

Exercises on DFT method

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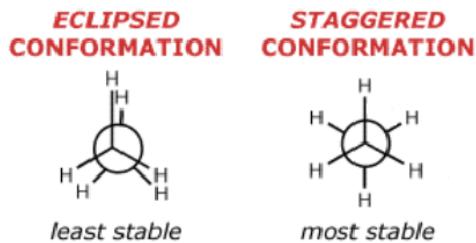


Introduction

All quantum chemical calculations in this study were performed using the ORCA software package [1], employing Density Functional Theory (DFT) [2].

Exercise 1

The rotational energy barrier between the eclipsed and staggered conformations in ethane is a fundamental parameter in quantum chemistry and molecular spectroscopy. In this study, we calculated the rotational barriers for ethane, 1,1-dichloroethane, and 1,1-difluoroethane using different computational basis sets and functionals to determine the most suitable basis set in terms of accuracy and computational cost.



1.1)

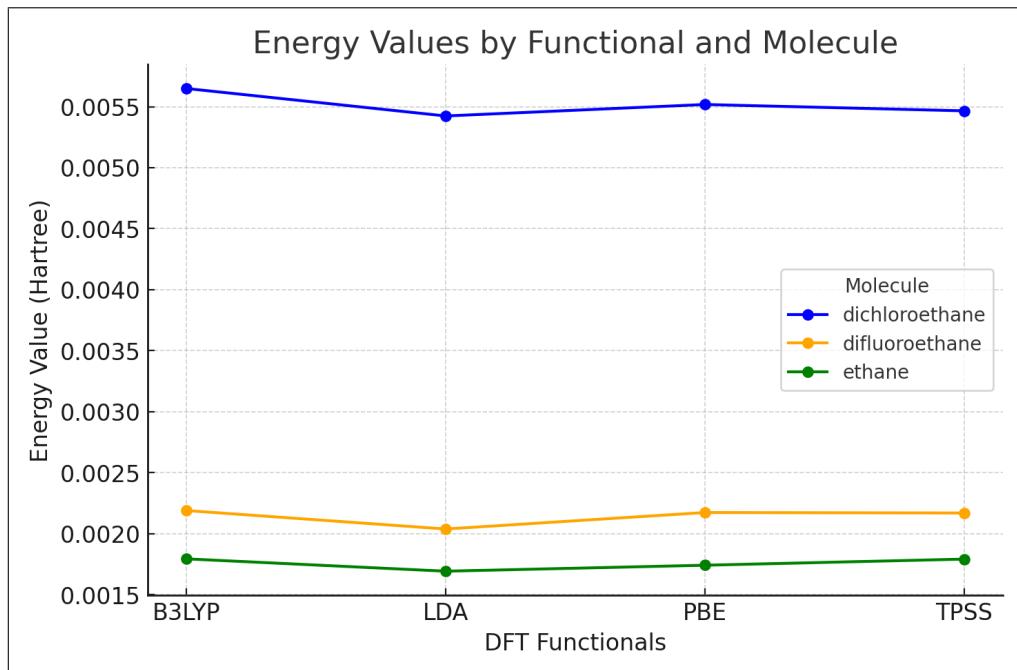


Figure 1: Potential energy barriers def2-TZVP/B3LYP,PBE,LDA,TPSS

In Figure 1, the potential energy barriers are represented, calculated as follows:

$$\Delta E = E_{\text{eclipsed}} - E_{\text{staggered}} \quad (1)$$

As shown in Figure 1, the energy barrier increases with molecular size.

