Density Functional Theory - FAQ's

1. What is computational chemistry?

Quantum many body problem can not be solved analytically. Often numerical solutions are employed to solve them. Results obtained from them are often referred as computational chemistry or theoretical materials science. The accuracy of the results varies with respect to the type of computational chemistry method.

2. What are the types of computational chemistry methods?

There are three types of methods: (i) *ab intio* method (ii) density functional theory and (iii) semiempirical method. In *ab intio* method (or first principles) each and every interaction in the atom has been considered and every electronic state will be calculated. In density functional theory calculations, instead of calculating electronic wave function, chemical properties are calculated as the function of electron density. Where as in the case of semiempirical methods, known experimental or theoretical data will be used for initial approximation and then the properties are calculated from that point.

3. How accurate are these methods?

First principle methods provide good results. Especially methods like CCSD(T) are considered as the golden standard among the methods. By properly choosing the potential and basis sets comparable results can be achieved using DFT methods. Particularly DFT provide very satisfying results in organic compounds and the predictions are very accurate. Severe optimization and bench-marking is required in the case of semiempirical methods.

4. So, what do we do exactly using DFT?

DFT is a numerical solution to quantum n-body problem. The solution is based on Hohenberg-Kohn theorem, which states that ground state properties of a molecule can be determined from its electron density. That is there is a connection between n-body wave function to the total electron density of the

system. So, by solving the functional of the density, real electron density can be calculated. In programming level, the molecule of interest is optimized by comparing its electron density with a pre-defined Kohn-Sham potential.

5. What are these Kohn-Sham potentials?

The pre-defined exchange or correctional functional such as wave functions or density is often expressed as functions (functional is a function of a function) either as Gaussian function or as a plane wave function. Gaussian is a localised model so it is suitable for single molecules. Whereas in the case of periodic systems such as crystal structure plane waves (technically sine and cosine waves will be fitted to the electronic distribution and fast Fourier transform will be done to extract the relaxed (or optimized) structure). These planes waves will be approximated to different elements and called as pseudo potentials. So, in every DFT calculation we have a define a functional (for example if it is a Gaussian calculation we will provide B3LYP and if it is a crystal system we will provide PBE) and in addition a basis set (that contains electronic wave functions). The system will combine our input file molecular coordinates with this functional and basis set to provide as optimized results.

6. What are the packages available for DFT calculations?

Depending upon the type of potential two kind of software packages are available. For molecular materials Gaussian type potentials are preferred and packages like Gaussian, Orca, Dalton are widely used. For Pseudo potentials Quantum Espresso, WIEN2k and VASP are often considered.

7. How to do a simple calculation in Quantum Espresso?

The following links provide the basic idea:

(a) http://www.iiserpune.ac.in/~smr2626/hands_on/week1/jun30/simple_calcs_qe_mastani.pdf

(b) http://flex.phys.tohoku.ac.jp/QE/workshop_QE_2016/DFT-hands-on-nguyen.pdf

(c) http://indico.ictp.it/event/a12255/session/1/contribution/1/material/0/0.pdf

8. How to do simple calculation using Orca?

Details available in this link: http://www.prvn.info/oec/dft.pdf