RICE UNIVERSITY

Inclusion of Triples Correction in the Coupled Cluster Method

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF ARTS

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June, 2002
ABSTRACT

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The Coupled Cluster theory has proven itself as an effective method for the accurate calculations of correlation energy. A computational program for the full coupled-cluster model (CCSDT) single, double and triple excitation method has been integrated into the Gaussian program. This interface is based on original code that had been developed in late 80’s. Single point energy calculations for the HF and OH⁻ molecules verify the accuracy and stability of the newly developed code compared to the old one. Research on the potential energy curve of the MnO₄⁻ anion has been conducted. Energy calculations for various Mn – O bond lengths using Hartree-Fock, MP2, MP3, MP4(SDQ), CCSD(T), B3LYP, VSXC, PBE and CCSDT method exist. The CCSDT result is in excellent agreement with the experimental value of the Mn – O bond length.
Acknowledgments

I am very thankful to my advisor Professor Gustavo E. Scuseria for helping me to understand first of all the basics of coupled cluster theory and secondly his coupled cluster program. Thank you also to Dr. Phillipe Ayala for explaining to me how to retrieve the double bar integral values from Gaussian 99 and the rest members of Dr. Scuseria's group for their helpful discussions.
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Chapter 1
Introduction

One of the biggest challenges in quantum chemistry is the qualitative and quantitative understanding of chemical bonding, which is the description of interactions between or within chemical systems. This challenge is due to complexity that exists in nature (different types of bonds) and makes very difficult the use of a single unique mathematical formula. If we consider a simple diatomic molecular system, its atoms contain electrons which interact and form a chemical bond. Quantum mechanics can provide us the appropriate mathematical tools to describe the behavior of these electrons which in many cases answer fundamental questions in chemical problems.

A fundamental equation is the time-independent Schrödinger equation [1]:

\[ H\Psi = E\Psi \]  \hspace{1cm} (1.1)

where \( H \) corresponds to the Hamiltonian operator, \( \Psi \) is the wavefunction and \( E \) is the total energy of the system. A simple form of the Hamiltonian operator for the case of a \( n \)-electron atom is expressed as:

\[ H = -\frac{\hbar}{2m_e} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Ze_i^2}{r_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{e^2}{r_{ij}} \]  \hspace{1cm} (1.2)

The first term is the kinetic-energy operator for the \( n \) electrons, the second term represents the potential energy for the attractions between the electrons and the nucleus and the third term is the potential energy for the interelectronic repulsions. Because
of the last term, the Schrödinger equation is not separable and the exact wave function cannot be written as the product of \( n \) one-electron functions. Thus, we cannot find exact, analytical solutions. For this reason, many approximation methods have been developed that elaborate the interelectronic repulsion from different perspectives.

Among the different approximation methods, we can find Hartree-Fock [16], Many Body Perturbation Theory [17–25], Configuration Interaction [29, 30], Density Functional Theory [31–34, 38] and the Coupled Cluster method [26–28]. Each of these uses a different approach to the problem of solving the Schrödinger equation.

This thesis deals with the inclusion of the triples correction in the coupled cluster method (CCSDT). This is done by modifying a program (Fcceg) that was developed in the 1980s which calculates the triples correction. Those modifications will allow us to include it in the Gaussian program. Gaussian is one of the most popular quantum chemistry programs and is widely used. We can divide the whole project in four parts: a) understand the coupled cluster theory and the old code, b) modify the old code and link it to Gaussian, c) verify the accuracy and stability of the linked code and d) use the CCSDT method to explore the potential energy curve of the \( MnO_4^- \) anion.

1.1 Motivation and Scope of the Thesis

The original code for CCSDT was developed almost 15 years ago [10, 11] and is an independent module that has its own format of input and output data. Our idea
was to transform this code by modifying certain parts, so that it can be included in Gaussian. Gaussian can carry out calculations up to the CCSD(T) level which doesn't include all the terms for the full triple correction. The benefit of this project would be that the CCSDT method will be available to many people that already use Gaussian.

Furthermore, in Fceg no more that 256 basis functions can be used. This is because of the molecular integrals that are saved using a specific algorithm. By removing this constraint the new code will be more dynamic since it will be able to be used for bigger molecules or for larger, more efficient basis sets.

Also, by using the simple user interface of Gaussian, we can give flexibility to the old program concerning the format of the input data (basis sets are already stored in Gaussian, using graphical interface (GaussView), changing units etc.).

After the interface has been completed, the next logical step will be to test its accuracy, efficiency and stability by using molecular systems for which result from the old program already exist.

Finally, the CCSDT method will be used for calculations of the potential energy of $MnO_4^-$ anion. Comparison with other methods will follow. Our preliminary calculations have shown that CCSD(T) fails to predict the correct equilibrium bond length between manganese and oxygen atoms which should be corrected with the inclusion of the full triples model (CCSDT).
1.2 Hartree-Fock method

The first approach to the problem of interacting electrons is the one that was introduced by Hartree [2], Fock [3] and Slater [4] who treated the electrons as independent particles and introduced the idea of the Self-Consistent Field (SCF). The self-consistent field is the interaction field that an electron experiences, if we consider a spatial average over the positions of all other electrons.

For the case of closed-shell orthogonal Hartree-Fock, the molecular orbitals must satisfy the equation:

\[ F \phi_i = \varepsilon_i \phi_i \]  \hspace{1cm} (1.3)

where \( F \) is the Fock operator that acts on \( \phi_i \) spatial orbitals to return the one-electron orbital energy \( \varepsilon_i \). The Hartree-Fock (HF) method is a variational method because it looks for those orbitals \( \phi_i \) that minimize the Hartree-Fock energy, \( E_{HF} \). In order to calculate the average potential for an electron, we need to know the wavefunction for all the other electrons.

The calculation is started by guessing the form of the wavefunctions and for a certain electron, we solve the Schrödinger equation. The resulting wavefunction is used to calculate the potential experienced by one of the other electrons. The Schrödinger equation is solved again and the new wavefunction is used to refine the potential experienced by another electron. We repeat this process for every electron and at the end we recalculate the potential experienced by the first electron. The whole cycle is
repeated until the solutions we get don’t change in a cycle of calculation and thus, the computed orbitals are self-consistent.

1.3 Importance of Correlation Energy

The results of Hartree-Fock method are in error of 0.5% to 1% which in absolute values is not big but in terms of chemical accuracy is very large. The main problem with the Hartree-Fock method is that it treats the interaction between electrons in an average way. Specifically, Hartree-Fock wavefunctions do not contain $r_{ij}$ explicitly, they are not very sensitive to electron repulsion for small $r_{ij}$ and they don’t describe how electrons correlate their motion in order to avoid each other as much as possible. When we refer to electron correlation, we mean that the motion of each electron is correlated to the motion of the others. The correlation energy is the difference between the exact energy and the Hartree-Fock energy.

Usually, correlation energy represents 1% of the Hartree-Fock energy and as was mentioned before in order to achieve chemical accuracy, we will have to calculate correlation energy in a more accurate way.

