学位論文（要約）

Molecular wave functions of H_2 by multiconfiguration time-dependent Hartree-Fock method

（多配置時間依存Hartree-Fock法によるH_2の分子波動関数 ）

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申請

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Abstract

In Chapter 1, インターネット公表に関する共著者全員の同意が得られていないため，本章については，非公開

In Chapter 2, I introduce basic ideas of the MCTDHF method and the equations of motion for determining wave functions of a molecule are derived by using a time-dependent variational principle. In Chapter 3, インターネット公表に関する共著者全員の同意が得られていないため，本章については，非公開

In Chapter 4, インターネット公表に関する共著者全員の同意が得られていないため，本章については，非公開

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1 Introduction

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2 The Multi-configuration time-dependent Hartree-Fock (MCTDHF) method

By following the descriptions in Ref. [15], I introduce the basic ideas of the MCTDHF method.

2.1 Hamiltonian for an N-electron system

The Hamiltonian for the N-electron system is written as

$$\hat{H} = -\sum_{j=1}^{N} \frac{\hbar^2}{2m_\mathrm{e}}\nabla_j^2 - \sum_{j=1}^{N}\sum_{A=1}^{N_\mathrm{nucl}} \frac{1}{4\pi\epsilon_0}\frac{Z_A e^2}{|\vec{r}_j - \vec{R}_A|} + \sum_{i=1}^{N}\sum_{j(>i)}^{N} \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian, $\hbar = h/2\pi$ is Planck constant, and m_e is the mass of an electron. The number of nuclei is denoted as N_nucl, Z_A represents the charge number of the Ath nucleus, and e is the elementary charge. The positions of jth electron and Ath nucleus are denoted as $\vec{r}_j$ and $\vec{R}_A$, respectively.

Here, the first and second terms in Eq.(2.1) are the sums of the one-electron operators. To sum up these terms, the following operator is introduced:

$$\hat{h}(\vec{r}_j) = -\frac{\hbar^2}{2m_\mathrm{e}}\nabla_j^2 - \sum_{A=1}^{N_\mathrm{nucl}} \frac{1}{4\pi\epsilon_0}\frac{Z_A e^2}{|\vec{r}_j - \vec{R}_A|}. \quad (2.2)$$

The second term in Eq.(2.1) is the sum of the two-electron operators:

$$\hat{\omega}(r_i, r_j) = \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}. \quad (2.3)$$

In the MCTDHF approach, the wave function of the N-electron system is written as [15]

$$|\Phi(t)\rangle = C_I(t)\,|\Phi_I(t)\rangle\,, \quad (2.4)$$

where $C_I(t)$ is the CI-coefficients and $\Phi_I(t)$ is the Slater determinants constructed from time-dependent spin-orbitals $\phi_k(t)$. The set of the CI-coefficients and the electronic spin-orbitals are determined to fulfill the Dirac-Frenkel time-dependent variational principle [22, 23] by which the time-dependent wave function represented in the form of multiconfiguration expansion by Eq.(2.4) leads to the exact time-dependent wave function.

2.2 Matrix elements of Hamiltonian

(i) Zero-substitution case

The matrix elements are as follows:

$$\langle \Phi_I | \Phi_I \rangle = 1, \tag{2.5}$$

$$\langle \Phi_I | \hat{h} | \Phi_I \rangle = \sum_{k}^{occI} \langle k | \hat{h} | k \rangle, \tag{2.6}$$

$$\langle \Phi_I | \hat{\omega} | \Phi_I \rangle = \sum_{k}^{occI} \sum_{l(>k)}^{occI} ([kk|ll] - [kl|lk]), \tag{2.7}$$

$$\langle \Phi_I | \frac{\partial}{\partial t} | \Phi_I \rangle = \sum_{k}^{occI} \langle k | \frac{\partial}{\partial t} | k \rangle, \tag{2.8}$$

$$\langle \Phi_I | \hat{H} | \Phi_I \rangle = \sum_{k}^{occI} \langle k | \hat{h} | k \rangle + \sum_{k}^{occI} \sum_{l(>k)}^{occI} ([kk|ll] - [kl|lk]), \tag{2.9}$$

where $\sum_k^{occI}$ denotes the summation over the constituent orbitals of Φ_I, and the following notation is adopted for two-electron integrals:

$$[jk|lm] = \iint dx dx' \phi_j(x)^* \phi_k(x) \frac{1}{4\pi\epsilon_0} \frac{1}{|r - r'|} \phi_l(x')^* \phi_m(x'). \tag{2.10}$$

.

(ii) One-substitution case

The matrix elements are as follows:

$$\langle \Phi_I | \, \Phi_{kI}^{m} \rangle = 0, \tag{2.11}$$

$$\langle \Phi_I | \, \hat{h} \, | \Phi_{kI}^{m} \rangle = (-1)^{p_I(k)+p_J(m)} \, \langle k | \, \hat{h} \, | m \rangle \, , \tag{2.12}$$

$$\langle \Phi_I | \, \hat{\omega} \, | \Phi_{kI}^{m} \rangle = (-1)^{p_I(k)+p_J(m)} \sum_{n}^{occI} ([km|nn] - [kn|nm]), \tag{2.13}$$

$$\langle \Phi_I | \, \frac{\partial}{\partial t} \, | \Phi_{kI}^{m} \rangle = (-1)^{p_I(k)+p_J(m)} \, \langle k | \, \frac{\partial}{\partial t} \, | m \rangle \, , \tag{2.14}$$

$$\langle \Phi_I | \, \hat{H} \, | \Phi_{kI}^{m} \rangle = (-1)^{p_I(k)+p_J(m)} \left[\langle k | \, \hat{h} \, | m \rangle + \sum_{n}^{occI} ([km|nn] - [kn|nm]) \right] , \tag{2.15}$$

where $p_I(k)$ denotes the position of the kth spin-orbitals in the Ith Slater determinant Φ_I. Φ_{kI}^{m} denotes a determinant that is constructed from a determinant Φ_I by a single spin-orbital substitution $\phi_m \leftarrow \phi_k$. Φ_J is the electronic Slater determinant constructed by the spin-orbitals substitution in Φ_I.

