

Time-dependent multiconfiguration theory for electronic dynamics of molecules in an intense laser field

Tsuyoshi Kato ^{*}, Hirohiko Kono

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, 980-8578 Japan

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Abstract

A multiconfiguration theory for electronic dynamics of molecules in an intense laser field is developed based on the Dirac–Frenkel time-dependent variational principle. The equations of motion for spin–orbitals and configuration–interaction coefficients are explicitly given. Numerical calculations of electronic dynamics of a hydrogen molecule in an intense electronic field are performed as a practical application of the theory.

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1. Introduction

The light intensity of $I = 3.5 \times 10^{16}$ W/cm² exerts on an electron a force that is as strong as the electron–nucleus interaction in a hydrogen atom. Interactions of atoms or molecules with near-infrared intense laser fields of light intensity of $I > 10^{12}$ W/cm² induce non-perturbative phenomena such as above-threshold ionization, tunnel ionization, and higher-order harmonic generation. An epoch is marked by the advent of attosecond light pulses generated by superposition of higher-order harmonics, which opened the door to tracing ultrafast electronic dynamics in atoms or molecules with attosecond time resolution. A lifetime of 8 fs of M-shell vacancies of Kr has been measured by varying the delay between a few-femtosecond visible light pulse (probing Auger electrons) and a synchronized sub-femtosecond soft X-ray (generating a core hole) [1].

Interest has recently been shown in questions as to how ionization of a molecule in an intense field is affected by molecular structure [2] or by electronic structure. Early measurements indicated that the ionization

rates of diatomics in an intense field are nearly equal to those of atoms with similar electron binding energies. In recent works, however, the ionization yield of O₂ has been found to be greatly suppressed, relative to Xe, an atom with nearly the same ionization potential as O₂[3,4]. Faisal and coworkers [5] attributed the suppression effect to a one-electron character, i.e., the symmetry of the highest occupied molecular orbital of O₂; the antibonding orbital causes a destructive interference between the two subwaves of the ionizing electron emerging from the two atomic centers.

In order to elucidate above-mentioned experimentally observed phenomena, it is necessary to reveal the role of multi-electron dynamics in atoms or molecules interacting with intense laser fields. Theoretical treatments beyond the single active electron approximation have been begun. By incorporating the electron–electron repulsion term into the so-called intense-field many body S-matrix theory, Becker and Faisal [6] reproduced the observed momentum distribution of doubly charged ions in nonsequential double ionization of He. Effects of multi-electron dynamics on field-induced intramolecular electron transfer accompanied by ionization [7] have been investigated by solving the time-dependent Schrödinger equation using a grid point wave packet method [8]. It has been shown that the proper description of ionization processes in intense fields requires an

^{*} Corresponding author. Fax: +81-22-217-7715.

E-mail address: kato@mcl.chem.tohoku.ac.jp (T. Kato).

adequate treatment of intramolecular electronic dynamics [9]. However, the applicability of ‘exact’ grid point wave packet method is restricted to few-electron systems for the present.

In this Letter, in order to investigate dynamics of many-electron systems, we take an alternative approach, i.e., a quantum chemistry approach. Based on a time-dependent variation principle, we develop a method to systematically approximate the exact electronic wave packet by a linear combination of small number of Slater determinants built from *time-dependent single-particle orbitals*, namely, a time-dependent multiconfiguration self-consistent field (TDMCSCF) method. We derive the equations of motion (EOM) for time-dependent orbitals and configuration-interaction (CI) coefficients. It is shown that the prescription includes the full-CI expansion as an exact solution and it is reduced to the time-dependent Hartree–Fock (TDHF) theory as a single Slater determinantal approximation. We present the results of the first application of the present TDMCSCF method to electronic dynamics of a hydrogen molecule in an intense laser field. Here we have used Gaussian-type atomic orbital functions as a basis set. Incorporating this approach, which can adequately describe intramolecular electronic dynamics, into the framework of scattering theory [10], one can calculate the probability of ionization of a many-electron molecule in an intense laser field.

