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An Implementation of the SIESTA code for Electronic Simulations and Its Application in Ordinary Hexagonal Ices

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We consider descriptions of a Density Functional Theory (DFT), a flexible LCAO method, and an implementation of the SIESTA code for electronic simulations in crystalline solids. We have defined equilibrium lattice parameters and relaxed atomic positions of ordinary hexagonal ices(disordered and ordered) with 16 water molecules by an *Ab Initio* total energy calculation using the SIESTA code. These results will be compared with the results of a plane wave (PW) ultrasoft-pseudopotential method by the CASTEP code.

I. INTRODUCTION

One of studies in the condensed matter physics is a study of structures of hydrogen bonded molecular solids. Such solids include various phases of ice and crystalline organic acids, which have been interesting biological applications.

Theoretical and computational parts of these studies have been developing by first - principles methods (*Ab Initio* methods), which are based on a DFT [1–4] with norm - conserving pseudopotentials [5]. These methods consist of the *Ab Initio* Total Energy Calculations [6, 7] and the Car - Parrinello Molecular Dynamics (MD) [8]. In this area, there are different methodologies as embodied in the CAmbridge Serial Total Energy Package (CASTEP) [6] and Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) [7] codes. The CASTEP code is very accurately, and PW basis sets with a ultrasoft-pseudopotential method are used to solve a self - consistent Kohn - Sham (KS)equation of the DFT. In the SIESTA code, the self - consistent KS equation will be also solved by using a flexible LCAO method in a Tight Binding Approximation (TBA).

The TBA is a widely used to electronic structure studies, and has proven its usefulness for a wide range of systems ranging from transition metals to covalent materials. The main advantage of the TBA is that it is significantly faster than the ***Ab Initio*** Plane Wave Total Energy Calculation [6] and Car - Parrinello MD simulations [8] but still gives accurate enough results in many cases. The TBA is not highly accurate. Therefore it is not necessary to calculate quantities with very high precision in the SIESTA code.

In this overview, we will first introduce to the DFT and an implementation of the SIESTA code. In the SIESTA code, the Numerical Atomic Orbital (NAO) basis sets [9?] are used to calculate a ground state total energy. In second section, we consider the brief description of the DFT: the self - consistent KS equation and a total energy functional. The implementation of the SIESTA code on the flexible LCAO method is described in the third section. The fourth section, we will have presented results of total energy calculation, to define equilibrium lattice parameters and relaxed atomic positions of ordinary hexagonal ices (disordered and ordered) with 16 water molecules by using the SIESTA and CASTEP codes.

II. THE DENSITY FUNCTIONAL THEORY (DFT)

In 1964, P. Hohenberg and W. Kohn derived a method to solve many electronic systems, as introduced a concept of an electronic density by basic variables within the framework of DFT [10]. The DFT will be based on the below two theorems: ***i.)*** ***The density as basic variables.*** The ground state energy of the system is a "unique functional "of the electronic density. *ii.)* ***The variational principle.*** The total energy functional attains its minimum value with respect to variation of the electronic density subject to the normalization condition when the density has its correct values. These theorems are the formal justification for working with electronic densities instead of wave functions.

In 1965, a practical scheme for DFT calculations became possible by a work of W. Kohn and L. J. Sham [11]. They chose the electronic density, which is expressed as:

$$\rho(\vec{r}) = \sum_{j=1}^{occ} |\psi_j(\vec{r})|^2, \qquad (1)$$

and one obtains $n(\vec{r})$, which satisfies the below equation:

$$[-\frac{\hbar^2}{2m_e}\Delta + V_{eff}^{KS}(\vec{r})]\psi_j(\vec{r}) = \epsilon_j \psi_j(\vec{r}), \qquad (2)$$

$$V_{eff}^{KS}(\vec{r}) = V_{ext}(\vec{r}) + e^2 \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}(\vec{r}) \quad (3)$$

where the first term is an external potential, the second term is an electrostatic potential, which is classical and is included by the Hartree-Fock approximation(HFA), the last term is an exchange-correlation potential, which is defined as:

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}. \quad (4)$$

Here ϵ_j is eigenvalues of an j^{th} ground state with the eigenfunction $\psi_j(\vec{r})$ at the given $V_{xc}(\vec{r})$. $E_{xc}[\rho(\vec{r})]$ is an exchange correlation functional of the system. This equation must be solved self-consistently, and is called the self-consistent Kohn - Sham (KS) equation [11].

