Lab 6: Density Functional Theory
CHE 525/PHY 567, Spring 2021, Stony Brook University

1   Introduction

Density functional theory (DFT) is among the most widely used methods in quantum chemistry, thanks to its ease of use and low computational cost. In DFT, the exchange and correlation energies are approximated by a density functional. A very large number of density functionals exist. For a list of density functionals available in Psi4, for example, see this page. Which functional should you use for a particular problem? Well, it is not so easy to know. Unlike wave function theories, there is no strict hierarchy of density functional theories that approach the exact solution of the Schrodinger equation. Instead, we rely on empirical knowledge about when certain functionals work and when they do not. Often it is necessary to develop this knowledge on a case-by-case basis.

A very rough starting point for assessing density functionals is the so-called Jacob's Ladder of functionals. It has been argued that one can expect more accurate results as one moves to functionals higher up this ladder:

- Rung 1 - Local density approximations (LDsA; which approximate exchange and correlation energies using only the local value of the electron density)

- Rung 2 - Generalized gradient appoximations (GGAs; which use only the local density and density gradient)

- Rung 3 - Meta-GGA (mGGA; which adds the second derivative of the density in addition to those used in a GGA)

- Rung 4 - Hybrid functionals (which add Hartree-Fock exchange between Kohn-Sham orbitals, aka *exact exchange*, on top of a GGA or mGGA)

- Rung 5 - Functionals that incorporate virtual orbitals (many, called *double hybrids*, include the virtuals via MP2-like correlation terms)

While there is certainly some truth that performance improves for some problems as you move up the ladder, there is no guarantee.

Another important consideration is dispersion. As you saw when we computed the PES for Ar_2 in Lab 4, many DFT functionals do not properly treat Van der Waals interactions. This is not surprising, given the local nature of density functionals, and the non-local nature of the electron correlation responsible for Van der Waals interactions. For this reason, empirical corrections for disperision are common, and it is often a good idea to use one.

Given the large number of functionals, and their unpredictable behavior, benchmarking density functionals for accuracy can be a useful thing to do prior to a large study. One could apply several different strategies:

- Choose a small system that is chemically similar to the system you are interested in. Compute some properties of interest using a trustworthy wave function method, such as coupled cluster theory. Then, search for density functional approximations that reproduce these properties.

- Choose a system that is chemically similar to the system you are interested in. Find experimentally measured properties of interest. Then, search for density functional approximations that reproduce these properties.

- If you are lucky, you might find enough computational data on chemically similar systems in the literature to choose a functional based on literature data, rather than having to do all of the work yourself.

In this exercise, we will apply the first strategy. Let's pretend that we are interested in modeling the reaction of O_3 with unsaturated hydrocarbons on the surface of a heterogeneous catalyst. Studying such a large system as a surface with wave function methods can be unweildy, so many in the field of computational

catalysis rely on DFT. In order to choose a functional, we might first benchmark the accuracy of several functionals for a set of smaller, but related systems. In this case, we might choose to use two reactions, the decomposition of ozone into oxygen:

$2 \, O_3 \rightarrow 3 \, O_2$
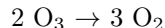
and the ozonolysis of ethene:
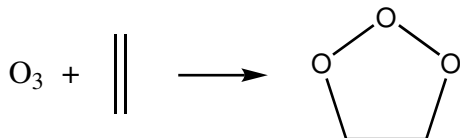
These systems are small enough that we can employ high-level wave function methods to benchmark various density functional approximations, but the chemistry is representative of what might happen on the catalyst surface of interest.

So that is what we will do. Below, we will benchmark various density functionals against a more accurate method that we trust (in this case, CCSD(T)) in order to pick one that accurately predicts the ΔU of these reactions. Of course accurately predicting ΔU is no guarantee that other properties are also accurately predicted. A very broad and interesting demonstration of this point recently made a big splash. Check out this paper. Still, our benchmarking strategy it is a good start, and better than nothing.

Note: This project was inspired by a recent tutorial review by Morgante and Peverati. The supporting information of this review contains a series of very informative computational exercises that you may find worthwhile if you plan to use DFT in your research.

2 Procedure

1. Pull down and look at the starter code `Lab6starter.dat`. As usual please read the script all the way throught, because the comments contain essential information. This code will compute ΔU for the first reaction (the break down of O_3 into O_2 at several levels of theory. This script will optimize the structure just once, using the widely used B3LYP functional. Then, at the B3LYP-optimized structure, we will compute compute single-point energies at three levels of theory: CCSD(T) (which we trust to give a reasonably reliable value of ΔU and two popular density functional: PBE (a GGA) and B3LYP (a hybrid functional). (Note to physicists: The PBE functional is so ubiquitous in solid state physics, that many in this field simply call it "GGA." In chemistry, there are other popular GGAs, so we call it by its full name.) You can run this script to see it work.

2. Now we will benchmark a large set of functionals in different categories. Modify the starter script so that it will compute ΔU for the following representative functionals:

   - LDAs: SVWN
   - GGAs: PBE, BLYP, BP86
   - Meta-GGAs: TPSS, M11-L
   - Hybrid: B3LYP, PBE0, M11
   - Double Hybrid: B2PLYP
   - Dispersion Corrected: B3LYP-D3BJ, PBE-D3BJ (these are dispersion-corrected versions of B3LYP and PBE, respectively)

3. Now compute ΔU for the the ozonolysis of ethene (second reaction above) using the same procedure and set of functionals. Again, use CCSD(T) energies as your reference point for comparison.

3 Deliverables

- Present figures showing the error of each functional for each reaction. Sort the functionals by "rungs," clearly labeling them (LDA, GGA, etc.).

- Which functional would you choose for your study, if you could choose any of the above functionals? How large are the errors in the reaction energies computed with this functional? At room temperature, how many kT is this?

- Now, consider the fact that it is difficult to apply hyrbrid and double-hybrid functionals to large, periodic systems (as you might use to model a catalytic surface). Which functional would you choose now? How large are the errors in the reaction energies computed with this functional? At room temperature, how many kT is this?

- Which functionals show the largest errors compared to CCSD(T)? How large are the errors in reaction energies? At room temperature, how many kT is this?

- Consider the different "rungs" of functionals. Does Jacob's Ladder correctly predict the relative accuracies of the functionals?

- Do dispersion corrections improve the agreement with CCSD(T) compared to B3LYP and PBE (even though one would not expect dispersion to play a roll in the thermochemistry of this reaction)?

- If you were interested in modeling these reactions on a gold surface, what other reactions might you benchmark in order to choose a suitable density functional? What data might you use?

Note: This is important enough that it bears repeating. Remember that, just because a particular functional works well for this reaction, it does not mean it will work well for others. That is why we are benchmarking a particular case.