1.4 Beyond Hartree-Fock limit

In order to recover more correlation energy, higher level methods have been developed. In many body perturbation theory (MBPT), we express the real hamiltonian as a summation of the hamiltonian of a simpler system and a hamiltonian representing a
perturbation. In configuration interaction (CI), we use configuration state functions, which are linear combination of Slater determinants and correspond to different orbital occupancies. In density functional theory (DFT), we express the wavefunction in terms of electron density $\rho$. In coupled cluster method (CC), we use the exponential ansatz to express the wavefunction. We truncate the Hamiltonian to the desired level depending on what kind of excitations we want to include.

In the next chapters, we will thoroughly discuss the coupled cluster method and specifically show how the triples correction has been implemented.
Chapter 2
Coupled Cluster Method

2.1 General Remarks

The Coupled-Cluster was first introduced by Cizek [5] as the Coupled Pair Many-Electron Theory (CPMET). Later on, algebraic equations for CCD were developed. CC became more popular in mid-70s where the spin-orbital CCD was derived [6]. After that, efficient algorithms were implemented and the different CC methods have moved to the mainstream of quantum chemistry.

2.2 The Exponential Ansatz

Traditional coupled-cluster theory begins with the expression of wavefunction according to the exponential ansatz,

$$\Psi_{CC} = e^T \Phi_0$$

(2.1)

where $$\Phi_0 = |0\rangle$$ is a single determinant based on the independent particle model (usually it is a Hartree-Fock determinant). The cluster operator is

$$T = T_1 + T_2 + T_3 + ...$$

(2.2)

where

$$T_n = \frac{1}{(n!)^2} \sum_{\alpha \beta \gamma \delta \cdots \mu \nu \cdots} t_{\alpha \beta \gamma \delta \cdots \mu \nu \cdots}^{\alpha \beta \gamma \delta \cdots} \{A^\dagger B^\dagger J C^\dagger K \cdots\}$$

(2.3)

where the i, j, k, ... and I, J, K, ... indices refer to spin orbital and operator labels, respectively, for occupied orbitals in $$\Phi_0$$, while a, b, c, ... and A, B, C, ... correspond
to orbitals and operator labels for unoccupied (virtual) orbitals in $\phi_0$. Also, $A^\dagger_p$ is a creation operator which by its action on a Slater determinant produces one more column (orbital) and one more row (electron) in the new determinant:

$$A^\dagger_p|\phi_0 \ldots \phi_s\rangle = |\phi_p \phi_0 \ldots \phi_s\rangle,$$
(2.4)

and $I$ is an annihilation operator which removes a column and a row from a Slater determinant:

$$I_p|\phi_p \phi_0 \ldots \phi_s\rangle = |\phi_0 \ldots \phi_s\rangle,$$
(2.5)

The $t_{ij\ldots}^{abc\ldots}$ quantities are the cluster coefficients whose specific values are determined via the electronic Schrödinger equation.

Each $T_i$ operator corresponds to the $i$th excitation, for example the $T_2$ operator refers to the 2nd excitations. We have to keep in mind that all orbitals are orthonormal and the normal ordering of the operators is denoted by $\{\}$.

If we expand the 2.2 equation in a power series, we obtain

$$e^T = 1 + T_1 + T_2 + T_3 + \ldots + \frac{1}{2!} T_1^2 + \frac{1}{3!} T_1 T_2 + \frac{1}{4!} T_1^3 + \frac{1}{2!} T_2^2 + T_1 T_3 + \frac{1}{2!} T_2^3 + \ldots$$
(2.6)

and we also know that

$$T_1 = \sum_A \sum_I t_A^I X_A^\dagger X_I,$$
(2.7)

and

$$T_2 = \sum_{A>B} \sum_{I>J} t_{ij}^{AB} X_B^\dagger X_J X_A^\dagger X_I$$
(2.8)

so

$$T_2^2 = \sum_{I>J} \sum_{K>L} \sum_{A>B} \sum_{C>D} t_{ij}^{AB} t_{kl}^{CD} X_B^\dagger X_J X_A^\dagger X_I X_D^\dagger X_L^\dagger X_C^\dagger X_K$$
(2.9)
where $X_A^\dagger$ is a creation operator and $X_i$ is annihilation operator. The $t_i^A$ and $t_{ij}^{AB}$ are the unknown cluster amplitudes.

Finally, we can re-write Equation 2.1

$$
\Psi_{CC} = (1 + T_1 + T_2 + T_3 \cdots + \frac{1}{2!} T_1^2 + T_1 T_2 + \frac{1}{3!} T_1^3 + \frac{1}{4!} T_1^4 + \frac{1}{2!} T_1^2 T_2 + T_1 T_3 + \frac{1}{2!} T_2^2 \cdots) \Phi_0
$$

(2.10)

The exponential ansatz is one of the main equations of coupled cluster theory. The exponentiated cluster operator when applied to the reference determinant, produces a new wavefunction containing cluster functions, each of which correlates the motion of electrons within specific orbitals. If $T$ includes contributions from all possible orbital groupings for the N-electron system (that is, $T_1$, $T_2$, ..., $T_N$), then the exact wavefunction within the given one-electron basis may be obtained from the reference function. The cluster operators are frequently referred to as excitation operators, since the determinants they produce resemble excited states in Hartree-Fock theory. Truncation of the cluster operator at specific excitation levels leads to different coupled cluster techniques: CCSD, CCSDT, CCSDTQ etc., where "S", "D", "T" and "Q" indicate that single, double, triple and quadruple excitations, respectively, are included in the wavefunction expansion.

In order to determine the coupled cluster coefficients, we will use the exponential ansatz described above to find the desired set of coupled cluster equations. Substituting Equation 2.1 into 1.1 derives

$$
He^T |\Phi_0\rangle = Ee^T |\Phi_0\rangle
$$

(2.11)
and by projecting onto $\Phi_0$, we obtain an expression for the energy,

$$\langle \Phi_0 | H e^T | \Phi_0 \rangle = E \langle \Phi_0 | e^T \Phi_0 \rangle \quad \text{(2.12)}$$

We have assumed the normalization $\langle \Phi_0 | \Psi_{CC} \rangle = 1$. One more expression can be obtained by left-projecting the Schrödinger equation by the excited determinants produced by the action of the cluster operator on the reference,

$$\langle \Phi_{i,j,...}^a | H e^T | \Phi_0 \rangle = E \langle \Phi_{i,j,...}^a | e^T | \Phi_0 \rangle \quad \text{(2.13)}$$

where $\Phi_{i,j,...}^a$ represents an excited determinant in which orbitals $\phi_i$, $\phi_j$ have been replaced with orbitals $\phi_a$, $\phi_b$.

Equations 2.12 and 2.13 represent the set of non-linear equations that must be solved in order to calculate the coupled cluster amplitudes. There are many formulations that have been developed in order to get the coupled cluster non-linear equations. We will focus on that which uses the Hausdorff theorem.

