5 Density Functional Theory

Density functional theory (DFT) has become very popular in recent years. This is justified based on the pragmatic observation that it is less computationally intensive than other methods with similar accuracy. This theory has been developed more recently than other *ab initio* methods. Because of this, there are classes of problems not yet explored with this theory, making it all the more crucial to test the accuracy of the method before applying it to unknown systems.

5.1 BASIC THEORY

The premise behind DFT is that the energy of a molecule can be determined from the electron density instead of a wave function. This theory originated with a theorem by Hoenburg and Kohn that stated this was possible. The original theorem applied only to finding the ground-state electronic energy of a molecule. A practical application of this theory was developed by Kohn and Sham who formulated a method similar in structure to the Hartree–Fock method.

In this formulation, the electron density is expressed as a linear combination of basis functions similar in mathematical form to HF orbitals. A determinant is then formed from these functions, called Kohn–Sham orbitals. It is the electron density from this determinant of orbitals that is used to compute the energy. This procedure is necessary because Fermion systems can only have electron densities that arise from an antisymmetric wave function. There has been some debate over the interpretation of Kohn–Sham orbitals. It is certain that they are not mathematically equivalent to either HF orbitals or natural orbitals from correlated calculations. However, Kohn–Sham orbitals do describe the behavior of electrons in a molecule, just as the other orbitals mentioned do. DFT orbital eigenvalues do not match the energies obtained from photoelectron spectroscopy experiments as well as HF orbital energies do. The questions still being debated are how to assign similarities and how to physically interpret the differences.

A density functional is then used to obtain the energy for the electron density. A functional is a function of a function, in this case, the electron density. The exact density functional is not known. Therefore, there is a whole list of different functionals that may have advantages or disadvantages. Some of these

functionals were developed from fundamental quantum mechanics and some were developed by parameterizing functions to best reproduce experimental results. Thus, there are in essence *ab initio* and semiempirical versions of DFT. DFT tends to be classified either as an *ab initio* method or in a class by itself.

The advantage of using electron density is that the integrals for Coulomb repulsion need be done only over the electron density, which is a three-dimensional function, thus scaling as N^3. Furthermore, at least some electron correlation can be included in the calculation. This results in faster calculations than HF calculations (which scale as N^4) and computations that are a bit more accurate as well. The better DFT functionals give results with an accuracy similar to that of an MP2 calculation.

Density functionals can be broken down into several classes. The simplest is called the Xα method. This type of calculation includes electron exchange but not correlation. It was introduced by J. C. Slater, who in attempting to make an approximation to Hartree–Fock unwittingly discovered the simplest form of DFT. The Xα method is similar in accuracy to HF and sometimes better.

The simplest approximation to the complete problem is one based only on the electron density, called a local density approximation (LDA). For high-spin systems, this is called the local spin density approximation (LSDA). LDA calculations have been widely used for band structure calculations. Their performance is less impressive for molecular calculations, where both qualitative and quantitative errors are encountered. For example, bonds tend to be too short and too strong. In recent years, LDA, LSDA, and VWN (the Vosko, Wilks, and Nusair functional) have become synonymous in the literature.

A more complex set of functionals utilizes the electron density and its gradient. These are called gradient-corrected methods. There are also hybrid methods that combine functionals from other methods with pieces of a Hartree–Fock calculation, usually the exchange integrals.

In general, gradient-corrected or hybrid calculations give the most accurate results. However, there are a few cases where Xα and LDA do quite well. LDA is known to give less accurate geometries and predicts binding energies significantly too large. The current generation of hybrid functionals are a bit more accurate than the present gradient-corrected techniques. Some of the more widely used functionals are listed in Table 5.1.

5.2   LINEAR SCALING TECHNIQUES

One recent development in DFT is the advent of linear scaling algorithms. These algorithms replace the Coulomb terms for distant regions of the molecule with multipole expansions. This results in a method with a time complexity of N for sufficiently large molecules. The most common linear scaling techniques are the fast multipole method (FMM) and the continuous fast multipole method (CFMM).

DFT is generally faster than Hartree–Fock for systems with more than 10–

TABLE 5.1   Density Functionals

Acronyms	Name	Type
Xα	X alpha	Exchange only
HFS	Hartree–Fock Slater	HF with LDA exchange
VWN	Vosko, Wilks, and Nusair	LDA
BLYP	Becke correlation functional with Lee, Yang, Parr exchange	Gradient-corrected
B3LYP, Becke3LYP	Becke 3 term with Lee, Yang, Parr exchange	Hybrid
PW91	Perdue and Wang 1991	Gradient-corrected
G96	Gill 1996	Exchange
P86	Perdew 1986	Gradient-corrected
B96	Becke 1996	Gradient-corrected
B3P86	Becke exchange, Perdew correlation	Hybrid
B3PW91	Becke exchange, Perdew and Wang correlation	Hybrid

15 nonhydrogen atoms, depending on the numeric integral accuracy and basis set. Linear scaling algorithms do not become advantageous until the number of heavy atoms exceeds 30 or more, depending on the general shape of the molecule.

