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Density Functional Theory

Project 3–Properties of the water molecule

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A report submitted in partial fulfilment of the requirements of
the University of Caen for the degree of
Erasmus Mundus Master in Nuclear Physics

January 6, 2025

Contents

Chapter 1

Theoretical study

1.1 Recall the statement of the first theorem of Hohenberg and Khon. Demonstrate, assuming there are two different external potentials V'_{ext} and V''_{ext}, both of which give the same electron density.

The first Hohenberg-Kohn theorem states that no two different external potentials V'_{ext} and V''_{ext} yield the same ground-state electron density $\rho(r)$. Let us assume that the density $\rho(r)$ corresponds to the ground state solution of H' with external potential V'_{ext} and also of H'' with external potential V''_{ext}. That is,

$$E' = \langle \psi'|H'|\psi' \rangle$$
$$E'' = \langle \psi''|H''|\psi'' \rangle$$

The difference between the two being,

$$E' - E'' = \int \left(V'_{\text{ext}} - V''_{\text{ext}} \right) \rho(r) dr$$

Then since the ground state corresponds to the minimum energy solution of a Hamiltonian,

$$E' < \langle \psi''|H'|\psi'' \rangle$$
$$E'' < \langle \psi'|H''|\psi' \rangle$$

Adding the two inequalities leads to a contradiction as follows,

$$
\begin{aligned}
E' + E'' &< \langle \psi''|H'|\psi'' \rangle + \langle \psi'|H''|\psi' \rangle \\
&< \langle \psi''|T + V'_{\text{ext}}|\psi'' \rangle + \langle \psi'|T + V''_{\text{ext}}|\psi' \rangle \\
&< \langle \psi''|T|\psi'' \rangle + \int V'_{\text{ext}}\rho(r)dr + \langle \psi'|T|\psi' \rangle + \int V''_{\text{ext}}\rho(r)dr \\
&< \langle \psi''|T|\psi'' \rangle + \int V''_{\text{ext}}\rho(r)dr + \langle \psi'|T|\psi' \rangle + \int V'_{\text{ext}}\rho(r)dr \\
&< E'' + E'
\end{aligned}
$$

This contradiction shows that two different external potentials V'_{ext} and V''_{ext} cannot lead to the same ground-state electron density $\rho(r)$.

1.2 Explain briefly the principle of the MPn method (in 10 lines maximum). Recall the energy obtained with the MP2 method and compare it to the HF energy.

The Møller-Plesset perturbation theory (MPn) is a post-Hartree-Fock method that systematically includes electron correlation by treating the difference between the exact Hamiltonian and the Hartree-Fock (HF) Hamiltonian as a perturbation. The energy is expanded as a series $E = E^{(0)} + E^{(1)} + E^{(2)}...$, where $E^{(0)}$ is the HF energy, and higher-order terms $E^{(n)}$ account for correlation effects.

In the MP2 method, second-order perturbation theory is used, with the energy correction $E^{(2)}$ calculated from the virtual orbitals and interaction between occupied and virtual orbitals. The MP2 energy is lower than the HF energy since it includes the correlation energy neglected in HF. Specifically, MP2 improves upon HF by considering instantaneous electron-electron repulsion, leading to a more accurate total energy.

Mathematically, the MP2 correction is:

$$E^{(2)} = \sum_{ij,ab} \frac{\langle ij|H|ab\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

1.3 Explain briefly the principle of the CI and CC methods and discuss the differences and the similarities between these two theories (in one page maximum).

Configuration Interaction (CI) is a quantum chemistry method that improves the Hartree-Fock wavefunction by constructing a more accurate wavefunction as a linear combination of multiple Slater determinants. These determinants represent different electronic configurations obtained by exciting electrons from occupied orbitals to virtual orbitals. The CI wave function is expressed as:

$$\Psi_{\mathsf{CI}} = c_0\Psi_{\mathsf{HF}} + \sum_i c_i\Psi_i + \sum_{ij} c_{ij}\Psi_{ij} + \dots$$

Here Ψ_{HF} is the Hartree-Fock wavefunction, and are singly and doubly excited determinants, respectively. The CI method systematically accounts for electron correlation by including higher-order excitations. However, CI is computationally expensive, as the number of determinants grows rapidly with the number of electrons and orbitals.

