Thesis

The electronic properties and optimized structures of the alkali adsorbed Si(001) surface by using the first principles molecular dynamics

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December 25, 1990

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Chapter 1

Introduction

The structural determination is a very important first step toward understanding the material properties from a microscopic view point. For perfect crystal, very accurate structural information can be obtained by means of the x-ray and neutron diffraction experiments. On the other hand, the structures with defects, surfaces and interfaces are generally very hard to be determined experimentally. Therefore, it is highly desirable that theories provide some useful complementary information in those cases. However, it is necessary to consider a very large system in the theoretical structural determination.

In traditional and standard electronic structure calculations based on the local density approximation (LDA) in the density functional (DF) theory, it is possible to obtain an accurate electronic properties (charge density, dispersion curves, density of states, etc.). Several works have also demonstrated that the total energy difference between different atomic structures can be calculated fairly accurately by LDA [1, 2]. Therefore, it is in principle possible to determine the lowest energy structure by calculating the total energy for every possible structure. However, this brute force approach becomes practically impossible for systems with more than three degrees of freedom.

It is necessary to calculate the forces to determine the structure efficiently. In the standard electronic structure calculation by using the norm-conserving pseudopotential and plane wave basis sets, it is easy to calculate the Hellmann-Feynman forces [3, 4, 5] which are acting on the ions. However, such an approach so far has generally used the standard matrix diagonalization method in order to obtain the eigen-vectors and eigen-values. The matrix diagonalization method requires an N^3 order task of calculation and an N^2 order memory with N denoting the number of plane waves. Therefore, the limitation of system size imposed by these aspects is also severe in practice.

On the other hand, a standard molecular dynamics can be used to obtain the optimized structure for a relatively large system. However, in this method, empirical or semi-empirical potentials are adopted whose accuracy is not necessarily guaranteed. In addition, the electronic properties of the optimized system are not given by this method.

Consequently, it is impossible to optimize the electronic and ionic structures simultaneously for a large system by using the traditional calculational methods. It has been hoped that a new method which solves above problems would appear.

In 1985, a new method was developed by Car and Parrinello [6]. Usually, this is called 'Car-Parrinello method', but in this thesis, it will be called 'The first principles molecular dynamics (FPMD) method'. The concept of this method is described as follows. In the density functional theory, the total energy of the system for a fixed ionic configuration takes a minimum for the true ground state. Therefore, solving the self-consistent solution of the ground state electronic structure can be regarded as an optimization of the total energy functional with regard to the electronic degrees of freedom. Based on this idea, the FPMD method calculates the electronic and ionic parts simultaneously. The electronic part is treated in a similar way to the ionic part by introducing an equation of motion like a Newton equation and its dynamics is totally fictitious. The wave function is solved dynamically by integrating the differential equation given by a Lagrange equation of motion and the process does not include matrix diagonalization. Therefore, this FPMD method requires no more than an N^2 order task of calculation and an N order memory, i.e., this method is very fast and saves a memory compared with the traditional one. Furthermore, it is possible to reduce the task of calculation from N^2 to $\alpha N log N$(α: numerical factor) as a result of some technical considerations. It is possible to treat larger systems, which cannot be imagined in the usual method.

In this thesis, we shall develop the program of the FPMD method and apply it to the Si(001) clean surface and the alkali adsorbed Si(001) surface systems. The surface is a very interesting system because it provides varieties of interesting phenomena, such as catalysis, anticorrosion, silicide formation at metal-semiconductor interfaces important in device applications, epitaxial growth, reconstruction and so on. Recently it has become possible to perform very accurate experiments for clean surface systems because of the development of the ultra high vacuum technique. In addition, a new experimental technique 'STM(Scanning Tunneling Microscope)' appeared in 1982 [7], which can clarify a local structure with single-atom resolution. Therefore, the research of surface systems has been developed remarkably both theoretically and experimentally.

Within the framework of the standard electronic structure calculation, it is very hard to calculate the surface systems because these semi-infinite systems do not have a periodicity. In order to solve this problem, a repeated slab geometry and supercell method are frequently adopted. The supercell is a very large unit cell which includes several tens and sometimes more than a hundred of atoms. In the repeated slab geometry, the unit cell includes atomic layers and a vacuum region. Since this unit cell is very large, it is necessary to use a huge number of plane waves in this calculation. Therefore, the FPMD method is more favorable than the traditional standard method for the study of surface problems.

We focus on the Si(001) surface system among a variety of surface systems, and study the clean and alkali adsorbed surfaces. A Si atom in the ideal (001) surface has two dangling bonds as shown in Fig. 1.1(a). The existence of dangling bonds unstabilizes the surface structure and a dimer structure is formed by changing the atomic positions to reduce the number of dangling bonds. There are two kinds of dimer structures: one is a symmetric dimer as shown in Fig. 1.1(b) and the other is an asymmetric dimer structure. Figure 1.1(c) shows the p(2×2) structure, one of the possible arrangements of the asymmetric dimers. In STM experiments [8, 9], the symmetric dimer structure is observed. On the contrary, in LEED (Low-Energy Electron Diffraction) [10] and ARUPS (Angle-Resolved Ultraviolet Photoelectron Spectroscopy) [11] experiments, the asymmetric dimer structure is observed.

On the other hand, in most of the theoretical electronic structure calculations, it is indicated that the asymmetric dimer structure is more stable than the symmetric one [12, 13, 14, 15]. We also attempt to obtain the optimized structure of the clean surface by allowing the ions to move automatically within the limitation of the (2×1) unit cell and calculate the electronic structure of this system simultaneously. As a result, we find that the asymmetric dimer is more favorable in three different conditions (a cutoff energy, k-points – [6.25Ry, 8k], [6.25Ry, 32k], [9.0Ry, 32k]). In some other theoretical groups [13, 14, 15, 16, 17, 18, 19], they have obtained the results that the antiferro-type asymmetric dimer c(4×2) [15] or p(2×2) [17, 18, 19] structure is the most stable one by using a larger unit cell [2×2, 4×2, etc.] than ours.

We shall extend our study to the alkali adsorbed Si(001)-2×1 and 2×3 surface systems. The kinds of adsorbed atoms are Li and Na. Several theoretical and experimental works on the alkali adsorbed Si(001) surface are available. Generally speaking, adsorption will be definitely accompanied by a structural relaxation of the substrate, which will modify the energetics of the adsorption. In this sense, theoretical works are not available so far which can give reliable answers to the actual adsorption sites among various possibilities. Therefore, the FPMD method is very suitable to the study of these cases.

Some fundamental aspects are controversial. For example, the saturation coverage of Na or K has not been well defined in the absolute scale: controversies are still going on about the single-layer model (like the Levine model) [20, 21, 22, 23, 24] versus the double-layer model [25, 26, 27]. The optimum adsorption sites have not been obtained yet. The alkali adsorbed surface structure for the 2×3 (or 3×2) unit cell [23] is not known. It is also interesting that the adsorption site of alkali adatoms depends strongly on the coverage and the kind of alkali atoms. With the aim of obtaining a consistent understanding of all these problems, we shall try in this thesis a determination of optimum structures with full relaxation of ions and study the dependences of the structures on the coverage and the kind of alkali atoms.

We obtain the optimized structures and electronic properties for these alkali adsorbed surface systems by using the FPMD method. The important results are summarized as follows. In the case of Na adsorption we treat three coverage types: the first one is a full coverage (two alkali atoms per a 2×1 surface unit cell [θ=1] and it is called a 'double-layer model'), the second one is a half coverage (one alkali atom per a 2×1 surface unit cell [$\theta = 0.5$] and is called a 'single-layer model'), and the third one is a $\theta = \frac{1}{6}$ coverage (one alkali atom per a 2×3 surface unit cell).

For the full coverage Na case, the most stable structure is the combination of the hollow (HH) site along the dimer chain and trough (valley bridge, T3) site on-top of the third layer Si atom. The optimized substrate structure turns out to be a nearly symmetric dimer with a significant movement of the substrate atoms toward the ideal position. For the half coverage Na case, the adsorption at the cave (T4) site is slightly more stable than the hollow (HH) one. In this case, the asymmetric dimer structure does not change to the symmetric one unlike the full coverage case, but the degree of asymmetry is reduced compared with the initial one of the clean surface.

Next, we consider the Si(001)-2×3 surface system with $\theta = \frac{1}{6}$. In this case, the Na atom is adsorbed on the bridge (B2) site between the two raised Si atoms of the neighboring Si-Si dimers. This adsorption site of Na is consistent with the STM results for K and Cs [28, 29, 30].

In the case of Li adsorption, we treated two coverage types, one is a full coverage, the other is a $\theta = \frac{1}{6}$ coverage. For the full coverage Li case, Li atoms are adsorbed at low symmetry positions. In this case, there are two energetically almost degenerate structures where the two possible adsorption sites along the trough are significantly off the valley bridge (T3) and the cave (T4) sites. Accordingly, the adsorption site of Li along the dimer chain is also slightly off the hollow (HH) site. In the $\theta = \frac{1}{6}$ coverage case, the result is almost similar to the Na adsorption case. This is inconsistent with the STM result [28, 29, 30]. The following two reasons are conceivable for the inconsistency: first, the present coverage $\theta = \frac{1}{6}$ is much higher than the experimental one (only a few percent); second, the number of the plane wave basis functions is not sufficient to treat the deep pseudopotential of Li. An improvement of the calculation in either of the two aspects requires too much of the computer resource and is left as a future task.

In most of the present calculations, we assume that the charge density of the core states is spatially separated from that of the valence states. This allows us to use a simple treatment of the exchange-correlation potential and energy, which works fairly well for Si. However, in the case of Na, the interatomic distance is underestimated by this simplification. Therefore, we implemented a partial core correction [31] for $\theta = 1$ and 0.5 in order to improve the calculation. We find that the calculated Na-Si bond length becomes closer to the experimental estimation [24].

The plan of the present thesis is as follows. In Chapter II, we will describe the method of calculation about 1)pseudopotential, 2)total energy calculation by using the standard matrix diagonalization, 3)Hellmann-Feynman forces, 4)the first principles molecular dynamics method(Car-Parrinello method), and 5)molecular dynamics method for the ionic system. The results and discussion are presented in Chapter III. The results are shown for 1)test calculations for bulk systems, 2)the clean Si(001)-2×1 surface for symmetric and asymmetric dimer cases, and 3)alkali adsorption on the Si(001)-2×1, 2×3 surfaces. Chapter IV is devoted to concluding remarks of this thesis.

Chapter 2

Method of calculation

2.1 Pseudopotential

2.1.1 Norm-conserving pseudopotential

The basic concept of pseudopotential is a frozen core approximation which assumes that the electronic states of core electrons are insensitive to the neighboring atomic configuration. The pseudopotential is constructed from the atomic potential so that the lowest eigenstate of the pseudopotential may correspond to the lowest valence state of the atomic potential. As a consequence, the pseudopotential does not have a $\frac{1}{r}$-like part in the vicinity of $r = 0$ unlike an atomic potential. It is possible to use the plane wave expansion in the electronic structure calculation because of the smoothed potential in the core region.

We would like to make some comments on the use of the pseudopotential and the plane wave expansion. As for the total energy per atom, five effective digits are sufficient in most cases in the pseudopotential approach because of the absence of the core contribution, while at least eight effective digits are required in the all-electron calculation. This nice aspect of the pseudopotential approach is obscured to some extent by the plane wave expansion because of very slow convergence in the total energy with respect to the number of plane wave basis functions. However, we should note that only the difference in the total energy between different situations is meaningful and that the convergence is much faster in the total energy difference than in the total energy itself. As force is essentially a total energy difference, relatively good convergence may be expected in the force calculation. Except such a convergence problem, forces acting on ions can easily be calculated with the plane wave expansion by using the Hellmann-

Feynman theorem [3, 4, 5]

Traditionally, empirical pseudopotentials constructed by using some experimental data have been adopted [32, 33, 34, 35, 36]. Such empirical pseudopotentials, however, have a weak point that the charge density does not coincide with that of the real atom even outside the core region $r > r_c$.

In 1979, Hamann, Schlüter and Chiang proposed a new *ab initio* pseudopotential [37]. A slight modification was made and a complete tabulation of pseudopotentials was given by Bachelet, Hamann and Schlüter (B-H-S) in 1982 [38]. The following conditions are imposed in this new pseudopotential:

1. Real and pseudo valence eigen-values agree for a chosen atomic configuration.
2. In the region of $r > r_c$, the amplitude of the pseudo-wave function coincides with that of the real atomic-wave function.
3. The pseudo-wave function does not have a node, so the plane wave basis can be used in the electronic structure calculation.
4. In the region of $r < r_c$, the norm of the pseudo-wave function coincides with that of the real wave function.
5. The first order energy derivatives of the logarithmic derivative of the pseudo- and atomic-wave functions coincide with each other at r_c.

   $$-\frac{1}{2}r^2R(r)^2\frac{d}{dE}(\frac{\partial R(r)}{\partial r}\frac{1}{R(r)})|_{r=r_c}\equiv\int_0^{r_c}R^*(r)R(r)r^2dr, \qquad (2.1)$$

   where R is a radial wave function. The Hartree atomic units ($e^2 = \hbar = m_e = 1$) are adopted throughout in this thesis. The cutoff radius r_c is defined as $r_c = \frac{r_{max}}{cc}$ with r_{max} is an outermost peak of the wave function and cc is an adjustable parameter in the range of $1.5 \sim 2.0$ as seen in Table I in the paper of B-H-S [38].

This B-H-S pseudopotential has a desirable feature that the charge density in the region of $r > r_c$ is sufficiently accurate. It has some weak points. The plane wave expansion cannot be applied in practice to some materials which have a strong core electron effect. For example, B, C, N, O and most of transition and noble metals have deep p or d potentials, which requires a huge number of plane waves in the electronic structure calculation.

