

# Improvement on Quasi-Variational Coupled Cluster(QVCC) method

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## **Abstract**

The thesis starts from mathematically introducing the ab-initio theoretical chemistry, beginning with the energy and variation of a Slater determinant, then the Hartree-Fock and Coupled Cluster theory. In the second chapter the methodological background of the project is introduced, starting from the detailed description of Traditional Coupled Cluster method and the Variational Coupled Cluster one, then introducing the early methods developed by my group: Linked Pair Functional method, Orbital-Optimized Quasi-Variational Coupled Cluster method and possible improvement. The rest of the thesis gives the detail of my research that is improvement made to the current Quasi-Variational Coupled Cluster method.



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# Chapter 1

## The ab-initio theoretical chemistry methods[1]

In the seventeenth century, Isaac Newton from United Kingdom developed classical mechanics. When the experiment is carried out in the microfield, the situation becomes very different. In the twentieth century, quantum mechanics was developed to predict the properties of very small particles such as electrons or atoms. Quantum chemistry applies quantum mechanics to the field of chemistry[2].

### 1.1 Schroedinger equation

The system in Quantum chemistry is described by wavefunction  $\Psi$ . The physical quantity observable is the square of the absolute value of  $\Psi$ , which equals to the product of  $\Psi$  and its complex conjugate:

$$|\Psi|^2 = \Psi^* \Psi \quad (1.1)$$

namely, probability density.

The wavefunction can be written as the product of the spatial function and a function of time,

$$\Psi(x, t) = f(t)\psi(x) \quad (1.2)$$

in which the one-dimensional case is presented.

The time-dependent Schroedinger equation in one-dimensional case is:

$$-\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t)$$

where the partial derivative of the wavefunction is:

$$\begin{aligned} \frac{\partial \Psi(x, t)}{\partial t} &= \frac{df(t)}{dt} \psi(x) \\ \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= f(t) \frac{d^2 \psi(x)}{dx^2} \end{aligned}$$

substituting into the equation, we get,

$$\begin{aligned} -\frac{\hbar}{i} \frac{df(t)}{dt} \psi(x) &= -\frac{\hbar^2}{2m} f(t) \frac{d^2 \psi(x)}{dx^2} + V(x) \psi(x) f(t) \\ -\frac{\hbar}{i} \frac{1}{f(t)} \frac{df(t)}{dt} &= -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + V(x) \end{aligned} \quad (1.3)$$

Because the left hand side of the equation is a function of t while right hand side is that of x, they should both be a constant, which can be denoted as  $E$ :

$$\begin{aligned} -\frac{\hbar}{i} \frac{1}{f(t)} \frac{df(t)}{dt} &= E \\ \frac{df(t)}{dt} &= -\frac{iE}{\hbar} f(t) \end{aligned} \quad (1.4)$$

The exponential function  $Ae^{-\frac{iEt}{\hbar}}$  is a solution to this equation. Generally, the constant coefficient  $A$  can be included in the spatial function  $\psi(x)$  as it multiplies  $f(t)$  eventually in  $\Psi(x, t)$ . The time function  $f(t)$  is therefore  $e^{-\frac{iEt}{\hbar}}$ .

The right hand side of this derived time dependent Schroedinger equation is,

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x) \quad (1.5)$$

This is the time independent Schroedinger equation for one-dimensional particle with mass  $m$ . Generally, the  $E$  is considered to be the energy of the system.

The time dependent wavefunction  $\Psi(x, t)$  is therefore,

$$\Psi(x, t) = e^{-\frac{iEt}{\hbar}} \psi(x) \quad (1.6)$$

Substitute this into the expression of the probability density above, we get

$$\begin{aligned}\Psi^* \Psi &= (e^{-\frac{iEt}{\hbar}} \psi(x))^* e^{-\frac{iEt}{\hbar}} \psi(x) \\ &= e^{\frac{iEt}{\hbar}} e^{-\frac{iEt}{\hbar}} \psi^*(x) \psi(x) = |\psi(x)|^2\end{aligned}$$

Because the probability density does not change with time, such state which can be separated into the product of time and spatial function is called stationary state.

## 1.2 Born-Oppenheimer approximation

The Hamiltonian operator for many particle system is,

$$\begin{aligned}\hat{H} = \sum_{\alpha} -\frac{\hbar^2}{2m_{\alpha}} \nabla_{\alpha}^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e'^2}{r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e'^2}{r_{i\alpha}} + \sum_i -\frac{\hbar^2}{2m_i} \nabla_i^2 \\ + \sum_i \sum_{j > i} \frac{e'^2}{r_{ij}}\end{aligned}\quad (1.7)$$

where  $\alpha, \beta$  are nuclei indices and  $i, j$  are electron indices. The first term is the nuclei kinetic energy and the fourth one electron kinetic energy, which describe the motion of the particles. The second term is the potential energy of nuclei and the fifth one is that of electrons, which describe the repulsion between particles, in which  $r_{\alpha\beta}$  is the distance between nuclei and  $r_{ij}$  is that between electrons. The third term is the potential energy between electrons and nuclei describing the attraction between them, in which the  $r_{\alpha i}$  is the distance between nuclei and electrons.

The full Hamiltonian operator can be simplified by certain approximation. By assuming that the configuration of nuclei is unchanged during the motion of the electron, or more simply speaking that the nuclei are fixed relative to the electron, the kinetic energy terms would become zero, and the potential energy term describing the repulsion between nuclei would become constant as  $r_{\alpha\beta}$  is fixed.

The original Schroedinger equation can be separated into the one only with respect to electron, on the basis that the wavefunction  $\Psi(\tau_{nu}, \tau_{el})$  depends on the coordinates of nuclei and electrons.

$$(\hat{H}_{el} + V_{NN})\psi_{el} = U\psi_{el}\quad (1.8)$$

$U = E_{el} + V_{NN}$  is the electronic energy including internuclear repulsion, because it can be proved that subtracting a constant from Hamiltonian

operator would not affect the wavefunction but only decrease each eigenvalue by a number. The Schroedinger equation can therefore be simplified to the pure electronic one

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el} \quad (1.9)$$

This approximation which separates the motion of electrons from that of nuclei is called Born-Oppenheimer approximation, it is very fundamental to quantum chemistry[3].

Hartree-Fock method is usually the starting point of the approximation to the electronic structure of the molecule. More advanced method can be made based on the Hartree-Fock wavefunction by adding higher order approximation to it.

The bra-ket notation used for representing wavefunction and its complex conjugate and their expectation value is defined as,

$$\langle x|\Psi\rangle = \int x\Psi dx = \Psi(x) \quad (1.10)$$

$$\langle\Psi|x\rangle = \int \Psi^* x dx = \Psi(x)^* \quad (1.11)$$

$$\langle\Psi|\hat{H}|\Psi\rangle = \int \Psi^* \hat{H}\Psi d\tau \quad (1.12)$$

$$\langle\Psi|\Psi\rangle = \int \Psi^* \Psi d\tau \quad (1.13)$$

where 'ket' of right angle bracket stands for the wavefunction while 'bra' of left angle bracket denotes the complex conjugate of it. When they close up, it represents the integral over all electron coordinates.

### 1.3 The energy of a Slater determinant

Each electron is described by an orbital. The one-electron functions of a molecule are thus Molecular Orbitals(MO), which are the product of a spatial orbital and a spin function( $\alpha$  or  $\beta$ ), also known as spin-orbitals, which may be taken as orthonormal. In the Hartree-Fock model, the total wavefunction is given as a product of orbitals. The overall wavefunction must be antisymmetric that is changing the sign with respect to interchanging any two orbitals, which is achieved by arranging orbitals in a Slater Determinant. The columns of a Slater determinant are single-electron wavefunctions that are orbitals, and the electron indices coordinate is along the rows. For

the case of  $N$  orbitals and  $N$  electrons, it is expressed as,

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix} \quad (1.14)$$

where  $\langle \phi_i | \phi_j \rangle = \delta_{ij}$  that is the orthonormal condition.

The expected set of orbitals is determined by Variational Principle. The Variational Principle states that the approximate wavefunction always has an energy higher than or equal to the exact Schroedinger equation energy, only for the wavefunction being exact Schroedinger equation function holds the equality. Therefore, the set of orbitals becomes expected one when it gives the lowest energy under the restriction of the wavefunction being a single Slater determinant.

The norm of a wavefunction is  $\langle \Psi | \Psi \rangle$ , for a normalized wavefunction  $\langle \Psi | \Psi \rangle = 1$ . The energy of a wavefunction is the expectation value of a Hamiltonian operator  $\hat{H}_e$ , divided by the norm of the wavefunction,

$$E = \frac{\langle \Psi | \hat{H}_e | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

therefore the energy of a normalized wavefunction is  $\langle \Psi | \hat{H}_e | \Psi \rangle$ .

The Hamiltonian operator  $\hat{H}_e$  could be written in atomic units as the sum of the kinetic energy operator  $\hat{T}_e$  describing the motion of electrons, the nuclear-nuclear repulsion operator  $\hat{V}_{nn}$ , the nuclear-electron repulsion operator  $\hat{V}_{ne}$  and the electron-electron repulsion operator  $\hat{V}_{ee}$ , which describe the potential energy of the system.

$$\hat{H}_e = \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \quad (1.15)$$

where,

$$\begin{aligned} \hat{T}_e &= - \sum_i^{N_{\text{elec}}} \frac{1}{2} \hat{\nabla}_i^2 \\ \hat{V}_{nn} &= \sum_a^{N_{\text{nucl}}} \sum_{b>a}^{N_{\text{nucl}}} \frac{Z_a Z_b}{|\vec{R}_a - \vec{R}_b|} \\ \hat{V}_{ne} &= - \sum_a^{N_{\text{nucl}}} \sum_i^{N_{\text{elec}}} \frac{Z_a}{|\vec{R}_a - \vec{r}_i|} \end{aligned}$$

$$\hat{V}_{ee} = \sum_i^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

The electron operators could be rewritten as one electron Hamiltonian operator  $\hat{h}_i$  and two electron operator  $\hat{g}_{ij}$ ,

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_a^{N_{\text{nucl}}} \frac{Z_a}{|\vec{R}_a - \vec{r}_i|}$$

$$\hat{g}_{ij} = \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\hat{H}_e = \sum_i^{N_{\text{elec}}} \hat{h}_i + \sum_i^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} \hat{g}_{ij} + \hat{V}_{nn} \quad (1.16)$$

The antisymmetrizing operator  $\hat{A}$  used for expressing the Slater determinant in a way suitable for deriving the energy is,

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_{p=0}^{N-1} (-1)^p \hat{P} = \frac{1}{\sqrt{N!}} (\hat{1} - \hat{P}_{ij} + \hat{P}_{ijk} - \dots)$$

where  $\hat{P}$  containing  $p$  as a parameter, permutes the orbital indices after it. The different order permutation operators include whole-electron interactions in each level, for example  $\hat{P}_{ijk}$  permutes orbitals  $\{ijk\}$  to  $\{jki\}$  or  $\{kij\}$ .

The antisymmetrizing operator  $\hat{A}$  commutes with the Hamiltonian operator  $\hat{H}$ ,

$$\hat{A}\hat{H} = \hat{H}\hat{A}$$

The Slater determinant could be expressed as the antisymmetrizing operator  $\hat{A}$  acting on the product of the diagonal elements  $\Pi$  of the determinant,

$$\Pi = \phi_1(1)\phi_2(2)\cdots\phi_N(N)$$

$$\Phi = \hat{A}(\phi_1(1)\phi_2(2)\cdots\phi_N(N)) = \hat{A}\Pi$$

The energy of a Slater determinant is the expectation value of the Hamiltonian operator  $\hat{H}_e$ ,

$$\begin{aligned}
E &= \frac{\langle \Phi | \hat{H}_e | \Phi \rangle}{\langle \Phi | \Phi \rangle} \\
&= \langle \Phi | \hat{H}_e | \Phi \rangle \\
&= \langle \hat{A}\Pi | \hat{H}_e | \hat{A}\Pi \rangle \\
&= \sqrt{N!} \langle \Pi | \hat{H}_e | \hat{A}\Pi \rangle \\
&= \sum_{p=0}^{N-1} (-1)^p \langle \Pi | \hat{H}_e | \hat{P}\Pi \rangle \\
&= \sum_{p=0}^{N-1} (-1)^p \langle \Pi | \sum_i \hat{h}_i + \sum_i \sum_{j>i} \hat{g}_{ij} + \hat{V}_{nn} | \hat{P}\Pi \rangle \\
&= \sum_{p=0}^{N-1} (-1)^p \langle \Pi | \sum_i \hat{h}_i | \hat{P}\Pi \rangle \\
&+ \sum_{p=0}^{N-1} (-1)^p \langle \Pi | \sum_i \sum_{j>i} \hat{g}_{ij} | \hat{P}\Pi \rangle + \sum_{p=0}^{N-1} (-1)^p \langle \Pi | \hat{V}_{nn} | \hat{P}\Pi \rangle \\
&= \sum_{p=0}^{N-1} \sum_i \langle \Pi | \hat{h}_i | \hat{P}\Pi \rangle \\
&+ \sum_{p=0}^{N-1} \sum_i \sum_{j>i} \langle \Pi | \hat{g}_{ij} | \hat{P}\Pi \rangle + \sum_{p=0}^{N-1} (-1)^p \hat{V}_{nn} \langle \Pi | \hat{P}\Pi \rangle \quad (1.17)
\end{aligned}$$

For the expectation value of the one-electron Hamiltonian operator  $\hat{h}_i$ , only the identity operator  $\hat{1}$  within  $\hat{P}$  will give the non-zero contribution.

$$\begin{aligned}
\langle \Pi | \hat{h}_i | \hat{1}\Pi \rangle &= \langle \phi_1(1)\phi_2(2)\cdots\phi_N(N) | \hat{h}_i | \phi_1(1)\phi_2(2)\cdots\phi_N(N) \rangle \\
&= \langle \phi_i(i) | \hat{h}_i | \phi_i(i) \rangle \langle \phi_2(2) | \phi_2(2) \rangle \cdots \langle \phi_N(N) | \phi_N(N) \rangle \\
&= \langle \phi_i(i) | \hat{h}_i | \phi_i(i) \rangle = h_i
\end{aligned}$$

For the expectation value of  $\hat{g}_{ij}$ , the identity operator  $\hat{1}$  within  $\hat{P}$  will give,

$$\langle \Pi | \hat{g}_{ij} | \hat{1}\Pi \rangle$$

$$\begin{aligned}
&= \langle \phi_1(1) \cdots \phi_i(i) \cdots \phi_j(j) \cdots \phi_N(N) | \hat{g}_{ij} | \phi_1(1) \cdots \phi_i(i) \cdots \phi_j(j) \cdots \phi_N(N) \rangle \\
&= \langle \phi_i(i) \phi_j(j) | \hat{g}_{ij} | \phi_i(i) \phi_j(j) \rangle \langle \phi_1(1) | \phi_1(1) \rangle \cdots \langle \phi_N(N) | \phi_N(N) \rangle \\
&= \langle \phi_i(i) \phi_j(j) | \hat{g}_{ij} | \phi_i(i) \phi_j(j) \rangle = J_{ij}
\end{aligned}$$

the  $\hat{P}_{kl}$  permuting two orbitals within  $\hat{P}$  will give

$$\begin{aligned}
&-\langle \Pi | \hat{g}_{ij} | \sum_k^N \sum_{l>k}^N \hat{P}_{kl} \Pi \rangle \\
&= -\sum_k^N \sum_{l>k}^N \langle \Pi | \hat{g}_{ij} | \hat{P}_{kl} \Pi \rangle
\end{aligned}$$

when  $j > i$ , only the orbital indices  $i=k$  and  $j=l$  will the result be non-zero,

$$\begin{aligned}
&= -\langle \phi_1(1) \cdots \phi_i(i) \cdots \phi_j(j) \cdots \phi_N(N) | \hat{g}_{ij} | \phi_1(1) \cdots \phi_j(i) \cdots \phi_i(j) \cdots \phi_N(N) \rangle \\
&= -\langle \phi_i(i) \phi_j(j) | \hat{g}_{ij} | \phi_j(i) \phi_i(j) \rangle \langle \phi_1(1) | \phi_1(1) \rangle \cdots \langle \phi_N(N) | \phi_N(N) \rangle \\
&= -\langle \phi_i(i) \phi_j(j) | \hat{g}_{ij} | \phi_j(i) \phi_i(j) \rangle = -K_{ij}
\end{aligned}$$

The expectation value of  $\hat{V}_{nn}$  is a constant with respect to the integral over the electron coordinates.

The energy of a Slater determinant could therefore be derived as,

$$E = \sum_i^{N_{\text{elec}}} h_i + \sum_i^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} (J_{ij} - K_{ij}) + \hat{V}_{nn} \quad (1.18)$$

The second term in the energy expression could become sum over full range of  $i$  and  $j$ ,

$$E = \sum_i^{N_{\text{elec}}} h_i + \frac{1}{2} \sum_i^{N_{\text{elec}}} \sum_j^{N_{\text{elec}}} (J_{ij} - K_{ij}) + \hat{V}_{nn} \quad (1.19)$$

The energy could be re-expressed in terms of Coulomb operator  $\hat{J}_i$  and exchange operator  $\hat{K}_i$  in order to conveniently derive the variation of the energy,

$$\begin{aligned}
\hat{J}_i | \phi_j(j) \rangle &= \langle \phi_i(i) | \hat{g}_{ij} | \phi_i(i) \rangle | \phi_j(j) \rangle \\
\hat{K}_i | \phi_j(j) \rangle &= \langle \phi_i(i) | \hat{g}_{ij} | \phi_j(i) \rangle | \phi_i(j) \rangle
\end{aligned}$$

$$\begin{aligned}
E &= \sum_i^{N_{\text{elec}}} \langle \phi_i(i) | \hat{h}_i | \phi_i(i) \rangle \\
&+ \frac{1}{2} \sum_i^{N_{\text{elec}}} \sum_j^{N_{\text{elec}}} (\langle \phi_j(j) | \hat{J}_i | \phi_j(j) \rangle - \langle \phi_j(j) | \hat{K}_i | \phi_j(j) \rangle) + \hat{V}_{nn} \quad (1.20)
\end{aligned}$$

Under the definition of the combination of the operators, we can find that

$$\langle \phi_j(j) | \hat{J}_i | \phi_j(j) \rangle - \langle \phi_j(j) | \hat{K}_i | \phi_j(j) \rangle = \langle \phi_j(j) | \hat{J}_i - \hat{K}_i | \phi_j(j) \rangle$$

therefore, the energy could be expressed as,

$$E = \sum_i^{N_{\text{elec}}} \langle \phi_i(i) | \hat{h}_i | \phi_i(i) \rangle + \frac{1}{2} \sum_i^{N_{\text{elec}}} \sum_j^{N_{\text{elec}}} \langle \phi_j(j) | \hat{J}_i - \hat{K}_i | \phi_j(j) \rangle + \hat{V}_{nn} \quad (1.21)$$

## 1.4 The variation of the energy of a Slater determinant

The variation of the energy with respect to orbital change is,

$$\begin{aligned}
\delta E &= \sum_i^{N_{\text{elec}}} (\langle \delta \phi_i(i) | \hat{h}_i | \phi_i(i) \rangle + \langle \phi_i(i) | \hat{h}_i | \delta \phi_i(i) \rangle) \\
&+ \frac{1}{2} \sum_i^{N_{\text{elec}}} \sum_j^{N_{\text{elec}}} (\langle \delta \phi_i(i) | \hat{J}_j - \hat{K}_j | \phi_i(i) \rangle + \langle \phi_i(i) | \hat{J}_j - \hat{K}_j | \delta \phi_i(i) \rangle) \\
&\quad + \langle \delta \phi_j(j) | \hat{J}_i - \hat{K}_i | \phi_j(j) \rangle + \langle \phi_i(i) | \hat{J}_i - \hat{K}_i | \delta \phi_i(i) \rangle \quad (1.22)
\end{aligned}$$

By altering the order of sum and relating i and j, the third element is same as the first one in the second term. So is the fourth element as the

second one. The expression could therefore be combined as,

$$\begin{aligned}
\delta E &= \sum_i^{N_{\text{elec}}} (\langle \delta\phi_i(i) | \hat{h}_i | \phi_i(i) \rangle + \langle \phi_i(i) | \hat{h}_i | \delta\phi_i(i) \rangle) \\
&+ \sum_i^{N_{\text{elec}}} \sum_j^{N_{\text{elec}}} (\langle \delta\phi_i(i) | \hat{J}_j - \hat{K}_j | \phi_i(i) \rangle + \langle \phi_i(i) | \hat{J}_j - \hat{K}_j | \delta\phi_i(i) \rangle) \\
\delta E &= \sum_i^{N_{\text{elec}}} (\langle \delta\phi_i(i) | \hat{h}_i + \sum_j^{N_{\text{elec}}} (\hat{J}_j - \hat{K}_j) | \phi_i(i) \rangle \\
&+ \langle \phi_i(i) | \hat{h}_i + \sum_j^{N_{\text{elec}}} (\hat{J}_j - \hat{K}_j) | \delta\phi_i(i) \rangle) \quad (1.23)
\end{aligned}$$

where  $\hat{h}_i + \sum_j^{N_{\text{elec}}} (\hat{J}_j - \hat{K}_j)$  is defined as the Fock operator  $\hat{F}_i$ ,

$$\delta E = \sum_i^{N_{\text{elec}}} (\langle \delta\phi_i(i) | \hat{F}_i | \phi_i(i) \rangle + \langle \phi_i(i) | \hat{F}_i | \delta\phi_i(i) \rangle) \quad (1.24)$$

The orbital set should keep orthonormal during the variation. It is achieved by using the Lagrange multipliers  $\lambda_{ij}$ . The Lagrange function  $L$  containing them will keep stationary with respect to a small change of the orbital  $\delta\phi$  at its local minimum,

$$L = E - \sum_{ij}^N \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \quad (1.25)$$

$$\delta L = \delta E - \sum_{ij}^N \lambda_{ij} (\langle \delta\phi_i | \phi_j \rangle + \langle \phi_i | \delta\phi_j \rangle) = 0 \quad (1.26)$$

Substituting the variation of energy  $\delta E$  into the stationary expression, we obtain that

$$\begin{aligned}
&\sum_i^{N_{\text{elec}}} (\langle \delta\phi_i(i) | \hat{F}_i | \phi_i(i) \rangle + \langle \phi_i(i) | \hat{F}_i | \delta\phi_i(i) \rangle) \\
&= \sum_{ij}^N \lambda_{ij} (\langle \delta\phi_i | \phi_j \rangle + \langle \phi_i | \delta\phi_j \rangle) \quad (1.27)
\end{aligned}$$

There is a kind of relationship between the expectation value and its complex conjugate,

$$\begin{aligned}\langle \phi_i(i) | \hat{F}_i | \delta \phi_i(i) \rangle &= \langle \delta \phi_i(i) | \hat{F}_i | \phi_i(i) \rangle^* \\ \langle \phi_i | \delta \phi_j \rangle &= \langle \delta \phi_j | \phi_i \rangle^*\end{aligned}$$

the stationary expression therefore becomes,

$$\begin{aligned}\sum_i^{N_{\text{elec}}} (\langle \delta \phi_i(i) | \hat{F}_i | \phi_i(i) \rangle + \langle \delta \phi_i(i) | \hat{F}_i | \phi_i(i) \rangle^*) \\ = \sum_{ij}^N (\langle \delta \phi_i | \phi_j \rangle + \langle \delta \phi_j | \phi_i \rangle^*)\end{aligned}\quad (1.28)$$

It seems that the variation  $\langle \phi_i(i) |$  and  $\langle \phi_i(i) |^*$  should cancel themselves with their counterparts on the right hand side of the equation,

$$\begin{aligned}\sum_i^{N_{\text{elec}}} \langle \delta \phi_i(i) | \hat{F}_i | \phi_i(i) \rangle &= \sum_{ij}^N \langle \delta \phi_i | \phi_j \rangle \\ \sum_i^{N_{\text{elec}}} \langle \delta \phi_i(i) | \hat{F}_i | \phi_i(i) \rangle^* &= \sum_{ij}^N \lambda_{ij} \langle \delta \phi_j | \phi_i \rangle^*\end{aligned}$$

Taking the complex conjugate of the second equation and subtracting it from the first one, we can obtain that

$$\begin{aligned}\sum_i^{N_{\text{elec}}} \langle \delta \phi_i(i) | \hat{F}_i | \phi_i(i) \rangle - \sum_i^{N_{\text{elec}}} \langle \delta \phi_i(i) | \hat{F}_i | \phi_i(i) \rangle \\ = \sum_{ij}^N \lambda_{ij} \langle \delta \phi_i | \phi_j \rangle - \sum_{ij}^N \lambda_{ij}^* \langle \delta \phi_j | \phi_i \rangle\end{aligned}\quad (1.29)$$

the left hand side of the equation is zero, and because  $\sum_{ji}^N \lambda_{ij}^* \langle \delta \phi_j | \phi_i \rangle = \sum_{ij}^N \lambda_{ji}^* \langle \delta \phi_i | \phi_j \rangle$ , we can eventually obtain that

$$\sum_{ij}^N (\lambda_{ij} - \lambda_{ji}^*) \langle \delta \phi_i | \phi_j \rangle \quad (1.30)$$

It seems that the coefficient  $\lambda_{ij} - \lambda_{ji}^*$  must be zero. Therefore the Hermitian conjugate relation is found within Lagrange multipliers  $\lambda_{ij} = \lambda_{ji}^*$ , i.e.  $\lambda_{ij}$  is Hermitian matrix element.

