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Density functional simulation of water molecule with Ab-initio pseudo potential

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Abstract
In the present work, we have firstly discussed about the role of computer simulations in physics, molecular dynamics, DFT and SIESTA code. After that we discussed various approximations to solve the many body Schrodinger equation. To study the behaviour of interacting electron, density functional theory is studied along with different formulations. Further we discussed about the pseudopotentials and its types and generated ab-inito pseudopotential of hydrogen and oxygen with the help of ATOM program using Troullier and Martin's scheme and also explained the basic DFT simulation of water molecule with help of SIESTA code.

Keywords: Density functional theory, computational physics, simulations, molecular dynamics.

Introductions
Computer simulations plays crucial role in physics by enabling scientists to study and understand complex physical phenomena that may be challenging or even impossible to investigate through traditional experimental methods. It plays a vital role in physics, molecular dynamics, and DFT [1], study of behaviour of materials under conditions such as high pressure or temperature, design new materials with some specific properties. Computer simulations are an essential tool for physicists. They allows us to study complex systems and phenomena that would be difficult to investigate through experiments. Modern theoretical methodology added to the advantage of high-speed computing, the work of computational physics is closely integrated with experimental effort at various laboratories and universities the world over.
The present work is an overview of the ab initio calculations using the SIESTA code. In this, our main emphasis is on the pseudopotential generation of hydrogen and oxygen and on studying basic DFT simulation of water molecules. The pseudopotential of hydrogen and oxygen are used for studying water molecules and molecular DFT simulation of water molecule are performed.

Theoretical Formalism
There are various types of pseudo potentials such as model pseudo potential, ab-initio pseudopotential, norm conserving pseudopotential and ultrasoft pseudopotential. We will discuss about trollies and martin's pseudopotential [3] as we have used this scheme in pseudopotential generation.
In this case also, all-electron computations of free atoms in a reference configuration are used to create unscreened ab-initio pseudopotentials first. After obtaining the valence states and all-electron potential, we build the screened pseudopotentials using the Troullier-Martins approach. Here, the pseudo wave function is taken to have the following form.

$$R_{TM}^{l}(r) = r^{l} e^{p(r)} p(r) = c_0 + \sum_{i=2}^{n} c_i r^{l}$$

The r^l behaviour for small r is included to avoid a hard-core pseudo potential, the criteria given by Troullier and Martins for the constructing the norm-conserving pseudopotential are the following:
1. Charge conservation inside the cut off radius.
2. R_psis node less and is exactly similar to the all-electron wave function outside a suitably chosen cutoff radius r_c

$$R_{ps} = \begin{cases} R_{ps}(r)\ for\ r < r_c, \\ R_{AE}(r) for\ r \geq r_c \end{cases}$$

3. The norm of the pseudo and true-wave functions inside the pseudized region ($r < r_c$) is the same:

$$\int_0^{r_c} |r\, R_{ps}(r)|^2 dr = \int_0^{r_c} |r\, R_{AE}(r)| dr$$

4. The logarithmic derivatives of the all electron and pseudo-wave functions match for $r \geq r_c$.
The polynomial is chosen of sixth order in r^2

$$p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}$$

Ab-initio Pseudopotentials of Oxygen and Hydrogen
Here, our interest is to study water molecular system using SIESTA. For this we require pseudopotentials of O, H. We have generated these by using the Atom program [3].

Oxygen
Our input file is named as O.tm2.inp and contains the electronic configuration as follows: $1s^2 2s^2 2p^4 3d^0 4f^0$. In input file we chose type of method used for generating pseudopotentials. Out of which 1s is the core orbital and rest are valence orbitals, by running the all electron configuration we plotted all electron wave functions and from these plots we choose the cut off radius, which corresponds to the maxima of the all electron wave function. This cut off radius is then used in the next step that is the pseudopotential generation step, and we checked whether all-electron and pseudopotential wave function are matching. If not we matched them by varying the cut off radius

Hydrogen
Here the electronic configuration used is $1s^1 2p^0 3d^0 4f^0$ and our input file is named as H.tm2.inp. Other method is similar as that of Oxygen atom.

Molecule of water
An arrangement of atomic nuclei and electrons that is stable enough to have observable characteristics is called a molecule. One molecule of water [4] is made up of two hydrogen atoms covalently bound to one oxygen atom.

Setting up a DFT Simulation
For setting up a DFT Simulation using SIESTA, following steps are to be performed:
1. Identification of atomic species.
2. Generation and testing of pseudopotentials of atomic species.
3. Setting up of input file for SIESTA
4. Analysis and visualization of output.