Coupled Cluster (CC) theory also improves the Hartree-Fock wavefunction by incorporating electron correlation but uses an exponential ansatz for the wavefunction:

$$\Psi_{\mathsf{CC}} = e^{\hat{T}}\Psi_{\mathsf{HF}}$$

Here $\hat{T} = \hat{T}_1 + \hat{T}_2 + ...$ is the cluster operator that includes single ($\hat{T}_1$) and higher excitations. Unlike CI, CC includes these excitations in a nonlinear way, allowing it to better capture correlation effects with fewer terms. For example, the CCSD method includes singles and doubles excitations and indirectly accounts for higher excitations through the exponential form. This makes CC highly accurate, especially for chemical systems dominated by dynamic correlation.

Both CI and CC aim to improve the Hartree-Fock description by including electron correlation, but they differ in approach. CI uses a variational method and is conceptually simpler, with a straightforward truncation scheme (e.g., CISD includes singles and doubles). However, it is not size-extensive, meaning the energy does not scale correctly with system size. CC, on the other hand, is size-extensive due to its exponential form, making it more reliable for large systems. While CC method is more accurate than truncated CI, it is also computationally more intensive due to the iterative solution of nonlinear equations. Both methods complement each other in understanding and predicting molecular electronic structures.

1.4 Among the following methods: CIS, CISD, CCD and CCSD which are suitable for describing the ground state energy?

Among the given methods, CCSD (Coupled Cluster Singles and Doubles) is the most suitable for describing ground-state energy due to its ability to account for both single and double excitations and its size-extensive nature, ensuring accurate scaling with system size. CCD (Coupled Cluster Doubles) is also suitable for systems where double excitations dominate, but it neglects single excitations, which may limit its applicability in some cases. CISD (Configuration Interaction Singles and Doubles) provides a reasonable approximation for small systems by including single and double excitations, but it is not size-extensive, making it less reliable for larger systems. CIS (Configuration Interaction Singles), however, is unsuitable for ground-state energy as it focuses only on single excitations, which do not contribute to electron correlation in the ground state.

Chapter 2

Analysis and Discussion

2.1 Exploration of the PES.

2.1.1 **For each OH bonds $\left(R_1 = R_2 = R \right.$ with $R = 0.80, 0.90, 1.00$ and 1.10Å), plot the energy calculated at the RHF, MP2, DFT(LDA, PBE, BLYP, B3LYP and M062X) and CCSD levels in function of the angle α where the energy will be expressed in a.u.**

Figure 2.1: Energy dependence on OH bond distance R and angle α calculated at the RHFlevel

Figure 2.2: Energy dependence on OH bond distance R and angle α calculated at the MP2level

Figure 2.3: Energy dependence on OH bond distance R and angle α calculated at the LDAlevel

Figure 2.4: Energy dependence on OH bond distance R and angle α calculated at the PBElevel

Figure 2.5: Energy dependence on OH bond distance R and angle α calculated at the BLYPlevel

Figure 2.6: Energy dependence on OH bond distance R and angle α calculated at the B3LYPlevel
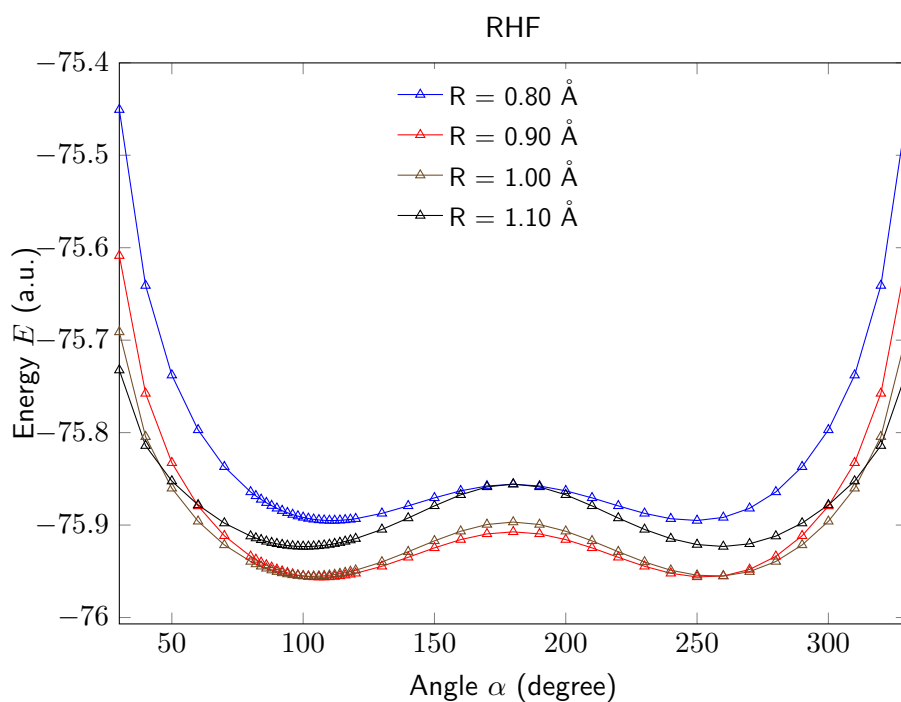

