CH3D5: Density Functional Theory: A Primer

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Background

So far we have been talking about the wave function, and how the wave function may be calculated using electronic structure theory. The most simple example we gave was Hartree-Fock theory. By now, you will have seen for yourself that Hartree-Fock theory does a pretty good job of approximating both the wave function and the total energy of a system. However, like most models, there is scope for improvement.

In the last set of notes, we mentioned a quantity known as the electron correlation. Correlation is defined as the difference between the Hartree-Fock total energy (and therefore the Hartree-Fock wave function) and the **exact** total electronic energy (and wave function). One of the outstanding problems in the field of theoretical chemistry today is how we can effectively and accurately model this correlation energy. Both the development of models of correlation, and also the calculation (on a computer) using such models are not easy tasks. Most electronic structure calculations that account for electron correlation are very computationally intensive (take a long time to finish)! A correlated model that is perhaps the least computationally intentsive to use is known as **density functional theory** otherwise referred to as DFT.

Density Functional theory (DFT)

The basic idea behind DFT has similarities and differences with Hartree-Fock theory. Remember from your reading material from last week that Hartree-Fock theory is concerned with the wave function. If we have $\mathcal{N}$ electrons, then the wave function is a function of the $\mathcal{N}$ positions (and spins) of these electrons $(r_1 \ldots r_N)$. The electron density ρ is related to the wave function. We obtain the electron density at a given position (say, r_1), by taking the square of the wave function, and integrating it over all positions (and spins) **except** those for r_1. This yields $\rho(r_1)$. In principle, if we know where the nuclei are in the molecule, and what their charges are, and we know the electron density, then we know **everything** about the electronic structure of a molecule.

Unlike Hartree-Fock theory, the emphasis in DFT is on the electron density (as opposed to emphasising the wave function, as in Hartree-Fock theory). In DFT, we still use a self-consistent field in the calculations, but this time, we iterate until the **electron density** is converged. Remember that in Hartree-Fock theory, we use self-consistency to converge the wave function. **In principle, a DFT calculation goes directly from the density to the total electronic energy, without having to calculate the wave function first.**

In DFT, the total energy can be written down as a **functional** of the density. **A functional is a function of a function**. Remember from the last set of notes that we

can break down the total energy into several parts (electron kinetic energy, electron-electron repulsion, electron-nuclear attraction, and, nuclear-nuclear repulsion). In DFT, the first three of these terms can be expresses as a functional of the electron density, *i.e.*

$$T[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)]$$

We'll now look at each of these three terms.

Starting with the easiest, the electron-nuclear attraction is straightforward to calculate as a functional of the density. Next, let's consider the kinetic energy. It turns out that for doing chemistry, using $T[\rho(r)]$ is not an accurate enough picture of the electron kinetic energy. In 1965, two people called Kohn (now Nobel prizewinner for his work on DFT) and Sham figured out a way to decompose the density into molecular orbitals (MO's), and use MO's to describe the kinetic energy (just like we do in Hartree-Fock theory). This works pretty well for chemical applicatons! This is called Kohn-Sham DFT, and is basically the most popular variant of DFT used worldwide. It is what you will be using in the lab. Note that since MO's get (indirectly) involved in a Kohn-Sham DFT calculation, we again have to make use of basis functions to expand the MO's.

Finally, we have the electron-electron repulsion term. This term actually comprises 3 components: a classical electrostatic part (Coulomb term, $J[\rho(r)]$), and two non-classical (quantum) parts—the exchange term, $E_x[\rho(r)]$, and the correlation term, $E_c[\rho(r)]$. **These last two terms, the exchange and correlation, are at the heart of DFT**. There are all sorts of exchange functionals and correlation functionals available to use in calculations. Most of these exchange and correlation functionals can be combined in a mix'n'match way.

In principle, if we know what the exact formulae for the exchange and correlation functionals are, we can get exact solutions from our calculations. The bad news is that no-one at present knows what the ideal formulae for exchange and correlation are—so theorists come up with models that approximate the exact contributions from exchange and correlation. Finding the correct $E_x[\rho(r)]$ and $E_c[\rho(r)]$ would be on par with finding the Holy Grail of the theoretical chemistry world!

Two very common (approximate) exchange functionals are Dirac exchange and Becke exchange. Dirac exchange was developed by assuming that molecules have a uniform electron density(!). Becke exchange improves on this model by adding in extra terms that include the gradient of the density. Two very common correlation functionals are Vosko-Wilks-Nusair correlation and Lee-Yang-Parr correlation. Similarly to exchange, Vosko-Wilks-Nusair correlation is based on a uniform electron density, while Lee-Yang-Parr correlation improves this by adding extra terms from the gradient of the density.

You can see that some of these functionals have very long names, so theorists tend to use abbreviations when they refer to the functionals they have used in their calculation. Dirac exchange is often abbreviated to "S", Becke exchange is abbreviated to "B" (or sometimes "B88"), the Vosko-Wilks-Nusair functional is called "VWN", and the Lee-Yang-Parr exchange is called "LYP". When referring to the level of theory used in DFT, the nomenclature is
"Exchange functional" "Correlation Functional"/"Basis set".
As an example, if a theorist is reporting results of a (Kohn-Sham) DFT calculation using Becke exchange and Lee-Yang-Parr correlation, using the 6-31G basis set, this calculation

would be referred to as a BLYP/6-31G calculation. One other ideosyncrasy is that the combination SVWN is often referred to as "LDA" (stands for local density approximation).

Hybrid density-functional theory (hybrid DFT) also deserve a mention. In hybrid DFT, we go one step further by writing down the total electronic energy as a blend of Hartree-Fock energy and DFT energies. Mixing in a bit of Hartree-Fock energy improves the total electronic energy in quite a few cases where DFT doesn't perform so well. The most common hybrid DFT functional is abbreviated to "B3LYP". It contains mixtures of Hartree-Fock, Becke exchange, Dirac exchange, VWN correlation and LYP correlation (basically, a bit of everything!). B3LYP calculations are probably the most popular DFT calculations worldwide at the present time.

On a closing note, it can't be emphasised enough that our exchange and correlation functionals in DFT are **approximate**. So, although we can account for the correlation energy in DFT (something we can't do using Hartree-Fock theory), this correlation term is approximate. DFT doesn't provide a route to systematically improving our description of correlation—each new correlation functional is different, but won't necessarily be consistently better than the previous one. We also have the exchange functional to worry about. In Hartree-Fock theory, exchange is treated exactly. So in DFT, we have to be careful that **both** exchange and correlation are being described properly.