The following is the process of constructing the B-H-S pseudopotential.

Step1) The first step pseudopotential $V_1(r)$ is made from an atomic potential which is calculated by considering all electrons.

$$V_1(r) = V_{atom}(r)[1 - f_{cut}\left(\frac{r}{r_c}\right)] + Cf_{cut}\left(\frac{r}{r_c}\right), \tag{2.2}$$

with

$$f_{cut}\left(\frac{r}{r_c}\right) = e^{-(\frac{r}{r_c})^{\lambda}}, \tag{2.3}$$

where $V_{atom}(r)$ is an atomic potential, $f_{cut}(r)$ a cutoff function, C an adjustable parameter, r_c a core radius (cutoff radius), and $\lambda = 3.5$. The cutoff function should satisfy the conditions

$$\lim_{r \to 0} f_{cut}\left(\frac{r}{r_c}\right) = 1, \tag{2.4}$$

and

$$\lim_{r \to \infty} f_{cut}\left(\frac{r}{r_c}\right) = 0. \tag{2.5}$$

The adjustable parameter C is determined so that the eigen-energies for the pseudopotential coincide with those of valence states for the original atomic potential.

Step 2) The first step pseudo-wave function $W_1(r)$ is obtained by solving the Schrödinger equation with $V_1(r)$.

Step 3) The second step pseudo-wave function is calculated to give the same amplitude of the atomic-wave function in the region of $r > r_c$.

$$W_2(r) = \gamma[W_1(r) + \delta \cdot r^{(l+1)} f_{cut}\left(\frac{r}{r_c}\right)], \tag{2.6}$$

where γ and δ are adjustable parameters which are determined to satisfy the norm conservation.

Step 4) The second step pseudopotential is obtained by inverting the Schrödinger equation as follows,

$$V_2(r) = V_1(r) + \frac{\gamma\, \delta \cdot r^{(l+1)} f_{cut}(\frac{r}{r_c})}{2W_2(r)}$$

$$\times \left\{\frac{\lambda^2(\frac{r}{r_c})^{2\lambda} - [2\lambda l + \lambda(\lambda+1)](\frac{r}{r_c})^{\lambda}}{r^2} + 2\epsilon - 2V_1(r)\right\}. \quad (2.7)$$

Step 5) $V_{ps}(r)$ is obtained by subtracting the Hartree potential $V_H(r)$ and exchange-correlation potential $V_{xc}(r)$ due to the valence electrons from $V_2(r)$,

$$V_{ps}(r) = V_2(r) - V_H(r) - V_{xc}(r). \quad (2.8)$$

Step 6) The $V_{ps}(r)$ is divided into two parts, one is a local part $V_{local}(r)$ and the other is a non-local part $V^l_{non-local}(r)$ dependent on the angular momentum l:

$$V_{ps}(r) = V_{local}(r) + \sum_l \mid l > V^l_{non-local}(r) < l \mid. \quad (2.9)$$

This $V_{ps}(r)$ is the final form of the B-H-S pseudopotential. We shall use this pseudopotential in the present FPMD. There are some calculations in which only the local part is used [39]. However the local part is generally very deep, so that more plane waves are required. Further, the neglect of l-dependent non-local parts destroys the norm conservation.

2.1.2 Kleinman-Bylander separable form

In this subsection, we focus on the non-local pseudopotential term $V^l_{non-local}(r)$. Its matrix element is

$$\begin{aligned} V^{B-H-S}_{\vec{k}+\vec{G},\vec{k}+\vec{G}'} &= \sum_l \int e^{-i(\vec{k}+\vec{G})\vec{r}} V^l_{non-local}(\vec{r}) e^{i(\vec{k}+\vec{G}')\vec{r}} d\vec{r} \\ &= \sum_l 4\pi(2l+1) P_l(\cos\theta_{\vec{k}+\vec{G},\vec{k}+\vec{G}'}) \int_0^\infty j_l(\mid \vec{k}+\vec{G} \mid r) j_l(\mid \vec{k}+\vec{G}' \mid r) \\ &\times \ V^l_{non-local}(r) r^2 dr, \end{aligned} \quad (2.10)$$

where $P_l(\cos\theta_{\vec{k}+\vec{G},\vec{k}+\vec{G}'})$ is a Legendre function, $\theta_{\vec{k}+\vec{G},\vec{k}+\vec{G}'}$ is an angle between vectors $\vec{k}+\vec{G}$ and $\vec{k}+\vec{G}'$, and $j_l(x)$ is a spherical Bessel function. The right hand side of eq. (2.10) is approximated by a separable form by using the Kleinman and Bylander (K-B) method [40]. The detailed formulation will be given in Appendix A. Equation (2.10) is transformed into

$$V^{B-H-S}_{\vec{k}+\vec{G},\vec{k}+\vec{G'}} \Rightarrow V^{K-B}_{\vec{k}+\vec{G},\vec{k}+\vec{G'}} = \sum_l 4\pi(2l+1)P_l(\cos\theta_{\vec{k}+\vec{G},\vec{k}+\vec{G'}})\frac{S^{KB}_{\vec{k},l}(\vec{G})S^{KB}_{\vec{k},l}(\vec{G'})}{W_l}, \tag{2.11}$$

where $\phi_l(r)$ is a pseudo-wave function and

$$S^{KB}_l(\vec{k}+\vec{G}) = \int_0^\infty j_l(\mid \vec{k}+\vec{G} \mid r)\phi_l(r)V^l_{non-local}(r)r^2dr, \tag{2.12}$$

$$W_l = \int_0^\infty \phi^*_l(r)V^l_{non-local}(r)\phi_l(r)r^2dr. \tag{2.13}$$

In the s and p potentials, Legendre functions are

$$P_0(\cos\theta_{\vec{k}+\vec{G},\vec{k}+\vec{G'}}) = 1, \tag{2.14}$$

and

$$P_1(\cos\theta_{\vec{k}+\vec{G},\vec{k}+\vec{G'}}) = \frac{(\vec{k}+\vec{G})\cdot(\vec{k}+\vec{G'})}{\mid \vec{k}+\vec{G} \mid \mid \vec{k}+\vec{G'} \mid}. \tag{2.15}$$

Therefore, the final form is given by

$$V^{K-B}_{\vec{q},\vec{q'}} \mid_{l=0} = \frac{V^{NL}_{l=0}(\vec{q})V^{NL}_{l=0}(\vec{q'})}{W_0}, \tag{2.16}$$

with

$$V^{NL}_{l=0}(\vec{q}) = (4\pi)^{\frac{1}{2}}\, S^{KB}_{\vec{k},0}(\vec{q}), \tag{2.17}$$

and

$$V^{K-B}_{\vec{q},\vec{q_c},\vec{q'},\vec{q'}_c} \mid_{l=1} = \frac{V^{NL}_{l=1}(\vec{q},\vec{q_c})V^{NL}_{l=1}(\vec{q'},\vec{q'}_c)}{W_1}, \tag{2.18}$$

with

$$V^{NL}_{l=1}(\vec{q},q_c) = (12\pi)^{\frac{1}{2}}\,\frac{q_c}{q}S^{KB}_{\vec{k},1}(\vec{q}), \tag{2.19}$$

where $\vec{q}=\vec{k}+\vec{G}$, $q = \mid \vec{q} \mid$, and q_c is the $c(=x,y,z)$ component of $\vec{q}$.

In the actual calculations, the following simplification is assumed

$$V^l_{non-local}(r) = V^2_{non-local}(r) \qquad \text{for } \; l \geq 3. \tag{2.20}$$

This approximation may be allowed for Li, Na and Si for which mixing of states with $l > 1$ into the valence states is small. Then eq.(2.9) is rewritten as

$$\begin{aligned}
V_{ps}(r) &= V_{local}(r) + \sum_{l} \mid l > V^{l}_{non-local}(r) < l \mid \\
&= V_{local}(r) + \sum_{l=0}^{1} \mid l > V^{l}_{non-local}(r) <\mid + V^{2}_{non-local}(r) \sum_{l=2}^{\infty} \mid l >< l \mid \\
&= \{V_{local}(r) + V^{2}_{non-local}(r)\} \\
&+ \sum_{l=0}^{1} \mid l > \{V^{l}_{non-local}(r) - V^{2}_{non-local}(r)\} < l \mid, \qquad (2.21)
\end{aligned}$$

where use has been made of the relation $\sum_{l=2}^{\infty} \mid l >< l \mid = 1 - \sum_{l=0}^{1} \mid l >< l \mid$. Therefore, in our practical calculations, we take ($V_{local}(r) + V^{2}_{non-local}(r)$) as the local part of the pseudopotential and ($V_{local}(r) - V^{2}_{non-local}(r)$) as the non-local one. The results of test calculations for bulk systems of Li, Na, Al and Si with these pseudopotentials will be mentioned in detail in Chapter 3.

Other types of separable forms have also been proposed for the non-local part of the pseudopotential. For example, corresponding to our V_l^{NL}, Hohl et al. [41, 42, 43] proposed

$$l = 0 : \quad \int j_0(\mid \vec{k} + \vec{G} \mid r) V^{0,s}_{non-local}(r) T_{i,\vec{k}}(r) r^2 dr, \qquad (2.22)$$

where

$$T_{i,\vec{k}} = \sum_{\vec{G'}} j_0(\mid \vec{k} + \vec{G'} \mid r) \Psi_{i,\vec{k}}(\vec{G'}), \qquad (2.23)$$

and

$$l = 1 : \quad \int j_1(\mid \vec{k} + \vec{G} \mid r) V^{1,s}_{non-local}(r) U_{i,\vec{k}}(r) r^2 dr, \qquad (2.24)$$

where

$$U_{i,\vec{k}} = \sum_{\vec{G'}} \frac{(\vec{k} + \vec{G'})}{\mid \vec{k} + \vec{G'} \mid} j_1(\mid \vec{k} + \vec{G'} \mid r) \Psi_{i,\vec{k}}(\vec{G'}). \qquad (2.25)$$

These formulae require an integration of the radial direction in the real space in every iteration, while such a radial part integration is performed only at the initial setting in the K-B method.

2.2 Total energy calculation

We describe the total energy calculation for an electronic system by using the norm-conserving pseudopotential and the plane wave basis sets based on the local density approximation (LDA) [44, 45, 46] in the density functional (DF) theory [47, 48].

At the first step, we describe the DF theory and LDA. The DF theory [47] is one of the variational methods with the one-electron density $n(\vec{r})$ as the variational parameter. The ground state energy for the electronic part is expressed as

$$E[n(\vec{r})] = F[n(\vec{r})] + \int V_{ext}(\vec{r})n(\vec{r})d\vec{r}, \tag{2.26}$$

where $V_{ext}(\vec{r})$ is an external potential (a potential from nuclei) and F is a universal functional which does not depend on $V_{ext}(\vec{r})$. The external potentials are the local and non-local pseudopotentials in this study. The universal functional F is expressed as

$$F[n(\vec{r})] = T[n(\vec{r})] + \frac{1}{2}\int\int \frac{n(\vec{r})n(\vec{r'})}{\mid \vec{r} - \vec{r'} \mid} d\vec{r}d\vec{r'} + E_{xc}[n(\vec{r})], \tag{2.27}$$

where $T[n(\vec{r})]$ is a kinetic energy in a non-interacting electron system, the second term is a classical Coulomb interaction and $E_{xc}[n(\vec{r})]$ is an exchange-correlation energy. The one-electron density $n(\vec{r})$ and the kinetic energy are obtained by the following Kohn-Sham (K-S) equation [48]:

$$[-\frac{1}{2}\Delta + V_{eff}(\vec{r})]\Psi_i(\vec{r}) = \lambda_i \Psi_i(\vec{r}), \tag{2.28}$$

$$V_{eff}(\vec{r}) = V_{ext}(\vec{r}) + \int \frac{n(\vec{r'})}{\mid \vec{r} - \vec{r'} \mid} d\vec{r'} + \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}, \tag{2.29}$$

$$T[n(\vec{r})] = \sum_{i=1}^{M} \int \Psi_i^*(\vec{r})(-\frac{1}{2}\Delta)\Psi_i(\vec{r})d\vec{r}, \tag{2.30}$$

and

$$n(\vec{r}) = \sum_{i}^{M} \mid \Psi_i(\vec{r}) \mid^2, \tag{2.31}$$

where i specifies the one-electron eigenstate, $\Psi_i(\vec{r})$ is its wave function and M is a number of occupied states. The normalization constraint is imposed on the wave function as follows

$$\int \mid \Psi_i^*(\vec{r}) \mid^2 d\vec{r}, = 1. \tag{2.32}$$

As the functional of $E_{xc}[n(\vec{r})]$ is not known in general, the LDA is commonly used which assumes the following expression.

$$E_{xc}[n(\vec{r})] = \int \epsilon_{xc}(n(\vec{r}))n(\vec{r})d\vec{r}, \tag{2.33}$$

where $\epsilon_{xc}(n(\vec{r}))$ is called the exchange-correlation energy density and is a function of the value of the one-electron density $n(\vec{r})$ at every $\vec{r}$. As for the actual functional form of $\epsilon_{xc}(n(\vec{r}))$, the results for the homogeneous electron gas with the density $n(\vec{r})$ is utilized. Among many variations [44, 45, 49], the result by Ceperley and Alder [50] as parametrized by Perdew and Zunger [46] is widely used recently. We adopt in this thesis Wigner's interpolation formula [51].