In practice, the convergence of solutions for the self-consistent KS equation with the given $V_{xc}(\vec{r})$ is given as a tolerance of a self-consistent charge density, which is usually chosen to be $10^{-4} - 10^{-7}$. The exchange-correlation effect is the quantum effect of the system with many electrons. In the DFT, the exchange - correlation potential not only includes exchange effects, but also correlation effects due to the Coulomb repulsion between the electrons (Dynamical Correlation Effects). In the HFA the exchange interaction is treated exactly, but we do not know the exact form of the exchange - correlation potential: both exchange and dynamical correlation effects are practically treated approximately. We therefore use a Local Spin Density Approximation (LSDA) [12], and a Generalized Gradient Approximation (GGA) [13] in the exchange - correlation functional.

Thus the total energy of the system can be written as a functional depending on orbitals $\psi_j(\vec{r}, \vec{R})$ and of the nuclear co - ordinates, collected together in the variables $\vec{R}$. We minimize total energy with respect to the above orbitals, according to the variational principle. Usually, a finite basis sets $\zeta_\mu(\vec{r} - \vec{R})$ are used, in the terms of which the orbitals are given as:

$$\psi_j(\vec{r}, \vec{R}) = \sum_\mu C_{j\mu}\zeta_\mu(\vec{r} - \vec{R}). \quad (5)$$

Only the minimum value of KS functional has physical meaning. At the minimum, the KS energy functional is equal to the ground state total energy of the system of electrons with the ions at the positions $\vec{R}$, and we can write by the below form [14]:

$$E_{GS}^{KS}(\vec{R}) = \min_{C_{j\mu} \rightarrow n(\vec{r})} E_{tot}^{KS}(C_{j\mu}, \vec{R}). \quad (6)$$

III. THE SIESTA CODE FOR ELECTRONIC SIMULATIONS

A. *The Tight Binding Approximation (TBA)*

To solve equations for electronic states in a crystal, there exist many methods for band structure calculations: *i.*) Augmented plane wave method (APW), *ii.*) Orthogonalized plane wave method (OPW), *iii.*) Green's function method of Korringa, Kohn and Rostoker (KKP), *iv.*) ($\vec{k}\vec{p}$) method, *v.*) Empirical pseudopotential method, *vi.*) Self - Consistent Field (SCF) Iteration method or *Ab Initio* pseudopotential method and etc. From these methods, in the limiting cases, there are below two methods: *i.*) The nearly free electron approximation, in which the potential is considered to be weak everywhere *ii.*) The TBA is important in calculations of states, which are tightly bound to the nuclei. The TBA deals with the case in which the overlap of atomic wavefunctions is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description completely irrelevant. This method is particularly useful for "insulators" and the "d - levels of transition metals", consists essentially of a flexible LCAO type of approach, in which the atomic states are used as basis orbitals.

In crystals, due to the translation symmetry, the crystalline KS orbitals are included as the Bloch theorem. The crystalline KS eigenstates are characterized by a reciprocal vector $\vec{k}$, and can be expanded in sets of Bloch functions $\zeta_\mu^{\vec{k}}(\vec{r})$, in which we expand as LCAO:

$$\psi_j^{\vec{k}}(\vec{r}) = \sum_\mu C_{j\mu}(\vec{k})\zeta_\mu^{\vec{k}}(\vec{r})$$

$$= \sum_\mu \sum_{n=-\infty}^{+\infty} C_{j\mu}(\vec{k})e^{i\vec{k}\vec{R}_n}\phi_\mu(\vec{r} - \vec{R}_n) \quad (7)$$

where $\vec{R}_n$ are direct lattice vectors, which are defined as $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ with basis vectors $\vec{a}_1, \vec{a}_2$ and $\vec{a}_3$ of the direct lattice, and $\phi_\mu(\vec{r} - \vec{R}_n)$ are NAO basis sets. By using a diagonalization method [15], the coefficients $C_{j\mu}(\vec{k})$ can be determined self-consistently by solving coupled matrix equations for chosen sets of $\vec{k}$-points within the reference unit cell:

$$\sum_\mu [H_{\eta\mu}^{KS}(\vec{k}) - \epsilon_j(\vec{k})S_{\eta\mu}^{\vec{k}}]C_{\mu j}(\vec{k}) = 0 \quad (8)$$

with

$$H_{\eta\mu}^{KS}(\vec{k}) = \sum_{n=-\infty}^{+\infty} e^{i\vec{k}\vec{R}_n}\langle\phi_\eta(\vec{r})|\hat{H}^{KS}|\phi_\mu(\vec{r} - \vec{R}_n)\rangle, \quad (9)$$

$$S^{\vec{k}}_{\eta\mu} = \sum_{n=-\infty}^{+\infty} e^{i\vec{k}\vec{R}_n} \langle \phi_\eta(\vec{r}) | \phi_\mu(\vec{r} - \vec{R}_n) \rangle. \qquad (10)$$

