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A New Theoretical Treatment on Quantum Chemical Studies for Electronic Structures of Extended Aperiodic Systems by Molecular Orbital and Crystal Orbital Methods

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主論文

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CONTENTS

Chapter 3.

Chapter 4.

General Conclusion.

LIST OF PUBLICATIONS

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General Introduction

Problems on the Theoretical Treatment of Electronic Structures for Extended Aperiodic Systems by Quantum Chemical Calculations

In this chapter, some problems on the conventional study by the molecular orbital and crystal orbital methods for the theoretical treatment of aperiodic polymers and perturbed crystals are summarized, and the brief discussion to overcome those points is given.

Recently, the computer-aided approach has come into wide use in the study of science by the remarkable progress in technology, and nowadays, the rapid development and the extensive improvement of various program packages enable every chemists to carry out the computational studies by the methods as quantum chemical calculations, molecular dynamics simulations, and so on. Therefore, the role of theoretical chemists will become more and more important, and thus, the cooperation between theoretical and experimental studies will contribute to the advance of chemical research such as the design of new functional materials.

In the field of quantum chemistry, the methods to calculate the electronic structures of small molecules and completely periodic systems have already been well established at the present time. The molecular orbital (MO) method is available for small molecules, while the crystal orbital (CO) method for periodic systems. These theoretical approaches are very useful in studying the electronic property of the systems, and therefore, those are widely applied to various systems.

The MO calculation is a very powerful tool on the theoretical study for electronic states of small molecules. By this method, various properties of molecules, for example, molecular structures, spectroscopic parameters, electron density distributions, energetic, and so on, can be obtained theoretically.[1] Furthermore, the methodology of MO approach including the treatment of electron correlation is much sophisticated, and many advanced program packages are developed and used.

The CO theory enables us to obtain the electronic characters of the bulk systems as one-dimensional polymers, two-dimensional surfaces, and three-dimensional crystals with perfect periodic arrangements. For instance, band structures and density of states which characterize the periodicity can be determined from the CO approach.[2,3] However, the improvement and spread of general programs for the crystal computation is delayed in comparison with the molecule computation.

On the other hand, there are some problems in applying these quantum chemical treatments to the large systems without periodicity or the extended systems with both periodic and aperiodic parts. In other words, it is difficult to calculate random polymers or perturbed crystals by the MO or CO method directly. The cluster or supercell model is used in the usual MO or CO study, but the model has the difficulty which is mainly due to the limitation for the capacity of computer in practical computations.

Generally, it is obvious for anyone that the computational studies largely depend on the ability of computer (cpu time, memory, cost, and so on) and also the economical environment of user. That is, the practical works by the applications of the MO or CO calculation to extended aperiodic systems are restricted within the upper limit which can be permitted in the above-mentioned situation. Thus, it is hoped that a new manner is developed to study such systems more efficiently and more systematically instead of the conventional approaches.

Here, the conventional approaches and the main problems on their applications to the theoretical treatment of aperiodic polymers and perturbed crystals are summarized as follows.

At first, the computational approach on aperiodic polymer systems is described.

In studying the electronic structure of a polymer system based on the quantum chemical calculation, the most different situation in comparison with the calculation of a small molecule is that it is impossible to calculate the whole molecule of polymer with large size. For that reason, we need a model system of extended polymer by any way in the practical study.

One approach to deal with a polymer is the cluster model in which a polymer is approximated by a molecule with several units of the polymer. However, we can not know the electronic properties of the polymer from the calculated result of a cluster having the specific size because the electronic natures may depend on the cluster size. Therefore, to extract the characters of the polymer by this model, the MO calculations of various clusters must be performed individually by taking the size of cluster larger. In the iterative calculations, we regard the converged properties of the energy per unit, the electron density distribution, and so on as that for the bulk limit of the polymer. This cluster approach can be applied to any nonperiodic polymers because the units which form a cluster are not limited to be the same with each other, but its application is restricted by the size of cluster and the upper limit of cluster size is determined by the capacity of computer. Also, the detection of periodic state such as the band structure in a periodic polymer is not necessarily clear.

Another is the CO calculation by assuming the perfect periodicity of a polymer, that is, a polymer is approximated as a one-dimensional crystal with periodic sequence of its constituent unit. In this approach, the eigenvalue problem of polymer is solved under the periodic boundary condition to obtain the COs which satisfy the translational symmetry of polymer. By this crystal model, we can know the electronic property of the bulk state without the end effect and obtain the band structure or the density of states which characterizes the periodic nature. However, this method is so restricted by the periodic boundary condition itself, that is, it requires the periodical sequence of same units in molecular geometry by which it is difficult to treat the aperiodic effect. Thus, if the supercell which is a large periodic unit including aperiodic part is employed, polymers with local aperiodic part can be treated by the CO method, but it has little power on the study of electronic structures for random polymers.

As is pointed out above briefly, the MO calculation and the CO calculation may be applied to random polymers and local aperiodic polymers, respectively, but, the methods have the problems on the treatment of the size effect in the cluster model and the aperiodic effect in the crystal model for nonperiodic polymer systems. In particular, for periodic polymers with aperiodic part within a local region, the most difficulty in studying the systems is caused by the fact that we must take into account the following two states connecting with each other in a polymer chain simultaneously, that is, the periodic-extended state which can be represented appropriately by the CO as a polymer with periodicity and the aperiodic-localized state which is suitable to be described by the MO as a cluster in periodic surroundings. Moreover, the optimal size of cluster or supercell can not be determined beforehand.

At second, the computational approach on perturbed crystal systems is described.

In these systems, because the periodicity of systems is broken in a local region, it is not easy to apply the CO theory to the perturbed systems. This theory assumes the perfect periodicity of whole systems, and, the periodic boundary condition is a serious restriction itself. In contrast with the CO approach, the MO approach has no limitation concerning the periodic sequence of constituent in the systems. However, this method can not reproduce the bulk electronic distributions since neighboring molecules are absent by its free boundary condition, thus, the electronic states at the center and at the edge are different.

In applying the CO and MO methods to the perturbed crystal systems, we must take the systems larger to satisfy the local or the bulk nature of the electronic states as follows. In the crystal approach, a supercell which is an extended unit for the periodicity of the system must be large enough so that the interactions among perturbed parts in neighboring cells are negligible small and do not affect on the local electronic states with each other. In the molecule approach, the size of a cluster molecule has to be sufficiently large in which the influences of molecular edges do not reach to the region around a local perturbed part and do not disturb the bulk electronic condition in its surrounding. However, it is impossible to know *a priori* the effective size of supercell or cluster in which the electronic structures of the perturbed systems can be described correctly without the effects of boundary conditions. Therefore, we need to repeat the calculations against the systems with different sizes to find the optimal size by monitoring the convergence of the local perturbed electronic property. These situations suggest the serious problem that the larger the perturbed systems become, the more enormous the computational efforts like as the calculations of integrals or the diagonalization of matrices in the CO or MO study become.

A local perturbation in an extended periodic system has mainly been dealt with by using the cluster model. Several reasons for using the cluster model instead of the supercell model may exists. Important one of them may be that the MO theory is very advanced and the calculations at the Hartree-Fock and the beyond-Hartree-Fock levels can be carry out by the general program packages with easy use. In other words, there is few packaged tools with popularity which can be used handily in the field of CO calculation. However, as for the evaluation of the bulk electronic structures in the pure and perfect periodic systems, it should be expected that the COs are more advantageous than the MOs, because the former satisfies the translational symmetry of the perfect periodic system without the boundary effect while the latter includes the edge effect by the free boundary condition. Furthermore, the program package which enable us to calculate the bulk electronic properties for one-, two-, and three-dimensional crystalline systems at the *ab initio* level is developed and released recently. That is, we have now arrived at the starting stage toward the development of a new method to examine the effects of local disordering in periodic systems effectively.

Next, the brief discussion to conquer the subjects on the theoretical approach described above is given in the following.

Many trials for the calculations of large extended molecular systems and their results for various molecules have been reported. However, the fragmentation of system is pre-assumed, thus, further calculations against the different selection of fragments must be required in order to find the suitable size of fragment.[4-12]

Several attempts to treat locally perturbed periodic systems by Green function technique have been carried out. This method may surely be useful, but it may appear as to be more complicated in the practical works for computation of its formulation. Moreover, the partition for perturbed and unperturbed regions in the system is assumed in advance, and also, the former region is calculated exactly while the latter region is dealt with approximately in evaluating the total electronic structure of system. Therefore, the determination of interacting range is arbitrary and the calculated results may largely depend on its selection.[13-19]

To overcome the size effect in the cluster or supercell model, we should determine uniquely the general interaction space among the partitioned fragments in extended aperiodic molecule or between the periodic and aperiodic parts in perturbed periodic system with no assumption for its range. It may be available by the following calculation of two-step procedure. Firstly, we obtain the electronic structure of appropriate cluster or periodic system exactly to use as the starting point. Secondly, the interaction space is extracted from the starting system under a perturbation such as the connection with other fragments or aperiodic parts, and then, the eigenvalue problem is solved within the interaction space only to evaluate the electronic state of whole system successively. The most important point is that this approach should not have any assumptions with regard to the range of given perturbation in the system when we estimate the electronic property of perturbed system. In other words, the key point in the idea is the separation of system into the size-dependent and size-independent parts at the MO or CO level.

In order to realize this idea in practical works, the total orbital space of system must be divided into the following two subspaces constructed with the interaction and noninteraction spaces under a given perturbation by the general formulation theoretically. The method has been proposed as the elongation method by the MO calculation.[20,21]

In this thesis, the general MO and CO approaches in place of the usual treatments, which enable us to carry out the efficient and systematic studies of electronic structures for extended aperiodic systems based on the concept explained above, are proposed. Those are the extension of the elongation method.

This thesis consists of the following chapters. In Chaps. 1 and 2, the CO-based elongation method is developed at the CNDO/2 level and the results of its application to the local aperiodicity in polymer and the molecular stacking on surface are reported. In Chap. 3, the extraction of periodicity in the electronic structures of nonperiodic polymers by the MO-based elongation calculation using AM1 parameters is discussed. In Chap. 4, *Ab initio* treatment of locally perturbed periodic systems are described by the two-dimensional CO method. Finally, as the general conclusion, the progresses on the theoretical treatment of electronic structures for extended aperiodic systems is summarized contrasting the present approach with the conventional method.

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Chapter 1

Calculations of Polymer Systems with Local Aperiodic Part: Elongation Method with Supercell Method

In this chapter, we propose a new theoretical approach to treat polymer systems with local aperiodic part efficiently. This approach is the combination of the elongation method with the supercell method which has been developed in our group, and we developed this approach to obtain the electronic structure of a polymer having local aperiodicity by considering the locality of the interaction between periodic and local aperiodic parts. In order to confirm the validity of this method, several model calculations were performed at the complete neglect of differential overlap (CNDO/2) level. That is, we applied this method to all-*trans* polyacetylene interacting with a small molecule, and to all-*trans* polyacetylene with partial substitution of hydrogen atoms by fluorine atoms. We compared the results obtained by this calculation with those obtained by usual crystal orbital calculation concerning total energy, computational time and electron density distribution. The charge extension on polymer chain under the influence of aperiodicity was also discussed.

1.1. INTRODUCTION

A theoretical method to calculate the electronic structures of complete periodic polymers has already been established as the crystal orbital method,[1] and it has been applied to various periodic polymers at the Hartree-Fock level.[2] In the approach, a periodic polymer is considered as a one-dimensional crystal and the eigenvalue problem is solved under the Bórn-von-Káman periodic boundary condition to obtain the crystal orbitals which satisfy the translational symmetry of the system. Moreover, the treatment at the post-Hartree-Fock level including the electron correlation effect has been developed in recent years.[3-7] Thus, the application of the methods in quantum chemical calculations to polymer systems with no periodicity remains as one important problem at present. The study in this direction is now in progress by various groups.[8-10]

Our group has developed the methods to deal with the aperiodicity of polymer systems. We have proposed two approaches, that is, the molecular orbital and the crystal orbital approaches. As an approach using the molecular orbital method, we considered the extension of the molecular cluster system, and proposed the method to obtain the electronic structure for the extension process of the system as the elongation method.[11] In this approach, we combine a small molecule or a molecular fragment with the end part of the starting cluster with appropriate size one after another by taking an important interaction into the eigenvalue problem of the extended system and dropping the unimportant part. By repeating this procedure, it is possible to calculate the electronic structure of periodic or aperiodic polymers systematically and efficiently, that is, a theoretical synthesis of polymers. Furthermore, the information about an electronic state in the local region of polymers can be extracted, for instance, local density of states in aperiodic polymers[12] or stationary condition of the electronic structure against the extension.[13] On the other hand, as an approach using the crystal orbital method (the supercell method),[14] a perturbational treatment by using the iterative transfer perturbation method was reported, and we applied is to the interaction between a periodic polymer and a small molecule,[15-18] or to polymers including the local aperiodic part.[19]

In the present chapter, as a new approach using the crystal orbital method, we propose a variational treatment to calculate the electronic structure of polymer systems with local aperiodicity. In order to develop this approach, we combined the elongation method[11,13] with the supercell method.[14] In this method, the crystal orbitals for the unit cell, which is a minimum periodic unit for the translational symmetry, are transformed into those for the supercell, which is a large periodic unit including several unit cells, at first. Next, we choose the orbital set interacting strongly with the local aperiodic part from the crystal orbitals for the supercell by an analogous procedure in the elongation method.[13] Then, we solve the eigenvalue problem represented with the selected orbital set. The procedure mentioned above, namely, selecting the orbital set under the effect of local aperiodic part and solving the eigenvalue problem represented with the orbital set, is repeated until the local interaction converges.

In order to demonstrate the generality and validity of our approach, we formulated and programmed these procedures at the complete neglect of differential overlap (CNDO/2) level,[20,21] and several model calculations were carried out. We applied this method to all-*trans* polyacetylene interacting with one small molecule HX (X=H,F,Li). We chose a hydrogen molecule as a model of the simple system, and hydrogen fluoride or lithium hydride as a model of the polar system. Furthermore, all-*trans* polyacetylene substituted hydrogen atoms by fluorine atoms partially was dealt with by this method. In the following sections, we describe the outline of this methodology and show the reliability of this treatment by comparing the results obtained by using this method with those obtained by using the usual crystal orbital method.

1.2. METHOD

Crystal orbitals of a periodic polymer can be obtained by using the tight-binding approximation under the periodic boundary condition in the following form:

$$\Psi_i(k_u) = (1/N)^{1/2} \sum_{l=0}^{N-1} \sum_{t=1}^{M} \exp(\tilde{i} k_u l)\, C_{ti}(k_u)\, \chi_t(\mathbf{r} - \mathbf{r}_t - l\mathbf{a}), \tag{1.1}$$

$$k_u = 2\pi p / N \quad (p = 1, \ldots, N), \tag{1.2}$$

where l specifies a unit cell in the polymer consisting of N cells, k_u is the wave number vector, $\mathbf{a}$ the lattice vector, i an energy level, t an atomic orbital, and $\mathbf{r}$ the position vector of an electron, $\tilde{i}$ denotes the imaginary unit $\sqrt{-1}$. Here, the periodic polymer is approximated as a one-dimensional crystal containing infinite unit cells, that is, infinite sequence of a minimum periodic unit for translational symmetry.

The crystal orbitals for the unit cell can be transformed into those for the supercell by using the method proposed by us before. Here, supercell is a large periodic unit consisting of m unit cells with the lattice vector $m\mathbf{a}$. Namely, the wave number vector k_u, and the atomic orbital coefficients C_{ti} of crystal orbitals for unit cell are transformed into those for the supercell as follows:

$$k_s = mk_u - 2j\pi \quad (j;\text{integer}), \tag{1.3}$$

$$C_{ti(n)}(k_s) = C_{ti}(k_u) \exp[\tilde{i}(n-1)k_u], \tag{1.4}$$

where n denotes the nth cell in the central supercell and j should be selected in order that k_s is in the range of the first Brilloin zone. The explanation of these relations is shown in Refs.[14-19]

In the present approach, since we study the local aperiodicity in a periodic polymer, it is convenient to treat the system based on the supercell. Thus, as the first step, after solving the eigenvalue problem to obtain the crystal orbitals for unit cell, we transform the crystal orbitals into those for supercell. This transformation corresponds to that from reduced zone scheme to extended zone scheme, which means the extension of periodic unit for translational symmetry.

Now, we consider the interaction with local aperiodic part added to supercell. In the case of local interaction in a large system, there is no need to deal with the interaction with all orbitals of the large system. Thus, we divide the whole system into two subsystems at the orbital level, and solve the eigenvalue problem represented with the interaction orbital set in two subsystems. Namely, the crystal orbitals for the supercell are divided into active orbitals which may be affected by the local interaction and frozen orbitals which will have no change after interacting with the local aperiodic part, and we choose the specific orbital pairs interacting strongly with each other from the active and frozen orbitals, respectively.

In order to perform the subdivision mentioned above, the following interaction block of the Fock matrix is calculated,

$$\mathbf{F}^{\mathrm{occ}} = \langle \Phi^{\mathrm{vac}} | \overline{F} | \Psi^{\mathrm{occ}} \rangle, \tag{1.5a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \Phi^{\mathrm{occ}} | \overline{F} | \Psi^{\mathrm{vac}} \rangle, \tag{1.5b}$$

where $\overline{F}$ is Fock operator, $\{\Phi_i\}$ $(i=1,\ldots,N)$ and $\{\Psi_j\}$ $(j=1,\ldots,M)$ indicate the specific orbitals that are interacting with each other, occ and vac represent occupied and vacant orbitals, respectively. The matrix elements in Eq. (1.5) correspond to the orbital-based interaction terms of the Fock matrix between $\{\Phi_i\}$ and $\{\Psi_j\}$. To find the orbital set in $\{\Psi\}$ which interacts with $\{\Phi\}$ strongly, the following technique is applied to $\mathbf{F}^{\mathrm{occ}}$ and $\mathbf{F}^{\mathrm{vac}}$, respectively. That is, if there are N^o occupied and N^v vacant orbitals in $\{\Phi\}$, M^o and M^v orbitals in $\{\Psi\}$, we multiply the above $N^v \times M^o$, $N^o \times M^v$ matrix by its adjoint $M^o \times N^v$, $M^v \times N^o$ matrix from the left side and diagonalize the obtained $M^o \times M^o$, $M^v \times M^v$ matrix $\mathbf{F}^{+}\mathbf{F}$,

$$\mathbf{U}^{+}\mathbf{F}^{+}\mathbf{F}\mathbf{U} = \mathbf{E}, \tag{1.6}$$

where $\mathbf{U}$ is the matrix whose columns are eigenvectors and $\mathbf{E}$ is the diagonal matrix of the eigenvalues. As the eigenvalues obtained here correspond to the magnitude of interaction between $\{\Phi\}$ and $\{\Psi\}$, we perform unitary transformation on $\{\Psi\}$ by using $\mathbf{U}$ and choose the orbital set with greater eigenvalue than an appropriate threshold from occupied and vacant spaces of transformed $\{\Psi\}$. This procedure is analogous to that for the corresponding orbital[22] or the interaction frontier molecular orbital (MO).[23,24] In this way, the orbital space is modified to satisfy the variational condition approximately in which Fock matrix elements between occupied and vacant orbitals are nearly equal to zero.

In the following, we describe the method to solve the eigenvalue problem for the polymer systems with local aperiodic part by using the procedure mentioned above in detail. The schematic illustration of the calculation procedure at a viewpoint of the division in orbital space of the system is given in Fig. 1.1 and the corresponding matrix representation is summarized in Fig. 1.2. We explain the procedure along with these figures below. The starting point is the crystal orbitals for the supercell obtained in the first step. Next, we find the orbital set in the supercell which will be affected by the interaction with the aperiodic part according to the techniques in Eqs. (1.5) and (1.6). In other words, we select the orbitals which are not satisfied with the variational condition in total orbital space. The interaction blocks of the Fock matrix in Eqs. (1.5a) and (1.5b) are shown as the shaded parts in Fig. 1.2 for each calculation step. We refer to "active" orbitals as the orbitals which are perturbed by the local interaction through the eigenvalue problem including the effect of the aperiodic part. Since "frozen" orbitals means the orbitals which only are transformed by the unitary matrix in Eq.

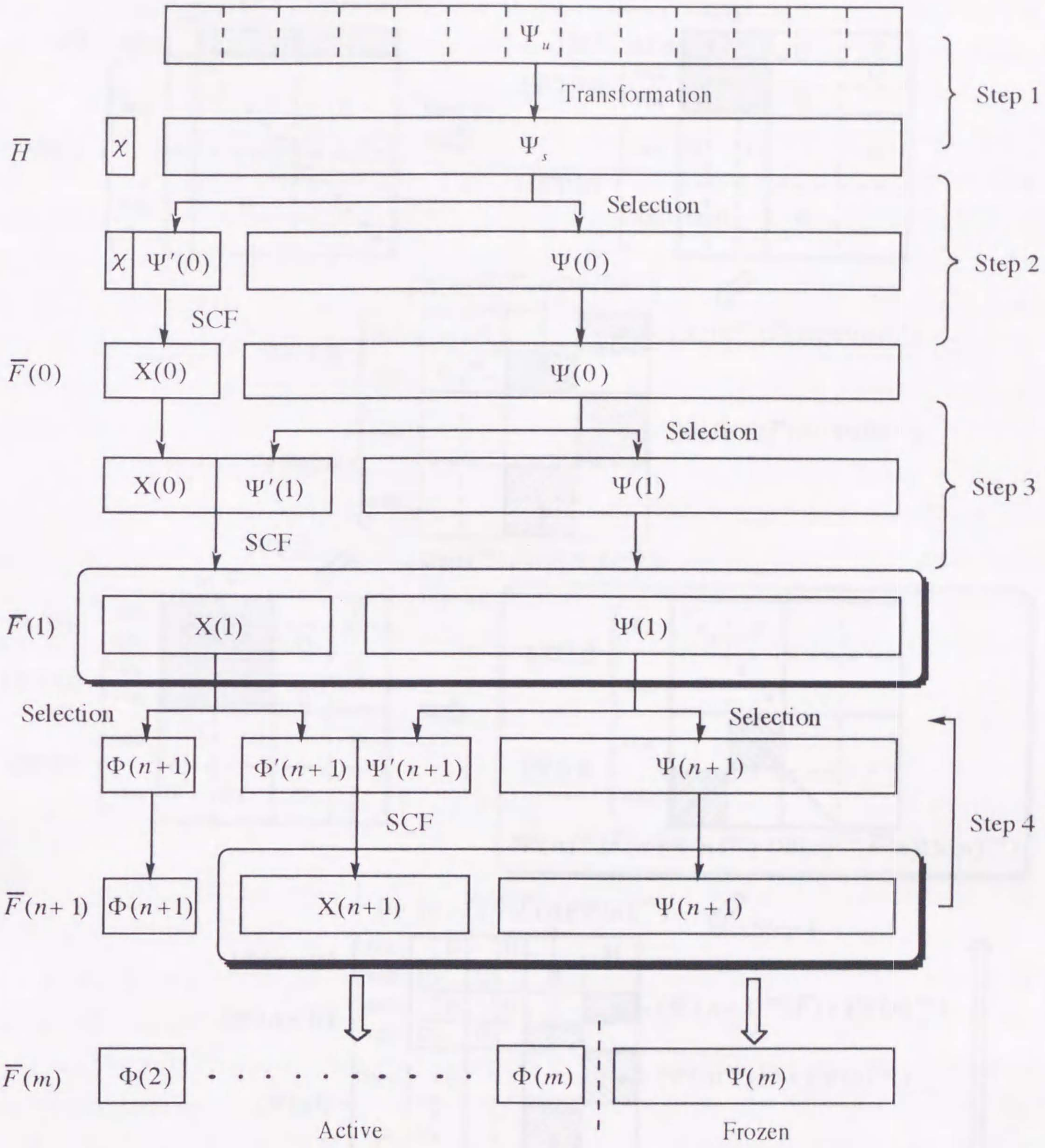

FIG. 1.1. Schematic illustration of the calculation procedure at a viewpoint of the division of orbital space of the system. The notation in this figure corresponds to that in the text.

(1.6) and separated from the basis orbitals of the eigenvalue problem of the interacting system, these orbitals keep the bulk nature of the periodic polymer described by the crystal orbital. Now, we note that because the Fock operator and crystal orbital depend on the wave number vector, we must carry out steps 2-4 in Figs. 1.1 and 1.2 for each value of the wave number vector for the supercell in Eq. (1.3).

As the second step, because the electronic state of the supercell is known and the variational condition is satisfied within the supercell, we consider the interaction between aperiodic and periodic parts in the system through core Hamiltonian (at the starting point, Fock operator including the interaction is unknown), that is, the interaction block is taken as follows:

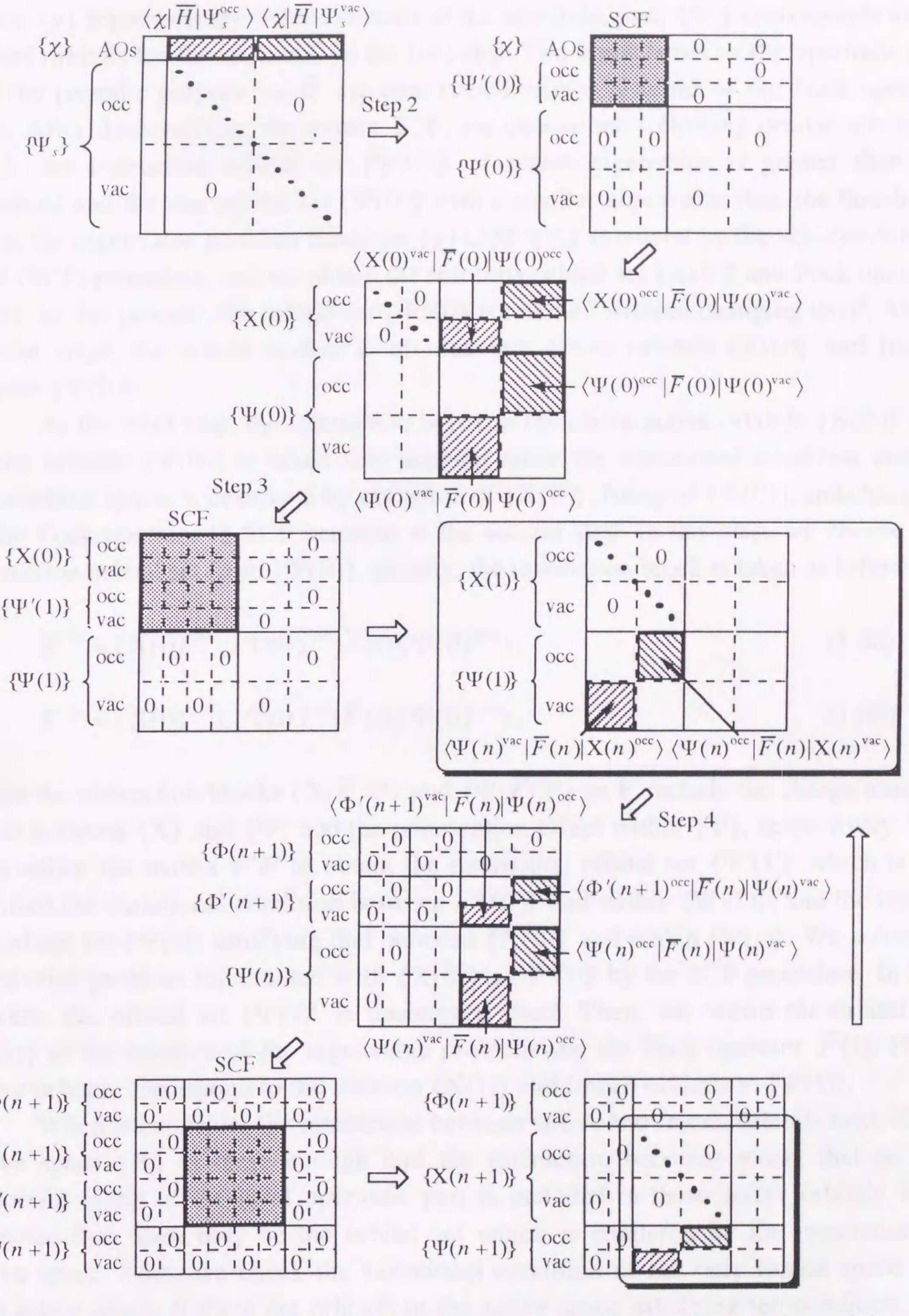

FIG. 1.2. Matrix representation of the calculation procedure in Fig. 1.1. The shaded part of the matrix at each calculation step corresponds to the interaction block of the Fock matrix in the text.

$$\mathbf{F}^{\rm occ} = \langle\chi|\overline{H}|\Psi_s^{\rm occ}\rangle, \tag{1.7a}$$

$$\mathbf{F}^{\rm vac} = \langle\chi|\overline{H}|\Psi_s^{\rm vac}\rangle, \tag{1.7b}$$

where $\{\chi\}$ represents the atomic orbitals at the aperiodic part, $\{\Psi_s\}$ corresponds to the crystal orbitals for the supercell in the first step. The terms between the aperiodic part and the periodic polymer in $\overline{H}$ are constructed with core terms of the Fock operator only. After diagonalizing the matrix $\mathbf{F}^{+}\mathbf{F}$, we choose the following orbital sets from $\{\Psi_s\}$; the interaction orbital set $\{\Psi'(0)\}$ of which eigenvalue is greater than the threshold and the rest orbital set $\{\Psi(0)\}$ with a smaller eigenvalue than the threshold. Then, the eigenvalue problem based on $\{\chi\}\cup\{\Psi'(0)\}$ is solved by the self-consistent-field (SCF) procedure, and we obtain the resulting orbital set $\{\mathrm{X}(0)\}$ and Fock operator $\overline{F}(0)$. In this process, the orbital set $\{\Psi(0)\}$ is retained without changing itself. At the present stage, the whole system is divided into active orbitals $\{\mathrm{X}(0)\}$ and frozen orbitals $\{\Psi(0)\}$.

As the third step, the interaction between the above active orbitals $\{\mathrm{X}(0)\}$ and frozen orbitals $\{\Psi(0)\}$ is taken into account since the variational condition among these orbital spaces is destroyed by extension of $\{\mathrm{X}(0)\}$, fixing of $\{\Psi(0)\}$, and changing of the Fock operator in SCF iteration at the second step. In this step, we choose the interaction orbital set from $\{\Psi(0)\}$, namely, the interaction block is taken as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \mathrm{X}(0)^{\mathrm{vac}} \cup \Psi(0)^{\mathrm{vac}} | \overline{F}(0) | \Psi(0)^{\mathrm{occ}} \rangle, \tag{1.8a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \mathrm{X}(0)^{\mathrm{occ}} \cup \Psi(0)^{\mathrm{occ}} | \overline{F}(0) | \Psi(0)^{\mathrm{vac}} \rangle, \tag{1.8b}$$

where the interaction blocks $\langle \mathrm{X}|\overline{F}|\Psi\rangle$ and $\langle \Psi|\overline{F}|\Psi\rangle$ in $\mathbf{F}$ include the charge transfer effect between $\{\mathrm{X}\}$ and $\{\Psi\}$ and the polarization effect within $\{\Psi\}$, respectively. We diagonalize the matrix $\mathbf{F}^{+}\mathbf{F}$ to obtain the interaction orbital set $\{\Psi'(1)\}$ which is not satisfied the variational condition between $\{\mathrm{X}(0)\}$ and within $\{\Psi'(1)\}$, and the rest of the orbital set $\{\Psi(1)\}$ satisfying that between $\{\mathrm{X}(0)\}$ and within $\{\Psi(1)\}$. We solve the eigenvalue problem represented with $\{\mathrm{X}(0)\}\cup\{\Psi'(1)\}$ by the SCF procedure. In this process, the orbital set $\{\Psi(1)\}$ is unchanged itself. Then, we obtain the orbital set $\{\mathrm{X}(1)\}$ as the solution of the eigenvalue problem and the Fock operator $\overline{F}(1)$. Here, active orbitals correspond to the solution $\{\mathrm{X}(1)\}$ and frozen orbitals to $\{\Psi(1)\}$.

When we consider the interaction between active and frozen orbitals next, if the active space $\{\mathrm{X}\}$ is large enough and the interaction becomes weak, that is, the important effect of the local aperiodic part is included in these active orbitals, it is expected that there may be the orbital set which is unaltered by the interaction in active space. Thus, we check the variational condition of not only frozen space but also active space. If there are orbitals in the active space satisfying the condition, we can consider that the orbitals are separated from the interaction space of the system. We take into account this situation in the next step.

As the fourth step, the following procedure is repeated until the interaction converges, that is, there are no interaction orbital sets with a greater eigenvalue than the threshold for the interaction block, which is not satisfied with the variational condition in the orbital space. In this step, we consider the interaction space as $\{\mathrm{X}\}$

and $\{\Psi\}$, and choose the interaction orbital set from $\{X\}$ and $\{\Psi\}$, respectively. Now, we consider the $n+1$th cycle in this step (the 1st cycle corresponds to the third step mentioned above). First, we use the interaction block as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \Psi(n)^{\mathrm{vac}} | \overline{F}(n) | \mathrm{X}(n)^{\mathrm{occ}} \rangle, \tag{1.9a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \Psi(n)^{\mathrm{occ}} | \overline{F}(n) | \mathrm{X}(n)^{\mathrm{vac}} \rangle, \tag{1.9b}$$

where the orbital set $\{\Psi(n)\}$ represents the nth frozen orbitals, and the orbital set $\{\mathrm{X}(n)\}$ corresponds to the eigenvectors of the nth eigenvalue problem by the SCF procedure. We choose the interaction orbital set $\{\Phi'(n+1)\}$ and the rest orbital set $\{\Phi(n+1)\}$ from the preceding solution $\{\mathrm{X}(n)\}$ by diagonalizing the matrix $\mathbf{F}^{+}\mathbf{F}$. Next, we take into account the interaction between $\{\Phi'(n+1)\}$ and the preceding frozen orbitals $\{\Psi(n)\}$, and the interaction block is defined as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \Phi'(n+1)^{\mathrm{vac}} \cup \Psi(n)^{\mathrm{vac}} | \overline{F}(n) | \Psi(n)^{\mathrm{occ}} \rangle, \tag{1.10a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \Phi'(n+1)^{\mathrm{occ}} \cup \Psi(n)^{\mathrm{occ}} | \overline{F}(n) | \Psi(n)^{\mathrm{vac}} \rangle. \tag{1.10b}$$

Here, we note that the block $\langle \Phi' | \overline{F} | \Psi \rangle$ in $\mathbf{F}$ corresponds to the charge transfer between $\{\Phi'\}$ and $\{\Psi\}$, and the block $\langle \Psi | \overline{F} | \Psi \rangle$ in $\mathbf{F}$ corresponds to the polarization within $\{\Psi\}$. We diagonalize the matrix $\mathbf{F}^{+}\mathbf{F}$, and choose the interaction orbital set $\{\Psi'(n+1)\}$ and the rest orbital set $\{\Psi(n+1)\}$ from $\{\Psi(n)\}$. Then, the eigenvalue problem is solved within $\{\Phi'(n+1)\} \cup \{\Psi'(n+1)\}$ by the SCF procedure to obtain the resulting orbital set $\{\mathrm{X}(n+1)\}$ and Fock operator $\overline{F}(n+1)$. In this process, the rest orbital set $\{\Phi(n+1)\}$ and $\{\Psi(n+1)\}$ have no change themselves.

Next, we assume the interaction space for the $n+2$th cycle as $\{\mathrm{X}(n+1)\}$ and $\{\Psi(n+1)\}$, and repeat the procedure in this step as mentioned above. Thus, at each cycle in this step, if there is, $\{\Phi\}$ is removed from the interaction space because it is possible to consider that the interaction between $\{\Phi(n+1)\}$ and $\{\Psi(n)\}$ is small enough since the eigenvalues of the interaction block between them are smaller than the threshold, and each $\{\Phi\}$ is maintained itself unchanging through all cycles. Finally, if the interaction converges at the mth cycle, we obtain the active orbitals as $\{\Phi(2)\}, \ldots, \{\Phi(m)\}$ and frozen orbitals as $\{\Psi(m)\}$.

We explain the concept and outline of this method as summary. We take the isolated system as a starting point. The Fock matrix based on orbitals in the system is diagonal within the supercell, and the matrix elements between the supercell and the aperiodic part have some values. If the eigenvalue problem of the whole system is solved completely, the matrix elements between occupied and vacant orbitals vanish (the variational condition). Therefore, we develop the method by which the total orbital space is forced to satisfy the variational condition finally. For that purpose, the specific orbital pairs that the matrix element between occupied and vacant orbitals has nonzero value were selected as an interaction orbital set. Then, the eigenvalue problem is solved within the selected space. After this step, the matrix elements between the interaction orbitals and the rest orbitals may have finite values by mixing through the density matrix. Thus, this selection must be done iteratively.