## 1.5 Hartree-Fock theory

The set of Hartree-Fock equation [4, 5] may be written as,

$$\hat{F}_i \phi_i(i) = \sum_{ij} \lambda_{ij} \phi_j \quad (1.31)$$

the unitary transformation can be done to the orbital set  $\phi$  so that the coefficients  $\lambda_{ij}$  on the right hand side can become diagonal, i.e.  $\lambda_{ij} = 0$  when  $i \neq j$  and  $\lambda_{ii} = \epsilon_i$ . The transformed orbitals are called Canonical Molecular orbitals denoted as  $\phi'$ ,

$$\hat{F}_i \phi'_i(i) = \lambda_{ii} \phi'_i = \epsilon_i \phi'_i \quad (1.32)$$

The elements within the set of orbitals  $\phi'$  are dependant to each other when the equations are solved, they are called self-consistent field orbitals.

The electron-electron repulsion is treated in a mean-field approximation due to the use of single Slater determinant.

The energy of a molecule with N electrons described by a Slater determinant is,

$$E_N = \sum_i^{N_{\text{elec}}} h_i + \frac{1}{2} \sum_i^{N_{\text{elec}}} \sum_j^{N_{\text{elec}}} (J_{ij} - K_{ij}) + V_{nn} \quad (1.33)$$

Now we ionize an electron from orbital k, suppose all the orbitals are remaining unchanged, the energy of the rest system is,

$$E_{N-1} = \sum_{i \neq k}^{N_{\text{elec}}} h_i + \frac{1}{2} \sum_{i \neq k}^{N_{\text{elec}}} \sum_{j \neq k}^{N_{\text{elec}}} (J_{ij} - K_{ij}) + V_{nn} \quad (1.34)$$

The ionization energy is,

$$E_N - E_{N-1} = h_k + \frac{1}{2} \sum_{j \neq k}^{N_{\text{elec}}} (J_{kj} - K_{kj}) + \frac{1}{2} \sum_{i \neq k}^{N_{\text{elec}}} (J_{ik} - K_{ik}) \quad (1.35)$$

There is symmetrical relationship within the Coulomb integral matrix elements  $J_{ij}$ ,

$$\begin{aligned} J_{ij} &= \langle \phi_i(i) \phi_j(j) | \frac{1}{|\vec{r}_i - \vec{r}_j|} | \phi_i(i) \phi_j(j) \rangle \\ &= \langle \phi_j(j) \phi_i(i) | \frac{1}{|\vec{r}_j - \vec{r}_i|} | \phi_j(j) \phi_i(i) \rangle = J_{ji} \end{aligned}$$

So is  $K_{ij} = K_{ji}$ .

The second term in the ionization energy is therefore equal to the third one,

$$E_N - E_{N-1} = h_k + \sum_{i \neq k}^{N_{\text{elec}}} (J_{ik} - K_{ik}) \quad (1.36)$$

which equals to the expectation value of the Fock operator that is the energy of the orbital,

$$E_N - E_{N-1} = \langle \phi_k(k) | \hat{F}_k | \phi_k(k) \rangle = \epsilon_k \quad (1.37)$$

This is the Koopman's theorem stating that the ionization energy is that of the ionized orbital  $\epsilon_k$ , based on the 'frozen Molecular orbital' approximation supposing that the orbitals are remaining unchanged during the process.

In the same way, the electron affinity is obtained as the energy of the  $k$ th unoccupied orbital in the neutral molecule, which becomes part of its relative anion after the process,

$$E_{N+1} - E_N = \epsilon_k \quad (1.38)$$

### 1.5.1 the Hartree-Fock equations made of atomic orbitals

According to the LCAO principle, Molecular Orbitals(MO) can be expanded as the linear combination of atomic orbitals, denoted as  $\chi$ :

$$\phi = \sum_a c_{ai} \chi_a \quad (1.39)$$

The set of Hartree Fock equations therefore becomes

$$\hat{F}_i \sum_{\alpha} c_{\alpha i} \chi_{\alpha} = \epsilon_i \sum_{\alpha} c_{\alpha i} \chi_{\alpha} \quad (1.40)$$

This equation is not stable unless for a complete basis set, however it can be compensated by projecting onto another atomic orbital.

Pre-multiply another atomic orbital  $\chi_{\beta}$  then take the integral over the whole coordinates space, we get the Roothan-Hall equation expressed by matrix:

$$(\mathbf{FC})_i = \mathbf{SC}\epsilon_i \quad (1.41)$$

where  $\mathbf{F}$  and  $\mathbf{S}$  are Fock matrix and overlap matrix:

$$F_{\alpha\beta} = \langle \chi_\alpha | \hat{F} | \chi_\beta \rangle S_{\alpha\beta} = \langle \chi_\alpha | \chi_\beta \rangle \quad (1.42)$$

Because there are  $N_{basis}$ , number of basis functions, possible  $\chi_\beta$  to pre-multiply, there are  $N_{basis}$  equations existing simultaneously.

The Fock matrix element  $F_{\alpha\beta}$  is,

$$\begin{aligned} \langle \chi_\alpha | \hat{h}_i + \sum_j (\hat{J}_j - \hat{K}_j) | \chi_\beta \rangle &= \langle \chi_\alpha | \hat{h}_i | \chi_\beta \rangle + \sum_j \langle \chi_\alpha | \hat{J}_j - \hat{K}_j | \chi_\beta \rangle \\ &= \langle \chi_\alpha | \hat{h}_i | \chi_\beta \rangle + \sum_j (\langle \chi_\alpha \phi_j | \hat{g} | \chi_\beta \phi_j \rangle - \langle \chi_\alpha \phi_j | \hat{g} | \phi_j \chi_\beta \rangle) \\ &= \langle \chi_\alpha | \hat{h}_i | \chi_\beta \rangle + \sum_j \sum_{\gamma\delta} c_{\gamma j} c_{\delta j} (\langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\delta \chi_\beta \rangle) \end{aligned} \quad (1.43)$$

where  $\sum_j c_{\gamma j} c_{\delta j}$  is called density matrix, denoted as  $D_{\gamma\delta}$ , and two-electron integrals following it describe the electron-electron repulsion.

The energy of a Slater determinant can be expressed in term of atomic orbitals as:

$$\begin{aligned} \sum_i \langle \phi_i | \hat{h}_i | \phi_i \rangle + \frac{1}{2} \sum_{ij} (\langle \phi_i \phi_j | \hat{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g} | \phi_j \phi_i \rangle) + V_{nn} \\ = \sum_i \sum_{\alpha\beta} c_{\alpha i} c_{\beta i} \langle \chi_\alpha | \hat{h}_i | \chi_\beta \rangle \\ + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} \sum_{\gamma\delta} c_{\alpha i} c_{\beta i} c_{\gamma j} c_{\delta j} (\langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\delta \chi_\beta \rangle) + V_{nn} \end{aligned} \quad (1.44)$$

in which the density matrices  $D_{\alpha\beta} = \sum_i c_{\alpha i} c_{\beta i}$  and  $D_{\gamma\delta} = \sum_j c_{\gamma j} c_{\delta j}$  can be defined. The energy can therefore be expressed in term of density matrices as

$$\sum_{\alpha\beta} D_{\alpha\beta} h_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta} \sum_{\gamma\delta} D_{\alpha\beta} D_{\gamma\delta} (\langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \hat{g} | \chi_\delta \chi_\beta \rangle) + V_{nn} \quad (1.45)$$

The one-electron integral can be expanded using the definition of  $\hat{h}_i$  operator:

$$\langle \chi_\alpha | \hat{h}_i | \chi_\beta \rangle = \int \chi_\alpha^*(i) \left( -\frac{1}{2} \nabla_i^2 \right) \chi_\beta(i) d\vec{r}_i - \sum_a \int \chi_\alpha^*(i) \left| \frac{Z_a}{\vec{R}_a - \vec{r}_i} \right| \chi_\beta(i) d\vec{r}_i \quad (1.46)$$

## 1.6 Coupled Cluster theory[59]

Coupled Cluster method was invented initially by Čížek and Faldus in the 1960s[6, 7, 8], it has become an effective tool in approximately solving electronic Schroedinger equation and predicting molecular properties, which is computationally affordable as well. Hurley presented the Coupled-Cluster Doubles(CCD) equations in a more easily-understandable way after it was invented[9]. Monkhorst then developed the general coupled cluster response theory which is used for calculating molecular properties[10]. In the 1970s, the software implementation was started by Pople[11] and Bartlett[12] with spin-orbital Coupled Cluster Doubles(CCD) program. After then, Purvis and Bartlett developed the method including Singles excitation(CCS) and have it implemented in a computer program[13]. A lot of exploration on the efficient Coupled Cluster code has been achieved after then[from reference [13] to [19]], inclusion of higher order excitations has also been developed[from reference[20] to [39]]. The equations are tried to spin-adapted into open-shell case, as well[from reference [40] to [47]].

### 1.6.1 the mathematical framework

Coupled Cluster theory tries including any type of correction, which is Single excitation, Double or Triple... with unlimited order that is square and cubic and so on to the reference wavefunction. It attempts to overcome the mean-field description of Hartree-Fock on the electron-electron repulsion, by including higher excitation to the original wavefunction.

The excitation operator  $\hat{T}$  is defined as,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_{N_{\text{elec}}}$$

where

$$\begin{aligned} \hat{T}_1 \Phi_0 &= \sum_i^{N_{\text{elec}}} \sum_a^{N_{\text{virt}}} t_i^a \Phi_i^a \\ \hat{T}_2 \Phi_0 &= \sum_i^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} \sum_a^{N_{\text{virt}}} \sum_{b>a}^{N_{\text{virt}}} t_{ab}^{ij} \Phi_{ij}^{ab} \end{aligned}$$

in which the coefficients  $t_i^a, t_{ab}^{ij}$  are called Single, Double excitation amplitudes. The Configuration Interaction(CI) wavefunction is,

$$\Phi_{\text{CI}} = (\hat{1} + \hat{T})\Phi_0 = (\hat{1} + \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_{N_{\text{elec}}})\Phi_0 \quad (1.47)$$

The Coupled Cluster excitation operator is,

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots = \sum_{k=0}^{N_{\text{elec}}} \frac{1}{k!}\hat{T}^k$$

Substitute the  $\hat{T}$  with the full expression, expand what obtained, collect the terms with same order together, we can express the excitation operator as,

$$\begin{aligned} e^{\hat{T}} = & 1 + \hat{T}_1 + (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) + (\hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{1}{6}\hat{T}_1^3) \\ & + (\hat{T}_4 + \hat{T}_3\hat{T}_1 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{24}\hat{T}_1^4) + \dots \end{aligned} \quad (1.48)$$

The Schroedinger equation with Coupled Cluster wavefunction could therefore be written as,

$$\hat{H}e^{\hat{T}}\Phi_0 = Ee^{\hat{T}}\Phi_0 \quad (1.49)$$

The energy of Coupled Cluster wavefunction could be determined as the expectation value of the Hamiltonian operator  $\hat{H}$ ,

$$E = \frac{\langle \Psi_{CC} | \hat{H} | \Psi_{CC} \rangle}{\langle \Psi_{CC} | \Psi_{CC} \rangle} = \frac{\langle e^{\hat{T}}\Phi_0 | \hat{H} | e^{\hat{T}}\Phi_0 \rangle}{\langle e^{\hat{T}}\Phi_0 | e^{\hat{T}}\Phi_0 \rangle} \quad (1.50)$$

The standard Coupled Cluster theory projects the Schroedinger equation onto the Slater determinant,

$$\langle \Phi_0 | \hat{H} e^{\hat{T}} | \Phi_0 \rangle = \langle \Phi_0 | E e^{\hat{T}} | \Phi_0 \rangle = E \langle \Phi_0 | e^{\hat{T}} | \Phi_0 \rangle \quad (1.51)$$

As the Slater determinants are orthonormal to each other, only the integral of the identity term on the right-hand side of the equation will give the non-zero contribution, the equation therefore becomes,

$$E = \langle \Phi_0 | \hat{H} e^{\hat{T}} | \Phi_0 \rangle \quad (1.52)$$

After expanding the Coupled Cluster excitation operator  $e^{\hat{T}}$ , the order terminates at 2 that is  $\hat{T}_2$  or  $\hat{T}_1^2$ .

$$\begin{aligned} E_{CC} = & \langle \Phi_0 | \hat{H} (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2) | \Phi_0 \rangle \\ = & \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \hat{T}_1 | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle + \frac{1}{2} \langle \Phi_0 | \hat{H} \hat{T}_1^2 | \Phi_0 \rangle \end{aligned} \quad (1.53)$$

Substituting  $\hat{T}_1$  and  $\hat{T}_2$  into  $E_{CC}$ , we derive the expression as,

$$\begin{aligned}
E_{CC} = E_0 + \sum_i^{N_{elec}} \sum_a^{N_{virt}} t_i^a \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle + \sum_i^{N_{elec}} \sum_{j>i}^{N_{elec}} \sum_a^{N_{virt}} \sum_{b>a}^{N_{virt}} t_{ab}^{ij} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle \\
+ \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} \sum_a^{N_{virt}} \sum_b^{N_{virt}} t_i^a t_j^b \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle
\end{aligned} \tag{1.54}$$

According to the Brillouin's theorem, the first matrix element  $\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle$  is zero and the last one  $\langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle$  is about two-electron integrals,

$$\begin{aligned}
E_{CC} = E_0 + \sum_i^{N_{elec}} \sum_{j>i}^{N_{elec}} \sum_a^{N_{virt}} \sum_{b>a}^{N_{virt}} t_{ab}^{ij} (\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle) \\
+ \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} \sum_a^{N_{virt}} \sum_b^{N_{virt}} t_i^a t_j^b (\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle)
\end{aligned} \tag{1.55}$$

The amplitudes could be determined by making similarity transformation on the Schroedinger equation, that is multiplying  $e^{-\hat{T}}$  on both sides of the equation,

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} \Phi_0 = e^{-\hat{T}} E e^{\hat{T}} \Phi_0 \tag{1.56}$$

It is supposed that  $e^{-\hat{T}}$  will cancel with  $e^{\hat{T}}$ . After projecting the expression onto the complex conjugate of the Slater determinant  $\Phi_0^*$ , we obtain that

$$E = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle \tag{1.57}$$

which is same as the energy obtained in standard Coupled Cluster theory.

By projecting the similarity transformed Coupled Cluster Schroedinger equation onto the excited Slater determinant,

$$\langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E_{CC} \langle \Phi_i^a | \Phi_0 \rangle = 0 \tag{1.58}$$

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 \tag{1.59}$$

$$\langle \Phi_{ijk}^{abc} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 \tag{1.60}$$

we can obtain the equations for the amplitudes.

## Chapter 2

# Variational Coupled Cluster(VCC) method and its approximation

Hartree-Fock method adapts single Slater determinant as the system wavefunction which is used for describing the ground state electronic structure of the system.

Traditional Coupled Cluster method adds higher order corrections to the single determinant of Hartree-Fock, which holds the important methodological properties rigorous extensivity meaning correct scaling of the energy with respect to system size, and exactness which has the energy equivalent to the Full Configuration Interaction(FCI) when the excitation operator  $\hat{T}$  is complete.

When more than one Slater determinant become important in describing the electronic structure of the molecule, single Slater determinant is limited in reflecting the electronic correlation, which is called the ‘static correlation effect’. The cluster operator  $\hat{T}$  in Traditional Coupled Cluster based methods are usually truncated to single and double levels, which encounter difficulty when such effect becomes dominant[58]. The higher level excitation such as Triple can be added to the methods to try overcoming the problem.

Advanced Coupled Cluster methods have been raised such as Quadratic Coupled Cluster(QCC) method[66], Improved Coupled Cluster(ICC) method[67] and Variational Coupled Cluster(VCC) method[68]. VCC has been demonstrated in prior studies[69, 75] to outperform other methods; it holds the upper bound property that the energy is always higher than the

Full Configuration Interaction(FCI) one[56].

James Robinson has developed approximate Variational Coupled Cluster methods[56], which keeps the upper bound property of the Variational one and holds the same computational complexity as the Traditional one. The developed methods have the important methodological property of rigorous extensivity with respect to system size, and exactness of the energy on the isolated two-electron subsystem.

## 2.1 Traditional Coupled Cluster method[59]

Following the Coupled Cluster theory in Chapter 1, Traditional Coupled Cluster method is based on making Similarity transformation to the electronic Hamiltonian operator,

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$$

then projecting the Schroedinger equation onto the ground or excited state Slater determinant,

$$\langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E_{\text{TCC}} \quad (2.1)$$

$$\langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 \quad (2.2)$$

$$\langle \Phi_{ij\dots}^{ab\dots} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 \quad (2.3)$$

where the energy  $E_{\text{TCC}}$  equation is independent from the rest ones determining the cluster amplitudes. The similarity transformed Hamiltonian operator could be expressed in terms of the commutators of Hamiltonian operator  $\hat{H}$  with excitation operator  $\hat{T}$ ,

$$\begin{aligned} e^{-\hat{T}} \hat{H} e^{\hat{T}} &= \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!} [[[ \hat{H}, \hat{T} ], \hat{T}], \hat{T}] \\ &\quad + \frac{1}{4!} [[[[ \hat{H}, \hat{T} ], \hat{T}], \hat{T}], \hat{T}] + \dots \end{aligned} \quad (2.4)$$

which is called Hausdorff expansion.

The Hamiltonian operator in second quantized form could be expressed as,

$$\hat{H} = \sum_{pq} h_{pq} c_p^\dagger c_q + \sum_{pqrs} \langle \phi_p \phi_q | | \phi_r \phi_s \rangle c_p^\dagger c_q^\dagger c_s c_r$$

where  $h_{pq} = \langle \phi_p | \hat{h}_i | \phi_q \rangle$  is the matrix element of the one-electron hamiltonian operator  $\hat{h}_i$  in the electronic Hamiltonian,  $\langle \phi_p \phi_q | | \phi_r \phi_s \rangle = \langle \phi_p \phi_q | \phi_r \phi_s \rangle -$

$\langle \phi_p \phi_q | \phi_s \phi_r \rangle$  is the two-bar notation of the two-electron integral,  $p, q, r, s$  are the general orbital indices which could either be occupied or virtual ones.

The positive commutator of the creation and annihilation operators  $c^\dagger, c$  is[65]:

$$\begin{aligned} [c_p, c_q]_+ &= c_p c_q + c_q c_p = 0 \\ [c_p^\dagger, c_q^\dagger]_+ &= c_p^\dagger c_q^\dagger + c_q^\dagger c_p^\dagger = 0 \\ [c_p^\dagger, c_q]_+ &= c_p^\dagger c_q + c_q c_p^\dagger = \delta_{pq} \end{aligned}$$

These are the ‘fermion commutation rules’.

For example, the commutator of creation and annihilation operators sequence in the one-electron part of the Hamiltonian operator  $\hat{H}$ ,  $c_p^\dagger c_q$  with that in the single excitation operator  $\hat{T}_1$ ,  $c_a^\dagger c_i$  is therefore derived as:

$$\begin{aligned} [c_p^\dagger c_q, c_a^\dagger c_i] &= c_p^\dagger c_q c_a^\dagger c_i - c_a^\dagger c_i c_p^\dagger c_q \\ &= c_p^\dagger \delta_{aq} c_i - c_a^\dagger \delta_{ip} c_q \end{aligned} \quad (2.5)$$

The number of creation and annihilation operators is decreased in the result, where the general indices ones  $c_p^\dagger, c_q$  coming from the Hamiltonian operator  $\hat{H}$  are reduced in number by one.

As the Hamiltonian operator  $\hat{H}$  contains at most four creation or annihilation operators, the Hausdorff expansion composed of the commutator of  $\hat{H}$  with excitation operator  $\hat{T}$  is terminated at the fourth order:

$$\begin{aligned} e^{-\hat{T}} \hat{H} e^{\hat{T}} &= \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!} [[[ \hat{H}, \hat{T} ], \hat{T}], \hat{T}] \\ &\quad + \frac{1}{4!} [[[[ \hat{H}, \hat{T} ], \hat{T}], \hat{T}], \hat{T}] \end{aligned} \quad (2.6)$$

We can then derive the energy  $E_{\text{TCC}}$  and cluster amplitudes equations based on terminated similarity transformed Hamiltonian operator  $e^{-\hat{T}} \hat{H} e^{\hat{T}}$ .

## 2.2 Variational Coupled Cluster method[59]

The energy functional of Variational Coupled Cluster(VCC) method is,

$$\begin{aligned} E_{\text{VCC}} &= \frac{\langle \Phi_0 | (e^{\hat{T}})^\dagger \hat{H} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | (e^{\hat{T}})^\dagger e^{\hat{T}} | \Phi_0 \rangle} \\ &= \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \end{aligned} \quad (2.7)$$

which is found minimum with respect to the cluster amplitudes, based on the variational principle.

The numerator of  $E_{\text{VCC}}$  could be expanded as,

$$\langle \Phi | (1 + \hat{T}^\dagger + \frac{1}{2}(\hat{T}^\dagger)^2 + \dots) \hat{H} (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \dots) | \Phi \rangle$$

as the power of  $\hat{T}$  becomes higher it will not terminate. The power series makes the expression much more complex than Traditional Coupled Cluster method.

Different methods based on Variational Coupled Cluster one has been raised. The Unitary Coupled Cluster(UCC) method researched by Hoffmann and Simons[60, 61] replaces the excitation operator  $\hat{T}$  with  $\hat{T} - \hat{T}^\dagger$ . The expectation value Coupled Cluster(XCC) method of Bartlett and Noga[62] where power series in VCC is truncated based on perturbation theory. The extended Coupled Cluster method(ECCM) developed by Arponen and Bishop [63, 64] adapted a modified energy functional including an exponentiated de-excitation operator similar to  $(e^{\hat{T}})^\dagger$ .

### 2.3 The approximation to the Variational Coupled Cluster method[48, 57]

In my project an accurate approximation to the Variational coupled cluster method is explored[48, 57].

There are a lot of attempts made by other authors to approximate the Variational Coupled Cluster method, the simplest of which is to truncate the power series in the ground state energy expression to  $1 + \hat{T}$ , and substitute it in the energy expression. It will lead to the Variational Configuration Interaction(VCI) which is known not to be extensive for a truncated cluster operator,

$$E_{\text{VCI}} = \frac{\langle \Phi_0 | (1 + \hat{T}^\dagger) \hat{H} (1 + \hat{T}) | \Phi_0 \rangle}{\langle \Phi_0 | (1 + \hat{T}^\dagger) (1 + \hat{T}) | \Phi_0 \rangle} \quad (2.8)$$

Due to the presence of uncanceled unlinked terms, the calculated energies do not scale correctly with the system size.

The CEPA(0) method substitutes the truncation into another form of the VCC energy composed of linked diagram terms below is not exact, which does not agree with Full Configuration Interaction, even when the cluster

operator is complete.

$$E_{\text{VCC}} = \langle \Phi_0 | (e^{\hat{T}})^\dagger \hat{H} e^{\hat{T}} | \Phi_0 \rangle_{\text{Linked}} \quad (2.9)$$

$$E_{\text{CEPA}} = \langle \Phi_0 | (1 + \hat{T}^\dagger) \hat{H} (1 + \hat{T}) | \Phi_0 \rangle_{\text{Linked}} \quad (2.10)$$

The problem could be understood more generally. In the exponential parameterization, the unlinked term in the numerator  $\langle \Phi_0 | (e^{\hat{T}})^\dagger \hat{H} e^{\hat{T}} | \Phi_0 \rangle$  cancels exactly with the denominator  $\langle \Phi_0 | (e^{\hat{T}})^\dagger e^{\hat{T}} | \Phi_0 \rangle$ , while the truncation made the cancellation fails and the unlinked term which is unphysical remains. So the variational Configuration Interaction loses the property of extensivity and the unlinked term remains in the CEPA(0) expression made the approximation not exact.

## 2.4 Linked Pair Functional method[55]

The theoretical method that underpins the approximation in my project is the Linked pair functional(LPF) or LPFD because of the double excitations being the only nature of the theory.

In LPFD, the exponential parameterization is replaced by the closed-form geometric series of cluster amplitudes, these series are tuned so that certain Variational coupled cluster doubles(VCCD) terms are reproduced exactly through all orders.