In practice, the sum over n restricts as the first few shells of neighbouring atoms or only nearest neighbours, and the electronic density in solids becomes:

$$\rho(\vec{r}) = \sum_j \int_{BZ} n_j(\vec{k}) |\psi_j^{\vec{k}}(\vec{r})|^2 d\vec{k} = \sum_{\eta\mu} \rho_{\eta\mu} \phi^*_\eta(\vec{r}) \phi_\mu(\vec{r}) \qquad (11)$$

where $\rho_{\eta\mu}$ is a density matrix of electrons, which is obtained as an integral over the volume of the BZ:

$$\rho_{\eta\mu} = \frac{V}{(2\pi)^3} \sum_j \int_{BZ} n_j(\vec{k}) C^*_{\eta j}(\vec{k}) C_{j\mu}(\vec{k}) e^{i\vec{k}(\vec{R}_\mu - \vec{R}_\eta)} d\vec{k} \qquad (12)$$

where V is a volume of the primitive cell in real space, $n_j(\vec{k})$ is an occupation of electrons in the j^{th} state. This integral is performed in a finite uniform grid of the BZ [16].

B. *The Numerical Atomic Orbital (NAO) basis sets*

In the flexible LCAO method, the basis sets can be classified into two groups: *i.)* Slater-type and Gaussian-type Orbitals (STO and GTO), *ii.)* Pseudo Atomic Orbitals (PAO) [9], which are provided as the numerical solution of atomic problem (with the same atomic pseudopotential as used in the PW calculation).

Within the cut-off radius, the atomic basis orbitals are written as products of a numerical radial function and spherical harmonics. For atom I, located at $\vec{R}_I$, the wave function is written as:

$$\psi_{Inlm}(\vec{r}) = R_{Inl}(r_I) Y_{lm}(\hat{r}_I) \qquad (13)$$

where $\vec{r}_I = \vec{r} - \vec{R}_I$. The radial functions are defined by a cubic spline interpolation [15] from the given values on a fine radial mesh. Each radial function may have a different cut-off radius and, up to that radius, its shape is completely free and may be introduced by the user in an input file. *i.e.* These radial functions and their charge densities are derived by pseudopotential generation methods for an atom [6]. Their basis orbitals are the eigenfunctions of the pseudo-atom within a spherical box (although the radius of the box may be different for each orbital.). In other words, they are the (angular momentum dependent) numerical eigenfunctions $R_l(r)$ of the atomic pseudoptential $V_l^{PS}(r)$ for an energy $\epsilon_l + \delta\epsilon_l$ chosen so that the first node occurs at the desired cut-off radius r_l^c:

$$[-\frac{1}{2}\frac{d^2}{dr^2}r + V_l^{PS}(r) + \frac{l(l+1)}{2r^2}]R_l(r) = (\epsilon_l + \delta\epsilon_l)R_l(r) \qquad (14)$$

with $R_l(r_l^c) = 0$.. Here $\delta\epsilon_l$ is an energy shift. In order to obtain a well balanced basis orbital, in which the effect of the confinement is similar for all the orbitals, it is usually better to fix a common "energy shift" rather than a common cut-off radius r_l^c, for all the atoms and angular momentums. This means that the orbital cut-off radii depend on the atomic species and angular momentum.

To achieve good converged results, in addition to the atomic valence orbitals, it is generally necessary to also include polarization orbitals, to account for the deformation induced by bond formation. In the valence pseudo-atomic orbitals there are no valence orbital with angular momentum $l+1$. As included a small electric field in the z-direction of an atom, we can calculate the polarization orbital with angular momentum $l+1$ using the first-order perturbation theory [7].

