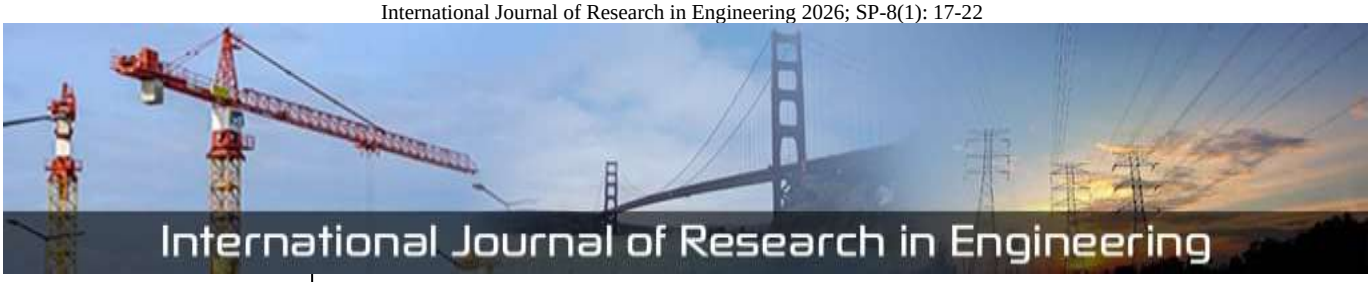

E-ISSN: 2664-8784
P-ISSN: 2664-8776
Impact Factor: RJIF 8.26
IJRE 2026; SP-8(1): 17-22

www.engineeringpaper.net
Received: xx-03-2025
Accepted: xx-04-2025

Swapna Department of Physics, DPG Degree College, Gurugram, Haryana, India

Corresponding Author:
Swapna Department of Physics, DPG Degree College, Gurugram, Haryana, India

Recent Advancement in Multidisciplinary innovation and research RAMIR-25

DFT-driven quantum simulation of molecules employing first-principles pseudopotentials

Swapna

DOI: https://www.doi.org/10.33545/26648776.2026.v8.i1a.172

Abstract
In the present work, we have discussed about molecular dynamics, simulations, DFT and SIESTA code. To solve many body Schrodinger equation, we discussed various approximation. Further we discussed about various types of pseudopotentials. Pseudopotentials are used to simplify the calculation of the electronic properties of atoms and molecules by replacing the strongly bound core electrons with an effective potential that acts on the valence electrons. With the help of ATOM program, we generated ab-initio pseudopotentials of hydrogen, oxygen and carbon using Troullier and Martin's scheme and also explained the basic DFT simulation of water and CO_2 molecule with help of SIESTA code. SIESTA is employed to carry out electronic structure calculations as well as ab-initio molecular dynamics simulations for various molecular systems.

Keywords: Density Functional Theory, Computational Physics, Simulations, Molecular Dynamics, Pseudopotentials

Introduction
Computational approaches have become indispensable in modern physics for exploring systems that are difficult
to investigate experimentally. In this work, we present an overview of first-principles simulation techniques with emphasis on Density Functional Theory (DFT) and its implementation using the SIESTA package. The theoretical background of many-body electronic structure calculations is discussed, along with the approximations employed to make the problem computationally tractable. Norm-conserving ab initio pseudopotentials for hydrogen and oxygen are generated using the Troullier-Martins scheme via the ATOM program. These pseudopotentials are subsequently applied to perform a DFT-based simulation of an isolated water molecule. The study highlights the role of pseudopotentials, basis sets, and convergence parameters in achieving reliable electronic structure results.

