it allows to visit phase space with a very small σ_j. For numerical stability the smallest value of σ_j is 10^{-8}.

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 $[6$ x $N_{\text{sweep}}]$)
4	p_{acc}	p_acc	Vector of acceptance rates with 6 entries: $p_{\text{acc}}(1)$: Acceptance rate of $\underline{\lambda}_1$ $p_{\text{acc}}(2)$: Acceptance rate of $\underline{\lambda}_2$ $p_{\text{acc}}(3)$: Acceptance rate of σ_1 $p_{\text{acc}}(4)$: Acceptance rate of σ_2 $p_{\text{acc}}(5)$: Acceptance rate of ξ_i $p_{\text{acc}}(6)$: Acceptance rate of ξ_e $p_{\text{acc}}(7)$: Acceptance rate of $q^{(1)}$ $p_{\text{acc}}(8)$: Acceptance rate of $q^{(2)}$

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.

PEPICOBayes($n^{(\beta)}$, $n^{(\alpha)}$, N_{run}, N_{sweep}, parameter, $q_0^{(1)}$, $q_0^{(2)}$)
    read all input variables
    for $k < N_{\text{sweep}}$
        for $i < N_{\text{run}}$
            suggest Monte Carlo step in $\underline{\lambda}_1$, $\underline{\lambda}_2$, σ_1, σ_2, ξ_e, ξ_i, $q^{(1)}$ or $q^{(2)}$
            compute Monte Carlo step probability
            if update is accepted
                overwrite corresponding variable with the new value
            else
                do nothing
            end
        end
        copy $\underline{\lambda}_1$, $\underline{\lambda}_2$, σ_1, σ_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. [3]. 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.

Attention: Using this starting point may decrease convergence time but it is important to test the stability of the result by starting at different starting points to ensure convergence and minimize the probability to be trapped at a local maximum.

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.

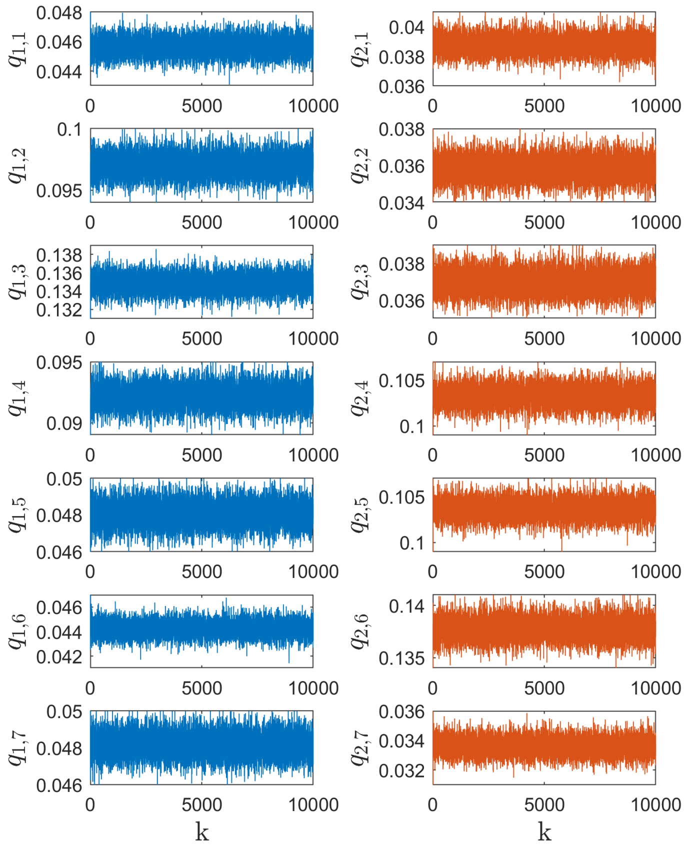

Figure 1: Time series of $q^{(2)}$.