The energy functional of the theory is like that of CEPA(0) mentioned above,

$$E_{\text{LPF}} = \langle \hat{H} \rangle + 2\langle \hat{H}_2 \hat{T} \rangle + \langle {}_1\hat{T}^\dagger (\hat{H} - \langle \hat{H} \rangle) {}_1\hat{T} \rangle \quad (2.11)$$

where the transformed cluster operator  ${}_q\hat{T}$  is defined as,

$$\begin{aligned} {}_q\hat{T}|\Phi_0\rangle &= \sum_{ij} \sum_{ab} \frac{1}{4} {}_qT_{ab}^{ij} |\Phi_{ij}^{ab}\rangle \\ {}_qT_{ab}^{ij} &= ({}_q\mathbf{U}^{qP_u} \mathbf{T})_{ab}^{ij} = \sum_{kl} \frac{1}{2} ({}_qU^{qP_u})_{kl}^{ij} T_{ab}^{kl} \\ {}_qU_{kl}^{ij} &= \delta_{kl}^{ij} + {}_qS_u \Delta_{kl}^{ij} \\ \Delta_{kl}^{ij} &= \lambda \eta_{kl}^{ij} + \frac{1}{2} (1 - \lambda) (\delta_k^i \eta_l^j - \delta_l^i \eta_k^j - \delta_k^j \eta_l^i + \delta_l^j \eta_k^i) \\ &= \lambda \eta_{kl}^{ij} + \frac{1}{2} (1 - \lambda) (1 - \tau_{ij}) (1 - \tau_{kl}) \delta_k^i \eta_l^j \end{aligned}$$

where  $\tau_{ij}$  permutes  $i$  and  $j$  in the term following it.

In the expression we find the transformed cluster amplitudes are finally defined by the density matrix:

$$\eta_{kl}^{ij} = \langle \Phi_0 | \hat{T}^\dagger c_k c_l c_j^\dagger c_i^\dagger \hat{T} | \Phi_0 \rangle = \sum_{ab} \frac{1}{2} t_{ab}^{ij} t_{kl}^{ab}$$

$$\eta_j^i = \langle \Phi_0 | \hat{T}^\dagger c_j c_i^\dagger \hat{T} | \Phi_0 \rangle = \sum_{ab} \sum_k \frac{1}{2} t_{ab}^{ik} t_{jk}^{ab}$$

The parameter  ${}_q P_u$  and  ${}_q S_u$  are determined uniquely by the requirement of the exactness of the method, here it means the equivalence to Configuration Interaction with double excitations(CID), in the limiting case of two electrons,

$${}_q P_u = -\frac{q}{2}$$

$${}_q S_u = 1$$

Through the series of a power of matrix for  $q=1$  or  $q=2$ ,

$${}_q \mathbf{U}^{P_u} = (\mathbf{1} + {}_q S_u \mathbf{\Delta})^{P_u} = \mathbf{1} + {}_q P_u {}_q S_u \mathbf{\Delta} + \dots$$

LPFD generates VCCD-like terms to infinite order in cluster amplitudes, and the particular VCCD terms captured in the approximation along with their weighting are controlled by the value of parameter  $\lambda$ .

In the approximation of Variational Coupled Cluster Doubles(VCCD) method, the terms of  $O(T^3)$  is the lowest order in which the LPFD differs. The contributing terms are given in the graph[ Table I in reference [57]: Linked  $O(T^4)$  contributions to VCCD, where  $\eta = \frac{1}{4} T_{ab}^{ij} T_{ij}^{ab}$ , where  $e\bar{e}$  and  $h\bar{h}$  label the two spin-orbitals occupied and unoccupied in the reference wavefunction, respectively.],

The VCCD possesses an internal mathematical structure that, in the limiting case of two electrons, results the mutual cancellation of the terms through all orders of cluster amplitudes.

In the terms of  $O(T^3)$ , the following relationship holds:

$$A + D = 0$$

$$B + 2C = 0$$

where A,B,C,D are the indices of the contributing terms.

The  $O(T^3)$  terms  $A+B+C+D$  in the VCCD could thus be approximated with parameter  $\lambda$  by,

$$A + B + C + D = (1 - \lambda)B/2 - \lambda C$$

## 2.5 Orbital optimized Quasi variational Coupled Cluster (OQVCCD) method[48, 57]

The current direct approximation to the Variational Coupled Cluster method(VCC) is the recently proposed Orbital-optimized Quasi-variational Coupled Cluster Doubles (OQVCCD) method. It is recognized that an infinite-order approximation scheme is what is required. In the method, the predicted ground-state energy is defined to be the variational minimum of the following CEPA(0)-like functional:

$$E_{\text{OQVCCD}} = \langle \hat{H} \rangle + 2\langle \hat{H} \hat{T}_2 \rangle + \langle {}_1\hat{T}_2^\dagger (\hat{H} - \langle \hat{H} \rangle) {}_1\hat{T}_2 \rangle \quad (2.12)$$

with respect to both the double amplitudes and the orbitals.

The renormalized cluster operator is defined through,

$${}_q\hat{T}_2|\Phi_0\rangle = \sum_{ab} \sum_{ij} \frac{1}{4} {}_qT_{ab}^{ij} c_b^\dagger c_j c_a^\dagger c_i |\Phi_0\rangle = \sum_{ab} \sum_{ij} \frac{1}{4} {}_qT_{ab}^{ij} |\Phi_{ab}^{ij}\rangle$$

where the renormalized cluster amplitudes are as follows,

$$\begin{aligned} {}_qT_{ab}^{ij} = & 2\left[\sum_c \frac{1}{2}(1 - \tau_{ab})(AU^{qP_u})_a^c T_{cb}^{ij}\right] \\ & + 2\left[\sum_k \frac{1}{2}(1 - \tau_{ij})(BU^{qP_u})_k^i T_{ab}^{kj}\right] \\ & - 1\left[\sum_{kl} \frac{1}{2}(CU^{qP_u})_{kl}^{ij} T_{ab}^{kl}\right] \\ & - 2\left[\sum_k \sum_c \frac{1}{4}(1 - \tau_{ij})(1 - \tau_{ab})(DU^{qP_u})_{ak}^{ic} T_{cb}^{kj}\right] \end{aligned}$$

where the  $\mathbf{U}$  matrices are,

$$\begin{aligned} AU_b^a &= \delta_b^a + {}_a\eta_b^a \\ BU_j^i &= \delta_j^i + {}_b\eta_j^i \\ CU_{kl}^{ij} &= \delta_{kl}^{ij} + {}_c\eta_{kl}^{ij} \\ DU_{aj}^{ib} &= \delta_{aj}^{ib} + {}_d\eta_{aj}^{ib} \end{aligned} \quad (2.13)$$

in which the density matrices are defined as,

$$\begin{aligned}
{}_a\eta_b^a &= \langle \hat{T}^\dagger c_a^\dagger c_b \hat{T} \rangle = \sum_{ij} \sum_c \frac{1}{2} t_{bc}^{ij} t_{ij}^{ac} \\
{}_b\eta_j^i &= \langle \hat{T}^\dagger c_j c_i^\dagger \hat{T} \rangle = \sum_{ab} \sum_k \frac{1}{2} t_{ab}^{ik} t_{jk}^{ab} \\
{}_c\eta_{kl}^{ij} &= \langle \hat{T}^\dagger c_k c_l c_j^\dagger c_i^\dagger \hat{T} \rangle = \sum_{ab} \frac{1}{2} t_{ab}^{ij} t_{kl}^{ab} \\
{}_d\eta_{aj}^{ib} &= \langle \hat{T}^\dagger c_j c_b^\dagger c_a c_i^\dagger \hat{T} \rangle = \sum_k \sum_c t_{ac}^{ik} t_{jk}^{bc}
\end{aligned}$$

### 2.5.1 the calculation on small molecules

The potential energy curve of BH is calculated using different methods with basis set cc-pVQZ. The benchmark curve is the Multi-Reference Configuration Interaction(MRCI). Because multiple configurations are needed to construct the wavefunction of MRCI, the Complete Active Space Self-Consistent Field(CASSCF) is pre-calculated to generate enough excited Slater Determinant for MRCI. The traditional Coupled Cluster based methods: CCSD, BCCD are performed compared with OQVCCD.

As shown in the Figure 2.1, CCSD, BCCD perform similarly with OQVCCD. However, the inclusion of (T) makes CCSD(T) appear unphysical maximum. This is because (T) keeps singular when highest occupied and lowest unoccupied become degenerate. BCCD(T), using transformed orbitals, behaves well together with OQVCCD(T).

Figure 2.2 is the potential energy curve of the bond stretching experiment on HF molecule. The Traditional Coupled Cluster(TCC) based methods: CCSD, BCCD are runned together with the ones including perturbative triples correction (T). The benchmark calculation is MRCI containing multiple Slater Determinants as reference wavefunction. The OQVCCD method is performed together with its triple excitation version OQVCCD(T). The basis set is aug-cc-pVQZ.

This calculation is designed for demonstrating the performance of different electron correlation methods in the system containing such effect. The Traditional Coupled Cluster(TCC) based methods CCSD, BCCD perform similarly with OQVCCD. However, the inclusion of (T) correction makes CCSD(T) generate unphysical maximum, while BCCD(T) and OQVCCD(T) show exactness in the long range bond stretching.

The traditional coupled cluster based methods are performed on the

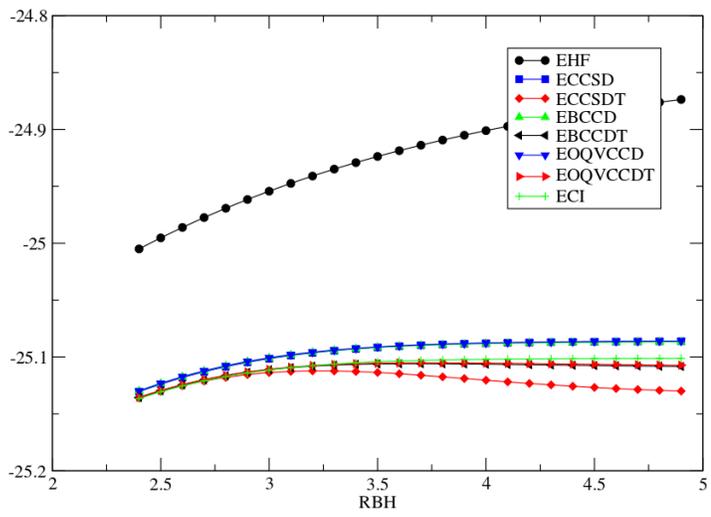


Figure 2.1: the potential energy curve of BH

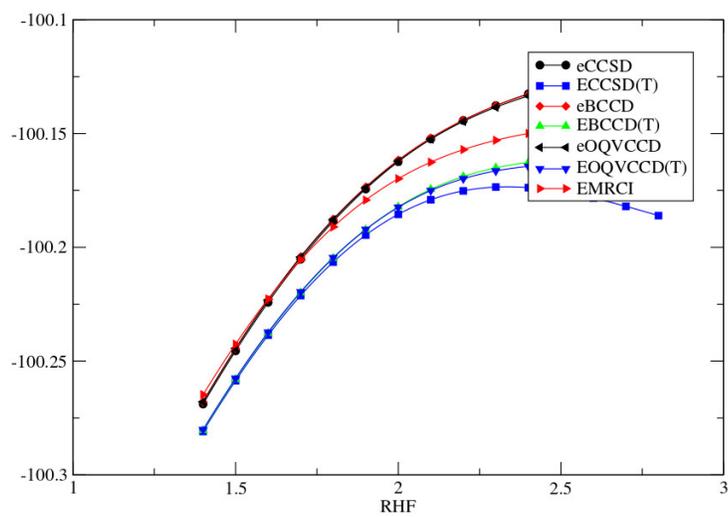


Figure 2.2: the potential energy curve of the bond stretching experiment on HF molecule

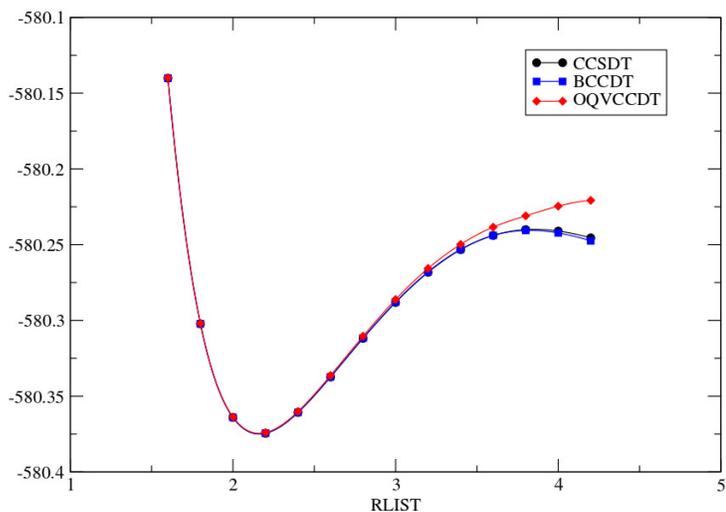


Figure 2.3: the potential energy curve of the bond stretching experiment on  $\text{Si}_2\text{H}_4$  molecule

bond stretching experiment of  $\text{Si}_2\text{H}_4$ . There is no benchmark calculation in this experiment as the Multi-Reference Configuration Interaction(MRCI) is too computational expensive to carry out. The triple correction made the CCSD and BCCD show unphysical maximum at the dissociation area where the correlation effect is strong.

## 2.6 $O(T^4)$ terms correction to Quasi-Variational Coupled Cluster(QVCC) method[48]

The current QVCCD method underestimates the bond length of small molecules at their equilibrium geometry and overestimates their spectroscopic constants[56], this is where the inclusion of  $T^4$  terms expected to improve.

In the Table 2.1 illustrated, the calculations are extrapolated based on small basis set. The empirical results are those coming from experiment, which could be considered as benchmark values. The QOVCCD method overesti-

Table 2.1: Comparison of equilibrium bond lengths and spectroscopic constants for some diatomic molecules. Basis set: cc-pVQZ, with correction energy  $x^{-3}$ -extrapolated using cc-pVTZ and cc-pVQZ[56]

System	Method	$R_e$ / Angstrom	$w_e/cm^{-1}$	$w_e x_e/cm^{-1}$
HF	CCSD	0.913	4203.5	89.1
	OAVCCD	0.913	4209.2	86.8
	OQVCCD	0.913	4210.7	87.2
	Empirical	0.917	4138.3	89.9
F <sub>2</sub>	CCSD	1.389	1020.5	8.5
	OAVCCD	1.386	1034.9	8.2
	OQVCCD	1.386	1030.3	8.6
	Empirical	1.412	916.6	11.2
N <sub>2</sub>	CCSD	1.092	2445.3	12.8
	OAVCCD	1.091	2456.4	12.6
	OQVCCD	1.090	2461.0	12.5
	Empirical	1.098	2358.6	14.3

mates the spectroscopic constant  $w_e$  in those small molecules whereas CCSD performs better.

The lowest-order discrepancy between Quasi-variational Coupled Cluster Doubles(QVCCD) method and Variational Coupled Cluster Doubles (VCCD) method occurs at the terms of  $T^4$  order. Although the term  $\langle \hat{T}_2^\dagger \hat{H} \hat{T}_2^2 \rangle_{\text{Linked}}$  is accounted for exactly in Quasi- method, the term  $(\frac{1}{2!})^2 \langle (\hat{T}_2^\dagger)^2 \hat{H} \hat{T}_2^2 \rangle_{\text{Linked}}$  is not.

It has already been established, however, that the one-electron  $T^4$  order terms, are complete in Quasi- method, and the omitted terms are therefore associated only with the two-electron part of the Hamiltonian(the fluctuation potential in the Moller-Plesset partitioning).

The individual diagram contribution may be grouped according to whether they involve the all-internal orbitals integrals,  $\langle ij||kl \rangle$ , the two-internal-two-external ones integrals,  $\langle ia||jb \rangle$ , or the all-external integrals,  $\langle ab||cd \rangle$ .

The sum of the omitted  $T^4$  order terms involving the set of all-internal integrals  $\langle ij||kl \rangle$  is denoted as  $\alpha$ , the sum of the terms involving the set of two-internal-two-external integrals  $\langle ia||jb \rangle$  as  $\beta$  and that involving the set of all-external integrals  $\langle ab||cd \rangle$  as  $\gamma$ .

Suppose all those terms omitted by the Quasi- method at  $T^4$  order are

added directly to the energy expression, the modified functional is expressed as:

$$E_{\text{QVCCD}} = \langle \hat{H} \rangle + 2\langle \hat{H} {}_2\hat{T}_2 \rangle + \langle {}_1\hat{T}_2^\dagger (\hat{H} - \langle \hat{H} \rangle) {}_1\hat{T}_2 \rangle + \alpha + \beta + \gamma \quad (2.14)$$

which is still minimized with respect to the double excitation amplitudes  $t_{ab}^{ij}$  and the orbitals.

The  $\alpha$ ,  $\beta$ ,  $\gamma$  terms consisting only of linked diagram vanish independently at the limitation of 2 electrons or 2 holes. Therefore the inclusion of these terms keeps the methodological property of current QVCCD method. However, the computational complexity of the  $\gamma$  term scales as  $O(v^6)$  which exceed that of CCSD(T) like methods.

$\alpha$  term is what my project should explore in order to approximate the Variational Coupled Cluster Doubles(VCCD) method in  $T^4$  order, the detail of each term is listed in the Table 2.2 below,

$$\alpha = \frac{1}{2}(B_1 + B_2 + D_1 + D_2) + M_1 + M_2 + M_3$$

$\beta$  term is also relatively high in computational cost at least  $O(o^3v^3)$ . The expected energy functional contains only  $\alpha$  term of  $O(o^4v^2)$  computational complexity at the moment. Because of the erroneous asymptotics of M1, it is replaced by M3 as they are same at the limitation of 2-electrons or 2-holes.

As the introduction of the QVCCD method above, the explicit mathematical formulae of those discrepant terms in  $\alpha$  and their partial derivative with respect to the cluster amplitudes, namely gradient, are what needs to be derived in my project in order to improve the current method.

Table 2.2: Linked  $\mathcal{O}(T^4)$  contributions to VCCD involving the all-internal 2-electron integrals,  $\{\langle ij||kl\rangle\}$ , along with fraction of the term captured by QVCCD[48].

	Diagram	$(\frac{1}{2!})^2 \langle (\hat{T}_2^\dagger)^2 \hat{\mathcal{H}} \hat{T}_2 \rangle_L$ Term	2 Electrons	2 Holes	QVCCD Fraction
A		$-\frac{1}{4} \langle ij  kl\rangle T_{ab}^{kl} T_{ij}^{ac} a_l^b$	$-(e\bar{e}  e\bar{e}) a_l^a a_l^b$	$-\frac{1}{2} \langle ij  kl\rangle T_{hh}^{kl} T_{ij}^{hh} \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	1
B1		$-\frac{1}{2} \langle ij  kl\rangle a_{im}^{kl} a_j^m$	$-2 \langle e\bar{e}  e\bar{e} \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	$-\frac{1}{2} \langle ij  kl\rangle a_{im}^{kl} a_j^m$	$\frac{1}{2}$
B2		$-\frac{1}{2} \langle ij  kl\rangle a_{ij}^{km} a_m^l$	$-2 \langle e\bar{e}  e\bar{e} \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	$-\frac{1}{2} \langle ij  kl\rangle a_{ij}^{km} a_m^l$	$\frac{1}{2}$
C		$+\frac{1}{8} \langle ij  kl\rangle a_{ij}^{mn} a_{mn}^{kl}$	$+\langle e\bar{e}  e\bar{e} \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	$+\frac{1}{4} \langle ij  kl\rangle T_{hh}^{kl} T_{ij}^{hh} \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	1
D1		$+\frac{1}{4} \langle ij  kl\rangle T_{ab}^{kl} T_{mi}^{ca} a_j^{bm}$	$+\langle e\bar{e}  e\bar{e} \rangle a_l^a a_l^b$	$+\frac{1}{2} \langle ij  kl\rangle a_{im}^{kl} a_j^m$	$\frac{1}{2}$
D2		$+\frac{1}{4} \langle ij  kl\rangle T_{ij}^{ab} T_{ca}^{mk} a_{lm}^{lc}$	$+\langle e\bar{e}  e\bar{e} \rangle a_l^a a_l^b$	$+\frac{1}{2} \langle ij  kl\rangle a_{ij}^{km} a_m^l$	$\frac{1}{2}$
M1		$+\frac{1}{2} \langle ij  kl\rangle a_i^k a_j^l$	$+\langle e\bar{e}  e\bar{e} \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	$+\frac{1}{2} \langle ij  kl\rangle a_i^k a_j^l$	0
M2		$+\frac{1}{2} \langle ij  kl\rangle a_{aj}^{kb} a_{ib}^{al}$	$-\langle e\bar{e}  e\bar{e} \rangle a_l^a a_l^b$	$-\langle ij  kl\rangle a_i^k a_j^l$	0
M3		$+\frac{1}{2} \langle ij  kl\rangle a_{im}^{nl} a_{nj}^{km}$	$+\langle e\bar{e}  e\bar{e} \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	$+\frac{1}{2} \langle ij  kl\rangle a_i^k a_j^l$	0

## Chapter 3

# The Formulae of $O(T^4)$ Terms to Quasi-Variational Coupled Cluster(QVCC) Method and its Software Implementation

### 3.0.1 the definition of closed shell double excitations operator[50]

The double excitations operator  $\hat{T}_2$ , in closed-shell form, is defined as:

$$\hat{T}_2 = \frac{1}{2} \sum_{ia} \sum_{jb} T_{ab}^{ij} \hat{E}_{ai} \hat{E}_{bj}$$

in which the  $\hat{E}_{ai}$ ,  $\hat{E}_{bj}$  are the usual spin-coupled one-particle excitation operators:

$$\hat{E}_{ai} = \tilde{c}_a^\dagger \tilde{c}_i + \bar{c}_a^\dagger \bar{c}_i$$

in which the tilde means the  $\alpha$  spin and the overbar means the  $\beta$  spin. Generally, in the closed-shell expression, a,b,c,d refer to the virtual (external) orbitals in the reference wavefunction, i,j,k,l refer to the occupied (internal) ones, which are all doubly occupied spatial orbitals in the reference wavefunction.

When the double excitations operator  $\hat{T}_2$  acts on the reference ground-state configuration  $|\Phi_0\rangle$ , it will generate combinations of the double excitations

configurations  $|\Phi_{ij}^{ab}\rangle$ :

$$\hat{T}_2|\Phi_0\rangle = \frac{1}{2} \sum_{ia} \sum_{jb} T_{ab}^{ij} |\Phi_{ij}^{ab}\rangle$$

The symmetry relation of the double excitations cluster amplitudes  $T_{ab}^{ij} = T_{ba}^{ji}$  can be justified as follows: Because the range of sum is over the full range of ia pair and jb,

$$\frac{1}{2} \sum_{ia} \sum_{jb} T_{ab}^{ij} \hat{E}_{ai} \hat{E}_{bj} |\Phi_0\rangle = \frac{1}{2} \sum_{jb} \sum_{ia} T_{ba}^{ji} \hat{E}_{bj} \hat{E}_{ai} |\Phi_0\rangle$$

Relying on the definition of the operator and its linear property; we can expand the double spin-coupled excitations operator as,

$$\hat{E}_{ai} \hat{E}_{bj} \Phi_0 = \hat{E}_{ai} (\Phi_j^{\bar{b}} + \Phi_j^{\bar{b}}) = \hat{E}_{ai} \Phi_j^{\bar{b}} + \hat{E}_{ai} \Phi_j^{\bar{b}} = \Phi_{ij}^{\bar{a}\bar{b}} + \Phi_{ij}^{\bar{a}\bar{b}} + \Phi_{ij}^{\bar{a}\bar{b}} + \Phi_{ij}^{\bar{a}\bar{b}}$$

and  $\hat{E}_{bj} \hat{E}_{ai} \Phi_0$  can be expanded in the same way,

$$\hat{E}_{bj} \hat{E}_{ai} \Phi_0 = \Phi_{ij}^{\bar{a}\bar{b}} + \Phi_{ij}^{\bar{a}\bar{b}} + \Phi_{ij}^{\bar{a}\bar{b}} + \Phi_{ij}^{\bar{a}\bar{b}}$$

which equals to  $\hat{E}_{ai} \hat{E}_{bj} \Phi_0$ . In fact, this process can be expressed in a more advanced way as the commutator equals to zero:  $[\hat{E}_{ai}, \hat{E}_{bj}] = 0$ .

Because the order of the indices can be altered in the sum, the definition above can therefore be rewritten as:

$$\frac{1}{2} \sum_{ia} \sum_{jb} T_{ab}^{ij} \hat{E}_{ai} \hat{E}_{bj} |\Phi_0\rangle = \frac{1}{2} \sum_{ia} \sum_{jb} T_{ba}^{ji} \hat{E}_{bj} \hat{E}_{ai} |\Phi_0\rangle$$

Therefore,  $T_{ba}^{ji} = T_{ab}^{ij}$ .

### 3.1 Spin-adaption

In most equations, the orbitals are one-electron functions[26], which are product of spin functions  $\alpha$  or  $\beta$ , they are called spin-orbital. The working equations software implemented are only composed of spatial part of spin-orbital, which is doubly occupied.

Therefore, the original expressions need to be transformed into the spatial orbital form in order to have them implemented into Molpro software. This process is called spin-adaption or spin-free formulation.

If spin-orbital I is of  $\alpha$  spin,  $I = \tilde{i}$  where  $i$  is the spatial index of orbital I. If I is of  $\beta$  spin,  $I = \bar{i}$ . This is the fundamental mathematical principle that underpins the transformation of the expression from spin-orbital form to spatial-orbital form.

### 3.1.1 the relationship between spin and spatial forms of cluster amplitudes

The relationship between the cluster amplitudes of spin-orbital and spatial-orbital forms in their double excitations operators is derived as follows.

The double excitations operator  $\hat{T}_2$  is

$$\hat{T}_2 = \frac{1}{4} \sum_{IJAB}^{\text{Spin}} t_{AB}^{IJ} c_A^\dagger c_B^\dagger c_J c_I = \sum_{A>B}^{\text{Vir}} \sum_{I>J}^{\text{Occ}} t_{AB}^{IJ} c_A^\dagger c_B^\dagger c_J c_I$$

in spin-orbital form.

It could be written as

$$\hat{T}_2 = \frac{1}{2} \sum_{ai} \sum_{bj} T_{ab}^{ij} (\tilde{c}_a^\dagger \tilde{c}_i + \bar{c}_a^\dagger \bar{c}_i) (\tilde{c}_b^\dagger \tilde{c}_j + \bar{c}_b^\dagger \bar{c}_j)$$

in the open-shell form.

The cluster operator  $\hat{T}_2$  can be expanded as follows in the spin-orbital form:

$$\begin{aligned} \hat{T}_2 = \sum_{a>b}^{\text{Vir}} \sum_{i>j}^{\text{Occ}} & (t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \bar{c}_a^\dagger \bar{c}_b^\dagger \bar{c}_j \bar{c}_i + t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \bar{c}_a^\dagger \bar{c}_b^\dagger \tilde{c}_j \bar{c}_i + t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \tilde{c}_a^\dagger \bar{c}_b^\dagger \tilde{c}_j \bar{c}_i + t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \tilde{c}_a^\dagger \tilde{c}_b^\dagger \tilde{c}_j \bar{c}_i \\ & + t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \tilde{c}_a^\dagger \tilde{c}_b^\dagger \tilde{c}_j \bar{c}_i + t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \tilde{c}_a^\dagger \tilde{c}_b^\dagger \bar{c}_j \tilde{c}_i) \end{aligned}$$

in the spatial-orbital form, it can be expanded as:

$$\hat{T}_2 = \frac{1}{2} \sum_{ij} \sum_{ab} (T_{ab}^{ij} \tilde{c}_a^\dagger \tilde{c}_i \tilde{c}_b^\dagger \tilde{c}_j + T_{ab}^{ij} \bar{c}_a^\dagger \bar{c}_i \tilde{c}_b^\dagger \tilde{c}_j + T_{ab}^{ij} \tilde{c}_a^\dagger \tilde{c}_i \bar{c}_b^\dagger \bar{c}_j + T_{ab}^{ij} \bar{c}_a^\dagger \bar{c}_i \bar{c}_b^\dagger \bar{c}_j)$$

By re-ordering the creation and annihilation operators, splitting the full range sum in the spatial expansion above, then comparing with the relevant terms in the spin form, we can get the spin-adaption relationship of cluster amplitudes between the spin-orbital and spatial-orbital form:

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = \frac{1}{2} (T_{ab}^{ij} - T_{ab}^{ji} - T_{ba}^{ij} + T_{ba}^{ji}) \quad (3.1)$$

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \quad (3.2)$$

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = \frac{1}{2} (T_{ab}^{ij} + T_{ba}^{ji}) \quad (3.3)$$

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \quad (3.4)$$

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = \frac{1}{2} (-T_{ab}^{ji} - T_{ba}^{ij}) \quad (3.5)$$

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \quad (3.6)$$

By applying the symmetry relation in the double excitations amplitudes derived in the last subsection, we can obtain the concise expressions:

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = T_{ab}^{ij} - T_{ba}^{ij} \quad (3.7)$$

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = T_{ab}^{ij} \quad (3.8)$$

$$t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = -T_{ba}^{ij} \quad (3.9)$$

### 3.1.2 the spin-adaption relation of two-electron integrals

The two-electron integral, in two-bar notation  $\langle IJ||KL \rangle = \langle IJ|KL \rangle - \langle IJ|LK \rangle$ , is an essential part of the energy terms, which is originally coming from the Hamiltonian operator. The angle bracket notation is called ‘physical notation’:  $\langle IJ|KL \rangle = \int \phi_I(i)\phi_J(j)|_{\frac{1}{\vec{r}_i-\vec{r}_j}}|\phi_K(i)\phi_L(j)d\vec{r}_i d\vec{r}_j$ . It can also be expressed in Chemical notation  $(IK|JL)$  in which the electron indices are same on both sides of the bar:

$$(IK|JL) = \int \phi_I(i)\phi_K(i)|_{\frac{1}{\vec{r}_i-\vec{r}_j}}|\phi_J(j)\phi_L(j)d\vec{r}_i d\vec{r}_j$$

Considering different spin cases of two-electron integral  $\langle IJ||KL \rangle$ , we get the spin-adaption relation as,

$$\langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle - \langle \bar{i}\bar{j}|\bar{l}\bar{k} \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle \quad (3.10)$$

Or, in chemical notation as:  $(ik|jl) - (il|jk)$

$$\langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle - \langle \bar{i}\bar{j}|\bar{l}\bar{k} \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle \quad (3.11)$$

$$\langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle - \langle \bar{i}\bar{j}|\bar{l}\bar{k} \rangle = \langle ij|kl \rangle \quad (3.12)$$

Or, in chemical notation as:  $(ik|jl)$

$$\langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle - \langle \bar{i}\bar{j}|\bar{l}\bar{k} \rangle = \langle ij|kl \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle \quad (3.13)$$

$$\langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle - \langle \bar{i}\bar{j}|\bar{l}\bar{k} \rangle = -\langle ij|lk \rangle \quad (3.14)$$

Or, in the chemical notation as:  $-(il|jk)$

$$\langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle - \langle \bar{i}\bar{j}|\bar{l}\bar{k} \rangle = -\langle ij|lk \rangle = \langle \bar{i}\bar{j}|\bar{k}\bar{l} \rangle \quad (3.15)$$

### 3.1.3 the spin-adaption of density matrices

The energy terms are composed of density matrices, which are made of cluster amplitudes.

The expression of the  $\mathcal{M}$  density matrix in M2 is,

$$\mathcal{M}_{AJ}^{IB} = \langle \hat{T}^\dagger c_J c_B^\dagger c_A c_I^\dagger \hat{T} \rangle = t_{AC}^{IK} t_{JK}^{BC}$$

the spin-adaption of which is,

$$\begin{aligned} d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} &= t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} + t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} \\ &= \sum_k \sum_c (T_{ac}^{ik} - T_{ca}^{ik}) (T_{bc}^{jk} - T_{cb}^{jk}) + \sum_k \sum_c T_{ac}^{ik} T_{bc}^{jk} \end{aligned} \quad (3.16)$$

$$\begin{aligned} d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} &= t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} + t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} \\ &= \sum_k \sum_c T_{ac}^{ik} T_{bc}^{jk} + \sum_k \sum_c (T_{ac}^{ik} - T_{ca}^{ik}) (T_{bc}^{jk} - T_{cb}^{jk}) \end{aligned} \quad (3.17)$$

$$d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} = d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} \quad (3.18)$$

$$\begin{aligned} d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} &= t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} + t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} \\ &= \sum_k \sum_c (T_{ac}^{ik} - T_{ca}^{ik}) T_{bc}^{jk} + \sum_k \sum_c T_{ac}^{ik} (T_{bc}^{jk} - T_{cb}^{jk}) \end{aligned} \quad (3.19)$$

$$\begin{aligned} d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} &= t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} + t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} \\ &= \sum_k \sum_c T_{ac}^{ik} (T_{bc}^{jk} - T_{cb}^{jk}) + \sum_k \sum_c (T_{ac}^{ik} - T_{ca}^{ik}) T_{bc}^{jk} \end{aligned} \quad (3.20)$$

$$d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} = d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} \quad (3.21)$$

$$\begin{aligned} d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} &= t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} \\ &= \sum_k \sum_c (-T_{ca}^{ik}) (-T_{cb}^{jk}) \\ &= \sum_k \sum_c T_{ca}^{ik} T_{cb}^{jk} \end{aligned} \quad (3.22)$$

$$\begin{aligned} d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} &= t_{\bar{a}\bar{c}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{b}\bar{c}} \\ &= \sum_k \sum_c T_{ca}^{ik} T_{cb}^{jk} \end{aligned} \quad (3.23)$$

$$d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} = d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}} \quad (3.24)$$

The  $\eta$  density matrix in M3 is,

$$\eta_{KL}^{IJ} = \langle \hat{T}^\dagger c_K c_L c_J^\dagger c_I^\dagger \hat{T} \rangle = \sum_A \sum_B \frac{1}{2} t_{AB}^{IJ} t_{KL}^{AB}$$

The spin-adaption of  $\mathcal{H}$  is,

$$\begin{aligned}\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} &= \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} \\ &= \sum_a \sum_b \frac{1}{2} (T_{ab}^{ij} - T_{ba}^{ij})(T_{ab}^{kl} - T_{ba}^{kl})\end{aligned}\quad (3.25)$$

$$\begin{aligned}\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} &= \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} + \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} \\ &= \sum_a \sum_b T_{ab}^{ij} T_{ab}^{kl}\end{aligned}\quad (3.26)$$

$$\begin{aligned}\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} &= \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} + \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} \\ &= -\sum_a \sum_b T_{ab}^{ij} T_{ba}^{kl}\end{aligned}\quad (3.27)$$

$$\begin{aligned}\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} &= \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} + \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} \\ &= \mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}\end{aligned}\quad (3.28)$$

$$\begin{aligned}\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} &= \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} + \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} \\ &= \mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}\end{aligned}\quad (3.29)$$

$$\begin{aligned}\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} &= \sum_a \sum_b \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} t_{\bar{k}\bar{l}}^{\bar{a}\bar{b}} \\ &= \mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}\end{aligned}\quad (3.30)$$

The relationship between the density matrices is used so as to express  $\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}$  in  $\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}$ :

$$\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} = \mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} = -\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}} = -\mathcal{H}_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}\quad (3.31)$$

### 3.2 the energy functional of $T^4$ terms

The energy functional of QVCCD method is

$$\begin{aligned}E_{\text{QVCCD}} &= \langle \hat{H} \rangle + 2\langle \hat{H} \hat{T}_2 \rangle + \langle {}_1\hat{T}_2^\dagger (\hat{H} - \langle \hat{H} \rangle) {}_1\hat{T}_2 \rangle \\ &\quad + \frac{1}{2}(B_1 + B_2 + D_1 + D_2) + M_2 + 2M_3\end{aligned}\quad (3.32)$$

with the additional M2, M3, B1, B2, D1, D2  $T^4$  terms.

Their explicit energy expressions are explored so as to be added to the original QVCCD energy functional.

### 3.2.1 The energy expression of M2 term

The spin-orbital expression of M2 is,

$$+\frac{1}{2}\langle IJ||KL\rangle d\eta_{AJ}^{KB} d\eta_{IB}^{AL}$$

Considering different spin possibility of the spin-orbital expression of M2, we can split it into ten possibilities,

$$M2_i, \frac{1}{2}\langle \tilde{i}\tilde{j}||\tilde{k}\tilde{l}\rangle d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} = M2_x, \frac{1}{2}\langle \bar{i}\bar{j}||\bar{k}\bar{l}\rangle d\eta_{\bar{a}\bar{j}}^{\bar{k}\bar{b}} d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}} \quad (3.33)$$

$$M2_v, \frac{1}{2}\langle \tilde{i}\tilde{j}||\tilde{k}\bar{l}\rangle d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\bar{b}} d\eta_{\tilde{i}\bar{b}}^{\tilde{a}\bar{l}} = M2_{vi}, \frac{1}{2}\langle \bar{i}\bar{j}||\bar{k}\tilde{l}\rangle d\eta_{\bar{a}\bar{j}}^{\bar{k}\tilde{b}} d\eta_{\bar{i}\tilde{b}}^{\bar{a}\tilde{l}} \quad (3.34)$$

$$M2_{iii}, \frac{1}{2}\langle \tilde{i}\tilde{j}||\bar{k}\bar{l}\rangle d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\bar{b}} d\eta_{\tilde{i}\bar{b}}^{\tilde{a}\bar{l}} = M2_{viii}, \frac{1}{2}\langle \bar{i}\bar{j}||\tilde{k}\tilde{l}\rangle d\eta_{\bar{a}\bar{j}}^{\bar{k}\tilde{b}} d\eta_{\bar{i}\tilde{b}}^{\bar{a}\tilde{l}} \quad (3.35)$$

$$M2_{ii}, \frac{1}{2}\langle \tilde{i}\bar{j}||\tilde{k}\bar{l}\rangle d\eta_{\tilde{a}\bar{j}}^{\tilde{k}\bar{b}} d\eta_{\tilde{i}\bar{b}}^{\tilde{a}\bar{l}} = M2_{ix}, \frac{1}{2}\langle \tilde{i}\bar{j}||\bar{k}\tilde{l}\rangle d\eta_{\tilde{a}\bar{j}}^{\tilde{k}\tilde{b}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \quad (3.36)$$

$$M2_{iv}, \frac{1}{2}\langle \bar{i}\tilde{j}||\bar{k}\tilde{l}\rangle d\eta_{\bar{a}\tilde{j}}^{\bar{k}\tilde{b}} d\eta_{\bar{i}\tilde{b}}^{\bar{a}\tilde{l}} = M2_{vii}, \frac{1}{2}\langle \tilde{i}\tilde{j}||\tilde{k}\tilde{l}\rangle d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \quad (3.37)$$

The energy expression of M2 in spatial-orbital form, which is the sum of all spin possibilities, is:

$$\begin{aligned} & \sum_{ijkl} ((ik|jl) - (il|jk)) \sum_{ab} (d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} + d\eta_{\bar{a}\bar{j}}^{\bar{k}\bar{b}} d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}}) \\ & + \sum_{ijkl} -(il|jk) \sum_{ab} (d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\bar{b}} d\eta_{\tilde{i}\bar{b}}^{\tilde{a}\bar{l}} + d\eta_{\bar{a}\bar{j}}^{\bar{k}\tilde{b}} d\eta_{\bar{i}\tilde{b}}^{\bar{a}\tilde{l}}) \\ & + \sum_{ijkl} (ik|jl) \sum_{ab} d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \end{aligned} \quad (3.38)$$

### 3.2.2 The energy expression of M3 term

The spin-orbital expression of M3 term is,

$$\sum_{IJKL} +\frac{1}{2}\langle IJ||KL\rangle \sum_{MN} c\eta_{IM}^{NL} c\eta_{NJ}^{KM}$$

The M3 term could be splitted into ten spin possibilities,

For  $I, L \in \alpha, M, N \in \alpha, K, J \in \alpha$ , the term denoted as  $M3_i$  is,

$$\sum_{ijkl} +\frac{1}{2}\langle \tilde{i}\tilde{j}||\tilde{k}\tilde{l}\rangle \sum_{m,n} c\eta_{\tilde{i}\tilde{m}}^{\tilde{n}\tilde{l}} c\eta_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{m}} \quad (3.39)$$

For  $I, L \in \alpha, M, N \in \alpha, K, J \in \beta$ , the term denoted as  $M\mathfrak{Z}_{ii}$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{m,n} \mathcal{A}_{\tilde{m}\tilde{n}}^{\tilde{n}\tilde{l}} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{m}} \quad (3.40)$$

For  $I, L \in \alpha, M, N \in \beta, K, J \in \alpha$ , the term denoted as  $M\mathfrak{Z}_{iii}$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{m,n} \mathcal{A}_{\tilde{m}\tilde{n}}^{\tilde{n}\tilde{l}} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{m}} \quad (3.41)$$

For  $I, L \in \alpha, M, N \in \beta, K, J \in \beta$ , the term denoted as  $M\mathfrak{Z}_{iv}$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{m,n} \mathcal{A}_{\tilde{m}\tilde{n}}^{\tilde{n}\tilde{l}} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{m}} \quad (3.42)$$

For  $I \in \alpha, L \in \beta, M \in \beta, N \in \alpha, K \in \alpha, J \in \beta$ ,  
the term denoted as  $M\mathfrak{Z}_v$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{m,n} \mathcal{A}_{\tilde{m}\tilde{n}}^{\tilde{n}\tilde{l}} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{m}} \quad (3.43)$$

For  $I \in \beta, L \in \alpha, M \in \alpha, N \in \beta, K \in \beta, J \in \alpha$ ,  
the term denoted as  $M\mathfrak{Z}_{vi}$  which equals to  $M\mathfrak{Z}_v$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{m,n} \mathcal{A}_{\tilde{m}\tilde{n}}^{\tilde{n}\tilde{l}} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{m}} \quad (3.44)$$

$$M\mathfrak{Z}_{vi} = M\mathfrak{Z}_v \quad (3.45)$$

For  $I, L \in \beta, M, N \in \alpha, K, J \in \alpha$ ,  
the term denoted as  $M\mathfrak{Z}_{vii}$  which equals to  $M\mathfrak{Z}_{iv}$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{m,n} \mathcal{A}_{\tilde{m}\tilde{n}}^{\tilde{n}\tilde{l}} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{m}} \quad (3.46)$$

$$M\mathfrak{Z}_{vii} = M\mathfrak{Z}_{iv} \quad (3.47)$$

For  $I, L \in \beta, M, N \in \alpha, K, J \in \beta$ , the term denoted as  $M\mathfrak{Z}_{iix}$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{m,n} \mathcal{A}_{\tilde{m}\tilde{n}}^{\tilde{n}\tilde{l}} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{m}} \quad (3.48)$$

$$M\mathfrak{Z}_{iix} = M\mathfrak{Z}_{iii} \quad (3.49)$$

For  $I, L \in \beta$ ,  $M, N \in \beta$ ,  $K, J \in \alpha$ , the term denoted as  $M3_{ix}$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \bar{i}\bar{j} | \bar{k}\bar{l} \rangle \sum_{m,n} \mathcal{A}_{i\bar{m}}^{\bar{n}\bar{l}} \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \quad (3.50)$$

$$M3_{ix} = M3_{ii} \quad (3.51)$$

For  $I, L \in \beta$ ,  $M, N \in \beta$ ,  $K, J \in \beta$ , the term denoted as  $M3_x$  is,

$$\sum_{ijkl} + \frac{1}{2} \langle \bar{i}\bar{j} | \bar{k}\bar{l} \rangle \sum_{m,n} \mathcal{A}_{i\bar{m}}^{\bar{n}\bar{l}} \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \quad (3.52)$$

$$M3_x = M3_i \quad (3.53)$$

Therefore,

$$\sum_{IJKL} + \frac{1}{2} \langle IJ | KL \rangle \sum_{MN} \mathcal{A}_{IM}^{NL} \mathcal{A}_{NJ}^{KM}$$

could be written abbreviatively as:

$$\begin{aligned} & M3_i + M3_{ii} + M3_{iii} + M3_{iv} + M3_v \\ & + M3_{vi} + M3_{vii} + M3_{iix} + M3_{ix} + M3_x \\ & = 2(M3_i + M3_{ii} + M3_{iii} + M3_{iv} + M3_v) \end{aligned} \quad (3.54)$$

The terms with same two-bar notation can be combined together so that the M3 term becomes:

$$\begin{aligned} & 2(M3_i + M3_{iii}) + 2M3_v + 2(M3_{ii} + M3_{iv}) \\ & = \sum_{ijkl} \sum_{m,n} (\langle ij | kl \rangle - \langle ij | lk \rangle) (\mathcal{A}_{i\bar{m}}^{\bar{n}\bar{l}} \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} + \mathcal{A}_{i\bar{m}}^{\bar{n}\bar{l}} \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}}) \\ & \quad + \sum_{ijkl} \sum_{m,n} \langle ij | kl \rangle \mathcal{A}_{i\bar{m}}^{\bar{n}\bar{l}} \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \\ & \quad + \sum_{ijkl} \sum_{m,n} -\langle ij | lk \rangle (\mathcal{A}_{i\bar{m}}^{\bar{n}\bar{l}} \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} + \mathcal{A}_{i\bar{m}}^{\bar{n}\bar{l}} \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}}) \end{aligned} \quad (3.55)$$

### 3.3 The partial derivative of the energy functional

#### 3.3.1 the partial derivative of the density matrices

Since the energy expression is composed of density matrices, in order to explore the partial derivative of the energy functional, that of the density matrices should be explored first.

In order to explore the residual of M2, we must know the partial derivative of its component  $d\eta$  with respect to the cluster amplitudes  $T_{ef}^{mn}$ ,

$$\begin{aligned}
\frac{\partial d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}}}{\partial T_{ef}^{mn}} &= \frac{\partial((T_{ac}^{ik}-T_{ca}^{ik})(T_{bc}^{jk}-T_{cb}^{jk})+T_{ac}^{ik}T_{bc}^{jk})}{\partial T_{ef}^{mn}} \\
&= 2 \sum_k \sum_c (\delta_{ae}\delta_{cf}\delta_{im}\delta_{kn} T_{bc}^{jk} + T_{ac}^{ik} \delta_{be}\delta_{cf}\delta_{jm}\delta_{kn}) \\
&\quad - \sum_k \sum_c (\delta_{ae}\delta_{cf}\delta_{im}\delta_{kn} T_{cb}^{jk} + T_{ac}^{ik} \delta_{ce}\delta_{bf}\delta_{jm}\delta_{kn}) \\
&\quad - \sum_k \sum_c (\delta_{ce}\delta_{af}\delta_{im}\delta_{kn} T_{bc}^{jk} + T_{ca}^{ik} \delta_{be}\delta_{cf}\delta_{jm}\delta_{kn}) \\
&\quad + \sum_k \sum_c (\delta_{ce}\delta_{af}\delta_{im}\delta_{kn} T_{cb}^{jk} + T_{ca}^{ik} \delta_{ce}\delta_{bf}\delta_{jm}\delta_{kn}) \\
&= 2(\delta_{ae}\delta_{im}T_{bf}^{jn} + T_{af}^{in}\delta_{be}\delta_{jm}) \\
&\quad - (\delta_{ae}\delta_{im}T_{fb}^{jn} + T_{ae}^{in}\delta_{bf}\delta_{jm}) \\
&\quad - (\delta_{af}\delta_{im}T_{be}^{jn} + T_{fa}^{in}\delta_{be}\delta_{jm}) \\
&\quad + (\delta_{af}\delta_{im}T_{eb}^{jn} + T_{ea}^{in}\delta_{bf}\delta_{jm}) \tag{3.56}
\end{aligned}$$

$$\frac{\partial d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}}}{\partial T_{ef}^{mn}} = \frac{\partial d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}}}{\partial T_{ef}^{mn}} \tag{3.57}$$

$$\begin{aligned}
\frac{\partial d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}}}{\partial T_{ef}^{mn}} &= 2 \sum_k \sum_c (\delta_{ae}\delta_{cf}\delta_{im}\delta_{kn} T_{bc}^{jk} + T_{ac}^{ik} \delta_{be}\delta_{cf}\delta_{jm}\delta_{kn}) \\
&\quad - \sum_k \sum_c (\delta_{ae}\delta_{cf}\delta_{im}\delta_{kn} T_{cb}^{jk} + T_{ac}^{ik} \delta_{ce}\delta_{bf}\delta_{jm}\delta_{kn}) \\
&\quad - \sum_k \sum_c (\delta_{ce}\delta_{af}\delta_{im}\delta_{kn} T_{bc}^{jk} + T_{ca}^{ik} \delta_{be}\delta_{cf}\delta_{jm}\delta_{kn}) \\
&= 2(\delta_{ae}\delta_{im}T_{bf}^{jn} + T_{af}^{in}\delta_{be}\delta_{jm}) \\
&\quad - (\delta_{ae}\delta_{im}T_{fb}^{jn} + T_{ae}^{in}\delta_{bf}\delta_{jm}) \\
&\quad - (\delta_{af}\delta_{im}T_{be}^{jn} + T_{fa}^{in}\delta_{be}\delta_{jm}) \tag{3.58}
\end{aligned}$$

$$\frac{\partial d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}}}{\partial T_{ef}^{mn}} = \frac{\partial d\eta_{\bar{a}\bar{j}}^{\bar{i}\bar{b}}}{\partial T_{ef}^{mn}} \tag{3.59}$$

$$\begin{aligned}
\frac{\partial d\eta_{ef}^{\bar{a}\bar{j}}}{\partial T_{ef}^{mn}} &= \frac{\partial(T_{ca}^{ik}T_{cb}^{jk})}{\partial T_{ef}^{mn}} \\
&= \sum_k \sum_c (\delta_{im}\delta_{kn}\delta_{ce}\delta_{af}T_{cb}^{jk} + T_{ca}^{ik}\delta_{jm}\delta_{kn}\delta_{ce}\delta_{bf}) \\
&= \delta_{im}\delta_{af}T_{eb}^{jn} + T_{ea}^{in}\delta_{jm}\delta_{bf}
\end{aligned} \tag{3.60}$$

$$\frac{\partial d\eta_{ef}^{\bar{a}\bar{j}}}{\partial T_{ef}^{mn}} = \frac{\partial d\eta_{\bar{a}\bar{j}}^{\bar{b}}}{\partial T_{ef}^{mn}} \tag{3.61}$$

### 3.3.2 the partial derivative of the energy expression

The partial derivative of the energy expression is used for constructing residual vector  $\vec{V}$ , which updates the cluster amplitudes in each iteration based on first order perturbation theory[50]:

$$T_{ab}^{ij} = -\frac{V_{ab}^{ij}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \tag{3.62}$$

where  $\epsilon$  is the eigenvalue of Fock operator.

