Correlated many-electron dynamics in real time using wavefunction methods

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In recent years, in part due to the progress made in generating and controlling intense laser fields, the timescale of dynamical processes in atomic and molecular systems has been pushed into the so-called attosecond domain. In parallel to the experimental work, theoretical methods are being developed to treat explicitly time-dependent electronic motion after photoexcitation. This talk describes correlated, explicitly time-dependent wavefunction-based N-electron methods and their application to selected molecular problems.

The focus of the talk is on many-electron methods in which the time-dependent N-electron wavefunction is represented as a sum of Slater determinants. The first approach of this type to be used here is time-dependent configuration interaction (TD-CI), where only the coefficients of the determinants are time-dependent. The second approach adopted here is the time-dependent complete active space SCF method (TD-CASSCF), for which both the coefficients of, and the Slater determinants themselves are time-dependent. Extensions of the methods to include ionization, dissipation, and optimal control strategies for excited electron dynamics, are also presented.

The methods will then be applied (i) for laser-pulse excitation and switching of real molecules without [1,2,3] and with [4] a dissipative environment, (ii) for the calculation of response properties of small molecules [5], (iii) for long-range intermolecular charge transfer [6], and (iv) for controlled electron dynamics in molecules [7].

[1] P. Krause, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **123**, 074105 (2005).
[2] M. Nest, R. Padmanaban, and P. Saalfrank, J. Chem. Phys. **126**, 214106 (2007).
[3] F. Remacle, M. Nest, and R.D. Levine, Phys. Rev. Lett. **99**, 183902 (2007).
[4] J.C. Tremblay, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **129**, 0843201 (2008).
[5] P. Krause, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **127**, 034107 (2007).
[6] S. Klinkusch, T. Klamroth, and P. Saalfrank, PCCP **11**, 3875 (2009).
[7] J.C. Tremblay and P. Saalfrank, Phys. Rev. A **78**, 063408 (2008).