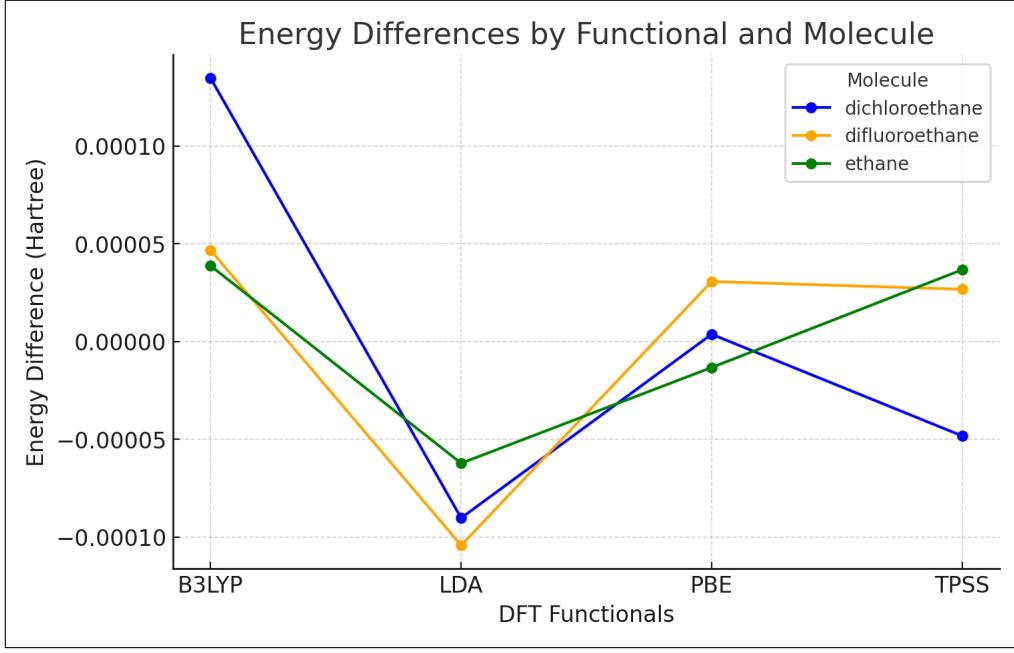


Figure 2: Relative potential energy barriers def2-TZVP/B3LYP,PBE,LDA,TPSS

Figure 2 represents the values of the relative potential energy barriers, calculated as follows:

$$\Delta E_{\text{relative}} = \Delta E - \langle \Delta E \rangle \quad (2)$$

where $\langle \Delta E \rangle$ is the mean energy barrier calculated for each molecule. This representation is useful for comparing the different functionals.

LDA (Local Density Approximation).[3] This is the simplest functional among the four. It treats the electron density as locally uniform and often overbinds, leading to an underestimation of energy barriers.

PBE (Perdew-Burke-Ernzerhof).[4] This GGA functional includes the density gradient and generally improves upon LDA by partially correcting its overbinding.

TPSS (Tao-Perdew-Staroverov-Scuseria).[5] A meta-GGA functional that incorporates the kinetic energy density, aiming to refine barrier predictions without relying on exact exchange.

B3LYP (Becke-3-Parameter-Lee-Yang-Parr).[6] A hybrid GGA functional that introduces a fraction of exact exchange, enhancing accuracy in energy barrier calculations.

In the plot (Figure 2), LDA exhibits the lowest values, reflecting its tendency to underestimate energies. PBE lies at intermediate values, correcting some of LDA's limitations. TPSS produces results between pure GGA functionals (like PBE) and hybrids (like B3LYP),

though its performance depends significantly on the specific system. B3LYP, owing to partial Hartree-Fock exchange, yields the highest barriers, as the inclusion of exact exchange reduces self-interaction errors and enhances the description of electronic repulsion.

1.2)

Density Functional Theory (DFT) calculations were performed using the basis sets QZVP, SVP, TZVP, and TZV to determine the rotational energy barrier for each molecule.

Table 1 presents the calculated rotational energy barriers for each molecule using different basis sets.

Molecule	QZVP	SVP	TZVP	TZV
1,1-Dichloroethane	3.37	4.27	3.54	2.17
1,1-Difluoroethane	1.35	1.63	1.37	0.25
Ethane	1.10	1.26	1.12	1.12

Table 1: Rotational energy barriers (in kcal/mol) calculated with different basis sets.

