

Exercise Ex6

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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

```
\begin{lstlisting}[language=Python]
\end{lstlisting}
```

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

Exercise 1

Why is it important to construct the starting structures in a specific conformation, although one is carrying out a geometry optimisation? Don't we risk to end up in the same conformation after the optimization, since we are dealing in both cases with the same molecule, i.e. methylcyclohexane?

The algorithm uses gradient descent and follows the steepest slope on the curve of the Potential Energy Surface during geometry optimization, but the curve associated to the system we are studying does not necessarily have only one global minimum and might have many local minima. In fact the methylcyclohexane has two local minima corresponding to the equatorial and axial position. If we start with the same initial configuration we will likely converge towards the same local minimum, this is why we need to construct different starting structures.

Exercise 2

Compute the energy of the two conformations and calculate the energy difference at 0 K, $\Delta E_{0K} = E_{\text{axial}} - E_{\text{equatorial}}$, i.e. the A-value, filling the table below. Compare the results of different methods with the experi-

mental value for the A-Value of the methyl group in a methylcyclohexane molecule, **1.74 kcal/mol**. For each method, use both 6-31+G* and 6-31+G** basis sets.

By adding **%time** at the beginning of each cell, the execution time will be printed out. This quantity is related to the computational cost of the calculation and can help you to compare the different methods.

You can split up the calculations among yourselves to speed up the process.

Method	E _{equatorial} (Hartrees)	E _{axial} (Hartrees)	$\Delta E(0K)$ (kcal/mol)	Relative error %	Basis set	Remark (ψ/ρ based ?)	Wall time
HF							
MP2							
BLYP							
MPW1PW91							
B97-2							
PBE							
TPSS							
M06-							
L							
M06-							
2X							
B3LYP-							
D3BJ							
Reference//	//		1.74	Experimental			

Method	$E_{\text{equatorial}}$ (Ha)	E_{axial} (Ha)	$\Delta E(0K)$ (kcal/mol)	Rel. error %	Basis set	Remark	Wall time
HF	-273.245841	-273.2420724	2.364817875	35.922	6-31+G*	ψ -based	25.29619908 s
HF	-273.2665356	-273.2628123	2.336406943	34.276	6-31+G**	ψ -based	38.41029763 s
MP2	-274.20746	-274.203995	2.1742875	24.959	6-31+G*	ψ -based	1h46min
MP2	-	-	0	100.000	6-31+G**	ψ -based	-
BLYP	-275.010229	-275.006325	2.44976	40.791	6-31+G*	ρ -based	3min58
BLYP	-275.006325	-275.025069	2.431631	39.749	6-31+G**	ρ -based	5min45
MPW1PW91	-275.141547	-275.138088	2.1705225	24.743	6-31+G*	ρ -based	3min17
MPW1PW91	-275.159045	-275.155645	2.1335	22.615	6-31+G**	ρ -based	3min30
B97-2	-275.102755	-275.09912	2.2809625	31.090	6-31+G*	ρ -based	1min8
B97-2	-275.120988	-275.117408	2.24645	29.106	6-31+G**	ρ -based	1min9
PBE	-274.801163	-274.797587	2.24394	28.962	6-31+G*	ρ -based	2min12
PBE	-274.818718	-274.815191	2.2131925	27.195	6-31+G**	ρ -based	3min22
TPSS	-275.244162	-275.240922	2.0331	16.845	6-31+G*	ρ -based	7min28
TPSS	-275.26039	-275.257202	2.00047	14.970	6-31+G**	ρ -based	8min 47
M06-L	-275.14381	-275.141905	1.1953875	31.300	6-31+G*	ρ -based	41min10
M06-L	-275.168237	-275.166418	1.1414225	34.401	6-31+G**	ρ -based	57min6
M06-2X	-275.053087	-275.050456	1.650983	5.116	6-31+G*	ρ -based	1min52
M06-2X	-275.067426	-275.064829	1.6296175	6.344	6-31+G**	ρ -based	57min6
B3LYP-D3BJ	-275.234567	-275.231718	1.7877475	2.744	6-31+G*	ρ -based	2min19
B3LYP-D3BJ	-275.253253	-275.250442	1.7639025	1.374	6-31+G**	ρ -based	4min41
Reference	//	//	1.74	Experimental			

The experimental A-value is 1.74 kcal/mol. Among all tested methods, only

B3LYP-D3BJ with 6-31+G** (1.76 kcal/mol, $\approx 1.4\%$ error) reproduces it smallest error among all methods used; B3LYP-D3BJ/6-31+G* provide also close results to the experimental values (1.79 kcal/mol, $\approx 2.7\%$ high). M06-2X/6-31+G** (1.63 kcal/mol, $\approx 6\%$ low) is acceptable but slightly underestimates the equatorial preference. In absolute terms several methods are within 1 kcal/mol, but in this set, B3LYP-D3BJ/6-31+G** is the closest to experimental value and most non-dispersion DFT GGAs/hybrids (BLYP, PBE, B97-2, MPW1PW91, TPSS) overestimate the A-value (2.2–2.45 kcal/mol), i.e. 25–40% too large, so they predict the axial form as too unstable (HF and MP2 also overestimate). On the other hand MP2 is much costlier than DFT for comparable accuracy.

