Time-dependent multiconfiguration theory for ultrafast electronic dynamics of molecules in an intense laser field: Electron correlation and energy redistribution among natural orbitals

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ABSTRACT

We propose a new definition of molecular orbital energy in order to investigate the energetics of constituent molecular orbitals in the many-electron wave function calculated based on time-dependent multiconfiguration theory. It is shown that when energies are assigned to natural orbitals by a similar manner to that used in the Hartree–Fock theory, we can quantify a correction energy to the total electronic energy that represents electron correlation, and thus we can evaluate the time-dependence of the correlation energy. Our attempt is illustrated by numerical results on the time-dependence of the spatial density of the correlation energy and the orbital energies for a H_2 molecule interacting with an intense, near-infrared laser field. We compared the energy $\zeta_j(t)$ supplied by the applied field with the net energy gain $\Delta\bar{\epsilon}_j(t)$ for respective natural orbitals $\phi_j(t)$. ϕ_j and found that the natural orbitals with $\Delta\bar{\epsilon}_j(t) > \zeta_j(t)$ play a key role in the ionization process.

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1. Introduction

The quantum chemical approach using molecular orbitals can provide precise electronic structures of many-electron systems. This approach can be extended to time-dependent problems such as electronic dynamics of molecules interacting with laser light, although the concept of molecular orbitals is not necessarily required for investigation of multielectron dynamics, as pointed out in Ref. [1]. However, the possible tractability of such methods to treat many-electron systems makes them attractive for development. Moreover, recent progresses in experimental attoscience [2,3] motivate the development of theoretical methods for quantum simulations and analysis of laser driven electron dynamics. As one of the attempts, time-dependent multiconfiguration theory for electronic dynamics has been developed [4–7]. In this theory, an *N*-electron wave function is expanded as a linear combination of Slater determinants (or configuration state functions, CSFs) (see Eq. (4)) [8] in which the spin-orbitals and the CI-coefficients are both treated as time-dependent quantities to fully utilize their flexibility as variational parameters to describe the wave function.

In a previous study [5], we formulated the equations of motion (EOMs) for spin-orbitals and CI-coefficients on the basis of time-dependent multiconfiguration self-consistent field theory (TDMCSCF) and used Gaussian-type atomic orbital functions as a basis set to describe the intra-molecular charge transfer in a H_2 molecule interacting with an intense laser field. Recently, we have formulated the EOMs for spin-orbitals in coordinate representation to use numerical orbital functions (multiconfiguration time-dependent Hartree–Fock theory, MCTDHF). This MCTDHF method can describe the large amplitude attosecond time-scale deformations of electron density related to the intense field-induced phenomena such as ultrafast intra-molecular charge transfer, ionization, and correlated electron dynamics of a molecule [7]. We concentrated on obtaining the EOMs tailored for realistic diatomic (or linear) molecules. Recent theoretical developments have confirmed that the multiconfiguration wave function for electronic systems within the clamped nuclear model is actually able to describe the large amplitude deformations of the electron density as mentioned above [9–14].

The difficulty in obtaining the exact time-dependent wave functions for many-electron systems requires the development of new methods such as the MCTDHF method. The use of the orbital concept to reduce the dimensionality of the total wave function is the key for the applicability of the MCTDHF theory. It should be moreover noted that affirmative usage of the orbital concept in the analysis of a variety of electronic dynamics, such as core excitation and electronic relaxation, is promising for the elucidation of underlying physics.

In the electronic structure calculations, the Hartree–Fock (HF) orbital energies are definitely assigned to the canonical HF orbitals

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as the eigenvalues of the Fock operator and the HF energy can explain the formation of stable atoms and molecules. The single determinantal approximation, i.e., the time-dependent HF theory, however, cannot provide an accurate description of many-electron dynamics induced by a strong perturbation such as an intense laser field [5]. Therefore, we need to use multiconfiguration theory to investigate the many-electron dynamics. However, once a multiconfiguration description of the wave function is adopted we have a problem in defining the motion of an electron occupying a molecular orbital with some amount of energy. To strengthen the MCTDHF approach in practical applications, it is necessary to establish firm and quantitative methodologies to analyze the time-dependent multiconfiguration wave function in terms of electron correlations [15].

In this paper, we examine a scheme in which the total energy of an electronic system is divided into single-particle energies associated with natural orbitals by taking an analogy with the energy expression in the HF theory. This is the first step for the establishment of quantitative methodologies to analyze the time-dependent multiconfiguration wave function in terms of electron correlations. The reason to adopt the natural orbitals are two-fold; (i) the natural orbitals are uniquely defined quantities for a given multiconfiguration wave function and (ii) the electron density of an N-electron system is decomposed as a weighted sum of the modulus squares of the natural orbitals. If we consider a situation where an N-electron system can be asymptotically decomposed into an electron and the remaining $(N-1)$-electron system in space, for example, the projectile electron in electron scattering experiments, it might be rational to quantify the single-particle properties for the projectile electron out of the N-electron wave function. In Section 2, we formulate for a general N-electron system the notion of the energy and potential of natural orbitals and newly define the electron correlation energy. In Section 3, we numerically calculate the time-dependence of the electron correlation density for a H_2 molecule interacting with an intense laser field, and show that we can quantify the time-dependence of the electron correlations. We also compare the energy supplied by the applied field with the net energy gain on the basis of the viewpoint of the natural orbital potential to discuss the mechanism of intense field ionization.

2. Theory

In this section, we will formulate the energies associated with natural spin-orbitals (NSOs). We arrange the expression of the electronic energy for the use of NSOs and heuristically partition off the electronic energy into individual natural orbitals. This approach is different from standard procedures, for instance, the Hartree–Fock theory and the Kohn–Sham density functional theory, in the sense that the canonical orbital energies are calculated simultaneously with the relevant orbitals by solving the eigenvalue problems. In the present paper, we intend to partition off the total energy into those of NSOs abstracted from a multiconfiguration many-electron wave function. Although we will present the numerical results only for the case of $N = 2$ in this paper, our formulation has a general applicability to *non-stationary many-electron wave functions*.