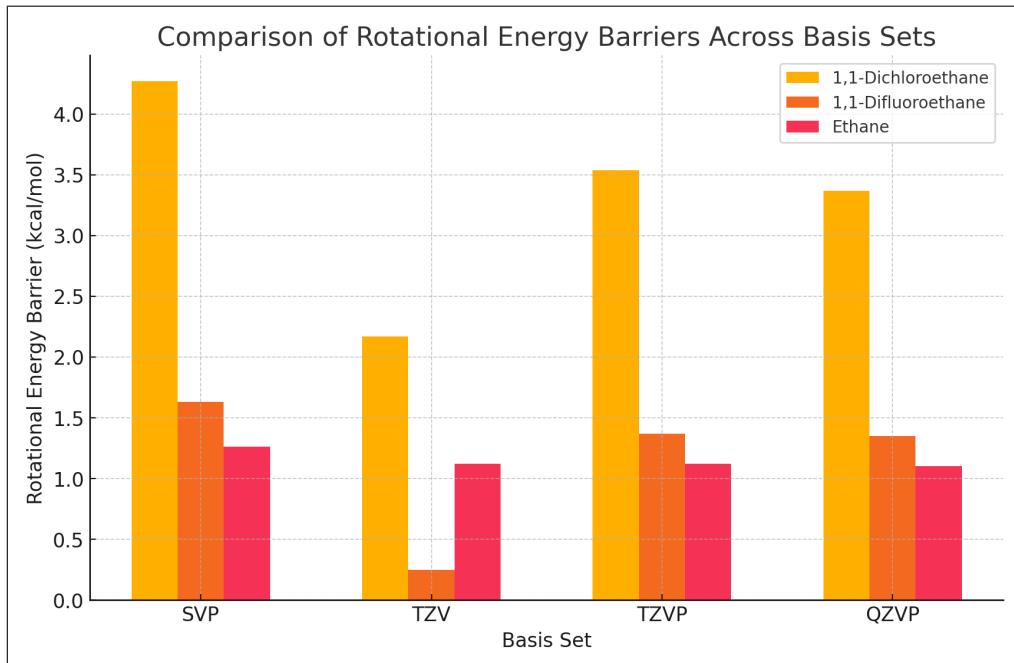


Figure 3: Relative potential energy barriers def2-SVP, def2-TZV, def2-TZVP, def2-QZVP/B3LYP

The analysis shows that for all basis sets except TZV, the energy value increases as the molecular weight increases.

- TZVP and QZVP appear to provide the most consistent results among the tested basis sets, yielding similar results.

- SVP overestimates the barrier, particularly for 1,1-dichloroethane.
- TZV significantly underestimates the barrier in 1,1-difluoroethane.

QZVP offers the highest level of accuracy among the tested basis sets; however, this comes at a significant computational expense. On the other hand, TZVP is the most balanced option, effectively combining precision with computational efficiency. SVP, while being a computationally cheap choice, often overestimates the rotational energy barriers. Meanwhile, TZV proves to be unreliable due to its inconsistent results, making it a less favorable option for these calculations.

1.3)