2. Theory

2.1. Dirac–Frenkel time-dependent variational principle

We begin with the definition of the many-electron Hamiltonian. In the second-quantization formalism, the time-dependent electronic Hamiltonian is expressed as

$$\hat{H}(t) = \sum_{ij} h_{ij}(t) \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{ijkl} [ki|lj] \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i, \quad (1)$$

where \hat{a}_i and \hat{a}_i^\dagger denote the annihilation and creation operators for an electron in the i th spin-orbital, respectively. In the present Letter, we assume the total number of spin-orbitals to be finite, although the restriction for the number is not essential for the following derivation. The single-particle integral $h_{ij}(t)$ includes the kinetic energy, the nuclear attraction potential $V_{\text{nuc}}(\vec{r})$, and the time-dependent external potential $V_{\text{ext}}(t)$ and is given by

$$h_{ij}(t) = \int d\vec{x} \phi_i^*(\vec{x}) \left\{ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{nuc}}(\vec{r}) + V_{\text{ext}}(t) \right\} \phi_j(\vec{x}), \quad (2)$$

where m_e is the electron mass and $\vec{x} = (\vec{r}, \sigma)$ denotes the spatial and spin coordinates of an electron. $\phi_i(\vec{x}) = \langle \vec{x} | i \rangle$ is the i th spin-orbital function. The two-particle integral

$[ki|lj]$ represents the Coulomb interaction among electrons, and is given by

$$[ki|lj] = \frac{1}{4\pi\epsilon_0} \int d\vec{x}_1 d\vec{x}_2 \phi_k^*(\vec{x}_1) \phi_i(\vec{x}_1) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \phi_l^*(\vec{x}_2) \phi_j(\vec{x}_2), \quad (3)$$

where e is the electron charge and ϵ_0 is the permittivity of vacuum. We express the time-dependent N -electron wave function $\Phi(t)$ by a linear combination of Slater determinants as

$$\Phi(t) = \sum_{I=1}^M C_I(t) \Phi_I(t), \quad (4)$$

where $C_I(t)$ is a complex coefficient (called CI-coefficient) and $\Phi_I(t)$ denotes an N -electron Slater determinant built from the spin-orbitals

$$\Phi_I = \|\phi_{i_1} \phi_{i_2} \cdots \phi_{i_N}\| = \hat{a}_{i_1}^\dagger \hat{a}_{i_2}^\dagger \cdots \hat{a}_{i_N}^\dagger |\text{vac}\rangle \langle i_1 < i_2 < \cdots < i_N|, \quad (5)$$

where $|\text{vac}\rangle$ is the electron vacuum. The determinants depend on time because we consider here the time-dependent spin-orbitals, and therefore the Fermi operators as well as the individual integrals in Eq. (1) depend on time (see Eq. (21)).

To derive the EOM for the spin-orbitals and the CI-coefficients, we utilize the Dirac–Frenkel time-dependent variational principle (DF-TDVP) expressed by [11–22]

$$\langle \delta\Phi(t) | \left(\hat{H}(t) - i\hbar \frac{\partial}{\partial t} \right) | \Phi(t) \rangle = 0, \quad (6)$$

where $\delta\Phi(t)$ denotes possible variations of the wave function with respect to the spin-orbital functions and the CI-coefficients.

2.2. Equation of motion for spin-orbitals

First, we shall derive the EOM for the spin-orbitals by considering the variation with respect to the spin-orbitals. We assume L independent spin-orbitals. In the following, we refer to the spin-orbitals that are used to build the Slater determinants to describe the wave function of Eq. (4) as *occupied* spin-orbitals, and we refer to those not used as *unoccupied* spin-orbitals. The number of the occupied and the unoccupied spin-orbitals are assumed to be N_o and $N_u = L - N_o$, respectively. In deriving the EOM for the occupied spin-orbitals, we require that the time evolution of the occupied spin-orbitals satisfies the following unitary condition:

$$\langle k(t) | m(t) \rangle = \langle k(t_0) | m(t_0) \rangle = \delta_{km} \quad (1 \leq k, m \leq N_o) \quad (7)$$

holds for $t \geq t_0$ with the initial orthonormal spin-orbitals at $t = t_0$. To take into account this constraint, we introduce Lagrange multipliers $\lambda_{km}(t)$ and rewrite Eq. (6) as

$$\left\langle \frac{\delta \Phi(t)}{\delta k} \right| \left(i\hbar \frac{\partial}{\partial t} - \hat{H}(t) \right) \left| \Phi(t) \right\rangle - \sum_m \lambda_{km}(t) \langle \delta k | m(t) \rangle = 0 \quad (8)$$

for the variation with respect to the k th occupied spin-orbital. After straightforward algebra, an explicit variation equation is derived from Eq. (8)

$$\begin{aligned} i\hbar \sum_I \sum_m^{occ} (-1)^{p_I(k)+p_J(m)} C_I(t)^* C_{kl}^m(t) \langle \delta k | \frac{\partial}{\partial t} | m(t) \rangle \\ = \sum_I \sum_m^{occ} (-1)^{p_I(k)+p_J(m)} C_I(t)^* \langle \delta k | \\ \times \left[C_{kl}^m(t) \left\{ \hat{h}_I(t) - \left(\hat{J}_k(t) - \hat{K}_k(t) \right) \right\} \right. \\ \left. + \sum_{\substack{n \\ (\neq k)}}^{occ I} \sum_{\substack{l \\ l(\neq m) \\ (k,n) \neq (m,l)}}^{occ} (-1)^{p_I(n)+p_J(l)} C_{knl}^{lm}(t) \text{sgn}(k-n) \right. \\ \left. \times \text{sgn}(m-l) \hat{f}_{nl}(t) \right] | m(t) \rangle - \sum_m^{occ} \lambda_{km}(t) \langle \delta k | m(t) \rangle. \end{aligned} \quad (9)$$

