DFT Lab Assignment

Part 1: Convergence & Error Cancellation

Objective: Generate convergence plots for energy and properties to investigate the dipole moment of Carbon Monoxide.
System: Carbon Monoxide (CO).

- Experimental Dipole Moment: $\mu = 0.112$ Debye.

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

1. `def2-SVP` (Small)
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?

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 a result closer to experiment than the largest basis set (QZVP). Explain why this happens.

Please submit one of your output files alongside your solutions.

Part 2: Functional Performance

Objective: Determine if standard DFT can predict the binding of noble gases (dispersion forces) compared to Wavefunction Theory.
System: Argon Dimer (Ar–Ar) fixed at the experimental equilibrium distance of 3.8 Å.
Task: Calculate the Interaction Energy (ΔE_{int}) using Single Point Energy calculations with the `def2-TZVP` basis set.

$$\Delta E_{int} = E_{\text{Dimer}} - 2 \times E_{\text{Atom}}$$

Required Calculations:

1. **Argon Dimer ($r = 3.8$ Å):**
   Run using `! B3LYP def2-TZVP Freq` and `! B3LYP-D4 def2-TZVP Freq`.
2. **Argon Atom:**
   Run using `! B3LYP def2-TZVP Freq` and `! B3LYP-D4 def2-TZVP Freq`.

Analysis Requirements

2.a) Calculation Table: Fill in the table below (convert Hartree to kJ/mol).

Method	$E_{\mathbf{Dimer}}$ **(Eh)**	$2 \times E_{\mathbf{Atom}}$ **(Eh)**	ΔE_{int} **(kJ/mol)**
B3LYP			
B3LYP-D4			
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?

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:

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

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

Please submit one of your output files alongside your solutions.