Figure 2.7: Energy dependence on OH bond distance R and angle α calculated at the M062Xlevel
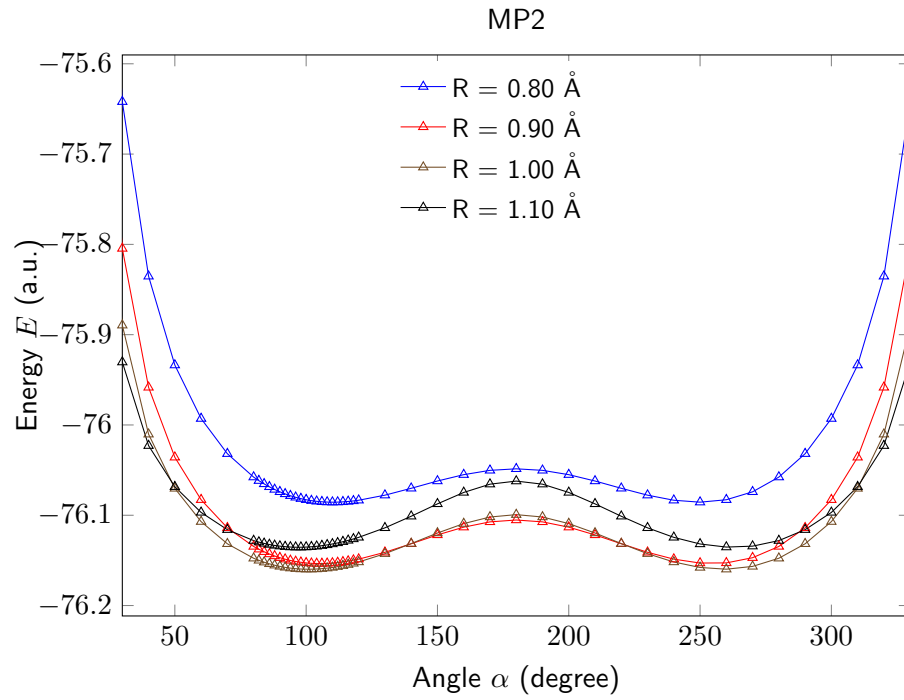