The partial derivative of the energy expression of M2 with respect to  $T_{ef}^{mn}$  is,

$$\begin{aligned}
&\sum_{ijkl} (\langle ij|kl\rangle - \langle ij|lk\rangle) \sum_{ab} \left( \frac{\partial d\eta_{ef}^{\bar{k}\bar{b}}}{\partial T_{ef}^{mn}} d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}} + d\eta_{\bar{a}\bar{j}}^{\bar{k}\bar{b}} \frac{\partial d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}}}{\partial T_{ef}^{mn}} \right. \\
&\quad \left. + \frac{\partial d\eta_{ef}^{\bar{k}\bar{b}}}{\partial T_{ef}^{mn}} d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}} + d\eta_{\bar{a}\bar{j}}^{\bar{k}\bar{b}} \frac{\partial d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}}}{\partial T_{ef}^{mn}} \right) \\
&- \sum_{ijkl} \langle ij|lk\rangle \sum_{ab} \left( \frac{\partial d\eta_{ef}^{\bar{k}\bar{b}}}{\partial T_{ef}^{mn}} d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}} + d\eta_{\bar{a}\bar{j}}^{\bar{k}\bar{b}} \frac{\partial d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}}}{\partial T_{ef}^{mn}} \right. \\
&\quad \left. + \frac{\partial d\eta_{ef}^{\bar{k}\bar{b}}}{\partial T_{ef}^{mn}} d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}} + d\eta_{\bar{a}\bar{j}}^{\bar{k}\bar{b}} \frac{\partial d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}}}{\partial T_{ef}^{mn}} \right) \\
&+ \sum_{ijkl} \langle ij|kl\rangle \sum_{ab} \left( \frac{\partial d\eta_{ef}^{\bar{k}\bar{b}}}{\partial T_{ef}^{mn}} d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}} + d\eta_{\bar{a}\bar{j}}^{\bar{k}\bar{b}} \frac{\partial d\eta_{\bar{i}\bar{b}}^{\bar{a}\bar{l}}}{\partial T_{ef}^{mn}} \right)
\end{aligned} \tag{3.63}$$

which could be simplified using the relationship within the two-electron in-

tegrals as:

$$\begin{aligned}
& 2 \sum_{ijkl} ((ik|jl) - (il|jk)) \sum_{ab} \frac{\partial d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}}}{\partial T_{ef}^{mn}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \\
& + 2 \sum_{ijkl} ((ik|jl) - (il|jk)) \sum_{ab} \frac{\partial d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}}}{\partial T_{ef}^{mn}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \\
& \quad + 2 \sum_{ijkl} -(il|jk) \sum_{ab} \frac{\partial d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}}}{\partial T_{ef}^{mn}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \\
& \quad + 2 \sum_{ijkl} -(il|jk) \sum_{ab} \frac{\partial d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}}}{\partial T_{ef}^{mn}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \\
& \quad + 2 \sum_{ijkl} (ik|jl) \sum_{ab} \frac{\partial d\eta_{\tilde{a}\tilde{j}}^{\tilde{k}\tilde{b}}}{\partial T_{ef}^{mn}} d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \tag{3.64}
\end{aligned}$$

After substituting the partial derivative of  $d\eta$ , expanding the expression, eliminating the delta terms, we can obtain the explicit expression of the partial derivative of M2 with respect to  $T_{ef}^{mn}$ ,

$$\begin{aligned}
& 2 \sum_{ijl} ((im|jl) - (il|jm)) \sum_b (2T_{bf}^{jn} - T_{fb}^{jn}) d\eta_{\tilde{i}\tilde{b}}^{\tilde{a}\tilde{l}} \\
& + 2 \sum_{ikl} ((ik|ml) - (il|mk)) \sum_a (2T_{af}^{kn} - T_{fa}^{kn}) d\eta_{\tilde{i}\tilde{e}}^{\tilde{a}\tilde{l}} \\
& - 2 \sum_{ijl} ((im|jl) - (il|jm)) \sum_b (T_{be}^{jn} - T_{eb}^{jn}) d\eta_{\tilde{i}\tilde{b}}^{\tilde{f}\tilde{l}} \\
& - 2 \sum_{ikl} ((ik|ml) - (il|mk)) \sum_a (T_{ae}^{kn} - T_{ea}^{kn}) d\eta_{\tilde{i}\tilde{f}}^{\tilde{a}\tilde{l}} \\
& \quad + 2 \sum_{ijl} ((im|jl) - (il|jm)) \sum_b T_{eb}^{jn} d\eta_{\tilde{i}\tilde{b}}^{\tilde{f}\tilde{l}} \\
& \quad + 2 \sum_{ikl} ((ik|ml) - (il|mk)) \sum_a T_{ea}^{kn} d\eta_{\tilde{i}\tilde{f}}^{\tilde{a}\tilde{l}}
\end{aligned}$$

$$\begin{aligned}
& +2 \sum_{ijl} -(il|jm) \sum_b (2T_{bf}^{jn} - T_{fb}^{jn}) d\eta_{i\bar{b}}^{\bar{e}\bar{l}} \\
& +2 \sum_{ikl} -(il|mk) \sum_a (2T_{af}^{kn} - T_{fa}^{kn}) d\eta_{i\bar{e}}^{\bar{a}\bar{l}} \\
& -2 \sum_{ijl} -(il|jm) \sum_b (T_{be}^{jn} - T_{eb}^{jn}) d\eta_{i\bar{b}}^{\bar{f}\bar{l}} \\
& -2 \sum_{ikl} -(il|mk) \sum_a (T_{ae}^{kn} - T_{ea}^{kn}) d\eta_{i\bar{f}}^{\bar{a}\bar{l}} \\
& \quad +2 \sum_{ijl} -(il|jm) \sum_b T_{eb}^{jn} d\eta_{i\bar{b}}^{\bar{f}\bar{l}} \\
& \quad +2 \sum_{ikl} -(il|mk) \sum_a T_{ea}^{kn} d\eta_{i\bar{f}}^{\bar{a}\bar{l}} \\
& +2 \sum_{ijl} (im|jl) \sum_b (2T_{bf}^{jn} - T_{fb}^{jn}) d\eta_{i\bar{b}}^{\bar{e}\bar{l}} \\
& +2 \sum_{ikl} (ik|ml) \sum_a (2T_{af}^{kn} - T_{fa}^{kn}) d\eta_{i\bar{e}}^{\bar{a}\bar{l}} \\
& \quad -2 \sum_{ijl} (im|jl) \sum_b T_{be}^{jn} d\eta_{i\bar{b}}^{\bar{f}\bar{l}} \\
& \quad -2 \sum_{ikl} (ik|ml) \sum_a T_{ae}^{kn} d\eta_{i\bar{f}}^{\bar{a}\bar{l}} \tag{3.65}
\end{aligned}$$

Based on the experience in the previous work of M2, the above explicit expression could be further simplified using the relationship within two-

electron integrals and density matrices  $d\eta$ ,

$$\begin{aligned}
& 4 \sum_{ijl} ((im|jl) - (il|jm)) \sum_b (2T_{bf}^{jn} - T_{fb}^{jn}) d\eta_{ib}^{\bar{e}l} \\
& -4 \sum_{ijl} ((im|jl) - (il|jm)) \sum_b (T_{be}^{jn} - T_{eb}^{jn}) d\eta_{ib}^{\bar{f}l} \\
& +4 \sum_{ijl} ((im|jl) - (il|jm)) \sum_b T_{eb}^{jn} d\eta_{ib}^{\bar{f}l} \\
& +4 \sum_{ijl} -(il|jm) \sum_b (2T_{bf}^{jn} - T_{fb}^{jn}) d\eta_{ib}^{\bar{e}l} \\
& -4 \sum_{ijl} -(il|jm) \sum_b (T_{be}^{jn} - T_{eb}^{jn}) d\eta_{ib}^{\bar{f}l} \\
& +4 \sum_{ijl} -(il|jm) \sum_b T_{eb}^{jn} d\eta_{ib}^{\bar{f}l} \\
& +4 \sum_{ijl} (im|jl) \sum_b (2T_{bf}^{jn} - T_{fb}^{jn}) d\eta_{ib}^{\bar{e}l} \\
& -4 \sum_{ijl} (im|jl) \sum_b T_{be}^{jn} d\eta_{ib}^{\bar{f}l} \tag{3.66}
\end{aligned}$$

By making contraction between two-electron integrals and density matrices, we can write the expression in the form having lower computational cost in

the software implementation,

$$\begin{aligned}
& 4 \sum_{jb} (2T_{bf}^{jn} - T_{fb}^{jn}) \sum_{il} ((im|jl) - (il|jm)) d\eta_{ib}^{\bar{e}l} \\
& -4 \sum_{jb} (T_{be}^{jn} - T_{eb}^{jn}) \sum_{il} ((im|jl) - (il|jm)) d\eta_{ib}^{\bar{f}l} \\
& +4 \sum_{jb} T_{eb}^{jn} \sum_{il} ((im|jl) - (il|jm)) d\eta_{ib}^{\bar{f}l} \\
& +4 \sum_{jb} (2T_{bf}^{jn} - T_{fb}^{jn}) \sum_{il} -(il|jm) d\eta_{ib}^{\bar{e}l} \\
& -4 \sum_{jb} (T_{be}^{jn} - T_{eb}^{jn}) \sum_{il} -(il|jm) d\eta_{ib}^{\bar{f}l} \\
& +4 \sum_{jb} T_{eb}^{jn} \sum_{il} -(il|jm) d\eta_{ib}^{\bar{f}l} \\
& +4 \sum_{jb} (2T_{bf}^{jn} - T_{fb}^{jn}) \sum_{il} (im|jl) d\eta_{ib}^{\bar{e}l} \\
& -4 \sum_{jb} T_{be}^{jn} \sum_{il} (im|jl) d\eta_{ib}^{\bar{f}l} \tag{3.67}
\end{aligned}$$

Defining  $\sum_{il} ((ik|jl) - (il|jk)) d\eta_{ib}^{\bar{a}l}$  as intermediate quantity  ${}_1H_{jkab}$ ,

$\sum_{il} ((ik|jl) - (il|jk)) d\eta_{ib}^{\bar{a}l}$  as intermediate quantity  ${}_2H_{jkab}$ ,  $\sum_{il} -(il|jk) d\eta_{ib}^{\bar{a}l}$  as

intermediate quantity  ${}_3H_{jkab}$ ,  $\sum_{il} -(il|jk) d\eta_{ib}^{\bar{a}l}$  as intermediate quantity

${}_4H_{jkab}$ ,  $\sum_{il} (ik|jl) d\eta_{ib}^{\bar{a}l}$  as intermediate quantity  ${}_5H_{jkab}$ . The final expression

suitable for software implementation is therefore,

$$\begin{aligned}
& 4 \sum_{jb} (2T_{bf}^{jn} - T_{fb}^{jn}) {}_1H_{jmeb} - 4 \sum_{jb} (T_{be}^{jn} - T_{eb}^{jn}) {}_1H_{jmfb} \\
& \qquad \qquad \qquad + 4 \sum_{jb} T_{eb}^{jn} {}_2H_{jmfb} \\
& + 4 \sum_{jb} (2T_{bf}^{jn} - T_{fb}^{jn}) {}_3H_{jmeb} - 4 \sum_{jb} (T_{be}^{jn} - T_{eb}^{jn}) {}_3H_{jmfb} \\
& \qquad \qquad \qquad + 4 \sum_{jb} T_{eb}^{jn} {}_4H_{jmfb} \\
& + 4 \sum_{jb} (2T_{bf}^{jn} - T_{fb}^{jn}) {}_5H_{jmeb} - 4 \sum_{jb} T_{be}^{jn} {}_5H_{jmfb} \quad (3.68)
\end{aligned}$$

### 3.4 Contravariant Configuration

The Slater determinant generated by the double excitations operator  $\hat{T}_2$  in the spatial orbital form  $|\Phi_{ij}^{ab}\rangle$  holds the inner product as following[49]:

$$\langle \Phi_{ij}^{ab} | \Phi_{kl}^{cd} \rangle = 4\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl} + 4\delta_{ad}\delta_{bc}\delta_{jk}\delta_{il} - 2\delta_{ac}\delta_{bd}\delta_{il}\delta_{jk} - 2\delta_{bc}\delta_{ad}\delta_{ik}\delta_{jl}$$

The ‘contravariant’ transformation is performed on the double excitations configuration space  $\{\Phi_{ij}^{ab}\}$  in order to have the orthogonality relation[50, 51]:

$$\tilde{\Phi}_{ij}^{ab} = \frac{1}{6}(2\Phi_{ij}^{ab} + \Phi_{ji}^{ab})$$

$$\langle \tilde{\Phi}_{ij}^{ab} | \Phi_{kl}^{cd} \rangle = \delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl} + \delta_{ad}\delta_{bc}\delta_{il}\delta_{jk}$$

the normalization relation of which is a special case of the above equation,

$$\langle \tilde{\Phi}_{ij}^{ab} | \Phi_{ij}^{ab} \rangle = 1 + \delta_{ab}\delta_{ij}$$

The adoption of the ‘Contravariant Configuration’ will raise certain effect on the relevant expectation values of certain physical variables. Taking the matrix element of the double excitations operator  $\hat{T}_2$  as an example:

$$\hat{T}_2|\Phi_0\rangle = \frac{1}{2} \sum_{ia} \sum_{jb} T_{ab}^{ij} |\Phi_{ij}^{ab}\rangle$$

$$\langle \Phi_{ij}^{ab} | \hat{T}_2 | \Phi_0 \rangle = \frac{1}{2} \sum_{kc} \sum_{ld} T_{cd}^{kl} \langle \Phi_{ij}^{ab} | \Phi_{kl}^{cd} \rangle$$

By substituting the orthogonality relation into the expression, applying the symmetry relation  $T_{ab}^{ij} = T_{ba}^{ji}$ , we find that:

$$\langle \Phi_{ij}^{ab} | \hat{T}_2 | \Phi_0 \rangle = 4T_{ab}^{ij} - 2T_{ab}^{ji}$$

We can also expand the matrix element made from contravariant configuration in the same way:

$$\langle \tilde{\Phi}_{ij}^{ab} | \hat{T}_2 | \Phi_0 \rangle = T_{ab}^{ij}$$

The transformation in same pattern as the one done on the double excitations configuration space  $\{\Phi_{ij}^{ab}\}$  can be done here:  $T_{ab}^{ij}$  is substituted by  $\frac{1}{6}(2T_{ab}^{ij} + T_{ab}^{ji})$

$$\begin{aligned} & 4\left(\frac{1}{6}(2T_{ab}^{ij} + T_{ab}^{ji})\right) - 2\left(\frac{1}{6}(2T_{ab}^{ji} + T_{ab}^{ij})\right) \\ & = T_{ab}^{ij} \end{aligned}$$

It lets the expectation value(the matrix element) made from the original double excitations configuration equal to the one made from contravariant configuration.

The technical job in my project focuses on calculating the derivative of the energy functional, and its software implementation. In order to be consistent with the calculation made by contravariant configuration, the derived gradient is transformed from  $G_{ab}^{ij}$  to  $\frac{1}{6}(2G_{ab}^{ij} + G_{ab}^{ji})$ . Since the transformation halves the overall magnitude, we need to pre-multiply a factor of 2 to cancel this side effect.

In the software implementation of CCSD method in the Molpro program[50], the residual is defined as,

$$\begin{aligned} V_{ab}^{ij} &= \langle \tilde{\Phi}_{ij}^{ab} | (\hat{H} - E) \\ & (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle \end{aligned} \quad (3.69)$$

which is expected to be zero at the convergence. The range of the indices is  $i \geq j, \forall a, b$ .

After substituting the expression of the contravariant component  $\tilde{\Phi}_{ij}^{ab}$  into

the equation, it becomes:

$$\begin{aligned}
V_{ab}^{ij} &= \langle \frac{1}{6}(2\Phi_{ij}^{ab} + \Phi_{ji}^{ab}) | (\hat{H} - E) \\
(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle \\
& \quad (3.70) \\
&= \frac{1}{3} \langle \Phi_{ij}^{ab} | (\hat{H} - E) \\
(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle \\
& \quad + \frac{1}{6} \langle \Phi_{ji}^{ab} | (\hat{H} - E) \\
(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle \\
& \quad (3.71)
\end{aligned}$$

Because the gradients derived in my project supposed the wavefunction to be normal, and in Molpro source file ccmp2.F it becomes part of  $V_{ab}^{ij}$  in the software implementation. I need to have it in this form in order to merge with the rest of the program, which is used for making a bi-orthogonal precondition for DIIS extrapolation[52, 15]:

$$V_{ab}^{ij} = \frac{1}{6}(2G_{ab}^{ij} + G_{ab}^{ji}) \quad (3.72)$$

### 3.4.1 the simple model of ‘contravariant’ transformation

The simplest closed-shell energy expression of Coupled-Cluster based method could be written as

$$E = \sum_{ijab} K_{ab}^{ij} (2T_{ab}^{ij} - T_{ab}^{ji}) \quad (3.73)$$

where  $K_{ab}^{ij}$  is the external exchange integral  $\langle ij|ab \rangle$  and  $T_{ab}^{ij}$  the cluster amplitudes.

The partial derivative of the energy expression with respect to a cluster amplitude  $T_{ef}^{mn}$  would be

$$\begin{aligned}
\frac{\partial E}{\partial T_{ef}^{mn}} &= \sum_{ijab} K_{ab}^{ij} (2\delta_{im}\delta_{jn}\delta_{ae}\delta_{bf} - \delta_{jm}\delta_{in}\delta_{ae}\delta_{bf}) \\
&= 2K_{ef}^{mn} - K_{ef}^{nm} \quad (3.74)
\end{aligned}$$

If the external exchange integral  $K_{ab}^{ij}$  in this energy expression is substituted by  $2K_{ab}^{ij} - K_{ab}^{ji}$ ,

$$E' = \sum_{ijab} (2K_{ab}^{ij} - K_{ab}^{ji})(2T_{ab}^{ij} - T_{ab}^{ji}) \quad (3.75)$$

the partial derivative with respect to  $T_{ef}^{mn}$  would then become:

$$\begin{aligned}\frac{\partial E'}{\partial T_{ef}^{mn}} &= \sum_{ijab} (2K_{ab}^{ij} - K_{ab}^{ji})(2\delta_{im}\delta_{jn}\delta_{ae}\delta_{bf} - \delta_{jm}\delta_{in}\delta_{ae}\delta_{bf}) \\ &= 4K_{ef}^{mn} - 2K_{ef}^{nm} - 2K_{ef}^{nm} + K_{ef}^{mn} = 5K_{ef}^{mn} - 4K_{ef}^{nm}\end{aligned}\quad (3.76)$$

The effect of the 'Contravariant' transformation introduced above can be seen by having,

$$\begin{aligned}&\frac{1}{6}\left(2\frac{\partial E'}{\partial T_{ef}^{mn}} + \frac{\partial E'}{\partial T_{ef}^{nm}}\right) * 2 \\ &= \frac{1}{6}\left(2(5K_{ef}^{mn} - 4K_{ef}^{nm}) + (5K_{ef}^{nm} - 4K_{ef}^{mn})\right) * 2 \\ &= 2K_{ef}^{mn} - K_{ef}^{nm}\end{aligned}\quad (3.77)$$

which exactly restores to  $\frac{\partial E}{\partial T_{ef}^{mn}}$ .

On the contrary, if the set of two-electron integral  $\{K_{ab}^{ij}\}$  in  $\frac{\partial E}{\partial T_{ef}^{mn}}$  is replaced by  $\{2K_{ab}^{ij} - K_{ab}^{ji}\}$ , it would become

$$2(2K_{ef}^{mn} - K_{ef}^{nm}) - (2K_{ef}^{nm} - K_{ef}^{mn}) = 5K_{ef}^{mn} - 4K_{ef}^{nm}\quad (3.78)$$

which turns into  $\frac{\partial E'}{\partial T_{ef}^{mn}}$ .

The actual  $O(T^4)$  energy terms are much more complicated than the simplest example above, which is a linear combination of the set of cluster amplitudes  $\{T_{ab}^{ij}\}$ . The relationship demonstrated above does not hold for the QVCCD  $O(T^4)$  energy functional.

### 3.4.2 the transformation made in the current QVCCD program

The QVCCD method implemented in ITF code by Joshua Black transforms the  $V_{ab}^{ij}$  matrices storing electron integral to  $2V_{ab}^{ij} - V_{ab}^{ji}$ . Although the old Molpro shares the same energy functional with ITF one made from V matrices and transformed cluster amplitudes [53]:

$$E = \sum_{IJAB} 2_2V_{AB}^{IJ} 2t_{AB}^{IJ} + \sum_{IJAB} 1V_{AB}^{IJ} 1t_{AB}^{IJ}\quad (3.79)$$

$$2V_{AB}^{IJ} = \langle \Phi_0 | \hat{H} | \Phi_{AB}^{IJ} \rangle\quad (3.80)$$

$$1V_{AB}^{IJ} = \langle \Phi_0 | 1\hat{T}^\dagger (\hat{H} - \langle \hat{H} \rangle) | \Phi_{ab}^{ij} \rangle\quad (3.81)$$

there is no such transformed V matrices intermediate quantity defined in the execution file `comp2.F`, which updates the energy in each iteration. It is surprisingly that the outcomes of those two programmes agree. The relevant subroutines are thus explored to find out the reason.

The subroutine `tracem2` calculating the trace of the product of matrices in the file, carries out the product of  $\vec{V}$  and  $\vec{T}$ :

$$trij = (2 - \delta_{ij}) \sum_{ab} T_{ab}^{ij} V_{ab}^{ij} \quad (3.82)$$

$$trji = (2 - \delta_{ij}) \sum_{ab} T_{ab}^{ij} V_{ba}^{ij} \quad (3.83)$$

An extra step was found after that command line calling `tracem2` subroutine. It assigned the energy by  $2trij - trji$ , which actually equals to

$$\begin{aligned} & (2 - \delta_{ij}) \sum_{ab} 2T_{ab}^{ij} V_{ab}^{ij} - (2 - \delta_{ij}) \sum_{ab} T_{ab}^{ij} V_{ba}^{ij} \\ & = (2 - \delta_{ij}) \sum_{ab} T_{ab}^{ij} (2V_{ab}^{ij} - V_{ba}^{ij}) \end{aligned} \quad (3.84)$$

There is symmetry relation within V matrices. For  ${}_2\vec{V}$ , which is the external exchange integrals  $\langle ij|ba \rangle = \langle ji|ab \rangle$ , therefore  ${}_2V_{ba}^{ij} = {}_2V_{ab}^{ji}$ .

As a result, when the above equation applies on  ${}_2V$ , it becomes

$$(2 - \delta_{ij}) \sum_{ab} T_{ab}^{ij} (2{}_2V_{ab}^{ij} - {}_2V_{ab}^{ji}) \quad (3.85)$$

then sum over  $i \geq j$ , would have the same effect as the intermediate process Joshua did in his code. Because as long as the function is symmetrized, the full range sum over the  $i, j$  pair would become

$$B(i, j) = \frac{A(i, j) + A(j, i)}{2} = B(j, i) \quad (3.86)$$

$$\sum_{ij} B(i, j) = \sum_{i < j} B(i, j) + B(i, i) + \sum_{i > j} B(i, j) = \sum_{i > j} B(i, j) * 2 + B(i, i) \quad (3.87)$$

which equals to  $\sum_{i \geq j} (2 - \delta_{ij}) B(i, j) = B(i, i) + \sum_{i > j} 2B(i, j)$ .

Because the external exchange integral

$\langle ij|ab \rangle = \int \phi_i(1)\phi_j(2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_a(1)\phi_b(2) d\vec{r}_1 d\vec{r}_2$  is same in the form as the all-internal integral  $\langle ij|kl \rangle$  illustrated in the above section. I need to do the same transformation to the two-electron integrals in my project in order to merge with the current QVCCD method in the old Molpro program.

## 3.5 Numerical means applied during the software implementation

### 3.5.1 Newton-Raphson method

Newton-Raphson method is based on the Taylor expansion of a function. It is designed for finding the root of a function, at which its value is zero.

If in the neighbour area of a point  $a$ , a function  $f(x)$  has its definition on derivative to  $n - 1$  order, and on point  $a$  it has  $n$ th order derivative, the function in this neighbour area  $|x - a| \ll \delta$  can be expanded as

$$f(x) = f(a) + f'(a)(x - a) + \frac{1}{2!}f''(a)(x - a)^2 + \dots + \frac{1}{n!}f^{(n)}(a)(x - a)^n \quad (3.88)$$

This is the Taylor expansion for single variable function  $f(x)$ .