The total Hamiltonian of an electronic system is given within the Born–Oppenheimer approximation by

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

where $\hat{a}_i$ and $\hat{a}_i^\dagger$ denote, respectively, the annihilation and creation operators for an electron in the ith spin-orbital. The single-particle integral $h_{ij}(t)$ includes the kinetic energy, the nuclear attraction potential $V_{\text{nucl}}(\vec{r})$, and the time-dependent external potential $V_{\text{int}}(t)$, and is given by

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

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 ith spin-orbital function. The two-particle integral $[ki|lj]$ represents the Coulomb interaction among electrons, and is given by

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

where $-e$ is the electron charge and ϵ_0 is the permittivity of vacuum. A normalized multiconfiguration many-electron wave function serves as the starting point. The N-electron wave function is approximated by a finite linear combination of Slater determinants as

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

where $C_I(t)$ is a complex coefficient (called CI-coefficient), M is the maximum number of the Slater determinants for a given active space of N_o ($\geqslant N$) spin-orbitals, i.e., complete active space expansion. An N-electron Slater determinant Φ_I is explicitly represented by specifying N constituent spin-orbitals $\{\phi_i\}$ belonging to the active space as

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

We calculate the time-dependent wave function by a time-dependent multiconfiguration method in which both the spin-orbitals and the CI-coefficients are optimized during the time-evolution [4,5]. In this case, therefore, the Fermi operators as well as the respective integrals in Eq. (1) depend on time. Note that we are approximating the wave function with a finite number of spin-orbital functions. Accordingly, the Hamiltonian of Eq. (1) is also represented by the finite number of spin-orbital functions.

2.1. Definition of the natural spin-orbitals

In this section, we summarize the properties of the NSOs [8] and the induced transformation of the wave function associated with the transformation of the spin-orbital functions. We consider the first-order reduced density matrix (RDM) γ which is defined as an $N_o \times N_o$ matrix as

$$(\gamma(t))_{mk} = \langle\Phi|\hat{a}_k^\dagger(t)\hat{a}_m(t)|\Phi\rangle = \sum_I^{(k)}(-1)^{p_I(k)+p_J(m)}C_I^*(t)C_{kl}^m(t) \quad (1 \leqslant m, k \leqslant N_o), \tag{6}$$

for the wave function of Eq. (4). The RDM is a Hermitian matrix and is usually normalized so that its trace is N. In the above equation, the symbol $\sum^{(k)}$ represents the summation with respect to the electron configurations that include an orbital ϕ_k as a constituent, and the symbol $p_I(k)$ stands for the position of the kth spin-orbital in Φ_I, e.g., $p_I(k) = j$ if $i_j = k$ in Eq. (5). $\Phi_J \equiv \Phi_{kl}^m$ represents the determinant that corresponds to the single-particle substitution $\phi_m \leftarrow \phi_k$ in Φ_I.

The NSOs are defined to diagonalize the representation of the RDM as

$$\langle\Phi|\hat{a}_j'^\dagger(t)\hat{a}_i'(t)|\Phi\rangle = \delta_{ij}\omega_j(t) \quad (1 \leqslant i, j \leqslant N_o), \tag{7}$$

where $\omega_j(t)$ is the eigenvalue (called occupation number) of the RDM associated with the jth NSO ϕ_j' and the corresponding Fermi operators are denoted as $\{\hat{a}_j'^\dagger\}$ and $\{\hat{a}_j'\}$. The conservation of the trace of the RDM guarantees the occupation numbers to be

$$0 \leqslant \omega_j(t) \leqslant 1 \quad (1 \leqslant j \leqslant N_o) \qquad \text{and} \qquad \sum_{j=1}^{N_o} \omega_j(t) = N. \tag{8}$$

The transformation from given molecular orbitals $\{\phi_j\}$ to the NSOs $\{\phi'_j\}$ is carried out by

$$\phi'_j(t) = \sum_{i=1}^{N_o} \phi_i(t) U_{ij}(t) \quad (1 \leqslant j \leqslant N_o), \tag{9}$$

with the use of an $N_o \times N_o$ unitary matrix $\boldsymbol{U}$ which is determined by solving the eigenvalue problem of Eq. (7). In order to keep the wave function unchanged under this orbital transformation, we must transform the CI-coefficients $\{C_I\}$ to $\{C'_I\}$ so that

$$\Phi(t) = \sum_{I=1}^{M} C_I(t) \Phi_I(t) = \sum_{J=1}^{M} C'_J(t) \Phi'_J(t), \tag{10}$$

where the prime denotes the representation for the natural orbitals [the equivalence is rigorous for use of the complete active space in Eq. (4)]. If we denote the inner-products between Slater determinants as $\langle \Phi'_J | \Phi_I \rangle$, the transformation to $\{C'_I\}$ is written as

$$C'_J(t) = \sum_{I=1}^{M} \langle \Phi'_J(t) | \Phi_I(t) \rangle C_I(t) \quad (1 \leqslant J \leqslant M). \tag{11}$$

The values of inner-products are given by determinants as $\langle \Phi'_J(t) | \Phi_I(t) \rangle = \det\{\boldsymbol{D}^{JI}(t)\}$, where $\boldsymbol{D}^{JI}(t)$ is an $N \times N$ matrix with elements of $(\boldsymbol{D}^{JI}(t))_{kl} = \langle \phi'_{J_k}(t) | \phi_{I_l}(t) \rangle$.

2.2. Formulation of the orbital energy and correlation energy for the natural spin-orbitals

We shall adopt a specific expression of the electronic energy evaluated by using NSOs. In the followings, we assume that we are using the NSOs to represent the wave function and we omit primes used in Eqs. (9)–(11). We note that the single-particle part of the Hamiltonian is evaluated by using the definition of the NSOs, Eq. (7); i.e., the expectation value of *any* single-particle operator $\hat{f}$ is expressed as a linear combination of products of two types of quantities, namely the occupation numbers and diagonal matrix elements for natural spin-orbitals $\{\phi_j(t)\}$:

$$\langle \Phi(t) | \hat{f} | \Phi(t) \rangle = \sum_{j=1}^{N_o} \omega_j(t) \langle \phi_j(t) | \hat{f} | \phi_j(t) \rangle = \sum_{j=1}^{N_o} \omega_j(t) f_{jj}(t). \tag{12}$$