The linear scaling DFT methods can be the fastest *ab initio* method for large molecules. However, there has been a lot of misleading literature in this field. The literature is ripe with graphs indicating that linear scaling methods take an order of magnitude less CPU time than conventional algorithms for some test systems, such as *n*-alkanes or graphite sheets. However, calculations with commercial software often indicate speedups of only a few percent or perhaps a slightly slower calculation. There are a number of reasons for these inconsistencies.

The first factor to note is that most software packages designed for efficient operation use integral accuracy cutoffs with *ab initio* calculations. This means that integrals involving distant atoms are not included in the calculation if they are estimated to have a negligible contribution to the final energy, usually less than 0.00001 Hartrees or one-hundredth the energy of a van der Waals interaction. In the literature, many of the graphs showing linear scaling DFT performance compare it to an algorithm that does not use integral accuracy cutoffs. Cases where the calculation runs faster without the linear scaling method are due to the integral accuracy cutoffs being more time-efficient than the linear scaling method.

The second consideration is the geometry of the molecule. The multipole estimation methods are only valid for describing interactions between distant regions of the molecule. The same is true of integral accuracy cutoffs. Because of this, it is common to find that the calculated CPU time can vary between different conformers. Linear systems can be modeled most efficiently and

folded, globular, or planar systems less efficiently. In our test calculations on the $C_{40}H_{82}$ *n*-alkane, the energy calculation on a folded conformation took four times as much CPU time as the calculation on the linear conformation.

The bottom line is that linear scaling methods can use less CPU time than conventional methods, but the speedup is not as great as is indicated by some of the literature. We ran test calculations on a C_{40} *n*-alkane in various conformations and a C_{40} graphite sheet with two software packages. These calculations showed that linear scaling methods required 60–80% of the amount of CPU time required for the conventional calculation. It is possible to obtain better performance than this by manually setting the multipole order used by the algorithm, but researchers have advised extreme caution about doing this because it can affect the accuracy of results.

5.3   PRACTICAL CONSIDERATIONS

As mentioned above, DFT calculations must use a basis set. This raises the question of whether DFT-optimized or typical HF-optimized basis sets should be used. Studies using DFT-optimized basis sets have shown little or no improvement over the use of a similar-size conventional basis sets. Most DFT calculations today are being done with HF-optimized GTO basis sets. The accuracy of results tends to degrade significantly with the use of very small basis sets. For accuracy considerations, the smallest basis set used is generally 6−31G* or the equivalent. Interestingly, there is only a small increase in accuracy obtained by using very large basis sets. This is probably due to the fact that the density functional is limiting accuracy more than the basis set limitations.

Since DFT calculations use numerical integrals, calculations using GTO basis sets are no faster than those using other types of basis sets. It is reasonable to expect that STO basis sets or numeric basis sets (e.g., cubic splines) would be more accurate due to the correct representation of the nuclear cusp and exponential decay at long distances. The fact that so many DFT studies use GTO basis sets is not a reflection of accuracy or computation time advantages. It is because there were a large number of programs written for GTO HF calculations. HF programs can be easily turned into DFT programs, so it is very common to find programs that do both. There are programs that use cubic spline basis sets (e.g., the dMol and Spartan programs) and STO basis sets (e.g., ADF).

The accuracy of results from DFT calculations can be poor to fairly good, depending on the choice of basis set and density functional. The choice of density functional is made more difficult because creating new functionals is still an active area of research. At the time of this book's publication, the B3LYP hybrid functional (also called Becke3LYP) was the most widely used for molecular calculations by a fairly large margin. This is due to the accuracy of the B3LYP results obtained for a large range of compounds, particularly organic molecules. However, it would not be surprising if this functional's

dominance changed within a few years. Table 5.1 lists a number of commonly used functionals.

Due to the newness of DFT, its performance is not completely known and continues to change with the development of new functionals. The bibliography at the end of this chapter includes references for studies comparing the accuracy of results. At the present time, DFT results have been very good for organic molecules, particularly those with closed shells. Results have not been so encouraging for heavy elements, highly charged systems, or systems known to be very sensitive to electron correlation. Also, the functionals listed in Table 5.1 do not perform well for problems dominated by dispersion forces.

5.4   RECOMMENDATIONS

Given the fact that DFT is newer than the other *ab initio* methods, it is quite likely that conventional wisdom over which technique works best will shift with the creation of new techniques in the not too distant future. DFT's recent heavy usage has been due to the often optimal accuracy versus CPU time. At the time of this book's publication, the B3LYP method with basis sets of $6-31G^*$ or larger is the method of choice for many organic molecule calculations. Unfortunately, there is no systematic way to improve DFT calculations, thus making them unusable for very-high-accuracy work. Researchers are advised to look for relevant literature and run test calculations before using these methods.

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