Benchmarking Electron Density in the Benzene Molecule

Carlos F. Perez-Cruz, Yueqing Chang, Kiel Williams and Lucas K. Wagner

Department of Physics, College of Engineering, University of Illinois at Urbana-Champaign

INTRODUCTION

Modern problems in physics often give rise to equations that - if solved - would provide great insight into the natural world. However, these equations are often too difficult to solve, even with the most powerful computers currently in existence. We must resort to various approximation schemes to make progress.

Given this reality, we must carefully assess how different approximations perform, relative to one another. We have attempted in this work to compare the performance of several methods within a single molecules of benzene.

AIM

We identified how electron density shifts from one method to another in a benzene molecule. We identified how the density redistributes itself from the molecule by subtracting one method from another.
We believe that this work could be generalized to other systems of interest and promote better understanding of different approximations used in computational condensed matter physics.

Choose Molecule

↓

Choose Approximation

↓

Compute Energy, Density, etc.

METHOD

We applied the following methods to compute the approximate ground-state electronic density in a single molecule of benzene.
- Hartree-Fock (HF)
- Density Functional Theory (LDA, PBE, B3LYP) [1]
- Coupled-Cluster Single Double (CCSD) [2]

We computed these densities using the Python-based simulations of chemistry framework (PySCF) computational package [3]. By subtracting the densities from one another we identified how the methods differ from one another. We used VESTA [4] to visualize the resulting electron densities and differences.

The total densities vary from method to method by a few percent, and visually appear similar.
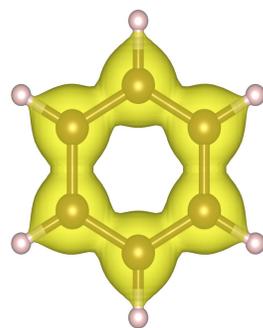

This is the molecular structure of Benzene. Yellow color represents the isosurfaces of electron density.

In order to show the differences between the applied methods, we subtract the electronic density calculated using HF by the densities computed using other approximations. For example, for LDA, we compute and visualize the following quantity
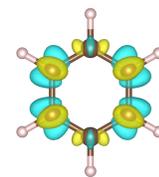
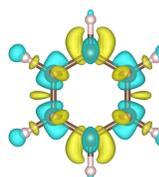$$\Delta\rho(\vec{r}) = \rho_{HF}(\vec{r}) - \rho_{LDA}(\vec{r})$$

RESULTS

As illustrative examples, we compare each method to the uncorrelated Hartree-Fock approach:
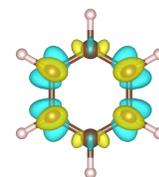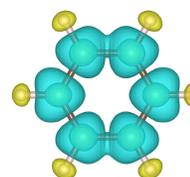

HF-LDA. Blue indicates regions where LDA density is greater.

HF-PBE. Blue indicates regions where PBE density is greater.

HF-B3LYP. Blue indicates regions where B3LYP density is greater.

HF-CCSD. Blue indicates regions where CCSD density is greater.

DISCUSSIONS

In comparing the different methods to the uncorrelated Hartree-Fock approach, several key trends appear:

- Compared to DFT, HF places too little density between the carbon sites of the ring

- HF tends to place too much density near the atoms. CCSD corrects this, allowing electrons to move further away from the ionic sites.

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