Coherent multiphoton spectroscopy for Hamiltonian reconstruction

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Multidimensional coherent spectroscopy has been extensively used to reveal quantum properties of complex molecular systems and can map system resonances to various dimensions in multidimensional frequency plots. At third order three dimensional maps are primary independent spectral elements, which encode underlying Hamiltonian of the system. However, is the inverse problem solvable?

The complete datasets at fifth order nonlinearity are five-dimensional, at seventh order are seven-dimensional, etc. Hence, the full amount of information becomes intractable at high orders. A simple two-pulse approach has been suggested for revealing full quantum ladder of an oscillator, thus allowing to map full potential surface of an oscillator [1] (Fig. 1).

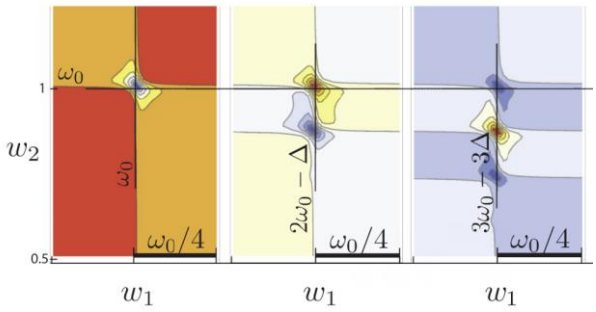

Figure 1. Coherent two-pulse spectra at third, fifth, seventh order ordered from left to right of a Morse oscillator.

The same approach could be used for revealing Hamiltonian of an excitonic molecular aggregate system in visible region. Our recent study of molecules with three electronic transitions (per chromophore) demonstrated that coherent 2D spectra reveal molecular transition energies of a molecular dimer [2]. By combining the two approaches we demonstrate that high nonlinear order two-pulse coherent spectra in the spirit of ref. [1] can be used to reveal complete map of chromophore transition energies for an arbitrary number of coupled molecules [3].

References

[1] D. Abramavicius, Revealing full quantum ladder by non-linear spectroscopy, Lith. J. Physics, **60**, 154-166 (2020).

[2] K. Zakutauskaitė, M. Mačernis, H. H. Nguyen, J. P. Ogilvie, D. Abramavičius, Extracting the excitonic Hamiltonian of a chlorophyll dimer from broadband two-dimensional electronic spectroscopy, *J. Chem. Phys.* **158**, 015103 (2023).

[2] J. P. Ogilvie, D. Abramavičius, Quantum protocol for unraveling excitonic system molecular Hamiltonian, *in preparation*.