(iii) Two-substitution case

The matrix elements are as follows:

$$\langle \Phi_I | \, \Phi_{klI}^{mn} \rangle = 0, \tag{2.16}$$

$$\langle \Phi_I | \, \hat{h} \, | \Phi_{klI}^{mn} \rangle = 0, \tag{2.17}$$

$$\langle \Phi_I | \, \hat{\omega} \, | \Phi_{klI}^{mn} \rangle = (-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} ([km|ln] - [kn|lm]), \tag{2.18}$$

$$\langle\Phi_I|\frac{\partial}{\partial t}|\Phi_{klI}^{mn}\rangle = 0, \tag{2.19}$$

$$\langle\Phi_I|\hat{H}|\Phi_{klI}^{mn}\rangle = (-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)}([km|ln]-[kn|lm]), \tag{2.20}$$

where $k<l$ and $m<n$. Φ_{klI}^{mn} denotes a determinant that is constructed from a determinant Φ_I by a double spin-orbital substitution $(\phi_m,\phi_n)\leftarrow(\phi_k,\phi_l)$.

(iv) Three- or more-substitution case

Scalar products of the Slater determinants and all the matrix elements of $\hat{h}$, $\hat{\omega}$, $\partial/\partial t$, and $\hat{H}$ are zero.

2.3 Time differentiation of Hamiltonian matrix elements

For the time differentiation and the Hamiltonian, their variations with respect to the kth spin-orbital is evaluated as follows;

(i) Zero-substitution case

$$\langle\Phi_I(\delta k)|\frac{\partial}{\partial t}|\Phi_I\rangle = \sum_k^{occI}\langle\delta k|\frac{\partial}{\partial t}|k\rangle, \tag{2.21}$$

$$\begin{aligned}\langle\delta\Phi_I(\delta k)|\hat{H}|\Phi_I\rangle = &\sum_k^{occI}\langle\delta k|\hat{h}|k\rangle + \sum_k^{occI}\sum_{l(>k)}^{occI}([(\delta k)k|ll]-[(\delta k)l|lk])\\ &+\sum_l^{occI}\sum_{k(>l)}^{occI}([ll|(\delta k)k]-[lk|(\delta k)l]).\end{aligned} \tag{2.22}$$

The second and third terms are summed up as

$$\langle\delta\Phi_I(\delta k)|\hat{H}|\Phi_I\rangle = \sum_k^{occI}\langle\delta k|\hat{h}|k\rangle + \sum_k^{occI}\sum_l^{occI}([(\delta k)k|ll]-[(\delta k)l|lk]). \tag{2.23}$$

By defining an operator $\hat{V}^{(I)}$ so that its matrix element is defined as

$$\langle l|\hat{V}^{(I)}|r\rangle = \sum_s^{occI}([lr|ss]-[ls|sr]), \tag{2.24}$$

we obtain

$$\langle \delta\Phi_I(\delta k)|\, \hat{H}\, |\Phi_I\rangle = \sum_k^{occI} \langle \delta k|\, \hat{h}\, |k\rangle + \sum_k^{occI} \langle \delta k|\, \hat{V}^{(I)}\, |k\rangle\,. \tag{2.25}$$

(ii) One-substitution case

$$\langle \Phi_I(\delta k)|\, \frac{\partial}{\partial t}\, |\Phi_{kI}^m\rangle = (-1)^{p_I(k)+p_J(m)} \langle \delta k|\, \frac{\partial}{\partial t}\, |m\rangle\,, \tag{2.26}$$

$$\begin{aligned}\langle \delta\Phi_I(\delta k)|\, \hat{H}\, |\Phi_{kI}^m\rangle = (-1)^{p_I(k)+p_J(m)} \Bigg[&\langle \delta k|\, \hat{h}\, |m\rangle + \sum_n^{occI} ([(\delta k)m|nn] - [(\delta k)n|nm]) \\ &+ [km|(\delta k)k] - [kk|(\delta k)m] \Bigg]\,. \end{aligned} \tag{2.27}$$

By introducing the Coulomb and exchange operators we write their matrix elements respectively as

$$\langle l|\, \hat{J}_k\, |r\rangle = [lr|kk], \tag{2.28}$$

and

$$\langle l|\, \hat{K}_k\, |r\rangle = [lk|kr], \tag{2.29}$$

and the equation Eq.(2.27) becomes

$$\langle \delta\Phi_I(\delta k)|\, \hat{H}\, |\Phi_{kI}^m\rangle = (-1)^{p_I(k)+p_J(m)} \langle \delta k| \left[\hat{h} + \hat{V}^{(I)} - (\hat{J}_k - \hat{K}_k)\right] |m\rangle\,. \tag{2.30}$$

(iii) Two-substitution case

$$\langle \Phi_I(\delta k)|\, \frac{\partial}{\partial t}\, |\Phi_{klI}^{mn}\rangle = 0, \tag{2.31}$$

$$\begin{aligned}\langle \delta\Phi_I(\delta k)|\, \hat{H}\, |\Phi_{klI}^{mn}\rangle =& (-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \\ &\times \begin{cases} [(\delta k)m|ln] - [(\delta k)n|lm] & \text{for } k < l \\ [lm|(\delta k)n] - [ln|(\delta k)m] & \text{for } k > l \end{cases}\,. \end{aligned} \tag{2.32}$$

By introducing a notation of $\hat{f}_{kl}$ to represent a Coulombic interaction mediated by the orbitals ϕ_k and ϕ_l as

$$\langle i| \hat{f}_{kl} |j\rangle = [ij|kl], \tag{2.33}$$

Eq.(2.32) becomes

$$\begin{aligned} \langle \delta\Phi_I(\delta k)| \hat{H} |\Phi^{mn}_{klI}\rangle =&(-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \operatorname{sgn}(k-l) \\ &\times \Big(\langle \delta k| \hat{f}_{lm} |n\rangle - \langle \delta k| \hat{f}_{ln} |m\rangle \Big). \end{aligned} \tag{2.34}$$

(iv) Three- or more-substitution case

The matrix elements of $\partial/\partial t$ and $\hat{H}$ are zero.