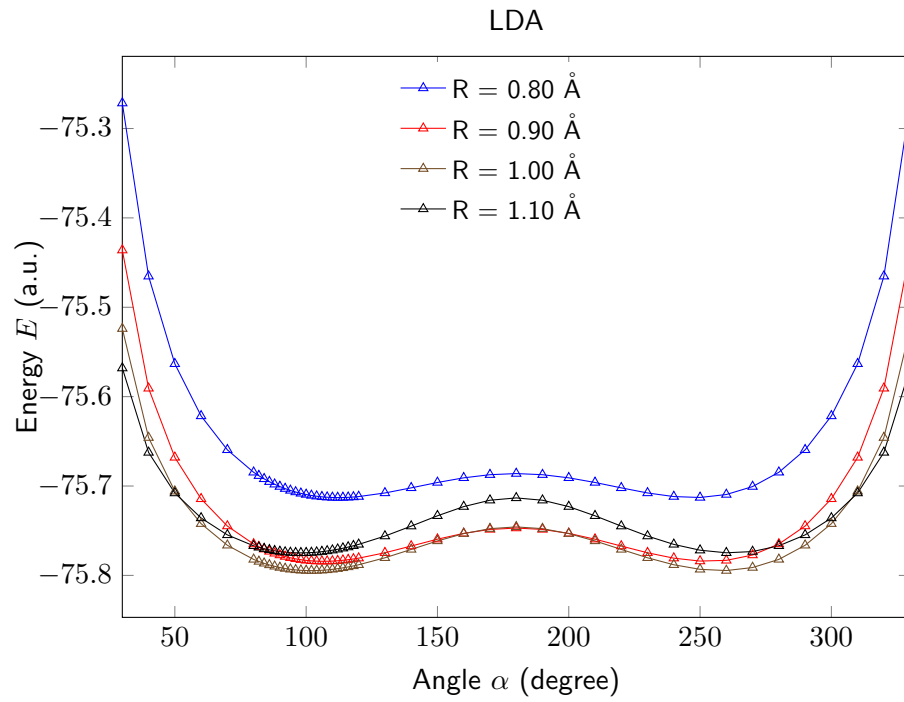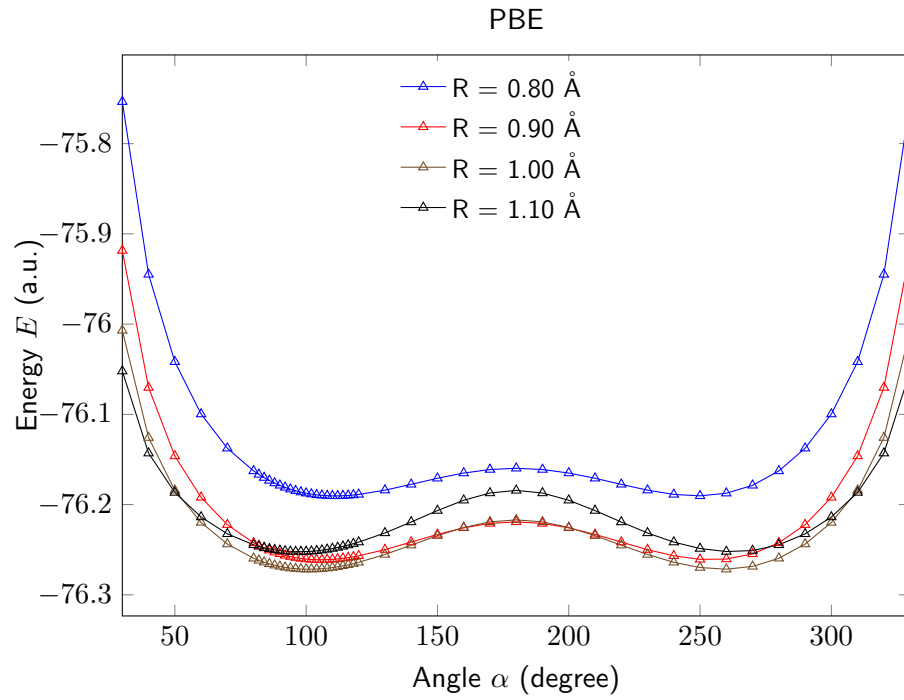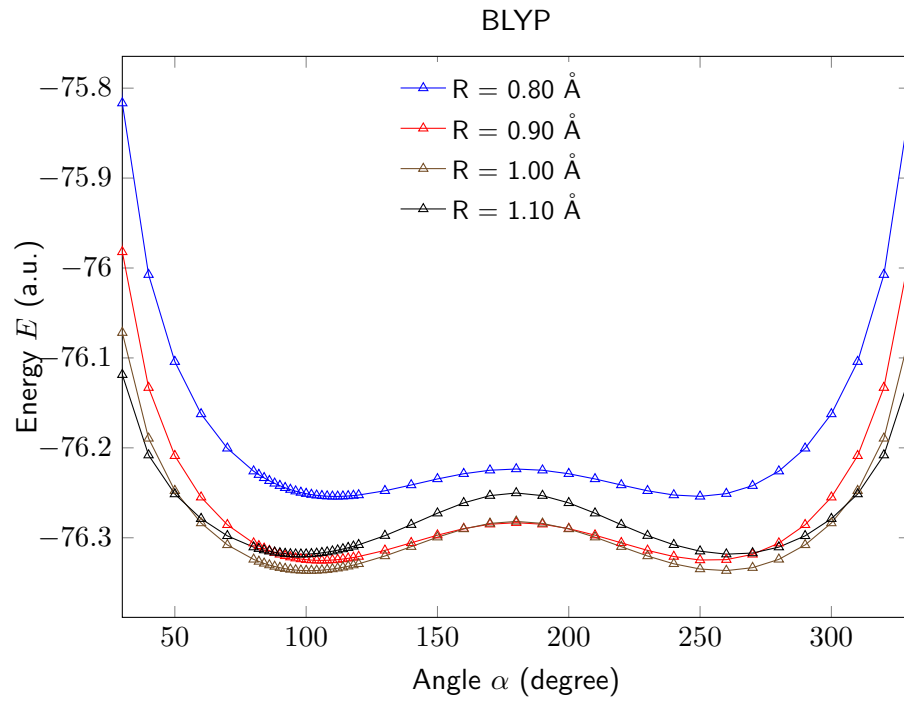