The angular momentum may be arbitrarily large, and there will be several orbitals (labelled by index n) with the same angular dependence, but different radial dependence, which is conventionally called a "multiple -ζ" basis. The term steams from the fact that the exponent of STO basis functions is often denoted by the greek letter ζ. The most important factor is the number of functions to be used. The small number of functions possible is a minimum basis set. Only enough functions are employed to contain all the electrons of the neutral atom. For hydrogen (and helium), this means a single s- function. For the first row in the periodic table, it means two s-functions ($1s$ and $2s$) and one set of p-functions ($2p_x, 2p_y$ and $2p_z$). Lithium and beryllium formally only require two s-functions, but a set of p-functions is usually added. For the second row elements, three s-functions ($1s$, $2s$ and $3s$) and two sets of p-functions ($2p$ and $3p$) are used.

The next improvement in the basis sets is a doubling of all basis functions, producing a Double-ζ (DZ) basis. A DZ basis employs: *i.)* two s-functions for hydrogen ($1s$ and $1s'$), *ii.)* four s-functions ($1s$, $1s'$, $2s$ and $2s'$) and two p-functions ($2p$ and $2p'$) for first row elements, *iii.)* six s-functions and four p-functions for second row elements.

In most cases, higher angular momentum functions are also important and these are denoted as polarization functions. Polarization functions are added to the chosen sp-basis. Adding a single set of polarization functions (p-functions on hydrogen and d-functions on heavy atoms) to the DZ basis forms a Double-ζ plus Polarization (DZP) basis. There is a variation where polarization functions are only added to non-hydrogen atoms. This does not mean that polarization functions are not important on hydrogen. However, hydrogen atoms often have a "passive" role, sitting at the end of bond, which does not take an active part in the property of interest.

The multiple-ζ basis set may be seen that the SZ basis are comparable to PW cut-offs typically used Car-Parrinello molecular dynamics (MD) simubasis set, while DZP sets are comparable to the cut-offs used in geometry relaxations and energy comparisons. In the SIESTA code, the multiple-ζ basis sets can be used together with the LSDA and GGA in the exchange-correlation functionals. Scalar relativistic effects and the non-linear partial core corrections to treat XC in the core region are also included in the SIESTA code [17].

In our work, the basis sets are defined through the following three parameters: (i) PAO.basis size, (ii) PAO.energy shift and (iii) PAO.split norm. The first parameter defines the number of orbitals per atom in the basis set. For a water molecule, a DZP which means two shells of s-orbital, two shells of p-orbitals, a polarization shell of d-orbitals for oxygen, and two shells of s-orbital and one shell of polarization p-orbitals for hydrogen). The second parameter describes the energy shift, that determines the cut-off radius of each of the orbitals, and third parameter defines the radius of the second-ζ orbital in the split valence double-ζ basis [16].

C. *The Total Energy Calculations in the SIESTA code*

In the Non-local Pseudopotential Approximation (NPA), the standard KS one-electron Hamiltonian may be written as:

$$\hat{H}^{KS} = \hat{T} + \sum_I V_I^{local}(r) + \sum_I V_I^{KB} + V_H(\vec{r}) + V_{xc}(\vec{r}) \tag{15}$$

where $\hat{T}$ is the kinetic energy operator. $V_H(\vec{r})$ and $V_{xc}(\vec{r})$ are the operators of total Hartree and XC potentials. The construction of the Hartree potential is the equivalent with the solution of Poisson equation with periodic boundary conditions [15]. $V_I^{local}(r)$ and V_I^{KB} are the local and non-local Kleinman Byalander (KB) parts of the pseudopotential of atom I [19]. In order to eliminate long range of $V_I^{local}(r)$, we screen it with the potential V_I^{atom} as created by an atomic electron density n^{atom}. Since the atomic basis orbitals are zero beyond the cut-off radius $r_I^c = \max_l(r_{Il}^c)$, and the screened "neutral atom" (NA) potential $V_I^{NA}(r) = V_I^{local}(r) + V_I^{atom}$ is also beyond this radius [20]. Then the total Hamiltonian may be rewritten as:

$$\hat{H}^{KS} = \hat{T} + \sum_I V_I^{KB} + \sum_I V_I^{NA}(r) + \delta V_H(r) + V_{xc}(r) \tag{16}$$

where $\delta V_H(r)$ is the electrostatic potential generated by the difference between the self-consistent electron density $n(\vec{r})$ and the sum of atomic densities $n^{atom} = \sum_I n_I^{atom}$ [7?]. The matrix elements of the first two terms involve only two-centre integrals, which are calculated in reciprocal space and tabulated as a function of inter-atomic distance. The remaining terms involves potentials, which are calculated on a 3D real space grid [7, 20].

In the calculation of the SIESTA code, the KS total energy can be written as a sum of band - structure (BS) energies plus some correction terms [7]. The BS term is a sum of the energies of the occupied states $\psi_i(\vec{r})$:

$$E_{BS}^{KS} = \sum_i \int_{occ} \psi_i(\vec{r}) H^{KS} \psi_i(\vec{r}) = \sum_{\mu\nu} H_{\mu\nu}\rho_{\nu\mu} = Tr(H\rho) \tag{17}$$

The correction terms are simple functionals of the electronic density, which can be obtained from the expression of electronic density and the atomic positions. The KS total energy can be written as:

$$E_{tot}^{KS} = E_{BS}^{KS} - \frac{1}{2}\int V_H(\vec{r})\rho(\vec{r})d\vec{r} - \int [\epsilon_{xc}(\vec{r}) - V_{xc}(\vec{r})]\rho(\vec{r})d\vec{r} + \sum_{I<J}\frac{Z_I Z_J}{R_{IJ}} \tag{18}$$

where $R_{IJ} = |\vec{R}_I - \vec{R}_J|$, Z_I, Z_J are the valence ion pseudo - atom charges at the positions $\vec{R}_I$ and $\vec{R}_J$ respectively, and $\epsilon_{xc}(\vec{r})n(\vec{r})$ is the exchange-correlation energy density. In order to also avoid the long range interactions of last term, we construct a diffuse ion charge density from the local pseudopotential $V_I^{local}(r)$, which has an asymptotic behavior of $-Z_I/R$ [7].

In finally, atomic forces and stresses can be calculated efficiently and accurately. Forces on the ions are obtained by the Hellman - Feynman theorem [3, 6], and are used to relax ionic positions to the minimum energy by the conjugate gradient method [6?]. The main convergence of total energy depends on: *i.*) a mesh cut-off energy E_{cut}, which depends on elements in the system, *ii.*) a number of $\vec{k}$- points, which is used to accurately integrate over all the BZ [16]. In the calculation of geometry optimization, the speed of convergence depends on a given tolerance of atomic forces and a given displacement of atoms. In the SIESTA code, the relaxed internal co-ordinates of atoms are found as with a given tolerance of atomic forces.

IV. AN APPLICATION OF THE SIESTA CODE IN ORDINARY HEXAGONAL ICES

A. *Structures of Ordinary Hexagonal Ices*

A ordinary hexagonal ice is obtained when a liquid water freezes at atmospheric pressure. It is called as IceIh, which has a disordered arrangement of water molecules. The space group is P_6/mmc[21]. An ordered arrangement of IceIh is IceXI, which was discovered below $72K$ by calorimetric measurements on

KOH-doped iceIh in 1982 [22]. The space group of iceXI is $Cmc2_1$ [21]. In these ices, the oxygen atoms lie on a hexagonal "wurtzite" lattice, and each oxygen atom is tetrahedrally coordinated. In iceIh, to create a disordered arrangement of molecular orientations, hydrogen atoms were randomly distributed into two potential minima along each hydrogen bond in order to satisfy the Bernal and Fowler "ice rules" [23]. In iceXI, hydrogen atoms were located at one of the two minima according to Whitworth et al. In iceIh, there are four kinds of hydrogen bond, and two kinds of them are found in the iceXI as shown on the figure 1.

The ordering transformation from iceIh to iceXI cannot take place in pure ice, because there is insufficient hydrogen mobility at the transition temperature for the ordering to occur. Therefore doping with KOH introduces sufficient mobility for iceXI to be formed during suitable annealing below the transition temperature. Doping ice with the alkali hydroxides has the remarkable effect of maintaining sufficient proton mobility at low temperatures for the transition to the ordered orientation of hydrogen atoms, to occur at $72K$.

We have done total energy calculations on the above two supercells for iceXI and iceIh with 16 water molecules [21?].