Exercise 3

What kind of basis sets were used for ψ based calculations? On which atoms will polarization and diffuse functions be included? Are we close to the basis set limit? Why, or why not?

For the calculations, we used the following two different basis sets: 6-31+G* and 6-31+G**. These two basis sets are split valence Double Zeta sets. The 6-31G means that we put in 1 contraction basis function, 6 primitive gaussian type orbitals (PGTO) for the 1s orbital which is the core, then we split the valence shell in two different basis sets for each orbital, 3 PGTO are given for 2s and in one contracted basis function and another 1 PGTO in a new contracted basis function. For 2p orbitals it is similar than 2s but now we take into account each spatial direction. 6-31+G* means that we add *sp* diffuse functions for the heavy atoms and a d-polarization also for the heavy atoms (not H atoms), this adds respectively for *s* diffuse 1 basis function with 1 PGTO, for *p*-diffuse 3 basis functions with each 1 PGTO, and for *d*-polarization 6 basis functions with each 1 PGTO. 6-31+G** keeps the same structure for heavy atoms but we now add for light atoms (for H) *p*-polarization, meaning 3 basis functions with each 1 PGTO. We are not close to the basis set limit since larger and more flexible basis sets can be used such as 6-31++G**, 6-311++G**, aug-cc-pVTZ and also Quadruple Zeta basis sets etc. We choose to stop at this point since methods used lead to calculations already computationally costly.

Exercise 4

Comment on the performance of the wavefunction based methods and DFT, comparing both accuracy and computational time.

Can you imagine why some DFT methods perform better than others? How does DFT compare to MP2 and HF? Would you expect the exchange-correlation functionals to give similar errors in different systems?

An often cited target for the development of exchange-correlation functionals is an error below *chemical accuracy*, i.e. within 1 kcal mol⁻¹ of the accurate result. Explain the accuracy of the results also in light of this.

Wavefunction-based HF is cheap (tens of s) but overestimates the A-value by $\approx 35\%$, so accuracy is poor. MP2 improves to $\approx 25\%$ error but is extensively time consuming (1h46min), so the gain is modest for this system. On the

other hand for Density-based methods, most DFTs are much faster (1–5 min) and several already reach improved accuracy over HF/MP2. B3LYP-D3BJ/6-31+G** gives 1.76 kcal/mol, only 1.4% off 1.74, which is within the chemical accuracy of 1 kcal/mol. Differences between DFTs come from how E_x and E_c are built (GGA, meta, hybrid). Hybrid functionals (B3LYP-D3BJ, M06-2X) capture the axial-equatorial balance better than pure GGAs (PBE, BLYP). Compared to MP2, DFTs providing acceptable results appear to be both more accurate and cheaper in computational cost; and if we compare them to HF, they are slightly slower but much more reliable. We cannot expect one XC functional to yield the same error on all molecules and all XC functionals to yield the same error for the same molecule: error cancellation is system and approximation dependent. In most cases we are within the chemical accuracy. However the relative errors are large because the quantity we aim to predict is small. So the criterion of "within the 1 kcal/mol" is not really discriminative here and it is important to look at the relative errors which show that most methods are not acceptable. This justifies the continuing search for improved XC functionals.

Exercise 5

Fill the above table with the results of your calculations. Compare the performance of the structures. Is there a trend relating the complexity of the exchange-correlation functional to the accuracy?

****Bonus**:** For the DFT methods, specify what approximations are used in the exchange functional (you may refer to {ref}'dfttheory').

Method	ϕ_1 [°]	ϕ_2 [°]	$r_1(\text{O}-\text{N})$ [Å]	$r_2(\text{O}-\text{N})$ [Å]	$r_3(\text{O}-\text{N})$ [Å]	Symmetry
Exp.	120	120	1.24	1.24	1.24	D_3^h
HF	114.214	114.242	1.175	1.175	1.335	C1
MP2	113.552	113.551	1.218	1.218	1.388	C1
mpw1pw91	123.505	112.990	1.205	1.245	1.245	C1
b3lyp-d3bj	120.035	119.931	1.240	1.240	1.240	C1

From the documentation of p Psi4, the main difference between mPW1PW91 and B3LYP-D3BJ is not really in term of computational cost but in the fact that mPW1PW91 is an hybrid Generalized Gradient Approximation (GGA) method while B3LYP-D3BJ is an hybrid GGA method with dispersion added (as the name shows "D3"). The dispersion aims to account for the attraction that arises from instantaneous and correlated electron-density fluctuations inside a neutral system. This is where a trend appears as seen in the above table where B3LYP-D3BJ reproduces correctly the length of the O – N bonds and a relative error of order 10⁻²% with respect to the correct angles.

Bonus : mPW1PW91 is an hybrid GGA : Exchange used is a modified PW91 (mPW) GGA exchange mixed with a single HF-exchange fraction (the

“1” denotes a one-parameter hybrid, typically $\sim 25\%$ of the exact exchange). Correlation = PW91.