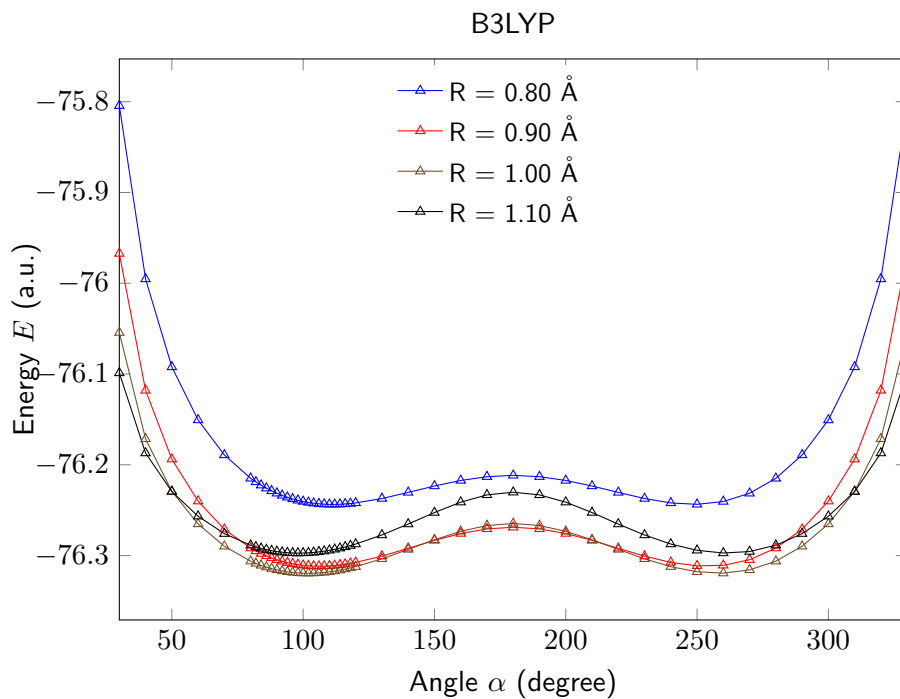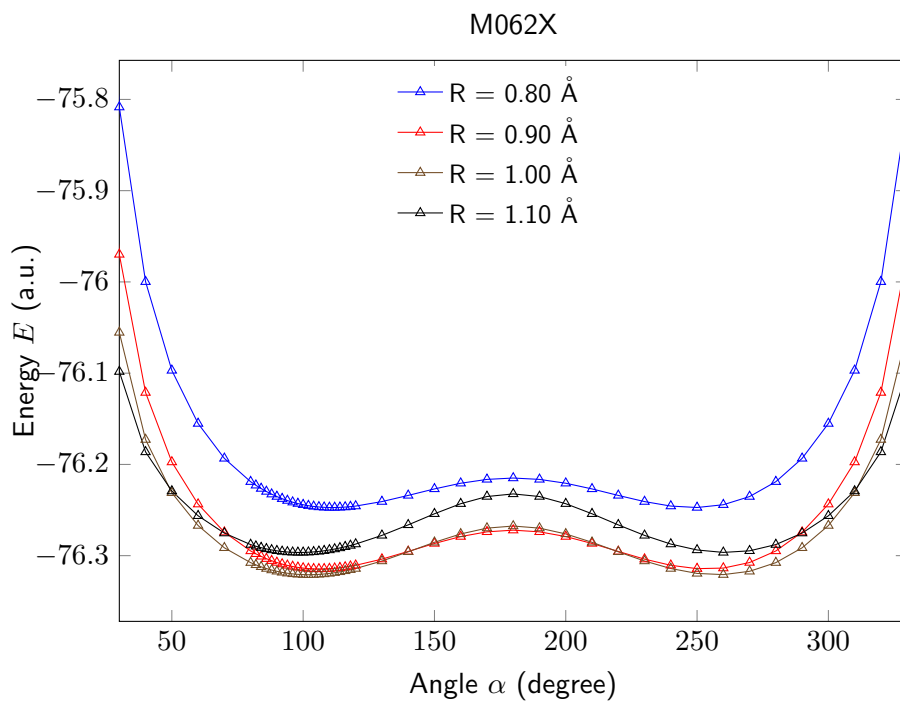
