

Chapter 9: Density Functional Theory (DFT) Methods

Key Notes:

Fundamental Aspects:

Density Functional Theory (DFT) is a computational method that derives properties of the molecule based on a determination of the *electron density* of the molecule. Unlike the *wavefunction*, which is not a physical reality but a mathematical construct, electron density is a physical characteristic of all molecules.

A *functional* is defined as a function of a function, and the energy of the molecule is a functional of the electron density. The electron density is a function with three variables – x-, y-, and z-position of the electrons. Unlike the wavefunction, which becomes significantly more complicated as the number of electrons increases, the determination of the electron density is independent of the number of electrons.

Methods:

There are roughly three types, or categories, of density functional methods. *Local density approximation (LDA)* methods assume that the density of the molecule is uniform throughout the molecule, and is typically not a very popular or useful method. *Gradient-corrected (GC)* methods look to account for the non-uniformity of the electron density. *Hybrid* methods, as the name suggests, attempt to incorporate some of the more useful features from *ab initio* methods (specifically Hartree-Fock methods) with some of the improvements of DFT mathematics. Hybrid methods, such as B3LYP, tend to be the most commonly used methods for computational chemistry practitioners.

Applications:

DFT is a general-purpose computational method, and can be applied to most systems. Like all computational methods, DFT methods are more useful for some types of calculations than others. DFT methods, unlike *ab initio* methods, can be used for calculations involving metals. Hybrid methods, such as B3LYP, are often the method of choice for reaction calculations. Some DFT methods are specifically designed for specific applications, such as the MPW1K hybrid method, designed for determination of kinetics problems.

Software Tools:

DFT methods are now standard in virtually all of the most popular software packages, including Gaussian, GAMESS, HyperChem, and Spartan. On the WebMO interface to the North Carolina High School Computational Chemistry Server, DFT methods are part of the standard options presented to the user. In addition, the user can customize a calculation to include advanced DFT methods, such as time-dependent DFT for determination of excited states.

Advantages:

The most significant advantage to DFT methods is a significant increase in computational accuracy without the additional increase in computing time. DFT methods such as B3LYP/6-31G(d) are oftentimes considered to be a standard model chemistry for many applications.

Disadvantages:

One of the main disadvantages of DFT methods is the challenge in determining the most appropriate method for a particular application. The practitioner should, prior to choosing a DFT method, consult the literature to determine the suitability of that choice

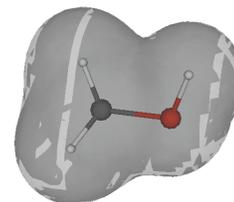
for that particular problem or application. As such, DFT usage tends to favor the more sophisticated user. In general practice (including educational environments), the B3LYP/6-31g(d) model chemistry is considered by most to be a good general-purpose choice.

Fundamental Aspects:

Density functional theory (DFT) is the newest method of the four, although the theory has been around for close to 40 years. It addresses one of the major criticisms of the *ab initio* method. In that method, the energy of the molecule and all of its derivative values depend on the determination of the wavefunction. The problem is that the wavefunction is not a *physical observable*; that is, the wavefunction is purely a mathematical construct. In reality, the wavefunction does not exist! When squared and multiplied by the area of the molecule, the wavefunction is simply a statistical probability that the electron(s) will be at a specific place or part of the molecule. Even though the wavefunction does not exist as a physical, observable property of an atom or molecule, the mathematical determination of the wavefunction (and with it, the atomic and molecular orbitals) has been a good predictor of energy and other actual properties of the molecule.

For a long time, computational chemists have been trying to find some property of atoms and molecules that actually exists, and that can be used to determine the energy and derivative properties of atoms and molecules. Llewellyn Thomas and Enrico Fermi were able to determine that there was a *one-to-one* correspondence between the *electron density* of a molecule and the wavefunction of a molecule with multiple electrons. Thomas was a professor at North Carolina State in the later years of his career, and he died in Raleigh in 1992. All of his teaching and research notes are on special collection at the NCSU Library. Fermi built the first nuclear reactor and was instrumental in the development of the atom bomb as a part of the Manhattan Project.