B3LYP-D3BJ is an hybrid GGA + dispersion : Exchange used is a Becke 3-parameter hybrid, this corresponds to a fitted mix of HF ($\approx 20\%$) and B88 GGA exchange on top of LSDA. Correlation = Local Spin-Density Approximations (LYP). “D3BJ” is an a-posteriori dispersion correction (Grimme D3) added to the energy; this dispersion is not part itself of the exchange functional,

Exercise 6

Take a screenshot of the MP2 and DFT SOMOs. How do the orbitals differ from each other? How does the symmetry of the SOMO relate to the predicted structure?

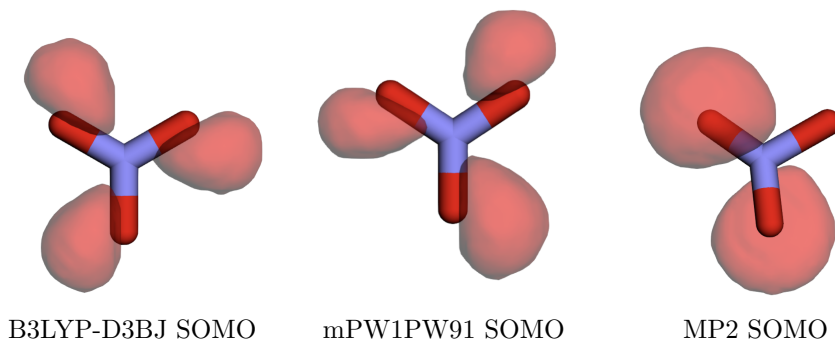


Figure 1: Singly occupied molecular orbitals (SOMO) from three methods.

As shown here, we see that the orbitals differ subsequently from one to another, first between DFT methods and *MP2* and then between the two different DFT methods. First, *MP2* compared to DFT, fails to reproduce the symmetric distribution of the unpaired electron of the radical NO_3 . (SOMO) by giving half the probability of finding it to only two of the three *O* atoms. Not enough correlation is taken into account by *MP2* which localizes the distribution instead of delocalizing it as expected for this radical. On the other hand DFT is able to delocalize the distribution between the three *O* atoms, but only it only partially reproduce the exact symmetric distribution depending on the method. Indeed *mPW1PW91* seems to overestimate the distribution on the longest bond as if the orbitals of the shorter bonds overlap with the latter, increasing its marginal. Concerning B3LYP-D3BJ, by adding dispersion, is able to symmetrically delocalize the distribution so that it reproduces correctly the D_3^h symmetry of the radical NO_3 . Therefore, SOMO symmetry mirrors the predicted geometry : B3LYP-D3BJ relates correctly the predicted structure.

Exercise 7

Explain the difference between static and dynamic correlation. Relate this

to the different results you obtained for the nitrate radical. What kind of correlation do HF, MP2 and DFT take into account?

Dynamic correlation corresponds to electrons avoiding each other instant-to-instant around a single reference which consists in the HF reference. It corresponds to the cusp and the short range contribution and is well captured by methods built from adding excitations around the single HF reference such as *MP* and *CC/CI*. On the other hand, *Static correlation* corresponds to the situation where more than one configuration is nearly degenerate, therefore a single reference determinant is inadequate. We need multiple references with comparable weights in order to avoid localization or symmetry breaking.

In our case the $\text{NO}_3\cdot$ radical has a near degenerate π -orbital in the D_3^h limit. This induces a non negligible static correlation energy and a method that is not able to capture it, tends to break the symmetry with unequal $N-O$ length bonds and $O-N-O$ angles and/or localizes the SOMO.

This is what we witness with first HF that typically lacks the electron correlation and therefore breaks the symmetry in the lengths and angles obtained. Similarly, as *MP2* is a method built from a single reference (HF), it fails to reproduce the symmetric behaviour in the length bounds and angles, leading to asymmetric localized orbitals on two of the three O atoms. Concerning DFT methods, results in *mPW1PW91* are improved by including dynamic correlation (introduced in the XC correlation term) and mitigates HF and *MP2* over-localization even if some asymmetry remains. *B3LYP-D3BJ* is able to recover the symmetry in length bounds, angles and SOMO distribution thanks to the correction brought to the energy by adding dispersion, capturing the static correlation due to nearly degeneracy.

Exercise 8

If you needed a highly accurate structure and energy for $\text{NO}_3\cdot$, which method would you use? Why?

Based on what was answered in the previous questions, I would use DFT. Indeed depending on the approximations used in the exchange correlation term and if dispersion is added, DFT methods are able to recover the static correlation where the single reference methods as HF, *MP(n)*, *CC*, *CI* struggle. Indeed the last 3 are often truncated to a certain and fails to capture the near degeneracy contribution. Also, multi-reference methods can be used, where these methods start from a set of important configurations. Finally, based on the notes, Meta-GGA seems to be the most efficient methods. They take into account how the density varies, its derivatives and the Kohn-Sham kinetic energy.