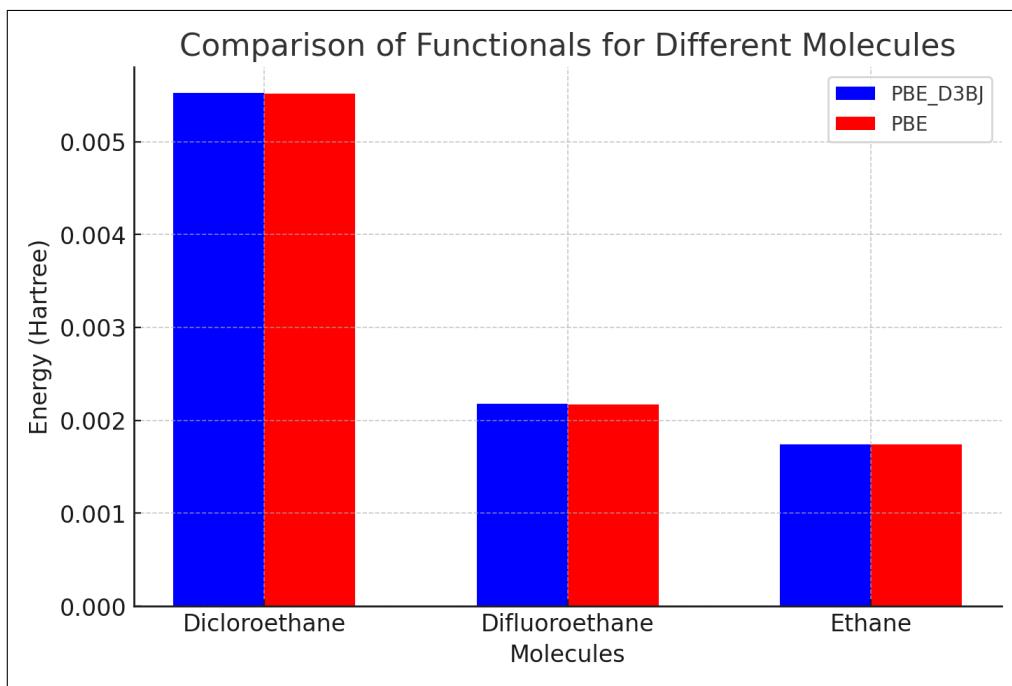


Figure 4: Comparison between def2-TZVP/PBE and def2-TZVP/PBE D3BJ

The graph in Figure 4 compares the potential energy barriers calculated with equation 1 using the functionals PBE and PBE-D3BJ with the def2-TZVP basis set for three molecules: dichloroethane, difluoroethane, and ethane.

The D3BJ [7] correction is an empirical dispersion correction introduced by Grimme, often applied to density functionals to improve the description of long-range dispersion interactions.

The graph suggests that including the D3BJ dispersion correction in PBE has a relatively small impact on energy values for these molecules since the result is practically the same.

Exercise 2

In this exercise I am going to study the following equations:



Table 2 presents the reaction enthalpies for propane, butane, and hexane calculated using different density functionals.

Molecule	B3LYP	PBE0	PBE-D3	PBE	SVWN5	TPSS
Propane	6.85	7.98	9.55	7.95	12.24	6.23
Butane	13.28	15.70	19.08	15.58	24.30	12.20
Hexane	25.55	30.56	37.74	30.19	47.56	23.62

Table 2: Calculated reaction enthalpies (kJ/mol).

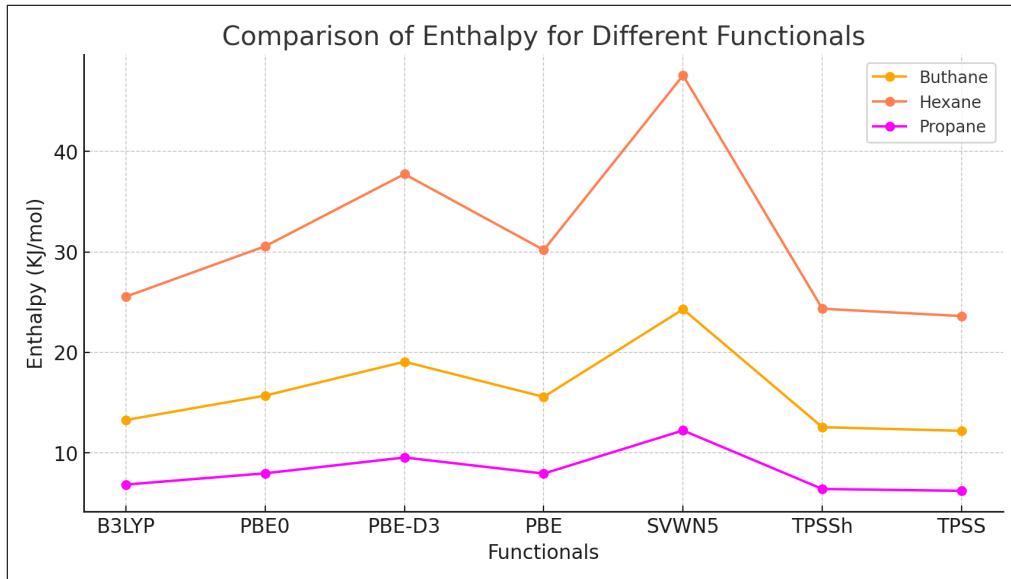


Figure 5: Comparison of Enthalpies by DFT Functional using def2-TZVP/B3LYP, PBE, PBE-D3, SVWN5, TPSS, TPSSh

The graph in Figure 5 shows the reaction enthalpies for butane, hexane, and propane using different DFT functionals with the def2-TZVP basis set. The reaction enthalpy (ΔH) is computed as the difference between the total enthalpies of the products and the reactants:

$$\Delta H = \sum H_{\text{products}} - \sum H_{\text{reactants}} \quad (3)$$

A positive enthalpy ($\Delta H > 0$) indicates an endothermic reaction, while a negative enthalpy ($\Delta H < 0$) suggests an exothermic process.