In the above equation, $C_{kl}^m(t)$ denotes the coefficient for a determinant that is constructed from the determinant Φ_I by a single substitution $\phi_m \leftarrow \phi_k$, and similarly $C_{knl}^{lm}(t)$ denotes the coefficient for a determinant that is constructed from Φ_I by a double substitution $(\phi_l, \phi_m) \leftarrow (\phi_k, \phi_n)$. We do not take care of the order of orbitals involved in the double substitutions; for instance, $C_{knl}^{lm}(t)$, $C_{nkl}^{lm}(t)$, $C_{mkl}^{lm}(t)$ and $C_{nkl}^{lm}(t)$ just denote a CI-coefficient associated with only one Slater determinant of Φ_{knl}^{lm} . We refer to the determinant that is made from these substitution(s) in Φ_I as just Φ_I as long as there is no confusion. The symbol $\sum_I^{(k)}$ represents the summation over determinants that include the spin-orbital ϕ_k , and $\sum_k^{occ I}$ represents the summation over the constituent spin-orbitals of Φ_I . Summations with respect to m and l are taken for all the occupied orbitals. The symbol $p_I(k)$ stands for the *position* of the k th spin-orbital in Φ_I , e.g., $p_I(k) = j$ if $i_j = k$ in Eq. (5). The single-particle operator $\hat{h}_I(t)$ associated with Φ_I is defined by

$$\hat{h}_I(t) = \hat{h}(t) + \hat{V}^{(I)}(t) \quad (10a)$$

with the single-particle operator $\hat{h}(t)$ corresponding to the first term of Eq. (1) and a potential

$$\hat{V}^{(I)}(t) = \sum_s^{occ I} \left(\hat{J}_s(t) - \hat{K}_s(t) \right), \quad (10b)$$

where \hat{J}_s and \hat{K}_s are Coulomb and exchange operators, respectively, defined to give the matrix elements, $\langle i | \hat{J}_s(t) | j \rangle = [ij|s(t)s(t)]$, and $\langle i | \hat{K}_s(t) | j \rangle = [is(t)|s(t)j]$. The general two-particle operator f_{kl} is defined by $\langle i | \hat{f}_{kl}(t) | j \rangle = [ij|k(t)l(t)]$.

Eq. (9) must hold for any variation of $\langle \delta k |$ in the functional space spanned by the *unoccupied* spin-orbitals ($1 \leq k \leq N_o$). Therefore, we obtain N_o -coupled

EOM for the occupied spin-orbitals. To concisely represent the equation, let us introduce the following notations:

$$(\mathbf{A}(t))_{km} = \sum_I^{(k)} (-1)^{p_I(k)+p_J(m)} C_I(t)^* C_{kl}^m(t), \quad (11a)$$

$$\begin{aligned} (\hat{\mathbf{K}}(t))_{km} = \sum_I^{(k)} (-1)^{p_I(k)+p_J(m)} C_I(t)^* \\ \times \left[C_{kl}^m(t) \left\{ \hat{h}_I(t) - \left(\hat{J}_k(t) - \hat{K}_k(t) \right) \right\} \right. \\ \left. + \sum_{\substack{n \\ (\neq k)}}^{occ I} \sum_{\substack{l \\ l(\neq m) \\ (k,n) \neq (m,l)}}^{occ} (-1)^{p_I(n)+p_J(l)} C_{knl}^{lm}(t) \right. \\ \left. \times \text{sgn}(k-n) \text{sgn}(m-l) \hat{f}_{nl}(t) \right], \end{aligned} \quad (11b)$$

$$(\mathbf{A}(t))_{km} = \lambda_{km}(t), \quad (11c)$$

and

$$(\vec{X}(t))_m = |m(t)\rangle, \quad (11d)$$

where $1 \leq k, m, n$, and $l \leq N_o$. Eq. (9) now reads

$$i\hbar \frac{\partial}{\partial t} \vec{X}(t) = \mathbf{A}^{-1}(t) [\hat{\mathbf{K}}(t) - \mathbf{A}(t)] \vec{X}(t), \quad (12)$$

where the existence of the inversion of \mathbf{A} is assumed [23,24]. The unitary condition expressed by Eq. (7) is satisfied if the matrix \mathbf{A} is chosen so that the product of the matrices, $\mathbf{A}^{-1}(t)[\hat{\mathbf{K}}(t) - \mathbf{A}(t)]$, appeared in Eq. (12) is hermite.

