Time-dependent complete-active-space self-consistent field method for multielectron dynamics in intense laser fields

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We propose a flexible time-dependent many-electron theoretical method for multielectron dynamics in intense laser fields, based on the concept of the complete-active-space self-consistent field (CASSCF) [1]. The method, called TD-CASSCF, allows compact yet accurate representation of ionization dynamics in many-electron systems, thus largely extends the applicability of the rigorous MCTDHF (multiconfigurational time-dependent Hartree-Fock) method [2, 3], while keeping the accuracy.

It is reasonable to expect that in a large molecule interacting with high-intensity, long wavelength laser, the deeply bound electrons remain non-ionized, while only the higher-lying valence electrons ionize appreciably. For the bound electrons, a closed shell description of the Hartree-Fock type would be acceptable. However, fully correlated treatment is required for ionizing electrons to describe the seamless transition from the closed-shell-dominant ground-state to the symmetry-breaking continuum. The CASSCF provides an ideal *ansatz* for such problem. It introduces the concept of *core* and *active* orbital subspaces, and configuration-interaction expansion is limited to the determinants with core orbitals being doubly occupied. It is possible to further split the core space to *frozen-core* (timely fixed) and *dynamical-core* (allowed to vary in time, in response to the field) subspaces. See Fig. 1.

Figure 2 shows the ionization probabilities of one-dimensional LiH-LiH model, induced by a 3-cycle laser pulse of $\sin^2$ envelope with wavelength 750 nm and peak intensity 4×10^{14} W/cm^2. As seen in the figure, TD-CASSCF with 4 active electrons closely reproduces the results of MCTDHF with the same number of orbitals. Details of the theory and numerical applications will be presented in this contribution to ECAMP11.

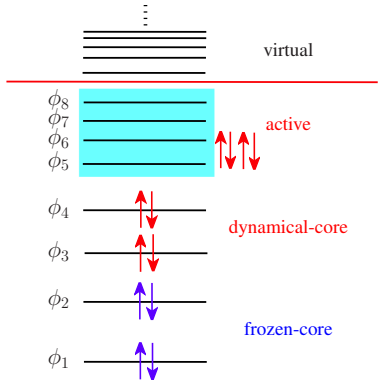

Fig.1: TD-CASSCF concept, illustraing a 12 electron system with 4/4/4 electrons in frozen-core/dynamical-core/active orbital subspaces, respectively.

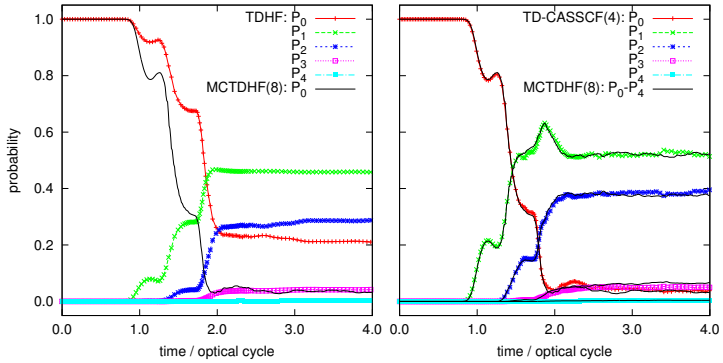

Fig. 2: Ionization probabilities (P_n for n-electron ionization) of 1D LiH-LiH as a function of time. Results of TDHF (left), TD-CASSCF with 4 active electron (right), and MCTDHF (black solid lines). Total numer of orbitals in both TD-CASSCF and MCTDHF is 8.

References:
[1] O. Roos, P. R. Taylor, and P. E. Siegbahn, Chem. Phys. **48**, 157 (1980).
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[3] T. Kato and H. Kono, Chem. Phys. Lett. **392**, 533 (2004).