The one-dimensional Newton-Raphson method only considers the first-order derivative of the function, and the expression is linear with respect to the variable

$$f(x) = f(a) + f'(a)(x - a) \quad (3.89)$$

suppose  $x$  is the root tried to find,  $x : f(x) = 0$ .

$$0 = f(a) + f'(a)(x - a)$$
$$x = a - \frac{f(a)}{f'(a)}$$

The algorithm needs to have the value of function  $f(x)$  and its first derivative at point  $a$ , then determine the approximate value of  $x$ . Note that this expression is an approximation, as it neglects its higher order terms. It takes the initial guessed  $x$  as the input of next iteration, and calculates its function and derivative value, then determine the following approximate root value. The algorithm runs iteratively until it converges.

The Taylor expansion can be applied to multi-variable functions, and the multi-dimensional Newton-Raphson formula can be written as,

$$f(x_1 + \delta x_1, x_2 + \delta x_2, \dots, x_N + \delta x_N) = f(x_1, x_2, \dots, x_N) + \sum_{i=1}^N \frac{\partial f(x_1, x_2, \dots, x_N)}{\partial x_i} \delta x_i + O(\delta x^2) \quad (3.90)$$

in which the higher order terms can be neglected.

Although the formula cannot be applied directly on the energy functional of

QVCCD method as the energy minimum is what explored, this formula can still be applied to find the point at which the gradient is zero. The second-order derivative of the energy functional is approximated by the difference of eigenvalues of Fock matrix. It becomes the working equation for the current CCSD programme in Molpro[50],

$$\Delta T_{ab}^{ij} = \frac{V_{ab}^{ij}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (3.91)$$

in which  $V_{ab}^{ij}$  is the residual matrix formed by gradient and  $T_{ab}^{ij}$  is the variables of the energy functional, cluster amplitudes. The programme runs iteratively until the residual vanishes.

### 3.5.2 Numerical differentiation

Numerical differentiation finds the derivative of a function numerically, through dividing the difference of the function value by the difference of the variable values. According to the mathematical definition of derivative of a function, the simplest numerical differentiation can be expressed as:

$$\frac{f(x+h) - f(x)}{h}$$

when the function  $f(x)$  is known and  $h$ , namely, stepsize is set manually as a small number.

Numerical differentiation can be performed when the explicit derivative expression is not available, for example, only the graph of a function is provided. In my project, it acts as a tool to check whether the explicit derivative expression, namely, analytical derivative is correct or not.

The formula involving more points on the curve provides a more accurate result. For example, the two point formula is

$$\frac{f(x+h) - f(x-h)}{2h}$$

The formula involving more points can be found through the combination of Taylor expansion series[76][77, 78]:

$$f(x + 2h) = f(x) + f'(x)2h + \frac{1}{2}f''(x)(2h)^2 + \frac{1}{6}f^{(3)}(x)(2h)^3 + \frac{1}{24}f^{(4)}(x)(2h)^4 + \frac{1}{5!}f^{(5)}(x)(2h)^5 + \dots \quad (3.92)$$

$$f(x + h) = f(x) + f'(x)h + \frac{1}{2}f''(x)h^2 + \frac{1}{6}f^{(3)}(x)h^3 + \frac{1}{24}f^{(4)}(x)h^4 + \frac{1}{5!}f^{(5)}(x)h^5 + \dots \quad (3.93)$$

$$f(x - h) = f(x) + f'(x)(-h) + \frac{1}{2}f''(x)(-h)^2 + \frac{1}{6}f^{(3)}(x)(-h)^3 + \frac{1}{24}f^{(4)}(x)(-h)^4 + \frac{1}{5!}f^{(5)}(x)(-h)^5 + \dots \quad (3.94)$$

$$f(x - 2h) = f(x) + f'(x)(-2h) + \frac{1}{2}f''(x)(-2h)^2 + \frac{1}{6}f^{(3)}(x)(-2h)^3 + \frac{1}{24}f^{(4)}(x)(-2h)^4 + \frac{1}{5!}f^{(5)}(x)(-2h)^5 + \dots \quad (3.95)$$

By subtracting  $f(x - 2h)$  from  $f(x + 2h)$  and  $f(x - h)$  from  $f(x + h)$ , the second and fourth order derivative terms would vanish, then multiply the latter combination by a factor of -8 and add them together, we get:

$$(f(x + 2h) - f(x - 2h)) - 8(f(x + h) - f(x - h)) = -12f'(x)h + o(h^5)$$

$$f'(x) = -\frac{(f(x + 2h) - f(x - 2h)) - 8(f(x + h) - f(x - h))}{12h} + o(h^4) \quad (3.96)$$

This is the four point formula for numerical differentiation, in which the error is the fourth power of the stepsize. It is considered to be very accurate. The storage of the cluster amplitudes in Molpro is not full, only  $T_{ef}^{mn}$  ( $m \leq n$ ) is stored in double excitation amplitudes, for the  $m < n$  cases the counterpart  $T_{fe}^{nm}$  is visited.

Therefore, there is problem when the numeric differentiation is carried out: because the variation of  $T_{ef}^{mn}$  ( $m > n$ ) will cause the change on  $T_{fe}^{nm}$  as well, the variation of the energy expression made of  $\vec{T}$  will be incorrect as a result. The actual situation of numerical differentiation in Molpro is:

$$\frac{E(T_{ef}^{mn} + \Delta T, T_{fe}^{nm} + \Delta T) - E(T_{ef}^{mn}, T_{fe}^{nm})}{\Delta T} \quad \text{for } (m > n)$$

Mathematically it equals to,

$$\frac{\partial E}{\partial T_{ef}^{mn}} + \frac{\partial E}{\partial T_{fe}^{nm}} + \frac{o(\vec{T}^2)}{\Delta T} \quad \text{for } (m > n)$$

Because  $\frac{\partial E}{\partial T_{fe}^{nm}}$  is not necessarily equalling to  $\frac{\partial E}{\partial T_{ef}^{mn}}$ , the analytic partial derivative with respect to  $T_{ef}^{mn}$  needs to plus its transposed counterpart with respect to  $T_{fe}^{nm}$  so as to compare with the numeric one.

For  $m = n$ , the numeric differentiation results match the analytical one directly because the cluster amplitudes are stored independently.

### 3.5.3 the merging problem with the old Molpro program

The code of  $T^4$  terms are combined with the current QVCCD one and are eventually built on CCSD program in Molpro[50]. The vector used to update the cluster amplitudes in each iteration is called the residual which is expected to vanish at the convergence.

$$V_{ab}^{ij} = \frac{1}{6}(2G_{ab}^{ij} + G_{ab}^{ji}) \quad (i \geq j) \quad (3.97)$$

The  $G_{ab}^{ij}$  is named gradient which is made of original partial derivative with respect to the cluster amplitudes. The current  $G_{ab}^{ij}$  in the program can be symmetrized:

$$G_{ab}^{ij} = \frac{\frac{\partial E}{\partial T_{ab}^{ij}} + \frac{\partial E}{\partial T_{ba}^{ji}}}{2} \quad (3.98)$$

so that

$$G_{ba}^{ji} = \frac{\frac{\partial E}{\partial T_{ba}^{ji}} + \frac{\partial E}{\partial T_{ab}^{ij}}}{2} = G_{ab}^{ij} \quad (3.99)$$

There is a way of updating the energy functional relying on the first-order derivative using Newton-Rhapson method.

$$E_{\text{New}}(\vec{T}) = E_{\text{Old}}(\vec{T}) + \sum_{ijab} \frac{\partial E}{\partial T_{ab}^{ij}} \Delta T_{ab}^{ij} \quad (3.100)$$

If the symmetrised gradient  $G_{ab}^{ij}$  is used as the derivative, as long as  $\Delta T_{ba}^{ji} = \Delta T_{ab}^{ij}$ ,

$$\begin{aligned}
E_{\text{New}}(\vec{T}) &\approx E_{\text{Old}}(\vec{T}) + \sum_{ijab} G_{ab}^{ij} \Delta T_{ab}^{ij} = E_{\text{Old}}(\vec{T}) + \sum_{i>j} \sum_{ab} G_{ab}^{ij} \Delta T_{ab}^{ij} \\
&+ \sum_{i<j} \sum_{ab} G_{ba}^{ji} \Delta T_{ba}^{ji} + \sum_i \sum_{a>b} G_{ab}^{ii} \Delta T_{ab}^{ii} + \sum_i \sum_{a<b} G_{ba}^{ii} \Delta T_{ba}^{ii} + G_{aa}^{ii} \Delta T_{aa}^{ii} \\
&= E_{\text{Old}}(\vec{T}) + 2 \sum_{i>j} \sum_{ab} G_{ab}^{ij} \Delta T_{ab}^{ij} + 2 \sum_i \sum_{a>b} G_{ab}^{ii} \Delta T_{ab}^{ii} + G_{aa}^{ii} \Delta T_{aa}^{ii} \\
&= E_{\text{Old}} + \sum_{i>j} \left( \frac{\partial E}{\partial T_{ab}^{ij}} + \frac{\partial E}{\partial T_{ba}^{ji}} \right) \Delta T_{ab}^{ij} + \sum_{a>b} \sum_i \left( \frac{\partial E}{\partial T_{ab}^{ii}} + \frac{\partial E}{\partial T_{ba}^{ii}} \right) \Delta T_{ab}^{ii} + \\
&\qquad\qquad\qquad \frac{1}{2} \left( \frac{\partial E}{\partial T_{aa}^{ii}} + \frac{\partial E}{\partial T_{aa}^{ii}} \right) \Delta T_{aa}^{ii}
\end{aligned} \tag{3.101}$$

$$\begin{aligned}
&= E_{\text{Old}} + \sum_{i>j} \sum_{ab} \frac{\partial E}{\partial T_{ab}^{ij}} \Delta T_{ab}^{ij} + \sum_{i<j} \sum_{ab} \frac{\partial E}{\partial T_{ab}^{ij}} \Delta T_{ab}^{ij} + \sum_{a>b} \sum_i \frac{\partial E}{\partial T_{ab}^{ii}} \Delta T_{ab}^{ii} \\
&\qquad\qquad\qquad + \sum_{a<b} \sum_i \frac{\partial E}{\partial T_{ab}^{ii}} \Delta T_{ab}^{ii} + \frac{\partial E}{\partial T_{aa}^{ii}} \Delta T_{aa}^{ii} \\
&= E_{\text{Old}} + \sum_{ijab} \frac{\partial E}{\partial T_{ab}^{ij}} \Delta T_{ab}^{ij}
\end{aligned} \tag{3.102}$$

which equals to equation 3.100.

However, the current CCSD program does not update like this. As discussed in the previous subsection, it applies Newton-Raphson method on the root-finding of the first-order derivative instead. Therefore, according to equation 3.72, the symmetrisation will make the gradient not mathematically ideal as it is no longer the pure partial derivative.

The current QVCCD method assigns  $\frac{\partial E}{\partial T_{ab}^{ij}}$  to  $G_{ba}^{ji}$  ( $i \leq j$ ), which leaves serious problem to its further development, as it is not the normal gradient used in equation 3.97.

Even if the program accepts this gradient, what actually runs in each iteration would be

$$\Delta T_{ba}^{ji} = \frac{V_{ba}^{ji}}{\epsilon_b + \epsilon_a - \epsilon_j - \epsilon_i} \quad (i \leq j) \tag{3.103}$$

which actually create an update  $\Delta T_{ba}^{ji}$  until the residual  $V_{ba}^{ji}$  vanishes.

Because in Molpro the set of cluster amplitudes is stored incompletely relying

on its internal symmetric relationship:

$$T_{ab}^{ij} = \begin{cases} T_{ab}^{ij}, & \text{when } i \geq j \\ T_{ba}^{ji}, & \text{when } i < j \end{cases}$$

The update,  $\Delta T_{ba}^{ji}$  ( $i < j$ ), added onto the set of cluster amplitudes would by coincidence be added to the correct place so that the full range of  $T_{ab}^{ij}$  doesn't make mistake in further use.

However, the development of extra  $T^4$  gradient must be treated specially in order to merge with the current QVCCD method.

$\frac{\partial E}{\partial T_{ba}^{ji}}$  needs to be added to the gradient  $G_{ba}^{ji}$  ( $i < j$ ), but not  $\frac{\partial E}{\partial T_{ab}^{ij}}$  added to the gradient  $G_{ab}^{ij}$  ( $i > j$ ).

When  $i = j$ , the situation is more complicated because the cluster amplitudes  $T_{ab}^{ii}$  is stored completely. The  $\frac{V_{ba}^{ii}}{\epsilon_b + \epsilon_a - \epsilon_i - \epsilon_i}$  would generate  $\Delta T_{ba}^{ii}$  and add to  $T_{ab}^{ii}$ , which will not be correct as it needs to be added to  $T_{ba}^{ii}$  stored independently.

Therefore, the  $T^4$  gradient  $G_{ab}^{ij}$  used to construct residual needs to be constructed specially from the mathematical partial derivative,

$$G_{ba}^{ji} \quad (i \leq j) = \begin{cases} \frac{\partial E}{\partial T_{ba}^{ji}}, & \text{when } i = j \\ \frac{\partial E}{\partial T_{ba}^{ji}}, & \text{when } i < j \end{cases}$$

## 3.6 Appendix: the working equations of M2, M3, B1 and D1 terms

### 3.6.1 the expression of ${}_b\eta$ density matrix

The expression of  ${}_a\eta$  density matrix has been derived above, that of  ${}_b\eta$  is,

$${}_b\eta_J^I = \sum_{AB} \sum_K \frac{1}{2} t_{AB}^{IK} t_{JK}^{AB}$$

The spin-adaption of  $\vartheta\eta$  is,

$$\begin{aligned}
\vartheta\eta_{\bar{j}}^{\bar{i}} &= \sum_{ab} \sum_k \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{a}\bar{b}} + \sum_{ab} \sum_k \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{a}\bar{b}} + \sum_{ab} \sum_k \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{a}\bar{b}} \\
&= \sum_{ab} \sum_k \frac{1}{2} (T_{ab}^{ik} - T_{ba}^{ik}) (T_{ab}^{jk} - T_{ba}^{jk}) + \sum_{ab} \sum_k \frac{1}{2} T_{ab}^{ik} T_{ab}^{jk} \\
&\quad + \sum_{ab} \sum_k \frac{1}{2} (-T_{ba}^{ik}) (-T_{ba}^{jk}) \\
&= \sum_{ab} \sum_k \frac{1}{2} (T_{ab}^{ik} - T_{ba}^{ik}) (T_{ab}^{jk} - T_{ba}^{jk}) + \sum_{ab} \sum_k T_{ab}^{ik} T_{ab}^{jk} \quad (3.104)
\end{aligned}$$

There is relationship between the expressions of  $\vartheta\eta$  and  $\mathcal{A}\eta$  terms,

$$\vartheta\eta_{\bar{j}}^{\bar{i}} = \sum_k (\mathcal{A}\eta_{\bar{j}\bar{k}}^{\bar{i}\bar{k}} + \mathcal{A}\eta_{\bar{j}\bar{k}}^{\bar{i}\bar{k}}) \quad (3.105)$$

$$\vartheta\eta_{\bar{j}}^{\bar{i}} = 0 \quad (3.106)$$

$$\vartheta\eta_{\bar{j}}^{\bar{i}} = 0 \quad (3.107)$$

$$\begin{aligned}
\vartheta\eta_{\bar{j}}^{\bar{i}} &= \sum_{ab} \sum_k \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{a}\bar{b}} + \sum_{ab} \sum_k \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{a}\bar{b}} + \sum_{ab} \sum_k \frac{1}{2} t_{\bar{a}\bar{b}}^{\bar{i}\bar{k}} t_{\bar{j}\bar{k}}^{\bar{a}\bar{b}} \\
&= \vartheta\eta_{\bar{j}}^{\bar{i}} \quad (3.108)
\end{aligned}$$

In order to explore the residual of M3, we must know the partial derivative of  $\mathcal{A}\eta$  density matrix with respect to the cluster amplitudes,

$$\frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} = \delta_{im} \delta_{jn} T_{ef}^{kl} + T_{ef}^{ij} \delta_{km} \delta_{ln} - \delta_{im} \delta_{jn} T_{fe}^{kl} - T_{fe}^{ij} \delta_{km} \delta_{ln} \quad (3.109)$$

$$\frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} = \frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} \quad (3.110)$$

$$\frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} = \delta_{im} \delta_{jn} T_{ef}^{kl} + T_{ef}^{ij} \delta_{km} \delta_{ln} \quad (3.111)$$

$$\frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} = \frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} \quad (3.112)$$

$$\frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} = -\delta_{im} \delta_{jn} T_{fe}^{kl} - T_{fe}^{ij} \delta_{km} \delta_{ln} \quad (3.113)$$

$$\frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} = \frac{\partial \mathcal{A}\eta_{\bar{k}\bar{l}}^{\bar{i}\bar{j}}}{\partial T_{ef}^{mn}} \quad (3.114)$$

### 3.6.2 the partial derivative of M3 term

The partial derivative of M3 term with respect to  $T_{ef}^{pq}$  is,

$$\begin{aligned}
& \sum_{ijkl} \sum_{m,n} (\langle ij|kl\rangle - \langle ij|lk\rangle) \left( \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} + \mathcal{H}_{im}^{\bar{n}l} \frac{\partial \mathcal{H}_{\bar{n}j}^{\bar{k}m}}{\partial T_{ef}^{pq}} \right. \\
& \quad \left. + \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} + \mathcal{H}_{im}^{\bar{n}l} \frac{\partial \mathcal{H}_{\bar{n}j}^{\bar{k}m}}{\partial T_{ef}^{pq}} \right) \\
& + \sum_{ijkl} \sum_{m,n} \langle ij|kl\rangle \left( \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} + \mathcal{H}_{im}^{\bar{n}l} \frac{\partial \mathcal{H}_{\bar{n}j}^{\bar{k}m}}{\partial T_{ef}^{pq}} \right) \\
& + \sum_{ijkl} \sum_{m,n} -\langle ij|lk\rangle \left( \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} + \mathcal{H}_{im}^{\bar{n}l} \frac{\partial \mathcal{H}_{\bar{n}j}^{\bar{k}m}}{\partial T_{ef}^{pq}} \right. \\
& \quad \left. + \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} + \mathcal{H}_{im}^{\bar{n}l} \frac{\partial \mathcal{H}_{\bar{n}j}^{\bar{k}m}}{\partial T_{ef}^{pq}} \right) \tag{3.115}
\end{aligned}$$

after combining the equivalent elements in each term in the expression, it could be simplified as(expression a):

$$\begin{aligned}
& \sum_{ijkl} \sum_{m,n} 2(\langle ij|kl\rangle - \langle ij|lk\rangle) \left( \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} + \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} \right) \\
& \quad + \sum_{ijkl} \sum_{m,n} 2\langle ij|kl\rangle \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} \\
& + \sum_{ijkl} \sum_{m,n} -2\langle ij|lk\rangle \left( \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} + \frac{\partial \mathcal{H}_{im}^{\bar{n}l}}{\partial T_{ef}^{pq}} \mathcal{H}_{\bar{n}j}^{\bar{k}m} \right) \tag{3.116}
\end{aligned}$$

Then substituting the partial derivatives of density matrices with actual formulae, expanding the expression, eliminating the delta terms inside, we

can get the explicit mathematical expression for the residual of M3 term:

$$\begin{aligned}
& \sum_{ijk} \sum_m 2(\langle ij|kq\rangle - \langle ij|qk\rangle) T_{ef}^{im} \mathcal{A}_{\tilde{p}\tilde{j}}^{\tilde{k}\tilde{m}} \\
& + \sum_{jkl} \sum_n 2(\langle pj|kl\rangle - \langle pj|lk\rangle) T_{ef}^{nl} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{q}} \\
& - \sum_{ijk} \sum_m 2(\langle ij|kq\rangle - \langle ij|qk\rangle) T_{fe}^{im} \mathcal{A}_{\tilde{p}\tilde{j}}^{\tilde{k}\tilde{m}} \\
& - \sum_{jkl} \sum_n 2(\langle pj|kl\rangle - \langle pj|lk\rangle) T_{fe}^{nl} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{q}} \\
& - \sum_{ijk} \sum_m 2(\langle ij|kq\rangle - \langle ij|qk\rangle) T_{fe}^{im} \mathcal{A}_{\tilde{p}\tilde{j}}^{\tilde{k}\tilde{m}} \\
& - \sum_{jkl} \sum_n 2(\langle pj|kl\rangle - \langle pj|lk\rangle) T_{fe}^{nl} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{q}} \\
& + \sum_{ijk} \sum_m 2\langle ij|kq\rangle T_{ef}^{im} \mathcal{A}_{\tilde{p}\tilde{j}}^{\tilde{k}\tilde{m}} \\
& + \sum_{jkl} \sum_n 2\langle pj|kl\rangle T_{ef}^{nl} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{q}} \\
& - \sum_{ijk} \sum_m 2\langle ij|qk\rangle T_{ef}^{im} \mathcal{A}_{\tilde{p}\tilde{j}}^{\tilde{k}\tilde{m}} \\
& - \sum_{jkl} \sum_n 2\langle pj|lk\rangle T_{ef}^{nl} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{q}} \\
& + \sum_{ijk} \sum_m 2\langle ij|qk\rangle T_{fe}^{im} \mathcal{A}_{\tilde{p}\tilde{j}}^{\tilde{k}\tilde{m}} \\
& + \sum_{jkl} \sum_n 2\langle pj|lk\rangle T_{fe}^{nl} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{q}} \\
& + \sum_{ijk} \sum_m 2\langle ij|qk\rangle T_{fe}^{im} \mathcal{A}_{\tilde{p}\tilde{j}}^{\tilde{k}\tilde{m}} \\
& + \sum_{jkl} \sum_n 2\langle pj|lk\rangle T_{fe}^{nl} \mathcal{A}_{\tilde{n}\tilde{j}}^{\tilde{k}\tilde{q}}
\end{aligned} \tag{3.117}$$

The contraction of two-electron integrals with density matrices are made so as to decrease the number of loops in the software implementation to be

carried on. Then we combine those terms with same contraction and get:

$$\begin{aligned}
& \sum_{im} 2(T_{ef}^{im} - T_{fe}^{im}) \sum_{jk} (\langle ij|kq\rangle - \langle ij|qk\rangle) \mathcal{A}_{\bar{p}\bar{j}}^{\bar{k}\bar{m}} \\
& + \sum_{ln} 2(T_{ef}^{nl} - T_{fe}^{nl}) \sum_{jk} (\langle pj|kl\rangle - \langle pj|lk\rangle) \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{q}} \\
& - \sum_{im} 2T_{fe}^{im} \sum_{jk} (\langle ij|kq\rangle - \langle ij|qk\rangle) \mathcal{A}_{\bar{p}\bar{j}}^{\bar{k}\bar{m}} \\
& - \sum_{ln} 2T_{fe}^{nl} \sum_{jk} (\langle pj|kl\rangle - \langle pj|lk\rangle) \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{q}} \\
& + \sum_{im} 2T_{ef}^{im} \sum_{jk} \langle ij|kq\rangle \mathcal{A}_{\bar{p}\bar{j}}^{\bar{k}\bar{m}} \\
& + \sum_{nl} 2T_{ef}^{nl} \sum_{jk} \langle pj|kl\rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{q}} \\
& - \sum_{im} 2(T_{ef}^{im} - T_{fe}^{im}) \sum_{jk} \langle ij|qk\rangle \mathcal{A}_{\bar{p}\bar{j}}^{\bar{k}\bar{m}} \\
& - \sum_{ln} 2(T_{ef}^{nl} - T_{fe}^{nl}) \sum_{jk} \langle pj|lk\rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{q}} \\
& + \sum_{im} 2T_{fe}^{im} \sum_{jk} \langle ij|qk\rangle \mathcal{A}_{\bar{p}\bar{j}}^{\bar{k}\bar{m}} \\
& + \sum_{ln} 2T_{fe}^{nl} \sum_{jk} \langle pj|lk\rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{q}} \tag{3.118}
\end{aligned}$$

We define the intermediate quantity  $\mathbf{H}$  as:

$${}_1H_{ilmn} = \sum_{jk} (\langle ij|kl\rangle - \langle ij|lk\rangle) \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \tag{3.119}$$

$${}_2H_{ilmn} = \sum_{jk} (\langle ij|kl\rangle - \langle ij|lk\rangle) \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \tag{3.120}$$

$${}_3H_{ilmn} = \sum_{jk} \langle ij|kl\rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \tag{3.121}$$

$${}_4H_{ilmn} = \sum_{jk} \langle ij|lk\rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \tag{3.122}$$

$${}_5H_{ilmn} = \sum_{jk} \langle ij|lk\rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \tag{3.123}$$

The compactest expression of the residual of M3 term could then be expressed as:

$$\begin{aligned}
& \sum_{im} 2(T_{ef}^{im} - T_{fe}^{im}) {}_1H_{iqmp} + \sum_{ln} 2(T_{ef}^{nl} - T_{fe}^{nl}) {}_1H_{plqn} \\
& \quad - \sum_{im} 2T_{fe}^{im} {}_2H_{iqmp} - \sum_{ln} 2T_{fe}^{nl} {}_2H_{plqn} \\
& \quad + \sum_{im} 2T_{ef}^{im} {}_3H_{iqmp} + \sum_{ln} 2T_{ef}^{nl} {}_3H_{plqn} \\
& - \sum_{im} 2(T_{ef}^{im} - T_{fe}^{im}) {}_4H_{iqmp} - \sum_{ln} 2(T_{ef}^{nl} - T_{fe}^{nl}) {}_4H_{plqn} \\
& \quad + \sum_{im} 2T_{fe}^{im} {}_5H_{iqmp} + \sum_{ln} 2T_{fe}^{nl} {}_5H_{plqn} \tag{3.124}
\end{aligned}$$

Combining those terms with same sum indices, we get the form suitable for programming:

$$\begin{aligned}
& \sum_{im} (2(T_{ef}^{im} - T_{fe}^{im}) {}_1H_{iqmp} - 2T_{fe}^{im} {}_2H_{iqmp} \\
& \quad + 2T_{ef}^{im} {}_3H_{iqmp} - 2(T_{ef}^{im} - T_{fe}^{im}) {}_4H_{iqmp} \\
& \quad \quad \quad + 2T_{fe}^{im} {}_5H_{iqmp}) \\
& + \sum_{ln} (2(T_{ef}^{nl} - T_{fe}^{nl}) {}_1H_{plqn} - 2T_{fe}^{nl} {}_2H_{plqn} \\
& \quad + 2T_{ef}^{nl} {}_3H_{plqn} - 2(T_{ef}^{nl} - T_{fe}^{nl}) {}_4H_{plqn} \\
& \quad \quad \quad + 2T_{fe}^{nl} {}_5H_{plqn}) \tag{3.125}
\end{aligned}$$

There is a smarter way of deriving the residual expression of M3 term in which the contraction of two-electron integrals with density matrices is

made immediately after the simplest expression of derivative(expression a):

$$\begin{aligned}
& \sum_{ilmn} 2 \frac{\partial \mathcal{A}_{i\bar{m}}^{\bar{n}l}}{\partial T_{ef}^{pq}} \sum_{jk} (\langle ij|kl \rangle - \langle ij|lk \rangle) \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \\
& + \sum_{ilmn} 2 \frac{\partial \mathcal{A}_{i\bar{m}}^{\bar{n}l}}{\partial T_{ef}^{pq}} \sum_{jk} (\langle ij|kl \rangle - \langle ij|lk \rangle) \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \\
& \quad + \sum_{ilmn} 2 \frac{\partial \mathcal{A}_{i\bar{m}}^{\bar{n}l}}{\partial T_{ef}^{pq}} \sum_{jk} \langle ij|kl \rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \\
& \quad + \sum_{ilmn} -2 \frac{\partial \mathcal{A}_{i\bar{m}}^{\bar{n}l}}{\partial T_{ef}^{pq}} \sum_{jk} \langle ij|lk \rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \\
& \quad + \sum_{ilmn} -2 \frac{\partial \mathcal{A}_{i\bar{m}}^{\bar{n}l}}{\partial T_{ef}^{pq}} \sum_{jk} \langle ij|lk \rangle \mathcal{A}_{\bar{n}\bar{j}}^{\bar{k}\bar{m}} \tag{3.126}
\end{aligned}$$

Then substituting the partial derivative of density matrices, expanding the expression, eliminating the delta terms, we can get the result in a smarter way.