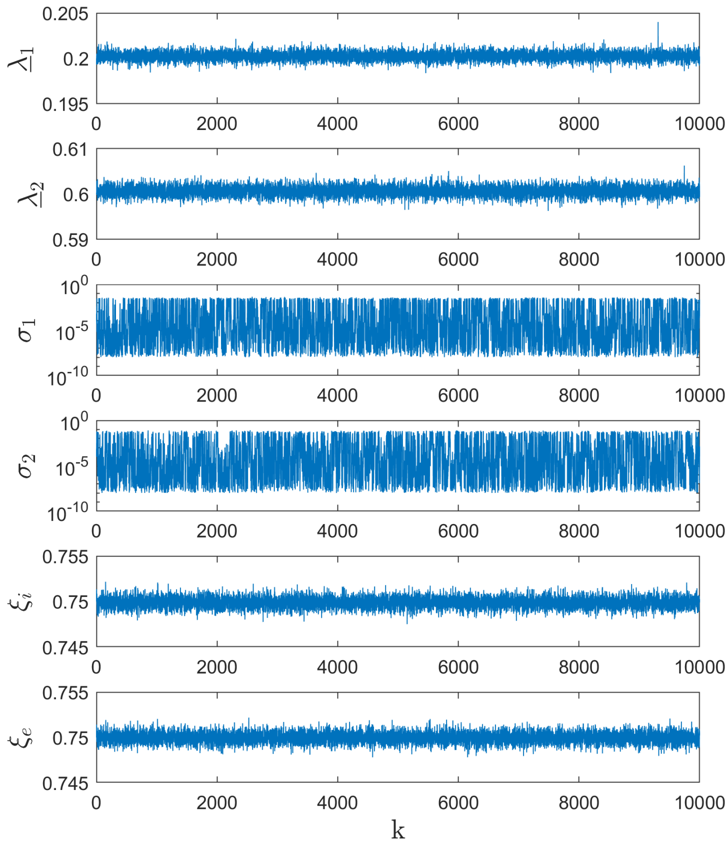

Figure 2: Time series of π. The real values are $\lambda_1 = 0.2$, $\lambda_2 = 0.6$, $\sigma_1 = 0$, $\sigma_2 = 0$, $\xi_i = 0.75$, $\xi_e = 0.75$. The algorithm can only evaluate that σ_j is very small but cant pin it down because in this regime it has no influence.

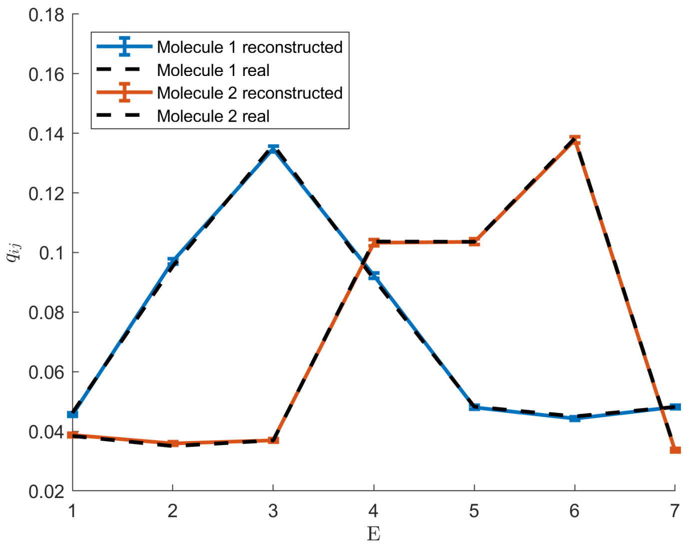

Figure 3: Reconstructed spectrum $q^{(2)}$.

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 computation. 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 *Windows10* and *Debian 9.6* - MATLAB version 2017b, 2018b). 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 pump-probe photoelectron-photoion coincidence measurements applying bayesian probability theory. *Phys. Rev. A*, 97:062503, Jun 2018.

[2] P. Heim, M. Rumetshofer, S. Ranftl, B. Thaler, W.E. Ernst, M. Koch, and W. von der Linden. Bayesian analysis of femtosecond pump-probe photoelectron-photoion coincidence spectra with fluctuating laser intensities. *Manuscript in preparation.*

[3] 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.