INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6” x 9” black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700  800/521-0600
TOTAL ENERGY CALCULATIONS
OF LARGE SCALE SYSTEMS
IN A TIGHT-BINDING REPRESENTATION

DISSERTATION
Presented in Partial Fulfillment of the Requirement for
the Degree of Doctor of Philosophy in the Graduate
School of The Ohio State University

by
JEONGNIM KIM, B.S.

The Ohio State University
1996

Dissertation Committee:
John W. Wilkins
Furrukh S. Khan
Jonathan Pelz

Approved by

Advisor
Department of Physics
ABSTRACT

We present two recent improvements in total energy calculations based on the tight-binding Hamiltonian scheme to study the electronic ground state and to perform molecular dynamics simulations of large scale systems: (i) a parallel implementation using iterative energy minimization schemes; and (ii) an orbital-based linear scaling method using non-orthogonal localized orbitals. We apply the new methods to study phonons in Si systems and extended Si defects. **Phonons in Si systems.** We perform molecular dynamics simulations using our parallel algorithm to extract phonon spectra of bulk Si and the Si(111)-7×7 reconstructed surface. Since these simulations last for long physical times (≈ 10 psec), the phonon frequencies are identified with a resolution of an order of 0.1 THz by fast Fourier transform of the ionic velocities. We identify localized vibrations on adatoms on the top layer of the Si(111)-7×7 reconstructed surface at 15 THz and 16.3 THz as those observed by electron-energy-loss spectroscopy. We observe a new highly symmetrical collective mode of the first-layer atoms at 12.5 THz. **Extended Si defects.** We study extended {311} defects using our orbital-based linear scaling method implemented on Cray-T3D. We investigate the {311} defects systematically from few-interstitial clusters to planar defects. We study the structural properties and energetics of the {311} defects depending upon their dimensions and interstitial concentrations and find possible mechanisms of interstitial capture by and release from the {311} defects.
We find that interstitial chain structures along the (011) direction are stable interstitial defects with respect to isolated interstitials. The interstitial chains provide basic building blocks of the extended {311} defects, i.e., the extended {311} defects are formed by condensation of the interstitial chains side by side in the (233) direction. We find successive rotations of pairs of atoms in the (011) plane are efficient mechanisms for propagation of interstitial chains. The mechanism together with the interstitial chain structure can explain the growth of the {311} defects and related structures such as V-shape bend structures and atomic steps observed in transmission electron microscopy images.
To My Parents
ACKNOWLEDGMENTS

I would like to express my great appreciation to my adviser, Professor John Wilkins, for his encouragement and understanding. Many things would not be possible without his support. Although he appeared to be too tough for a nice unexperienced Korean student (I borrow the expression from my adviser), I came to understand and appreciate his kindness and sense of humor in many ways. In particular, I'm thankful for him to give me opportunities to contact people in the electronic structure community and to partcipate in the exciting development of new methods.

I want to thank my co-adviser, Professor Furrukh S. Khan, who introduced me into the field and encouraged me to explore new possibilities. His enthusiasm and creativity has been an inspiration to enjoy the research as my best hobby.

Many thanks to Professor Jonathan Pelz for serving on my graduate committee. I could have precious experiences working with experimentalists through the collaboration with Professor Pelz and his students. Thanks for faculty members, postdocs and visitors at the Ohio State University who have taught me a lot.

I want to thank my collaborators, Dr. Giulia Galli, Dr. Francesco Mauri and Dr. Andrew Canning for the helpful discussions. The new development of $O(N)$ method with them was an exciting experience. I am especially grateful to Dr. Giulia Galli for her support and the great time I had with her family. Also, I like to thank Professor Roberto Car, who made the valuable stay at IRRMA (Institute Romand de Recherche Numérique en Physique des Matériaux) possible.

One of the most unforgettable things in my graduate study is the group meeting where I learn much about the physics beyond my narrow scope. I enjoyed the lively discussions with my group members: Meb Alouani, Wilfried Aulbur, Herve Castella, Jian Chen, Lars Jonsson, Alex Kuznetsov, Jeff LePage, Carlos Egues
Menezes, Michael Reyzer, Sven Rudin, Matthew Steiner, and Shiwei Zhang. I'd like to especially thank Lars Johsson giving me critial readings of the manuscript and his thoughtful advices on many things.

I owe many thanks to my physics teacher at the high school, who first showed me the world of physics and didn't stop me to become a physicist. Also, I have been very lucky to have many friends who are supportive and loving, back in my high school and college in Korea.

I'm deeply thankful for my parents who gave me a life and taught me how to love it. They have believed in me and have encouraged me to do what I like most. I want to attribute my graduation specially to my father who was a good teacher, a good husband, and most of all, a great father.

The research reported in this thesis is supported by grants from the Department of Energy — Basic Sciences, Division of Materials Research. The computational facilities are provided by the National Super-Oak Ridge National Laboratory, Pittsburgh Supercomputer Center and the Ohio Supercomputer Center. The parallel implementation of the generalized $O(N)$ method is developed as part of the Parallel Application Technology Program (PATP) joint project between École Polytechnique Fédérale de Lausanne (EPFL) and Cray Research. Copyright 1995 by Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA) and EPFL.
CURRICULUM VITAE

April 18, 1968 . . . . . . Born — Incheon, Republic of Korea

February 1991 . . . . . . B. S., Korea Advanced Institute of Science and Technology

June 1991—August 1992 . . University Fellowship, The Ohio State University, Columbus, Ohio, USA

September 1992—present . . Teaching and research assistant, Department of Physics, The Ohio State University, Columbus, Ohio, USA

PUBLICATIONS


FIELD OF STUDY

Major Field: Physics
# TABLE OF CONTENTS

Abstract ................................................................. ii
Dedication ................................................................. iv
Acknowledgements ....................................................... v
Vita ........................................................................ vii
Table of contents ........................................................ viii
List of Tables ................................................................. x
List of Figures ................................................................. xi

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Total energy calculations in a tight-binding representation</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Introduction and overview</td>
<td>1</td>
</tr>
<tr>
<td>1.2. Total energy expression for group IV atoms in a tight-binding representation</td>
<td>7</td>
</tr>
<tr>
<td>1.3. Molecular dynamics simulations</td>
<td>13</td>
</tr>
<tr>
<td>1.4. Molecular dynamics simulations based on the Car-Parrinello fictitious Lagrangian scheme</td>
<td>16</td>
</tr>
<tr>
<td>1.5. Total energy calculations of bulk Si in the TB representation</td>
<td>19</td>
</tr>
<tr>
<td>1.6. Conclusions</td>
<td>23</td>
</tr>
<tr>
<td>References for Chapter 1</td>
<td>24</td>
</tr>
</tbody>
</table>

| 2. Parallel implementation of TB-MD by iterative energy minimization schemes | 26 |
| 2.1. Introduction | 26 |
| 2.2. Parallel implementation of the iterative minimization schemes | 30 |
| 2.3. Phonons of the bulk silicon system | 36 |
| 2.4. Total energy minimization of the 7×7 surface | 41 |
| 2.5. Dynamics simulations of the 7×7 surface | 50 |
| 2.6. Conclusions | 58 |
| References for Chapter 2 | 61 |
3. Total energy global optimization using non orthogonal localized orbitals . 63
   3.1. Introduction ........................................... 63
   3.2. Electronic structure calculations at a given chemical potential .... 66
      3.2.1. Definition of the functional ......................... 66
      3.2.2. Role of the chemical potential ..................... 68
   3.3. $O(N)$ calculations with overlapping localized orbitals .......... 71
      3.3.1. Localization of orbitals and practical implementation ......... 71
      3.3.2. The multiple minima problems ...................... 73
      3.3.3. Overcome of the multiple minima problems ........... 81
      3.3.4. Improvement on variational estimates of the ground state properties 84
   3.4. Molecular dynamics simulations .................................. 87
   3.5. Conclusions ............................................. 90
       References for Chapter 3 .................................... 91

4. Extended Si defects .................................................. 92
   4.1. Introduction ............................................ 92
   4.2. Calculational details ...................................... 97
   4.3. Interstitial chains along the (011) direction .................. 101
   4.4. Extended rod-like {311} defects ............................. 107
   4.5. Propagation of interstitial chains .......................... 114
   4.6. Planar {311} defects ....................................... 124
   4.7. Conclusions ................................................ 129
       References for Chapter 4 .................................... 133

Bibliography

Bibliography .......................................................... 135

Appendix

A. TB Hamiltonian matrix elements ............................. 139
B. The conjugate gradient method ............................... 141
C. TB parameters by Khan et al. ................................. 144
D. TB parameters by Kwon et al. ................................. 148
     References for Appendix .................................... 151
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table Number</th>
<th>Table Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Bulk properties of the diamond Si by total energy calculations in the tight-binding Hamiltonian schemes</td>
<td>20</td>
</tr>
<tr>
<td>2.1</td>
<td>The phonon frequencies of bulk silicon.</td>
<td>39</td>
</tr>
<tr>
<td>2.2</td>
<td>Bond lengths of the surface atoms of the fully relaxed 7x7 surface.</td>
<td>45</td>
</tr>
<tr>
<td>2.3</td>
<td>The energies of the surface states with respect to the HOMO energy.</td>
<td>47</td>
</tr>
<tr>
<td>3.1</td>
<td>Cohesive energy $E_{coh}$ (eV) of a 256 carbon atom slab.</td>
<td>74</td>
</tr>
<tr>
<td>3.2</td>
<td>Cohesive energy (eV) and length (Å) of the double and single bonds of C60.</td>
<td>85</td>
</tr>
<tr>
<td>3.3</td>
<td>Cohesive energy $E_{coh}$ (eV) of different forms of solid carbon.</td>
<td>86</td>
</tr>
<tr>
<td>4.1</td>
<td>Formation energies of point defects calculated by using the TB Hamiltonian</td>
<td>100</td>
</tr>
<tr>
<td>4.2</td>
<td>Formation energy per interstitial ($E_{int}^f$ in Eq. (4.1)) and the binding energy ($E^b$ in Eq. (4.2)) of few-interstitial clusters</td>
<td>106</td>
</tr>
<tr>
<td>4.3</td>
<td>Formation energy of extended {311} defects consisting of interstitial chains.</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>Formation energies per interstitial ($E_{int}^f$) of planar {311} defects.</td>
<td>125</td>
</tr>
</tbody>
</table>


**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
</table>

1.1: Relative fluctuations of $E^{ion}$, the constant energy of motions during the MD simulations. .......................................................... 15

2.1: (a) Top view of a unit cell of the dimer-atom-stacking fault (DAS) model of the 7×7 reconstructed surface. ................................. 28-29

2.2: Flowchart to perform molecular dynamics simulations in the TB Hamiltonian scheme using iterative energy minimizations. 31-32

2.3: Decomposition of the Hamiltonian matrix and the wave functions to perform the parallel matrix-matrix multiplication. 34-35

2.4: Power spectrum of bulk silicon at Γ, X and L. 40

2.5: The Local Density of States per atom, $D_{middle}(ε)$ of the two bulklike layers 43

2.6: The LDOS obtained from Eq. (19) in the text for, (a) the adatoms, (b) the surface-free atoms of the 1st-layer, (c) the corner atom. 48-49

2.7: Power spectrum of the surface atoms; (a) the adatoms, (b) the surface-free atoms (c) the back-bone atoms and (d) the dimers. 52-53

2.8: Power spectra of the adatoms, the back-bone atoms and the 2nd-layer atoms underneath ................................................................. 55-56

2.9: Polarization vectors of localized phonons at adatomic sites indicated by $P_1$, $P_2$ and $P_3$ in Figure 2.8: 57

2.10: The polarization vectors of the surface mode at 12.5 THz projected on the (111)-plane. 59

3.1: Plot of the function $f(a_i, η) = (c_i - η)a_i^2(2 - a_i^2)$ 69

3.2: Differential atomic charge ($Δρ$) on each atomic site of a 256 carbon... 75-76
3.3: Differential atomic charge ($\Delta \rho$) on each atomic site for the same system as in Figure 3.2. ................................................................. 78
3.4: Total energy, $E_{\text{tot}}$, (upper panel) and total charge (lower panel) per atom ................................................................ ..................................................... 82-83
3.5: Energy per atom ($E_{\text{const}}$) as a function of the simulation time ($t$) for constant temperature ($T$) molecular dynamics (MD) simulations of liquid C. ................. 88

4.1: An orthorombic unit cell used to describe the $\{311\}$ defects. ................................................................. 99
4.2: An interstitial chain obtained by stacking pair interstitials with a periodicity of $L_{x0}$ along the $(011)$ direction. ......................................................................... 103-104
4.3: Projections on the $(0\overline{1}1)$ plane of rod-like $\{311\}$ defects containing two interstitial chains. ........................................................................ 108-109
4.4: By subsequent rotations of solid atoms connected by solid bonds, an interstitial chain with the $\{311\}$ habit plane is displaced by ........................................ 116-117
4.5: By rotation of three solid bonds, a rod-like $\{311\}$ defect containing two $I$-chains on the $\{311\}$ plane (a) is transformed to ........................................ 119-120
4.6: Bend configuration of the $\{311\}$ defects (bottom) obtained by addition of two interstitial chains to an $I$-chain on the $\{100\}$ plane (top). ......................... 122-123
4.7: Formation energy ($E^f$) per unit width ($L_{yo}$) with respect to the number of interstitials per unit width (left); ................................................................. 128
4.7: Initial configurations to obtain the extra energy required to add one interstitial to the bulk system in the presence of a planar defect ........................................ 132-131
CHAPTER 1

TOTAL ENERGY CALCULATIONS IN A TIGHT-BINDING REPRESENTATION

1.1. Introduction and overview

Computer modelling is an important tool to understand the properties of condensed-matter systems at a microscopic level [1]. Simulation studies of the interacting atoms are increasingly applied to predict properties of real materials, e.g., the ground-state atomic configuration of a reconstructed surface [2] and the melting of bulk Si [3]. Simulation techniques – (i) atomic relaxations by total energy minimization and (ii) molecular dynamics (MD) simulations – require the calculation of forces acting on the atoms. The atomic degrees of freedom move along the force directions in order to obtain an atomic configuration of a lower energy or to follow the trajectories of atoms during a period of time. The atomic forces are derived from interatomic potentials which describe the interaction of the atoms in the condensed-matter systems.

Constructing a reliable interatomic potential to describe interactions of covalently bonded atoms has been an important task for modelling and control of the
technologically important semiconducting devices. As a computationally efficient method, classical potentials of group IV atoms have been extensively developed [4,5] and have been successfully applied to study properties of surfaces, clusters and amorphous phases [6,7]. These potentials include two- and three-body potentials which are empirically fitted to describe phase diagrams of the crystal structures and other properties known from experiments and first-principle calculations. The molecular dynamics simulations using the classical potentials are computationally efficient and can handle large scale systems consisting of $10^3$ to $10^6$ atoms [6]. However, the classical potentials are inadequate to study phenomena that are originated from the quantum nature of the electronic structure, e.g., an energy lowering by Jahn-Teller distortion around a vacancy in a diamond Si.

On the other hand, as an accurate but rather slow method, the total energy calculation based on the density functional theory in the local density approximation (DFT-LDA) can be used to calculate the interatomic potentials without introducing any empirical parameter [1,8,9]. In the DFT-LDA scheme, a total energy is expressed as a functional of the ionic configuration and the electronic structure. Due to the much smaller mass of the electrons than that of ions, the electron system responds quickly to a change in the ionic positions and therefore the ions move on the interatomic potential surface represented by the ground-state solution of the total energy functional with respect to the electronic degrees of freedom (Born-Oppenheimer approximation). For a given ionic configuration, the electronic ground state is calculated by total energy minimizations with respect to single-particle electron wave functions. Then, the ionic forces are calculated by taking the derivatives of the ground-state energy with respect to the ionic positions. Recent developments
in the algorithms, in particular iterative energy minimization schemes [10,11,12], and in the computational powers have made it possible to perform MD simulations within the DFT-LDA scheme to a greater extent. However, the simulation is still limited to a few hundred atom systems for a short time (~ psec) because of the large memory requirements and the long computational time.

Total energy calculations based on a tight-binding representation can provide an alternative way to perform atomic relaxations and MD simulations with a desirable efficiency and accuracy in describing the covalent systems [13,14,15,16,17,18]. In the tight-binding scheme, the electronic structure is calculated by using a minimal basis set, localized sp^3 orbitals. The use of a small number of basis functions (e.g., 4N basis functions for a system containing N group IV atoms) greatly improves the efficiency in calculating the electronic ground state compared to the DFT-LDA method. Although the tight-binding Hamiltonian is very simple, it can contain the essential quantum nature of the electronic structure and thus describe the system with a better accuracy than the classical potentials.

The evaluation of the electronic ground state in the TB representation requires an order of N^3 steps, where N is the number of atoms in a system [19]. This unfavorable O(N^3) scaling results from the orthonormality constraints on the single-particle wave functions to describe the electrons that are Fermi particles governed by Pauli exclusion principle. This limits the size of the systems that can be treated to about a thousand when conventional methods—the diagonalization of Hamiltonian matrix or the iterative minimization schemes—are employed on the most powerful modern supercomputers.

In this dissertation, I present two approaches which have been developed to
study large scale systems with an improved efficiency and a comparable accuracy of the conventional total energy methods in a TB representation: (1) a parallel implementation using iterative energy minimization schemes; and (2) an orbital-based linear scaling method using non-orthogonal localized orbitals.

As the system size increases, the memory requirements and the computational time increase accordingly. Parallel computations can provide a solution for the increasing computational load to study large scale systems by dividing data and tasks among a number of processors [20,21]. The most time consuming procedure to evaluate the electronic ground state in the TB Hamiltonian representation can be done by parallelized matrix manipulations. When the number of processors is scaled linearly to the system size, the parallelization leads to an effective $O(N^2)$ scaling of the computational time for the calculation of the electronic structure.

We perform MD simulations using the parallel algorithm to extract phonon spectra of bulk Si and the Si(111)-7×7 reconstructed surface (Chapter 2). A large unit cell is required to realistically include all features of the complex reconstruction of the Si(111) surface. Furthermore, a long time MD simulation, of the order of ten psec, is necessary to resolve surface phonons of the system consisting of many degrees of freedom with a low symmetry.

In the last few years, new methods, for which the computational effort scales linearly to the system size ($O(N)$-method), have been introduced independently by several groups. Some of these approaches are based on an orbital formulation (single-particle electron wave functions) [22,23,24,25], while others are based on the one-electron Green's function [26,27] or density matrix [28,29,30]. The basic ingredients of the orbital-based $O(N)$ methods are a suitably defined total energy
*functional* and the *spatial localization of the orbitals*. The total energy expression is defined so that the minimum of the energy functional coincides with the true ground state energy of the electronic structure in the absence of localization constraints. The orthogonality constraints on the orbitals are implicitly imposed in the energy functional to eliminate the $O(N^3)$-scaling procedure either by an orthogonalization of the orbitals or by an inversion of an overlap matrix of the orbitals. Then, the energy functional is minimized with respect to orbitals constrained to be localized in finite regions of real space, called localization regions. The localization of the orbitals together with the short-rangeness of the TB Hamiltonian matrix elements reduce the calculation of the electronic structure to sparse matrix manipulations – multiplications and additions. The computational efforts of the sparse matrix manipulations scale linearly with respect to the system size.

The use of localized orbitals in describing the electronic structure can be a good approximation, if the local properties of a region can be computed from knowledge of the electronic structure in some vicinity of that region. For example, it is well known that the periodic insulators can be represented by exponentially localized orbitals (Wannier type functions) [31] and therefore the total energy and the ionic forces might be well described by using the localized orbitals. In the orbital-based $O(N)$ scaling methods, there is only one variational parameter – the size of the localization regions – to control the error in calculating the total energy and ionic forces. Therefore, the error can be systematically reduced by increasing the size of the localization regions.

The orbital-based $O(N)$ scaling method has been implemented on the Cray T3D parallel computers [21]. Localization of the orbitals within the energy func-
tional, which excludes the explicit matrix inversion or the orthogonalization of the orbitals, reduces computations to evaluate the electronic structure to sparse matrix manipulations, which can be efficiently parallelized. This parallel code allows us to explore larger systems than what could be studied on the conventional supercomputer platforms.

We present total energy calculations of extended Si defects, namely the \{311\} defects, by using the parallelized orbital-based $O(N)$ method (Chapter 4). Large supercells containing few thousand atoms are used to describe the long-range atomic relaxation in the presence of the defects and a large configurational space is investigated to study the \{311\} defects systematically from few-interstitial clusters to planar defects.

The rest of the dissertation is organized in a following way. In section 1.2, the tight-binding Hamiltonian scheme is generally described and the conventional methods to obtain the electronic ground state are presented. I discuss the scaling problem inherited in the electronic structure calculations, so called $O(N^3)$ scaling, in detail. Molecular dynamics simulations in the tight-binding representation and Car-Parrinello fictitious Lagrangian method are discussed in section 1.3 and 1.4, respectively. In section 1.5, I present the total energy calculations of the bulk Si to discuss the accuracy of the TB Hamiltonian scheme to describe the covalent systems in comparison with the first principle methods.

In chapter 2, I present a parallel implementation of the iterative minimization schemes. I show that calculation of the electronic ground state by the iterative minimizations can be done by matrix manipulations, which are straightforwardly parallelized. In following sections, I present the study of phonon spectra of the
bulk Si and the Si(111)-7×7 reconstructed surface using the microcanonical MD simulations based on the Car-Parrinello fictitious Lagrangian method.

In chapter 3, I present the generalized orbital-based linear scaling method. In section 3.2, I first introduce an energy functional, which eliminates the $O(N^3)$ scaling operations and depends on a number of electronic wave functions larger than the occupied states, and then discuss its properties and the role of the chemical potential. In section 3.3 and 4, I present the results of tight-binding calculations based on the generalized $O(N)$ method, showing that the novel approach allows one to obtain the electronic ground state without trapping in multiple minima and to improve on the efficiency of MD simulations.

In chapter 4, I present total energy calculations of the extended Si defects, so-called rod-like {311} defects, by using the generalized $O(N)$ method. I discuss the structural properties and the energetics of a class of Si defects which can store Si interstitials. I present a mechanism which can account for the growth/shrinkage of the {311} defects.

1.2. Total energy expression for group IV atoms in a tight-binding Hamiltonian representation

The total energy of a system containing $N$ covalently bonded atoms is expressed as an energy functional of the ionic positions $\{\mathbf{R}_i\}$ and the electronic wave functions $\{\psi_i\}$. The ground state of the electronic structure is described by $N_{occ} = 4N/2$ wave functions of the occupied states: the number of valence electrons of the group IV atoms is $4N$ and the spin degeneracy of the non-magnetics systems reduce the number of independent wave functions by a factor of $1/2$. The wave functions are
expanded in an orthogonal basis set. In the tight-binding scheme, a minimal basis set consisting of localized $sp^3$-orbitals is used to expand the electron wave functions as

$$|\psi_i\rangle = \sum_l \sum_\alpha^4 |\phi_{l\alpha}\rangle \langle \phi_{l\alpha} |\psi_i\rangle. \quad (1.1)$$

Here, $|\phi_{l\alpha}\rangle$ denotes a basis function localized at the $l$-th atom and the index $\alpha$ specifies four atomic orbitals – $s, p_x, p_y$ and $p_z$ orbitals. Introducing an overlap matrix, $S_{ij} = \langle \psi_i | \psi_j \rangle$, the total energy is given as

$$E^{tot}[\{\psi\}, R] = 2 \sum_i^{N_{tot}} S_{jj}^{-1} \langle \psi_i | H | \psi_j \rangle + \sum_{ll'} R_i | R_i - R_i'|. \quad (1.2)$$

The first term, which we label as $E^{TB}$, describes the electronic structure for a fixed ion configuration. The second term is the ionic pair potential which takes account of the repulsive interaction of ion cores, exchange-correlation energy of the electrons and the double counting of the electron-electron interaction of the $E^{TB}$.