The feature of this treatment is the simplicity in practical calculation. In this approach, we diagonalize the matrix $\mathbf{F}^{+}\mathbf{F}$ only to find the interaction orbital set, and solve the eigenvalue problem within the interaction orbital space. Thus, there is no need to treat the whole system with a large dimension and solve a large eigenvalue problem directly. The important effects of charge transfer and exchange between periodic and aperiodic parts can be taken into account, and the polarization effect within the periodic part can be also taken in this calculation by the procedure mentioned in this section. Furthermore, the interaction orbital space is not an external parameter and the determination of that is included in our calculation procedure itself.

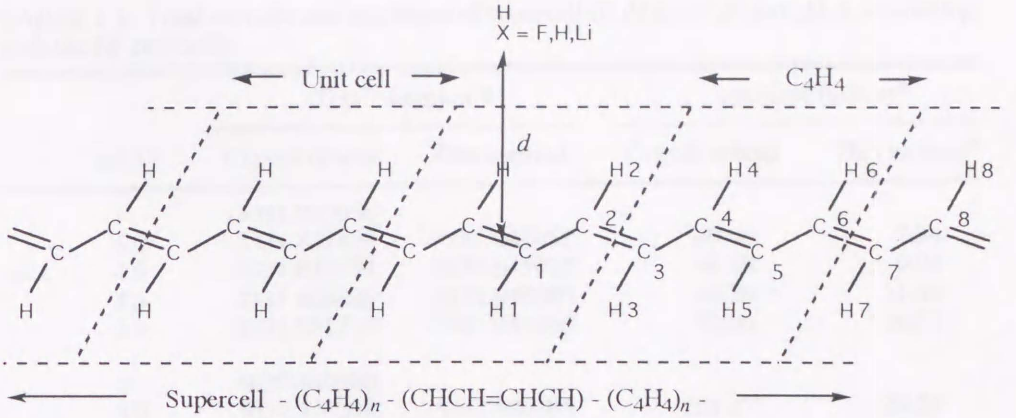

FIG. 1.3. The interacting system of polyacetylene and a small molecule HX (X=F,H,Li). The geometrical parameters used in this calculation are taken as follows: C-C = 1.460 Å, C=C = 1.350 Å, C-H = 1.090 Å, all bond angle = 120° and H-F = 0.917 Å, H-H = 0.742 Å, H-Li = 1.594 Å. A small molecule is placed on the central double bond between carbon atoms C1 apart from polymer chain by the distance d.

1.3. RESULTS AND DISCUSSION

We performed several test calculations for the method described in the previous section in order to check the reliability and usefulness. The models used in test calculations and their structural parameters are shown in Figs. 1.3 and 1.4. The first model systems are all-*trans* polyacetylene interacting with one small molecule. We put a small molecule on the central double bond apart from the polymer plane by the distance d. The second model system is all-*trans* polyacetylene substituted two hydrogen atoms bonding with the central double bond by fluorine atoms. In these models, we consider (C_4H_4) as a unit cell and $(C_4H_4)_n$-(C_4H_4)-$(C_4H_4)_n$ as a supercell. By taking the size of supercell large, the models in Fig. 1.3 may be correspond to low level doping and in Fig. 1.4 to local abnormal bonding for periodic polymer systems.

In this work, we took 10^{-5} as the threshold value and all calculations were performed at the CNDO/2 level. As the polyacetylene supercell is large itself, we used

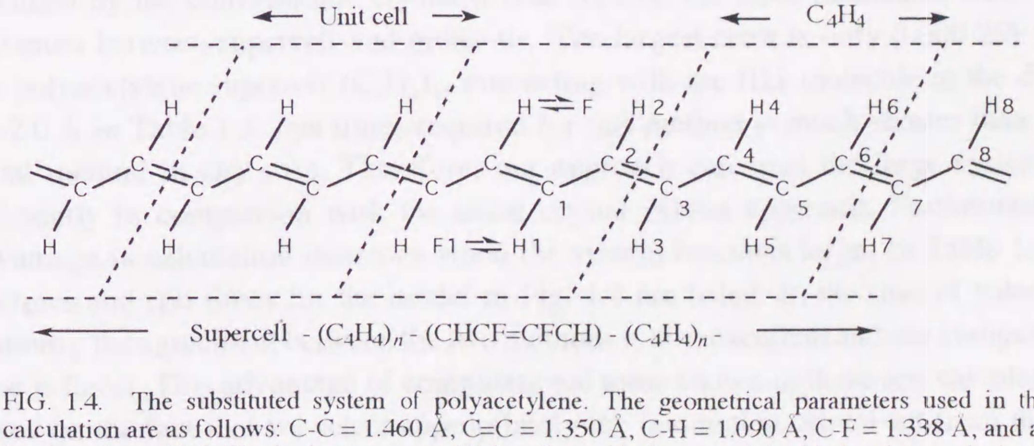

FIG. 1.4. The substituted system of polyacetylene. The geometrical parameters used in this calculation are as follows: C-C = 1.460 Å, C=C = 1.350 Å, C-H = 1.090 Å, C-F = 1.338 Å, and all bond angles = 120°. The hydrogen atoms H1 bonding with the central double bond are substituted by fluorine atoms F1.

TABLE 1.1. Total energies and cpu times of supercell $(C_4H_4)_n$-(C_4H_4)-$(C_4H_4)_n$ interacting with the HF molecule.

		Total energy (eV)		cpu time (min:s)[a]	
	d (Å)	Crystal orbital	This method	Crystal orbital	This method[b]
n=1	∞	-3331.837656			
	5.0	-3331.842459	-3331.842451	40:06	7:36
	4.0	-3331.843033	-3331.843021	43:20	9:05
	3.0	-3331.848886	-3331.848880	46:26	11:36
	2.0	-3331.951273	-3331.951264	53:06	16:31
n=2	∞	-5037.540280			
	5.0	-5037.546296	-5037.546285	254:47	25:21
	4.0	-5037.546932	-5037.546907	270:07	26:09
	3.0	-5037.552888	-5037.552869	288:05	31:47
	2.0	-5037.655475	-5037.655450	322:56	41:47
n=3	∞	-6743.245051			
	5.0	-6743.251852	-6743.251834	865:59	65:45
	4.0	-6743.252501	-6743.252468	933:34	73:59
	3.0	-6743.258476	-6743.258444	987:14	71:55
	2.0	-6743.361096	-6743.361060	1099:30	87:45
n=4	∞	-8448.951470			
	5.0	-8448.958850	-8448.958829	2241:14	172:56
	4.0	-8448.959502	-8448.959462	2407:44	153:40
	3.0	-8448.965481	-8448.965438	2562:51	153:31
	2.0	-8449.068109	-8449.068069	2805:14	166:46
n=5	∞	-10154.659159			
	5.0	-10154.666996	-10154.666973	4713:16	331:26
	4.0	-10154.667649	-10154.667607	5098:45	323:59
	3.0	-10154.673630	-10154.673563	5396:29	289:56
	2.0	-10154.776260	-10154.776189	5953:47	295:58

[a] cpu time on IBM RISC System/6000 340.
[b] Including calculation time for unit cell.

nearest neighbor approximation.

The total energies and cpu times of the models in Fig. 1.3 are listed in Tables 1.1, 1.2, and 1.3. Total energies calculated by using our method agree with those obtained by the conventional crystal orbital method for three molecules with various distances between supercell and molecule. The largest error is only 0.000 299 eV for the polyacetylene supercell $(C_4H_4)_{11}$ interacting with the HLi molecule at the distance d=2.0 Å in Table 1.3. cpu times required for this method is much shorter than for the usual method in any case. Therefore, our approach can treat the large system more efficiently in comparison with the usual crystal orbital approach. Furthermore, this advantage in calculation increases when the system becomes large. In Table 1.4, total energies and cpu times for the model in Fig. 1.4 are listed. In the case of substitution of atoms, the agreement between the two methods is also excellent and our computational time is faster. This advantage of computational tome shown in these test calculations is based on the fact that we select appropriately the interaction orbital set from the large system. That is, it is not required to solve the whole eigenvalue problem of the system.

TABLE 1.2. Total energies and cpu times of supercell $(C_4H_4)_n$-(C_4H_4)-$(C_4H_4)_n$ interacting with the HH molecule.

		Total energy (eV)		cpu time (min:s)[a]	
	d (Å)	Crystal orbital	This method	Crystal orbital	This method[b]
	∞	-2598.668058			
	5.0	-2598.669266	-2598.669266	37:47	5:35
n=1	4.0	-2598.669758	-2598.669758	38:49	5:51
	3.0	-2598.682212	-2598.682208	40:23	7:00
	2.0	-2598.823883	-2598.823859	43:54	9:14
	∞	-4304.370576			
	5.0	-4304.372068	-4304.372069	250:18	17:43
n=2	4.0	-4304.372562	-4304.372561	257:54	21:10
	3.0	-4304.385017	-4304.384979	267:40	29:57
	2.0	-4304.526762	-4304.526740	289:04	28:36
	∞	-6010.075342			
	5.0	-6010.077026	-6010.077026	878:33	39:20
n=3	4.0	-6010.077520	-6010.077518	900:07	52:07
	3.0	-6010.089975	-6010.089920	938:56	80:46
	2.0	-6010.231734	-6010.231710	1015:21	73:52
	∞	-7715.781767			
	5.0	-7715.783593	-7715.783593	2296:14	88:21
n=4	4.0	-7715.784087	-7715.784084	2355:07	109:45
	3.0	-7715.796543	-7715.796487	2471:27	179:08
	2.0	-7715.938306	-7715.938279	2657:57	165:25
	∞	-9421.489460			
	5.0	-9421.491400	-9421.491400	4889:27	183:16
n=5	4.0	-9421.491894	-9421.491891	5054:25	227:40
	3.0	-9421.504350	-9421.504295	5247:17	371:59
	2.0	-9421.646114	-9421.646084	5668:53	321:25

[a] cpu time on IBM RISC System/6000 340.
[b] Including calculation time for unit cell.

For example, the dimensions of the eigenvalue problem to be diagonalized in SCF iterations for the case of substituted polyacetylene supercell $(C_4H_4)_4$-$(C_4H_2F_2)$-$(C_4H_4)_4$ are as follows: 186×186 [number of atomic orbitals (AOs) in the system] by the crystal orbital method while 18×18 (at the step 2), 44×44 (at the step 3), 67×67 (at the 1st cycle in the step 4), 38×38 (at the 2nd cycle in the step 4) by this calculation. In this case, the number of final active orbitals is 126 and frozen orbitals is 60.

The electron density distributions at the central part and end part in the supercell and small molecule HF are summarized in Tables 1.5(a) (model in Fig. 1.3) and 1.6(b) (model in Fig. 1.4). Because the results from our method reflect the symmetry of the system completely, the values for half-side of the chain are listed. From these tables, it is shown that the atomic populations at both aperiodic and periodic parts (central and end parts) calculated by using the two methods are in excellent agreement with each other. The agreement of the results by both methods for other models in Fig. 1.3 is also very good.

These results shown above support the validity of this method, and the accuracy

TABLE 1.3. Total energies and cpu times of supercell $(C_4H_4)_n$-(C_4H_4)-$(C_4H_4)_n$ interacting with the HLi molecule.

		Total energy (eV)		cpu time (min:s)[a]	
	d (Å)	Crystal orbital	This method	Crystal orbital	This method[b]
n=1	∞	-2588.137732			
	5.0	-2588.413058	-2588.413053	48:13	13:40
	4.0	-2589.564576	-2589.564568	50:01	18:39
	3.0	-2593.326889	-2593.326882	52:16	25:32
	2.0	-2597.345509	-2597.345493	61:06	29:45
n=2	∞	-4293.840923			
	5.0	-4294.117089	-4294.117068	303:48	33:52
	4.0	-4295.270574	-4295.270543	307:48	51:19
	3.0	-4299.041081	-4299.041002	317:01	70:15
	2.0	-4303.074287	-4303.074158	367:46	91:22
n=3	∞	-5999.545808			
	5.0	-5999.822327	-5999.822289	1030:30	74:10
	4.0	-6000.976230	-6000.976167	1057:29	101:14
	3.0	-6004.748346	-6004.748235	1085:13	138:08
	2.0	-6008.784270	-6008.784094	1252:41	161:17
n=4	∞	-7705.252269			
	5.0	-7705.528981	-7705.528931	2638:34	153:40
	4.0	-7706.683000	-7706.682881	2724:16	172:01
	3.0	-7710.455543	-7710.455409	2784:38	229:08
	2.0	-7714.492146	-7714.491904	2893:13	276:34
n=5	∞	-9410.959977			
	5.0	-9411.236821	-9411.236764	5608:13	273:50
	4.0	-9412.390878	-9412.390745	5751:46	302:34
	3.0	-9416.163561	-9416.163395	5868:06	392:34
	2.0	-9420.200380	-9420.200081	6086:34	438:37

[a] cpu time on IBM RISC System/6000 340.
[b] Including calculation time for unit cell.

of the calculated results can be controlled by the threshold value for the orbital selection.

In Table 1.6, the convergence of total energies for the polyacetylene supercell $(C_4H_4)_{11}$ interacting with small molecules HX (X=F,H,HLi) at the distances d=5.0 and 2.0 Å is summarized in detail. The number of basis orbitals (number of AOs) and SCF iterations in crystal orbital calculations are as follows: 225 and 8 (HF and HLi), 222

TABLE 1.4. Total energies and cpu times of substituted supercell $(C_4H_4)_n$-$(C_4H_2F_2)$-$(C_4H_4)_n$.

		Total energy (eV)		cpu time (min:s)[a]	
n	No-substituted	Crystal orbital	This method	Crystal orbital	This method[b]
1	-2558.542622	-4027.314727	-4027.314620	41:49	15:11
2	-4264.245143	-5733.020895	-5733.020634	251:18	48:11
3	-5969.949911	-7438.727146	-7438.726811	851:09	100:33
4	-7675.656336	-9144.434493	-9144.434125	2166:41	185:55
5	-9381.364030	-10850.142878	-10850.142499	4589:31	375:19

[a] cpu time on IBM RISC System/6000 340.
[b] Including calculation time for unit cell.

TABLE 1.5. (a) The electron density distributions of polyacetylene supercell $(C_4H_4)_5$-(C_4H_4)-$(C_4H_4)_5$ interacting with the HF molecule.[a] The distance between the supercell and the HF molecule is 2.0 Å. (b) The electron density distributions of substituted polyacetylene supercell $(C_4H_4)_5$-$(C_4H_2F_2)$-$(C_4H_4)_5$.[b]

(a) Atom	H	F	C1	C2	C3	C4	C19	C20	C21	C22
Crystal orbital	0.7913	7.2139	3.9881	3.9996	4.0089	4.0009	4.0034	4.0032	4.0034	4.0033
This work	0.7914	7.2138	3.9878	3.9995	4.0091	4.0015	4.0033	4.0032	4.0033	4.0032
Atom			H1	H2	H3	H4	H19	H20	H21	H22
Crystal orbital			0.9985	0.9975	0.9975	0.9978	0.9968	0.9968	0.9968	0.9968
This work			0.9988	0.9977	0.9976	0.9977	0.9968	0.9968	0.9968	0.9968

(b) Atom	C1	C2	C3	C4	C19	C20	C21	C22
Crystal orbital	3.8434	4.0338	3.9864	4.0092	4.0029	4.0033	4.0031	4.0032
This work	3.8436	4.0331	3.9871	4.0087	4.0031	4.0032	4.0032	4.0032
Atom	F1	H2	H3	H4	H19	H20	H21	H22
Crystal orbital	7.1917	0.9729	0.9870	0.9946	0.9967	0.9967	0.9967	0.9967
This work	7.1908	0.9722	0.9863	0.9948	0.9968	0.9968	0.9968	0.9968

[a] The numbering of atoms is defined in Fig. 1.3.
[b] The numbering of atoms is defined in Fig. 1.4.

and 8 (HH). The weak interaction between the polyacetylene and hydrogen molecule at the distance d=5.0 Å converges very fast, and interaction orbital space is very small. In the other interacting systems, the total energy is converged at the 2nd cycle in step 4 completely. The total SCF iteration cycles are more than crystal orbital calculation, but the number of basis orbitals of the eigenvalue problem in much smaller.

TABLE 1.6. Convergence of total energies for supercell $(C_4H_4)_5$-(C_4H_4)-$(C_4H_4)_5$ interacting with the HX molecule.

	d=5.0 Å	Basis MOs	Iteration	d=2.0 Å	Basis MOs	Iteration
X=F						
Step 2[a]	-0.124409[b]	6	5	-0.686310[b]	15	6
Step 3	-0.000159	46	2	-0.020006	69	3
Step 4	-0.000007	8	1	-0.000043	38	1
Step 4	-0.000002	4	1	-0.000003	2	1
X=H						
Step 2[a]	-0.000008[b]	3	1	-0.326096[b]	6	4
Step 3	-0.000001	4	1	-0.074093	33	4
Step 4				-0.000078	28	1
Step 4				-0.000004	9	1
X=Li						
Step 2[a]	-0.439005[b]	12	4	-18.889920[b]	15	5
Step 3	-0.040715	70	3	-0.704510	89	7
Step 4	-0.000057	44	1	-0.001301	97	3
Step 4	-0.000004	8	1	-0.000031	28	1

[a] Calculation step in Fig. 1.1.
[b] Energies in eV.

Thus, total computation time is faster in this calculation. That is, our method solves the small eigenvalue problem iteratively instead of solving the large eigenvalue problem of the whole system in the usual calculation.

Next, we show the interaction energies between polymer and a small molecule obtained by this approach in Table 1.7. The interaction energy is obtained as the energy difference between the interacting system and the isolated system. The interacting system is stabilized when the size of the supercell is larger (from n=1 to n=2). The reason for this stabilization may be considered that the repulsive interaction between a small molecule in the central supercell and one in the nearest neighbor supercell decreases in the large supercell because of the long distance between small molecules. The interaction energies might appear at first glance to be almost converged at n=4 or n=5, but, the differences between successively larger n (for n>5) are often nondecreasing and, thus, the convergence behavior is not obvious. This slow convergence of the interaction is caused by the long range interaction of the pi electron system. The weak interaction between polyacetylene and HF or HH is almost of the same order, while there is a larger interaction energy of the polymer with HLi than those with HF and HH.

The electron densities of each small molecule HX (X=F,H,Li) on the polyacetylene supercell $(C_4H_4)_{15}$ are shown in Table 1.8. The top line in this table displays the atomic population of the isolated molecule. There is no electron transfer from polyacetylene to HF molecule at all distances between the polymer and the molecule. A small amount of electron transfer is found from polymer to HH molecule only at the distance d=2.0 Å. In the case of the interaction with the HLi molecule, the amount of electron

TABLE 1.7. Interaction energies between supercell $(C_4H_4)_n$-(C_4H_4)-$(C_4H_4)_n$ and HX molecule[a]

d (Å)	n=1	n=2	n=3	n=4	n=5	n=6	n=7
X=F							
5.0	-0.0048	-0.0060	-0.0068	-0.0074	-0.0078	-0.0082	-0.0085
4.0	-0.0054	-0.0066	-0.0074	-0.0080	-0.0084	-0.0088	-0.0092
3.0	-0.0112	-0.0126	-0.0134	-0.0140	-0.0144	-0.0148	-0.0151
2.0	-0.1136	-0.1152	-0.1160	-0.1166	-0.1170	-0.1174	-0.1177
X=H							
5.0	-0.0012	-0.0015	-0.0017	-0.0018	-0.0019	-0.0020	-0.0021
4.0	-0.0017	-0.0020	-0.0022	-0.0023	-0.0024	-0.0025	-0.0026
3.0	-0.0142	-0.0144	-0.0146	-0.0147	-0.0148	-0.0149	-0.0150
2.0	-0.1558	-0.1562	-0.1564	-0.1565	-0.1566	-0.1567	-0.1568
X=Li							
5.0	-0.2753	-0.2761	-0.2765	-0.2767	-0.2768	-0.2769	-0.2770
4.0	-1.4268	-1.4296	-1.4304	-1.4306	-1.4308	-1.4309	-1.4310
3.0	-5.1892	-5.2001	-5.2024	-5.2031	-5.2034	-5.2036	-5.2037
2.0	-9.2078	-9.2332	-9.2383	-9.2396	-9.2401	-9.2403	-9.2404

[a] Energies in eV.

TABLE 1.8. Electron densities of small molecules HX (X=F,H,Li) on polyacetylene supercell $(C_4H_4)_7$-(C_4H_4)-$(C_4H_4)_7$.

d (Å)	HF	HH	HLi
∞	8.0000	2.0000	2.0000
5.0	8.0000	2.0000	2.0114
4.0	8.0000	2.0000	2.0603
3.0	8.0002	2.0007	2.2151
2.0	8.0051	2.0189	2.4903

transfer is remarkable even apart from the polymer by d=5.0 Å and the tendency of electron transfer increases by approaching the polymer. The larger interaction energies in Table 1.7 between polyacetylene and HLi in comparison with the other molecules (HF and HH) are caused by this electron transfer effect.

The net charge on each carbon atom on supercell $(C_4H_4)_{15}$ interacting with small molecules at the distance d=2.0 Å is summarized in Fig. 1.5. For each case, the net charges at the edge of the supercell is consistent with the value -0.003 of the isolated polyacetylene. In the case of the interaction with the HH molecule, the convergence of net charge is rapid and the extension of charges is limited within almost seven carbons from the central carbon. On the other hand, in polymer chains interacting with HF or HLi molecule, charges are extended with oscillation around the isolated value. The range of charge extension is C15 for HF and C21 for HLi in one side of the chain. Particularly, by electron transfer from the polymer to the HLi molecule, considerable deviation from the isolated case is found in the charge distribution

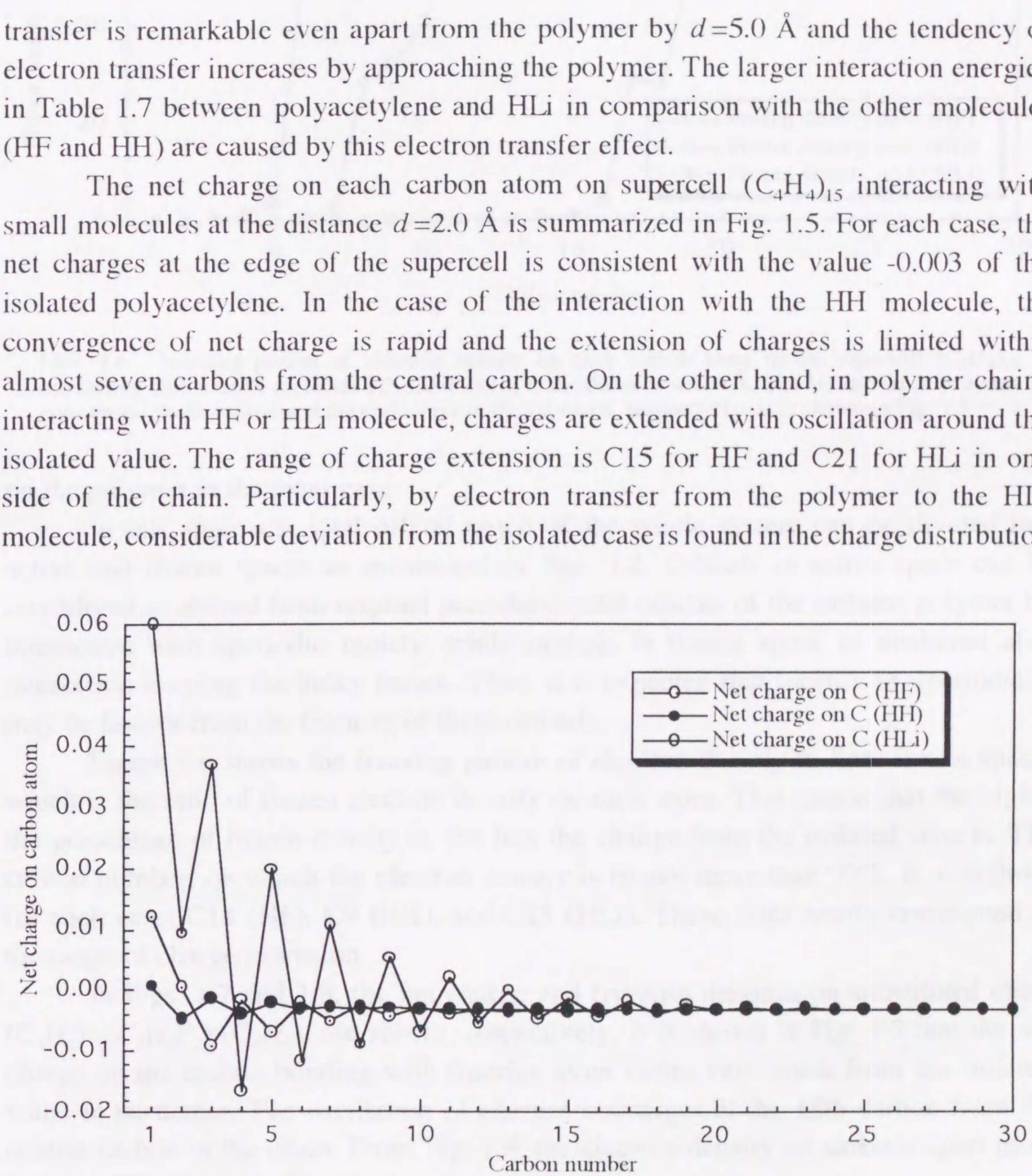

FIG. 1.5. Net charge on each carbon atoms in the supercell $(C_4H_4)_{15}$ interacting with a small molecule HX (X=F,H,Li) at the distance d=2.0 Å. The 1st and the 30th atoms correspond to the central and the end atoms in the supercell, respectively, as is shown in Fig. 1.3.

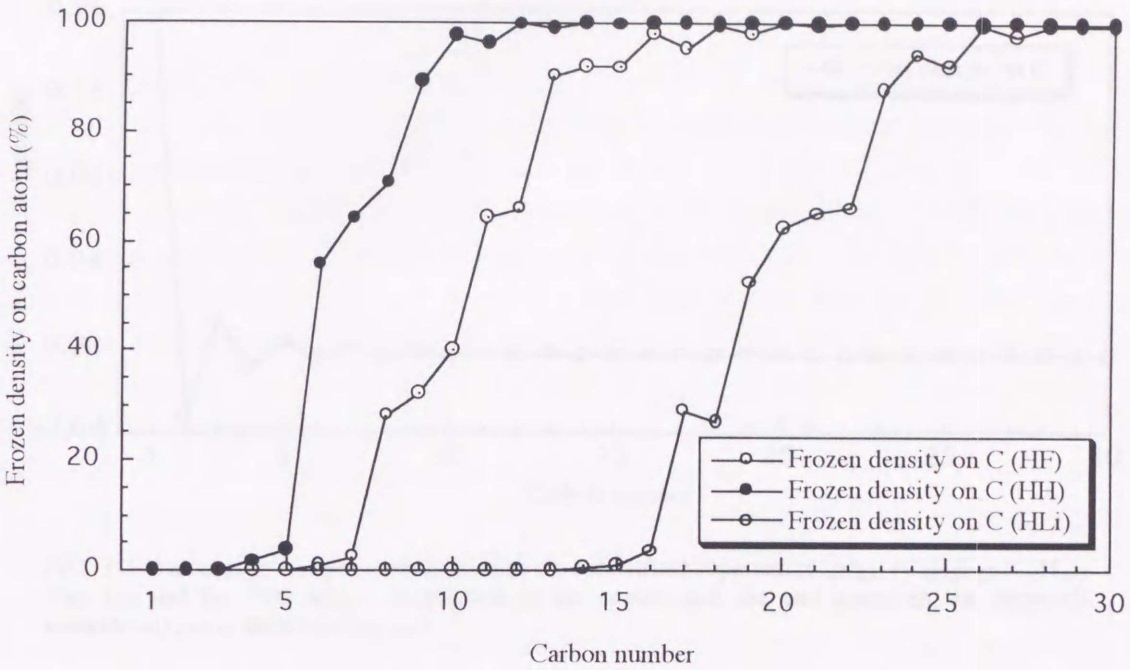

FIG. 1.6. Freezing pattern of electron density on each carbon atom in the supercell $(C_4H_4)_{15}$ interacting with a small molecule HX (X=F,H,Li) at the distance *d*=2.0 Å. The 1st and the 30th atoms correspond to the central and the end atoms in the supercell, respectively, as is shown in Fig. 1.3.

on the polymer in the latter case.

In our approach, total orbital space of the whole system can be divided into active and frozen spaces as mentioned in Sec. 1.2. Orbitals in active space can be considered as altered from original periodic crystal orbitals of the isolated polymer by interaction with aperiodic moiety, while orbitals in frozen space as unaltered after interaction keeping the bulky nature. Thus, it is expected that locality of aperiodicity may be known from the features of these orbitals.

Figure 1.6 shows the freezing pattern of electron density in final frozen space, which is the ratio of frozen electron density on each atom. This means that the higher the percentage of frozen density is, the less the change from the isolated state is. The carbon number, on which the electron density is frozen more than 90%, is as follows for each case: C14 (HF), C9 (HH), and C23 (HLi). These sizes nearly correspond to the range of charge extension.

In Figs. 1.7 and 1.8, the net charge and freezing diagram on substituted chain $(C_4H_4)_7$-$(C_4H_2F_2)$-$(C_4H_4)_7$ are shown, respectively. It is shown in Fig. 1.7 that the net charge on the carbon bonding with fluorine atom varies very much from the isolated value in particular. The oscillation of charges converges at the 15th carbon from the central carbon in the chain. From Fig. 1.8, the electron density on carbons apart more than the 17th carbon is frozen more than 90%.

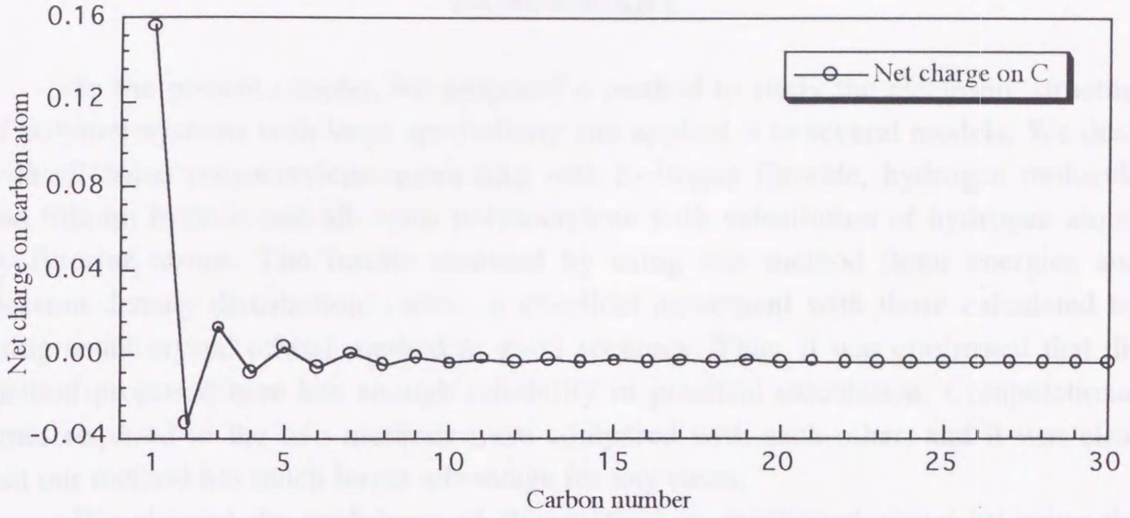

FIG. 1.7. Net charge on each carbon atom in the substituted supercell $(C_4H_4)_7$-$(C_4H_2F_2)$-$(C_4H_4)_7$. The 1st and the 30th atoms correspond to the central and the end atoms in the supercell, respectively, as is shown in Fig. 1.4.

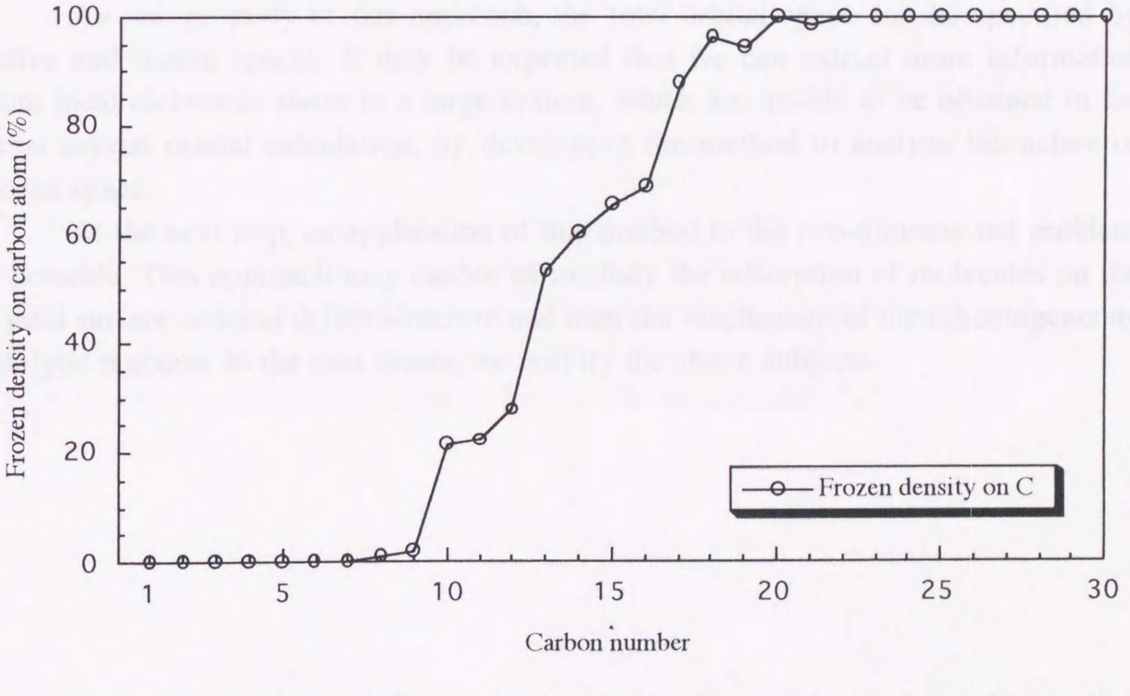

FIG. 1.8. Freezing pattern of electron density on each carbon atom in the substituted supercell $(C_4H_4)_7$-$(C_4H_2F_2)$-$(C_4H_4)_7$. The 1st and the 30th atoms correspond to the central and the end atoms in the supercell, respectively, as is shown in Fig. 1.4.

1.4. SUMMARY

In the present chapter, we proposed a method to study the electronic structure of polymer systems with local aperiodicity and applied it to several models. We dealt with all-*trans* polyacetylene interacting with hydrogen fluoride, hydrogen molecule and lithium hydride and all-*trans* polyacetylene with substitution of hydrogen atoms by fluorine atoms. The results obtained by using this method (total energies and electron density distributions) were in excellent agreement with those calculated by using usual crystal orbital method in good accuracy. Thus, it was confirmed that the method proposed here has enough reliability in practical calculation. Computational times required in the two methods were compared with each other, and it was clear that our method has much larger advantage for any cases.

We showed the usefulness of this method as mentioned above by using the CNDO/2 approximation. Of course, the calculation has no satisfying level of approximation. But, it is easy to develop this method in more advanced semiempirical calculations since this method has no special limitation. Moreover, it can be applicable to *ab initio* calculations if we select the orbital set which satisfy the orthonormal condition in the same manner as described in the previous study of our group.[13]

As one property of our approach, the total orbital space can be specified by active and frozen spaces. It may be expected that we can extract more information from local electronic states in a large system, which are unable to be obtained in the usual crystal orbital calculation, by developing the method to analyze the active or frozen space.

At the next step, an application of this method to the two-dimensional problem is possible. This approach may enable us to study the adsorption of molecules on the crystal surface or local defect structure and then the mechanism of the inhomogeneous catalytic reaction. In the near future, we will try the above subjects.

