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Coherent Control from Nano- to Macroscales

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Coherent control of molecules is generally performed such that a microscopic sample volume, as determined by the laser focus diameter, is irradiated with a shaped laser pulse, then the photophysical or photochemical outcome is measured, and the next (modified) pulse shape is applied to a fresh ensemble of molecules under identical initial conditions. Two restrictions of this now well-established scheme of "microscale" learning control can be identified: (1) The best spatial resolution for control is limited by diffraction to half the wavelength of the light field, and (2) the efficiency of the photoreaction may be very low, generating only small amounts of photoproducts. It will be shown how both limitations can be overcome by developing coherent control methods for applications not only on the microscale, but also on (1) the nanoscale and (2) the macroscale.

For nanoscale coherent control, we combine adaptive polarization shaping of femtosecond laser pulses with concepts from nano-optics. Exploiting the properties of electromagnetic near fields in the vicinity of suitable nanostructures, one can generate user-specified control fields with subwavelength spatial resolution and femtosecond timing in a flexible fashion [1]. The feasibility of such schemes was shown in a recent experiment [2] by measuring the nano-optical field properties via photoemission electron microscopy and providing control through adaptive polarization shaping. Apart from the field itself, it is also possible to manipulate nanoscale forces, possibly leading to a new type of single-molecule "mechanical" control.

For macroscale coherent control and spectroscopy, we developed an accumulative approach that allows us time-resolved analysis of photochemical reactions that have extremely low quantum yields and would not be visible in conventional transient absorption [3]. The experimental setup allows for the interaction of many identical laser pulses with one sample volume. After a well-controlled time, the accumulated stable photoproducts are detected. Time-resolved or pulse-shaping experiments can be implemented by changing delays or pulse shapes after automatically exchanging the sample volume. The accumulative scheme was applied to the photoconversion reaction of green fluorescent protein (GFP). Effects of accumulation and diffusion of products and reactants in the detection and interaction volume are described quantitatively, providing a calibration of the setup. The detection sensitivity is better than 0.01 mOD per pulse.

References:
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