2.4 Time-dependent variational principle with respect to spin-orbitals

The Dirac-Frenkel time-dependent variational principle [22, 23] is written as

$$\langle \delta\Psi(\delta k)| \hat{H} - i\hbar\frac{\partial}{\partial t} |\Psi\rangle = 0. \tag{2.35}$$

Substituting Eq.(2.4) into Eq.(2.35), the resultant equation is

$$\sum_I^{(k)} \sum_J C_I^*(t) \langle \delta\Phi_I(\delta k)| \hat{H} - i\hbar\frac{\partial}{\partial t} \{C_J(t) |\Phi_J\rangle\} = 0, \tag{2.36}$$

where $\sum_I^{(k)}$ denotes the summation over the Slater determinants composed of the spin-orbital ϕ_k.

The first term of Eq.(2.36) is written by distinguishing the substitution relation between Φ_I and Φ_J as

$$
\begin{aligned}
&\sum_I^{(k)} \sum_J C_I^*(t) C_J(t) \langle \delta\Phi_I(\delta k)| \hat{H} |\Phi_J\rangle \\
&= \sum_I |C_I(t)|^2 \langle \delta\Phi_I(\delta k)| \hat{H} |\Phi_I\rangle \\
&+ \sum_I^{(k)} \sum_{m(\neq k)}^{occ} C_I^*(t) C_{kI}^m(t) \langle \delta\Phi_I(\delta k)| \hat{H} |\Phi_{kI}^m\rangle \\
&+ \sum_I^{(k)} \sum_{l(\neq k)}^{occI} \sum_{\substack{m<n \\ (k,l)\neq(m,n)}}^{occ} C_I^*(t) C_{klI}^{mn}(t) \langle \delta\Phi_I(\delta k)| \hat{H} |\Phi_{klI}^{mn}\rangle ,
\end{aligned}
\tag{2.37}
$$

where C_{kI}^m denotes the coefficient for the determinant Φ_{kI}^m, C_{klI}^{mn} denotes the coefficient for the determinant Φ_{klI}^{mn}, and $\sum_m^{occ}$ denotes the summation over all the occupied spin-orbitals. By substituting Eqs.(2.25), (2.30), and (2.34) into Eq.(2.37), we obtain

$$
\begin{aligned}
&\sum_I^{(k)} \sum_J C_I^*(t) C_J(t) \langle \delta\Phi_I(\delta k)| \hat{H} |\Phi_J\rangle \\
&= \sum_I^{(k)} \sum_m^{occ} C_I^*(t) C_{kI}^m(t) (-1)^{p_I(k)+p_J(m)} \langle \delta k| \left[\hat{h} + \hat{V}^{(I)} - (\hat{J}_k - \hat{K}_k)\right] |m\rangle \\
&+ \sum_I^{(k)} \sum_{l(\neq k)}^{occI} \sum_{\substack{m<n \\ (k,l)\neq(m,n)}}^{occ} C_I^*(t) C_{klI}^{mn}(t) (-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \\
&\qquad \times \mathrm{sgn}(k-l) \Big(\langle \delta k| \hat{f}_{lm} |n\rangle - \langle \delta k| \hat{f}_{ln} |m\rangle \Big) .
\end{aligned}
\tag{2.38}
$$

A more compact form of Eq.(2.38) can be written as

$$
\begin{aligned}
&\sum_{I}^{(k)}\sum_{J} C_I^*(t)C_J(t)\left\langle\delta\Phi_I(\delta k)\right|\hat{H}\left|\Phi_J\right\rangle \\
&=\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)C_{kI}^{m}(t)(-1)^{p_I(k)+p_J(m)}\left\langle\delta k\right|\left[\hat{h}+\hat{V}^{(I)}-(\hat{J}_k-\hat{K}_k)\right]\left|m\right\rangle \\
&+\sum_{I}^{(k)}\sum_{l(\neq k)}^{occI}\sum_{\substack{m,n\\(k,l)\neq(m,n)}}^{occ} C_I^*(t)C_{klI}^{mn}(t)(-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \\
&\qquad\qquad\times\operatorname{sgn}(k-l)\operatorname{sgn}(m-n)\left\langle\delta k\right|\hat{f}_{ln}\left|m\right\rangle . \qquad (2.39)
\end{aligned}
$$

The second term of Eq.(2.36) is written as

$$
\begin{aligned}
&\sum_{I}^{(k)}\sum_{J} C_I^*(t)\left\langle\delta\Phi_I(\delta k)\right| i\hbar\frac{\partial}{\partial t}\left\{C_J(t)\left|\Phi_J\right\rangle\right\} \\
&= i\hbar\sum_{I}^{(k)}\sum_{J} C_I^*(t)\left\{\frac{\partial}{\partial t}C_J(t)\right\}\left\langle\delta\Phi_I(\delta k)\middle|\Phi_J\right\rangle \\
&+ i\hbar\sum_{I}^{(k)}\sum_{J} C_I^*(t)C_J(t)\left\langle\delta\Phi_I(\delta k)\right|\frac{\partial}{\partial t}\left|\Phi_J\right\rangle . \qquad (2.40)
\end{aligned}
$$

The first term in the right-hand side of Eq.(2.40) is calculated as

$$
\begin{aligned}
&\sum_{I}^{(k)}\sum_{J} C_I^*(t)\left\langle\delta\Phi_I(\delta k)\right| i\hbar\frac{\partial}{\partial t}\left\{C_J(t)\left|\Phi_J\right\rangle\right\} \\
&= i\hbar\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)\left\{\frac{\partial}{\partial t}C_{kI}^{m}(t)\right\}(-1)^{p_I(k)+p_J(m)}\left\langle\delta k\middle| m\right\rangle \\
&+ i\hbar\sum_{I}^{(k)}\sum_{J} C_I^*(t)C_J(t)\left\langle\delta\Phi_I(\delta k)\right|\frac{\partial}{\partial t}\left|\Phi_J\right\rangle . \qquad (2.41)
\end{aligned}
$$