### 2.3 Hausdorff Theorem

The CC equations derived previously can’t be used for practical computer implementation. One must first transform these expressions in terms of the one- and two-electron integrals as well as the cluster amplitudes. In order to do that we have to use the Hausdorff Theorem. First, we will use the Schrödinger equation

$$H e^T \Psi_0 = E e^T \Psi_0 \quad \text{(2.14)}$$

and we multiply on the left by $e^{-T}$. Thus, we obtain

$$e^{-T} H e^T \Psi_0 = E \Psi_0 \quad \text{(2.15)}$$
The next step would be to use the Hausdorff commutator expansion:
\[ e^A Be^{-A} = B + [A, B] + \frac{1}{2!} [A, [A, B]] + \cdots \]  \hfill (2.16)

The excitation operator \( X^+_A X_I \) commutes with the operator \( T \) but the general creation/annihilation operator product \( X^+_P X_Q \) does not so \( H \) doesn’t commute with \( T \).

We can also see that
\[ X^+_P X_Q X^+_A X_I = \delta_{AQ} X^+_P X_I - X^+_P X^+_A X_Q X_I \]
\[ = \delta_{AQ} X^+_P X_I - X^+_A X^+_P X_I X_Q \]
\[ = \delta_{AQ} X^+_P X_I - \delta_{PI} X^+_A X_Q + X^+_A X_I X^+_P X_Q \]  \hfill (2.17)

thus,
\[ [X^+_P X_Q, X^+_A X_I] = \delta_{AQ} X^+_P X_I - \delta_{PI} X^+_A X_Q \]  \hfill (2.18)

where \( \delta_{AQ} \) and \( \delta_{IP} \) are Kronecker delta functions. So, we can rewrite \( H \) as
\[ H = \sum_{PQ} \langle P|H|Q \rangle X^+_P X_Q + \sum_{PQRS} \langle PR|QS \rangle X^+_P X^+_Q X_S X_R \]  \hfill (2.19)

and the \( P, Q, R, S \) creation and annihilation operators will be eliminated. The only operators that will remain are those like \( X^+_A X_I \), that commute with \( T \). Thus, the Hausdorff expansion is given from the below equation
\[ e^T H e^{-T} \Psi_0 = H + [H, T] + \frac{1}{2} [[H, T], T] + \frac{1}{3!} [[[H, T], T], T] + \frac{1}{4!} [[[[[H, T], T], T], T], T] \]  \hfill (2.20)

The next step will be to project onto a basis of functions (usually a Hartree-Fock) where excited configurations are produced by the excitations operators in \( T \). If we suppose that \( \Psi_{ABC \ldots} \) is an arbitrary excited configuration, then by using 2.20, we get
\[ \langle \Psi_0 | H + [H, T] + \frac{1}{2} [[H, T], T] + \frac{1}{3!} [[[H, T], T], T] + \frac{1}{4!} [[[[[H, T], T], T], T], T]| \Psi_0 \rangle = E \]  \hfill (2.21)
and
\[
\langle \Psi_{IJK,\ldots}^{ABC,\ldots} | H + [H, T] + \frac{1}{2} [[H, T], T] + \\
\frac{1}{3!} [[[H, T], T], T] + \frac{1}{4!} [[[H, T], T], T], T] \rangle | \Psi_0 \rangle = 0
\]  \tag{2.22}
for every $IJK \ldots$ and $ABC \ldots$

Using the truncated Hausdorff expansion, we may obtain analytic expressions for the commutators and insert these into the coupled cluster energy and amplitude equations 2.21 and 2.22. However, this is only the first step in obtaining expressions which may be efficiently implemented on the computer. We must next choose a truncation of $T$ and then derive expressions containing only one- and two-electron integrals and cluster amplitudes.

We define an operator
\[
D_n T_n = [Ee^T]_c
\]  \tag{2.23}
where the subscript $c$ denotes that only "connected terms" will be included [28]. The normal ordered Hamiltonian will be expressed as
\[
H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle = \sum_{p,q} f_{pq} \{ p^T q \} + \frac{1}{2!} \sum_{p,q,r,s} \langle pq || rs \} \{ p^T q^T r s \} = F_N + W_N \tag{2.24}
\]

If we suppose that $T = T_1 + T_2$ then
\[
D_1 T_1 = WT_1 + WT_2 + WT_1 T_2 + \frac{1}{2} WT_1^2 + \frac{1}{3!} WT_1^3
\]  \tag{2.25}
\[
D_2 T_2 = W + WT_1 + WT_2 + \frac{1}{2} WT_2^2 + WT_1 T_2 + \\
\frac{1}{2} WT_1^2 T_2 + \frac{1}{2} WT_1^2 + \frac{1}{3!} WT_1^3 + \frac{1}{4!} WT_1^4
\]  \tag{2.26}
and we can find the correlation energy by the equation
\[
\epsilon_{CCSD} = \langle \Psi_0 | W \left( \frac{1}{2} T_1^2 + T_2 \right) | \Psi_0 \rangle
\]  \tag{2.27}
We will use only connected contributions in the expansion $W e^{T_1+T_2}$. If we expand
the previous two equations, we will have
\[
(\epsilon_I - \epsilon_A) = \langle \Psi_I^A | W T_1 | \Psi_0 \rangle + \langle \Psi_I^A | W T_2 | \Psi_0 \rangle + \langle \Psi_I^A | W T_1 T_2 | \Psi_0 \rangle + \langle \Psi_I^A | \frac{1}{2} W T_1^2 | \Psi_0 \rangle + \langle \Psi_I^A | \frac{1}{3!} W T_1^3 | \Psi_0 \rangle
\] (2.28)
and
\[
(\epsilon_I + \epsilon_J - \epsilon_A - \epsilon_B) t^{AB}_{IJ} = \langle \Psi_{IJ}^{AB} | W | \Psi_0 \rangle + \langle \Psi_{IJ}^{AB} | W T_1 | \Psi_0 \rangle + \langle \Psi_{IJ}^{AB} | \frac{1}{2} W T_2 | \Psi_0 \rangle + \langle \Psi_{IJ}^{AB} | \frac{1}{2} W T_1 T_2 | \Psi_0 \rangle + \langle \Psi_{IJ}^{AB} | \frac{1}{2} W T_1^2 | \Psi_0 \rangle + \langle \Psi_{IJ}^{AB} | \frac{1}{3!} W T_1^3 | \Psi_0 \rangle
\] (2.29)

The next step will be to expand the terms of the above equation with respect to
the coupled cluster coefficients as shown in the example below:
\[
\langle \Psi_{IJ}^{AB} | W T_2 | \Psi_0 \rangle = \sum_{K>L} \sum_{C>D} \langle \Psi_{IJ}^{AB} | W | \Psi_{KL}^{CD} \rangle t^{CD}_{KL}
\] (2.30)

From the Slater-Condon rules we can see that the indices K, L, C, D can not be
different from the I, J, A, B. At least two of the former must match with the latter,
so
\[
\langle \Psi_{IJ}^{AB} | W T_2 | \Psi_0 \rangle = \sum_{C>D} \langle AB || CD \rangle t^{CD}_{IJ} + \sum_{K>L} \langle IJ || KL \rangle t^{AB}_{KL} + \sum_K \sum_L \{ \langle KA || JC \rangle t^{BC}_{IK} - \langle KB || JC \rangle t^{AC}_{IK} - \langle KA || IC \rangle t^{BC}_{JK} + \langle KB || IC \rangle t^{AC}_{JK} \}
\] (2.31)

