Time-dependent optimized coupled-cluster method for multielectron dynamics II. A coupled electron-pair approximation

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We report the implementation of a cost-effective approximation method within the framework of time-dependent optimized coupled-cluster (TD-OCC) method [J. Chem. Phys. 148, 051101 (2018)] for real-time simulations of intense laser-driven multielectron dynamics. The method, designated as TD-OCEPA0, is a time-dependent extension of the simplest version of the coupled-electron pair approximation with optimized orbitals [J. Chem. Phys. 139, 054104 (2013)]. It is size extensive, gauge invariant, and computationally much more efficient than the TD-OCC with double excitations (TD-OCCD). We employed this method to simulate the electron dynamics in Ne and Ar atoms exposed to intense near infrared laser pulses with various intensities. The computed results, including high-harmonic generation spectra and ionization yields, are compared with those of various other methods ranging from uncorrelated time-dependent Hartree-Fock (TDHF) to fully-correlated (within the active orbital space) time-dependent complete-active-space self-consistent-field (TD-CASSCF). The TD-OCEPA0 results show a good agreement with TD-CASSCF ones for moderate laser intensities. For higher intensities, however, TD-OCEPA0 tends to overestimate the correlation effect, as occasionally observed for CEPA0 in the ground-state correlation energy calculations.

I. INTRODUCTION

In recent years there has been a significant breakthrough in the experimental techniques to measure and control the motions of electrons in atoms and molecules, for example, measurement of the delay in photoionization1,2, migration of charge in a chemical process3,4 and dynamical change of the orbital picture during the course of bond breaking or formation5,6. Atoms and molecules interacting with laser pulses of intensity $10^{14}$ W/cm$^2$ or higher in the visible to mid-infrared region, show highly nonlinear response to the fields such as above-threshold ionization (ATI), tunneling ionization, nonsequential double ionization (NSDI) and high-harmonic generation (HHG). All these phenomena are by nature nonperturbative5. The essence of the attosecond science lies in the HHG9–11, one of the most successful means to generate ultrashort coherent light pulses in the wavelength ranging from extreme-ultraviolet (XUV) to the soft x-ray regions12–15, which can be used to unravel the electronic structure5,6 or dynamics16 of many-body quantum systems. The HHG spectrum is characterized by a plateau where the intensity of the emitted light remains nearly constant up to many orders, followed by a sharp cutoff7.

A whole lot of numerical methods have been developed to understand atomic and molecular dynamics in the intense laser field (For a comprehensive review on various wavefunction-based methods for the study of laser-induced electron dynamics, see Ref. 18) to catch up with the progress in the experimental techniques. In principle, “the best” one could do is to solve the time-dependent Schrödinger equation (TDSE) to have an exact description. However, the exact solution of the TDSE is not feasible for systems containing more than two electrons19–28. As a consequence, single-active electron (SAE) approximation has been widely used, in which the outermost electron is explicitly treated with the effect of the other electrons modeled by an effective potential. The SAE model has been successful in numerically exploring various high-field phenomena29,30. However, the missing electron correlation in SAE makes this method at best qualitative.2

Among other established methods, the multiconfiguration time-dependent Hartree-Fock (MCTDF)31–35 and time-dependent complete-active-space self-consistent-field (TD-CASSCF)36–38 are the most competent theoretical methods for the study of the laser-driven multielectron dynamics where both configuration interaction (CI) coefficients and the orbitals are propagated in time. The time-dependent (or optimized in the sense of time-dependent variational principle) orbital formulation widens the applicability of these methods by allowing to use a fewer number of orbitals than the case of fixed orbital treatments. Though powerful, the dilemma with these full CI-based methods is the applicability to large atomic or molecular systems due to the factorial escalation of the computational cost with respect to the number of electrons. To subjugate this difficulty, more approximate, thus computationally more efficient time-dependent multiconfiguration self-consistent-field (TD-MCSCF) methods have been developed, based on the truncated CI expansion within the chosen active orbital space39–42, compromising size extensivity.

To regain the size extensivity, the coupled-cluster expansion43–45 of the time-dependent wavefunction emerges...
naturally as an alternative to the truncated CI expansion. The initial ideas of developing time-dependent coupled-cluster go back to as early as 1978 by Schönhammer and Gunnarsson, and Hoodbhoy and Negele. Here we take note of a few theoretical works on the time-dependent coupled-cluster method for time-independent Hamiltonian and Hoodbhoy and Negele. (OATDCC) method for time-independent Hamiltonian and dynamics of molecules, using time-independent orbitals and the CI wavefunction reconstructed from the propagated CC amplitudes to evaluate the expectation value of operators.