### 3.6.3 the energy and partial derivative expression of B1 and B2 terms

The spin-orbital expression of B1 term is,

$$\sum_{IJKL} -\frac{1}{2} \langle IJ||KL \rangle \sum_M \mathcal{A}_{IM}^{KL} \mathcal{B}_J^M$$

Considering the different spin possibilities of the set of two-bar integrals and  $\mathcal{A}$ ,  $\mathcal{B}$  density matrices, we can convert the current B1 expression into

that with respect to spatial part of the orbital,

For  $I \in \alpha, J \in \alpha, K \in \alpha, L \in \alpha$ , the relevant B1 term is,

$$\sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m a_{i\tilde{m}}^{\tilde{k}\tilde{l}} b_{\tilde{j}}^{\tilde{m}} = \sum_{ijkl} -\frac{1}{2} (\langle ij | kl \rangle - \langle ij | lk \rangle) \sum_m a_{i\tilde{m}}^{\tilde{k}\tilde{l}} b_{\tilde{j}}^{\tilde{m}} \quad (3.127)$$

For  $I \in \alpha, J \in \beta, K \in \alpha, L \in \beta$ , the relevant B1 term is,

$$\sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m a_{i\tilde{m}}^{\tilde{k}\tilde{l}} b_{\tilde{j}}^{\tilde{m}} = \sum_{ijkl} -\frac{1}{2} \langle ij | kl \rangle \sum_m a_{i\tilde{m}}^{\tilde{k}\tilde{l}} b_{\tilde{j}}^{\tilde{m}} \quad (3.128)$$

For  $I \in \alpha, J \in \beta, K \in \beta, L \in \alpha$ , the relevant B1 term is,

$$\sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m a_{i\tilde{m}}^{\tilde{k}\tilde{l}} b_{\tilde{j}}^{\tilde{m}} = \sum_{ijkl} \frac{1}{2} \langle ij | lk \rangle \sum_m a_{i\tilde{m}}^{\tilde{k}\tilde{l}} b_{\tilde{j}}^{\tilde{m}} \quad (3.129)$$

For  $I \in \beta$ ,  $J \in \alpha$ ,  $K \in \alpha$ ,  $L \in \beta$ , the relevant B1 term is,

$$\sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} = \sum_{ijkl} \frac{1}{2} \langle ij | lk \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} \quad (3.130)$$

$$= \sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} \quad (3.131)$$

For  $I \in \beta$ ,  $J \in \alpha$ ,  $K \in \beta$ ,  $L \in \alpha$ , the relevant B1 term is,

$$\sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} = \sum_{ijkl} -\frac{1}{2} \langle ij | kl \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} \quad (3.132)$$

$$= \sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} \quad (3.133)$$

For  $I \in \beta$ ,  $J \in \beta$ ,  $K \in \beta$ ,  $L \in \beta$ , the relevant B1 term is,

$$\sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} = \sum_{ijkl} -\frac{1}{2} (\langle ij | kl \rangle - \langle ij | lk \rangle) \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} \quad (3.134)$$

$$= \sum_{ijkl} -\frac{1}{2} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} \quad (3.135)$$

Looking at the different B1 terms carefully, we find that the third one could be expressed as following using the relationship between  $\mathcal{A}$  matrices,

$$\sum_{ijlk} -\frac{1}{2} \langle ij | lk \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}}$$

which in fact equals to the second one.

Therefore, the energy expression with respect to spatial-orbital, which is the sum of all these possibilities is eventually,

$$\sum_{ijkl} -(\langle ij | kl \rangle - \langle ij | lk \rangle) \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} + 2 \sum_{ijkl} -\langle ij | kl \rangle \sum_m \mathcal{A}_{i\tilde{m}}^{\tilde{k}\tilde{l}} \vartheta \eta_j^{\tilde{m}} \quad (3.136)$$

B2 has the same mathematical expression as B1 term and therefore having the same expression of partial derivative with respect to  $T_{ef}^{pq}$  as B1.

In order to derive the residual of B1, we must know the partial derivative of  $\vartheta\eta$  with respect to the cluster amplitude. The expression of the partial derivative of  $\vartheta\eta$  term with respect to the cluster amplitudes could be expressed in that of the  $\mathcal{A}\eta$  term.

$$\begin{aligned}
\frac{\partial \vartheta\eta_{\tilde{j}}}{\partial T_{ef}^{mn}} &= \frac{\partial \sum_k (\mathcal{A}\eta_{\tilde{j}k}^{\tilde{i}k} + \mathcal{A}\eta_{\tilde{j}k}^{\tilde{i}k})}{\partial T_{ef}^{mn}} \\
&= \sum_k \left( \frac{\partial \mathcal{A}\eta_{\tilde{j}k}^{\tilde{i}k}}{\partial T_{ef}^{mn}} + \frac{\partial \mathcal{A}\eta_{\tilde{j}k}^{\tilde{i}k}}{\partial T_{ef}^{mn}} \right) \\
&= \sum_k (\delta_{im}\delta_{kn} T_{ef}^{jk} + T_{ef}^{ik} \delta_{jm}\delta_{kn} - \delta_{im}\delta_{kn} T_{fe}^{jk} - T_{fe}^{ik} \delta_{jm}\delta_{kn} \\
&\quad + \delta_{im}\delta_{kn} T_{ef}^{jk} + T_{ef}^{ik} \delta_{jm}\delta_{kn}) \\
&= \sum_k (2\delta_{im}\delta_{kn} T_{ef}^{jk} + 2T_{ef}^{ik} \delta_{jm}\delta_{kn} - \delta_{im}\delta_{kn} T_{fe}^{jk} - T_{fe}^{ik} \delta_{jm}\delta_{kn}) \\
&= 2\delta_{im} T_{ef}^{jn} + 2T_{ef}^{in} \delta_{jm} - \delta_{im} T_{fe}^{jn} - T_{fe}^{in} \delta_{jm} \quad (3.137)
\end{aligned}$$

$$\frac{\partial \vartheta\eta_{\tilde{j}}}{\partial T_{ef}^{mn}} = 0 \quad (3.138)$$

$$\frac{\partial \vartheta\eta_{\tilde{j}}}{\partial T_{ef}^{mn}} = 0 \quad (3.139)$$

$$\frac{\partial \vartheta\eta_{\tilde{j}}}{\partial T_{ef}^{mn}} = \frac{\partial \vartheta\eta_{\tilde{j}}}{\partial T_{ef}^{mn}} \quad (3.140)$$

The partial derivative of B1 term with respect to the cluster amplitude  $T_{ef}^{pq}$  is,

$$\frac{\partial (\sum_{ijkl} -(\langle ij|kl\rangle - \langle ij|lk\rangle) \sum_m \mathcal{A}\eta_{im}^{\tilde{k}l} \vartheta\eta_j^{\tilde{m}} + 2 \sum_{ijkl} -\langle ij|kl\rangle \sum_m \mathcal{A}\eta_{im}^{\tilde{k}l} \vartheta\eta_j^{\tilde{m}})}{\partial T_{ef}^{pq}}$$

$$\begin{aligned}
&= \sum_{im} T_{ef}^{im} \sum_j -(\langle ij|pq\rangle - \langle ij|qp\rangle) \vartheta \eta_j^{\bar{m}} \\
&\quad + \sum_{kl} T_{ef}^{kl} \sum_j -(\langle pj|kl\rangle - \langle pj|lk\rangle) \vartheta \eta_j^{\bar{q}} \\
&\quad + \sum_{im} T_{fe}^{im} \sum_j (\langle ij|pq\rangle - \langle ij|qp\rangle) \vartheta \eta_j^{\bar{m}} \\
&\quad + \sum_{kl} T_{fe}^{kl} \sum_j (\langle pj|kl\rangle - \langle pj|lk\rangle) \vartheta \eta_j^{\bar{q}} \\
&\quad + \sum_j 2T_{ef}^{jq} \sum_{ikl} -(\langle ij|kl\rangle - \langle ij|lk\rangle) \mathcal{A}_{i\bar{p}}^{\bar{kl}} \\
&\quad + \sum_m 2T_{ef}^{mq} \sum_{ikl} -(\langle ip|kl\rangle - \langle ip|lk\rangle) \mathcal{A}_{i\bar{m}}^{\bar{kl}} \\
&\quad - \sum_j T_{fe}^{jq} \sum_{ikl} -(\langle ij|kl\rangle - \langle ij|lk\rangle) \mathcal{A}_{i\bar{p}}^{\bar{kl}} \\
&\quad - \sum_m T_{fe}^{mq} \sum_{ikl} -(\langle ip|kl\rangle - \langle ip|lk\rangle) \mathcal{A}_{i\bar{m}}^{\bar{kl}} \\
&\quad + 2 \sum_{im} T_{ef}^{im} \sum_j -\langle ij|pq\rangle \vartheta \eta_j^{\bar{m}} \\
&\quad + 2 \sum_{kl} T_{ef}^{kl} \sum_j -\langle pj|kl\rangle \vartheta \eta_j^{\bar{q}} \\
&\quad + 2 \sum_j (2T_{ef}^{jq} - T_{fe}^{jq}) \sum_{ikl} -\langle ij|kl\rangle \mathcal{A}_{i\bar{p}}^{\bar{kl}} \\
&\quad + 2 \sum_m (2T_{ef}^{mq} - T_{fe}^{mq}) \sum_{ikl} -\langle ip|kl\rangle \mathcal{A}_{i\bar{m}}^{\bar{kl}} \tag{3.141}
\end{aligned}$$

Define  $\sum_j -(\langle ij|kl\rangle - \langle ij|lk\rangle) \vartheta \eta_j^{\bar{m}}$  as intermediate quantity  ${}_1H_{iklm}$  and  $\sum_{ikl} -(\langle ij|kl\rangle - \langle ij|lk\rangle) \mathcal{A}_{i\bar{m}}^{\bar{kl}}$  as intermediate quantity  ${}_2H_{jm}$ ,  $\sum_j -\langle ij|kl\rangle \vartheta \eta_j^{\bar{m}} = \sum_j -\langle ij|kl\rangle \vartheta \eta_j^{\bar{m}}$  as intermediate quantity  ${}_3H_{iklm}$  and  $\sum_{ikl} -\langle ip|kl\rangle \mathcal{A}_{i\bar{m}}^{\bar{kl}}$  as intermediate quantity  ${}_4H_{jm}$ , we can express it in the way suitable for software

implementation,

$$\begin{aligned}
& \sum_{im} (T_{ef}^{im} - T_{fe}^{im}) {}_1H_{ipqm} + \sum_{kl} (T_{ef}^{kl} - T_{fe}^{kl}) {}_1H_{pklq} \\
& + \sum_j (2T_{ef}^{jq} - T_{fe}^{jq}) {}_2H_{jp} + \sum_m (2T_{ef}^{mq} - T_{fe}^{mq}) {}_2H_{pm} \\
& \quad + 2 \sum_{im} T_{ef}^{im} {}_3H_{ipqm} + 2 \sum_{kl} T_{ef}^{kl} {}_3H_{pklq} \\
& + 2 \sum_j (2T_{ef}^{jq} - T_{fe}^{jq}) {}_4H_{jp} + 2 \sum_m (2T_{ef}^{mq} - T_{fe}^{mq}) {}_4H_{pm} \tag{3.142}
\end{aligned}$$

### 3.6.4 The D1 term

The spin-orbital expression of D1 is,

$$\sum_{IJKL} \frac{1}{4} \langle IJ || KL \rangle \sum_{ABC} \sum_M t_{AB}^{KL} t_{MI}^{CA} d\eta_{JC}^{BM}$$

which could be divided into different spatial-orbital possibilities,

For  $I \in \alpha, J \in \alpha, K \in \alpha, L \in \alpha, A \in \alpha, B \in \alpha, C \in \alpha, M \in \alpha$ , the D1 is:

$$\begin{aligned}
& \sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} || \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{ab}}^{\tilde{k}\tilde{l}} t_{\tilde{mi}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\
& = \sum_{ijkl} \frac{1}{4} ((ik|jl) - (il|jk)) \sum_{abc} \sum_m (T_{ab}^{kl} - T_{ba}^{kl}) (T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \tag{3.143}
\end{aligned}$$

For  $I \in \alpha, J \in \alpha, K \in \alpha, L \in \alpha, A \in \alpha, B \in \alpha, C \in \beta, M \in \beta$ , the D1 is:

$$\begin{aligned}
& \sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} || \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{ab}}^{\tilde{k}\tilde{l}} t_{\tilde{mi}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\
& = \sum_{ijkl} \frac{1}{4} ((ik|jl) - (il|jk)) \sum_{abc} \sum_m (T_{ab}^{kl} - T_{ba}^{kl}) T_{ca}^{mi} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \tag{3.144}
\end{aligned}$$

For  $I \in \alpha, J \in \beta, K \in \alpha, L \in \beta, A \in \alpha, B \in \beta, C \in \alpha, M \in \alpha$ , the D1 is:

$$\begin{aligned} & \sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\ &= \sum_{ijkl} \frac{1}{4} (ik|jl) \sum_{abc} \sum_m T_{ab}^{kl} (T_{ca}^{im} - T_{ac}^{im}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \end{aligned} \quad (3.145)$$

For  $I \in \alpha, J \in \beta, K \in \alpha, L \in \beta, A \in \alpha, B \in \beta, C \in \beta, M \in \beta$ , the D1 is:

$$\begin{aligned} & \sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\ &= \sum_{ijkl} \frac{1}{4} (ik|jl) \sum_{abc} \sum_m T_{ab}^{kl} T_{ca}^{mi} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \end{aligned} \quad (3.146)$$

For  $I \in \alpha, J \in \beta, K \in \alpha, L \in \beta, A \in \beta, B \in \alpha, C \in \alpha, M \in \beta$ , the D1 is:

$$\begin{aligned} & \sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\ &= \sum_{ijkl} \frac{1}{4} (ik|jl) \sum_{abc} \sum_m (-T_{ba}^{kl})(-T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \end{aligned} \quad (3.147)$$

For  $I \in \alpha, J \in \beta, K \in \beta, L \in \alpha, A \in \alpha, B \in \beta, C \in \alpha, M \in \alpha$ , the D1 is:

$$\begin{aligned} & \sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\ &= \sum_{ijkl} -\frac{1}{4} (il|jk) \sum_{abc} \sum_m (-T_{ba}^{kl})(T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \end{aligned} \quad (3.148)$$

For  $I \in \alpha, J \in \beta, K \in \beta, L \in \alpha, A \in \alpha, B \in \beta, C \in \beta, M \in \beta$ , the D1 is:

$$\begin{aligned} & \sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\ &= \sum_{ijkl} -\frac{1}{4} (il|jk) \sum_{abc} \sum_m (-T_{ba}^{kl}) T_{ca}^{mi} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \end{aligned} \quad (3.149)$$

For  $I \in \alpha, J \in \beta, K \in \beta, L \in \alpha, A \in \beta, B \in \alpha, C \in \alpha, M \in \beta$ , the D1 is:

$$\begin{aligned} & \sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\ &= \sum_{ijkl} -\frac{1}{4} (il|jk) \sum_{abc} \sum_m T_{ab}^{kl} (-T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \end{aligned} \quad (3.150)$$

For  $I \in \beta, J \in \alpha, K \in \alpha, L \in \beta, A \in \alpha, B \in \beta, C \in \beta, M \in \alpha$ , the D1 is:

$$\sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} = \text{the eighth term} \quad (3.151)$$

For  $I \in \beta, J \in \alpha, K \in \alpha, L \in \beta, A \in \beta, B \in \alpha, C \in \alpha, M \in \alpha$ , the D1 is:

$$\sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} = \text{the seventh term} \quad (3.152)$$

For  $I \in \beta, J \in \alpha, K \in \alpha, L \in \beta, A \in \beta, B \in \alpha, C \in \beta, M \in \beta$ , the D1 is:

$$\sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} = \text{the sixth term} \quad (3.153)$$

For  $I \in \beta, J \in \alpha, K \in \beta, L \in \alpha, A \in \alpha, B \in \beta, C \in \beta, M \in \alpha$ , the D1 is:

$$\sum_{ijkl} \frac{1}{4} \langle \tilde{i}\tilde{j} | \tilde{k}\tilde{l} \rangle \sum_{abc} \sum_m t_{\tilde{a}\tilde{b}}^{\tilde{k}\tilde{l}} t_{\tilde{m}\tilde{i}}^{\tilde{c}\tilde{a}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} = \text{the fifth term} \quad (3.154)$$



$$= \sum_{ijkl} -\frac{1}{4}(ik|jl) \sum_{abc} \sum_m (-T_{ba}^{kl})(T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}}$$

which equals to,

$$\sum_{ijkl} \frac{1}{4}(ik|jl) \sum_{abc} \sum_m T_{ab}^{kl}(T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}}$$

which is the third case.

So are the seventh case replaced by the fourth one and the eighth case by the fifth.

The compactest energy expression of D1 is therefore:

$$\begin{aligned} \sum_{ijkl} \frac{1}{2}((ik|jl) - (il|jk)) \sum_{abc} \sum_m (T_{ab}^{kl} - T_{ba}^{kl})((T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} + T_{ca}^{mi} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}}) \\ + \sum_{ijkl} (ik|jl) \sum_{abc} \sum_m (T_{ab}^{kl}(T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} + T_{ab}^{kl} T_{ca}^{mi} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \\ + (-T_{ba}^{kl})(-T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}}) \end{aligned} \quad (3.160)$$

The partial derivative of D1 with respect to  $T_{ef}^{pq}$  is,

$$\begin{aligned} \sum_{ijkl} \frac{1}{2}((ik|jl) - (il|jk)) \sum_{abc} \sum_m \frac{\partial(T_{ab}^{kl} - T_{ba}^{kl})((T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} + T_{ca}^{mi} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}})}{\partial T_{ef}^{pq}} + \\ \frac{\partial \sum_{ijkl} (ik|jl) \sum_{abc} \sum_m (T_{ab}^{kl}(T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} + T_{ab}^{kl} T_{ca}^{mi} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} + (-T_{ba}^{kl})(-T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}})}{\partial T_{ef}^{pq}} \end{aligned} \quad (3.161)$$

The first term becomes,

$$\begin{aligned} \sum_{ijkl} \frac{1}{2}((ik|jl) - (il|jk)) \sum_{abc} \sum_m \left( \frac{\partial(T_{ab}^{kl} - T_{ba}^{kl})}{\partial T_{ef}^{pq}} ((T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} + T_{ca}^{mi} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}}) \right. \\ \left. + (T_{ab}^{kl} - T_{ba}^{kl}) \left( \frac{\partial(T_{ca}^{mi} - T_{ac}^{mi})}{\partial T_{ef}^{pq}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \right. \right. \\ \left. \left. + \frac{\partial T_{ca}^{mi}}{\partial T_{ef}^{pq}} d\eta_{\tilde{j}\tilde{c}}^{\tilde{b}\tilde{m}} \right) \right) \end{aligned} \quad (3.162)$$

Making the contraction of  $(T_{ab}^{kl} - T_{ba}^{kl})$  with the two-electron integral,  $T_{ca}^{mi} \dots$  with the density matrices, we can then define

$$\sum_m \sum_c ((T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{j\bar{c}}^{\bar{b}\bar{m}} + T_{ca}^{mi} d\eta_{j\bar{c}}^{\bar{b}\bar{m}}) \text{ as the intermediate function } H_1(i, a, j, b),$$

$$\sum_{kl} \frac{1}{2} ((ik|jl) - (il|jk))(T_{ab}^{kl} - T_{ba}^{kl}) \text{ as the intermediate function } H_2(i, j, a, b).$$

Substituting the partial derivative, expanding the expressions, we can obtain the explicit expression of the first term after eliminating the delta terms.

Making the contraction of two-electron integral with  $T_{ab}^{kl}, T_{ca}^{mi} \dots$  with the density matrices within the energy expression itself before having differentiation on it, we can rewrite the second term of the derivative of D1 after rearranging the order of sum in certain terms:

$$\begin{aligned} & \sum_{ijkl} \sum_{a,b} (ik|jl) \frac{\partial T_{ab}^{kl}}{\partial T_{ef}^{pq}} \sum_m \sum_c (T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{j\bar{c}}^{\bar{b}\bar{m}} \\ & \sum_{ij} \sum_{a,b} \sum_m \sum_c \frac{\partial (T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{j\bar{c}}^{\bar{b}\bar{m}}}{\partial T_{ef}^{pq}} \sum_{kl} (ik|jl) T_{ab}^{kl} \\ & \sum_{ijkl} \sum_{a,b} (ik|jl) \frac{\partial T_{ab}^{kl}}{\partial T_{ef}^{pq}} \sum_m \sum_c T_{ca}^{mi} d\eta_{j\bar{c}}^{\bar{b}\bar{m}} \\ & \sum_{ij} \sum_{a,b} \sum_m \sum_c \frac{\partial T_{ca}^{mi} d\eta_{j\bar{c}}^{\bar{b}\bar{m}}}{\partial T_{ef}^{pq}} \sum_{kl} (ik|jl) T_{ab}^{kl} \\ & \sum_{ijkl} \sum_{a,b} (ik|jl) \frac{\partial (-T_{ba}^{kl})}{\partial T_{ef}^{pq}} \sum_m \sum_c (-T_{ac}^{mi}) d\eta_{j\bar{c}}^{\bar{b}\bar{m}} \\ & \sum_{ij} \sum_{a,b} \sum_m \sum_c \frac{\partial (-T_{ac}^{mi}) d\eta_{j\bar{c}}^{\bar{b}\bar{m}}}{\partial T_{ef}^{pq}} \sum_{kl} (ik|jl) (-T_{ba}^{kl}) \end{aligned} \quad (3.163)$$

We can therefore define  $\sum_m \sum_c (T_{ca}^{mi} - T_{ac}^{mi}) d\eta_{j\bar{c}}^{\bar{b}\bar{m}}$  as the intermediate function  $H_3(i, a, j, b)$ ,  $\sum_{kl} (ik|jl) T_{ab}^{kl}$  as the intermediate function  $H_4(i, j, a, b)$ ,  $\sum_m \sum_c T_{ca}^{mi} d\eta_{j\bar{c}}^{\bar{b}\bar{m}}$  as the intermediate function  $H_5(i, a, j, b)$ ,  $\sum_m \sum_c (-T_{ac}^{mi}) d\eta_{j\bar{c}}^{\bar{b}\bar{m}}$  as the intermediate function  $H_6(i, a, j, b)$ ,  $\sum_{kl} (ik|jl) (-T_{ba}^{kl})$  as the intermediate function  $H_7(i, j, a, b)$ .