In order to solve the CC equations, we start with an initial guess for the $t_2 = 0$ for
the $t_2$ amplitudes that correspond to the right-hand side of the equation 2.26. The
next step is to solve for a first-order estimation \( t_2(1) \) where \( D_2 T_2 \approx W \). Each side operates on \( \Psi_0 \) and all values of \( \Psi_{ij}^{AB} \) are taken into account so

\[
(\epsilon_I + \epsilon_J - \epsilon_A - \epsilon_B)\Psi_{ij}^{AB}(1) = \langle \Psi_{ij}^{AB} | W | \Psi_0 \rangle = \langle AB || IJ \rangle
\]  

(2.32)

thus

\[
t_{ij}^{AB} = \frac{\langle AB || IJ \rangle}{\epsilon_I + \epsilon_J - \epsilon_A - \epsilon_B}
\]  

(2.33)

The first order perturbation wavefunction is

\[
|1\rangle = \sum_{I>J} \sum_{A>B} \Psi_{ij}^{AB} t_{ij}^{AB}(1)
\]  

(2.34)

and the second order correction to energy (MBPT2) is

\[
\epsilon(2) = \sum_{I>J} \sum_{A>B} \frac{\langle IJ || AB \rangle \langle AB || IJ \rangle}{\epsilon_I + \epsilon_J - \epsilon_A - \epsilon_B}
\]  

(2.35)

It is obvious that for any given estimate of the amplitudes the equation 2.29 will not vanish and the CC solution will not vanish. In order CC to converge lets assume that we have an estimate of the amplitudes \( t \). We wish to determine a correction \( \delta t \).

In perturbation theory we will have

\[
(\epsilon_i - \epsilon_a)\delta t_{i}^{a} = G(i, a)
\]  

(2.36)

and

\[
(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\delta t_{ij}^{ab} = G(i, j, a, b)
\]  

(2.37)

where \( G(i, a) \) and \( G(i, j, a, b) \) are the right-hand sides of the amplitudes equations. We can get the amplitude corrections by dividing with the energy denominators. Then, we proceed for every iteration and \( t^{[n+1]} = t^{[n]} + \delta t^{[n]} \) and specifically for the doubles equation will have

\[
(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\delta t_{ij}^{ab[n]} = G(i, j, a, b)^{[n]}
\]  

(2.38)
Although one might expect this scheme to be efficient, for high orders of correction is rather slow and inconvenient. Instead, we use a new guess after a specific number of iterations and a certain number of amplitudes is available. For instance if we have m sets of amplitudes \( t^{[n]} \) and vectors \( G^{[n]} \) we represent the solution as linear combination \( \sum_n t^{[n]} c_n \) and by using direct inversion in the iterative subspace (DIIS) we can find the coefficients that minimize the residuals. That means, we have to minimize the squared norm \( ||\sum_n c_n G^{[n]}||^2 \) when \( \sum_n c_n = 1 \).

Many times in the case of closed shell systems, we have the problem of nondynamical correlation. This is the case where the Hartree-Fock dominates the wavefunction. That is why we need a variable that can predict when the nondynamical correlation is not negligible. The quantity \( T_1 \) was introduced by Lee [7]:

\[
T_1 = \frac{||t_1||}{\sqrt{N}}
\]  

(2.39)

In the unfortunate case that the orbitals do not describe very well the excited configurations we will note increased orbital relaxation. The main contributors to the orbital relaxation are the single excitations. That is why we use \( t_1 \) to monitor the nondynamical correlation.

### 2.4 Size Consistency

We will illustrate the property of size-extensivity with an example. We want to calculate the binding energy of a dimer by using MBPT2, CISD and CCSDT. We perform the same calculation when the monomers are far apart and we compare
the estimations. The result for MBPT2 and CCSDT are comparable and physically plausible (for the case of water around 4.3 Kcal/mol). But for the case of CISD, we will estimate -8.0 Kcal/mol. We understand that the result of CISD is not the expected. That is because CISD includes disconnected terms in the $T$ operator while CCSD will include only the connected ones. Thus a great advantage of coupled cluster method is that it is size-consistent.

In the general case we define the size-consistency [8] as

$$E_{AB}(r_{AB} \to \infty) = E_A + E_B$$  \hspace{1cm} (2.40)

where $E_{AB}$ the energy of the dimer and $E_A,E_B$ the energies of the monomers.

### 2.5 Size Extensivity

Size extensivity [9] is related to the proper scaling of the energy with the size of the system. It is more general than the size-consistency. For example, if we use frozen core in our calculations, we will expect our results to scale properly with the number of electrons. In other words the wavefunction should be able to describe a fragmentation process correctly.

At this point it is obvious that we have to truncate the operator $T$ for practical reasons. If we use $T = T_1$, we will not include dynamical correlation effects and the single excitations will not interact with the reference function. Also, we will clearly have to include double excitations, which are the dominant terms. For other properties than energy the contributions from $E_1^T$ are very crucial. Furthermore, a
comparison with Configuration Interaction results suggests that we have to include at least single and double excitations in order to increase accuracy. But if we want to move beyond CCSD we have to include the triple excitations.
Chapter 3

Inclusion of Triple Excitations

3.1 General Remarks

As we mentioned before, we can truncate the $T$ operator in different levels depending on the excitations that we want to include. When we refer to the full triples correction, we mean that the $T$ operator will include all the connected terms up to the 3rd excitation and it will be expressed as

$$T = T_1 + T_2 + T_3$$  \hspace{1cm} (3.1)

where $T_3$ is

$$T_3 = \sum_{I>J>K} \sum_{A>B>C} t_{IIJK}^{ABC} X_C X_K X_B X_J X_I X_I$$  \hspace{1cm} (3.2)

In this case, we will have a new operator $D_3T_3$ which we can express as

$$D_3T_3 = WT_2 + WT_3 + \frac{1}{2} WT_2^2 + WT_1T_2 + WT_1T_3 + WT_2T_3$$ \hspace{1cm} (3.3)

$$+ \frac{1}{2} WT_1^2T_2 + \frac{1}{2} WT_1T_2^2 + \frac{1}{2} WT_1^2T_3 + \frac{1}{3!} WT_1^3T_2$$

In Chapter 2, it was described how to solve CC equations. The same principles apply in the case of CCSDT, only this time, we have an extra amplitude, the $t_{IIJK}^{ABC}$ which will be included in the process and a third equation which is Equation 3.3.