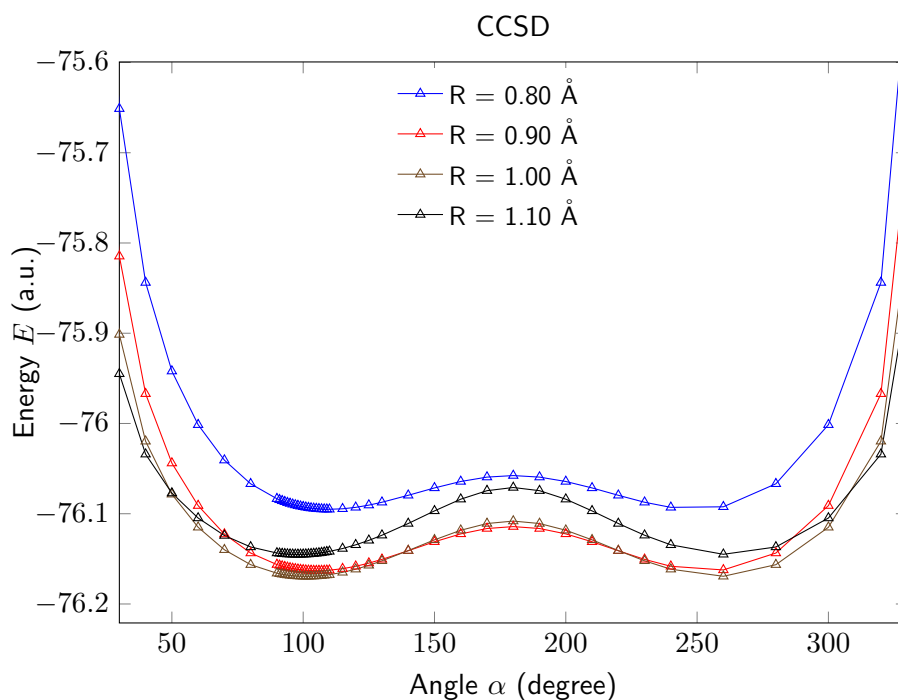Figure 2.8: Energy dependence on OH bond distance R and angle α calculated at the CCSDlevel