B. *Computational Methods*

When relaxed structures for ordinary hexagonal ices find, a structural geometry optimisation will be done by the conjugate gradient minimization method [6?] of the energy functional in the framework of the Self-Consistent Iteration (SCI) method in the DFT. We have done the structural geometry optimisation by both the SIESTA and CASTEP codes. The DFT can not describe Van Der Waals interaction. We will use pseudoptential methods, to describe the hydrogen and covalent bonds in ice. A Local Density Approximation (LDA) can not be used for a description of the properties of hydrogen bonded complexes. But gradient corrected functionals should be used to the exchange-correlation functional. Therefore the GGA is needed to use in hydrogen bonded systems [24]. The state of valence electrons is expressed as the KS equations of the DFT with an exchange correlation functional of GGA by PBE [25]. In all the calculations of a diagonalization method, we used the $8K$ points as to be $2x2x3$ by a scheme of Monkhorst and Pack [26]. We have got the values of measurement of ratio c/a for iceIh and iceXI as 1.6280 at $253K$, and 1.6277 at $10K$ respectively (where a and c are cell parameters of unit cells), and the experimental values are: $a = 4.519Ang$, $c = 7.357Ang$ for iceIh, and $a = 4.4934(1)Ang$, $c = 7.3139(1)Ang$ for iceXI [? ?]. Using a LAPACK math library, we will use a serial version for the SIESTA 1.3 code on the SUNFIRE V880 cluster node with 8 processors and $16G$ of memory.

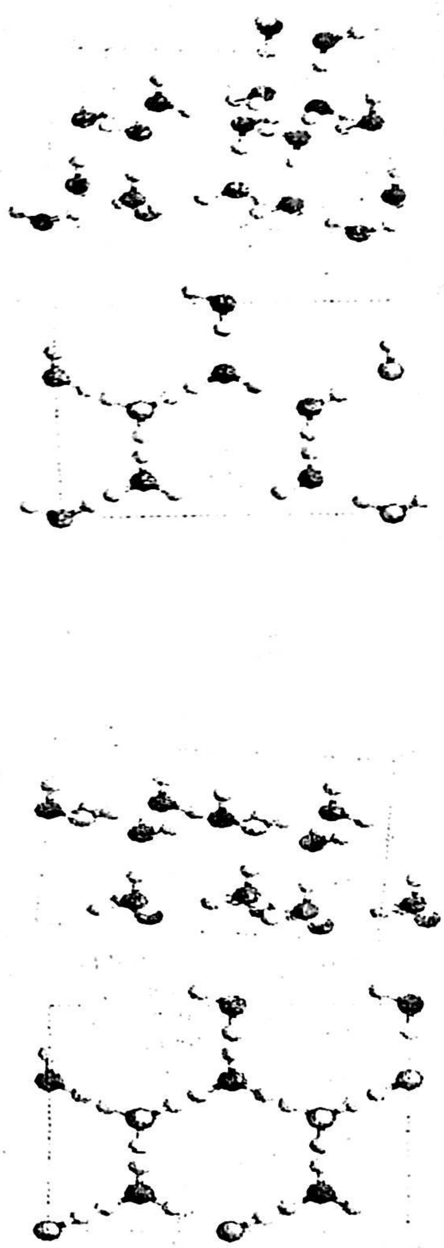

FIG. 1: The structures and projections of supercell for IceIh and IceXI with 16 water molecules respectively

In the calculation of the CASTEP code we have got SCF convergence criterion per atom as $10^{-7}eV$, and the tolerance for total energy per atom as $0.2\cdot 10^{-4}eV$. The interactions will be expressed as an ultrasoft - pseudopotential. The maximum force tolerance and the atomic maximum displacement were

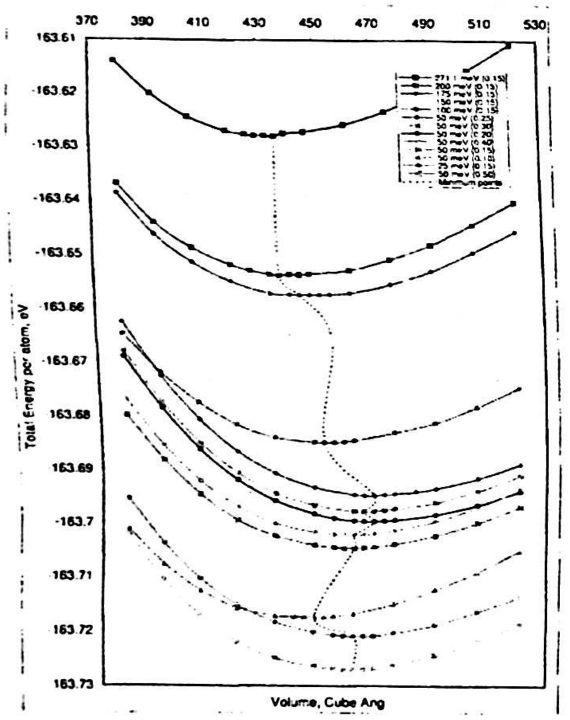

FIG. 2: The calculations of total energy curves for iceIh by the SIESTA code

chosen as $0.001 eV/Ang$ and $0.005 Ang$ respectively. The cut-off energy of PW's is $500 eV$.