In Equation 3.4, we have expanded all the terms that are needed to perform the calculation.
\[
\ell_{ij}^{abc} L_{ij}^{abc} = \sum_{P_{ia,jk,ke}} \left( \sum_{e} x_{1}(a, b, i, e) t_{ej}^{ce} - \sum_{m} x_{2}(a, m, i, j) t_{be}^{mk} \right) + \\
\sum_{P_{ia,jk,ke}} \left( \sum_{e} x_{v}(a, e) t_{ij}^{ebc} - \sum_{m} x_{o}(i, m) t_{mjk}^{abc} \right) + \\
\sum_{mn} x_{3}(j, k, m, n) t_{ijm}^{abc} + \sum_{ef} x_{4}(b, c, e, f) t_{ij}^{ae} + \\
\sum_{ml} x_{6}(a, m, i, e) \left( 2t_{mj}^{bec} - t_{mjk}^{bec} - t_{mjk}^{cbe} \right) - \\
\sum_{ml} \left( x_{5}(a, m, i, e) t_{mji}^{bec} + x_{5}(b, m, e, i) t_{mij}^{ae} + x_{5}(c, m, e, i) t_{mji}^{ab} \right)
\]

The intermediate quantities used in Equation 3.4 are given below:

\[
\chi_{1}(a, b, i, e) = \langle ab | i e \rangle + \sum_{mn} f(e, i, m, n) t_{nm}^{ab} + \sum_{mf} \left( \langle 2f(b, m, e, f) - f(b, m, e, f) t_{mi}^{af} - f(a, m, f, e) t_{mi}^{bf} \right) - \\
\sum_{m} (f(a, m, i, e) t_{mi}^{b} + f(b, m, e, i) t_{mi}^{a}) + \sum_{f} \langle ab | f e \rangle t_{i}^{f} - \\
\sum_{mn} \langle mn | ef \rangle \left( 2t_{inn}^{abf} - t_{nmi}^{abf} - t_{inn}^{abf} \right)
\]

\[
\chi_{2}(a, m, i, j) = \langle am | ij \rangle + \sum_{ef} f(a, m, e, f) t_{ij}^{ef} + \sum_{ne} \left( \langle 2f(e, j, m, n) - f(e, j, m, n) t_{im}^{ae} - f(e, i, n, m) t_{jm}^{ea} \right) - \\
\sum_{m} (f(i, e, m, a) t_{ij}^{e} + f(j, e, m, a) t_{ji}^{e}) - \sum_{f} \langle ij | nm \rangle t_{i}^{n} + \\
\sum_{m} f(m, e) t_{ij}^{ae} + \sum_{nef} \langle mn | ef \rangle \left( 2t_{ijn}^{afe} - t_{ij}^{afe} - t_{ijn}^{afe} \right)
\]
\chi_3(j, k, m, n) = \langle jk|mn \rangle + \sum_{ef} \langle jk|ef \rangle \tau_{mn}^{ef} + \sum_e \langle je|mn \rangle t_e^e + \\
\langle ek|mn \rangle t_j^e

(3.7)

\chi_4(b, c, e, f) = \langle bc|ef \rangle + \sum_{mn} \langle bc|mn \rangle \tau_{mn}^{bc} - \sum_m \langle bm|ef \rangle t_m^c - \\
\langle mc|ef \rangle t_m^b

(3.8)

\chi_5(a, m, e, i) = \langle am|ei \rangle - \sum_{nf} \langle mn|fe \rangle \tau_{in}^{fa} - \sum_n \langle nm|ei \rangle t_n^a + \\
\sum_f \langle am|ef \rangle t_i^f

(3.9)

\chi_6(a, m, i, e) = \langle am|ie \rangle - \sum_{nf} \langle mn|ef \rangle t_n^af - \langle mn|ef \rangle \tau_{in}^{fa} - \\
\sum_n \langle nm|ie \rangle t_n^a + \sum_f \langle ae|fm \rangle t_i^f

(3.10)

\chi_7(i, m) = \langle i|f|m \rangle + \sum_{ne} \langle ie||mn \rangle t_n^a + \sum_{nef} \langle mn|ef \rangle \tau_{in}^{ef}

(3.11)

\chi_8(a, e) = \langle a|f|e \rangle + \sum_{ef} \langle am||ef \rangle t_i^f - \sum_{nmf} \langle mn|ef \rangle \tau_{mn}^{fa}

(3.12)

f_1(a, m, e, f) = \langle am|ef \rangle - \sum_n \langle nm|ef \rangle t_n^a

(3.13)

f_2(e, i, m, n) = \langle ei|mn \rangle + \sum_f \langle mn|ef \rangle t_i^f

(3.14)

f_3(a, m, i, e) = \langle am|ie \rangle + \sum_f \langle am|ef \rangle t_i^f

(3.15)
\[ f_4(a, m, e, i) = \langle am|ei \rangle + \sum_f \langle am|ef \rangle t_f^i \] (3.16)

\[ f_5(i, e, a, m) = \langle ie|am \rangle - \sum_n \langle ie|nm \rangle t_n^a \] (3.17)

\[ f_6(i, e, m, a) = \langle ie|ma \rangle - \sum_n \langle ie|mn \rangle t_n^a \] (3.18)

\[ f_6(m, e) = \langle m|f|e \rangle + \sum_{nf} \langle mn|ef \rangle t_n^f \] (3.19)

\[ \tau_{mn}^{ef} = t_{mn}^{ef} + t_{mn}^{ef} \] (3.20)

The above equations show that once we have all the needed integrals, we can calculate the intermediates and thus solve the CC equations as described earlier. Also, in the above equations, the antisymmetrized spin independent integrals have been used:

\[ \langle pq||rs \rangle = 2\langle pq|rs \rangle - \langle pq|sr \rangle \] (3.21)

### 3.2 Modifications

In this section, we will focus on the major modifications that should be done on Fcceg [10,11] in order to link it with Gaussian.

- First, we have to retrieve all the basic geometrical parameters of the molecular system from Gaussian. That includes bond lengths, angles and so on. Because Fcceg uses cartesian coordinates, in the case that the geometry of the molecule
is given as Z-matrix, we have to convert it to cartesian coordinates. Also the reference energy (Hartree-Fock energy) and the nuclear repulsion are needed. Another point is to make sure that we have enough memory for the calculation. For this reason, we used Gaussian's subroutines to allocate the maximum available memory (Fcceg had its own subroutine for memory allocation). Moreover, we need other information like number of shells, total number of electrons, number of occupied and virtual orbitals etc.

- After making sure that all the initial information described before was retrieved correctly, we continue with the recovery of the molecular orbitals which will be used for the formation of many intermediates. In Fcceg the integrals were saved using a specific algorithm. Also, along with the integrals a label was written to the output file that was containing the information concerning the indices of a specific integral. In order to save disk space, a single word was used to describe all four indices and by using bit operations, we could retrieve the four indices. Because we have 8 bits available for a word, that means that the larger number of combinations is $2^8$ which is 256. Since the indices refer to basis functions, no more than 256 basis function can be used in a calculation.

We solve that shortcoming by reading the integrals from the Gaussian output. Gaussian saves the integrals in a specific order. Thus, by simply knowing this order, we can assign certain indices for certain integrals and thus, there is no
limitation concerning the number of basis functions that can be used.

- The next step is to form the Fock matrix in the molecular basis. In Fcceg that was done directly from the one-electron integrals but in Gaussian we already have the Fock matrix in the atomic basis. By applying the correct subroutines, we can transform the Fock matrix in the molecular basis with the help of the molecular coefficients.

- In Fcceg the CC coefficients (amplitudes) were saved in different files. Gaussian simply creates a file and all the needed variables are saved over there. Thus, we had to save a part of this file for the CCSDT intermediates which mainly are the CC amplitudes.

- Special care needed to be taken for the case of the VV|VV integrals ($\chi_4$), where V denotes virtual orbitals. Because those integrals were sorted in a specific way, a new module needed to be included into Gaussian that will sort those integrals in the appropriate way. The sorted integrals were saved separately and they were retrieved later on the calculation. The VV|VV integrals were used though out the program not as arrays like the other type integrals but as two-dimension variables.

