

## Research Article

# Utilizing the Hartree-Fock Method to Analyze Carbon Dioxide Molecule

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## Abstract

The determination of the ground state of the carbon dioxide molecule is conducted through matrix Hartree-Fock computations for a polyatomic molecule. Utilization of basis sets is implemented to achieve a precision that approaches the sub- $\mu$  Hartree of the  $\text{CO}_2$  molecule for the energy levels. Utilizing a 28s14p14d14f atom-centered and a 24s10p11d bond-centered Gaussian basis set, the upper limit for the Hartree-Fock ground state energy of  $\text{CO}_2$  at its practical picture has been calculated, yielding a value of -187.125408 Hartree. Utilizing our knowledge in diatomic molecules, we approximate the precision of this measurement to fall within 5-6  $\mu$  Hartree. The current computations offer a methodology to assess the precision of different basis sets frequently utilized in molecular self-consistent field investigations. These basis sets encompass STOJG, 4-31G, 6-31G, 6-31G(3d), 6-31IG, 6-311+G(3d0, D95, and D95V+(3d)), alongside cc-pVDZ, uug-cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ, which have been proposed for the purpose of investigating electron correlation. We have recently performed calculations on the  $\text{CO}$  ground state at the nuclear geometry employed in the present work using the basis sets proposed by Dunning and co-workers and designated cc-pVQZ, aug-cc-pVQZ, cc-pVSZ and nupcc-pVSZ. The estimated basis set truncation errors for these sets are 0.00371, 0.00319, 0.00047 and 0.00039 Hartree respectively.

## Keywords

Hartree-Fock Approximation, Polyatomic Molecules,  $\text{CO}_2$ 

## 1. Introduction

In the preceding publications within this series [1-3], the primary emphasis was placed on the evaluation of the attainable accuracy in the computation diatomic molecules ground-state energies utilizing the Hartree-Fock framework. This task was completed by utilizing the theoretical approach, more precisely, finite basis set expansions means. In the initial segment of the series, it was illustrated that atom-centered basis sets comprising functions of Gaussian-type have the capacity to attain sub- $\mu$  Hartree precision for monoatomic system operating under the Hartree-Fock framework.

Progressing to the subsequent section, an examination was conducted on the employment of elliptical basis functions for diatomic molecules within the context of the Hartree-Fock model. Finally, the third section of the study demonstrated that through the integration of atom-centered and bond-centered functions within basis sets comprised of Gaussian-type functions, it is possible to achieve a level of accuracy that nears the sub- $\mu$  Hartree threshold for the total Hartree-Fock energy pertaining to the ground state of the nitrogen molecule.

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In this work, explore the properties of polyatomic molecules, expanding on our previous studies. Illustrated through a specific case, we analyze the lowest energy state in CO<sub>2</sub> at its most stable atomic arrangement. Our primary objective is to assess the precision in determining the Hartree-Fock energy of this system. This evaluation is conducted using basis sets comprised of Gaussian-type functions, which encompass both atom-centered and bond-centered functions. To approximate the occupied orbitals and electron density within the framework of the Hartree-Fock approximation, we utilize finite basis set expansions. These expansions rely on global basis functions that ensure continuity throughout the entire system. Furthermore, the algebraic approximation serves a crucial role in representing the virtual spectrum, which is of utmost importance in applying methods of many-body to address the problem of electron correlation. In the realm of the relativistic formulation, the algebraic approximation also assumes the responsibility of representing the negative energy system.

Moreover, the algebraic approximation finds application in representing the virtual spectrum. In the case of diatomic systems, effective implementations of the finite difference [4-6] and finite element methods [7] have been accomplished through the utilization of spheroidal coordinates. By adopting this approach, the problem is effectively reduced to two dimensions. Specifically, in the case of the finite difference method, the currently employed approach yields the occupied orbitals values on a grid that has been purposefully constructed for this specific purpose. In a recent study [8], we conducted a comparison between Hartree-Fock calculations using finite basis sets and finite difference methods for the CO ground state. The results of the study revealed a disparity of approximately 1.5 $\mu$  Hartree in the energies obtained from the two methods. Although the comparison utilized the finite difference method, it is important to highlight that finite element techniques offer approximations to the orbitals that exhibit only piecewise continuity. This is because the orbitals are constructed using segmented regions, which can lead to discontinuities at the boundaries between these segments.