In 2012, Kvaal pioneered a time-dependent coupled-cluster method using time-dependent orbitals for electron dynamics, designated as orbital-adaptive time-dependent coupled-cluster (OATDCC) method. Based on Arponen’s bi-orthogonal formulation of the coupled-cluster theory, the OATDCC method is derived from the complex-analytic action functional using time-dependent biorthonormal orbitals. Recently, we have also developed time-dependent optimized coupled-cluster (TD-OCC) method based on the real action functional using time-dependent orthonormal orbitals. The TD-OCC method is a time-dependent extension of the orbital optimized coupled-cluster method popular in the stationary electronic structure theory. It is not only size extensive, but also gauge invariant, and scales polynomially with respect to the number of active electrons $N$. Theoretical as well as numerical comparison of closely-related OATDCC and TD-OCC methods is yet to be done, and will be discussed elsewhere. (See Refs. 64 and 65 for recent theoretical accounts on orbital-optimized and time-dependent coupled-cluster methods, and Refs. 66 and 67 for the gauge-invariant coupled-cluster response theory with orthonormal and biorthonormal orbitals, respectively.)

We have implemented TD-OCC method with double excitations (TD-OCCD) and double and triple excitations (TD-OCCDT) within the chosen active space, of which the computational cost scales as $N^6$ and $N^9$, respectively. Such scalings are milder than the factorial one in the MCTDHF and TD-CASSCF methods; nevertheless, a lower cost alternative within the TD-OCC framework is highly appreciated to further extend the applicability to heavier atoms and larger molecules interacting with intense laser fields.

One such low-cost model is a family of the methods called coupled-electron pair approximation (CEPA), originally introduced in 1970’s. In particular, the simplest version of the family, denoted as CEPA0 (See Sec. II for the definition), is recently attracting a renewed attention due to its high cost-performance balance. The orbital-optimized version of this method (OCEPA0) has been also developed and applied to the calculation of, e.g. equilibrium geometries and harmonic vibrational frequencies of molecules, which motivated us to extend it to the time-dependent problem.

In the present article, we report the implementation of the time-dependent, orbital-optimized version of the CEPA0 theory, hereafter referred to as TD-OCEPA0. Pilot applications to the simulation of induced dipole moment, high-harmonic spectra, and ionization probability in three different laser intensities for Ne and Ar are reported. We compare TD-OCEPA0 results with those of other methods ranging from uncorrelated TDHF, TD-MCSCF with a truncated CI expansion, TD-OCCD, and fully correlated TD-CASSCF, using the same number of active orbitals (except for TDHF) to quantitatively explore the performance of TD-OCEPA0. The computational cost of TD-OCEPA0 scales as $N^6$, which is formally the same as that of TD-OCCD; however as shown in Sec. II, one need not solve for the double deexcitation operator $A_2$, but it is sufficient to propagate the double excitation operator $T_2$ since $A_2 = T_2$. This leads to a great saving of the computational time as numerically demonstrated in Sec. III.

The manuscript is arranged as follows. A concise description of the TD-OCEPA0 method is presented in Sec. II. Section III discusses the computational results. Finally, we made our concluding remark in Sec. IV. We use Hartree atomic units unless stated otherwise, and Einstein convention is implied throughout for summation over orbital indices.

II. METHOD

A. Background

We consider a system with $N$ electrons governed by the following Hamiltonian,

$$H = \sum_{i=1}^{N} h(\mathbf{r}_i, \mathbf{p}_i) + \sum_{i=1}^{N-1} \sum_{j=2}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and canonical momentum of an electron $i$. The corresponding second quantized Hamiltonian reads

$$\hat{H} = h_{\mu}^{\nu} \hat{E}_{\mu}^{\nu} + \frac{1}{2} w_{\mu\lambda}^{\nu\gamma} \hat{E}_{\mu\gamma}^{\nu\lambda},$$

where $\hat{E}_{\mu}^{\nu} = \hat{c}_{\mu}^\dagger \hat{c}_{\nu}$ and $w_{\mu\lambda}^{\nu\gamma} = \hat{c}_{\mu}^\dagger \hat{c}_{\lambda}^\dagger \hat{c}_{\gamma} \hat{c}_{\nu}$, with $\hat{c}_{\mu}^\dagger$ ($\hat{c}_{\mu}$) being a creation (annihilation) operator in a complete, orthonormal set of $2n_{\text{bas}}$ spin-orbitals $\{\psi_{\mu}\}$, where $n_{\text{bas}}$ is the number of basis functions (or the number of grid points) to expand the spatial part of $\psi_{\mu}$, and

$$h_{\mu}^{\nu} = \int dx_1 \psi_{\mu}^*(x_1) h(\mathbf{r}_1, \mathbf{p}_1) \psi_{\nu}(x_1),$$

$$w_{\mu\lambda}^{\nu\gamma} = \int dx_1 dx_2 \psi_{\mu}^*(x_1) \psi_{\nu}^*(x_2) \psi_{\lambda}(x_1) \psi_{\gamma}(x_2) \frac{1}{|r_1 - r_2|},$$

where $x_i = (r_i, \sigma_i)$ is a composite spatial-spin coordinate.