We will express the total energy in the momentum space [52]. The wave function is expanded in plane waves

$$\Psi_{i,\vec{k}}(r) = \sum_{\vec{G}} \Psi_{i,\vec{k}}(\vec{G})e^{i(\vec{k}+\vec{G})\vec{r}}, \tag{2.34}$$

where i is a band index, $\vec{k}$ a wave vector in the first Brillouin zone, $\vec{G}$ a reciprocal lattice vector and $\Psi_{i,\vec{k}}(\vec{G})$ a coefficient of the expanded plane wave. The K-S equation, eq. (2.28), in the momentum space is written as

$$\sum_{\vec{G}'}[\frac{1}{2}(\vec{k}+\vec{G}')^2\delta_{\vec{G},\vec{G}'} + V_{\vec{k}+\vec{G},\vec{k}+\vec{G}'}]\Psi_{i,\vec{k}}(\vec{G}') = \lambda_{i,\vec{k}}\Psi_{i,\vec{k}}(\vec{G}), \tag{2.35}$$

with

$$\begin{aligned} V_{\vec{k}+\vec{G},\vec{k}+\vec{G}'} &= V_H(\vec{G}-\vec{G}') + V_{xc}(\vec{G}-\vec{G}') + V_{local}(\vec{G}-\vec{G}') \\ &+ \sum_l V^l_{non-local}(\vec{k}+\vec{G},\vec{k}+\vec{G}')\hat{P}_l, \end{aligned} \tag{2.36}$$

where $\lambda_{i,\vec{k}}$ is the eigen-value and $\hat{P}_l$ is a projection operator for l.

The eigen-vectors and eigen-values are obtained by diagonalizing the matrix of the K-S equation, eq.(2.35). However, the matrix diagonalization method requires an N^3 order task of calculation and an N^2 order memory in the case of N plane waves. It becomes virtually impossible to calculate the electronic structure in the case of a large unit cell (supercell). For example, in the case of double precision complex with $N = 10000$, the memory region amounts to an order of $(N^2 \times 16 =)$ 1.6Gbytes and the number of numerical operations an order of $(N^3 =)\ 10^{12}$.

The charge density is needed for obtaining the Hartree and exchange-correlation potentials or energies. As the task for obtaining the charge density is very heavy in our calculation, we have to adopt an efficient procedure of calculating the charge density. The charge densities in the real and momentum spaces are

$$\rho(\vec{r}) = \sum_{i}^{occupied} \sum_{\vec{k}} \rho_{i,\vec{k}}(\vec{r}), \tag{2.37}$$

with

$$\rho_{i,\vec{k}}(\vec{r}) = \mid \sum_{\vec{G}} \Psi_{i,\vec{k}}(\vec{G}) e^{i\vec{G}\vec{r}} \mid^2, \tag{2.38}$$

and in $\vec{G}$ space

$$\rho(\vec{G}) = \frac{1}{\Omega} \int \rho(r) e^{-i\vec{G}\cdot\vec{r}} d\vec{r} = \sum_{i}^{occupied} \sum_{\vec{k}} \rho_{i,\vec{k}}(\vec{G}), \tag{2.39}$$

with

$$\begin{aligned} \rho_{i,\vec{k}}(G) &= \frac{1}{\Omega} \int \rho_{i,\vec{k}}(\vec{r}) e^{-i\vec{G}\vec{r}} d\vec{r} \\ &= \sum_{\vec{G}'} \Psi^*_{i,\vec{k}}(\vec{G}' - \vec{G}) \Psi_{i,\vec{k}}(\vec{G}'), \end{aligned} \tag{2.40}$$

where the integration is over the unit cell volume Ω.

We first obtain $\Psi_{i,\vec{k}}(\vec{G})$ as eigen-vectors of the eigen-value problem and then calculate $\rho_{i,\vec{k}}(\vec{G})$, $\rho(\vec{G})$, $\rho_{i,\vec{k}}(\vec{r})$ and $\rho(\vec{r})$. If we adopt eq. (2.40) for calculating $\rho_{i,\vec{k}}(\vec{G})$, preparation of the set $\{\rho(\vec{G})\}$ requires an N^2 order task of calculations. This can be reduced to an $N \log N$ order task by calculating $\rho_{i,\vec{k}}(\vec{r})$ of eq. (2.38) by using inverse FFT and then $\rho_{i,\vec{k}}(\vec{G})$ again by using FFT as

$$\rho_{i,\vec{k}}(\vec{G}) = \frac{1}{\Omega}\int \rho_{i,\vec{k}}(\vec{r})e^{-i\vec{G}\vec{r}}d\vec{r}. \tag{2.41}$$

This procedure has another merit that $\rho(\vec{r})$ is obtained as a byproduct of $\rho(\vec{G})$. It should be noted that even if a plane wave expansion is adopted, $\rho(\vec{r})$ is a necessary quantity in the calculation of the exchange-correlation potential and energy.

Finally, the expression for the total energy in our calculation is

$$\begin{aligned} E^{(n)}_{total} &= \sum_{i}^{occupied}\sum_{\vec{k}}\lambda_{i,\vec{k}} - 4\pi\Omega\sum_{G\neq 0}\frac{\rho^{*(n-1)}(\vec{G})}{\vec{G}^2}\rho^{(n)}(\vec{G}) \\ &- \sum_{\vec{G}} V^{*(n-1)}_{xc}(\vec{G})\rho^{(n)}(\vec{G}) + 4\pi\Omega\frac{1}{2}\sum_{G\neq 0}\frac{\rho^{*(n)}(\vec{G})}{\vec{G}^2}\rho^{(n)}(\vec{G}) \\ &+ \sum_{\vec{G}} E^{*(n)}_{xc}(\vec{G})\rho^{(n)}(\vec{G}) + \alpha_1 Z + \gamma_{Ewald}, \end{aligned} \tag{2.42}$$

where the superscript n implies the n-th step iteration, $\alpha_1 Z$ is the correction term of a local pseudopotential [53] and γ_{Ewald} is the Ewald term which is an electrostatic energy of ions and the uniform part of the electron density. In the above equation, $\sum_i^{occupied}$ means that a summation over the energy bands at each k-point for sampling are up to the Fermi energy.

Although the last term of the total energy equation includes the diverging terms for the ionic and electronic parts, it can be properly evaluated by the Ewald method. The expression for γ_{Ewald} is given by

$$\begin{aligned} \gamma_{Ewald} &= \frac{1}{2}\sum_{s,s'} 2Z_s Z_{s'}\Big[\frac{4\pi}{\Omega}{\sum_{\vec{G}}}'\frac{1}{\mid \vec{G}\mid^2}e^{i\vec{G}(\vec{\tau}_s-\vec{\tau}_{s'})}e^{-\frac{|\vec{G}|^2}{4\alpha}} - \frac{1}{\Omega}\frac{\pi}{\alpha} \\ &+ {\sum_{\vec{l}}}'\frac{1-erf(\alpha^{\frac{1}{2}}\mid \vec{l}+\vec{\tau}_s-\vec{\tau}_{s'}\mid)}{\mid \vec{l}+\vec{\tau}_s-\vec{\tau}_{s'}\mid} - 2(\frac{\alpha}{\pi})^{\frac{1}{2}}\delta_{s,s'}\Big], \end{aligned} \tag{2.43}$$

where $\vec{l}$ is a lattice vector, Z_s the valence of the s-th ion, $\vec{\tau}_s$ its basis vector in the unit cell, α a numerical factor for convergence in the Ewald summation and $erf(x)$ an error function. In this equation, the prime of $\sum$ means that it excludes the term of $\vec{G}=0$ and also the one of $\vec{l}=0$ when $s=s'$.

The Fermi energy must be obtained before calculating the total energy and charge density. The summation over k-points for sampling in the first

Brillouin zone is usually performed by the tetrahedron method [54, 55] for accurate calculations. However, in supercell calculations, the number of sampling k-points is only a few in general so that the tetrahedron method is not applicable. Therefore, in our calculation the Fermi energy ϵ_f is obtained by summing up the artificially broadened energy spectrum: the energy spectrum at each k-point is broadened with an adequate width. The width is not necessary for non-metallic systems with a band gap. However, if the width is very small for metallic systems, the Fermi energy oscillates in the process of calculation because of the possible interchange between the occupied and unoccupied states.

After the eigen-vectors and eigen-values are obtained by using the matrix diagonalization, the Fermi energy is determined by counting the occupied states. The charge density is obtained from the eigen-vectors. After these calculations, the total energy of the electronic part is calculated for a given ionic configuration. The final step is a convergence check and charge mixing. The input and output charge densities are mixed for faster convergence. The calculation is continued until the difference between input and output values (charge density, potential, total energy, etc) is smaller than a given criterion. Here, the flow chart of the above calculation is shown in Fig. 2.1.

2.3 Hellmann-Feynman force

It is possible to calculate the forces [52] which act on the ions in the unit cell on the basis of the Hellmann-Feynman theorem [3, 4, 5]. The force acting on the s-th ion is divided into two contributions:

$$\vec{F}_s = -\frac{\partial E_{total}}{\partial \vec{\tau}_s} = \vec{F}_s^e + \vec{F}_s^{Ewald}. \tag{2.44}$$

The electronic part $\vec{F}_s^e$ is given by

$$\begin{aligned}
\vec{F}_s^e &= i\Omega \sum_{\vec{G}} \rho^*(\vec{G})\vec{G}e^{-i\vec{G}\vec{\tau}_s} V_{local}^s(\vec{G}) \\
&- i\Omega \sum_{i}^{occupied} \sum_{\vec{k}} \sum_{l} \sum_{\vec{G},\vec{G}'} (\vec{G}' - \vec{G})\Psi_{i,\vec{k}}^*(\vec{G})\Psi_{i,\vec{k}}(\vec{G}')e^{i(\vec{G}'-\vec{G})\vec{\tau}_s} \\
&\times V_{non-local}^{l,s}(\vec{k}+\vec{G}, \vec{k}+\vec{G}'),
\end{aligned} \tag{2.45}$$

and the ionic part $\vec{F}_s^{Ewald}$ originating from γ_{Ewald} is given by

$$\begin{aligned}\vec{F}_s^{Ewald} &= Z_s \sum_{s\neq s'} Z'_s \Big[\frac{4\pi}{\Omega} \sum_{\vec{G}\neq 0} [\frac{\vec{G}}{\mid \vec{G} \mid^2} \sin [\vec{G}(\vec{\tau}_s - \vec{\tau}'_s)] e^{-\frac{|\vec{G}|^2}{4\alpha}}]\Big] \\ &+ \sum_{\vec{l}} \Big[\frac{\vec{x} erfc(\alpha^{\frac{1}{2}} \mid \vec{x} \mid)}{\mid \vec{x} \mid^3} + (\frac{\alpha}{\pi})^{\frac{1}{2}} \frac{2\vec{x}}{\mid \vec{x} \mid^2} e^{-\alpha|\vec{x}|^2}\Big]_{\vec{x}=\vec{l}+\vec{\tau}_s-\vec{\tau}_{s'}}, \qquad (2.46)\end{aligned}$$

where $erfc(x) = 1 - erf(x)$. In the above equations based on the plane wave basis, it is interesting to note that several contributions originating from the $\vec{\tau}_s$ dependence of the electron density $\rho(\vec{r})$ cancel out and that only the terms including $V_{local}(\vec{G})$ and $V^l_{non-local}(\vec{k}+\vec{G}, \vec{k}+\vec{G}')$ remain.

In $\vec{F}^e_s$, the second term in the right hand side of eq. (2.45) is a double summation with respect to $\vec{G}$ and $\vec{G}'$. Therefore, the task of calculation of this term is very heavy. As is shown below, however, it is possible to reduce this task by using the K-B separable form of the non-local part of the pseudopotential [40]. In the second term of eq. (2.45), we consider the following quantity

$$\begin{aligned}\vec{F}^{e,NL}_{s,i,\vec{k}} &= -i\Omega \sum_{\vec{G},\vec{G}'} (\vec{G} - \vec{G}') \Psi^*_{i,\vec{k}}(\vec{G}) \Psi_{i,\vec{k}}(\vec{G}') e^{i(\vec{G}'-\vec{G})\vec{\tau}_s} \\ &\times V^{l,s}_{non-local}(\vec{k}+\vec{G}, \vec{k}+\vec{G}'). \qquad (2.47)\end{aligned}$$

By using eqs. (2.17) and (2.19), we define

$$\vec{A}_{s,i,\vec{k}} = \sum_{\vec{G}} \vec{G} \Psi_{i,\vec{k}}(\vec{G}) e^{i\vec{G}\vec{\tau}_s} V^{NL}_{s,l}(\vec{k}+\vec{G}), \qquad (2.48)$$

and

$$\vec{B}_{s,i,\vec{k}} = \sum_{\vec{G}} \Psi^*_{i,\vec{k}}(\vec{G}) e^{i\vec{G}\vec{\tau}_s} V^{NL}_{s,l}(\vec{k}+\vec{G}), \qquad (2.49)$$

with which eq. (2.47) is reduced to

$$\vec{F}^{s,NL}_{e,i,\vec{k}} = -i\Omega(\vec{A}_s \vec{B}_s - \vec{A}^*_s \vec{B}^*_s). \qquad (2.50)$$

The task of the calculation for the non-local pseudopotential part in the force is very heavy with the non-separable form. With the increase of the number of atoms and plane waves, this task becomes heavier and heavier so that it becomes difficult to perform the molecular dynamics for ions by using these forces. Therefore, the reduction of the task from an N^2 order to an N order by using the K-B separable form is crucial in practice.

2.4 Car-Parrinello method

So far, we have described the standard electronic structure calculation by using the norm-conserving pseudopotential, the plane wave basis and the matrix diagonalization on the basis of the local density approximation in the density functional theory. The problems in the matrix diagonalization method are an N^3 order task of calculation and an N^2 order memory.

In 1985, Car and Parrinello developed a new and epochal method for the electronic and ionic structure calculation [6]. In this method, the electronic and ionic parts of the system are solved simultaneously by using the differential equations like a Newton equation. It is possible to obtain the ground state of the electronic structure and optimize the ionic structure simultaneously. In addition, this method does not include matrix diagonalization and the task of the calculation and the memory are reduced. For these reasons, it is advantageous to use this method in order to optimize electronic and ionic structures in large systems.