We consider a particular choice of the Lagrange multipliers that ensures the following relations:

$$\langle k(t) | \frac{\partial}{\partial t} | m(t) \rangle = 0 \quad (1 \leq k, m \leq N_o). \quad (13)$$

Eq. (13) means that the time derivatives of occupied spin-orbitals are expressed in terms of unoccupied spin-orbitals. The condition of Eq. (7) is automatically satisfied if Eq. (13) holds. From Eq. (12), it turns out that Eq. (13) is satisfied by setting the multipliers to be

$$(\mathbf{A})_{nm} = \sum_k^{occ} \langle m | \hat{\mathbf{K}}_{nk} | k \rangle \quad (1 \leq n, m \leq N_o). \quad (14)$$

By substituting this expression back into Eq. (12), we obtain

$$i\hbar \frac{\partial}{\partial t} \vec{X}(t) = \hat{\mathbf{Q}}(t) \mathbf{A}^{-1}(t) \hat{\mathbf{K}}(t) \vec{X}(t), \quad (15)$$

where we used a resolution relation that is valid within the present framework of a finite number of spin-orbitals,

$$\hat{1} \equiv \sum_k^{occ} |k\rangle \langle k| + \sum_s^{unocc} |s\rangle \langle s| = \hat{P} + \hat{Q}. \quad (16)$$

The presence of \hat{Q} in Eq. (15) clearly represents that the occupied spin-orbitals are coupled to unoccupied spin-orbitals, i.e.,

$$i\hbar \frac{\partial}{\partial t} |m\rangle = \sum_s^{\text{unocc}} (\mathbf{T})_{ms} |s\rangle \quad (1 \leq m \leq N_o) \quad (17a)$$

with a $N_o \times N_u$ matrix

$$(\mathbf{T}(t))_{ms} = \sum_{p,q=1}^{\text{occ}} (A^{-1}(t))_{mp} \langle s(t) | \hat{\mathbf{K}}(t)_{pq} | q(t) \rangle, \quad (17b)$$

where s is the index for the unoccupied spin-orbitals. The unoccupied spin-orbitals should also evolve in time so that the occupied and unoccupied spin-orbitals form an orthonormal basis set. One way to achieve this is as follows. We define a $L \times L$ hermite matrix \mathbf{F} from \mathbf{T} as

$$\mathbf{F} = \begin{bmatrix} \mathbf{0} & \mathbf{T} \\ \mathbf{T}^\dagger & \mathbf{0} \end{bmatrix}, \quad (18)$$

and a L th order column vector \vec{W} by

$$(\vec{W})_n = \begin{cases} |k_n\rangle & \text{if } 1 \leq n \leq N_o; \text{ occupied orbital,} \\ |s_{n-N_o}\rangle & \text{if } N_o + 1 \leq n \leq L; \text{ unoccupied orbital.} \end{cases} \quad (19)$$

Because of the hermiticity of \mathbf{F} , the required unitary transformation condition for all the spin-orbitals is satisfied if we regard the following nonlinear Schrödinger equation as the EOM

$$i\hbar \frac{\partial}{\partial t} \vec{W}(t) = \mathbf{F}(t) \vec{W}(t). \quad (20)$$

We recall that the single-particle field \mathbf{F} is defined by specifying a set of orthonormal spin-orbitals and the Slater determinants. If we denote the orbital transformation for a small time-step Δt by

$$\hat{a}_k^\dagger(t + \Delta t) = \exp[-i\hat{\kappa}] \hat{a}_k^\dagger(t) \exp[i\hat{\kappa}] \quad (21a)$$

with a linear operator

$$\hat{\kappa} = \sum_{ij} \kappa_{ij} \hat{a}_i^\dagger(t) \hat{a}_j(t) \quad (1 \leq i, j \leq L), \quad (21b)$$

we can relate the hermite matrix κ to the single-particle field \mathbf{F} as $\kappa = \mathbf{F}(t)^\dagger \Delta t / \hbar$, where the superscript T means the transposed matrix [25]. This explicit formula for the orbital transformation plays a central role in the time integration of the EOM [26].

