

# Time-resolved Pump–Probe Spectroscopy to Follow Valence Electron Motion

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One of the major endeavors of chemical physics over the last decades has been the study of microscopic dynamics on ever shorter time scales. Recent advances in light sources make it timely to consider probing the fastest time scales relevant to chemistry, the motions of valence electrons. Anticipating the experimental realization of attosecond pulses [1] with photon energies up to 1 keV [2], we have developed a simple theory, which connects the evolution of a non-stationary electronic state (presumed to be created by a few-cycle UV pump pulse) to an XUV/X-ray probe signal. The electronic states we wish to follow evolve on time scales of a few to several femtoseconds. The essential principle is that the dynamic valence occupancy structure of these states can be probed, resolved in both space and time, by taking advantage of the inherent locality of core–valence transitions and the comparatively short time scale on which they can be produced. The presented formalism is built in terms of the time-dependent single-particle reduced density matrix; it provides a compact theoretical framework for understanding experimental results, and it can be supported by any ab initio electronic structure model. This has been applied to dynamic density matrices obtained from time-domain electronic structure calculations at the extended, second-order algebraic diagrammatic construction [ADC(2)-x] level [3].

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[2] T. Popmintchev, M.-C. Chen, P. Arpin, M. M. Murnane and H.C. Kapteyn, *Nat. Photonics* 4, 822 (2010).

[3] A. B. Trofimov and J. Schirmer, *J. Phys. B* 28, 2299 (1995).