By using the wave function represented by the NSOs (rightmost of Eq. (10)), the Fermi-commutation relation, and a resolution relation applicable to a wave function expanded by $\{\Phi_K(t)\}$,

$$\hat{1}(t) = \sum_{K=1}^{M} |\Phi_K(t)\rangle \langle \Phi_K(t)| \tag{13}$$

for the N-electron subspace [16], we obtain the energy expression as

$$E(t) = \langle \Phi(t) | \hat{H}(t) | \Phi(t) \rangle = \sum_{j}^{N_o} \omega_j(t) \tilde{\epsilon}_j(t)$$
$$- \frac{1}{2} \sum_{i \neq j}^{N_o} \{[i(t)i(t)|j(t)j(t)] - [j(t)i(t)|i(t)j(t)]\} \sum_{I}^{(ij)} |C_I(t)|^2 + E_{\text{rem}}(t), \tag{14}$$

where the symbol $\sum^{(ij)}$ represents the summation with respect to the electron configurations that include orbitals ϕ_i and ϕ_j as constituents (see Appendix A). The *natural spin-orbital energy* $\tilde{\epsilon}_j$ associated with the jth NSO is defined as

$$\tilde{\epsilon}_j(t) = h_{jj}(t)$$
$$+ \sum_{i(\neq j)}^{N_o} \{[i(t)i(t)|j(t)j(t)] - [j(t)i(t)|i(t)j(t)]\} \sum_{I}^{(ij)} |C_I(t)|^2 / \omega_j(t), \tag{15}$$

where the quantity $\sum_{I}^{(ij)} |C_I|^2 / \omega_j = \langle \Phi | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_i | \Phi \rangle / \langle \Phi | \hat{a}_j^\dagger \hat{a}_j | \Phi \rangle$ is considered as the conditional probability to find an electron in the ith NSO if we know with certainty that an electron is in the $j(\neq i)$th NSO. Therefore, Eq. (15) quantifies the total amount of the single-particle energy including the quantum electrostatic potential energy felt by an electron occupying the jth NSO. The second term of Eq. (14) compensates for the double counting of the electron–electron interactions already included in the first term. The energy correction term, denoted by E_{rem}, which may represent a kind of electron correlation energy, is given by

$$E_{\text{rem}}(t) = \frac{1}{2} \sum_{i \neq j}^{N_o} \sum_{\substack{k \neq l \\ \neq (i,j)}}^{N_o} [k(t)i(t)|l(t)j(t)]$$
$$\times \sum_{I}^{(il)} (-1)^{p_I(i)+p_I(l)+p_J(k)+p_{J'}(j)} \left(C_{il}^k(t) \right)^* C_{ll}^j(t), \tag{16}$$

where we used J and J' to specify the electron configurations $\Phi_J = \Phi_{il}^k$ and $\Phi_{J'} = \Phi_{ll}^j$, respectively. This term is evaluated to be negative as the conventional correlation energy E_{corr}. If we do not use the NSOs, the expectation value that stems from the single-particle part in Eq. (15) includes the off-diagonal elements of the RDM. The diagonal elements are only normalized as $\sum_{i=1}^{N_o} (\gamma)_{ii} = N$ and each diagonal element is not uniquely determined for the use of general spin-orbitals. We also note that $E_{\text{rem}}(t) = 0$ if $\omega_j = 1$ for $1 \leqslant j \leqslant N = N_o$; the NSO energy defined by Eq. (15) is reduced to the canonical HF orbital energy and the energy expression of Eq. (14) is nothing but the HF energy.

From Eq. (16), we may define a correlation energy density:

$$E_{\text{rem}}(t) = \int d\vec{r}_1 \, \mathscr{E}_{\text{rem}}(\vec{r}_1, t), \tag{17}$$

where

$$\mathscr{E}_{\text{rem}}(\vec{r}_1, t) = \frac{1}{2} \sum_{\sigma_1} \sum_{i \neq j}^{N_o} \sum_{\substack{k \neq l \\ \neq (i,j)}}^{N_o} \int d\vec{x}_2 \, \frac{e^2 \phi_k^*(\vec{x}_1, t) \phi_i(\vec{x}_1, t) \phi_l^*(\vec{x}_2, t) \phi_j(\vec{x}_2, t)}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$
$$\times \sum_{I}^{(il)} (-1)^{p_I(i)+p_I(l)+p_J(k)+p_{J'}(j)} \left(C_{il}^k(t) \right)^* C_{ll}^j(t). \tag{18}$$

The correlation energy density $\mathscr{E}_{\text{rem}}(\vec{r}, t)$ quantifies an instantaneous spatial distribution of energy that the mean field picture defined by the instantaneous natural orbitals [the first two terms in rhs of Eq. (14)] cannot take into account. Since the spatial integral of $\mathscr{E}_{\text{rem}}(\vec{r}, t)$ is negative, we expect that the dominant part of $\mathscr{E}_{\text{rem}}(\vec{r}, t)$ as a function of $\vec{r}$ is negative. There is no guarantee that the numerical values of $\mathscr{E}_{\text{rem}}(\vec{r}, t)$ reproduce the correlation energy distribution with equal accuracy at all times since the mean field itself is a time-dependent quantity. However, at least, the correlation energy density is expected to reflect the correlated motion of electrons in real space.

In order to estimate the energy of an electron occupying a NSO, we may define an "effective" single-particle energy $\bar{\epsilon}_j$ for the jth NSO. By distributing the correction energy of Eq. (16) into NSOs in an appropriate manner, we define the correction energy for the jth NSO as

$$\Delta_j(t) = \frac{1}{2}\mathrm{Re}$$

$$\times \left[\sum_{\substack{i(\neq j)}}^{N_o} \sum_{\substack{k\neq l \\ \neq (ij)}}^{N_o} [k(t)i(t)|l(t)j(t)] \sum_{l}^{(il)} (-1)^{p_l(i)+p_l(l)+p_j(k)+p_{j'}(j)} \left(C_{ii}^k(t)\right)^* C_{ll}^j(t)/\omega_j(t) \right],$$

(19)

where we note that $E_{\mathrm{rem}}(t)$ is a real-valued quantity. We can then define the energy $\bar{\epsilon}_j$ as

$$\bar{\epsilon}_j(t) = h_{jj}(t) + \frac{1}{2}\sum_{i(\neq j)}^{N_o}\{[i(t)i(t)|j(t)j(t)] - [j(t)i(t)|i(t)j(t)]\}$$

$$\times \sum_{l}^{(ij)}|C_l(t)|^2/\omega_j(t) + \Delta_j(t).$$

(20)

From Eqs. (14), (19), and (20), we obtain a simple expression for the electronic energy as

$$E(t) = \sum_{j=1}^{N_o}\omega_j(t)\bar{\epsilon}_j(t).$$

(21)

This equation has the same structure of the Gibbs free energy expressed in terms of chemical potentials. Therefore we refer those energies $\bar{\epsilon}_j(t)$ as *natural spin-orbital potentials* in this paper.

