

Electrons in motion, or: Can we make a Hartree-Fock state?

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Recent progress in generating intense laser fields, has pushed the timescale for probing dynamical processes in atomic and molecular systems down to the attosecond domain ($1 \text{ as} = 10^{-18} \text{ s}$). In parallel with experiments, theoretical methods are being developed to treat explicitly time-dependent electronic motion after photoexcitation. This talk describes our efforts to extend *ab initio* wavefunction based methods of stationary electronic structure theory, to the explicitly time-dependent domain. In particular, time-dependent configuration interaction (TD-CI) and time-dependent complete active space SCF method (TD-CASSCF) [1] will be introduced as systematically improvable, correlated methods for propagating electronic wavefunctions in real time.

Armed with these methods, we seek to control electron motion at will, using shaped, ultrashort laser pulses. For instance, we may ask as to whether it is possible to create a *Hartree-Fock state* – a hitherto purely theoretical concept – starting from the (correlated) ground state of an atom or molecule [3]. In particular alkaline earth atoms seem suitable for an actual experiment to realize controlled, correlated electron motion, *cf.* Fig.1. A Hartree-Fock state is an electron wavepacket, a non-stationary state whose fate is also of interest: We find that electron correlation reappears on an attosecond timescale, when starting from a Hartree-Fock reference. Finally, we also demonstrate how explicitly time-dependent methods can be used to calculate response properties of molecular systems after non-resonant or resonant, excitation with ultrashort laser pulses [2]

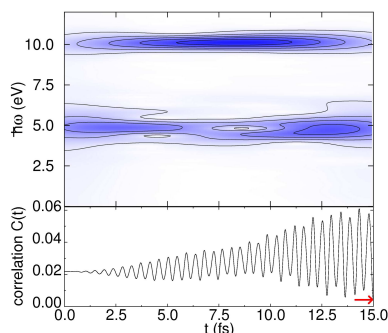


Fig.1: A series of laser pulses obtained from optimal control theory (upper), controls the amount of “correlation” in a Mg atom (below) [3].

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[3] M. Nest, M. Ludwig, I. Ulusoy, T. Klamroth, and P. Saalfrank, *J. Chem. Phys.*, 138, 164108, 2013.