Gauge-invariant formulation of time-dependent configuration interaction singles method

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We propose a gauge-invariant formulation of the channel orbital-based time-dependent configuration interaction singles (TDCIS) method [Phys. Rev. A. 74, 043420 (2006)], one of the powerful ab initio methods to investigate electron dynamics in atoms and molecules subject to an external laser field. In the present formulation, we derive the equations of motion (EOMs) in the velocity gauge using gauge-transformed orbitals, not fixed orbitals, that are equivalent to the conventional EOMs in the length gauge using fixed orbitals. The new velocity-gauge EOMs avoid the use of the length-gauge dipole operator, which diverges at large distance, and allows to exploit computational advantages of the velocity-gauge treatment over the length-gauge one, e.g., a faster convergence in simulations with intense and long-wavelength lasers, and the feasibility of exterior complex scaling as an absorbing boundary. The reformulated TDCIS method is applied to an exactly solvable model of one-dimensional helium atom in an intense laser field to numerically demonstrate the gauge invariance. We also discuss the consistent method for evaluating the time derivative of an observable, relevant e.g. in simulating high-harmonic generation.

I. INTRODUCTION

Time-dependent configuration interaction singles (TDCIS) method is one of the powerful ab initio methods to investigate laser-driven electron dynamics in atoms and molecule [1–24]. In the TDCIS method, the time-dependent electronic wavefunction is given by the configuration interaction (CI) expansion,

$$
\Psi(t) = \Phi C_0(t) + \sum_{\text{occ}} \sum_{a} \Phi_{ia} C_{ia}(t),
$$

where $\Phi$ is the ground-state Hartree-Fock (HF) wavefunction, and $\Phi_{ia}$ is a singly-excited configuration-state function (CSF), replacing an occupied HF orbital $\phi_i$ with a virtual (unoccupied in $\Phi$) orbital $\phi_a$, and the electron dynamics is described through the time evolution of the CI coefficients, $C_0$ and $\{C_{ia}\}$. Compared to more involved ab initio wavefunction-based approaches [25] such as time-dependent multiconfiguration self-consistent-field (TD-MCSCF) methods [26–33], time-dependent $R$-matrix based approaches [34–56], or time-dependent reduced density-matrix approach [57–63], distinct advantages of the TDCIS method include a low computational cost and the conceptual simplicity to analyze simulation results. Furthermore, an equivalent, effective one-electron theory with coupled channels has been developed [2], which introduces the orbital-like quantity, called channel orbital,

$$
\chi_i(r,t) = \sum_a \phi_a(r) C_{ia}(t),
$$

and rewrites EOMs for CI coefficients with those for channel orbitals $\{\chi_i(r,t)\}$ with no reference to virtual orbitals. This reformulation removes the bottleneck of the CI coefficient-based TDCIS method to compute all (or, at least sufficiently many, including bound and continuum) virtual orbitals prior to the simulation, and thus particularly useful in grid-based simulations.

Despite this advantage, numerical applications of the channel orbital-based TDCIS method has been limited to Refs. [2] [14] [15] for a one-dimensional Hamiltonian and Ref. [1] for noble gas atoms with a Hartree-Slater potential, as far as we know, and the vast majority of applications to date have adopted the CI coefficient-based approach [2–24], except for the use of $\{\chi_i\}$ as intermediate quantities in evaluating photoelectron spectra [13]. The preference of CI coefficient-based approach might be partially due to the high symmetry of atomic systems, for which the stationary Hartree-Fock operator decouples for different angular momenta [4], making it a relatively feasible task to obtain all virtual orbitals (within a given radial grids or radial basis functions) for the lowest few angular momenta. The channel orbital-based approach would be more suited, on the other hand, to simulations of electron dynamics with intense and/or long-wavelength laser fields, requiring much longer angular momentum expansion [39–41], and moreover to grid-based molecular applications, where obtaining a sufficient spectrum of virtual levels could be unacceptably expensive.

However, the TDCIS method, either in the CI coefficient-based or channel orbital-based formulation, suffers from the lack of gauge invariance, as a general consequence of relying on truncated CI expansion with fixed orbital functions. Previously, the length gauge (LG) has been employed e.g., in Ref. [2] [16], and the velocity gauge (VG) in Ref. [17–21]. Although gauge dependence of the TDCIS method using fixed orbitals has been noted already in Ref. [2], comparative assessment of the LG and VG treatments (within the grid-based TDCIS) has not been reported to the best of our knowledge, except for being briefly mentioned in Ref. [42]. In particular, the channel orbital-based approach [2] has been applied only in the LG [2, 4], and as shown below in this paper, the VG treatment with fixed orbitals is not very appropriate for applications to high-field phenomena. This is a serious drawback, since for an efficient simulation of molecules, it is highly ap-

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precluded to take advantage of the velocity-gauge treatment, e.g., the feasibility of exterior complex scaling [43, 44] as an absorbing boundary, to reduce the computational cost related to the number of grid points.

In the present work, we propose a gauge-invariant reformulation of the channel orbital-based TDCIS method. To this end, instead of applying the fixed-orbital TDCIS ansatz to the velocity-gauge time-dependent Schrödinger equation (TDSE), we adopt the formulation using unitary-orbital orbital \( \phi_p(t) = U(t)\phi_p \), where \( U(t) \) is the gauge transformation operator connecting the (exact) solution of TDSE in the LG and VG. The resulting EOMs in the reformulated VG is equivalent to the LG ones with fixed orbitals by construction, and at the same time allows to exploit advantages of the velocity-gauge simulations as mentioned above.

This paper proceeds as follows. In Sec. II after defining the target Hamiltonian and the gauge transformation in Sec. II A and reviewing the TDCIS method using fixed orbitals both in the CI coefficient-based [Sec. II B] and channel orbital-based [Sec. II C] approaches, we present the gauge-invariant reformulation in Sec. II D and a consistent method for evaluating the time derivative of one-electron observables in Sec. II E. Then in Sec. II I we apply the channel orbital-based TDCIS method, using LG with fixed orbitals, VG with fixed orbitals, and the reformulated VG, to the model one-dimensional (1D) Hamiltonian to compare the results of various TDCIS approaches with numerically exact TDSE results, and demonstrate the importance of non-Ehrenfest method to compute dipole acceleration. Finally, concluding remarks are given in Sec. IV. The Hartree atomic units are used throughout unless otherwise noted.

II. THEORY

A. System Hamiltonian and gauge transformation

Let us consider an atom or a molecule consisting of \( N \) electrons interacting with an external laser field. In this work, we restrict our treatment in the clamped-nuclei approximation and the electron-laser interaction within the electric dipole approximation. Then the exact description of the system dynamics is given by the solution \( \Psi_L(t) \) of TDSE,

\[
i\dot{\Psi}_L(t) = H_L(t)\Psi_L(t),
\]

with the system Hamiltonian \( H_L(t) = H_0 + H_{\text{ext}}^L(t) \), where \( H_0 \) is the field-free electronic Hamiltonian

\[
H_0 = \sum_{k=1}^N \hbar \langle r_k, p_k \rangle + \sum_{k=1}^N \sum_{l>k} \frac{1}{\lvert r_k - r_l \rvert},
\]

where \( r_k \) and \( p_k = -i\nabla r_k \) are the coordinate and canonical momentum of an electron, \( \hbar \langle r_k, p_k \rangle = \frac{1}{2} p_k^2 + v_n(r_k) \), with \( v_n \) being the electron-nucleus interaction. Here we are considering the LG treatment, where the electron-laser interaction \( H_{\text{ext}}^L(t) \) is given by

\[
H_{\text{ext}}^L(t) = E(t) \cdot \sum_{k=1}^N r_k,
\]

where \( E(t) \) is the laser electric field.

As well known, the system dynamics is equivalently described in the VG, of which the wavefunction \( \Psi_V \) is connected with the LG one through

\[
\Psi_V(t) = U(t)\Psi_L(t),
\]

with a unitary transformation

\[
U(t) = \exp \left[ -i \sum_{k=1}^N \left\{ A(t) \cdot r_k - \frac{1}{2} \int_{-\infty}^t dt' \lvert A(t') \rvert^2 \right\} \right],
\]

where \( A(t) = -\int_{-\infty}^t E(t') dt' \) is the vector potential, and we arbitrarily include the second term in the exponential, which is a \( c \)-number, to avoid appearance of terms proportional to \( \lvert A \rvert^2 \) in subsequent equations. Then we substitute \( \Psi_L = U^{-1} \Psi_V \) into the LG TDSE, Eq. [4], use \( du/dt = i \sum_{k=1}^N (E \cdot r_k + \lvert A \rvert^2/2) p_k \), and note \( U p_k U^{-1} = p_k + A \) to derive the VG TDSE,

\[
i\dot{\Psi}_V(t) = H_V(t)\Psi_V(t),
\]

with \( H_V(t) = H_0 + H_{\text{ext}}^V(t) \), and

\[
H_{\text{ext}}^V(t) = A(t) \cdot \sum_{k=1}^N p_k.
\]

One should carefully note that the present proof of equivalence of the LG and VG treatments, Eqs. [4] and [5], with the transformation of Eq. [7], applies only to the exact solution of TDSE. See e.g., Ref. [45, 47] for deeper discussions on the gauge transformation within TDSE, and Ref. [48] for the gauge invariance of TD-MCSCF methods.

For a compact presentation of the many-electron theory, we rewrite the system Hamiltonian in the second quantization,

\[
\hat{H}_L(t) = \hat{H}_0 + \hat{H}_{\text{ext}}^L(t),
\]

\[
\hat{H}_V(t) = \hat{H}_0 + \hat{H}_{\text{ext}}^V(t),
\]

\[
\hat{H}_0 = \hat{h} + \frac{1}{2} \sum_{\sigma \tau} \sum_{pqrs} \langle pr|qs \rangle \hat{c}^\dagger_{p\sigma} \hat{c}_{q\tau} \hat{c}_{r\tau} \hat{c}^\dagger_{s\sigma},
\]

\[
\hat{H}_{\text{ext}}^L(t) = E(t) \cdot \hat{r},
\]

\[
\hat{H}_{\text{ext}}^V(t) = A(t) \cdot \hat{p},
\]

where \( \{ \hat{c}_{p\sigma} \} \) and \( \{ \hat{c}^\dagger_{p\sigma} \} \) are the creation and annihilation operators, respectively, for the set of spin-orbitals given as a direct product \( \{ \phi_p \} \otimes \{ s_\uparrow, s_\downarrow \} \) of orthonormal spatial orbitals \( \{ \phi_p \} \) and up-spin (down-spin) functions \( s_\uparrow (s_\downarrow) \). The operators \( \hat{h} \), \( \hat{r} \), and \( \hat{p} \) are defined, respectively, as

\[
\hat{h} = \sum_{\sigma} \sum_{pq} \hat{h}_{pq} \hat{c}^\dagger_{p\sigma} \hat{c}_{q\sigma},
\]

\[
\hat{r} = \sum_{\sigma \tau} \sum_{pq} \hat{r}_{pq} \hat{c}^\dagger_{p\sigma} \hat{c}_{q\tau},
\]

\[
\hat{p} = \sum_{\sigma \tau} \sum_{pq} \hat{p}_{pq} \hat{c}^\dagger_{p\sigma} \hat{c}_{q\tau},
\]

where \( \hat{h}_{pq} \), \( \hat{r}_{pq} \), and \( \hat{p}_{pq} \) are the matrix elements of \( h \), \( r \), \( p \), respectively, in terms of \( \{ \phi_p \} \), and

\[
\langle pr|qs \rangle = \int \! dr_1 \int \! dr_2 \phi^\dagger_{p\sigma}(r_1)\phi_{q\tau}(r_2)\rho_{r_1} \phi_{s\sigma}(r_1)\phi_{\tau}(r_2).
\]
The TDSE of the LG, Eq. (3), and VG, Eq. (5), read
\[ i\frac{\partial \Psi_L(t)}{\partial t} = \hat{H}_L(t)|\Psi_L(t)\rangle, \]
\[ i\frac{\partial \Psi_V(t)}{\partial t} = \hat{H}_V(t)|\Psi_V(t)\rangle, \]
with the transformation
\[ \Psi_V = \hat{U}(t)|\Psi_L\rangle, \]
\[ \hat{U}(t) = \exp \left[ -i \int^t_{-\infty} \mathbf{A}(t') \cdot \mathbf{r} - \frac{\hat{N}}{2} \int^t_{-\infty} dt' \mathbf{A}(t')^2 \right], \]
where \( \hat{N} = \sum \alpha \sum_{\sigma} \hat{c}_{\alpha\sigma}^\dagger \hat{c}_{\alpha\sigma} \) is the number operator.

In this work, we consider a closed-shell system with even number of electrons, and choose as \( \{\phi_p\} \) the time-independent Hartree-Fock (HF) orbitals satisfying the canonical, restricted HF equation
\[ \hat{f}\phi_p = \hat{h}\phi_p + 2 \sum_j \hat{W}^\phi_j |\phi_p\rangle - \sum_j \hat{W}^\phi_j |\phi_j\rangle = \epsilon_p |\phi_p\rangle, \]
where \( \epsilon_p \) is the orbital energy, and \( \hat{W}^\phi_j \) is the electronegative potential of a product \( \phi^*(r)\phi(r) \) of given orbitals, defined in the real space as
\[ \hat{W}^\phi_j = \int dr_2 \phi^*(r_2) \phi(r_2) |r_1 - r_2| \]
As usual, we separate the full set of HF orbitals \( \{\phi_p\} \) into the occupied orbitals \( \{\phi_i\} \) which are occupied in the HF ground-state wavefunction (also referred to as the reference) \( |\Phi\rangle = \prod_i \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\downarrow} |\rangle \) is the vacuum.), and the virtual orbitals \( \{\phi_a\} \) which are unoccupied in \(|\Phi\rangle\).

B. Review of CI coefficient-based TDCIS with fixed orbitals

We write the second-quantized version of Eq. (1), for the LG case, as
\[ |\Psi_L(t)\rangle = |\Phi\rangle C_0(t) + \sum_{i}^{occ} \sum_{a}^{vir} \langle \Phi|_{ia} \rangle C_{ia}(t), \]
where \( \langle \Phi|_{ia} \rangle = \sum_{\alpha}^{i\dagger} \hat{c}_{\alpha\sigma} c_{i\sigma} |\Phi\rangle / \sqrt{2} \). The equations of motion for the CI coefficients have been derived by inserting Eq. (19) into the LG TDSE, Eq. (14a), and closing from the left with the reference and singly-excited CSFs,
\[ \langle \Phi| (\hat{H}_L - i\partial_t) |\Phi\rangle C_0 + \sum_{j}^{occ} \langle \Phi|_{jb} \rangle C_{jb} = 0, \]
\[ \langle \Phi|_{ia} (\hat{H}_L - i\partial_t) |\Phi\rangle C_0 + \sum_{j}^{occ} \langle \Phi|_{ja} \rangle C_{ja} = 0. \]
Conceptually, more proper derivation of Eqs. (20) is based on Dirac-Frenkel variational principle, which considers the Lagrangian
\[ L_L(t) = \langle \Psi_L | (\hat{H}_L - i\partial_t) |\Psi_L\rangle, \]
and requires \( \partial L_L / \partial C_{ia} = \partial L_L / \partial C_{ia} = 0 \). Substituting \( \hat{H}_L \) of Eq. (16a) into Eqs. (20), using the Slater-Condon rule for the Hamiltonian matrix elements, and noting the canonical condition \( f_{pp} = \epsilon_p \delta_{pq} \), the EOMs for the length gauge are derived as
\[ i\hat{C}_0 = \sqrt{2} |E\rangle \langle \phi_j | \mathbf{r} |\phi_j\rangle C_{jb}, \]
\[ i\hat{C}_{ia} = \langle \phi_a| \left\{ \sum_{b} (\hat{E}_i + \mathbf{E} \cdot \mathbf{r}) |\phi_b\rangle C_{ib} + \sqrt{2} |E\rangle \langle \phi_i | \mathbf{r} \langle \phi_i| C_0 \right\} - \mathbf{E} \sum_{j} C_{ja} \langle \phi_j | \mathbf{r} |\phi_i\rangle. \]

References [17] [24] have used the same expansion in terms of fixed CSFs also in the VG case,
\[ |\Psi_V(t)\rangle = |\Phi\rangle D_0(t) + \sum_{i}^{occ} \sum_{a}^{vir} \langle \Phi|_{ia} \rangle D_{ia}(t), \]
and required Eqs. (20) to hold, with \( \hat{H}_L, C_0, \) and \( C_{ia} \) replaced with \( \hat{H}_V, D_0, \) and \( D_{ia} \). This is equivalent to consider the following Lagrangian,
\[ L_V(t) = \langle \Psi_V | (\hat{H}_V - i\partial_t) |\Psi_V\rangle, \]
and to require \( \partial L_V / \partial D_{0}^* = \partial L_V / \partial \partial D_{ia}^* = 0 \), which derives
\[ i\hat{D}_0 = \sqrt{2} \mathbf{A} \cdot \sum_{j} |\phi_j\rangle |\bar{p}\rangle |\phi_b\rangle D_{jb}, \]
\[ i\hat{D}_{ia} = \langle \phi_a| \left\{ \sum_{b} (\hat{E}_i + \mathbf{A} \cdot \mathbf{p}) |\phi_b\rangle D_{ib} + \sqrt{2} \mathbf{A} \cdot \mathbf{p} |\phi_i\rangle D_0 \right\} - \mathbf{A} \sum_{j} D_{ja} \langle \phi_j | \mathbf{p} |\phi_i\rangle. \]

C. Review of Channel orbital-based TDCIS with fixed orbitals

An interesting reformulation of the above-described TDCIS method, as mentioned in Sec. 1, has been proposed in Ref. 2 which introduces the time-dependent channel orbitals \( |\chi_i\rangle \) that collects all the single excitations originating from an occupied orbital \( |\phi_i\rangle \),
\[ |\chi_i\rangle = \sum_{a} |\phi_a\rangle C_{ia}(t), \]
and rewrites the EOMs in terms of \( C_0 \) and \( \{ |\chi_i\rangle \} \) as
\[ i\hat{C}_0 = \sqrt{2} |E\rangle \langle \phi_j | \mathbf{r} |\chi_j\rangle, \]
\[ i|\chi_i\rangle = \hat{P} |(\hat{E}_i + \mathbf{E} \cdot \mathbf{r}) |\chi_i\rangle + \sqrt{2} |E\rangle \langle \phi_i | \mathbf{r} |\chi_i\rangle \]
\[ - \sum_j |\chi_j\rangle \langle \phi_j | \mathbf{E} \cdot \mathbf{r} |\phi_i\rangle. \]
where \( \hat{P} = \hat{1} - \sum_j |\phi_j\rangle\langle\phi_j| \). According to these EOMs and the initial conditions \( |C_0(t \to -\infty) = 1, \{C_{ia}(t \to -\infty) = 0 \} \to \{x_i(t \to -\infty) = 0 \} \), the channel orbitals \( |\chi_i\rangle \) gets gradually populated along with the laser-electron interaction, measuring an exciton of an electron out of \( |\phi_i\rangle \).

See Ref. [2] for interesting properties of the channel orbitals.

It is also possible to formulate the channel orbital-based scheme based on the velocity gauge TDCIS using fixed orbitals, although not previously considered. We, therefore, introduce the analogous quantity

\[
|\eta_i\rangle = \sum_a |\phi_{ia}\rangle D_{ia}(t),
\]

and rewrite Eqs. (26) as

\[
i\hat{D}_0 = \sqrt{2A} \sum_j \langle\phi_j|\hat{p}|\eta_i\rangle, \tag{30a}
\]

\[
i\hat{\eta}_i = \hat{P}((\hat{F}_i + A \cdot \hat{p})|\eta_i\rangle + \sqrt{2A} \cdot \hat{p}|\phi_i\rangle D_0)
- \sum_j |\eta_j\rangle \langle\phi_j|A \cdot \hat{p}|\phi_i\rangle.
\]

(30b)

Hereafter, we refer to the method based on Eqs. (28), i.e., the channel orbital-based TDCIS in the length gauge with fixed orbitals, simply as LG method, and that based on Eqs. (30), i.e., the channel orbital-based TDCIS in the velocity gauge with fixed orbitals, as VG method, for notational brevity.

D. Channel orbital-based TDCIS in the velocity gauge with rotated orbitals

The gauge dependence of the LG and VG treatments, Eqs. (28) and (30), results from the fact that the ansatz of Eqs. (19) and (24), both using fixed orbitals, cannot be connected with the transformation, Eq. (16), as is generally the case for truncated CI expansion using fixed orbitals. For a method to be gauge invariant, the underlying Lagrangian in LG and VG cases should be numerically the same when evaluated with the solution of respective EOMs, which does not hold in the present case, \( L_L(t) \neq L_V(t) \), with Eqs. (21) and (25).

Thus we define the total wavefunction \( |\Psi_V(t)\rangle \), transformed from \( |\Psi_L(t)\rangle \) to the velocity gauge, as

\[
|\Psi_V(t)\rangle = \hat{U}(t)|\Psi_L(t)\rangle
= |\Phi\rangle C_0(t) + \sum_{i\sigma} \sum_{a} |\Phi_{ia}\rangle C_{ia}(t), \tag{31}
\]

with \( |\Psi_L(t)\rangle \) constructed with the solution of CI coefficient-based EOMs in the LG, Eqs. (22). Here \( |\Phi\rangle = \hat{U}(t)|\Phi\rangle \) and \( |\Phi_{ia}\rangle = \hat{U}(t)|\Phi_{ia}\rangle = \sum_{\sigma} \alpha_{ia}\beta_{ia}|\Phi'\rangle /\sqrt{2} \) are the reference and singly-excited CSF constructed with unitary rotated orbitals, i.e., \( |\phi'_{ia}\rangle = \hat{U}|\phi_{ia}\rangle \) and \( \beta_{ia} = \hat{U}(t)\alpha_{ia} \hat{U}^{-1}(t) \). It should be noted that \( |\Psi_V\rangle \) cannot be rewritten into the form of Eq. (24) in general. Associated with this wavefunction, we consider the following Lagrangian,

\[
L_V(t) = \langle \Psi_V'(t)|\hat{H}_V - i\partial_t|\Psi_V(t)\rangle. \tag{32}
\]

The equivalence of this approach to the LG treatment is readily confirmed by seeing

\[
L_V(t) = \langle \Psi_L|\hat{U}^{-1}(t)|\hat{H}_V - i\partial_t\hat{U}|\Psi_L\rangle
= \langle \Psi_L|(|\hat{H}_L - i\partial_t\rangle)|\Psi_L\rangle = L_L(t). \tag{33}
\]

One may naively expect that \( L'_V \) of Eq. (32), which differs from \( L_V \) of Eq. (25) only by the replacement of \( \Psi_V \) with \( \Psi'_V \), leads to the EOMs of Eq. (30) with \( D_0, \{D_{ia}\}, \{\phi_p\} \) replaced with \( C_0, \{C_{ia}\}, \{\phi_p\} \). This is not the case, however, due to the time dependence of the rotated CSFs, e.g., \( \langle \Phi|\Phi'\rangle = iE(t) \cdot \hat{p}|\phi'_p\rangle \), and after extracting these time dependence, Eq. (32) reads

\[
L'_V(t) = \langle \Psi'_L|\hat{H}_V + E(t) \cdot \hat{p} - i\partial_t\rangle|\Psi'_L\rangle, \tag{34}
\]

where \( \partial_t \) time differentiates CI coefficients only. Now requiring \( dL'_V/dC_0^\ast = 0 \), equivalently, substituting the back transformation \( |\phi_p\rangle = U^{-1}|\phi'_p\rangle \) into Eqs. (22) derives

\[
i\hat{C}_0 = \sqrt{2E} \sum_{jb} \langle \phi'_j|\hat{p}|\phi'_b\rangle C_{jb}, \tag{35a}
\]

\[
i\hat{C}_{ia} = \langle \phi'_i|\sum_{b} (\hat{F}_i + A \cdot \hat{p} + E \cdot \hat{r})|\phi'_b\rangle C_{ib}
+ \sqrt{2E} \cdot \hat{r}|\phi'_i\rangle C_0
- \sum_j C_{ja} \langle \phi'_j|\hat{p}|\phi'_i\rangle. \tag{35b}
\]

where \( \hat{F}_i \) is given by Eq. (23) with \( \{\phi\} \) replaced with \( \{\phi'_i\} \). Equations (35) are the CI coefficient-based TDCIS EOMs based on the Lagrangian of Eq. (32). Although this approach is guaranteed to be equivalent to the CI coefficient-based LG TDCIS, it brings no numerical gain over Eqs. (22), peculiarly including both \( E \cdot r \) and \( A \cdot p \), and requiring extensive gauge transformation of all occupied and virtual orbitals.

None the less, a useful method can be derived, if one switches to the channel orbital-based scheme by defining the rotated channel functions,

\[
|\chi_i(t)\rangle = \hat{U}(t)|\chi_i\rangle = \sum_{a} |\phi'_{ai}\rangle C_{ia}. \tag{36}
\]

Then we use \( d\hat{U}/dt = i(E \cdot \hat{r} + \hat{N}|A|^2/2)|\hat{U}\rangle \), and note \( \hat{U}\hat{U}^{-1} = \hat{p} + \hat{N}A \) to derive

\[
i\hat{C}_0 = \sqrt{2E} \sum_{j} \langle \phi'_j|\hat{p}|\chi'_i\rangle, \tag{37a}
\]

\[
i\hat{C}_{ia} = \hat{P}'((\hat{F}_i + A \cdot \hat{p})|\chi'_i\rangle + \sqrt{2E} \cdot \hat{p}|\phi'_i\rangle C_{0})
- \sum_j \langle \chi'_j\rangle \langle \phi'_j|E \cdot \hat{r}|\phi'_i\rangle C_{ja} + \langle \phi'_j|A \cdot \hat{p}|\chi'_i\rangle, \tag{37b}
\]

where \( \hat{P}' = 1 - \sum |\phi'_j\rangle\langle \phi'_j\rangle \). Equations (37) are the main results of this work, which are called the rotated velocity-gauge (rVG) EOMs for brevity. The rVG scheme is equivalent to the LG scheme with fixed orbitals by construction, while replacing the length-gauge dipole operator \( E \cdot r \) [the second term of Eq. (30)] with the spatially uniform \( A \cdot p \) [the second term of
Although several terms in the EOMs still involve the dipole operator, they all apply to the (rotated) occupied orbital which is localized around nuclei, thus posing no difficulty in enjoying the same advantages of VG propagations of orbitals \[39\]-\[41\].

E. Evaluation of the time derivative of an observable

Let us next consider how to compute expectation value of a one-electron operator \(\langle \hat{O}(t) \rangle = \langle \Psi(t)|\hat{O}|\Psi(t)\rangle\), and its time derivative \(d\langle \hat{O}(t) \rangle/dt\). For exact solution of TDSE, \(|\Psi\rangle = -i\hat{H}|\Psi\rangle\), the time derivative is given by

\[
\frac{d}{dt}\langle \Psi|\hat{O}|\Psi \rangle = \langle \Psi|\hat{O}|\Psi \rangle + \langle \hat{O}\Psi|\Psi \rangle
\]  

(38a)

\[
= -i\langle \Psi|\{\hat{O}, \hat{H}\}|\Psi \rangle,
\]  

(38b)

The TDCIS expectation value of a one-electron operator \(\hat{O}\) is given \[2\] by

\[
\langle \Psi_L|\hat{O}|\Psi_L \rangle = 2 \sum_j \langle \phi_j|\hat{O}|\phi_j \rangle + \sum_j \langle \chi_j|\hat{O}|\chi_j \rangle + 2\sqrt{2} Re\{C^*_0 \sum_j \langle \phi_j|\hat{O}|\chi_j \rangle\} - \sum_{ij} \langle \chi_i|\chi_j \rangle \langle \phi_j|\phi_i \rangle,
\]  

(39)

in the LG case. That for the VG is given by replacing \(C_0\) with \(D_0\) in the above equation, and for the rVG by replacing \(\{\phi_j, \chi_j\}\) with \(\{\phi'_j, \chi'_j\}\). The expression for the time derivative, in the LG case, is derived by using Eqs. (28) in Eq. (38a) as

\[
\frac{d}{dt}\langle \Psi_L|\hat{O}|\Psi_L \rangle = 2\Re\left[ \sum_j \langle \chi_j|\hat{O}|\chi_j \rangle + \sqrt{2}(C^*_0 \langle \phi_j|\hat{O}|\chi_j \rangle + C^*_0 \langle \phi_j|\hat{O}|\chi_j \rangle) - \sum_{ij} \langle \chi_i|\chi_j \rangle \langle \phi_j|\phi_i \rangle \right].
\]  

(40)

The VG expression is also given by the above equation with \(C_0\) replaced with \(D_0\), and that for the rVG is

\[
\frac{d}{dt}\langle \Psi'_L|\hat{O}|\Psi'_L \rangle = 2\Re\left[ \sum_j \langle \chi'_j|\hat{O}|\chi'_j \rangle + \sqrt{2}(C^*_0 \langle \phi'_j|\hat{O}|\chi'_j \rangle + C^*_0 \langle \phi'_j|\hat{O}|\chi'_j \rangle) - \sum_{ij} \langle \chi'_i|\chi'_j \rangle \langle \phi'_j|\phi'_i \rangle \right] + \sqrt{2}\text{Im}\left[ 2E \cdot \sum_j C^*_0 \langle \phi'_j|\hat{r}|\chi'_j \rangle + |A|^2 \sum_j C^*_0 \langle \phi'_j|\hat{O}|\chi'_j \rangle - iE \cdot \sum_{ij} (2\delta_{ij} - \langle \chi'_i|\chi'_j \rangle) \langle \phi'_j|\hat{r}|\phi'_i \rangle.\right.
\]  

(41)

Although Eqs (40) and (41) look rather complicated, their evaluations are straightforward given the time derivatives of working variables \(C_0\), \{\chi_i\}, etc, which are necessary, in any case, to propagate the EOMs.

III. NUMERICAL EXAMPLES

In this section, we numerically apply the channel orbital-based TDCIS method in the LG, VG, and rVG to the 1D model Helium atom, using the computational code developed by modifying an existing TDHF code used in our previous work \[30\]-\[33\]-\[48\]. The field-free electronic Hamiltonian is given by

\[
H_0 = \sum_{k=1}^2 \left\{ \frac{1}{2} \frac{\partial^2}{\partial z_k^2} - \frac{2}{z_k + 1} \right\} + \frac{1}{\sqrt{(z_1 - z_2)^2 + 1}},
\]  

(42)

for two electronic coordinates \(z_1\) and \(z_2\), and the laser-electron interaction \(E(t) \cdot \hat{r}\) and \(A(t) \cdot \hat{p}\) are replaced with \(E(t)z\) and \(A(t)\hat{p}_z = -iA(t)\partial/\partial z\), respectively, in Eqs. (28), (30) and (37). Orbitals are discretized on equidistant grid points with spacing \(\Delta z = 0.4\) within a simulation box \(-1000 \leq z \leq 1000\), with an absorbing boundary implemented by a mask function of \(\cos^{1/4}\) shape at 10% side edges of the box. Each EOM is solved by the fourth-order Runge-Kutta method with a fixed time step size (1/10000 of an optical cycle). Spatial derivatives are evaluated by the eighth order finite difference method, and spatial integrations are performed by the trape-
First, we compare the time-dependent dipole moment \( \langle z(t) \rangle \) obtained with TDCIS approaches with that of TDSE in Fig. 1 which immediately reveals a strong gauge dependence of fixed-orbital approaches, i.e., the large difference between LG and VG results. One should note that the comparison of LG and VG results alone can tell nothing about the preference of either approach; TDCIS method in both LG and VG are the first approximation in the hierarchy of CI expansions, which, at the full-CI limit, would be gauge invariant. The point here is that the LG scheme outperforms the VG scheme in comparison to the exact TDSE result as clearly seen in Fig. 1 which convinces one an empirical preference of the LG treatment. On the other hand, the results of LG and rVG agree perfectly within the graphical resolution, numerically demonstrating the theoretical gauge invariance.

Next, we consider the dipole acceleration \( \langle a(t) \rangle \) defined as the time derivative of the kinematic momentum,

\[
\langle a(t) \rangle = \frac{d\langle \hat{p}_z \rangle}{dt},
\]

where \( \hat{p}_z = \hat{p}_z \) for the LG, and \( \hat{p}_z + A(t) \) for the VG. In the exact TDSE case, applying Eqs. (44) and \( \hat{O} = \hat{\pi} \) (also taking into account the trivial, explicit time dependence of \( \pi(t) \) in the VG case) derives

\[
\langle a(t) \rangle = -\langle \Psi | \frac{\partial v_{\text{ion}}}{\partial z} | \Psi \rangle - 2E(t),
\]

where \( \partial v_{\text{ion}}/\partial z = -\partial /\partial z \left( 2z^2 + 1 \right)^{-1/2} = 2z(z^2 + 1)^{-3/2} \) for the 1D Hamiltonian. Numerically achieving the theoretical equivalence of Eq. (44) and (45), even for the exact TDSE method, requires a simulation to be converged with respect to computational parameters (time-step size, etc.). Therefore, we first applied both Eq. (44) and Eq. (45) in the TDSE simulation, and confirmed a perfect agreement (not shown), suggesting the convergence of the simulation. Then we compare the results of TDCIS in the LG, using Eqs. (44) and (45) with \( \hat{O} = \hat{\pi} \), and with that of TDSE in Fig. 2, clearly showing a better agreement of the results of the former approach with that of TDSE. From this result, and also by the fact that being based on Eq. (44) guarantees that the HHG spectra obtained from the velocity \( \langle \pi \rangle(t) \) and the acceleration \( \langle a \rangle(t) \), at the convergence, properly relate to each other and the LG, rVG, and TDSE results should be adopted as a consistent method for evaluating the dipole acceleration.

Then we compare the time evolution of the dipole acceleration [Fig. 3] and the HHG spectrum [Fig. 4] obtained as the modulus squared of the Fourier transform of the dipole acceleration obtained with TDCIS method in LG, VG, and rVG [based on Eq. (44)] with those of TDSE. We observe that (1) the LG and rVG results are identical to within the scale of the figure, (2) they also show a good agreement with TDSE.
FIG. 3. Time evolution of the dipole acceleration of 1D-He exposed to a laser pulse with a wavelength of 750 nm and an intensity of (a) $5 \times 10^{14}$ W/cm$^2$ and (b) $1 \times 10^{15}$ W/cm$^2$. Comparison of the results with TDCIS in the LG, VG, and rVG with that of TDSE.

FIG. 4. HHG spectrum of 1D-He exposed to a laser pulse with a wavelength of 750 nm and an intensity of (a) $5 \times 10^{14}$ W/cm$^2$ and (b) $1 \times 10^{15}$ W/cm$^2$. Comparison of the results with TDCIS in the LG, VG, and rVG with that of TDSE.

results, (3) and in contrast, the VG results strongly deviate from all the other results. Especially, Fig. 4 shows a remarkable agreement of the TDCIS spectra in the LG and rVG and the TDSE one, suggesting that the TDCIS method would be a useful computational method for studying HHG process in more complex atoms and molecules, in particular, when the present rVG treatment is combined with advanced, velocity gauge-specific computational techniques.

IV. CONCLUSIONS

In this work, we propose a gauge-invariant formulation of the channel orbital-based TDCIS method for ab initio investigations of electron dynamics in atoms and molecules. Instead of using fixed orbitals both in length-gauge and velocity-gauge simulations, we adopt, in the velocity-gauge case, the EOMs derived with unitary rotated orbitals $|\phi_p(\tau)\rangle = U(\tau)|\phi_p\rangle$ using gauge-transforming operator $U(t)$, which replaces the length-gauge operator $\hat{E} \cdot \hat{r}$ appearing in the length-gauge EOMs with the velocity-gauge counterpart $\mathbf{A} \cdot \mathbf{p}$, while keeping the equivalence to the length-gauge treatment. This would make it possible to take advantages of the velocity-gauge simulation over the length-gauge one, e.g., the faster convergence of simulations of atoms interacting with an intense and/or long-wavelength laser field, with respect to the maximum angular momentum included to expand orbitals, and the native feasibility of advanced absorbing boundaries such as the exterior complex scaling. Applications to real atoms and molecules with the three-dimensional Hamiltonian will be presented elsewhere.

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