Exercise Ex5

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Please use this template to submit your answers.
If you had to modify code from the notebook, please include the modified code in your submission either as screenshot or in a

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\begin{lstlisting}[language=Python]
\end{lstlisting}
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environment.

You only need to include the code cells that you modified.

Note, that references to other parts of the documents aren't resolved in this template and will show as **??**. Check the text of the exercises on website for the reference

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Exercise 1

- Calculate the HF energy for Boron using the 6-311+G** basis set, then determine the value of the correlation energy for boron assuming an "experimental" energy of -24.608 Hartrees ([**?**]).

- Using the same basis set, perform an energy calculation with CISD and full CI.

- Using the same basis set, perform an energy calculation with MP2, MP3 and MP5.

- Using the same basis set, perform an energy calculation with CCSD and CCSD(T).

Determine the percentage of the correlation energy recovered for HF, MP2, MP5, CCSD, CCSD(T).

Compare the performances of the different methods. In particular, you will see that some of the methods seem to overestimate the correlation

recovered. How is it possible? (*Hint:* Think both about the theoretical aspects of the methods and *how* we are computing the recovered correlation energy).

	% correlation recovered
hf	0.000000
mp2	72.042401
mp3	90.729937
mp5	100.785294
ccsd	100.711378
ccsd(t)	102.150181
cisd	99.259774
fci	102.632129

Figure 1: % of E_{corr} recovered

In 6-311+G**, the HF run sets the correlation gap $\Delta E = E_{\text{exact}} - E_{\text{HF}} = -0.07765$ Ha with $E_{\text{exact}} = -24.608$ Ha; the recovered fraction is $100 \cdot \frac{(E_{\text{HF}} - E_M)}{\Delta E}$. We are not able to recover 100% of the correlation energy since we are truncating the wavefunction, also incomplete basis sets introduce errors of accuracy. The overestimations of the correlation energy ($\geq 100\%$) arises because MP, CC and CI are non variational leading methods to possible smaller energies.

Exercise 2
Perform the calculations below and complete the following table.

Method:	HF	MP2	MP3	Exp.
$E^{F\cdot}$	-99.381098	-99.537740	-99.547730	n/a
$E^{H_3C\cdot}$	-39.565801	-39.700946	-39.720405	n/a
E^{CH_3F}	-139.057552	-139.422653	-139.436919	n/a
E^{BDE}	69.435479	115.440741	105.913684	109.2 kcal mol^{-1}

Exercise 3
Why is it a reasonable choice to use Hartree-Fock geometries and wavefunctions as a starting point for optimisations at the Post-Hartree-Fock level? What is the advantage and how is this approach justified?

While Hartree Fock geometries do not take into account correlations between electrons, we can still use it as initial guess since it is a relatively good approximation of the ground state wavefunction and energy. From this we will perform $MP(n)$ method which adds electron correlation through small perturbative terms. Thanks to our HF calculations, we use it as initial guess for the ground state and construct the small perturbative terms from this unperturbed

term. Indeed the most common choice is to take the sum of the single particle Fock operators as the unperturbed Hamiltonian, and the difference between the full Hamiltonian and the HF Hamiltonian as perturbation. When summing the first two order $E^{(0)}$ with $E^{(1)}$ we retrieve the HF energy E_{HF}, justifying our choice of using HF-geometries as starting point. Similarly for CI and CC, we first need to construct excited states from the reference namely the HF slater determinant. The convergence of post-HF methods is therefore speed-up since we start from a close guess of the ground state.

Exercise 4

Why do you think it is reasonable to choose not to carry out a geometry optimisation for mp3?

Since we are adding smaller and smaller perturbative terms, the geometry is not supposed to change drastically under these addings. From HF geometry optimization, then $MP(2)$ geometry, we are already capturing an important overview of the geometry. Redoing the optimization would incredibly increase the computation cost since we should re-compute higher perturbative terms for each iteration. We chose balance between accuracy and computational cost.

Exercise 5

Is the homolytic cleavage of the H_3C-F bond likely, based on the BDE that you calculated? (Think of radical processes in general.)

We learned from experimental results that BDE is at 109.2 kcal/mol while we obtained MP3 at 105.9 kcal/mol (closest method), the high energy shows a strong C-F bond, making homolytic cleavage unlikely. In fact it is because of the high electronegativity difference between carbon and fluorine. We also know that radical processes generally favor weaker bonds for feasibility without extreme inputs like heat or light. The results suggest that this reaction requires significant activation, consistent with the fact that the molecule is stable. The cleavage is unlikely.

