

Band Structure of Si and Geometric Optimization of SiO₂ Cluster

A dissertation Submitted in partial fulfillment

For the degree of Master of Science in Physics

Under the Academic autonomy
National Institute of Rourkela

By

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CERTIFICATE

This is to certify that the dissertation entitled "Band Structure of Si and Geometric Optimization of SiO₂ Cluster" being submitted by Miss Santripati Khandai to the Department of Physics, National Institute of Technology, Rourkela, Orissa for the award of the degree of Master of Science, is a record of bonafide research carried out by her under my supervision in the session 2008-09 at N.I.T., Rourkela.

BIPLAB GANGULI

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Santripty Khandai

ABSTRACT

In this project we have carried out a computer simulation for the study of electronic structure of the bulk silicon and geometric structure of SiO_2 cluster. We found the charge density and energy band gap for the bulk silicon. The geometric optimization of the cluster SiO_2 was undertaken in this project. Finally we supply our results and state the future works in this field.

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SYNOPSIS

This thesis entitled "Band Structure of Si and Geometric Optimization of SiO_2 Cluster" is submitted by Santripati Khandai to the Department of Physics, National Institute of Technology, Rourkela in the partial fulfilment of the requirements of the M.Sc. degree.

The problem in dealing with the clusters is that they are considered to be intermediate between atoms and bulk matter. Also some of their properties cannot be determined directly by the experimental measurements and so researchers working in this field have developed computer simulation for the study of clusters.

In the second section we see one of the methods of computer simulation called the 'Molecular Dynamics' which is rendered useful for the study of clusters. The molecular dynamics uses the concept of density functional theory which is also discussed therein.

We then discuss the use of a computer package named the 'Quantum Espresso' used for carrying out the simulation and later discuss the application of its codes to the study of physical system. The code PWscf is used here for the study electronic structure of bulk silicon

We use the code Car-Parinello for the geometrical optimization of SiO_2 cluster.

Finally we come up with the conclusion from our present study and also suggest the future works that can be carried in this field.

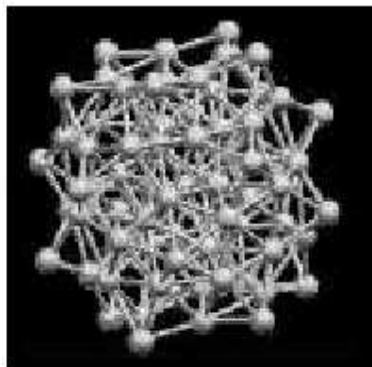
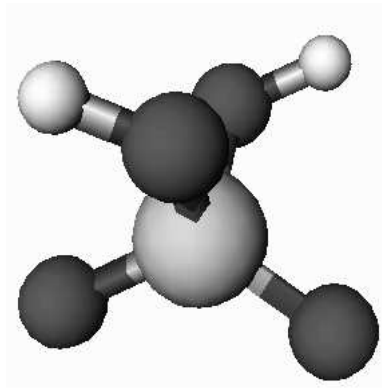
INTRODUCTION

We study the properties of different systems by modelling it in accordance to our convenience but in certain cases we really get messed up due to the complexities that arise. We can model our system using quantum mechanics like we are able to solve the hydrogen atom problem very well with it arriving at the exact solution for the wavefunction. This is possible because the exact form of the potential is known to us. Basically a hydrogen atom consists of a proton and an electron in which the only form of potential is the Coulombic repulsion. This is the simplest problem solved by quantum mechanics. Also quantum mechanics is equally beneficial for solving for the wavefunctions in solids. In this case the supporting factor remains the known boundary conditions and the assumed periodicity of the potential. The periodicity is based on the fact that the solids constitute the periodic arrangement of the atoms at the lattice sites. But what if there is only a group of atoms to be studied, it would represent a system of which we do not know the potential and also the solution using quantum mechanics would surely land us in trouble for the solution would then be quite complicated. In those cases quantum mechanics cannot be helpful in studying a system because we cannot solve the complex equations for arriving at desired wavefunctions. Also we could use classical mechanics to model our system but the problem with it is the simplified assumptions which renders it unfruitful because of less accuracy. It actually neglects the interactions between the particles which might be effectively contributing to the phenomena involved. So researchers working on this field developed a very effective way to study the system formed from the conglomeration of group of atoms known as the CLUSTERS. This is known

as 'MOLECULAR DYNAMICS' based on the computer simulation. It is best suited for the study of the solids and clusters. Earlier the study of any system consisted of the experimental data but now a days we can go for computer simulation. It is helpful in a way that we study the system even under extreme conditions of temperature and pressure which is not possible in experimental techniques because we always have a limitations of the apparatus we use. We usually cannot go for very high or very low temperature and pressure range. The molecular dynamics makes use of the density functional theory in order to explain the properties of the system. To study the molecular dynamics we selected the QUANTUM ESPRESSO package out of the various packages available and herein discuss the use of the package in the study of our physical system.

CLUSTERS AND BULK MATTER

Clusters are the aggregates of atoms or molecules with a well defined number of constituents ranging from few to several thousands of atoms. They form the intermediate between atoms (or molecules) and the bulk matter and the study of clusters actually speaks of the evolution of the physical quantities from atoms towards solids. Below are some figures depicting the structure of clusters. So the study of physical and chemical properties of clusters is



presently the most active and emerging trends in physics, chemistry and material science. Clusters are therefore not just the fragments of solids rather they possess their own unique geometric and electronic structure. Their electronic, magnetic, optical and chemical properties have been found to be very

different from their bulk form. Moreover their above mentioned properties are dependent on their size, shape and composition. For example, the chemical reactivity can change drastically on going from a specific cluster size to other. Subsequently to make the potential utilization of the clusters in the technological applications we should gain a fundamental understanding of them. This includes, how the clusters are different from atoms and bulk, their evolution with size, their geometry and structure, variations in their properties related to the electronic, magnetic, optical and chemical properties with size. The above knowledge about clusters will truly help us to tailor their properties to obtain a desired property.

The existing literature and previous works shows that on comparison of the cluster and the bulk matter there are variation in their properties. While the size is the most important controlling factor for the clusters and the addition or removal of atoms from clusters can drastically vary their properties, the addition or removal of atoms from bulk matter almost have no effect on their size. Also the bulk matter and clusters have a difference when they are compared with respect to their structures. The bulk matter are crystalline and arrange themselves in a periodic form this is not the case for the clusters. They are usually non-periodic aggregates of atoms. Due to variations in the properties of clusters and bulk matter all the theories used to describe the bulk matter cannot be simply used for clusters. So the researchers face problems while investigating clusters as they cannot be categorised under atoms or bulk materials.

As many of the clusters properties cannot be just obtained from the direct experimental measurements we prefer to go for a theoretical model complemented by the computer simulations. The computer simulation we used here is the Molecular dynamics simulation. Moreover in order to handle these

clusters a theory which was developed to handle a large number of electrons called the Density functional theory has been found to be very effective. The description of both the molecular dynamics and density functional theory follows henceforth.

MOLECULAR DYNAMICS

We go for computer simulation because it is complement to the conventional experiments enabling us to learn something that cannot be found with the direct experimental methods. There are two families of computer simulation technique one Molecular dynamics and the other is Monte-Carlo simulation. Simulations act as a bridge between theory and experiment. We may test a theory by conducting a simulation using the same model. We here concentrate on the technique of molecular dynamics. Molecular dynamics is the study of interaction of atoms where we allow the atoms to be added one by one and study its dynamics using computer simulation in which atoms are allowed to interact with each other for a certain period of time. Molecular dynamics makes the study of complex systems easier because it handles with numerical methods rather the usual analytical way. But long MD simulations end up with error which can be corrected by the proper selection of algorithms and parameters. So why do we need to study MD simulation here? The reason being molecular dynamics simulations illuminates how the properties of a system evolve as the size increases. The basic ingredient of molecular dynamics are the calculation of forces on each atom, and from that information, the position of each atom.

Density functional Theory

In 1964 Hohenberg and Kohn published a paper where they stated the fundamental theorem which gave birth to modern DFT an alternative approach to deal with the many body problem in electronic structure theory. Density functional theory is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many body systems, in particular atoms, molecules and the condensed phases. With the help of this theory the properties of a many electron systems can be determined by using functionals (Function of another functions), in this case the properties are determined as spatially dependent electron density and hence the name “density functional theory”. DFT is most popular and versatile methods available in condensed matter physics and computational physics for determination of electronic and other ground state properties of matter. The conceptual roots for dft was laid by Thomas-Fermi model but was put on firm footing by Hohenberg-Kohn theorems. The original H-K theorems held only for non-degenerate ground states in absence of magnetic field, although they have since been generalized to encompass them. The first H-K theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial co-ordinates which reduces our problem to 3 spatial co-ordinates from $3N$ spatial co-ordinates for N body problem because of the use of density functionals. This theorem can be extended to the time dependent domain for the development of time dependent density functional theory. At first sight it would seem that many ground state wave functions could yield the same density and therefore this statement seem s unrealistic. But it can be shown that for a given ground state density ρ , there

is a unique one to one correspondence between the potential V_{ext} , the many body ground state $\Psi(r_1, r_2, \dots, r_N)$ and the ground state charge density ρ . The second H-K theorem defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional.

Density functional theory has become the workhorse in electronic structure calculations. Its success derives from the ability to produce accurate results with reasonable computational effort. The drawback of dft is that it is bound to the ground state properties. However the time dependent density functional theory extends its applicability to the excited states. DFT can be better understood with reference to the Kohn-Sham equations.

Important insight in the properties of many particle systems can be obtained from the study of effective non-interacting particle models. With the Kohn-Sham approach to DFT the interacting system of particles in a static potential is replaced by a non-interacting system of particles in an effective potential.

For a non-interacting particle system with Hamiltonian \hat{H} , ground state density ρ , external potential V_{ext} the Schrodinger equation can be written as

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(r)\right]\psi(r) = \epsilon\psi(r)$$

with $\int |\psi|^2 = \rho(r)$ If we apply the Hohenberg-Kohn theorem to this non-interacting system we find that there is at most one external potential V_{ext} to within a constant which generates ρ . Therefore for a given ground state density ρ , all the properties of the system are determined. Thus one can write the total energy as a functional of charge density.

$$E[\rho] = T[\rho] + \int V_{ext}(r)\rho(r)dr + V_H[\rho] + E_{xc}[\rho]$$

where, $T[\rho]$ =kinetic energy

$E_{xc}[\rho]$ = exchange-correlation function

V_{ext} =potential on electron due to the nuclei.

It is this Kohn-Sham equation which is solved using the QUANTUM ESPRESSO package in order to determine the properties of our system. Next we should understand the package used for the above calculation.

QUANTUM ESPRESSO

We use the QUANTUM ESPRESSO which a computer package to study the electronic structure and optimization using the molecular dynamics simulation. This package contains two codes in addition with some auxiliary codes for the study of calculation of electronic structure properties within density functional theory, using the plane wave basis set and pseudopotentials. The two codes are

- PWscf(plane wave self-consistent field)
- CP(Car-Parinello)

and the auxiliary codes are

- PWgui (graphical user interface for PWscf): a graphical interface for producing input data files for PWscf.
- atomic : a program for atomic calculations and generation of pseudopotentials.
- iotk : an input-output toolkit

The codes used in the package are capable of performing different kinds of calculations. The PWscf code can currently perform the following kinds of calculations :

- ground state energy and one electron (Kohn Sham) orbitals.

- atomic forces, stresses and structural optimization.
- molecular dynamics on the ground state Born-Oppenheimer surface also with variable cell.
- Nudged elastic band (NEB) and Fourier string method dynamics (SMD) for energy barriers and reaction paths.
- phonon frequencies and eigenvectors at a generic wavevector, using DF perturbation theory.
- effective charges and dielectric tensors.
- electron-phonon interaction coefficients for metals.
- interatomic force constants in real space.
- third order anharmonic phonon lifetime.
- IR and Raman (non-resonant) cross-section.
- macroscopic polarization via Berry phase.

The above calculations can be performed for both the insulators and metals, in any crystal structure for many exchange-correlation functionals.

CP can currently perform the following kinds of calculations :

- CP molecular dynamics simulation.
- geometry optimization by damped dynamics.

- constant temperature simulation.
- variable cell (Parinello-Rahman) dynamics.
- NEB for energy barriers and reaction paths.
- String method dynamics (in real space).
- dynamics with Wannier functions and under finite electric fields.
- Spin polarized calculations.

CP works with both norm-conserving and ultrasoft pseudopotentials.

PWscf

The input data for the various calculations listed above are organized as several namelists followed by the other fields introduced by keywords. The various namelists are:

- `&control` : the general variables controlling the run are specified here
- `&system` : structural information on the system under investigation is being specified in this namelist
- `&electrons` : electronic variable self-consistency, smearing.
- `&ions (optional)` : ionic variables, relaxation, dynamics
- `&phonon(optional)` : information required to produce data for phonon calculations.
- `&cell(optional)` : variable cell dynamics.

Optional namelists can be omitted if the calculations to be performed does not require them. Those depends on the value of variable "calculation" in namelist &control. Most variables in the namelists have default values. Only the following variables in &system must be always be specified.

ibrav : takes an integer value, it is the Bravais lattice index or the structure index.

celldm : it represents the crystallographic constants.

nat(integer) : indicates the number of atoms in the unit cell.

ntyp(integer) : number of types of atoms in the unit cell.

ecutwfc : kinetic energy cutoff(Ry) for wavefunctions.

RESULTS AND DISCUSSIONS

Application of PWscf code to the Silicon system

We applied the PWscf code to silicon solid to study the charge density and its energy band gap whose plot are shown below.

The charge density plot shows the distribution of fractional charges from

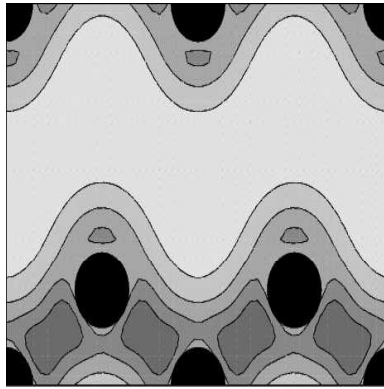


Figure 1: Charge density plot of silicon

which the information about the strength of bonding can be known.

The plot representing the Energy versus the k-points

We find the energy eigen values by solving the Kohn-Sham equations and plot it against various k-points and interpret the plot to predict the energy gap. From the above plot we find the band gap of silicon which is represented by the difference between the maximum of the valence band and the minimum of the conduction band. The value of band gap is about 1eV which is nearly same as the experimental results. This also confirms that silicon has a indirect band gap.

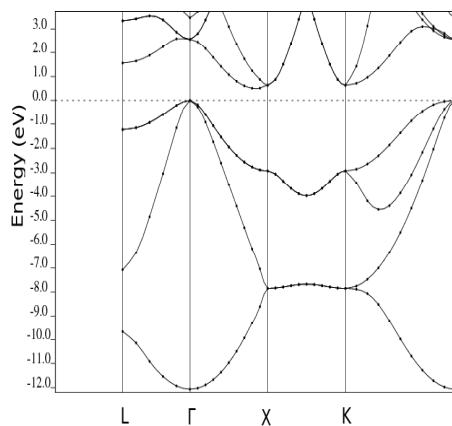


Figure 2: Energy vs k-points

CAR-PARINELLO

In this section we discuss how to perform the basic Car-Parinello (CP) simulations using the CP codes as given in the Quantum Espresso package. The CP simulation is a sequence of different runs, some of them used to prepare the system and other performed to collect the statistics, or to modify the state of the system itself: i.e. modify the temperature or the pressure. The CP simulation can be used to study the geometry optimization of the molecule under consideration. We should know what geometry optimization and why it is so essential while running the computer simulations.

Geometry Optimization

The geometry of the molecule determines many of its physical and chemical properties. This is why it becomes extremely essential that we understand the geometry of molecule while running the computations. The geometry of a molecule is determined by the repulsion forces of its valence pairs. The repulsion forces of the pairs effect the size of the bond angle. The lone pair electrons bring a twist to the idea of molecular geometry. Molecular geome-

try is the molecules arrangement inspace.it doesnot describe the placement of the electrons around each atom.Determination of molecular geometry is fairly simple : identify the valence electron pairs and determine the geometry using VSPER theory but actually this doesnot provide the detail needed for the computational methods.For computational methods we need more precise information like the atomic positions(cartesian co-ordinates),bond lengths and bond angles to find the optimal molecular geometry.The arrangement of atoms in the molecules and more specifically the electrons around the atom determine the energy level of that molecule.Infact the energy of a molecular system varies even with the small changes in its structure.This is why geometry is so important when performing calculations.The objective of geometry optimization is to find the poit at which the energy is at a minimum because this is where the molecule is most stable and is most likely to be found in nature.Hence the geometry optimization is also referred to as the 'energy minimization'.It is therefore the purpose of geometry optimizations to locate the minima based on some geometry for the molecule.Programs generally works to find a stationary point, a point on the potential energy surface where the forces are zero.they do this by calculating the first derivative of energy (also known as the gradient).At the minima of the gradient the derivative of the energy with respect its co-ordinates is zero and we can say that the system has thus reached a stationary point.algorithms are also available that can vary the bond angles,bond lengths in a molecule,calculating the energy and continuing until confirmation that corresponds to an energy minimum is found.

Use of CP code for the geometry optimization

- **Geometry optimization of SiO_2 system**

We have applied the CP simulation code to the SiO_2 system by

1. Here we have considered the cluster of six SiO_2 molecules and the input in the input file is accordingly specified. The atomic positions of each atomic species are supplied and the electronic minimization is carried out.

Initial Atomic Positions

| type of atom | x-position | y-position | z-position |
|--------------|------------|------------|------------|
| O | 3.0 | 14.8 | 1.2 |
| O | 7.2 | 6.8 | 1.0 |
| O | 2.0 | 6.0 | 4.7 |
| O | 6.5 | 14.0 | 4.8 |
| O | 4.0 | 11.2 | 7.9 |
| O | 9.0 | 3.2 | 8.0 |
| O | 3.9 | 4.8 | 9.1 |
| O | 8.6 | 12.8 | 9.1 |
| O | 3.2 | 1.2 | 5.5 |
| O | 7.8 | 9.3 | 5.5 |
| O | 2.0 | 10.0 | 2.0 |
| O | 6.5 | 2.0 | 2.0 |
| Si | 0.3 | 8.0 | 3.4 |
| Si | 5.0 | 0.0 | 3.4 |
| Si | 2.1 | 12.2 | -0.0 |
| Si | 6.7 | 4.2 | -0.0 |
| Si | 2.2 | 3.8 | 6.8 |
| Si | 7.0 | 11.8 | 6.8 |

As the time step specified is 20 after 20 steps we land up at the following atomic positions and velocities.

Atomic Positions after 20 steps

| type of atom | x-position | y-position | z-position |
|--------------|--------------|--------------|---------------|
| O | 0.318829E+01 | 0.148324E+02 | 0.122883E+01 |
| O | 0.783231E+01 | 0.678704E+01 | 0.122883E+01 |
| O | 0.207443E+01 | 0.599538E+01 | 0.473758E+01 |
| O | 0.672031E+01 | 0.140423E+02 | 0.473758E+01 |
| O | 0.396307E+01 | 0.112699E+02 | 0.787861E+01 |
| O | 0.860802E+01 | 0.322296E+01 | 0.787861E+01 |
| O | 0.396307E+01 | 0.481915E+01 | 0.914625E+01 |
| O | 0.860802E+01 | 0.128645E+02 | 0.914625E+01 |
| O | 0.318736E+01 | 0.125668E+01 | 0.558030E+01 |
| O | 0.783324E+01 | 0.930201E+01 | 0.558030E+01 |
| O | 0.207536E+01 | 0.100921E+02 | 0.207359E+01 |
| O | 0.671938E+01 | 0.204673E+01 | 0.207359E+01 |
| Si | 0.288916E+00 | 0.804533E+01 | 0.340456E+01 |
| Si | 0.493387E+01 | 0.000000E+00 | 0.340456E+01 |
| Si | 0.213389E+01 | 0.122772E+02 | -0.418803E-01 |
| Si | 0.677884E+01 | 0.423184E+01 | -0.418803E-01 |
| Si | 0.213389E+01 | 0.381349E+01 | 0.685203E+01 |
| Si | 0.677884E+01 | 0.118588E+02 | 0.685203E+01 |

Atomic Velocities after 20 steps

| type of atom | x- | y- | z- |
|--------------|--------------|--------------|--------------|
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |

This just tells us that the ions are fixed while the electronic configuration is being brought to the ground state.

2. Sometimes it may so happen that the electronic configuration is not being brought to the ground state by just one run. In that case we have to rerun the program.

3. Once the ground state of electronic configuration is reached we move on to minimize the ionic positions. For this we need to specify the ion dynamics. Using this we arrive at the following positions and velocities after 20 steps.

Atomic positions after 20 steps

| type of atom | x-position | y-position | z-position |
|--------------|--------------|---------------|---------------|
| O | 0.318643E+01 | 0.148399E+02 | 0.121331E+01 |
| O | 0.783638E+01 | 0.679773E+01 | 0.121869E+01 |
| O | 0.208727E+01 | 0.599663E+01 | 0.471585E+01 |
| O | 0.674031E+01 | 0.140461E+02 | 0.471678E+01 |
| O | 0.395966E+01 | 0.112480E+02 | 0.783277E+01 |
| O | 0.861023E+01 | 0.320846E+01 | 0.784150E+01 |
| O | 0.395529E+01 | 0.483368E+01 | 0.912939E+01 |
| O | 0.860607E+01 | 0.128743E+02 | 0.913167E+01 |
| O | 0.318801E+01 | 0.124313E+01 | 0.557079E+01 |
| O | 0.783747E+01 | 0.928612E+01 | 0.556785E+01 |
| O | 0.209544E+01 | 0.100868E+02 | 0.207251E+01 |
| O | 0.674311E+01 | 0.203900E+01 | 0.207471E+01 |
| Si | 0.288142E+00 | 0.804160E+01 | 0.339162E+01 |
| Si | 0.493608E+01 | -0.101833E-02 | 0.339404E+01 |
| Si | 0.213567E+01 | 0.122748E+02 | -0.431943E-01 |
| Si | 0.678457E+01 | 0.423078E+01 | -0.419012E-01 |
| Si | 0.213636E+01 | 0.381171E+01 | 0.682936E+01 |
| Si | 0.678608E+01 | 0.118557E+02 | 0.682876E+01 |

Atomic velocities after 20 steps

| type of atom | x- | y- | z- |
|--------------|---------------|---------------|---------------|
| O | -0.815350E-05 | 0.547370E-04 | -0.113948E-04 |
| O | -0.179083E-04 | 0.404174E-04 | -0.235676E-04 |
| O | 0.419929E-04 | 0.150723E-04 | -0.199907E-04 |
| O | 0.422602E-04 | 0.113748E-04 | -0.152130E-04 |
| O | -0.219101E-04 | -0.576041E-04 | -0.538556E-04 |
| O | -0.160356E-04 | -0.618509E-04 | -0.616328E-04 |
| O | -0.408225E-05 | 0.613513E-04 | 0.710963E-04 |
| O | -0.127947E-04 | 0.606509E-04 | 0.649406E-04 |
| O | -0.153791E-04 | -0.417056E-04 | 0.216495E-04 |
| O | -0.140632E-04 | -0.406276E-04 | 0.214824E-04 |
| O | 0.375518E-04 | -0.168902E-04 | 0.149520E-04 |
| O | 0.431374E-04 | -0.894594E-06 | 0.407441E-05 |
| Si | -0.737197E-06 | 0.529625E-05 | 0.240347E-05 |
| Si | -0.598602E-05 | -0.415104E-05 | -0.683880E-06 |
| Si | -0.414508E-05 | -0.852147E-05 | -0.791960E-06 |
| Si | -0.763526E-05 | -0.446646E-05 | 0.688794E-05 |
| Si | -0.759440E-05 | -0.122235E-05 | -0.644139E-05 |
| Si | -0.511095E-05 | -0.666704E-06 | -0.854030E-05 |

This time the ionic velocities unlike previous cases is not zero as the ions are under some dynamics to come to the ground state. This is the ionic minimization step which is then followed by the ionic randomization.

4. The ionic minimization is followed by the ionic randomization because if the ions are in their equilibrium positions they won't move in the

dynamics simulation. After the run we achieve both the old and new positions of both atomic species 1 and 2.

Atomic positions of species 1 before randomization

| type of atom | x-position | y-position | z-position |
|--------------|--------------|--------------|--------------|
| O | 0.318643E+01 | 0.148399E+02 | 0.121331E+01 |
| O | 0.783638E+01 | 0.679773E+01 | 0.121869E+01 |
| O | 0.208727E+01 | 0.599663E+01 | 0.471585E+01 |
| O | 0.674031E+01 | 0.140461E+02 | 0.471678E+01 |
| O | 0.395966E+01 | 0.112480E+02 | 0.783277E+01 |
| O | 0.861023E+01 | 0.320846E+01 | 0.784150E+01 |
| O | 0.395529E+01 | 0.483368E+01 | 0.912939E+01 |
| O | 0.860607E+01 | 0.128743E+02 | 0.913167E+01 |
| O | 0.318801E+01 | 0.124313E+01 | 0.557079E+01 |
| O | 0.783747E+01 | 0.928612E+01 | 0.556785E+01 |
| O | 0.209544E+01 | 0.100868E+02 | 0.207251E+01 |
| O | 0.674311E+01 | 0.203900E+01 | 0.207471E+01 |

Atomic positions of species 1 after randomization

| type of atom | x-position | y-position | z-position |
|--------------|------------|------------|------------|
| O | 0.343736 | 0.921841 | 0.120756 |
| O | 0.843367 | 0.421717 | 0.120281 |
| O | 0.222841 | 0.372292 | 0.463650 |
| O | 0.723230 | 0.872524 | 0.463441 |
| O | 0.427031 | 0.700329 | 0.771247 |
| O | 0.926774 | 0.199999 | 0.771448 |
| O | 0.426758 | 0.299390 | 0.895748 |
| O | 0.926494 | 0.799318 | 0.895859 |
| O | 0.343206 | 0.078207 | 0.546258 |
| O | 0.843017 | 0.577851 | 0.546550 |
| O | 0.223514 | 0.627336 | 0.203389 |
| O | 0.723470 | 0.126983 | 0.203110 |

The atomic positions of the species 2 and its velocities both before and after randomizations.

Atomic positions of species 2 before randomization

| type of atom | x-position | y-position | z-position |
|--------------|--------------|---------------|---------------|
| Si | 0.288142E+00 | 0.804160E+01 | 0.339162E+01 |
| Si | 0.493608E+01 | -0.101833E-02 | 0.339404E+01 |
| Si | 0.213567E+01 | 0.122748E+02 | -0.431943E-01 |
| Si | 0.678457E+01 | 0.423078E+01 | -0.419012E-01 |
| Si | 0.213636E+01 | 0.381171E+01 | 0.682936E+01 |
| Si | 0.678608E+01 | 0.118557E+02 | 0.682876E+01 |

Atomic positions of species 2 after randomization

| type of atom | x-position | y-position | z-position |
|--------------|------------|------------|------------|
| Si | 0.031615 | 0.500310 | 0.333062 |
| Si | 0.531155 | 0.000099 | 0.333353 |
| Si | 0.230214 | 0.763250 | -0.003945 |
| Si | 0.729946 | 0.262939 | -0.003680 |
| Si | 0.229321 | 0.237108 | 0.671064 |
| Si | 0.729527 | 0.736761 | 0.670912 |

This shows that the ionic randomization is successful and the ions are displaced from their equilibrium positions. Now that we have achieved the electronic minimization and ionic randomization we start the CP dynamics. The atomic velocities are now

Atomic velocities after randomization

| type of atom | x- | y- | z- |
|--------------|--------------|--------------|--------------|
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| O | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |
| Si | 0.000000E+00 | 0.000000E+00 | 0.000000E+00 |

The velocities are zero because we have specified the ion dynamics as none.

5. To begin the first CP simulations after minimizations we change both the electron and ion dynamics and the both the electron and ion velocities as 'zero'. After CP simulations we have the following atomic positions and velocities.

Atomic positions after first CP run

| type of atom | x-position | y-position | z-position |
|--------------|--------------|---------------|---------------|
| O | 0.318469E+01 | 0.148496E+02 | 0.121063E+01 |
| O | 0.783399E+01 | 0.680838E+01 | 0.120963E+01 |
| O | 0.209279E+01 | 0.599284E+01 | 0.470691E+01 |
| O | 0.675135E+01 | 0.140436E+02 | 0.470745E+01 |
| O | 0.395657E+01 | 0.112360E+02 | 0.782488E+01 |
| O | 0.860921E+01 | 0.319365E+01 | 0.783218E+01 |
| O | 0.394659E+01 | 0.484612E+01 | 0.914169E+01 |
| O | 0.859619E+01 | 0.128776E+02 | 0.915349E+01 |
| O | 0.318503E+01 | 0.123475E+01 | 0.557300E+01 |
| O | 0.783157E+01 | 0.927496E+01 | 0.557539E+01 |
| O | 0.210502E+01 | 0.100888E+02 | 0.207955E+01 |
| O | 0.676240E+01 | 0.203105E+01 | 0.207938E+01 |
| Si | 0.287360E+00 | 0.804058E+01 | 0.339018E+01 |
| Si | 0.493337E+01 | -0.297518E-02 | 0.339513E+01 |
| Si | 0.213563E+01 | 0.122743E+02 | -0.410871E-01 |
| Si | 0.678171E+01 | 0.422888E+01 | -0.390885E-01 |
| Si | 0.213749E+01 | 0.381082E+01 | 0.682742E+01 |
| Si | 0.678718E+01 | 0.118581E+02 | 0.682798E+01 |

Atomic velocities after first CP run

| type of atom | x- | y- | z- |
|--------------|---------------|---------------|---------------|
| O | -0.155156E-04 | 0.611578E-04 | -0.199210E-04 |
| O | -0.302284E-04 | 0.368654E-04 | -0.369685E-04 |
| O | 0.527848E-04 | 0.109873E-04 | -0.172918E-04 |
| O | 0.479264E-04 | 0.110626E-04 | -0.954606E-05 |
| O | -0.340035E-04 | -0.595444E-04 | -0.560207E-04 |
| O | -0.378366E-04 | -0.663575E-04 | -0.561125E-04 |
| O | 0.581899E-06 | 0.694576E-04 | 0.798805E-04 |
| O | -0.230163E-04 | 0.709698E-04 | 0.605798E-04 |
| O | -0.234218E-04 | -0.419045E-04 | 0.363919E-04 |
| O | -0.909712E-05 | -0.519401E-04 | 0.186856E-04 |
| O | 0.373082E-04 | -0.318370E-04 | 0.246452E-04 |
| O | 0.451629E-04 | 0.145786E-04 | -0.868336E-05 |
| Si | 0.302586E-05 | 0.220046E-04 | 0.904551E-05 |
| Si | 0.628317E-05 | -0.564081E-05 | -0.547645E-05 |
| Si | 0.236351E-06 | -0.109277E-04 | -0.372922E-05 |
| Si | 0.849588E-06 | -0.124336E-04 | 0.939898E-05 |
| Si | -0.113911E-04 | -0.114315E-05 | -0.110027E-04 |
| Si | -0.508662E-05 | -0.528530E-05 | -0.717274E-05 |

These are the final positions and velocities which we obtain from the CP simulations. These are, as we infer the most preferred positions for the atomic species which is obtained after the run and hence we can say that the system is now geometrically optimized. The atoms have velocities implying that they are undergoing continuous vibrations about their mean positions.

CONCLUSIONS

The comparative study of clusters and bulk matter from the literature survey shows wide variations in their properties. The size of the clusters is a controlling factor of their properties and it becomes extremely essential to study the size and structure of clusters to determine its properties. We find the Car-Parinello method as a powerful method to study the geometric optimization of clusters and that it can very accurately find the optimum structure of the clusters.

FUTURE WORKS

The study in the field of clusters has enormous potential, one can try out the other calculations possible by the two codes along with the plotting of the final geometrically optimized structures obtained from the CP simulation. One can also study the electrical, magnetic, optical and chemical properties of the clusters. Also the variations of these properties with the size of clusters is a good piece of work one can get interested to do.

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