The tight-binding energy term can be rewritten as

$$E^{TB} = 2 \sum_{ij}^{N_{tot}} \sum_\alpha \sum_{\alpha'} S_{ji}^{-1} \langle \psi_i | H_{l\alpha, l'\alpha'} | \psi_j \rangle, \quad (1.3)$$

in terms of the basis functions, where $H_{l\alpha, l'\alpha'} = \langle \phi_{l\alpha} | H | \phi_{l'\alpha'} \rangle$ is a parameterized Hamiltonian matrix element (Appendix A). The Hamiltonian matrix at the $\Gamma$ point is a real symmetrical matrix with the size of $4N \times 4N$. The Hamiltonian matrix elements take simple functional forms which depend on the distance and direction cosines of the $l$-th and $l'$-th atoms [14,15,16,17]. The TB Hamiltonian matrix elements are short-ranged, i.e. $H_{l\alpha, l'\alpha'} \neq 0$, only if $|R_l - R_{l'}| \leq R_c$ for a cutoff radius of $R_c$. In contrast to the DFT-LDA method, the tight-binding scheme is not a self-consistent method. The electron structure is not taken into account in constructing the Hamiltonian. Therefore, the Hamiltonian elements can be calculated...
trivially for a given ionic configuration by using the parameters. Once the Hamiltonian matrix is set up, the next step is to search a set of coefficients, $C_{i\alpha} = \langle \psi_i | \phi_{i\alpha} \rangle$, which minimizes the tight-binding energy, i.e., the wave functions which represent the electronic ground state.

Traditionally, a direct diagonalization of the Hamiltonian matrix has been used to obtain all the eigenstates [15]. Then, the minimum energy is calculated as a sum of the $N_{occ}$ lowest eigenvalues as

$$E^{TB} = 2 \sum_{i=1}^{N_{occ}} \epsilon_i,$$

where $H|\chi_i\rangle = \epsilon_i|\chi_i\rangle$. Although the diagonalization can provide a straightforward solution of the tight-binding energy, the use of diagonalizations is limited to a system of few hundred atoms even when highly-optimized routines are used on the state-of-art computers. The main difficulty comes from the fact that the computational effort of matrix diagonalizations scales cubically with the size of the Hamiltonian matrix -- the $O(N^3)$ scaling. In particular, to perform molecular dynamics (MD) simulations, one has to diagonalize the Hamiltonian matrix at each atomic step as many as $10^3$ to $10^4$ steps.

An alternative method to obtain the tight-binding energy is to use iterative minimization schemes [10,11,12]. The calculation of the sum of the $N_{occ}$ lowest eigenenergies can be viewed as a minimization of the energy functional with respect to the coefficients of the electron wave functions ($C_{i\alpha}$). Starting from an initial guess of the wave functions, $|\psi^0_i\rangle$'s, a new set of the wave functions is obtained as $|\psi_i\rangle \leftarrow |\psi^0_i\rangle + |\Delta_i\rangle$. The change in the wave functions, $\{|\Delta\rangle\}$, is chosen so that the tight-binding energy decreases. The wave functions are updated until the
energy converges to its global minimum. At the minimum of the energy functional, the functional derivatives of the TB energy functional with respect to the wave functions vanishes as

\[
\frac{\delta E}{\delta (\langle \psi_i \rangle)} = -4 \sum_j S^{-1}_{ij} H |\psi_j\rangle + 4 \sum_j \sum_k S^{-1}_{ij} \langle \psi_j | H |\psi_k\rangle S^{-1}_{ik} |\psi_k\rangle = 0. \tag{1.5}
\]

It can be shown that the wave functions, which satisfy the Eq. (1.5), are related to the the \(N_{occ} = 2N\) lowest eigenstates by a unitary transformation. The iterative method is particularly appealing for the MD simulations of large scale systems: (i) only \(N_{occ}\) wave functions are used for the energy minimization instead of \(4N\) wave functions for the diagonalization of the Hamiltonian matrix; and (ii) once the electron wave functions of the ground state are obtained for a given ionic configuration, they can be used as the initial wave functions for the next ionic configuration and only few iterations would be required to converge to the ground state.

The simplest way to minimize the energy is to use the steepest descent (SD) method, by taking \(|\Delta\rangle\) along the gradient direction as

\[
|\Delta_i\rangle = \lambda \frac{\delta E}{\delta (\langle \psi_i \rangle)}.
\]

For a set of the wave functions and the gradient directions, the increment (\(\lambda\)) is calculated to satisfy the extreme condition,

\[
\frac{\partial E[|\psi_0\rangle + \lambda |\Delta\rangle]}{\partial \lambda} = 0. \tag{1.7}
\]

Then, the value of the TB energy for a new set of wave functions is the minimum along the gradient directions. However, the steepest descent method usually requires many iterations to converge to the global minimum of the energy, because
there is no guarantee that the energy minimization along a gradient direction is the global optimization of the energy.

The convergence of the energy minimization can be improved by using corrected gradient directions – conjugate gradient directions, so that each minimization along the conjugate gradient directions is a global optimization of the energy [32]. In the conjugate gradient method (Appendix B), the conjugate gradient direction is constructed by a combination of the present gradient direction and previous gradient directions during the iterative procedure [11,12]. The energy minimization along the conjugate gradient direction ensures the global optimization of the energy and therefore much fewer iterations are required to converge to the energy minimum compared to the SD method.

Although the iterative minimization schemes, such as the conjugate gradient method, have improved the efficiency in solving the Hamiltonian problem over the diagonalization, the unfavorable $O(N^3)$-scaling problem still exists [1]. As seen in Eq. (1.3) and Eq. (1.5), obtaining the gradient direction by taking derivatives of the energy functional with respect to the wave functions involves an inversion of the overlap matrix. The inversion of the overlap matrix, whose size is $2N \times 2N$, also requires computational efforts proportional to $N^3$.

The overlap matrix inversion is introduced to implicitly impose the orthonormality constraints on the wave functions to keep the number of electrons at $4N$:

$$Q = 2 \sum_{ij}^{N_{occ}=2N} S_{ji}^{-1} \langle \psi_i | \psi_j \rangle .$$

(1.8)

The orthonormal constraints can be imposed explicitly by using Lagrangian multipliers. For the orthogonal wave functions, $\langle \psi_i | \psi_j \rangle = \delta_{ij}$, the number of electrons is
always $4N$ and the tight-binding energy becomes

$$E^{TB} = 2 \sum_{i}^{N_{ec}} \langle \psi_{i} | H | \psi_{i} \rangle .$$

(1.9)

The gradient is modified by the orthogonal constraints as

$$\frac{\delta E}{\delta (\psi_{i})} = -4H|\psi_{i}\rangle + 2 \sum_{j} \Lambda_{ij}|\psi_{j}\rangle ,$$

(1.10)

with the Lagrangian multipliers, $\Lambda_{ij} = \langle \psi_{i} | H | \psi_{j} \rangle + \langle \psi_{j} | H | \psi_{i} \rangle$. However, the calculation of the second term of Eq. (1.10) requires a computational time proportional to the cubic power of the system size as well.

We have shown that the $O(N^{3})$ scaling to obtain the electronic structure energy ($E^{TB}$) is originated from the orthonormality constraint on the electron wave functions. The orthonormality constraints are necessary to represent electrons, Fermi particles, by single-particle wave functions. Recently, there have been major developments in the methodology and the algorithms to overcome the $O(N^{3})$-scaling problem. One example is a parallel implementation of the iterative minimization schemes which will be discussed in detail in chapter 2. We show that parallelization of the algorithms lead to an effective $O(N^{2})$ scaling when the number of processors increases linearly with the system size [20]. In the last few years, a class of methods, whose computation scales linearly with the system size [22,23,24,25,28], has been developed by several groups and has proven its efficiency in studying large systems. In chapter 3, we present an orbital-based linear scaling method which relies upon a novel functional, depending on a number of localized states larger than the number of occupied states, and on a parameter which determines the total number of electrons in the system. We show that the new approach incorporated with massively parallel computations makes it possible to explore increasingly larger scale quantum systems.
1.3. Molecular dynamics simulations

Molecular dynamics simulations provide a direct way to study the dynamics of ions in a system. Conventional molecular dynamics simulations use the propagators of ionic positions and velocities derived from the Lagrangian, which consists of the ionic potential and ionic kinetic energy. In the TB scheme, the ionic potential is expressed as the energy functional of the ionic positions and the electron wave functions (Eq. (1.2)). Due to the much smaller mass of the electrons than that of ions, the electron system responds quickly to a change in the atomic positions and, therefore, the potential surface is represented by the ground-state solution with respect to the electron wave functions during the MD simulations (Born-Oppenheimer approximation). This approximation gives a reliable description of ions in a semiconducting system, because the excitation of the electrons to the unoccupied states is negligible at the temperature scale we are interested in (< 5000 K). Then, the Lagrangian of the system is

\[ L = \frac{1}{2} M \sum_{l} (\ddot{R}_l)^2 - E_{\text{tot}}[\{\psi\}, \{R\}], \quad (1.11) \]

where \( M \) is the mass of ions.

The equation of motions of the ions can be derived from the Lagrangian as

\[ M \ddot{R}_l = -\frac{\partial E_{\text{tot}}[\{\psi\}, \{R\}]}{\partial R_l}. \quad (1.12) \]

Since the electrons are in the ground state, the wave functions satisfies the condition in Eq. (1.5), and the ionic forces are

\[ -\frac{\partial E_{\text{tot}}[\{\psi\}, \{R\}]}{\partial R_l} = -2 \sum_{i} N_{\text{occ}} \langle \psi_i | \frac{\partial H}{\partial R_l} | \psi_i \rangle - \sum_{l'} \frac{\partial E_{R}[|R_l - R_{l'}|]}{\partial R_l}, \quad (1.13) \]
assuming that the wave functionals are orthogonal [33]. A similar force expression can be obtained for the energy functional with the inversion of the overlap matrix. With the force calculated from the total energy functional, the atomic position is updated using a time integration algorithm, such as the Beeman [34] or Verlet [35] algorithms.

In performing MD simulations in the TB representation, the most time-consuming part is to obtain the electronic ground state (to quench the electron wave functions on the Born-Oppenheimer surface). Previously in section 1.2, we have compared the diagonalization method and the iterative minimization schemes. Using the conjugate gradient method is an efficient way of obtaining the electronic ground state during the MD simulations, because the wave functions of the previous ionic step provides good initial wave functions for the energy minimization at the present ionic step.

The number of iterations to quench the electron wave functions on the Born-Oppenheimer surface determines the accuracy of the ionic forces. A fluctuation in a constant of the motions can be a measure of the accuracy of the iterative minimization method. For the constant energy MD simulations – microcanonical ensemble MD simulations, the total energy including the ionic potential and kinetic energy,

$$E^{\text{ion}} = E^{\text{tot}} + \frac{1}{2M} \sum_i (\dot{\mathbf{R}}_i)^2,$$  \hspace{1cm} (1.14)

has to be conserved. It has been observed that an extremely accurate quench is required to keep the total energy fluctuation bounded within reasonable limits, when an iterative method is used to quench the electronic wave functions to the Born-Oppenheimer surface at each molecular dynamics step [1,25]. In Figure 1.1,
FIGURE 1.1 Relative fluctuations of $E_{\text{ion}}$, the constant energy of motions during the MD simulations (Eq. 1.15). The system consists of 64 Si atoms in the diamond structure and the simulations start with an initial temperature 300 K. For the MD simulation using the conjugated gradient minimization (CG-MD), the time step ($\Delta t$) to update the ionic positions is 1 fsec and $N_{\text{int}} = 20$ iterative minimizations are performed at each ionic step. For the MD simulation based on the Car-Parrinello fictitious Lagrangian method (CPMD), we chose $\Delta t = 0.5$ fsec. The CG-MD takes about 10 times longer than the CPMD for the simulations of the same period of time.
we show the relative fluctuation of the energy during a MD simulation,

\[
\frac{\Delta E^{\text{ion}}}{E^{\text{ion}}(t = 0)} = \frac{[E^{\text{ion}}(t) - E^{\text{ion}}(t = 0)]}{E^{\text{ion}}(t = 0)},
\]

with respect to the energy at a reference time \( t = 0 \). The microcanonical ensemble simulation is performed for bulk Si of 64 atoms with an initial temperature 300 K. At each ionic step, the TB energy is minimized by the conjugate gradient method with \( N_{\text{int}} = 20 \) iterations. The figure shows that the ion energy decreases as the MD simulation proceeds. The energy loss is about 1 meV/atom/psec. The energy conservation can be systematically improved by using a larger number of iterations.

1.4. Molecular dynamics simulations based on the Car-Parrinello fictitious Lagrangian scheme

An alternative method, which combines the iterative minimization scheme with a fictitious motions of the electronic wave functions, was introduced by Car and Parrinello [10]. In their method, electronic wave functions are treated as additional degrees of freedoms and the deviation of the electronic energy from the exact ground state is permitted by including a fictitious kinetic energy term in the Lagrangian. The fictitious Lagrangian is

\[
L_{CP} = \frac{1}{2} \mu \sum_i \langle \hat{\psi}_i | \hat{\psi}_i \rangle + \frac{1}{2} M \sum_i (\hat{R}_i)^2 - E^{\text{tot}}[\{\psi\}, \{R\}],
\]

where \( \mu \) is the fictitious electronic mass. The equation of motions for the electronic wave functions are given as

\[
\mu \ddot{\psi}_i = -\frac{\partial E_{\text{tot}}[\{\psi\}, \{R\}]}{\partial (\langle \psi_i \rangle)} + 2 \sum_j \Lambda_{ij} \psi_j,
\]
Here, $\Lambda_{ij}$'s are the Lagrangian multipliers introduced to satisfy the orthonormality constraints on the electronic wave functions as in Eq. (1.10). Instead of being quenched to the Born-Oppenheimer surface at every molecular dynamics time step, the electronic wave functions evolve according to the equations of motions (Eq. (1.17)). Performing molecular dynamics simulations in the framework of the Car-Parrinello fictitious Lagrangian method (CPMD) is computationally equivalent to use the steepest descent/conjugate gradient minimization with one iteration. Once the ground state of the electronic structure is obtained for a given ionic configuration, the electron wave functions follow the motions of the ions adiabatically, remaining on the average in the ground state.

To describe the ionic trajectories correctly in the presence of the fictitious motion of the wave functions, the fictitious mass $\mu$ must be chosen in such a way that i) error in the ionic forces caused by electrons being not exactly in the ground state is canceled by the fictitious oscillations of electronic wave functions about the Born-Oppenheimer surface with characteristic frequencies, $\sqrt{E_{\text{gap}}/\mu} < \omega_{el} < \sqrt{\Delta E/\mu}$, and ii) the fictitious kinetic energy of the electronic system remains small and bounded during the entire duration of the simulation [36]. Here, $E_{\text{gap}}$ is the energy gap between the occupied and the unoccupied bands and $\Delta E$ is the difference between the highest and the lowest eigenenergy of the Hamiltonian. It can be shown that if the fictitious mass, $\mu$, satisfies the condition,

$$\omega_{\text{ph}}^{\text{max}} \ll \omega_{el}^{\text{min}} \equiv \sqrt{\frac{E_{\text{gap}}}{\mu}},$$

(1.18)

for the maximum phonon frequency, $\omega_{\text{ph}}^{\text{max}}$, of the system, then the energy mixing between the ionic system and the fictitious electronic system is negligible. Our results show that for simulations as long as a few tens of psec, the ionic energy is
well conserved to within an accuracy of \( \Delta E_{\text{ion}}/E_{0}^{\text{ion}} < 10^{-5} \). When performing CPMD simulations, it is important to choose a molecular dynamics time step, \( \Delta t \), according to the condition,

\[
\omega_{\text{el}}^{\text{max}} = \sqrt{\frac{\Delta E \mu}{\mu}} \ll \frac{1}{\Delta t},
\]

(1.19)

to stabilize the molecular dynamics algorithm with respect to the integration of the equations of motions numerically, either by the Beeman [34] or the Verlet [35] algorithms.

Computationally, CPMD is equivalent to one iterative energy minimization by the SD or CG method [37]. When the system has a gap, CPMD simulations can be more effective than minimizing the TB energy by the CG method. In Figure 1.1, the fluctuation of the \( E_{\text{ion}} \) during the microcanonical ensemble CPMD simulation is shown in comparison with that during a MD simulation using the CG minimization. The energy fluctuation is much smaller (a factor of \( 10^{-3} \)) and, furthermore, it oscillates with a bounded amplitude. The computational time for the one-pscc MD simulation by the Car-Parrinello method is at least 20 times less than that by the conjugate gradient method.

However, the Car-Parrinello method requires a factor of 10 to 100 smaller time step, \( \Delta t \), for the integration of the equations of the motions to study gapless systems than the CG minimization scheme. The smaller time step results in increase in the computational time inversely proportional to \( \Delta t \). In addition, the fictitious electron system is coupled to the physical ionic system, since \( \omega_{\text{ph}}^{\text{max}} \sim \omega_{\text{el}}^{\text{min}} \) for a finite fictitious mass. The adiabatic approximation – the electron wave functions follow the motions of the ions adiabatically remaining on the average in the ground state – is not valid anymore. This leads to a significant energy transfer from the ionic
system to the electron system. Therefore, we have used both the conjugate gradient minimization and the Car-Parrinello fictitious Lagrangian method to perform molecular dynamics simulations of covalent systems depending upon the energy gap of the system.

1.5. Total energy calculations of bulk Si in the TB representations

The tight-binding Hamiltonian scheme has been widely used to investigate not only bulk systems but also other complex systems such as reconstructed surfaces and defects [17,18,2]. The tight-binding molecular dynamics (TBMD) simulation scheme has the desirable computational efficiency and accuracy to describe complex covalent systems. Due to the small number of basis functions (4N localized atomic orbitals), the computation is reasonably fast compared to the \textit{ab initio} method. The TB total energy provides much greater accuracy than the classical potentials by capturing essential quantum nature of the electronic structure in the simplest way. Furthermore, recent developments in linear scaling methods and parallel computers have made it possible for the TBMD scheme to explore much bigger systems and to be competitive with the classical potentials.

We have applied two sets of TB Hamiltonian parameters to study reconstructed surfaces and Si defects. Here, we discuss the quality of the TB Hamiltonians to describe the Si systems in comparison to the more accurate \textit{ab initio} method in the local density approximation (LDA). In Table 1.1, the values of the physical properties of the diamond Si obtained by using the tight-binding Hamiltonian parameters are listed. The cohesive energy is defined as

\[ E_{coh} = \frac{E_{tot}(N)}{N} - E_{atom}, \]  

(1.20)
TABLE 1.1 Bulk properties of the diamond Si by total energy calculations in the tight-binding Hamiltonian schemes. The values are compared with those by total energy calculations in the local density approximation and from experiments.
where $E_{\text{atom}}$ is an energy of an isolated atom. The error in $E_{\text{coh}}$ and the lattice constant of the diamond structure is less than 1% for both TB Hamiltonians. The bulk modulus (B) is calculated with a larger error about 10%. The tight-binding Hamiltonian by Khan et al. [15] (the first column of Table 1.1) gives a good description of the phonon frequencies with errors about 5%. However, the elastic constants ($C_{11} - C_{12}$ and $C_{44}$) are different from those of LDA calculations and experiments by 30%. Another set of TB Hamiltonian parameters [18] improves the elastic constants but gives a poor description of the phonon frequencies.

These differences come from the scaling of the Hamiltonian matrix elements and the pair potentials with respect to a distance ($R_{ll'}$) between two atoms, $l$ and $l'$. A tight-binding Hamiltonian matrix element is expressed as

$$H_{l\alpha,l'\alpha'}[R_l, R_{l'}] = E_{l\alpha,l'\alpha'} h_{\alpha\alpha'}(\frac{R_{ll'}}{R_0}) ,$$

where $E_{l\alpha,l'\alpha'}$ is a hopping integral of two localized basis functions at a distance of $R_0$ - the bond length in the equilibrium diamond structure. The hopping integrals depend on the directional cosines of position vectors $R_l$ and $R_{l'}$. The distance dependence of the Hamiltonian matrix elements is taken care of by the scaling function, $h_{\alpha\alpha'}(R_{ll'}/R_0)$.

For the tight-binding Hamiltonian by Khan et al. [15] (Appendix C), the scaling function of the TB Hamiltonian matrix elements is

$$h_{\alpha\alpha'}(\frac{R_{ll'}}{R_0}) = \left(\frac{R_0}{R_{ll'}}\right)^2 f_c(R_{ll'}) ,$$

independently of the $\alpha$ and $\alpha'$ and the pair potential is given as

$$E_R = \phi\left(\frac{R_{ll'}}{R_0}\right) .$$
The leading scaling of the pair potential for \( R_{\|} \sim R_0 \) is \((R_0/R_{\|})^m\) with \( m = 3.37 \).

A smooth cutoff function, \( f_c \), is introduced

\[
f_c(R_{\|}) = \frac{1}{2} \left[ 1 - \tanh \left( \frac{R_{\|} - \gamma R_0}{\Delta} \right) \right].
\]

(1.24)

to maintain the \((R_0/R_{\|})^2\) scaling of the hopping terms for \( R_{\|} \sim R_0 \) [13] and to decay smoothly beyond \( \gamma R_0 \) with a length scale of \( \Delta \). The parameters, \( \gamma \) and \( \Delta \), were not included for the fitting procedure, but empirically determined after obtaining the set of the hopping parameters \( H_{\alpha\alpha'}^0 \). The choice of \( \gamma \) and \( \Delta \) is made to exclude the second nearest neighbor interactions, while maintaining the \((R_0/R_{\|})^2\) scaling for the first nearest neighbor interactions. Since there is no unique way of choosing \( \gamma \) and \( \Delta \) to restrict the TB Hamiltonian elements to the first neighbor shells of all crystalline structures, the ability to predict other crystalline structures of Si of metallic phases is rather limited. However, these TB Hamiltonian parameters provide a good description of the vibrational properties of the diamond structure. We have applied them to study surface reconstructions and surface phonons, which will be discussed in Chapter 2.

The tight-binding Hamiltonian by Kwon et al. [18] uses short-range scaling functions proposed by Goodwin, Skinner, and Pettifor [16], as

\[
h_{\alpha\alpha'}(R_{\|}/R_0) = \left( \frac{R_0}{R_{\|}} \right)^2 \exp \left( 2 \left[ - \left( \frac{R_{\|}}{R_{c,\alpha\alpha'}} \right)^{n_{c,\alpha\alpha'}} + \left[ \frac{R_0}{R_{c,\alpha\alpha'}} \right]^{n_{c,\alpha\alpha'}} \right] \right).
\]

(1.25)

In this scaling, the \( R_{c,\alpha\alpha'} \) controls the range of the interaction and \( n_{c,\alpha\alpha'} \) the decay of the interactions. In comparison to the scaling function used by Khan et al., the \( R_c \) is analogous to \( \gamma R_0 \) and \( n_{c,\alpha\alpha'} \) to \( \Delta \). The scaling function in Eq. (1.25) have been shown to reproduce diverse bulk phases of silicon and the elastic constants of the diamond structure better than the simple inverse-square scaling functions.
in Eq. (1.22). However, the pair potential scales \((R_0/R_{ui})^m\) with a high value of \(m = 6.87\), which is responsible for the overestimation of the optical phonons (Table 1.1). We applied this TB Hamiltonian model to study extended defects in Si, for which a good description of the elastic properties of the bulk Si is especially important.

1.6. Conclusions

In this chapter, we introduced the total energy expression in the tight-binding representations to study covalent systems. For the molecular dynamics simulations of large scale systems, iterative minimizations of the TB energy are effective to quench the electronic wave functions on the Born-Oppenheimer surfaces than the diagonalization method. We showed that the MD simulations based on Car-Parrinello fictitious Lagrangian method can be applied to study dynamical properties of systems with an energy gap with an improved computational efficiency. We discuss the unfavorable \(O(N^3)\)-scaling in solving the TB Hamiltonian in detail and show that the scaling problem arises due to the orthonormality constraint on the single-particle wave functions to represent electrons. In following chapters, we introduce two approaches to overcome the \(O(N^3)\)-scaling problem—(1) parallel implementation and (2) an orbital-based linear scaling method—and present total energy calculations based on the new methods.
REFERENCES

1. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. 64, 1045 (1992), and references there in.


19. The scaling of the DFT-LDA scheme is also \( N^3 \) with a much greater prefactor than the TB Hamiltonian scheme.


37. For the first iteration of conjugate gradient minimization, the gradient direction is used for the conjugate gradient direction.