In the optimization process for the ionic structure, the electronic state should be close to the Born-Oppenheimer surface of the ground state. Otherwise the accurate forces are not obtained and therefore, it is impossible to perform accurate molecular dynamics for ionic systems. In the Car-Parrinello method, it is possible to keep the electronic state close to the Born-Oppenheimer surface by adjusting some parameters so that the electronic degrees of freedom may follow the ionic motion quickly.

In the following, we describe the basic idea of the Car-Parrinello method briefly. We express the total energy of the system as $E[\{\Psi_{i,\vec{k}}\},\{\vec{R}_I\}]$. $\{\Psi_{i,\vec{k}}\}$ denotes a set of trial Kohn-Sham orbitals occupied by electrons and $\{\vec{R}_I\}$ is a set of ionic positions. The ground state of the system for the optimized ionic positions corresponds to the global minimum of $E[\{\Psi_{i,\vec{k}}\},\{\vec{R}_I\}]$ in the extended space spanned by $\{\Psi_{i,\vec{k}}\}$ and $\{\vec{R}_I\}$. In this sense, the structural optimization based on the DF electronic structure calculation corresponds to the minimization of $E[\{\Psi_{i,\vec{k}}\},\{\vec{R}_I\}]$ with respect to $\{\Psi_{i,\vec{k}}\}$ and $\{\vec{R}_I\}$.

Car and Parrinello adopted a molecular dynamics method for the minimization of $E[\{\Psi_{i,\vec{k}}\},\{\vec{R}_I\}]$ and introduced a fictitious equation of motion for $\Psi_{i,\vec{k}}$ through the following Lagrangian.

$$\begin{aligned} L &= \sum_{i,\vec{k}} \int m \mid \dot{\Psi}_{i,\vec{k}}(\vec{r}) \mid^2 d\vec{r} + \sum_I \frac{1}{2} M_I \dot{\vec{R}}_I^2 - E[\{\Psi_{i,\vec{k}}\},\{\vec{R}_I\}] \\ &+ \sum_{i,j,\vec{k}} \Lambda_{ij,\vec{k}} \left(\int \Psi^*_{i,\vec{k}}(\vec{r}) \Psi_{j,\vec{k}}(\vec{r}) d\vec{r} - \delta_{ij} \right), \end{aligned} \tag{2.51}$$

where m is a fictitious mass, M_I is the mass of an ion and the last term with the Lagrange multiplier $\Lambda_{ij,\vec{k}}$ originates from the orthonormality constraints

$$\int \Psi^*_{i,\vec{k}}(\vec{r}) \Psi_{j,\vec{k}}(\vec{r}) d\vec{r} = \delta_{ij}. \tag{2.52}$$

With eq. (2.51), the equations of motion are given by

$$\frac{d}{dt}\left(\frac{\delta L}{\delta \dot{\Psi}^*_{i,\vec{k}}} \right) = \frac{\delta L}{\delta \Psi^*_{i,\vec{k}}}, \tag{2.53}$$

and

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{R}_I} \right) = \frac{\partial L}{\partial R_I}. \tag{2.54}$$

Therefore

$$m \ddot{\Psi}_{i,\vec{k}}(\vec{r},t) = -\frac{\delta E}{\delta \Psi^*_{i,\vec{k}}(\vec{r},t)} + \sum_j \Lambda_{ij,\vec{k}} \Psi_{j,\vec{k}}(\vec{r},t), \tag{2.55}$$

and

$$M_I \ddot{\vec{R}}_I = - \nabla_{\vec{R}_I} E. \tag{2.56}$$

By using $\frac{\delta E}{\delta \Psi^*} = H\Psi$, eq. (2.55) is reduced to

$$m \ddot{\Psi}_{i,\vec{k}}(\vec{r},t) = -H \Psi_{i,\vec{k}}(\vec{r},t) + \sum_j \Lambda_{ij,\vec{k}} \Psi_{j,\vec{k}}(\vec{r},t), \tag{2.57}$$

where H is the Kohn-Sham one-electron Hamiltonian. Equation (2.57) is solved numerically by the Verlet algorithm [56] combined with the Ryckaert et al. method [57] for determine $\Lambda_{ij,\vec{k}}$. It should be noted here that the time-dependence of the wave function does not have any real physical meaning.

It is completely a mathematical trick for solving the eigen-value problem for the Kohn-Sham equation iteratively. In fact, if $\Psi_{i,\vec{k}}$ comes close to the solution of the Kohn-Sham equation, $\Psi_{i,\vec{k}}$ becomes stationary and eq.(2.57) is reduced to the K-S equation.

As for the optimization process for the structure of ions, the system generally has some local minimum states. In the case of searching the local or global minimum states of $E[\{\Psi_{i,\vec{k}}\},\{\vec{R}\}]$, the first step of the optimization process is to cooling down only the electronic state to the Born-Oppenheimer surface (ground state) for the initial fixed ionic position. This is shown as a process (1) in Fig. 2.2. After this step, the electronic and ionic states are solved simultaneously as a process (2). Finally, the process of calculation will stop when the system comes sufficiently close to the local or global minimum state as a process (3).

There are some methods which are different from the original Car-Parrinello method. The steepest descent (SD) and the modified steepest descent (MSD) methods [58, 59, 60, 61] which originate from Williams and Soler [62] are used in this study and will be described in detail in the following subsections.

2.4.1 Steepest descent method

We adopted two methods, one is the steepest descent (SD) method which will be described in this subsection, the other is the modified steepest descent (MSD) method which will be described in the next subsection. In the SD method, the eigen-vectors are solved dynamically by integrating the first order differential equation.

$$\begin{aligned}
\nu\dot{\Psi}_{i,\vec{k}}(\vec{G},t) &= -\frac{1}{2}\mid \vec{k}+\vec{G}\mid^2 \Psi_{i,\vec{k}}(\vec{G},t) \\
&- \sum_{G'}\{V_H(\vec{G}-\vec{G'})+V_{xc}(\vec{G}-\vec{G'})+V_{local}(\vec{G}-\vec{G'})\}\Psi_{i,\vec{k}}(\vec{G'},t) \\
&- \sum_{G',l} V^l_{non-local}(\vec{k}+\vec{G},\vec{k}+\vec{G'})\Psi_{i,\vec{k}}(\vec{G'},t) \\
&+ \sum_j \Lambda_{ij,\vec{k}}\Psi_{j,\vec{k}}(\vec{G},t), \qquad (2.58)
\end{aligned}$$

where ν is a fictitious friction parameter. The simplest way of solving eq. (2.58) is

$$\Psi_{i,\vec{k}}(\vec{G},t+\Delta t) = \Psi_{i,\vec{k}}(\vec{G},t) + \Delta t\dot{\Psi}_{i,\vec{k}}(\vec{G},t), \tag{2.59}$$

where Δt is a time step. The explicit expression for $\Lambda_{ij,\vec{k}}$, which is valid to the first order in Δt, is given by

$$\Lambda_{ij,\vec{k}}(t) = \int \Psi^*_{j,\vec{k}}(\vec{r},t)H(t)\Psi_{i,\vec{k}}(\vec{r},t)d\vec{r}. \tag{2.60}$$

The derivation of eq.(2.60) is given in Appendix B. In this thesis, we replace $\Lambda_{ij,\vec{k}}$ with a diagonal matrix $\lambda_{i,\vec{k}}\delta_{ij}$. This means that only the normalization constraint for the wave functions is taken into account. The Gram-Schmidt orthogonalization process is introduced after every time step in order to guarantee the orthonormality for $\{\Psi_{i,\vec{k}}(\vec{G},t+\Delta t)\}$. In order to save computational time, we further introduce a following approximation, bearing the following situation in mind. The initial stage of the calculation is fairly efficient in the sense that the system approaches the equilibrium configuration rather quickly. Then the force acting on each atom becomes small and the time evolution of the system becomes slow. The calculation for this part requires a lot of computer time to attain the convergence criterion. The slow time evolution of the system in the latter part of the time steps allows us to use the following expression for $\lambda_{i,\vec{k}}$:

$$\lambda_{i,\vec{k}}(t+\Delta t) = \int \Psi^*_{i,\vec{k}}(\vec{r},t+\Delta t)H(t)\Psi_{i,\vec{k}}(\vec{r},t+\Delta t)d\vec{r}, \tag{2.61}$$

which can be transformed into an efficient expression as

$$\begin{aligned}
\lambda_{i,\vec{k}}(t+\Delta t) &= \sum_{\vec{G},\vec{G}'} \Psi^*_{i,\vec{k}}(\vec{G},t+\Delta t) < \vec{G} \mid H(t) \mid \vec{G}' > \Psi_{i,\vec{k}}(\vec{G}',t+\Delta t) \\
&= \lambda_{i,\vec{k}} - \nu \sum_{\vec{G}} \{\dot{\Psi}^*_{i,\vec{k}}(\vec{G},t)\Psi_{i,\vec{k}}(\vec{G},t+\Delta t) - \Psi^*_{i,\vec{k}}(\vec{G},t+\Delta t)\dot{\Psi}_{i,\vec{k}}(\vec{G},t) \\
&\quad + \Psi^*_{i,\vec{k}}(\vec{G},t)\dot{\Psi}_{i,\vec{k}}(\vec{G},t)\} + \mathrm{O}(\Delta t^2),
\end{aligned} \tag{2.62}$$

where $< \vec{G}|$ means the bra of plane waves. This expression is derived in Appendix C. Although the first expression of $\lambda_{i,\vec{k}}(t+\Delta t)$ in eq. (2.62) includes the double summation over $\vec{G}$ and $\vec{G}'$, the second approximate expression includes only the single summation over $\vec{G}$. Therefore, an N^2 order task is reduced to an N order one. As all the expressions from eq. (2.59) to eq. (2.62) are approximations, the time dependence of $\Psi_{i,\vec{k}}(\vec{G},t)$ is described only approximately. Nevertheless, the starting differential equation for $\Psi_{i,\vec{k}}(\vec{G},t)$ is an artificial one and thereby it is not necessary to solve it very accurately. We should emphasize that the final stationary solution is not affected by the approximations introduced above. The flow chart of the SD (or MSD) calculation is shown in Fig. 2.3.

2.4.2 Modified steepest descent method

In the MSD method, the differential equation in eq. (2.58) is solved analytically on the assumption that only the diagonal part of Hamiltonian, $< \vec{G} \mid H(t) \mid \vec{G} >$, depends on time [58, 59, 60, 63]. Therefore, the allowed Δt is the time interval during which $\Psi_{i,\vec{k}}(\vec{G}')$ $(\vec{G}' \neq \vec{G})$ can be regarded as a constant. As a result, it is possible to perform the calculation with a larger time step Δt than that of the SD case, so that the number of steps in the MSD method for attaining a convergence is $\frac{1}{2} \sim \frac{1}{5}$ of that in the SD method.

The explicit expression for the MSD is derived as follows,

$$\begin{aligned}
\nu\dot{\Psi}_{i,\vec{k}}(\vec{G},t) = & - [\frac{1}{2} \mid \vec{k}+\vec{G} \mid^2 + V(\vec{G}=0) \\
& + \sum_l V^l_{non-local}(\vec{k}+\vec{G},\vec{k}+\vec{G}) - \lambda_{i,\vec{k}}]\Psi_{i,\vec{k}}(\vec{G},t) \\
& - \sum_{\vec{G}'(\neq\vec{G})} [V(\vec{G}-\vec{G}') + \sum_l V^l_{non-local}(\vec{k}+\vec{G},\vec{k}+\vec{G}')] \\
& \times\Psi_{i,\vec{k}}(\vec{G}',t), \qquad (2.63)
\end{aligned}$$

where $V(\vec{G}-\vec{G}') = V_H(\vec{G}-\vec{G}') + V_{xc}(\vec{G}-\vec{G}') + V_{local}(\vec{G}-\vec{G}')$, the first term is a diagonal part of Hamiltonian with the time dependence taken into account and the second term is an off-diagonal part which is assumed to be time independent. By defining the following quantities W and R by

$$\begin{aligned}
W = & \frac{1}{\nu}\Big[\frac{1}{2} \mid \vec{k}+\vec{G} \mid^2 + V(\vec{G}=0) \\
& + \sum_l V^l_{non-local}(\vec{k}+\vec{G},\vec{k}+\vec{G}) - \lambda_{i,\vec{k}}\Big], \qquad (2.64)
\end{aligned}$$

and

$$R = \frac{1}{\nu} \sum_{\vec{G}'(\neq\vec{G})} [V(\vec{G}-\vec{G}') + \sum_l V^l_{non-local}(\vec{k}+\vec{G},\vec{k}+\vec{G}')]$$

$$\times \Psi_{i,\vec{k}}(\vec{G}', t), \tag{2.65}$$

eq. (2.63) becomes

$$\begin{aligned}
\dot{\Psi}_{i,\vec{k}}(\vec{G}, t) &= -W\Psi_{i,\vec{k}}(\vec{G}, t) - R \\
&= -W(\Psi_{i,\vec{k}}(\vec{G}, t) + \frac{R}{W}).
\end{aligned} \tag{2.66}$$

The solution of eq. (2.66) is

$$\Psi_{i,\vec{k}}(\vec{G}, t + \Delta t) = e^{-W\Delta t}\Psi_{i,\vec{k}}(\vec{G}, t) + (e^{-W\Delta t} - 1)\frac{R}{W}. \tag{2.67}$$

In this treatment, the error originates from the assumption that R is time-independent. From our experience, the time step Δt for the MSD calculation can be five times as large as that of the SD case. If we use an even larger time step, the calculation does not converge.