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Chapter 2

Electronic Structures of Large, Extended, Nonperiodic Systems: Cluster Series of Polymer and Molecular Stacking on Surface

The elongation method based on the molecular orbital (MO) theory, which enables us to extend a polymer with any molecular fragments theoretically, has recently been developed by our group. As the next step, we introduced an approach based on the crystal orbital (CO) theory into above treatment. In the present chapter, the elongation method was developed at the Hartree-Fock level with CNDO/2 parameters, and was applied to model systems composed of the cluster series of polymer and the molecular stacking on surface. In the cluster-series calculations, hydrogen molecule [$(H_2)_n$], hydrogen fluoride [$(HF)_n$], polyethylene (PE), and polyacetylene (PA) were created successively to approximate their one-dimensional periodic polymers by using the MO-based elongation method. In the molecular-stacking models, we described the hypothetical surface of crystal as periodically arranged hydrogen molecules by the COs, and several hydrogen molecules were stacked up on the surface one after another with the elongation procedure. Furthermore, the lattice defect on surface in which a part of stacked layer is lacking was dealt with by our approach. We also treated carbon monoxide chemisorption on periodic magnesium chain as a more realistic model. Results for these systems support the applicability of our method for nonperiodic interactions in one- and two-dimensional large systems.

2.1. INTRODUCTION

In the field of quantum chemistry, the methods to calculate the electronic structures of small molecules or completely periodic polymers have already been established at the present time. The MO method is available for small molecules, while the CO method for periodic polymers.[1,2] These methods are very useful in studying the electronic property and therefore widely applied to various systems. However, we can not use them to study large molecules or aperiodic polymers straightforward because of the limit in the memory of computer as well as the computer time. In the case that it is impossible to calculate the whole system as it is, we approximate a part of large molecule as a cluster or a nonperiodic polymer as a periodic polymer with a supercell including an aperiodic part. Then, the calculation for each cluster or supercell with different size is carried out individually by using the MO method or the CO method for their various sizes. We consider the converged physicochemical properties of the cluster or supercell as those of the large molecule or aperiodic polymer itself, respectively. As mentioned above, however, the conventional methods have the limitation of application to large, extended, nonperiodic systems. For this reason, it will be inevitable to develop a new theoretical approach to treat those systems efficiently and systematically. Several approaches with regard to this subject have been developed in recent years.[3-7]

Our group has proposed the elongation method as a new approach which enables us to calculate the electronic structures of large molecular systems with nonperiodicity.[8] In this approach, we extend a cluster by the manner in which a small molecule or a molecular fragment is connected with the end part of the starting cluster with appropriate size one by one. In this way, what we called, a cluster is propagated by a unit. This propagation is performed by taking into account only local interaction between the cluster molecule and the adding fragment. In this propagation process, we can separate the MOs of the cluster into two spaces, one is the orbitals which are altered by the interaction with fragment and another is those which are unaltered, and then, we solve the eigenvalue problem based on the former only. That is, we incorporate only the important interaction into the eigenvalue problem of the extended system and drop out the unimportant part. Thus, the dimension of the matrix which should be diagonalized in each step of the propagation calculation can be retained almost constant. When we repeat this procedure any times, we can synthesize periodic or aperiodic polymers with any length theoretically. Since the calculation procedure of this approach includes the extension process of the system itself systematically at the orbital level, we can calculate the electronic structures of large, extended, nonperiodic systems efficiently. Moreover, as already reported in the previous studies of our group such as local density of states in aperiodic polymers,[9] stationary condition of the electronic structure against the extension,[10] and stationary space analysis by the cluster-series model,[11,12] information on electronic states in local region of large polymers can be extracted.

On the other hand, the CO method can be applied to the systems with complete periodicity (polymer, surface, and crystal)[13] and has been used in the band structure calculations of periodic systems. In this approach, the eigenvalue problem is solved under the Bórn-von-Kárman periodic boundary condition in order to obtain the COs which satisfy the translational symmetry of the system. Thus, we can obtain the electronic property of bulk systems by using the CO method. However, this method is so restricted by the periodic boundary condition itself, which requires the completely periodic structure of the system, and thus, can not be applied to the system with local aperiodicity.

Consequently, we have developed a method to calculate the electronic state of polymers with local aperiodic part, for instance, interaction with a small molecule, defective structure or abnormal bonding, based on the supercell method using COs.[14] That is, the COs of minimum translational unit (unit cell) are transformed into those of large translational unit (supercell) in order to treat the local aperiodicity embedded in the periodic polymer. In the previous work, we considered the interaction between the supercell and the aperiodic part as a perturbation, and treated this by using the iterative transfer perturbation theory.[15] This treatment has been applied to the interaction between a periodic polymer and a small molecule or to the local aperiodicity within a polymer.[16,17]

In the chapter 1,[18] we proposed a new theoretical approach using the variational treatment based on the SCF CO method to calculate efficiently the polymer system with local aperiodic part. This can be regarded as the combination between the elongation method and the supercell method. In practical calculations, this approach has proved to be reliable enough and it has great advantage in the computational time compared to the usual CO calculations. In this study, we have dealt with the system in which a small molecule is interacting with a periodic polymer, thus, this approach should correspond to the propagation of the system only by one unit. As the next step, we developed this method to calculate the continuous propagation of the system by the elongation procedure.

In the present chapter, we report the results of model calculations for both of the cluster propagation and the molecular stacking on surface by using the elongation method. As mentioned already, the former is based on the MO method and the latter is based on the CO method. The main part of the calculation procedure for the two systems is almost the same. That is, as the first step, we calculate the starting cluster by using the MO method and the starting surface by the CO method. Then, as the next step, the orbital separation of the cluster or the surface is carried out under the influence of adding fragment or stacking layer, respectively, and then, the eigenvalue problem of the extended system is solved. In this step, we use the same manner for the both extensions of the cluster and the surface. By repeating this procedure, we extend the cluster or the surface successively. For the molecular stacking on surface, we must take into account both of the extension process in a local region and the bulky nature in an extended surface. For this purpose, we employed the both of the elongation method and the supercell method, that is, we transform the COs of the starting surface for the unit cell into those for the supercell according to the procedure of the supercell method at first. Next, the orbital separation of the system is carried out and the eigenvalue problem is solved by a similar manner as in the case of the propagation of cluster. This procedure is repeated according to the elongation method in order to pile up layers on the surface.

We formulated the procedures to treat the extension process of system mentioned above and developed the program for these procedures at the CNDO/2 level.[19-21] At first, in order to confirm the generality of this method, the calculations for the propagation of cluster based on the MO method were performed. In these calculations, the hypothetical one-dimensional clusters which consist of hydrogen molecule or hydrogen fluoride, and the realistic one-dimensional periodic polymers, polyethylene or polyacetylene, are elongated. Next, we calculated three models which correspond to the growth of crystal surface by using the elongation method based on the CO theory. In these calculations, as the first step of our study toward this direction, we considered one-dimensional chain constructed with hydrogen molecules as a "quasi" crystal surface. Although the real surface is periodic in two dimension in fact, we approximate the surface by one-dimensional periodical chain. Several layers of hydrogen molecules were approached on the quasi surface one by one to simulate the growth of the surface. Also, the model which may correspond to the defective structure on the surface was calculated by this method. Finally, as a more realistic application, we treated the chemisorption of carbon monoxide on a periodic atomic chain composed of magnesium extending in one dimension. In the following sections, we describe the outline of this methodology and show the reliability of this treatment by comparing the results with those obtained by the usual MO or CO calculations for the cluster or surface.

Finally, it should be pointed out that the main purpose of this study is to confirm the usefulness of our approach in the calculations of the electronic structures of large, extended, nonperiodic systems. If the generality of this method is confirmed, we will apply it to the more realistic systems like as aperiodic biopolymers or two-dimensional crystal surfaces. Moreover, we expect that the three-dimensional extension will be possible by using the elongation method based on the two-dimensional COs. Attempt for this direction is now in progress and will be published in the near future.

2.2. METHOD

When the size of system is too large to calculate the electronic structure of the whole molecule by the quantum chemical method, we usually use the cluster model. The electronic character of the system is determined as the stationary nature against the size extension of clusters. But this model requires the calculations for each cluster individually, and thus the approach is not necessarily more systematic and efficient. For example, in the case of the calculation for the cluster A including appropriate units and the its extended cluster $A+B$ with one more unit, we must perform the calculations on the both clusters individually and compare the energy per unit, the electron density distribution, and so on with each other in order to check the convergency for electronic nature of the system. If the dimension of the clusters is comparatively small, this approach will be useful. However for large extended systems, the effort for the computations becomes enormous.

How can we obtain the electronic property of extended systems by a systematic manner? Now, we consider the case that the electronic structure of the cluster A is known, and then the fragment B is connected with the cluster A. Surely, we can obtain the electronic states of the extended cluster $A+B$ by solving the eigenvalue problem based on the MOs for A and the atomic orbitals (AOs) for B directly. If we can select specific orbitals in the cluster A which are affected by the addition of the fragment B, we may use them instead of the all orbitals in the cluster A. Those selected orbitals thus obtained must be more effective basis orbitals in solving the eigenvalue problem in the extended system $A+B$. In extending the cluster, the above-mentioned selection of orbitals should be advantageous.

However, the effects of the fragment B on the cluster A can be evaluated exactly only if the interaction between the cluster A and the fragment B is exactly evaluated. In other words, if the electronic structure of the extended cluster $A+B$ is known, we can classify the orbitals in the system into two groups; one is altered orbitals and another is unaltered ones by the interaction with the fragment B. The method to extract and separate the orbital space in cluster-extending calculations has already been published as the stationary conditions of the electronic structures against the extension of molecular systems and has been applied to the elongation calculations.[10-12]

In order to develop the method to perform the elongation calculation, at the starting point, the interaction between the cluster A and the fragment B through core Hamiltonian is taken into account and the effective bases are selected based on the interaction. At this stage, if we solve the eigenvalue problem represented with the effective orbitals in the cluster A and the AOs in the fragment B, the Fock operator of the extended cluster $A+B$ which includes a part of the interaction between the cluster A and the fragment B can be determined. At the same time, the orbitals which are obtained as the solution of the eigenvalue problem also include the effect of the fragment B partially. In contrast to the above-mentioned orbitals, the other orbitals which are removed from the basis orbitals are not affected by the interaction. Thus, in order to introduce the perturbation by the fragment B completely, we treat the interaction between the selected orbitals and the remaining orbitals successively. For this purpose, we again select the basis orbitals based on the Fock operator obtained here and determine new Fock operator by solving the eigenvalue problem within new basis orbital space. In this way, by repeating the procedure, the influence of the fragment B on the cluster A based on the interaction with each other can be included in the electronic structure of extended system $A+B$ by degrees. Finally, we can determined the specific orbitals in the system which are altered (active orbitals) and unaltered (frozen orbitals) by the cluster extension. The frozen orbitals can be regarded as also stationary orbitals against the extension by one more unit as discussed in the previous works of our group.[10-12]

The situation mentioned above is also true in the case that the molecule B is stacked up on the extended crystal surface A. Thus, the applicability of the method is not limited to the cluster-extending calculation.

The elongation method is the method to perform the quantum chemical calculations on the largely extended chemical systems such as one-dimensional polymers connected by chemical bondings between units or molecular crystals without bonds between them. Also, this approach includes the orbital mixing between the cluster A and the fragment B as the results of the charge transfer and exchange interactions together with the polarization effect as shown in Subsection 2.2.3 in detail.

In this study, we performed elongation calculations on the two systems, that is, the propagation of cluster based on the MO method and the stacking of molecules on surface based on the CO method. However, the main technique used in the both calculations, which is the selection of effective basis orbitals for the eigenvalue problem and the division of the system at the orbital level, is the same. In this section, at first, we explain only the outline of the calculation procedure for the both systems in Subsections 2.2.1 and 2.2.2. Next, the procedure of orbital separation in the system, which is common technique for the two systems, is described in detail in Subsection 2.2.3.

2.2.1. Elongation Calculation Based on the MO Method

In Fig. 2.1, the calculation procedure for the propagation of cluster molecule is summarized schematically. At first, we carry out the MO calculation for the cluster including a small number of units. Next, we consider the system in which one adding fragment, C in Fig. 2.1, connected with the end part of the starting cluster. When we solve the eigenvalue problem of the propagated cluster, we can select the specific orbitals from the orbital space of the starting cluster which give a large influence on the eigenvalue problem. After that we use the selected MOs in the starting cluster and the AOs in the adding fragment as the basis of the eigenvalue problem. In practice, we must select the MOs and solve the eigenvalue problem iteratively in one-unit propagation so as to reach the self-consistent field as will be described in Subsection 2.2.3. In this

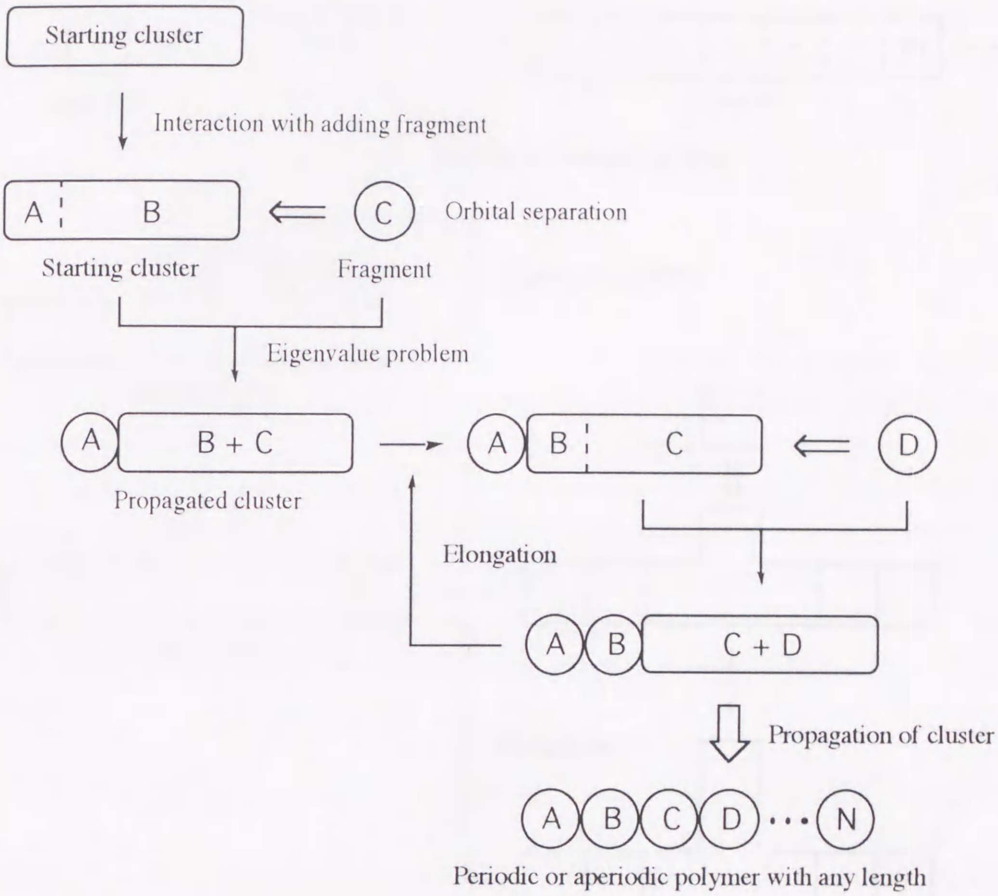


FIG. 2.1. Schematic illustration of the calculation procedure in the molecular-orbital-based elongation method for the propagation of cluster.

process, finally, we can determine the MOs in the propagated cluster which are altered by the interaction with adding fragment (active MOs) and the MOs which are unchanged by the interaction (frozen MOs). That is, total orbital space in a cluster molecule is divided into active space ($B+C$ in Fig. 2.1) and frozen space (A in Fig. 2.1). In the next propagation of the cluster, we regard the finally obtained active MOs as the MOs of the new starting cluster, and include only the interaction between the final active MOs and the newly adding AOs of the next fragment, D in Fig. 2.1, into the eigenvalue problem. On the other hand, final frozen MOs are fixed against the addition of the next fragment as the stationary orbitals. By repeating these procedures mentioned above, the total orbital space of extended systems is divided into a series of $A, B, C, D, \ldots, N$ as shown in Fig. 2.1, the electronic structures of periodic or aperiodic polymers with any length can be calculated without increasing the dimension of the matrix which must be diagonalized in the successive elongation cycle. The method to select the interaction orbitals used in this work is described in Subsection 2.2.3 in detail.

2.2.2. Elongation Calculation Based on the CO Method

We show the schematic illustration of the calculation procedure for the stacking

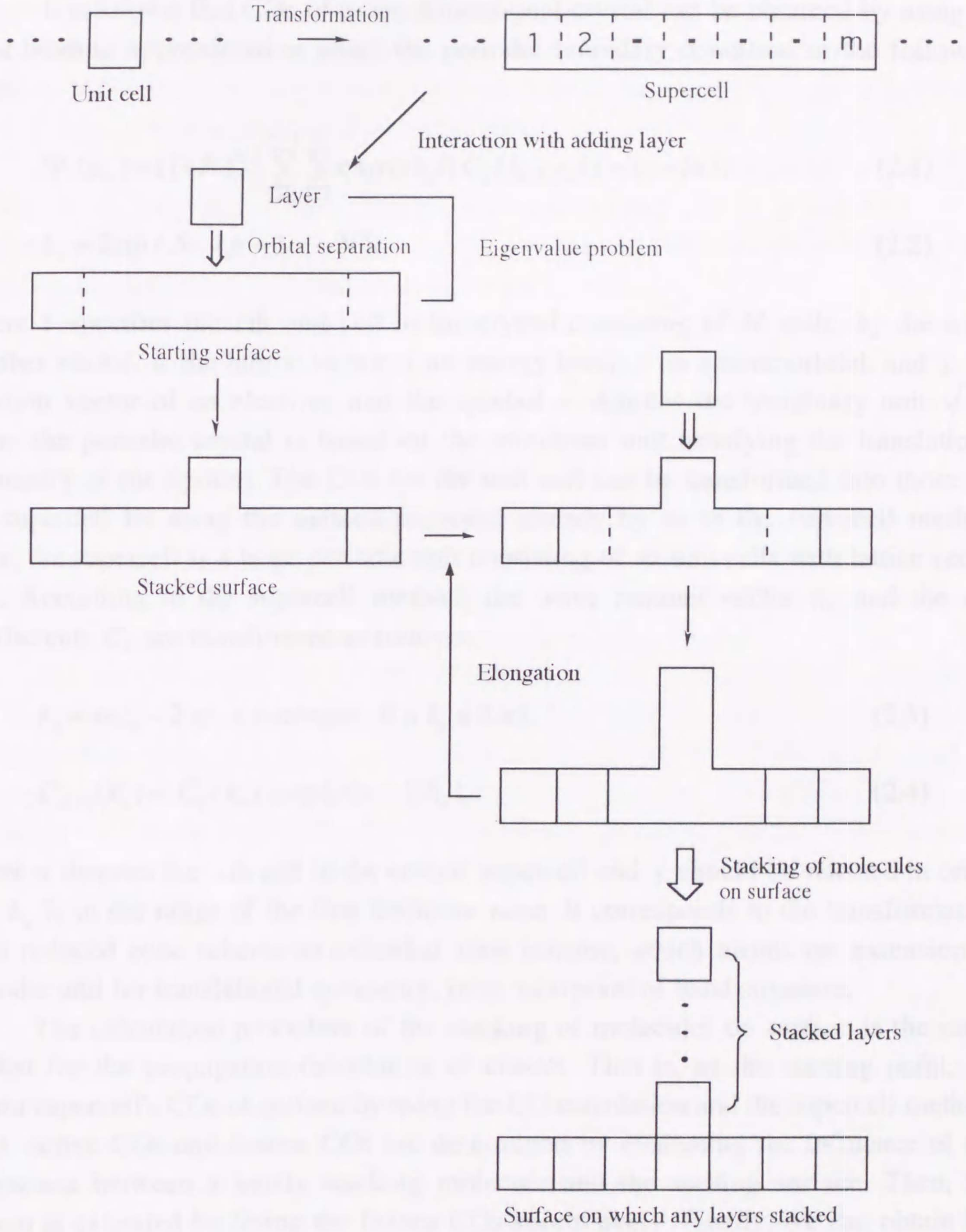


FIG. 2.2. Schematic illustration of the calculation procedure in the crystal-orbital-based elongation method for the stacking of molecules on surface.

of molecules on surface in Fig. 2.2. Because we are interested in the extension within a local region on surface, it is convenient to treat the system based on the supercell. For that purpose, we transform the COs of the surface for a unit cell into the COs for a supercell. Except using the COs of the starting surface instead of the MOs of the starting cluster, the similar procedures as those described in the previous subsection are employed in the extension calculation of the system. In the following, we explain the transformation method of the COs from the unit cell to those for the supercell.

It is known that COs of a one-dimensional crystal can be obtained by using the tight-binding approximation under the periodic boundary condition in the following form:

$$\Psi_i(k_u) = (1/N)^{1/2} \sum_{l=0}^{N-1} \sum_{t=1}^{M} \exp(\tilde{i}\, k_u l)\, C_{ti}(k_u)\, \chi_t(\mathbf{r} - \mathbf{r}_t - l\mathbf{a}), \tag{2.1}$$

$$k_u = 2\pi p / N \quad (p = 1, \ldots, N), \tag{2.2}$$

where l specifies the lth unit cell in the crystal consisting of N cells, k_u the wave number vector, $\mathbf{a}$ the lattice vector, i an energy level, t an atomic orbital, and $\mathbf{r}$ the position vector of an electron, and the symbol $\tilde{i}$ denotes the imaginary unit $\sqrt{-1}$. Here, the periodic crystal is based on the minimum unit satisfying the translational symmetry of the system. The COs for the unit cell can be transformed into those for the supercell by using the method proposed already by us as the supercell method. Here, the supercell is a large periodic unit consisting of m unit cells with lattice vector $m\mathbf{a}$. According to the supercell method, the wave number vector k_u and the AO coefficients C_{ti} are transformed as follows:

$$k_s = mk_u - 2\pi j \quad (j\text{: integer, } 0 \le k_s \le 2\pi), \tag{2.3}$$

$$C_{ti(n)}(k_s) = C_{ti}(k_u) \exp[\tilde{i}\,(n-1)k_u], \tag{2.4}$$

where n denotes the nth cell in the central supercell and j should be selected in order that k_s is in the range of the first Brillouin zone. It corresponds to the transformation from reduced zone scheme to extended zone scheme, which means the extension of periodic unit for translational symmetry, from viewpoint of band structure.

The calculation procedure of the stacking of molecules on surface is the same as that for the propagation calculation of cluster. That is, as the starting point, we obtain supercell's COs of surface by using the CO calculation and the supercell method. Next, active COs and frozen COs are determined by evaluating the influence of the interaction between a newly stacking molecule and the starting surface. Then, the system is extended by fixing the frozen COs successively. Finally, we can obtain the electronic structure of surface on which several layers of molecules are piled up.

2.2.3. Orbital Separation (Determination of Active and Frozen Orbitals)

In the case of dealing with local interaction in a large system, we need not consider the interactions among all orbitals in the large system. For example, in extending the chemical system by connecting molecules successively with each other, it is conceivable that the influence of the newly connected species on the electronic structure of the extended system is limited within the local region around the connecting region between the two systems when total system becomes larger. In other words, when the selection of interaction orbitals which are influenced by an adding fragment can be done effectively from the total orbital space of the whole system, all that we have to do is to solve the eigenvalue problem only within the interaction space instead of solving the eigenvalue problem in the total space.

By using the elongation method based on the idea described in the above paragraph, in the present case, the MOs of the starting cluster or the COs of the starting surface can be divided into active and frozen MOs or COs after one-unit extension as mentioned in Subsections 2.2.1 and 2.2.2.

The problem is that how can we select the interaction orbitals which can be used as the effective bases of the eigenvalue problem? In this work, we apply the variational condition in order to perform the selection of orbitals as has been used to extract the stationary orbitals.[10-12]

That is, when a given cluster or surface is elongated by one unit by connection with an adding fragment, the variational condition is that the matrix elements of MO- or CO-based Fock matrix between occupied and vacant orbitals in the extended system should be zero. Thus, we define the orbitals which do not satisfy the variational condition in the cluster or surface as effective interaction orbitals.

To show the procedure for the orbital selection in the system, it is considered that the orbitals $\{\Psi_j\}$ $(j=1,...,M)$ are known at first, and then, those are perturbed by the interaction with $\{\Phi_i\}$ $(i=1,...,N)$ which are combined to $\{\Psi\}$. Here, to find the interaction orbitals and perform the division of orbital space mentioned above, the following rectangular blocks of MO- or CO-based Fock matrix should be obtained,

$$\mathbf{F}^{\text{occ}} = \langle \Phi^{\text{vac}} | \hat{F} | \Psi^{\text{occ}} \rangle, \tag{2.5a}$$

$$\mathbf{F}^{\text{vac}} = \langle \Phi^{\text{occ}} | \hat{F} | \Psi^{\text{vac}} \rangle, \tag{2.5b}$$

where $\hat{F}$ is the Fock operator for the perturbed system, and occ or vac indicates occupied or vacant orbital, respectively. The matrix elements in Eq. (2.5) correspond to the terms between occupied and vacant spaces of Fock matrix based on the orbitals $\{\Phi\}$ and $\{\Psi\}$. To satisfy the variational condition, the matrix elements should be zero. Our purpose is to extract specific orbitals from $\{\Psi\}$ which have nonzero values of the matrix elements in Eq. (2.5). In order to find the orbitals in $\{\Psi\}$ which interact with $\{\Phi\}$ effectively, the following technique is applied to $\mathbf{F}^{\text{occ}}$ and $\mathbf{F}^{\text{vac}}$, respectively. That is, if the number of the occupied orbitals is N^o and that of the vacant orbitals is N^v in $\{\Phi\}$ and those in $\{\Psi\}$ are M^o and M^v orbitals, respectively, we multiply the above $N^v \times M^o$ and $N^o \times M^v$ matrices by those adjoint $M^o \times N^v$ and $M^v \times N^o$ matrices from the left side. The $M^o \times M^o$ and $M^v \times M^v$ matrices are thus obtained, that is the matrix $\mathbf{F}^{+}\mathbf{F}$, are diagonalized. This means that,

$$\mathbf{U}^{+}\mathbf{F}^{+}\mathbf{F}\mathbf{U} = \mathbf{E}, \tag{2.6}$$

where **U** is the matrix whose columns are eigenvectors and **E** is the diagonal matrix composed of the eigenvalues. The eigenvalues obtained here reflect the magnitude of the Fock matrix elements between occupied and vacant spaces of the orbitals $\{\Phi\}$ and $\{\Psi\}$. Therefore, the eigenvalues should be measures to indicate whether the variation condition is satisfied or not. Thus, we perform unitary transformation on $\{\Psi\}$ by using **U** and select the orbitals which have greater eigenvalue than an appropriate threshold value (10^{-5} in this work) in occupied and vacant spaces of the transformed $\{\Psi\}$. These orbitals can be regarded as the interaction orbitals which do not satisfy the variational condition against the extension by the addition of orbitals $\{\Phi\}$. This procedure is analogous to that for the corresponding orbital[22] or the interaction frontier orbital.[23,24] A similar manner is also applied in the elongation calculation to extract the stationary space of electronic states against the extension of molecular systems.[10-12] We refer to the selected orbitals with greater eigenvalues as "interaction orbitals" (MOs or COs) and to the rest orbitals with smaller eigenvalues as "noninteraction orbitals" hereafter. In other words, we define "interaction orbitals" as the orbitals which do not satisfy the variational condition and "noninteraction orbitals" as the orbitals which satisfy the condition in the total orbital space of system. Then, we solve the eigenvalue problem based on "interaction orbitals" only by the self-consistent-field (SCF) procedure, and the "noninteraction orbitals" are removed from the basis orbitals in the eigenvalue problem. In this way, we modify the orbital space of the extended system so as to satisfy approximately the variational condition in which Fock matrix elements between occupied and vacant orbitals are nearly equal to zero. Now, in practice, it is noted that this selection must be done iteratively in order to satisfy the condition as explained below.

In the following, we describe in detail the method to solve the eigenvalue problem for extended system by using the technique mentioned in the previous paragraph. The schematic illustration of the calculation procedure at the viewpoint of orbital separation is given in Fig. 2.3 and the matrix representations which correspond to each step in Fig. 2.3 are summarized in Figs. 2.4(a)-2.4(c). The interaction blocks of the Fock matrix in Eq. (2.5) are also shown as the shaded parts in Fig. 2.4. We explain the procedures along with these figures. Here, we note in stacking calculation based on the CO method that the Steps 2-4 must be carried out for each wave number vector k_s for supercell, because Fock operator and COs depend on the wave number vector under the periodic boundary condition. But, the procedures for MO and CO treatments are the same except for the k-dependence.

In Step 1, COs for unit cell $\{\Psi_u\}$ are transformed into those for supercell $\{\Psi\}$ as mentioned in the subsection B [Eqs. (2.1)-(2.4)]. This step is needed only for stacking calculation based on the CO method.

In Step 2, we take into account the interaction between starting orbitals (MOs in starting cluster or COs in starting surface) and adding AOs (in fragment or layer) through core Hamiltonian at the first because Fock operator of the extended system is unknown at the starting point. As shown in Fig. 2.4(a), the Fock matrix based on MOs

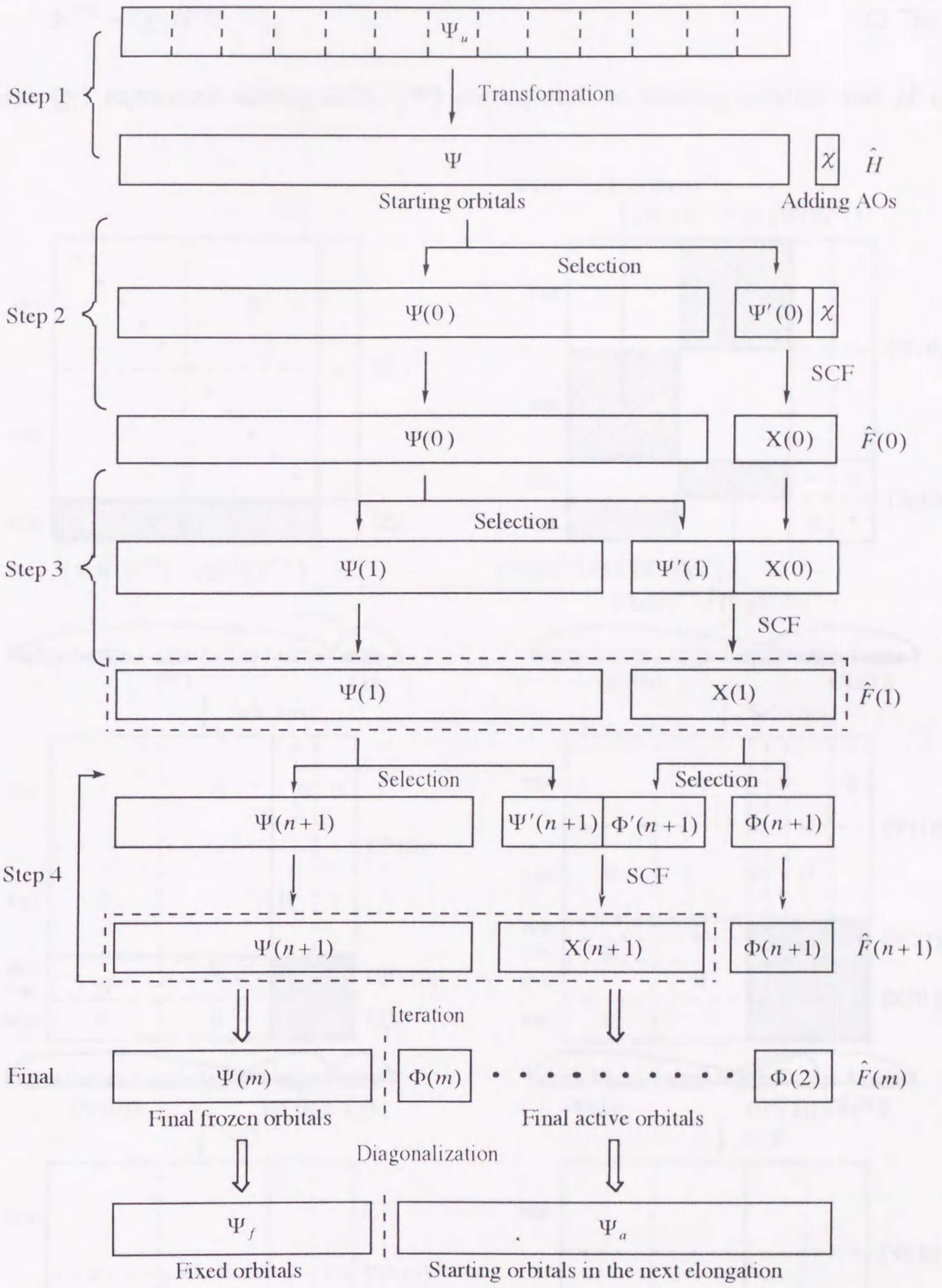


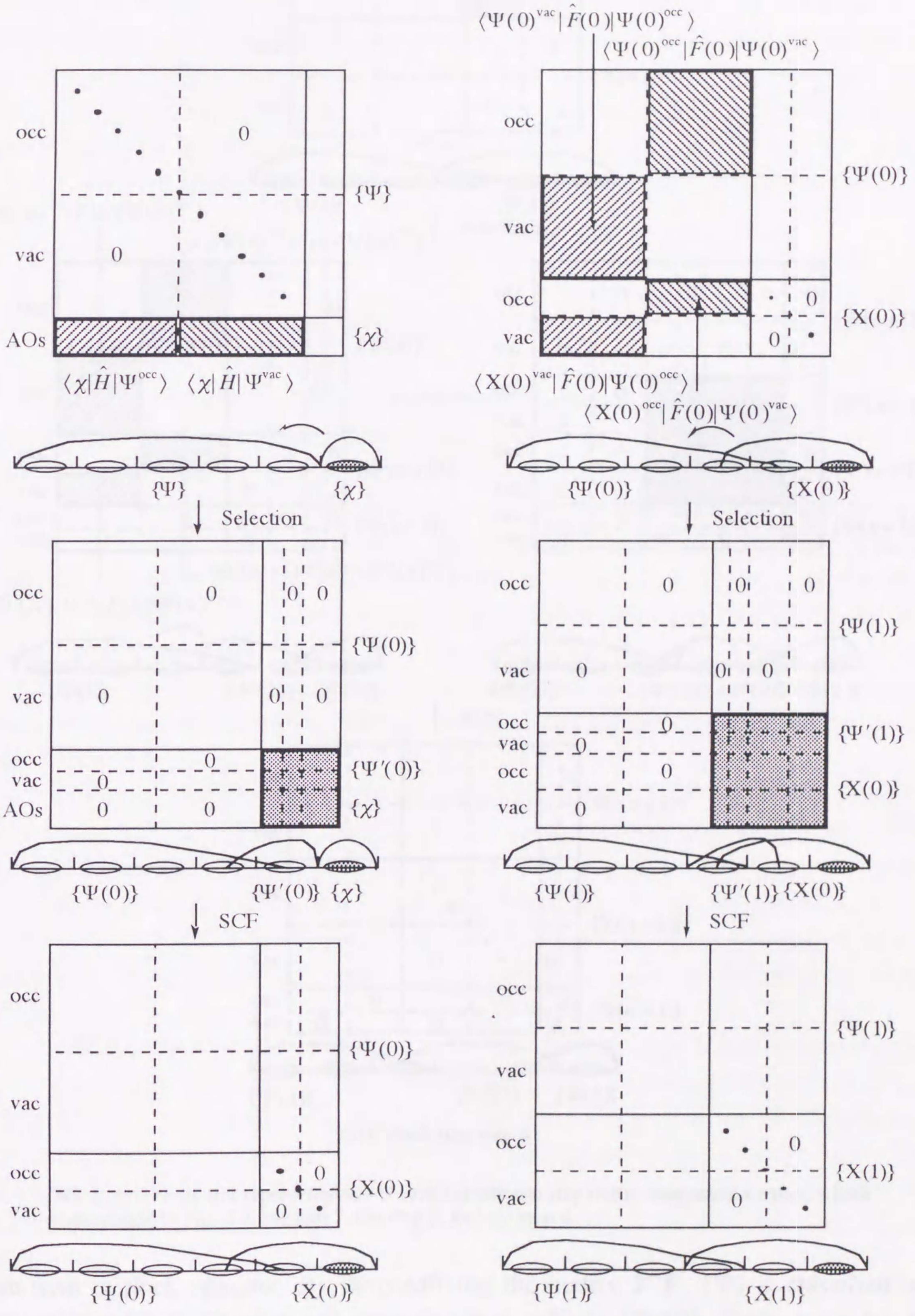
FIG. 2.3. The process of orbital separation of the system to determine the active and frozen orbitals in the elongation method.

or COs is diagonal within starting cluster or surface, and the interaction blocks are shown as shaded parts and taken as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \chi | \hat{H} | \Psi^{\mathrm{occ}} \rangle, \tag{2.7a}$$

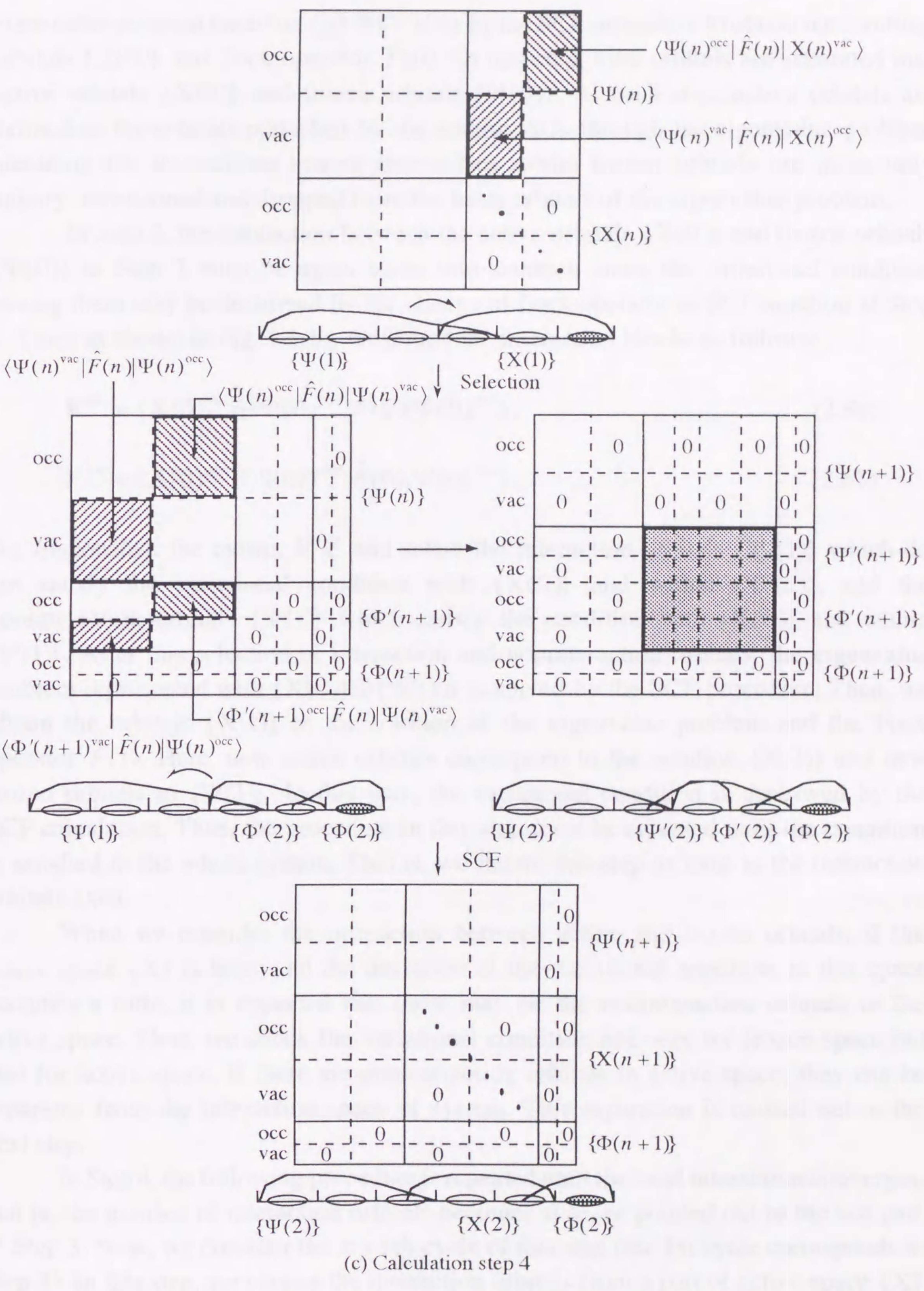
$$\mathbf{F}^{\text{vac}} = \langle \chi | \hat{H} | \Psi^{\text{vac}} \rangle, \tag{2.7b}$$

where $\{\chi\}$ represents adding AOs, $\{\Psi\}$ corresponds to starting orbitals and $\hat{H}$ is the



(a) Calculation step 2

(b) Calculation step 3



(c) Calculation step 4

FIG. 2.4. The matrix representation of each calculation step in the elongation method which corresponds to Fig. 2.3, (a) step 2, (b) step 3, and (c) step 4.

core term in Fock operator. By diagonalizing the matrix $\mathbf{F}^{+}\mathbf{F}$, $\{\Psi\}$ is classified into interaction orbitals $\{\Psi'(0)\}$ and noninteraction orbitals $\{\Psi(0)\}$. Then, we solve the eigenvalue problem based on $\{\chi\}\oplus\{\Psi'(0)\}$ by the SCF procedure to obtain the resulting orbitals $\{X(0)\}$ and Fock operator $\hat{F}(0)$. In this step, total orbitals are separated into active orbitals $\{X(0)\}$ and frozen orbitals $\{\Psi(0)\}$. At each step, active orbitals are defined as the orbitals perturbed by the adding AOs through the eigenvalue problem including the interactions among themselves, while frozen orbitals are those only unitary transformed and dropped from the basis orbitals of the eigenvalue problem.