2.3. Equation of motion for CI-coefficients

Next, we consider the EOM for the CI-coefficients. It is easily obtained by putting $\langle \delta\Phi | = \langle \partial\Phi(t) / \partial C_I^*(t) |$ in Eq. (6) as

$$i\hbar \frac{\partial}{\partial t} C_I(t) = \sum_J C_J(t) \langle \Phi_I(t) | \hat{H}(t) | \Phi_J(t) \rangle. \quad (22)$$

In our formulation, the terms $\langle \Phi_I | \partial / \partial t | \Phi_J \rangle$ vanish identically due to Eq. (13). Therefore, the EOM for CI-coefficients is identical to the standard time-dependent

secular equation for time-independent orbitals. The explicit expression of Eq. (22) is given by

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} C_I(t) = & C_I(t) \sum_k^{\text{occ } I} \langle k | \left[\hat{h}(t) + \frac{1}{2} \hat{V}^{(I)}(t) \right] | k \rangle \\ & + \sum_k^{\text{occ } I} \sum_{\substack{m \\ (\neq k)}}^{\text{occ}} (-1)^{p_I(k)+p_J(m)} C_{kl}^m(t) \langle k | \hat{h}_I(t) | m \rangle \\ & + \sum_{k < n}^{\text{occ } I} \sum_{\substack{m, l \\ (\neq n, k)}}^{\text{occ}} (-1)^{p_I(k)+p_I(n)+p_J(l)+p_J(m)} C_{knl}^{ml}(t) \\ & \times \langle k | \hat{h}_{nl}(t) | m \rangle \text{sgn}(l - m). \end{aligned} \quad (23)$$

Eqs. (20) and (23) are the central results of this study. We can trace the time-dependence of the wave function by simultaneously integrating these coupled EOMs. We used the Euler method or a leapfrog Crank–Nicholson method for the numerical integration [26].

2.4. Connection to the full-CI approach and the time-dependent Hartree–Fock (TDHF) theory

We will clarify the relations of the present formulation with two limiting descriptions of the wave function; the full-CI approach and the TDHF theory.

If we consider all the possible determinants built from a given set of spin-orbitals, the physical contents of the wave function described by Eq. (4) should be identical to the ordinary full-CI wave function built from time-independent spin-orbitals. It is easy to see this connection, since there is no unoccupied spin-orbital in the full-CI treatment. The dimension of \mathbf{T} becomes zero, and thus $\mathbf{F} = \mathbf{0}$ and the spin-orbitals becomes time-independent from Eq. (20). Therefore, the full-CI approach is contained in the present formulation as a limiting case. (Note that the number of the unoccupied orbitals can be zero, even if we do not consider the full-CI expansion.) On the other extreme, if the wave function is approximated by a single Slater determinant Φ_I at all times, we obtain an EOM for the constituent spin-orbitals from Eq. (9) or Eq. (12) as

$$i\hbar \frac{\partial}{\partial t} |k(t)\rangle = \hat{h}_I(t) |k(t)\rangle - \sum_m^{\text{occ } I} \lambda_{km}(t) |m(t)\rangle. \quad (24)$$

In order to make the time evolution be unitary (Eq. (7)), $\mathbf{A}(t)$ in Eq. (24) should be hermite. The special choice of $\mathbf{A}(t) \equiv \mathbf{0}$ results in the ordinary TDHF equation. The difference between the ordinary TDHF equation and Eq. (20) stems from the choice of $\mathbf{A}(t) \equiv \mathbf{0}$ or Eq. (14) [i.e., Eq. (13)]. These two equations lead to two single Slater determinantal wave functions. However, the two Slater determinants differ only in the global phase factor and hence they are physically the same.

2.5. Imaginary-time propagation for initial wave function preparation

To conclude the theoretical formulation, we shall mention the so-called relaxation method in order to prepare the ground state wave function [27]. This method is based on the following replacement in which the wave function is propagated in imaginary time ($t \rightarrow -i\tau$) to eliminate the excited state components in a trial wave function $|\Phi_{\text{try}}(0)\rangle$

$$\exp\left[-\frac{i}{\hbar}\hat{H}_0 t\right]|\Phi_{\text{try}}(0)\rangle \rightarrow \exp\left[-\frac{1}{\hbar}\hat{H}_0 \tau\right]|\Phi_{\text{try}}(0)\rangle, \quad (25)$$

where \hat{H}_0 is the electronic Hamiltonian without an external perturbation. The convergence of the wave function into the ground state wave function is obvious if we expand $|\Phi_{\text{try}}(-i\tau)\rangle$ in terms of eigenstates of \hat{H}_0 . The EOM for the CI-coefficients is readily obtained by changing the time argument $t \rightarrow -i\tau$ in Eq. (23). During the imaginary time evolution, the norm of the wave function $\mathcal{N}(\tau) = \sum_I |C_I(-i\tau)|^2$ decreases from its initial value of unity, and thus renormalization steps are needed. From a variational viewpoint, we have to take into account the *relaxation of the spin-orbitals* in addition to the relaxation of the CI-coefficients. The initial spin-orbitals that we prepare are not optimized for the relaxed CI-coefficients in general. The EOM for the spin-orbitals are formally obtained from Eq. (20) as

$$\frac{\partial}{\partial \tau} \vec{W}(-i\tau) = -\frac{1}{\hbar} \mathbf{F}(-i\tau) \vec{W}(-i\tau), \quad (26)$$

where the evolution of the spin-orbitals is no longer unitary. Accordingly, the spin-orbitals thus obtained should not be used as an orthonormal basis set. Here, we propose a way to avoid this problem by applying the Schmidt orthonormalization procedure to the spin-orbitals at every imaginary time-step. Schmidt's method is simply implemented by using a standard QR decomposition routine. Eq. (26) together with Schmidt orthonormalization works well as shown in the following section.

3. Application to a hydrogen molecule

In this section, we apply the present theory to a hydrogen molecule in an intense laser field. The distance between two protons is fixed at $R = 1.6a_0$, where a_0 is the Bohr radius. The basis set 6-311++G(2d,2p) of Cartesian Gaussian-type atomic orbital functions is used for the HF molecular orbital calculation [28,29]. We assume that the spin-orbitals are expressed as

$$\phi_k(\vec{r}) = \begin{cases} \chi_j(\vec{r}) & \alpha(\sigma) \text{ if } k = 2j, \\ \chi_j(\vec{r}) & \beta(\sigma) \text{ if } k = 2j + 1, \end{cases} \quad (27)$$

and thus the number of the independent molecular orbitals χ_j reduces to $L/2$. In the present calculation, $L/2 = 20$. The total number of possible Slater determinants M is $M_{\text{full-CI}} = 400$ in Eq. (4) (the total number of configuration state functions is 210) for singlet states, and the full-CI ground state energy is $E_{\text{full-CI}} = 1.7900 E_h$, where E_h is the atomic unit of energy. We start by examining the electronic energy convergence for the imaginary time propagation (Fig. 1). In this Letter, we activate the lowest three HF orbitals ($1\sigma_g$, $1\sigma_u$, and $2\sigma_g$) as the occupied orbitals ($N_o = 3$) and then the number of Slater determinants used to expand the wave function of Eq. (4) is $M = 9$ for the singlet ground state. We took the HF state as the trial wave function ($E_{\text{HF}} = -1.7508 E_h$). For the EOM of the orbitals, we tested Eq. (26) (imaginary time propagation) and Eq. (20) with $t = \tau$ (real time propagation). The time-step $\Delta\tau = 0.001 \hbar/E_h$ ($\hbar/E_h = 0.0242$ fs) is used for the discrete time integration. As shown in Fig. 1, the approximate energy obtained with the help of Eq. (26) monotonically converges to the value of $E_{\text{conv}} = -1.7786 E_h$, while the real time propagation with

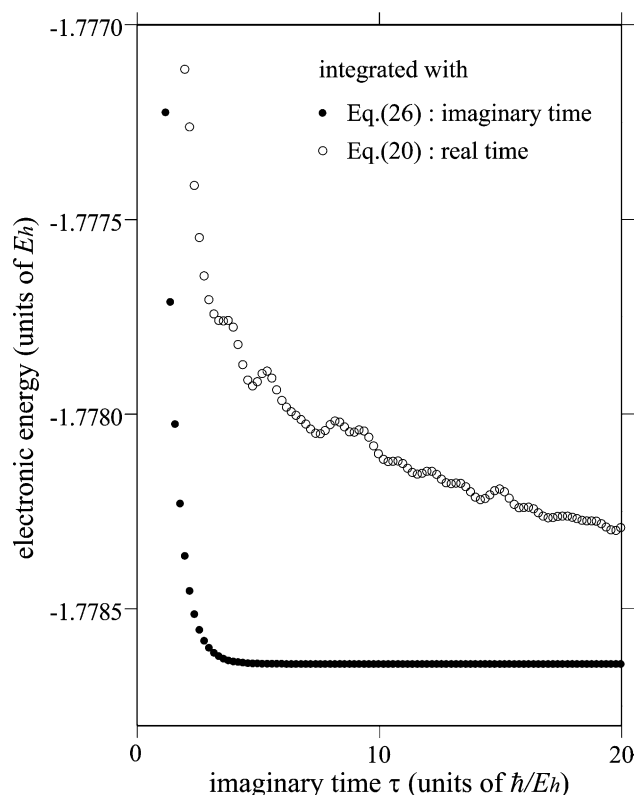


Fig. 1. Energy expectation values of the ground state wave function of H_2 obtained by relaxation methods in time domain τ . The trial wave function is the HF wave function. The 6-311G++(2d,2p) basis set is used, and the lowest three HF orbitals are activated as the occupied orbitals ($N_o = 3$ and $M = 9$). The HF energy is $-1.7508 E_h$ and the full-CI ground state energy is $-1.7900 E_h$. The results calculated by the EOM for the orbitals of Eq. (26) (imaginary time) and of Eq. (20) (real time) are plotted by solid and open circles, respectively.