Within the dipole approximation in the length gauge the energy supplied to the system from the radiation field per unit time is given by [17]

$$\frac{dW(t)}{dt} = \frac{d\vec{\mu}(t)}{dt}\cdot\vec{\mathscr{E}}(t),$$

(22)

where $\vec{\mu}(t)$ is the dipole moment expressed by

$$\vec{\mu}(t) = -e\sum_j\omega_j(t)\langle\phi_j(t)|\hat{r}|\phi_j(t)\rangle = \sum_j\omega_j(t)\vec{\mu}_j(t),$$

(23)

with

$$\vec{\mu}_j(t) = -e\langle\phi_j(t)|\hat{r}|\phi_j(t)\rangle.$$

(24)

$\vec{\mathscr{E}}(t)$ represents the vector of the external electric field. We can distribute the energy supply to the electrons in different orbitals as

$$\frac{dW(t)}{dt} = \frac{d}{dt}\left[\sum_j\omega_j(t)\vec{\mu}_j(t)\right]\cdot\vec{\mathscr{E}}(t).$$

(25)

Therefore it is reasonable to regard the piece of energy

$$\frac{dW_j(t)}{dt} = \frac{d\vec{\mu}_j(t)}{dt}\cdot\vec{\mathscr{E}}(t)$$

(26)

as energy supply to the electron occupying the jth NSO per unit time. The net energy supply to the jth NSO is given by

$$\zeta_j(t) = \int_0^t d\tau\frac{d\vec{\mu}_j(\tau)}{d\tau}\cdot\vec{\mathscr{E}}(\tau).$$

(27)

If the energy gain

$$\Delta\bar{\epsilon}_j(t) = \bar{\epsilon}_j(t) - \bar{\epsilon}_j(0) - \left(-\vec{\mu}_j(t)\cdot\vec{\mathscr{E}}(t)\right) \quad (\vec{\mathscr{E}} = 0 \text{ at } t = 0)$$

(28)

is thoroughly due to the energy supply from the external field $\zeta_j(t)$, $\Delta\bar{\epsilon}_j(t) = \zeta_j(t)$ follows, and if the energy supply from the field does not play a role in the energy gain of the NSO, $\zeta_j(t)$ should be zero; then, the energy gain (or loss) is thoroughly due to the electron–electron interactions. The situation can be mathematically expressed by *assuming* the single-electron Hamiltonian $\hat{h}(t)$ for a natural spin-orbital function $\phi(\vec{x}, t)$ expressed as

$$\hat{h}(t) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{\mathrm{eff}}(\vec{r}, t) + e\vec{r}\cdot\vec{\mathscr{E}}(t) \equiv \hat{h}_0(t) + e\vec{r}\cdot\vec{\mathscr{E}}(t)$$

(29)

with an effective potential $V_{\mathrm{eff}}(\vec{r}, t)$ [18] which contains all the effects of the electron correlation. The spin-orbital function $\phi(\vec{x}, t)$ evolves in time according to the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\phi(\vec{x}, t) = \left[\hat{h}_0(t) + e\vec{r}\cdot\vec{\mathscr{E}}(t)\right]\phi(\vec{x}, t).$$

(30)

Therefore, the effective single-electron energy, namely, natural spin-orbital potential, $\bar{\epsilon}(t) \equiv \langle\phi(\vec{x}, t)|\hat{h}(t)|\phi(\vec{x}, t)\rangle$, satisfies the following relations:

$$\frac{d\bar{\epsilon}(t)}{dt} = \langle\phi(\vec{x}, t)|\frac{\partial V_{\mathrm{eff}}(\vec{r}, t)}{\partial t}|\phi(\vec{x}, t)\rangle - \vec{\mu}(t)\cdot\frac{d\vec{\mathscr{E}}(t)}{dt}$$

(31)

and

$$\Delta\bar{\epsilon}(t) = \int_0^t d\tau\langle\phi(\vec{x}, \tau)|\frac{\partial V_{\mathrm{eff}}(\vec{r}, \tau)}{\partial\tau}|\phi(\vec{x}, \tau)\rangle + \zeta(t),$$

(32)

which can be obtained by integrating Eq. (31) by parts and using the definitions of Eqs. (27) and (28). Here, the dipole moment is given by $\vec{\mu}(t) = -e\langle\phi(\vec{x}, t)|\vec{r}|\phi(\vec{x}, t)\rangle$.

From Eqs. (31) and (32), we notice that if the time-derivative of $V_{\mathrm{eff}}(\vec{r}, t)$ is zero, which means that the dynamics of the relevant spin-orbital is not driven by the electron correlation, $\Delta\bar{\epsilon}(t) = \zeta(t)$ is obtained. This condition can also be fulfilled when the orbital dynamics is recognized as a field following adiabatic process. The adiabatic condition is expressed by the eigen equation:

$$\left[\hat{h}_0(t) + e\vec{r}\cdot\vec{\mathscr{E}}(t)\right]\phi(\vec{x}, t) = F(t)\phi(\vec{x}, t),$$

(33)

where $F(t)$ is a time-dependent eigenvalue. This equation implies that $\bar{\epsilon}(t) = F(t)$ holds for the process where the eigenvalue $F(t)$ depends only on the electric field vector $\vec{\mathscr{E}}(t)$. Thus we have a relation

$$\frac{d\bar{\epsilon}(t)}{dt} = \frac{dF(t)}{dt} = \frac{dF(t)}{d\vec{\mathscr{E}}(t)}\cdot\frac{d\vec{\mathscr{E}}(t)}{dt} = -\vec{\mu}(t)\cdot\frac{d\vec{\mathscr{E}}(t)}{dt}.$$

(34)

By comparing Eq. (34) with Eq. (31), we find that the adiabatic response to the field is a sufficient condition for $\Delta\bar{\epsilon}(t) = \zeta(t)$ or

$$\langle\phi(\vec{x}, t)|\frac{\partial V_{\mathrm{eff}}(\vec{r}, t)}{\partial t}|\phi(\vec{x}, t)\rangle = 0.$$

(35)

3. Numerical results and discussion

Armed with the above definitions, we now calculate the time-dependent characteristics of the NSOs.