In this document, a methodical utilization of the algebraic approximation is utilized, a technique that has been previously established and employed in the examination of the CO molecule. We employ this methodology to perform finite basis set Hartree-Fock analyses of the ground state of CO<sub>2</sub>. Although in theory finite difference and finite element methodologies could be applied to tri-atomic systems, they lack the capability of exploiting specialized coordinate systems tailored for addressing the Coulomb singularities found in atomic and diatomic entities. These special coordinate systems offer more efficient and accurate treatment of such singularities, which can significantly impact the accuracy of calculations for systems with strong electron-electron interactions. Consequently, these methods often necessitate a larger number of points to attain the desired level of accuracy [9]. In light of this, we propose A basis set, which possesses

the capability of accurately describing the Hartree-Fock ground state of the carbon monoxide (CO) molecule with a precision of approximately 1 $\mu$  Hartree, the utilization of this method can be employed to attain a comparable degree of precision for the CO<sub>2</sub> molecule.

The structure of this work is outlined as follows:

Section 2 provides a brief description of the methods employed in our study. Section 3 presents the results obtained from our calculations. In Section 4, we discuss the results and draw conclusions based on our findings.

## 2. Procedure

In accordance with the Hartree-Fock approach, the ground-state arrangement of the CO<sub>2</sub> molecule is determined at its equilibrium nuclear configuration can be described by a set of 11 orbitals. Each of these orbitals is occupied by two electrons, consistent with the Pauli Exclusion Principle. This configuration accounts for the electronic structure and distribution of electrons in the CO<sub>2</sub> molecule within the framework of the Hartree-Fock approximation.

$$X^1 \sum_g^+ :1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 4\sigma_g^2 2\sigma_u^2 3\sigma_u^2 1\pi_u^4 1\pi_g^4. \quad (1)$$

In its ground electronic state, the CO<sub>2</sub> molecule possesses a linear molecular geometry, meaning that the carbon (C) and oxygen (O) atoms are arranged in a straight line. The CO<sub>2</sub> molecule belongs to the point symmetry group  $D_{\infty h}$ , which reflects its cylindrical symmetry along the molecular axis. Experimental measurements have determined the C=O bond lengths in CO<sub>2</sub> to be approximately 1.160 Å [10]. This measurement refers to the distance between the carbon atom and one of the oxygen atoms in the molecule. The bond length provides insight into the spatial arrangement and strength of the chemical bonds within the CO<sub>2</sub> molecule.

The expansion of the one-electron functions in this research is accomplished through the utilization of a basis set consisting of even-tempered spherical harmonic Gaussian-type functions. The establishment and attributes of these basis sets have been delineated in a prior publication by our research group [8]. The methodologies for constructing these fundamental sets have been thoroughly expounded in prior literature, offering in-depth information. The fundamental sets employed in this investigation consist of functions that are focused on atomic as well as bond centers. These basis sets were initially developed for investigating the N<sub>2</sub> molecule ground state [3, 11]. They have also been successfully applied in studies involving various diatomic species, such as the carbon monoxide (CO) molecule [8, 12]. The utilization of these basis sets facilitates the accurate description of the electronic structure and properties of the CO<sub>2</sub> molecule within the Hartree-Fock framework.

The molecular foundation for the carbon dioxide molecule may be characterized in the subsequent manner:

$$S_O \oplus S_C \oplus S'_O \oplus S_{CO} \oplus S'_{CO} \quad (2)$$

In the instance of CO<sub>2</sub>, the molecular foundation set comprises atom-centered basis sets for oxygen (S<sub>O</sub>) and carbon (S<sub>C</sub>), in addition to bond-centered basis sets (S<sub>CO</sub>). The incorporation of bond-centered functions in calculations of molecular electronic structure has a extensive historical background [13-25]. Nonetheless, recent research has indicated that these functionalities provide a proficient method for reaching the Hartree-Fock threshold [3, 11, 12, 8, 26]. It is imperative to highlight that the employment of bond-centric functionalities ought to be approached judiciously. Before integrating the bond-centric collections (S<sub>CO</sub>), it is essential to verify that the atom-centric foundational collections (S<sub>O</sub> and S<sub>C</sub>) are fully saturated in accordance with the specific theoretical framework in use. This guarantees that the enhancement in energy due to the incorporation of S<sub>CO</sub> is credited to an improved depiction of bonding, rather than the atoms per se. It is important to note that a basis set at the atomic level, which is complete in relation to the Hartree-Fock framework, may not be complete for treatments involving correlation.