Eq. (20) does not converge for the time period $[0, 20 \hbar/E_h]$. The converged energy agrees with the ground state energy calculated by the GAMESS code with a MCSCF option [30] for seven digits.

To check the accuracy of our real time propagation scheme, we confirmed that the converged energy E_{conv} is conserved for the unperturbed real time propagation. Next, we apply an intense laser field to the ground state wave function. The electric field is assumed to have the form $\vec{\mathcal{E}}(t) = \vec{e}_z f(t) \sin(\omega t)$, where the polarization vector \vec{e}_z is assumed to be parallel to the molecular axis. The envelope function $f(t)$ is linearly ramped in time so that $f(t)$ attains its maximum value of $f(t) = 0.12 E_h/ea_0$ (light intensity $I = 5.0 \times 10^{14} \text{ W/cm}^2$) at $t = T_c = 2\pi/\omega$. We set the frequency at $\omega = 0.06 E_h/\hbar$ (wavelength $\lambda = 760 \text{ nm}$, $T_c = 104.7 \hbar/E_h = 2.53 \text{ fs}$), which is much smaller than the energy difference between the ground state and the first singlet excited state $B^1\Sigma_u^+$ ($\Delta E \simeq 0.5 E_h$). The interaction potential $V_{\text{ext}}(t)$ in Eq. (2) is the dipole interaction with the field. The time-step $\Delta t = \Delta\tau$ is used for the real time propagation [26].

In order to visualize the wave function, we consider the reduced density function defined by $\Psi(z_1, z_2, t) = \sum_{\sigma_1, \sigma_2} \int dx_1 dx_2 dy_1 dy_2 |\Phi(\vec{x}_1, \vec{x}_2, t)|^2$. In the two-dimensional plot of $\Psi(z_1, z_2, t)$, the amplitudes around the anti-diagonal points $z_1 = -z_2 = \pm R/2$ represent the contributions of the covalent electron configuration, and

the diagonal points around $z_1 = z_2 = \pm R/2$ represent the ionic configuration.

In Fig. 2, we depict the contour plots of the reduced density functions: (a)–(c) the ground state density functions at $t = 0$ and (a')–(c') the snapshots at $t = 3T_c/4$. We compare here the results of the present method (panels a and a') with those calculated by two well-defined approaches: (b) and (b') the full-CI; (c) and (c') the TDHF method (i.e., $N_o = 1$ and $M = 1$). We have confirmed that the shape of the full-CI reduced density (panels b and b') quantitatively agrees with the corresponding ‘exact’ reduced density calculated by a grid point method (Fig. 2 in [31]). As is shown in Fig. 2b, the ground state reduced density is mainly composed of the covalent components. The HF description (panel c) fails to describe such the structure because the HF wave function is composed of the covalent and the ionic electron configurations with equal weights. This defect is cured by introducing the multiconfiguration structure of the wave function *and* the orbital optimization, as shown in Fig. 2a. At $t = 3T_c/4$, where $\mathcal{E}(t) = -0.09 E_h/\hbar$, the ionic component is created around $z_1 = z_2 = R/2$, where the electrostatic potential of the electrons $ez_1\mathcal{E}$ and $ez_2\mathcal{E}$ are negative. We can clearly see that the fine structures of the full-CI reduced density in Fig. 2(b') are well reproduced by the present method (panel a'), e.g., the polarization of the electron distri-