In the following, we consider the electronic dynamics of a H_2 molecule in an intense near-infrared laser field. To obtain the singlet ground state wave function, we used 9 spatial orbital functions $(N_o = 18), (1\sigma_g), (1\sigma_u, 1\pi_u^\pm, 2\sigma_g)$ and $(1\pi_g^\pm, 3\sigma_g, 2\sigma_u)$, of which the HF orbital energies are roughly grouped into three. The total number of electron configurations (Slater determinants) used to expand the wave function of Eq. (4) is 81. We used the cylindrical coordinate to describe the orbital functions together with the so-called ABC discretization of the nuclear Coulomb attraction potential [19]. The grid points to describe the numerical orbital functions are set in the rectangular space of $|z| \leqslant 49.8\ a_0$ and $\rho \leqslant 40.0\ a_0$, where a_0 is the Bohr radius. The numbers of the grid points for z and ρ are 250 and 100, respectively. The electronic ground state energy is calculated by imaginary time propagation to be $E_g = -1.7403\ E_h$ for the fixed internuclear distance of $R = 1.6\ a_0$ (the positions of two protons are $z = \pm 0.8\ a_0$ at $\rho = 0$), where E_h is the Hartree energy. The equilibrium internuclear distance is 1.4 a_0 but we calculated with $R = 1.6\ a_0$ for purely computational reasons. The exact electronic energy is $E_g^{\mathrm{exact}} = -1.7936\ E_h$ with the correlation energy of $E_{\mathrm{corr}}^{\mathrm{exact}} = E_g^{\mathrm{exact}} - E_g^{\mathrm{HF}} = -0.0422\ E_h$ [20,21], where E_g^{HF} is the energy at the HF limit. The deviation of the calcu-

Table 1
The calculated values of the orbital occupation ω_j, orbital energy $\tilde{\epsilon}_j$, and orbital potential $\bar{\epsilon}_j$ for the electronic ground state of H_2 for the fixed internuclear distance at $R = 1.6\ a_0$ [22]. Note that the occupation number is defined for the spin-orbitals but in the table we symbolized the orbitals by their spatial symmetries. Therefore, the sum of the occupation numbers in the table is normalized to 1.

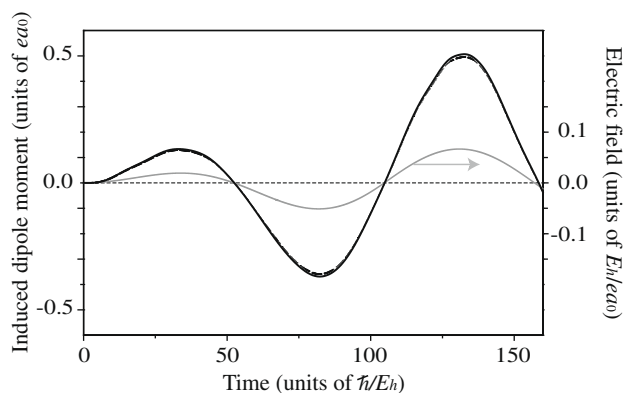| Spatial orbitals	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$3\sigma_g$	$2\sigma_u$	$\pi_u^\pm$	$\pi_g^\pm$
ω_j	0.9781	0.01367	3.391×10^{-3}	1.247×10^{-4}	1.146×10^{-4}	2.237×10^{-3}	7.766×10^{-5}
$\tilde{\epsilon}_j/E_h$	−0.5431	0.08192	0.4283	1.7855	2.1527	0.4875	1.9636
$\bar{\epsilon}_j/E_h$				−0.8702			

Fig. 1. Time-dependence of the induced dipole moment of H_2 interacting with an intense, near-IR laser field in the 9 MO case (solid line). The dashed line is the result obtained by the use of 6 MOs of $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, and $1\pi_u^\pm$. The gray line shows the applied laser electric field (wavelength: $\lambda = 760$ nm, intensity for the maximum field strength: $I = 1.0 \times 10^{14}$ W/cm²).

lated ground state energy from E_g^{exact}, denoted by E^{error}, is +0.0533 E_h, and is ascribed to the large distance of the first grid point from the z-axis along the ρ direction ($\Delta\rho = 0.4\ a_0$). Improvement of the ground state energy is accomplished just by using a smaller grid size in the calculation. Since the correlation energy in the present grid representation, $E_{\text{corr}} = -0.0402\ E_h$, is smaller than E^{error} in magnitude, it seems inaccurate. However, a scaling law against the total energy holds; $E_{\text{corr}}/E_g = 0.0231$ is almost the same as $E_{\text{corr}}^{\text{exact}}/E_g^{\text{exact}} = 0.0235$. We therefore expect that the small energy values related to electron correlation presented in this section have a similar scaling law against the total energy and reflect how the exact values change temporally.