In the calculation of the SIESTA code, the interactions of valence electrons with the ionic cores are described as a norm - conserving pseudopotential by Troullier and Martins [27]. By using diagonalization and Order-N methods we have found relaxed internal co - ordinates and lattice parameters in the above two supercells of ices by using a DZP basis set and pseudoptentials with the partial core correction (PCC) of 0.6 a.u. on the oxygen atom [17]. The maximum force tolerance and the atomic maximum displacement were chosen as $0.02 eV/Ang$ and $0.02 Ang$ respectively. The mesh cut off energy is $350 Ry$ in the all supercells. In the Order-N method [28], a localized basis set is used, and we chose a cut-off radius of Localized Wave Functions (LWF's) and energy tolerance as $7 Ang$ and 10^{-8} respectively.

C. *Calculations and results*

As the CASTEP code, the equilibrium lattice parameters was found that there were 2.5 and 3.0 percent less than the experimental values in iceXI and iceIh respectively, at which the equilibrium volume corresponds to $474.06 Ang^3$ as shown on the figure 4.

In the SIESTA code, the default value of the energy shift is $272.1 meV$, and the default cut-off radius of the basis sets is short. In our case, we have to get a large cut-off radius of the basis sets. Therefore, at the default split norm, which is chosen as 0.15, we have found a convergence of equilibrium lattice parameters as a function of the energy shifts. In these cases, the equilibrium lattice parameters are found to be 4 percent less than the experimental values as shown on the table I. In next case, we have shown a effect of split norms at the energy shift $50.0 meV$. At the split norm 0.20 the equilibrium lattice parameters are found to be 3.5 percent less than the experimental values as shown on the table II. These results of the total energy calculations are shown on the figure 2.

Therefore, we will calculate the total energy curve at the energy shift $50.0 meV$ with the split norm of 0.20, then we have calculated the total energy curves by the SIESTA code. By using the SIESTA code, in the delocalized DZP basis set, we have found that the equilibrium lattice parameters are 3.0 and 3.5 percent less than the experimental values in iceXI and iceIh respectively.

As used eigenvalues of the Hamiltonian operator in the diagonalization method, we can show electronic densities of states, and we used a Gaussian "broadened" function of half width at half maximum of $0.25 eV$. In the occupied bands, one could notice two high peaks at the $-13.99 eV$ and $-8.39 eV$ in the both ices. The peak at the $-13.99 eV$ is a combination of $2p$ orbital for oxygen atoms and $1s$ orbital for hydrogen atoms, while the peak at the $-8.39 eV$ is almost a pure $2p$ orbital for oxygen atoms. Moreover,

TABLE I: The convergence of equilibrium lattice parameters as an energy shift at the split norm 0.15

at energy shift, meV	272.1	200.0	175.0	150.0	100.0	50.0	25.0
percent less than experimental lattice parameters	5.75	5.75	5.25	4.5	4.75	4.0	3.75 -4.0

TABLE II: The effect of equilibrium lattice parameters as a split norm at the energy shift $50.0 meV$

at different split norms	0.10	0.15	0.20	0.25	0.30	0.40	0.50
percent less than the experimental lattice parameters	5.0	4.0	3.5	3.5	3.75	4.0	4.0

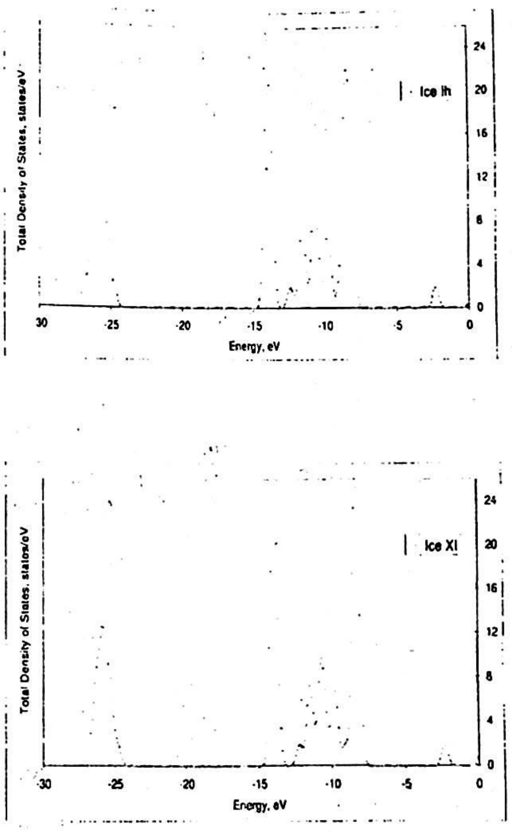

FIG. 3: The Electronic Total Densities of States for iceIh and iceXI at the Γ point by the SIESTA code

