10.637: IN CLASS WORKSHEET, LAB 5

This worksheet should be filled in to the best of your ability during in-class time and returned to myself or the TA at the end of the class period on **10/17/23** or uploaded to Canvas by **11:59PM EDT** (Mon). Please answer questions to the best of your ability. You may work with a partner and ask questions, but you must hand in your own work.

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A. C_2H_4 basis set extrapolation energies

1. What is the difference between HF/cc-pVTZ and the complete basis set result from the exponential fit? Convert your answer to kcal/mol. **0.0023**

2. Which choice of *n* -1 and *n* in the two-point formula gives the closest agreement with the exponential decay fitting formula? *n* = **4**

B. Basis set error and structure: planar or pyramidal NH_3?

1. Fill in the table below with the total energy (in Ha) you obtained for each structure (bent/planar) and basis set (STO-3G/6-31G/6-31G*/6-311++G(d,p)) combination. Then calculate the relative energy of the bent structure with respect to the planar structure ($\Delta E = E_{bent}-E_{planar}$) **and convert to kcal/mol**.

	E_{planar} (Ha)	E_{bent} (Ha)	ΔE (kcal/mol)
STO-3G	**-55.438**	**-55.455**	**-11.1**
6-31G	**-56.166**	**-56.166**	**-0.00063**
6-31G*	**-56.174**	**-56.184**	**-6.51**
6-311++G(d,p)	**-56.207**	**-56.215**	**-4.63**

2. Of the three basis sets (STO-3G/6-31G/6-31G*), which one **gives the most incorrect** ΔE with respect to the large basis (6-311++G(d,p))? **STO-3G**

3. Of the three basis sets (STO-3G/6-31G/6-31G*) which one gives the **most accurate** ΔE with respect to the large basis (6-311++G(d,p)) ? **6-31G***

4. Fill in the table below with the N-H distance (in Å) and H-N-H angle (in degrees) you obtained for each structure (bent/planar) and basis set (STO-3G/6-31G/6-31G*/6-311++G(d,p)) combination.

	$d(N\text{-}H)_{bent}$ (Å)	$d(N\text{-}H)_{planar}$ (Å)	$\angle H\text{-}N\text{-}H_{bent}$ (°)
STO-3G	**1.0032**	**1.0055**	**104.2**
6-31G	**0.9913**	**0.9914**	**116.1**
6-31G*	**1.0025**	**0.9885**	**107.2**
6-311++G(d,p)	**1.0003**	**0.9875**	**108.3**

5. Of the three basis sets (STO-3G/6-31G/6-31G*), which gives the **best** agreement for the planar ammonia N-H bond length with respect to 6-311++G(d,p)? **6-31G***

6. Of the three basis sets (STO-3G/6-31G/6-31G*, which gives the **worst** agreement for the bent H-N-H angle with respect to 6-311++G(d,p)? **6-31G**

C. Orthogonal basis set contributions: the tetracene molecule.

1. Fill in the table below with the total energy you obtained for each basis set for the tetracene molecule.

	6-31G	6-31G**	6-311G	6-31++G	6-311++G(d,p)
E (Ha)	**-688.380**	**-688.640**	**-688.491**	**-688.498**	**-688.761**

2. Fill in the table below with the rel. energy in (kcal/mol) you obtained for pairs of basis sets that measure the contribution of triple-zeta/double-zeta split valence, polarization, and diffuse:

	triple-zeta split valence	polarization	diffuse functions
relative E (kcal/mol)	**-69.6**	**-163.2**	**-74.0**

Hint: If you don't remember which symbol corresponds to what basis function, consult your notes

from *Topic 5.*

3. Rank the contributions from largest to smallest: triple-zeta split valence (i.e., vs double-zeta split valence), polarization, or diffuse functions according to their contribution to the total energy. *Put the rank order to the left of each contribution below*:

_3_ triple-zeta split valence

_1_ polarization

_2_ diffuse functions

4. Estimate the energy (in Ha) of the tetracene molecule at the HF/6-311++G(d,p) level using the additivity concept discussed in class. **-688.869**

5. What % of the energy difference between HF/6-311++G(d,p) and HF/6-31G did the additivity concept estimate recover? **128**

6. What % of the total wall time did the sum of the four needed individual calculations that you carried out take vs. the large calculation result? **71%**

7. If we gave you a much bigger molecule to study that had > 50 heavy atoms, how do you expect your answer to the last question to change? **the time will differ more largely**