

## Density Function Theory (DFT)

DFT is a more recent addition to electronic structure methods, particularly for single molecule calculations.

The basic premise is that there is a one-to-one mapping from the ground state electron density to the ground state electronic wavefunction. This gives us another method for solving the electronic Schrödinger equation. Furthermore, the electron density is only a function of three variables rather than the  $3n$  (three for each of the  $n$  electrons) variables that are present in the many-electron wavefunction. In practice, this leads to a much quicker and simpler calculation.

The nature of DFT means that it includes some part of electron correlation although the amount and type is functional dependent and generally not well defined.

### Functionals

#### Basic Functionals

A significant problem in DFT is that the exact form of the functional (function of a function) that maps the electron density to the electronic wavefunction is not known for any system other than a free electron gas. Different approximations have been used to provide the functionals required.

In the *local density approximation* (LDA) the functional only depends on the value of the density at the coordinate where the functional is evaluated. The LDA has been used widely and successfully in solid state physics but is an inadequate approximation for molecular calculations.

The next level of complexity is to also include the gradient of the electron density at the coordinate where the functional is evaluated. This is the *generalized gradient approximation* (GGA) and has yielded good results for molecular ground state geometries and energies.

In order to increase the accuracy and reliability of functionals, there has been (and continues to be) much work dedicated to generating better functionals for molecular systems.

#### Advanced Functionals

There are many different functionals available in most computational chemistry packages and they are generally described by two parts, the *exchange* functional and the *correlation* functional. For example, a commonly seen functional (for molecular calculations) is BLYP; this uses the exchange functional of Becke (hence the 'B') and the correlation function of Lee, Yang and Parr (hence the 'LYP').

#### Hybrid Functionals

Hybrid functionals try to overcome some of the deficiencies of 'pure' DFT exchange functionals by mixing in a component of the exact exchange energy from HF theory. Possibly the most widely used hybrid functional in molecular calculations is the ubiquitous B3LYP functional. This uses the B exchange functional, the LYP correlation functional along with 3 parameters controlling the amount of exact HF exchange energy mixed in.

Hybrid functionals are generally fitted to a training set of molecules and so are not *ab initio* methods in the true sense as they include some empirical input. Care is needed when using hybrid functionals to make sure that they have been fitted to molecules that resemble your system.

### **Advantages**

DFT includes some component of electron correlation for much the same computational cost as HF methods. This means that it is a highly efficient way of performing a more advanced calculation on your system and that you can treat more accurately systems that are too large for post-HF methods (MP2, CCSD(T), CISD).

DFT methods (along with plane-wave basis sets) also allow us to use electronic structure methods on the condensed phase (particularly crystalline or metallic solids).

### **Disadvantages**

How do you choose the best functional for your system? DFT methods are not systematically improvable like wavefunction based methods and so it is impossible to estimate the error associated with your calculations without reference to experimental data or other types of calculation. The choice of functionals is daunting and can have a real impact on your calculations.

There are difficulties in using DFT to describe intermolecular interactions, especially those involving dispersion (VDW) forces or systems in which dispersion forces compete with other interactions (biomolecules).

### **Applications**

- Calculation and stability of structures: equilibrium, transition state and reaction intermediates.
- Characterization of the MOs – predictions of reactivity.
- Vibrational analysis – calculating IR and Raman spectra.
- Charge distribution and unpaired spin densities.

### **Software Available on the EaStCHEM RCF**

- **Gaussian 03** – Includes a very wide choice of functionals for use on molecular systems. Good choice for small to medium systems.
- **MOLPRO** – Includes a smaller choice of functionals than Gaussian but is better at treating large molecular systems due to better parallel algorithms.
- **CASTEP, VASP, CPMD, CRYSTAL** – DFT codes for solid state calculations. CASTEP, VASP and CPMD use plane-wave basis sets while CRYSTAL uses localized GTO basis sets.