Time-Dependent Multiconfiguration Methods for Multielectron Dynamics in Intense Laser Fields

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Abstract: Time-dependent complete-active-space and *general* multiconfiguration self-consistent-field methods are formulated. The concept of orbital subspacing in these methods enables compact yet accurate description of multielectron dynamics in intense laser fields.

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1. Introduction

One of the main objectives of strong field physics and attosecond science is a direct measurement and control of electron motions in atoms and molecules. The time-dependent Schrödinger equation (TDSE) provides the rigorous theoretical framework for investigating such electron dynamics. However, direct real-space simulations of TDSE for multielectron systems are extremely difficult. The multiconfiguration time-dependent Hartree-Fock (MCTDHF) method adopts the full configuration interaction (Full-CI) expansion of the total wavefunction with adaptive (timely varying) orbital functions [1]. The total wavefunction of an N-electron system is given by

$$\Psi(t) = \sum_I C_I(t)\Phi_I(t), \quad \Phi(t) = |\phi_i(1)\phi_j(2)\cdots\phi_k(N)\rangle, \tag{1}$$

where $\Phi_I(t)$ is an N-electron determinant constructed from orbital functions $\{\phi_i\}$. Though powerful, this method suffers from the limitation in the applicability due to the exponential increase of the complexity against N.

2. Theory

To circumvent this difficulty, we proposed the time-dependent complete-active-space self-consistent-field (TD-CASSCF) method [2]. The CASSCF *ansatz* introduces the concept of core and active orbital subspaces, and CI expansion of Eq.(1) is limited to the determinants including doubly occupied core orbitals. See Fig. 1 (a). The core orbitals are formulated either as frozen-core (timely fixed) or dynamical-core (allowed to vary in time). The equations of motion for the method is derived based on the time-dependent variational principle.

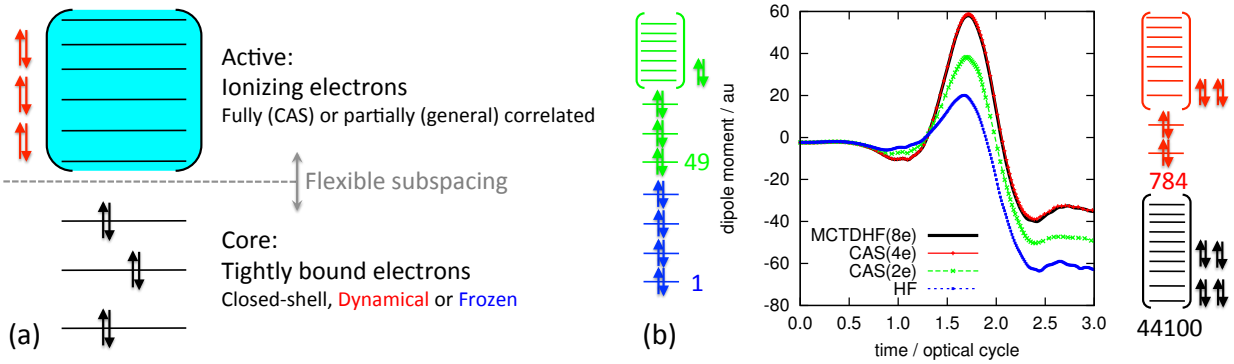

Fig. 1. (a) The concept of orbital subspacing, illustrating the 12 electron wavefunction with 6 core and 6 active electrons. The active electrons are fully (TD-CASSCF) or partially (general TD-MCSCF) correlated among the active orbitals. The core orbitals are doubly occupied by core electrons. (b) Time evolution of dipole moment of 1D-$(LiH)_2$ exposed to an intense femto second laser pulse. See text for more details. The subspacing schemes and the CI dimension in Eq. (1) are given for each method.

3. Numerical assessments

To test the performance of the TD-CASSCF method, we applied it to the ionization dynamics of various one-dimensional (1D) multielectron models. Computational details are given in Ref. [2]. Figure 1 (b) shows the time evolution of the dipole moment of 1D LiH dimer (8 electrons) induced by a three-cycle laser pulse with wavelength 750 nm and peak intensity 4×10^{14} W/cm^2. As seen in the figure, the TD-CASSCF(4e) method with four active electrons closely reproduces the MCTDHF(8e) results with all eight electron correlated. The CI dimension of the former wavefunction is less than 2% of the latter.