Because of their work, it was determined that if we can determine the electron density of a molecule, we can say numerous things about the molecule, and this forms the basis for density functional theory. The molecule shown is methanol (CH_3OH), and the electron density mapping is visualized. There are several major advantages of this approach. The first is that the method is based on a property that exists in real molecules, not a purely mathematical invention. The second is that the wavefunction becomes more complicated mathematically as the number of electrons increases. In DFT, the density depends only on the x-y-z coordinates of the individual electron. In practical terms, DFT can be said to *scale* three-dimensionally, or as N^3 , where N is the number of basis functions. *Ab initio* methods, on the other hand, scale as N^4 , and as a result DFT calculations are faster with better accuracy. There are, of course, still major approximations that are used in DFT that affect the computing time and accuracy of molecules that are evaluated with DFT methods.



The fundamental underlying mathematics of this method is the *functional*. Most readers should have encountered the idea of a *function* in one or more mathematics classes. We say something is a function of some other factor. For example, we might say that “height is a function of age”. In this case, the mathematics might be represented by age being the independent variable (represented by “x” on a graph) and height being represented by the dependent variable (“y” on a graph). This function is probably fairly linear, at least until the age of 20 or so. Mathematically, we use the notation $f(x)$, read as the “the function of x”. Our age-height function might be represented by the slope equation, where $f(x)=mx+b$, where $f(x)$ is the height (y), m is the slope, x is the age (in years), and b is the y-intercept. In mathematical terms, a function is denoted as follows:

$$y = f(x)$$

A *functional* is a function of a function. Conceptually, this is no more difficult than the concept of a function, but it is not a mathematical concept encountered by most high school or college students. In a function, the dependent variable (y) depends on one or more *single variables*. In the example above, the dependent variable (height) depends on *one* single variable (age). In *ab initio methods*, we are interested in the *wavefunction*. In theory, the wavefunction depends on the electron coordinates – x , y , and z . In practice, however, the wavefunction depends on other variables, and the complexity of the wavefunction increases as we increase the number of electrons. The wavefunction is dependent on $3N$ variables, where N is the number of atoms. In computational chemistry, a number of approximations need to be made in order to solve the mathematics with our current computational capabilities. Schrödinger's equation states that the energy of the molecule is a function of the wavefunction. Determining the wavefunction becomes the goal of modern computational chemistry.

Mathematically, a *functional* is denoted as follows:

$$y = F[f(x)]$$

In this notation, the value of y is in and of itself dependent on another function. The first $f(x)$ function becomes the input for the functional, that is, a function of a function.

In DFT methods, the energy of the molecule is a *functional* of the electron density. Electron density is a function, with three variables: x -position, y -position, and z -position of the electrons. Regardless of the number of electrons, the electron density function is *always* only dependent on those three numbers. The *functional* (F) of electron density gives us the energy of the molecule. The practical advantage is that the mathematics does not spiral out of control as we increase the number of electrons.

$$\text{Electron density} = \rho(x, y, z)$$

$$\text{Energy} = F[\rho(x, y, z)]$$

The goal in DFT now becomes to find the value of the functional F , and to do this we need to make approximations. Indeed, one of the reasons why there are so many different DFT methods is that there are multiple ways of approximating the functional. For purposes of this *Guide*, and to avoid overwhelming the reader, the number of approximations presented will be limited to three or four.

It is perhaps instructive, however, to delve a little more deeply into the mathematics. In the 1960s, Hohenberg and Kohn were able to use the Thomas-Fermi theorem to develop a more detailed version of the theory. This in turn was adapted by Kohn and Sham (1965) into a practical version of the density functional theory. The KS theory, which describes the mathematics of electron densities and their subsequent correlations to molecular energies, is shown in its simplest form as follows”

$$E_{DFT}[\rho] = T[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho]$$

where E is the energy, T is the kinetic energy of the electrons, E_{ne} is the nuclear-electron attraction (Coulombic) energy, J is the electron-electron repulsive (Coulombic) energy, and E_{xc} is the electron-electron exchange-correlation energy. Notice that each of these terms is a function of the function ρ , the electron density, which is itself a function of the three positional coordinates (x , y , and z). As such, each of the terms above – T , E_{ne} , J , and E_{xc} is a functional. The challenge now becomes to determine the value of each of these four functionals.