In Step 3, the interaction between the active orbitals $\{X(0)\}$ and frozen orbitals $\{\Psi(0)\}$ in Step 2 must be again taken into account, since the variational condition among them may be destroyed by the change of Fock operator in SCF iteration at Step 2. Thus, as shown in Fig. 2.4(b), we define the interaction blocks as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle X(0)^{\mathrm{vac}} \oplus \Psi(0)^{\mathrm{vac}} | \hat{F}(0) | \Psi(0)^{\mathrm{occ}} \rangle, \tag{2.8a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle X(0)^{\mathrm{occ}} \oplus \Psi(0)^{\mathrm{occ}} | \hat{F}(0) | \Psi(0)^{\mathrm{vac}} \rangle. \tag{2.8b}$$

We diagonalize the matrix $\mathbf{F}^{+}\mathbf{F}$ and select the interaction orbitals $\{\Psi'(1)\}$ which do not satisfy the variational condition with $\{X(0)\}$ and within $\{\Psi'(1)\}$, and the noninteraction orbitals $\{\Psi(1)\}$ which satisfy the condition with $\{X(0)\}$ and within $\{\Psi(1)\}$. After this selection of interaction and noninteraction orbitals, the eigenvalue problem represented with $\{X(0)\}\oplus\{\Psi'(1)\}$ is solved by the SCF procedure. Then, we obtain the orbitals $\{X(1)\}$ as the solution of the eigenvalue problem and the Fock operator $\hat{F}(1)$. Here, new active orbitals correspond to the solution $\{X(1)\}$ and new frozen orbitals to $\{\Psi(1)\}$. In this way, the variational condition is destroyed by the SCF calculation. Thus, the procedure in this step must be repeated until the condition is satisfied in the whole system. That is, we iterate this step as long as the interaction orbitals exist.

When we consider the interaction between active and frozen orbitals, if the active space $\{X\}$ is large and the deviation of the variational condition in this space becomes a little, it is expected that there may be the noninteraction orbitals in the active space. Thus, we check the variational condition not only for frozen space but also for active space. If there are noninteracting orbitals in active space, they can be separated from the interaction space of system. This separation is carried out in the next step.

In Step 4, the following procedure is repeated until the local interaction converges, that is, the number of interaction orbitals becomes zero, as pointed out in the last part of Step 3. Now, we consider the $n+1$th cycle of this step (the 1st cycle corresponds to Step 3). In this step, we choose the interaction orbitals from a part of active space $\{X\}$ and frozen space $\{\Psi\}$ by the following two-step procedure (see Fig. 2.3). First, we confirm the variational condition of active space by using the interaction blocks as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \Psi(n)^{\mathrm{vac}} | \hat{F}(n) | X(n)^{\mathrm{occ}} \rangle, \tag{2.9a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \Psi(n)^{\mathrm{occ}} | \hat{F}(n) | \mathrm{X}(n)^{\mathrm{vac}} \rangle, \tag{2.9b}$$

where $\{\Psi(n)\}$ represents the nth frozen orbitals, $\{\mathrm{X}(n)\}$ corresponds to the solution of the nth eigenvalue problem. By diagonalizing the matrix $\mathbf{F}^{+}\mathbf{F}$, we select the interaction orbitals $\{\Phi'(n+1)\}$ and noninteraction orbitals $\{\Phi(n+1)\}$ from $\{\mathrm{X}(n)\}$ in active space. Here, $\{\Phi'(n+1)\}$ does not satisfy the variational condition and $\{\Phi(n+1)\}$ does. Next, we test the condition also for the frozen orbitals by taking the interaction blocks as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \Phi'(n+1)^{\mathrm{vac}} \oplus \Psi(n)^{\mathrm{vac}} | \hat{F}(n) | \Psi(n)^{\mathrm{occ}} \rangle, \tag{2.10a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \Phi'(n+1)^{\mathrm{occ}} \oplus \Psi(n)^{\mathrm{occ}} | \hat{F}(n) | \Psi(n)^{\mathrm{vac}} \rangle. \tag{2.10b}$$

Diagonalization of the matrix $\mathbf{F}^{+}\mathbf{F}$ is carried out to determine the interaction orbitals $\{\Psi'(n+1)\}$ which does not satisfy the variational condition and the noninteraction orbitals $\{\Psi(n+1)\}$ which satisfy the condition. After selecting the interaction orbitals $\{\Phi'(n+1)\}$ and $\{\Psi'(n+1)\}$ from active and frozen spaces, respectively, the eigenvalue problem is solved within the orbital space $\{\Phi'(n+1)\}\oplus\{\Psi'(n+1)\}$ by the SCF procedure to obtain the resulting orbitals $\{\mathrm{X}(n+1)\}$ and Fock operator $\hat{F}(n+1)$. This step is summarized in Fig. 2.4(c). In this step, we can separate total orbital space into the active space $\{\Phi\}\oplus\{\mathrm{X}\}$ and the frozen space $\{\Psi\}$.

Next, we take $\{\mathrm{X}(n+1)\}$ and $\{\Psi(n+1)\}$ as the interaction space for the $n+2$th cycle, and repeat the procedure in this step as mentioned above. Thus, at each cycle of this step, if there is, $\{\Phi\}$ is removed from the interaction space and each $\{\Phi\}$ remains invariant through all cycles, because the interaction between $\{\Phi(n+1)\}$ and $\{\Psi(n)\}$ is considered to be small enough. That is, we assume that the variational condition of $\{\Phi(n+1)\}$ is not destroyed by the interaction with $\{\Psi(n+1)\}$ through the change in Fock operator. Finally, when the interaction converges, the interaction orbitals vanish and the variational condition is satisfied approximately in the total orbital space of the system. That is, at the mth cycle, the active orbitals can be determined as $\{\Phi(2)\}$,..., $\{\Phi(m)\}$ and the frozen orbitals as $\{\Psi(m)\}$. At this point, we obtain the electronic structure of the system with one-unit extension, ultimately, the cluster is elongated by one unit or the surface is stacked by one layer.

Now, it is noteworthy that the important effects of charge transfer and exchange between starting orbitals and adding AOs are included in the blocks of $\langle \mathrm{X} | \hat{F} | \Psi \rangle$ and $\langle \Phi' | \hat{F} | \Psi \rangle$, and also, the polarization effect within starting orbitals is included in the block $\langle \Psi | \hat{F} | \Psi \rangle$ at Steps 3 and 4.

In the continuous extension of the system, the Steps 2-4 are repeated any times with the following treatment. We diagonalize the Fock matrix within the active space and within the frozen space to determine final active orbitals $\{\Psi_a\}$ and frozen orbitals $\{\Psi_f\}$. As the starting orbitals of next elongation cycle, the active orbitals $\{\Psi_a\}$ are used, which correspond to $\{\Psi\}$ in Step 2, and the frozen orbitals $\{\Psi_f\}$ are fixed in the next elongation. That is, the frozen orbitals are separated from the total orbital space of the system and are kept without any changes through all calculation cycles. In other words, the Steps 2-4 are carried out within the orbital space which includes the active orbitals and the adding orbitals of the fragment or layer. We show a schematic illustration of orbital separation by this procedure in Fig. 2.5.

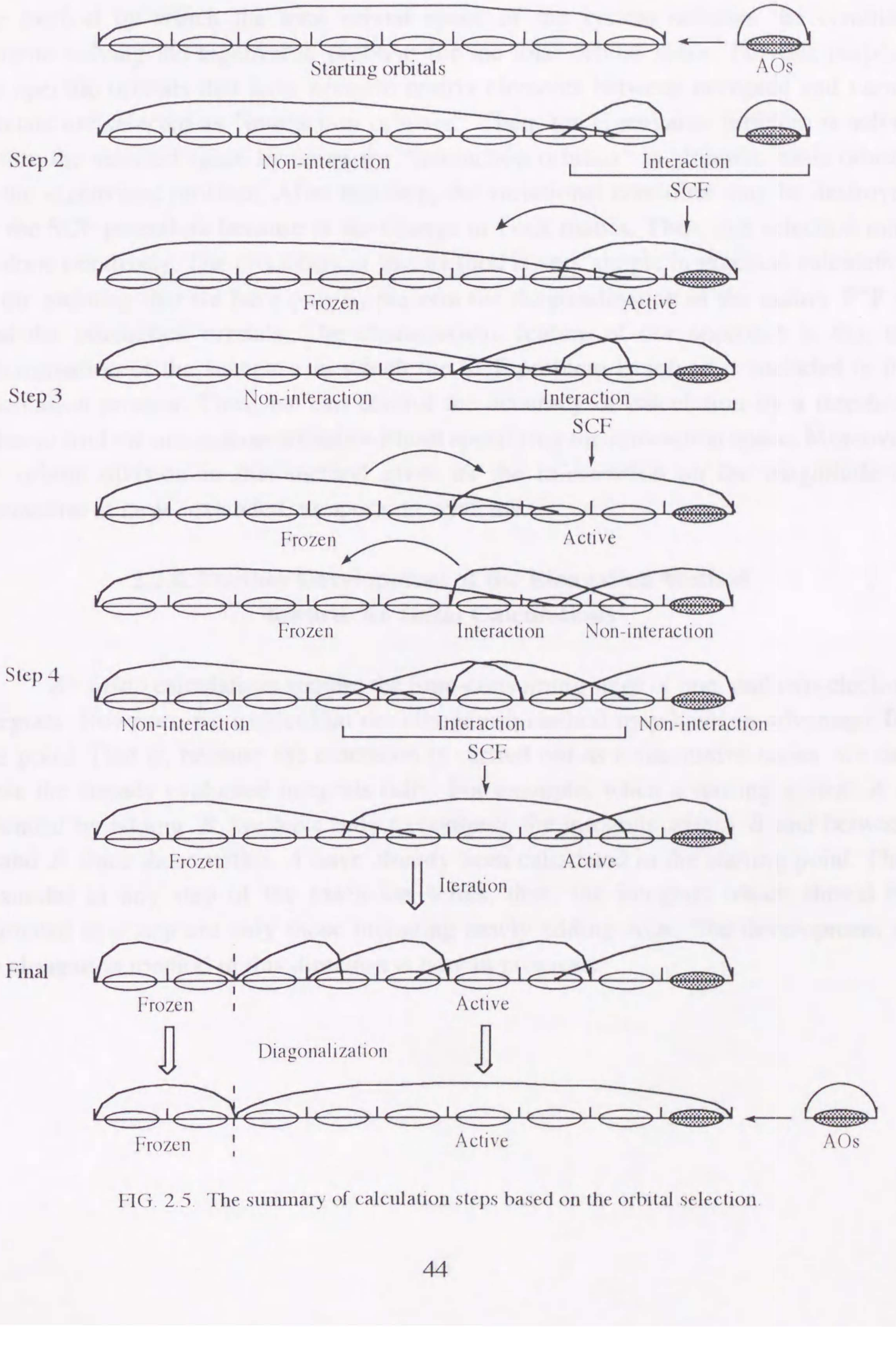


FIG. 2.5. The summary of calculation steps based on the orbital selection.

Finally, we summarize briefly the concept and the outline of this elongation method. We take the isolated system (cluster or surface) as the starting point, and combine it with the adding molecule (fragment or layer). At the starting point, the Fock matrix is diagonalized within the starting orbital space, and the matrix elements between the starting orbitals and adding AOs have nonzero values. If the eigenvalue problem of the whole system is solved completely, the matrix elements between occupied and vacant orbitals must vanish (the variational condition). Therefore, we developed the method by which the total orbital space of the system satisfies the condition without solving the eigenvalue problem for the total orbital space. For this purpose, the specific orbitals that have nonzero matrix elements between occupied and vacant orbitals are selected as "interaction orbitals". Then, the eigenvalue problem is solved within the selected space by using the "interaction orbitals" as effective basis orbitals of the eigenvalue problem. After this step, the variational condition may be destroyed by the SCF procedure because of the change in Fock matrix. Thus, this selection must be done iteratively. The procedure of this method is very simple in practical calculation in the meaning that we have only to perform the diagonalization of the matrix $\mathbf{F}^{+}\mathbf{F}$ to find the interaction orbitals. The characteristic feature of our approach is that the determination of the subspace in which the SCF problem is solved is included in the calculation process. Thus, we can control the accuracy of calculation by a threshold value to find the interaction orbitals without specifying the interaction space. Moreover, the orbital division in this method gives us the information on the magnitude of interaction in large, extended, nonperiodic systems.

2.2.4. Further Development of the Elongation Method toward *Ab Initio* Calculations

Ab initio calculations require the time-consuming steps of one- and two-electron integrals. However, we expect that the elongation method may have an advantage for this point. That is, because the extension is carried out as a successive series, we can reuse the already-evaluated integrals fully. For example, when a starting system A is extended by adding B, we have only to compute the integrals within B and between A and B since those within A have already been calculated in the starting point. This is similar in any step of the extension series, thus, the integrals which should be estimated at a step are only those including newly adding AOs. The development of the elongation method in this direction is now in progress.

2.3. RESULTS AND DISCUSSION

We performed several model calculations by using the method described in the section 2.2. At first, we demonstrate the results for the propagation of cluster in order to check the reliability. Next, this elongation method is applied to three models for the stacking of molecules on surface. Finally, we report briefly the results for local chemisorption of carbon monoxide on magnesium chain.

In this section, we do not analyze the electronic structures obtained by the calculations in detail, because the purpose of this study is to test the applicability of our approach for various extended systems.

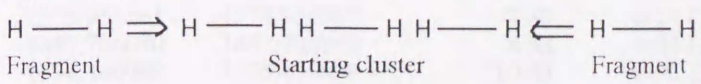
In this work, we assumed 10^{-5} as the threshold value of orbital selection and all results were obtained at the SCF level by using the CNDO/2 approximation. We specify "usual" calculation as the MO calculation for each cluster molecule with different size in Subsection 2.3.1 and as the CO calculation under nearest neighbor approximation of each surface with different number of stacked layers in Subsection 2.3.2. These calculations were also carried out for the comparison with the results by the elongation method.

2.3.1. Propagation of Various Clusters

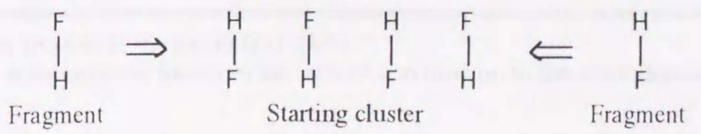
We applied the MO-based elongation method to several extended systems of hydrogen molecule, hydrogen fluoride, polyethylene, and polyacetylene. Since the purpose of these test calculations is to confirm the validity of our method, we show only the total energies of the systems together with computational times in comparison with usual cluster calculations.

The models and their geometrical parameters used in the propagation calculations are shown in Figs. 2.6(a)-2.6(d). Each of them corresponds to model polymer of hydrogen molecule, hydrogen fluoride, polyethylene, and polyacetylene, respectively. In performing these calculations, the clusters were propagated by arranging periodically in one dimension. We carried out two-directional elongations, that is, the molecular fragments were added to the both ends of the cluster by one unit. The polymers with chemical bondings in Figs. 2.6(c) and 2.6(d) were extended by substituting the end hydrogen atom by the adding fragment, that is, we substitute the 1s coefficient of the hydrogen atom by the 2s coefficient of carbon atom of the adding fragment.

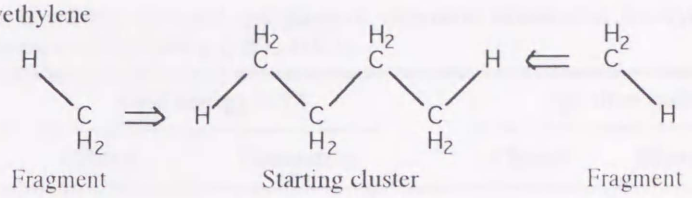
(a) Hydrogen molecule



(b) Hydrogen fluoride



(c) Polyethylene



(d) Polyacetylene

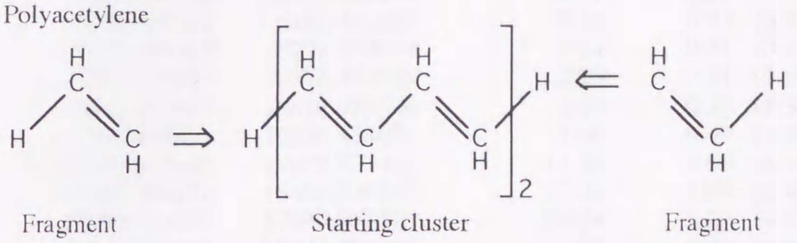


FIG. 2.6. The clusters calculated by the elongation process. We assumed and fixed the following geometrical parameters; (a) bond length of hydrogen molecule = 0.742 Å and intermolecular distance = 1.0 Å, (b) bond length of hydrogen fluoride = 0.917 Å and intermolecular distance = 1.5 Å, (c) r(C-C) = 1.45 Å, r(C-H) = 1.09 Å, and all bond angles = 109.5°, and (d) r(C-C) = 1.476 Å, r(C=C) = 1.326 Å, r(C-H) = 1.084 Å, ∠CCC = 124.0°, and ∠C=CH = 120.0°.

The results of the calculations are listed in Tables 2.1-2.4. In these tables, n denotes the number of elongated units and the starting cluster corresponds to n=0. From these tables, it is obvious that our approach has enough reliability and great advantage in the computational time in comparison with the usual cluster calculations.

TABLE 2.1. Total energies and cpu times of extension calculation for hydrogen molecular cluster $(H_2)_n$-$(H_2)_3$-$(H_2)_n$.

	Total energy (eV)		cpu time (min:s)[a]	
n	Cluster	Elongation	Cluster	Elongation[b]
1	-197.628026	-197.628026	0:01	0:01 (-----)
2	-276.383418	-276.383418	0:02	0:02 (0:03)
3	-355.138332	-355.138327	0:04	0:02 (0:05)
4	-433.893127	-433.893122	0:08	0:03 (0:08)
5	-512.647897	-512.647890	0:14	0:04 (0:12)
6	-591.402673	-591.402661	0:22	0:06 (0:18)
7	-670.157461	-670.157443	0:34	0:07 (0:25)
8	-748.912265	-748.912241	0:50	0:08 (0:33)
9	-827.667083	-827.667056	1:11	0:10 (0:43)
10	-906.421915	-906.421883	1:39	0:11 (0:54)
11	-985.176761	-985.176723	2:15	0:13 (1:07)
12	-1063.931619	-1063.931575	2:59	0:16 (1:23)
13	-1142.686489	-1142.686437	3:44	0:18 (1:41)
14	-1221.441369	-1221.441311	4:33	0:21 (2:02)
15	-1300.196260	-1300.196194	5:59	0:24 (2:26)
16	-1378.951161	-1378.951087	7:37	0:27 (2:53)
17	-1457.706070	-1457.705989	8:53	0:31 (3:24)
18	-1536.460988	-1536.460899	10:42	0:32 (3:56)
19	-1615.215914	-1615.215817	13:32	0:37 (4:33)
20	-1693.970848	-1693.970743	16:02	0:41 (5:14)

[a] cpu time on IBM RISC System/6000 530H.

[b] The value in parentheses indicates the sum of cpu time up to the nth extension.

TABLE 2.2. Total energies and cpu times of extension calculation for hydrogen fluoride molecular cluster $(HF)_n$-$(HF)_4$-$(HF)_n$.

	Total energy (eV)		cpu time (min:s)[a]	
n	Cluster	Elongation	Cluster	Elongation[b]
1	-4636.959158	-4636.959169	0:11	0:07 (-----)
2	-6182.449012	-6182.449020	0:32	0:14 (0:21)
3	-7727.939661	-7727.939674	1:14	0:21 (0:42)
4	-9273.430921	-9273.430936	2:29	0:31 (1:13)
5	-10818.922682	-10818.922698	4:29	0:37 (1:50)
6	-12364.414871	-12364.414889	7:06	0:47 (2:37)
7	-13909.907432	-13909.907452	11:16	1:00 (3:37)
8	-15455.400322	-15455.400327	17:02	1:09 (4:46)
9	-17000.893509	-17000.893516	24:24	1:27 (6:13)
10	-18546.386966	-18546.386976	33:53	1:48 (8:01)
11	-20091.880670	-20091.880682	46:04	2:06 (10:07)
12	-21637.374601	-21637.374616	61:10	2:38 (12:45)
13	-23182.868744	-23182.868762	79:51	3:02 (15:47)
14	-24728.363084	-24728.363105	102:06	3:30 (19:17)
15	-26273.857609	-26273.857633	128:48	4:22 (23:39)
16	-27819.352308	-27819.352335	160:05	5:06 (28:45)
17	-29364.847171	-29364.847183	197:27	5:37 (34:22)
18	-30910.342190	-30910.342204	242:25	6:19 (40:41)
19	-32455.837357	-32455.837374	288:44	6:44 (47:25)
20	-34001.332665	-34001.332685	327:49	8:02 (55:27)

[a] cpu time on IBM RISC System/6000 530H.

[b] The value in parentheses indicates the sum of cpu time up to the *n*th extension.

Moreover, since the increment of the errors in the continuous elongation is very small, the validity of the calculated results should be maintained in the more extensions. The diagrams of computational times for polyethylene and polyacetylene systems are given

TABLE 2.3. Total energies and cpu times of extension calculation for polyethylene molecular cluster H-$(CH_2)_n$-$(CH_2)_4$-$(CH_2)_n$-H.

	Total energy (eV)		cpu time (min:s)[a]	
n	Cluster	Elongation	Cluster	Elongation[b]
1	-1457.451870	-1457.451871	0:26	0:17 (-----)
2	-1930.278904	-1930.278905	1:09	0:30 (0:47)
3	-2403.106253	-2403.106240	2:46	0:55 (1:42)
4	-2875.934106	-2875.934093	5:24	1:16 (2:58)
5	-3348.762143	-3348.762129	9:12	1:49 (4:47)
6	-3821.590439	-3821.590422	15:17	2:15 (7:02)
7	-4294.418996	-4294.418974	23:48	2:41 (9:43)
8	-4767.247724	-4767.247702	35:26	2:55 (12:38)
9	-5240.076677	-5240.076643	50:19	3:31 (16:09)
10	-5712.905766	-5712.905730	70:25	3:49 (19:58)
11	-6185.735020	-6185.734971	94:53	4:52 (24:50)
12	-6658.564431	-6658.564380	126:37	4:57 (29:47)
13	-7131.393984	-7131.393920	164:49	6:19 (26:06)
14	-7604.223839	-7604.223772	209:28	6:53 (32:59)
15	-8077.053677	-8077.053596	256:15	8:50 (41:49)

[a] cpu time on IBM RISC System/6000 530H.

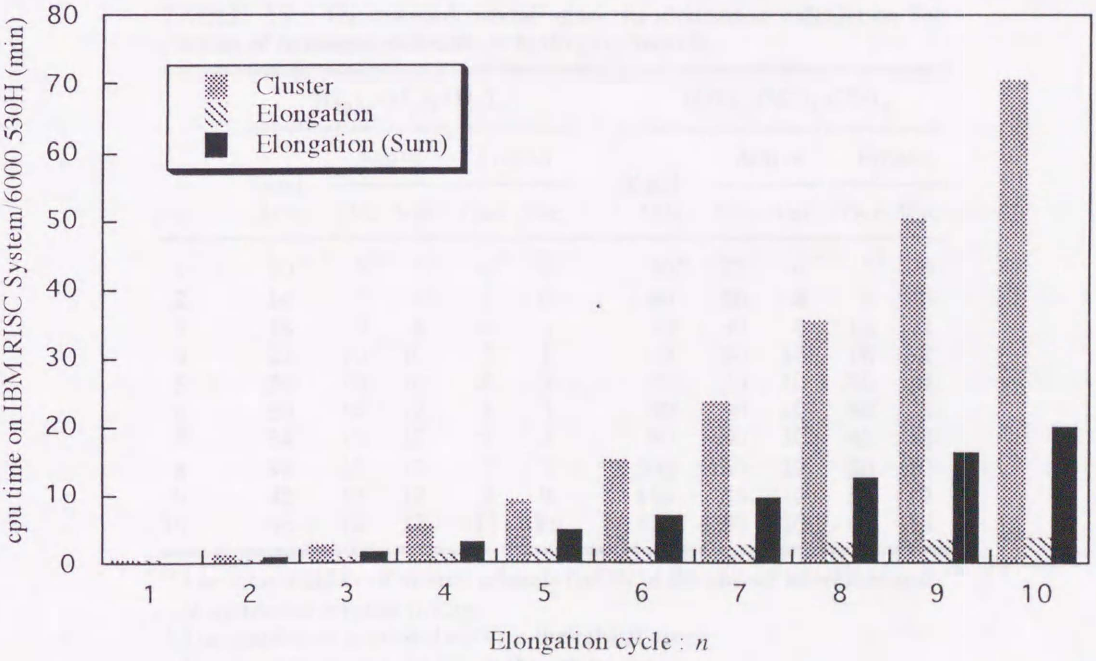
[b] The value in parentheses indicates the sum of cpu time up to the *n*th extension.

TABLE 2.4. Total energies and cpu times of extension calculation for polyacetylene molecular cluster H-$(C_2H_2)_n$-$(C_2H_2)_4$-$(C_2H_2)_n$-H.

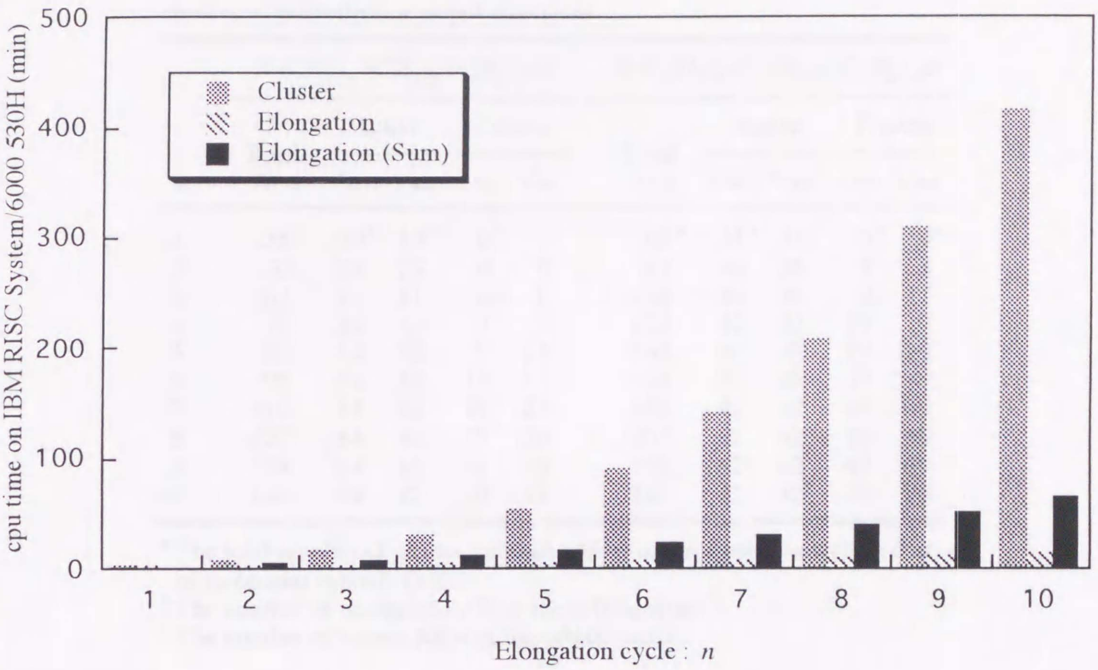
	Total energy (eV)		cpu time (min:s)[a]	
n	Cluster	Elongation	Cluster	Elongation[b]
1	-2596.502795	-2796.502795	2:22	1:36 (-----)
2	-3449.362937	-3449.362937	6:44	2:11 (3:47)
3	-4302.223779	-4302.223773	15:23	3:30 (7:17)
4	-5155.085125	-5515.085116	30:25	4:30 (11:47)
5	-6007.946920	-6007.946897	54:06	5:04 (16:51)
6	-6860.809139	-6860.809106	89:37	6:09 (23:00)
7	-7713.671683	-7713.671639	140:23	7:33 (30:33)
8	-8566.534563	-8566.534506	207:03	9:37 (40:10)
9	-9419.397820	-9419.397750	309:25	11:19 (51:29)
10	-10272.261231	-10272.261148	415:59	13:24 (64:53)

[a] cpu time on IBM RISC System/6000 530H.
[b] The value in parentheses indicates the sum of cpu time up to the *n*th extension.

in Figs. 2.7(a) and 2.7(b) to compare our approach with the usual cluster approach. In the extension of the system, the elongation method can calculate the system as cluster series successively by connecting each cluster, that is, we need not to calculate the whole molecules with different sizes individually as the usual cluster model. In the elongation calculation, noninteraction orbitals which are removed from the basis of the eigenvalue problem can be determined. Therefore, eigenvalue problem with small dimension having only the interaction orbitals is solved iteratively instead of large eigenvalue problem of the whole system. Thus, the cpu time consumed in one-unit extension by our calculation is much shorter than the usual calculation. Moreover, total cpu time up to nth extension of the elongation method is also shorter than the



(a) Polyethylene



(b) Polyacetylene

FIG. 2.7. The computational times for the propagation of clusters which approximate one-dimensional periodic polymers by using usual cluster model or the MO-based elongation method, (a) polyethylene and (b) polyacetylene.

time required for the one cluster with size n. From the comparison of the both methods, it is expected that the advantage of our method increases more and more when the system becomes much larger as aperiodic biopolymers.

TABLE 2.5. The divided orbital space in elongation calculation for clusters of hydrogen molecule or hydrogen fluoride.

	$(H_2)_n$-$(H_2)_3$-$(H_2)_n$					$(HF)_n$-$(HF)_4$-$(HF)_n$				
		Active		Frozen			Active		Frozen	
n	Total AOs	Occ.	Vac.	Occ.	Vac.	Total AOs	Occ.	Vac.	Occ.	Vac.
1	10[a]	5[b]	5[c]	0[b]	0[c]	30[a]	22[b]	6[c]	2[b]	0[c]
2	14	7	7	0	0	40	26	8	6	0
3	18	9	8	0	1	50	30	8	10	2
4	22	10	10	1	1	60	30	10	18	2
5	26	10	10	3	3	70	30	10	26	4
6	30	12	12	3	3	80	30	10	34	6
7	34	12	12	5	5	90	30	10	42	8
8	38	12	12	7	7	100	30	10	50	10
9	42	12	12	9	9	110	30	10	58	12
10	46	12	12	11	11	120	30	10	66	14

[a] The total number of atomic orbirals (AOs) in the cluster as well as that of molecular orbitals (MOs).

[b] The number of occupied MOs in the orbital space.

[c] The number of vacant MOs in the orbital space.

TABLE 26. The divided orbital space in elongation calculation for clusters of polyethylene or polyacetylene.

	$H-(CH_2)_n-(CH_2)_4-(CH_2)_n-H$					$H-(C_2H_2)_n-(C_2H_2)_4-(C_2H_2)_n-H$				
	Total	Active		Frozen		Total	Active		Frozen	
n	AOs	Occ.	Vac.	Occ.	Vac.	AOs	Occ.	Vac.	Occ.	Vac.
1	38[a]	19[b]	19[c]	0[b]	0[c]	62[a]	31[b]	31[c]	0[b]	0[c]
2	50	25	25	0	0	82	38	38	3	3
3	62	31	31	0	0	102	42	40	9	11
4	74	34	32	3	5	122	42	42	19	19
5	86	34	32	9	11	142	42	42	29	29
6	98	34	32	15	17	162	42	42	39	39
7	110	34	32	21	23	182	42	42	49	49
8	122	34	32	27	29	202	42	42	59	59
9	134	34	32	33	35	222	42	42	69	69
10	146	34	32	39	41	242	42	42	79	79

[a] The total number of atomic orbirals (AOs) in the cluster as well as that of molecular orbitals (MOs).