The calculated values of the orbital occupation ω_j, orbital energy $\tilde{\epsilon}_j$, and orbital potential $\bar{\epsilon}_j$ for the ground state are summarized in Table 1 [22]. In the course of the ground state calculation, we have found that the natural orbital potentials $\{\bar{\epsilon}_j\}$ degenerate to be $\bar{\epsilon}_j = -0.8702\ E_h = E_g/2$ independent of the orbital indices (we have observed a 12 digit agreement). This degeneracy may be peculiar to the two-electron system, and may be related to the inherent structure of the spatial wave function of the two-electron system. It is expressed by a linear combination of the diagonal binary products as $\Phi(\vec{x}_1, \vec{x}_2, t) = 2^{-1/2}(\alpha_1\beta_2 - \beta_1\alpha_2)\sum_j \omega_j(t)^{1/2} \psi_j(\vec{r}_1, t)\psi_j(\vec{r}_2, t)$ by using the spatial natural orbitals $\{\psi_j(\vec{r}, t)\}$ [23]. The mathematical proof for this degeneracy
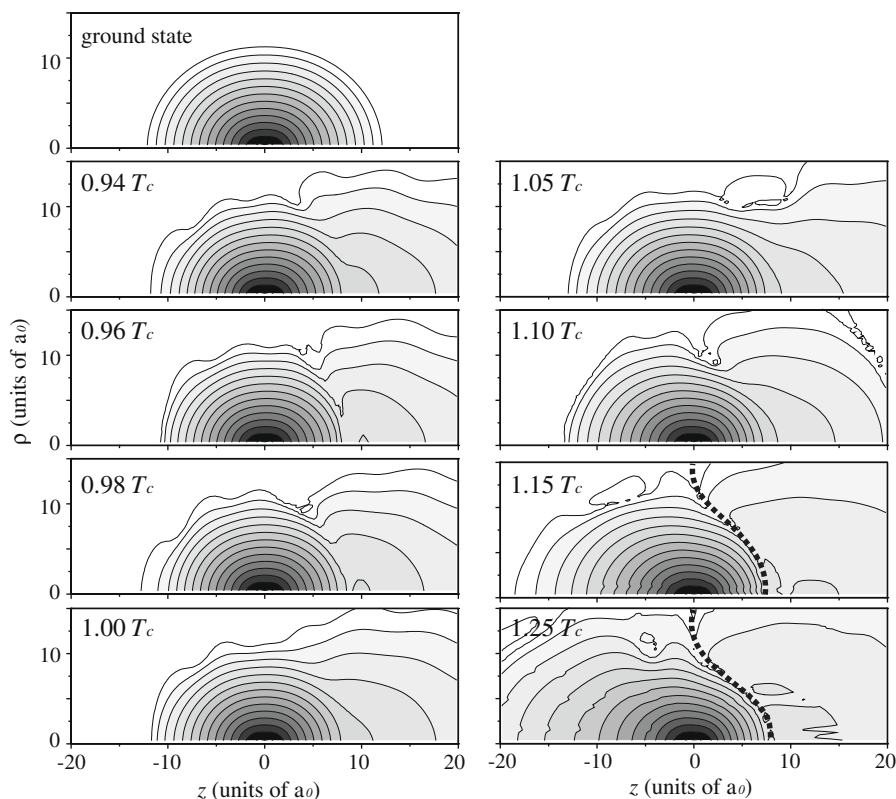

Fig. 2. Snapshots of the correlation energy density. The left-top panel shows the correlation energy density for the electronic ground state. The time for each panel is indicated in units of the laser optical cycle T_c. A logarithmic scale is employed for the modulus values from 10^{-2} to 10^{-15}. The broken lines drawn in the panels at $t = 1.15T_c$ and $1.25T_c$ show the zeros of the correlation density. In the two panels, the correlation density is positive in the right domain of the broken line while it is negative in the left domain.

has yet to be obtained. In a preliminary calculation for a N_2 molecule, we did not observe the degeneracies of the natural orbital potentials.

Now, we consider a H_2 molecule interacting with an intense laser field. We adopt the dipole approximation in the length gauge for the laser–molecule interaction. The electric field is assumed to have a form $\vec{\mathscr{E}}(t) = \vec{e}_z\, f(t) \sin(\omega t)$, where the polarization vector $\vec{e}_z$ is parallel to the molecular axis. The envelope function $f(t)$ is linearly ramped so that $f(t)$ attains its maximum value of f_{max} at the end of the first optical period of $t = T_c = 2\pi/\omega$ and kept constant after the first optical period. The laser frequency is $\omega = 0.06\ E_h/\hbar$ (wavelength $\lambda = 760$ nm, $T_c = 104.7\ \hbar/E_h = 2.53$ fs), and the field amplitude is set to be $f_{max} = 0.0534\ E_h/ea_0$ (the light intensity for the maximum field strength is $I = 1.0 \times 10^{14}$ W/cm^2).

We confirmed that the difference between the electronic energies calculated by the (directly propagated) time-dependent orbital functions and by the natural orbital functions is less than $10^{-7}\ E_h$. In Fig. 1 we show the time-dependence of the induced dipole moment of H_2. For comparison, we also plot the result obtained by the use of 6 spatial orbital functions, i.e., $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, and $1\pi_u^{\pm}$. From the figure, we can see that the convergence of the electronic response of H_2 to the external field is accomplished by the use of 9 spatial orbital functions.

Fig. 2 shows snapshots of the correlation energy density. The calculated correlation density is represented as a contour map of $\log_{10}|\mathscr{E}_{rem}(\rho, z, t)|$. The left-top panel shows the correlation energy density for the electronic ground state. From the plot we can see that the correlation energy density is larger near the nuclei because the motion of two electrons is entangled and the electron–electron interaction is stronger compared with the external region. The other plots correspond to a period of time when the electron freed by the interaction with the laser field during the first optical period recollides with the ion core from the positive z direction.

In addition to the high correlation energy density near the nuclei, it can clearly be seen that the external portion of the correlation energy density corresponding to the freed electron passes by the ion core from the positive z region to the negative z region. Note that this movement of the external portion of the correlation energy density reflects the dynamics of a wave packet comprising of continuum-state components, but the calculated energy density is of the two-body quantity. If the ejected electron is really isolated from the ion core or adequately described by the mean field [the first two terms in rhs of Eq. (14)], it cannot interact with the remaining electron(s) within the ion core and will be transparent from the view point of the correlation energy. Therefore the appearance of the finite correlation energy density outside the ion core region means that the interaction of an ejected electron with the remaining electron(s) in the ion core region during the rescattering event cannot be properly described by the mean field mentioned above.