It turns out that the first three can be determined reasonably well using *ab initio* or semi-empirical methods. This, by the way, makes it difficult to classify DFT. Some computational chemists consider it to be a variation of the *ab initio* method. Some consider it to have connections to semi-empirical, while others

classify it as a completely separate method. For purposes of this *Guide*, DFT is considered to be one of the four basic methods – molecular mechanics, semi-empirical, *ab initio*, and DFT. Regardless of how one determines the first three terms, the last one – the electron exchange-correlation energy – is the term that causes the most concern.

There are a large number of approximations that attempt to calculate the electron exchange-correlation energy. The electron correlation aspect addresses how an electron in an atom or molecule interacts, or “sees”, another electron. The electron exchange aspect describes a quantum mechanical property of electrons that is related to their exchange between a fermion and a boson (a *fermionic* or *bosonic* electron). This exchange is well beyond the scope of this *Guide*, but suffice it to say that it is related to the Pauli Exclusion principle, which states that no two electrons can occupy the same energy state.

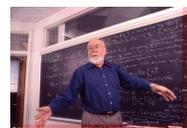
Given this discussion, the next section addresses various methods.

Methods:

Methods in DFT are complicated and diverse, but can roughly be divided into three classes:

1. Methods that use a *local density approximation (LDA)*. The LDA is determined solely based on the properties of the electron density. The *critical assumption* of this approximation is that, for a molecule with many electrons in a gaseous state, the density is uniform throughout the molecule. This is not the case for molecules, where the electron density is decidedly not uniform. This approximation does, however, work well with electronic band structures of solids, which describes the range of energies in which electrons are permitted or not permitted (forbidden). Outside of this application, however, local density approximations are not very satisfactory.
2. Methods that combine the electron density calculations with a *gradient correction factor*. A gradient in mathematics is a function that measures the rate of change of some property. In this case, the gradient looks to account for the non-uniformity of the electron density, and as such is known as *gradient-corrected*. Another term for this is *non-local*.
3. Methods that are a combination of a Hartree-Fock approximation to the exchange energy and a DFT approximation to the exchange energy, all combined with a functional that includes electron correlation. These methods are known as *hybrid* methods, and are currently (Fall of 2006) the most common and popular DFT method used in practice.

The table below provides a good summary of sample methods by name, acronym, and type. [Historical aside: it should be noted that two of the chemists noted are North Carolinians: Bob Parr (shown below) is a quantum chemist at the University of North Carolina at Chapel Hill (read the article: <http://research.unc.edu/endeavors/fall2004/parr.html>) and Weitao Yang is chemistry faculty at Duke University. Chengteh Lee was Dr. Parr’s graduate student and Dr. Yang was his post-doctoral student. Their 1988 paper, “Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density”, is one of the most cited papers in the chemistry literature. The paper is routinely referred to as the “LYP” paper.]



Name of the method	Type	Acronym
Hartree-Fock Slater functional	Hartree-Fock with local density approximation exchange	HFS
Vosko, Wilks, and Nusair	Local Density Approximation (emphasis on electron correlation approximation)	VWN
Becke correlation functional; Lee, Yang, Parr electron exchange functional	Gradient-corrected LDA functional	BLYP
Becke 3-term correlation functional; Lee, Yang, and Parr exchange functional	Hybrid DFT	B3LYP

Perdew 1986 functional	Gradient-corrected LDA functional	P86
Becke 3-term correlation functional; Perdew correlation term	Hybrid DFT	P3P86
Modified Perdew-Wang one parameter hybrid for kinetics	Hybrid DFT	MPW1K

For the mathematically inclined readers, the B3LYP functional has this form:

$$E_{xc} = (1 - a_0)E_x(LDA) + a_0E_x(HF) + a_xE_x(B88_x) + a_cE_c(LYP88_c) + (1 - a_c)E_cVWN80_c$$

where $a_0 = 0.2, a_x = 0.72, a_c = 0.81$

The purpose of including this complex mathematical function (functional) is to suggest the hybrid nature of the mathematics. Note that various approximations – local density approximation (LDA), Hartree-Fock (HF), Becke-1988 (B88), Lee-Yang-Parr 1988 (LYP88), and Vosko, Wilks, Nusair 1980 (VWN80) – are part of this hybrid functional. The lower case x refers to the determination of the electron exchange while the lower case c refers to the determination of the electron correlation.