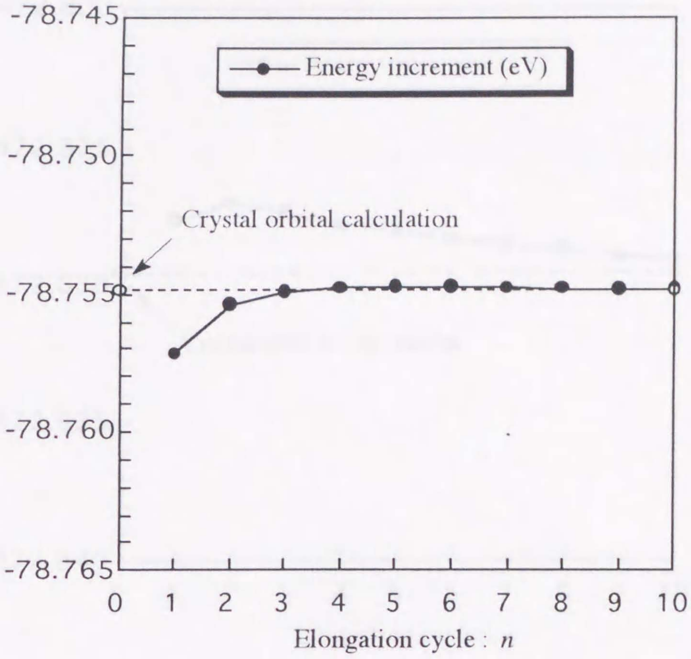
[b] The number of occupied MOs in the orbital space.

[c] The number of vacant MOs in the orbital space.

The divided orbital spaces which are final active and frozen orbitals in these calculations are summarized in Tables 2.5 and 2.6. The first freezing of occupied orbitals appears at n=4 for hydrogen molecule, at n=1 for hydrogen fluoride, at n=4 for polyethylene, and at n=2 for polyacetylene. This means that the orbitals begin to be frozen against the following propagation of clusters; from $(H_2)_9$ to $(H_2)_{11}$ for hydrogen molecule, from $(HF)_4$ to $(HF)_6$ for hydrogen fluoride, from $H-(CH_2)_{10}-H$ to $H-(CH_2)_{12}-H$ for polyethylene, and from $H-(CH)_{12}-H$ to $H-(CH)_{16}-H$ for polyacetylene. In repeating the extension, the active space becomes constant, and constant number of orbitals is newly frozen against each extension. This situation has been discussed in our previous study on stationary orbitals[10] and it has been pointed out that the analysis of the stationary space gives us the information on the electronic state from cluster to polymer.[11] As described in these works, it is expected that the band structure can be reconstructed from our cluster-series calculation.[12]

Next, energy increments $\Delta E(n) = E(n) - E(n-1)$ which corresponds to the energy per two units of polymer are shown in Figs. 2.8(a)-2.8(d). For comparison, the energies of periodic polymers obtained by the CO calculations including up to the 15th neighbor interaction are also shown together. For all cases, the energies per two units are converged into those of the periodic polymers at n=10. In the case of hydrogen molecule, the convergence is very fast in comparison with other cases because of the weak interaction between molecules. The converged values are listed below together with the values of the CO calculations.

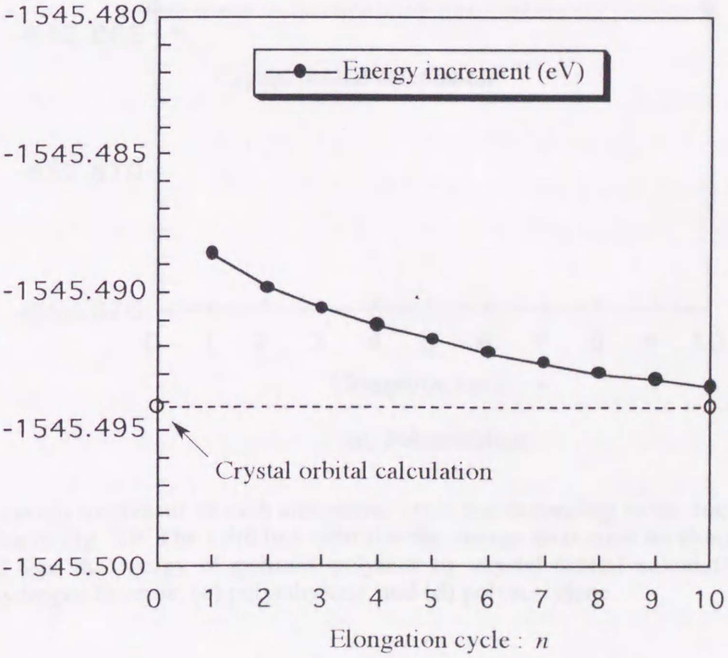
		$\Delta E(10)$	E(Crystal)
Hydrogen molecule	:	-78.7548 eV	-78.7548 eV
Hydrogen fluoride	:	-1545.4935 eV	-1545.4941 eV



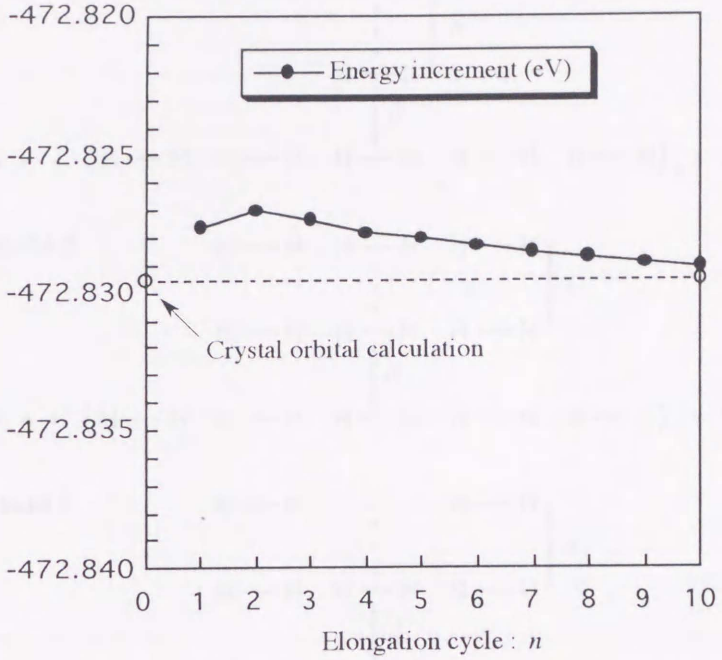
(a) Hydrogen molecule

Polyethylene	:	-472.8291 eV	-472.8296 eV
Polyacetylene	:	-852.8634 eV	-852.8640 eV

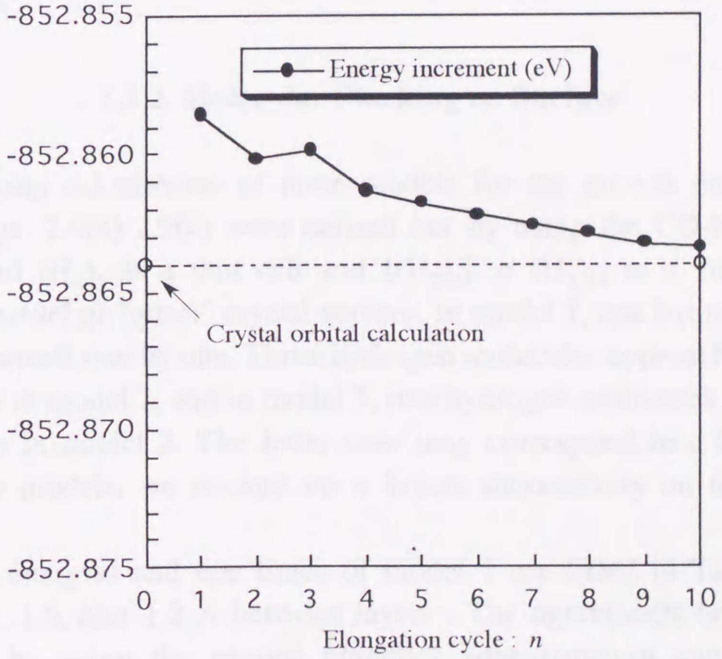
The energy increment ΔE corresponds to the energy of periodic polymer exactly. Thus, the elongation method can reproduce the property of periodic polymer in the case of the periodical propagation.



(b) Hydrogen fluoride



(c) Polyethylene



(d) Polyacetylene

FIG. 2.8. The energy increment in each elongation cycle corresponding to the energy per two units of clusters shown in Fig. 2.6. The solid line indicates the energy increment by elongation calculation and the dashed line the energy of periodic polymer by crystal orbital calculation, (a) hydrogen molecule, (b) hydrogen fluoride, (c) polyethylene, and (d) polyacetylene.

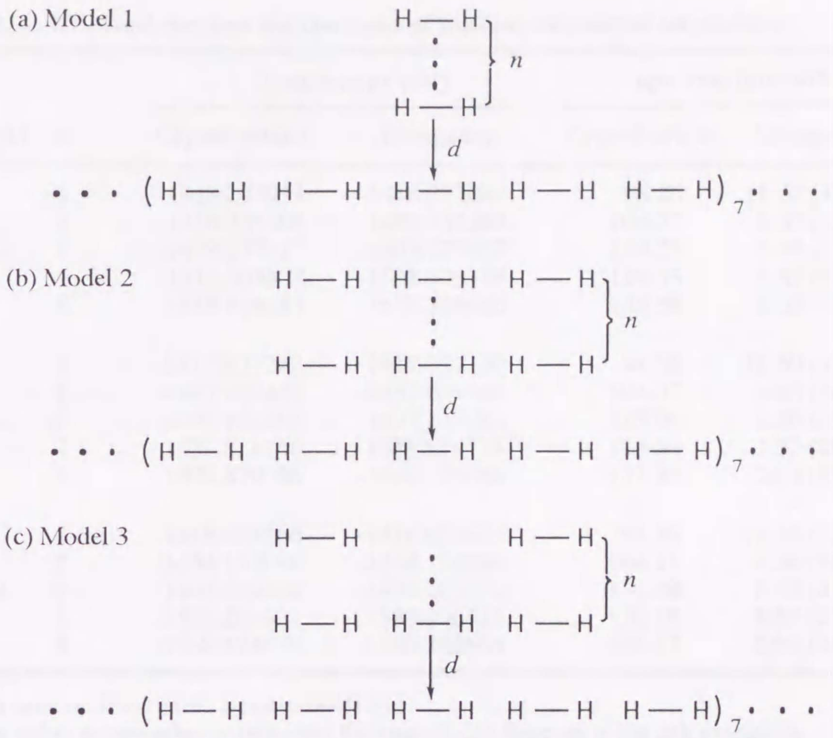


FIG. 2.9. The models used in the calculation for stacking of molecules on surface. The following geometrical parameters were assumed; bond length of hydrogen molecule = 0.742 Å and intermolecular distance = 1.0 Å. The layers of hydrogen molecules are approached on surface at equal interval *d*.

2.3.2. Molecular Stacking on Surface

The stacking calculations of three models for the growth on crystal surface illustrated in Figs. 2.9(a)-2.9(c) were carried out by using the CO-based elongation method. We used $(H_2)_5$ as a unit cell and $[(H_2)_5]_7 = (H_2)_{35}$ as a supercell, and the supercell is the model of "quasi" crystal surface. In model 1, one hydrogen molecule is added on the supercell one by one. Three hydrogen molecules approach to the supercell one after another in model 2, and in model 3, two hydrogen molecules are put upon the top of the layers in model 2. The latter case may correspond to a lattice defect on surface. In these models, we stacked up n layers successively on the surface at an equal interval.

The total energies and cpu times of model 1 are listed in Table 2.7 at three distances d=2.0, 1.6, and 1.2 Å between layers . The agreements between the usual CO calculation by using the nearest neighbor approximation and the elongation calculation are excellent. The computational time by our approach is much faster than the usual CO method. In our calculation, when we need to obtain the result at $n=m$, we have to calculate from n=1 to $n=m$. However, the cpu time required for the elongation calculation from n=1 to $n=m$ is shorter than that in the usual CO calculation only at $n=m$. In other words, our approach can calculate up to mth cycle in shorter time than the usual CO calculation for the only one value for n.

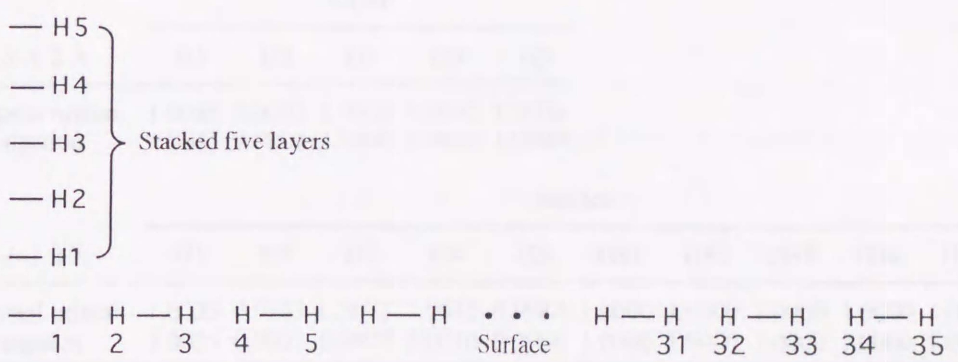
TABLE 2.7. Total energies and cpu times of stacking calculation for model 1.

		Total energy (eV)		cpu time (min:s)[a]	
d (Å)	*n*	Crystal orbital	Elongation	Crystal orbital	Elongation[b]
2.0	1	-1418.227053	-1418.227049	95:16	11:52 (13:12)
	2	-1458.252508	-1458.252508	104:27	2:40 (15:52)
	3	-1498.277917	-1498.277917	114:23	1:48 (17:40)
	4	-1538.303308	-1538.303308	124:35	1:55 (19:35)
	5	-1578.328685	-1578.328686	135:58	2:03 (21:38)
1.6	1	-1417.827242	-1417.827240	94:58	11:50 (13:10)
	2	-1457.490382	-1457.490382	104:37	3:45 (16:55)
	3	-1497.153286	-1497.153286	115:06	1:50 (18:45)
	4	-1536.816176	-1536.816176	125:56	1:57 (20:42)
	5	-1576.479056	-1576.479056	137:41	2:04 (22:46)
1.2	1	-1416.093566	-1416.093533	94:36	12:18 (13:38)
	2	-1454.152076	-1454.152068	104:11	4:38 (18:16)
	3	-1492.209366	-1492.209360	114:38	2:54 (21:10)
	4	-1530.266521	-1530.266515	126:18	1:57 (23:07)
	5	-1568.323670	-1568.323664	138:27	2:05 (25:12)

[a] cpu time on IBM RISC System/6000 340.

[b] The value in parentheses indicates the sum of cpu time up to the *n*th extension.

(a) Model 1



(b) Models 2 and 3

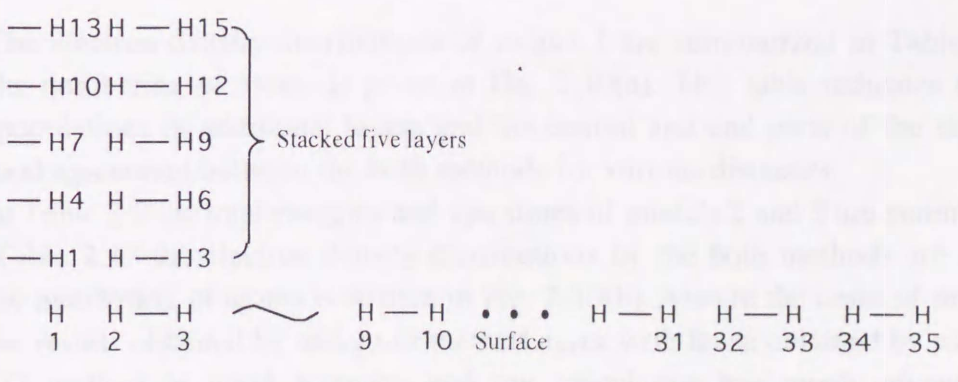


FIG. 2.10. The numbering of atoms in the following models, (a) model 1 in Table 2.8 and (b) models 2 and 3 in Table 2.10. The model is symmetrical and only half side of the system is shown.

TABLE 2.8. The electron density distributions on surface on which stacked five layers and on atoms in five layers for model 1.[a]

	Layer				
d=2.0 Å	H1	H2	H3	H4	H5
Crystal orbital	1.0005	1.0000	1.0000	1.0000	1.0000
Elongation	1.0005	1.0000	1.0000	1.0000	1.0000

	Surface									
d=2.0 Å	H1	H2	H3	H4	H5	H31	H32	H33	H34	H35
Crystal orbital	1.0002	0.9995	0.9998	1.0001	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000
Elongation	1.0002	0.9994	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

	Layer				
d=1.6 Å	H1	H2	H3	H4	H5
Crystal orbital	1.0018	1.0000	1.0000	1.0000	1.0000
Elongation	1.0018	1.0000	1.0000	1.0000	1.0000

	Surface									
d=1.6 Å	H1	H2	H3	H4	H5	H31	H32	H33	H34	H35
Crystal orbital	1.0008	0.9984	0.9992	1.0004	0.9995	1.0000	1.0000	1.0000	1.0000	1.0000
Elongation	1.0008	0.9984	0.9992	1.0003	0.9996	1.0000	1.0000	1.0000	1.0000	1.0000

	Layer				
d=1.2 Å	H1	H2	H3	H4	H5
Crystal orbital	1.0055	1.0002	1.0000	1.0000	1.0000
Elongation	1.0055	1.0002	1.0000	1.0000	1.0000

	Surface									
d=1.2 Å	H1	H2	H3	H4	H5	H31	H32	H33	H34	H35
Crystal orbital	1.0025	0.9953	0.9973	1.0012	0.9984	1.0000	1.0000	1.0000	1.0000	1.0000
Elongation	1.0025	0.9951	0.9974	1.0010	0.9986	1.0000	1.0000	1.0000	1.0000	1.0000

[a] The numbering of atoms is shown in Fig. 2.10(a).

The electron density distributions of model 1 are summarized in Table 2.8 in which the numbering of atoms is given in Fig. 2.10(a). This table indicates that the atomic populations of additional layers and the central and end parts of the supercell are in good agreement between the both methods for various distances.

In Table 2.9 the total energies and cpu times of models 2 and 3 are summarized, and in Table 2.10 the electron density distributions by the both methods are shown, where the numbering of atoms is written in Fig. 2.10(b). Also in the cases of models 2 and 3, the results obtained by using our method agree with those obtained by using the usual CO method in good accuracy and our calculation has much advantage in computational time.

TABLE 2.9. Total energies and cpu times of stacking calculation for models 2 and 3.

d=1.6 Å		Total energy (eV)		cpu time (min:s)[a]	
Model	n	Crystal orbital	Elongation	Crystal orbital	Elongation[b]
2	1	-1495.426436	-1495.426433	116:02	13:17 (14:37)
	2	-1612.684387	-1612.684386	152:55	9:05 (23:42)
	3	-1729.941864	-1729.941863	198:37	10:42 (34:24)
	4	-1847.199353	-1847.199350	254:12	12:35 (46:59)
	5	-1964.456913	-1964.456909	318:32	14:41 (61:40)
	6	-2081.714558	-2081.714553	394:28	17:09 (78:49)
	7	-2198.972288	-2198.972282	488:04	19:42 (98:31)
	8	-2316.230099	-2316.230092	590:34	22:26 (120:57)
	9	-2433.487988	-2433.487981	709:46	25:31 (146:28)
	10	-2550.745952	-2550.745943	847:27	28:42 (175:10)
3	1	-1457.444361	-1457.444350	106:10	11:08 (12:28)
	2	-1574.709550	-1574.709545	140:21	8:39 (23:16)
	3	-1691.967362	-1691.967359	180:06	9:40 (33:22)
	4	-1809.224873	-1809.224869	234:14	12:34 (46:58)
	5	-1926.482423	-1926.482417	296:36	14:42 (61:41)
	6	-2043.740045	-2043.740038	368:16	17:20 (79:00)
	7	-2160.997749	-2160.997741	454:08	20:27 (99:16)
	8	-2278.255534	-2278.255525	551:25	22:50 (121:21)
	9	-2395.513397	-2395.513388	668:22	26:05 (147:02)
	10	-2512.771336	-2512.771326	800:28	29:23 (175:51)

[a] cpu time on IBM RISC System/6000 340.

[b] The value in parentheses indicates the sum of cpu time up to the nth extension.

TABLE 2.10. The electron density distributions on surface on which stacked five layers at d=1.6 Å and on atoms in five layers for models 2 and 3. [a]

Model 2 Layer	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Crystal orbital	0.9981	0.9651	1.0387	0.9981	0.9670	1.0349	0.9982	0.9674	1.0344	0.9982
Elongation	0.9981	0.9651	1.0387	0.9981	0.9670	1.0349	0.9982	0.9674	1.0344	0.9982

Layer	H11	H12	H13	H14	H15
Crystal orbital	0.9676	1.0342	0.9977	0.9615	1.0407
Elongation	0.9676	1.0342	0.9977	0.9615	1.0407

Surface	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Crystal orbital	1.0008	1.0052	0.9957	0.9991	0.9975	1.0005	0.9992	1.0002	0.9997	1.0000
Elongation	1.0008	1.0050	0.9959	0.9988	0.9978	1.0002	0.9995	1.0000	0.9999	1.0000

Surface	H31	H32	H33	H34	H35
Crystal orbital	1.0000	1.0000	1.0000	1.0000	1.0000
Elongation	1.0000	1.0000	1.0000	1.0000	1.0000

TABLE 2.10. (*Continued.*)

Model 3 Layer	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Crystal orbital	0.9981	0.9651	1.0387	0.9981	0.9670	1.0349	0.9982	0.9675	1.0343	0.9950
Elongation	0.9981	0.9651	1.0387	0.9981	0.9670	1.0349	0.9982	0.9675	1.0343	0.9950

Layer	H11	H12	H13	H14	H15
Crystal orbital	0.9641	1.0389	--------	1.0036	0.9984
Elongation	0.9641	1.0389	--------	1.0036	0.9984

Surface	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Crystal orbital	1.0008	1.0052	0.9957	0.9991	0.9975	1.0005	0.9992	1.0002	0.9997	1.0000
Elongation	1.0008	1.0050	0.9959	0.9988	0.9978	1.0002	0.9995	1.0000	0.9999	1.0000

Surface	H31	H32	H33	H34	H35
Crystal orbital	1.0000	1.0000	1.0000	1.0000	1.0000
Elongation	1.0000	1.0000	1.0000	1.0000	1.0000

[a] The numbering of atoms is shown in Fig. 2.10(b).

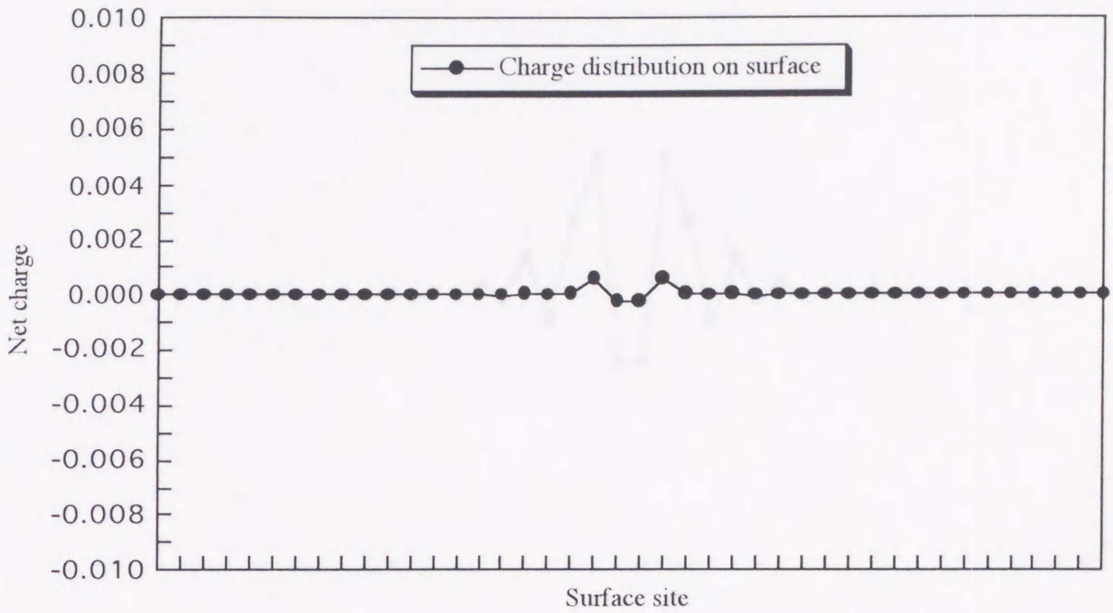
Next, the sum of electron density on each hydrogen atom in the surface is listed in Table 2.11 for the three models. In models 1 and 2, no electron transfers are found between the surface and the layers at the two distances of d=2.0 and 1.6 Å. Small amounts of electron transfer from the surface to the layers are found only at d=1.2 Å. In model 3 for lattice defect, electron transfer from the surface to the layers appears in the case of n=1, in which the defect site is created on the surface directly. For the systems having more than n=2, the perfect layers between the surface and the defective layer may screen electron transfer, and thus the tendency of the electron transfer is the same as that of model 2.

The net charges on each site of the surface for model 1, in which five layers are piled up on at the equal interval d, are shown in Figs. 2.11(a)-2.11(c). In the case of d =2.0 Å, the deviation of the charge density from the value for bulky chain is little recognized, and of d=1.6 Å, it is observed a little around the central molecule. For d =1.2 Å, the effect of the stacking layers is extended within nearly five molecules at the center of the surface. For the all cases, the central site on which layers are stacked has minus charge and its neighboring sites have plus.

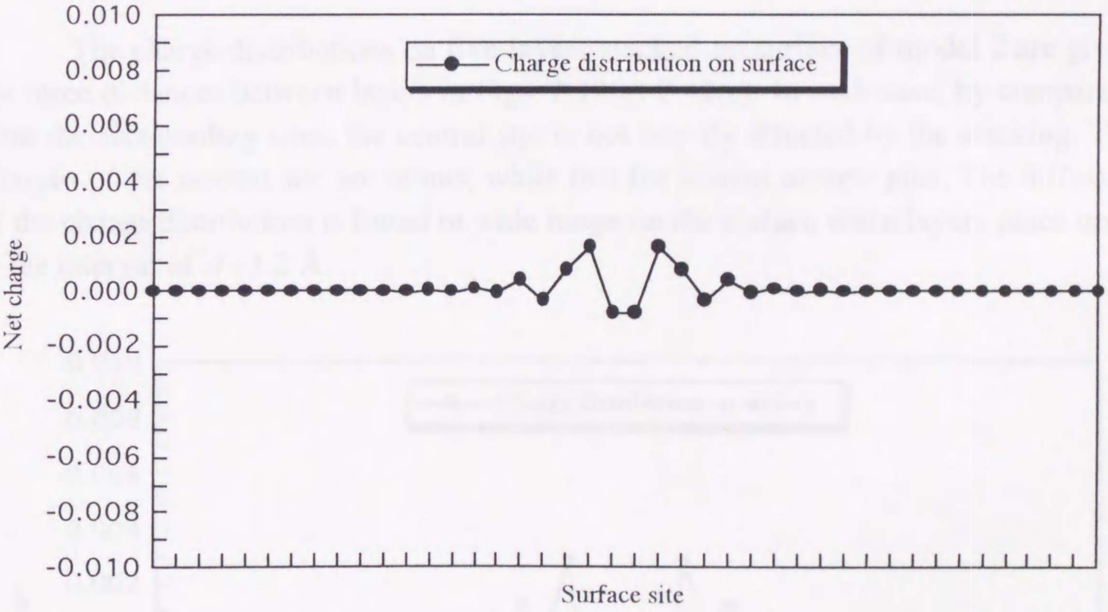
TABLE 2.11. The sum of electron density on surface of models 1, 2, and 3.[a]

	Model 1			Model 2			Model 3		
n d=	2.0 Å	1.6 Å	1.2 Å	2.0 Å	1.6 Å	1.2 Å	2.0 Å	1.6 Å	1.2 Å
1	69.999	69.996	69.989	69.999	69.996	69.988	69.998	69.993	69.979
2	69.999	69.996	69.989	69.999	69.996	69.987	69.999	69.996	69.987
3	69.999	69.996	69.989	69.999	69.996	69.987	69.999	69.996	69.987
4	69.999	69.996	69.989	69.999	69.996	69.987	69.999	69.996	69.987
5	69.999	69.996	69.989	69.999	69.996	69.987	69.999	69.996	69.987

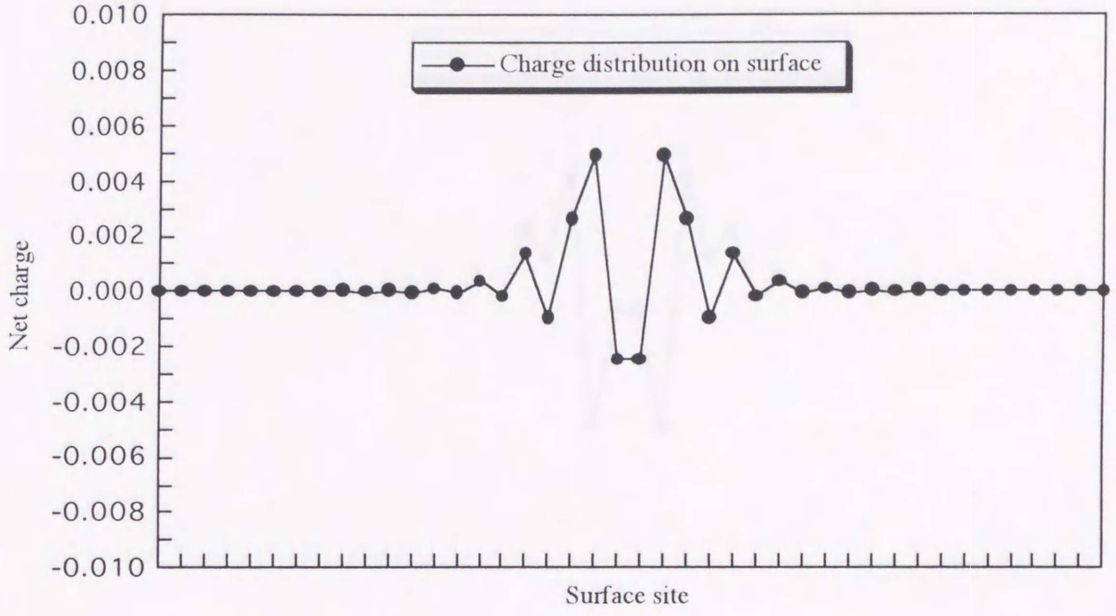
[a] The sum of electron density on isolated surface $-(H_2)_{35}-$ = 70.


Charge distribution on surface
Net charge
0.010
0.008
0.006
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
Surface site

(a)


Charge distribution on surface
Net charge
0.010
0.008
0.006
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
Surface site

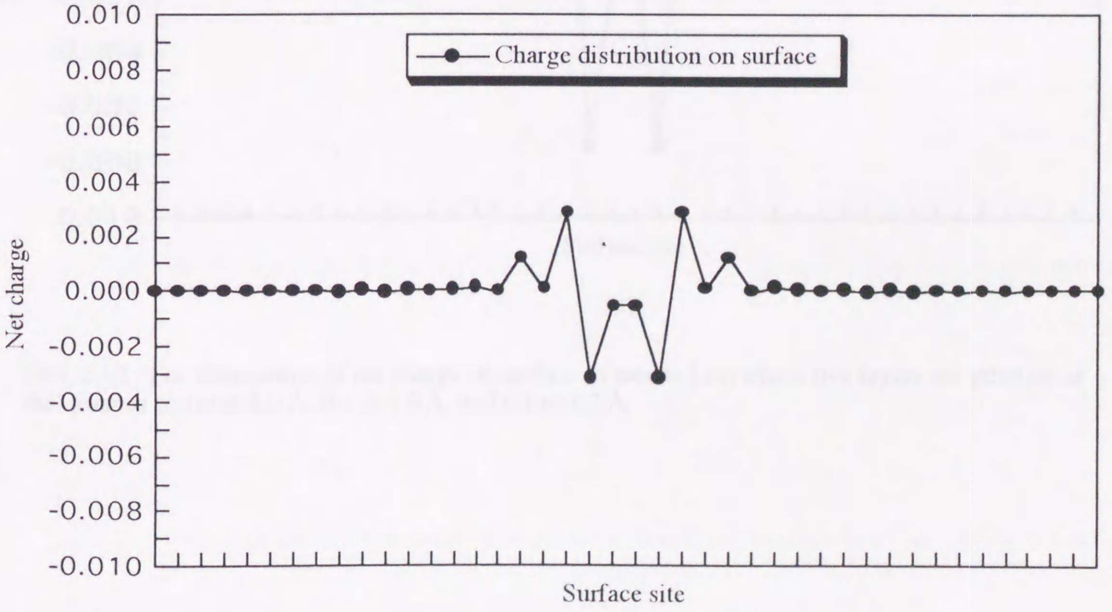
(b)



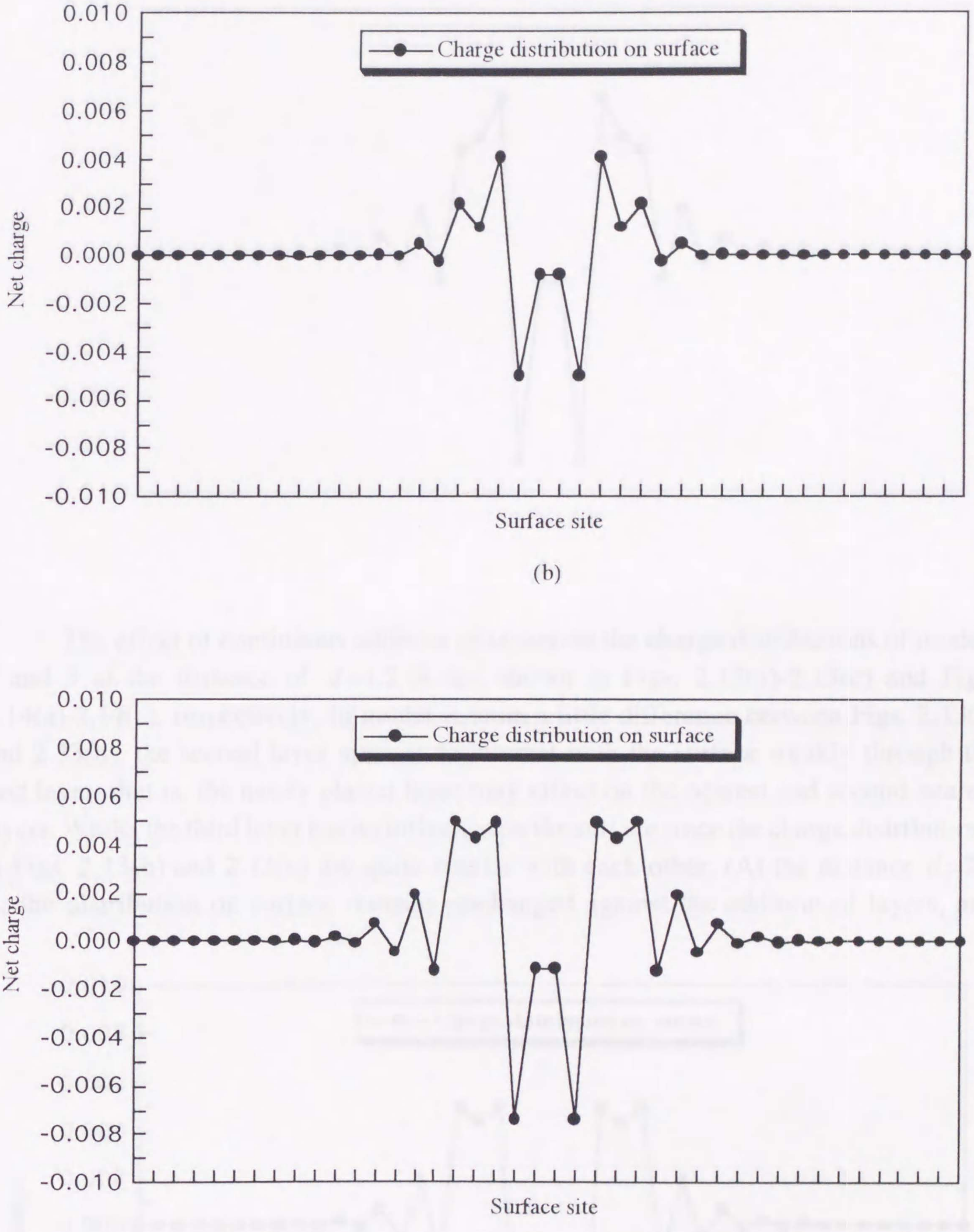
(c)

FIG. 2.11. The distribution of net charge on surface in model 1 on which five layers are piled up at the distance *d*, (a) *d*=2.0 Å, (b) *d*=1.6 Å, and (c) *d*=1.2 Å.