By distinguishing the permutation relation between Φ_I and Φ_J, we obtain

$$\begin{aligned}
&\sum_I^{(k)} \sum_J C_I^*(t) \langle \delta\Phi_I(\delta k)| \, i\hbar \frac{\partial}{\partial t} \{C_J(t) \, |\Phi_J\rangle\} \\
&= i\hbar \sum_I^{(k)} \sum_m^{occ} C_I^*(t) \left\{ \frac{\partial}{\partial t} C_{kI}^m(t) \right\} (-1)^{p_I(k)+p_J(m)} \langle \delta k| \, m\rangle \\
&+ i\hbar \sum_I^{(k)} \sum_J |C_I^*(t)|^2 \langle \delta\Phi_I(\delta k)| \frac{\partial}{\partial t} |\Phi_I\rangle \, . \\
&+ i\hbar \sum_I^{(k)} \sum_{m(\neq k)}^{occ} C_I^*(t) C_{kI}^m(t) (-1)^{p_I(k)+p_J(m)} \langle \delta\Phi_I(\delta k)| \frac{\partial}{\partial t} |\Phi_{kI}^m\rangle \, . \\
&+ i\hbar \sum_I^{(k)} \sum_{l(\neq k)}^{occI} \sum_{\substack{m<n \\ (k,l)\neq(m,n)}}^{occ} C_I^*(t) C_{klI}^{mn}(t) (-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \\
&\qquad\qquad\qquad\qquad \times \langle \delta\Phi_I(\delta k)| \frac{\partial}{\partial t} |\Phi_{klI}^{mn}\rangle \, . \qquad (2.42)
\end{aligned}$$

By substituting Eq.(2.21), (2.26), and (2.31) into Eq.(2.42), we obtain

$$\begin{aligned}
&\sum_I^{(k)} \sum_J C_I^*(t) \langle \delta\Phi_I(\delta k)| \, i\hbar \frac{\partial}{\partial t} \{C_J(t) \, |\Phi_J\rangle\} \\
&= i\hbar \sum_I^{(k)} \sum_m^{occ} C_I^*(t) \left\{ \frac{\partial}{\partial t} C_{kI}^m(t) \right\} (-1)^{p_I(k)+p_J(m)} \langle \delta k| \, m\rangle \\
&+ i\hbar \sum_I^{(k)} \sum_m^{occ} C_I^*(t) C_{kI}^m(t) (-1)^{p_I(k)+p_J(m)} \langle \delta k| \frac{\partial}{\partial t} |m\rangle \, . \qquad (2.43)
\end{aligned}$$

Therefore, we obtain an explicit form of the time-dependent variational principle with respect to the spin-orbitals as

$$\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)C_{kI}^m(t)(-1)^{p_I(k)+p_J(m)}\left\langle\delta k\right|\left[\hat{h}+\hat{V}^{(I)}-(\hat{J}_k-\hat{K}_k)\right]\left|m\right\rangle$$

$$+\sum_{I}^{(k)}\sum_{l(\neq k)}^{occI}\sum_{\substack{m,n\\(k,l)\neq(m,n)}}^{occ} C_I^*(t)C_{klI}^{mn}(t)(-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)}$$

$$\times\,\mathrm{sgn}(k-l)\,\mathrm{sgn}(m-n)\left\langle\delta k\right|\hat{f}_{ln}\left|m\right\rangle$$

$$=i\hbar\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)\left\{\frac{\partial}{\partial t}C_{kI}^m(t)\right\}(-1)^{p_I(k)+p_J(m)}\left\langle\delta k\middle| m\right\rangle$$

$$+\,i\hbar\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)C_{kI}^m(t)(-1)^{p_I(k)+p_J(m)}\left\langle\delta k\right|\frac{\partial}{\partial t}\left|m\right\rangle. \tag{2.44}$$

2.5 Equations of motion with respect to the spin-orbitals

The orthonormalization conditions with respect to the spin-orbitals are expressed as

$$\left\langle k\middle| m\right\rangle=\delta_{km}, \tag{2.45}$$

where δ_{km} is the Kronecker delta. The variation with respect to the spin-orbital ϕ_k is evaluated as

$$\left\langle\delta k\middle| m\right\rangle=0. \tag{2.46}$$

The Dirac-Frenkel time-dependent variational principle with the orthonormalization conditions of the spin-orbitals is expressed by using (2.46) as

$$\left\langle\delta\Psi(\delta k)\right|\hat{H}-i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle-\sum_{m}^{occ}\lambda_{km}\left\langle\delta k\middle| m\right\rangle=0, \tag{2.47}$$

where λ_{km} is the Lagrange multiplier. From Eq.(2.44), this equation is rewritten as

$$
\begin{aligned}
&\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)C_{kI}^m(t)(-1)^{p_I(k)+p_J(m)}\langle\delta k|\left[\hat{h}+\hat{V}^{(I)}-(\hat{J}_k-\hat{K}_k)\right]|m\rangle \\
&+\sum_{I}^{(k)}\sum_{l(\neq k)}^{occI}\sum_{\substack{m,n\\(k,l)\neq(m,n)}}^{occ} C_I^*(t)C_{klI}^{mn}(t)(-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \\
&\qquad\qquad\qquad\times\operatorname{sgn}(k-l)\operatorname{sgn}(m-n)\langle\delta k|\hat{f}_{ln}|m\rangle \\
&-\sum_{m}^{occ}\lambda_{km}\langle\delta k|\,m\rangle \\
&=i\hbar\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)\left\{\frac{\partial}{\partial t}C_{kI}^m(t)\right\}(-1)^{p_I(k)+p_J(m)}\langle\delta k|\,m\rangle \\
&+i\hbar\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)C_{kI}^m(t)(-1)^{p_I(k)+p_J(m)}\langle\delta k|\frac{\partial}{\partial t}|m\rangle\,.
\end{aligned}
\tag{2.48}
$$