In Fig. 3, we compare the temporal profiles of the net energy supplies $\zeta_j(t)$ [Eq. (27)] and the energy gains $\Delta\bar{\epsilon}_j(t)$ [Eq. (28)] for NSOs. The assignment of the natural orbitals are based on the symmetry in the electronic ground state. From the plots, we may categorize the temporal behavior of the two energy values $\zeta_j(t)$ and $\Delta\bar{\epsilon}_j(t)$ into two groups; (i) natural orbitals of which the two energy values have almost the same time-dependence ($1\sigma_g$, $1\pi_u$ and $1\pi_g$) and (ii) natural orbitals of which the two energy values show different behaviours. Further, in the latter group there are two patterns of the time-dependence; (ii-a) $\Delta\bar{\epsilon}_j(t) \geqslant \zeta_j(t)$ ($2\sigma_g$ and $3\sigma_g$) and (ii-b) $\zeta_j(t) \geqslant \Delta\bar{\epsilon}_j(t)$ ($1\sigma_u$ and $2\sigma_u$). The behavior of the group (i) is characterized by $\langle\phi_j(t)|\partial V_{eff}(\vec{r}, t)/\partial t|\phi_j(t)\rangle \simeq 0$. We call the orbitals in the group (i) "spectator orbital". As shown in Fig. 3, the response of the $1\sigma_g$ orbital is most adiabatic. The values of $\zeta(t)$ and $\Delta\bar{\epsilon}(t)$ for $1\sigma_g$ hit zero at $\vec{\mathscr{E}}(t) = 0$ and reach a
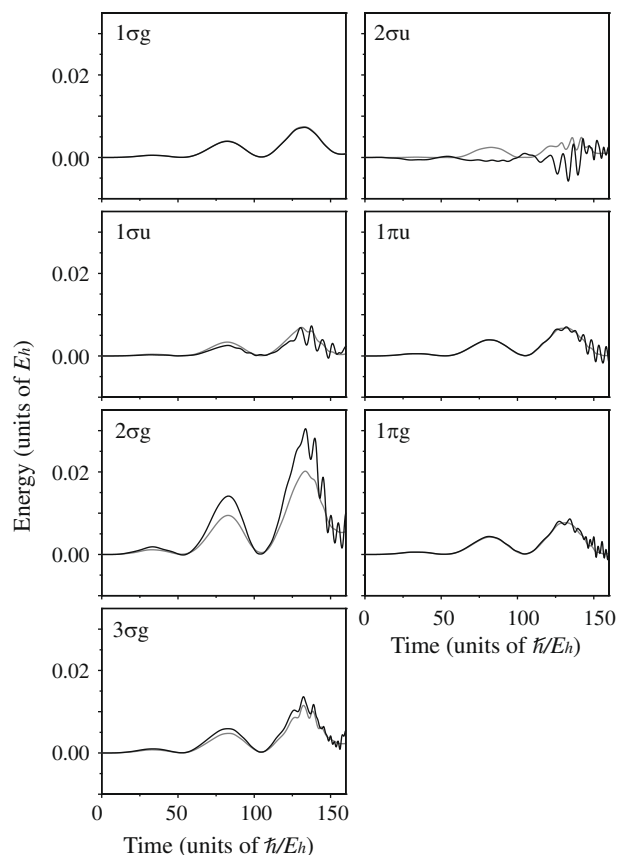

Fig. 3. Comparison of the temporal profiles of the net energy supply $\zeta_j(t)$ (gray line) [Eq. (27)] and the energy gain $\Delta\bar{\epsilon}_j(t)$ (solid line) [Eq. (28)] for each natural orbital. The assignment of the natural orbitals is based on the symmetry in the electronic ground state.

maximum value when $|\vec{\mathscr{E}}(t)|$ takes a maximum, indicating that the $1\sigma_g$ orbital adiabatically changes according to the change in the field $\vec{\mathscr{E}}(t)$. This is consistent with the conclusion in the preceding section; when the response is adiabatic, the condition $\langle\phi_j(t)|\partial V_{eff}(\vec{r}, t)/\partial t|\phi_j(t)\rangle = 0$ or $\zeta(t) = \Delta\bar{\epsilon}(t)$ should hold.

From the view point of the energy gain, the orbitals in the group (ii-a) is supplied energy more than the energy gain from the external field (work done by the external field) and the opposite can be said about the orbitals in the group (ii-b). The origin of the difference in the two energy values can be attributed to the electron–electron interaction. In other words, the natural spin-orbital potential energies are exchanged among orbitals belonging to the group (ii); the orbitals in the group (ii-a) can be said to be energy acceptor orbitals (for which $\langle\phi_j(t)|\partial V_{eff}(\vec{r}, t)/\partial t|\phi_j(t)\rangle > 0$) and those in the group (ii-b) energy donor orbitals (for which $\langle\phi_j(t)|\partial V_{eff}(\vec{r}, t)/\partial t|\phi_j(t)\rangle < 0$).

In a previous study of ionization of H_2, we concluded that an electron is predominantly ejected from the time-developing molecular orbital assigned as $2\sigma_g$ for the case of the present intensity of the laser field. The conclusion is drawn from the analysis of the time-dependence in the orbital norms and CI-coefficients [24]. We eliminated the portions of orbitals reaching the grid boundaries to calculate the ionization probability and also to avoid an artificial reflection of the wave function. On the other hand, we keep the norms of the orbital functions being unity during the propagation by taking advantage of the redundancy between the CI-coefficients and the orbital functions, i.e., the decreases in the norms of orbital functions at every time step are converted into the decreases in the absolute values of CI-coefficients.

The above conclusion is consistent with the present single-particle picture of the natural orbital potential since the $\zeta(t)$ value of the acceptor orbital assigned as $2\sigma_g$ has the largest amplitude and the amount of energy supply from the other orbitals is also the largest. These two observations are reasonable as the attributes of the single-particle function that is occupied by the freed electron.

4. Concluding remarks

In this paper, the notion of the natural orbital energy and potential is formulated in the framework of time-dependent multiconfiguration theory and their dynamical properties are shown for a H_2 molecule interacting with a laser field. By defining the natural orbital energy that formally generalizes the HF orbital energy, we newly quantified an energy that reflects dynamical electron correlations on the attosecond time-scale as shown in Fig. 2. Ultrafast energy exchange among natural orbitals within a half optical cycle is also quantified (see Fig. 3). We believe that the notion of the natural orbital energy will extend the ability of the recently developing time-dependent multiconfiguration theory in elucidating the role of electron correlations for many-electron dynamics in a strong external field. The present work is the first step to that purpose.

We presented numerical results on the time-dependence of the spatial density of the newly defined correlation energy and the orbital potentials for H_2 interacting with an intense, near-infrared field. We compared the energy $\zeta_j(t)$ supplied by the applied field with the net energy gain $\Delta\bar{\epsilon}_j(t)$ for respective natural orbitals $\phi_j(t)$. The responses of natural orbitals can be classified into three: (a) $\Delta\bar{\epsilon}_j(t) = \zeta_j(t)$ (spectator orbital); $\Delta\bar{\epsilon}_j(t) < \zeta_j(t)$ (donor orbital); and $\Delta\bar{\epsilon}_j(t) > \zeta_j(t)$ (acceptor orbital). We concluded that acceptor natural orbitals play a key role in the ionization process and that ionization predominantly occurs from the time-developing acceptor $2\sigma_g$ orbital for the case of the present applied field.

