Time-dependent Coupled-cluster Theory for Laser-driven multielectron dynamics

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[Abstract] This contribution deals with the implementation of time-dependent optimized coupled-electron pair approximation (TD-OCEPA) method as an approximate version of the time-dependent optimized coupled-cluster (TD-OCC) method [T. Sato et al., J. Chem. Phys. 148, 051101 (2018)] to broaden the applicability to the larger chemical systems for the study of laser-driven multielectron dynamics. As a numerical test, we have employed the method to understand laser-induced dynamics in Kr atom and compared with the results of time-dependent Hartree-Fock (TDHF), time-dependent optimized coupled-cluster double (TD-OCCD), and time-dependent complete-active-space self-consistent field (TD-CASSCF) methods. The implemented method retains the size-extensive and gauge-invariant description of multielectron dynamics of the parent TD-OCC formulation.

[Introduction] The theoretical study of laser-driven multielectron dynamics [1] demands comprehensive treatment of the electron correlation [2, 3]. The multiconfiguration time-dependent Hartree-Fock (MCTDHF) method [4, 5] and time-dependent complete-active-space self-consistent-field (TD-CASSCF) method [2, 6] are the most suited for this purpose. However, factorial escalation of computational cost limits the applicability of these methods to small chemical systems. Efficient methods have been developed by retaining configuration interaction (CI) expansion of the wavefunction up to a certain practical level [7, 8], however, which resulted in the loss of the criteria of size-extensivity. Therefore, the choice of the coupled-cluster wavefunction instead of the truncated CI wavefunction is a worthy choice. Recently, we have derived and implemented a polynomial cost-scaling time-dependent optimized coupled-cluster (TD-OCC) method considering double and triple excitation amplitudes (TD-OCCDT) with optimized orthonormal orbitals, where both the orbitals and the amplitudes are time-dependent and propagated in time [9]. In the present work, we consider the formulation and implementation of orbital optimized coupled-electron pair approximation [10] method in the time-dependent framework (TD-OCEPA). The TD-OCEPA method scales \(N^6\) where \(N\) is the number of active orbitals. The solution of the \(T_2\) amplitude equation is sufficient, and we do not need to solve for the \(\Lambda_2\) amplitudes since \(\Lambda_2 = T_2^+\) due to the real-valued [6], linear structure of the functional.

[Method] We choose to work with the real-action formulation of the time-dependent variational principle which requires the definition of a Lagrangian,

\[
\delta S = 0, \quad S = \Re \int_{t_0}^{t_1} L(t)dt = \frac{1}{2} \int_{t_0}^{t_1} (L(t) + L^*(t))dt,
\]

\[
L_{TD-OCC} = \langle \Phi | (1 + \hat{\Lambda}) e^{-\hat{T}} (\hat{H} - i \hat{\partial}_t) e^{\hat{T}} | \Phi \rangle,
\]

\[
\hat{T} = \tau_{ij}^{ab} \hat{E}_{ij}^{ab} + \tau_{ijk}^{abc} \hat{E}_{ijk}^{abc} + \ldots
\]

\[
\hat{\Lambda} = \lambda_{ab}^{ij} \hat{E}_{ab}^{ij} + \lambda_{abc}^{ijk} \hat{E}_{abc}^{ijk} + \ldots
\]

\[
L_{TD-OCEPA} = \langle \Phi | (1 + \hat{\Lambda}_2) \{(\hat{H} - i \hat{\partial}_t)(1 + \hat{T}_2)\} | \Phi \rangle, \quad \hat{\Lambda}_2 = T_2^+
\]

The EOMs for the amplitudes \(\tau_{ij}^{ab}\) and orbitals are obtained from the stationary conditions, \(\delta S / \delta \lambda_{ab}^{ij} = 0, \delta S / \delta \Delta_\mu^\nu = 0\), respectively, as

\[
i \tau_{ij}^{ab} = \langle \Phi_{ij}^{ab} | [(\hat{H} - i \hat{X})(1 + \hat{T}_2)] c | \Phi \rangle,
\]
\[ i|\psi_p\rangle = (1 - \hat{p})|\psi_p\rangle + \hat{W_s}^T|\psi_q\rangle P_{or}^{qs}(D^{-1})^{qs}_p + i|\psi_q\rangle X^q_p, \tag{7} \]

\[
D^p_q = \frac{1}{2}(\rho^p_q + \rho^{qs}_{qs}), \quad P^{qs} = \frac{1}{2}(\rho^{qs} + \rho^{qs})^r, \\
p^p_q = \langle \Phi|(1 + \Lambda_2)[c_q^s c_p(1 + \hat{T}_2)]|\Phi\rangle_c, \\
\rho^{qs} = \langle \Phi|(1 + \Lambda_2)[c_q^s c_p(1 + \hat{T}_2)]|\Phi\rangle_c,
\]

where \(c\) stands for the connectedness of the diagrams. The effect of the laser electric field is introduced through the one-body part of the Hamiltonian

\[
H(t) = \sum_i N \left[ h_0(r, p) + V_{\text{ext}}(t) + \sum_{i<j} \frac{1}{r_{ij}} \right] \tag{8}.
\]

The Hamiltonian \(H\) is given by Eq. 8, where \(h_0\) is the one-electron part of the atomic Hamiltonian, and \(V_{\text{ext}}\) is the laser-electron interaction.

**Results and Discussion** In our simulation, we opted for the wavelength of 1500 nm with three cycle laser pulse having \(\sin^2\) envelope. Dipole approximation and velocity gauge are invoked to include the laser electric field. We have studied time-dependent dipole-moment, probability of finding an electron outside a sphere of a radius of 20 a.u., and high-harmonic generation (HHG) spectra of Kr atom using TDHF, TD-OCEPA, TD-OCCD, and TD-CASSCF methods presented in Fig. 1. The performance of the TD-OCEPA method is found to be better than the TD-OCCD method in comparison to the TD-CASSCF method with a substantial reduction in the computational cost. On the other hand, TDHF tends to underestimate for both dipole moment and ionization probability. For HHG spectra, all the methods qualitatively predict near-identical spectra with TD-OCEPA method except for the TDHF which lacks finer details, especially at the higher plateau region.

![Fig. 1](image-url) Time-dependent dipole moment (left), single ionization probability (middle), and HHG spectra (right) of Kr exposed to a laser pulse with a wavelength of 1500 nm and intensity of \(1.8 \times 10^{14}\) W/cm\(^2\). Comparison of the results of TD-CASSCF, TD-OCCD, TD-OCEPA, and TDHF methods. Eight valence electrons are correlated among 13 active orbitals for the correlated methods.

**References**