Of these methods, the B3LYP functional is considered to be the “industry standard” in terms of practical applications, and it is this method that is available as a pull-down option on the North Carolina High School Computational Chemistry server.

Applications:

Density functional theory is a general-purpose computational chemistry method, and as such, can be applied to most systems. With the number of variations of this method – we have only shown seven in the table above – there is no simple guide to the “correct” choice of a DFT method. On average, there is considerable consensus that DFT methods are “better” than *ab initio* methods, and are generally stated to be more accurate with lower computational expense. There are, of course, some general guidelines for the choice of a DFT method:

1. B3LYP, run with a 6-31G* or better basis set, is *on average* the best choice of a model chemistry for most systems. B3LYP/6-31G* is particular good for organic molecules, but less so for metal-containing compounds.
2. BLYP with most basis sets is the opposite of B3LYP: not particularly accurate with organics, but provides reasonably good energy values for metal-containing compounds.
3. BLYP and B3LYP methods perform close to the same for determination of charge densities on atoms in molecules.
4. Both gradient-corrected and hybrid methods provide high levels of accuracy in the determination of a geometry optimization.
5. B3LYP methods clearly provide better results for reaction chemistry calculations
6. DFT methods are considered by some, but not all, to produce unacceptable results for weak hydrogen bonding interactions.

This incomplete list points to the challenge facing all computational chemists, whether they are using computational chemistry to solve problems or are trying to develop new methodologies. That challenge is finding a method or methods that are a suitable compromise between accuracy and computational expense. Most chemists do not have unlimited computing resources, and as such need to use approximation methods in order to generate results. For theoreticians, the challenge is to develop new approximations that closely mimic the actual chemistry of the atoms and/or molecules, all the while being appreciative and responsive to the needs of the practitioner.

Software Tools:

DFT methods are embedded as “standard” model chemistries in most of the *ab initio* software packages, including GAMESS and Gaussian. On the North Carolina High School Computational Chemistry server, the use of Gaussian is recommended for DFT calculations.

On the WebMO server, one can modify jobs by hand using the “Preview” tab on the Configure window. For example, for excited state chemistry (NMR determinations), the use of the time-dependent (TD) DFT method is recommended. For example, an NMR job for water was set up using the pull-down menus. From the “Preview” tab, we clicked on the Generate button, resulting in the line below:

```
#N B3LYP/6-31G(d) NMR
```

We modified this input file to include time-dependent DFT, calculating 12 excited states (**nstates**) for the water molecule. Notice we also added a “+” to the basis set, indicating the use of a diffuse basis set, recommended for excited state calculations.

```
#N B3LYP td=nstates=12/6-31+g*
```

In short, the various software packages have a wide range of additional options beyond what is indicated by the available pull-down menus from WebMO. As your experience increases, you can take advantage of this flexibility.

Advantages:

One important advantage of DFT was described early in this chapter: that being that DFT scales three-dimensionally, or as N^3 , (N = number of basis functions). *Ab initio* methods, on the other hand, scale as N^4 . As a result DFT calculations are slightly faster with better accuracy. Perhaps more importantly, DFT methods overcome one of the main disadvantages of *ab initio* methods such as Hartree-Fock: the complete neglect of electron correlation. Electron correlation is defined as the difference between the Hartree-Fock energy and the exact solution of the Schrödinger equation. DFT methods account for some of this difference with no increase in computational time.

DFT can also perform calculations on some molecules that are not possible with *ab initio* methods, most notably transition metals.

Disadvantages:

Not unlike other methods, the computational chemist must make decisions about which DFT method to use for a particular application. For example, the BLYP method is considered by some (most?) to be appropriate for transition metal applications, but not for organic compounds. B3LYP, on the other hand, has the opposite characteristics. MPW1K, as the name suggests, is particularly well suited for use in modeling kinetics of reactions via determination of transition states. It is, however, a bad choice for stable molecules.

Having said that, we frequently recommend the use of DFT methods to students doing independent research, unless the focus of their research is on comparing model chemistries. For example, we encourage students to use the B3LYP/6-31G(d) model chemistry as the “standard” for projects involving relatively small molecules. With this model chemistry, students can obtain sufficiently accurate results without consuming significant amounts of computing resources.