25
CHAPTER 2

PARALLEL IMPLEMENTATION OF TB-MD BY
THE ITERATIVE MINIMIZATION SCHEMES

2.1. Introduction

Molecular dynamics simulation provides a direct way to study the dynamics of ions in a system. Conventionally empirical interatomic potentials have been used for the dynamical simulation of very large systems consisting of neutral atoms [1,2]. Although classical potentials can be used to simulate $10^3$ to $10^6$ atoms, they are inadequate to describe those dynamical properties of semiconducting systems for which the quantum nature of the electronic bond is important. On the other hand, it is computationally demanding to use first principle \textit{ab initio} methods based on the local density approximation (LDA) to simulate large systems with a few hundred atoms, for long physical times of the order of psecs. Molecular dynamics simulation using a tight-binding Hamiltonian is an alternate method to describe quantum systems dynamically in practically feasible computational times [3]. Recent developments in massively parallel computation have made it possible to handle increasingly larger systems.
We have developed a parallel algorithm for molecular dynamics simulations using a tight-binding Hamiltonian. The electronic structures are handled by the iterative minimization schemes to improve the speed of the calculation [4,5,6]. We have used the total energy expression for silicon due to Tománek and Schlüter [7] which is based on the original tight-binding parameterization scheme of Chadi [8]. This TB Hamiltonian parameters have been applied to study bulk, surfaces and clusters, and have been shown to give surprisingly good results compared with the local density approximation [3].

For a benchmark test, phonon frequencies of bulk silicon were extracted from the ionic velocity data of a dynamical simulation of bulk silicon consisting of a 128-atom supercell. Comparison of bulk silicon data with experiments showed that Car-Parrinello Molecular Dynamics (CPMD) describes the dynamics of the system properly without giving fictitious ionic modes. The power spectrum obtained from a 10-psec simulation of a 128-atom supercell displayed very sharp peaks corresponding to the phonon modes existing in the finite system. Because of a small molecular dynamics time step (1 fs) and a long simulation time (10 psecs), direct FFT of the ionic velocities was sufficient for the estimation of the power spectrum, without any need of techniques like the maximum entropy method [9].

I present molecular dynamics simulation study to extract the vibrational modes of the Si(111)-7×7 reconstructed surface. The dimer-adatom-stacking-fault (DAS) model by Takayanagi et al. [10] is consistent with the experimental observations on the Si(111)-7×7 reconstructed surface and it is generally accepted to be the correct model of the atomic structure of the surface. A unit cell of the DAS model consists of 12 adatoms on the outer most surface, two subcells with different stacking
FIGURE 2.1 (a) Top view of a unit cell of the dimer-adatom-stacking fault (DAS) model of the 7\times7 reconstructed surface. Atoms in different layers are shown by circles of different sizes. The size of the circles decreases for the atoms further from the surface. A dimer row divides the cell into two subcells; the “fault” left subcell has a stacking sequence different from the bulk sequence (of the “unfaulted” right subcell) in that the 1st-layer atoms are on top of the 4th-layer atoms. Numbers label unique atoms of the surface layers according to Ref. [11]. Identical atoms are related by symmetry operations; three-fold symmetry in a subcell and mirror symmetry about the long diagonal of the unit cell. The three classes of dangling-bond atoms are, the twelve adatoms (1, 2, 3 and 4), the six surface-free atoms (7 and 12) and a corner atom (26). Dimer rows are present in the 2nd-layer along the cell boundaries (16, 17 and 21). Atoms (5, 6, 7, 8, 10, 11, 13 and 14) are the back-bone atoms in the 1st-layer, which are connected to the adatoms. (b) Side view of the slab along the long diagonal. The adatoms are on the “top” sites right above the 2nd-layer atoms (15, 20, 22 and 25) rather than on the “hollow” sites. The lower part of the slab is constructed by inversion with respect to the “\times” drawn in the middle of the slab. The computational cell consists of a slab bounded by infinite vacuum layers on both sides along the [111]-direction and periodic boundary conditions are applied in the (111)-plane.
FIGURE 2.1
sequences and dimerization along the cell boundaries (Figure 2.1). Theoretical calculations of the relaxation of Si(111)-7×7 have confirmed the DAS geometry of the model and shown that it is an energetically favorable reconstruction of the Si(111)-surface [11,12,13]. Relaxation over a few surface layers and the large 7×7 unit cell in the (111)-plane requires a large computational supercell consisting of a few hundred atoms. We use a supercell consisting of 400 atoms with a slab geometry and an initial ionic configuration from Ref. [11]. The ions are initially relaxed by total energy minimization until forces have converged to less than 0.1eV/A.

The dynamical simulations are performed by Car-Parrinello fictitious Lagrangian method using a tight-binding Hamiltonian at 20 K. The simulations presented in this chapter have been performed on the Intel/Paragon distributed memory parallel computers, for a long physical time of about 8 psecs to study surface phonons. Electron-energy-loss (EEL) spectroscopy by Daum et al. observed a high frequency mode at 17 THz localized at adatomic sites [14], which we found at 16.3 THz and 15 THz from the power spectrum of surface atoms. This mode involves out-of-phase vibration of adatoms and the 2nd-layer atoms underneath. We relate the broad peak at 7.5 THZ by EEL [14] to the surface phonons observed on the adatomic sites at a lower frequency range (6~10 THz). We observe a new mode involving planar vibrations of the 1st-layer atoms and dimers. This mode is three-fold symmetric with respect to the center of the two subcells and the two subcells show out-of-phase breathing vibrations.

2.2. Parallel implementation of the iterative minimization schemes

In solving the eigenvalue problems by iterative minimizations of an energy func-
FIGURE 2.2 Flowchart to perform molecular dynamics simulations in the TB Hamiltonian scheme using iterative energy minimizations. One cycle of the outer loop corresponds to one MD step. At each time step, the Hamiltonian matrix elements are calculated by using the linked-lists of the atoms and stored. The inner loop is the TB energy minimization by the iterative methods: (a) a multiplication of the Hamiltonian matrix by the wave functions; (b) construction of the Lagrangian multipliers; (c) a multiplication of the Lagrangian multipliers by the wave functions; (d) construction of the gradient directions; and (e) calculation of the λ to minimize the TB energy along the gradient direction and construction of a new set of wave functions. For the conjugate gradient minimization, an extra step to calculate the conjugate gradient directions is added between step (d) and (e). To quench the electronic wave functions on the Born-Oppenheimer surface at every ionic step, the inner loop is repeated. We use either a fixed number of iterations or unlimited number of iterations, until the total energy converges within a certain tolerance (typically, less than 10^{-6} eV per atom). For the MD simulation based on the Car-Parrinello fictitious Lagrangian method, the inner loop is not repeated.
Set up the Hamiltonian matrix for the ionic configuration at \( t \)

- (a) \( H |\psi_i> \)
- (b) \( \Lambda_{ij} \leftarrow <\psi_i | H |\psi_j> + <\psi_j | H |\psi_i> \)
- (c) \( \sum_j \Lambda_{ij} |\psi_j> \)
- (d) \( |\Delta_i> \leftarrow -4H |\psi_i> + 2 \sum_j \Lambda_{ij} |\psi_j> \)
- (e) \( |\psi_i> \leftarrow |\psi_i> + \lambda |\Delta_i> \)

Calculate ionic forces and update the ionic positions

\( t \leftarrow t + \Delta t \)

FIGURE 2.2
tional, the most important step is to obtain the gradient directions. The $O(N^3)$ scaling is the result of either the matrix inversion or the constraint term by Lagrangian multipliers. Due to its simplicity of parallelization, we have used the energy functional without the inversion of the overlap matrix. Lagrangian multipliers take care of the orthogonality constraints on the wave functions. In this case, calculations of the gradients and energy minimizations can be done by the manipulation of matrices. In Figure 2.2, we show the algorithm to obtain the ground state by iterative minimization schemes in the framework of MD simulations. The outer loop is to update the ionic positions and the inner loop is to calculate the electronic ground state. The inner loop can be substituted by a diagonalization of the Hamiltonian matrix. More than 90% of computational time is spent on the inner loop even for a system of few tens of atoms.

We have implemented the parallel algorithm to perform the TB-MD simulations using iterative minimization schemes on Intel/Paragon and Cray-T3D [15]. Both parallel computer systems belong to the multiple instruction and multiple data stream architecture (MIMD): each processor has its own memory and microprocessor to perform computations in parallel. Although most of the computation can be done on each processor independently, communications between processors are necessary to pass global information and data. We have used machine specific communication libraries to achieve fast communication. In particular, the shared memory library routines (SHMEM) are used in the code implemented on Cray-T3D.

To maximize the performance of the parallel algorithms, it is important to balance the computational load on each processor and to reduce the communication between the processors. Since the TB Hamiltonian matrix elements, $H_{\alpha\beta\alpha'} = $
FIGURE 2.3 Decomposition of the Hamiltonian matrix and the wave functions to perform the parallel matrix-matrix multiplication. For a system containing $N$ covalent atoms, each processor (total $N_p$ number of processors) has information of (a) a band of the Hamiltonian matrix and (b) $2N/N_p$ number of wave functions. The multiplication of the Hamiltonian matrix by the wave functions is schematically illustrated. For the initial data distribution, a set of block matrices are simultaneously calculated by matrix-matrix multiplications (shaded area). Then, the wave functions are transferred to the next processors and another set of block matrices are calculated. For the $p = N_p - 1$ processor, the wave functions are transferred to the $p = 0$ processor to form a ring structure of the processors. This procedure is repeated until the matrix elements of $H|\psi\rangle$ are completed.
Figure 2.3
\begin{equation}
\langle \phi_{l a} | H | \phi_{l' a'} \rangle, \text{ are not zero, only if } |\mathbf{R}_l - \mathbf{R}_{l'}| < R_c, \text{ we use the data distribution based on the physical location of the atoms. We partition the atoms into cells of equal size. Each cell is mapped over a processor which contains the information of the atoms that belong to the cell. Linked-lists of the atoms are constructed to set up the Hamiltonian matrix. Only the non-zero elements of the Hamiltonian matrix are precalculated using the parameters and then stored (Figure 2.3(a)). Decomposition of the wave functions is done by distributing } 2N/N_p \text{ wave functions per processor (Figure 2.3(b)). The parallel procedure to multiply the Hamiltonian matrix by the wave functions is illustrated in Figure 2.3. Calculations of the Lagrangian multipliers and the second term in Eq. (1.10) can be done similarly to the multiplication of the Hamiltonian matrix by the wave functions.}
\end{equation}

The computational time to perform one iteration of SD or CG minimization is proportional to \( N^3/N_p \) when the calculation of an \( N \)-atom system is performed on \( N_p \) processors. The communication time increase as the square of the number of atoms with a smaller prefactor than the computational time. Therefore, if the number of processors is made to scale linearly with the number or atoms, then the computational time scales as \( O(N^2) \).

2.3. Phonons of the bulk silicon system

The nearest neighbor distance of the diamond structure is 2.38 Å (experiment 2.35 Å) for the total energy given by Eq. (1.2). The band gap, \( E_{\text{gap}} \), at \( T \) is 1.2 eV for a 128-atom supercell. Based on the criteria for the fictitious mass (\( \mu \)) and the molecular dynamics time step (\( \Delta t \)) given by Eq. (1.18) and Eq. (1.19) [16], different masses and time steps were tested and the conservation of ionic energy
and the boundedness of the electronic fictitious kinetic energy were monitored. For
the bulk case we chose the fictitious mass $\mu_b = 511$ AU and the time step $\Delta t = 1$
fs. For this choice, the minimum electronic frequency $\omega_{el}^{\text{min}}$ is about four times
larger than $\omega_{ph}^{\text{max}}$, i.e.,

$$\omega_{el}^{\text{min}} \equiv \sqrt{\frac{E_{gap}}{\mu_b}} \approx 4 \times \omega_{ph}^{\text{max}}.$$  \hspace{1cm} (2.1)

The ionic energy given by Eq. (1.14) is conserved with a fractional fluctuation
of $\Delta E^{\text{ion}}/E^{\text{ion}}(t = 0) < 10^{-5}$ and the fictitious kinetic energy remains bounded
throughout a simulation of more than $10$ psecs.

The molecular dynamics time step, $\Delta t = 1$ fs, is considerably large compared
to that used in Car-Parrinello molecular dynamics based on LDA and the plane
wave basis. In the case of LDA with plane waves, the MD time step is smaller
for larger supercells as the highest electronic eigenenergy depends on the highest
kinetic energy term in the Hamiltonian. This small time step is another factor in
increasing the computational load for LDA simulations [17]. However, the highest
eigenvalue of the the TB Hamiltonian doesn’t depend upon the system size, i.e.,
the size of the supercell; thus, the same fictitious mass and time step can be used
for the dynamical simulation of bulk silicon regardless of the size of the supercell.

Phonons of bulk silicon have been studied in the literature mainly by using per­
turbation theory [18]. The alternate method of extracting phonon frequencies is to
perform molecular dynamics simulations over long physical times. Similarly, surface
phonons of the Si(111)-2×1 reconstructed surface were studied by ab initio molecular
dynamics simulations [19]. Our supercell consisting of 128 atoms corresponds
to 64 fcc-primitive cells. Initially, ions are randomly displaced from equilibrium.
positions and random velocities are assigned to the ions consistent with an initial temperature of 300 K. After a few 10's of fs, the system reaches microcanonical equilibrium and the simulation is performed for 11 pscc with a fluctuation, $\Delta E^{\text{ion}} / E^{\text{ion}}(t = 0)$, of less than $10^{-5}$.

Phonon spectra are extracted by velocity-velocity autocorrelation functions,

$$P(q, \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle v_q(t)v_q(0) \rangle = \int_{-\infty}^{\infty} dt e^{i\omega t} \int_0^\infty d\tau v_q(t+\tau)v_q(\tau)$$

$$= |v_q(\omega)|^2,$$

for wave vector $q$. Since the simulation time is long ($\sim 10$ psec), power spectrum estimation by the FFT can be used without making any assumptions. First, $v_q^i(t_k)$ for the $i$th atom in a primitive cell is obtained by the fourier transform as

$$v_q^i(t_k) = \sum_l e^{iR_l \cdot q} v^i(R_l),$$

where $l$ runs over the primitive cells in a supercell. Next, the power spectrum, $P(q, \omega)$, is calculated as

$$P(q, \omega) = \sum_{i=1,2} |v_q^i(\omega)|^2,$$

where

$$v_q^i(\omega) = \sum_k e^{i\omega t_k} v_q^i(t_k),$$

for the fcc-primitive unit cell.

The peaks in the power spectra correspond to the frequencies of phonons of allowed wave vector $q$. The resolution in the frequency is proportional to $1/T \approx 0.1$ THz for a total simulation time $T \approx 10$ psec. We obtain very sharp peaks for each
<table>
<thead>
<tr>
<th></th>
<th>Experiment (THz)</th>
<th>CPMD (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{\text{TO}}(\Gamma_{25'})$</td>
<td>15.53</td>
<td>16.21</td>
</tr>
<tr>
<td>$\nu_{\text{TA}}(X_3)$</td>
<td>4.49</td>
<td>4.68</td>
</tr>
<tr>
<td>$\nu_{\text{LO}}(X_1)$</td>
<td>12.32</td>
<td>12.01</td>
</tr>
<tr>
<td>$\nu_{\text{TO}}(X_4)$</td>
<td>13.90</td>
<td>14.26</td>
</tr>
<tr>
<td>$\nu_{\text{TA}}(L_3)$</td>
<td>3.43</td>
<td>3.42</td>
</tr>
<tr>
<td>$\nu_{\text{LA}}(L_{2'})$</td>
<td>11.35</td>
<td>10.25</td>
</tr>
<tr>
<td>$\nu_{\text{LO}}(L_1)$</td>
<td>12.60</td>
<td>12.50</td>
</tr>
<tr>
<td>$\nu_{\text{TO}}(L_{3'})$</td>
<td>14.68</td>
<td>15.33</td>
</tr>
</tbody>
</table>

**TABLE 2.1** The phonon frequencies of bulk silicon at $\Gamma$, $X$ and $L$. Experimental data are from inelastic neutron scattering by Dolling [20]. The error of our results is approximately 5%.

39
FIGURE 2.4 Power spectrum of bulk silicon at Ω, X and L. Power spectrum is calculated via Eq. 2.2, the ionic velocity-velocity autocorrelation function using the FFT. The frequency of the optical phonon (Γ′ 25) is 16.2 THz. The frequency of each mode is listed in table 2.1.
q. The overlap of the power spectra of several q's whose results are tabulated in Table 2.1 is shown in Figure 2.4. The frequency of the optical phonon at Γ is 16.2 THz, while the experimental value from inelastic neutron scattering by Dolling [20] is 15.5 THz. Fine splitting of the optical modes is found along the Δ-direction and the dispersion relation is reproduced in a good agreement with experiments. Phonon frequencies obtained by our simulation compared with experimental results are listed in Table 2.1. The error is about 5%.

2.4. Total energy minimization of the 7×7 surface

It is believed that the annealed Si(111) surface undergoes a 7 x 7 reconstruction described by the Dimer-atom-stacking-fault (DAS) model by Takayanagi [10]. A unit cell of the DAS model is shown in Figure 2.1. The numbers on the atoms label the unique atoms in a cell. Identical atoms in a cell are related by symmetry operations [11], consisting of three-fold symmetry in a subcell and mirror symmetry about the long diagonal of the unit cell in Figure 2.1(a). There are 12 adatoms on the top layer and two subcells formed by the division of the unit cell by a dimer row along the short diagonal. The left subcell in the figure is said to have a stacking fault because its stacking sequence is different from that of bulk silicon. The 1st-layer atoms on the faulted side are located on top of the 4th-layer atoms. Nine dimers are present on the 2nd-layer in a unit cell along the cell boundaries. The adatoms are located on “top” sites, directly above the second-layer atoms rather than on “hollow” sites [21]. At the corner of a unit cell, a hole is surrounded by 12 atoms, which is a 3rd-layer atom with a dangling bond. There are 6 surface-free atoms with a dangling bond on the 1st-layer which are not connected to the adatoms.
Supercells with slab geometries have been widely used in the literature to determine the optimized geometry of the reconstructed surface and to perform dynamical simulations [17]. In our calculation, a slab of finite thickness is located in the middle of the cell and is bounded by vacuum layers on both sides along the [111]-direction (Figure 2.1(b)) with periodic boundary conditions applied in directions perpendicular to the [111]-direction. Infinite cell size is assigned along the [111]-direction as only the nearest neighbor interactions within the cutoff radius are included in the tight-binding Hamiltonian. The lower part of the slab is constructed by inversion with respect to the “x” in the middle of the slab in Figure 2.1(b). The slab has to be thick enough so that the two surfaces do not interact with each other through the middle layers. We choose a 10-layer-thick slab including adatomic layers, to study the 7x7 reconstructed surface. The total number of atoms in the cell is 400. We use the same slab for the total energy minimization and the dynamical simulations.

We started the total energy minimization from the ionic configuration obtained from Ref. [11], where a supercell geometry of 196 atoms with a hydrogen saturated bottom layer was used for the model calculation. The coordinates were scaled by the lattice constant of 2.38 Å consistent with the Hamiltonian used in our calculations. During the total energy minimization, two innermost layers were fixed and 8-surface layers were relaxed until all the forces on the ions were less than 0.1eV/Å. Total configurational energy minimization was performed by using the steepest descent method.

The Local Density of States (LDOS) of the middle bulk-like layers, $D_{middle}(\epsilon)$, was obtained to make sure that the 10-layer-thick slab was suitable for the description of the 7x7 DAS model. For comparison, a plot of $D_{middle}(\epsilon)$ is displayed along
FIGURE 2.5 The Local Density of States per atom, $D_{\text{middle}}(e)$ of the two bulklike layers in the middle of the 7×7 slab (the thick solid line) is compared to the DOS of bulk silicon at $\Gamma$ (the thin solid line) with the same normalization. The computational supercell for the bulk silicon calculation is chosen to be 6-layer thick along the [111]-direction with periodic boundary conditions applied in the [111]-direction as well as in the (111)-plane. By using this unit cell, the DOS of bulk silicon at $\Gamma$ has the same band-folding as the surface slab so that direct comparison is possible, without the need of k-sum.
with the plot of the DOS of bulk silicon in Figure 2.5. $D_{\text{middle}}(\epsilon)$ is obtained by projecting the DOS onto atoms of the bulk-like middle layers, i.e.,

$$D_{\text{middle}}(\epsilon) = \sum_{i} \sum_{\alpha} \sum_{i} 2N \delta(\epsilon - \epsilon_i) |\langle \psi_i | \phi_{\alpha}^i \rangle|^2,$$  

where $N_{\text{middle}} = 98$ for the two middle layers and $\epsilon_i$ is the $i$th eigenenergy of the tight-binding Hamiltonian. The supercell we used for the bulk system consists of 6 layers along the [111]-direction with periodic boundary conditions applied along the [111]-direction as well as in the (111)-plane. This supercell in the (111)-plane has a $7 \times 7$ geometry. With this choice of the bulk supercell, the DOS at $\Gamma$ for the bulk calculation has the same band folding as the DOS obtained from the supercell of the $7 \times 7$ reconstructed surface, so direct comparison is possible without the need of a $k$-sum. Figure 2.5 shows that the LDOS of bulk-like middle layers of the slab shows an excellent agreement with that of the actual bulk calculation, indicating that our slab satisfies the condition of the isolation of the two surfaces on both sides, and providing an environment of ideal bulk silicon substrate to the surface.

Our results, after the complete relaxation of the surface, can be summarized as follows: i) adatoms show large stretching toward the vacuum. The nearest neighbor distance of the adatoms is stretched by 8% of the bulk value, and the corner adatoms move along the [111]-direction more than adatoms in the middle of the subcells; ii) atoms underneath adatoms are pushed into the bulk-layer but the distortion of 3rd-layer atoms from bulk configuration is less significant compared to that of a previous calculation [11]; and iii) surface free atoms move to the vacuum resulting in stretching of the bond length but maintaining tetrahedral structure with less distortion than adatomic sites.
<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length (Å)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adatom – Back-bone atom</td>
<td>2.58 ± 0.04</td>
<td>+8</td>
</tr>
<tr>
<td>Adatom – 2nd-layer atom</td>
<td>2.57 ± 0.02</td>
<td>+8</td>
</tr>
<tr>
<td>Surface-free atom – 2nd-layer atom</td>
<td>2.43 ± 0.02</td>
<td>+2</td>
</tr>
<tr>
<td>Dimer</td>
<td>2.45 ± 0.02</td>
<td>+3</td>
</tr>
<tr>
<td>Dimer – 3rd-layer atom</td>
<td>2.39 ± 0.02</td>
<td>+0.4</td>
</tr>
<tr>
<td>Corner atom – 4th-layer atom</td>
<td>2.40 ± 0.01</td>
<td>+1</td>
</tr>
</tbody>
</table>

**TABLE 2.2** Bond lengths of the surface atoms of the fully relaxed 7×7 surface and the error in percentage with respect to the bond length of bulk silicon (2.38 Å). Each adatom has four nearest neighbors, namely three back-bone atoms and a 2nd-layer atom, on top of which the adatom is located. Each surface-free atom with one dangling bond is connected to three 3rd-layer atoms while maintaining tetrahedral configuration. Dimers have a bond length of 2.45 Å. The third column in the table is the percentage difference of the bond length compared to the ideal bond length of the bulk diamond structure.
Bond lengths of the surface atoms are listed in Table 2.2. The nearest neighbor distance of bulk silicon is 2.38 Å. The average bond length between an adatom and the back-bone atoms is 2.58 Å and that of an adatom and a 2nd-layer atom is 2.57 Å. The 2nd-layer atoms labeled as 16, 20, 22 and 25 in Figure 2.1 have 5 nearest neighbors, namely, one adatom, three back-bone atoms, and one 3rd-layer atom. The bond length between surface-free atoms and the connected atoms on the 2nd-layer atoms is 2.43 Å, i.e., it is stretched by 2% of the nearest neighbor distance of the ideal tetrahedral structure. The average length of the dimers is calculated to be 2.45 Å, compared with 2.49 Å, which is the result of the x-ray measurements by Robinson et al. [22]. Finally, the corner atoms move towards the vacuum with a bond-length of 2.40 Å.