By taking the new Lagrange-multiplier as

$$
\lambda'_{km}=\lambda_{km}+i\hbar\sum_{I}^{(k)} C_I^*(t)\left\{\frac{\partial}{\partial t}C_{kI}^m(t)\right\}(-1)^{p_I(k)+p_J(m)},
\tag{2.49}
$$

the variational equation is written simply as

$$
\begin{aligned}
&\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)C_{kI}^m(t)(-1)^{p_I(k)+p_J(m)}\langle\delta k|\left[\hat{h}+\hat{V}^{(I)}-(\hat{J}_k-\hat{K}_k)\right]|m\rangle \\
&+\sum_{I}^{(k)}\sum_{l(\neq k)}^{occI}\sum_{\substack{m,n\\(k,l)\neq(m,n)}}^{occ} C_I^*(t)C_{klI}^{mn}(t)(-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \\
&\qquad\qquad\qquad\times\operatorname{sgn}(k-l)\operatorname{sgn}(m-n)\langle\delta k|\hat{f}_{ln}|m\rangle \\
&-\sum_{m}^{occ}\lambda'_{km}\langle\delta k|\,m\rangle \\
&=i\hbar\sum_{I}^{(k)}\sum_{m}^{occ} C_I^*(t)C_{kI}^m(t)(-1)^{p_I(k)+p_J(m)}\langle\delta k|\frac{\partial}{\partial t}|m\rangle\,.
\end{aligned}
\tag{2.50}
$$

By defining (i) the matrix of the Lagrange-multiplier as

$$
\mathbf{\Lambda}_{km}=\lambda'_{km},
\tag{2.51}
$$

(ii) the first-order reduced density matrix as

$$\boldsymbol{A}_{km} = \sum_{I}^{(k)} C_I^*(t) C_{kI}^m(t) (-1)^{p_I(k)+p_J(m)}, \tag{2.52}$$

and (iii) a new matrix operator as

$$\begin{aligned}\hat{\boldsymbol{K}}_{km} =& \sum_{I}^{(k)} C_I^*(t) C_{kI}^m(t) (-1)^{p_I(k)+p_J(m)} \left[\hat{h} + \hat{V}^{(I)} - (\hat{J}_k - \hat{K}_k)\right] \\ &+ \sum_{I}^{(k)} \sum_{l(\neq k)}^{occI} \sum_{\substack{n \\ (k,l)\neq(m,n)}}^{occ} C_I^*(t) C_{klI}^{mn}(t) (-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \\ &\times \mathrm{sgn}(k-l)\,\mathrm{sgn}(m-n) \hat{f}_{ln},\end{aligned} \tag{2.53}$$

the variational equation with respect to the spin-orbitals is expressed as

$$\sum_{m}^{occ} \langle \delta k | \hat{\boldsymbol{K}}_{km} | m \rangle - \sum_{m}^{occ} \boldsymbol{\Lambda}_{km} \langle \delta k | \, m \rangle = i\hbar \sum_{m}^{occ} \boldsymbol{A}_{km} \langle \delta k | \frac{\partial}{\partial t} | m \rangle \,. \tag{2.54}$$

Because the variation $\langle \delta k|$ is arbitrary in Eq.(2.54), we obtain

$$\sum_{m}^{occ} \hat{\boldsymbol{K}}_{km} | m \rangle - \sum_{m}^{occ} \boldsymbol{\Lambda}_{km} | m \rangle = i\hbar \sum_{m}^{occ} \boldsymbol{A}_{km} \frac{\partial}{\partial t} | m \rangle \,. \tag{2.55}$$

By introducing the column vector of the spin-orbitals as

$$\vec{X}_m = | m \rangle \,, \tag{2.56}$$

the equation of motion with respect to the spin-orbitals is written in a compact form as

$$\hat{\boldsymbol{K}} \vec{X} - \boldsymbol{\Lambda} \vec{X} = i\hbar \boldsymbol{A} \frac{\partial}{\partial t} \vec{X}. \tag{2.57}$$

By assuming that $\boldsymbol{A}^{-1}$ exists and multiplying it from the left side, the equation of motion with respect to the spin-orbitals is written as

$$i\hbar \frac{\partial}{\partial t} \vec{X} = \boldsymbol{A}^{-1} \left[\hat{\boldsymbol{K}} - \boldsymbol{\Lambda}\right] \vec{X}. \tag{2.58}$$

The Lagrange-multiplier of Eq.(2.58) is determined so that the spin-orbitals are kept orthonormalized at all times:

$$\langle k(t)|\, m(t)\rangle = \langle k(t_0)|\, m(t_0)\rangle = \delta_{km}. \tag{2.59}$$

This means that the scalar product between spin-orbitals are conserved in time.

As long as

$$\frac{d}{dt}\langle k(t)|\, m(t)\rangle = 0 \tag{2.60}$$

is fulfilled, Eq.(2.59) holds. Because Eq.(2.60) means

$$\begin{aligned} 0 &= \langle k(t)| \left[\frac{\partial}{\partial t}|m(t)\rangle\right] + \left[\frac{\partial}{\partial t}\langle k(t)|\right]|m(t)\rangle \\ &= \langle k(t)| \left[\frac{\partial}{\partial t}|m(t)\rangle\right] + \left(\langle m(t)| \left[\frac{\partial}{\partial t}|k(t)\rangle\right]\right)^{*}, \end{aligned} \tag{2.61}$$

it can be expressed as

$$\forall k, m, \qquad \langle k(t)| \left[\frac{\partial}{\partial t}|m(t)\rangle\right] = 0. \tag{2.62}$$

This equation shows that $(\partial/\partial t)\,|m(t)\rangle$ is in the space spanned by the unoccupied spin-orbitals.

From Eq.(2.58), the time-derivative of the spin-orbital is obtained as

$$\begin{aligned} \frac{\partial}{\partial t}|m\rangle &= (i\hbar)^{-1}\sum_{k}^{occ}\sum_{l}^{occ}(\boldsymbol{A}^{-1})_{mk}\left[\hat{\boldsymbol{K}}_{kl} - \boldsymbol{\Lambda}_{kl}\right]|l\rangle\,. \\ &= (i\hbar)^{-1}\sum_{k}^{occ}(\boldsymbol{A}^{-1})_{mk}\sum_{l}^{occ}\left[\hat{\boldsymbol{K}}_{kl} - \boldsymbol{\Lambda}_{kl}\right]|l\rangle\,. \end{aligned} \tag{2.63}$$

Therefore, the sufficient conditions represented by Eq.(2.62) is expressed as:

$$\sum_{l}^{occ}\left[\hat{\boldsymbol{K}}_{kl} - \boldsymbol{\Lambda}_{kl}\right]|l\rangle = \left[\hat{1} - \sum_{s}^{occ}|s\rangle\langle s|\right] f(|m\rangle), \tag{2.64}$$

where $f(|m\rangle)$ is a linear combination of the occupied and unoccupied spin-orbitals, that is $\sum_l^{occ}\left[\hat{\boldsymbol{K}}_{kl}-\boldsymbol{\Lambda}_{kl}\right]|l\rangle$ is in the space spanned by the unoccupied spin-orbitals.