Overall, for all the hydrocarbons the enthalpy of the reaction is positive which indicates that the reaction is endothermic, however the trend suggests that as molecular size increases, the reaction enthalpy increases.

The different enthalpies of reactants and products have been calculated by adding the zero-point energy, vibrational, rotational, and translational thermal corrections, as well as the thermal enthalpy correction, to the electronic energy.

2.1) Which functionals lead to better results? which are worse? Can you rationalize why?

The experimental values for these reactions are shown in table 3

Molecule	Exp. (kJ/mol)
Propane	9.36
Butane	21.85
Hexane	42.98

Table 3: Experimental reaction enthalpies (kJ/mol).

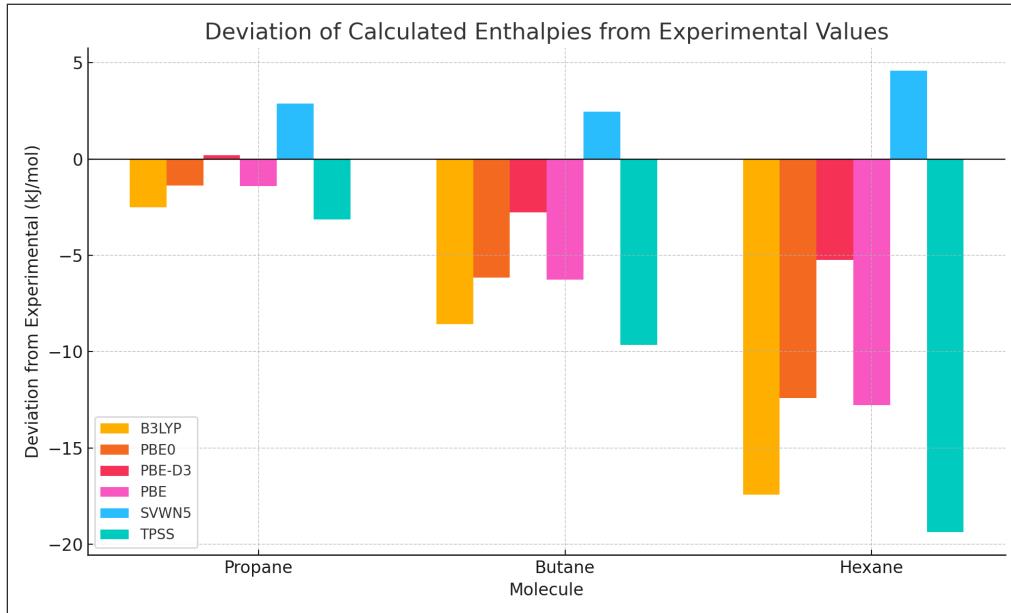


Figure 6: Enthalpies relative to the experimental values using def2-TZVP/B3LYP, PBE, PBE-D3, SVWN5, TPSS, TPSSh

Looking at the bar chart of Figure 6 we compare each functional's deviation from the experimental result: **PBE-D3** and **SVWN5**[8] tend to remain closer to the experimental values for propane, butane, and hexane. **PBE** and **PBE0**, Their deviations are not as small

as PBE-D3 or SVWN5, but generally better than the worst cases. **B3LYP** and **TPSS**, Both show more significant discrepancies, especially for hexane (the largest molecule).

Hydrocarbons (particularly longer chains like butane and hexane) exhibit significant London dispersion forces. Functionals that do not include an explicit treatment of dispersion often underestimate these interactions, leading to larger errors.

PBE-D3 incorporates Grimme's D3 dispersion term, improving the description of long-range electron correlation.

Although SVWN5 (Local Density Aproximation, LDA) is conceptually simpler and often less accurate for complex systems, it can yield fortuitously good results for certain hydrocarbons. SVWN5 may benefit from accidental error compensation.