Electronic structure of the 7×7 surface has been studied extensively in the literature, both theoretically and experimentally. Early studies by LEED at low temperatures (T=15 K) [23] showed half-filled surface states at the Fermi level, thus indicating the metallicity of the surface. We obtain localized surface states by projecting the DOS onto specific atomic sites. The LDOS projected onto the \( l \)-type atom is obtained as

\[
D_l(\epsilon) = \sum_{i} \sum_{a} \sum_{i} \delta(\epsilon - \epsilon_i) |\langle \psi_i | \phi_{l,a}^i \rangle|^2.
\]  

(2.7)

The plots of the LDOS projected onto adatoms, surface-free atoms, the corner atom and the dimers are shown in Figure 2.6. The energy of the highest occupied band \( (E_{\text{HOMO}}) \) is \( \approx 0.3 \) eV and the band gap, \( E_{\text{gap}} \), is 0.05 eV at \( \Gamma \). Surface states identified by localized peaks at surface atoms are compared to current-imaging-tunneling spectroscopy (CITS) data by Hammers et al. [24] in Table 2.3. This table lists the localized states at specific atomic sites obtained by CITS and our
TABLE 2.3 The energies of the surface states with respect to the HOMO energy ($E_{\text{HOMO}} = 2.94 \times 10^{-1}$ eV). Projected density of states are calculated to obtain the localized surface states at specific atomic sites. The experimental results by current-imaging tunneling spectroscopy [22] are also listed for comparison, where $E_f$ is the Fermi energy.
FIGURE 2.6 The LDOS obtained from Eq. (19) in the text for, (a) the adatoms, (b) the surface-free atoms of the 1st-layer, (c) the corner atom and (d) the dimers, all drawn to the same scale. The energy of the highest occupied orbital, $E_{\text{HOMO}} = 0.03 \text{ eV}$, is indicated by an arrow on the energy axis. The energy of the surface states around the Fermi level, localized at specific atomic sites, which are identified by the peaks in the LDOS, are listed in Table 2.3 and compared with those observed by current-imaging-tunneling spectroscopy (CITS) [22]. The electronic structure of 7×7 is metallic with a small but finite gap ($E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \approx 0.05 \text{ eV}$ at $\Gamma$). The surface states at the Fermi level are localized at the adatomic sites (the adatoms and the back-bone atoms) and the dimers.
FIGURE 2.6
calculations. There is a clear gap in the LDOS of the surface-free atoms and the corner atom with dangling bonds (Figure 2.6(b) and (c)). Highly localized states at $E_{\text{LUMO}} - 0.9$ eV originate from the dangling bonds. Surface states at the Fermi level are localized on adatoms and dimers, which are responsible for the metallicity of the surface.

2.5. Dynamics simulation of $7 \times 7$ surface

In Car-Parrinello fictitious Lagrangian method, a well defined band gap is a crucial element in determining the reliability of simulations with fictitious degrees of freedoms related to the electronic wave functions. Appreciable heat transfer from the ionic subsystem to the electronic subsystem during the CPMD simulations has been commonly observed for metallic systems and additional degrees of freedoms related to temperatures have been introduced in the literature to maintain thermal inequilibrium of the two subsystems by using various thermostats [25]. Even though 7×7 surface is metallic, there are only a few surface states at the Fermi level and a small but finite band gap, $E_{\text{gap}} = 0.05$ eV, is obtained from direct diagonalization of the Hamiltonian in the ground state. Therefore, instead of using thermostats to fix the temperatures of the ions and the electronic wave functions separately, we used a small fictitious mass and a correspondingly small molecular dynamics time step according to the conditions given by Eq. (1.18) and Eq. (1.19).

First we note that the maximum phonon frequency, $\omega_{\text{ph}}^{\text{max}}$, is of the same order, for both bulk and the 7×7 surface. To obtain the same quality of simulations for the 7 × 7 surface as the bulk simulations, we choose the same value for $\omega_{\text{el}}^{\text{min}}$ for the 7 × 7 surface as was used for the bulk case. This fixes $\mu_{7 \times 7} = 0.04 \mu_{\text{bulk}}$. by
using Eq. (1.18) and the fact that the ratio of $E_{gap}$ for bulk and the $7 \times 7$ surface is equal to $1.2/0.05 = 0.04$. Having fixed $\mu_{7 \times 7}$, the maximum electronic frequency, $\omega_{el}^{max}$, is fixed via Eq. (1.19). Now we choose $\omega_{el}^{max} \Delta t$ to have the same value as in the bulk case. This fixes the molecular dynamics time step, $\Delta t = 0.2$ fsec, which is about a factor of 5 smaller than the bulk value of $\Delta t$. These chosen values of $\mu_{7 \times 7}$ and $\Delta t$, give us the same accuracy in the energy conservation of the $7 \times 7$ simulations as was obtained in the bulk calculations.

Initial velocities of the ions were randomly distributed consistent with a temperature of 20 K. The total physical time of our simulation is about 8 psec. Ionic energy is conserved to an accuracy of $\Delta E_{ion} / E_{ion}(t = 0) < 10^{-5}$ throughout the duration of our simulation, indicating that there is no significant heat transfer between the ionic and the fictitious electronic systems. The power spectrum is estimated by using the FFT and relative phases of the fourier transform of the velocities are analyzed to study the polarization vectors of the modes corresponding to specific frequencies.

We obtain normalized power spectrum of the $l$-type atom on the surface layers by

$$ P_l(\omega) = \frac{1}{N_l} \sum_{l^*} \frac{|v_{l^*}(\omega)|^2}{}, $$

(2.8)

where $N_l$ is the number of atoms related by symmetry operations in a cell to the $l$-type atom. Power spectra of various surface atoms are shown in Figure 2.7, for (a) adatoms ($N_l = 12$), (b) surface-free atoms ($N_l = 6$), (c) back-bone atoms ($N_l = 36$) and (d) dimers ($N_l = 18$). The peaks labeled as $P_1, P_2$ and $P_3$ in Figure 2.7(a) are localized at adatoms and polarized along the [111]-direction. Relatively high energy phonon at 17.1 THz has been observed by EEL using carbon contamination.
FIGURE 2.7 Power spectrum of the surface atoms: (a) the adatoms, (b) the surface-free atoms (c) the back-bone atoms and (d) the dimers. The height of the spectrum is properly normalized using Eq. 2.8 in the text. The solid lines are power spectrum of polarization vectors projected along the [111]-direction while the dotted lines are projected in the (111)-plane. There are three prominent peaks in the power spectra of the adatoms (a), $P_1$, $P_2$ and $P_3$, which are polarized along the [111]-direction. We associate these peaks with the surface phonons localized at the adatomic sites, which have been observed experimentally by EEL [14]. A new mode at 12.5 THz ($P_4$) is found, which involves vibrations of most of the 1st-layer atoms, i.e. the surface-free atoms (b) and the back-bone atoms (c). The same mode is observed in the spectrum the dimers (d).
FIGURE 2.7
on 7×7 surface [14]. We associate the peak, \( P_3 \), in Figure 2.7(a) with this phonon. The high frequency phonon is a common feature of the reconstructed surface with adatoms, which has also been found on the Si(111)-2×2 surface [26]. It has been suggested in the literature that the \( P_3 \) peak is the optical mode of adatom and atoms underneath [14,26,27]. As discussed later, our results are consistent with this observation.

Power spectra of each adatomic sites are compared and relative phases of vibration are analyzed. Adatoms labeled as 1, 2, 3 and 4 in Figure 2.1 having different relaxations are analyzed separately and for each case, power spectrum projected on the atoms directly connected to that particular adatom are displayed in Figure 2.8. The corner adatoms on the faulted side in Figure 2.8(a) show peaks at different frequencies, 6 THz and 15 THz, indicated by \( P_1 \) and \( P_3 \) respectively, while the middle adatoms on the faulted side in Figure 2.8(b) have prominent peaks at \( P_1(8 \text{ THz}), P_2(10 \text{ THz}) \) and \( P_3(16.3 \text{ THz}) \). The power spectrum of the atoms on the unfaulted side is similar to that in Figure 2.8(b). The modes, \( P_3 \) and \( P_3' \), have identical motions whose polarization vectors involve out-of-phase oscillations of atoms along the [111]-direction as shown in Figure 2.9. This is consistent with previous theoretical calculations [14,26,27]. The amplitude of the 2nd-layer atom is quite big compared to those of the adatom and the 3rd-layer atom. Back-bone atoms move mainly in the plane but their oscillation strength is quite small.

We relate two distinct localized modes, \( P_1 \) and \( P_2 \), to the broad peak at 7.5 THz observed by EEL [23]. The adatoms have a large amplitude while the 2nd-layer atoms moving in-phase with adatoms have a small amplitude (Figure 2.9(a) and (b)). Significant splitting of the localized modes at different adatomic sites is
FIGURE 2.8 Power spectra of the adatoms, the back-bone atoms and the 2nd-layer atoms underneath, of (a) the corner adatomic site on the faulted side and (b) the middle adatomic site on the faulted side. The numbers on the top right hand side are consistent with the labels on the atoms in Figure 2.1, i.e., (a)-(1) is the power spectrum of the adatom on the faulted side. Power spectrum is estimated by the FFT and properly normalized. The solid lines are power spectrum of polarization vectors projected along the [111]-direction while the dotted lines are projected in the (111)-plane. The power spectra of the atoms on the unfaulted side are similar to those of the middle adatomic site on the faulted side (b). There is a difference in frequency between the identical modes ($P_{1}$ vs $P_{1}$, and $P_{2}$ vs $P_{2}$) depending upon the location of the adatoms, which is believed to be caused by the difference in the local environment of the adatoms.
FIGURE 2.8
FIGURE 2.9 Polarization vectors of localized phonons at adatomic sites indicated by $P_1$, $P_2$ and $P_3$ in Figure 2.8: (a) in-phase vibrations of an adatom and atoms underneath along the [111]-direction with a large amplitude on the adatom at 8 THz. (b) Oscillation of the 3rd-layer atom is out-of-phase with respect to the adatom. The amplitudes of the 2nd-layer atom and the backbone atoms are small compared to those of the adatom and the 3rd-layer atom (10 THz). (c) The high frequency mode at 16 THz has a large amplitude on the 2nd-layer atoms, vibrating out of phase with respect to the adatoms. This mode has a small amplitude on the back-bone atoms on the 1st-layer.
attributed to the difference in the local environment of these adatoms. The local electronic structure of different adatoms is different depending upon the location of the adatoms in a cell; the electronic structure is directly related to the amount of relaxation of the particular adatoms [24].

Finally, we have observed a new mode which involves the motion of many surface atoms. The peak ($P_4$) at 12.5 THz is present in the spectra of most of the surface atoms as can be seen in Figure 2.7. The amplitudes of the surface-free atoms and the back-bone atoms (labeled as 8 and 9 in Figure 2.1) are comparable for this mode. The projected surface mode on the (111)-plane is shown in Figure 2.10. This mode is three-fold symmetric within a subcell and the polarization vectors in the two subcells are 180° out-of-phase with respect to each other. Considering the left subcell in Figure 2.10, inward vibration of three-surface-free atoms is accompanied by outward motion of the rest of the 1st-layer atoms. Back-bone atoms connected to the middle adatoms have larger amplitude than those connected to the corner adatoms. The dimer row behaves as a boundary between the subcells and atoms show optical polarization along the dimer row.

We also observe a strong peak at 3 THz, decaying in amplitude for the inner layer atoms, whose frequency is close to the Rayleigh mode observed by inelastic He-atom scattering measurements of Si(111) [28]. We believe that this peak originates from the Rayleigh mode of the unreconstructed Si(111) surface at the zone boundaries, folded back at $\Gamma$.

2.6. Conclusions

We have determined the phonon frequencies of bulk silicon and the 7×7 recon-
FIGURE 2.10 The polarization vectors of the surface mode at 12.5 THz projected on the (111)-plane. The mode is three-fold symmetric with respect to the center of the subcells. The adatoms, the 1st-layer and the 2nd-layer atoms take part in this mode and are shown with the same labeling of atoms as in Figure 2.1. The back-bone atoms of a subcell move outwards from the center while the surface-free atoms (gray circles) breathe inwards. The modes in the two subcells are out-of-phase with respect to each other. The length of the arrows is proportional to the amplitudes of atoms.
structured surface by performing Car-Parrinello Molecular Dynamics (CPMD) simulations based on a tight-binding Hamiltonian. Since the physical time spanned by these simulations is comparatively long, of the order of ten psecs, the peaks in the power spectrum obtained from the FFT of the ionic velocities are quite sharp. Simulations of such large systems over these physical times is made possible by the parallelization of the algorithm for distributed memory parallel computers. For bulk silicon, our results are about 5% of the experimental results. For the 7×7 reconstructed surface, in addition to the localized modes which have been observed before, we have seen a new surface mode which involves the vibrations of most of the 1st-layer atoms. Since our simulation involved all the 400 atoms in the supercell, we were able to directly observe the peak corresponding to this mode in the power spectrum and determine its polarization vectors from the simulation data.
REFERENCES

3.1. Introduction

Most electronic structure calculations performed nowadays in condensed matter physics are based on a single particle orbital formulation. Within this framework, the ground state energy ($E_0$) of a multi-atomic system is obtained by solving a set of eigenvalue equations. Until recently, this has been accomplished by searching directly the eigenstates of the single particle Hamiltonian ($\hat{H}$), which in general are extended states, e.g. Bloch states in a periodic system [1].

In the last few years, methods for electronic structure (ES) calculations have been introduced, which are based on a Wannier-like representation of the electronic wave functions [2,3,4,5,6,7,8]. The main motivation for choosing such a representation was the search for methods for which the computational effort scales linearly with system size ($O(N)$ methods). Very recently, real space Wannier-like formulations were also used to describe the response of an insulator to an external electric field [9]. Within these approaches, a suitably defined total energy functional ($E$) is
minimized with respect to orbitals constrained to be localized in finite regions of real space, called localization regions. The minimization of the energy functional does not require the computation of either eigenvalues or eigenstates of $\hat{H}$.

In the absence of localization constraints, one can prove [4] that the absolute minimum of $E$ ($E_0$) coincides with $E_0$. In the presence of localization constraints, a variational approximation to the electronic wave functions is introduced and therefore $\tilde{E}_0$ lies above $E_0$. However, the difference between $\tilde{E}_0$ and $E_0$ can be reduced in a systematic way, by increasing the size of the localization regions. We note that localization constraints do not introduce any approximation when the resulting localized orbitals can be obtained by a unitary transformation of the occupied eigenstates. Therefore the use of localized orbitals is well justified for, e.g., periodic insulators, for which exponentially localized Wannier functions can be constructed by a unitary transformation of occupied Bloch states [10].

The minimization of the functional $E$ with respect to extended states can be easily performed so as to lead directly to the ground state energy $E_0$, without traps at local minima or metastable configurations [5]. On the contrary, the minimization of $E$ with respect to localized orbitals can lead to a variety of minima [5,7]. In order to attain the minimum representing the ground state, information about the bonding properties of the system has to be included in the input wave functions. This implies a knowledge of the system that may be available only in particular cases, and it constitutes the major drawback of the orbital based $O(N)$ method, which has otherwise been shown to be an effective framework for large scale quantum simulations [11].

In this chapter, we propose a functional for orbital based $O(N)$ calculations,
whose minimization with respect to localized orbitals leads directly to a physical approximation of the ground state, without traps at local minima. This overcomes the multiple minima problem present within the original formulation [4,5] and makes it possible to perform $O(N)$ calculations for an arbitrary system, with totally unknown bonding properties. The present formulation has also other advantages with respect to the original one. While retaining the same computational cost, it allows one to decrease the error in the variational estimate of $E_0$, for a given size of the localization regions, and to improve the energy conservation during a molecular dynamics run.

The novel functional depends on a number of electronic orbitals ($M$) larger than the number of occupied states ($N/2$) of the $N$-electron system, and contains a parameter $\eta$ determining the total charge. During the functional minimization $\eta$ is varied until the total charge of the system equals the total number of electrons; thus when convergence is achieved, i.e. the ground state is attained, the value of $\eta$ coincides with that of the electronic chemical potential $\mu$. Once the ground state is obtained for a given ionic configuration, the corresponding wave functions and ionic positions can be used as a starting point for molecular dynamics simulations, which are then performed at fixed chemical potential. This is at variance with conventional ES calculations based on orbital formulations, where $N$ is always fixed, e.g. by imposing orthonormality constraints. Similar to the present approach, $O(N)$ calculations based on a density matrix formulation [12] are performed at fixed chemical potential. Consistently, the functional describing the total energy does not have multiple minima in the subspace of localized density matrices. However, whereas a density matrix approach presupposes the use of all the occupied and
unoccupied states (i.e. a number of states equal to \( n_{\text{basis}} \), where \( n_{\text{basis}} \) is the number of basis functions), in our formulation only a limited number of unoccupied states needs to be added to the set of occupied states, regardless of the basis set size. Therefore the present formulation can be efficiently applied also in computations where the number of basis functions is much larger than the number of occupied states in the system (e.g. first principles plane wave calculations).

3.2 Electronic structure calculations at a given chemical potential

3.2.1 Definition of the functional

We consider the energy functional \( E \) defined in Ref. 5, which depends on \( N/2 \) occupied orbitals, for a \( N \) electron system. We generalize \( E \) so as to depend on an arbitrary number \( M \) of orbitals, which can be larger than the number of occupied states \( N/2 \). For simplicity, we consider a non self-consistent Hamiltonian. The energy functional is written as:

\[
E[\{\psi\}, \eta, M] = 2 \sum_{ij=1}^{M} Q_{ij} < \psi_j | \hat{H} - \eta | \psi_i > + \eta N .
\] (3.1)

Here \( \{\psi\} \) is a set of \( M \) overlapping orbitals, \( \hat{H} \) the single particle Hamiltonian, \( \eta \) a parameter and \( Q \) a \((M \times M)\) matrix:

\[
Q = 2I - S .
\] (3.2)

\( S \) is the overlap matrix: \( S_{ij} = < \psi_i | \psi_j > \) and \( I \) is the identity matrix. This definition of the \( Q \) matrix corresponds to truncate the series expansion of the inverse of the overlap matrix to the first order (\( \mathcal{N} = 1 \), in the notation of Ref. 5). The charge
density is defined as

\[ \rho(r) = 2 \sum_{ij=1}^{M} < \psi_j | r | \psi_i > Q_{ij} . \] (3.3)

For \( M = N/2 \), one recovers the original energy functional for \( O(N) \) calculations.

We note that the energy functional in Eq. (3.1) can be expressed in terms of a density matrix \( \hat{\sigma} \{ \{ \psi \} \} \):

\[ E \{ \{ \psi \}, \eta, M \} = 2 \text{Tr} [(\hat{H} - \eta) \hat{\sigma}] + \eta N . \] (3.4)

Here the trace is computed over the \( n_{\text{basis}} \) functions used for the expansion of the \( \{ \psi \} \), and \( \hat{\sigma} \{ \{ \psi \} \} = \sum_{ij=1}^{M} | \psi_i > Q_{ij} < \psi_j | \).

Before discussing the use of the functional of Eq. (3.1) within a localized orbital formulation, it is useful to assess some of its general properties.

(i) \( E \{ \{ \psi \}, \eta, M \} \) is invariant under unitary transformations: \( \psi'_i = \sum_{j=1}^{M} U_{ij} \psi_j \), where \( U \) is a \( (M \times M) \) unitary matrix.

(ii) Orbitals with vanishing norms do not give any contribution to the energy functional \( E \{ \{ \psi \}, \eta, M \} \). If the overlap matrix \( S \) entering Eq. (1) has \( (M - M') \) eigenvalues equal to zero, then a unitary transformation \( U \) exists, such that \( \{ \psi' \} \) satisfies the condition:

\[ < \psi'_i | \psi'_i > = 0, \quad \text{for} \quad i = M' + 1, ..., M . \] (3.5)

Under this condition:

\[ E \{ \{ \psi \}, \eta, M \} = E \{ \{ \psi' \}, \eta, M' \} . \] (3.6)

We note that if \( Q \) is replaced by \( S^{-1} \) in the definition of \( E \{ \{ \psi \}, \eta, M \} \) (Eq. (3.1)), then orbitals with a vanishing norm give a non zero contribution to
the total energy, since for $< \psi_i | \psi_i > \rightarrow 0$ the eigenvalues of $S^{-1}$ go to infinity. Therefore the functional $E[\{\psi\}, \eta, M]$, with $Q$ replaced by $S^{-1}$, does not satisfy property (ii).

(iii) The ground state energy $E_0$ is a stationary point of $E[\{\psi\}, \eta, M]$. In order to prove this statement, we consider the following set of orbitals $\{\psi^0\}$:

$$|\psi^0_i > = |\chi_i > \quad \text{for} \quad i = 1, N/2$$
$$= |0 > \quad \text{for} \quad i = N/2 + 1, M,$$

where $|\chi_k >$ are the $n_{\text{basis}}$ eigenvectors of $\hat{H}$ with eigenvalue $\epsilon_k$. Hereafter we assume that $< x_k | x_k > = 1$ and $\epsilon_k \leq \epsilon_{k+1}$. The set $\{\psi^0\}$ fulfills Eq. (3.5), and therefore $E[\{\psi^0\}, \eta, M] = E[\{\psi^0\}, \eta, N/2] = E_0$. In addition, the set $\{\psi^0\}$ is a stationary point of $E[\{\psi\}, \eta, M]$, since $\partial E / \partial \psi^0_k(\{\psi^0\}) = 0$, where

$$\frac{\delta E}{\delta \psi_k} = 4 \sum_{j=1}^{M} [(\hat{H} - \eta)\psi_j > (Q_{jk}) - |\psi_j > < \psi_j | (\hat{H} - \eta)\psi_k >].$$

(iv) The stationary point $E_0$ is a minimum of $E[\{\psi\}, \eta, M]$ if $\eta$ is equal to the electronic chemical potential $\mu$. We will only consider electrons at zero temperature, and therefore we choose $\mu$ such that $\epsilon_{N/2} < \mu < \epsilon_{N/2+1}$. This property will be proved in the next section.

3.2.2 Role of the chemical potential

Before giving a proof of property (iv) stated in section 3.2.1, we discuss a simple example which is useful to illustrate the role played by $\eta$ in the minimization of the energy functional $E$. For this purpose, we evaluate the functional $E[\{\psi\}, \eta, M]$ for
FIGURE 3.1 Plot of the function $f(a_i, \eta) = (\epsilon_i - \eta)a_i^2(2 - a_i^2)$ for a positive and a negative value of $(\epsilon_i - \eta)$. 
a set of $M$ eigenstates of the Hamiltonian. In particular, we choose a set $\{\psi\}$ such that $|\psi_i\rangle = a_i|\chi_i\rangle$, with arbitrary $a_i$. In this case the energy functional becomes:

$$E[\{a\}, \eta, M] = 2 \sum_{i=1}^{M} (c_i - \eta)(2 - a_i^2)a_i^2 + \eta N$$

(3.9)

As illustrated in Fig. 3.1, the function $(c_i - \eta)(2 - a_i^2)a_i^2$ has a minimum at $a_i = 0$ if $c_i > \eta$, and a minimum at $a_i = 1$ if $c_i < \eta$. Thus the functional $E[\{a\}, \eta, M]$ has a minimum for a set $\{a^0\}$ such that $a_i^0 = 1$ if $c_i < \eta$, and $a_i^0 = 0$ if $c_i > \eta$. At the minimum, Eq. (3.9) becomes

$$E_{\text{min}} = 2 \sum_{i=1}^{M'} c_i + \eta(N - 2M')$$

(3.10)

where $c_{M'} < \eta < c_{M'+1}$ and the total charge of the system is $\rho_{\text{tot}} = 2 \sum_{i=1}^{M}(2 - a_i^2)a_i^2 = 2M'$. We can now choose $\eta$ so that $\rho$ is equal to the actual number of electrons in the system. This is accomplished by setting $\rho_{N/2} < \eta < \rho_{N/2+1}$, i.e. by choosing $\eta$ equal to the electronic chemical potential $\mu$. We then have $\rho_{\text{tot}} = 2M' = N$ and $E_{\text{min}} = E_0$. In order to give a general proof of property (iv) (section 3.2.1), we show that the Hessian matrix $(h)$ of the functional $E[\{\psi\}, \eta, M]$ at the ground state is positive definite, if $\eta = \mu$. The computation of the eigenvalues of $h$ follows closely the procedure used in Ref. [5] to calculate the Hessian matrix of $E[\{\psi\}, \eta, N/2]$ at the ground state. Since the functional $E[\{\psi\}, \eta, M]$ is invariant under unitary rotations of the $\{\psi\}$, we can write a generic variation of the wave function with respect to the ground state as

$$|\psi_i^0\rangle = |\chi_i\rangle + |\Delta_i\rangle \quad \text{for} \quad i = 1, N/2$$

$$|0\rangle + |\Delta_i\rangle \quad \text{for} \quad i = N/2 + 1, M$$

(3.11)
where

\[ |\Delta_i> = \sum_{l=1}^{n_{\text{basis}}} c_l^i |x_l> . \]  

(3.12)

By inserting Eq.(3.11) into Eq. (3.1), it is straightforward to show that the first order term in the \{c\} coefficients vanishes for any value of the parameter \(\eta\), consistently with property (iii) stated in section 3.2.1. The remaining second order term can be written as follows:

\[
E^{(2)} = \sum_{i=1}^{N/2} \sum_{m=N/2+1}^{n_{\text{basis}}} 2[\epsilon_m - \epsilon_i](c_m^i)^2 + \sum_{ij=1}^{N/2} 8[\eta - (\epsilon_i + \epsilon_j)/2](1/\sqrt{2})(c_j^i + c_i^j)^2 + \sum_{i=N/2+1}^{M} \sum_{m=N/2+1}^{n_{\text{basis}}} 4[\epsilon_m - \eta](c_m^i)^2 .
\]

(3.13)

The eigenvalues \(2[\epsilon_m - \epsilon_i]\) are independent of \(\eta\) and always positive, whereas the eigenvalues \(8[\eta - (\epsilon_i + \epsilon_j)/2]\) and \(4[\epsilon_m - \eta]\) are positive, if and only if \(\eta\) coincides with the chemical potential \(\mu\). This proves property (iv) of section 3.2.1.

### 3.3 \(O(N)\) calculations with overlapping localized orbitals

#### 3.3.1 Localization of orbitals and practical implementation

We now turn to the discussion of the functional defined in section 3.2.1 within a localized orbital formulation. The use of localized orbitals is a key feature to achieve linear system-size scaling [5] calculations. Orbitals are constrained to be localized in appropriate regions of space, called localization regions, i.e. they have non zero components only inside a given localization region, whereas they are zero outside the localization region. The choice of the number of localization regions...
and of their centers is arbitrary. In the calculations that will be discussed in the next sections, we chose a number of localization regions equal to the number of atoms, each centered at an atomic site \( I \). We then associated an equal number of localized orbitals \( n_s \) to a localization region, e.g. two and three localized orbitals for \( M = N/2 \) and \( M = 3N/4 \), respectively. \( M = N n_s/n_{\text{val}} \), where \( n_{\text{val}} \) is the number of valence electrons per atom).

We will present electronic structure calculations and molecular dynamics simulations of various carbon systems, carried out within a tight binding approach. We adopted the TB Hamiltonian proposed by Xu et al. [13,14], which includes non zero hopping terms only between the first nearest neighbors. In a tight-binding picture, a localization region centered on the atomic site \( I \) can be identified with the set \( \{LR_I\} \) of atoms belonging to the localization region. Atoms are included in \( \{LR_I\} \), if they belong to the \( N_h \) nearest neighbor of the center atom. Then, the localized orbital \( |\psi^L_I > \), whose center is the \( I \)th atom, is expressed as

\[
|\psi^L_I > = \sum_{J \in \{LR_I\}} \sum_{\alpha} C^J_{\alpha} |\phi_{J\alpha} > ,
\]

where \( |\phi_{J\alpha} > \)'s are the atomic basis functions of the atom \( J \) and the index \( \alpha \) indicates the atomic components \( (s, p_x, p_y \text{ or } p_z) \). In our computations, the generalized energy functional was minimized with respect to the localized orbitals \( \{\psi^L\} \) by performing a conjugate gradient (CG) procedure, both for structural optimizations and molecular dynamics simulations. For some calculations it was necessary to use a non zero Hubbard-like term [13] to prevent unphysical charge transfers. In this case the line minimization required in a CG procedure reduces to the minimization of a polynomial of eighth degree in the variation of the wave function along the
conjugate direction. We performed an exact line minimization by evaluating the coefficients of the polynomial.

3.3.2 The multiple minima problem

As mentioned in the introduction, the major drawback of the original formulation of orbital based $O(N)$ calculations is the so called multiple minima problem. Experience has shown that the minimization of $E[\{\psi\}, \eta, N/2]$ with respect to localized orbitals usually leads to a variety of minima [5,7], and that the physical properties of the minimum reached during a functional minimization depend upon the choice for the input wave functions. If the input wave functions are constructed by taking advantage of bonding information about the ground state, then a minimum representing a physical approximation to the ground state may be reached, after an iterative minimization. On the contrary, if no information on the ground state is included in the localized orbitals from the start, the functional minimization usually leads to a local minimum, which is characterized by an unphysical charge density distribution.

This is illustrated for a particular case in Table 3.1 and Fig. 3.2, where we present the results of a series of tight binding (TB) calculations using localized orbitals, for a 256 carbon atom slab. The slab, consisting of 16 layers, represents bulk diamond terminated by a C(111)-2 × 1 Pandey reconstructed surface on each side. We considered localization regions (LRs) extending up to second neighbors ($N_a=2$). We performed conjugate gradient minimizations of the electronic structure using two localized orbitals per LR ($n_x=2$), which correspond to the case $M = N/2$ in Eq. (3.1), i.e. to the original formulation of $O(N)$ calculations. These minimiza-
TABLE 3.1 Cohesive energy $E_{coh}$ (eV) of a 256 carbon atom slab. The slab, consisting of 16 layers, represents bulk diamond terminated by a C(111)-2 x 1 Pandey reconstructed surface on each side. $E_c$ was obtained by performing localized orbital calculations with two and three states ($n_s$) per atom (see text), and with three different inputs for the starting wave functions. *Totally random* input: the wave function expansion coefficients ($C_j^i, \text{sec Eq. 3.(14)}$) on each site of a localization region (LR) are random numbers, and orbitals belonging to the same LR are orthonormalized at the beginning of the calculations. *Atom by atom* input: each orbital has a non zero $C_j^i$ only on the atomic site to which it is associated, and for each atomic site this coefficient is chosen to be the same. *Layer by layer* input: each orbital has a non zero $C_j^i$ only on the atomic site to which it is associated, and the value of this coefficient is chosen to be the same for each equivalent atom in a layer. In the case of *atom by atom* and *layer by layer* inputs, the initial wave functions are an orthonormal set. The calculations were performed with $\eta=7.5$ eV and $\eta=3.1$ eV for $n_s=2$ and $n_s=3$, respectively, and with LRs extending up to second neighbors ($N_h=2$, amounting at most to 17 atoms per LR). The value for $E_c$ obtained by direct diagonalization is 7.04 eV. (See also Figure 3.1). The highest occupied and lowest unoccupied eigenvalues are 2.85 and 3.42 eV, respectively. In all calculations the Hubbard like term was set at zero.

<table>
<thead>
<tr>
<th>Wave Function input</th>
<th>$E_{coh}$ [$n_s=2$]</th>
<th>$E_{coh}$ [$n_s=3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Totally random</em></td>
<td>6.837</td>
<td>6.978</td>
</tr>
<tr>
<td><em>Atom by atom</em></td>
<td>6.721</td>
<td>6.978</td>
</tr>
<tr>
<td><em>Layer by layer</em></td>
<td>6.930</td>
<td>6.978</td>
</tr>
</tbody>
</table>
FIGURE 3.2 Differential atomic charge ($\Delta \rho$) on each atomic site of a 256 carbon atom slab. The slab, consisting of 16 layers, represents bulk diamond terminated by a C(111)-2 × 1 Pandey reconstructed surface on each side. The ionic index indicates individual atomic sites belonging to the slab, which are ordered layer by layer, starting from the uppermost surface. The arrow indicates the slab center. $\Delta \rho_K = \rho_K - \rho^0$, where $\rho_K = 2 \sum_{ij=1}^{M} \sum_{\alpha} < \psi_i | \phi_{K\alpha} > Q_{ij} < \phi_{K\alpha} | \psi_j >$, $\rho^0 = 4$, and $K$ is the atomic site. In panels A, B and C we show the results of calculations performed with two orbitals per atomic site, and with the three different wave function inputs listed in Table 3.1, respectively.
1. Ionic Index 256

(A) Random

(B) Atom by Atom

(C) Layer by Layer

\[ \Delta p \]

1  Ionic Index 256

FIGURE 3.2
tions were carried out by starting from different wave function inputs. The only calculation which lead to a physical minimum was the one started with orbitals containing symmetry information about the system, as shown by comparing the results of Figure 3.2C with those of direct diagonalization, reported in Figure 3.3B. The other calculations lead to unphysical minima: when starting with a totally random input (Figures 3.2A), we found a local minimum with charged sites, located predominantly in the surface layers and in the middle of the slab. When starting from an atom by atom input (Figure 3.2B) we obtained a local minimum corresponding to two differently charged surfaces, one positively and the other negatively charged.

The local minima problem present in the original $O(N)$ formulation can be illustrated with a simple one dimensional model [15]. We consider a linear chain with $N_{\text{site}}$ sites and 2 $N_{\text{site}}$ electrons in a uniform electric field of magnitude $F$, with Hamiltonian:

$$\hat{H} = \sum_{K=1}^{N_{\text{site}}} (E_{\text{gap}}|e_K||-F|K(|e_K|+|g_K|)).$$

(3.15)

Here $|e_K>\text{ and }|g_K>$ are the highest and the lowest level of the isolated site $K$, respectively, and $E_{\text{gap}}$ is the splitting between these two levels. Since the hopping terms between different sites are set at zero, $|e_K>$ and $|g_K>$ are also eigenfunctions of the linear chain Hamiltonian. We now study the ground state of the system as a function of the electric field $F$. If $0 < F < E_{\text{gap}}/(N_{\text{site}} - 1)$, the total energy of the system is minimized by the set of orbitals $\psi_i^0$ given by:

$$|\psi_i^0> = |g_i> \quad \text{for} \quad i = 1, N_{\text{site}}.$$

(3.16)

If $E_{\text{gap}}/(N_{\text{site}} - 1) < F < E_{\text{gap}}/(N_{\text{site}} - 2)$, the eigenvalue of $|g_1>$ is higher than that of $|e_{N_{\text{site}}}>$, and therefore the total energy of the system is minimized by the
FIGURE 3.3 Differential atomic charge ($\Delta \rho$) on each atomic site for the same system as in Figure 3.2. The ionic index is the same as in Figure 3.2. In the upper panel we report the results of a calculation carried out with three orbitals ($n_s$) per atomic site, and with a totally random input for the initial wave functions (see Table 3.1). Contrary to the calculation started from a totally random input and performed with $n_s=2$ (see Figure 3.2A), the calculation with $n_s=3$ gives a ground state charge density very close to that obtained by direct diagonalization, shown in the lower panel.
following set of orbitals $|\psi_i^0>$:

$$|\psi_i^0> = |g_{i+1}>, \quad \text{for} \quad i = 1, N_{\text{site}} - 1,$$

$$|e_i>, \quad \text{for} \quad i = N_{\text{site}}.$$ \hspace{1cm} (3.17)

In both cases, the total energy of the linear chain system can be obtained exactly within a localized orbital picture, by considering $N_{\text{site}}$ LRs centered on atomic sites, which extend up to the first neighbors of a given site.

We first describe the total energy of the system with the functional $E[\{\psi \}, \eta, N/2]$. Within this framework, the set $|\psi_i^0>$ which minimizes $E[\{\psi \}, \eta, N/2]$ in the presence of a small field, i.e. when $0 < F < E_{\text{gap}}/(N_{\text{site}} - 1)$, is also a local minimum of $E[\{\psi \}, \eta, N/2]$ in the presence of a large field, i.e. when $E_{\text{gap}}/(N_{\text{site}} - 1) < F < E_{\text{gap}}/(N_{\text{site}} - 2)$. This can be easily seen from the second order expansion ($E^{(2)}$) of $E[\{\psi \}, \eta, N/2]$ around the set of orbitals defined in Eq. (3.16):

$$E^{(2)} = \sum_{i=1}^{N_{\text{site}}} \sum_{m \in \{LR_i\}} \sum_{m \neq 1} 2[E_{\text{gap}} - F(m - i)](e_m^i)^2$$

$$+ \sum_{i=1}^{N_{\text{site}}} \sum_{j \in \{LR_i\}} 8[\eta + F(i + j)] \frac{1}{\sqrt{2}} (g_j^i + g_j^i)^2,$$ \hspace{1cm} (3.18)

where $g_k^i$ and $e_k^i$ are the projection of the vector $|\psi_i> = |\psi_i^0>$ on the state $|g_k>$ and $|e_K>$, respectively. If the orbital are extended, the difference $(m - i)$ can be as large as $(N_{\text{site}} - 1)$ and the eigenvalues $[E_{\text{gap}} - F(m - i)]$ can be negative when $E_{\text{gap}}/(N_{\text{site}} - 1) < F < E_{\text{gap}}/(N_{\text{site}} - 2)$. However, if the orbital are localized the difference $(m - i)$ is smaller than $(N_{\text{site}} - 1)$ and the eigenvalues $[E_{\text{gap}} - F(m - i)]$ are always positive also for $E_{\text{gap}}/(N_{\text{site}} - 1) < F < E_{\text{gap}}/(N_{\text{site}} - 2)$. 

79
We now turn to a description of the total energy of the linear chain system with
the functional $E[\{\psi\}, \mu, M]$, where $M$ is larger than the number of occupied states
$N/2$, e.g. $M = 2N_{\text{site}}$. It is straightforward to show that contrary to a description
with $E[\{\psi\}, \eta, N/2]$, when using $E[\{\psi\}, \mu, M]$ the set of orbitals of Eq. (3.16) is not
a local minimum of the system in the presence of a large field. Indeed, according
to Eq. (3.13), the second order expansion $E^{(2)}$ is now given by:

$$E^{(2)} = \sum_{i=1}^{N_{\text{site}}} \sum_{m \in \{LR_i\}} 2[E_{\text{gap}} - F(m - i)](c_m^i)^2$$
$$+ \sum_{i=1}^{N_{\text{site}}} \sum_{j \in \{LR_i\}} 8[\mu + F\frac{i + j}{2}][\frac{1}{\sqrt{2}}(g_j^i + g_i^j)]^2$$
$$+ \sum_{i=N_{\text{site}}+1}^{2N_{\text{site}}} \sum_{m \in \{LR_i\}} 4[E_g - Fm - \mu](g_m^i)^2.$$  

(3.19)

Here the LOs with indices $i$ and $i + N_{\text{site}}$ are assigned to the localization region
$\{LR_i\}$. Both within an extended and a localized orbital picture, the eigenvalue
$4[E_g - FN_{\text{site}} - \mu]$ is negative when $E_{\text{gap}}/(N_{\text{site}} - 1) < F < E_{\text{gap}}/(N_{\text{site}} - 2)$.

This simple model shows that the extremum properties of $E[\{\psi\}, \eta, N/2]$ and
$E[\{\psi\}, \mu, M]$ are in general different, and in particular that local minima of the en-
ergy functional $E[\{\psi\}, \eta, N/2]$ are not necessarily so for $E[\{\psi\}, \mu, M]$. This suggests
that the use of the functional $E[\{\psi\}, \mu, M]$ may overcome the multiple minima prob-
lem encountered within a formulation based on $E[\{\psi\}, \eta, N/2]$. This simple model
suggests also the reason why the multiple minima problem should be overcome:
the minimization of $E[\{\psi\}, \mu, M]$ is performed by adjusting $\mu$ until the total charge
equals the total number of electrons in the system; this means that the appropriate
filling of the orbitals is determined by the $\text{global}$ variable $\mu$. This allows for long-
range charge transfers in the minimization process, irrespective of the extent of the localization in the wave functions. Therefore the presence of the *global* variable $\mu$, together with the augmented variational freedom of extra orbitals added to the definition of the functional, is expected to account for global changes taking place in the system.

### 3.2.3 Overcome of the multiple minima problem

We now present a series of numerical examples, showing that the minimization of the generalized functional $E[\{\psi\}, \eta, M]$ (Eq. (3.1)) with respect to localized orbitals can be performed without traps at local minima, as indicated by the simple model discussed in the previous section. We performed calculations for various carbon systems (bulk solids, surfaces, clusters and liquids), by using again LRs extending up to second neighbors ($N_h=2$). We considered three LOs per site ($n_s=3$), i.e. $M = 3N/2$ in Eq. (1). In all cases, using $n_s=3$ was sufficient to overcome the multiple minima problem present in the original formulation. We note that the generalized functional, although it includes a number of localized orbitals larger than the number of occupied states, still allows one to carry out electronic minimizations and molecular dynamics simulations with a computational effort scaling linearly with system size.

In Figure 3.4, we show the energy and the charge per atom during a conjugate gradient minimization of $E[\{\psi\}, \eta, M]$, for a 256 carbon atom slab, starting from a totally random input. The system is the same as the one studied in the previous section with $n_s=2$. The minimization was started with $\eta = 20$ eV; the parameter was then decreased every 20 iterations, and finally set at 3.1 eV, which corresponds to the value of the chemical potential. As discussed in section 3.2.2, for a given $\eta$
FIGURE 3.4 Total energy, $E_{\text{tot}}$, (upper panel) and total charge (lower panel) per atom, as a function of the number of iterations, for an electronic minimization of the same system as in Figures 3.1, 2 and Table 3.1. $E_{\text{tot}} = E\{\psi, \eta, M\}$ (see text). The minimization was carried out with three states per atom ($n_s = 3$) and was started from a totally random input. The chemical potential ($\eta$) was varied from 20 to 3.1 eV during the minimization. The final value of $\eta$ was chosen so that the total charge eventually be equal to the number of electrons in the system. In the upper panel, the inset shows $E_{\text{tot}}$ as a function of 500 iterations, converging to the value reported in Table 3.1, and indicated as a dotted line.
FIGURE 3.4
the integral of the charge density converges to a value which corresponds to filling all the orbitals with energies smaller than $\eta$. For example, for $\eta = 20$ eV the total charge per atom is equal to 6, i.e. all the $3N/2$ orbitals are filled. Eventually, when $\eta = \mu$ the total charge becomes equal to the number of electrons in the system. The way $\eta$ is varied during a minimization is not unique; however the final value of $\eta$ must be always adjusted so as to obtain the correct charge in the system. It is seen in Table I that all the minimizations with $n_s=3$ converge to the same value, irrespective of the input chosen for the wave function. This value corresponds to a physical minimum, as shown in Fig. 3 where we compare the charge density distribution with that obtained by direct diagonalization.

3.3.4 Improvement on variational estimates of the ground state properties

The use of the generalized functional and LOs not only overcomes the problem of multiple minima, but it also improves the variational estimate of $E_0$, for a given size of the LRs. This is shown in Table 3.2 and 3.3, where we compare the results of calculations using the same LRs but different number of orbitals ($n_s=2$ and 3), for various carbon systems. The improvement is particularly impressive in the case of $C_{60}$, where we also performed an optimization of the ionic structure. The error on the cohesive energy is decreased from 3 to 1.5% by increasing $n_s$ from 2 to 3. Most importantly the optimized ionic structure obtained with $n_s=3$ is in excellent agreement with that obtained with an extended orbital calculation. We note that localization constraints introduce a symmetry breaking in the system, i.e. LOs do not satisfy all the symmetry properties of the Hamiltonian eigenstates. In
<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Cohesive Energy (eV/atom)</th>
<th>Double-bond distance (Å)</th>
<th>Single-bond distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LO[N_{h}=2, n_{s}=2]</td>
<td>6.69 (6.89)</td>
<td>1.358-1.407</td>
<td>1.420-1.512</td>
</tr>
<tr>
<td>LO[N_{h}=2, n_{s}=3]</td>
<td>6.81 (6.91)</td>
<td>1.386-1.388</td>
<td>1.445-1.453</td>
</tr>
<tr>
<td>Extended Orbitals</td>
<td>6.91</td>
<td>1.393</td>
<td>1.440</td>
</tr>
</tbody>
</table>

**TABLE 3.2** Cohesive energy (eV) and length (Å) of the double and single bonds of C_{60}, as obtained from structural optimizations using localized (LO) and extended orbitals. In all calculations the Hubbard like term was set at zero. For comparison, cohesive energies obtained by direct diagonalization are given in parentheses. Computations with LO were performed by including two shells in a localization region (N_{h}=2, amounting to 10 atoms per localization region), and by considering two and three orbitals (n_{s}) per atom (see text).
### TABLE 3.3 Cohesive energy $E_{coh}$ (eV) of different forms of solid carbon computed at a given bond length $r_0$. The calculations were performed with supercells containing 216, 128 and 100 atoms for diamond, two-dimensional graphite and the linear chain, respectively. In calculations with localized orbitals we used 2 and 3 orbitals per atom ($n_\sigma$, see text). The LRs included two shells of neighbors ($N_h=2$), amounting to 17, 10 and 5 atoms per LR in the case of diamond, two-dimensional graphite and the linear chain, respectively.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Diamond ($r_0 = 1.54$ Å)</th>
<th>2D-Graphite ($r_0 = 1.42$ Å)</th>
<th>1D-Chain ($r_0 = 1.25$ Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{coh}$ [$N_h=2$, $n_\sigma=2$]</td>
<td>7.16</td>
<td>7.09</td>
<td>5.62</td>
</tr>
<tr>
<td>$E_{coh}$ [$N_h=2$, $n_\sigma=3$]</td>
<td>7.19</td>
<td>7.12</td>
<td>5.67</td>
</tr>
<tr>
<td>$E_{coh}$ [$N_h=\infty$]</td>
<td>7.26</td>
<td>7.28</td>
<td>5.93</td>
</tr>
</tbody>
</table>
The symmetry breaking is large when using \( n_s = 2 \); the deviation of the double and single bond lengths with respect to their average values are 3.5 and 6.3 %, respectively. On the contrary, in the optimized geometry obtained with \( n_s = 3 \) the symmetry breaking is very small (0.1 and 0.5 %, for the double and single bonds, respectively), compared to the icosahedral structure.

When using \( n_s = 2 \), the ground state LOs are nearly orthonormal [5], whereas minimizations with \( n_s = 3 \) yield overlapping LOs. Indeed when using \( n_s = 3 \), at the minimum the overlap matrix \( S \) has \( 2n_s \) eigenvalues close to 1 and \( n_s \) eigenvalues close to 0, and this condition can be satisfied with a non diagonal \( S \) matrix. We define a quantity measuring the orthogonality of the orbitals as

\[
\Delta^2 = \frac{(\sum_{ij=1}^{M} (\delta_{ij} - S_{ij})^2)/M}{\sum_{ij=1}^{M} \delta_{ij}^2/M}.
\]

In the case of \( C_{60} \), \( \Delta^2 \) is 2.5 \( 10^{-3} \) and 0.17 for \( n_s = 2 \) and \( n_s = 3 \), respectively. We also note that for various systems, the centers of the LOs \( \langle r^L \rangle \), defined as

\[
\langle r^L \rangle = \frac{\sum_K \sum_\alpha <\psi^L|\phi_{K\alpha}> \langle r_K \rangle \langle \phi_{K\alpha} |\psi^L \rangle}{\langle \psi^L |\psi^L \rangle},
\]

were always found to be located at distances shorter than one bond length from the center of their own LRs, when using \( n_s = 3 \). In the case of \( n_s = 2 \), we instead found cases, e.g. the \( C_{60} \) molecule, where some orbitals were centered far from their atomic sites and close to the border of their LRs.

3.4 Molecular dynamics simulations

In order to investigate the performances of the generalized functional (Eq. (3.1)) for molecular dynamics (MD) simulations, we carried out MD runs for liquid carbon at low density (2 gr cm\(^{-3}\)) and at 5000 K. We used a 64 atom cell with simple cubic
FIGURE 3.5 Energy per atom (E_{const}) as a function of the simulation time (t) for constant temperature (T) molecular dynamics (MD) simulations of liquid C. E_{const}=E_{kin} + E[\{\psi\}, \eta, M] + E_{thrm}, where E_{kin} is the ionic kinetic energy, E[\{\psi\}, \eta, M] is the ground state value of the electronic energy functional (see text) and E_{thrm} is the sum of the potential and kinetic energies associated to the Nose' thermostat. The LRs extend up to second neighbors (N_a=2, amounting on average to 18 atoms per LR). Lines (a) and (b) correspond to MD runs with three states per atom (n_a=3), whereas line (c) corresponds to a simulation with n_a=2. The time step used in the three MD runs was 30 a.u.(0.73 fs). At each step, the electronic structure was minimized by a conjugate gradient procedure with a fixed number of iterations (N_{iter}). The simulations represented by lines (b) and (c) require the same computational cost.
periodic boundary conditions and only the $\Gamma$ point to sample the BZ. We used a
cutoff radius of 2.45 Å for the hopping parameters entering the TB Hamiltonian
and for the two body repulsive potential [13] and $U = 8$ eV. In the case of 1-C it
was necessary to add an Hubbard like term to the Hamiltonian, in order to prevent
unphysical charge transfers during the simulations. Equilibration of the system was
performed in the canonical ensemble by using a Nosé thermostat [16].

Within the original $O(N)$ approach, MD runs for 1-C were found to be partic­
ularly demanding from the computational point of view, since they required many
iterations ($N_{\text{iter}}$) per ionic move (e.g. $N_{\text{iter}}=300$ for $\Delta t=30$ a.u.), in order to mini­
mize the energy functional [5]. Most importantly, during the simulation the system
could be trapped at a local minimum, evolve adiabatically from that minimum for
some time, and suddenly jump to another minimum lower in energy. This shows
up as a spike in the constant of motion of the system ($E_{\text{const}}$), as can be seen in
the line (c) of Figure 3.5, which displays $E_{\text{const}}$ for a run performed with $n_s=2$.
Because of local minima, a perfect conservation of energy could never be achieved
with $n_s=2$, even by increasing $N_{\text{iter}}$ to a very large number.

When MD runs are performed with $n_s=3$, the problem of local minima is over­
come; furthermore a significant improvement in the conservation of energy can be
achieved at the same computational cost as simulations with $n_s=2$. This is seen
in Figure 3.5 by comparing lines (b) and (c). When the generalized functional
is used, the accuracy of the energy conservation during a MD run is related only
to the convergence of the electronic minimization scheme: a good conservation of
energy can be obtained just by increasing $N_{\text{iter}}$. This is shown by the line (a) in
Figure 3.5. We note that the behavior of $E_{\text{const}}$ observed for all the simulations was
not affected by the presence of the thermostat. This was checked by repeating all
MD runs with three different masses ($Q_s$) for the Nosé thermostat ($Q_s=1,4,100$ in
the same units). The structural properties of 1-C computed from the MD runs with
$n_s=3$ showed a very good agreement with those previously obtained with $n_s=2$.

3.5 Conclusions

We have presented a generalization of orbital based $O(N)$ approaches, which relies
upon a novel functional, depending on a number of localized states larger than the
number of occupied states, and on a parameter which determines the total number
of electrons in the system. We have shown that the minimization of this functional
with respect to localized orbitals can be carried out without traps at local minima,
irrespective of the input chosen for the wave functions. In this way, the multiple
minima problem present in the original formulation is overcome, and $O(N)$ com­
putations can be performed for an arbitrary system, without knowing any bonding
properties of the system for the calculation input. We have also presented a series of
tight binding calculations for various carbon systems, showing that the generalized
$O(N)$ approach allows one to decrease the error in the variational estimate of the
ground state properties, and to improve energy conservation, i.e. efficiency, during
a molecular dynamics run. This can be accomplished at the same computational
cost as within the original formulation. At variance from $O(N)$ density matrix ap­
proaches, our formulation requires that only a limited number of unoccupied states
be included in the energy functional, regardless of the basis set size. Therefore
the present formulation can be efficiently applied also in computations where the
number of basis functions is much larger than the number of occupied states in the
system (e.g. first principles plane wave calculations).
REFERENCES


14. We used a cutoff radius of 2.30 Å for the hopping parameters of $\hat{H}$ and for the two body repulsive potential, and $U=0$ eV for the Hubbard like term (see Ref.(13)).

15. A similar model was used by D. Vanderbilt to show numerically the presence of local minima in the functional $E[\{\varphi^0\}, \eta, N/2]$ (private communication).

4.1. Introduction

The decreasing size of semiconductor devices requires precise control of device structures, particularly dopant distributions. Ion implantation introduces energetic charged atomic particles in a substrate for the purpose of changing electrical, metallurgical and chemical properties of the substrate. The wide use of ion implantation is due to its precise control over total dopant doses, depth profiles and the area uniformity. However, ion implantation induces transient enhanced diffusion (TED) of dopants: the diffusivity of the dopants is abnormally enhanced for a transient period of time after ion-implantation [1]. Many studies have suggested that lattice damages, introduced during ion implantation, are responsible for fast diffusion of dopants [2,3].

In particular, the diffusivity of boron during annealing in ion-implanted samples is enhanced by many orders of magnitude greater than B diffusivity in a thermal equilibrium [2]. This transient enhanced diffusion of B places limitations of the use
of B⁺-implantation in fabricating submicron devices. Boron TED occurs due to excessive Si interstitials, which are created by B⁺-implantation and contribute to the fast diffusion of B [1,3]. The boron diffusion via pairing of B and Si interstitials has been supported by experiments and theories [1]. Experiments observe enhancement of the B diffusivity when Si interstitials are selectively injected by surface oxidation [4] and by Si⁺-implantation [3]. First principle calculations reported that the activation energy of B diffusion associated with Si interstitials is the lowest among possible diffusion mechanisms [5,6]. Therefore, the concentration of Si interstitials after the ion implantation and during the thermal annealing process is an important parameter to determine the final depth profile of B in the ion-implanted samples.

The concentration of Si interstitials depends on (1) the ion implantation conditions – the incident energy and the dose – and (2) the temperature at which thermal annealing is performed. Implantation at a higher incident energy or with a higher dose of the ions generates more Si interstitials. As the name transient enhanced diffusion indicates, the enhancement factor of the B diffusivity decays as the thermal annealing proceeds, and eventually the diffusivity of the B converges to that in a thermal equilibrium. The temporal extent of the enhanced diffusion of B decrease at higher annealing temperatures, since the excessive Si interstitials migrate to the regular lattice sites in a shorter period of time [2]. It is observed that the temporal extent (duration of the boron TED) is exponentially activated. The activation energy, depending on the ion implantation conditions, shows a large variance: 1–5 eV [7,8].

This activation energy summarizes complex processes for B diffusion in ion-implanted samples – generation, diffusion and annihilation of the Si interstitials as
well as the interactions of B with the B and Si interstitials. Studies showed that the time evolution of the interstitial concentration during the boron TED is governed by trapping mechanisms of Si interstitials to interstitial storage region [9,10]. The energy required to release a Si interstitial from the possible interstitial storages can be one of many contributing variables to determine the activation energy. A higher energy would be required to release interstitials from more stable interstitial storages and, therefore, the TED would last longer at a given annealing temperature until all interstitials are evaporated from the storages.

Recently, Eaglesham et al. [10] and Stolk et al. [11] suggested that emission of Si interstitials from particular extended defects, namely {311} defects, causes the boron TED. They observed that the dissolution of the {311} defects occurs at the same time and the temperature conditions as boron TED. The extended {311} defects are detected under B⁺-implantation at an incident energy of few tens of eV [3,11] and the corresponding activation energy of the boron TED was obtained at 3-5 eV [7]. The high value of the activation energy can be related to the stability of the {311} defects with respect to isolated interstitials. However, boron TED has been also observed without detecting any macroscopic defect, when the energy of the B⁺-implantation decreases below 10 keV [8]. A lower activation energy (about 1 eV) was estimated for this low-energy ion implantation. This low-energy B⁺-implantation experiment suggests that the formation of stable {311} defects depends on the interstitial concentrations. Furthermore, the observation of boron TED in the absence of the observable {311} defects suggests that microscopic interstitial clusters may exist and contribute to the B diffusion by releasing interstitials at a lower energy cost. It is possible that the microscopic interstitial clusters are
related to the \{311\} defects and the formation and dissolution of the defects, from the interstitial clusters to the extended \{311\} defects, can be explained by common mechanisms.

The proposition that the \{311\} defects are formed by condensation of interstitials and provide interstitial sources during boron TED has been supported by experiments using a variety of procedures to inject Si interstitials into bulk systems: the \{311\} defects are observed to be formed by surface oxidation \[4\], and by GeV-electron irradiation \[12\] and by ion implantations \[11\].

The \{311\} defects are often called rod-like, because they are typically elongated along the (011) direction as much as a micron \[12,13\]. The width of the \{311\} defects ranges 1 - 100 nm along the (233) direction, perpendicular to the elongation direction. The name \{311\} defects indicates the observed habit plane \[14\] on which the rod-like defects lie, namely the \{311\} plane formed by the (011) and (233) directions.

Here, we present total energy calculations based on the tight-binding Hamiltonian scheme (i) to study the structural properties and energetics of the \{311\} defects as function of their dimensions and interstitial concentrations and (ii) to find possible mechanisms of interstitial capture by and release from the \{311\} defects. We investigate the \{311\} defects systematically from few-interstitial clusters to planar defects. Our results can be summarized as follows.

1. **Interstitial chain – the basic building block of the \{311\} defects**: we show that an interstitial chain along the (011) direction is stable with respect to isolated interstitials. The formation energy of the interstitial chains, $E_{\text{int}}^f = 2 \text{ eV per interstitial}$, is smaller than the formation energies of isolated interstitials, $3 - 5$
cV. Interstitial chains constitute basic building blocks of the \{311\} defects, i.e., extended defects on the \{311\} habit plane can be constructed by arranging the interstitial chains along the (233) direction.

(2) Stability of the \{311\} defects: interstitial chains along the (011) direction are stable against the isolated interstitials if they contain more than 2 interstitials. The formation energy per interstitial decreases linearly with the length of the interstitial chains along the (011) directions. More stable extended \{311\} defects than isolated interstitial chains are formed by condensation of interstitial chains along the (233) direction. The interstitial concentration of the most stable \{311\} defect, a planar defect, is \(5.45 \times 10^{14}/\text{cm}^2\).

(3) Growth mechanism: the stability dependence of the \{311\} defects on the interstitial concentration indicates that finite-size interstitial clusters capture interstitials to grow into the interstitials chains along the (011) direction. The elongated interstitial chains are then further stabilized by capturing interstitials or interstitial chains side by side along the (233) direction. This growth mechanism based on the stability study is in a good agreement with the experimental claims that the elongation of the rod-like \{311\} defects along the (011) direction precedes the growth in the width along the (233) direction.

(4) Propagation of the interstitial chains: we propose a mechanism which can account for the motion of interstitial chains in the direction perpendicular to the chain direction with a relatively small energy barrier. Successive rotations of pair atoms on the \{011\} plane displace the interstitial chains. The growth of the \{311\} defects along the (233) direction can be explained by propagations of interstitial chains which are attracted to and captured by the already existing \{311\} defects.
We show that V-shaped bend structure and atomic steps found in the transmission electron microscopy (TED) images can be formed by combinations of the interstitial chains and the planar rotations.

4.2. Calculational details

We perform total energy calculations based on a linear-scaling method in a tight-binding representation [15], using supercell methods at the \( \Gamma \) point. A tight-binding Hamiltonian developed by Kwon et al. [16] is used to study the defect structures. This TB Hamiltonian gives a good description of the relative energies and equilibrium volumes of the diamond structure and the metallic phases. One flaw of this Hamiltonian is that its ground state structure of the crystalline silicon is the clathrate structure, which has the same coordination of the diamond structure and consists of five- and six-member rings [17]. We find the cohesive energy of the clathrate structure is calculated indeed 0.07 eV lower than that of the diamond structure. In addition, the optical phonon frequencies of the diamond structure are overestimated by 30% compared to the experimental values. On the other hand, this TB Hamiltonian describes the elastic properties of the diamond structure with an error less than 5% compared to experiments and, more importantly, gives the formation energies of the point defects such as vacancies and interstitials which are in good agreements with those by the LDA calculations [18,19,20,21].

The total energy calculations of defects requires large supercells to obtain converged formation energies, mainly due to the long-range structural relaxation. We use the orbital-based linear-scaling method implemented on Cray-T3D [22]. We choose a spherical localization of 6 Å for less than 1% error in the total energy.
(about 30 meV per atom) compared to those obtained by exact calculations by diagonalizations. The chemical potential, $\mu$, is adjusted to achieve the correct number of electrons with an error less than $10^{-5}$ electron charge. Significant charge transfer is prevented by using a finite Hubbard-like term ($U = 4$ eV); however, little differences are observed from a finite $U$ and $U = 0$ in the relaxed atomic structures and in the total energies.

Figure 4.1 shows the smallest orthorombic unit cell used to study $\{311\}$ defects. The $[311]$ direction, normal to the habit plane of the defects, is chosen as the $z$ axis and the $[0\bar{1}1]$ and $[\bar{2}3\bar{3}]$ directions as the $x$ and $y$ axes, respectively. The unit lengths along the three principal axes are $L_{x0} = a/\sqrt{2}$, $L_{y0} = a\sqrt{11}/\sqrt{2}$ and $L_{z0} = a\sqrt{11}$, for the lattice constant $a$ of the diamond structure Si. The lengths of a computational cell along the $[0\bar{1}1]$ and $[\bar{2}3\bar{3}]$ directions are varied by choosing integer multiples $(n_x, n_y)$ of $L_{x0}$ and $L_{y0}$ and the length along the $[311]$ direction at $L_z = 2L_{z0}$. Values for $n_x$ and $n_y$ are chosen so that the displacement of the atoms far from the defect core is less than 0.02 Å with respect to the regular lattice sites of the perfect diamond structure. Periodic boundary conditions are applied along all three directions. For the structural optimizations, initial configurations of the model structures are given properly by hands and constant temperature MD simulations are performed at 300 - 600 K for about 1 psec to avoid trapping in the local minima of the atomic structures with small energy barriers. Then, atomic positions are fully relaxed until the atomic force on each atom is less than 0.01 eV/Å.

We define formation energy of a defect structure which contains $N_{\text{int}}$ interstitials
FIGURE 4.1 An orthorombic unit cell used to describe the \{311\} defects. The three principal axes are along the [011], [233] and [311] directions. For the Si lattice constant \((a = 5.43 \text{ Å})\), the dimensions of the unit cell are \(L_{xo} = a/\sqrt{2}\), \(L_{yo} = a\sqrt{11}/\sqrt{2}\) and \(L_{zo} = a\sqrt{11}\). Supercell calculations at the \(\Gamma\) point are performed by taking a computational cell whose size is \(L_x = n_x \times L_{xo}, L_y = n_y \times L_{yo}\), and \(L_z = 2 \times L_{zo}\). Periodic boundary conditions are applied in all three directions.
TABLE 4.1 Formation energies of point defects calculated by using the TB Hamiltonian by Kwon et al. [16] compared with those from LDA calculations. A cubic unit cell is used for the calculation with three principal axes in the [100], [010] and [001] directions. For $a$, the lattice constant of the diamond structure, the sizes of the 64-, 512- and 1000-atom unit cell are $2a \times 2a \times 2a$, $4a \times 4a \times 4a$ and $5a \times 5a \times 5a$, respectively. The numbers in the parenthesis are calculated by taking 512-atom computational cells at the defect concentration of one per 64 atoms to mimic the integration over the Brillouin zone of the 64-atom supercell. For the vacancy calculation, an atom is removed from the diamond structure and then a small Jahn-Teller distortion –pairing of atoms around the vacancy– is introduced to the initial configuration to break the tetrahedral symmetry around the vacancy. The T-interstitial denotes an additional atom at the tetragonal site and the coordination of the interstitial is $(1/2, 1/2, 1/2)a$ in a cubic unit cell. An additional atom at the hexagonal site is called the H-interstitial whose coordination is $(3/8, 3/8, 5/8)a$ in a cubic unit cell. The (110)-interstitialcy is constructed by substituting a lattice atom with two atoms bonded along the (110) direction. In order to maintain the initial symmetry of the defects, constant temperature MD simulations are not performed to obtain relaxed atomic configurations around the defect. In particular, the T- and H-interstitial atoms are fixed at the initial positions, while the rest of atoms are free to move.

<table>
<thead>
<tr>
<th>Defect</th>
<th>One defect per</th>
<th>TB Calculations</th>
<th>LDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>64 atoms</td>
<td>512 atoms</td>
<td>1000 atoms</td>
</tr>
<tr>
<td>Vacancy</td>
<td>3.4 (4.5)</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>T Interstitial</td>
<td>3.7 (4.1)</td>
<td>3.9</td>
<td>4.1</td>
</tr>
<tr>
<td>H Interstitial</td>
<td>4.8 (5.2)</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>(110) interstitialcy</td>
<td>3.5 (4.0)</td>
<td>3.9</td>
<td>3.9</td>
</tr>
</tbody>
</table>
and $N_{\text{bulk}}$ Si atoms in a computational cell as

$$E_I \equiv E_{\text{tot}}[N_{\text{int}} + N_{\text{bulk}}] - \frac{N_{\text{int}} + N_{\text{bulk}}}{N_{\text{bulk}}} E_{\text{tot}}[N_{\text{bulk}}]. \tag{4.1}$$

The formation energy per interstitial, $E_{\text{int}}^f = E_I / N_{\text{int}}$, is used to compare defects at a wide range of interstitial concentrations. A smaller $E_{\text{int}}^f$ corresponds to a more stable interstitial defect. The formation energies of point defects – the vacancy, T-interstitial, H-interstitial and (011) interstitialcy – are listed in Table 4.1. Calculations by first-principle LDA [18,19,20,21] and by using this TB Hamiltonian [16] found that the (110)-interstitialcy is the most stable point defect among the point defects in Table 4.1. Our total energy calculation using a 1000-Si supercell gives $E_{(110)}^f = 3.9$ eV.

A binding energy of interstitials with respect to isolated interstitials is defined as

$$-E^b \equiv E_I - N_{\text{int}} E_{(110)}^f, \tag{4.2}$$

for $E_{(110)}^f$, the formation energy of an isolated (110)-interstitialcy. A positive binding energy of a defect containing interstitials indicates that the interstitial defect is stable with respect to isolated interstitials.

### 4.3. Interstitial chains along the (011) direction

Here, we discuss an interstitial chain structure which is stable against isolated interstitials and which constitutes a building block of the (311) defects. The interstitial chain structure in Figure 4.2 shows that interstitial chains along the (011) direction can be inserted into bulk Si without introducing any dangling bond by stacking pair interstitials with a periodicity of $L_x$. This arrangement of interstitials along
the (011) direction is favorable, since only two dangling bonds would be required for any finite-length interstitial chain [4,23]. Since the number of dangling bonds per interstitial is inversely proportional to the length of the chain, the interstitial chain becomes more stable as it grows along the (011) direction. The interstitial chain structures have also been used for an atomic model of planar {311} defects by Takeda et al. [24,25,26,27]

The most simple defect configuration containing interstitial chains, the structure in Figure 4.2(a), is obtained by inserting an interstitial chain into bulk Si. By adding two interstitials per plane, two bonds (dotted line) are broken and two seven-members are introduced along the ±[311] directions. The six-member ring at the center turns into two adjacent five-member rings. The bond-angle distortion ranges from -23° to 20° and the bond-length distortion from -0.13 to 0.03 Å. This chain configuration is a stable interstitial complex with a relatively small formation energy per interstitial, $E_{\text{int}} = 2.2$ eV, compared to that of isolated interstitials (3-5 eV).

More stable structures can be obtained by eliminating five-member rings which share common bonds. A rotation of the atoms, connected by a solid bond indicated by an arrow, converts the right five-member ring in Figure 4.2(a) into a six-member ring in Figure 4.2(b) and lowers the formation energy to 1.7 eV. This defect structure is characterized by a six-member ring surrounded by five- and seven-member rings and has a mirror symmetry with respect to the center of the six-member ring [28]. While the concentration of the additional atoms is two per unit length ($L_{2\theta}$), this configuration appears to have two interstitial chains due to its symmetry.

A rotation of the other solid bond results in an interstitial chain surrounded
FIGURE 4.2 An interstitial chain obtained by stacking pair interstitials with a periodicity of $L_{xo}$ along the (011) direction. The solid atoms are $L_{xo}/2$ into the plane with respect to the open-circled atoms. (a) An interstitial chain inserted into bulk Si is surrounded by two adjacent five-member rings. The dotted lines denote the bonds which are broken by addition of interstitial chains. This structure has a formation energy of 2.2 eV per interstitial. (b) By a rotation of atoms connected by a solid bond (arrow), a more stable structure with $E_{int}^f = 1.7$ eV is obtained. The structure has a mirror symmetry with respect to the center of the six-member ring. The dashed line indicates the $\{100\}$ plane normal to the center line. (c) A rotation of the other bond results in an interstitial chain configuration of $E_{int}^f = 1.7$ eV. The symmetry of the structure is an inversion symmetry with respect to the center of pair interstitials on the $\{311\}$ plane (dashed line).
FIGURE 4.2

(a) $E_{\text{int}} = 2.2 \text{ eV}$

(b) $E_{\text{int}} = 1.7 \text{ eV}$

(c) $E_{\text{int}} = 1.7 \text{ eV}$
by six- and five-member rings in Figure 4.2(c). This configuration has an inversion symmetry with respect to the center of the interstitial pairs. The formation energy is 1.7 eV per interstitial and the corresponding bond-angle and bond-length distortions are $-15^\circ$ to $20^\circ$ and -0.1 to 0.03 Å. We label the structure in Figure 4.2(b) as an $I$-chain on {100} plane and that in Figure 4.2(c) as an $I$-chain on {311} plane, based on the symmetry of the interstitial chains. These stable interstitial chains constitute basic building blocks of the {311} defects. Arranging interstitial chains side by side in the (233) direction results in the formation of even more stable extended defects lying on the {311} plane.

The small formation energy per interstitial (< 2 eV) of the interstitial chain structures in Figures 4.2(b) and (c) suggests that microscopic defects containing only a few interstitials may exist as stable structures as well. Interstitial clusters containing 2–6 interstitials are constructed by inserting finite-length interstitial chains into bulk Si. Table 4.2 gives the formation energies per interstitial ($E_{int}^f$) of finite-size interstitial clusters. Generally, $E_{int}^f$ decreases as the size of interstitial defects increases, while the binding energy increases. This $E_{int}^f$ dependence on the number of interstitials, i.e., the length of the interstitial chain, is consistent with experimental observation that the rod-like defects are extended along the (011) direction as long as a submicron [12,13,25]. The elongation of the {311} defects in the (011) direction is the consequence of the formation of the energetically favorable interstitial chain structures. This observation agrees with the energetic argument based on the minimum dangling bond ratio of the (011) chain structures.

Table II shows that microscopic defects containing more than two interstitials are stable with respect to isolated interstitials. A binding energy per interstitial
### TABLE 4.2

<table>
<thead>
<tr>
<th>( N_{\text{int}} )</th>
<th>( E_f/N_{\text{int}} )</th>
<th>( E^b )</th>
<th>( E^b/N_{\text{int}} )</th>
<th>( E_f/N_{\text{int}} )</th>
<th>( E^b )</th>
<th>( E^b/N_{\text{int}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.7</td>
<td>-1.6</td>
<td>-0.8</td>
<td>4.9</td>
<td>-2.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>3</td>
<td>3.7</td>
<td>0.6</td>
<td>0.2</td>
<td>3.4</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>3.4</td>
<td>2.0</td>
<td>0.5</td>
<td>3.3</td>
<td>2.4</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>4.5</td>
<td>1.0</td>
<td>2.9</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>2.8</td>
<td>6.6</td>
<td>1.1</td>
<td>2.8</td>
<td>6.6</td>
<td>1.1</td>
</tr>
<tr>
<td>( \infty )</td>
<td>1.7</td>
<td>2.2</td>
<td>1.7</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Orientation of the computational cell:

- \( ^a[0\bar{1}1] \times [\bar{3}2\bar{2}] \times [311] \)
- \( ^b[0\bar{1}1] \times [0\bar{1}1] \times [100] \)

**TABLE 4.2** Formation energy per interstitial, \( E_f^i \) in Eq. (4.1), and the binding energy, \( E^b \) in Eq. (4.2), of few-interstitial clusters. The interstitial clusters are constructed by inserting interstitial chains between bulk layers whose length is at least \( 6 \times L_{zo} \) along the [0\bar{1}1] direction. The length of an \( N_{\text{int}} \)-interstitial cluster along the (011) direction is \( N_{\text{int}} L_{zo} / 2 \). The orientation of the computational cells is chosen according to the symmetry of the interstitial chains. The bottom row shows \( E_f^i \) and \( E^b / N_{\text{int}} \) for the line defects: infinite interstitial chains along the [1\bar{1}0] direction (Figure 4.2). The size dependence of \( E_f^i \) shows that the interstitial clusters can trap interstitials to form more stable elongated structures.
can be interpreted as an average energy required to release interstitials from the interstitial clusters and the interstitial chains. The energy cost to evaporate interstitials increases as the size of the interstitial cluster grows: a smaller interstitial cluster would be dissolved at a lower annealing temperature or in a shorter period of time. Few-interstitial clusters, which are stable against isolated interstitials, and interstitial chains may be responsible for the boron TED with a small activation energy (< 2 eV) when no extended defects are detected [8].

4.4. Extended rod-like \{311\} defects

Here we show that extended \{311\} defects can be constructed by arranging the interstitial chains along the (233) direction. It has been observed that the rod-like defects elongated along the (011) direction grow thicker along the (233) direction, when there is a constant supply of interstitials [13]. Possible configurations consisting of two interstitial chains are shown in Figure 4.3. Extended \{311\} defects can be constructed by adding more interstitial chains along the [233] direction. As seen in Figure 4.3, the \{311\} habit plane of the defects is made of two orthogonal directions, the (011) and (233) directions. In forming defects extended along the [233] direction, the arrangement of interstitial chains should satisfy following conditions: when two interstitial chains are separated by $L_{ya}/2$ as in Figure 4.3(a), the pair include an $I^1$ and an $I^1$; when separated by $L_{ya}$, the pair consist of two identical interstitial chains, two $I^{11}$'s as in Figure 4.3(b) or two $I^{11}$'s. Otherwise, dangling bonds are introduced and the corresponding distortions in bond angles become much larger than typical bond-angle distortions of ±20° of the stable \{311\} defects. Indeed, molecular dynamics simulations at 600 K about 1 psec remove such configurations.
FIGURE 4.3 Projections on the \{0\overline{1}1\} plane of the rod-like \{311\} defects containing two interstitial chains. The solid atoms (\bullet) are deeper into the plane than the open-circled atoms (O) by $L_{20}/2$. Interstitial chains are specified by the upper atoms with respect to the \{311\} plane (dashed lines): (1) $I^1$, when the upper atoms are out-of the \{0\overline{1}1\} plane; and (2) $I^1$, when the upper atoms are into the \{0\overline{1}1\} plane. The rod-like \{311\} defects are believed to grow by adding interstitial chains along the [233] direction. Total energy calculations give the formation energy per interstitial at 1.5 eV for (a) and at 1.6 eV for (b). Seven-member rings ($E_7$'s) form boundaries between the defects and the bulk Si, and they can be converted into six-member rings ($E_6$) by rotations of the solid bonds (heavy lines). In a similar way, an eight-member ring $O_8$ can be converted into either a seven-member ring ($O_7$) or a six-member ring ($O_6$). The stability of the $E_7$ and $O_8$ units depends on the arrangement of interstitial chains. A rotation of any solid bond of (a) increases the total energy. However, more stable structures can be obtained by rotations of the solid bonds in (b) as far as the transformation doesn't introduce adjacent five-member rings.
A new structure, an eight-member ring, is shown in Figure 4.3(b). When two interstitial chains are separated by $L_{y0}$ in the [233] direction, there are three possible configurations: an eight-member ring ($O_8$); a seven-member ring ($O_7$); and a six-member ring ($O_6$). The three structures between two interstitial chains are related to each other by the same kind of planar rotations in Figure 4.2. The eight-member ring in Figure 4.3(b) can be converted into an $O_7$ or an $O_6$ unit by rotations of the solid bonds (heavy lines) on the $\{0\bar{1}1\}$ plane. An atomic model proposed by Takeda uses the eight-member ring as a basic unit in constructing the planar defects [24,26,27]. However, we consider three possibilities, the $O_8$, $O_7$ and $O_6$ units between two interstitial chains separated by $L_{y0}$. For all the structures we have studied, the six-member rings ($O_6$) between interstitial chains are found to be unstable with respect to the $O_8$ or $O_7$ units. A structure which forms a boundary between the defects and the bulk Si is denoted as $E_7$ according to the notation, introduced by Takeda [26,27]. Similarly to the eight-member rings, the seven-member rings ($E_7$) can be converted into six-member rings ($E_6$) by planar rotations of the solid bonds in Figure 4.3.

The formation energies of rod-like $\{311\}$ defects containing few interstitial chains are listed in Table 4.3. For example, the $E_711O_811E_7$ model structure has the elements: $I$ – interstitial chains; $O_8$ – eight-member rings between the interstitial chains; and $E_7$ – seven-member rings at the defect boundaries. Among possible combinations of the $O$ and $E$ units for the given arrangement of interstitial chains, configurations with a lower formation energy are listed in Table 4.3. The rod-like defects become more stable with increasing number of interstitial chains ($I$ units) in the [233] direction as seen the $E_{int}^f$'s of Table 4.3: the formation energy
decreases (i) when interstitial chains are added side by side in the [233] direction with a distance \( L_{y0}/2 \), Table 4.3 (a) \( \rightarrow \) (e); and (ii) when interstitial chains are added in the [233] direction in the presence of an \( O \) unit, Table 4.3 (f) \( \rightarrow \) (i).

As seen in Table 4.3, the eight-member rings (\( O_8 \)) are stable when they are separated by a distance equal to or larger than \( L_{y0} \). The formation energy of the \( E_7IIO_8IE_7 \) model structure is lowered by 0.1 eV by transformation of the \( O_8 \) unit to a seven-member ring (\( O_7 \)). On the other hand, the eight-member ring of \( E_7IIO_8IE_7 \) model is stable with respect to the \( E_7IIO_7IE_7 \) structure. Similarly, we observe that the seven-member ring at a defect boundary is stable, if there are more than 2 \( I \) units inserted between \( E_7 \) and the closest \( O \) or \( E \) unit. For example, the total energy increases when the seven-member rings (\( E_7 \)'s) are converted into six-member rings for the \( E_7IIIE_7 \) and \( E_7IIO_8IE_7 \) models.

We define an energy release \( \Delta E_I \), when an interstitial chain is added to a rod-like defect \( X \) containing \( N_{int} \) interstitials per \( L_{x0} \), as

\[
\Delta E_I = (N_{int}E_{int}^{I}[X] + 2E_{int}^{I}[E_7IE_7]) - (N_{int} + 2) \times E_{int}^{I}[X + I \rightarrow Y]. \tag{4.3}
\]

The formation energy, \( E_{int}^{I}[E_7IE_7] = 1.8 \) per interstitial, is used as the formation energy of an isolated interstitial chain, which contains two interstitials per unit length \( L_{x0} \). The energy release \( \Delta E_I \) for the \( E_7IIO_8IE_7 \) structure to capture an interstitial chain and become the \( E_7IIO_8IE_7 \) structure is 1.6 eV per unit length \( (L_{x0}) \). On the other hand, \( \Delta E_I = 1.0 \) eV for the \( E_7IIIIE_7 \) structure to become the \( E_7IIIIE_7 \) structure. The larger \( \Delta E_I \) for the \( E_7IIO_8IE_7 \) structure indicates that the \( E_7IIO_8IE_7 \) structure provides a more efficient sink of interstitials than the \( E_7IIIIE_7 \) structure, which contains the same number of interstitials per unit cell. The \( \Delta E_I \)'s for the \( E_7IIIE_7 \) structure suggest that the interstitials can be evaporated
<table>
<thead>
<tr>
<th>Model structure</th>
<th>$N_{\text{int}}$ (% of I units per unit cell*)</th>
<th>$E_{\text{int}}^I$ (eV)</th>
<th>$\Delta E_I : X + I \rightarrow Y$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) $E_7IIE_7^*$</td>
<td>2 (67)</td>
<td>1.8$^\dagger$</td>
<td>1.2: (a)+I $\rightarrow$ (b) 0.9: (a)+I $\rightarrow$ (f)</td>
</tr>
<tr>
<td>(b) $E_7IIIE_7$</td>
<td>4 (50)</td>
<td>1.5</td>
<td>1.6: (b)+I $\rightarrow$ (c) 1.0: (b)+I $\rightarrow$ (g)</td>
</tr>
<tr>
<td>(c) $E_7IIIIIE_7$</td>
<td>6 (60)</td>
<td>1.3</td>
<td>1.2: (c)+I $\rightarrow$ (d) 0.6: (c)+I $\rightarrow$ (h)</td>
</tr>
<tr>
<td>(d) $E_7IIIIIIIE_7$</td>
<td>8 (67)</td>
<td>1.3</td>
<td>1.0: (d)+I $\rightarrow$ (e)</td>
</tr>
<tr>
<td>(e) $E_7IIIIIIIE_7$</td>
<td>10 (71)</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>(f) $E_7IO_7IE_7$ or $E_7IO_8IE_6$</td>
<td>4 (40)</td>
<td>1.6</td>
<td>1.3: (f)+I $\rightarrow$ (g)</td>
</tr>
<tr>
<td>(g) $E_7IIIO_7IE_7$ or $E_7IIIO_8IE_6$</td>
<td>6 (50)</td>
<td>1.4</td>
<td>1.1: (g)+I $\rightarrow$ (h) 1.3: (g)+I $\rightarrow$ (i)</td>
</tr>
<tr>
<td>(h) $E_7IIIO_8IE_7$</td>
<td>8 (57)</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>(i) $E_7IIIO_8IIIE_7$</td>
<td>8 (57)</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

* Unit cell: $L_{x0} \times 6L_{y0} \times 2L_{z0}$
** Identical to the I-chain on the {311} plane in Figure 4.2(c).

$^\dagger$ $E_{\text{int}}^I = 1.7$ eV for a unit cell $L_{x0} \times 3L_{y0} \times 2L_{z0}$

**TABLE 4.3** Formation energy of extended {311} defects consisting of interstitial chains. The computational cell is $3L_{x0} \times 6L_{y0} \times 2L_{z0}$ containing three unit cells in the [011] direction for all listed model structures. The ratio of the I unit to the extent of defects is given in percentage, e.g., $3/6 = 50\%$ for the $E_7IIIO_8IE_7$ structure. The energy release, $\Delta E_I$, is defined in Eq. 4.3 upon adding an interstitial chain (I) to the rod-like defect X. Y denotes a defect structure constructed by adding an I with a distance of either $L_{y0}/2$ or $L_{y0}$ from the boundary interstitial chain of the defect X.
with a smaller energy cost from the $E_{T1081E7}$ structure than from the $E_{T111E7}$ structure.

Growth mechanism of the $\{311\}$ defects are suggested by both the $E_{int}^f$ at different interstitial concentrations and the energy release $\Delta E_I$, when an interstitial chain is added to an existing $\{311\}$ defect. Previously we showed that an interstitial chain can exist as a stable structure against isolated interstitials with an $E_{int}^f < 2.2$ eV, which is smaller than that of isolated interstitials. The interstitial chain can provide a sink of interstitials to capture interstitial chains along the $[233]$ direction. Reactions which release a larger energy to capture an interstitial chain are more likely to happen during the growth process.

We express the capturing of an interstitial chain by a rod-like $\{311\}$ defect symbolically as

\[
\cdots I E + I \rightarrow \cdots I I E_7 \quad \text{for } d = L_{yo}/2, \quad (4.4a)
\]

\[
\cdots I E + I \rightarrow \cdots I O I E \quad \text{for } d = L_{yo}, \quad (4.4b)
\]

Here, $d$ is the distance of the additional interstitial chain from the boundary interstitial chain. Table 4.3 shows that the energy release by addition of an interstitial chain is similar for either $d = L_{yo}/2$ or $d = L_{yo}$, which suggests that the interstitial-chain capturing mechanisms in Eq. (4.4) are equally likely to happen. In other words, an interstitial chain can be added next to the boundary interstitial chain with a distance either $L_{yo}/2$ or $L_{yo}$. Consequently, the $O$ units would be randomly introduced and the $\{311\}$ defects would have no particular periodic arrangement of the interstitial chains. In fact, experiments observe no particular periodicity of the
{311} defects in the (233) direction [25], while the periodicity in the (011) direction is identified to be \( L_{x0} \), which results from the interstitial chain structure.

We denote the "interstitial density" to be ratio of the number of interstitial chains to the total number of units in the defects:

\[
\text{"interstitial density"} \equiv \frac{N[I]}{N[I] + N[O] + N[E]}.
\]  (4.5)

We obtain the optimal ratio of the interstitial chains of 67% for the {311} defects based on following results: (i) the formation energy for the extended defects (3) – (5) in Table 4.3 is same with differences less than 0.1 eV. This formation energy, \( E_{\text{int}} = 1.3 \) eV, is smaller than \( E_{\text{int}} = 1.4 \) eV of a planar defect – an infinite sequence of the interstitial chains in the [233] direction (\( \cdots I I I I \cdots \equiv /I/ \)). (ii) The planar defect consisting of sequences of \( I I O_8 \) structure, \( \cdots I I O_8 I I O_8 \cdots \equiv /I I O_8/ \) model, is found to be very stable with the smallest \( E_{\text{int}} = 1.2 \) eV among the model structures we have investigated. This interstitial density (67%) is in a good agreement with the observed ratio of \( I \) units, 62% from HRTEM images [24].

4.5. Propagation of interstitial chains

So far we have discussed the energetics of classes of defects, from the interstitial clusters to the extended {311} defects, solely in terms of the formation energies. It has been shown that the interstitial clusters can bind interstitials and become elongated interstitial chains along the (011) direction. The interstitial chains in turn grow to the extended {311} defects by capturing interstitials along the (233) direction. We propose that successive planar rotations, which are shown to introduce eight-member rings between interstitial chains separated by \( L_{y0} \), can also displace
interstitial chains. By successive rotations of atoms connected by solid bonds in Figure 4.4, an interstitial chain characterized by the \{311\} habit plane is displaced by \( \Delta = 2a/\sqrt{2} \) along the arrow (the \{0\bar{1}\} direction), perpendicular to the \{0\bar{1}\} chain direction. The planar rotations connect two interstitial chain structures with the same \( E_{\text{int}}^I = 1.7 \text{ eV} \) - the \( I \)-chain on the \{311\} plane, Figure 4.4(a)(c)(d), and the \( I \)-chain on the \{100\} plane, Figure 4.4(b)(e).

This kind of coordinated atomic motions was first introduced by Pandey as a diffusion mechanism of Si atoms in a thermal equilibrium without introducing point defects [29]. He suggested that successive rotations of nearest neighboring atoms in the \{0\bar{1}\} plane and the \{011\} plane result in exchanges of atoms and eventually displacements of Si atoms. The interstitial chain configurations shown in Figure 4.4 are related to each other by \( \phi \sim 70^\circ \) rotation of the pair atoms (solid circles) in the \{0\bar{1}\} plane.

For a formation energy of interstitial chain, \( E_f \), an energy barrier for the propagation, \( E_b \), and an entropy involved with the propagation, \( S \), the probability for an interstitial chain to propagate is proportional to \( \exp \{-(E_f + E_b - TS)/k_B T\} \). The propagation mechanism of the interstitial chains via planar rotations has such desirable features: (1) no dangling bond is introduced during the transformation due to atomic relaxations and thus a small energy barrier is expected; and (2) the entropy involved with the rotation may be high because of the large extent of atomic relaxations and many possible paths.

An energy barrier for the transformation from the structure of Figure 4.4(a) to (b) is estimated in two ways. First, an energy barrier for the rotation is estimated by calculating total energies of saddle points and comparing the total energies with
FIGURE 4.4 By successive rotations of solid atoms connected by solid bonds, an interstitial chain on the \{311\} habit plane is displaced by $\Delta = 2a/\sqrt{2}$ along the perpendicular direction of the interstitial chain (arrow). The \(\otimes\) denotes a reference atom. Intermediate structures are characterized by the habit planes, the \{100\} plane for (b) and (d) and the \{311\} plane for (c), indicated by dashed lines. The formation energy per interstitial of the illustrated structures is 1.7 eV for a fixed computational cell. The dimension of the cell is $4L_{x_0} \times 3L_{y_0} \times 2L_{z_0}$. 

116
FIGURE 4.4
those of the interstitial chain structures. The calculations are performed at a fixed computation cell of $4L_{x0} \times 3L_{y0} \times 2L_{z0}$. This computational cell contains four solid bonds into the $\{0\overline{1}1\}$ plane which are not shown in Figure 4.4(a). The saddle point configurations are initially given by simultaneously rotating the atoms connected by the solid bonds by $\phi = 15^\circ, 30^\circ, \text{and } 45^\circ$ on the $\{0\overline{1}1\}$ plane. The bond length of the two atoms is chosen at the average value of the bond lengths of two structures in Figure 4.4(a) and (b). Then, structural relaxations of the initial configurations are performed by allowing all atoms to move except for the two rotated atoms. The rotated atoms are fixed at the intermediate positions. The calculated energy barrier is 1.7 eV per bond. When the similar rotation of two atoms is performed in the bulk Si without any interstitial, the energy barrier is about 2.7 eV per bond.

Alternatively, the energy barrier is estimated by rotating one bond at a time among four solid bonds in a computational cell, which are underneath of the solid bond in Figure 4.4(a) in the $[0\overline{1}1]$ direction. For rotations of one to three bonds, the total energy increases by $1.2 \pm 0.1$ eV in comparison with those of the interstitial chains in Figure 4.4(a) and (b). The corresponding increase in the formation energies is less than 0.2 eV per interstitial. No dangling bond is introduced by these planar rotations and the intermediate structures have bond-angle distortions of $\pm 22^\circ$, slightly larger than $-15^\circ$ to $20^\circ$ bond-angle distortions of the interstitial chain configurations in Figure 4.4(a) and (b). The energy barriers estimated by two different paths suggest that many possible combinations of the planar rotations, which has an energy barrier less than 2 eV per bond, can lead to the displacements of interstitial chains.

*Step structures and V-shaped bends found in the extended $\{311\}$ defects can*
FIGURE 4.5 By rotations of three solid bonds, a rod-like \( \{311\} \) defect containing two \( I \)-chains on the \( \{311\} \) plane (a) is transformed to a step configuration with a height of \( \Delta = \frac{a}{\sqrt{11}} \) along the \( [311] \) direction (b). The solid atoms are deeper into the plane by \( L_{zo} / 2 \) than the open-circled atoms. The difference of the total energies per unit cell of the two structures, which contains 528 bulk Si atoms, is less than 0.1 eV, and the corresponding \( \Delta E_{\text{int}}^{f} \) is less than 0.05 eV. Intermediate states after rotations of one or two solid bonds have the same \( E_{\text{int}}^{f} \).
be constructed by combination of rotations of nearest neighboring atoms on the \{0\tilde{1}1\} plane together with the interstitial chain structures. Rotations of three solid bonds in Figure 4.5(a) result in a displacement of the right interstitial chain. The formation energy of the structures before and after the transformation is the same at $E_{\text{int}}^f = 1.5$ eV. The structure in Figure 4.5(b) is similar to the core model of the atomic steps observed in HRTEM images [25]. Addition of interstitial chains to this defect structure along $\pm y$ direction (the [2\tilde{3}3] direction) leads to the formation of a defect structure containing an atomic step. The two \{311\} habit planes shown as dashed lines are separated by a step height of $\Delta = a/\sqrt{11}$ along the \{311\} direction, which agrees with that predicted in Ref. [25].

It has been observed that the \{311\} defects change habit planes, for example, between the \{311\} and \{3\tilde{1}1\} planes [25]. The atomic configuration around the bend where the habit planes change can be identified as the $I$-chain in the \{100\} plane in Figure 4.2(b). We show in Figure 4.6 that the interstitial chains can be added to an $I$-chain \{100\} plane to form a $V$-shaped defect. The initial configuration, when two interstitial chains are added, is chosen so as to avoid the generation of adjacent five-member rings by bond rotations on the \{0\tilde{1}1\} plane. The lowest energy configuration of the bend structure is found to have seven-member rings at the edges ($E_7$): by transformation of the six-member rings to $E_7$'s, the total energy is lowered by 3.8 eV per cell [30], corresponding to $\Delta E_{\text{int}}^f = -0.2$ eV. The bond-angle distortion ranges between $-17^\circ$ and $26^\circ$ and the bond-length distortion between $-0.1$ Å and $0.02$ Å. The formation energy, 1.3 eV per interstitial, is comparable to that of the $E_7IIIIE_7$ model structure at the same interstitial concentration of 6 per unit length, $L_{20} = a/\sqrt{2}$. The defect can grow on both habit planes, the \{311\} and
FIGURE 4.6 Bend configuration of the \{311\} defects (bottom) obtained by addition of two interstitial chains to an \(I\)-chain on the \{100\} plane (top). Insertion of interstitial chains results in breaking of bonds (dotted lines). The bottom structure contains 6 interstitials per unit length of \(L_{\text{zo}}\): 2 interstitials associated with the \(I\)-chain on the \{100\} plane and 4 additional atoms indicated by arrows. A row of the center six-member rings along the [011] direction forms a boundary of the defects which have the \{311\} and \{3\overline{1}1\} habit planes (dashed lines). This V-shaped defect has a mirror symmetry with respect to the center of the six-member rings. The formation energies per interstitial are 1.7 eV (top) and 1.3 eV (bottom). Further growth of the defect can occur by addition of interstitial chains on the both habit planes.
planes, by capturing interstitials or interstitial chains.

4.6. Planar \{311\} defects

Extended \{311\} defects as wide as 100 nm along the (233) direction are studied by approximating them as planar defects which are periodic both in the (011) and the (233) directions [31]. Formation energies of planar defects, constructed by combinations of interstitial chains (I) and eight-member rings (O₈) along the [233] direction, are listed in Table 4.4. As introduced by Takeda et al. [26], the periodicity of a planar defect along the [233] direction is specified by an arrangement of I's and O's within a unit cell, which is denoted by /\cdots/. For example, the /IIO₈/ model contains two I units separated by a distance of L_yo/2 in the [233] direction and one O₈ unit within a unit cell. The periodicity of the /IIO₈/ model along the [233] direction is 3(L_yo/2), where L_yo/2 is the average width of each unit and the factor 3 is the total number of units within a unit cell.

The formation energy per interstitial of the planar \{311\} defects is significantly smaller than that of isolated interstitials and comparable to that of the extended \{311\} defects with finite widths along the [233] direction (Table 4.3). The stability of the planar defects against isolate interstitials indicates that the \{311\} defects can grow indefinitely as long as the interstitials are supplied, e.g., during the ion implantation process. Among the model structures we have investigated, the /IIO₈/ model is the lowest in the formation energy per interstitial (E_{int} = 1.2 eV). The density of the I units of the /IIO₈/ planar defect is 67%, corresponding the interstitial concentration of \(5 \times 10^{14}/\text{cm}^2 = \frac{4}{(L_zo \times 3(L_yo/2))}.\)
<table>
<thead>
<tr>
<th>Model structure</th>
<th>$N_{\text{int}}^*$</th>
<th>$E_{\text{int}}^f$(eV)</th>
<th>Stability of $O_8$ units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2L_{z0}$</td>
<td>$3L_{z0}$</td>
<td></td>
</tr>
<tr>
<td>/I/</td>
<td>12</td>
<td>1.35</td>
<td>1.27</td>
</tr>
<tr>
<td>/IO$_8$/</td>
<td>6</td>
<td>1.68</td>
<td>1.59</td>
</tr>
<tr>
<td>$/II/O_8$/</td>
<td>8</td>
<td>1.23</td>
<td>1.16</td>
</tr>
<tr>
<td>$/IIIIO_8$/</td>
<td>8</td>
<td>1.35</td>
<td>1.26</td>
</tr>
<tr>
<td>$/IIIIO_8$/</td>
<td>10</td>
<td>1.24</td>
<td>1.18</td>
</tr>
<tr>
<td>$/IIIIO_8O_8$/</td>
<td>8</td>
<td>1.48</td>
<td>Unstable, /IIIIO$_7$O$_7$/</td>
</tr>
</tbody>
</table>

* Per unit area: $L_{z0} \times 3L_{y_0}$ on the $\{311\}$ plane

**TABLE 4.4** Formation energies per interstitial ($E_{\text{int}}^f$) of planar $\{311\}$ defects consisting of interstitial chains and eight-member rings. The periodicity of the structures along the $[233]$ direction is denoted by /···/. The number of interstitials and the formation energy are given per unit area, $L_{z0} \times 3L_{y_0}$, in order to compare structures with different periodicities along the $[233]$ direction. The same computational cell is used for the total energy calculations of all the listed structures with two choices for the length of the cell in the $[311]$ direction, $2L_{z0}$ and $3L_{z0}$. The last column shows the stability of the eight-member rings and the most stable planar defects which can be obtained by rotations of atoms on the $\{0\bar{1}1\}$. 
The model structure with adjacent \(O_8\) units along the [233] direction is energetically least favorable at the same interstitial concentration in comparing the /IIIO\(O_8/\), /IIIO_8IO_8/ and /IIIIO_8O_8/ models. In fact, segments including two adjacent eight-member rings, \(O_8O_8O_8\ldots\), have not been identified as local structures of the extended {311} defects [24,25]. When a planar rotation is applied on the common bond shared by the neighboring eight-member rings of the /IIIIO_8O_8/ model, \(E_{\text{int}}^f\) is lowered by 0.2 eV. The stability of the eight-member rings of each structure is studied by applying planar rotations of the atoms which form boundaries between the eight-member rings and six-member rings along the [233] direction. The last column of Table 4.4 shows that the \(O_8\)'s are stable when their separation is equal to or larger than \(L_{y0}\), consistently with the result of the finite-width {311} defects.

The difference of the \(E_{\text{int}}^f\)'s of the /IIIO_8/ and /IIIIO_8IO_8/ models implies that the stability of the planar defects is determined not only by the density of interstitial chains but also the arrangement of interstitial chains. Planar defects containing isolated interstitial chains between \(O\) units (\(OIO\ldots\)) have higher formation energies than those without them at the same interstitial concentration. The energy gain by transformation of one of the eight-member rings to a seven-member ring is insufficient to change the relative stabilities of the planar defects. Based on the \(E_{\text{int}}^f\) of the planar defects listed in Table 4.4, we expect that the /IIIIO_8IIO_8/ and /IIIO_8/ planar defects to have comparable \(E_{\text{int}}^f\) to the most stable planar defect, the /IIIO_8/ model.

The formation energy of the planar defects we have discussed is obtained without allowing relaxation of the supercells. A supercell relaxation would have generated the displacement vector (Burger vector) around the core of the {311} defects.
identified by TEM observations. However, we anticipate that the relative stability is correctly described by the fixed cell calculations. The critical dimension for the convergent formation energy for the planar defects is \( L_z \), the length of the supercell in the [311] direction. We obtain the formation energies of the planar defects at \( L_z = 3L_{20} \), which are also listed in Table 4.4. The formation energy is lowered by 0.08 eV on average for all the planar defects. The relative stability of the planar defects is the same for \( L_z = 2L_{20} \) and \( 3L_{20} \).

In Figure 4.7, we show the formation energy of the defects which are infinite along the [233] direction and finite \( (L_D = n_D L_{20}) \) along the [011] direction. The elongation direction of the {311} defects is always along the (011) direction. However, we study the hypothetical defect structures with lengths \( L_D \) shorter than the width in the [233] direction to compare with the planar defects. Since the infinite limits of these defects \( (L_D \propto \infty) \) are planar defects, we can compare the formation energy of the planar defects in Table 4.4 with \( E_{\text{int}}^f(\infty) \), which can be extracted from the finite-length-defect calculations.

The defect structures in Figure 4.7 are constructed by inserting a finite-length planar defect between bulk layers. The defects become either the /1/ or /108/ model structure at the infinite limits. The formation energy increase linearly to the length along the [011] direction:

\[
E_f = E_{\text{edge}}^f + N_{\text{int}} E_{\text{int}}^f(\infty). \tag{4.6}
\]

Then the \( E_{\text{int}}^f \) of the defects with respect to the length is written as

\[
E_{\text{int}}^f = E_{\text{int}}^f(\infty) + E_{\text{edge}}^f/N_{\text{int}} \propto 1/L_D. \tag{4.7}
\]

The slopes, \( E_{\text{int}}^f(\infty) \), of two kinds of defects is the formation energy per interstitial at the infinite limits, i.e., \( N_{\text{int}} \propto L_D \rightarrow \infty \). The slopes obtained from linear fittings
FIGURE 4.7 Formation energy ($E_f^I$) per unit width ($L_y0$) with respect to the number of interstitials per unit width (left); a schematic diagram to show how the computational cell is constructed (right). A slab with a finite length of $n_D L_{x0}$, for an integer $n_D = 1 \cdots 4$, contains defect structures based on the /IO8/ and /I/ models. The slab is sandwiched between Si bulk layers along the [011] direction with a fixed total length of $6L_{x0}$. A common width along the [233] direction is chosen at $L_y0$. The number of interstitials per unit width ($L_y0$) is proportional to the length of the defects: $N_{int} = 4n_D$ for the defects based on the /I/ model and $N_{int} = 2n_D$ for those based on the /IO8/ model. The formation energy is fitted by Eq. (4.6). For the defects based on the /I/ model, the values of $E_{edge}^f$ and $E_{int}^f[\infty]$ are 8.4 and 1.4 eV respectively; $E_{edge}^f = 6.1$ eV and $E_{int}^f[\infty] = 1.7$ eV for the defects derived from the /IO8/ model. The formation energy per interstitial decreases as the length increases as in Eq. (4.7). At $N_{int} \to \infty$, the $E_{int}^f$'s converge to those of the planar defects, 1.4 eV for the /I/ model and 1.7 eV for the /IO8/ model.
are in good agreements with the $E^i_{\text{int}}$'s in Table 4.4, 1.4 eV and 1.7 eV for the /I/ model and /IO8/ model, respectively. This result confirms that the /I/ model is more stable than the /IO8/ model.

Finally, the ability of the \{311\} defects to capture or release interstitials is studied by calculating an energy required to add an interstitial to the bulk Si in the presence of the planar defects (Figure 4.8). An interstitial is added at the hexagonal site at a distance of $h$ from the \{311\} habit plane. The eight-member rings of the /IO8/ planar defect can provide efficient sinks of interstitials: the extra energy to add an interstitial to the /IO8/ planar defect decreases with decreasing $h$, 3.2 eV at 16.5 Å and 1.5 eV at 10.1 Å. When the interstitial is added right above the eight-member ring (3.8 Å from the habit plane), about 0.1 eV energy is released. On the other hand, an additional interstitial is not bounded by the /II08/ planar defect. The energy required to add an interstitial is 4.7 – 5.1 eV. This energy is comparable to the formation energy of an isolated interstitial at the hexagonal sites and larger than that of the \(\text{\{110\}}\) interstitials. These results support the calculations showing that the saturation of interstitials is achieved at the $I$ density about 67% in the /II08/ structure (Table 4.4).

4.7 Conclusions

We have showed that interstitial chain structures elongated along the \(011\) direction constitute the basic building blocks of the extended \{311\} defects. This interstitial chain configuration is favored due to the minimum ratio of dangling bonds per interstitial and small distortions in bond angles and bond lengths. Even finite-size interstitial chains, as small as 2-interstitial clusters, are found to be stable
FIGURE 4.8 Initial configurations to obtain the extra energy required to add one interstitial to the bulk system in the presence of a planar defect. The additional interstitial is located at a hexagonal site with a distance $h$ measured from the $\{311\}$ plane on which the center of interstitial chains lie (the dashed line). Two cases with $h_1 = 16.5$ Å and $h_2 = 3.8$ Å are illustrated at the same time. The computational cell is $6L_x \times 3L_y \times 2L_z$. The distance of interstitials in the neighboring cells, i.e. the distances between images related by periodic boundary conditions, is larger than the distance of the additional interstitial to the habit plane of the planar defect. The interstitials associated with the interstitial chains of the $\text{IO}_8$ model structure are indicated by arrows.
against isolated interstitials. A growth mechanism of the $\{311\}$ defects can be speculated from the dependence of the $E_{\text{int}}^f$'s on the dimensions of the defects and the interstitial concentrations. The growth of the $\{311\}$ defects would occur first by (1) elongation of interstitial chains along the $(011)$ direction and (2) the widening of the defects follows by capturing interstitial chains alongside the $(233)$ direction. We present an efficient mechanism, rotations of atoms on the $\{011\}$ plane, which can lead to propagation of interstitial chains. The planar rotation together with the interstitial chain structures can be applied to explain growth process of the $\{311\}$ defects and related structures such as the V-shape bend structure and atomic steps. We observed that the most stable arrangement of interstitial chains of the extended $\{311\}$ defects is $\cdots 110_8 110_8 \cdots$ and the optimal density of interstitial chains is $67\%$ which is in a good agreement with the experimental value of $62\%$. 

132
REFERENCES

1. P. M. Fahey, P. B. Griddin and J. D. Plummer, Rev. Mod. Phys. 61, 289 (1989), and references there in.


26. M. Kohyama and S. Takeda, Phys. Rev. B, 46, 12305 (1992), the symbols of the structural units (I, O and E) are adapted to describe the extended {311} defects.


28. The same $E_{int} = 1.7$ eV is obtained from a calculation using a computational cell oriented as [011] x [011] x [100].


30. The orientation and size of the computational cell is $3a/\sqrt{2}[011] \times 12a/\sqrt{2}[011] \times 7a[100]$ for the lattice constant $a$. The cell contains 1008 bulk Si atoms.

31. Experimentally, a displacement vector of the perfect crystals around the core of the {311} defects was identified as $0.14a/\sqrt{11}$ along the [233] direction and $0.64a/\sqrt{11}$ along the [311] direction. Our structural optimizations are performed by fixed cell calculations without a rigid body translation. All the atoms in the computational cells are allowed to relax.
BIBLIOGRAPHY


[26] P. M. Fahey, P. B. Griddin and J. D. Plummer, Rev. Mod. Phys. 61, 289 (1989), and references there in.


[63] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and and J. D. Joannopoulos, Rev. Mod. Phys. 64, 1045 (1992), and references there in.
Appendix A: TB Hamiltonian matrix elements

For atoms \( l' \) and \( l \) with a distance \( R_{ll'} = |R_l - R_{l'}| \) apart, the Hamiltonian matrix element is given as \( E_{l\alpha, l'\alpha'} \) is an hopping integral of two localized basis functions at a distance of \( R_0 \) – the bond length in the equilibrium diamond structure. The hopping integrals depend on the directional cosines of position vectors \( R_l \) and \( R_{l'} \) [1].

For the onsite terms, when \( l = l' \), the Hamiltonian matrix elements are given as

\[
\langle \phi_{l'\alpha'} | H | \phi_{l\alpha} \rangle = \begin{cases} 
E_s & \text{for } \alpha = \alpha' = s \\
E_p & \text{for } \alpha = \alpha' = p_x, p_y, p_z \\
0 & \text{for } \alpha \neq \alpha'
\end{cases} \quad (A1)
\]

For the direction cosines of the vectors \( R_{l'} - R_l \):

\[
l = \frac{R_{l'x} - R_{lx}}{R_{ll'}} \\
m = \frac{R_{l'y} - R_{ly}}{R_{ll'}} \\
n = \frac{R_{l'z} - R_{lz}}{R_{ll'}} \quad (A2)
\]
\( E_{l\alpha,l'\alpha'} \) is determined as follow:

\[
E_{l\alpha,l's} = V_{ss\sigma}
\]

\[
E_{l\alpha,l'p_c} = -Elp_x, l's = lV_{sp\sigma}
\]

\[
E_{l\alpha,l'p_y} = -Elp_y, l's = mV_{sp\sigma}
\]

\[
E_{l\alpha,l'p_z} = -Elp_z, l's = nV_{sp\sigma}
\]

\[
Elp_x,l'p_y = Elp_z,l'p_x = ln(V_{pp\sigma} - V_{ppx})
\]

\[
Elp_x,l'p_z = Elp_z,l'p_x = ln(V_{pp\sigma} - V_{ppx})
\]

\[
Elp_y,l'p_x = Elp_z,l'p_y = mn(V_{pp\sigma} - V_{ppx})
\]

\[
Elp_z,l'p_x = l^2V_{pp\sigma} + (1 - l^2)V_{ppx}
\]

\[
Elp_z,l'p_y = m^2V_{pp\sigma} + (1 - m^2)V_{ppx}
\]

\[
Elp_z,l'p_z = n^2V_{pp\sigma} + (1 - n^2)V_{ppx}.
\]

The TB parameters - \( E_\sigma, E_p, V_{ss\sigma}, V_{sp\sigma}, V_{pp\sigma} \) and \( V_{ppx} \) - and the scaling function, 
\( h_{\alpha\alpha'}(R_{l\alpha'}/R_0) \), are determined empirically in the TB total energy scheme.
Appendix B: The Conjugate Gradient method

The conjugate gradient method is a scheme for minimizing a function along the direction \([2,3]\), which is a combination of the new gradient and the previous conjugate gradient direction as

\[
| h^m \rangle = | g^m \rangle + \gamma^m | h^{m-1} \rangle ,
\]

where \(| g \rangle \) and \(| h \rangle \) denote the gradient and the conjugate gradient respectively, and \(m\) is the iteration index. By taking \(\gamma\) as

\[
\gamma^m = \frac{\langle g^m | g^m \rangle - \langle g^m | g^{m-1} \rangle}{\langle g^{m-1} | g^{m-1} \rangle} ,
\]

\(\langle h^m | h^{m-1} \rangle = 0\) is satisfied.

The gradients are computed by the same subroutine for the electronic forces under orthogonality constraint as presented earlier in this paper and the conjugate gradients are calculated by Eq.(1.10). For the new trial wave functions which are the linear combination of the wave functions and the conjugate gradient directions,

\[
| \psi^m_i \rangle = | \psi_i \rangle + \lambda | h^m_i \rangle ,
\]

the energy functional

\[
E(\alpha) = \sum_{ij} S^{-1}_{ij} \langle \psi_i \mid H \mid \psi_j \rangle ,
\]
is to be minimized with respect to $\alpha$, where $S_{ij} = \langle \psi_i^l | \psi_j^l \rangle$ are the overlap matrix elements. It is computationally costly to get the minimum exactly since the total energy is a highly nonlinear function of $\alpha$.

If we orthogonalize the conjugate gradients to the wave functions and normalize them, then the off diagonal elements of the overlap matrix are quite negligible around the minimum and the overlap matrix can be approximated as the unit matrix. As the gradients are already orthogonalized to the wave functions by the Lagrangian multiplier (Eq. (1.10)), the conjugate gradient needs to be orthogonalized to its band only as

$$| h_i^l \rangle = | h_i^{lm} \rangle - \langle \psi_i | h_i^{lm} \rangle | \psi_i \rangle.$$  \hspace{1cm} (B5)

Then, the normalization is performed as

$$| h_i^{ll} \rangle = \frac{| h_i^l \rangle}{\langle h_i^l | h_i^l \rangle}.$$  \hspace{1cm} (B6)

The new trial wave functions are

$$| h_i^{ll} \rangle = \frac{| h_i^l \rangle}{\langle h_i^l | h_i^l \rangle},$$  \hspace{1cm} (B6)

and the total energy is expanded as

$$| \psi_i^l \rangle = \cos \theta | \psi_i \rangle + \sin \theta | h_i^{ll} \rangle,$$  \hspace{1cm} (B7)

where the coefficients of the wave functions, $C_{l\alpha}^i$'s, are obtained as,

$$E_{tot}(\theta) \approx E_0 + E_1 \cos 2\theta + E_2 \sin 2\theta.$$  \hspace{1cm} (B8)

Gram-Schmidt orthonormalization must be performed to get rid of the slight non-orthogonality of the wave functions as we have neglected the off diagonal elements of the overlap matrix.
The $\theta_o$ minimizing the energy is calculated analytically as

$$E_0 = \sum_i \langle \psi_i | H | \psi_i \rangle + \sum_i \langle h_i'' | H | h_i'' \rangle$$

$$E_1 = \sum_i \langle \psi_i | H | \psi_i \rangle - \sum_i \langle h_i'' | H | h_i'' \rangle$$

$$E_2 = 2 \sum_i \langle \psi_i | H | h_i'' \rangle.$$  \hspace{1cm} (B9)

To quench the electronic system to the BO surface, the minimizations should be repeated until $\epsilon = \Delta E_{\text{tot}}/N$ becomes less than a certain predetermined tolerance. The simulations show that a tolerance of $\epsilon < 10^{-9}$ is required if the ionic energy is to remain bounded during the course of the simulations, and each step requires about 20 iterations.
Appendix C: TB parameters by Khan et al. [4]

We use a total energy expression for silicon due to Tománek and Schlüter [5] which is based on the original tight-binding parameterization scheme of Chadi [6]. The total energy of the group IV atoms is described by an energy functional of the ionic positions and the electron wave functions as

\[ E_{\text{tot}} = E_{TB} + E_R. \]  

(C1)

The first term is the tight-binding energy as in Eq. (1.9),

\[ E_{TB} = 2 \sum_{i}^{N_{\text{site}}=2N} \langle \psi_i | H | \psi_i \rangle - N E_{Si}^0 \]

\[ = 2 \sum_{i} \sum_{l,l'} \sum_{\alpha \alpha'} \langle \psi_i | \phi_{l \alpha} \rangle \langle \phi_{l' \alpha'} | H | \phi_{l' \alpha'} \rangle \langle \phi_{l' \alpha'} | \psi_i \rangle - N E_{Si}^0, \]  

(C2)

where \( | \phi_{l \alpha} \rangle \) denotes an atomic orbital localized at the \( l \)-th atomic site with \( \alpha = s, p_x, p_y \) and \( p_z \). The tight-binding energy of an isolated neutral atom is set to zero by \( E_{Si}^0 = 2(E_s + E_p) \), where \( E_s \equiv \langle \phi_{ls} | H | \phi_{ls} \rangle = -5.25 \) eV and \( E_p \equiv \langle \phi_{lp} | H | \phi_{lp} \rangle = 1.20 \) eV for \( p = p_x, p_y \) and \( p_z \).

The scaling function of the Hamiltonian matrix elements in Eq. (A1) is assumed to decay with a factor

\[ h_{\alpha \alpha'}(\frac{R_{ll'}}{R_0}) = f_c(\frac{R_{ll'}}{R_0})^2. \]  

(C3)

144
$R_0 = 2.35 \, \text{Å}$ is the nearest neighbor distance in diamond-structure silicon and $f_c$ is a smooth cutoff function introduced to benefit molecular dynamics simulations.

$$f_c(R_{ll'}) = \frac{1}{2} \left[ 1 - \tanh \left( \frac{R_{ll'} - R_b}{\Delta} \right) \right]. \quad \text{(C4)}$$

We choose $R_b = 1.4R_0$ and $\Delta = 0.1 \, \text{Å}$ to ensure only the first-nearest neighboring interaction in the diamond Si. The hopping integrals at $R_0$ are following:

$$V_{ss\sigma} = -1.938 \, \text{eV} \quad V_{sp\sigma} = 1.745 \, \text{eV} \quad \text{(C5)}$$

$$V_{pp\sigma} = 3.050 \, \text{eV} \quad V_{pp\pi} = -1.075 \, \text{eV}.$$  

The ionic potential ($E_R$) consists of three terms,

$$E_R = E_2 - E_3 + E_4, \quad \text{(C6)}$$

where

$$E_2 = \sum_{l=2}^{N} \sum_{l'=1}^{l-1} \phi(|\mathbf{R}_l - \mathbf{R}_{l'}|)$$

$$E_3 = N \left[ \phi_1 \left( \frac{n_b}{N} \right)^2 + \phi_2 \left( \frac{n_b}{N} \right) + \phi_3 \right]$$

$$E_4 = U \sum_{l=1}^{N} (q_l - q_l^0)^2.$$

$E_2$ is the repulsive energy needed to correct the double counting of electron-electron interactions, the exchange correlation energies, and the ion-ion interactions. The $\phi$ term appearing in $E_2$ is

$$\phi(R_{ll'}) = E_{St_2}^{\text{tot}}(R_{ll'}) f_c(R_{ll'}) - \left[ E_{St_2}^{TB}(R_{ll'}) - 2E_{St_2}^{\text{tot}} \right], \quad \text{(C8)}$$

where $E_{St_2}^{\text{tot}}$ and $E_{St_2}^{TB}$ are the total and tight-binding energies of silicon dimer, respectively. For $E_{St_2}^{\text{tot}}$ we use the total energy of diatomic molecule calculated by

145
Raghavachari [7]:

\[
P_{Si_2}^{tot} = \begin{cases} 
A\left(\frac{R_{ll'}}{R^*}\right)^p - \left(\frac{R_{ll'}}{R^*}\right)^q \exp\left[\frac{\gamma}{\left(\alpha - (R_{ll'}/R^*)\right)^\nu}\right] & \text{if } \frac{R_{ll'}}{R^*} < a_c \\
0 & \text{if } \frac{R_{ll'}}{R^*} \geq a_c
\end{cases}, \quad (C9)
\]

with

\[
A = 80716.277\text{eV}
\]
\[
R^* = 1.7814354\text{Å}
\]
\[
\gamma = -10.706328
\]
\[
p = -3.3720658
\]
\[
q = -0.4758296
\]
\[
\nu = 0.31040657
\]
\[
a_c = 2.8067254\text{Å}.
\]

\[E_3\] is included to reproduce bulk-diamond-cubic and body-centered-cubic structures of silicon and to determine phase diagrams of the crystalline Si systems. \(n_b\) is the number of bonds and sums over all pairs of atoms of \(f_c\) function.

\[
n_b = \sum_{l=2}^{N} \sum_{l'=1}^{l-1} f_c(|R_l - R_{l'}|). \quad (C11)
\]

The parameters \(\phi_1, \phi_2,\) and \(\phi_3\) are given 0.225, 1.945, and -1.03 eV, respectively. These parameters are chosen by Tománek and Schlüter [5] to obtain the absolute cohesive energies of both diamond and bcc silicon. For a given crystal structure, this term is a constant which doesn't contribute to physical properties such as the elastic constants and phonon frequencies.
The last term $E_4$ is to prevent large charge transfer among the atoms and vanishes for neutral system.

$$q_l = 2 \sum_{i=1}^{2N} \sum_{\alpha=1}^{4} (c_{i\alpha}^j)^2, \quad q_l^0 = 4.0.$$  \hfill (C12)
Appendix D: TB parameters by Kwon et al. [8]

Similarly to the tight-binding Hamiltonian of Khan et al., the total energy consists of the tight-binding energy \( E^{TB} \) and the ionic repulsive potential \( E_R \). The parameters of the TB Hamiltonian matrix elements are

\[
\begin{align*}
E_b &= -5.250 \text{ eV} & E_p &= 1.200 \text{ eV} \\
V_{ss\sigma} &= -2.038 \text{ eV} & V_{sp\sigma} &= 1.745 \text{ eV} \\
V_{pp\sigma} &= 2.750 \text{ eV} & V_{ppx} &= -1.075 \text{ eV}.
\end{align*}
\]

The scaling function of the Hamiltonian matrix is

\[
h_{\alpha\alpha'}(\frac{R_{ll'}}{R_0}) = \left(\frac{R_0}{R_{ll'}}\right)^2 \exp\left(2\left[-\frac{R_{ll'}}{R_c,\alpha\alpha'}\right]^{n_{\epsilon,\alpha\alpha'}} + \left[\frac{R_0}{R_c,\alpha\alpha'}\right]^{n_{\epsilon,\alpha\alpha'}}\right),
\]

according to Goodwin, Skinner, and Pettifor [9].

The ionic potential is

\[
E_R = \sum_l f \left[ \sum_{l'} \phi\left(\frac{R_{ll'}}{R_0}\right) \right],
\]

where

\[
\phi\left(\frac{R_{ll'}}{R_0}\right) = \left[\frac{R_0}{R_{ll'}}\right]^m \times \exp\left\{m\left[-\left(\frac{R_{ll'}}{d_c}\right)^{m_e} + \left(\frac{R_0}{d_c}\right)^{m_e}\right]\right\},
\]

and

\[
f(x) = C_1 x + C_2 x^2 + C_3 x^3 + C_4 x^4.
\]
Parameters for the TB total energy functional defined in Eqs. (D2)-(D5).

<table>
<thead>
<tr>
<th>TB Hamiltonian matrix parameters</th>
<th>( (\alpha, \alpha') )</th>
<th>( sso )</th>
<th>( spo )</th>
<th>( pp\sigma, \pi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{c,\alpha\alpha'} )</td>
<td>9.5</td>
<td>8.5</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>( R_{c,\alpha\alpha'} )</td>
<td>3.4</td>
<td>3.55</td>
<td>3.7</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pair-potential parameters</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( m )</td>
<td>6.8755</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( m_c )</td>
<td>13.017</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( d_c )</td>
<td>3.66995</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_1 ) (eV)</td>
<td>2.1604385</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_2 ) (eV)</td>
<td>-0.1384393</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_3 ) (eV)</td>
<td>(5.8398423 \times 10^{-3} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_4 ) (eV)</td>
<td>(-8.0263577 \times 10^{-5} )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium volumes and bulk moduli of the bulk crystal structures of Si by this TB Hamiltonian are in good agreements with the LDA calculations. We calculate the cohesive energy and the equilibrium unit cell of ST-12 structure, which can provide a stringent test for the transferability of the TB parameters. The ST-12 structure contains 12 atoms in a tetragonal unit cell with a dimension of \( a \times a \times c \). All atoms are four-coordinated with bond-angles \( 90 - 130^\circ \). Differently from the diamond structure with only six-member rings, the ST-12 structure consists of five- and seven-member rings. Experimentally, the cohesive energy of the ST-12 structure is obtained to be \(0.123 \pm 0.007\) eV higher than that of the diamond structure [10]. We optimize both (i) the atomic positions in a unit cell and (ii)
the ratio \( c/a \) at a fixed volume per atom of 19.1 \( \text{Å}^3 \), which corresponds to the experimental density. We obtain the cohesive energy 0.27 eV higher than that of the diamond structure and the ratio \( c/a = 0.94 \).
REFERENCES