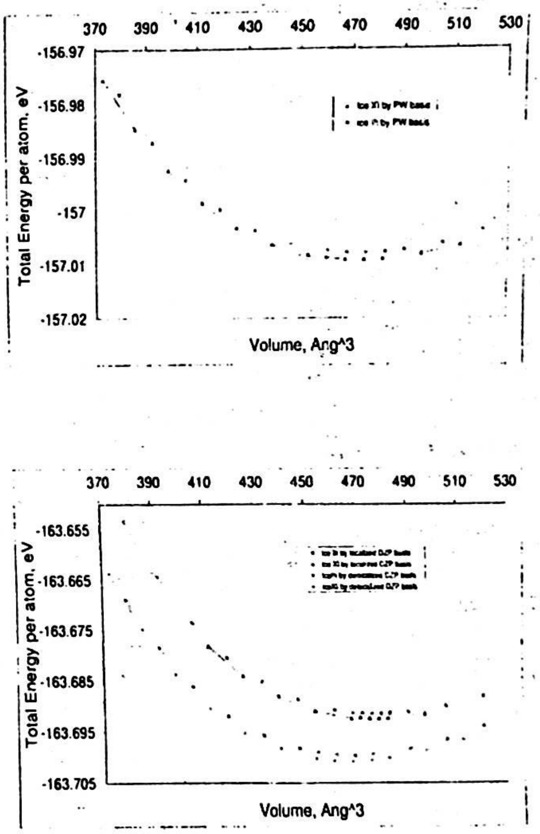

FIG. 4: Our main results of the total energy calculation for iceXI and iceIh by both the codes

one can notice that the highest occupied bands are mostly a conbination of $2p$ orbital for oxygens and $1s$ orbital for hydrogens with a small $2s$ orbital for oxygens at the $-25.90eV$ [29]. But the other small peak at the $-2.39eV$ corresponds to an unoccupied band as shown in the figure 3. Therefore, the Fermi level of Kim functional in the Order-N method [28] has found to be $-5.3eV$ in the both ices. In localized DZP basis set, the equilibrium lattice parameters are found to be 2.25 and 3.0 percent less than the experimental values of iceXI and iceIh respectively, as shown in the figure 4.

The CPU time of single point calculations at the obtained relaxed structures was 1.49 hours for iceIh, and 1.45 hours for iceXI in the diagonalization method, and it was 1.62 hours for iceIh, and 1.56 hours for iceXI in the Order-N method.

V. CONCLUSION

We have done *Ab Initio* total energy calculations for ordinary hexagonal ices, using a SCI method in the flexible LCAO method with norm-conserving pseudopotentials, within a framework of the DFT. When the transferability of the charge density between core and valence electrons for the oxygen atom is decreased, we included the partial core correction to the pseudopotential for oxygen atoms.

By using the delocalized basis set, we have found the relaxed lattice parameters of the supercell in hexagonal ices, which are 3.0 and 3.5 percent less than the experimental values of iceXI and iceIh respectively. By using the localized basis set, we have also found the relaxed lattice parameters of the supercell in hexagonal ices, which are 2.25 and 3.0 percent less than the experimental values of iceXI and iceIh respectively. As used the CASTEP code with the ultrasoft- pseudoptential in the GGA, we also found that there are 2.5 and 3.0 percent less than the experimental values of iceXI and iceIh respectively.

In the case of the delocalized basis set, the relaxed lattice parameters of unit cell have found to be $4.3608Ang$ and $c = 7.0995Ang$ for iceIh, and $a = 4.3586Ang$ and $c = 7.0945Ang$ for iceXI. In the case of the localized basis set, the relaxed lattice parameters have found to be $4.3834Ang$ and

$c = 7.1363 Ang$ for iceIh, and $a = 4.3923 Ang$ and $c = 7.1493 Ang$ for iceXI.

In these calculations of the SIESTA code, we have shown that the range of basis sets plays important role, and the split norm is to be very sensitive to the total energy calculations.

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