In the original Car-Parrinello method, the sum of the kinetic energy of the electronic and ionic parts and the total energy of the electronic part which includes the electrostatic term of ions (Ewald term) is constant exactly in the process of calculation if the Ryckaert method [57] for orthonormalization of eigen-vectors is adopted:

$$\sum_{i,\vec{k}}^{occupied} \frac{1}{2} m \int |\ \dot{\Psi}_{i,\vec{k}}\ |^2\ d\vec{r} + \sum_I \frac{1}{2} M_I \dot{\vec{R}}_I^2 + E_{tot}[\{\Psi_{i,\vec{k}}\}, \{\vec{R}_I\}] = \text{const.} \tag{2.68}$$

However, in the SD and MSD methods, such an energy conservation does not hold. The terms in the left hand side in eqs. (2.58) and (2.63) have a friction parameter ν, so that an energy dissipation should occur in the process of calculation.

This energy dissipation is explained in the following. Let us calculate the following quantity:

$$\frac{d}{dt}\{\frac{1}{2}\sum_I M_I \dot{\vec{R}}_I^2\} + \frac{dE_{tot}}{dt}. \tag{2.69}$$

The derivative of the total energy is

$$\frac{dE_{tot}}{dt} = \sum_i^{occupied} \sum_{\vec{k}} \int (\frac{\delta E_{tot}}{\delta \Psi_{i,\vec{k}}} \frac{d\Psi_{i,\vec{k}}}{dt} + \frac{\delta E_{tot}}{\delta \Psi^*_{i,\vec{k}}} \frac{d\Psi^*_{i,\vec{k}}}{dt}) d\vec{r}$$

$$+ \sum_I \frac{\partial E_{tot}}{\partial \vec{R}_I} \frac{d\vec{R}_I}{dt}. \tag{2.70}$$

In this equation, the first and second terms are reduced to

$$\frac{\delta E_{tot}}{\delta \Psi_{i,\vec{k}}} \frac{d\Psi_{i,\vec{k}}}{dt} = (H\Psi^*_{i,\vec{k}})\dot{\Psi}_{i,\vec{k}}, \tag{2.71}$$

$$\frac{\delta E_{tot}}{\delta \Psi^*_{i,\vec{k}}} \frac{d\Psi^*_{i,\vec{k}}}{dt} = (H\Psi_{i,\vec{k}})\dot{\Psi}^*_{i,\vec{k}}, \tag{2.72}$$

and the last term is transformed into

$$\sum_I \frac{\partial E_{tot}}{\partial \vec{R}_I} \frac{d\vec{R}_I}{dt} = -\sum_I M_I \ddot{\vec{R}}_I \dot{\vec{R}}_I = -\frac{d}{dt}(\frac{1}{2}\sum_I M_I \mid \dot{\vec{R}}_I \mid^2). \tag{2.73}$$

Therefore, the last term in eq.(2.73) cancels with the first term in eq.(2.69). The remaining terms can be rewritten by using the equation $\nu\dot{\Psi}_i = -H\Psi_i + \sum_j \Lambda_{ij}\Psi_j$:

$$\begin{aligned} & \sum_i < \dot{\Psi}_i \mid H \mid \Psi_i > + \sum_i < \dot{\Psi}_i \mid H \mid \Psi_i >^* \\ = & \sum_{ij} \{< \dot{\Psi}_i \mid H\delta_{ij} - \Lambda_{ij} \mid \Psi_j > + < \dot{\Psi}_i \mid \Lambda_{ij} \mid \Psi_j >\} + \ c.c. \\ = & -2\nu \sum_i < \dot{\Psi}_i \mid \dot{\Psi}_i > + \sum_{ij} \Lambda_{ij} \{< \dot{\Psi}_i \mid \Psi_j > + < \Psi_i \mid \dot{\Psi}_j > \} \end{aligned} \tag{2.74}$$

where the index $\vec{k}$ and the summation over it are implicitly included. Noticing that $\frac{d}{dt} < \Psi_i \mid \Psi_j >= 0$ for the second term of eq. (2.74), we obtain

$$\frac{d}{dt}\left\{\frac{1}{2}\sum_I M_I \dot{\vec{R}}_I^2 + E_{tot}[\{\Psi_{i,\vec{k}}\}, \{\vec{R}_I\}]\right\} = -2\nu \sum_{i,\vec{k}}^{occupied} \int \mid \dot{\Psi}_{i,\vec{k}} \mid^2 d\vec{r}. \tag{2.75}$$

This relation suggests that the total energy of the ionic part is decreasing monotonously.

In our calculation, the charge density is mixed in each iteration in order to suppress the charge oscillation which seems to be enhanced in surface systems. In our test calculations for some bulk systems, it is not necessary to introduce this charge mixing. The effect of this charge mixing on the energy balance problem discussed above is not sufficiently understood at present.

In our SD and MSD calculations, the initial wave function expanded in plane waves is given by using the matrix diagonalization. In this case, the cutoff energy, which determines the number of plane waves, is set to be about half of that in the following iterations in order to save memory and CPU-time. Of course, the final results are not affected by this initial wave function.

2.5 Molecular dynamics for ionic part

The ionic motion is governed by the Hellmann-Feynman forces [3, 4, 5] which were discussed in Section 2.3. The ionic coordinates in the unit cell are updated by the Verlet algorithm [56] as follows,

$$\vec{R}_I(t+\Delta t) = 2\vec{R}_I(t) - \vec{R}_I(t-\Delta t) + \frac{\vec{F}_{HF}(\vec{R}_I)}{M_I}(\Delta t)^2 \tag{2.76}$$

where $\vec{R}_I(t+\Delta t)$ is the coordinate of I-th ion at time $t+\Delta t$, $\vec{F}_{HF}$ is the Hellmann-Feynman force and Δt is a time step.

In our calculation, the ions are initially displaced from symmetry points sufficiently in order to allow them to move toward a lower energy configuration. At first, the ions are accelerated by the forces and temperature of the ionic system increases. However, due to the relation given by eq. (2.75) the sum of the total energy and kinetic energy of the ions starts to decrease after some time. The temperature of the ionic part eventually decreases to zero Kelvin after taking some peaks. The process of calculation is terminated when the convergence criterion that forces acting on ions is less than $1.0 \times 10^{-3} Ry/a.u.$ is satisfied. A word of warning is necessary here. The use of the SD and MSD method for the electronic part tends to quickly reduce the kinetic energy of ions and therefore lead to a local minimum instead of the global minimum. To obtain the global minimum configuration, it may be better to adopt the original Car-Parrinello method for the electronic part.

Chapter 3

Results and discussion

3.1 Test calculations for bulk systems

In this section, we will describe the results of test calculations for bulk systems in order to check the pseudopotentials and the program. The calculated systems are Li, Na, Al and Si for which some theoretical calculations have already been performed with the same norm-conserving pseudopotential with the plane wave basis [64, 65, 66, 67]. We calculate the electronic properties (the total energy and the dispersion curve) and obtain the equilibrium lattice constants and bulk moduli for these systems. The bulk systems of Li and Na are metals and their crystal structures are bcc. Al is also a metal and its crystal structure is fcc. Si is a semiconductor and takes a diamond structure.

The conditions (the cutoff energy E_{cut} and number of k-points for sampling N_k) and results of the calculations are summarized in Table 3.1. The results of Al and Si agree fairly well with the experimental data [68]. On the other hand, the agreement is poor for Li and Na: the equilibrium lattice constants are underestimated and the bulk moduli are overestimated accordingly. It is known that a partial core correction [31] plays an important role in the case of alkali metals. As a matter of fact, the results are improved significantly by considering the partial core correction for Na. Most of the results presented in this thesis are those without the partial core correction except some results presented in section 3.3.

Next, we attempt a test of the FPMD for the electronic and ionic parts. The following simple model is set for a test calculation. We prepare a cubic unit cell which includes two Al atoms. The Al atoms are initially displaced along the [111] direction from the positions corresponding to the bcc structure. We first calculate only the electronic part to bring it to the Born-Oppenheimer surface for the ground state corresponding to the initial condition. After this procedure, the electronic and ionic parts are solved simultaneously to optimize the structure. The displaced atoms start to return to the equilibrium bcc positions in the process of calculation and the final equilibrium structure becomes the perfect bcc structure.

3.2 Calculation of Si(001) surface

The purpose of this thesis is the clarification of the optimized structures of the alkali adsorbed Si(001) surfaces and their dependences on the coverage and adsorbed atomic type.

The geometry of the possible adsorption sites for Na is schematically shown in Fig. 3.1. Here the following notations are used: HH and HB denote the hollow site and the bridge site respectively along the hill of the dimer chain, T3(T4) is the site along the trough on-top of the third(fourth) layer Si atom, B1 is the on-top site of the raised Si atom of an asymmetric Si-Si dimer, and B2 denotes the bridge site between the two raised Si atoms of the neighboring Si-Si dimers. HH site is called a hollow or pedestal site, HB is called a bridge site, T3 is called a valley bridge site, and T4 is called a cave site by other research groups.

The starting substrate configuration is set to be the asymmetric dimer for all systems, which is optimized separately for the clean surface. In each case, the alkali atoms are put slightly off ($5\% \sim 12.5\%$ of the side length of the unit cell) the symmetry positions HH, HB, T3, and T4 in order to allow them to move toward lower energy configurations.

A repeated slab geometry and supercell method are adopted for surface systems. A supercell is a large unit cell which includes several tens to a hundred of atoms. In a repeated slab geometry, the unit cell includes the atomic layers and vacuum region as schematically illustrated in Fig. 3.2. The thickness of the vacuum region should be chosen in such a way that the interaction between the atomic slabs through the vacuum region can be neglected and the number of the atomic layers should be chosen in such a way that the interaction between two surfaces through bulk can be neglected. In our calculation, the number of atomic (Si) layers is ten, and the thickness of the vacuum region is the same as that of the atomic layers. The thickness of the vacuum region is sufficient since the wave functions for the occupied states decay into the vacuum exponentially and the electron density near the center of the vacuum region is vanishingly small. Figure 3.3 shows an example of the electron density for the full coverage Na adsorption case. On the other hand, the thickness of the atomic layers may not be sufficient but is near the upper limit imposed by the present computer capability.

The distributions of sampling k-points adopted in the following for the (2×1) unit cell are shown in Fig. 3.4. The cutoff energy E_{cut}, the number of plane waves N_w, the number of sampling k-points N_k, and some results of calculations are listed in Table 3.2. They include the total energies, the heights of alkali atoms, the nearest interatomic distance between the alkali adatom and the substrate Si atom and the distance of the Si-Si dimer atoms.

3.2.1 Clean surface

Some LEED experiments demonstrate that the clean surface of Si(001) exhibits a c(4×2) pattern which is generally believed to be an ordering state of asymmetric dimers [10]. On the other hand, asymmetric dimers can be clearly observed only near the step or some other defects by STM measurements [8, 69]. In the clean surface region of Si(001) without step or vacancies, STM observes a symmetric dimer. The symmetric dimers observed by STM may be due to thermal oscillations of the asymmetric dimers, since it observes an average for time of the order of 1.0×10^{-2} seconds [69].

We study whether the asymmetric dimer is stabilized or not with three different conditions for the cutoff energy and the k-space sampling and show the results in Table 3.3. Although the energy difference has not converged yet with respect to the cutoff energy E_{cut}, the asymmetric dimer has a lower energy for all three cases, being consistent with other calculations [13, 14, 15, 16, 17, 18, 19]. The energy separation between the π and π^* band gap states becomes wider by about 0.01 a.u. (0.27eV) when the symmetric Si-Si dimer is transformed to the asymmetric one as seen in Fig. 3.5. The Si-Si dimer distance in our calculation is 2.30 Å being shorter than the experimental estimate of 2.45 Å by 6%.

In Fig. 3.6, the electron density for the clean surface is shown. Its dimer structure is asymmetric and the raised Si atom of the asymmetric dimer is slightly more populated by electrons than the lower one. This charge transfer was first discussed by Chadi [16] based on the empirical tight-binding calculation and also discussed by Zhu et al. [15] based on the conventional pseudopotential band calculation.

3.2.2 Full coverage Na/Si(001)-2×1 surface

The computational condition is such that $E_{cut} = 6.25$ Ry and $N_k = 8$ as seen in Table 3.2. As the system has an insulating gap for $\theta = 1$, this small N_k is expected to be sufficient. We found two stable configurations, the combinations HH-T3 and HH-T4. The former combination is lower in energy by 28meV per dimer than the latter, being consistent with the double layer model proposed for the K adsorption [26].

In contrast to the present result, Batra suggested that the T4 site is energetically more stable than T3 [70]. He optimized the height of Na but fixed the substrate atomic configuration as the symmetric dimer model, which was optimized separately for the clean surface. He also studied the adsorption on the bulk terminated surface and concluded that such an adsorption configuration would not be realized. We have confirmed that the optimization of the Na position only gives us a result almost identical to that of Batra. Recently, he found that the substrate relaxation has a tendency of stabilizing the HH-T3 configuration to make it nearly degenerate with HH-T4 [71].

The HB site of the Si-Si dimer is not a stable position for Na adsorption. The top views of the optimized atomic positions for the Na adsorption with the full coverage in the HH-T3 and HH-T4 configurations are shown in Fig. 3.7(a) and (b), respectively. Both for the HH-T3 and HH-T4 cases, a substantial relaxation of the Si substrate is induced (Fig.3.7(c)): the Si-Si dimers are now symmetric and the dimer distance is 2.65 Å (2.51 Å) for the HH-T3 (HH-T4) case. The details of geometrical parameters for the optimized structures are listed in Tables 3.4 and 3.5. The total energy and temperature of the ionic part in the process of calculation for the HH-T3 case are shown in Figs.3.8(a) and (b), respectively. In the first hundred iteration steps, only the electronic part was cooled down to the ground state.