This Eq.(2.64) is written also as

$$\sum_l^{occ}\boldsymbol{\Lambda}_{kl}|l\rangle=\sum_l^{occ}\hat{\boldsymbol{K}}_{kl}|l\rangle-f(|m\rangle)+\sum_s^{occ}|s\rangle\langle s|\{f(|m\rangle)\}\,. \tag{2.65}$$

When $f(|m\rangle)$ is chosen as

$$f(|m\rangle)=\sum_l^{occ}\hat{\boldsymbol{K}}_{kl}|l\rangle\,, \tag{2.66}$$

the sum of the first term and the second term in the right-hand side vanishes, and Eq.(2.65) is written as

$$\sum_l^{occ}\boldsymbol{\Lambda}_{kl}|l\rangle=\sum_s^{occ}|s\rangle\langle s|\left[\sum_l^{occ}\hat{\boldsymbol{K}}_{kl}|l\rangle\right]. \tag{2.67}$$

By exchanging the dummy indices, s and l, in the right-hand side of Eq.(2.67), we obtain

$$\sum_l^{occ}\boldsymbol{\Lambda}_{kl}|l\rangle=\sum_l^{occ}|l\rangle\sum_s^{occ}\langle l|\hat{\boldsymbol{K}}_{ks}|s\rangle\,. \tag{2.68}$$

This means that the Lagrange-multiplier is written as

$$\boldsymbol{\Lambda}_{kl}=\sum_s^{occ}\langle l|\hat{\boldsymbol{K}}_{ks}|s\rangle\,. \tag{2.69}$$

Because this choice of the Lagrange-multiplier satisfies Eq.(2.64) as well as Eq.(2.62), Eqs.(2.60) and (2.59) also hold.

Inserting Eq.(2.69) into Eq.(2.58), the mth component becomes

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}|m\rangle &=\sum_k^{occ}(\boldsymbol{A}^{-1})_{mk}\sum_l^{occ}\left[\hat{\boldsymbol{K}}_{kl}-\boldsymbol{\Lambda}_{kl}\right]|l\rangle\,.\\
&=\sum_k^{occ}(\boldsymbol{A}^{-1})_{mk}\sum_l^{occ}\left[\hat{\boldsymbol{K}}_{kl}-\sum_s^{occ}\langle l|\hat{\boldsymbol{K}}_{ks}|s\rangle\right]|l\rangle\,.\\
&=\sum_k^{occ}(\boldsymbol{A}^{-1})_{mk}\left[\sum_l^{occ}\hat{\boldsymbol{K}}_{kl}|l\rangle-\sum_l^{occ}\sum_s^{occ}|l\rangle\langle l|\hat{\boldsymbol{K}}_{ks}|s\rangle\right].
\end{aligned} \tag{2.70}$$

By exchanging the suffixes, s and l, in the last term, the resultant equation is

$$i\hbar\frac{\partial}{\partial t}\left|m\right\rangle = \sum_{k}^{occ}(\boldsymbol{A}^{-1})_{mk}\left[\sum_{l}^{occ}\hat{\boldsymbol{K}}_{kl}\left|l\right\rangle - \sum_{s}^{occ}\sum_{l}^{occ}\left|s\right\rangle\left\langle s\right|\hat{\boldsymbol{K}}_{kl}\left|l\right\rangle\right]$$
$$= \sum_{k}^{occ}(\boldsymbol{A}^{-1})_{mk}\sum_{l}^{occ}\left[\hat{1} - \sum_{s}^{occ}\left|s\right\rangle\left\langle s\right|\right]\hat{\boldsymbol{K}}_{kl}\left|l\right\rangle. \tag{2.71}$$

By introducing the projection operator to the space spanned by the unoccupied orbitals as

$$\hat{Q} = \hat{1} - \sum_{s}^{occ}\left|s\right\rangle\left\langle s\right|, \tag{2.72}$$

the equation of motion is written as

$$i\hbar\frac{\partial}{\partial t}\left|m\right\rangle = \hat{Q}\sum_{k}^{occ}\sum_{l}^{occ}(\boldsymbol{A}^{-1})_{mk}\hat{\boldsymbol{K}}_{kl}\left|l\right\rangle, \tag{2.73}$$

which can be expressed in a matrix form as

$$i\hbar\frac{\partial}{\partial t}\vec{X} = \hat{Q}\boldsymbol{A}^{-1}\hat{\boldsymbol{K}}\vec{X}. \tag{2.74}$$

2.6 The equation of motion for CI-coefficients

The Dirac-Frenkel time-dependent variational principle is written as

$$\left\langle\delta\Psi(\delta C_I)\right|\hat{H} - i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle = 0. \tag{2.75}$$

Because

$$\left\langle\Psi\right|\hat{H}\left|\Psi\right\rangle = \sum_{IJ}C_I^*C_J\left\langle\Psi_I\right|\hat{H}\left|\Psi_J\right\rangle, \tag{2.76}$$

and

$$\left\langle\delta\Psi(\delta C_I)\right|\hat{H}\left|\Psi\right\rangle = \sum_{J}(\delta C_I)^*C_J\left\langle\Psi_I\right|\hat{H}\left|\Psi_J\right\rangle, \tag{2.77}$$

the time-dependent variational principle is written as

$$i\hbar \langle \delta\Psi(\delta C_I)| \frac{\partial}{\partial t} |\Psi\rangle = \sum_J (\delta C_I)^* C_J \langle \Psi_I | \hat{H} |\Psi_J\rangle . \tag{2.78}$$

We also have

$$\begin{aligned}\langle \Psi| \frac{\partial}{\partial t} |\Psi\rangle &= \sum_{IJ} C_I^* \langle \Psi_I | \frac{\partial}{\partial t} \{C_J |\Psi_J\rangle\} \\ &= \sum_{IJ} C_I^* \langle \Psi_I | \left\{ \frac{\partial C_J}{\partial t} |\Psi_J\rangle + C_J \frac{\partial}{\partial t} |\Psi_J\rangle \right\} .\end{aligned} \tag{2.79}$$