Figure 2.9: Energy dependence on OH bond distance R and angle α calculated at R = 0.90 Å for different methods.
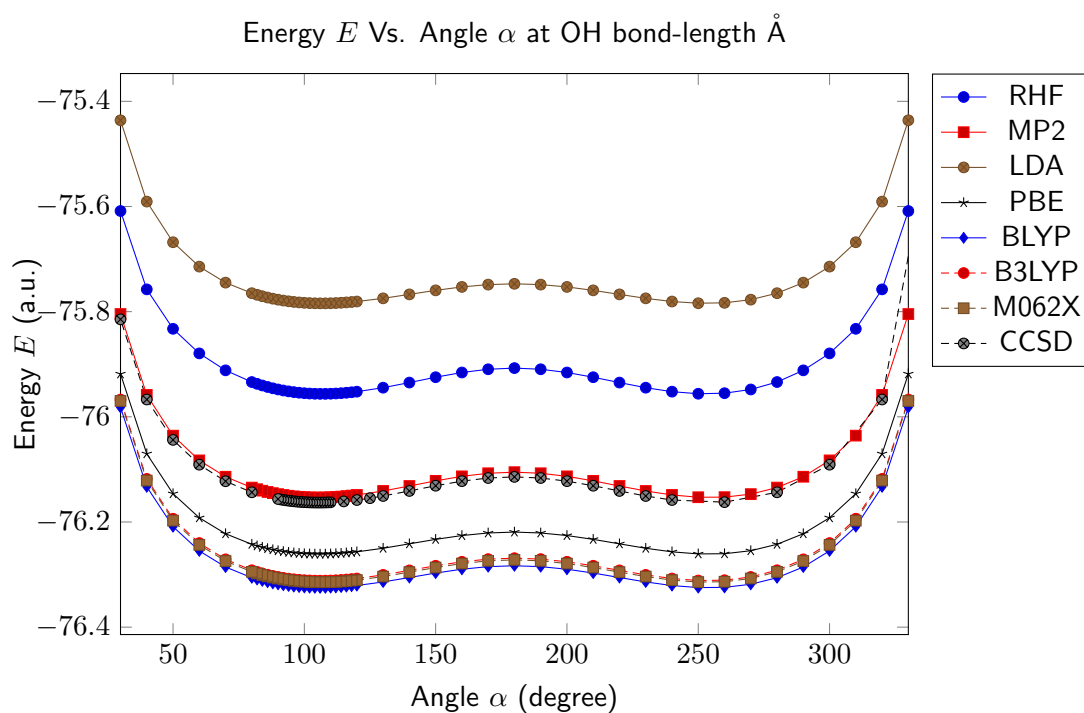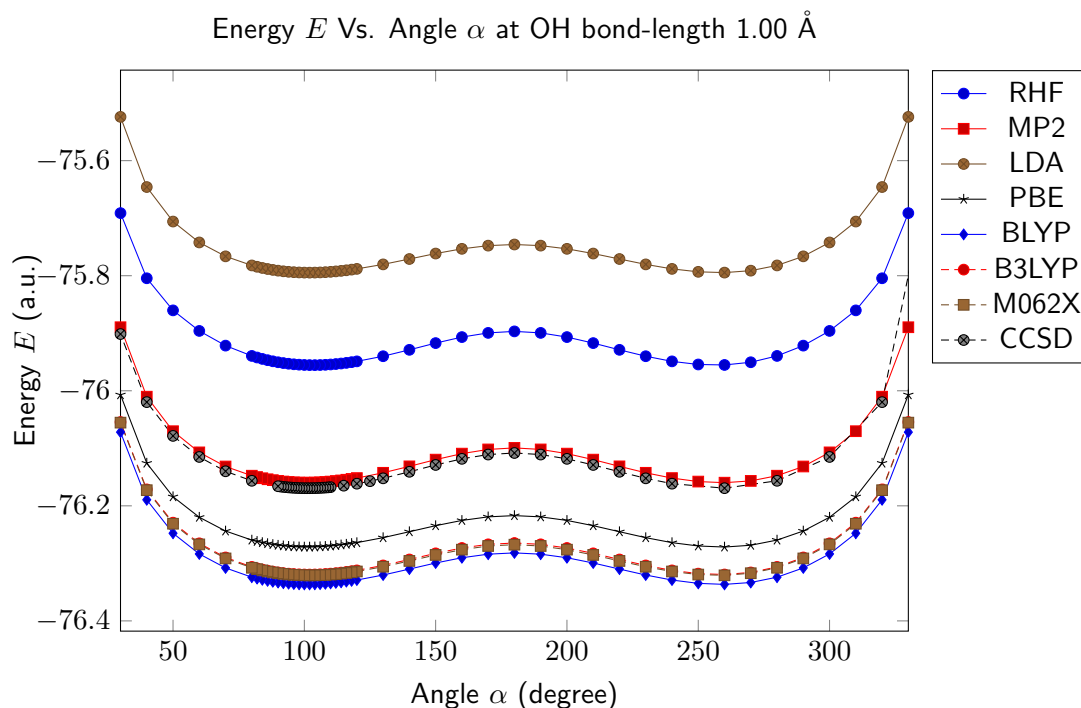
Figure 2.10: Energy dependence on OH bond distance R and angle α calculated at R = 1.00 Å for different methods.