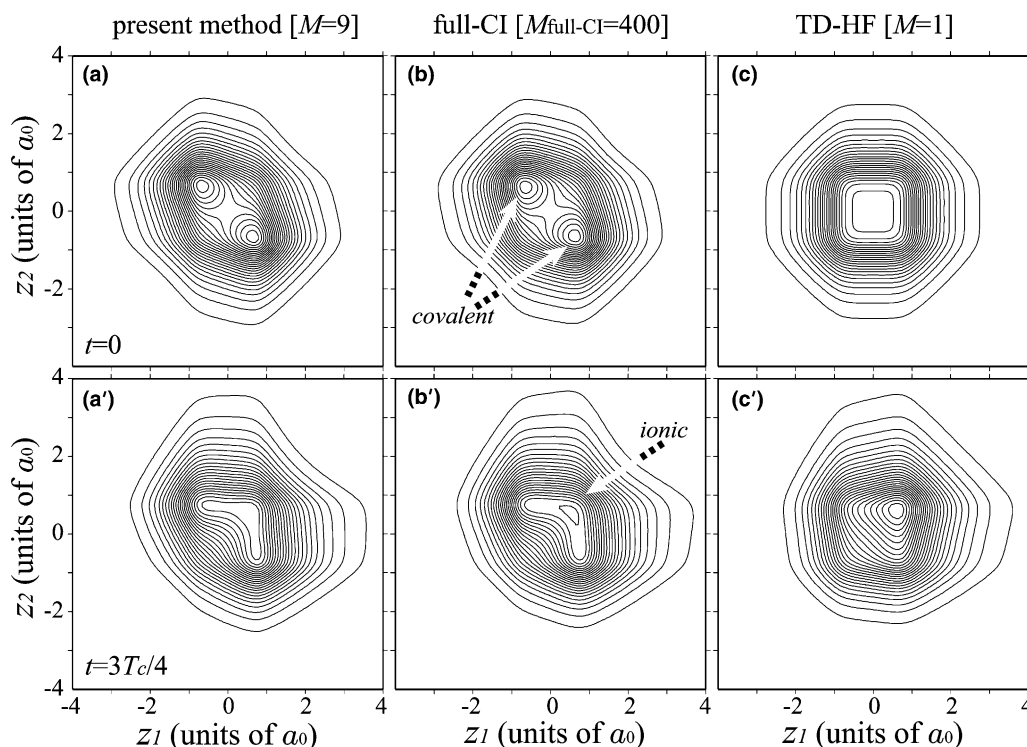


Fig. 2. Contour plots of the reduced density functions: (a)–(c) the ground state density functions at $t = 0$ and (a')–(c') the snapshots at $t = 3T_c/4$. We compare the results of the present method (a and a') with those of the full-CI (b and b') and of the TDHF (c and c'). The length of the determinantal expansion of the wave function M is depicted for each method. The contour lines in the six panels are plotted at the same intervals.

bution (intramolecular charge transfer) in the region of $-R/2 \leq z_1, z_2 \leq R/2$, the valley along a line $z_1 = z_2 \geq R/2$, and the less correlated electron distributions at the exterior regions in z_1 or $z_2 \geq R/2$. Within the single determinantal approximation of TDHF (panel c'), the deformation of the reduced density in Fig. 2(b') is only partially reproduced. The effect of electron–electron repulsion is underestimated in the less correlated TDHF wave function. Thus, as shown in Fig. 2(c'), an ionic component around $z_1 = z_2 = R/2$ is highly peaked compared with the covalent components. The localized ionic component caused by intramolecular electron transfer is the main doorway state to the subsequent ionization (detailed discussions are given in [8,31]). Therefore, for the calculation of the intense field ionization probability, we need to properly describe intramolecular electron transfer affected by electron correlation. The results shown in Fig. 2 indicate that the present method fulfills these requirements.

Finally, we comment on the results of the multiconfiguration treatment of the wave function based on time-independent molecular orbitals, namely: (i) HF orbitals; (ii) orbitals optimized for the ground state by the relaxation method ($N_o = 3$ and $M = 9$ case). As is apparent from the variational viewpoint, these results show poor agreement with the full-CI result compared with the present TDMCSCF results. For instance, at $t = 3T_c/4$, the reduced density calculated by using the HF orbitals does not provide the proper electronic polarization, and that calculated by using the orbitals optimized for the ground state fails to describe the electron distributions at the exterior regions in z_1 or $z_2 \geq R/2$, although it provides a fine intramolecular electronic polarization as shown in Fig. 2(a').

4. Concluding remarks

In this Letter, on the basis of the DF-TDVP, we developed a theory to describe the electronic dynamics of a many-electron system in a strong perturbation. EOMs for the spin–orbitals and the CI-coefficients are explicitly derived. The principal feature of the present prescription is optimization of the single-particle orbitals and the CI-coefficients in real and imaginary time propagation. By numerical calculations of electronic dynamics of a hydrogen molecule in an intense laser field, we confirmed that under the same length of the determinantal expansion, the present approach yields a more suitable description of the wave function compared with the conventional time-dependent secular equation formalism with time-independent orbitals. Therefore, efficient improvement of the quality of the wave function from the level of the TDHF to that of full-CI is systematically feasible.

In order to apply the present TDMCSCF theory to large molecules, it is necessary to develop advanced solution algorithms for solving the EOMs. A solid theoretical framework to reduce the number of Slater determinants for electronic structure calculations for stationary states [32] can be used to make the present theory more practical.

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