

# Exercise Session 6

## IESM Fall 2025-2026

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# Exercise 6 - DFT vs (Post) HF Methods

## Learning goals

Compare accuracy and efficiency of electron density based methods to wavefunction based methods

Compare exchange-correlation functionals used in DFT calculations

Learn how frontier orbital visualization supports the analysis of electronic structure calculations

## Chapter in script

Chapter 8 - Density Functional Theory

## Resources

Introduction to Density Functional Theory (DFT) by David Sherrill [video](#)

Review of DFT Methods by Axel D. Becke [article](#)

## Exercise 6 - DFT vs (Post) HF Methods: Theory

- (Post) HF methods are wavefunction-based (we need to find the system (many-electrons) wavefunction)
- DFT shifts the focus: we need to find the electron density
- Why? For  $N$  electrons, the system wavefunction is a complex function of  $3N$  variables, but the electron density is a function of 3 variables
- The universal functional not known, but proven to exist
- Everything that is unknown is contained in  $E_{XC}[\rho]$

$$E[\rho] = T_s[\rho] + J[\rho] + \int v_{\text{ext}}(r)\rho(r)dr + E_{XC}[\rho]$$

- Each computational functional will treat the XC part differently

## Exercise 6 - DFT (continued)

DFT is the workhorse of electronic structure methods:



- In the **top 100** most cited papers (ever!!) in the scientific community, 12 are on DFT

# Comments on DFT

- Kohn-Sham formulation: fictitious molecular orbitals (non-interacting)
- If the exact XC functional is known - ground-state energies, electron/charge density and HOMO (Koopman's theorem) are known
- Usually fast and widely available
- What can DFT do?
  - Atomic and cell geometries (fixed V,P)
  - Formation energy
  - Properties related to the ground state

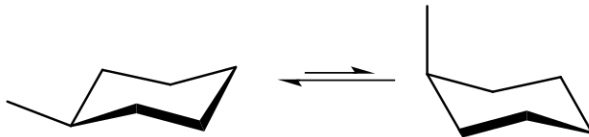
## Comments on DFT - downsides

- DFT also has some downsides - we will see this in practice
  - Difficulties capturing systems with dispersion
  - Band gap problem - LUMO cannot be associated with KS orbitals (derivative discontinuity, deviation from piecewise linearity)
  - No magic solutions :( we must make approximations and test our decisions

## Comments on orbitals

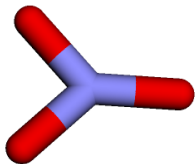
- Orbitals are spatial wavefunctions, essentially probability amplitudes
- In practice, our calculated orbitals are mathematical formulations which approximate our true system
- Different calculations of orbitals (KS orbitals, canonical HF orbitals, Dyson orbitals) can disagree qualitatively
- Be careful with overinterpreting orbitals

## Exercise 6.1 - Methylcyclohexane A-value



- You will perform calculations with HF and MP2 and different DFT functionals, add results to [collaborative spreadsheet](#) (link also on Moodle)
- Points of comparison:
  - $\psi$  or  $\rho$  based?
  - how accurate (w.r.t. experimental reference)?
  - computational time
- DFT is a world on its own - depending on the functional chosen you can go from cheap, very off calculations to expensive and more reliable ones

## Exercise 6.2 - Geometric properties: $\text{NO}_3$ radical



- Calculate N-O bond lengths and O-N-O bond angles
  - Experiments:  $D_3^h$ , N-O 1.24 Å and O-N-O 120°
- Compare results (HF, MP2 vs DFT)
- You will visualize the KS orbitals - what can they tell us?
  - Changes in the electronic structure between different species
  - General size, shape of expected one-electron orbitals (hopefully)

## Exercise 6 - Tips

- Calculations for Exercise 6.1 will be done in a collaborative way to speed up the exercise, add your results to [collaborative spreadsheet](#) (linked also on Moodle)
- You can monitor your calculations by opening a terminal window in noto and typing “tail -f name\_output\_log”
- DFT will be further explored during lectures and the next exercises
- Here we used as reference some papers that can be useful for further understanding [DFT1](#), [DFT2](#), [orbitals](#)