The complete set of $2n_{\text{bas}}$ spin-orbitals (labeled with $\mu, \nu, \gamma, \lambda$) is divided into $n_{\text{occ}}$ occupied $(o, p, q, r, s)$ and $2n_{\text{bas}} - n_{\text{occ}}$ virtual spin-orbitals having nonzero and vanishing occupations, respectively, in the coupled-cluster (MCSCF) expansion of the total wavefunction. The occupied spin-orbitals are classified into $n_{\text{core}}$ core spin-orbitals which are occupied in the reference $\Phi$ and kept uncorrelated, and $n_{\text{act}} = n_{\text{occ}} - n_{\text{core}}$ active spin-orbitals $(t, u, v, w)$ among which the $N_{\text{act}} = N - n_{\text{core}}$ active electrons are correlated.
The active spin-orbitals are further splitted into those in the hole space \((i,j,k,l)\) and the particle space \((a,b,c,d)\), which are occupied and unoccupied, respectively, in \(\Phi\). The core spin-orbitals can also be split into those in the frozen-core space \((i'j'k'l')\) which are fixed in time, and the dynamical-core space \((i'j'k'l')\) which are propagated in time.

Hereafter we refer to spin-orbitals simply as orbitals. [Note that Refs. 36,37,42 for TD-MCSCF methods deal with the equations of motion (EOMs) for spatial orbitals.] The system Hamiltonian (2) is equivalently written as
\[
\hat{H} = E_0 + f^p_{pr} \hat{E}^p_{pr} + \frac{1}{4} \sum_{\nu \lambda} \hat{E}^{\nu \lambda}_{\nu \lambda},
\]
where \(E_0 = \langle \Phi | \hat{H} | \Phi \rangle\), \(f^p_{pr} = h^p_{pr} + v^p_{ij} (j \text{ running over core and hole spaces})\), \(v^p_{ij} = v^p_{ij} - u^p_{ij}\), and the bracket \(\{ \cdots \} \) implies that the operator inside is normal ordered relative to the reference.

B. Review of TD-OC Methods

Let us begin with a generic TD-OC framework, which relies on the time-dependent variational principle with real action functional,
\[
S = \text{Re} \int_{t_0}^{t_1} \text{L}dt = \frac{1}{2} \int_{t_0}^{t_1} (L + L^*)dt,
\]
where
\[
L = \langle \Phi | \{ (\hat{H} - i \hat{\Lambda} \} e^{-\hat{T} (\hat{H} - i \hat{\Lambda} \} e^{\hat{T}} \} | \Phi \rangle, \tag{7}
\]
and, respectively using \(L\) of Eq. (16) derives
\[
i \hat{\lambda}_{ij} = \langle \Phi | \hat{E}^{ij}_{ab} \{ (\hat{H} - i \hat{X}) (1 + \hat{T}_2) \} | \Phi \rangle = v_{ij}^{ab} - p(\hat{f}_{ij}^{ab} \hat{r}_{ij} + p(ab) f_{ij}^{ab} \hat{r}_{ij} + \frac{1}{2} \hat{r}_{ij}^{ab} \hat{r}_{ij}^{ab} + p(ij) p(ab) v_{ij}^{ab} r_{ij}, \tag{18}
\]
and, accordingly the correlation RDMs [Eqs. (15)],
\[
\gamma_{ij}^{ab} = \langle \Phi | \hat{E}^{ij}_{ab} \{ (\hat{H} - i \hat{X}) (1 + \hat{T}_2) \} | \Phi \rangle, \tag{17a}
\]
\[
\gamma_{ij}^{ab} = \langle \Phi | \hat{E}^{ij}_{ab} \{ (\hat{H} - i \hat{X}) (1 + \hat{T}_2) \} | \Phi \rangle. \tag{17b}
\]
Requiring \(\delta S/\delta \lambda_{ij} = 0\) and \(\delta S/\delta \lambda_{ij} = 0\), respectively, using \(L\) of Eq. (16) derives
\[
\gamma_{ij}^{ab} = \langle \Phi | \hat{E}^{ij}_{ab} \{ (\hat{H} - i \hat{X}) (1 + \hat{T}_2) \} | \Phi \rangle = v_{ij}^{ab} - p(\hat{f}_{ij}^{ab} \hat{r}_{ij} + p(ab) f_{ij}^{ab} \hat{r}_{ij} + \frac{1}{2} \hat{r}_{ij}^{ab} \hat{r}_{ij}^{ab} + p(ij) p(ab) v_{ij}^{ab} r_{ij}, \tag{19}
\]
where \(\hat{f}_{ij}^{ab} = f_{ij}^{ab} - i X_{ij}^p \hat{E}^{ij}_{ab} \) and \(p(\mu \nu) A_{\mu \nu} = A_{\mu \nu} - A_{\nu \mu}\). Comparing Eqs (18) and (19), and noting that the orbitals are orthonormal, one sees that the EOM for \(\lambda_{ij}^{ab}\) is the complex conjugate of that for \(\epsilon_{ij}^{ab}\), concluding that \(\Lambda_0 = \hat{T}_2\). As a result, the first and second terms of Eq. (16) are real, and
\[
\text{Im} \int_{t_0}^{t_1} \text{L}dt = \frac{1}{2} \int_{t_0}^{t_1} (L - L^*)dt = \frac{1}{2} \left\{ |\epsilon_{ij}^{ab}(t_1)|^2 - |\epsilon_{ij}^{ab}(t_0)|^2 \right\} \tag{20}
\]
is independent of the integration path and irrelevant in taking its variation. Therefore, given the orthonormal orbitals, \( L \) is essentially real, and one could equally base oneself on
\[
S = \int_{t_0}^{t_1} L dt, \tag{21}
\]
for TD-OCEPA0 ansatz. See Sec. II D below for more explicit account of this point.