Exercise 6

What is the trend in energies when moving from HF over MP2 to MP3 for your calculations? Does this series converge? Do you expect the same trend for higher order MPn methods? Why?

Hint: You can check the convergence for MP2 and MP3 by running the code cell below.

In the first three graphs, the energy is monotically decreasing. Looking at the fourth graph (BDE), we see that the series may not converge or slowly, indeed it seems to oscillate around the experimental value of 109.2 (Same observation for the first three graphs with respect to the true ground state).The error comes generally from our initial guess that might be imperfect, impacting higher order perturbative orders since they directly depend on smaller orders.

Also adding higher perturbative terms will not drastically improve the convergence since matrix elements will not have significant contribution according to Slater-Condon rules.
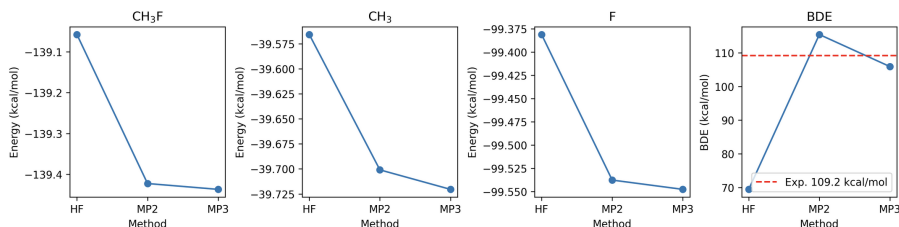

Figure 2: Energy value for CH_3F, CH_3, F and BDE for different methods and for last iteration when convergence is reached

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Exercise 7

Comment on the accuracy of the HF approach for this system. Is the error associated with HF or with MPn bigger, and why? (*Hint*: Think in terms of the scale of the absolute energy of the reaction, as well as of the different components of the system.)

HF underestimates BDE $\approx$ 40kcal/mol by neglecting correlation between electrons, and treat them independetly as a mean-field approximation, which is inadequate for radicals where dynamic correlation is crucial. $MP(n)$ errors are smaller ($MP(2)$): +6 kcal/mol, $MP(3)$: -3 kcal/mol) as they include perturbative corrections up to order n, this allows to recover more correlation energy. On the absolute scale ($\approx$100 kcal/mol reaction energy), neglecting the correlation from HF amplifies errors, while $MP(n)$ truncates the infinite series but better approximates the full CI limit.

Exercise 8

Assess and comment on the performance of the different methods with respect to experimental values. Can you think of possible reasons for differences between the experimental and computed values?

	HF	MP2	MP3	Exp.
r(O0–N) Å	1.172597	1.215742	1.199054	1.198000
error	-0.025403	0.017742	0.001054	n/a
rel. error (%)	2.120	1.481	0.088	n/a
r(O2–N) Å	1.189170	1.226783	1.214052	1.213000
error	-0.023830	0.013783	0.001052	n/a
rel. error (%)	1.965	1.136	0.087	n/a
r(O3–N) Å	1.334134	1.415244	1.383966	1.410000
error	-0.075866	0.005244	-0.026034	n/a
rel. error (%)	5.381	0.372	1.846	n/a
ϕ(O–N–O) °	129.046342	130.551919	129.715694	130.200000
error	-1.153658	0.351919	-0.484306	n/a
rel. error (%)	0.886	0.270	0.372	n/a

The performance of HF, $MP2$, and $MP3$ methods for HNO_3 geometry improves from HF to $MP2$ and $MP3$. We see that for two quantities $MP2$ performs better than $MP3$ ($r(O_3-N)$ and $\phi(O-N-O)$) but overall $MP3$ shows the smallest relative errors as seen in the above table. HF over(/under)estimates bond lengths due to the correlation between electron that is neglected, while $MP2$ and $MP3$ refine this through perturbative approach, though deviations remain. Overall $MP(n)$ methods outperforms HF since they capture better correlation between electrons, notably where the third O has an additional H atoms where the interaction with its electron may affect the energy and geometry optimization. But $MP(n)$ methods may also oscillate since for some bonds length higher perturbative orders under perform compared to lower orders as seen. Differences may arise from basis set limitations (6-31+G*). Indeed, due to its moderate size, 6-31+G* potentially underrepresents electron correlation and polarization effects. Higher-level perturbation orders or larger basis sets could reduce errors, but at higher computational cost.