B3LYP and PBE0 combine GGA exchange-correlation with a fraction of exact (Hartree-Fock) exchange. Without a dispersion correction these hybrids typically underestimate non-covalent interactions, becoming less accurate as molecule size (and dispersion contribution) increases.

TPSS (Meta-GGA) includes dependence on the kinetic-energy density, theoretically improving short- and medium-range correlation. Like the other functionals without an explicit dispersion term, it struggles with large alkanes, leading to more pronounced errors in hexane.

PBE-D3 and **SVWN5** consistently provide the closest agreement with experimental reaction enthalpies for propane, butane, and hexane. Functionals **PBE** and **PBE0** exhibit moderate deviations, better than the worst but not as accurate as PBE-D3 or SVWN5. **B3LYP** and **TPSS** show the largest errors, especially for longer hydrocarbon chains, highlighting the need for a proper description of dispersion.

2.2) There has been some discussion about whether the functional "rung", the type of exchange term used or medium-range correlation (dispersion) is responsible for the deviations from the experimental data. What is your opinion based in your results?

In our study of hydrocarbon reaction enthalpies (propane, butane, and hexane), the clearest conclusion is that the **presence or absence of an explicit dispersion correction** drives the most significant differences between computed and experimental values. Although the "rung" of the functional (*e.g.*, LDA, GGA, meta-GGA, or hybrid) and the amount of exact (Hartree–Fock) exchange certainly affect thermochemical performance, our data show that:

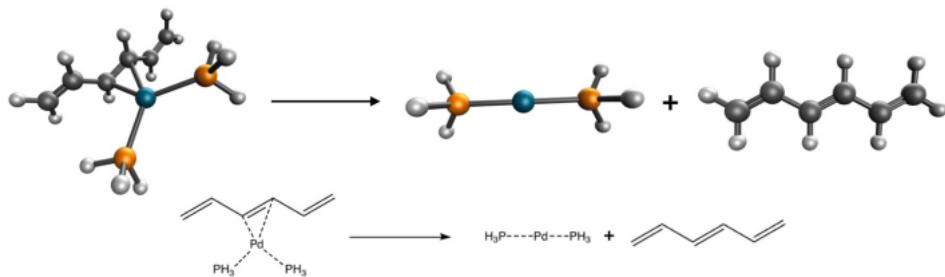
- **PBE vs. PBE-D3:** Adding Grimme's D3 dispersion correction to a base GGA (PBE) dramatically reduces deviations, more than moving to a higher-rung functional without dispersion.
- **TPSS vs. PBE-D3:** Although TPSS is a meta-GGA (nominally higher rung), it still underperforms compared to PBE-D3, again highlighting the importance of an explicit long-range correlation correction.
- **SVWN5 (LDA):** Surprisingly, an LDA functional like SVWN5 can achieve acceptable accuracy through *fortunate* error cancellation, despite being considered a lower-rung approach.

- **Hybrid Functionals Without Dispersion:** Both B3LYP and PBE0, which include a fraction of exact exchange, fail to fully capture dispersion.

Hence, while the theoretical sophistication of a higher-rung functional or the inclusion of exact exchange matters, the most critical factor for accurately predicting hydrocarbon thermochemistry in this context is capturing dispersion properly through an explicit -D3.

Exercise 3

Study of an organometallic reaction



The dissociation energy (E_{diss}) was computed by calculating the total electronic energy of the complex ($E_{complex}$) and the sum of the energies of the dissociated fragments ($E_{products}$). The dissociation energy is obtained as:

$$E_{diss} = E_{products} - E_{complex} \quad (4)$$

where $E_{products}$ includes the individual energies of the separated fragments. Each energy term was calculated using the same computational method to ensure consistency. This energy was compared with the experimental value of 16.2 kcal mol⁻¹

To do this I tested multiple functionals and basis sets in ORCA, refining my approach based on both theoretical considerations and literature recommendations.

I began by using the **PBE0-D3 functional** with the **DEF2-TZVP basis set**, as PBE0 is a widely used hybrid functional that balances accuracy and computational cost, while the DEF2-TZVP basis provides a reasonable description of transition metals. This calculation established the baseline for comparison.