Because we assume that the spin-orbitals satisfy the conditions of Eq.(2.62), we obtain

$$\langle \Psi_I | \frac{\partial}{\partial t} |\Psi_J\rangle = 0. \tag{2.80}$$

Consequently, we obtain

$$\langle \Psi| \frac{\partial}{\partial t} |\Psi\rangle = \sum_{IJ} C_I^* \frac{\partial C_J}{\partial t} \langle \Psi_I | \Psi_J\rangle . \tag{2.81}$$

From the orthonormalization of the spin-orbitals, we can write

$$\begin{aligned}\langle \Psi| \frac{\partial}{\partial t} |\Psi\rangle &= \sum_{IJ} C_I^* \frac{\partial C_J}{\partial t} \delta_{IJ} \\ &= \sum_{I} C_I^* \frac{\partial C_I}{\partial t} .\end{aligned} \tag{2.82}$$

Therefore, the variation can be written as

$$\langle \delta\Psi(\delta C_I)| \frac{\partial}{\partial t} |\Psi\rangle = (\delta C_I)^* \frac{\partial C_I}{\partial t}, \tag{2.83}$$

and consequently, the time-dependent variational principle is written as

$$i\hbar (\delta C_I)^* \frac{\partial C_I}{\partial t} = \sum_J (\delta C_I)^* C_J \langle \Psi_I | \hat{H} |\Psi_J\rangle . \tag{2.84}$$

Because the variation of δC_I is arbitrary, the time-dependent variational principle is rewritten as

$$i\hbar \frac{\partial C_I}{\partial t} = \sum_J C_J \langle \Psi_I | \hat{H} | \Psi_J \rangle . \tag{2.85}$$

This is the equation of motion for the CI-coefficients.

The right-hand side of Eq.(2.85) is written by distinguishing between Φ_I and Φ_J and by using the case (iv) in the subsection 2.2, we obtain

$$\begin{aligned} i\hbar \frac{\partial C_I}{\partial t} &= C_I \langle \Psi_I | \hat{H} | \Psi_I \rangle \\ &+ \sum_k^{occI} \sum_{m(\neq k)}^{occ} C_{kI}^m \langle \Psi_I | \hat{H} | \Psi_{kI}^m \rangle \\ &+ \sum_k^{occI} \sum_{l(>k)}^{occI} \sum_{\substack{m<n \\ (k,l)\neq(m,n)}}^{occ} C_{klI}^{mn} \langle \Psi_I | \hat{H} | \Psi_{klI}^{mn} \rangle . \end{aligned} \tag{2.86}$$

By substituting the equations in Eqs.(2.9), (2.15), and (2.20) into the right-hand side of Eq.(2.86), the resultant equation becomes

$$\begin{aligned} i\hbar \frac{\partial C_I}{\partial t} &= C_I \left[\sum_k^{occI} \langle k | \hat{h} | k \rangle + \sum_k^{occI} \sum_{l(>k)}^{occI} ([kk|ll] - [kl|lk]) \right] \\ &+ \sum_k^{occI} \sum_{m(\neq k)}^{occ} C_{kI}^m (-1)^{p_I(k)+p_J(m)} \left[\langle k | \hat{h} | m \rangle + \sum_n^{occI} ([km|nn] - [kn|nm]) \right] \\ &+ \sum_k^{occI} \sum_{l(>k)}^{occI} \sum_{\substack{m<n \\ (k,l)\neq(m,n)}}^{occ} C_{klI}^{mn} (-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} ([km|ln] - [kn|lm]). \end{aligned}$$

$$\tag{2.87}$$

By using the operators defined in Eqs.(2.24) and (2.33), we obtain

$$
\begin{aligned}
i\hbar\frac{\partial C_I}{\partial t} &= C_I \sum_{k}^{occI} \langle k| \left[\hat{h} + \frac{1}{2}\hat{V}^{(I)}\right] |k\rangle \\
&+ \sum_{k}^{occI} \sum_{m(\neq k)}^{occ} C_{kI}^{m} (-1)^{p_I(k)+p_J(m)} \langle k| \left[\hat{h} + \hat{V}^{(I)}\right] |m\rangle \\
&+ \sum_{k}^{occI} \sum_{l(>k)}^{occI} \sum_{\substack{m,n \\ (k,l)\neq(m,n)}}^{occ} C_{klI}^{mn} (-1)^{p_I(k)+p_I(l)+p_J(m)+p_J(n)} \\
&\qquad\qquad\qquad\qquad \times \operatorname{sgn}(n-m) \langle k| \hat{f}_{ln} |m\rangle \,. \qquad (2.88)
\end{aligned}
$$

This is the explicit form of the EOM for the CI-coefficients.

The MCTDHF method introduced here was extended in Ref. [21] to treat both nuclear dynamics and electron dynamics simultaneously.

3 Theory

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4 Results and Discussion

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5　Concluding remarks

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Appendix A: Expansion theorem

The expansion of the molecular wave function in Eq.(3.10) is derived from the expansion theorem in Ref. [33]. The molecular wave function of the left-hand side of Eq.(3.10) is expanded by the orthonormalized single-electronic function $\{\phi_i(x_1)\}$ as

$$\Phi(x_1, x_2, R) = \sum_j \phi_j(x_1) B_j(x_2, R), \tag{A.1}$$

where $B_j(x_2, R)$ is the expansion coefficients written as

$$B_j(x_2, R) = \int dx_1 \phi_j^*(x_1) \Phi(x_1, x_2, R). \tag{A.2}$$

By similar procedure, the expansion coefficients $B_j(x_2, R)$ is expanded as

$$B_j(x_2, R) = \sum_k \phi_k(x_2) D_{jk}(R), \tag{A.3}$$

where $D_{jk}(R)$ is the expansion coefficients written as

$$D_{jk}(R) = \int dx_2 \phi_k^*(x_2) B_j(x_2, R). \tag{A.4}$$

From Eqs.(A.1) and (A.3), the molecular wave function is written as

$$\Phi(x_1, x_2, R) = \sum_j \sum_k \phi_j(x_1) \phi_k(x_2) D_{jk}(R). \tag{A.5}$$