The charge distributions on five-layers-stacked-up surface of model 2 are given for three distances between layers in Figs. 2.12(a)-2.12(c). In each case, by comparing with the surrounding sites, the central site is not heavily affected by the stacking. The charges of the nearest site are minus, while that for second nearest plus. The diffusion of the charge distribution is found in wide range on the surface when layers place upon at the interval of d=1.2 Å.



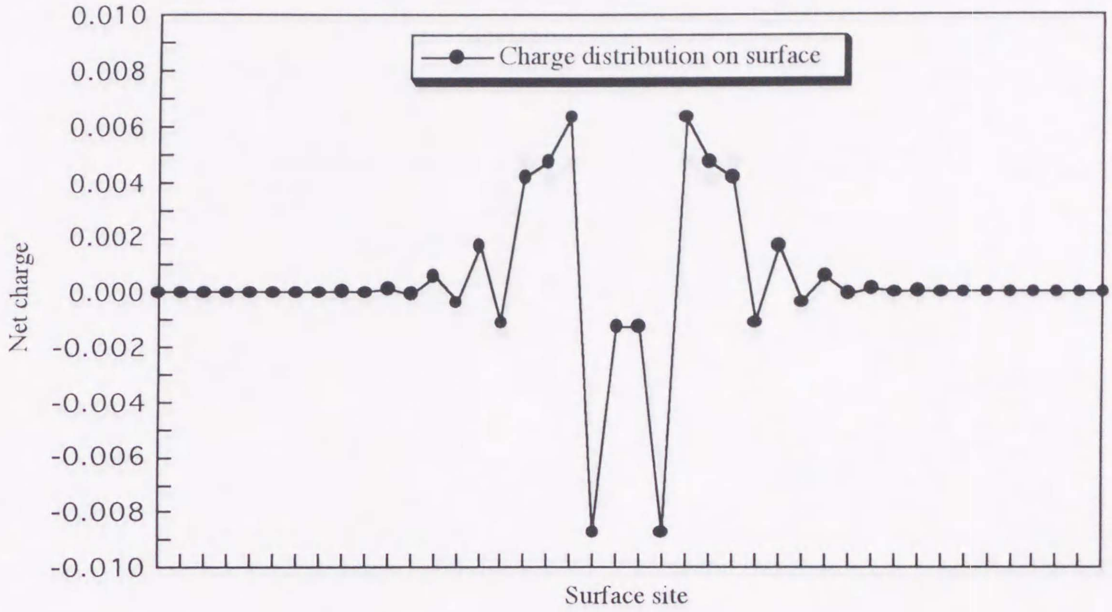
(a)



(b)

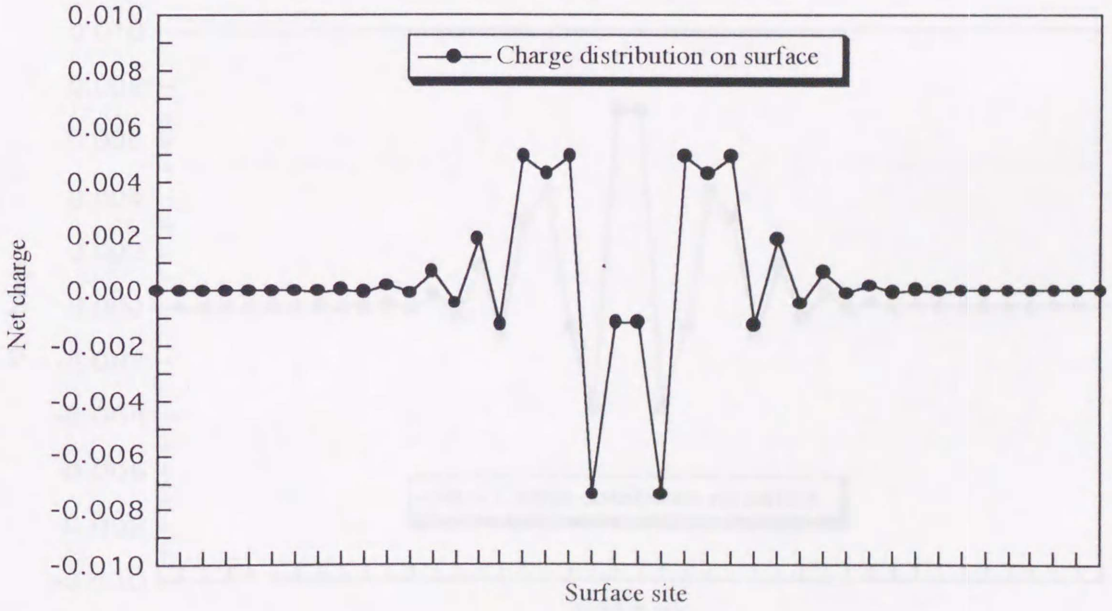
(c)

FIG. 2.12. The distribution of net charge on surface in model 2 on which five layers are piled up at the distance d, (a) d=2.0 Å, (b) d=1.6 Å, and (c) d=1.2 Å.

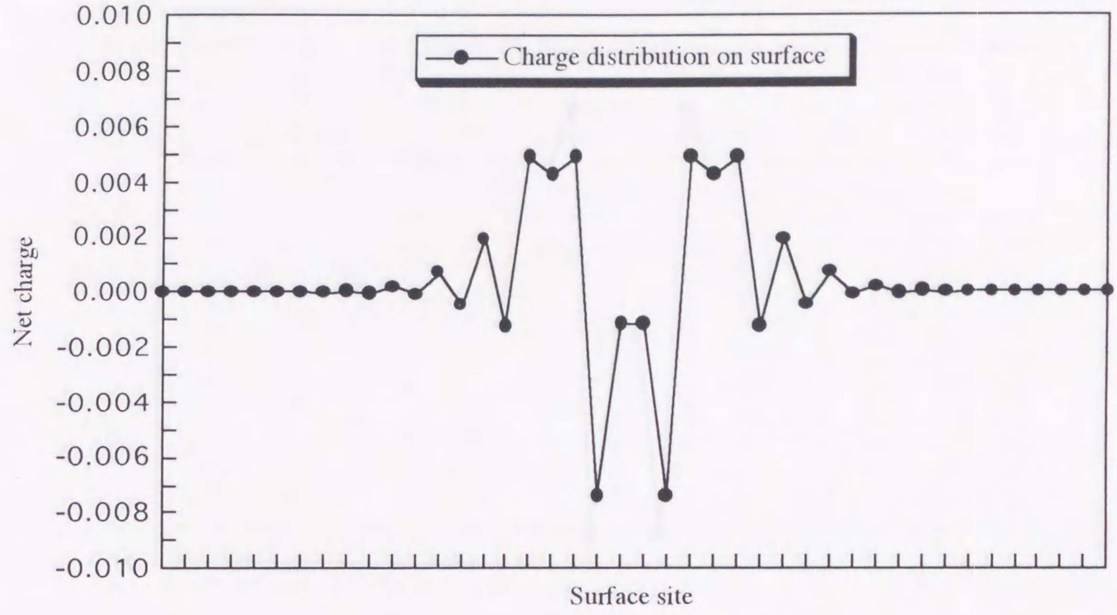


(a)

The effect of continuous addition of layers on the charge distributions of models 2 and 3 at the distance of d=1.2 Å are shown in Figs. 2.13(a)-2.13(c) and Figs. 2.14(a)-2.14(c), respectively. In model 2, from a little difference between Figs. 2.13(a) and 2.13(b), the second layer appears to interact with the surface weakly through the first layer, that is, the newly placed layer may effect on the nearest and second nearest layers. While, the third layer has no influence on the surface since the charge distributions in Figs. 2.13(b) and 2.13(c) are quite similar with each other. (At the distance d=2.0 Å, the distribution on surface remains unchanged against the addition of layers, and



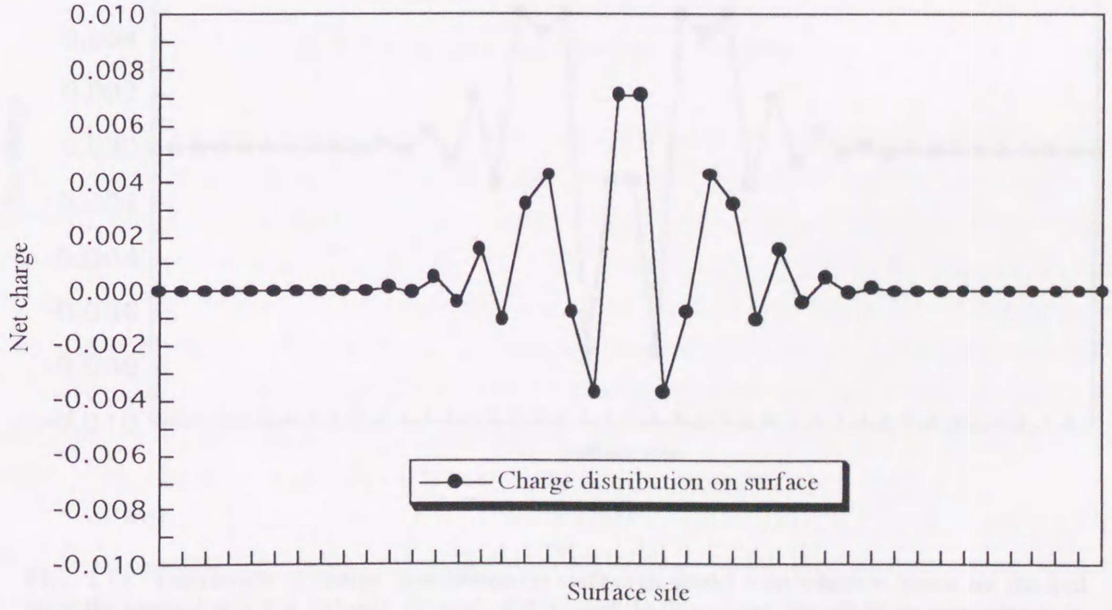
(b)



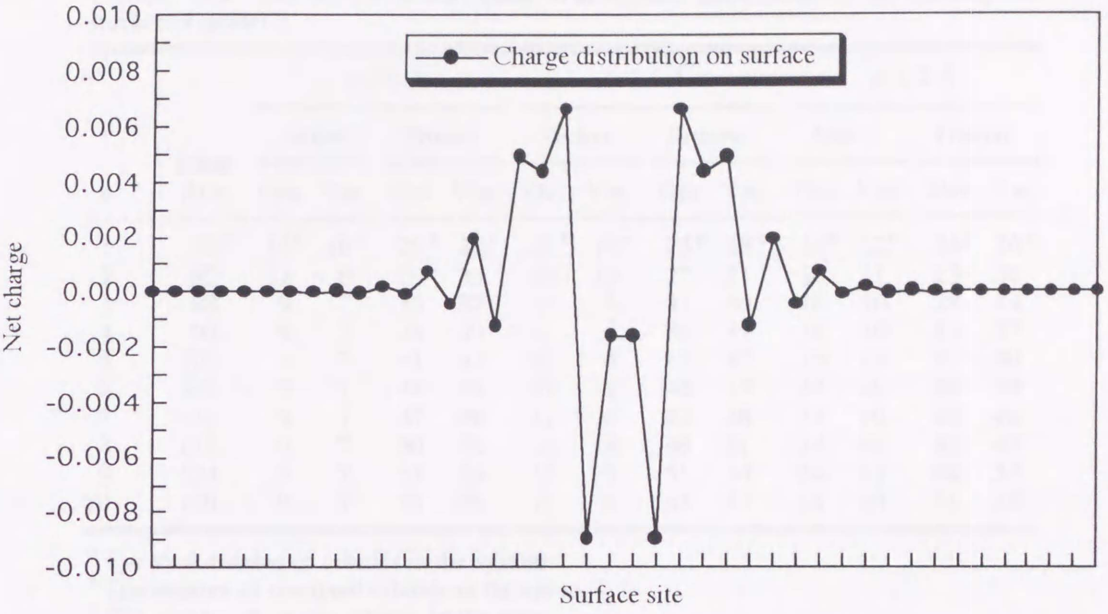
(c)

FIG. 2.13. The change of charge distribution on surface in model 2 on which n layers are stacked up at the interval d=1.2 Å, (a) n=1, (b) n=2, and (c) n=3.

the newly adding layer may interacts only with the nearest layer since the charge distributions on the layers apart from the top layer by more than two layers are not affected by the addition of top layer. This situation is the same as that at the distance d =1.6 Å.) In model 3, on the central molecule of the surface on which defect is created and on the second nearest molecule from the defect, atomic populations decrease, while on the nearest molecule, the populations increase in the case of first stacking as

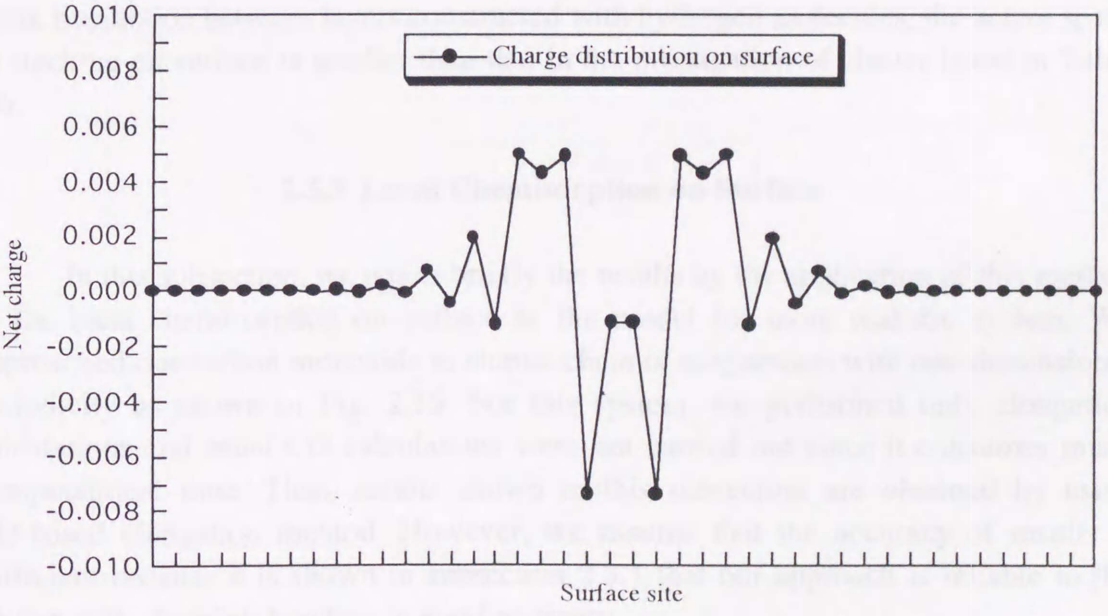


(a)



(b)

is shown in Fig. 2.14(a). In the case with more than two layers, there are several perfect layers between the top defect and the surface, and charge distributions on surface is shown in Figs. 2.14(b) and 2.14(c) and its tendency is almost similar with that of model 2 by comparison of Fig. 2.13 with Fig. 2.14. (From comparison like this, it finds that the charge distributions on the surface apart from the top defective layer



(c)

FIG. 2.14. The change of charge distribution on surface in model 3 on which n layers are stacked up at the interval d=1.2 Å, (a) n=1, (b) n=2, and (c) n=3. In this model, the nth layer corresponds to defective structure.

TABLE 2.12. The divided orbital space in elongation calculation for the stacking on surface of model 2.

		d=2.0 Å				d=1.6 Å				d=1.2 Å			
		Active		Frozen		Active		Frozen		Active		Frozen	
n	Total AOs	Occ.	Vac.	Occ.	Vac.	Occ.	Vac.	Occ.	Vac.	Occ.	Vac.	Occ.	Vac.
1	76[a]	12[b]	10[c]	26[b]	28[c]	13[b]	10[c]	25[b]	28[c]	14[b]	12[c]	24[b]	26[c]
2	82	12	8	29	33	14	10	27	31	16	11	25	30
3	88	9	7	35	37	13	8	31	36	16	10	28	34
4	94	9	7	38	40	11	8	36	39	16	10	31	37
5	100	9	7	41	43	11	8	39	42	15	10	35	40
6	106	9	7	44	46	11	8	42	45	14	10	39	43
7	112	9	7	47	49	11	8	45	48	14	10	42	46
8	118	9	7	50	52	11	8	48	51	14	10	45	49
9	124	9	7	53	55	11	8	51	54	14	10	48	52
10	130	9	7	56	58	11	8	54	57	14	10	51	55

[a] The total number of orbitals in the system.
[b] The number of occupied orbitals in the space.
[c] The number of vacant orbitals in the space.

by m layers in model 3 are consistent with those in model 2, that is, m=2 at d=2.0 Å, m=2 at d=1.6 Å, and m=4 at d=1.2 Å.) It is suggested that the effect of defect may reach to the m-1th layers from the defect.

The orbital space in stacking cycle of model 2 is listed in Table 2.12. The active spaces at three distances become larger in the following order; d=2.0 Å < d=1.6 Å < d=1.2 Å and become constant as follows; 16(total), 9(occ), 7(vac) at d=2.0 Å, 19(total), 11(occ), 8(vac) at d=1.6 Å, and 24(total), 14(occ), 10(vac) at d=1.2 Å. Because of the weak interaction between layers constructed with hydrogen molecules, the active space in stacking on surface is smaller than that in the propagation of cluster listed in Table 2.6.

2.3.3. Local Chemisorption on Surface

In this subsection, we report briefly the results by the application of this method to the local chemisorption on surface as the model for more realistic system. We approached one carbon monoxide to atomic chain of magnesium with one-dimensional periodicity as shown in Fig. 2.15. For this system, we performed only elongation calculations and usual CO calculations were not carried out since it consumes much computational time. Thus, results shown in this subsection are obtained by using CO-based elongation method. However, we assume that the accuracy of results is sufficient because it is shown in subsection 2.3.1 that our approach is reliable to the system with chemical bonding in good accuracy.

The potential energy curve and the change of net charge on each atom (carbon and oxygen atoms in carbon monoxide, magnesium atom at chemisorption site on surface) versus the distance between the surface and a molecule are summarized in

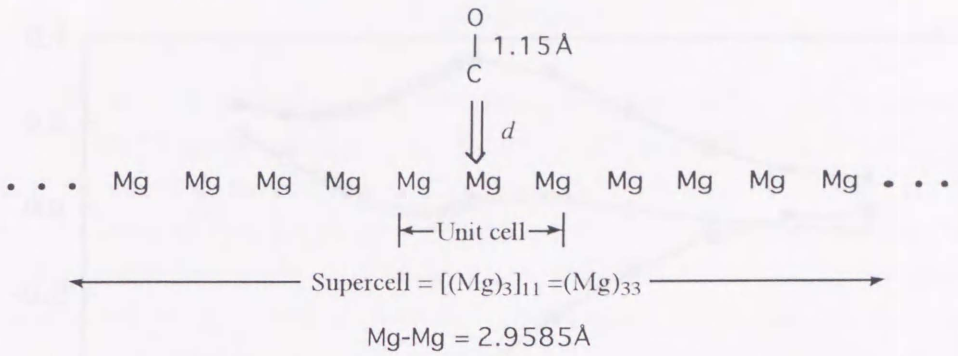
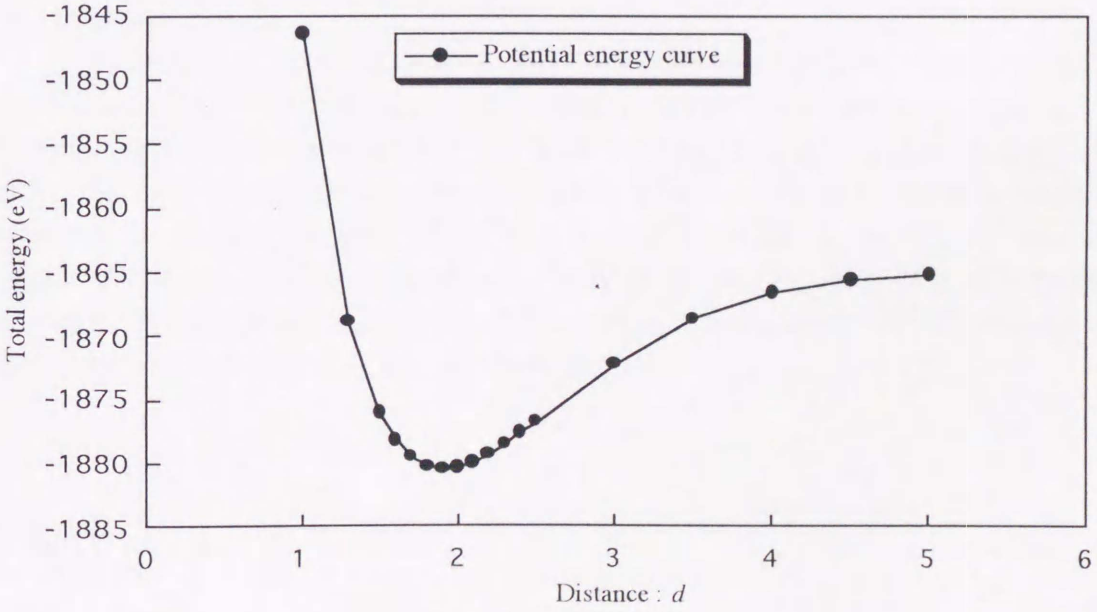


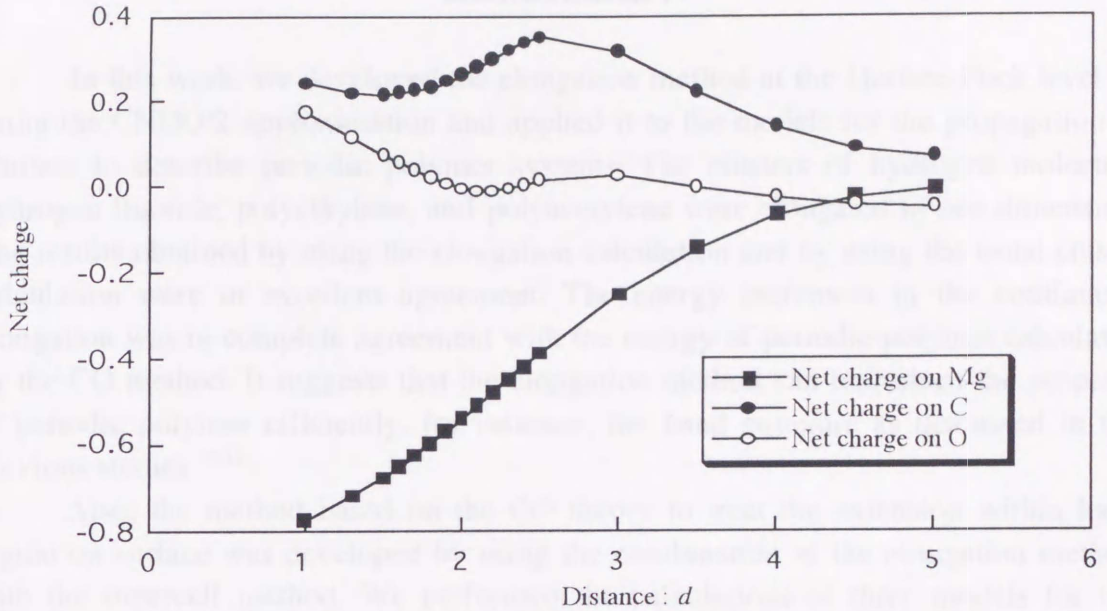
FIG. 2.15. The model system for local chemisorption of carbon monoxide on atomic chain of magnesium.

Figs. 2.16(a) and 2.16(b), respectively. The minimum point of the energy potential is almost at d=1.9 Å. The net charge on the oxygen atom has little change compared with the other atoms. The plus charge on carbon atom increases with approaching to magnesium chain, and magnesium atom has minus charge, because the charge transfer from carbon to magnesium occurs.

Of course, these calculations in this work can not reproduce the real system extended in three dimensions. But, we may expect that our approach to treat local chemisorption on periodic surface can mimic the real system efficiently. That is, usually, the periodic surface is approximated by the cluster of several layers, and a molecule is placed on the cluster. In this approach, however, the size of the cluster required for the estimation of bulk limit is not necessarily clear. With regard to this point, our CO-based elongation method is satisfactory and able to describe the electronic structure of the surface.



(a)



(b)

FIG. 2.16. The results of calculation for chemisorption, (a) potential energy curve and (b) net charge on magnesium atom at chemisorption site and each atom of carbon monoxide.

2.4. SUMMARY

In this work, we developed the elongation method at the Hartree-Fock level by using the CNDO/2 approximation and applied it to the models for the propagation of clusters to describe periodic polymer systems. The clusters of hydrogen molecule, hydrogen fluoride, polyethylene, and polyacetylene were elongated in one dimension. The results obtained by using the elongation calculation and by using the usual cluster calculation were in excellent agreement. The energy increment in the continuous elongation was in complete agreement with the energy of periodic polymer calculated by the CO method. It suggests that the elongation method can reproduce the property of periodic polymer efficiently, for instance, the band structure as discussed in the previous studies.[10-12]

Also, the method based on the CO theory to treat the extension within local region on surface was developed by using the combination of the elongation method with the supercell method. We performed the calculations of three models for the growth of crystal surface and good results were obtained. Although only the hypothetical models constructed with hydrogen molecules arranged in one dimension were dealt with, it should be emphasized that the obtained results suggest the applicability of our method to more realistic systems and it will be carried out in practice if this method is extended to two-dimensional systems.

We indicated the usefulness of our method within the CNDO/2 approximation in this chapter. However, since our method has necessarily no special limitations and conditions, it can be used in more advanced semiempirical calculations. Several calculations are now carrying out in our group and we will report the results in near future. Moreover, it can be applicable to *ab initio* calculations if we select the active and the frozen orbitals from both of the variational and the orthonormality conditions in the extended system.

As a next step, we will attempt to apply our method to two-dimensional problems and various realistic systems like as adsorptions on crystal surface or local defective structures, and moreover, catalytic effects. In studying in this direction, usually, the periodic surface is approximated by the cluster of several layers, and a molecule is placed on the cluster. In this approach, however, the size of the cluster which is required to estimate sufficiently the bulk limit of surface is not necessarily evident. With regard to this point, our CO-based elongation method would be satisfactory and able to describe the electronic states of bulk surface.

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Chapter 3

Interface and Local Defect States in a Polymer: Periodicity in Electronic States of a Nonperiodic Polymer

We have developed an approach at the Hartree-Fock level by which it is possible to calculate the electronic structures of large polymers with or without periodic sequences systematically. This elongation method is based on the concept of a cluster-series calculation which means the successive connection of cluster molecules at the molecular orbital level in approximating a large polymer as a cluster molecule. It has already been reported that we can extract the periodic condition of the electronic states within the series of extended clusters by using the cluster-series model. Recently, we tried to introduce the elongation method into the program package of semiempirical molecular orbital methods MOPAC. In the present chapter, we report results of applications to the calculations of three polymer systems by using AM1 parameters, that is, the first system is the periodic polymer, the second is the interface between two blocks in a polymer chain, and the third is the local defect within a periodic polymer. In calculations of periodic polymers, clusters of polyethylene, polytetrafluoroethylene, polyacetylene, or polydifluoroacetylene were elongated in one direction, and the interfaces between the above polymer blocks with ethylene- or acetylene-type chain were dealt with by the two-directional elongation method. Also, the solitonic structures with one plus or minus charge within polyacetylene chain were created in elongation calculations of the bidirectional extension as models for the local defect in a periodic polymer. Moreover, we discussed periodic states of electronic structures in these systems from cluster-series calculations.

3.1. INTRODUCTION

In studying the electronic structures of polymer systems based on the quantum chemical calculation, the most different point in comparison with the calculation of small molecules is that it is impossible to calculate whole molecules of polymer with large size. For that reason, we need a model system for the large polymer by any way in practical calculations.

One approach to deal with polymer systems is the cluster model in which a polymer is approximated by a cluster molecule with several units of the polymer. In applying this model to extract the electronic property of the polymer, the molecular orbital calculation of each cluster molecule with different size is performed individually, and in those calculations, we monitor the phycochemical property, e.g., the energy per unit or the electron density distribution, in which we take the cluster size larger, and regard the converged value as that for the bulk limit of the polymer. The merit of this cluster approach is the applicability to any nonperiodic polymers because the units which form the cluster molecule are not limited to be the same with each other, while, the demerit is that the size dependence of application and that the detection of the bulk limit is not necessary clear. Also, how can we extract the periodicity of electronic structures such as the band structure in the case of periodic polymers?

Another is the crystal orbital calculation in which the perfect periodicity of a polymer chain is assumed; that is, the polymer is approximated as the one-dimensional crystal with periodic sequence of its constituent unit. In this calculation, the eigenvalue problem of the system is solved under the periodic boundary condition to obtain the crystal orbitals which satisfy the translational symmetry of the system. By this crystal approach, we can know the electronic property of the bulk state without the end effect and obtain the band structure or the density of states based on the periodic nature. But, this method is so restricted by the periodic boundary condition itself, that is, it requires the periodic condition of molecules by which it is difficult to treat the effect of local aperiodicity in periodic polymers.

Surely, the methods based on the molecular orbital theory or the crystal orbital theory are well established and developed at present as very useful tools for the study of small molecules or one-, two-, and three-dimensional periodic systems, respectively, and those have been widely applied to various systems.[1-3] However, some problems still remain in the application of the methods to large, extended, nonperiodic polymer systems as is pointed out above briefly. Those are the treatment of the size effect in the cluster model and the aperiodic effect in the crystal model. In particular, for polymers with aperiodicity within a local region, the most difficulty in dealing with the systems is caused by the fact that we must take into account the following two states connecting with each other in a polymer chain simultaneously; that is, the periodic-extended state which can be represented appropriately by the crystal orbital as a polymer with periodicity and the aperiodic-localized state which is suitable to be described by the molecular orbital as a cluster molecule in periodic surroundings.

In order to investigate the electronic structures of large, extended, nonperiodic molecules, several approaches have been developed by various groups in recent years. For instance, local space approximation to combine fragments connected by a localized bonding interaction,[4,5] Green matrix method for a local perturbation in the periodic polymer,[6,7] localized electron pair theory for the calculation of ground state energies of large molecules,[8] NDDO fragment self-consistent field approximation for large electronic systems,[9] a divide-and-conquer approach to the *ab initio* computation of large molecules,[10] an *ab initio* method for approximation of the frozen molecular fragment,[11,12] and so on. Moreover, the treatments of local defects in a solid based on embedded-cluster approach are also in progress.[13-15]

On the other hand, our group has recently developed the elongation method for the study of any polymer systems with or without periodicity.[16] In this method, by extending a cluster molecule continuously, we can synthesize periodic or aperiodic polymers theoretically. Also, application of this method to the calculation of local density of states in aperiodic polymer has been reported.[17] Moreover, it has been shown that we can extract the periodic nature in a polymer chain by an analysis of stationary space in the cluster-series calculation based on the elongation method.[18] And, it has been confirmed to be able to reconstruct the band structure of periodic chains from the analysis.[19,20] Furthermore, the trials to develop the elongation method based on the crystal orbital theory were carried out[21,22] and now in progress.

The elongation method is a natural extension of cluster model, that is, a polymer chain is approximated as a cluster molecule. But, the calculations of clusters with different sizes can be carried out as a cluster series in our model instead of treating the clusters as one molecule individually in the usual cluster model by the following manner. In the elongation method, we extend a cluster molecule by connecting a molecular fragment with the end part of the cluster one after another as is shown in Fig. 3.1. This figure represents the outline of the cluster-series calculation by the elongation method schematically. A starting cluster with a suitable number of its constituent units is extended by connecting with any fragment molecules continuously. In order to carry out the successive size extension of the system efficiently and systematically, under the influence of newly combined fragments, the separation of orbital space in a cluster can be performed at the molecular orbital (MO) level. That is, we can determine the MOs which are affected (active MOs) and which are unaltered (frozen MOs) by the connection of a new fragment in one-unit extension. This situation is described in Fig. 3.1 in the following way; the orbital space in a starting cluster can be divided into frozen space A and active space B under the interaction with atomic orbitals C in the first fragment. The electronic structure of the extended cluster can be determined by solving only the eigenvalue problem within $B+C$. At this stage, all MOs in the one-unit-elongated cluster are separated into active MOs as $B+C$ and frozen MOs as A. Then, in extending one more unit, only the interaction between the active MOs and a next adding fragment is taken into account fully. In other words, the frozen MOs are fixed and kept unchanged in the following extension. The illustration

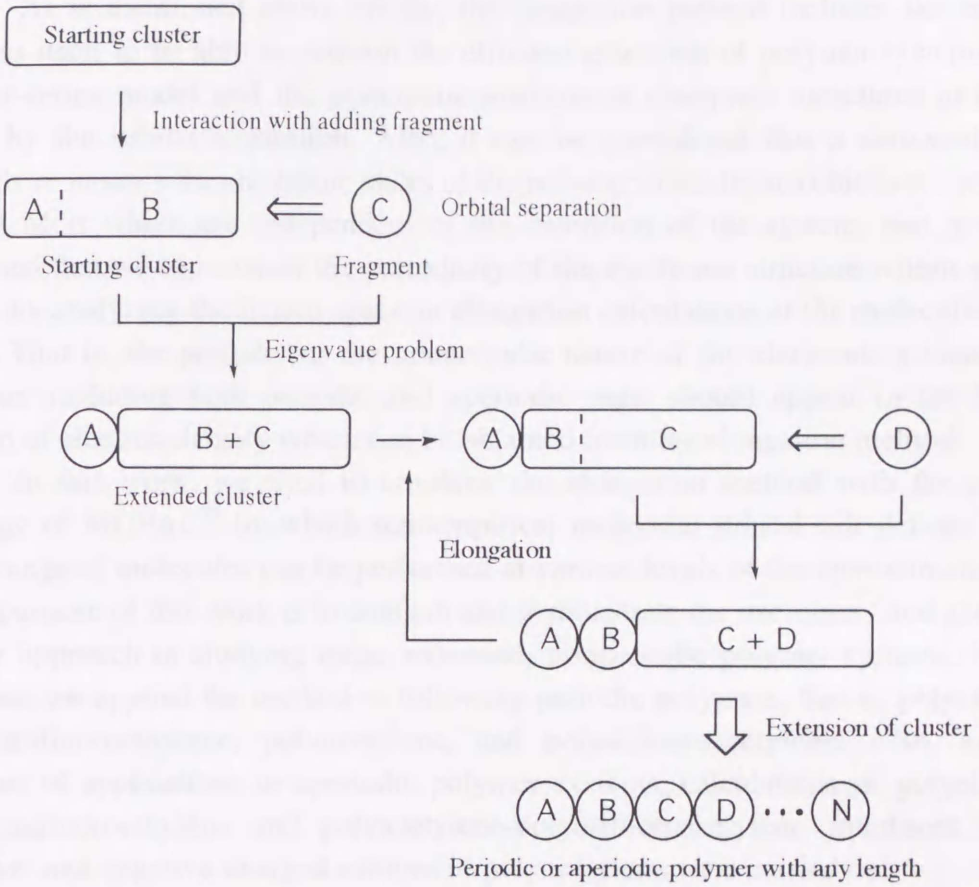


FIG. 3.1. Schematic illustration of the outline for the process of elongation calculation by which the cluster molecule is extended in one direction successively, that is, the cluster-series model for the theoretical synthesis of the electronic structure for periodic or aperiodic polymers with any lengths.

in Fig. 3.1 shows this stage as follows; the previous active space $B+C$ can be specified as the new frozen and active spaces B and C by the connection with new atomic orbitals D in the second fragment. The eigenvalue problem of the extended system can be solved by removing the frozen spaces A and B. That is, the electronic structure of a two-unit-extended cluster is determined by the old and new frozen MOs of A and B and the new active MOs of $C+D$. These procedures of separation and extension can be repeated until we can obtain the polymer with desired length. Furthermore, at the same time, we can obtain the series with separated orbital spaces of MOs in an any periodic or aperiodic polymer as $A, B, C, D, \ldots, N$ in Fig. 3.1. In practical elongation, in solving the eigenvalue problem of the extended cluster series only within the active space, the self-consistent-field (SCF) calculation for the active MOs in an original cluster plus the atomic orbitals in an added fragment can be replaced by a series of SCF steps with a largely reduced number of basis orbitals. The detail of explanation concerning the treatment of SCF procedure is described in the next section. Also, the active space of extended cluster series is retained as almost constant in successive connection with fragments, and thus, we can treat the large system without increasing the dimension of SCF step by the orbital division.