Based on the natively real action functional \( S \) of Eq. (21), the equation for \( X_p^{\mu} = \langle \psi_{\mu} | \psi_{\nu} \rangle \) is derived by requiring \( \delta S / \delta X_p^{\mu} = 0 \) using the Lagrangian expression of Eq. (10b) and RDMs of Eqs. (17) to obtain
\[
i (X_p^{\mu} \rho_p^{\nu} - \rho_p^{\nu} X_p^{\mu}) = F_p^{\mu} \rho_p^{\nu} - \rho_p^{\nu} F_p^{\mu*},
\]
where \( F_p^{\mu} = \langle \psi_{\mu} | \hat{F} | \psi_{\nu} \rangle \),
\[
\hat{F} \langle \psi_{\nu} | = \hat{h} \langle \psi_{\nu} | + W^{\nu}_{\gamma}(\rho_{\gamma}^{\nu}) (\rho^{-1})_{\mu},
\]
\[
W^{\nu}_{\gamma}(x_1) = \int dx_2 \langle \psi_{\nu} | x_2 \rangle \psi_{\gamma}(x_2) | \rho_1 - \rho_2 |.
\]
Subsequent analyses of Eq. (22) are parallel to those for TD-MCSCF methods, and one arrives at the orbital EOMs,
\[
i | \psi_{\mu} \rangle = \left( i \hat{P} \hat{F} | \psi_{\nu} \rangle + | \psi_{\nu} \rangle \hat{F}^\dagger \right) X_p^{\mu},
\]
where \( \hat{P} \) is the identity operator within the orbital space \( \{ \psi_{\mu} \} \), and \( \hat{P} = \sum_{\mu} | \psi_{\mu} \rangle \langle \psi_{\mu} | \) with non-redundant orbital rotations determined by
\[
i (\delta^a_{\mu} - \rho^a_{\mu}) X_p^{\mu} = F_p^{a} \rho_p^{\nu} - \rho_p^{\nu} F_p^{a*},
\]
\[
i (X_p^{\mu} \rho_p^{\nu} - \rho_p^{\nu} X_p^{\mu}) = F_p^{a} \rho_p^{\nu} - \rho_p^{\nu} F_p^{a*}.
\]
A careful consideration of the frozen-core orbitals within the electric dipole approximation derives
\[
i X_p^{\mu} = \left\{ \begin{array}{ll}
0 & (\text{length gauge}) \\
E(t) \cdot | \psi_{\mu} \rangle | \psi_{\mu} \rangle & (\text{velocity gauge})
\end{array} \right. \tag{28}
\]
where \( E \) is the external electric field, enabling gauge-invariant simulations with frozen-core orbitals.