To evaluate whether a more extensive basis set could improve the results, I repeated the calculation with **DEF2-TZVPP**, a larger triple-zeta basis. However, the dissociation energy was slightly worse. This suggested that further increasing the basis set size would not significantly enhance accuracy.

Next, I tested **B3LYP-D3**, a hybrid functional that incorporates a higher percentage of exact Hartree-Fock (HF) exchange than PBE0. This functional is commonly used in transition metal chemistry, but the calculated dissociation energy was far from the experimental value, significantly underestimating it. This result indicated that B3LYP was not well-suited for this system.

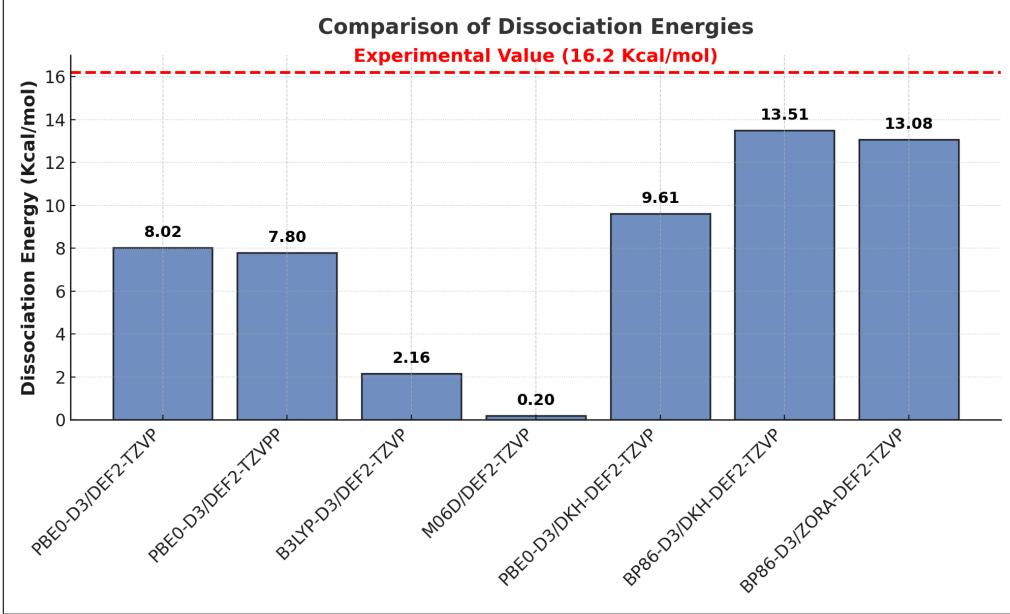


Figure 7: Comparison of Dissociation Energies

According to an study[9], the **M06D functional**[10] was recommended for similar systems. I tested M06D with the same DEF2-TZVP basis set, but the results were extremely poor, yielding an even lower dissociation energy.

After consulting another study[11], which emphasized the importance of relativistic basis sets for heavy elements like palladium, I tested a relativistic approach. Since PBE0-D3 had previously given the best results, I applied the **DKH (Douglas-Kroll-Hess) relativistic correction**[12] with DEF2-TZVP. This modification improved the dissociation energy compared to the non-relativistic calculations, confirming that relativistic effects were necessary for a more accurate description of the system.

The same paper also suggested that **BP86**[13] was particularly well-suited for palladium complexes. To verify this, I performed calculations using BP86-D3 with two different relativistic methods: DKH and ZORA[14] and a special basis set for palladium which was SARC-ZORA-TZVP. The results showed that BP86 yielded better agreement with the experimental dissociation energy than PBE0-D3. Among the two relativistic corrections, BP86-D3-DKH produced the best results.

In addition to providing the most accurate dissociation energy, BP86-D3-DKH/DEF2-TZVP drastically reduced computational time, completing the total energy calculation for the complex in just 2 minutes and 27 seconds, compared to 14 minutes and 42 seconds with PBE0-D3-DKH/DEF2-TZVP. This means that not only does BP86-D3-DKH produce more accurate results, but it is also nearly 6 times faster, making it the most efficient choice for this system.

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