PHYSICAL REVIEW A **98**, 023405 (2018)

Effective-potential theory for time-dependent many-electron wave functions

Tsuyoshi Kato[1,2,*] and Kaoru Yamanouchi[1]
[1]*Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[2]*Department of Theoretical and Computational Molecular Science, Institute for Molecular Science,*
Myodaiji, Okazaki, Aichi 444-8585, Japan

(Received 4 May 2018; published 10 August 2018)

We derive a variation equation for a time-dependent effective potential that is local both in time and in space and show that this potential generates and propagates spin orbitals with which a many-particle, time-dependent, multiconfigurational wave function $\Psi(t)$ is constructed. Within this approach, the wave function and the effective potential are determined simultaneously in a self-consistent manner both in time-independent and in time-dependent cases. We also derive an equation that determines a real-valued effective potential and show that the equation establishes a relation among the first-order and second-order reduced density matrices and the electron repulsion integrals in the spin-orbital representation. By introducing the first-order density equation, we show that the variation equation for the effective potential can be simplified for an exact wave function. We also show that we can derive an effective potential with which a ground-state wave function that fulfills the Brillouin-Brueckner condition is constructed and that we can derive the effective potential proposed by Slater, with which a ground-state wave function represented by the multiconfiguration expansion is calculated, when an additional constraint is imposed on the varitation equation.

DOI: 10.1103/PhysRevA.98.023405

I. INTRODUCTION

The multiconfiguration, time-dependent Hartree-Fock (MCTDHF) method [1,2] was developed for treating time-dependent electronic dynamics of atoms and molecules from first principles, and its basic formulations and proof-of-principle applications have been established by recent theoretical and computational efforts [1,3–5]. We are now entering the research phase in which we explore its practical applicability to many-electron atoms and molecules and implement program codes for practical calculations. For example, the elucidation of time-dependent many-electron dynamics induced by an ultrashort intense laser pulse is one of the most interesting themes currently [6–10].

In MCTDHF studies, the time-dependent Schrödinger equation (TDSE) is solved by time propagation of spin orbitals and configuration-interaction (CI) coefficients, with which a time-dependent, multiconfigurational wave function is constructed [1–4,11–14]. The time propagation of spin orbitals is carried out by the integration of the nonlinear equations of motion (EOMs) in time and the time propagation of the CI coefficients is carried out by the integration of a linear EOM [3]. These EOMs are formulated using the Dirac-Frenkel time-dependent variational principle [15,16].

Alternatively, time-dependent dynamics of many electrons can be represented by a single-particle TDSE with a time-dependent single-particle potential, which is derived from a time-dependent many-electron wave function. This type of single-particle-potential approach could give us a straightforward picture of ultrafast and correlated motion of electrons in a many-electron system. Schild and Gross [17] derived an exact single-particle TDSE with a time-dependent single-particle potential by adopting the wave-function factorization scheme proposed by Hunter [18], in which a stationary-state many-electron wave function is factorized as the product of a marginal amplitude and a conditional amplitude. Indeed, we can calculate the exact electron density of a many-electron system by taking the squared modulus of the marginal amplitude, which depends only on a single-electron coordinate. Recently, Ando [19] investigated higher-order harmonics generation by LiH using time-dependent single-particle potentials representing Li($2s$) and H($1s$) electrons.

In the present study, we propose a formulation for the time propagation of the spin orbitals governed by a single-particle TDSE with a time-dependent local effective potential $v_{\mathrm{eff}}(\vec{r},t)$. In the present approach, we derive the multiconfigurational wave function and the effective potential simultaneously in a self-consistent manner, and therefore, we can correlate the motion of the spin orbitals with the temporal variation of the time-dependent effective potential. We find an equation that determines a real-valued effective potential, which establishes a relation among the first-order and second-order reduced density matrices (RDMs) and the electron repulsion integrals in the spin-orbital representation.

In Sec. II, we formulate an effective-potential theory for a time-dependent multiconfigurational wave function and derive a variation equation by which the effective potential is determined. In Sec. III, we relate the present formulation to the density equation theory (DET) developed by Cho [20], Nakatsuji [21,22], and Cohen and Frishberg [23] and we derive the first member of the Born, Bogoliubov, Green, Kirkwood, and Yvon (BBGKY) hierarchy of equations [24] in terms of the effective potential. In Sec. IV, we clarify the properties of existing effective-potential theories [25,26] for many-electron wave functions through a comparison with the present theory.

---

[*] tkato@chem.s.u-tokyo.ac.jp

Finally, in Sec. V, we summarize the present study. Detailed derivations of the equations that are referred to in the text are summarized in Appendixes A–J.

II. FORMULATION OF AN EFFECTIVE-POTENTIAL THEORY

A. Multiconfiguration expansion approximation of a wave function

The exact time-dependent wave function $\Psi_{\rm exact}(t)$ of an N-electron system follows the TDSE,

$$i\hbar\frac{\partial}{\partial t}\Psi_{\rm exact}(x_1,x_2,\ldots,x_N,t) = \hat{H}(t)\Psi_{\rm exact}(x_1,x_2,\ldots,x_N,t), \tag{1}$$

where the symbol x_j represents the spatial coordinate $\vec{r}_j$ and the spin coordinates μ_j of the jth electron, i.e., $x_j=(\vec{r}_j,\mu_j)$. For simplicity, we consider a spin-singlet state with an even-N electron system. Within the Born-Oppenheimer approximation, the time-dependent total Hamiltonian $\hat{H}(t)$ is written as

$$\hat{H}(t)=\hat{T}+\hat{V}_{\rm ext}(t)+\hat{W}_{\rm ee}, \tag{2}$$

where the kinetic energy operator, the time-dependent external potential, and the electron-electron Coulombic potential are expressed, respectively, by

$$\hat{T}=\sum_{j=1}^{N}\hat{t}(\vec{r}_j)=\sum_{j=1}^{N}\left(-\frac{\hbar^2}{2m_{\rm e}}\right)\frac{\partial^2}{\partial\vec{r}_j^{\,2}}, \tag{3}$$

$$\hat{V}_{\rm ext}(t)=\sum_{j=1}^{N}v_{\rm ext}(\vec{r}_j,t)=\sum_{j=1}^{N}v_{\rm en}(\vec{r}_j)+\sum_{j=1}^{N}v_{\rm ptb}(\vec{r}_j,t), \tag{4}$$

and

$$\hat{W}_{\rm ee}=\frac{e^2}{4\pi\epsilon_0}\sum_{i<j}^{N}\frac{1}{r_{ij}}, \tag{5}$$

where $m_{\rm e}$ denotes the mass of the electron, e the elementary charge, and ϵ_0 the permittivity of vacuum. In Eq. (4), the external potential $v_{\rm ext}$ is expressed as the sum of the electron-nuclear attraction potential $v_{\rm en}$ and a time-dependent perturbation $v_{\rm ptb}(t)$. It should be noted that the electron-nuclear attraction potential $v_{\rm en}(\vec{r}_j)$ can be written as a single-particle potential for the jth electron in describing atoms as well as molecules. Throughout this paper, the operator $v_{\rm ptb}(t)$ is assumed to be a multiplicative real-valued function in the coordinate representation. For example, if we describe the interaction of an electron with an external laser electric field $\vec{\mathcal{E}}(t)$ in the length gauge, $v_{\rm ptb}(t)$ is explicitly represented by

$$v_{\rm ptb}(t)=e\vec{r}\cdot\vec{\mathcal{E}}(t). \tag{6}$$

We introduce the normalized approximate wave function $\Psi_{\rm approx}(t)$ represented by the multiconfiguration expansion of a finite length of $\mathcal{L}$ as

$$\Psi_{\rm approx}(x_1,x_2,\ldots,x_N,t) = \sum_{K=1}^{\mathcal{L}}C_K(t)\Phi_K(x_1,x_2,\ldots,x_N,t), \tag{7}$$

where the Slater determinant $\Phi_K(t)$ is constructed by time-dependent spin orbitals $\{\phi_k(x,t)\}$ $(k=1,2,3,\ldots,N,\ldots)$ as

$$\Phi_K(x_1,x_2,\ldots,x_N,t) = \frac{1}{\sqrt{N!}}\det\{\phi_{k_1}(x_1,t)\phi_{k_2}(x_2,t)\ldots\phi_{k_N}(x_N,t)\}. \tag{8}$$

The spin orbitals are assumed to form an orthonormal set as

$$\langle\phi_i(t)|\phi_j(t)\rangle=\int dx\,\phi_i^*(x,t)\phi_j(x,t)=\delta_{ij}, \tag{9}$$

and thus the orthonormalized relation among Slater determinants is automatically satisfied as

$$\langle\Phi_K(t)|\Phi_L(t)\rangle=\delta_{\rm KL}. \tag{10}$$

When the expansion length is increased as $\mathcal{L}\to\infty$ so that the set of spin orbitals becomes complete, the *expansion theorem* [27] states that we are able to construct an exact wave function $\Psi_{\rm exact}$ in the form of Eq. (7).

B. Variational formulation to optimize the effective potential

The derivation of the variation equation for the effective potential is based on McLachlan's norm-minimization principle [28]. By substituting $\Psi_{\rm approx}(t)$ from Eq. (7) on the left-hand side of Eq. (1), we obtain

$$\frac{\partial}{\partial t}\Psi_{\rm approx}(x_1,x_2,\ldots,x_N,t) = \sum_{K=1}^{\mathcal{L}}\frac{dC_K(t)}{dt}\Phi_K(x_1,x_2,\ldots,x_N,t) + \sum_{K=1}^{\mathcal{L}}C_K(t)\frac{\partial}{\partial t}\Phi_K(x_1,x_2,\ldots,x_N,t). \tag{11}$$

We assume that the time evolution of the spin orbitals $\{\phi_k(x,t)\}$ is governed by a single-particle TDSE specified by the time- and spatially local effective potential $v_{\rm eff}(\vec{r},t)$ as

$$\left[i\hbar\frac{\partial}{\partial t}-\left(-\frac{\hbar^2}{2m_{\rm e}}\frac{\partial^2}{\partial\vec{r}^{\,2}}+v_{\rm eff}(\vec{r},t)\right)\right]\phi_k(x,t)=0. \tag{12}$$

For a spin-singlet state with an even-N electron system, we can restrict the effective potential to be spin independent. The spin orbitals are represented by

$$\phi_k(x,t)=\begin{cases}\psi_k(\vec{r},t),\ \alpha(\mu) & \text{if}\quad k\quad \text{is odd},\\ \psi_k(\vec{r},t),\ \beta(\mu) & \text{if}\quad k\quad \text{is even},\end{cases} \tag{13}$$

where $\psi_k(\vec{r},t)$ denotes a time-dependent spatial orbital and α and β stand for the spin functions.

The assumption represented by Eq. (12) indicates that the time dependence of a Slater determinant is governed by the TDSE represented by

$$0=\left[i\hbar\frac{\partial}{\partial t}-(\hat{T}+\hat{V}_{\rm eff}(t))\right]\Phi_K(x_1,x_2,\ldots,x_N,t) = \left[i\hbar\frac{\partial}{\partial t}-\hat{H}_{\rm eff}(t)\right]\Phi_K(x_1,x_2,\ldots,x_N,t), \tag{14}$$

where

$$\hat{V}_{\text{eff}}(t) = \sum_{j=1}^{N} v_{\text{eff}}(\vec{r}_j, t) \tag{15}$$

and

$$\hat{H}_{\text{eff}}(t) = \hat{T} + \hat{V}_{\text{eff}}(t). \tag{16}$$

Therefore, using Eq. (14), Eq. (11) can be rewritten as

$$i\hbar\frac{\partial}{\partial t}\Psi_{\text{approx}}(t) = i\hbar\sum_{K}^{\mathcal{L}}\frac{dC_K(t)}{dt}\Phi_K(t) + \sum_{K}^{\mathcal{L}} C_K(t)[\hat{T} + \hat{V}_{\text{eff}}(t)]\Phi_K(t). \tag{17}$$

On the other hand, using Eqs. (2) and (7) we obtain

$$\hat{H}(t)\Psi_{\text{approx}}(t) = \sum_{K}^{\mathcal{L}} C_K(t)[\hat{T} + \hat{V}_{\text{ext}}(t) + \hat{W}_{\text{ee}}]\Phi_K(t). \tag{18}$$

If the wave function is exact, the left-hand side of Eq. (17) and the left-hand side of Eq. (18) must be equal. However, when an approximate wave function is adopted, they are not equal to each other, and the time-dependent effective potential $v_{\text{eff}}(\vec{r}, t)$ is defined so that the magnitude of this discrepancy is minimized.

We first subtract Eq. (18) from Eq. (17) to obtain

$$\left(i\hbar\frac{\partial}{\partial t} - \hat{H}(t)\right)\Psi_{\text{approx}}(t) = i\hbar\sum_{K}^{\mathcal{L}}\frac{dC_K(t)}{dt}\Phi_K(t) + \sum_{K}^{\mathcal{L}} C_K(t)[\tilde{V}(t) - \hat{W}_{\text{ee}}]\Phi_K(t), \tag{19}$$

where $\tilde{V}(t)$ in Eq. (19) is defined as

$$\tilde{V}(t) = \hat{V}_{\text{eff}}(t) - \hat{V}_{\text{ext}}(t) = \sum_{j=1}^{N}[v_{\text{eff}}(\vec{r}_j, t) - v_{\text{ext}}(\vec{r}_j, t)] = \sum_{j=1}^{N}\tilde{v}(\vec{r}_j, t). \tag{20}$$

The kinetic energy operators in Eqs. (17) and (18) cancel each other out in Eq. (19). We refer to $\tilde{v}(\vec{r}, t)$ in Eq. (20) as an internal effective potential.

Next, we define the time-dependent norm $\mathcal{N}(t)$ by

$$\mathcal{N}(t) = \langle\Psi_{\text{approx}}(t)|\left(i\hbar\frac{\partial}{\partial t} - \hat{H}(t)\right)^{\dagger} \times \left(i\hbar\frac{\partial}{\partial t} - \hat{H}(t)\right)|\Psi_{\text{approx}}(t)\rangle. \tag{21}$$

By setting the first variation of $\mathcal{N}(t)$ with respect to $\tilde{V}^{\dagger}(t)$ to be 0, we obtain the variation equation for the effective potential as

$$0 = i\hbar\sum_{\text{KL}}^{\mathcal{L}} C_K^*(t)\frac{dC_L(t)}{dt}\langle\Phi_K(t)|\delta\tilde{V}^{\dagger}(t)|\Phi_L(t)\rangle + \sum_{\text{KL}}^{\mathcal{L}} C_K^*(t)C_L(t)\langle\Phi_K(t)|\delta\tilde{V}^{\dagger}(t)(\tilde{V}(t) - \hat{W}_{\text{ee}})|\Phi_L(t)\rangle. \tag{22}$$

In Eq. (22), variations with respect to the spin orbitals are not considered. This is because, as pointed out by Nazarov in Ref. [29], spin orbitals remain unchanged at time t by the variation of the potential at time t, although the time derivatives of the spin orbitals at time t should be affected by the variation of the potential, $\delta\tilde{v}^{\dagger}(\vec{r}_j, t) = \delta v_{\text{eff}}^{\dagger}(\vec{r}_j, t)$, as can be seen in Eq. (12). This fact allows us to derive the variation equation for the time-local effective potential in a straightforward manner.

C. The variation equation for the effective potential and equations of motion for the CI coefficients

From the variation equation of Eq. (22), the effective potential $v_{\text{eff}}(\vec{r}, t) = \tilde{v}(\vec{r}, t) + v_{\text{ext}}(\vec{r}, t)$ needs to satisfy the following linear integral equation, i.e., a Fredholm equation of the second type (see Appendix A);

$$\begin{aligned}\tilde{v}(\vec{r}_1, t)\gamma_{\text{approx}}(x_1', t|x_1, t) &= 2\int dx_2\left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} - \tilde{v}(\vec{r}_2, t)\right]\Gamma^{(2)}_{\text{approx}}(x_1', x_2, t|x_1, x_2, t)\\ &\quad + 3\int dx_2\int dx_3\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}_{\text{approx}}(x_1', x_2, x_3, t|x_1, x_2, x_3, t)\\ &\quad - i\hbar\tilde{\gamma}_{\text{approx}}(x_1', t|x_1, t),\end{aligned} \tag{23}$$

where γ_{approx}, $\Gamma^{(2)}_{\text{approx}}$, and $\Gamma^{(3)}_{\text{approx}}$ denote, respectively, the first-, second-, and third-order reduced density matrices associated with the wave function Ψ_{approx} in the coordinate representation.

The RDMs are calculated in a manner similar to that in Ref. [27] by using the wave function defined by Eq. (7). The explicit definitions of RDMs are described in Appendix A. The last term in Eq. (23) is defined as

$$\begin{aligned}i\hbar\tilde{\gamma}_{\text{approx}}(x_1', t'|x_1, t) &= i\hbar N\int dx_2\cdots\int dx_N\ \Psi^*_{\text{approx}}(x_1', x_2, x_3, \ldots, x_N, t')\\ &\quad\times\sum_{K=1}^{\mathcal{L}}\frac{dC_K(t)}{dt}\Phi_K(x_1, x_2, \ldots, x_N, t).\end{aligned} \tag{24}$$

In Appendix B, we show that we can set the potential $\tilde{v}(\vec{r}, t)$ as well as the diagonal element $i\hbar\tilde{\gamma}_{\text{approx}}(x_1, t|x_1, t)$ to be real-valued functions. Because of this real-valuedness of $\tilde{v}(\vec{r}, t)$, the single-particle TDSE of Eq. (12) describes the unitary time propagation of the spin orbitals, Therefore, the assumption of Eq. (9) becomes valid as long as a set of initial spin orbitals is orthonormalized.

As shown in Appendix C, the EOMs for the CI coefficients are derived based on the Dirac-Frenkel time-dependent variational principle as

$$i\hbar\frac{d}{dt}\vec{C}(t) = \boldsymbol{V}(t)\vec{C}(t), \tag{25}$$

where we have introduced a column vector with $\mathcal{L}$ elements and an $\mathcal{L} \times \mathcal{L}$ Hermitian matrix defined as

$$(\vec{C}(t))_L = C_L(t), \tag{26}$$

and

$$(\boldsymbol{V}(t))_{\mathrm{KL}} = \langle \Phi_K(t)|\hat{W}_{\mathrm{ee}} - \tilde{V}(t)|\Phi_L(t)\rangle. \tag{27}$$

It should be noted that we need to know beforehand the EOMs for the spin orbitals in evaluating the terms of $\langle \Phi_K(t)|i\hbar\partial/\partial t|\Phi_L(t)\rangle$, which we use in the derivation of the EOMs for the CI coefficients.

D. Solution algorithm for the effective potential

Using the condition of the real-valuedness of $\tilde{v}(\vec{r},t)$ in Eq. (23), we can calculate the quantity defined by

$$\Delta(x_1',t|x_1,t) \equiv [\tilde{v}(\vec{r}_1,t) - \tilde{v}(\vec{r}_1',t)]\gamma_{\mathrm{approx}}(x_1',t|x_1,t). \tag{28}$$

By setting $x_1' = x_1$ in Eq. (28), we obtain $\Delta(x_1,t|x_1,t) = 0$, which leads to the necessary condition for the real-valuedness of $\tilde{v}(\vec{r},t)$ in Eq. (23) given by

$$\langle \Psi_{\mathrm{approx}}(t)|[\hat{\psi}^\dagger(x_1)\hat{\psi}(x_1),\, \tilde{V}(t) - \hat{W}_{\mathrm{ee}}]|\Psi_{\mathrm{approx}}(t)\rangle = 0, \tag{29}$$

where the symbol $[\cdot,\cdot]$ stands for a commutator. The derivation of Eq. (29) is shown in Appendix D and the fact that $\tilde{v}(\vec{r},t)$ could not be determined by simply solving Eq. (23) is explained in Appendix E.

We assume that we have a set of orthonormalized spin orbitals $\{\phi_k(x,t)\}$ $(1 \leqslant k \leqslant 2M$ and $N < 2M)$. The representations of the Fermi field operators in Eq. (29) are given using the set of spin orbitals as

$$\hat{\psi}^\dagger(x) = \sum_{k=1}^{2M} \phi_k^*(x,t)\hat{a}_k^\dagger(t) \tag{30}$$

and

$$\hat{\psi}(x) = \sum_{k=1}^{2M} \phi_k(x,t)\hat{a}_k(t), \tag{31}$$

where $\hat{a}_k^\dagger(t)$ and $\hat{a}_k(t)$ denote, respectively, the creation and annihilation operators of the single-particle state $|k(t)\rangle$, and the spin orbitals are defined by

$$\phi_k(x,t) = \langle x|k(t)\rangle = \langle x|\hat{a}_k^\dagger(t)|0\rangle, \tag{32}$$

with $|0\rangle$ representing the vacuum. The expressions of Eqs. (30) and (31) become exact as long as we use a complete orthonormalized set of time-independent or time-dependent spin orbitals, that is, when $M \to \infty$.

Using the representations of Eqs. (30) and (31) together with the commutation relation given by

$$[\hat{a}_k^\dagger(t)\hat{a}_m(t),\, \hat{a}_n^\dagger(t)\hat{a}_l(t)] = \delta_{nm}\hat{a}_k^\dagger(t)\hat{a}_l(t) - \delta_{kl}\hat{a}_n^\dagger(t)\hat{a}_m(t), \tag{33}$$

we can calculate the contribution of $\tilde{V}(t)$ in Eq. (29) as

$$\begin{aligned}
&\langle \Psi_{\mathrm{approx}}(t)|[\hat{\psi}^\dagger(x)\hat{\psi}(x),\, \tilde{V}(t)]|\Psi_{\mathrm{approx}}(t)\rangle \\
&= \sum_{ijs}(\phi_i^*(x,t)\phi_j(x,t)\gamma_{si}(t) \\
&\quad - \phi_s^*(x,t)\phi_i(x,t)\gamma_{ij}(t))\tilde{v}_{js}(t) \\
&= \sum_{ijs}\phi_i^*(x,t)(\gamma^T)_{is}(t)(\tilde{v}^T)_{sj}(t)\phi_j(x,t) \\
&\quad - \sum_{ijs}\phi_s^*(x,t)(\gamma^T)_{sj}(t)(\tilde{v}^T)_{ji}(t)\phi_i(x,t) \\
&= (\vec{\phi}(x,t))^\dagger[\boldsymbol{\gamma}^T(t),\, \tilde{\boldsymbol{v}}^T(t)]\vec{\phi}(x,t),
\end{aligned} \tag{34}$$

where the superscript T denotes the transpose of a vector or a matrix. We define here the column vector $\vec{\phi}(x,t)$ as

$$(\vec{\phi}(x,t))^T = (\phi_1(x,t), \phi_2(x,t), \ldots, \phi_{2M}(x,t)) \tag{35}$$

and the $2M \times 2M$ Hermitian matrices as

$$\begin{aligned}
\gamma_{ji}(t) &= \langle \Psi_{\mathrm{approx}}(t)|\hat{a}_i^\dagger(t)\hat{a}_j(t)|\Psi_{\mathrm{approx}}(t)\rangle \\
&= \sum_I^{(i)}(-1)^{p_I(i)+p_J(j)}C_I^*(t)C_{iI}^j(t)
\end{aligned} \tag{36}$$

and

$$\tilde{v}_{ij}(t) = \int dx\; \phi_i^*(x,t)\tilde{v}(\vec{r},t)\phi_j(x,t). \tag{37}$$

In Eq. (36), the symbol $\sum_I^{(i)}$ represents the summation over the configurations that include a spin orbital ϕ_i as a constituent, $C_{iI}^j(t)$ denotes the CI coefficient for a determinant that is constructed from the determinant Φ_I by a single substitution, $\phi_j \leftarrow \phi_i$, and the symbol $p_I(i)$ stands for the *position* of the ith spin orbital in Φ_I, i.e., $p_K(i) = j$, which means that $i = k_j$ in Eq. (8). In Eq. (36), J of $p_J(j)$ stands for Φ_{iI}^j representing the single substitution $\phi_j \leftarrow \phi_i$ in Φ_I, i.e., $\Phi_J = \Phi_{iI}^j$. The matrix $\boldsymbol{\gamma}(t)$ is the spin-orbital representation of the 1-RDM of $\gamma_{\mathrm{approx}}(x',t|x,t)$.

On the other hand, we evaluate the contribution of $\hat{W}_{\mathrm{ee}}$ in Eq. (29) as

$$\begin{aligned}
&\langle \Psi_{\mathrm{approx}}(t)|[\hat{\psi}^\dagger(x)\hat{\psi}(x),\, \hat{W}_{\mathrm{ee}}]|\Psi_{\mathrm{approx}}(t)\rangle \\
&= \sum_{ij}^{2M}\phi_i^*(x,t)(X_{ji}(t) - X_{ij}^*(t))\phi_j(x,t) \\
&= (\vec{\phi}(x,t))^\dagger(\boldsymbol{X}^T(t) - \boldsymbol{X}^*(t))\vec{\phi}(x,t),
\end{aligned} \tag{38}$$

where we have used the commutation relation

$$\begin{aligned}
&[\hat{a}_k^\dagger(t)\hat{a}_m(t),\, \hat{a}_p^\dagger(t)\hat{a}_r^\dagger(t)\hat{a}_s(t)\hat{a}_q(t)] \\
&= \delta_{mp}\hat{a}_k^\dagger(t)\hat{a}_r^\dagger(t)\hat{a}_s(t)\hat{a}_q(t) - \delta_{mr}\hat{a}_k^\dagger(t)\hat{a}_p^\dagger(t)\hat{a}_s(t)\hat{a}_q(t) \\
&\quad + \delta_{ks}\hat{a}_p^\dagger(t)\hat{a}_r^\dagger(t)\hat{a}_q(t)\hat{a}_m(t) - \delta_{kq}\hat{a}_p^\dagger(t)\hat{a}_r^\dagger(t)\hat{a}_s(t)\hat{a}_m(t)
\end{aligned} \tag{39}$$

and the expression of $\hat{W}_{\mathrm{ee}}$ given by Eq. (E2) in Appendix E.

We define the $2M \times 2M$ matrix $\boldsymbol{X}(t)$ in Eq. (38) by its matrix elements as

$$X_{ij}(t) = \sum_{pqr}^{2M} [i(t)q(t)|r(t)p(t)]\Gamma^{(2)}_{qpjr}(t), \tag{40}$$

where $\Gamma^{(2)}_{qpjr}(t)$ is the spin-orbital representation of $\Gamma^{(2)}_{\text{approx}}(x'_1, x'_2, t|x_1, x_2, t)$ given by

$$\Gamma^{(2)}_{qpjr}(t) = \langle \Psi_{\text{approx}}(t)|\hat{a}^{\dagger}_{j}(t)\hat{a}^{\dagger}_{r}(t)\hat{a}_{p}(t)\hat{a}_{q}(t)|\Psi_{\text{approx}}(t)\rangle \tag{41}$$

and the two-electron integrals, which are defined by

$$\begin{aligned}[j(t)q(t)|r(t)p(t)] = \int dx_1 dx_2\, \phi^*_j(x_1,t)\phi_q(x_1,t)\\ \times \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\phi^*_r(x_2,t)\phi_p(x_2,t).\end{aligned} \tag{42}$$

In calculating $\boldsymbol{\Gamma}^{(2)}(t)$, we can use the relation given by

$$\begin{aligned}\Gamma^{(2)}_{ijkl}(t) = &\sum_{K}^{\mathcal{L}} \langle \Psi_{\text{approx}}(t)|\hat{a}^{\dagger}_{k}(t)\hat{a}_{i}(t)|\Phi_K(t)\rangle\\ &\times \langle \Phi_K(t)|\hat{a}^{\dagger}_{l}(t)\hat{a}_{j}(t)|\Psi_{\text{approx}}(t)\rangle\\ &- \delta_{il}\langle \Psi_{\text{approx}}(t)|\hat{a}^{\dagger}_{k}(t)\hat{a}_{j}(t)|\Psi_{\text{approx}}(t)\rangle\\ = &\sum_{K}^{(il)} (-1)^{p_K(i)+p_K(l)+p_J(k)+p_{J'}(j)}\big(C^{k}_{iK}(t)\big)^* C^{j}_{lK}(t)\\ &- \delta_{kj}\gamma_{jk}(t),\end{aligned} \tag{43}$$

where the symbol $\sum_K^{(il)}$ represents the summation over the configurations that include spin orbitals ϕ_i and ϕ_l as the constituent orbitals.

We introduce the anti-Hermitian matrix $\boldsymbol{B}(t)$ given by

$$\boldsymbol{B}(t) = \boldsymbol{X}(t) - \boldsymbol{X}^{\dagger}(t). \tag{44}$$

By substituting Eqs. (34) and (38) into Eq. (29), we obtain

$$\begin{aligned}&\langle \Psi_{\text{approx}}(t)|[\hat{\psi}^{\dagger}(x)\hat{\psi}(x), \tilde{V}(t) - \hat{W}_{\text{ee}}]|\Psi_{\text{approx}}(t)\rangle\\ &= (\vec{\phi}(x,t))^{\dagger}([\boldsymbol{\gamma}^T(t), \tilde{\boldsymbol{v}}^T(t)] - \boldsymbol{B}^T(t))\vec{\phi}(x,t) = 0.\end{aligned} \tag{45}$$

Equation (45) should hold for any x, and thus, we obtain

$$[\tilde{\boldsymbol{v}}(t), \boldsymbol{\gamma}(t)] = \boldsymbol{B}(t), \tag{46}$$

which can be regarded as the equation with which the matrix $\tilde{\boldsymbol{v}}(t)$ is determined. When the Hermitian matrix $\boldsymbol{\gamma}(t)$ and the anti-Hermitian matrix $\boldsymbol{B}(t)$ are given, we can solve Eq. (46) for the *Hermitian* matrix $\tilde{\boldsymbol{v}}(t)$ [30]. The Hermiticity of the matrix $\tilde{\boldsymbol{v}}(t)$ is a necessary and sufficient condition for the multiplicative potential function $\tilde{v}(\vec{r},t)$ to be real-valued.

We can construct $\tilde{v}(\vec{r},t)$ using $\tilde{\boldsymbol{v}}(t)$ as

$$\begin{aligned}\tilde{v}(\vec{r},t) = \langle x|\tilde{v}(t)|x\rangle &= \sum_{ij}^{2M} \phi_i(x,t)\tilde{v}_{ij}(t)\phi^*_j(x,t)\\ &= (\vec{\phi}(x,t))^T\tilde{\boldsymbol{v}}(t)(\vec{\phi}(x,t))^*,\end{aligned} \tag{47}$$

where we have used the notation of Eq. (35). Equation (47) can be used to determine the effective potential using the spin orbitals $\{\phi_k(x,t)\}$ and the CI coefficients $\{C_K(t)\}$. By using the expression of Eq. (13), we can show that the right-hand side of Eq. (47) does not depend on the spin coordinate μ.

If we assume that a single exact effective potential $\hat{v}_{\text{eff}}(t)$ exists when $2M \to \infty$ and that the corresponding internal effective potential $\tilde{v}(t) = \hat{v}_{\text{eff}}(t) - \hat{v}_{\text{ext}}(t)$ also exists, the form of the potential defined by the right-hand side of Eq. (47) represents the orthogonal projection of the exact operator $\tilde{v}(t)$ onto the subspace spanned by the finite set of $\{\phi_k(x,t)\}$ $(1 \leqslant k \leqslant 2M)$ [27]. We can thus regard the expression of Eq. (47) as an approximation of the single exact effective potential $\hat{v}_{\text{eff}}(t)$ using a finite number of spin orbitals. The invariance of the effective potential under orbital rotation is discussed in Appendix F and the gauge transformation from the length gauge to the velocity gauge is shown in Appendix G.

In Fig. 1, we summarize the procedures introduced in Secs. II B–II D in a flowchart.

E. Propagation of the wave function

In order to perform time propagation of the wave function $\Psi_{\text{approx}}(t)$, we need to set the initial conditions. The initial conditions are the effective potential $v_{\text{eff}}(\vec{r})$ associated with the initial stationary-state wave function and the spin orbitals and CI coefficients constituting the initial stationary-state wave function.

Once the EOM for the real-time propagation of the wave function $\Psi_{\text{approx}}(t)$ is formulated, the wave function Ψ_{approx} of the ground state can be calculated using the imaginary-time propagation method as long as the ground state is not degenerated [31–33]. Obtaining the ground state Ψ_{approx} is equivalent to preparing the initial conditions for real-time propagation of the wave function, that is, we can use Ψ_{approx} as the initial wave function, as $\Psi_{\text{approx}}(t=0) = \Psi_{\text{approx}}$ and $v_{\text{eff}}(\vec{r}, t=0) = v_{\text{eff}}(\vec{r})$. The spin orbitals and the CI coefficients optimized for the ground state Ψ_{approx} are used as the initial conditions for Eqs. (12) and (25), respectively.

A possible iterative scheme for the imaginary-time propagation to obtain the optimized time-independent effective potential $v_{\text{eff}}(\vec{r})$ and the optimized time-independent CI coefficients for the ground state is shown in Appendix H. The spin orbitals are obtained as the eigenfunctions of a single-particle time-independent Schrödinger equation having the optimized time-independent effective potential $v_{\text{eff}}(\vec{r})$.

By using Eqs. (12), (23), and (25) we can show for real-time propagation that the norm of the wave function is conserved and that, as long as an external perturbation is absent, the energy expectation value is also conserved irrespective of the expansion length of $\mathcal{L}$. In Appendix H, we also show a possible leapfrog integration scheme for real-time propagation of the effective potential $v_{\text{eff}}(\vec{r},t)$ and the CI coefficients.

III. COMBINATION WITH THE DENSITY EQUATION THEORY

As long as the set of spin orbitals is complete or, equivalently, if $\mathcal{L} \to \infty$, we can apply the variation equation, Eq. (23), to describe an exact wave function. In this section, we consider this ideal limit of $\mathcal{L} \to \infty$ in Eq. (7) and assume that the

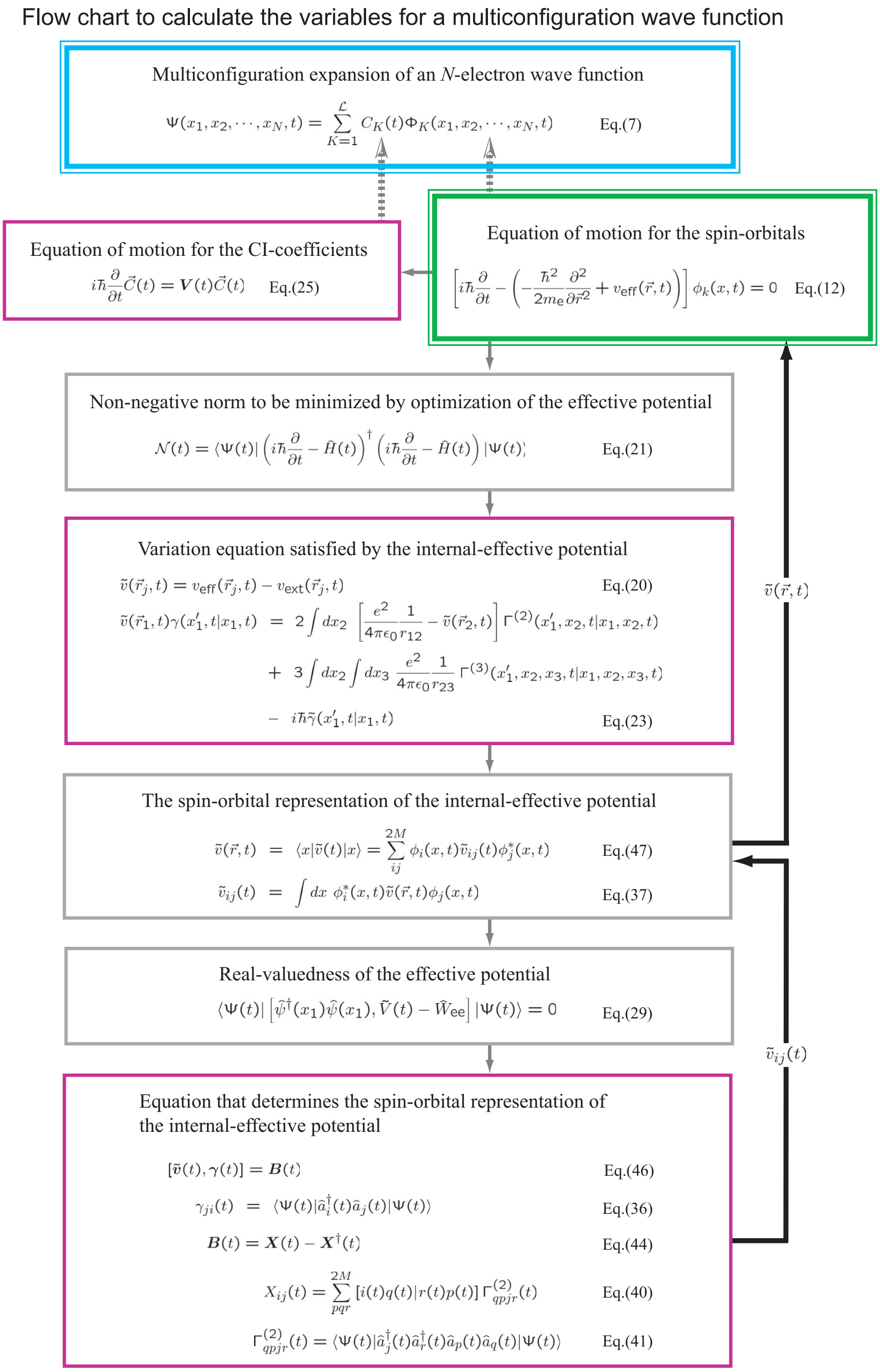

FIG. 1. Flowchart for the derivations of the equation of motion for the CI coefficients and the internal effective potential introduced in Sec. II.

exact ground-state wave function $\Psi_{\rm exact}$ is calculated by the imaginary-time propagation method. This $\Psi_{\rm exact}$ is the solution of the time-independent Schrödinger equation for the lowest eigenvalue $E_{\rm exact}$ of the relevant system as represented by

$$\hat{H}_0\Psi_{\rm exact}=E_{\rm exact}\Psi_{\rm exact}, \tag{48}$$

where $\hat{H}_0$ denotes the total Hamiltonian of the system having no external perturbation, which means that $v_{\rm ptb}(\vec{r},t)=0$ in Eq. (4).

We can simplify Eq. (23) by introducing the relations among exact RDMs, which were derived by the density equation theory [20,21,23]. It is shown by Nakatsuji in Ref. [21] that the density equation, also known as the contracted Schrödinger equation, is equivalent to the Schrödinger equation as long as the order (n) of the density equation is greater than or equal to 2 ($n \geqslant 2$) [34–37]. As pointed out in Refs. [21] and [38], the first-order ($n = 1$) density equation describes a necessary condition to be fulfilled by the Schrödinger equation.

We rewrite Eq. (23) using Eq. (20) for the exact ground-state wave function as

$$\begin{aligned}
&i\hbar\tilde{\gamma}_{\text{exact}}(x_1'|x_1) + [\hat{t}(\vec{r}_1) + v_{\text{eff}}(\vec{r}_1)]\gamma_{\text{exact}}(x_1'|x_1)\\
&\quad + 2\int dx_2\, [\hat{t}(\vec{r}_2) + v_{\text{eff}}(\vec{r}_2)]\Gamma^{(2)}_{\text{exact}}(x_1', x_2'|x_1, x_2)|_{x_2'=x_2}\\
&= [\hat{t}(\vec{r}_1) + v_{\text{ext}}(\vec{r}_1)]\gamma_{\text{exact}}(x_1'|x_1)\\
&\quad + 2\int dx_2 \left[\hat{t}(\vec{r}_2) + v_{\text{ext}}(\vec{r}_2) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\right]\\
&\quad \times \Gamma^{(2)}_{\text{exact}}(x_1', x_2'|x_1, x_2)|_{x_2'=x_2}\\
&\quad + 3\int dx_2 \int dx_3\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}_{\text{exact}}(x_1', x_2, x_3|x_1, x_2, x_3),
\end{aligned} \tag{49}$$

where we omit the time arguments in the RDMs and that in $\tilde{\gamma}_{\text{exact}}$. In Eq. (49), for convenience in the following discussion, we have added on both sides the kinetic energy operators $\hat{t}(\vec{r})$ operating on the 1-RDM as well as on the second-order reduced density matrix (2-RDM). The operator $\hat{t}(\vec{r}_j)$ acts on the unprimed argument x_j in the RDMs.

The first-order density equation, which was first reported by Nakatsuji [21] for exact RDMs, is given by

$$\begin{aligned}
&E_{\text{exact}}\gamma_{\text{exact}}(x_1'|x_1)\\
&\quad = [\hat{t}(\vec{r}_1) + v_{\text{ext}}(\vec{r}_1)]\gamma_{\text{exact}}(x_1'|x_1)\\
&\qquad + 2\int dx_2 \left[\hat{t}(\vec{r}_2) + v_{\text{ext}}(\vec{r}_2) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\right]\\
&\qquad \times \Gamma^{(2)}_{\text{exact}}(x_1', x_2'|x_1, x_2)|_{x_2'=x_2} + 3\int dx_2\\
&\qquad \times \int dx_3\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}_{\text{exact}}(x_1', x_2, x_3|x_1, x_2, x_3).
\end{aligned} \tag{50}$$

By subtracting Eq. (50) from Eq. (49), we obtain the relation

$$\begin{aligned}
&E_{\text{exact}}\gamma_{\text{exact}}(x_1'|x_1)\\
&\quad = i\hbar\tilde{\gamma}_{\text{exact}}(x_1'|x_1) + \hat{h}_{\text{eff}}(\vec{r}_1)\gamma_{\text{exact}}(x_1'|x_1)\\
&\qquad + 2\int dx_2\, \hat{h}_{\text{eff}}(\vec{r}_2)\Gamma^{(2)}_{\text{exact}}(x_1', x_2'|x_1, x_2)|_{x_2'=x_2},
\end{aligned} \tag{51}$$

where the single-particle effective Hamiltonian $\hat{h}_{\text{eff}}(\vec{r}_1)$ is defined by

$$\hat{h}_{\text{eff}}(\vec{r}_1) = \hat{t}(\vec{r}_1) + v_{\text{eff}}(\vec{r}_1). \tag{52}$$

Equation (51) should be satisfied by an exact wave function, and at this point, Eq. (51) is more stringent compared to the variation equation, Eq. (23). Because there is $i\hbar\tilde{\gamma}_{\text{exact}}(x_1'|x_1)$ on the right-hand side of Eq. (51), this equation is different from the first-order density equation describing a noninteracting electron system, that is, a model system that is described by a Hamiltonian composed of only single-particle operators. Because Eq. (51) is derived from the combination of the variation equation, Eq. (49), and the first-order density equation, Eq. (50), we refer to Eq. (51) as the variational first-order density equation. As shown in Appendix I, a formula with which we can calculate the total energy E_{exact} is obtained by performing the integration with respect to x_1 after setting $x_1' = x_1$ in Eq. (51) as

$$\begin{aligned}
E_{\text{exact}} &= \int dx_1\, \hat{h}_{\text{eff}}(\vec{r}_1)\gamma_{\text{exact}}(x_1'|x_1)|_{x_1'=x_1}\\
&\quad + \frac{1}{N}\int dx_1\, i\hbar\tilde{\gamma}_{\text{exact}}(x_1|x_1).
\end{aligned} \tag{53}$$

We note that we cannot determine the origin of the effective potential that can be treated as the common diagonal elements of Δ_{e} in $\tilde{\boldsymbol{v}}$ in Eq. (46), i.e., an energy displacement by Δ_{e} for all spin orbitals, because the diagonal matrix $\Delta_{\text{e}}\,\mathbf{1}$ always commutes with $\boldsymbol{\gamma}$. However, the displacement Δ_{e} does not change the ground-state energy of the system because the contribution of Δ_{e} in E_{exact} cancels out as

$$\begin{aligned}
&\Delta_{\text{e}}\int dx\, \gamma_{\text{exact}}(x|x) + \frac{1}{N}\int dx\, \langle\Psi_{\text{exact}}|\hat{n}(x)(-N\Delta_{\text{e}})|\Psi_{\text{exact}}\rangle\\
&\quad = 0
\end{aligned} \tag{54}$$

in Eq. (53).

The procedure adopted in the derivation of the variational first-order density equation can also be applied to an exact time-dependent wave function. Using the time-dependent DET developed by Nakatsuji in Ref. [22], the first-order time-dependent density equation for an exact wave function is expressed as

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}\gamma_{\text{exact}}(x_1', t'|x_1, t) &= [\hat{t}(\vec{r}_1) + v_{\text{ext}}(\vec{r}_1, t)]\gamma_{\text{exact}}(x_1', t'|x_1, t)\\
&\quad + 2\int dx_2 \left[\hat{t}(\vec{r}_2) + v_{\text{ext}}(\vec{r}_2, t) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\right]\Gamma^{(2)}_{\text{exact}}(x_1', x_2', t'|x_1, x_2, t)|_{x_2'=x_2}\\
&\quad + 3\int dx_2 \int dx_3\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}_{\text{exact}}(x_1', x_2, x_3, t'|x_1, x_2, x_3, t),
\end{aligned} \tag{55}$$

where the time derivative is taken only for the unprimed argument t in the same manner as in Ref. [22].

On the other hand, similarly to the derivation of Eq. (49) from Eq. (23), we rewrite Eq. (23) for the time-dependent case as follows:

$$\begin{aligned} & i\hbar\tilde{\gamma}_{\mathrm{exact}}(x_1', t'|x_1, t) + [\hat{t}(\vec{r}_1) + v_{\mathrm{eff}}(\vec{r}_1, t)]\gamma_{\mathrm{exact}}(x_1', t'|x_1, t) + 2\int dx_2\, [\hat{t}(\vec{r}_2) + v_{\mathrm{eff}}(\vec{r}_2, t)]\Gamma^{(2)}_{\mathrm{exact}}(x_1', x_2', t'|x_1, x_2, t)|_{x_2'=x_2} \\ & \quad = [\hat{t}(\vec{r}_1) + v_{\mathrm{ext}}(\vec{r}_1, t)]\gamma_{\mathrm{exact}}(x_1', t'|x_1, t) + 2\int dx_2 \left[\hat{t}(\vec{r}_2) + v_{\mathrm{ext}}(\vec{r}_2, t) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\right]\Gamma^{(2)}_{\mathrm{exact}}(x_1', x_2', t'|x_1, x_2, t)|_{x_2'=x_2} \\ & \qquad + 3\int dx_2 \int dx_3\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}_{\mathrm{exact}}(x_1', x_2, x_3, t'|x_1, x_2, x_3, t). \end{aligned} \tag{56}$$

By subtracting Eq. (56) from Eq. (55), we obtain the relation

$$i\hbar\frac{\partial}{\partial t}\gamma_{\mathrm{exact}}(x_1', t'|x_1, t) = i\hbar\tilde{\gamma}_{\mathrm{exact}}(x_1', t'|x_1, t) + \hat{h}_{\mathrm{eff}}(\vec{r}_1, t)\gamma_{\mathrm{exact}}(x_1', t'|x_1, t) + 2\int dx_2\, \hat{h}_{\mathrm{eff}}(\vec{r}_2, t)\Gamma^{(2)}_{\mathrm{exact}}(x_1', x_2', t'|x_1, x_2, t)|_{x_2'=x_2}, \tag{57}$$

where the single-particle time-dependent effective Hamiltonian is defined as

$$\hat{h}_{\mathrm{eff}}(\vec{r}_1, t) = \hat{t}(\vec{r}_1) + v_{\mathrm{eff}}(\vec{r}_1, t). \tag{58}$$

We refer to Eq. (57) as the variational time-dependent first-order density equation.

In solving Eq. (57), we may set the following initial conditions:

$$v_{\mathrm{eff}}(\vec{r}, t = 0) = v_{\mathrm{eff}}(\vec{r}), \tag{59}$$

$$\tilde{\gamma}_{\mathrm{exact}}(x_1', t' = 0|x_1, t = 0) = \tilde{\gamma}_{\mathrm{exact}}(x_1'|x_1), \tag{60}$$

$$\gamma_{\mathrm{exact}}(x_1', t' = 0|x_1, t = 0) = \gamma_{\mathrm{exact}}(x_1'|x_1), \tag{61}$$

and

$$\Gamma^{(2)}_{\mathrm{exact}}(x_1', x_2', t' = 0|x_1, x_2, t = 0) = \Gamma^{(2)}_{\mathrm{exact}}(x_1', x_2'|x_1, x_2), \tag{62}$$

where the quantities on the right-hand sides of the above equations are calculated for the exact ground-state wave function.

The variational time-dependent first-order density equation, Eq. (57) can be rewritten as an EOM for RDMs having a single time argument t by using the Hermitian property of the RDMs as

$$\begin{aligned} & i\hbar\frac{\partial}{\partial t}\gamma_{\mathrm{exact}}(x_1', t|x_1, t) \\ & \quad = [\hat{h}_{\mathrm{eff}}(\vec{r}_1, t) - \hat{h}_{\mathrm{eff}}(\vec{r}_1', t)]\gamma_{\mathrm{exact}}(x_1', t|x_1, t) \\ & \qquad + i\hbar[\tilde{\gamma}_{\mathrm{exact}}(x_1', t|x_1, t) + \tilde{\gamma}^{*}_{\mathrm{exact}}(x_1, t|x_1', t)]. \end{aligned} \tag{63}$$

where we use the relation

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\gamma_{\mathrm{exact}}(x_1', t|x_1, t) = {} & i\hbar\frac{\partial}{\partial t}\gamma_{\mathrm{exact}}(x_1', t'|x_1, t)|_{t'=t} \\ & - \left[i\hbar\frac{\partial}{\partial t}\gamma_{\mathrm{exact}}(x_1, t'|x_1', t)\right]^{*}\Bigg|_{t'=t}. \end{aligned} \tag{64}$$

By applying the expansion of Eq. (D5) to the second line of Eq. (63), we obtain

$$\begin{aligned} & i\hbar\frac{\partial}{\partial t}\gamma_{\mathrm{exact}}(x_1', t|x_1, t) \\ & \quad = [\hat{h}_{\mathrm{eff}}(\vec{r}_1, t) - \hat{h}_{\mathrm{eff}}(\vec{r}_1', t)]\gamma_{\mathrm{exact}}(x_1', t|x_1, t) \\ & \qquad + \langle\Psi_{\mathrm{exact}}(t)|[\hat{\psi}^{\dagger}(x_1')\hat{\psi}(x_1), \hat{H}(t) - \hat{H}_{\mathrm{eff}}(t)]|\Psi_{\mathrm{exact}}(t)\rangle. \end{aligned} \tag{65}$$

Alternatively, from the first-order time-dependent density equation, Eq. (55), we can derive

$$\begin{aligned} & i\hbar\frac{\partial}{\partial t}\gamma_{\mathrm{exact}}(x_1', t|x_1, t) \\ & \quad = [\hat{h}(\vec{r}_1, t) - \hat{h}(\vec{r}_1', t)]\gamma_{\mathrm{exact}}(x_1', t|x_1, t) \\ & \qquad + 2\int dx_2\, \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1'2}}\right]\Gamma^{(2)}_{\mathrm{exact}}(x_1', x_2, t|x_1, x_2, t). \end{aligned} \tag{66}$$

The expression of Eq. (66) corresponds to the first member of the BBGKY hierarchy equations [24] that describe the time evolution of a many-body fermionic system in a pure state in terms of RDMs. Equation (65) plays the same role as Eq. (66) within the present effective-potential theory. On the right-hand side of Eq. (66), the two-particle Coulombic potential appears in the second term. On the other hand, on the right-hand side of Eq. (65), the two-particle Coulombic potential contributes to both the first and the second terms. In the first term, a part of the two-particle Coulombic potential, which can be represented by single-particle operators, is included in the effective potential in $\hat{h}_{\mathrm{eff}}(\vec{r}, t)$. In the second term, the remaining part of the Coulomb potential is included in the two-particle operator represented by $\hat{H}(t) - \hat{H}_{\mathrm{eff}}(t) = \hat{W}_{\mathrm{ee}} - \hat{V}(t)$.

By taking steps similar to those used in the derivation of Eq. (45), we can further rewrite the second term on the right-hand side of Eq. (65) as

$$\begin{aligned} & \langle\Psi_{\mathrm{exact}}(t)|[\hat{\psi}^{\dagger}(x_1')\hat{\psi}(x_1), \hat{H}(t) - \hat{H}_{\mathrm{eff}}(t)]|\Psi_{\mathrm{exact}}(t)\rangle \\ & \quad = (\vec{\phi}(x_1', t))^{\dagger}\big(\boldsymbol{B}^{T}_{\mathrm{exact}}(t) - \big[\boldsymbol{\gamma}^{T}_{\mathrm{exact}}(t), \tilde{\boldsymbol{v}}^{T}(t)\big]\big)\vec{\phi}(x_1, t), \end{aligned} \tag{67}$$

where the matrix $\boldsymbol{B}_{\text{exact}}(t)$ is defined by Eq. (44). On the other hand, from the real-valuedness condition of the effective potential of Eq. (46), the right-hand side of Eq. (67) vanishes identically, and consequently, we can write Eq. (65) as

$$i\hbar\frac{\partial}{\partial t}\gamma_{\text{exact}}(x_1',t|x_1,t) = [\hat{h}_{\text{eff}}(\vec{r}_1,t) - \hat{h}_{\text{eff}}(\vec{r}_1{}',t)] \times \gamma_{\text{exact}}(x_1',t|x_1,t). \quad (68)$$

Equation (68) shows that the effect of the two-particle operators in the original Hamiltonian, Eq. (2), is properly described by the effective potential of the first member of the BBGKY hierarchy. Because the effective potential $v_{\text{eff}}(\vec{r},t)$ in $\hat{h}_{\text{eff}}(\vec{r},t)$ is determined by Eq. (46), $v_{\text{eff}}(\vec{r},t)$ is determined not only by the 1-RDM but also by the 2-RDM. This means that the 2-RDM is indirectly used in Eq. (68).

IV. COMPARISON WITH OTHER THEORIES

A. Comparison with localized Hartree-Fock theory

A variationally optimized time-dependent local effective-potential theory within a single-determinantal approximation is formulated by Nazarov in Ref. [29], which can be regarded as an extension of the existing localized Hartree-Fock (LHF) theory [39] to the time-dependent LHF (TDLHF) theory. The LHF theory for stationary-state calculations can be regarded as a good approximation [40] to the optimized effective-potential theory [41,42]. In LHF theory as well as TDLHF theory, the effective potential is optimized by using a single-determinantal wave function. On the other hand, in the present study, the multiconfiguration expansion of Eq. (7) is adopted for representing the wave function. Therefore, the present effective-potential theory can be regarded as an extension of the procedure developed in Ref. [29]. Indeed, we can obtain from Eq. (23) the expression of the time-dependent localized exchange potential derived in Ref. [29] by assuming a single-determinantal approximation in Eq. (7). We note that, within a single-determinantal approximation of the wave function, $i\hbar\dot{\gamma}_{\text{approx}}(x_1',t'|x_1,t) = 0$ in Eq. (24), and thus, Eq. (23) is expressed as

$$\begin{aligned}\tilde{v}(\vec{r}_1,t)\gamma_{\text{approx}}(x_1,t|x_1,t) &= 2\int dx_2\left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} - \tilde{v}(\vec{r}_2,t)\right]\Gamma^{(2)}_{\text{approx}}(x_1,x_2,t|x_1,x_2,t)\\ &\quad + 3\int dx_2\int dx_3\,\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\\ &\quad \times \Gamma^{(3)}_{\text{approx}}(x_1,x_2,x_3,t|x_1,x_2,x_3,t) \quad (69)\end{aligned}$$

for $x_1' = x_1$. We can see that Eq. (69) is exactly the same as the equation derived in Ref. [29] with which the time-dependent exchange potential $v_x(\vec{r},t)$ defined as

$$v_x(\vec{r},t) = \tilde{v}(\vec{r},t) - v_{\text{H}}(\vec{r},t) \quad (70)$$

was determined, where $v_{\text{H}}(\vec{r}_1,t)$ denotes the time-dependent Hartree potential given by

$$v_{\text{H}}(\vec{r}_1,t) = \frac{e^2}{4\pi\epsilon_0}\sum_{\sigma}\int d\vec{r}_2\frac{\gamma_{\text{approx}}(\vec{r}_2,\sigma,t|\vec{r}_2,\sigma,t)}{r_{12}}. \quad (71)$$

It is noted that the effective potential for the TDLHF is derived by deleting the last term on the right-hand side of Eq. (23). However, this term plays a central role in deriving the effective potential for a wave function represented by a multiconfigurational form as explained in Sec. II D.

B. Comparison with MCTDHF

In the present approach as well as in the MCTDHF, we adopt a multiconfigurational wave function as an approximation of an exact wave function and optimize the CI coefficients based on the Dirac-Frenkel time-dependent variational principle. However, in the present formulation, we optimize the effective potential to generate and propagate the spin orbitals. On the other hand, in the MCTDHF, we optimize the orbital functions directly. Consequently, the ground-state wave functions calculated by these two methods are different. Within the single-determinantal approximation of the ground state, the Hartree-Fock state [3] is obtained by the MCTDHF while the localized Hartree-Fock state is obtained by the present approach. This is because, within the MCTDHF, we take the variations with respect to all the spin orbitals to derive variation equations for spin orbitals. In the present formulation, by contrast, the variation equation is derived by taking the variation with respect to the effective potential under the constraint that the effective potential is local and real-valued. Because of this difference in the variational procedures, the ground-state energy calculated by the LHF theory is always higher than that calculated by the Hartree-Fock theory [39,40]. However, this difference is expected to be reduced when we adopt the multiconfiguration expansion as suggested by the expansion theorem [27].

The difference between the variations adopted in formulating the MCTDHF and the variations adopted in the present theory is also reflected in the property of the potentials that generate the spin orbitals by which the total wave function is constructed. Within the MCTDHF, if we rearrange the EOMs for the spin orbitals so that they are expressed in the form of the single-particle TDSE, all the operators other than the kinetic energy become complex-valued and orbital dependent as exemplified by the TDHF potential in the single-determinantal approximation [43,44]. Within the present formulation, we can always find the single real-valued effective potential, and thus, the EOM for the spin orbitals is a single-particle TDSE specified by the effective potential. Alternatively, the EOMs in the MCTDHF are derived as coupled nonlinear equations for the spin orbitals. Because a variety of established algorithms can be used in solving the single-particle TDSE, the numerical implementation of the propagation of the spin orbitals by the single-particle TDSE specified by the effective potential is more straightforward than that in the MCTDHF. According to the real-time propagation scheme proposed in Appendix H, the multiconfigurational wave function and the effective potential are determined simultaneously in a self-consistent manner. Therefore, using an EOM for the propagation of the spin orbitals, the variation of the time-dependent effective potential in time is reflected directly to the motion of the spin orbitals. This situation is in contrast to the conventional construction of a time-dependent single-particle potential [17,19]. Within the MCTDHF theory, the time-dependent single-particle potential for the time-dependent natural spin orbitals can be calculated after the calculation of the time-dependent many-electron wave function [43,44].

It is true that the present effective-potential theory defines only a necessary condition to be fulfilled by a many-electron TDSE. However, if the solution of a many-electron TDSE is obtained as the total number of spin orbits is increased, the converged solution can be regarded as a numerically exact solution based on the expansion theorem as in the case of MCTDHF calculations.

C. The N-representable problem

Within the DET, we cannot judge whether a given RDM is derived from an antisymmetrized N-particle wave function [45], that is, we cannot solve the N-representable problem [38,46]. However, the solution of the variation equation, Eq. (23), is free of the N-representable problem because the RDMs are constructed directly from the wave function of Eq. (7), and therefore, the density equations, Eqs. (50) and (57), can be used for the solution algorithms by which the effective potential is calculated.

We note that some necessary conditions for RDMs to be N-representable have been obtained [35–38], and therefore, the ground-state energy can be calculated without using a wave function by making accurate reconstruction functionals for the higher order RDMs using a trial 2-RDM [34–38,47–50]. It can be said that the original goal of the DET is satisfactorily achieved by adopting these accurate reconstruction functionals. Recently, the propagation algorithm of a 2-RDM without a wave function was tested and the numerical result confirms that the reconstruction functional for a time-dependent 3-RDM from a time-dependent 2-RDM is stable and accurate [51]. On the other hand, in the present theory, the RDMs are calculated using the time-dependent wave function of Eq. (7), in which the occupied spin orbitals and the CI coefficients are propagated in time by the explicit EOMs, Eqs. (12) and (25), respectively. Therefore, the RDMs treated in the present theory are free of the N-representable problem.

D. Comparison with Löwdin's effective-potential theory

Brenig [52] showed that CI coefficients that correspond to a single substitution from a reference configuration $\Phi_{K=1} \equiv \Phi_1$ can be eliminated when the magnitude of the norm $|\langle\Phi_1|\Psi_{\text{exact}}\rangle|$ is maximized, that is, the exact ground-state wave function Ψ_{exact} can be written as

$$\Psi_{\text{exact}} = C_1\Phi_1 + \sum_{i<j}\sum_{p<q} C_{ij}^{pq}\Phi_{ij}^{pq} + \sum_{i<j<k}\sum_{p<q<r} C_{ijk}^{pqr}\Phi_{ijk}^{pqr} + \cdots, \tag{72}$$

where the indices $i, j, k, \ldots$ denote spin orbitals constituting Φ_1, $p, q, r, \ldots$ denote other spin orbitals, and all the spin orbitals are orthonormalized. Φ_{ij}^{pq} denotes a Slater determinant obtained by the orbital substitutions of $(p, q) \leftarrow (i, j)$ in Φ_1, and Φ_{ijk}^{pqr} by $(p, q, r) \leftarrow (i, j, k)$ in Φ_1. An exact wave function having the structure of Eq. (72) is said to satisfy the Brillouin-Brueckner condition [53] and the spin orbitals are referred to as Brueckner orbitals.

Apparently, the multiconfiguration expansion that satisfies the Brillouin-Brueckner condition can readily be constructed using the general expansion of Eq. (7) by setting the CI coefficients to be 0 for the Slater determinants generated by the single substitution from Φ_1. This means that, by assuming the multiconfiguration expansion of the wave function that satisfies the Brillouin-Brueckner condition and by performing imaginary-time propagation, we can obtain the effective potential that generates Brueckner orbitals in the form of $\tilde{v}(\vec{r})$ defined by Eq. (47) using the solution of $\tilde{\boldsymbol{v}}$ for Eq. (46).

Note that the choice of the CI coefficients as shown in Eq. (72) works as a constraint for the orbital rotation discussed in Appendix F and fixes the spin orbitals uniquely to be Brueckner orbitals. Therefore, we can see that the present procedure to determine the effective potential based on the expansion of Eq. (72) establishes a way to construct the effective potential, whose existence was pointed out by Löwdin in Ref. [25], which generates the exact self-consistent field orbitals, i.e., Brueckner orbitals.

E. Comparison with Slater's effective-potential theory

In the effective-potential theory proposed by Slater for a multiconfigurational wave function [26], the effect of the electron-nuclear interaction is not included in the effective potential, and thus, the effective potential $V_{\text{e}}(x)$ defined in Ref. [26] corresponds to $\tilde{v}(\vec{r})$ in our formulation. For a spin-singlet state with an even-N electron system, Slater's effective potential is independent of spin variables, and thus, $V_{\text{e}}(x_1) = V_{\text{e}}(\vec{r}_1)$, and we can write the effective potential defined in Ref. [26] as

$$V_{\text{e}}(x_1) = \frac{\displaystyle\int (dx_1')\Psi^*(x_1, \ldots, x_N)\hat{W}_{\text{ee}}\Psi(x_1, \ldots, x_N)}{\displaystyle\int (dx_1')\Psi^*(x_1, \ldots, x_N)\Psi(x_1, \ldots, x_N)}, \tag{73}$$

which corresponds to $\tilde{v}(\vec{r})$ in the present study as explained below. Because the discussion below can be applied both to an approximated and an exact wave function, hereafter, in this section, we omit the subscripts "approx" and "exact" for the wave function and for the RDMs. For the ground state, our variation equation, Eq. (23), for the effective potential is represented by

$$\begin{aligned}
&\tilde{v}(\vec{r}_1)\gamma(x_1|x_1)\\
&\quad = 2\int dx_2\left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} - \tilde{v}(\vec{r}_2)\right]\Gamma^{(2)}(x_1, x_2|x_1, x_2)\\
&\qquad + 3\int dx_2\int dx_3\,\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}(x_1, x_2, x_3|x_1, x_2, x_3)\\
&\qquad - i\hbar\tilde{\gamma}(x_1|x_1).
\end{aligned} \tag{74}$$

Alternatively, we can rewrite Eq. (73) as

$$\tilde{v}(\vec{r}_1)\gamma(x_1|x_1) = 2\int dx_2\,\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\Gamma^{(2)}(x_1, x_2|x_1, x_2), \tag{75}$$

where we use the relation of

$$V_{\text{e}}(\vec{r}_1) \equiv \tilde{v}(\vec{r}_1). \tag{76}$$

From comparison of Eqs. (74) and (75), we find that

$$\begin{aligned} R(x_1|x_1) = {} & i\hbar\tilde{\gamma}(x_1|x_1) + 2\int dx_2\, \tilde{v}(\vec{r}_2)\Gamma^{(2)}(x_1,x_2|x_1,x_2) \\ & - 3\int dx_2 \int dx_3\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}} \\ & \times \Gamma^{(3)}(x_1,x_2,x_3|x_1,x_2,x_3) \end{aligned} \tag{77}$$

is missing in Slater's formulation. Using the relation expressed by Eq. (J7) in Appendix J, we can rewrite Eq. (77) as

$$\begin{aligned} R(x_1|x_1) = {} & 2\int dx_2\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\Gamma^{(2)}(x_1,x_2|x_1,x_2) \\ & - \tilde{v}(\vec{r}_1)\gamma(x_1|x_1), \end{aligned} \tag{78}$$

which will be 0 if we use Slater's assumption, Eq. (75). Therefore, we see that Slater's effective potential can be deduced within our approach by imposing a constraint represented by $R(x_1|x_1) = 0$ in Eq. (77) to the variation equation, Eq. (74). In this sense, the imaginary-time propagation scheme for obtaining the optimized spin orbitals for a ground state shown in Appendix H can be regarded as the exactification of Slater's approach based on the well-defined variational formulation.

As shown by Löwdin [27], we can derive Slater's effective potential as an averaged potential of the optimized spin orbitals starting from the so-called extended Hartree-Fock equation.

Finally, we note that Eq. (74) as well as Eq. (75) can be applied to describe a time-dependent wave function if they are used together with the EOM for the CI coefficients of Eq. (25).

V. SUMMARY

In the present study, we have proposed a theory to solve the time-dependent Schrödinger equation for many-electron systems in which a time-dependent local effective potential is introduced to determine the time-dependent spin orbitals. For the time-dependent problem, the spin orbitals are propagated by a time-dependent single-particle Schrödinger equation with the time-dependent effective potential starting from the initial spin orbitals determined for the many-electron ground-state wave function. In order to describe the many-electron ground-state wave function, we define the spin orbitals as the eigenfunctions of a time-independent single-particle Schrödinger equation with a time-independent effective potential.

Based on the time-dependent variational principle, we have derived a variation equation [Eq. (23)] by which the effective potential is determined. We have provided Eq. (46), with which we can determine the spin-orbital representation of the internal effective potential, establishing a relation among the first- and second-order reduced density matrices and the Coulombic interaction operator in the spin-orbital representation. Equation (46) ensures that the effective potential is a real-valued function. The effective potential is also shown to be invariant under the rotation of the spin orbitals.

We have introduced a possible iterative scheme for imaginary-time propagation to obtain the optimized time-independent effective potential and the optimized time-independent CI coefficients for the ground state and a leapfrog integration scheme for real-time propagation of the effective potential and the CI coefficients.

By combining the variation equation, Eq. (49), with the first-order density equation, Eq. (50), we obtain the variational first-order density equation, Eq. (51). For the time-dependent case, can also combine our variation equation, Eq. (56), with the time-dependent first-order density equation, Eq. (55), and derive the variational time-dependent first-order density equation, Eq. (57). By setting the two time arguments used in Eq. (57) to be identical, we can derive the first member of the BBGKY hierarchy using the time-dependent single-particle effective Hamiltonian as Eq. (68).

We have shown that the variational equation for the effective potential [Eq. (23)] gives the effective potential derived by Nazarov in Ref. [29] in the time-dependent localized Hartree-Fock theory and have derived the effective potential for the time-dependent localized Hartree-Fock theory by neglecting the last term on the right-hand side of Eq. (23). On the other hand, for a wave function represented in a multiconfigurational form, we have shown that the neglected term in Eq. (23) plays an essential role in deriving the equation by which the effective potential is determined [Eq. (46)].

Based on the comparison with the present formulation, we have clarified that we can calculate the effective potential that generates Brueckner orbitals proposed by Löwdin by the present formulation by assuming a wave function satisfying the Brillouin-Brueckner condition and that we can derive Slater's effective potential for a multiconfigurational wave function by imposing the constraint $R(x_1|x_1) = 0$ in Eq. (77) to the variation equation for the effective potential of Eq. (74) derived in the present study.

We can apply the present effective-potential approach to the description of the dynamics of bosonic systems and systems consisting of bosons and fermions. In order to describe a non-Born-Oppenheimer molecular wave function, we have to introduce nuclear amplitudes in the MCTDHF method [12,54]. It may also be possible to construct a non-Born-Oppenheimer wave function within the present effective-potential theory by introducing another effective potential for the nuclear motion in addition to the effective potential for the electronic motion. As proposed in an earlier MCTDHF paper [55], we are able to calculate the effective-potential functions for the excited states by projecting out numerically the wave functions for the electronic states, having lower energies, starting from the first excited state.

ACKNOWLEDGMENTS

The authors thank Prof. H. Goto of Butsuryo College of Osaka, Prof. K. Nobusada of the Institute for Molecular Science, Prof. A. D. Bandrauk of Université de Sherbrooke, and Prof. E. K. U. Gross of Max Planck Institute of Microstructure Physics for valuable discussions. This research was supported by JSPS KAKENHI Grant No. 24655005, JSPS KAKENHI Grant No. JP15H05696, and a Grant-in-Aid of the Institute for Molecular Science, Department of Theoretical and Computational Molecular Science.

APPENDIX A: DERIVATION OF EQ. (23) FROM EQ. (22)

In this Appendix, we omit the subscript "approx" for the wave function and for the RDMs because the derivations here can also be applied to an exact wave function.

The permutation symmetry of the wave function with respect to the coordinates of the particles simplifies the expression of Eq. (22) as

$$\begin{aligned}0 = i\hbar \sum_{K} \frac{dC_K(t)}{dt} \int dx_1 \cdots \int dx_N \Psi^*(x_1, x_2, \ldots, x_N, t)\delta\tilde{v}^\dagger(\vec{r}_1, t)\Psi(x_1, x_2, \ldots, x_N, t)\\ + \int dx_1 \cdots \int dx_N \Psi^*(x_1, x_2, \ldots, x_N, t)\delta\tilde{v}^\dagger(\vec{r}_1, t)\\ \times \left\{ \sum_{j=1}^{N} \tilde{v}(\vec{r}_j, t) - \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^{N} \frac{1}{r_{ij}} \right\} \Psi(x_1, x_2, \ldots, x_N, t).\end{aligned} \tag{A1}$$

Equation (A1) should hold for an arbitrary variation of $\delta\tilde{v}^\dagger(\vec{r}_1, t)$, and thus, we obtain

$$\begin{aligned}0 &= i\hbar \sum_{K} \frac{dC_K(t)}{dt} \int dx_2 \cdots \int dx_N \Psi^*(x_1, x_2, \ldots, x_N, t)\Phi_K(x_1, x_2, \ldots, x_N, t)\\ &\quad + \int dx_2 \cdots \int dx_N \Psi^*(x_1, x_2, \ldots, x_N, t) \left\{ \sum_{j=1}^{N} \tilde{v}(\vec{r}_j, t) - \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^{N} \frac{1}{r_{ij}} \right\} \Psi(x_1, x_2, \ldots, x_N, t)\\ &= i\hbar \sum_{K} \frac{dC_K(t)}{dt} \int (dx_1')\, \Psi^*\Phi_K + \int (dx_1')\, \Psi^* \left\{ \sum_{j=1}^{N} \tilde{v}(\vec{r}_j, t) - \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^{N} \frac{1}{r_{ij}} \right\} \Psi,\end{aligned} \tag{A2}$$

where we adopt the notation [27]

$$\int (dx_1') \equiv \int dx_2 \cdots \int dx_N. \tag{A3}$$

Using the permutation symmetry of the wave function Eq. (A2) can be rewritten as

$$\begin{aligned}0 = i\hbar \sum_{K} \frac{dC_K(t)}{dt} \int (dx_1')\, \Psi^*\Phi_K + \int (dx_1')\, \Psi^*\tilde{v}(\vec{r}_1, t)\Psi + (N-1) \int (dx_1')\, \Psi^*\tilde{v}(\vec{r}_2, t)\Psi - (N-1) \int (dx_1')\, \Psi^* \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}} \Psi\\ - \frac{1}{2}(N-1)(N-2) \int (dx_1')\, \Psi^* \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{23}} \Psi.\end{aligned} \tag{A4}$$

We introduce the notation given by Eq. (24) to the first term in Eq. (A4) as

$$i\hbar\tilde{\gamma}(x_1', t'|x_1, t) \equiv i\hbar N \int (dx_1')\, \Psi^*(x_1', x_2, x_3, \ldots, x_N, t') \sum_{K=1}^{\mathcal{L}} \frac{dC_K(t)}{dt} \Phi_K(x_1, x_2, \ldots, x_N, t). \tag{A5}$$

The 1-RDM γ associated with time-dependent many-electron wave functions $\Psi(t')$ and $\Psi(t)$ is defined by

$$\begin{aligned}\gamma(x_1', t'|x_1, t) &= \langle \Psi(t')|\hat{\psi}^\dagger(x_1')\hat{\psi}(x_1)|\Psi(t)\rangle\\ &= {}_N C_1 \int (dx_1')\, \Psi^*(x_1', x_2, x_3, \ldots, x_N, t')\Psi(x_1, x_2, x_3, \ldots, x_N, t),\end{aligned} \tag{A6}$$

where $\hat{\psi}^\dagger(x_1)$ and $\hat{\psi}(x_1)$ are the creation and annihilation field operators for the fermion, respectively, and $\Gamma^{(2)}$ and $\Gamma^{(3)}$ are defined, respectively, as

$$\begin{aligned}\Gamma^{(2)}(x_1', x_2', t'|x_1, x_2, t) &= \frac{1}{2!} \langle \Psi(t')|\hat{\psi}^\dagger(x_1')\hat{\psi}^\dagger(x_2')\hat{\psi}(x_2)\hat{\psi}(x_1)|\Psi(t)\rangle\\ &= {}_N C_2 \int (dx_{12}')\, \Psi^*(x_1', x_2', x_3, \ldots, x_N, t')\Psi(x_1, x_2, x_3, \ldots, x_N, t)\end{aligned} \tag{A7}$$

and

$$\begin{aligned}\Gamma^{(3)}(x_1', x_2', x_3', t'|x_1, x_2, x_3, t) &= \frac{1}{3!} \langle \Psi(t')|\hat{\psi}^\dagger(x_1')\hat{\psi}^\dagger(x_2')\hat{\psi}^\dagger(x_3')\hat{\psi}(x_3)\hat{\psi}(x_2)\hat{\psi}(x_1)|\Psi(t)\rangle\\ &= {}_N C_3 \int (dx_{123}')\, \Psi^*(x_1', x_2', x_3', x_4, \ldots, x_N, t)\Psi(x_1, x_2, x_3, x_4, \ldots, x_N, t').\end{aligned} \tag{A8}$$

In Eqs. (A7) and (A8), we adopt the notations [27]

$$\int (dx'_{12}) \equiv \int dx_3 \cdots \int dx_N \quad \text{and} \quad \int (dx'_{123}) \equiv \int dx_4 \cdots \int dx_N. \tag{A9}$$

By using Eqs. (A5), (A7), and (A8), Eq. (A4) is rewritten as

$$\begin{aligned} 0 &= i\hbar\tilde{\gamma}(x'_1 t'|x_1 t) + \tilde{v}(\vec{r}_1, t)\gamma(x'_1, t'|x_1, t) \\ &\quad + 2\int dx_2\, \tilde{v}(\vec{r}_2, t)\Gamma^{(2)}(x'_1, x_2, t'|x_1, x_2, t) - 2\int dx_2\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\Gamma^{(2)}(x'_1, x_2, t'|x_1, x_2, t) \\ &\quad - 3\int dx_2 dx_3\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}(x'_1, x_2, x_3, t'|x_1, x_2, x_3, t), \end{aligned} \tag{A10}$$

which is Eq. (23).

APPENDIX B: REAL-VALUEDNESS OF THE EFFECTIVE POTENTIAL

In this Appendix, we show that the effective potential $v_{\text{eff}}(\vec{r}, t)$ given as the solution of Eq. (23) can be taken as a real-valued function. We omit the subscript "approx" for the wave function as well as for the RDMs because the derivations here can also be applied to an exact wave function.

The diagonal element of the variation equation, Eq. (23), is rewritten using the relation of Eq. (20) as

$$\begin{aligned} &i\hbar\tilde{\gamma}(x_1, t|x_1, t) + v_{\text{eff}}(\vec{r}_1, t)\gamma(x_1, t|x_1, t) + 2\int dx_2\, v_{\text{eff}}(\vec{r}_2, t)\Gamma^{(2)}(x_1, x_2, t|x_1, x_2, t) = v_{\text{ext}}(\vec{r}_1, t)\gamma(x_1, t|x_1, t) \\ &+ 2\int dx_2 \left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} + v_{\text{ext}}(\vec{r}_2, t)\right]\Gamma^{(2)}(x_1, x_2, t|x_1, x_2, t) + 3\int dx_2 \int dx_3\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}(x_1, x_2, x_3, t|x_1, x_2, x_3, t). \end{aligned} \tag{B1}$$

On the right-hand side of Eq. (B1), the first, second, and third terms are all real-valued because they are represented by the operation of the Hermitian operators on the Hermitian RDMs. Consequently, the left-hand side of Eq. (B1) should be real-valued.

We rewrite the first term $i\hbar\tilde{\gamma}(x_1, t|x_1, t)$ in Eq. (B1) as

$$\begin{aligned} i\hbar\tilde{\gamma}(x_1, t|x_1, t) &= i\hbar\sum_K \frac{dC_K(t)}{dt}\, \langle\Psi(t)|\hat{n}(x_1)|\Phi_K(t)\rangle \\ &= \sum_{\text{KL}} V_{\text{KL}}(t)C_L(t)\, \langle\Psi(t)|\hat{n}(x_1)|\Phi_K(t)\rangle \\ &= \sum_{\text{KL}} C_L(t)\, \langle\Psi(t)|\hat{n}(x_1)|\Phi_K(t)\rangle\, \langle\Phi_K(t)|\hat{W}_{\text{ee}} - \hat{V}_{\text{eff}}(t) + \hat{V}_{\text{ext}}(t)|\Phi_L(t)\rangle \\ &= \langle\Psi(t)|\hat{n}(x_1)[\hat{W}_{\text{ee}} - \tilde{V}(t)]|\Psi(t)\rangle \\ &= \langle\Psi(t)|\hat{n}(x_1)[\hat{H}(t) - \hat{H}_{\text{eff}}(t)]|\Psi(t)\rangle, \end{aligned} \tag{B2}$$

where $\hat{n}(x_1)$ denotes the density operator represented by

$$\hat{n}(x_1) = \hat{\psi}^\dagger(x_1)\hat{\psi}(x_1). \tag{B3}$$

In the second line of Eq. (B2), we have used Eq. (25). In the third line, we have used the expression of the resolution operator onto the CI space spanned by a finite number of Slater determinants

$$\hat{1} = \sum_K |\Phi_K(t)\rangle\langle\Phi_K(t)|. \tag{B4}$$

In the fourth line, we have used the notation of Eq. (20).

In order to show that the effective potential $v_{\text{eff}}(\vec{r}, t)$ can be real-valued, we first assume that the effective potential is complex-valued and is described as $v_{\text{eff}}(\vec{r}, t) = v'_{\text{eff}}(\vec{r}, t) + i v''_{\text{eff}}(\vec{r}, t)$. The contribution of the imaginary part of the effective potential to the term $i\hbar\tilde{\gamma}(x_1, t|x_1, t)$ on the left-hand side of Eq. (B1) is given by using Eq. (B2) as

$$\begin{aligned} \Im\{i\hbar\tilde{\gamma}(x_1, t|x_1, t)\} &= -\,\langle\Psi(t)|\hat{n}(x_1)\int dx_2\, \hat{\psi}^\dagger(x_2)v''_{\text{eff}}(\vec{r}_2, t)\hat{\psi}(x_2)|\Psi(t)\rangle \\ &= -\int dx_2\, v''_{\text{eff}}(x_2, t)\, \langle\Psi(t)|\delta(x_1 - x_2)\hat{n}(x_1) + \hat{\psi}^\dagger(x_1)\hat{\psi}^\dagger(x_2)\hat{\psi}(x_2)\hat{\psi}(x_1)|\Psi(t)\rangle \\ &= -v''_{\text{eff}}(\vec{r}_1, t)\gamma(x_1, t|x_1, t) - 2\int dx_2\, v''_{\text{eff}}(\vec{r}_2, t)\Gamma^{(2)}(x_1, x_2, t|x_1, x_2, t). \end{aligned} \tag{B5}$$

On the other hand, the contribution of the imaginary part of the second term and that from the imaginary part of the third term on the right-hand side of Eq. (B1) are given by

$$\begin{aligned}\Im\Big[v_{\rm eff}(\vec{r}_1,t)\gamma(x_1,t|x_1,t)+2\int dx_2\; v_{\rm eff}(\vec{r}_2,t)\Gamma^{(2)}(x_1,x_2,t|x_1,x_2,t)\Big]\\ = v''_{\rm eff}(\vec{r}_1,t)\gamma(x_1,t|x_1,t)+2\int dx_2\; v''_{\rm eff}(\vec{r}_2,t)\Gamma^{(2)}(x_1,x_2,t|x_1,x_2,t).\end{aligned} \tag{B6}$$

The imaginary parts, Eqs. (B5) and (B6), cancel each other out in Eq. (B1) regardless of the value of $v''_{\rm eff}(\vec{r},t)$. Therefore, we are allowed to adopt the simplest condition of $v''_{\rm eff}(\vec{r},t)\equiv 0$ throughout the formulation, and consequently, from Eq. (B5), we find that $i\hbar\tilde{\gamma}(x_1,t|x_1,t)$ is real-valued.

APPENDIX C: DERIVATION OF EQ. (25)

In this Appendix, we derive the EOM for the CI coefficients based on the Dirac-Frenkel time-dependent variational principle [15,16], which is expressed as

$$\langle\delta\Psi(t)|i\hbar\frac{\partial}{\partial t}-\hat{H}(t)|\Psi(t)\rangle=0, \tag{C1}$$

where $\delta\Psi(t)$ denotes a possible variation of the wave function. In this section, we omit the subscript "approx" for the wave function and for the RDMs because the procedure below is applied not only to an approximated wave function but also to an exact wave function. In order to obtain the EOMs for the CI coefficients, we consider the variation of the wave function defined by

$$\delta\Psi(t)=\frac{\partial\Psi(t)}{\partial C_K(t)}=\Phi_K(t). \tag{C2}$$

By substituting Eq. (C2) into Eq. (C1), we obtain

$$\langle\Phi_K(t)|i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle=\langle\Phi_K(t)|\hat{H}(t)|\Psi(t)\rangle. \tag{C3}$$

The left-hand side of Eq. (C3) can be rewritten as

$$\begin{aligned}\sum_L\langle\Phi_K(t)|i\hbar\frac{\partial}{\partial t}|\Phi_L(t)\rangle\,C_L(t)&=\sum_L i\hbar\frac{dC_L(t)}{dt}\langle\Phi_K(t)|\Phi_L(t)\rangle+\sum_L\langle\Phi_K(t)|i\hbar\frac{\partial}{\partial t}|\Phi_L(t)\rangle\,C_L(t)\\&=\sum_L i\hbar\frac{dC_L(t)}{dt}\delta_{\rm KL}+\sum_L\langle\Phi_K(t)|\hat{H}_{\rm eff}(t)|\Phi_L(t)\rangle\,C_L(t)\\&=i\hbar\frac{dC_K(t)}{dt}+\sum_L\langle\Phi_K(t)|\hat{H}_{\rm eff}(t)|\Phi_L(t)\rangle\,C_L(t),\end{aligned} \tag{C4}$$

where we have used the definition of Eq. (12) in the first line to express the $\mathcal{L}\times\mathcal{L}$ matrix element of $\langle\Phi_K(t)|\hat{H}_{\rm eff}(t)|\Phi_L(t)\rangle$ and Eq. (10). Alternatively, using Eq. (7) we rewrite the right-hand side of Eq. (C3) as

$$\langle\Phi_K(t)|\hat{H}(t)|\Psi(t)\rangle=\sum_L\langle\Phi_K(t)|\hat{H}(t)|\Phi_L(t)\rangle\,C_L(t). \tag{C5}$$

By substituting Eqs. (C4) and (C5) into Eq. (C3) and by using Eqs. (2), (15), and (20), we obtain

$$i\hbar\frac{dC_K(t)}{dt}=\sum_L\langle\Phi_K(t)|\hat{W}_{\rm ee}-\tilde{V}(t)|\Phi_L(t)\rangle\,C_L(t), \tag{C6}$$

We note that the result expressed by Eq. (C6) can also be obtained by applying McLachlan's norm minimization principle [28].

APPENDIX D: DERIVATION OF EQ. (29)

In this Appendix, we derive Eq. (29). We omit the subscript "approx" for the wave function and for the RDMs because the procedure below can also be applied to an exact wave function. First, by taking the complex conjugate of Eq. (23), we obtain

$$\begin{aligned}\tilde{v}(\vec{r}_1,t)\gamma^*(x_1',t|x_1,t)&=2\int dx_2\left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}-\tilde{v}(\vec{r}_2,t)\right]\Gamma^{(2)*}(x_1',x_2,t|x_1,x_2,t)\\&\quad+3\int dx_2\int dx_3\;\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)*}(x_1',x_2,x_3,t|x_1,x_2,x_3,t)+i\hbar\tilde{\gamma}^*(x_1',t|x_1,t),\end{aligned} \tag{D1}$$

where we have used the fact that we have chosen the effective potential to be real-valued. Using the Hermiticity of the RDMs, the left-hand side of Eq. (D1) and the first and second terms on the right-hand side of Eq. (D1) can be rewritten as

$$\begin{aligned}\tilde{v}(\vec{r}_1,t)\gamma(x_1,t|x_1',t) &= 2\int dx_2\left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}-\tilde{v}(\vec{r}_2,t)\right]\Gamma^{(2)}(x_1,x_2,t|x_1',x_2,t)\\ &\quad+3\int dx_2\int dx_3\,\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}(x_1,x_2,x_3,t|x_1',x_2,x_3,t)+i\hbar\tilde{\gamma}^*(x_1',t|x_1,t).\end{aligned}\tag{D2}$$

If we exchange the coordinates x_1' and x_1 in Eq. (D2), we obtain

$$\begin{aligned}\tilde{v}(\vec{r}_1{}',t)\gamma(x_1',t|x_1,t) &= 2\int dx_2\left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{1'2}}-\tilde{v}(\vec{r}_2,t)\right]\Gamma^{(2)}(x_1',x_2,t|x_1,x_2,t)\\ &\quad+3\int dx_2\int dx_3\,\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}(x_1',x_2,x_3,t|x_1,x_2,x_3,t)+i\hbar\tilde{\gamma}^*(x_1,t|x_1',t).\end{aligned}\tag{D3}$$

By subtracting Eq. (D3) from Eq. (23), we obtain

$$\begin{aligned}\Delta(x_1',t|x_1,t) &= [\tilde{v}(\vec{r}_1,t)-\tilde{v}(\vec{r}_1{}',t)]\gamma(x_1',t|x_1,t) = 2\int dx_2\,\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}}-\frac{1}{r_{1'2}}\right]\Gamma^{(2)}(x_1',x_2,t|x_1,x_2,t)\\ &\quad-i\hbar[\tilde{\gamma}(x_1',t|x_1,t)+\tilde{\gamma}^*(x_1,t|x_1',t)]\\ &= 2\int dx_2\,\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}}-\frac{1}{r_{1'2}}\right]\Gamma^{(2)}(x_1',x_2,t|x_1,x_2,t)-\langle\Psi(t)|[\hat{\psi}^\dagger(x_1')\hat{\psi}(x_1),\hat{W}_{\mathrm{ee}}-\tilde{V}(t)]|\Psi(t)\rangle,\end{aligned}\tag{D4}$$

where, in the last line, we have used the relation

$$\begin{aligned}i\hbar\tilde{\gamma}(x_1',t|x_1,t) &= i\hbar\sum_K^{\mathcal{L}}\frac{dC_K(t)}{dt}\langle\Psi(t)|\hat{\psi}^\dagger(x_1')\hat{\psi}(x_1)|\Phi_K(t)\rangle = \sum_L^{\mathcal{L}}C_L(t)\,\langle\Psi(t)|\hat{\psi}^\dagger(x_1')\hat{\psi}(x_1)[\hat{W}_{\mathrm{ee}}-\tilde{V}(t)]|\Phi_L(t)\rangle\\ &= \langle\Psi(t)|\hat{\psi}^\dagger(x_1')\hat{\psi}(x_1)[\hat{W}_{\mathrm{ee}}-\tilde{V}(t)]|\Psi(t)\rangle,\end{aligned}\tag{D5}$$

which can be derived from the right-hand side of Eq. (24) in a manner similar to that used in the derivation of Eq. (B2). By setting $x_1' = x_1$ in Eq. (D4), we obtain Eq. (29).

APPENDIX E: DIFFICULTY IN DIRECT DETERMINATION OF THE POTENTIAL $\tilde{v}(\vec{r}_1, t)$ FROM EQ. (23)

In this Appendix, we show that we could not determine the effective potential as the solution of Eq. (23) as long as we use Eq. (25) in eliminating $dC_K(t)/dt$ in Eq. (24). The right-hand side of Eq. (D5) derived in Appendix D is evaluated by using the second quantized expression of the single-particle operator $\tilde{V}(t)$ defined by

$$\tilde{V}(t) = \int dx\ \hat{\psi}^\dagger(x)\tilde{v}(\vec{r},t)\hat{\psi}(x)\tag{E1}$$

and the two-particle operator $\hat{W}_{\mathrm{ee}}$ defined as

$$\hat{W}_{\mathrm{ee}} = \frac{1}{2}\int dx_2\int dx_3\ \hat{\psi}^\dagger(x_2)\hat{\psi}^\dagger(x_3)\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\hat{\psi}(x_3)\hat{\psi}(x_2).\tag{E2}$$

Then we obtain

$$\begin{aligned}i\hbar\tilde{\gamma}(x_1',t|x_1,t) &= 2\int dx_2\,\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\Gamma^{(2)}(x_1',x_2,t|x_1,x_2,t)+3\int dx_2\int dx_3\,\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{23}}\Gamma^{(3)}(x_1',x_2,x_3,t|x_1,x_2,x_3,t)\\ &\quad-\tilde{v}(\vec{r}_1,t)\gamma(x_1',t|x_1,t)-2\int dx\ \tilde{v}(\vec{r},t)\Gamma^{(2)}(x,x_1',t|x,x_1,t).\end{aligned}\tag{E3}$$

This *reproduction* of the variation equation, Eq. (23), essentially stems from the use of the assumption of the single-particle TDSE, Eq. (12), in deriving the EOMs for the CI coefficients as shown in Eq. (C4). In order to obtain $\tilde{v}(\vec{r},t)$ as the solution of Eq. (23), we need an additional condition imposed on Eq. (23). That condition is real-valuedness of the effective potential $\tilde{v}_{\mathrm{eff}}(\vec{r},t)$ or, equivalently, real-valuedness of the internal effective potential $\tilde{v}(\vec{r},t)$.

APPENDIX F: PROPERTY OF EQ. (46) UNDER ORBITAL ROTATION

In this Appendix, we consider the property of Eq. (46) under orbital rotation and transformation of the CI coefficients associated with the orbital rotation that keeps the wave function unchanged. Using a $2M \times 2M$ unitary matrix $\boldsymbol{u}$, the orbital rotation from a set of spin orbitals $\{\phi_l\}$ to a new set of spin orbitals $\{\phi'_k\}$ can be represented by

$$\phi'_k(t) = \sum_{l=1}^{2M} \phi_l(t) u_{lk} \quad (1 \leqslant k,\, l \leqslant 2M), \tag{F1}$$

that is,

$$(\vec{\phi}'(t))^T = (\vec{\phi}(t))^T\, \boldsymbol{u}, \tag{F2}$$

with the notation of Eq. (35). In order to keep the wave function unchanged under this orbital rotation, the associated change in the CI coefficients from $\{C_I(t)\}$ to $\{C'_I(t)\}$ should be determined so that $\Psi_{\text{approx}}(t)$ is represented as

$$\Psi_{\text{approx}}(t) = \sum_{I=1}^{\mathcal{L}} C_I(t)\Phi_I(t) = \sum_{J=1}^{\mathcal{L}} C'_J(t)\Phi'_J(t), \tag{F3}$$

where the prime denotes the wave function represented by the new set of spin orbitals. The transformation from $\{C_I(t)\}$ to $\{C'_I(t)\}$ can be expressed as

$$C'_J(t) = \sum_{I=1}^{\mathcal{L}} \langle \Phi'_J(t)|\Phi_I(t)\rangle\, C_I(t) \quad (1 \leqslant J \leqslant \mathcal{L}). \tag{F4}$$

The inner product $\langle \Phi'_J(t)|\Phi_I(t)\rangle$ in Eq. (F4) can be represented as $\langle \Phi'_J(t)|\Phi_I(t)\rangle = \det\{\boldsymbol{D}^{JI}(t)\}$, using $\boldsymbol{D}^{JI}(t)$, representing an $N \times N$ matrix with elements of $D^{JI}_{kl}(t) = \langle \phi'_{J_k}(t)|\phi_{I_l}(t)\rangle$. By using the definition of $\boldsymbol{\gamma}(t)$ in Eq. (36) and Eq. (F1), we can derive the representation of the 1-RDM as

$$\begin{aligned}\gamma_{\text{approx}}(x'_1, t|x_1, t) &= \langle \Psi(t)|\hat{\psi}^\dagger(x)\hat{\psi}(x)|\Psi(t)\rangle = \sum_{ab}^{2M} \phi^*_a(x'_1, t)\phi_b(x_1, t)\gamma_{ba}(t)\\ &= \sum_{pq}^{2M} \phi'^*_q(x'_1, t)\phi'_p(x_1, t)\left[\sum_{ab}^{2M} u^\dagger_{pb}\gamma_{ba}(t)u_{aq}\right],\end{aligned} \tag{F5}$$

which shows that the representation of $\gamma_{\text{approx}}(x'_1, t|x_1, t)$ using the rotated orbitals denoted $\boldsymbol{\gamma}'(t)$ is given by

$$\boldsymbol{\gamma}'(t) = \boldsymbol{u}^\dagger\, \boldsymbol{\gamma}(t)\, \boldsymbol{u}. \tag{F6}$$

Similarly, we can show that the matrix $\boldsymbol{X}$ of Eq. (40) is transformed to $\boldsymbol{X}'(t)$ as

$$\boldsymbol{X}'(t) = \boldsymbol{u}^\dagger\, \boldsymbol{X}(t)\, \boldsymbol{u}. \tag{F7}$$

From Eq. (F7) and Eq. (44), we obtain

$$\boldsymbol{B}'(t) = \boldsymbol{u}^\dagger\, \boldsymbol{B}(t)\, \boldsymbol{u}. \tag{F8}$$

Finally, we can show that the matrix $\tilde{\boldsymbol{v}}(t)$ of Eq. (37) is transformed as

$$\tilde{\boldsymbol{v}}'(t) = \boldsymbol{u}^\dagger \tilde{\boldsymbol{v}}(t)\, \boldsymbol{u}. \tag{F9}$$

From Eqs. (F6), (F8), and (F9), we conclude that the form of Eq. (46) determining the effective potential is invariant under the orbital rotation, that is,

$$[\tilde{\boldsymbol{v}}'(t),\, \boldsymbol{\gamma}'(t)] = \boldsymbol{B}'(t). \tag{F10}$$

We compared the internal effective potentials obtained from Eqs. (46) and (F10). If we substitute the relation of Eq. (F2) into Eq. (47), we obtain

$$\tilde{v}(\vec{r}, t) = (\vec{\phi}'(x, t))^T\, \boldsymbol{u}^\dagger \tilde{\boldsymbol{v}}(t)\, \boldsymbol{u}(\vec{\phi}'(x, t))^* = (\vec{\phi}'(x, t))^T \tilde{\boldsymbol{v}}'(t)(\vec{\phi}'(x, t))^* = \tilde{v}'(\vec{r}, t), \tag{F11}$$

where we have used the relation $\boldsymbol{u}\,\boldsymbol{u}^\dagger = \boldsymbol{1}$ in the first line and Eq. (F9) in the second line. Therefore, we can see that the internal effective potential $\tilde{v}(\vec{r}, t)$, and consequently the effective potential $v_{\text{eff}}(\vec{r}, t)$, is invariant under the orbital rotation.

Using Eq. (F11), we can also confirm that the single-particle TDSE of Eq. (12) is invariant under the orbital rotation of Eq. (F1). We rewrite Eq. (12) as

$$i\hbar\frac{\partial}{\partial t}(\vec{\phi}(x, t))^T = (\hat{t} + \tilde{v}_{\text{eff}}(\vec{r}, t))(\vec{\phi}(x, t))^T. \tag{F12}$$

By multiplying both sides by $\boldsymbol{u}$ from the right, we obtain

$$i\hbar\frac{\partial}{\partial t}(\vec{\phi}'(x, t))^T = (\hat{t} + \tilde{v}_{\text{eff}}(\vec{r}, t))(\vec{\phi}'(x, t))^T, \tag{F13}$$

where we have used the definition of Eq. (F2) and the conclusion from Eq. (F11). Therefore, for the time propagation of the wave function, there is an arbitrariness with respect to the orbital rotation, although the internal effective potential remains the same as shown by Eq. (F11). This invariance of the effective potential is suitable to analyze the motion of electrons because we only need to refer to a single effective potential regardless of the orbitals adopted.

We note that, except for possible sets of degenerate spin orbitals of the same spatial symmetry, we could not choose arbitrarily the unitary matrix $\boldsymbol{u}$, which is introduced in Eq. (F1), for the imaginary-time propagation because the initial spin orbitals are determined as the eigenfunctions of a single-particle time-independent Schrödinger equation.

APPENDIX G: GAUGE TRANSFORMATION

When we adopt the velocity gauge to describe the interaction of an electron and an external laser field instead of the interaction represented in the length gauge, Eq. (6), it is necessary to replace the kinetic energy operator in Eq. (12) with

$$\hat{t}(\vec{r}) = -\frac{\hbar^2}{2m_\mathrm{e}}\frac{\partial^2}{\partial\vec{r}^2} \Rightarrow \frac{1}{2m_\mathrm{e}}\left\{\frac{\hbar}{i}\frac{\partial}{\partial\vec{r}} + e\vec{\mathcal{A}}(t)\right\}^2, \tag{G1}$$

where

$$\vec{\mathcal{A}}(t) = -\int_{-\infty}^{t} dt'\,\vec{\mathcal{E}}(t') \tag{G2}$$

denotes the vector potential of the external field. Accordingly, the single-particle TDSE represented by Eq. (12) should be read as

$$\left[i\hbar\frac{\partial}{\partial t} - \left(\frac{1}{2m_\mathrm{e}}\left\{\frac{\hbar}{i}\frac{\partial}{\partial\vec{r}} + e\vec{\mathcal{A}}(t)\right\}^2 + v_\mathrm{eff}(\vec{r},t)\right)\right]\phi_k(x,t) = 0. \tag{G3}$$

In order to obtain the effective potential in the velocity gauge in Eq. (49), it is necessary to regard $\hat{t}(\vec{r})$ as the right-hand side of Eq. (G1) and assume that $v_\mathrm{ext}(\vec{r},t) = v_\mathrm{en}(\vec{r})$ by setting $v_\mathrm{ptb}(\vec{r},t) = 0$ in Eq. (4). Because the kinetic energy operators in Eqs. (17) and (18) cancel each other out in deriving Eq. (19), we can perform the gauge transformation from the length gauge to the velocity gauge by simply replacing the kinetic energy operator as shown in Eq. (G1) and by nullifying the perturbation represented using v_ptb in Eq. (6) in the length gauge.

APPENDIX H: POSSIBLE SCHEMES FOR TIME PROPAGATION

In this Appendix, we propose possible numerical schemes for both imaginary-time propagation of the wave function and real-time propagation. In this section, we omit the subscript "approx" for the wave function and the RDMs because the derivations below can be applied not only to an approximated wave function but also to an exact wave function.

First, we consider imaginary-time propagation to calculate the converged quantities that are used in the construction of a ground-state wave function in the form of Eq. (7). The calculation steps are as follows:

(i) We prepare a trial set of initial spin orbitals $\{\phi_k^{(n)}(x)\}$ and CI coefficients $\{\vec{C}^{(n)}(\tau)\}$, where the superscript integer "n" denotes the number of iterations and the argument τ is the imaginary time. For instance, if we assume the Hartree-Fock orbitals for the initial guess, we prepare N Hartree-Fock spin orbitals and set $C_1^{(n=0)}(\tau=0) = 1$ and $C_K^{(n=0)}(\tau=0) = 0$ for $K \geqslant 2$, where $\Phi_{K=1}^{(n=0)}$ is chosen as the Hartree-Fock state Φ_HF.

(ii) We propagate the CI coefficients for a time increment of $\delta\tau$ by adopting the EOM, Eq. (25), for the imaginary-time argument τ, which is represented by

$$-\hbar\frac{d}{d\tau}\vec{C}^{(n)}(\tau) = \boldsymbol{V}^{(n)}(\tau)\vec{C}^{(n)}(\tau), \tag{H1}$$

where the matrix element of $\boldsymbol{V}^{(n)}(\tau)$ is evaluated by using $\{\phi_k^{(n)}(x)\}$ and $\{\vec{C}^{(n)}(\tau)\}$. The norm of the CI coefficients is not maintained in the course of the time propagation represented by Eq. (H1) because the propagation is not unitary. We thus renormalize the propagated CI coefficients $\{\vec{C}^{(n)}(\tau+\delta\tau)\}$ so that they fulfill $\sum_K |C_K^{(n)}(\tau+\delta\tau)|^2 = 1$ and regard the renormalized CI-coefficients as $\{\vec{C}^{(n+1)}(\tau+\delta\tau)\}$.

(iii) Next, using $\{\phi_k^{(n)}(x)\}$ and $\{\vec{C}^{(n+1)}(\tau+\delta\tau)\}$, we calculate the spin-orbital representation of the first-order RDM as $\boldsymbol{\gamma}^{(n+1)}(\tau+\delta\tau)$ and that of the second-order as $\boldsymbol{\Gamma}^{(2)(n+1)}(\tau+\delta\tau)$. Using $\{\phi_k^{(n)}(x)\}$, we evaluate the two-electron integrals defined by Eq. (42).

(iv) We solve Eq. (46) for $\tilde{\boldsymbol{v}}$ using the quantities prepared in step iii. Then we construct the updated effective potential using Eq. (47) as $v_\mathrm{eff}^{(n+1)}(\vec{r},\tau+\delta\tau)$. If there is no external perturbation, we can set $\tilde{v} = v_\mathrm{eff} - v_\mathrm{en}$ from Eqs. (4) and (20).

(v) Finally, we calculate the spin orbitals for $k = 1, 2, \ldots, N, \ldots$ as the eigenfunctions of the single-particle time-independent Schrödinger equation obtained by numerical diagonalization,

$$\left[-\frac{\hbar^2}{2m_\mathrm{e}}\frac{\partial^2}{\partial\vec{r}^2} + v_\mathrm{eff}^{(n+1)}(\vec{r},\tau+\delta\tau)\right]\phi_k^{(n+1)}(x) = \epsilon_k^{(n+1)}\phi_k^{(n+1)}(x), \tag{H2}$$

where ϵ_k denotes the kth eigenvalue.

When the conditions

$$\{\phi_k^{(n+1)}(x)\} = \{\phi_k^{(n)}(x)\}$$

and

$$\{\vec{C}^{(n+1)}(\tau+\delta\tau)\} = \{\vec{C}^{(n)}(\tau)\}, \tag{H3}$$

are numerically satisfied, we regard that convergence is achieved. If convergence is not achieved, we have to iterate the above steps i–v using the spin orbitals $\{\phi_k^{(n+1)}(x)\}$ and the CI coefficients $\{\vec{C}^{(n+1)}(\tau+\delta\tau)\}$ as the trial spin orbitals and CI coefficients in step i.

We note that the eigenequation, Eq. (H2), in step v can also be solved by propagation of the single-particle TDSE in the imaginary-time domain, as discussed in Refs. [3] and [33], by rewriting the real-time EOM for the spin orbitals, Eq. (12), as

$$-\frac{\partial}{\partial\tau}\phi_k(x,\tau) = \left[-\frac{\hbar^2}{2m_\mathrm{e}}\frac{\partial^2}{\partial\vec{r}^2} + v_\mathrm{eff}(\vec{r},\tau)\right]\phi_k(x,\tau). \tag{H4}$$

By setting $v_\mathrm{eff}(\vec{r},\tau) = v_\mathrm{eff}^{(n+1)}(\vec{r},\tau+\delta\tau)$ and $\phi_k(x,\tau) = \phi_k^{(n)}(x,\tau)$ and integrating Eq. (H4) for $\delta\tau$, we obtain a propagated set of spin orbitals $\{\phi_k^{(n)}(x,\tau+\delta\tau)\}$, which may not be an orthonormalized set. When $\{\phi_k^{(n)}(x,\tau+\delta\tau)\}$ is not an orthonormalized set, by using the Gram-Schmidt orthogonalization method, we are able to reorthonormalize the set of $\{\phi_k^{(n)}(x,\tau+\delta\tau)\}$. Then we regard the renormalized set as $\{\phi_k^{(n+1)}(x,\tau+\delta\tau)\}$.