Theoretical Formalism
As density gradients are taken into additional account, GGA is able to capture important and subtle features of electronic structure that LDA might ignore. It enhances the precision of DFT computations for a variety of materials, such as solids, molecules, and surfaces, and is especially useful for systems with significant electron density fluctuations [1]. GGA has made it possible to predict various material properties, such as band gaps, reaction energies.
Pseudopotentials are constructed with complex balancing acts to minimize computational cost and accurately represent the effects of the core electrons. Pseudopotentials are essential tools in computational materials science in Siesta. Because they make it possible to accurately and efficiently model materials at the atomic and electronic levels, these pseudopotentials are essential. Pseudopotentials are used in DFT to handle the intricate interactions between electrons and atomic nuclei, where the electron density describes the electronic structure of a material [2]. Pseudopotentials generated by calculations on atoms (or atom-like states) are termed as ab-initio because they are not fitted to the experiment. The concept of norm conservation has a special place in the development of ab-initio pseudopotentials and it makes them accurate and transferable.

Pseudopotential Generation

There are generally three steps to generate pseudopotential using ab initio methods. First using DFT, atomic levels and wave functions are generated. From this one then generates the pseudopotentials. Finally, it is checked that whether what has been done is useful or not, and if it is not, then it is tried again in different way. The Kleinman-Bylander projection is used by Troullier and Martins approach to construct the numerical form of the pseudopotential, which has the benefit of providing a simple pseudopotential. The construction of pseudopotential is often done separately for each angular momentum quantum number l of the pseudo wavefunction. These pseudopotentials are called non-local pseudopotentials [3] which have the form:

$$V_{NL} = \sum |Y_{lm}\rangle V_l \langle Y_{lm}|$$

Where spherical harmonics Y_{lm} project out each angular momentum component. This type of pseudopotential requires projection operator to be used for each plane wave which needs efficient computational effort. Local pseudopotentials are pseudopotentials that employ the same potential for all angular moments. They are computationally more efficient than non-local pseudopotential but are less reliable.

Steps in ab-initio Pseudopotential generation

1. Selection of valence and core states.
2. Selection of reference configuration.
3. Generating the all electron wave function by running all electron script.
4. The matching radii be chosen from the wave functions at step three.
5. Choose the type of method. rc and the reference configuration for generating the screened pseudopotential [4].
6. Test the generated pseudopotential.
7. Visualizing whether the all-electron wave function match with the pseudo-wave function beyoud rc or not.
8. Check whether logarithmic derivative matches at rc.

Oxygen

Our input file is named as O.tm2.inp and contains the electronic configuration as follows: $1s^2 2s^2 2p^4 3d^0 4f^0$. Method of generation is choosen in input file. 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

