Extracting coupling mode spectral densities with 2D electronic spectroscopy

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Abstract

2D electronic spectroscopy (2DES) is an experimental tool that can image how energy excitations evolve in time with femtosecond resolution. This makes 2DES a powerful technique for investigating quantum mechanical processes in real time, such as the transport of energy in light-absorbing molecules.

In general, these types of quantum systems never exist in isolation, but are coupled to some larger vibrational environment. Therefore, methods that can reconstruct the spectral density of the environment from experimental data can yield key insights into the impact of the environment on the system. Although such experimental methods exist, they can generally only access vibrational modes that couple diagonally to the system. However, it remains challenging to effectively reconstruct the spectral density of modes that couple different system states (1).

I will present a potential method for extracting such coupling modes spectral densities using 2DES. For this, we use a process tensor method that can simulate 2DES measurements in a numerically exact way (2,3). We additionally find that with a Markovian master equation, the signal simulated for our extraction method disappears. Since these simulations correspond to the calculation of multi-time correlation functions, our method could be a step towards designing an experimental protocol for testing the presence of memory effects (4).

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(3) R. de Wit et al. arXiv:2402.15454

(4) S. Milz et al. Phys. Rev. Lett. 123, 040401 (2019)

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