- Finally, we included the main subroutine of the new program in Gaussian, just after the transformation of the integrals in the molecular basis.
After completing all the necessary modifications, we test the accuracy and stability of the new interface.
Chapter 4
Preliminary Results

In order to verify the accuracy and stability of the new software, a series of calculations was performed for different molecular systems.

4.1 Hydrogen Fluoride

By using the 6-311++G(2df,2p) basis set, we calculated the total energy of the HF molecule up to CCSDT theory level. The bond distance between hydrogen atom and fluoride atom is $r_{HF}=0.92 \text{ Å}$ [12]. The next table shows a comparison for the results produced by Gaussian and Fcceg programs for Hartree-Fock, MP2 and CCSDT methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Gaussian</th>
<th>Fcceg</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-100.05664272693</td>
<td>-100.05664272693</td>
</tr>
<tr>
<td>MP2</td>
<td>-100.35108135216</td>
<td>-100.35108135219</td>
</tr>
<tr>
<td>CCSDT</td>
<td>-100.39968978085</td>
<td>-100.39968978084</td>
</tr>
</tbody>
</table>

Table 4.1 Calculation of energy for the HF molecule by using Hartree-Fock, MP2 and CCSDT methods. The calculations were performed using Gaussian and Fcceg programs with the 6-311++G(2df,2p) basis set. All values in Hartrees.

From Table 4.1 we can see that the results for the case of MP2 and CCSDT match up to the 10th decimal digit. This is because the two-electron integrals in Gaussian
are calculated with 10 decimal digits accuracy and this limits the accuracy in the MP2 and CCSDT results. Unfortunately, the 10 digits accuracy is the maximum available accuracy for the two-electron integrals in Gaussian and we can not go further than that.

Furthermore, we performed energy calculations for the HF, MP2, MP3, MP4(SDQ), CCSD(T) and CCSDT methods by using the Gaussian program and the Gaussian interface of CCSDT. Because Gaussian is a very complex program, we wanted to assure that there will be no conflicts when we use other methods along with CCSDT method. The next table summarizes results for those methods. The calculations were successful for the case of CCSDT and for the other methods, as well.

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (Hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-100.05664273</td>
</tr>
<tr>
<td>MP2</td>
<td>-100.35108135</td>
</tr>
<tr>
<td>MP3</td>
<td>-100.33131987</td>
</tr>
<tr>
<td>MP4(SDQ)</td>
<td>-100.34445336</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-100.11571599</td>
</tr>
<tr>
<td>CCSDT</td>
<td>-100.39968978</td>
</tr>
</tbody>
</table>

Table 4.2 Energy calculations for different levels of theory for the HF molecule with the 6-311++G(2df,2p) basis set. Calculations were performed using Gaussian interface of CCSDT and all values are in Hartrees.
Inspection of Table 4.2 shows that CCSD(T) recovers 60 mHartrees of correlation energy, while with the inclusion of the full triples correction the correlation energy is almost 350 mHartrees.

Another point where we should be careful with our verification calculations is when we use frozen orbitals. When we perform calculations for large molecules, we can save a substantial amount of time by freezing the innermost molecular orbitals. We can freeze occupied and/or virtual molecular orbitals.

In order to make sure that our program gives us correct results when we use frozen orbitals, we used the HF molecule and we froze the 2 innermost molecular orbitals. Thus, we created a Ne – Ne core that will not react with the rest of the electrons of the molecule. Because we just want to demonstrate the accuracy of the software, we used the small STO-3G basis set.

<table>
<thead>
<tr>
<th>Method/Software</th>
<th>Gaussian</th>
<th>Fcceg</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-98.57084862810</td>
<td>-98.57084862810</td>
</tr>
<tr>
<td>MP2</td>
<td>-98.58385662764</td>
<td>-98.58385662770</td>
</tr>
<tr>
<td>CCSDT</td>
<td>-98.59048167813</td>
<td>-98.59048167817</td>
</tr>
</tbody>
</table>

**Table 4.3** Energy calculations for the HF molecule, where we have frozen the 2 innermost molecular orbitals. The STO-3G basis set was used and all values are in Hartrees.

From the Table 4.3, we can see that the Gaussian results match to those of the
Fceg program for all the methods that have been used.
4.2 Hydroxide Anion

The next example is the hydroxide anion, $OH^-$. The bond distance between hydrogen and oxygen is $r_{OH}=0.96$ Å. The Table shows 4.4 a comparison for the results produced by Gaussian and Fcceg programs for Hartree-Fock, MP2 and CCSDT methods by using the 6-311++G(2df,2p) basis set.

<table>
<thead>
<tr>
<th>Method/Software</th>
<th>Gaussian</th>
<th>Fcceg</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-75.40831333311</td>
<td>-75.40831333311</td>
</tr>
<tr>
<td>MP2</td>
<td>-75.70668469315</td>
<td>-75.70668469313</td>
</tr>
<tr>
<td>CCSDT</td>
<td>-75.71517707254</td>
<td>-75.71517707257</td>
</tr>
</tbody>
</table>

**Table 4.4** Calculation of energy for the $OH^-$ anion by using Hartree-Fock, MP2 and CCSDT methods. The calculations were performed by using Gaussian and Fcceg programs with the 6-311++G(2df,2p) basis set. All values are in Hartrees.

Again, we verify that the results given from Gaussian match the results of the original code for certain bounds of accuracy.

In Table 4.5, energy calculations are included for different methods using the same basis set.

From Table 4.5, we can see the gap between the CCSD(T) and CCSDT methods, which is approximately 250 mH. This is due to the full inclusion of the triple excitations in CCSDT that allow more correlation energy to be recovered.
<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (Hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-75.40831333</td>
</tr>
<tr>
<td>MP2</td>
<td>-75.70668469</td>
</tr>
<tr>
<td>MP3</td>
<td>-75.68174390</td>
</tr>
<tr>
<td>MP4(SDQ)</td>
<td>-75.70525827</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-75.46577248</td>
</tr>
<tr>
<td>CCSDT</td>
<td>-75.71517707</td>
</tr>
</tbody>
</table>

**Table 4.5**  
Energy calculations for different levels of theory for the $OH^-$ anion with the 6-311++G(2df,2p) basis set. Calculations were performed using Gaussian and all values are in Hartrees.
Chapter 5
Exploring the Permanganate Anion Potential Energy Curve

The scope of this project is to investigate the potential energy curve of the permanganate anion with respect to the $Mn - O$ bond length. Preliminary results show that perturbation methods (MP2, MP3 and MP4) and coupled cluster method CCSD(T) have failed to predict the correct equilibrium structure compared to the experimental value. We have utilized the CCSDT method to prove the high accuracy of coupled cluster theory and to explain the need to use the full triples correction model for this case.

5.1 Computational Details

The permanganate anion is a relatively large molecule for coupled cluster calculations. The total number of electrons is 58, where 25 electrons are given by $Mn$ atom, 32 electrons by $O$ atoms and there is one more electron because of the negative charge of the molecule.