Next we show in Fig. 2 the high-order harmonic generation (HHG) spectra of 1D LiH clusters, $(\mathrm{LiH})_n$ with $n = 1, 2, 3$. The laser profile is the same as in Fig. 1. The ground state of $(\mathrm{LiH})_n$ was found to consist of n deeply bound (core) and n weakly bound (valence) orbitals in the Hartree-Fock picture [2]. Thus n active electrons should be appropriate for the $(\mathrm{LiH})_n$ model. The three-step-model predictions (Koopmans) of the cutoff positions are indicated in the figure. We observe the followings: (i) Frozen-core and dynamical-core treatments highlights the physical origins of the first (valence) and second (core) cutoffs: the photon emission above the valence cutoff is absent in the frozen-core response. (ii) For $(\mathrm{LiH})_n$ with n =1 and 2, TD-CASSCF method with n active electrons well reproduces the HHG of MCTDHF method. The MCTDHF calculation of $(\mathrm{LiH})_3$ was impossible due to the excessively large CI dimension (more than 25 million), while the CASSCF expansion remains quite feasible with 48400 determinants. Also shown in Fig. 2 (c) is an example of the *general* TD-MCSCF approach [3], including a closed-shell reference determinant and up to triply excited configurations from the reference (TD-CISDT) with adaptive orbitals. This method uses as few as 7000 configurations, yet gives an accurate HHG spectrum, showing a good agreement with that of TD-CASSCF.

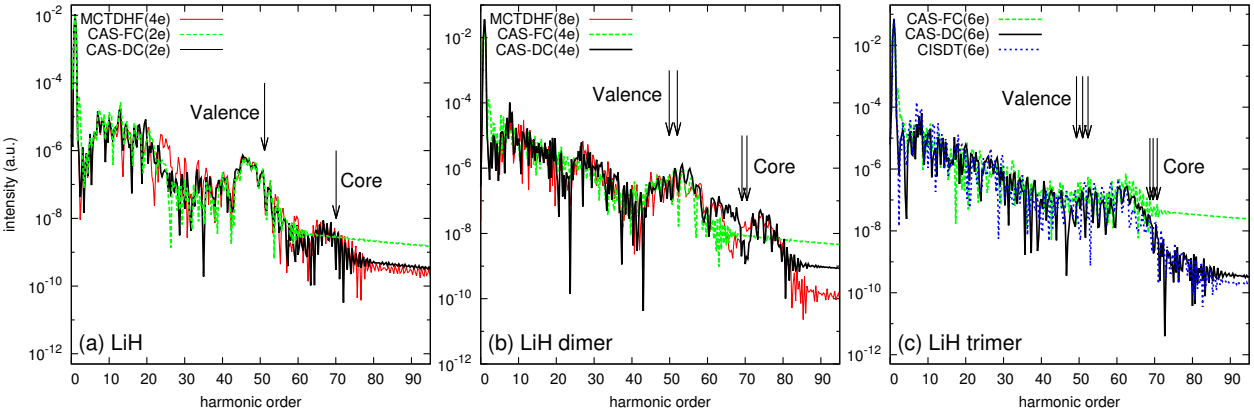

Fig. 2. HHG spectra of $(\mathrm{LiH})_n$ clusters with n = 1, 2, and 3 in panels (a), (b), and (c), respectively. Results of MCTDHF, TD-CASSCF with frozen-core (CAS-FC) and dynamical-core (CAS-DC) are compared. The HHG spectrum of TD-CISDT method is also shown for $(\mathrm{LiH})_3$. See text for more details.

4. Summary

The TD-CASSCF and general TD-MCSCF methods are developed. The concept of orbital subspacing enables accurate representation of electron dynamics of systems with large number of electrons, which was inaccessible with the MCTDHF method. The flexibility of these approaches provides deeper understanding of the physical mechanisms involved in an investigated process. These methods would open the new possibilities of first-principle theoretical study of intense laser induced ultrafast phenomena in realistic atoms and molecules.

References

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