Subsequently, the electronic and ionic parts were solved simultaneously. After iterations over 1500, the calculation attained a sufficient convergence and the optimized configuration was obtained. At first, the temperature of the ionic part increases rapidly and after several tens of steps, it begins to decrease due to the friction effect as described in Section 2.4.2. The remaining small asymmetry in the positional parameters in the final configuration may be some artifacts of our automatic optimization process. As the atomic arrangement approaches the optimum one, the force acting on each atom becomes vanishingly small (the criterion for stabilization is 1.0×10^{-3} Ry/a.u.) so that atoms may not reach their exact optimum positions. The disappearance of the asymmetry is a natural consequence of the full occupancy of the π^* band-gap states, because the energy gain caused by the lowering of the π band is cancelled out by the energy loss caused by the counter movement of the π^* band as seen in Fig. 3.5.

Enta et al. [25] found that the surface with the saturation coverage of K was insulating and suggested that the alkali atoms would be adsorbed not only at the raised sites of the Levine model but also at the trough sites between the dimer rows [26]. The saturation coverage was claimed to be the full coverage $\theta = 1.0$. Recent experiments support the existence of two different adsorption sites [27]. The Si(001)-2×1 surface with the saturation coverage of Na was also shown to be insulating by Enta et al. [72]. However, some experiments claimed that the saturation coverage will not be $\theta = 1$ but $\theta = 0.68$ or $\theta = 0.5$ for the Na and K adsorption [22, 23, 73, 74]. A realization of the adsorption pattern of the Levine model was claimed by the LEED analysis [24].

These experiments were carried out at room temperature or at even higher temperature, whereas the present calculation is for zero Kelvin. Therefore, a theoretical study on the effect of the finite temperature is needed to give a definitive conclusion about the saturation coverage. Finally, we note that the shortest Na-Si distance in the HH-T3 configuration is 2.62 Å (2.81 Å) for Na at the HH (T3) site. This relatively short Na-Si distance may imply that Na atoms are chemisorbed rather than physisorbed even for $\theta = 1$.

In Figs. 3.9(a) - (f), the contour maps of the electron density are shown for the side and top views of the Na adsorbed Si(001) surface (HH-T3) for the full coverage. The axes of x and y are shown in Fig. 3.1(a) by arrows, and the z axis is perpendicular to the Si(001) surface ([001] direction) as shown in Fig. 3.1(b). The filled circles denote the positions of Na and Si atoms projected on the cut plane. The Na atoms are indicated by arrows. In the figure of the side view, the cut plane is shown in the attached small figure. z(height) in Fig. 3.9(d) to (f) denotes a height of the cut plane for the top view measured from the bottom of the unit cell. (With this origin for z, the center of the substrate slab is located at z = 11.531 a.u.) The heights of the adsorbed Na on the T3 and HH are 23.998, 25.329(a.u.), respectively. In Fig. 3.9(a), the electron density in the dimer is symmetric and the covalent bond charge along the dimer, which is clearly seen in Fig. 3.6 for the clean surface, does not exist. In Fig. 3.9(b), although the cut plane contains the Na atoms adsorbed at the HH site as indicated by arrows, the electron density coming from the adsorbed Na cannot be identified. Figures 3.9(c) and (d) show the contour maps of the difference electron densities defined as the total electron density of Na/Si(001) minus the electron density of the Si substrate. In Fig. 3.9(c), it is found that the covalent bond charge is formed between the Na adatom on the T3 site and the second layer Si atoms. In Fig. 3.9(d), which is a top view of the electron density in the plane whose height is at the middle of the Na at HH and the dimer Si, the formation of the bond charge between the Na and the dimer Si atoms is observed. Figures 3.9(e) and (f) are the contour map of a top view and the bird's eye view for a plane at the height 30.329(a.u.) which is higher than that of the adsorbed Na on the HH site by 5.0(a.u.). In the bird's eye view, the electron density coming from the adsorbed Na at the T3 site is slightly seen but that from the Na at the HH site cannot be identified at all.

3.2.3 Half coverage Na/Si(001)-2×1 surface

$E_{cut} = 9.0$ Ry and $N_k = 32$ in this case. As the π^* band is half-filled for $\theta = 0.5$, the system is metallic and a large N_k is required. The fundamental question in the $\theta = 0.5$ case is whether the alkali atoms are adsorbed along the hill of the dimer chain or along the trough between the dimer chains. For Na adsorption, the pseudopotential calculation by Batra predicted that the HH site is more stable than T4 (T3) site by 0.12eV (0.22eV). On the other hand, a cluster calculation by Ling et al. [75] for K adsorption predicted that the T4 site is more favored. In these calculations, however, the possibility of asymmetry in the Si-Si dimer was not taken into account.

The top views of the optimized atomic positions for the Na adsorption with the half coverage in the HH and T4 configurations are shown in Fig. 3.10(a) and (b), respectively. As is shown in Figs. 3.10(c) and (d), the asymmetry of the Si-Si dimer remains for $\theta = 0.5$ in both cases of the adsorption along the hill and the trough of the dimer rows. There is still an energy gain caused by the asymmetry-induced increase of the $\pi - \pi^*$ band separation as the π^* band is only half-filled. Even if the Na atoms are put fairly close to the T3 sites, they move toward the T4 sites and stop there. Along the hill of the dimer, the HH site is stable while the HB site is unstable. The present calculation shows that the T4 adsorption is lower than the HH adsorption by 12meV/dimer. Unfortunately, this energy difference is already close to the limit of the numerical accuracy. Analysis of experiments suggest that the preferential adsorption at T4 rather than HH may not be plausible. It was shown by Ishida and Terakura [76] that the T4 site adsorption produces a much smaller lowering of the workfunction than observed. A recent LEED analysis concluded that the HH-site adsorption is more favorable than the T4-site adsorption [24]. However, a caution may be necessary to this LEED analysis. It was stated in the paper [24] that the double-layer model of the HH-T3 configuration is equally acceptable.

We calculate the binding energy of the Na adatom on the Si substrate in order to obtain an insight to the saturation coverage. The binding energy per one Na is defined as follows. For the full coverage,

$$E^{full}_{Batra} = \frac{1}{4}(E^{full}_{Na/Si} - E_{Si-sub} - E^{full}_{Na-lay}), \tag{3.1}$$

$$E^{full}_{bind} = E^{full}_{Batra} - \frac{1}{4}[4E_{Na-atom} - E^{full}_{Na-lay}], \tag{3.2}$$

and for the half coverage,

$$E^{half}_{Batra} = \frac{1}{2}(E^{half}_{Na/Si} - E_{Si-sub} - E^{half}_{Na-lay}), \tag{3.3}$$

$$E^{half}_{bind} = E^{half}_{Batra} - \frac{1}{2}[2E_{Na-atom} - E^{half}_{Na-lay}], \tag{3.4}$$

where $E^{full(half)}_{Batra}$ is the binding energy adopted by Batra [71] between the Na layer and the Si substrate for the full (half) coverage, $E^{full(half)}_{bind}$ is the adsorption energy with respect to the assembly of isolated Na atoms, $E_{Na/Si}^{full(half)}$ is the total energy of the Na adsorbed Si surface, E_{Si-sub} is the total energy of the Si substrate, $E_{Na-lay}^{full(half)}$ is the total energy of isolated Na layer corresponding to the full (half) coverage, and $E_{Na-atom}$ is the total energy of the Na (pseudo) atom. The factor $\frac{1}{4}$ ($\frac{1}{2}$) takes account of the fact that the unit cell contains 4(2) Na atoms, 2(1) from each of the slab surfaces, for the full (half) coverage. As for E_{Batra}^{half}, the obtained binding energy for the half coverage HH case is -2.21eV, being close to Batra's value of -2.23eV [71]. The other quantities are shown in Table 3.6.

In this table, the binding energy for the full coverage (HH-T3) is larger than that of the half coverage (HH or T4). And the binding energy for the $\theta = \frac{1}{6}$ is the largest. It should be noted that the condition (E_{cut} and N_k) for the full coverage is different from that for the half coverage and that the binding energies may depend on this difference. Nevertheless, an important conclusion here is that the binding energy is still significant for the full coverage.

In order to understand the real situation for the saturation coverage, more detailed studies including temperature effects are necessary. At the present stage, combining several experimental results as well as calculations, we speculate that the coexistence of the HH-site adsorption and the T4-(or T3-) site adsorption may be realized. The adatoms adsorbed along the trough are expected to give only a small influence on the workfunction, LEED, and STM.

3.2.4 $\frac{1}{6}$ coverage Na/Si(001)-2×1 surface

Figure 3.11(a) is the STM image for low coverage K on the Si(001) surface [28, 29, 30], and the corresponding schematic diagram for the atomic arrangement is shown in Fig. 3.11(b). In Fig. 3.11(a), the bright large spots correspond to adsorbed K and the neighboring zig-zag spots correspond to raised Si atoms along the alternating arrangement of the asymmetric dimers. This result suggests that the adsorption site for low coverage K is none of those sites considered for $\theta = 1$ and 0.5. It is the B2 site in our notation, i.e., the bridge site between the two raised Si atoms of the neighboring Si-Si dimers. It is also interesting to note that the adsorbed K atoms seem to enhance the contrast of the STM image associated with the asymmetry of the neighboring Si-Si dimers [28, 29, 30]. We attempt to analyze these aspects of the STM observations by using a supercell for $\theta = \frac{1}{6}$.

Because of the large system size, the present calculation uses a relatively small E_{cut} of 5.0 Ry corresponding to the number of plane waves of 3072. $N_k = 4$ is also small. The present calculation is therefore a preliminary one. The starting atomic configuration for the substrate is the 2×1-asymmetric dimer structure which was optimized for the clean surface. The Na atom is initially put slightly off the HB or T3 site. The crosses in Fig.3.12(a) denote two initial Na positions. As the optimization process proceeds starting from either of the two initial positions, the Na atom moves toward the inter-dimer bridge B2 site as denoted by a hatched sphere in Fig.3.12(a). This is the position that the STM image [28, 29, 30] suggests as the adsorption site for K in the low coverage region. Figure 3.12(b) is a side view containing Na and the Si atoms designated as A, A', B and B' in Fig. 3.12(a). In the above calculation, a ferromagnetic ordering of the asymmetric dimers for the substrate was assumed as a initial configuration and was not destroyed in the optimized configuration. However, as mentioned in Section 2.4.2, the kinetic energy of the ionic system dissipates quickly in the present MSD approach so that the system may be easily trapped at a local minimum. Therefore two additional initial arrangements of the asymmetric dimers are considered. First, the reversal of the asymmetry for the dimer designated as (C,C') in Fig. 3.12(a) lowers the total energy by 19.1meV per (2×3) surface unit cell without significant change in the geometry in the vicinity of the adsorbed Na. This result is consistent with the zig-zag image along the dimer row near the adsorbed K. However, for the initial configuration shown in Fig. 3.13, the optimum Na position turns out to be the hollow site as shown by a hatched sphere. However, the total energy of this configuration is higher than that of the previous one by 136meV per (2×3) surface unit cell.

The present coverage $\theta = \frac{1}{6}$ may not be low enough to make a direct comparison with the experiments and there may also be some difference between K and Na. Still it is very interesting that the present calculation does indicate a dramatic change in the preferred adsorption site between the high coverage and low coverage cases.

Here, we show the calculated electron density corresponding to the configuration of Fig. 3.12 in order to compare with the results of STM [28, 29, 30]. The contour maps of the electron density in the side view and top view are shown in Figs. 3.14(a)-(h). The cut plane of side view is shown in the attached small figure. The Na atom is indicated by an arrow. In Fig. 3.14(a), the electron density on the dimer is asymmetric and that arising from the adsorbed Na is not identified as in the full coverage case. In the side view of the electron density shown in Fig. 3.14(b), the arrows along the vertical axis denote the height of the cut plane for the top views (Figs. 3.14(c)-(h)). In these figures for the top view which may be compared with the STM results, the position of the adsorbed Na is around the center of the figure as shown by the hatched circle. The height of the cut plane in Fig. 3.14(c) is that of the raised Si atom of the asymmetric dimer. The height in Fig. 3.14(d) is that of the adsorbed Na atom. In Figs. 3.14(e)-(h), the electron density of the adsorbed Na can be seen clearly. The position of the cut plane in Fig. 3.14(e) is higher than that of the Na atom by 2.1 Å. The bird's eye view corresponding to Fig. 3.14(f) is shown in Fig. 3.14(g). The electron profiles given in Figs. 3.14(e)-(h) are consistent with the observed STM image [28, 29, 30].

3.2.5 Full coverage Li/Si(001)-2×1 surface

As Li is chemically fairly different from other alkali metal elements, it is interesting to see whether any qualitatively different aspect can be found between Li and Na as adsorbates on the Si surface. Even within the limited size of the present unit cell, we have in fact found that Li behaves quite differently from Na. The HB site is unstable for Li, too. However, unlike the case of Na, the Li atom along the trough is trapped at either of the two off-symmetry positions as shown in Fig. 3.15. Accordingly, the adsorption site of Li along the dimer chain is also slightly off the HH site. The two configurations are energetically almost degenerate with the energy difference of only 5.0meV. Nevertheless, the relaxation of the substrate is more or less similar to that for the Na case. The positional parameters corresponding to Fig. 3.15 are listed in Tables 3.7 and 3.8. Although the most stable atomic arrangement for Li at the saturation coverage should be searched for with probably a much larger unit cell to allow more degrees of freedom, the present calculation demonstrates very clearly a qualitative difference between Li and Na as adsorbates on the Si(001) surface. It was experimentally shown that Li behaves completely differently from other alkali atoms as adsorbates on the Si(001) surface in the high coverage regime (Silicide formation) [74].