### 3. Results and Discussion

The formulation of the equable foundation ground state sets for the CO<sub>2</sub> is delineated in Table 1. Within the tabular presentation, the symbol "A" signifies the basis set centered on the atom, while "B BC" denotes the basis set centered on the bond, N represents the overall number of primitive basis functions, denoted as E, provides insight into the calculated ground state Hartree-Fock energy  $E_{HF}$ . Additionally, the parameters m and  $\varepsilon$  are utilized to signify the computational linear dependency present in the basis set. In particular, the symbol m is used to denote the count of eigenvalues pertaining to the overlap matrix that have magnitudes smaller than  $10^{-5}$ , while the symbol  $\varepsilon$  stands for the minimum eigenvalue. In prior research pertaining to the CO ground state, the basis set centered on the atom, identified as 30s15p15d15f, was utilized. The application of this basis set resulted in the determination of the Hartree-Fock energy for the ground state of CO, at the nuclear geometry in equilibrium according to experiments, exhibiting a deviation of 196  $\mu$  Hartree from the outcome derived from calculations based on finite differences [8]. Similarly, the identical basis set resulted in a deviation of 216 Hartree [3, 11] in the Hartree-Fock energy calculated for the iso-electronic N<sub>2</sub> ground state compared to the finite difference outcome. The quantification of computational linear dependence was conducted as m = 5 and  $\varepsilon = 4.2 \times 10^{-7}$  for CO, and m = 5 and  $\varepsilon = 3.7 \times 10^{-7}$  for N<sub>2</sub> in these particular computations.

In the current calculations involving CO<sub>2</sub> utilizing the 30s15p15d15f basis set, a more pronounced a comparison

revealed the presence of computational linear dependency to CO with m = 15 and  $\varepsilon = 8.4 \times 10^{-8}$ . Consequently, an examination was conducted on the antecedent basis set within the progression 2ns np nd nf, denoted as 28s14p14d14f. In the case of the CO (N<sub>2</sub>), this particular basis set results in an energy discrepancy of 209 (227)  $\mu$  Hartree, where n = 4 (4) and  $\varepsilon = 6.8 \times 10^{-7}$  (  $5.8 \times 10^{-7}$  ). When using the 28s14p14d14f atom-centered basis set for CO<sub>2</sub>, the assessment of computational linear dependence was established through numerical values of m = 13 and  $\varepsilon = 1.5 \times 10^{-7}$ . A comparison of the energies calculated for CO1 with the 28s14p14d14f and the 30s15p15d15f atom-centered basis sets revealed a discrepancy of 23  $\mu$  Hartree, whereas for CO (N<sub>2</sub>), this difference was 13 (11)  $\mu$  Hartree. A basis set acquired through the addition of a bond-centered set to the 28s14p14d14f atom-centered sets for CO was previously demonstrated to yield a Hartree-Fock energy deviating by merely 3.2  $\mu$  Hartree.

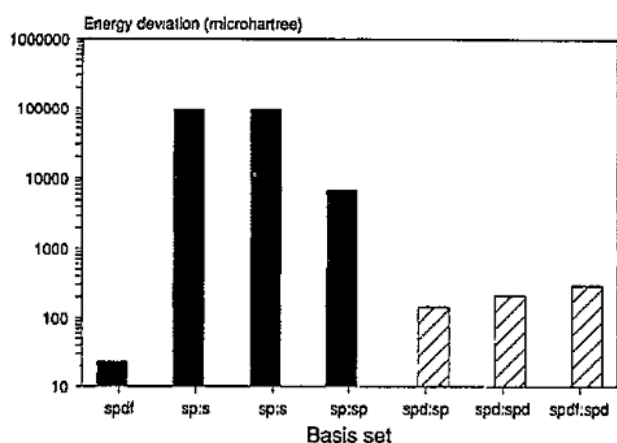
**Table 1.** The ground state energies of the CO<sub>2</sub> molecule in the Matrix Hartree-Fock method.

Basie state	N	E <sub>HF</sub> (Hartree)	[m, $\varepsilon$ ]
30s15p15d15f	510	-187.725114	[15,8.4 (-8)]
28s14p14d14f	476	-187.725091	[13,1.5(-7)]
28s14p:28s BC	168	-187.627251	[5,4.5(-8)]
28s 14p:26s BC	166	-187.627243	[1,4.7(-6)]
28s14p:26s BC	208	-187.718261	[8,1.1(-7)]
28s14p14d:25s 11p BC	388	-187.725259	[5,2.1(-7)]
28s14p14d:24s 11p 11d	388	-187.725259	[5,2.1(-7)]
28s14p14d 14f:24s 10p 11d BC	585	-187.725408	[19,1.1(-7)]

In Figure 1, the energy discrepancy for CO<sub>2</sub> is depicted in the bar located at the far left. This bar signifies the disparities in computed energies compared to the energy derived from the 30s15p15d15f basis set, expressed in  $\mu$  Hartree on a logarithmic scale. Upon analysis of these findings, it was deduced that a novel basis set should be formulated specifically for the CO<sub>2</sub> molecule. Subsequently, the resolution was taken to establish the foundation for CO<sub>2</sub> utilizing the 28s14p14d14f atom-centered groups.

We shall proceed to discuss the matter of augmenting atom-centered basis sets with bond-centered sets. The basis set 28s BC, denoted as 28s14p, generates an energy outcome deviation of 50029  $\mu$  Hartree for CO compared to the finite difference outcome, and a difference of 49 821  $\mu$  Hartree

from the outcome achieved using the 28s14p14d14f atom-centered basis group. For the  $N_2$  molecule, the energy discrepancy resulting from the 30s15p:30s BC basis set in comparison to the finite difference outcome is 58008  $\mu$  Hartree, and 57793  $\mu$  Hartree different from the 30s15p15d15f atom-centered basis set. In the case of  $CO_2$ , utilizing the 28s14p:28s BC basis set generates an energy value that surpasses the one derived from the 30s15p15d15f set by 97863  $\mu$  Hartree. This discrepancy in energy is illustrated by the second bar in Figure 1. However, a notable escalation in the realm of computational analysis, the presence of linear dependence becomes apparent in certain scenarios of the 28s14p:28s BC basis set for CO, displaying values of  $[m, \varepsilon] = [2, 3.5 \times 10^{-6}]$ , in contrast to  $[5, 4.7 \times 10^{-8}]$  for  $CO_2$ . The elimination of the two most widely dispersed bond-center functions arise from the 28s14p:28s BC basis set for  $CO_2$  resulted in a mere 8.4  $\mu$  Hartree increase in energy, yet effectively decreased the metrics of the concept of computational linear dependence is crucial to understand to  $[m, \varepsilon] = [1, 5.0 \times 10^{-6}]$ .



**Figure 1.** Discrepancy in the computed energy values compared to the energy derived from the specified basis set 30s15p15d15f is observed. Energy levels exceeding this threshold are denoted by horizontal bars, whereas those below it are indicated by diagonal lines.

Incorporating p-type bond-centered functions into the 28s14p:26s BC basis set resulted in a decrease in energy by 91018  $\mu$  Hartree, while ensuring that the computational linear dependence remains within acceptable limits to preserve the numerical accuracy of the calculation. The incorporation of p-type functions into a 30s15p:30s BC basis set for  $N_2$  resulted in a set labeled as 30s15p:30s15p BC, leading to a reduction in energy of 53610  $\mu$  Hartree and a deviation of 440  $\mu$  Hartree from the finite difference calculation. In the case of  $N_2$ , 92.6% of the energy difference between using the 30s15p:30s BC basis set and the finite difference energy can be accounted for by including p-symmetry bond-centered functions. This accounts for 93% of the discrepancy in ener-

gies calculated using the 30s15p:30s BC and the 30s15p15d15f basis sets. In the case of the  $CO_2$  ground state, the reduction in energy observed upon inclusion of a 14p BC set to the 28s14p:26s BC set corresponds to 92.8% of the difference between the energies computed with the 28s14p14d14f atom-centered set and the 28s14p:26s set. The third column depicted in Figure 1 illustrates the energy difference between the calculation with the 28s14p:26s14p BC basis set and our reference energy derived from the 30s15p15d15f basis set.

In the following phase of expanding the basis set, d-type functions were integrated into the atom-centered basis sets. Nevertheless, this led to heightened computational linear dependency. In order to alleviate this challenge, functions were deliberately excluded from the bond-centered sets. More specifically, the subsequent most diffused s-type function and the top three most diffused functions of p-type were eradicated from the basis set. This procedure facilitated the management of computational linear dependence while incorporating essential d-type functions in the atom-centered basis sets. The resultant basis set, achieved through the addition of d-type functions and exclusion of specific diffuse functions, leads to a reduction in energy of 7000  $\mu$  Hartree when compared to the 28s14p:26s14p BC set. The energy derived from the 28s14p14d:24s11p BC set is roughly ~146  $\mu$  Hartree lower than the minimum energy documented in Table 1 for an atom-centered basis set (specifically, the 30s15p15d15f set). Moreover, the novel basis set constitutes only 68% of the magnitude of the atom-centered set, underscoring its heightened effectiveness. The fourth bar in Figure 1 illustrates the described outcome. Previous studies conducted on  $N_2$  revealed that the utilization of a 30s15p15d:30s15p BC basis set led to a Hartree-Fock energy that was lower compared to that achieved with a 0s15p15d15f basis set by approximately ~182  $\mu$  Hartree. Moreover, the energy acquired through the 30s15p15d:30s15p BC set was in close proximity to about ~42  $\mu$  Hartree of the finite difference outcome. In contrast, in the case of CO, an energy calculation using a basis set denoted as 28s14p14d:28s14p BC resulted in an energy level that was roughly ~167  $\mu$  Hartree lower than the energy obtained with the 28s14p14d14f set. Nevertheless, it was approximately 455  $\mu$  Hartree higher than the outcome obtained from employing the finite difference method.

The integration of a group of d-type functions into the bond-centered sets led to a further decline in energy in comparison to the 28s14p14d:24s11p BC set, resulting in a decrease of 66 Hartree. Nevertheless, to prevent a significant rise in linear dependency, exclusion of the most diffuse s-type function that persisted in the bond-centered set was imperative. The resulting basis set is denoted as 28s14p14d:24splld BC. Utilizing this basis set leads to an energy reduction of around 214  $\mu$  Hartree compared to the lowest energy value documented in Table 1 for a basis set

centered on an atom. This outcome is depicted by the second-to-last bar in Figure 1. Regarding the fundamental state of the CO molecule, the basis set referred to as 30s15p15d15f:27s12p10d10f BC produced energy approximately 195  $\mu$  Hartree lower than that obtained with an atom-centered basis set (30s15p15d15f). Shifting focus to N<sub>2</sub>, the energy gap between the 30s15p15d15f and 30s15p15d15f:27s12p10d BC sets is approximately 215  $\mu$  Hartree.

**Table 2.** The ground state of CO<sub>2</sub> occupied energies are examined with length of bond measuring 1.160 angstroms.

Orbital	E (Hartree)
$1\sigma_g^2$	-21.64836
$1\sigma_u^2$	-21.64922
$2\sigma_g^2$	-11.45880
$3\sigma_g^2$	-1.63114
$4\sigma_g^2$	-1.57732
$2\sigma_u^2$	-0.90031
$3\sigma_u^2$	-0.75389
$1\pi_u^4$	-0.72612
$1\pi_g^4$	-0.55513

A basis set denoted as 28s14p14d14f: 25s11p9d BC was identified as yielding the total energy of Hartree-Fock calculated for the carbon monoxide (CO) molecule that remained within 3  $\mu$  Hartree of the finite difference outcome. In the ultimate computation for the ground state of carbon dioxide, the basis set utilized was specified as 28s14p14d14f: 24s10p11d BC. This computation yielded an energy that was 83  $\mu$  Hartree less than the energy acquired through the functions of symmetry belonging to s, p, and d orbitals are observed at both locations the atom and bond centers, and it was 394 Hartree lower than the reference energy acquired with the 30s15p15d15f atom-centered basis set. This outcome is depicted by the final bar in Figure 1. It is approximated that the computation utilizing the 28s14p14d14f: 24s10p11d BC basis set, as detailed in Table 1 for the CO<sub>2</sub> ground state, will entail an error of around 5-6  $\mu$  Hartree.

Utilizing basis sets with a proven track record of achieving sub-Hartree level precision for the ground states of carbon monoxide and nitrogen molecules, matrix Hartree-Fock

computations were performed for the ground state of the CO<sub>2</sub> molecule, which acts as an exemplary instance of polyatomic systems. The precision of our energy computations is estimated to fall within the 5-6  $\mu$  Hartree range. This accomplishment is deemed a notable progression in Hartree-Fock computations for multi-electron polyatomic molecules due to the unprecedented level of precision achieved. It is imperative to emphasize that the methodology adopted in this investigation is void of any presumptions that could impede the applicability of our approach to diverse polyatomic molecules.

The accuracy of matrix Hartree-Fock calculations using the correlation consistent basis sets, as developed by Dunning and colleagues [29-31] for studying electron correlation, was further assessed. Specifically, an analysis was conducted on the effectiveness of the basis sets recognized as ccpVDZ and aug-cc-pVDZ. For the ccpVDZ basis set, the matrix Hartree-Fock energy computed was -187.651108 Hartree, while the associated basis set truncation error amounted to 0.07430 Hartree. In relation to the aug-cc-pVDZ basis set, the calculated matrix Hartree-Fock energy was -187.662824 Hartree, accompanied by a basis set truncation error of 0.06258 Hartree. Moreover, an exploration was carried out on the cc-pVTZ and aug-cc-pVTZ basis sets.

The Hartree-Fock matrix energy obtained with the cc-pVTZ basis set was -187.707256 Hartree, and the corresponding basis set truncation error was 0.01815 Hartree. For the aug-cc-pVTZ basis set, the Hartree-Fock matrix energy was -187.709507 Hartree, and the basis set truncation error was 0.01590 Hartree. These results demonstrate the accuracy achieved by the correlation consistent basis sets in matrix Hartree-Fock calculations, with the computed energies and truncation errors reported for each basis set. It is of significance to compare the discrepancies in energy described in Table 3 with the correlation energies estimated using many-body perturbation theory. All orbitals are deemed 'active' in the correlation energy calculations outlined in this context and Cartesian. Unfortunately, due to the unavailability of Table 3 or specific information pertaining to the correlation energies estimated using many-body perturbation theory we are incapable of presenting a direct comparison or offering further details. If you have any particular inquiries or necessitate aid with related topics, kindly inform me, and I will gladly offer assistance.

**Table 3.** The accumulation of matrix Hartree-Fock coefficient for the carbon dioxide molecule's ground state utilizing specific standard basis sets of Cartesian Gaussian-type functions.

sets	N (bash)	E (Hartree)	$\epsilon_{\text{BEST}}$ (Hartree)
STO-3G	15	-185.064 77	2.7608
3-12G	27	-186.661183	1.1645

sets	N (bash)	E (Hartree)	$\epsilon_{\text{BEST}}$ (Hartree)
4-21G	27	-187.427960	0.39785
6-31G	27	-187.614955	0.2114
6-31G(d)	46	-187.632837	0.0930
6-31G(2d)	64	-187.744122	0.0816
6-31G(3d)	82	-187.749958	0.0759
6-31G(3df)	102	-187.658690	0.0669
6-31G(3df)	116	-187.664131	0.0618
6-311G	37	-178.666217	0.1698
6-311+G(3df)	118	-187.808767	0.0619

## 4. Conclusion

When Gaussian basis functions are employed, it becomes crucial to assess the discrepancy in energy inaccuracies highlighted in Table 2 and the correlation energies derived using many-body perturbation theory. The STO-3G basis set, although not originally tailored for correlation investigations, reports the second-order energy value as  $E_2 \approx -0.1995$  Hartree. This quantity represents only 7.5% of the pertinent error resulting from the truncation of the basis set, with the optimal truncation error  $\epsilon_{\text{BEST}}$  being 0.0813. The truncation error associated with the basis set 6-31G(2d) is measured at 0.0813 Hartree. The coefficients associated with the expansion of many-body perturbation theory are denoted as  $E_2 \approx -0.5440$  Hartree,  $E_3 \approx +0.0145$  Hartree, and  $E_4 \approx -0.0404$  Hartree, respectively. Of particular interest is the observation that the magnitude of the coefficient  $E_2$  is -16% relative to  $E_1$ , exceeding the values of the higher-order energy coefficients. Furthermore, the calculation of  $E_3$  is derived as -17.9% relative to  $E_1$ , and  $E_4$  as -50% relative to  $E_1$ . It is important to highlight that the specific numerical values assigned to  $E_1$ ,  $E_2$ ,  $E_3$ , and  $E_4$  are not specified, having been excluded from the original inquiry. Nonetheless, this information affords a comprehensive understanding of the contrast between energy discrepancies and coefficients in the many-body perturbation approach for the STO-3G and 6-31G(2d) basis sets.

## Author Contributions

**Enass Hammadi Hasan:** Formal Analysis, Writing – original draft

**Saad Naji Abood:** Supervision

## Conflicts of Interest

The authors declare no conflicts of interest.

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