Future work will focus on the identification of orbitals that correspond to electron rescattering and the clarification of the energy exchange between thus assigned "rescattering" orbitals and the other participating orbitals to elucidate the mechanism of non-sequential double ionization. Other ultrafast electronic processes in the attosecond regime, such as core excitation and electronic relaxation [25] induced by the interaction with intense laser fields, can also be treated in a unified way by using the MCTDHF method. MCTDHF techniques to partition the wave function into the bound-state and continuum-state components by using the Feschbach formalism have recently been developed [26]. This type of approach would be utilized for investigation of a variety of electronic dynamics if it is combined with the presently proposed notion of the time-dependent natural orbital energy.

Appendix A. The expression of the total electronic energy

In this appendix, we derive Eq. (14) which is a specific expression of the electronic energy for the use of the natural orbitals.

In calculating the electronic energy, the single-particle part of the Hamiltonian is evaluated as in Eq. (12) by using the definition of the NSOs (Eq. (7)). For the two-particle part, we make use of an identity

$$\langle\Phi|\hat{a}_k^\dagger\hat{a}_l^\dagger\hat{a}_j\hat{a}_i|\Phi\rangle = \sum_K \langle\Phi|\hat{a}_k^\dagger\hat{a}_i|\Phi_K\rangle\langle\Phi_K|\hat{a}_l^\dagger\hat{a}_j|\Phi\rangle - \delta_{il}\langle\Phi|\hat{a}_k^\dagger\hat{a}_j|\Phi\rangle$$
$$= \sum_K^{(il)} (-1)^{p_K(i)+p_K(l)+p_j(k)+p_{j'}(j)} \left(C_{iK}^k\right)^* C_{lK}^j - \delta_{kj}\delta_{li}\omega_j, \quad (A1)$$

which is derived by using the Fermi-commutation relation

$$\hat{a}_k^\dagger\hat{a}_l^\dagger\hat{a}_j\hat{a}_i = \hat{a}_k^\dagger\hat{a}_i\hat{a}_l^\dagger\hat{a}_j - \delta_{il}\hat{a}_k^\dagger\hat{a}_j, \quad (A2)$$

and the resolution relation of Eq. (13). $\Phi_J = \Phi_{iK}^k$ and $\Phi_{J'} = \Phi_{lK}^j$ represent the Slater determinants that correspond to the single-particle substitutions $\phi_k \leftarrow \phi_i$ and $\phi_j \leftarrow \phi_l$ in Φ_K, respectively. The symbol $\sum^{(il)}$ in Eq. (A1) represents the summation with respect to the electron configurations that include orbitals ϕ_i and ϕ_l as constituents. From the definition of the Hamiltonian of Eq. (1) and the expressions of Eqs. (7) and (A1), we may write the electronic energy as

$$E = \langle\Phi|\hat{H}|\Phi\rangle = \sum_j^{occ}\left\{h_{jj} - \frac{1}{2}\sum_{i(\neq j)}^{occ}[ji|ij]\right\}\omega_j$$
$$+ \frac{1}{2}\sum_{i\neq j}^{occ}\sum_{k\neq l}^{occ}[ki|lj]\sum_K^{(il)}(-1)^{p_K(i)+p_K(l)+p_j(k)+p_{j'}(j)}\left(C_{iK}^k\right)^* C_{lK}^j. \quad (A3)$$

We abstract the so-called Coulomb and exchange terms from the two-particle interactions as

$$E = \sum_j^{occ}\left\{h_{jj} - \frac{1}{2}\sum_{i(\neq j)}^{occ}[ji|ij]\right\}\omega_j$$
$$+ \frac{1}{2}\sum_{i\neq j}^{occ}[ii|jj]\sum_K^{(ij)}(-1)^{p_K(i)+p_K(j)+p_i(i)+p_{j'}(j)}\left(C_{iK}^i\right)^* C_{jK}^j$$
$$+ \frac{1}{2}\sum_{i\neq j}^{occ}[ji|ij]\sum_K^{(i)}(-1)^{p_K(i)+p_K(i)+p_j(j)+p_{j'}(j)}\left(C_{iK}^j\right)^* C_{iK}^j$$
$$+ \frac{1}{2}\sum_{i\neq j}^{occ}\sum_{\substack{k\neq l \\ \neq(ij)}}^{occ}[ki|lj]\sum_K^{(il)}(-1)^{p_K(i)+p_K(l)+p_j(k)+p_{j'}(j)}\left(C_{iK}^k\right)^* C_{lK}^j. \quad (A4)$$

Since the phase factors in the second and third terms in Eq. (A4) are unity, we obtain

$$E = \sum_j^{occ}\omega_j h_{jj} + \frac{1}{2}\sum_{i\neq j}^{occ}[ii|jj]\sum_K^{(ij)}|C_K|^2 - \frac{1}{2}\sum_{i\neq j}^{occ}[ji|ij]\left\{\omega_j - \sum_K^{(i)}|C_{iK}^j|^2\right\}$$
$$+ \frac{1}{2}\sum_{i\neq j}^{occ}\sum_{\substack{k\neq l \\ \neq(ij)}}^{occ}[ki|lj]\sum_K^{(il)}(-1)^{p_K(i)+p_K(l)+p_j(k)+p_{j'}(j)}\left(C_{iK}^k\right)^* C_{lK}^j. \quad (A5)$$

For $i \neq j$, Eq. (A1) is expressed as

$$\langle\Phi|\hat{a}_j^\dagger\hat{a}_i^\dagger\hat{a}_j\hat{a}_i|\Phi\rangle = \sum_K^{(i)}|C_{iK}^j|^2 - \omega_j. \quad (A6)$$

On the other hand, we have

$$\langle\Phi|\hat{a}_i^\dagger\hat{a}_i^\dagger\hat{a}_j\hat{a}_i|\Phi\rangle = -\langle\Phi|\hat{a}_i^\dagger\hat{a}_i^\dagger\hat{a}_i\hat{a}_i|\Phi\rangle = -\sum_K^{(ij)}|C_K|^2, \quad (A7)$$

to obtain

$$\omega_j - \sum_K^{(i)} |C_{iK}^j|^2 = \sum_K^{(ij)} |C_K|^2. \tag{A8}$$

The physical interpretation of the above equation is simple; [the probability to find an electron in the jth orbital] minus [the probability to find an electron in the jth orbital with certainty that no electron in the ith orbital] equals to [the probability to find two electron in the ith and jth orbitals ($i \neq j$)]. Substitution of Eq. (A8) into Eq. (A5) yields the final expression of Eq. (14).

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