A very important parameter that will influence the final results is the selection of the basis set. Since, the permanganate anion is a large molecule, we have to use a basis set that is not very large, which includes diffuse and polarization functions in order to supply the molecular orbitals with additional flexibility. For this reason
the 6-311++G(d) basis set [13,14] has been selected (pluses denote diffuse functions and d denotes polarization function). This is a triple valence basis set where the core orbitals consist of 6 GTOs (Gaussian-type orbitals) and the valence orbitals are described by 3 orbitals (one is constructed by 3 GTOs and the other two are single GTOs).

The total number of the contracted Gaussian functions is 146. For the case of the manganese atom there are 10 contracted GTOs on the s-shell, 7 contracted GTOs on the p-shell, 4 contracted GTOs on the d-shell and 1 contracted GTO on the f-shell, while for each of the O atoms there are 5 contracted GTOs on the s-shell, 4 contracted GTOs on the p-shell and 1 contracted GTO on the d-shell. The contracted basis set for the Mn atom can be written as [10s7p4d1f] and for the O atom as [5s4p1d]. The Table 5.1 contains the total number of contracted Gaussian-type functions for each type of shell for both Mn and O atoms.

A significant reduction of the computational effort in quantum chemical investigations can be achieved by freezing some of the molecular orbitals. Those orbitals are not included in the calculation of the correlation effects, when higher level methods are applied. This approach is based on the fact that mainly the valence electrons of an atom determine its chemical behavior. The selection of the frozen core was based on the energies of the molecular orbitals. In appendix A.2, we can find the molecular orbital energies for the case of $r_{Mn-O} = 1.58\, \text{Å}$ for the Hartree-Fock energy level. The
<table>
<thead>
<tr>
<th>Shell Type</th>
<th>Mn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>p</td>
<td>21</td>
<td>12</td>
</tr>
<tr>
<td>d</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>f</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>58</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 5.1  Contains the total number of contracted GTOs for Mn and O atoms for every shell.

first step was to freeze the 13 innermost occupied molecular orbitals (26 electrons), which correspond to an Ar atom (18 electrons) and four He atoms (8 electrons in total). Because of the high demand on computational resources, we had to freeze four more molecular orbitals. They mainly consist of the 2S atomic orbitals of the O atoms. In total, there are 17 frozen occupied molecular orbitals. The same scheme was applied for the virtual molecular orbitals. We have, also, frozen the 13 outermost virtual molecular orbitals which correspond to an Ar atom and four He atoms (26 electrons).

The structure of the permanganate ion can be described as a manganese atom surrounded by four oxygen atoms at the corners of a regular tetrahedron. From experimental results, it has been proved that the average Mn – O bond distance
Figure 5.1  The geometry of \( MnO_4^- \) molecule

is 1.629 Å, and the average \( O - Mn - O \) angle is 109.4° [15]. Table 5.2 contains the geometry of the molecule based on experimental results. The structure of the permanganate ion is depicted in Figure 5.1.

Because of the high demand of CCSDT on computational resources and since the structure of the \( MnO_4^- \) ion is a regular tetrahedron, we focused our research on the \( Mn - O \) bond length. That means that for every point on the potential curve, we kept fixed the angles and dihedral angles. Also, for a certain point on the potential curve the four \( Mn - O \) bond lengths are equal \((r_{Mn-O})\). Every point on the potential energy curve corresponds to a different \( r_{Mn-O} \) bond length. We used a range of values for the \( r_{Mn-O} \) bond length starting at 1.58 Å and ending at 1.63 Å in increments of
<table>
<thead>
<tr>
<th>Center</th>
<th>Atom</th>
<th>Bond length</th>
<th>Angle</th>
<th>Dihedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>O 1</td>
<td>1.629</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>O 1</td>
<td>1.629</td>
<td>2</td>
<td>109.4</td>
</tr>
<tr>
<td>4</td>
<td>O 1</td>
<td>1.629</td>
<td>2</td>
<td>109.4</td>
</tr>
<tr>
<td>5</td>
<td>O 1</td>
<td>1.629</td>
<td>2</td>
<td>109.4</td>
</tr>
</tbody>
</table>

**Table 5.2**  The Z-matrix for the experimental structure of the $MnO_4^-$ ion.

0.01 Å. For the case of the CCSDT method, in order to get a more accurate potential curve the 1.64 Å value has been added. The geometrical parameters for each case can be found in the Appendix A.1.
5.2 Results

The first calculations that have been carried out are shown in Table 5.3. We have summarized the results for the following methods:

- Hartree-Fock [16]
- MP2 [17–22], MP3 [23, 24], MP4(SDQ) [25]
- CCSD(T) [26, 27]
- B3LYP [31], VSXC [32] and PBE [33, 34]

MP2, MP3 and MP4(SDQ) methods are perturbation methods with orders of correction two, three and four respectively. In the case of MP4(SDQ), the single, double and quadrable excitations have been included. B3LYP, VSXC and PBE methods are based on density functional theory.

B3LYP is the Becke’s three-parameter hybrid functional that has the form:

\[ aE_x^{Slater} + (1 - a)E_x^{HF} + b\Delta E_x^{Becke} + E_c^{VWN} + c\Delta E_C^{non-local} \]  \hspace{1cm} (5.1)

where the non-local correlation is provided by the Lee, Yang, Parr [35, 36] correlation functional. VWN is the Vosko, Wilk and Nunair correlation functional [37]. The a, b, c constants are calculated by fitting the \( G_1 \) molecule set [39–41].

The exchange formula of VSXC is given by the following equation:

\[ E_x[\rho_\alpha, \rho_\beta] = \sum_\sigma \int \rho_\sigma^{4/3} f(x_\sigma, z_\sigma) dx \]  \hspace{1cm} (5.2)
where
\[
f(x_\sigma, z_\sigma) = \frac{a}{\gamma_\sigma(x, z)} + \frac{b x_\sigma^2 + c z_\sigma}{\gamma_\sigma^2(x, z)} + \frac{d x_\sigma^4 + e x_\sigma^2 z_\sigma + f z_\sigma^2}{\gamma_\sigma^3(x, z)}
\] (5.3)

and the Fermi momentum is given as \(\gamma_\sigma(x, z) = 1 + \alpha(x_\sigma^2 + z_\sigma)\). The correlation formulas for the same-spin and opposite-spin correlational functionals are:
\[
E_c^{\sigma\sigma'} = \int f^{\sigma\sigma'}(x, z) e^{LDA}_{c^{\sigma\sigma'}} d\mathbf{r}
\] (5.4)
\[
E_c^{\sigma\sigma} = \int f^{\sigma\sigma}(x_\sigma, z_\sigma) D_{\sigma} e^{LDA}_{c^{\sigma\sigma}} d\mathbf{r}
\] (5.5)

Finally the correlation form is
\[
E_c = E_c^{\alpha\beta} + E_c^{\alpha\alpha} + E_c^{\beta\beta}
\] (5.6)

Inspection of Table 5.3 shows that Hartree-Fock, MP2 and MP3 methods have no minimum in the potential energy curve. The Hartree-Fock method does not include correlation effects and such a result was expected. Even though MP2 and MP3 contain correlation effects, they fail to predict a minimum in the vicinity of 1.58\(\text{Å} - 1.63\text{Å}.