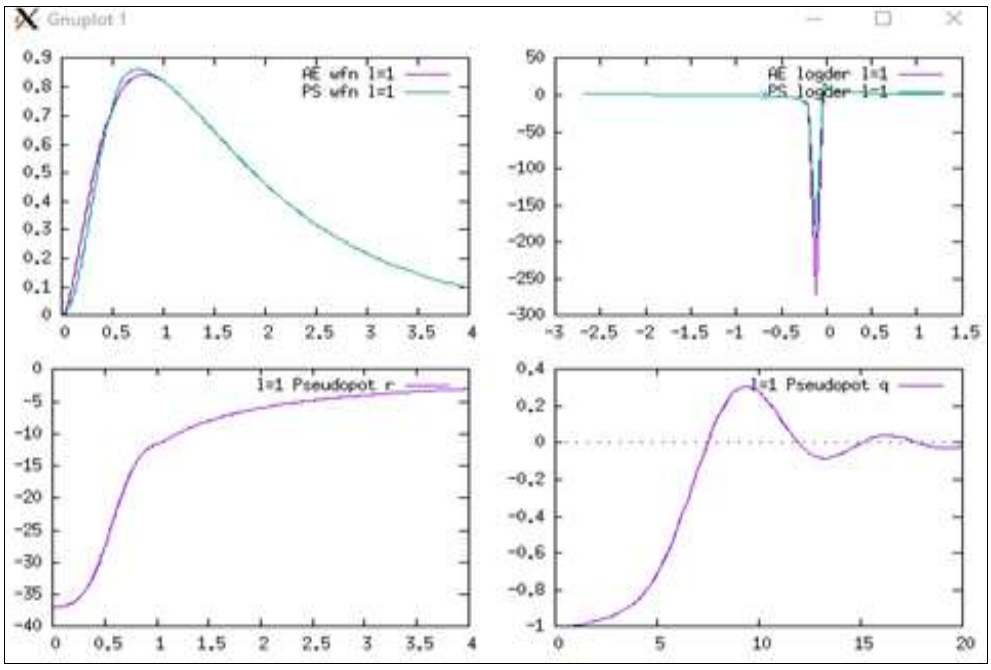

Fig 1: Output of Pseudopotential generation for oxygen using TM for (l = 1) (a) Plot of pseudo-wave function vs radius (r in bohr) (b) Plot of logarithmic derivative with energy (Ryd.) (c) Plot of radial pseudopotential with radius (bohr) (d) Plot of fourier transform of pseudo wave function with wave vector (q)

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. The type of method used for generating pseudopotentials is also chosen in the input file.

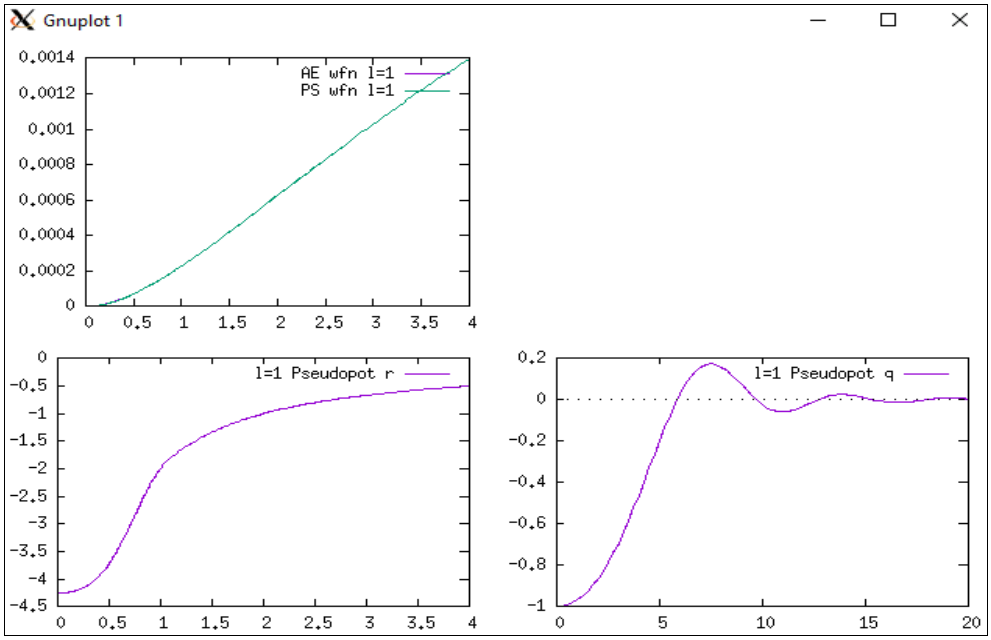

Fig 2: Output of Pseudopotential generation for Hydrogen using TM for (l = 1) (a) Plot of pseudo-wave function vs radius (r in bohr) (b) Plot of radial pseudopotential with radius (bohr) (c) Plot of fourier transform of pseudo wave function with wave vector (q).

Carbon

Our input file is named as O.tm2.inp and contains the electronic configuration as follows: $1s^2 2s^2 2p^2 3d^0 4f^0$. Method of generation is choosen in input file.