For preparing for simulation of water using SIESTA one needs pseudo potential files of hydrogen and water from the generated and tested pseudo potentials as described in previous chapter, and besides this one needs to prepare an input file in the flexible data format (FDF), which is read as a standard input. The simulation has been performed on ubuntu using SIESTA serial version 4.1-b4. First thing which is to be kept in mind for the present system is that since we are interested in various properties of a single molecule, the periodic simulation cell chosen in SIESTA should be large enough to neglect interaction among other molecules.

Various parameters in input FDF file
Since the input parameters control the simulation, it is worth going through these carefully. We can divide input FDF file in the following parts:
1. General system descriptors.
2. Simulation run parameters related to mesh cutoff and energy cutoffs.
3. Functional and solution method.
4. K-sampling.
5. SCF iterations.
6. Molecular dynamics options.
7. Basis set generation details.

Discussion and conclusion
We chose in FDF file set of parameters as given in the table 1 and the solution method used is diagnalization.

Table 1: Magnitude of lattice constant and mesh cutoff

Name	Value
Lattice constant (A°)	12
Mesh cutoff (Ryd.)	140

1. Egg box effect
The molecule is displaced along x-axis in the various steps, a graph is plotted between displacement and the total energy and the total force as shown in figures 1 and 2 respectively. From it that value of the displacement is chosen where energy total and total force is minimized. Thus, from the graph the value of the displacement chosen is $0.3A^0$.

2. Lattice constant and mesh cutoff
The values of lattice constant and mesh cutoff as shown in table 1 are those for which the total energy converges. This can be seen in Figures 3 and 4 respectively.

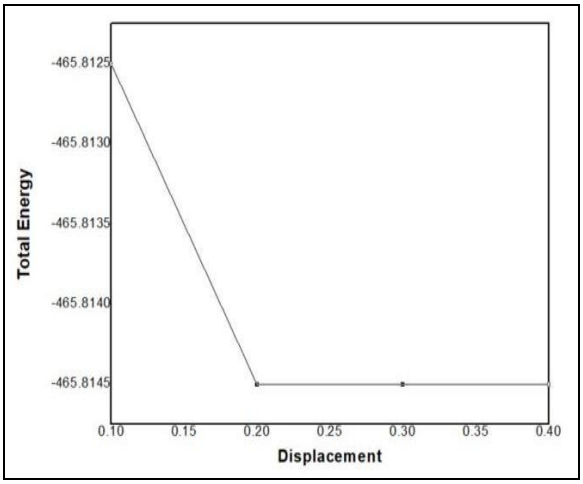

Fig 1: Plot of total energy (eV) vs displacement (Ang.)

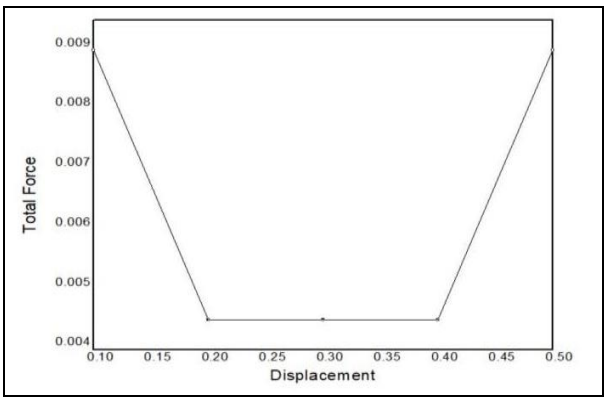

Fig 2: Plot of Total force (eV/Ang.) vs displacement (Ang.)

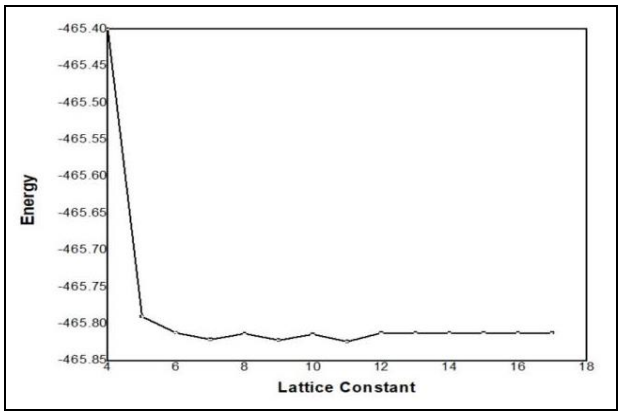

Fig 3: Plot of lattice constant (Ang.) vs total energy

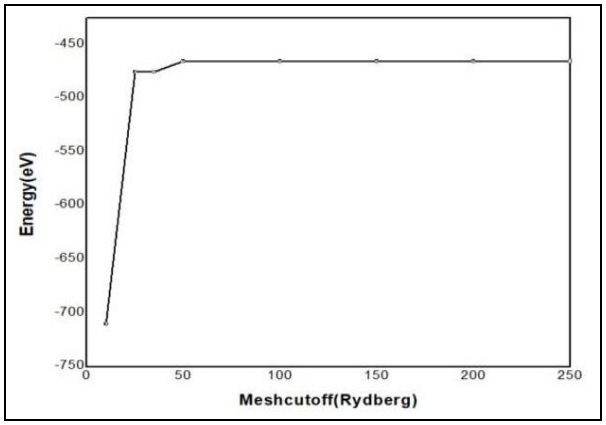

Fig 4: Plot of Total energy (ev) vs mesh cutoff (Rydberg)