As is mentioned above briefly, the elongation method includes the extension process itself to be able to perform the efficient extension of polymer systems by the cluster-series model and the systematic analysis of electronic structures at the MO level by the orbital separation. Also, it can be considered that a series of frozen orbitals represents the electronic states of the polymer since those orbitals are separated as the MOs which are independent of the extension of the system, and it may be expected that we can extract the periodicity of the electronic structure within a cluster series by analyzing the frozen space in elongation calculations at the molecular orbital level. That is, the periodic or the nonperiodic nature of the electronic structure in a polymer including both periodic and aperiodic parts should appear in the freezing pattern of electron density which can be obtained from the elongation method.

In this work, we tried to combine the elongation method with the program package of MOPAC[23] by which semiempirical molecular orbital calculations for the wide range of molecules can be performed at various levels of the approximation. The main purpose of this work is to confirm and demonstrate the usefulness and generality of our approach in studying large, extended, nonperiodic polymer systems. For that purpose, we applied the method to following periodic polymers, that is, polyethylene, polytetrafluoroethylene, polyacetylene, and polydifluoroacetylene. Also, as some samples of applications to aperiodic polymer systems, calculations of polyethylene-polytetrafluoroethylene and polyacetylene-polydifluoroacetylene interfaces and of positive- and negative-charged solitons in polyacetylene were carried out.

In the following sections, we describe the calculation procedure of the elongation method and show results obtained by using this method in comparison with those obtained by using original MOPAC. Also, we discuss the characteristic of electronic states with periodicity in a periodic or nonperiodic polymer chain.

3.2. METHOD

It has been pointed out in the previous works of our group that after the extension of cluster by one unit is finished, if we select the MOs in an original cluster which satisfy both the orthonormality condition and the variational condition between adding fragment and within the cluster in extended system, those orbitals are also good MOs in the extended cluster, that is, the MOs are stationary against the size extension and stationary orbitals are unaltered under the effect of additional fragments.[18-20] In this study, an analogous method by which we can extract the stationary orbitals mentioned above was employed in order to determine the active and the frozen orbitals for the one-unit extension. That is, we choose and distinguish the MOs which satisfy and do not satisfy the variational condition, which means that the matrix elements of the MO-based Fock matrix between occupied and vacant orbitals must be zero in the system. (Here, it must be noted that because we employ the semiempirical MO methods in this work, the orthonormality condition is self-satisfied in the system automatically.)

In the situation that the effect of a newly connected fragment is almost localized within the region at the cluster end (this situation is expected in the case that the size of the cluster is much larger than that of the fragment), it is not necessary to take into account the interaction between all orbitals in the cluster and atomic orbitals in the fragment. Thus, the selection of interaction and noninteraction orbitals in the total orbital space of the system can be done, and then, it is reasonable that we have only to solve the eigenvalue problem of the extended cluster within the interaction space. Several methods which can define the interaction and noninteraction orbitals of the system may be applicable. In this work, we determined the "interaction" orbital as the molecular orbital which does not satisfy the variational condition and the "noninteraction" orbital as the orbital which does the condition. That is, the SCF calculation can be replaced by the SCF series of eigenvalue problem with interaction orbitals as more effective basis orbitals. As described in the latter part in detail, under the influence of a newly connected fragment, by repeating the orbital selection of interaction and noninteraction orbitals and solving the eigenvalue problem within interaction space of the system, we can extract the following MOs in the extended cluster which are perturbed by the interaction of the adding fragment (active MOs) and which are not done (frozen MOs) finally in each extension process by using the elongation method.

In order to divide the total orbital space of the extended cluster into the interaction and the noninteraction orbital spaces at the MO level as described above, here, we consider the situation that given orbitals $\{\Phi_i\}$ $(i=1,...,N)$ and $\{\Psi_j\}$ $(j=1,...,M)$ interact with each other. How can we determine and select the specific orbitals in $\{\Psi\}$ which are affected by the interaction with $\{\Phi\}$ or which are unaltered? For that propose, the following technique can be applicable based on the variational condition, that is, the rectangular parts of MO-based Fock matrix is defined as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \Phi \oplus \Psi^{\mathrm{vac}} | \hat{F} | \Psi^{\mathrm{occ}} \rangle, \tag{3.1a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \Phi \oplus \Psi^{\mathrm{occ}} | \hat{F} | \Psi^{\mathrm{vac}} \rangle, \tag{3.1b}$$

where $\hat{F}$ denotes Fock operator, occ and vac indicate occupied and vacant molecular orbitals, respectively. In the above expression of Eqs. (3.1a) and (3.1b), the blocks of $\langle \Phi | \hat{F} | \Psi \rangle$ include the effects of charge transfer and exchange interaction between $\{\Phi\}$ and $\{\Psi\}$, and the blocks of $\langle \Psi | \hat{F} | \Psi \rangle$ describe the polarization effect within $\{\Psi\}$. The selection of MOs in $\{\Psi\}$ which interact with $\{\Phi\}$ effectively can be done by the following procedure on the matrices $\mathbf{F}^{\mathrm{occ}}$ and $\mathbf{F}^{\mathrm{vac}}$, respectively. That is, if the orbital space $\{\Psi\}$ includes M^o occupied MOs and M^v vacant MOs, we multiply the above $N^v \times M^o$, $N^o \times M^v$ matrices ($N^v = N + M^v$, $N^o = N + M^o$) by its adjoint $M^o \times N^v$, $M^v \times N^o$ matrices from the left-hand side, respectively, and then, we diagonalize the obtained $M^o \times M^o$, $M^v \times M^v$ matrices $\mathbf{F}^{\mathrm{a}+}\mathbf{F}^{\mathrm{a}}$ (a = occ or vac) individually. Next, we perform the unitary transformation on $\{\Psi\}$ by using obtained eigenvectors and choose orbitals with greater or smaller eigenvalue of the diagonalized matrix than an appropriate threshold value from both occupied and vacant orbital spaces of the unitary-transformed $\{\Psi\}$, respectively, because the square root of the eigenvalues of $\mathbf{F}^{+}\mathbf{F}$ represent the strength of the interaction between $\{\Psi\}$ and $\{\Phi\}$. Also, as is described above, the elements in Eq. (3.1) include all terms of polarization, charge transfer, and exchange interactions of the interacting system which cause orbital mixing. In other words, if we can create the orbital pairs with zero values of their matrix elements, they do not mix with each other without interacting. This procedure is analogous to that for the corresponding orbital[24] or the interaction frontier orbitals.[25,26] Also, the same manner was applied in the elongation calculation in order to extract stationary orbitals against the extension of the system as mentioned above.[18-20] We refer to selected molecular orbitals with greater or smaller eigenvalues than the appropriate threshold value to as "interaction" MOs or "noninteraction" MOs, respectively, through this text. In other words, we define "interaction" MOs as orbitals which are not satisfied with the variational condition and "noninteraction" MOs as orbitals which are satisfying the condition in the total orbital space of the system. We solve the eigenvalue problem within the interaction orbital space only by the self-consistent-field (SCF) procedure, and at the same time, the noninteraction orbital space is removed from basis orbitals of the eigenvalue problem to be retained unchanging in SCF iterations. In this way, we can specify the interactive and noninteractive orbital spaces in the total orbital space of the system.

As we explained the outline of the elongation calculation by Fig. 3.1 in the previous section, the size of cluster is extended continuously by adding molecular fragments one after another. In the elongation calculation by one unit, the SCF iteration of the extended cluster is required. But, by selecting (non)interaction orbitals in each step by the procedure mentioned above, we can replace the extended SCF calculation by a series of SCF steps with small dimension. This is one of the characteristic features of the elongation method. As another characteristic, after one-unit extension of the system, the orbital space can be separated into active and frozen orbitals. We show the practical steps of calculation in detail in the following.

We show the formulation to solve the eigenvalue problem of the extended system by using the technique which we mentioned in the previous paragraphs. The

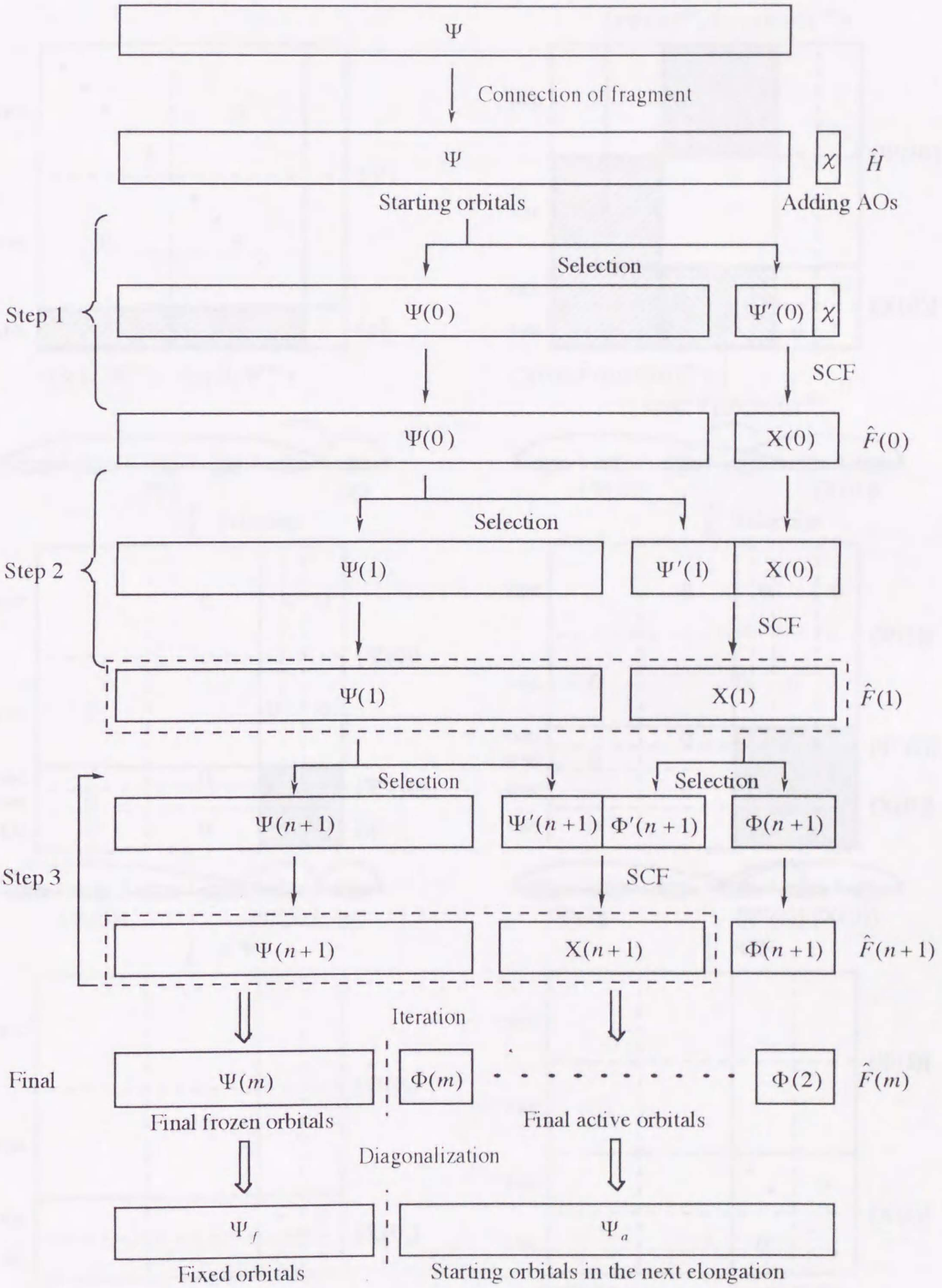
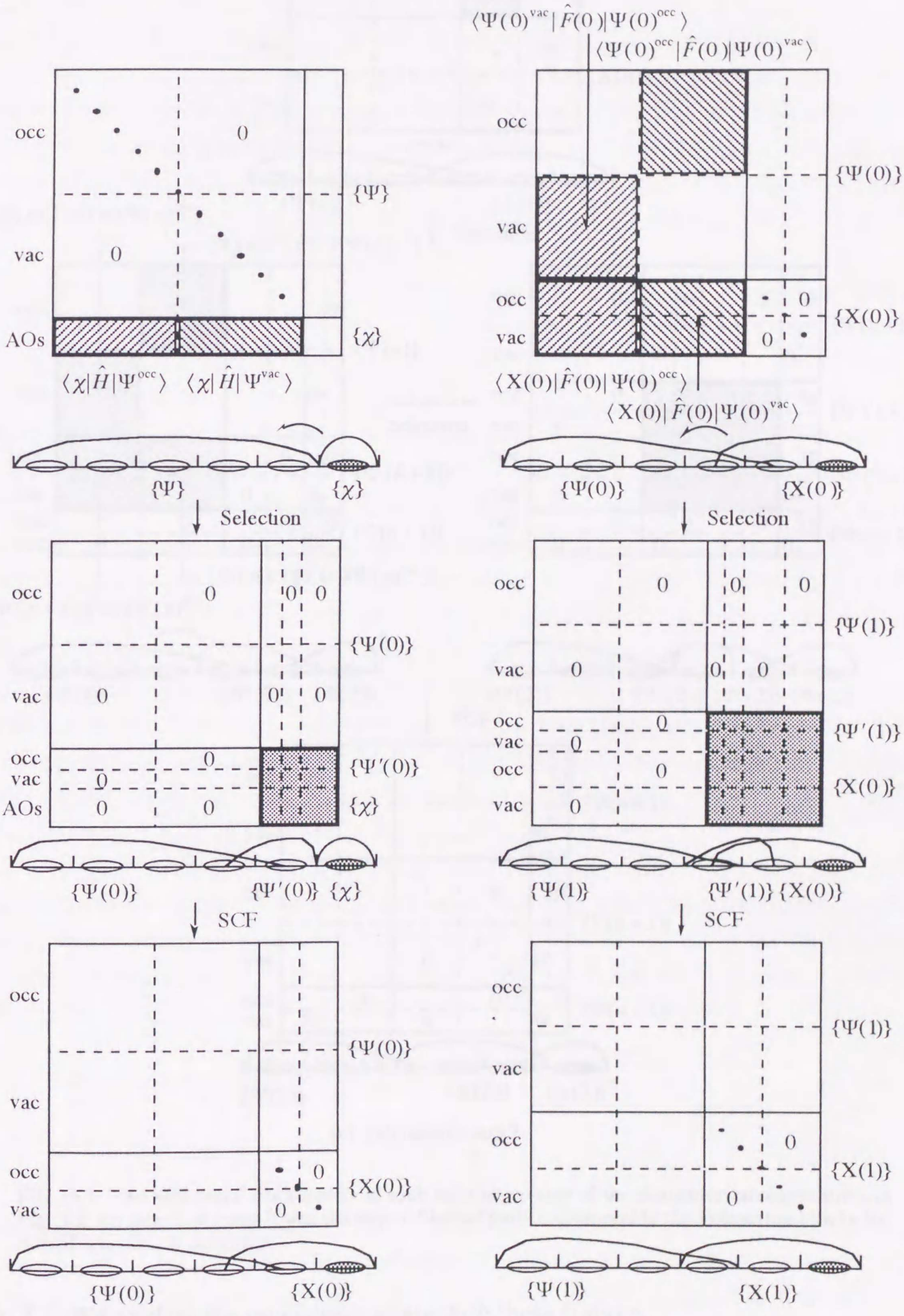


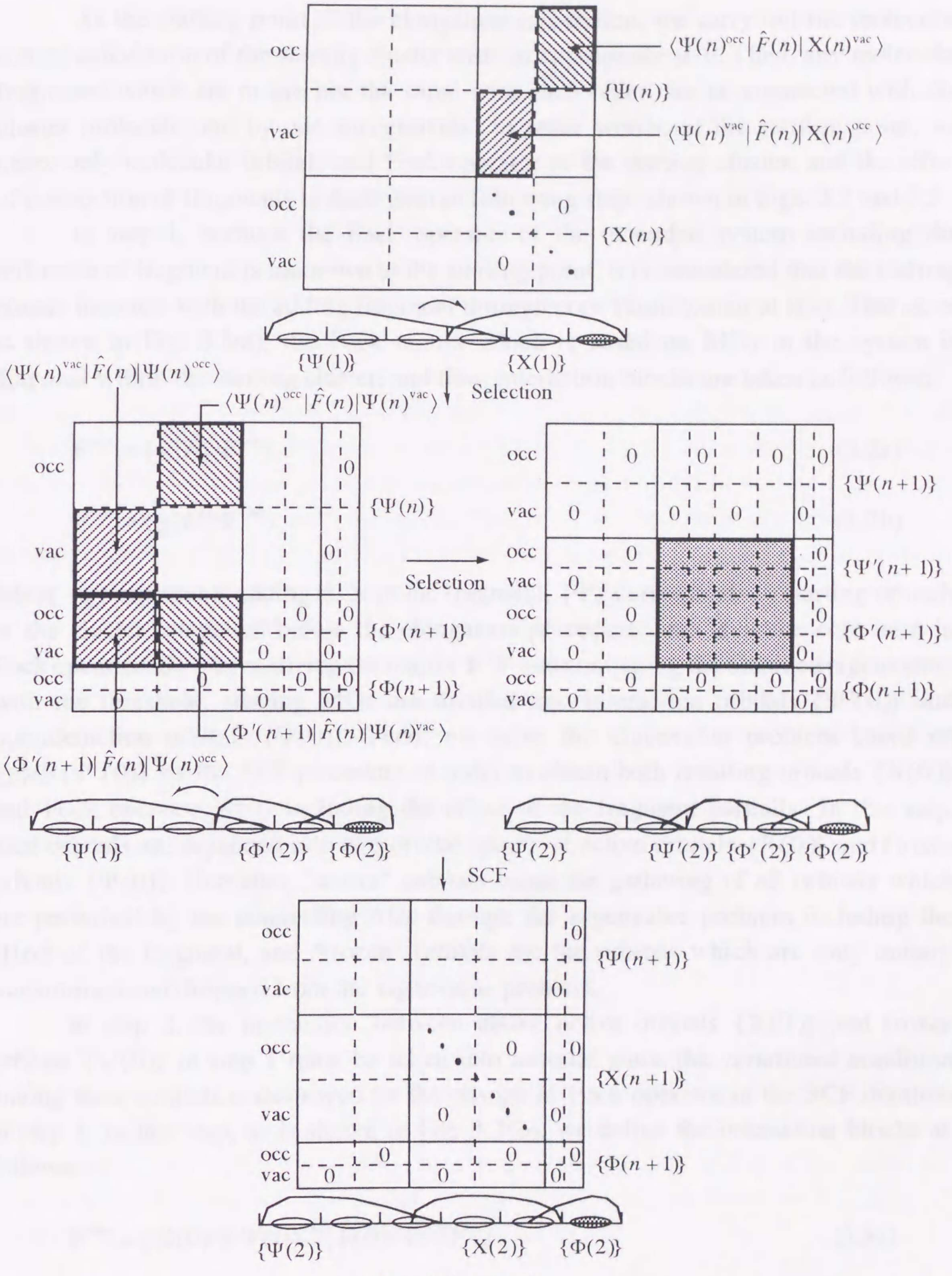
FIG. 3.2. The procedure for the orbital separation in the system to determine the active and the frozen orbitals in one-unit extension by the elongation method.

schematic illustration of the calculation procedure at a viewpoint of orbital separation is given in Fig. 3.2 and the MO-based matrix in each step is summarized in Figs. 3.3(a)-3.3(c). The interaction blocks in Eq. (3.1) are also shown as the shaded parts in



(a) Calculation step 1

(b) Calculation step 2



(c) Calculation step 3

FIG. 3.3. The MO-based Fock matrix in each calculation step of the elongation method shown in Fig. 3.2, (a) step 1, (b) step 2, and (c) step 3. Shaded parts correspond to the interaction blocks for orbital selection at each step.

Fig. 3.3. We explain the procedures along with these figures.

As the starting point of the elongation calculation, we carry out the molecular orbital calculation of the starting cluster with an appropriate size. Then, any molecular fragments which are or are not the same with each other can be connected with the cluster molecule one by one successively. In other words, at the starting point, we know only molecular orbitals and Fock operator of the starting cluster, and the effect of connection of fragments is dealt with in following steps shown in Figs. 3.2 and 3.3.

In step 1, because the Fock operator of the extended system including the influence of fragment is unknown at the starting point, it is considered that the starting cluster interacts with the adding fragment through core Hamiltonian at first. That is, as is shown in Fig. 3.3(a), the Fock matrix which is based on MOs in the system is diagonal within the starting cluster, and thus, interaction blocks are taken as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \chi | \hat{H} | \Psi^{\mathrm{occ}} \rangle , \tag{3.2a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \chi | \hat{H} | \Psi^{\mathrm{vac}} \rangle , \tag{3.2b}$$

where $\{\chi\}$ represents adding AOs in the fragment, $\{\Psi\}$ corresponds to starting orbitals of the cluster calculated before the elongation procedure, and $\hat{H}$ is the core term in Fock operator. By diagonalizing the matrix $\mathbf{F}^{+}\mathbf{F}$ and comparing the obtained eigenvalues with the threshold, starting MOs are divided into interaction orbitals $\{\Psi'(0)\}$ and noninteraction orbitals $\{\Psi(0)\}$. Then, we solve the eigenvalue problem based on $\{\chi\}\oplus\{\Psi'(0)\}$ by the SCF procedure in order to obtain both resulting orbitals $\{\mathrm{X}(0)\}$ and Fock operator $\hat{F}(0)$ including the effect of the fragment partially. In this step, total orbitals are separated into two orbital spaces of active orbitals $\{\mathrm{X}(0)\}$ and frozen orbitals $\{\Psi(0)\}$. Hereafter, "active" orbitals mean the gathering of all orbitals which are perturbed by the connecting AOs through the eigenvalue problem including the effect of the fragment, and "frozen" orbitals are the orbitals which are only unitary transformed and dropped from the eigenvalue problem.

In step 2, the interaction between above active orbitals $\{\mathrm{X}(0)\}$ and frozen orbitals $\{\Psi(0)\}$ in step 1 must be taken into account since the variational condition among these orbitals is destroyed by the change in Fock operator in the SCF iteration at step 1. In this step, as is shown in Fig. 3.3(b), we define the interaction blocks as follows:

$$\mathbf{F}^{\mathrm{occ}} = \langle \mathrm{X}(0) \oplus \Psi(0)^{\mathrm{vac}} | \hat{F}(0) | \Psi(0)^{\mathrm{occ}} \rangle , \tag{3.3a}$$

$$\mathbf{F}^{\mathrm{vac}} = \langle \mathrm{X}(0) \oplus \Psi(0)^{\mathrm{occ}} | \hat{F}(0) | \Psi(0)^{\mathrm{vac}} \rangle . \tag{3.3b}$$

According to the procedure in Eq. (3.1), we diagonalize the matrix $\mathbf{F}^{+}\mathbf{F}$ which consists of the blocks in Eq. (3.3) to specify interaction orbitals $\{\Psi'(1)\}$ which are not satisfied by the variational condition between $\{\mathrm{X}(0)\}$ and within $\{\Psi'(1)\}$ and also noninteraction orbitals $\{\Psi(1)\}$ which are satisfying the condition between $\{\mathrm{X}(0)\}$ and within $\{\Psi(1)\}$.

After this selection of orbitals, the eigenvalue problem represented with $\{X(0)\}\oplus\{\Psi'(1)\}$ is solved by the SCF procedure. Then, the orbitals $\{X(1)\}$ are obtained as the solution of the eigenvalue problem. Also, we obtain the Fock operator $\hat{F}(1)$. In this process, new active orbitals correspond to the solution $\{X(1)\}$ and new frozen orbitals to $\{\Psi(1)\}$. In this way, the variational condition is not necessary satisfied after the SCF calculation. Thus, the procedure in this step must be repeated until the condition is satisfied in the whole system. In this approach, the checkpoint for the satisfaction of the variational condition is the number of interaction orbitals in the system and we iterate this step by checking whether the number of interaction orbitals becomes zero or not as long as the number of interaction orbitals is not equal to zero.

In repeating step 2, when the active space becomes larger and the deviation from the variational condition becomes smaller, it is expected that noninteraction MOs may appear in this space. To confirm the situation, we check the variational condition not only in the frozen space but also in the active space in the next step. If there are any orbitals in the active space, we permit that those orbitals can be separated from the interaction space of the system. By this treatment, the dimension of the SCF problem can be largely reduced in the next step.

In step 3, we repeat the following treatment until the local interaction converges which can be confirmed by checking whether the number of interaction orbitals becomes zero or not. Now, the $n+1$ th cycle of this step is described and the first cycle corresponds to step 2. In this step, as is mentioned above, we choose the interaction orbitals from the active space $\{X\}$ and the frozen space $\{\Psi\}$, respectively, by the following two-step procedure. In the first step, we test the variational condition of the active space by using the interaction blocks as follows:

$$\mathbf{F}^{\text{occ}} = \langle \Psi(n)^{\text{vac}} | \hat{F}(n) | X(n)^{\text{occ}} \rangle, \tag{3.4a}$$

$$\mathbf{F}^{\text{vac}} = \langle \Psi(n)^{\text{occ}} | \hat{F}(n) | X(n)^{\text{vac}} \rangle, \tag{3.4b}$$

where $\{\Psi(n)\}$ is the set of frozen orbitals after the nth iteration, $\{X(n)\}$ corresponds to the solution of the eigenvalue problem in the nth cycle and Fock operator $\hat{F}(n)$ is determined by the nth procedure. At first, we find the sets of interaction and noninteraction MOs $\{\Phi'(n+1)\}$ and $\{\Phi(n+1)\}$ from $\{X(n)\}$ in the active space by diagonalizing the matrix $\mathbf{F}^{+}\mathbf{F}$. In the second step, we check also the condition of frozen space by taking the interaction blocks as follows:

$$\mathbf{F}^{\text{occ}} = \langle \Phi'(n+1) \oplus \Psi(n)^{\text{vac}} | \hat{F}(n) | \Psi(n)^{\text{occ}} \rangle, \tag{3.5a}$$

$$\mathbf{F}^{\text{vac}} = \langle \Phi'(n+1) \oplus \Psi(n)^{\text{occ}} | \hat{F}(n) | \Psi(n)^{\text{vac}} \rangle. \tag{3.5b}$$

Diagonalization of the matrix $\mathbf{F}^{+}\mathbf{F}$ enables us to determine interaction orbitals $\{\Psi'(n+1)\}$ and noninteraction orbitals $\{\Psi(n+1)\}$ in the frozen space. After these two-step selections of interaction orbitals $\{\Phi'(n+1)\}$ and $\{\Psi'(n+1)\}$, the eigenvalue problem is solved within $\{\Phi'(n+1)\}\oplus\{\Psi'(n+1)\}$ by the SCF procedure to obtain resulting orbitals $\{X(n+1)\}$ and Fock operator $\hat{F}(n+1)$. This step is summarized in Fig. 3.3(c). In this step, we can separate the total orbital space into the active space $\{\Phi\}\oplus\{X\}$ and the frozen space $\{\Psi\}$.

In the next cycle of this procedure, we assume $\{X(n+1)\}$ and $\{\Psi(n+1)\}$ as the interaction space for the $n+2$th cycle and repeat the procedure in this step as is stated above within the space. By this manner, at each cycle of step 3, if there is, $\{\Phi\}$ in the active space is removed from the interaction space and we regard each $\{\Phi\}$ as invariant through all cycles. This treatment of $\{\Phi\}$ is based on the fact that the interaction between $\{\Phi(n+1)\}$ and $\{\Psi(n)\}$ is weak enough as eigenvalues of interaction block between them are smaller than the threshold, that is, we assume that the variational condition of $\{\Phi(n+1)\}$ will not be destroyed by the interaction with $\{\Psi(n+1)\}$. Finally, if the interaction converges at the mth cycle in this step, the active MOs can be extracted as $\{\Phi(2)\},\ldots,\{\Phi(m)\}$ and the frozen MOs as $\{\Psi(m)\}$, thus, we can obtain the electronic structure of the system in which one-unit extension is finished. That is, the procedure in Fig. 3.1 that a starting cluster is elongated by the connection with the first fragment is completed, and the active and frozen MOs as $\{\Phi(2)\},\ldots,\{\Phi(m)\}$ and $\{\Psi(m)\}$ correspond to $B+C$ and A in Fig. 3.1, respectively. In the next addition of fragment D in Fig. 3.1, the active MOs of $B+C$ can be regarded as new starting MOs by the following manner.

In the continuous elongation of the system, that is, in the connection with more than the second fragment, steps 1-3 can be repeated in any times according to the following way. We diagonalize the active- and the frozen-MO-based Fock matrices in order to determine the final sets of active and frozen orbitals $\{\Psi_a\}$ and $\{\Psi_f\}$. Active orbitals $\{\Psi_a\}$ are used as starting orbitals in the next elongation cycle, which correspond to $\{\Psi\}$ in step 1 of the procedure in Fig. 3.2, while, frozen orbitals $\{\Psi_f\}$ are fixed in the next elongation calculation. That is, frozen MOs are separated from the total orbital space of the system and those are maintained without interaction through the successive extension cycle. In other words, steps 1-3 in the next elongation are carried out within the selected space which is constructed with active MOs in one-unit-extended cluster and adding AOs in a next-connecting fragment.

We show in Fig. 3.4 schematically the summary of the orbital separation in the system by this calculation procedure of each step in Fig. 3.2.

The characteristic feature and merit of the calculation procedures of this method is their simplicity in the practical calculation, that is, we have only to diagonalize the matrix $\mathbf{F}^{+}\mathbf{F}$ in order to find interaction orbitals and solve the eigenvalue problem based on those orbitals. And, the SCF calculation within active space can be carried out by a series of SCF steps only with small number of interaction orbitals as effective basis orbitals of the eigenvalue problem. Moreover, since our approach includes the determination of the divided subspaces in which the SCF problem must be solved in the calculation process as described in this section at the MO level, we need not to

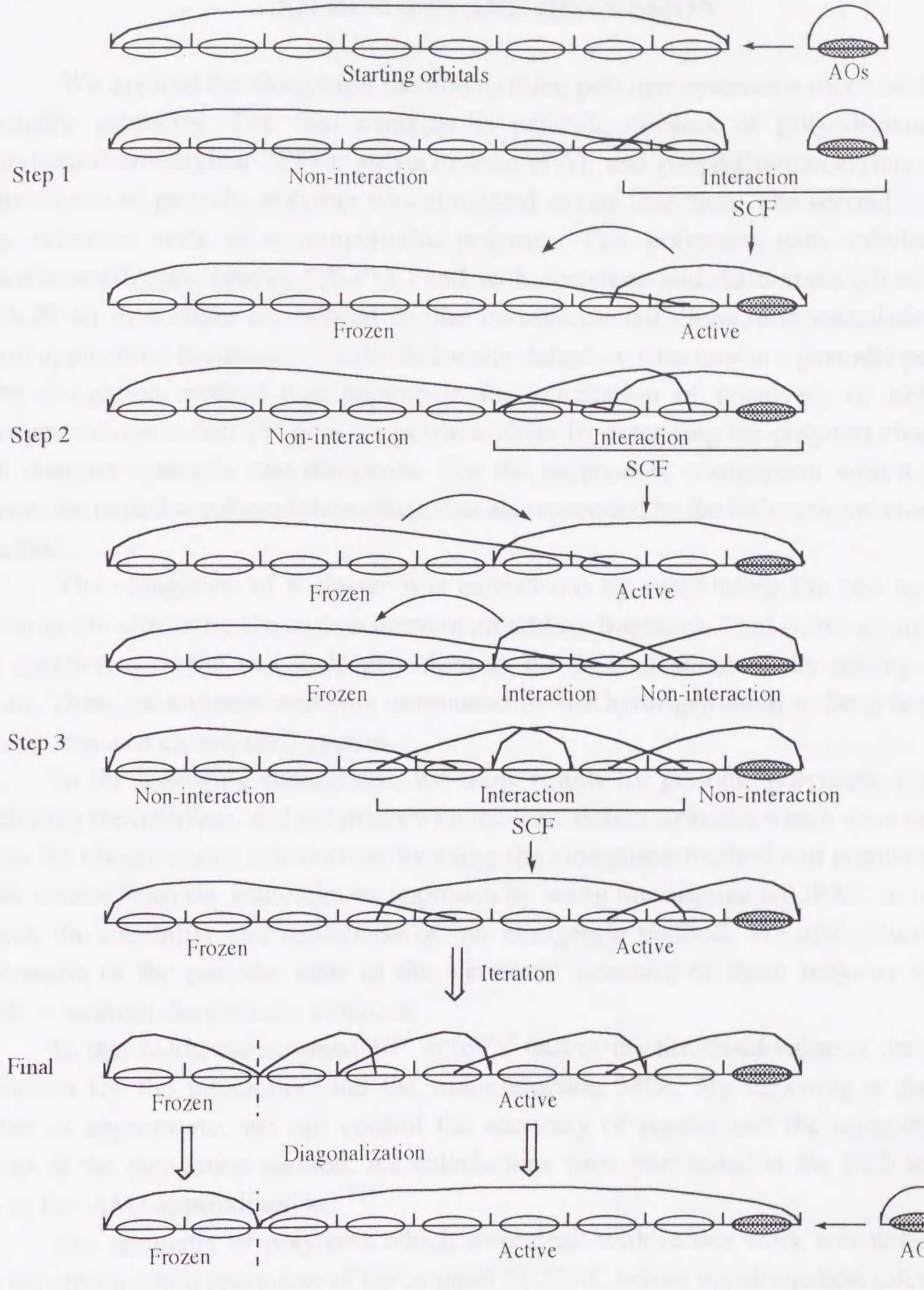


FIG. 3.4. The summary of calculation steps based on the viewpoint of orbital selection.

specify the interaction orbital space. Also, we can separate the total orbital space of the system as the active and frozen spaces, and the successive extension of a cluster series does not increase the active space after the extension by appropriate units. The division of the orbital space in this approach gives us the information on the periodicity in the electronic structure of a periodic or aperiodic polymer.

3.3. RESULTS AND DISCUSSION

We applied the elongation method to three polymer systems with or without the periodic geometry. The first example is periodic clusters of polyethylene (PE), polytetrafluoroethylene (PFE), polyacetylene (PA), and polydifluoroacetylene (PFA). The cluster of periodic polymer was elongated in one direction. The second system is the interface state in a nonperiodic polymer. The polymers with ethylene and tetrafluoroethylene blocks (PE-PFE) and with acetylene and difluoroacetylene blocks (PA-PFA) in a chain are treated by the two-directional elongation calculation. The third application is concerned with the locally defective structure in a periodic polymer. The elongation method was applied to the calculation of positively or negatively charged soliton defect (S^+ or S^-) in polyacetylene by extending the polymer chain from the charged center in two directions. For the purpose of comparison with a perfect chain, the periodic polyacetylene chain was also extended by the bidirectional elongation method.

The elongation of a cluster was carried out by substituting the end hydrogen atom in the cluster by the carbon atom in an adding fragment. That is, we regarded the 1s coefficient of the end hydrogen atom as the 2s coefficient of the adding carbon atom. Thus, each cluster end was terminated by the hydrogen atom to be able to treat the system as a closed shell system.

In the following subsections, we show results for periodic polymers, polymers including the interface, and polymers with the local defect structure which were obtained from the cluster-series calculations by using the elongation method and compare those with results from the usual cluster approach by using the original MOPAC in order to check the reliability and usefulness of our elongation method. We also describe the formation of the periodic state in the electronic structure of these polymer systems with or without the periodic structure.

In this work, we assumed 10^{-5} in $(eV)^2$ unit as the threshold value of the orbital selection for the interaction and the noninteraction MOs. By choosing a threshold value as appropriate, we can control the accuracy of results and the computational effort in the elongation method. All calculations were performed at the SCF level by using the AM1 approximation.[27,28]

The geometry of polymers which were dealt with in this work was determined by the optimization procedure of the original MOPAC before the elongation calculation was carried out. We assumed cluster molecules as planar molecules, and the optimization was performed only on the largest cluster for each polymer system by using "EF" and "PRECISE" options. Also, in the case of periodic polymer systems, "TV" option was applied to satisfy the periodic condition of the molecule. For periodic polymers, the cluster molecules of H-$[C_2H_4]_{10}$-H (PE), H-$[C_2F_4]_{10}$-H (PFE), H-$[C_2H_2]_{10}$-H (PA), and H-$[C_2F_2]_{10}$-H (PFA) were optimized by the following two-step procedures. That is, in this periodic case, the cluster including ten units was optimized at first by using "TV" option, and then, the cluster terminal at both ends was covered by two hydrogen atoms. Next, we optimized the terminal hydrogen atoms only by fixing the geometry of central units finally. The structures around the interface between different blocks of polymers were determined from the optimized geometry for the cluster molecules of H-$[C_2H_4]_{14}$-$[C_2F_4]_{14}$-H (PE-PFE) and H-$[C_2H_2]_{14}$-$[C_2F_2]_{14}$-H (PA-PFA). The defective structure of a charged soliton in polyacetylene was created from results of the geometry optimization for H-$[C_2H_2]_{20}$-$[C_5H_5]$-$[C_2H_2]_{20}$-H cluster molecule having plus or minus charge (S^+ or S^-). In extending the polymer systems, the clusters with optimized structures were divided into the unit including two carbon atoms, and then, each unit was connected with each other in accordance with the elongation method.