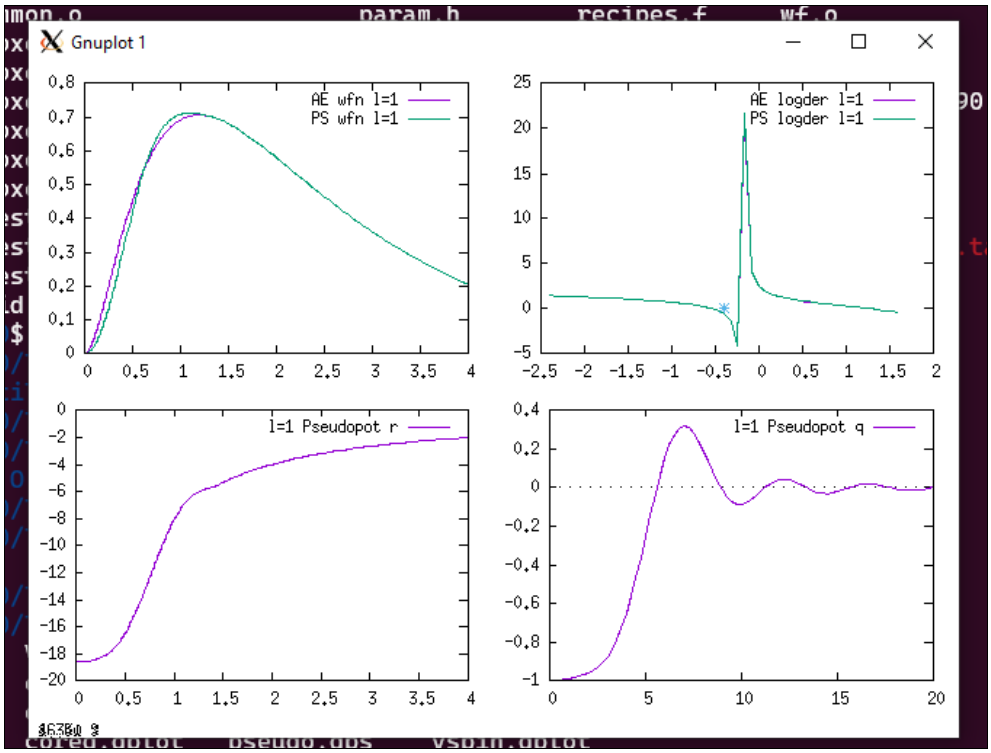

Fig 3: Output of Pseudopotential generation for carbon using TM for (l = 1) (a) Plot of pseudo-wave function vs radius (r in bohr) (b) Plot of logarithmic derivative with energy (Ryd.) (c) Plot of radial pseudopotential with radius (bohr) (d) Plot of fourier transform of pseudo wave function with wave vector (q)

The development of accurate electronic structure calculation based on density functional theory (DFT) is a best approach for electronic structure calculations The complex part of electronic structure calculation is in handling the many electron instructions the decomposition of full electronic wave function into single electron function leads to additional terms in the Hamiltonian, namely, the exchange term of the Hartree Fock method and correlation energy which swaps up the remaining effects. The difficulty in DFT in that these two terms are not tractable, and therefore an approximation is required. The first approximation that was used is the local density approximation (LDA) in which it is assumed that the exchange correlation energies at a point can be represented by the energy of a uniform gas of electron with the density of that point. This approximation has proven to be adequate for many purposes, but nevertheless, there was a strong motivation to improve upon LDA. The most obvious improvement was to take account

of the gradient of the electron density at the point. And this has been implemented through the generalized gradient approximation (GGA). Both the LDA and GGA interactions have been parameterized by calculations on the free electron gas, which is one of the few problems in many body calculations for which there are exact solutions. Full doing DFT calculations. Various codes are available mostly used codes are CASTEP (Cambridge Serial Total Energy Packages) and SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atom). We have used SIESTA for our work.

Setting up a DFT Simulation

Following steps are performed to set up DFT Simulation:

1. Firstly we identify the atomic species.
2. Pseudopotentials generation and testing of atomic species is done.
3. Then we set up input file for SIESTA.
4. Finally we do analysis and visualization of output.
5. Various parameters in input fdf file:

General system descriptors

- System name: It is the string of one word containing a descriptive name of the system, e.g. Water
- System label: A single word containing a nick name of the system, e.g. Water in our case.
- Number of atoms: There are three atoms in H_2O molecule, two of hydrogen and one of oxygen.

System Name Water molecule
System Label h2o
Number Of Atoms 3
Number Of Species 2

Simulation run parameters related to mesh cutoff and energy cutoffs

(i) Chemical species label: It explains the different chemical species which are present, assigning them a number for further identification here there are two atomic species 1 and 2 which are O and H respectively preceded by their atomic numbers.

