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

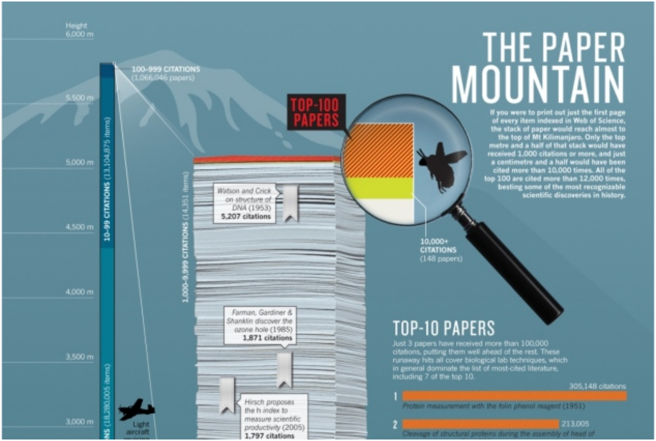
- (Post) HF methods are wavefunction-based (we need to find the system (many-electrons) wavefunction)
- DFT shifts the focus: we need to find the electron density
- Why? For N electrons, the system wavefunction is a complex function of 3N variables, but the electron density is a function of 3 variables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

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

- 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: ficticious 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

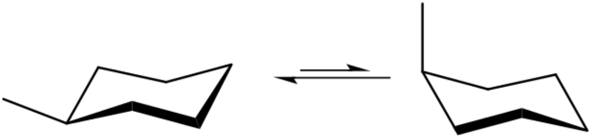
Comments on DFT - downsides

- 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

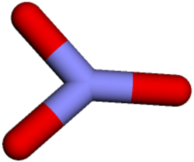
- Orbitals are spatial wavefunctions, essentially probability amplitudes
- In practice, our calculated orbitals are mathematical formulations which approximate our true system
- Different calculations of orbtials (KS orbitals, canoncial HF orbitals, Dyson orbitals) can disagree qualitatively
- Be careful 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:
  - 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
  - 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 papers that can be useful for further understanding DFT1, DFT2, orbitals