Energy E Vs. Angle α at OH bond-length 1.00 Å

2.1.2 From these graphs, identify the extrema of the PES and discuss about their nature (minima or not)

From the energy versus angle graphs for the water molecule, we observe a minimum around 100 degrees and a local maximum at 180 degrees. Due to the function's symmetry about 180 degrees, the minimum is mirrored at approximately 260 degrees.

2.2 Properties of the molecule

Table 2.1: Geometrical properties of the water molecule

Model	Energy (a.u.)	Angle α (°)	R_{OH} (Å)	Dipole μ (D)	$\triangle R_{OH}$	$\triangle \mu$
RHF	-76.05958	106.50759	0.94205	2.11101	0.01591	0.14294
MP2	-76.0587	104.59693	0.96223	2.11155	0.00517	0.14323
LDA	-75.9013	105.26632	0.97135	2.1098	0.01469	0.14229
PBE	-76.37691	104.29122	0.97102	2.03538	0.01435	0.10199
BLYP	-76.44548	104.53756	0.97297	2.0313	0.01639	0.09978
B3LYP	-76.42605	105.27116	0.96287	2.06247	0.00583	0.11666
M062X	-76.42621	105.52302	0.96004	2.09023	0.00289	0.13169

Experimental values from NIST (2022):

$$R_{\text{OH}}^{\text{exp}} = 1.809 \text{ cm}^{-1} \qquad \mu^{\text{exp}} = 1.847 \text{ Debeye} \qquad \alpha^{\text{exp}} = 104.3° NIST \text{ (2022)}$$

Table 2.2: Vibrational frequencies of the water molecule

Model	Scaling Factor	ω_{bend} cm^{-1}	$\omega_{\text{sym str}}$ cm^{-1}	$\omega_{\text{anti str}}$ cm^{-1}
RHF	0.9086	1576.03	3734.77	3827.32
MP2	0.9479	1529.38	3620.01	3740.29
LDA	0.9884	1517.50	3662.55	3772.05
PBE	0.9888	1570.59	3651.20	3752.59
BLYP	0.9975	1584.30	3630.61	3732.15
B3LYP	0.9654	1560.35	3650.54	3750.65
M062X	0.9462	1515.77	3644.39	3746.29

Experimental values from NIST (2022):

$$\omega_{\text{bend}}^{\text{exp}} = 1595 \text{ cm}^{-1} \qquad \omega_{\text{sym str}}^{\text{exp}} = 3657 \text{ cm}^{-1} \qquad \omega_{\text{anti str}}^{\text{exp}} = 3756 \text{ cm}^{-1}$$

2.2.1 Which method is best suited for determining the bond-lengths and dipole of the water molecule? Justify your answer.

B3LYP and M062X provided the most accurate bond lengths due to their ability to incorporate electron correlation effects effectively. B3LYP, as a hybrid functional, combines Hartree-Fock exchange with DFT correlation, offering a well-balanced description of the electron density. This balance often leads to more precise bond lengths for small molecules. Similarly, M062X is a meta-hybrid functional that includes advanced correlation terms, allowing it to perform well for systems involving hydrogen bonding or other non-covalent interactions, which are critical in water molecules. The treatment of exchange-correlation effects in both functionals ensures bond length predictions closely align with experimental values as reflected from small percentage errors.

BLYP, PBE, and B3LYP gave accurate dipole moments because they effectively describe the electron distribution across the water molecule. BLYP and PBE are generalized gradient approximation (GGA) functionals that improve over the simpler LDA by considering the gradient of the electron density. This enhances their ability to capture the asymmetry in the charge distribution of polar molecules like water. B3LYP further refines this by incorporating a fraction of exact Hartree-Fock exchange, leading to a more accurate description of molecular polarity. These functionals' capacity to model electron density and polarization effects makes them particularly reliable for predicting dipole moments.

2.2.2 Which method is more adapt to compute the IR spectrum of the water molecule?

For computing the IR spectrum of the water molecule, B3LYP is the most suitable method as reflected from its closeness with the experimental values of vibrational frequencies. IR spectrum is derived from vibrational frequencies and intensities, and the B3LYP method excels at

describing the potential energy surface (PES) accurately. Comparatively, PBE and BLYP underperform in predicting IR intensities while LDA is too simplistic. M062X is in principle more accurate for vibrational modes but is computationally expensive and so may not outperform B3LYP for smaller molecules like water.

2.2.3 Which method do you think is best suited to studying water clusters? Justify your answer.

For studying water clusters, M062X is the best-suited method due to its excellent performance in modeling non-covalent interactions such as hydrogen bonding, which is critical in water clusters. M062X is a meta-hybrid functional that includes advanced correlation effects, making it highly accurate for systems involving dispersion and polarization without excessively high computational cost.

Chapter 3

Conclusion

In this report, the bond length, geometry, and vibrational frequencies of the water molecule were investigated using computational methods such as RHF, MP2, LDA, PBE, BLYP, B3LYP, and M062X. The results demonstrated that B3LYP and M062X provided the most accurate bond lengths and geometry, closely aligning with experimental data. For vibrational frequencies relevant to IR spectra, the density functional methods B3LYP, BLYP, and PBE proved to be the most suitable, effectively capturing the key features of the water molecule's vibrational modes. These findings emphasize the reliability of hybrid and generalized gradient approximation (GGA) functionals for accurately modeling molecular properties and underscore the importance of method selection based on the property being studied.

References

NIST (2022), 'Computational chemistry comparison and benchmark database'.
   URL: *https://cccbdb.nist.gov/*