

Exercise Session 6

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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 wavefunction)
- DFT shifts the focus: we need to find the ground-state charge density
- Why? For N electrons, wavefunction is a complex function of $3N$ variables, but the ground-state charge density is a function of 3 variables
- The universal functional of DFT is not known, but proven to exist
- Everything that is unknown is contained in E_{XC}

$$E(\rho) = T_0(\rho) + J(\rho) + \int v_{\text{ext}}\rho + E_{XC}$$

- Each functional will treat the XC part differently

Exercise 6 - DFT (continued)

DFT is the workhorse of electronic structure methods:



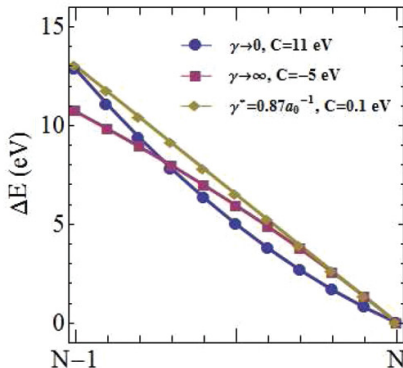
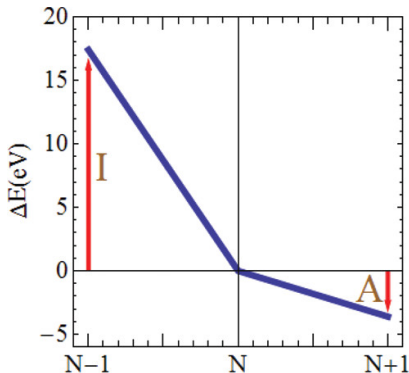
- In the **top 100** most cited papers (ever!!) in the scientific community, 12 are on DFT

Comments on DFT

- Kohn-Sham formulation: fictitious molecular orbitals (non-interacting)
- If the exact XC functional is known - ground state energies, charge densities 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 ground state

Comments on DFT - downsides

- DFT also has some downsides - we will see this in practice
 - Difficulties with dispersion
 - Band gap problem - LUMO cannot be associated with KS orbitals (derivative discontinuity, deviation from piecewise linearity) [ref](#)



Comments on orbitals

- Orbitals are spatial wavefunctions/probability amplitudes
- We work with approximations, orbitals are mathematical formulations that approximate reality
- “*Dyson orbitals*” show how electronic distribution varies with ionization
 - Can be measured in some ionization experiments
- Koopman’s theorem associates the Dyson orbital of an ionization process with the canonical HF orbital of the unionized state (for systems where we don’t have static correlation)
- Dyson and canonical HF orbitals can even disagree qualitatively (*the same goes for KS orbitals*)

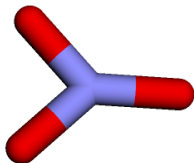
TAKE-HOME MESSAGE: be careful with overinterpreting orbitals!

Exercise 6.1 - Methylcyclohexane A-value



- You will perform calculations with HF and MP2 and different DFT functionals, add results to [collaborative spreadsheet](#) (linked also on Moodle)
- Points of comparison:
 - ψ or ρ 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: 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
 - Changes in a chemical transformation

Exercise 6 - Tips

Tips!

- DFT will be further explored during lectures and the next exercises
- Here we used as reference papers that can be useful for further understanding [DFT1](#), [DFT2](#), [orbitals](#)
- 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)