By using the converged spin orbitals and CI coefficients, we can construct the ground-state wave function as

$$\Psi(x_1,x_2,\ldots,x_N) = \sum_{K=1}^{\mathcal{L}} C_K\Phi_K(x_1,x_2,\ldots,x_N), \tag{H5}$$

where we omit the time argument τs because we treat a stationary-state wave function. We note that, similarly to the Hartree-Fock method, the orbital energy ϵ_k in Eq. (H2) is defined for the constituent spin orbitals [43] of a multiconfigurational wave function.

Next, we consider real-time propagation. For real-time propagation, there are many ways to implement numerically. When we adopt the split operator method [56], for instance, the orbitals are propagated as

$$\phi_k(x,t+\delta t) \simeq e^{-i\hat{t}(\vec{r})\frac{\delta t}{2\hbar}} e^{-iv_\mathrm{eff}(\vec{r},t+\delta t/2)\frac{\delta t}{\hbar}} e^{-i\hat{t}(\vec{r})\frac{\delta t}{2\hbar}}\phi_k(x,t), \tag{H6}$$

where δt denotes a time step. In order to perform the transformation of Eq. (H6), we need to have the effective potential at $t+\delta t/2$, that is, we need to know the wave function $\Psi(t+\delta t/2)$ or, equivalently, the spin orbitals $\{\phi_k(x,t+\delta t/2)\}$ and the CI coefficients $\{C_K(t+\delta t/2)\}$. Consequently, as the initial conditions, we need to know the spin orbitals $\{\phi_k(x,\delta t/2)\}$ and the CI coefficients $\{C_K(\delta t/2)\}$ in addition to $\{\phi_k(x,t=0)\}$ and $\{C_K(t=0)\}$. The quantities at $t=\delta t/2$ are calculated by using the results obtained from the imaginary-time propagation, i.e., the spin orbitals $\{\phi_k(x,t=0)\}$ are propagated for $\delta t/2$ using Eq. (12) as $\{\phi_k(x,t=\delta t/2) = e^{-i\epsilon_k\delta t/2\hbar}\phi_k(x,t=0)\}$ and the CI coefficients $\{C_K(t=0)\}$ are propagated using Eq. (25) under the condition that an external perturbation is absent. In this example, the external perturbation must be imposed on later than $t=\delta t/2$. In this way, real-time propagation with the split operator method will be performed by using the leapfrog integration scheme [56] with the two discretized time series $t_1 = (0,\delta t,2\delta t,\ldots)$ and $t_2 = (\delta t/2, 3\delta t/2, 5\delta t/2,\ldots)$ alternatively.

APPENDIX I: DERIVATION OF EQ. (53)

In this Appendix, we derive Eq. (53). By taking a trace of the left-hand side of Eq. (51), we obtain

$$\int dx_1 E_\mathrm{exact}\gamma_\mathrm{exact}(x_1|x_1) = NE_\mathrm{exact}. \tag{I1}$$

On the other hand, by taking a trace of the second term on the right-hand side of Eq. (51), we obtain

$$2\int dx_1\int dx_2\,\hat{h}_\mathrm{eff}(\vec{r}_2)\Gamma^{(2)}_\mathrm{exact}(x_1,x_2'|x_1,x_2)|_{x_2'=x_2} = (N-1)\int dx_1\,\hat{h}_\mathrm{eff}(\vec{r}_1)\gamma_\mathrm{exact}(x_1'|x_1)|_{x_1'=x_1}, \tag{I2}$$

where we have used a general relation applicable to a set of the 1-RDM and 2-RDM expressed as

$$\int dx_1dx_2\,\hat{t}(\vec{r}_2)\Gamma^{(2)}(x_1,x_2'|x_1,x_2)|_{x_2'=x_2} = \frac{N-1}{2}\int dx_1\,\hat{t}(\vec{r}_1)\gamma(x_1'|x_1)|_{x_1'=x_1}. \tag{I3}$$

Therefore, the contributions from the second and the third terms on the right-hand side of Eq. (51) become

$$\int dx_1\,\hat{h}_\mathrm{eff}(\vec{r}_1)\gamma_\mathrm{exact}(x_1'|x_1)|_{x_1'=x_1} + 2\int dx_1\int dx_2\,\hat{h}_\mathrm{eff}(\vec{r}_2)\Gamma^{(2)}_\mathrm{exact}(x_1,x_2'|x_1,x_2)|_{x_2'=x_2} = N\int dx_1\,\hat{h}_\mathrm{eff}(\vec{r}_1)\gamma_\mathrm{exact}(x_1'|x_1)|_{x_1'=x_1}, \tag{I4}$$

which shows that Eq. (53) holds.

APPENDIX J: THE INTEGRAL OF THE DIAGONAL ELEMENT OF EQ. (24)

We give an explicit expression of the integration of the diagonal element of Eq. (24) for a stationary state. The result is expressed as

$$\frac{1}{N}\int dx i\hbar\tilde{\gamma}(x|x) = \int dx_1 \int dx_2 \frac{1}{r_{12}}\Gamma^{(2)}(x_1, x_2|x_1, x_2) - \int dx_1 \tilde{v}(\vec{r}_1)\gamma(x_1|x_1). \tag{J1}$$

The proof of Eq. (J1) is shown below.

First, we rewrite the left-hand side of Eq. (24) as

$$i\hbar\tilde{\gamma}(x|x) = N\int dx_1 \cdots \int dx_N \,\langle\Psi|x_1\cdots x_N\rangle\, \delta(x - x_1)\langle x_1\cdots x_N|[\hat{W}_{\rm ee} - \tilde{V}]\Psi\rangle, \tag{J2}$$

where we have used the resolution of identity in the coordinate representation,

$$\hat{1} = \int dx_1 \cdots \int dx_N |x_1\cdots x_N\rangle\langle x_1\cdots x_N|, \tag{J3}$$

and the matrix element of $\hat{n}(x)$ expressed as

$$\langle x_1\cdots x_N|\hat{n}(x)|x'_1\cdots x'_N\rangle = \left[\Pi_{j=1}^{N}\delta(x_j - x'_j)\right]\left[\sum_{k=1}^{N}\delta(x - x_k)\right] \tag{J4}$$

in the coordinate representation and the permutation symmetry of each wave function with respect to the coordinates of the particles. Then the contribution from the single-particle part in Eq. (J2) is evaluated as

$$N\int dx_1 \cdots \int dx_N \,\langle\Psi|x_1\cdots x_N\rangle\, \delta(x - x_1)\,\langle x_1\cdots x_N|\tilde{V}|\Psi\rangle = \tilde{v}(x)\gamma(x|x) + 2\int dx'\tilde{v}(x')\Gamma^{(2)}(x, x'|x, x'), \tag{J5}$$

and that from the two-particle interaction is evaluated as

$$\begin{aligned} &N\int dx_1 \cdots \int dx_N \,\langle\Psi|x_1\cdots x_N\rangle\, \delta(x - x_1)\,\langle x_1\cdots x_N|\hat{W}_{\rm ee}|\Psi\rangle \\ &= 2\int dx_2 \frac{1}{|\vec{r} - \vec{r}_2|}\Gamma^{(2)}(x, x_2|x, x_2) + 3\int dx_2 \int dx_3 \frac{1}{r_{23}}\Gamma^{(3)}(x, x_2, x_3|x, x_2, x_3). \end{aligned} \tag{J6}$$

By substituting Eqs. (J5) and (J6) into Eq. (J2), we obtain

$$\begin{aligned} i\hbar\tilde{\gamma}(x|x) = &\, 2\int dx_2 \frac{1}{|\vec{r} - \vec{r}_2|}\Gamma^{(2)}(x, x_2|x, x_2) + 3\int dx_2 \int dx_3 \frac{1}{r_{23}}\Gamma^{(3)}(x, x_2, x_3|x, x_2, x_3) \\ &- \tilde{v}(x)\gamma(x|x) - 2\int dx'\tilde{v}(x')\Gamma^{(2)}(x, x'|x, x'). \end{aligned} \tag{J7}$$

Finally, by integrating Eq. (J7) with respect to x, we derive

$$\int dx i\hbar\tilde{\gamma}(x|x) = N\int dx_1 \int dx_2 \frac{1}{r_{12}}\Gamma^{(2)}(x_1, x_2|x_1, x_2) - N\int dx_1 \tilde{v}(x_1)\gamma(x_1|x_1), \tag{J8}$$

where we have utilized the recursive relation of the RDMs for $2 \leqslant p \leqslant N$ given by

$$\int dx_p \Gamma^{(p)}(x'_1, \ldots, x'_{p-1}, x_p|x_1, \ldots, x_{p-1}, x_p) = \frac{N - p + 1}{p}\Gamma^{(p-1)}(x'_1, \ldots, x'_{p-1}|x_1, \ldots, x_{p-1}). \tag{J9}$$

Equation (J8) is equivalent to Eq. (J1). As can be understood from the derivation, Eq. (J1) holds for an approximated wave function as well as for an exact wave function and can be used in both time-independent and time-dependent cases.

[1] J. Zanghellini, M. Kitzler, C. Fabian, T. Brabec, and A. Scrinzi, Laser Phys. **13**, 1064 (2003).

[2] H.-D. Meyer, F. Gatti, and G. A. Worth, *Multidimensional Quantum Dynamics: MCTDH Theory and Applications* (Wiley-VCH Verlag, Weinheim, 2009).

[3] T. Kato and H. Kono, Chem. Phys. Lett. **392**, 533 (2004).

[4] M. Nest, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **122**, 124102 (2005).

[5] O. E. Alon, A. I. Streltsov, and L. S. Cederbaum, Phys. Rev. A **79**, 022503 (2009).

[6] N. B. Delone and V. P. Krainov, *Multiphoton Processes in Atoms. Springer Series on Atoms + Plasmas* (Springer, Berlin, 2000), Vol. 13.

[7] C. J. Joachain, N. J. Kylstra, and R. M. Potvliege, *Atoms in Intense Laser Fields* (Cambridge University Press, Cambridge, UK, 2012).

[8] M. Kling and M. Vrakking, Annu. Rev. Phys. Chem. **59**, 463 (2008).
[9] F. Krausz and M. Ivanov, Rev. Mod. Phys. **81**, 163 (2009).
[10] P. M. Kraus, B. Mignolet, D. Baykusheva, A. Rupenyan, L. Horny, E. F. Penka, G. Grassi, O. I. Tolstikhin, J. Schneider, F. Jensen, L. B. Madsen, A. D. Bandrauk, F. Remacle, and H. J. Wörner, Science **350**, 790 (2015).
[11] R. P. Miranda, A. J. Fisher, L. Stella, and A. P. Horsfield, J. Chem. Phys. **134**, 244101 (2011).
[12] D. J. Haxton, K. V. Lawler, and C. W. McCurdy, Phys. Rev. A **83**, 063416 (2011).
[13] H. Miyagi and L. B. Madsen, Phys. Rev. A **87**, 062511 (2013).
[14] T. Sato and K. L. Ishikawa, Phys. Rev. A **91**, 023417 (2015).
[15] P. A. M. Dirac, Proc. Cambridge Philos. Soc. **26**, 376 (1930).
[16] J. Frenkel, *Wave Mechanics, Advanced General Theory* (Clarendon Press, Oxford, UK, 1934).
[17] A. Schild and E. K. U. Gross, Phys. Rev. Lett. **118**, 163202 (2017).
[18] G. Hunter, Int. J. Quantum Chem. **9**, 237 (1975).
[19] K. Ando, J. Chem. Phys. **148**, 094305 (2018).
[20] S. Cho, Sci. Rep. Gunma Univ. **11**, 1 (1962).
[21] H. Nakatsuji, Phys. Rev. A **14**, 41 (1976).
[22] H. Nakatsuji, Theor. Chem. Acc. **102**, 97 (1999).
[23] L. Cohen and C. Frishberg, Phys. Rev. A **13**, 927 (1976).
[24] A. Akbari, M. J. Hashemi, A. Rubio, R. M. Nieminen, and R. van Leeuwen, Phys. Rev. B **85**, 235121 (2012).
[25] P.-O. Löwdin, J. Math. Phys. **3**, 1171 (1962).
[26] J. C. Slater, Phys. Rev. **91**, 528 (1953).
[27] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).
[28] A. D. McLachlan, Mol. Phys. **8**, 39 (1964).
[29] V. U. Nazarov, Phys. Rev. B **87**, 165125 (2013).
[30] D. S. Bernstein, in *Matrix Mathematics: Theory, Facts, and Formulas with Application to Linear Systems Theory* (Princeton University Press, Princeton, NJ, 2005), p. 98.
[31] R. Kosloff and H. Tal-Ezer, Chem. Phys. Lett. **127**, 223 (1986).
[32] C. Lin and A. A. Demkov, Phys. Rev. B **90**, 235122 (2014).
[33] C. Lin and A. A. Demkov, Phys. Rev. B **92**, 155135 (2015).
[34] C. Valdemoro, Phys. Rev. A **45**, 4462 (1992).
[35] F. Colmenero, C. Perez del Valle, and C. Valdemoro, Phys. Rev. A **47**, 971 (1993).
[36] H. Nakatsuji and K. Yasuda, Phys. Rev. Lett. **76**, 1039 (1996).
[37] D. A. Mazziotti, Phys. Rev. A **57**, 4219 (1998).
[38] *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski (Springer Science+Business Media, New York, 2000).
[39] F. D. Sala and A. Görling, J. Chem. Phys. **115**, 5718 (2001).
[40] C. A. Ullrich, *Time-Dependent Density-Functional Theory* (Oxford University Press, Oxford, UK, 2012).
[41] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).
[42] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[43] T. Kato and H. Kono, Chem. Phys. **366**, 46 (2009).
[44] S. Ohmura, T. Kato, T. Oyamada, S. Koseki, H. Ohmura, and H. Kono, J. Phys. B: At. Mol. Opt. Phys. **51**, 034001 (2018).
[45] D. W. Smith, J. Chem. Phys. **43**, S258 (1965).
[46] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).
[47] D. A. Mazziotti, Phys. Rev. Lett. **93**, 213001 (2004).
[48] D. A. Mazziotti, Phys. Rev. Lett. **97**, 143002 (2006).
[49] D. B. Jeffcoat and A. E. DePrince III, J. Chem. Phys. **141**, 214104 (2014).
[50] P. Elliott and N. T. Maitra, Int. J. Quantum Chem. **116**, 772 (2016).
[51] F. Lackner, I. Březinová, T. Sato, K. L. Ishikawa, and J. Burgdörfer, Phys. Rev. A **91**, 023412 (2015).
[52] W. Brenig, Nucl. Phys. **4**, 363 (1957).
[53] R. K. Nesbet, Phys. Rev. **109**, 1632 (1958).
[54] T. Kato and K. Yamanouchi, J. Chem. Phys. **131**, 164118 (2009).
[55] J. Caillat, J. Zanghellini, M. Kitzler, O. Koch, W. Kreuzer, and A. Scrinzi, Phys. Rev. A **71**, 012712 (2005).
[56] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran 77: The Art of Scientific Computing* (Cambridge University Press, Cambridge, UK, 1992).