Relevant orbital rotations \( \{ X_j^j \} \), \( \{ X_j^i \} \), and \( \{ X_j^a \} \) can be arbitrary anti-Hermite matrix elements. In particular, if one chooses \( X_j^a = X_j^j = 0 \), the term \( -i \hat{X} \) is dropped in Eqs. (18) and (19). Again as a consequence of \( \hat{\Lambda}_2 = \hat{T}_2 \), both 1RDM and 2RDM are Hermitian, of which the algebraic expression of non-zero elements are given by
\[
\gamma_{ij} = -\frac{1}{2} \chi_{cd} c_{ij} c_{kl}, \quad \gamma_{ab} = \frac{1}{2} k_{cl} e_{ab} \tag{29a}
\]
\[
\gamma_{ij}^{cd} = -\frac{1}{2} k_{ab} c_{cd} k_{ij}, \quad \gamma_{kl}^{cd} = \frac{1}{2} k_{ab} c_{cd} k_{ij} \tag{29b}
\]
\[
\gamma_{ij}^{ab} = \chi_{cd} c_{ij} c_{kl}, \quad \gamma_{ij}^{ij} = \chi_{ij} \tag{29c}
\]
\[
\gamma_{ij}^{ab} = \gamma_{ij}^{ab} \tag{29d}
\]
In summary, the TD-OCEPA0 method is defined by the EOMs of \( \hat{T}_2 \) amplitudes [Eq. (18)] and orbitals [Eq. (25)], with the hole-particle mixing determined by solving Eq. (22) and RDMs given by Eqs. (29).

### D. Relation to other ansatz
As the name suggests, the TD-OCEPA0 method is a time-dependent extension of the stationary OCEPA0 method. In the stationary case, it is known that OCEPA0, D-MBPT(\( \infty \))84,85, third-order expectation value coupled-cluster [XCC(3)]86, and the linearized CCD (LCCD)87 energy functionals are all equivalent. The similar equivalence in the time-dependent case can be demonstrated by considering the Lagrangian of Eq. (7). In particular, the XCC Lagrangian can be written as
\[
L = \frac{1}{(\Phi^T e^{-\hat{H}}) \Phi} (\hat{H} - i \frac{\partial}{\partial t} e^{T} | \Phi \rangle)
\]
\[
= \langle \Phi | e^{T} (\hat{H} - i \frac{\partial}{\partial t}) e^{T} | \Phi \rangle
\]
\[
\sim (\Phi^{\dagger} (1 + \hat{T}^{\dagger})(\hat{H} - i \frac{\partial}{\partial t})(1 + \hat{T}))_{sc} | \Phi \rangle,
\]
\[
= L_0 + \langle \Phi | [(1 + \hat{T}^{\dagger})(\hat{H} - i \hat{X})(1 + \hat{T})]_{sc} | \Phi \rangle - i \tau_{ij}^{ab} \gamma_{ij}^{ab},
\]
where [\( \cdots \)\] restricts to strongly connected terms, and the third line introduces the XCC(3) approximation. This Lagrangian, which leads to the same working equations as derived in Sec. II C (with \( \hat{\Lambda}_2 = \hat{T}_2 \)), emphasizes the Hermitian nature of the TD-OCEPA0, of which a certain advantage over the standard non-Hermitian treatment is discussed in Ref. 88 in the stationary case.

The EOMs of the TD-OCEPA0 method is simpler than those of the closely-related TD-OCCD method (See Appendix A for algebraic details of the TD-OCCD method.) in that all terms quadratic to \( \gamma_{ij}^{ab} \) are absent in the \( \hat{T}_2 \) equation [comparing Eq. (18) and (A1)] and in the 2RDM expression [comparing Eq. (29d) and (A3d)]. It should also be noted that one need not solve for \( \hat{\Lambda}_2 \) for TD-OCEPA0 since \( \hat{\Lambda}_2 = \hat{T}_2 \), in

| Basis | Method | This work \(^{a}\) | PSI4 \(^{b}\) |
|-------|--------|----------------|-------------|
| Be 6-31G^{**} | HF | -14.5667 6405 | -14.5667 6403 |
| | CEPA0 | -14.6192 0335 | -14.6192 0335 |
| | OCEPA0 | -14.6196 5019 | -14.6196 5018 |
| | OCCD | -14.6138 6552 | -14.6138 6552 |
| | OCCDT | -14.6139 4064 | -14.6139 4064 |
| | FC1 | -14.6139 4255 | -14.6135 4253 |
| Ne cc-pVDZ \(^{**1}\) | HF | -128.4887 7555 | -128.4887 7555 |
| | CEPA0 | -128.6802 1409 | -128.6802 1409 |
| | OCEPA0 | -128.6802 9009 | -128.6802 9009 |
| | OCCD | -128.6795 9316 | -128.6795 9316 |
| | OCCDT | -128.6807 2135 | -128.6807 2135 |
| | FC1 | -128.6808 8113 | -128.6808 8113 |

\(^{a}\) The overlap, one-electron, and two-electron repulsion integrals over Gaussian basis functions are generated using Gaussian09 program (Ref. 82), and used to propagate EOMs in imaginary time in the orthonormalized Gaussian basis, with a convergence threshold of \( 10^{-15} \) Hartree of energy difference in subsequent time steps.
contrast to the fact that Eq. (A2) should be solved for TD-OCCD. These simplifications make TD-OCEPA0 computationally much more efficient than TD-OCCD, as numerically demonstrated in Sec. III.

III. NUMERICAL RESULTS AND DISCUSSIONS

A. Ground-state energy

We have implemented the TD-OCEPA0 method for atom-centered Gaussian basis functions and spherical finite-element discrete variable representation (FEDVR) basis for atoms, both with spin-restricted and spin-unrestricted treatments, by modifying the TD-OCCD code described in Ref. 59. Exploiting the feasibility of the imaginary time relaxation to obtain the ground state\(^{59}\), we first computed the ground-state energy of Be and Ne atoms with standard Gaussian basis sets, and compare the results with those obtained by PS14 program package\(^ {80}\), in which the time-independent OCEPA0 method is implemented. To facilitate the comparison, the number of active spatial orbitals \(n_{\text{act}}/2\) are set to be the same as the number of basis functions \(n_{\text{bas}}\), since this is the only capability of the PSI4 program. In this case, there are no virtual orbitals (See Sec. II B for the definition.), and therefore, the first term of Eq. (25) vanishes. We also take an option of imaginary-propagating amplitudes only, with all orbitals frozen at the canonical HF solution, to obtain the fixed-orbital CEPA0 energy.

The calculated total energies listed in Table I demonstrate a virtually perfect agreement of the results of this work and PS14 program, both for CEPA0 and OCEPA0 methods and for Be and Ne atoms (with a small discrepancy due to a digit truncation of Gaussian one- and two-electron integrals), which confirms the correctness of our implementation.

It is also observed that, for both Be and Ne, the OCEPA0 energies are noticeably lower than the OCCD ones, and for the Be case, the OCEPA0 energy is slightly lower than the FCI energy. Such an overestimation of the correlation energy is usually considered not critical, and more than compensated by the size extensivity in the stationary case.

B. Application to electron dynamics in Ne and Ar

Next, we apply the TD-OCEPA0 method to the laser-driven electron dynamics in Ne and Ar atoms. Within the dipole approximation in the velocity gauge, the one-electron Hamiltonian is given by

\[
h(r, p) = \frac{1}{2} |p|^2 - \frac{Z}{|r|} + A(t)p_z, \tag{31}\]

where \(Z\) is the atomic number, \(A(t) = -\int E(t')dt'\) is the vector potential, with \(E(t)\) being the laser electric field linearly polarized along \(z\) axis. It should be noted that TD-OCC method (including TD-OCEPA0) is gauge invariant; length-gauge and velocity-gauge simulations, upon numerical convergence, give the same result for observables. The velocity

FIG. 1. Time evolution of the dipole moment of Ne irradiated by a laser pulse of a wavelength of 800 nm and intensities of \(5 \times 10^{14}\) W/cm\(^2\) (a), \(8 \times 10^{14}\) W/cm\(^2\) (b), and \(1 \times 10^{15}\) W/cm\(^2\) (c), calculated with TDHF, TD-OCISD, TD-OCEPA, TD-OCCD, and TD-CASSCF methods.

FIG. 2. Time evolution of the single ionization probability of Ne irradiated by a laser pulse of a wavelength of 800 nm and intensities of \(5 \times 10^{14}\) W/cm\(^2\) (a), \(8 \times 10^{14}\) W/cm\(^2\) (b), and \(1 \times 10^{15}\) W/cm\(^2\) (c), calculated with TDHF, TD-OCISD, TD-OCEPA, TD-OCCD, and TD-CASSCF methods.
The dipole moment (Fig. 1) and the ionization probability (Fig. 2) of Ne atom show a general trend that the deviation of results for each method from TD-CASSCF ones decreases as TDHF ≫ TD-OCISD > TD-OCEPA0 ≈ TD-OCID > TD-OCCDT. The HHG spectra [Fig. 3 (a)-(c)] are well reproduced by all the methods, except a systematic underestimation of the intensity by TDHF, with the magnitude of the error amounting to 100% of the TD-CASSCF spectral amplitude as shown in Fig. 3 (d)-(f). The magnitude of the error depends weakly on the harmonic order at the plateau region, which decreases again as TDHF ≫ TD-OCISD > TD-OCEPA0 ≈ TD-OCID > TD-OCCDT. The Ne atom is characterized by its large ionization potential of 21.6 eV, resulting in relatively low ionization probabilities (Fig. 2) for the present laser pulses. In that case, TD-OCEPA0 and TD-OCID give a notably similar, and accurate description of dynamics, implying that the truncation after the doubles amplitude and the linearization of the Lagrangian [Eq. 16] are both justified.

The Ar atom, having a lower ionization potential of 15.6 eV, exhibits a richer dynamics than Ne, e.g., a larger-amplitude oscillation of the dipole moment (Fig. 4), ionization probabilities as high as 70% (Fig. 5), and HHG spectra characterized by a dip around 34th harmonic related to the Cooper minimum of the photoionization spectrum at the same energy (Fig. 6). The trend of the accuracy of each method is similar to the case for Ne, except that TD-OCEPA0 and TD-OCID give noticeably different descriptions of dynamics. In general, TD-OCEPA0 tends to capture a larger part of the correlation effect (the difference between TDHF and TD-CASSCF) than TD-OCCDT does. This results in, on one hand, a better agreement of the TD-OCEPA0 results (than TD-OCID) with TD-CASSCF ones for lower intensity cases [Fig. 4 (a),(b), Fig. 5 (a),(b), and Fig. 6 (d),(e)], and, on the other, leads to an overestimation of the correlation effect for the highest intensity [Fig. 4 (c), Fig. 5 (c), Fig. 6 (f)], somewhat analogous to the overestimation of the ground-state correlation energy as discussed in Sec. III A.

The nonlinear exponential parametrization in TD-OCCD seems to play a role in correcting the overestimation, and the inclusion of the triple excitations (TD-OCCDT) is essential.
to retain the decisive accuracy across the employed range of the laser intensity. Despite the aforementioned overestimation of the correlation effect for higher intensities, we judge that the present results of TD-OCEPA0 are quite encouraging; it clearly outperforms TD-OCISD for all properties of both atoms, and at least performs equally as TD-OCCD for a moderate laser intensity.

![Diagram](image)

**FIG. 3.** The HHG spectra from Ne irradiated by a laser pulse of a wavelength of 800 nm obtained with various methods (top), and the relative deviation of the spectral amplitude from the TD-CASSCF spectrum (bottom) defined as Eq. (33), for laser intensities of $5 \times 10^{14}$ W/cm$^2$ (a,d), $8 \times 10^{14}$ W/cm$^2$ (b,e), and $1 \times 10^{15}$ W/cm$^2$ (c,f).

![Diagram](image)

**FIG. 4.** Time evolution of the dipole moment of Ar irradiated by a laser pulse of a wavelength of 800 nm and intensities of $2 \times 10^{14}$ W/cm$^2$ (a), $4 \times 10^{14}$ W/cm$^2$ (b), and $6 \times 10^{14}$ W/cm$^2$ (c), calculated with TDHF, TD-OCISD, TD-OCEPA, TD-OCCD, and TD-CASSCF methods.

![Diagram](image)

**FIG. 5.** Time evolution of the single ionization probability of Ar irradiated by a laser pulse of a wavelength of 800 nm and intensities of $2 \times 10^{14}$ W/cm$^2$ (a), $4 \times 10^{14}$ W/cm$^2$ (b), and $6 \times 10^{14}$ W/cm$^2$ (c), calculated with TDHF, TD-OCISD, TD-OCEPA, TD-OCCD, and TD-CASSCF methods.
TABLE II. Comparison of the CPU time (in second) spent for the evaluation of the $T_2$ equation, $\Lambda_2$ equation, and 2RDM for TD-OCCD and TD-OCEPA0 methods with various active spaces. See text for more details.

| active space | TD-OCCD | TD-OCEPA0 |
|--------------|---------|-----------|
|              | $T_2$   | $\Lambda_2$ | 2RDM | $T_2$ | $\Lambda_2$ | 2RDM |
| (8e-9o)      | 8.1     | 11.4      | 20.7 | 3.3  | -           | 3.1  |
| (8e-13o)     | 40.8    | 55.5      | 109.4| 18.2 | -           | 19.8 |
| (8e-20o)     | 254.9   | 332.1     | 703.9| 131.4| -           | 187.9|
| (1e-16o)     | 248.2   | 307.2     | 555.5| 111.1| -           | 83.2 |
| (1e-17o)     | 314.4   | 437.0     | 852.1| 131.5| -           | 124.4|
| (1e-18o)     | 452.6   | 619.6     | 1024.8| 187.9| -           | 143.3|

$a$ CPU time spent for the simulation of Ar atom with $n_{act}$ active orbitals and $N_{F}^e$ active electrons ($n_{act} = N_{act} \cdot 2$), recorded and accumulated over 1000 time steps of a real-time simulation ($I_0 = 2 \times 10^{14}$ W/cm$^2$ and $\lambda = 800$ nm), using an Intel(R) Xeon(R) CPU with 12 processors having a clock speed of 3.33GHz.