%block Chemical Species Label
1 8 O # Species index, atomic number, species label
2 1 H
% endblock Chemical Species Label

(ii) The following block gives the position of the various atoms in angstrom present in water that is one O-atom and two H-atom as:

Atomic Coordinates Format Ang
% block Atomic Coordinates And Atomic Species
-2.81351637 3.05733200 -0.00478348 1 O
-2.81956763 2.26594233 0.55957050 2 H
-2.80538217 3.81765024 0.60040665 2 H
% endblock Atomic Coordinates And Atomic Species

(iii) Lattice constant: It gives the size of the supercell, and that value is choosen at which our system behaves as a molecule. Sometimes one gets confused about its meaning, since we are looking at a single molecule, therefore the size of the lattice constant should be so large so that their is enough vacuum around our molecule.

(iv) Meshcutoff: Choice of meshcutoff is a very crucial choice and the total energy convergence depends upon it. It is the parameter which defines the k-grid cutoff. To seeits role simulation is run by varying the meshcutoff, and then a graph between the total energy and meshcutoff is chosen at which energy converges.

(v) Denchar: Denchar is a program that uses SIESTA's output to compute charge densities in real space. The charge density can be visualised in 3d mode with xcrysden or vesta software.

(vi) Egg box effect [5]: SIESTA uses a finite 3D grid for the calculation of some integrals and representation of charge densities and potentials. Its fineness is determined by its plane-wave cut off i.e. meshcutoff parameter. It means that all periodic plane waves with kinetic energy lower than this cutoff can be represented in the grid. The existence of the grid causes the breaking of the translational symmetry which is called the eggbox effect, due to the fact that density and the potential have the plane wave components above the mesh cutoff. For reasonable values of the meshcutoff, the effect of the eggbox on the total energy or on the relaxed structure is unimportant. Here we do small displacement in the position of the molecule inside the box with SIESTA, a rigid translation of the system using the following block is done:

% block Atomic Coordinates Origin
0 0 0
% endblock Atomic Coordinates Origin

Functional and solution method

- **XC functional:** This parameter represents the exchange-functional type it may be local density approximation or generalized gradient approximation or hybrid.
- **Solution Method:** There are two types of solution methods to get energy eigen values available in siesta, dingnalization and order n. In the case of small systems with atoms less than hundred diagonalization method is the most appropriate one.

K-sampling

- **kgrid-Monkhorst-Pack:** It is the parameter [6] that is utilized in the k-point computations. For periodic systems, a K-mesh with several points is required; however, for molecules, a single K-point is sufficient.
- **kgrid – cutoff:** This parameter establishes how fine the k-grid is when it comes to Brillouin zone sampling. To achieve the same level of sampling precision with a single k-point, the length of the supercell's lattice vector must be cut in half. Its default value is 0.0 bohr.

SCF iterations

- MaxSCF iterations: This parameter shows the maximum number of SCF iterations per time step and its default value is 50.
- DM. Mixing Weiglit: It gives the proportion a of output density matrix to be used for the input density matrix of next SCF cycle, its default value is 0.25.
- DM.tolerance: This flag gives the tolerance of the density matrix. When the maximum difference between the output and input on each element of the DM in a SCF cycle is smaller than DM Tolerance then the self consistency has been achieved. Its default value is 10^{-4}.
- DM. Number Pulay: It controls the Pulay convergence accelerator. Pullay mixing accelerates convergence quite significantly and can reacli convergence in cases where linear mixing cannot. If its value is 0 or 1 simple

linear mixing is performed and its default value is 0.

Molecular dynamics options

- MD.TypeOfRun: This string explains the type of the molecular dynamics. Here we have used CG type of run means coordinate optimization by conjugate gradients.
- MD.NumCGsteps: It gives the maximum number of conjugate gradient minimization moves, the minimization is stopped if tolerance is reached.
- MD.MAX CGDispl: It gives the maximum atomic displacements on a CG optimization move. Its default value is.2 Bohr.
- MD. MaxForceTol: It gives the force tolerance in CG coordinate optimization. Run stops if the maximum atomic force is smaller than MD.MaxForceTol. Its default value is.04ev/Ang.