3.2.6 $\frac{1}{6}$ coverage Li/Si(001)-2×1 surface

The STM image for low coverage Li on the Si(001) surface [28, 29, 30] and its schematic illustration are shown in Fig. 3.16. Unlike the case for K shown in Fig. 3.11, the adsorption site for low coverage Li is the B1 site in Fig. 3.1, i.e., the on-top site of the raised Si atom of an asymmetric Si-Si dimer. The purpose of the study for this coverage of Li is the same as for the Na $\theta = \frac{1}{6}$ case. The condition of the calculation is also completely the same as the Na case. The initial Li atoms are put slightly off the HB or T3 site as in the case of Na in Fig. 3.12(a). As the optimization process proceeds from either of the two initial positions, the Li atom moves toward the inter-dimer bridge B2 site as in the Na case. The heights of adsorbed Li is lower than that of adsorbed Na. In addition, the other substrate configuration as the Na case of Fig. 3.13 is used and the optimized position is almost the same (HH site) as in the Na case. (The height of Li is also lower than that of Na.) These results do not agree with the STM measurement for Li. This inconsistency may arise from the fact that our surface unit cell is not large enough to simulate the experimental situation. Another problem is that as Li has a relatively deep pseudopotential, the present cutoff energy (5Ry) is definitely insufficient. More extended studies will be performed in near future.

3.3 Partial core correction

In all of the above results, we noticed an inconvenient aspect in the theoretically optimized structures : the interatomic distances in the surface region are significantly shorter than those estimated by experiments. These shorter distances are caused by the following reason. The pseudopotential for the core part is obtained from the neutral pseudoatomic potential by subtracting the Hartree and exchange-correlation potentials for valence electrons as described in Section 2.1. The subtracted Hartree and exchange-correlation potentials are made of only valence electrons. Although this unscreening process is exact for the Hartree potential because of its linear dependence on the electron density, it is only an approximation for the exchange-correlation potential. This simplified process for the exchange-correlation potential is justified if the core electron density is spatially separated from the valence electron density. Such a situation is not necessarily realized in alkali atoms and the approximate treatment for the exchange-correlation potential has a tendency of underestimating the bond length. It is necessary to introduce a partial core correction [31] to correct this underestimation.

We introduce this partial core correction for the adsorbed Na and the substrate Si atoms and study the difference from previous results for the full and half coverage cases. The optimized configurations without the partial core correction are adopted as the initial configurations for this correction. The obtained positional parameters and interatomic distances are listed in Table 3.2.

For the full coverage cases (HH-T3 and HH-T4) as well as for the half coverage ones (HH and T4), the interatomic distances in the surface region become significantly larger. The experimental values of the Na-Si distance for the saturation coverage are 2.975 Å [24] from LEED analysis and 2.8 Å [77] by surface EXAFS. If we assume that the experimental saturation coverage corresponds to $\theta = 1.0$, our new value of 3.13 Å for the HH-T3 case is slightly larger than the experimental values. A qualitatively new aspect is that the adsorbed atom on the T4 site moves to the T3 site and stops there for the full coverage. Therefore, in the case of considering the partial core correction, the relative stability of the optimized configuration of HH-T3 with reference to that of HH-T4 is enhanced. For the half coverage, the optimized configuration of T4 becomes significantly more stable than that of HH by 100meV per dimer. The corresponding value without the partial core correction is only 12meV per dimer. Nevertheless, we find that the qualitative aspect of the most stable configuration is not affected by the partial core correction.

Chapter 4

Concluding remarks

We have performed the FPMD calculation for the clean and alkali adsorbed Si(001) surfaces. The results are summarized as follows.
(1) Clean Si(001)-2×1 surface

- The asymmetric dimer is more stable than the symmetric one.

(2) Na adsorbed Si(001) surfaces

1. Full coverage
    - The configuration of HH-T3 is more favorable than that of HH-T4 (consistent with the XPD(X-ray photoelectron diffraction) result [26]).
    - The HB site is unstable.
    - The asymmetric dimer of substrate changes into the symmetric one.
2. Half coverage
    - The configuration of T4 is more favorable than that of HH (inconsistent with the LEED result [24]).
    - The HB site is unstable.
    - The asymmetry in the Si-Si dimer becomes weaker than that of the clean substrate.
3. $\frac{1}{6}$ coverage
    - The optimized site of Na is on the bridge site (B2) between the two raised Si atoms of the neighboring Si-Si dimers (consistent with the STM result [28, 29, 30]).

(3) Li adsorbed Si(001) surfaces

1. Full coverage
    - The Li atoms are adsorbed on off-symmetry sites as shown in Fig. 3.15.
2. $\frac{1}{6}$ coverage
    - The optimized site of Li is same as that of Na (inconsistent with STM result [28, 29, 30]).

(4) Partial core correction

- The interatomic distances of Na-Si become much closer to experimental values by considering the partial core correction [31].

We conclude from above results as follows. The stable configuration for the half coverage is such that the Na atoms are adsorbed on the T4 sites with forming linear chains of Na adatoms between dimer rows. Ling et al. [75] also arrived at the same conclusion for the K case, although they did not take account of the asymmetry of the Si-Si dimer. Even for the full coverage, the Na atoms can be chemisorbed on the Si substrate with a significant binding energy. The result seems to suggest that the saturation coverage may be $\theta = 1$. For the low coverage ($\theta = \frac{1}{6}$) case, the optimum site of the adsorbed Na is the B2 which is different from the adsorption sites for the higher coverage ($\theta = 0.5$ or 1.0) cases. The present FPMD calculation has been successful in reproducing the difference of the situation of adsorption for the low and high coverage cases but not in reproducing the STM result for the low coverage of Li adsorption.

There remain controversies on the saturation coverage. Enta et al. [72] suggested that the saturation coverage for Na is $\theta = 1.0$. On the other hand, Wei et al. [24] suggested that $\theta = 0.5$ is the saturation coverage. Furthermore, there is also a possibility $\theta = 0.68$ as suggested by Glander et al. [22, 23].

As mentioned above, our calculation supports Enta et al.'s [72] suggestion. However, we should note that the present calculations have covered only very limited possibilities for the atomic arrangement. Further, we assumed *a priori* the (2×1) unit cell for $\theta = 0.5$ and $\theta = 1$. Therefore, we cannot rule out a possibility of incommensurate configuration in the dimer direction: for example, four Na atoms on average per five Si dimers.

Theoretical analysis of such a possibility requires very heavy calculations and is left as a future task. Nevertheless, the present calculations strongly suggest the necessity of modifying the Levine model. All calculations performed up to present (the present calculations both with and without the partial core correction and the calculation by Ling et al. [75]) suggested adsorption of Na and K along the trough. In most experiments, Na seems to be adsorbed both at HH and T3 (or T4). This difference is highly likely to be due to finite temperature effects.

The cutoff energy, the number of k-points for sampling, the size of the unit cell, the number of plane waves, and the CPU-time of supercomputer (Hitac S820/80) for each calculation are listed in Table 4.1 in order to show the performance of the present calculations. It is found that the calculations for the half or $\frac{1}{6}$ coverage case are already close to the practical upper limit of the computer resource.

Some of the problems existing in the present calculations are listed below.

- The speed of the convergence for the SD calculation is slow for an electronic part. Besides, it is rather difficult to obtain the global minimum of the structure for ions. A future test of some other algorithms is necessary. (For example, the original Car-Parrinello method, the conjugate gradient method, etc [58, 59, 78])

- The temperature control by a constant temperature MD for an ionic part should be introduced.

- A shape of the unit cell has been fixed in the process of our FPMD calculation. The constant pressure MD for an ionic part [79, 80] is required for a more strict test of the structural stability.

- The materials which we can study by pseudopotentials with plane wave basis is fairly limited. For example, noble and transition metals, B, C, O, N [with deep 2p potentials], and so on cannot be treated so accurately. It is necessary to devise a new type of pseudopotentials [81, 82, 83, 84].

Finally, it should be noted that the FPMD method is useful for the search and design of new materials and the present study is a first step toward its real application.

Appendix A

Separable form for non-local pseudopotentials

Equation (2.9) is

$$V_{ps}(r) = V_{local}(r) + \sum_{l} \mid l > V^{l}_{non-local}(r) < l \mid . \tag{2.9}$$

In the second term of the right hand side of this eqaution, $V^{l}_{non-local}(r)$ is replaced by the Kleinman-Bylander form [85]

$$V^{l,KB}_{non-local}(r) = \frac{\mid V^{l}_{non-local} \mid \phi_l >< \phi_l \mid V^{l}_{non-local} \mid}{< \phi_l \mid V^{l}_{non-local} \mid \phi_l >}, \tag{A.1}$$

where $V^{l,KB}_{non-local}(r)$ is a separable non-local pseudopotential and $\phi_l(r)$ is a pseudo-wave function for an atomic eigen-state. Here, the pseudo-eigen energies for the separable and non-separable forms are obtained as follows

$$< \phi_l \mid V^{l,KB}_{non-local} \mid \phi_l >= \epsilon^{KB}_{l}, \tag{A.2}$$

$$< \phi_l \mid V^{l}_{non-local} \mid \phi_l >= \epsilon_l, \tag{A.3}$$

where the ϵ^{KB}_{l} is equal to ϵ_l.

But, the equality of these eigen-energies is not guaranteed in the general case with a wave function Ψ

$$< \Psi \mid V^{l,KB}_{non-local} \mid \Psi > \neq < \Psi \mid V^{l}_{non-local} \mid \Psi > . \tag{A.4}$$

The difference in these eigen-energies can be reduced within a sufficient accuracy by choosing the local pseudopotential of eq. (2.9). At present, there is no problem as for the accuracy of our calculation where the d-pseudopotential is adopted for the local pseudopotential.

Appendix B

Lagrange multiplier in steepest descent method

The following three equations are our starting point:

$$\nu\dot{\Psi}_i(t) = -H(t)\Psi_i(t) + \sum_j \Lambda_{ij}\Psi_j(t), \tag{B.1}$$

$$\Psi_i(t+\Delta t) = \Psi_i(t) + \Delta t\dot{\Psi}_i(t), \tag{B.2}$$

$$\int \Psi_i^*(t)\Psi_j(t)d\vec{r} = \delta_{ij}. \tag{B.3}$$

The Lagrange multiplier Λ_{ij} is determined so as to satisfy the orthonormalization constraint at $t + \Delta t$

$$\int \Psi_i^*(t+\Delta t)\Psi_j(t+\Delta t)d\vec{r} = \delta_{ij}. \tag{B.4}$$

Inserting eq. (B.2) into the left hand side of eq. (B.4), we obtain

$$\begin{aligned} & \int\{\Psi_i(t+\Delta t)\}^*\{\Psi_j(t+\Delta t)\}d\vec{r} \\ = & \int\{\Psi_i(t) + \Delta t\dot{\Psi}_i(t)\}^*\{\Psi_j(t) + \Delta t\dot{\Psi}_j(t)\}d\vec{r} \\ = & \int \Psi_i^*(t)\Psi_j(t)d\vec{r} + \Delta t\int\{\dot{\Psi}_i^*(t)\Psi_j(t) + \Psi_i^*(t)\dot{\Psi}_j(t)\}d\vec{r} \\ & +(\Delta t)^2\int \dot{\Psi}_i^*(t)\dot{\Psi}_j(t)d\vec{r}. \end{aligned} \tag{B.5}$$

By neglecting the second order term of Δt, eq. (B.4) is reduced to

$$\int\{\dot{\Psi}_i^*(t)\Psi_j(t) + \Psi_i^*(t)\dot{\Psi}_j(t)\}d\vec{r} = 0. \tag{B.6}$$

Substituting eq. (B.1) for $\dot{\Psi}_i(t)$ into eq. (B.6), we obtain

$$\int(-H\Psi_i(t)+\sum_l \Lambda_{il}\Psi_l(t))^*\Psi_j(t)d\vec{r}+\int \Psi_i^*(t)(-H\Psi_j(t)+\sum_m \Lambda_{jm}\Psi_m(t))d\vec{r}$$
$$= 2(- < \Psi_i \mid H \mid \Psi_j > +\Lambda_{ji}) = 0. \tag{B.7}$$

Therefore, Λ_{ji} is given by

$$\Lambda_{ji} =< \Psi_i \mid H \mid \Psi_j >. \tag{B.8}$$

Appendix C

Approximation to diagonal Lagrange multipliers

Here, the approximation in the calculation of $\lambda_{i,\vec{k}}$ in Section 2.4.1 is described in detail. Equation (2.62) is written here again

$$\begin{aligned}
\lambda_{i,\vec{k}}(t+\Delta t) &= \sum_{\vec{G},\vec{G}'} \Psi_{i,\vec{k}}(\vec{G},t+\Delta t) < \vec{G} \mid H(t) \mid \vec{G}' > \Psi_{i,\vec{k}}(\vec{G}',t+\Delta t) \\
&= \lambda_{i,\vec{k}} - \nu \sum_{\vec{G}} \{ \dot{\Psi}^*_{i,\vec{k}}(\vec{G},t)\Psi_{i,\vec{k}}(\vec{G},t+\Delta t) - \Psi^*_{i,\vec{k}}(\vec{G},t+\Delta t)\dot{\Psi}_{i,\vec{k}}(\vec{G},t) \\
&\quad +\Psi^*_{i,\vec{k}}(\vec{G},t)\dot{\Psi}_{i,\vec{k}}(\vec{G},t)\}. \qquad (2.62)
\end{aligned}$$

In order to derive this equation, we proceed in the following way:

$$\begin{aligned}
& \sum_{\vec{G},\vec{G}'} \Psi_{i,\vec{k}}(\vec{G},t+\Delta t) < \vec{G} \mid H(t) \mid \vec{G}' > \Psi_{i,\vec{k}}(\vec{G}',t+\Delta t) \\
= & \sum_{\vec{G},\vec{G}'} (\Psi^*_{i,\vec{k}}(\vec{G},t) + \delta\Psi^*_{i,\vec{k}}(\vec{G},t)) < \vec{G} \mid H(t) \mid \vec{G}' > (\Psi_{i,\vec{k}}(\vec{G}',t) + \delta\Psi_{i,\vec{k}}(\vec{G}',t)) \\
= & \sum_{\vec{G},\vec{G}'} \Psi^*_{i,\vec{k}}(\vec{G},t) < \vec{G} \mid H(t) - \lambda_{i,\vec{k}}(t) \mid \vec{G}' > \Psi_{i,\vec{k}}(\vec{G}',t) \\
+ & \sum_{\vec{G},\vec{G}'} \delta\Psi^*_{i,\vec{k}}(\vec{G},t) < \vec{G} \mid H(t) - \lambda_{i,\vec{k}}(t) \mid \vec{G}' > \Psi_{i,\vec{k}}(\vec{G}',t) \\
+ & \sum_{\vec{G},\vec{G}'} \Psi^*_{i,\vec{k}}(\vec{G},t) < \vec{G} \mid H(t) - \lambda_{i,\vec{k}}(t) \mid \vec{G}' > \delta\Psi_{i,\vec{k}}(\vec{G}',t) \\
+ & \sum_{vecG,\vec{G}'} \delta\Psi^*_{i,\vec{k}}(\vec{G},t) < \vec{G} \mid H(t) - \lambda_{i,\vec{k}}(t) \mid \vec{G}' > \delta\Psi_{i,\vec{k}}(\vec{G}',t) \\
+ & \sum_{\vec{G},\vec{G}'} (\Psi^*_{i,\vec{k}}(\vec{G},t) + \delta\Psi^*_{i,\vec{k}}(\vec{G},t)) < \vec{G} \mid \lambda_{i,\vec{k}}(t) \mid \vec{G}' > (\Psi_{i,\vec{k}}(\vec{G}',t) + \delta\Psi_{i,\vec{k}}(\vec{G}',t)) \\
= & \lambda_{i,\vec{k}}(t)
\end{aligned}$$

$$\begin{aligned}
&+ \sum_{\vec{G},\vec{G}'} \Psi^*_{i,\vec{k}}(\vec{G},t) < \vec{G} \mid H(t) - \lambda_{i,\vec{k}}(t) \mid \vec{G}' > \Psi_{i,\vec{k}}(\vec{G}',t) \\
&+ \sum_{\vec{G},\vec{G}'} \delta\Psi^*_{i,\vec{k}} < \vec{G} \mid H(t) - \lambda_{i,\vec{k}}(t) \mid \vec{G}' > \Psi_{i,\vec{k}}(\vec{G}',t) \\
&+ \sum_{\vec{G},\vec{G}'} \Psi^*_{i,\vec{k}}(\vec{G},t) < \vec{G} \mid H(t) - \lambda_{i,\vec{k}}(t) \mid \vec{G}' > \delta\Psi_{i,\vec{k}}(\vec{G}',t) \bigcirc (\Delta t^2) \\
&= \lambda_{i,\vec{k}}(t) - \nu \sum_{\vec{G}'} \dot{\Psi}^*_{i,\vec{k}}(\vec{G}',t)\Psi_{i,\vec{k}}(\vec{G}',t) \\
&- \nu \sum_{\vec{G}'} \delta\Psi^*_{i,\vec{k}}(\vec{G}',t)\dot{\Psi}_{i,\vec{k}}(\vec{G}',t) - \nu \sum_{\vec{G}'} \dot{\Psi}^*_{i,\vec{k}}(\vec{G}',t)\delta\Psi_{i,\vec{k}}(\vec{G}',t) + \bigcirc(\Delta t^2) \\
&= \lambda_{i,\vec{k}}(t) \\
&- \nu \sum_{\vec{G}} \dot{\Psi}^*_{i,\vec{k}}(\vec{G},t)[\Psi_{i,\vec{k}}(\vec{G},t) + \delta\Psi_{i,\vec{k}}(\vec{G},t)] \\
&- \nu \sum_{\vec{G}} [\Psi^*_{i,\vec{k}}(\vec{G},t) + \delta\Psi^*_{i,\vec{k}}(\vec{G},t)]\dot{\Psi}_{i,\vec{k}}(\vec{G},t) \\
&+ \nu \sum_{\vec{G}} \Psi^*_{i,\vec{k}}(\vec{G},t)\dot{\Psi}_{i,\vec{k}}(\vec{G},t). \qquad \text{(C.1)}
\end{aligned}$$

The final form is obtained as

$$\begin{aligned}
\lambda_{i,\vec{k}}(t+\Delta t) &= \lambda_{i,\vec{k}}(t) - \nu \sum_{\vec{G}} \{\dot{\Psi}^*_{i,\vec{k}}(\vec{G},t)\Psi_{i,\vec{k}}(\vec{G},t+\Delta t) \\
&- \Psi^*_{i,\vec{k}}(\vec{G},t+\Delta t)\dot{\Psi}_{i,\vec{k}}(\vec{G},t) + \Psi^*_{i,\vec{k}}(\vec{G},t)\dot{\Psi}_{i,\vec{k}}(\vec{G},t)\}, \qquad (2.62)
\end{aligned}$$

where $\delta\Psi$ means the change in the wave function after one time step including the Gram-Schmidt orthogonalization process. Schematically,

$$\begin{aligned}
\Psi_{i,\vec{k}}(\vec{G},t+\Delta t) &= \Psi_{i,\vec{k}}(\vec{G},t) + \Delta t\dot{\Psi}_{i,\vec{k}}(\vec{G},t), \qquad (2.59) \\
&\Downarrow \\
&Gram - Schmidt\ orthogonalization \\
&\Downarrow \\
\Psi_{i,\vec{k}}(\vec{G},t+\Delta t) &= \Psi_{i,\vec{k}}(\vec{G},t) + \delta\Psi_{i,\vec{k}}(\vec{G},t). \qquad \text{(C.2)}
\end{aligned}$$

We also made use of the relation

$$\sum_{\vec{G}} \Psi^*_{i,\vec{k}}(\vec{G},t+\Delta t)\Psi_{i,\vec{k}}(\vec{G},t+\Delta t) = 1. \qquad \text{(C.3)}$$

Acknowledgements

I would like to express my sincere thanks to Professor K. Terakura for continual guidance and encouragement throughout the course of the work of this thesis. I wish to thank Dr. S. Blügel for many helpful discussions and suggestions. I also wish to thank Mr. Y. Morikawa for helpful assistance in the calculations. The calculation by considering the partial core correction and the preparation of pseudopotentials with this correction were carried out with his assistance. I am grateful to Dr. H. Ishida for giving me the starting version of the program for the electronic structure calculation. Several helpful discussions with Drs. T. Oguchi, T. Sasaki, Y. Ishii, S. Takizawa, M. Ikeda and T. Yamazaki are gratefully acknowledged.

The numerical calculations were performed at the Computer Centers of University of Tokyo, Institute for Molecular Science and Institute for Solid State Physics.

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Figure Caption

- Fig.1.1. (a) A side view of the ideal clean Si(001) surface, (b) the clean Si(001) surface with symmetric dimer, (c) the clean Si(001) surface with p(2×2) configuration. These figures originate from

  Introduction to Surface Physics (in Japanese) by M. Tsukada (University of Tokyo Press, 1989).
- Fig. 2.1. A flow chart of the standard electronic structure calculation.
- Fig.2.2. A process of the FPMD calculation. The vertical line measures a total energy. The horizontal line means a configuration of ions.
- Fig. 2.3. The flow chart of the SD or MSD calculation.
- Fig.3.1. Top (a) and side (b) views of the asymmetric dimer configuration of the Si(001)-2×1 surface. The filled and the open circles denote the Si atoms in the topmost surface layer and those underneath, respectively. The possible adsorption sites for alkali atoms are denoted as HB, HH, T3, T4, B1 and B2.
- Fig.3.2. A supercell including atomic layers and vacuum region for the repeated slab model.
- Fig. 3.3. A bird's eye view of the electron density for the Na adsorbed Si(001) surface for the full coverage. The cut plane is parallel to the y-z plane and contains the Si-Si dimer. The axes x, y and z are shown in Fig. 3.1.
- Fig. 3.4. Positions of k-points for sampling in the whole surface Brillouin zone for Si(001)-2×1 unit cell. The open circles denote the k-points. The numbers of k-points are 8 in (a) and 32 in (b).

- Fig. 3.5. The energy dispersion curves of π and π^* bands for the symmetric and asymmetric dimer configurations. Solid lines are for the surface bands of the symmetric dimer and broken lines for those of the asymmetric dimer. The regions of the bulk bands are indicated by hatching. The position of the Fermi energy for $\theta = 0.0$, 0.5 and 1.0 are schematically shown.
- Fig. 3.6. Contour map of the electron density for the clean surface with the asymmetric dimer. The cut plane is parallel to the y-z plane and contains the Si-Si dimer.
- Fig. 3.7. (a),(b) Top views of the optimized atomic positions for the Na adsorption with the full coverage in the HH-T3 and HH-T4 configurations, with the hatched circles denoting Na. (c) A side view corresponding to the HH-T3 configuration. The dotted circles with and without cross denote the asymmetric dimer of the clean Si surface and the ideal bulk terminated Si surface, respectively. The circles denoted by A and B are Na.
- Fig. 3.8. The total energy (a) and the temperature (b) curves for the configuration of HH-T3. The vertical lines of (a) and (b) measure the total energy (Hartree) and the temperature (Kelvin), respectively. The horizontal lines means a number of iteration steps in the process of the calculation.
- Fig. 3.9(a). Contour map of the electron density for the Na adsorbed Si(001) surface for the full coverage (HH-T3). The filled circles denote the positions of the Na and Si atoms projected on the cut plane. The arrows indicate Na atoms. This is a side view for the cut plane shown by the attached small figure.
- Fig. 3.9(b). Same as in Fig. 3.9(a).
- Fig. 3.9(c). Same as in Fig. 3.9(a). This is a difference electron density.
- Fig. 3.9(d). Same as in Fig. 3.9(a). This is a top view for the difference electron density. Z(height) is a height from the bottom of the unit cell as shown in Fig. 3.2.
- Fig. 3.9(e). Same as in Fig. 3.9(a). This is a top view. Z(height) is a height from the bottom of the unit cell as shown in Fig. 3.2.

- Fig. 3.9(f). The bird's eye view corresponding to Fig. 3.9(e).
- Fig. 3.10. Top and Side views of the optimized atomic configuration for the Na adsorption with $\theta = 0.5$. The hatched circles denote the Na atoms and the others are the substrate Si atoms. The dotted circles with and without cross denote the ideal bulk terminated Si surface and the asymmetric dimer of the clean surface, respectively. (a) and (c) are for Na at the HH site and (b) and (d) for Na at the T4 site. In the present calculation, case (b) is more stable than case (a) by 12meV/dimer.
- Fig. 3.11. (a) STM image for low coverage K on the Si(001) surface. The bright large spots correspond to adsorbed K and the neighboring zig-zag spots correspond to raised Si atoms. (b) The corresponding schematic diagram for the atomic arrangement. The large double circle denotes the adsorbed K atom and the filled circles denote the raised Si atoms. (From reference [30])
- Fig. 3.12. (a) A top view of the 2×3 surface unit cell for the $\frac{1}{6}$ coverage of Na. The crosses denote two initial positions for Na and the hatched circle denotes Na at the optimized adsorption site. The filled and open circles denote the substrate Si atoms in the topmost surface layer and the second layer, respectively. (b) The corresponding side view. The hatched circle denotes the Na atom. The thin dotted circles with and without cross denote the ideal bulk terminated Si surface and the asymmetric dimer of the clean surface, respectively. Appreciable amount of displacements can also be seen in the second layer. The Si atoms designated by A, A', B, B', C and C' correspond to those in (a).
- Fig. 3.13. A top view of the 2×3 surface unit cell for the $\frac{1}{6}$ coverage of Na. The initial configuration of the Si substrate is different from that of Fig. 3.12(a). The cross denotes the initial position of Na and the hatched circle denotes Na at the optimized adsorption site. The filled and open circles denote the substrate Si atoms in the topmost surface layer and the second layer, respectively.

- Fig. 3.14(a). Contour map of the electron density for the Na adsorbed Si(001) surface for $\theta = \frac{1}{6}$ with Na on the B2 site. The filled circles denote the positions of the Na and Si atoms projected on the cut plane. The arrow indicates the Na atom. This is a side view for the cut plane shown by the attached small figure.

- Fig. 3.14(b). Same as in Fig. 3.14(a). Each arrow along the vertical axis indicates the height of the cut plane for the top view in each of Figs. 3.14(c)-(h).

- Fig. 3.14(c). Same as in Fig. 3.14(a). This is a top view. Z(height) is a height from the bottom of the unit cell as shown in Fig. 3.2. The hatched circle denotes the adsorbed Na atom.

- Fig. 3.14(d). Same as in Fig. 3.14(c).

- Fig. 3.14(e). Same as in Fig. 3.14(c).

- Fig. 3.14(f). Same as in Fig. 3.14(c).

- Fig. 3.14(g). The bird's eye view corresponding to Fig. 3.14(f).

- Fig. 3.14(h). Same as in Fig. 3.14(c).

- Fig.3.15. Top views of two possible optimized atomic positions (a) and (b) for the Li adsorption with the full coverage. The large filled and open circles denote the Si atoms in the top-most and second substrate layers. The small hatched circles denote the adsorbed Li atoms. The configurations (a) and (b) are nearly degenerate with (a) having a lower energy by only about 5 meV.

- Fig. 3.16. (a) STM image for low coverage Li on the Si(001) surface. The bright large spots correspond to adsorbed Li and the neighboring zig-zag spots correspond to raised Si atoms. (b) The corresponding schematic diagram for the atomic arrangement. The double circle near the center of the figure denotes the adsorbed Li atom and the filled circles denote the raised Si atoms. (From reference [30])