Jyvaskyla Summer School 2013
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Homework

1) In one of the first setups for 2D electronic spectroscopy in box geometry, a diffractive optical element generates the four beams and the delays are introduced by glass wedges. In another setup with conventional optics only, the beams are generated with broadband beam splitters and the delays are realized by pairwise beam manipulation with delay stages. In both cases, four pulses with identical spectra are employed.

   Imagine you have two samples. For the first one, the central wavelength of the employed laser beam is set to a certain value. For the second one, a different central wavelength is needed.

   Discuss briefly what changes within the setups when the central wavelength is set to a different value.

2) a) Look at the 2D spectra of the FMO complex published by the Fleming group in 2005. Explain why basically all off-diagonal signal is observed at one side of the diagonal only.

b) Would you expect to measure a 2D spectrum at a population time of a few nanoseconds? In the 2D spectra of the photoisomers of a molecular switch (Brixner group 2011), there is still a signal at a population time of several nanoseconds, although all molecules are in the electronic ground state at that time.

c) Where do these signals come from and how would photoisomerization between the two isomers show up at such a long population time?

3) You have a 2D setup in pump-probe geometry with a pulse shaper in the pump beam. The pulse shaper can both shape the amplitude and the phase of the incoming laser beam in a desired way. Explain why this allows both the recording of 2D spectra in the frequency-domain approach and in the time-domain approach.

4) In 2D electronic spectroscopy in pump-probe geometry with a pulse shaper, often a 4-step phase cycling scheme is employed. The phases of the two pump pulses are set to either a value of 0 or to a value of π, yielding four possible combinations. The signal is then obtained by combining the four measurements with the correct sign.

   Explain how this removes pump-probe signals as well as scattering contributions from a single pump pulse, and determine the right signs for the combination of the four measurements (i.e. which ones are added and which ones subtracted).

5) You have built a setup in box geometry for recording 2D electronic spectra. The signal and the local oscillator beam travel along the direction $-k_1+k_2+k_3$ and are detected with a spectrometer. The pulse pairs 1 and 2 as well as the pulse pair 3 and the local oscillator are inherently phase-locked. All pulses can be delayed independently.

   You would like to measure a double-quantum coherence 2D spectrum with the same setup, i.e. the phase-matching condition $k_1+k_2-k_3$. For this, two pulses arrive first simultaneously, and the delay between them and the third pulse is scanned to obtain the frequency axis ω_2.

a) How could this be done by not changing the position of the detector nor the beam directions?
b) Is the phase stability maintained?