Basis set generation related variables

PAO. basis type: SIESTA generates extended bases such as multiple zeta, polarization and diffuse orbitals applying different schemes of choice

The following are some of the parameters of the simulation:

The atomic coordinates input format used is cartesian coordinates and the method of calculation is diagonalization. The electronic temperature is.0019 Ry. The force tolerance in CG coordinate optimization in the present case is 0.04eV/Ang. In our fdf file there is parameter called "Write MDhistory" which is done true and accumulates the molecular dynamics trajectory in the files named as:

- H_2O.MD and H_2O.MDE: When this flag WriteMDhistory is made true, then these two files got make. Out of which first contains the information of atomic coordinates and velocities. And the second one contains the shorter description of the run.
- H_2O.EIG: When this flag Write Eigen values is made true then this file got make. It writes the Hamiltonian eigenvalues for the sampling $\vec{k}$ points, in the main output file.
- H_2O.XV: When MD.UseSaveXV flag is made true then,everytime the atoms move, either during coordinate relaxation or molecular dynamics, their updated positions and current velocities are stored in the H_2O.XV.
- H_2O.PLD: When WriteDenchar flag is made true then this file got make, it contains the information of the valence charge density contours.
- H_2O.CG: When MD. UseSaveCG flag is made true then this file got make and it contains the conjugate-gradient history information.
- H_2O.RHO: When SaveRho flag is made true then this file gets written and the information about the valence pseudocharge density is written in it.

At the end of the output file i.e. in H_2O.out file we get the information about final energy, stress tensor, pressure, electric dipole and CPU execution times as follows:

siesta: Final energy (eV):
siesta: Kinetic = 352.168784
siesta: Hartree = 476.700278
siesta: Ext. field = 0.000000
siesta: Exch.-corr. = -112.823966
siesta: Ion-electron = -1260.871383
siesta: Ion-ion = 79.013786
siesta: Ekinion = 0.000000
siesta: Total = -465.812502
siesta: Stress tensor (static) (eV/Ang**3):
siesta: -0.000010 0.000000 0.000000
siesta: 0.000000 0.000004 -0.000003
siesta: 0.000000 -0.000003 0.000014
siesta: Cell volume = 1728.000000 Ang**3
siesta: Pressure (static):
siesta: Solid Molecule Units
siesta: -0.00000003 -0.00000007 Ry/Bohr**3
siesta: -0.00000253 -0.00000163 eV/Ang**3
siesta: -0.00405213 -0.00261272 kBar
siesta: Electric dipole (a.u.) = -0.017561 -0.003784 0.543847
siesta: Electric dipole (Debye) = -0.044636 -0.009619 1.382322