For the rest of the methods, we have plotted the relative energy with respect to the \(r_{\text{Mn-O}}\) bond length, in Figure 5.2. The relative energy is given from the formula \(E - E_{eq.}\), where \(E_{eq.}\) is the energy at the minimum of the energy curve.

After locating the minimum on the potential energy curve (spline fitting), we interpolate the corresponding \(r_e\) for each case. We have summarized the results of the equilibrium bond lengths in Table 5.4 along with the percentage relative error and the corresponding energy values. In order to calculate the relative error, we have used the standard formula \(\frac{|r_{\text{calc}} - r_{\text{exp.}}|}{r_{\text{exp.}}}\), where \(r_{\text{exp.}}\) is the experimental value.
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Table 5.3  Energy calculations for different levels of theory for the $MnO_4^-$ molecule with the 6-311++G(d) basis set. All energy values are in Hartrees and bond distances are in Angstroms.
Figure 5.2  MP4(SDQ), CCSD(T), B3LYP, VSXC and PBE energy calculations for the $MnO_4^-$ molecule. The 6-311++G(d) basis set has been used.
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**Table 5.4**  Equilibrium Mn – O bond lengths, percentage relative errors with respect to the experimental value and the corresponding energies. Bond distances are in Angströms and energy values are in Hartrees.

Table 5.4 shows that the B3LYP, CCSD(T) and MP4(SDQ) values are too short compared to the experimental value. The relative errors in those cases are over 1%, where B3LYP gives the largest error of 1.75%. VSXC and PBE give better results with under 1% error. Especially PBE, gives the best results from the methods that were under consideration.

From Table 5.4, we can see that the CCSD(T) estimation of the equilibrium bond length is not in a good agreement with experiment.
5.3 CCSDT Results

It was previously shown that the CCSD(T) method fails to predict an equilibrium \( Mn - O \) bond length close to the experimental value. It is believed that this is related with the fact that not all the triples have been included. For this reason, we will calculate the equilibrium \( Mn - O \) bond length by using the CCSDT method.

In Table 5.5, we have reported the CCSDT energy results and in Figure 5.3, we have plotted the relative CCSDT energy values with respect to the \( r_{Mn-O} \). The minimum of the CCSDT energy curve is \(-1450.8535401\) Hartrees and the corresponding bond length is \(1.6224\, \text{Å} \). The percentage relative error in this case is \(0.40\% \).

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Table 5.5 CCSDT energy calculations for the \( MnO_4^- \) molecule with the 6-311++G(d) basis set. All energy values are in Hartrees and bond distances are in Angstroms.
Figure 5.3  MP2, CCSDT, CCSD(T) and PBEPBE energy calculations for MnO$_4^-$ molecule. The 6-311++G(d) basis set has been used.
If we compare the CCSDT results to those of Table 5.4, we can conclude that CCSDT has given the most accurate results, where the percentage relative error is under 0.5%. The comparison between CCSD(T) and CCSDT results is very interesting. By including all the terms in the triples correction (CCSDT), we reduced the relative error, almost three times compared to that where we have included only the connected terms (CCSD(T)). In summary, two main points have been clarified by this study:

- CCSDT is an extremely powerful method, which gives high accuracy results.

- In the case of $MnO_4^-$ is essential to apply the full triples correction to get the correct answer concerning the equilibrium $Mn - O$ bond length.
Chapter 6
Conclusions

This project was about interfacing old CCSDT software program (Fccg) into Gaussian. Modifications to the original coupled-cluster code were made in order to make it compatible with Gaussian. Verification results exist for the HF and OH− molecules. Also, original research has been performed in the potential energy curve of the MnO₄⁻ anion. The potential energy has been calculated with respect to the Mn − O bond length, by using different methods. Comparison of the results has shown the accuracy of the CCSDT method.

By using the Gaussian interface, we transformed the old inflexible code into an easy-to-use tool, where all the benefits of using Gaussian have been included:

- By interfacing the old software program into Gaussian, the CCSDT program is available to a large number of users because Gaussian is one of the most popular quantum chemistry programs.

- The limitation of using a maximum of 256 basis functions has been eliminated. In the new implementation, the two-electron integrals are being read directly from the output of Gaussian. The integrals in Gaussian are saved in a specific order without using a single word (8 bits) to describe the four indices. Thus, we can always restore the integrals knowing their order without using the single
word scheme.

Preliminary results were produced in order to verify the accuracy and stability and to demonstrate the flexibility of the new software.

- For the \( HF \) molecule, we have calculated the total energy by using both programs, Gaussian interface and Fcceu. The 6-311++G(2df,2p) basis set has been used. There was a total match of the results up to the 10th decimal digit. This is because the two-electron integrals in Gaussian are calculated with 10 digits accuracy. In general, the accuracy of 10 decimal digits is satisfactory and we can make sure that the new software is bug free. Also, we have tested the inclusion of frozen molecular orbitals, which was successful. Moreover, calculations for other methods than CCSDT have shown no conflicts when they are performed along with the CCSDT method.

- A second example is the \( OH^- \) anion. Again, results were produced by using both software programs. The 6-311++G(2df,2p) basis set was used and the energy results were an exact match.

- For the case of \( MnO_4^- \), we have used the 6-311++G(d) basis set. We have performed calculations for the location of the equilibrium \( r_{Mn-O} \) bond length, for different methods. The methods that have been used are: Hartree-Fock, MP2, MP3, MP4(SDQ), CCSD(T), B3LYP, VSXC, PBE and CCSDT. The
results indicate that the HF, MP2, MP3m MP4(SDQ), CCSD(T) and B3LYP methods have failed to predict an accurate value for the equilibrium \( Mn - O \) bond length. On the other hand, VSXC, PBE and CCSDT give results that are in good agreement with the theoretical value. Furthermore, a comparison between the CCSD(T) and CCSDT results indicate that in this case, inclusion of all the terms in the triple correction is mandatory in order to get the correct result, concerning the minimum of the potential energy curve.

This project sets the basis for further development of the CCSDT method in Gaussian. The next step would be to include symmetry elements in molecular orbitals which will narrow down the total single, double and triple excitations. This is because we will exclude from the computational loops intermediate elements that belong in different irreducible representations and thus are zero.

In the future directions of extension of the program, we should make available different methods like CCSDT-1a or CCSDT-2 etc. These methods make possible the investigation of the contributions of specific terms in the total triple correction for different kind of molecular systems. Also, this is the starting point for including energy gradients and calculating optical properties like dipole moments and polarizabilities.
Appendix A
Appendix

In the appendix, we have included input data that was used for the calculations.

A.1 $MnO_4^-$ Geometries

All the required input data is listed below. The geometry is in cartesian coordinates
and is expressed in atomic units.

• $r_{Mn-O} = 1.58\text{Å}$

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• $r_{Mn-O} = 1.59\text{Å}$

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A.2 MO Energies for $MnO_4^-$ for the Hartree-Fock method

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References

3. V. Fock, Z. Phys. 61, 126 (1930).
17. C. Moller and M. S. Plesset, Phys. Rev. 46, 618 (1934).