From the Pauli principle, the wave function change its sign against the exchange of two electrons:

$$\Phi(x_2, x_1, R) = -\Phi(x_1, x_2, R). \tag{A.6}$$

By inserting Eq.(A.5), we obtain

$$\sum_j \sum_k \phi_j(x_2) \phi_k(x_1) D_{jk}(R) = -\sum_j \sum_k \phi_j(x_1) \phi_k(x_2) D_{jk}(R). \tag{A.7}$$

By exchanging the suffixes in the left-hand side of Eq.(A.7), we obtain

$$\sum_k \sum_j \phi_k(x_2)\phi_j(x_1) D_{kj}(R) = -\sum_j \sum_k \phi_j(x_1)\phi_k(x_2) D_{jk}(R). \tag{A.8}$$

From Eq.(A.8), we obtain

$$\forall j,k \qquad D_{kj}(R) = -D_{jk}(R). \tag{A.9}$$

By setting $k = j$, we obtain

$$D_{jj}(R)(= -D_{jj}(R)) = 0. \tag{A.10}$$

From Eq.(A.5), the molecular wave function is expressed as

$$\begin{aligned}
\Phi(x_1, x_2, R) &= \frac{1}{2}\Phi(x_1, x_2, R) + \frac{1}{2}\Phi(x_1, x_2, R) \\
&= \frac{1}{2}\sum_j \sum_k \phi_j(x_1)\phi_k(x_2) D_{jk}(R) + \frac{1}{2}\sum_j \sum_k \phi_j(x_1)\phi_k(x_2) D_{jk}(R) \\
&= \frac{1}{2}\sum_j \sum_k \phi_j(x_1)\phi_k(x_2) D_{jk}(R) + \frac{1}{2}\sum_k \sum_j \phi_k(x_1)\phi_j(x_2) D_{kj}(R).
\end{aligned} \tag{A.11}$$

By inserting Eq.(A.10), we obtain

$$\begin{aligned}
\Phi(x_1, x_2, R) &= \frac{1}{2}\sum_j \sum_k \phi_j(x_1)\phi_k(x_2) D_{jk}(R) - \frac{1}{2}\sum_k \sum_j \phi_k(x_1)\phi_j(x_2) D_{jk}(R) \\
&= \frac{1}{2}\sum_j \sum_k \left\{\phi_j(x_1)\phi_k(x_2) - \phi_k(x_1)\phi_j(x_2)\right\} D_{jk}(R).
\end{aligned} \tag{A.12}$$

The right-hand side is devided into three parts as

$$\begin{aligned}
\Phi(x_1, x_2, R) = &\frac{1}{2}\sum_j \sum_{k(>j)} \left\{\phi_j(x_1)\phi_k(x_2) - \phi_k(x_1)\phi_j(x_2)\right\} D_{jk}(R) \\
&+ \frac{1}{2}\sum_j \left\{\phi_j(x_1)\phi_j(x_2) - \phi_j(x_1)\phi_j(x_2)\right\} D_{jj}(R) \\
&+ \frac{1}{2}\sum_j \sum_{k(<j)} \left\{\phi_j(x_1)\phi_k(x_2) - \phi_k(x_1)\phi_j(x_2)\right\} D_{jk}(R)
\end{aligned} \tag{A.13}$$

The second line in Eq.(A.13) vanishes due to Eq.(A.10). By exchanging the suffixes in the third line of Eq.(A.13), we obtain

$$\begin{aligned}\Phi(x_1, x_2, R) &= \frac{1}{2}\sum_j \sum_{k(>j)} \{\phi_j(x_1)\phi_k(x_2) - \phi_k(x_1)\phi_j(x_2)\}\, D_{jk}(R) \\ &+ \frac{1}{2}\sum_k \sum_{j(<k)} \{\phi_k(x_1)\phi_j(x_2) - \phi_j(x_1)\phi_k(x_2)\}\, D_{kj}(R). \end{aligned} \tag{A.14}$$

Because of $\sum_k \sum_{j(<k)} = \sum_j \sum_{k(>j)}$, Eq.(A.14) is expressed as

$$\begin{aligned}\Phi(x_1, x_2, R) &= \frac{1}{2}\sum_j \sum_{k(>j)} \{\phi_j(x_1)\phi_k(x_2) - \phi_k(x_1)\phi_j(x_2)\}\, D_{jk}(R) \\ &+ \frac{1}{2}\sum_j \sum_{k(>j)} \{\phi_k(x_1)\phi_j(x_2) - \phi_j(x_1)\phi_k(x_2)\}\, D_{kj}(R). \end{aligned} \tag{A.15}$$

By inserting Eq.(A.10) into Eq.(A.15), we obtain

$$\begin{aligned}\Phi(x_1, x_2, R) &= \frac{1}{2}\sum_j \sum_{k(>j)} \{\phi_j(x_1)\phi_k(x_2) - \phi_k(x_1)\phi_j(x_2)\}\, D_{jk}(R) \\ &- \frac{1}{2}\sum_j \sum_{k(>j)} \{\phi_k(x_1)\phi_j(x_2) - \phi_j(x_1)\phi_k(x_2)\}\, D_{jk}(R) \\ &= \sum_j \sum_{k(>j)} \{\phi_j(x_1)\phi_k(x_2) - \phi_k(x_1)\phi_j(x_2)\}\, D_{jk}(R) \end{aligned} \tag{A.16}$$

We number the combination of two indices (j, k) $(k > j)$ by I, introduce an Slater determinant $\Phi_I(x_1, x_2)$ as

$$\Phi_I(x_1, x_2) = \frac{1}{\sqrt{2!}} \{\phi_j(x_1)\phi_k(x_2) - \phi_k(x_1)\phi_j(x_2)\}, \tag{A.17}$$

and define $D_{jk}(R) \equiv C_I(R)$. By using these notations I, $\Phi_I(x_1, x_2)$, and $C_I(R)$, we write Eq.(A.16) as

$$\Phi(x_1, x_2, R) = \sum_I \Phi_I(x_1, x_2) C_I(R). \tag{A.18}$$

The expansion form in Eq.(A.18) is exactly the same as that in Eq.(3.10).

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