3.3.1. Periodic Polymers

Results for the application of the elongation method to periodic polymers are shown in this subsection. Periodic polyethylene (PE), polytetrafluoroethylene (PFE), polyacetylene (PA), and polydifluoroacetylene (PFA) were calculated at the AM1 level.

The calculated polymer systems with the periodicity and their geometrical parameters are shown in Figs. 3.5(a)-3.5(d). The extension was started from the cluster molecule with one unit including two carbon atoms and thirteen units was connected successively with the starting cluster one after another. Finally, the extended cluster had fourteen units in the chain.

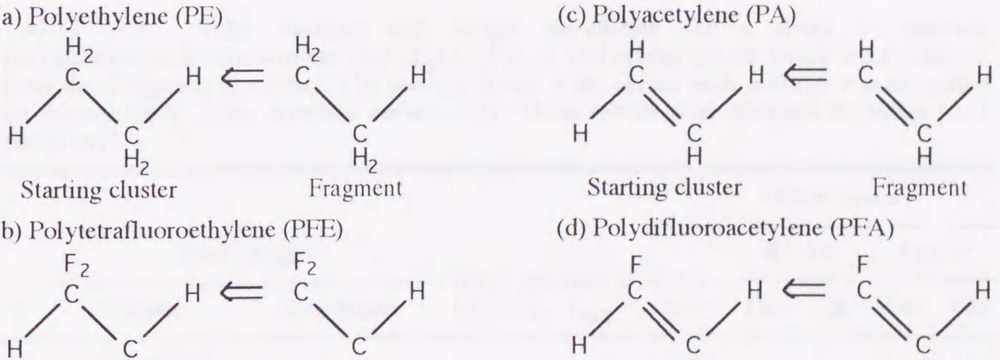

(a) Polyethylene (PE)
(b) Polytetrafluoroethylene (PFE)
(c) Polyacetylene (PA)
(d) Polydifluoroacetylene (PFA)

FIG. 3.5. The periodic polymers calculated by the one-directional elongation, (a) polyethylene, (b) polytetrafluoroethylene, (c) polyacetylene, and (d) polydifluoroacetylene. The optimized geometrical parameters are as follows: (a) r(C-C) = 1.51361 Å, r(C-H) = 1.12195 Å, ∠CCC = 111.28425° and the angle between CH bond and the polymer plane = 53.55811°, and for the terminal hydrogen atom, r(C-H) = 1.11319 Å and ∠HCC = 111.18802°; (b) r(C-C) = 1.61192 Å, r(C-F) = 1.36771 Å, ∠CCC = 109.53719° and the angle between CF bond and the polymer plane = 52.22245°, and for the terminal hydrogen atom, r(C-H) = 1.12897 Å and ∠HCC = 107.47552°; (c) r(C-C) = 1.44404 Å, r(C=C) = 1.34790 Å, r(C-H) = 1.10412 Å, ∠CCC = 122.96388° and ∠C=CH = 120.54100°, and for the terminal hydrogen atom, r(C-H) = 1.09464 Å and ∠HCC = 122.83133°; (d) r(C-C) = 1.47374 Å, r(C=C) = 1.37881 Å, r(C-F) = 1.34967 Å, ∠CCC = 123.02731° and ∠C=CF = 120.54061°, and for the terminal hydrogen atom, r(C-H) = 1.10034 Å and ∠HCC = 123.74935°. The geometry optimization was carried out for clusters which include ten units with twenty carbon atoms in the main chain.

TABLE 3.1. Total energies and energy increments for a series of periodic polyethylene clusters H-(C_2H_4)-$(C_2H_4)_n$-H and orbital spaces which were obtained from the elongation procedure. The starting cluster is the cluster with n=0 and was elongated by thirteen units in one direction successively. These results were obtained by using AM1 parameters.

					Orbital space			
	Total energy [a]				Active		Frozen	
n	Cluster	Elongation	Energy increment [b] $\Delta E_n = E_n - E_{n-1}$	Total AOs	Occ.	Vac.	Occ.	Vac.
0	-339.128714 [c]							
1	-650.800042	-650.800042 [c]	-311.671328 [c]	26	13	13	0	0
2	-962.469159	-962.469159	-311.669117	38	19	19	0	0
3	-1274.138279	-1274.138279	-311.669120	50	21	22	4	3
4	-1585.807401	-1585.807400	-311.669121	62	21	22	10	9
5	-1897.476524	-1897.476523	-311.669123	74	21	22	16	15
6	-2209.145647	-2209.145645	-311.669122	86	21	22	22	21
7	-2520.814770	-2520.814768	-311.669123	98	21	22	28	27
8	-2832.483893	-2832.483891	-311.669123	110	21	22	34	33
9	-3144.153017	-3144.153014	-311.669123	122	21	22	40	39
10	-3455.822140	-3455.822137	-311.669123	134	21	22	46	45
11	-3767.491264	-3767.491260	-311.669123	146	21	22	52	51
12	-4079.160387	-4079.160383	-311.669123	158	21	22	58	57
13	-4390.829511	-4390.829506	-311.669123	170	21	22	64	63

[a] Calculations were performed on IBM RISC System/6000 340.

[b] Values were obtained from results of the elongation method.

[c] Energies are shown in eV unit.

In Tables 3.1-3.4, total energies of each cluster with different size of PE, PFE,

TABLE 3.2. Total energies and energy increments for a series of periodic polytetrafluoroethylene clusters H-(C_2F_4)-$(C_2F_4)_n$-H and orbital spaces which were obtained from the elongation procedure. The starting cluster is the cluster with n=0 and was elongated by thirteen units in one direction successively. These results were obtained by using AM1 parameters.

					Orbital space			
	Total energy [a]				Active		Frozen	
n	Cluster	Elongation	Energy increment [b] $\Delta E_n = E_n - E_{n-1}$	Total AOs	Occ.	Vac.	Occ.	Vac.
0	-2225.512435 [c]							
1	-4422.297263	-4422.297263 [c]	-2196.784828 [c]	50	37	13	0	0
2	-6619.032676	-6619.032675	-2196.735412	74	55	19	0	0
3	-8815.756892	-8815.756887	-2196.724212	98	63	25	10	0
4	-11012.477469	-11012.477452	-2196.720565	122	64	28	27	3
5	-13209.196606	-13209.196578	-2196.719126	146	66	30	43	7
6	-15405.915099	-15405.915058	-2196.718480	170	66	30	61	13
7	-17602.633277	-17602.633221	-2196.718163	194	66	30	79	19
8	-19799.351292	-19799.351219	-2196.717998	218	66	30	97	25
9	-21996.069215	-21996.069124	-2196.717905	242	66	30	115	31
10	-24192.787087	-24192.786977	-2196.717853	266	66	30	133	37
11	-26389.504926	-26389.504797	-2196.717820	290	66	30	151	43
12	-28586.222746	-28586.222597	-2196.717800	314	66	30	169	49
13	-30782.940553	-30782.940384	-2196.717787	338	66	30	187	55

[a] Calculations were performed on IBM RISC System/6000 340.

[b] Values were obtained from results of the elongation method.

[c] Energies are shown in eV unit.

TABLE 3.3. Total energies and energy increments for a series of periodic polyacetylene clusters H-(C_2H_2)-(C_2H_2)$_n$-H and orbital spaces which were obtained from the elongation procedure. The starting cluster is the cluster with n=0 and was elongated by thirteen units in one direction successively. These results were obtained by using AM1 parameters.

	Total energy ^{a}				Orbital space			
					Active		Frozen	
n	Cluster	Elongation	Energy increment^{b} $\Delta E_n = E_n - E_{n-1}$	Total AOs	Occ.	Vac.	Occ.	Vac.
0	-310.336790^{c}							
1	-593.521691	-593.521691^{c}	-283.184901^{c}	22	11	11	0	0
2	-876.723249	-876.723249	-283.201558	32	16	16	0	0
3	-1159.927884	-1159.927882	-283.204633	42	20	18	1	3
4	-1443.133102	-1443.133098	-283.205216	52	21	18	5	8
5	-1726.338417	-1726.338409	-283.205311	62	21	18	10	13
6	-2009.543732	-2009.543719	-283.205310	72	21	18	15	18
7	-2292.749033	-2292.749013	-283.205294	82	21	18	20	23
8	-2575.954320	-2575.954294	-283.205281	92	21	18	25	28
9	-2859.159598	-2859.159564	-283.205270	102	21	18	30	33
10	-3142.364869	-3142.364827	-283.205263	112	21	18	35	38
11	-3425.570136	-3425.570084	-283.205257	122	21	18	40	43
12	-3708.775399	-3708.775339	-283.205255	132	21	18	45	48
13	-3991.980661	-3991.980591	-283.205252	142	21	18	50	53

[a] Calculations were performed on IBM RISC System/6000 340.

[b] Values were obtained from results of the elongation method.

[c] Energies are shown in eV unit.

PA, and PFA by using the conventional cluster model and the elongation approach are

TABLE 3.4. Total energies and energy increments for a series of periodic polydifluoroacetylene clusters H-(C_2F_2)-(C_2F_2)$_n$-H and orbital spaces which were obtained from the elongation procedure. The starting cluster is the cluster with n=0 and was elongated by thirteen units in one direction successively. These results were obtained by using AM1 parameters.

	Total energy ^{a}				Orbital space			
					Active		Frozen	
n	Cluster	Elongation	Energy increment^{b} $\Delta E_n = E_n - E_{n-1}$	Total AOs	Occ.	Vac.	Occ.	Vac.
0	-1253.552949^{c}							
1	-2479.189308	-2479.189309^{c}	-1225.636360^{c}	34	23	11	0	0
2	-3704.807765	-3704.807765	-1225.618456	50	34	16	0	0
3	-4930.420510	-4930.420506	-1225.612741	66	42	21	3	0
4	-6156.030379	-6156.030366	-1225.609860	82	45	26	11	0
5	-7381.638665	-7381.638635	-1225.608269	98	46	28	21	3
6	-8607.246033	-8607.245981	-1225.607346	114	46	29	32	7
7	-9832.852846	-9832.852764	-1225.606783	130	46	30	43	11
8	-11058.459309	-11058.459192	-1225.606428	146	46	30	54	16
9	-12284.065546	-12284.065386	-1225.606194	162	46	30	65	21
10	-13509.671633	-13509.671424	-1225.606038	178	46	30	76	26
11	-14735.277616	-14735.277355	-1225.605931	194	46	30	87	31
12	-15960.883529	-15960.883211	-1225.605856	210	46	30	98	36
13	-17186.489391	-17186.489015	-1225.605804	226	46	30	109	41

[a] Calculations were performed on IBM RISC System/6000 340.

[b] Values were obtained from results of the elongation method.

[c] Energies are shown in eV unit.

listed. Also, energy increments in extension cycles of clusters obtained from the results of the elongation method are summarized in Tables 3.1-3.4. Results of total energies obtained from both calculations are in good agreement within the order of almost 10^{-3}-10^{-5} in eV unit for all periodic polymers. This accuracy of results in the elongation calculation is quite satisfactory indeed. The absolute value of the largest error in our cluster-series approach is only 0.000 376 eV in the case of PFA with n=13. Furthermore, from the results of the energy per one connected unit which is defined as the increment in the total energy of two continuous elongation calculations listed in Tables 3.1-3.4, we see that the convergence of the energy per unit for the hydrocarbon polymers (PE and PA) is faster than for the fluorine-substituted polymers (PFE and PFA) as follows: the energy of PE or PA becomes almost constant at two-units extension while PFE or PFA has the converged energy after the fifth or sixth elongation. Finally, when the cluster includes fourteen units, each periodic polymer has the following converged energy per its unit, that is, -311.6691 eV (PE), -2196.7178 eV (PFE), -283.2053 eV (PA), and -1225.6058 eV (PFA).

The net charge on each carbon atom in the final polymer chain with fourteen units is shown in Fig. 3.6. The plotted line is flat in the central part of the periodic chain, and it suggests that the electronic state in the flat part is bulky. The end effect appears as the deviation from the flat line at both cluster ends, and the effect is much extended in the acetylene chains (PA and PFA) than the ethylene chains (PE and PFE). In these calculations, we merely elongated the clusters one after another successively

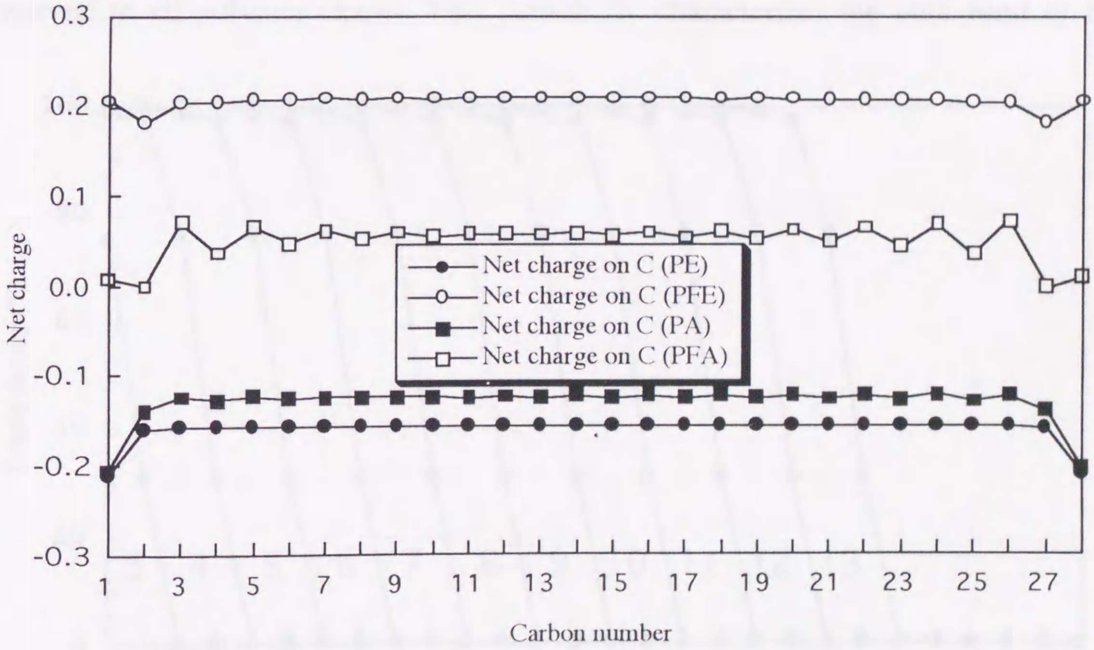
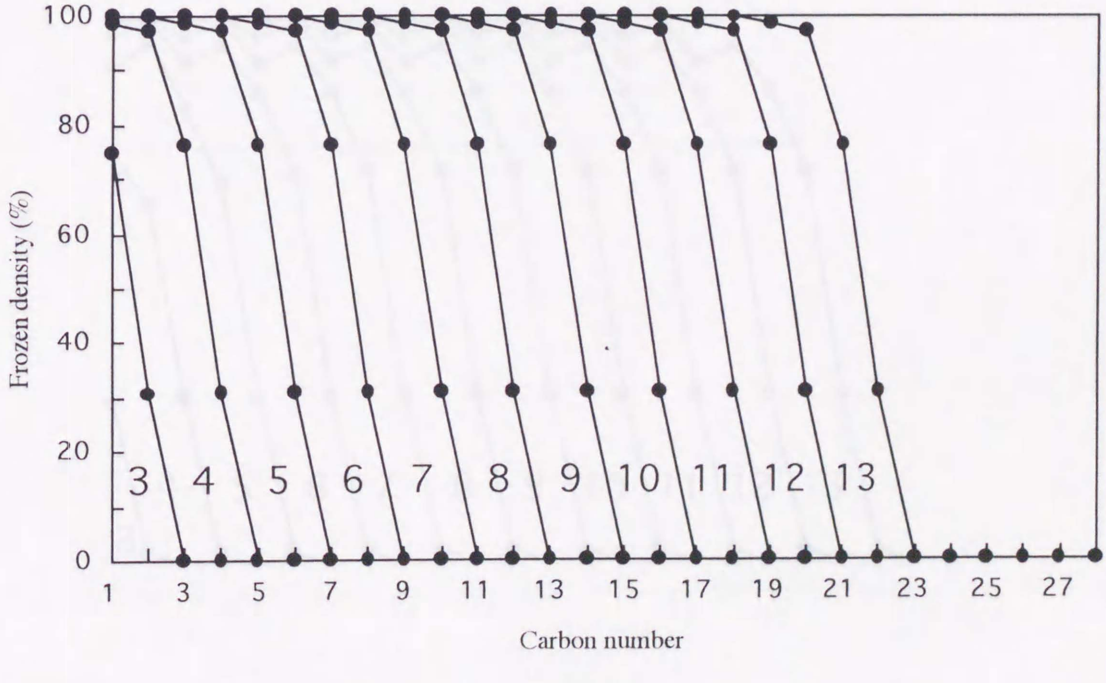


FIG. 3.6. The distribution of the net charge on each carbon atom in the final polymers of ethylene (PE), tetrafluoroethylene (PFE), acetylene (PA), and difluoroacetylene (PFA) with 14 units extended by the elongation method. The atom C1 is the end atom in the starting cluster and the atom C28 is the end atom in the last fragment.

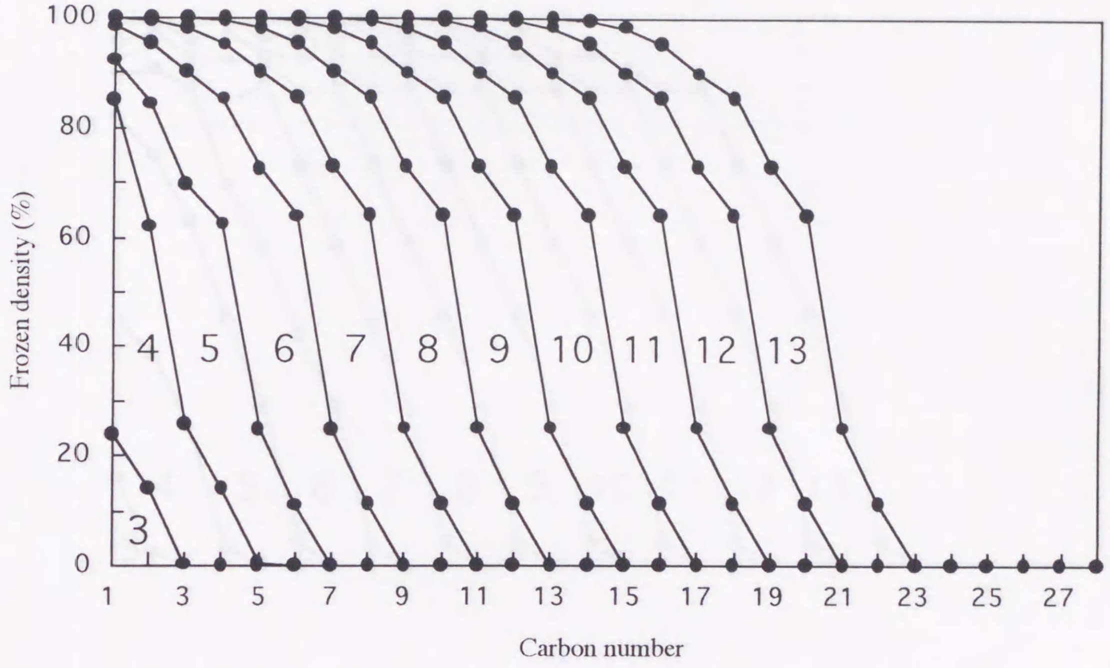
in one direction, that is, the special attention concerning the symmetry of molecules was not considered at all. But, resulting charge distributions on polymer chains reflect the symmetrical geometry of molecules.

We show orbital spaces which are determined in cluster-series calculations by using the elongation method in Tables 3.1 (PE), 3.2 (PFE), 3.3 (PA), and 3.4 (PFA). The freezing of molecular orbitals (MOs) in size-extending calculations of each polymer system appears in the third extension for all systems concerned. In elongation cycles, the number of active MOs becomes constant at n=3 (PE), n=5 (PFE), n=4 (PA), and n=7 (PFA). The number of active MOs remains as a constant at n=13 because we assumed the periodic sequence of geometry and the end effect in the geometry of terminal unit of polymers is not included. The constant active space indicates that the constant MOs are newly frozen against the connection of a new adding fragment, that is, six occupied and vacant MOs (PE), eighteen occupied and six vacant MOs (PFE), five occupied and vacant MOs (PA), and eleven occupied and five vacant MOs are newly frozen in each system. This situation suggests that the electronic state in the cluster is stationary against the size extension by the addition of fragments and the periodicity of the electronic structure can be extracted by the periodic freezing pattern of the electron density as has been pointed out in the previous works of our group.[18-20]

Next, to demonstrate the periodic condition based on the freezing pattern, diagrams of the frozen density on carbon atoms in each chain, which is the percentage of the frozen electron density obtained from frozen occupied MOs, are drawn in Figs. 3.7(a)-3.7(d). As is shown in these figures, the formation of highly periodic patterns are observed in all polymer chains. This periodicity characterizes the bulk limit of the

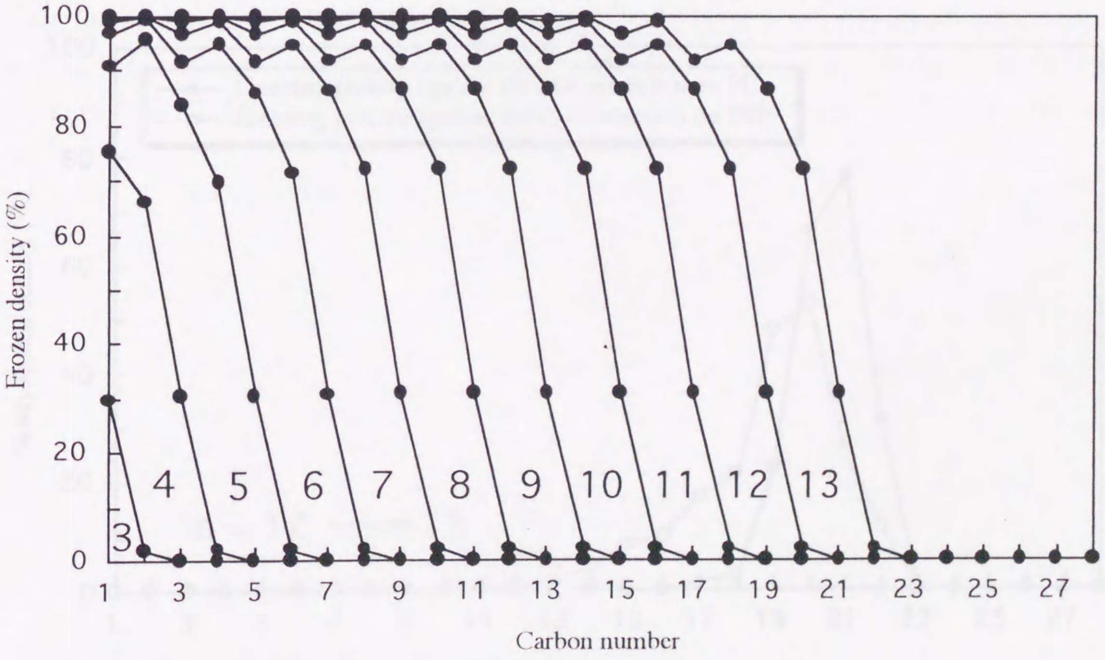


(a) PE

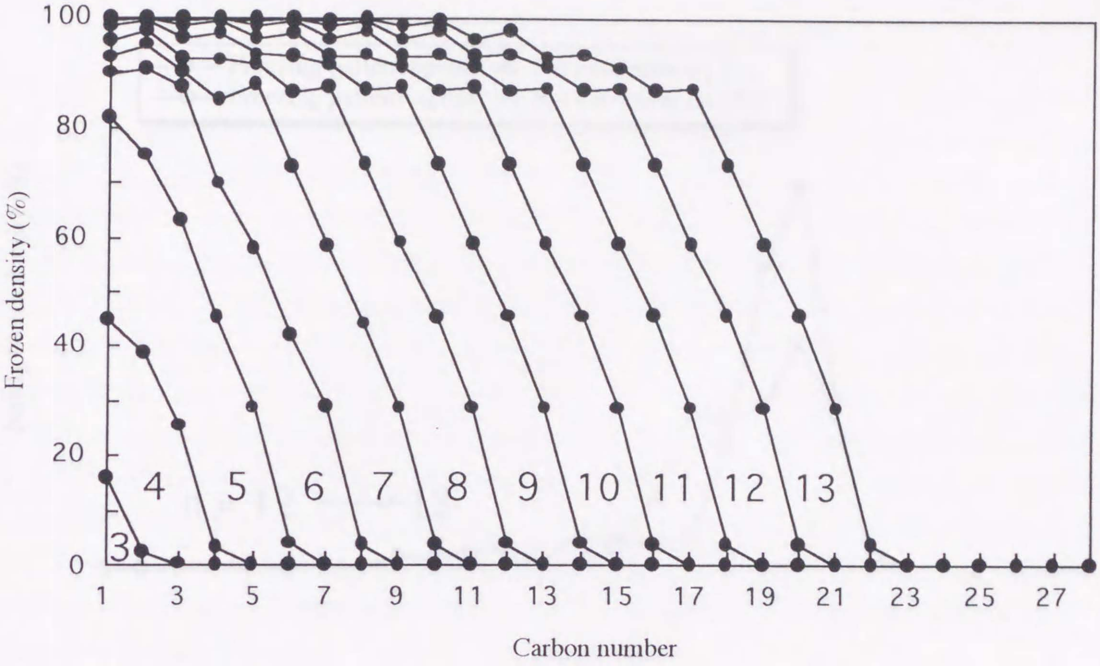


(b) PFE

electronic state with the translational symmetry. The freezing patterns of the last extension with n=13 are given in Figs. 3.8(a) and 3.8(b). In the case of hydrocarbon chains, the electron density around C20-C21 (PE) and C19-C20 (PA) can be frozen against the bonding with C27-C28. On the other hand, the frozen density in fluorine substituted systems of PFE and PFA is distributed in wide range of the chain in



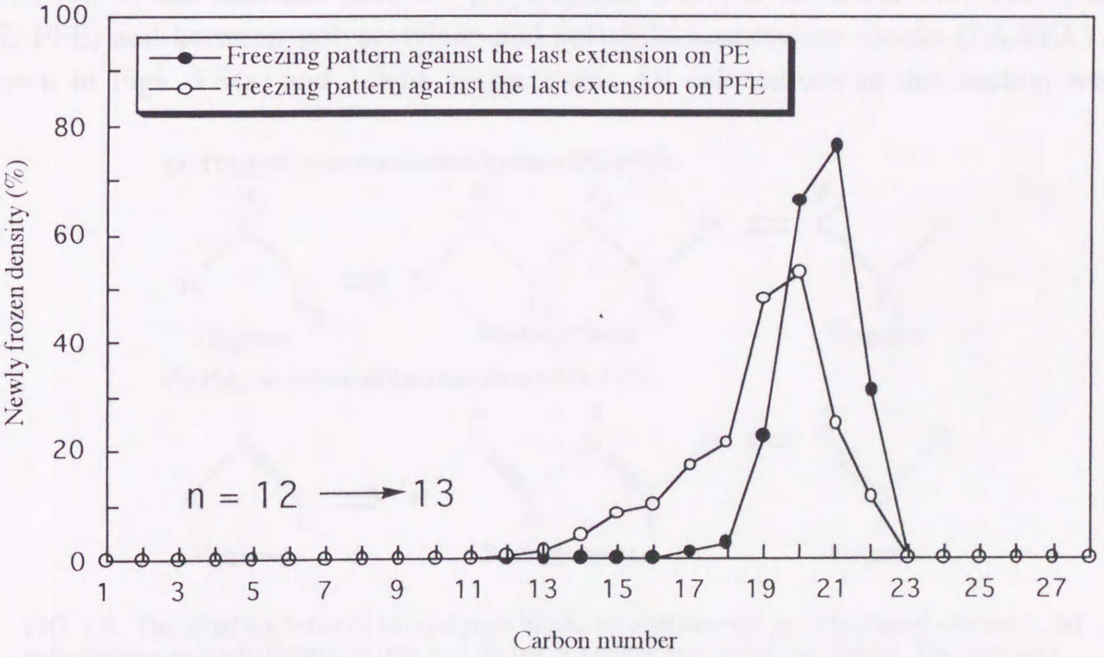
(c) PA



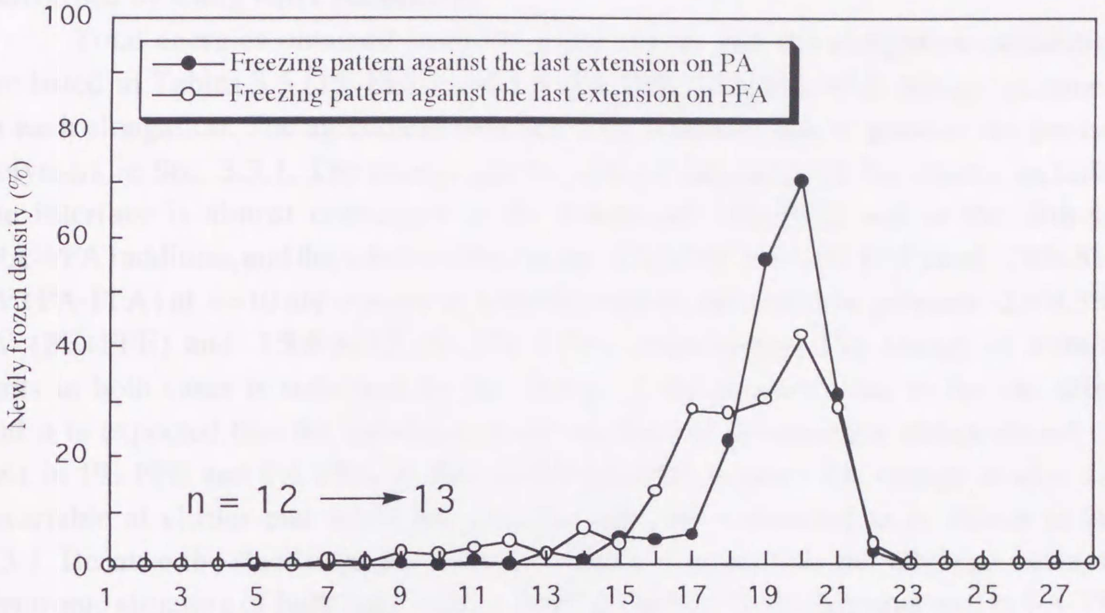
(d) PFA

FIG. 3.7. The freezing pattern of the electron density on each carbon atom in elongation cycles, (a) PE, (b) PFE, (c) PA, (d) PFA. The number of connected fragments with the starting cluster is included in the graph. The atom C1 is the end atom in the starting cluster and the atom C28 is the end atom in the last fragment.

comparison with PE and PA. In this way, we can know the periodicity at the MO level.



(a) PE and PFE



(b) PA and PFA

FIG. 3.8. The plot of the newly frozen density on each carbon atom against the last extension of the system, (a) ethylene system and (b) acetylene system. The C27 and C28 carbon atoms are included in the last connected fragment.

3.3.2. Interfaces between Polymer Blocks

In this subsection, we report results of the application by the two-directional extension to the interface between polyethylene and polytetrafluoroethylene blocks (PE-PFE) and between polyacetylene and polydifluoroacetylene blocks (PA-PFA) as shown in Figs. 3.9(a) and 3.9(b), respectively. All calculations in this section were

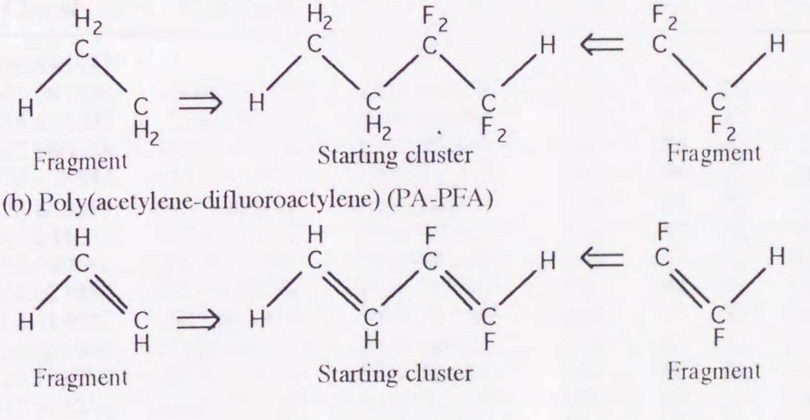


FIG. 3.9. The interface between two polymer blocks by applying the two-directional extension, (a) polyethylene-polytetrafluoroethylene and (b) polyacetylene-polydifluoroacetylene. The geometry of the system was obtained by the optimization calculation for the final polymer as is mentioned in the text.

performed by using AM1 parameters.

Total energies obtained from the usual cluster and the elongation calculations are listed in Tables 3.5 (PE-PFE) and 3.6 (PA-PFA) together with energy increments in each elongation. The agreement between both results is also as good as the periodic polymers in Sec. 3.3.1. The energy per two added fragments of the cluster including the interface is almost converged at the fourth-unit (PE-PFE) and at the fifth-unit (PA-PFA) addition, and the values of the energy -2508.3869 eV (PE-PFE) and -1508.8115 eV (PA-PFA) at $n=10$ are consistent with the sum of each periodic polymer -2508.3869 eV (PE+PFE) and -1508.8111 eV (PA+PFA), respectively. The energy of terminal units in both cases is stabilized by the change of the geometry due to the end effect, and it is expected that the influence of the cluster end is restricted within almost one unit in PE-PFE and PA-PFA at the cluster terminal because the energy is also kept invariable at cluster end when the periodic units are connected as is shown in Sec. 3.3.1. Because the stabilization in acetylene chain is larger than the ethylene chain, the electronic structure of bulk state may be more perturbed by the terminal unit in PA-PFA chain than in PE-PFE chain.

In order to view the influence of the interface bonding and the end effect of the cluster terminal on the electronic structure of the polymer system at the molecular orbital level, the orbital spaces of PE-PFE and PA-PFA interfaces in elongation cycles are shown in Tables 3.5 and 3.6. The freezing of molecular orbitals begins from $n=3$

TABLE 3.5. Total energies and energy increments for a cluster series of block copolymer which are including the interface between two blocks of polyethylene and polytetrafluoroethylene H-$(C_2H_4)_n$-$(C_2H_4$-$C_2F_4)$-$(C_2F_4)_n$-H and the number of molecular orbitals included in the divided orbital space at each extension cycle by the elongation method. The starting cluster with n=0 was elongated from both ends of the cluster by thirteen units in two directions successively. These results were obtained by using the AM1 method.

	Total energy [a]				Orbital space			
					Active		Frozen	
n	Cluster	Elongation	Energy increment [b] $\Delta E_n = E_n - E_{n-1}$	Total AOs	Occ.	Vac.	Occ.	Vac.
0	-2536.836533 [c]							
1	-5045.287508	-5045.287508 [c]	-2508.450975 [c]	74	49	25	0	0
2	-7553.692607	-7553.692607	-2508.405099	110	73	37	0	0
3	-10062.086653	-10062.086643	-2508.394036	146	83	47	14	2
4	-12570.476844	-12570.476821	-2508.390178	182	86	52	35	9
5	-15078.865419	-15078.865382	-2508.388561	218	87	52	58	21
6	-17587.253235	-17587.253182	-2508.387800	254	87	52	82	33
7	-20095.640661	-20095.640590	-2508.387408	290	87	52	106	45
8	-22604.027869	-22604.027780	-2508.387190	326	87	52	130	57
9	-25112.414942	-25112.414833	-2508.387053	362	87	52	154	69
10	-27620.801903	-27620.801774	-2508.386941	398	87	52	178	81
11	-30129.188709	-30129.188560	-2508.386786	434	87	52	202	93
12	-32637.575259	-32637.575089	-2508.386529	470	87	52	226	105
13	-35145.977028	-35145.976835	-2508.401746	506	87	51	250	118

[a] Calculations were performed on IBM RISC System/6000 340.

[b] