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Part 1 : Convergence & Error Cancellation

Objective

Generate convergence plots for energy and properties to investigate the dipole moment of Carbon Monoxide

Experimental Dipole : $\mu = 0.112$ *Debye*

Task

Optimize the geometry of CO using the B3LYP functional with three increasingly large basis sets :

1. `def2-SVP` *(Easy)*
2. `def2-TZVP` *(Medium)*
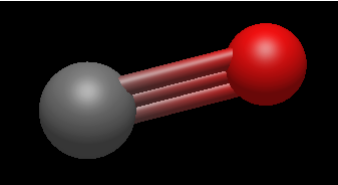3. `def2-QZVP` *(Large)*

Analysis Requirements

1.a) Convergence Plot

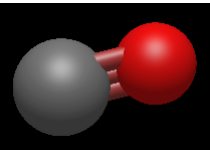*Plot Total Energy (Hartree) vs. Basis Set (SVP, TZVP, QZVP). Does the energy plateau?*

To start, we need to create an `XYZ` file of the Carbon Monoxide we want to simulate. To do this we use Avogadro 2.

A Carbon Monoxide Molecule is comprised of 1 Carbon triple Bonded to 1 Oxygen with no Hydrogen's Present. In Avogadro it's Design looks like the following :

Now a small trick I've learnt in the Nano Car club is to Pre-Optimize Molecules before running them through the Orca Geometry Optimization. This can be done using the Built In Avogadro Geo-Opt which can be found under `Extensions → Optimize Geometry` or by clicking `Ctrl` + `Alt` + `O`

Before this Pre-Optimization, the bond length was 2.011 Angstroms, and after it was reduced to 1.057 Angstroms :

This Molecule was then exported as a `XYZ` file with the following content :

```
2
XYZ file generated by Avogadro.
C    -1.5438288094    1.0737094824   -0.0000015062
O    -0.5230671226    1.3481080587   -0.0000048453
```

Now we need to create Input Files for the 3 Calculations, since we are only modifying the Basis Sets, we can use the same template for all 3. These 3 Input Files are written as follows :

```
! B3LYP def2-SVP OPT PAL8
* xyzfile 0 1 CO.xyz
```

```
! B3LYP def2-TZVP OPT PAL8
* xyzfile 0 1 CO.xyz
```

```
! B3LYP def2-QZVP OPT PAL8
* xyzfile 0 1 CO.xyz
```

> 🖉 **PAL8 Keyword**
>
> Note that I have added the PAL8 keyword, this is an extra Keyword used to enable multithreaded / multicore calculations. This specifically tells the Calculation to utilize 8 Cores giving a ~8x Speedup in Calculation time

After running these calculations we receive the following results when Grepping the Files :

SVP

```
$ grep "FINAL SINGLE POINT ENERGY" CO-Opt-SVP.out
FINAL SINGLE POINT ENERGY       -113.157770997763
FINAL SINGLE POINT ENERGY       -113.172643984369
FINAL SINGLE POINT ENERGY       -113.172820672673
FINAL SINGLE POINT ENERGY       -113.172830315281
FINAL SINGLE POINT ENERGY       -113.172830323047
```

TZVP

```
$ grep "FINAL SINGLE POINT ENERGY" CO-Opt-TZVP.out
FINAL SINGLE POINT ENERGY       -113.297963862751
FINAL SINGLE POINT ENERGY       -113.310081170919
FINAL SINGLE POINT ENERGY       -113.310336754123
FINAL SINGLE POINT ENERGY       -113.310348670257
FINAL SINGLE POINT ENERGY       -113.310348685374
```
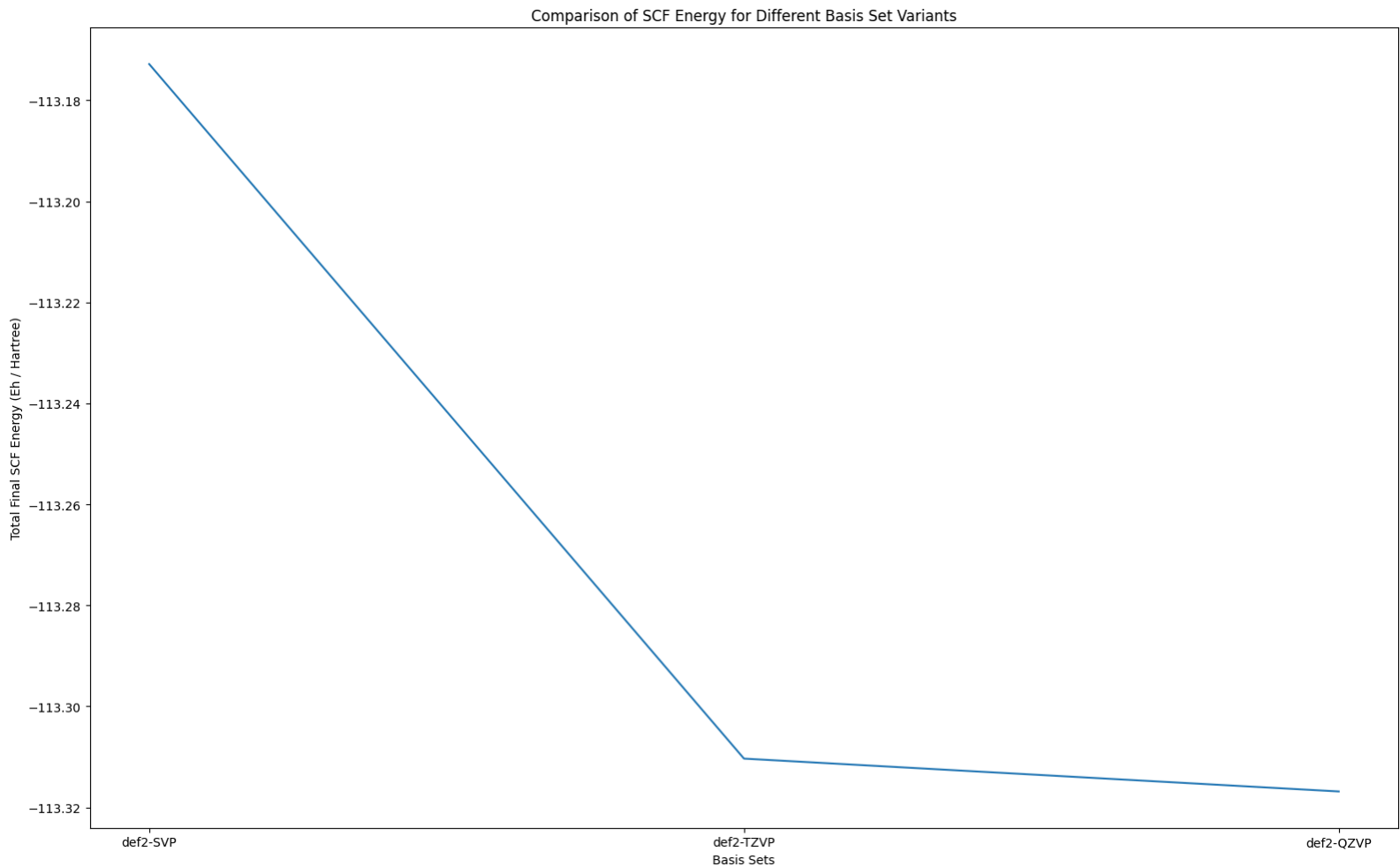
QZVP

```
$ grep "FINAL SINGLE POINT ENERGY" CO-Opt-QZVP.out
FINAL SINGLE POINT ENERGY       -113.304944696170
FINAL SINGLE POINT ENERGY       -113.316581391745
FINAL SINGLE POINT ENERGY       -113.316840548768
FINAL SINGLE POINT ENERGY       -113.316852244261
FINAL SINGLE POINT ENERGY       -113.316852256737
```

And to fill out the table and fill in the Graph we use the last values in the Grep Search :

Basis Set	Total Energy (Hartree)
def2-SVP	-113.172830323047
def2-TZVP	-113.310348685374
def2-QZVP	-113.316852256737

And when Graphed out, gives the following :

To answer the question, yes it does appear that as we increase the complexity of the Basis Set, the energy level does Plateau.

Extra

The code used to generate the Graph is as follows :

```python
# Imports
import numpy as np
import matplotlib.pyplot as plt

# Plot the SCF Energy
SVP = -113.172830323047
TZVP = -113.310348685374
QZVP = -113.316852256737

energies = [SVP, TZVP, QZVP]
labels = ["def2-SVP", "def2-TZVP", "def2-QZVP"]

plt.figure(figsize=(16, 10))
plt.plot(labels, energies)
plt.title("Comparison of SCF Energy for Different Basis Set Variants")
plt.ylabel("Total Final SCF Energy (Eh / Hartree)")
plt.xlabel("Basis Sets")
plt.tight_layout()
plt.show()
```

1.b) Error Cancellation Analysis

- *Create a Table comparing your calculated Dipole Moment (μ) to the experimental value (0.112 Debye)*
- *You may find that the smaller basis set (TZVP) gives results closer to the experiment than the largest basis set (QZVP). Explain why this happen.*

Basis Set	Dipole (μ)	Ideal Dipole (μ_T)	$\Delta(\mu - \mu_T)$	Relative Error % ($\frac{\mu - \mu_T}{\mu_T} \cdot 100$)
def2-SVP	0.219138904	0.112	0.107138904	95.66

Basis Set	Dipole (μ)	Ideal Dipole (μ_T)	$\Delta(\mu - \mu_T)$	Relative Error % ($\frac{\mu - \mu_T}{\mu_T} \cdot 100$)
def2-TZVP	0.107718598	0.112	-0.004281402	3.82
def2-QZVP	0.102315614	0.112	-0.009684386	8.65

The reason the smaller Basis Set `TZVP` is yielding a Dipole closer to the Ideal Dipole of 0.112 Debye is due to a phenomenon known as Fortuitous Error Correction, this is where the Overestimation Error that comes from running the SCF Convergence on the Carbon Monoxide gets cancelled out by the Basis Set Incompleteness Error. It just so happens that in the `TZVP` Basis Set they are nearly identical, which makes it come close to the Idea Dipole.

Part 2 : Functional Performance

Objective

Determine if standard DFT can predict the binding of noble gases (dispersion forces) compared to Wavefunction Theory.

Task

Calculate the Interaction Energy (ΔE_{int}) using Single Point Energy calculations with the `def2-TZVP` *basis set.*

Required Calculations

Argon Dimer

2 Argon Atoms separated by a radius of 3.8 Angstrom. Run using the following Calculations :

```
! B3LYP def2-TZVP FREQ
```

```
! B3LYP-D4 def2-TZVP FREQ
```

Argon Atom

A Single Argon Atom. Run using the following Calculations :

```
! B3LYP def2-TZVP FREQ
```
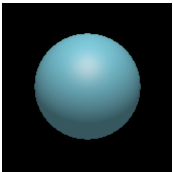
```
! B3LYP-D4 def2-TZVP FREQ
```

Analysis Requirements

2.a) Calculation Table

Fill in the table below (convert Hartree to kJ/mol)

Method	E_{Dimer} (Eh)	$2 \times E_{Atom}$ (Eh)	ΔE_{int} (Eh)	ΔE_{int} ($\frac{kJ}{mol}$)
B3LYP				
B3LYP-D4				
MP2 (Reference)				

Alright, to Start we again need to create the 2 molecules for this Calculation. This requires creating a XYZ File for a Single Argon Atom, and another with 2 Argon Atoms that are separated by 3.8 Angstroms, these are shown below :

Distance: 3.801 Å

Now we can create the Input files to run the Calculations.

> ✏️ **PAL8 Keyword**
>
> Note that I have added the PAL8 keyword, this is an extra Keyword used to enable multithreaded / multicore calculations. This specifically tells the Calculation to utilize 8 Cores giving a ~8x Speedup in Calculation time

Ar-B3LYP.inp

```
! B3LYP def2-TZVP FREQ PAL8
* xyzfile 0 1 Ar.xyz
```

Ar-B3LYP-D4.inp

```
! B3LYP-D4 def2-TZVP FREQ PAL8
* xyzfile 0 1 Ar.xyz
```

Ar2-B3LYP.inp

```
! B3LYP def2-TZVP FREQ PAL8
* xyzfile 0 1 Ar2.xyz
```

Ar2-B3LYP-D4.inp

```
! B3LYP-D4 def2-TZVP FREQ PAL8
* xyzfile 0 1 Ar2.xyz
```

Now, we run the calculations, and fill out the following table, where the conversion of $Eh \rightarrow \frac{kJ}{mol}$ is done by multiplying by $2626.5 \frac{\frac{kJ}{mol}}{Eh}$:

Method	E_{Dimer} (Eh)	$2 \times E_{Atom}$ (Eh)	ΔE_{int} (Eh)	ΔE_{int} ($\frac{kJ}{mol}$)
B3LYP	-1054.960550966105	-1054.960771	2.20455099 $\times 10^{-4}$	0.5788048624
B3LYP-D4	-1054.961176828013	-1054.960771	-4.05406809 $\times 10^{-4}$	-1.064395577
MP2 (Reference)	-1054.012202	-1054.011989	-	-0.56

2.b) Binding Analysis

- *Compare the MP2 result to the Experimental value: -1.18 kJ/mol. Does MP2 capture the binding correctly?*
- *Does standard B3LYP predict a bound state ($\Delta E < 0$) or a repulsive state ($\Delta E > 0$)?*
- *How much energy (in kJ/mol) does the D4 dispersion correction add? Based on this, is the description of electron correlation as "nature's chemical glue" accurate?*

Looking at the fact that our MP2 Reference has an interaction energy difference of -0.56 kJ/mol compared to experimental value that is more than double and that the relative error between the 2 is 52.54%, I would say that it does a poor job at capturing the Binding Energy.

The standard B3LYP Functional predicts a Repulsive state since it's ΔE is positive at $0.5788048624 \frac{kJ}{mol}$

To calculate the amount of energy that the Dispersion Correlation added, we need to take the difference between the Deltas. Therefor we calculate :

$$\Delta E_{int_{B3LYP-D4}} - \Delta E_{int_{B3LYP}} = -1.064395577 - 0.5788048624 = -1.643200439$$

Therefor the D4 Dispersion Correlation added an extra $-1.643200439 \frac{kJ}{mol}$. Based off this fact, and since the B3LYP-D4 functional is closer to the Experimental Value of -1.18 kJ/mol it is safe to say that the statement that the Electron Correlation is "Natures Chemical Glue" is accurate.

2.c) Thermodynamics

- *While the Interaction Energy (ΔE_{int}) tells you if the atoms attract, the Gibbs Free Energy (ΔG) tells you if the dimer actually forms spontaneously at room temperature.*
- *Calculate the Binding Free Energy at 298 K :*

$$\Delta G_{bind} = G_{Dimer} - 2 \times G_{Atom}$$

- *Based on the sign of ΔG_{bind} that you calculated, will the Argon dimer form spontaneously?*

Since we didn't specify the Temmperatures at which the Calculations occured, Orca will use the default Room Temperature which is set to 298.15 K. For this calculation we will determine this as close enough and use the Previously run calculations.

To extract the Gibbs Free Energy of all the Output Files :

Ar-B3LYP

```
$ grep "Final Gibbs free energy" Ar-B3LYP.out
Final Gibbs free energy         ...   -527.49559691 Eh
```

Ar-B3LYP-D4

```
$ grep "Final Gibbs free energy" Ar-B3LYP-D4.out
Final Gibbs free energy         ...   -527.49559691 Eh
```

Ar2-B3LYP

```
$ grep "Final Gibbs free energy" Ar2-B3LYP.out
Final Gibbs free energy         ...   -1054.98539408 Eh
```

Ar2-B3LYP-D4

```
$ grep "Final Gibbs free energy" Ar2-B3LYP-D4.out
Final Gibbs free energy         ...   -1054.98604336 Eh
```

Which results in the following table :

Method	G_{Dimer} (Eh)	$2 \times G_{Atom}$ (Eh)	ΔG_{bind} (Eh)	ΔG_{bind} ($\frac{kJ}{mol}$)	Spontaneous
B3LYP	-1054.98539408	-1054.991194	0.00579974	15.22721737	No
B3LYP-D4	-1054.98604336	-1054.991194	0.00515046	13.52253273	No

Based on the results from calculations using the 2 Functionals, Argon Dimers will not form Spontaneously at Room Temperature because the Binding Free Energy is Positive in both cases.