Expanding the derivatives of those products, substituting the partial derivatives of cluster amplitudes and density matrices with explicit expression, splitting the expression and eliminating the delta terms thereafter, we can obtain the final expression of the second term.

The final expression of the derivative of D1 which is that of the first term plus that of second term is,

$$\begin{aligned}
& \sum_{ij} \frac{1}{2} ((ip|jq) - (iq|jp)) H_1(i, e, j, f) \\
& - \sum_{ij} \frac{1}{2} ((ip|jq) - (iq|jp)) H_1(i, f, j, e) \\
& + \sum_{jb} d\eta_{j\bar{e}}^{\tilde{b}\bar{p}} H_2(q, j, f, b) - \sum_{jb} d\eta_{j\bar{f}}^{\tilde{b}\bar{p}} H_2(q, j, e, b) \\
& + \sum_i \sum_a \sum_m \sum_c (T_{ca}^{mi} - T_{ac}^{mi}) (2T_{cf}^{mq} - T_{fc}^{mq}) H_2(i, p, a, e) \\
& + \sum_{ij} \sum_{ab} (T_{ea}^{pi} - T_{ae}^{pi}) (2T_{bf}^{jq} - T_{fb}^{jq}) H_2(i, j, a, b) \\
& - \sum_i \sum_a \sum_m \sum_c (T_{ca}^{mi} - T_{ac}^{mi}) (T_{ce}^{mq} - T_{ec}^{mq}) H_2(i, p, a, f) \\
& - \sum_{ij} \sum_{ab} (T_{fa}^{pi} - T_{af}^{pi}) (T_{be}^{jq} - T_{eb}^{jq}) H_2(i, j, a, b) \\
& + \sum_j \sum_b d\eta_{j\bar{e}}^{\tilde{b}\bar{p}} H_2(q, j, f, b) \\
& + \sum_i \sum_a \sum_m \sum_c T_{ca}^{mi} (2T_{cf}^{mq} - T_{fc}^{mq}) H_2(i, p, a, e) \\
& + \sum_{ij} \sum_{ab} T_{ea}^{pi} (2T_{bf}^{jq} - T_{fb}^{jq}) H_2(i, j, a, b) \\
& - \sum_i \sum_a \sum_m \sum_c T_{ca}^{mi} T_{ce}^{mq} H_2(i, p, a, f) \\
& - \sum_{ij} \sum_{ab} T_{fa}^{pi} T_{be}^{jq} H_2(i, j, a, b)
\end{aligned}$$

$$\begin{aligned}
& + \sum_{ij} (ip|jq) H_3(i, e, j, f) \\
& + \sum_j \sum_b d\eta_{j\bar{e}}^{\bar{b}\bar{p}} H_4(q, j, f, b) - \sum_j \sum_b d\eta_{j\bar{f}}^{\bar{b}\bar{p}} H_4(q, j, e, b) \\
& + \sum_i \sum_a \sum_m \sum_c (T_{ca}^{mi} - T_{ac}^{mi}) (2T_{cf}^{mq} - T_{fc}^{mq}) H_4(i, p, a, e) \\
& \quad + \sum_{ij} \sum_{ab} (T_{ea}^{pi} - T_{ae}^{pi}) (2T_{bf}^{jq} - T_{fb}^{jq}) H_4(i, j, a, b) \\
& \quad - \sum_i \sum_a \sum_m \sum_c (T_{ca}^{mi} - T_{ac}^{mi}) T_{ce}^{mq} H_4(i, p, a, f) \\
& \quad \quad - \sum_{ij} \sum_{ab} (T_{fa}^{pi} - T_{af}^{pi}) T_{be}^{jq} H_4(i, j, a, b) \\
& \quad + \sum_{ij} (ip|jq) H_5(i, e, j, f) \\
& \quad + \sum_j \sum_b d\eta_{j\bar{e}}^{\bar{b}\bar{p}} H_4(q, j, f, b) \\
& + \sum_i \sum_a \sum_m \sum_c T_{ca}^{mi} (2T_{cf}^{mq} - T_{fc}^{mq}) H_4(i, p, a, e) \\
& \quad + \sum_{ij} \sum_{ab} T_{ea}^{pi} (2T_{bf}^{jq} - T_{fb}^{jq}) H_4(i, j, a, b) \\
& - \sum_i \sum_a \sum_m \sum_c T_{ca}^{mi} (T_{ce}^{mq} - T_{ec}^{mq}) H_4(i, p, a, f) \\
& \quad - \sum_{ij} \sum_{ab} T_{fa}^{pi} (T_{be}^{jq} - T_{eb}^{jq}) H_4(i, j, a, b) \\
& \quad - \sum_{ij} (ip|jq) H_6(i, f, j, e) \\
& \quad - \sum_j \sum_b d\eta_{j\bar{f}}^{\bar{b}\bar{p}} H_7(q, j, e, b) \\
& + \sum_i \sum_a \sum_m \sum_c (-T_{ac}^{mi}) T_{ec}^{mq} H_7(i, p, a, f) \\
& \quad + \sum_{ij} \sum_{ab} (-T_{af}^{pi}) T_{eb}^{jq} H_7(i, j, a, b) \tag{3.164}
\end{aligned}$$

The mathematical expression of D2 is equal to D1 and therefore their residual are same.

# Chapter 4

## Calculations and Discussions

### 4.1 the test of the method

#### 4.1.1 Extensivity and Exactness

The current Quasi-Variational Coupled Cluster Doubles(QVCCD) method possesses rigorous extensivity which means the energy scales correctly with respect to the system size. The improved method of my project therefore must keep this important methodological property.

The energy of single Helium atom and double ones separated infinitely are calculated using improved method with cc-pVDZ basis set:

	Energy
single Helium atom	-2.8876 Hartree
double Helium atoms separated 100 Angstrom	-5.7752 Hartree

where the double energy is two times as large as the single one.

H<sub>2</sub> containing only one occupied orbital is similar to the He atom, the energy of which is calculated compared with that of two H<sub>2</sub> separated infinitely using improved method,

	Energy
the energy of H <sub>2</sub> with cc-pVDZ basis set	-0.9260 Hartree
the energy of two H <sub>2</sub> separated 100 Angstrom	-1.8519 Hartree

the double relationship in which ensures the extensivity.

The current QVCCD method also possesses exactness at the limitation of 2 electrons or 2 holes, the energy at which agrees with that of Configuration Interaction Doubles(CID). The additional terms of my project to the current energy functional should therefore vanish on their own as designed at the

index 1	index 2	index 3	numerical derivative	analytic derivative
1	1	1	3.903E-004	3.903E-004
2	2	17	3.611E-004	3.611E-004
1	1	4	-5.698E-005	-5.698E-005
2	2	20	9.874E-005	9.874E-005
2	1	33	6.272E-004	6.272E-004

Table 4.1: the numerical differentiation test of M2 term on di-Helium molecule, where  $aE - b$  is the way number  $a * 10^{-b}$  presented in Fortran program output

very beginning. As derived in last chapter, because of the equivalence in  $\alpha$  term, it becomes,

$$\alpha = B1 + D1 + M2 + 2M3$$

The two-electron limitation of B1 term is,  $-2\langle e\bar{e}||e\bar{e}\rangle\langle\hat{T}_2^\dagger\hat{T}_2\rangle\langle\hat{T}_2^\dagger\hat{T}_2\rangle$  which is same as that of B2, that of M3 is  $+\langle e\bar{e}||e\bar{e}\rangle\langle\hat{T}_2^\dagger\hat{T}_2\rangle\langle\hat{T}_2^\dagger\hat{T}_2\rangle$ . The limitation of  $B1 + 2M3$ , which is part of the additional  $\alpha$  term, is 0.

The two-electron limitation of D1 term is expressed as,  $+\langle e\bar{e}||e\bar{e}\rangle a\eta_b^a a\eta_a^b$  which is same as that of D2, that of M2 is  $-\langle e\bar{e}||e\bar{e}\rangle a\eta_b^a a\eta_a^b$ . The limitation of  $D1 + M2$  which is the rest part of  $\alpha$  is therefore 0[48].

The initial value of those energy diagrams is calculated using improved method,

$$E_{B1} + 2E_{M3} = 0$$

$$E_{D1} + E_{M2} = 0$$

which ensures the exactness of the improved method.

#### 4.1.2 the numerical differentiation test

Every term in the energy expression,  $M_2, M_3, B_1$  and  $D_1$  are successfully tested by means of the numerical differentiation described in last Chapter.

In Table 4.1, the index 1 is the first occupied orbital  $i$  in the cluster amplitude  $T_{ab}^{ij}$  with respect to which the partial derivative is found, and the index 2 is the second occupied orbital  $j$ . The index 3 is the composed index made from the occupied ones  $i, j$  and virtual ones  $a, b$ , which uniquely relates to a cluster amplitude. As shown in the Table, the numerical derivative agree with the analytical one.

$N_2$  is a much larger molecule than  $He_2$ , in which hundreds of combinations

index 1	index 2	index 3	numerical derivative	analytic derivative
1	1	1	-1.431E-004	-1.431E-004
2	1	78	2.186E-004	2.186E-004
2	2	155	-7.168E-005	-7.168E-005
3	3	232	-2.261E-004	-2.261E-004
4	4	309	-2.261E-004	-2.261E-004

Table 4.2: the numerical differentiation test of M3 term on di-Nitrogen molecule, where  $aE - b$  is the way number  $a * 10^{-b}$  presented in Fortran program output

composed index	numerical derivative	analytic one	difference
1	1.739E-004	1.739E-004	-4.342E-016
78	3.080E-004	3.080E-004	5.616E-017
155	1.055E-003	1.055E-003	-1.064E-015
232	2.136E-004	2.136E-004	4.235E-016
309	2.136E-004	2.136E-004	-2.470E-016

Table 4.3: the numerical differentiation test of B1 term on di-Nitrogen molecule, where  $aE - b$  is the way number  $a * 10^{-b}$  presented in Fortran program output

of four indices  $i, j$  and  $a, b$  are possible. It means that there are hundreds of partial derivatives carried out by the software. Some of these combinations are symmetric to each other, ie the orbitals are degenerate, for example, the cluster amplitudes demonstrated in the last two rows of Table 4.2, with respect to which the partial derivatives are same.

Table 4.3 is the partial derivative of B1 term with respect to the cluster amplitudes in  $N_2$  molecule. As introduced in the last Chapter, because the numerical differentiation is not mathematical due to the incomplete storage of cluster amplitudes, the analytical result has to be transformed in order to compare with the numerical one that is considered to be the benchmark. The transformed results  $\frac{\partial E}{\partial T_{ab}^{ij}} + \frac{\partial E}{\partial T_{ba}^{ji}}$  ( $i > j$ ) agree with the numerical ones.

Table 4.4 is the comparison on D1 term using  $CO_2$  molecule, which is a larger system than  $N_2$ . As expected in the last Chapter, the error is reduced to the fourth power of the stepsize which is at  $1 * 10^{-16}$  level. The difference presented in the Tables listed are all around this level.

composed index	numerical derivative	analytic one	difference
1	-1.932E-004	-1.932E-004	-3.433E-015
180	1.864E-004	1.864E-004	6.392E-015
359	-1.492E-004	-1.492E-004	-1.684E-016
538	-3.335E-005	-3.335E-005	7.976E-016
717	-3.335E-005	-3.335E-005	-1.921E-015

Table 4.4: the numerical differentiation test of D1 term on Carbon di-Oxide molecule, where  $aE - b$  is the way number  $a * 10^{-b}$  presented in Fortran program output

### 4.1.3 energy variation test on QVCCD method

When the program converges, the energy of the molecule, as a function with respect to cluster amplitudes, reaches minimum. The energy is therefore numerically tested by being varied in its neighbour area to see whether it is the minimum.

When a cluster amplitude is selected and varied a small amount, the energy changed as a result should be higher than the equilibrium one because the latter is expected to be the local minimum.

In the experiment, the special cluster amplitudes representing  $T_{aa}^{ii}, T_{ab}^{ii}, T_{ab}^{ij}, T_{aa}^{ij}$  ( $i \neq j, a \neq b$ ) are selected, and a tiny amount is at first added then subtracted from them, the energy changed are demonstrated as a variable with respect to the varying cluster amplitudes. As shown in the Figure 4.1.3, Figure 4.2, Figure 4.3, the energies with respect to  $T_{aa}^{ii}, T_{ab}^{ij}, T_{aa}^{ij}$  ( $i \neq j, a \neq b$ ) are all satisfactorily demonstrating themselves to be the minimum. Although there is certain degree  $T_{ab}^{ii}$  ( $a \neq b$ ) in which the result is not the expected quadratic plot shape(Figure 4.1.3), it can due to the nature defect in Molpro, or simply because they are not dominant in magnitude.

## 4.2 spectroscopic constants of small molecules

Certain calculations have been done to re-estimate the performance of the methods on the equilibrium bond length and vibrational frequency of small molecules, based on the existing work introduced in Table 2.1 in Chapter 2 section 6.

The experiment was done using the diatomic molecule curve fit command in Molpro, which took a couple of points on the  $N_2$  potential energy curve

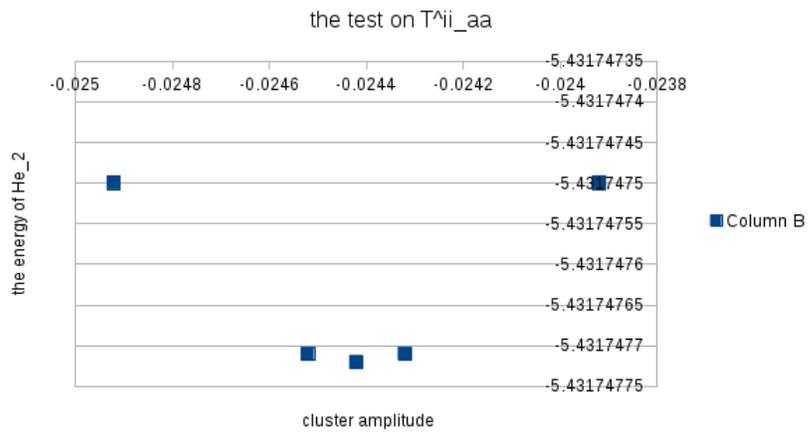


Figure 4.1: the energy variation test on He<sub>2</sub>, the unit of the energy is Hartree, the equilibrium energy is -5.43174772

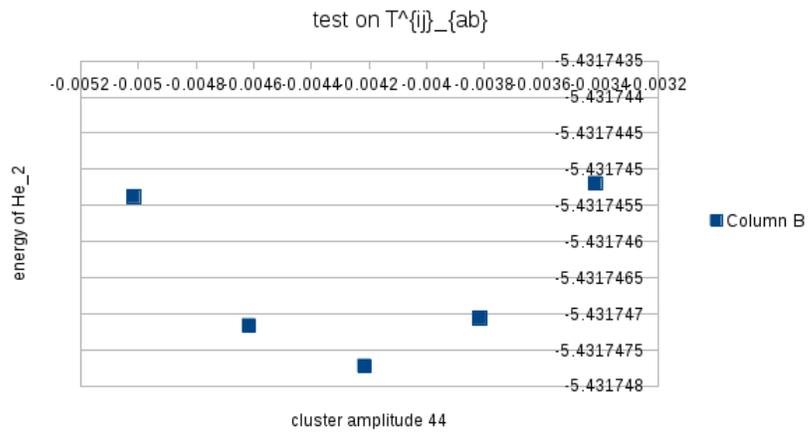


Figure 4.2: the energy variation test on He<sub>2</sub>, the unit of the energy is Hartree, the equilibrium energy is -5.43174772

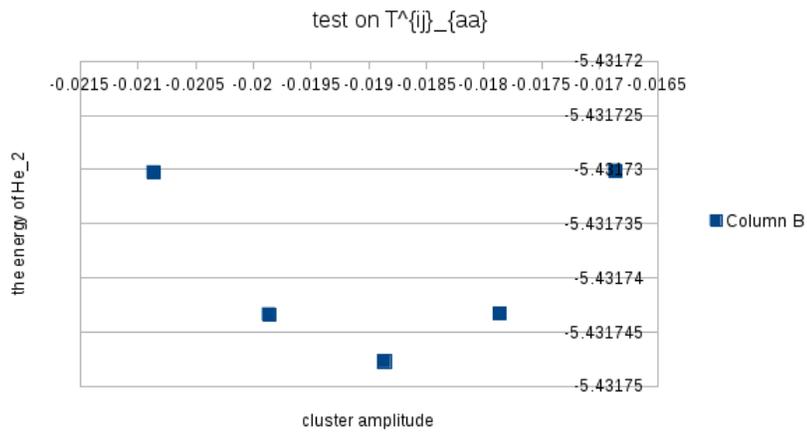


Figure 4.3: the energy variation test on He<sub>2</sub>, the unit of the energy is Hartree, the equilibrium energy is -5.43174772

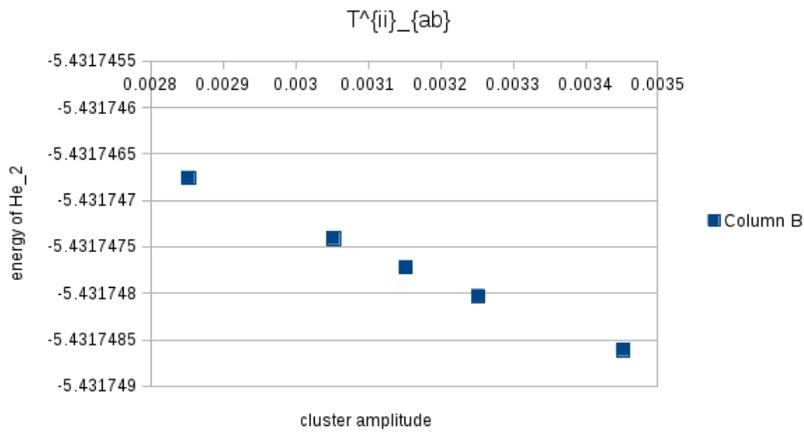


Figure 4.4: the energy variation test on He<sub>2</sub>, the unit of the energy is Hartree, the equilibrium energy is -5.43174772

N <sub>2</sub>	way of extrapolation	vibrational frequency
CCSD(T)	VTZ-VQZ extrapolation	2364.72
	VQZ-V5Z extrapolation	2363.08
	V5Z-V6Z extrapolation	2361.94
OQVCCD(T)	VTZ-VQZ extrapolation	2382.05
	VQZ-V5Z extrapolation	2379.93
	V5Z-V6Z extrapolation	2379.28
QVCCD	VTZ-VQZ extrapolation	2475.67
	VQZ-V5Z extrapolation	2473.79
	V5Z-V6Z extrapolation	2472.73
improved QVCCD	VTZ-VQZ extrapolation	2457.74
improved OQVCCD	VQZ-V5Z extrapolation	2444.75
improved OQVCCD(T)	V5Z-V6Z extrapolation	2364.37
F <sub>2</sub>	way of extrapolation	vibrational frequency
		(equilibrium bond length)
QVCCD	VTZ-VQZ extrapolation	1058.35(1.3794)
OQVCCD	VTZ-VQZ extrapolation	1030.06(1.3862)
OQVCCD(T)	VTZ-VQZ extrapolation	938.86(1.4082)
improved QVCCD	VTZ-VQZ extrapolation	1022.14(1.3866)
improved OQVCCD	VTZ-VQZ extrapolation	990.48(1.3944)
improved OQVCCD(T)	VTZ-VQZ extrapolation	889.63(1.4189)

Table 4.5: the calculation on N<sub>2</sub> and F<sub>2</sub>, the unit of the vibrational frequency is  $cm^{-1}$

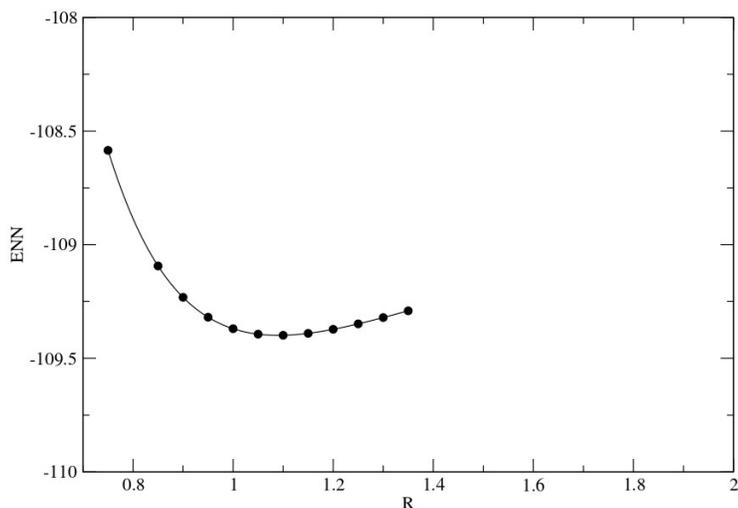


Figure 4.5: the points selected on the  $N_2$  potential energy curve used to estimate the diatomic molecule property

and works out the vibrational frequency and other molecular property (such as equilibrium bond length, energy) automatically, as demonstrated in Figure 4.5. The  $T^4$  terms improved the current QVCCD method in a magnitude expected, which is shown in the Table 4.5. The calculation is also done on the  $F_2$ . The improved magnitude should reflect its accuracy [79].

## 4.3 the prospective work to the project

### 4.3.1 the defect in current QVCCD with $T^4$ program

#### the reverse ordered residual

As described in subsection 3.5.3, the  $T^4$  terms are built onto the QVCCD platform containing disaster remained. The gradient stored are in reverse order to the convention in Molpro, which left enormous implicit effect in the running of the rest of the program. For example, in the DIIS extrapolation, the residual made of gradient are used to form the corresponding vector

$\vec{V}$ [50],

$$\vec{V} = \sum_n \lambda_n \vec{V}^{(n)} \quad (4.1)$$

where  $\lambda_n$  are determined by minimizing

$$\vec{V}^\dagger \vec{V} = \sum_{i \geq j} \text{tr}(\vec{V}^{ij\dagger} \vec{V}^{ij}) + \sum_i (\vec{v}^{i\dagger} \vec{v}^i) \quad (4.2)$$

with restriction

$$\sum_n \lambda_n = 1 \quad (4.3)$$

Noone can guarantee that the reverse ordered residual  $\vec{V}^{(n)}$  will not make any difference.

### the simple inclusion of D2 and B2 term

The D2 and B2 terms described in Chapter 3 do not have the full partial derivative expression developed, because their energy values are same as D1 and B1. Therefore, they are simply replaced by timing a factor of 2 in front of D1 and B1 terms in both the energy and partial derivative expressions. However, it can be seen from their expressions that the partial derivative with respect to the cluster amplitudes are not equal to D1 and B1 although their energy values are proved to be same. As a result, simply times a factor of 2 on the partial derivative of D1 and B1 would be less mathematically ideal.

It can ensure the partial derivative to be purely mathematical if the factor of 2 is not imposed, but the D2 and B2 terms would be totally neglected. Therefore, the full expression of D2 and B2 can be explored in the next project.

### 4.3.2 the reduction of computational cost

The current program implements the working equation in a normal way of programming design. It implements the product of two matrices which is a special form of multi-variable functions, for example  $\sum_k \sum_c T_{ac}^{ik} T_{bc}^{jk}$ , in a

multiple embedded loop:

```
DO i=1,N
  DO j=1,N
    DO a=1,v
      DO b=1,v
        DO c=1,v
          DO k=1,N
             $sum = T_{ac}^{ik} T_{bc}^{jk}$ 
          ENDDO
        ENDDO
      ENDDO
    ENDDO
  ENDDO
ENDDO
```

(4.4)

where  $N$  is the number of electrons and  $v$  is the number of virtual orbitals in the system. It is nearly the most efficient algorithm on its own. Because the execution of each variable needs at least one unit of time, if each loop is iterated  $N$  times, the 6-fold loop would be executed  $N^6$  times, which is generally of lowest complexity in whatever way it is implemented.

As far as I have heard, when the number  $N$  that each loop is iterated is a large number, for example 1000 or 10000, there is certain CPU branch prediction algorithm which relates to the miss rate calculation of memory cache[80, 81, 82]. It is of lower computational cost but far beyond basic way of software implementation, which requires the association of hardware as well.

There is internal subroutine stored in Molpro that does such matrix multiplication in a more efficient way instead of using normal multiple loops, which will greatly reduce the computational cost.

The current program involving  $T^4$  terms runs slowly and is only applicable for small molecules, therefore, it is quite urgent that the code needs to be updated using such intrinsic subroutines in Molpro.

### 4.3.3 the orbital optimized version of the QVCCD method involving $T^4$ term

The current QVCCD method has the version containing orbital optimized, which is described in Chapter 2. Now that the  $T^4$  terms are ready to QVCCD method, the orbital optimized version is what needs to be developed at the next stage. In fact, the current QVCCD method with  $T^4$  terms can already run with the optimized orbital input from the current OQVCCD method, which is also an effective way of including optimized orbitals just using the existing developed methods.

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