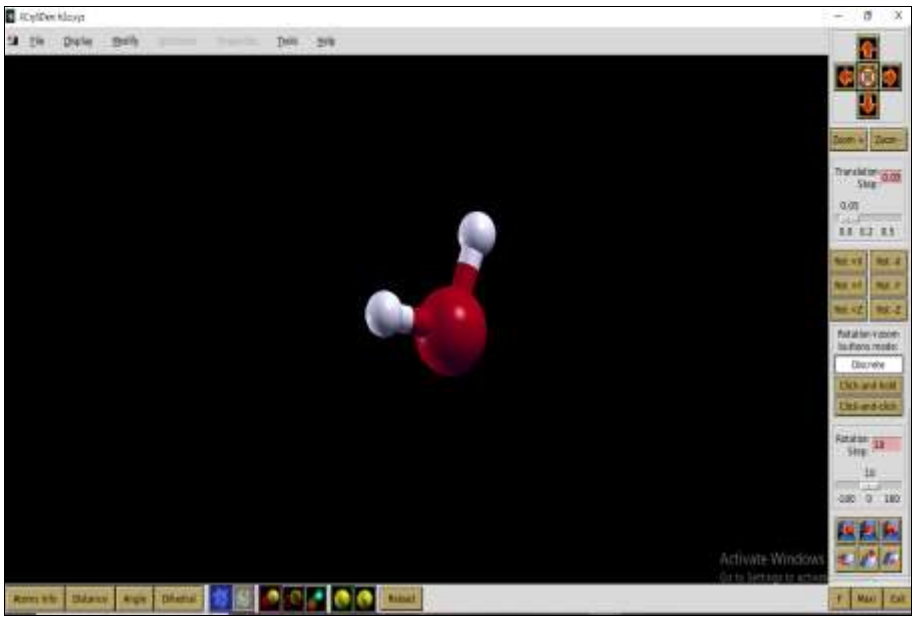

Fig 4: Water molecule simulation viewed in xcrysden

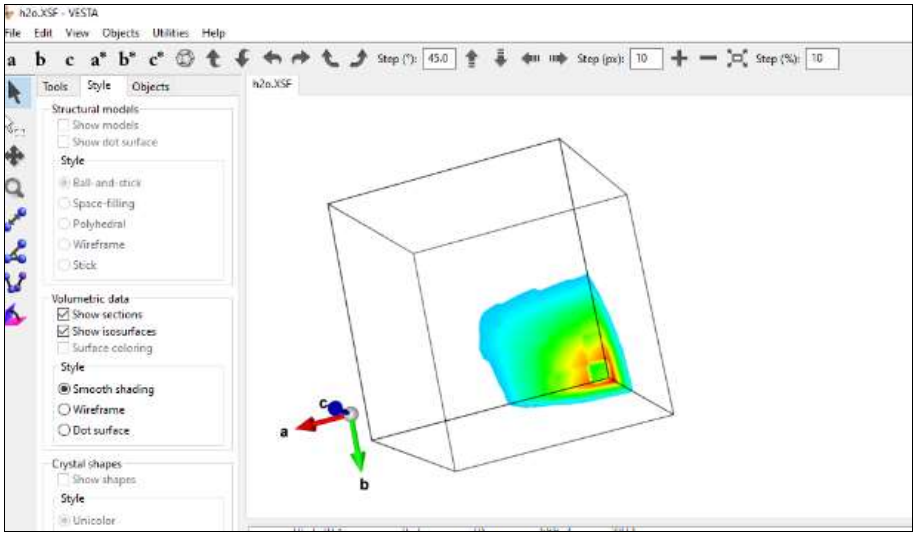

Fig 5: Charge Density of Water

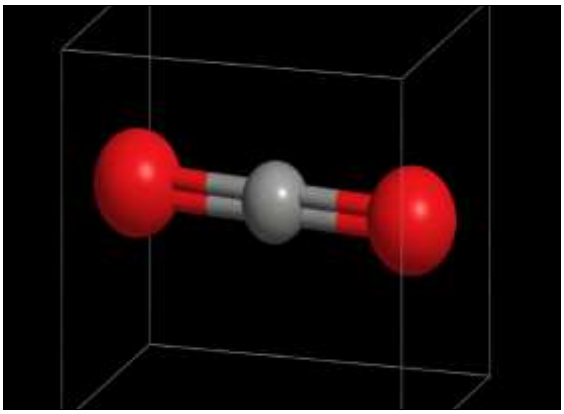

Fig 6: CO2 molecule simulation viewed in xcrysden

Conclusion

The present work consists of review of theoretical description of ab-inito calculation in material science. Here, DFT is computational 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 some other packages.

References

1. Shell DS, Stechell JA. Density functional theory. 2009;10.
2. Chelikowsky JR, Louie SG, editors. Quantum theory of real materials. Boston: Kluwer Press; 1996.
3. Kleinman L, Bylander DM. Phys Rev Lett. 1982;48:1425–1428.
4. Atom user manual. Version 4.2.7.
5. https://departments.icmab.es/leem/SIESTA_MATERIAL/Docs/Manuals/siesta-4.1-b4.pdf
6. http://surphy.fat.bme.hu/blog/sites/default/files/webfm/qchem/library / simulation / SIESTA-tuto.pdf