Finally, we compare the computational cost of TD-OCEPA0 and TD-OCCD methods. Table II reports the central processor unit (CPU) time for the computational bottlenecks differing in these two methods, with varying numbers of active electrons and active orbitals. The largest active space with 18 electrons and 18 orbitals (18e-18o) is challenging for the fully correlated TD-CASSCF.

First, depending on the active space configurations, the evaluation of the $T_2$ equation of the TD-OCEPA0 [Eq. (18)] is 1.9~2.5 times faster than that of TD-OCCD [Eq. (A1)]. A bigger computational gain comes from the fact that one need not solve for the $\Lambda_2$ equation, which, for TD-OCCD [Eq. (A2)] takes longer than that for the $T_2$ equation because of more mathematical operations involved. A further significant cost reduction is obtained by TD-OCEPA0 for the 2RDM evaluation [Eqs. (29d)], which is 5.5~7.2 times faster than the TD-OCCD case [Eqs. (A3d)]. As a whole, the TD-OCEPA0 simulation with, e.g., the (18e-18o) active space achieves 6.3 times speed up relative to the TD-OCCD simulation with the same active orbital space.

IV. SUMMARY

We have presented the implementation of TD-OCEPA0 method as a cost-effective approximation within the TD-OCC framework, for the first principles study of intense laser-driven multielectron dynamics. The TD-OCEPA0 method retains the important size-extensivity and gauge-invariance of TD-OCC, and computationally much more efficient than the full TD-OCC method. As a first numerical test, we applied the present implementation to Ne and Ar atoms irradiated by an intense near infrared laser pulses with three different intensities to compare the time-dependent dipole moment, the ionization probability, and HHG spectra with those obtained with other methods including the fully correlated TD-CASSCF methods with the same number of active orbitals. It is observed that, for the highest laser intensity, with sizable ionization, the TD-OCEPA0 tends to overestimate the correlation effect defined as the difference between TDHF and TD-CASSCF descriptions. For moderate intensities, however, the TD-OCEPA0 method performs at least equally well as TD-OCCD with a substantially lower computational cost. It is anticipated that the present TD-OCEPA0 method serves as an important theoretical tool to investigate ultrafast and/or high-field processes in chemically relevant large molecular systems.
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Appendix A: Algebraic details of TD-OCCD

The TD-OCCD method implemented in Ref. 59 employs the same truncation ($\hat{T} = \hat{T}_2$ and $\Lambda = \Lambda_2$) as for TD-OCEPA0, but retains the full exponential operator $e^{\hat{T}_2}$. As a result, the amplitude EOMs are given by

$$i\hat{\gamma}^{ab}_{ij} = \hat{\gamma}^{ab}_{ij} - p(ij)\hat{f}^{ab}_{ij} + p(ab)\hat{f}^{ab}$$
$$+ \frac{1}{2}p^{ab,cd}_{ij} + \frac{1}{2}\hat{\gamma}^{ab}_{ij} + p(ij)p(ab)\hat{f}^{ac}_{ik}\hat{f}^{cb}_{kj}$$
$$- \frac{1}{2}p^{ab,cd}_{ij} - \frac{1}{2}p^{ac,cd}_{ij} - \frac{1}{2}p^{bc,cd}_{ij}$$
$$+ \frac{1}{4}\hat{\gamma}^{ab}_{ij} + \frac{1}{4}\hat{\gamma}^{bc}_{ij} + \frac{1}{4}\hat{\gamma}^{cd}_{ij}$$

(A1)

The EOMs for orbitals are formally the same as that for TD-OCEPA0, Eqs. (25)-(27), but with RDMs $\rho$ replaced with Hermitianized ones, $\rho^H_{ij} = (\rho^H_{ij} + \rho^H_{ji})/2$ and $P^T_{ij} = (\rho^T_{ij} + \rho^T_{ji})/2$. Finally the algebraic expression for non-zero correlation RDM elements is

$$\lambda^{ab}_{ij} = -\frac{1}{2}\lambda^{cd}_{ij} - \frac{1}{2}\lambda^{bc}_{ij}$$

(A3a)

$$\gamma^{ab}_{cd} = \frac{1}{2}\lambda^{bc}_{ij} - \frac{1}{2}\lambda^{cd}_{ij}$$

(A3b)

$$\lambda^{bc}_{ij} = \frac{1}{2}\lambda^{cd}_{ij}$$

(A3c)

$$\lambda^{ab}_{ij} = \lambda^{cd}_{ij} + \frac{1}{2}p(ij)p(ab)\lambda^{cd}_{ij}$$

(A3d)
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