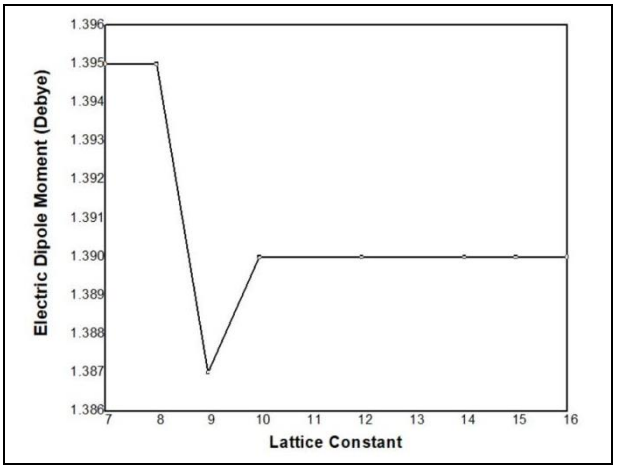

Fig 5: Plot of Electric dipole moment vs Lattice constant

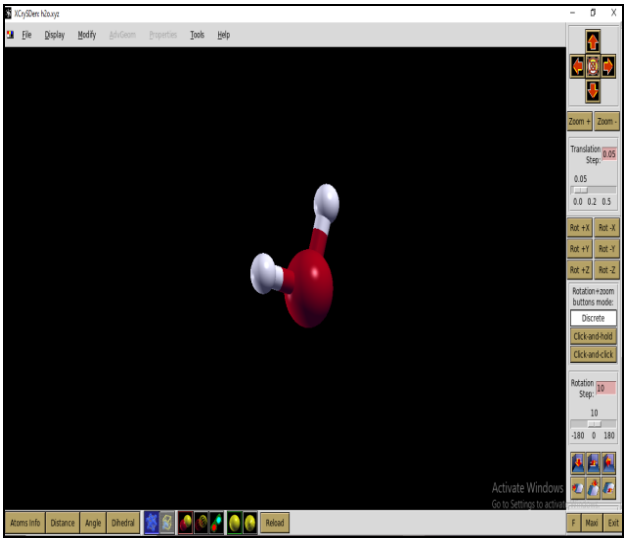

Fig 6: Water molecule simulation viewed in xcrysden

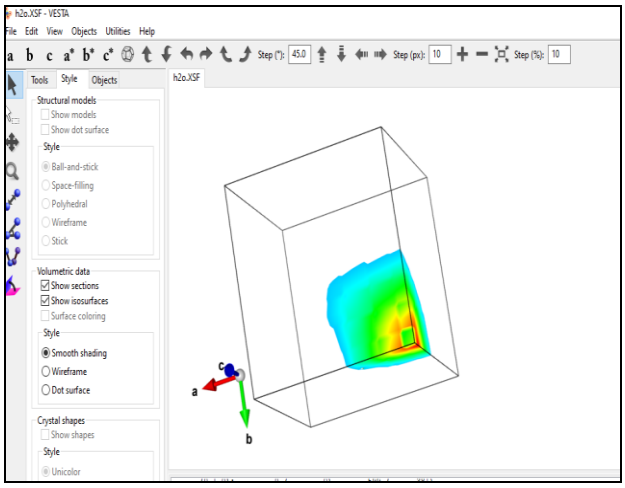

Fig 7: Charge density of water

Conclusion

The present work consist of review of theoretical description of ab-inito calculation in material science. We discussed various approximations, to solve the many body Schrodinger equation. The properties in material science depends on the interacting electrons. So to study the behaviour of these electrons, Density Functional Theory is most widely used. Here, DFT is computationally treated with SIESTA package, which is an open source code. It is

used to perform electronic structure calculations and ab-initio molecular dynamics simulations of molecules. SIESTA is very efficient as it used a basis set of strictly-localized atomic orbitals. Its accuracy and cost varied in wide range, from quick calculations to highly accurate simulations. Also it take less time for calculation as compared to other some other packages.

In the present work, we have performed pseudopotential generation of Hydrogen and oxygen which are further used to study water molecule using Troullier Martins schemes. In last chapter, we have discussed various parameter of input FDF file like mesh cut off, lattice parameter etc and Basis set generation related variables. At the end of the output file we get the information about final energy, stress tensor, pressure, and electric dipole and plotted graphs using them.

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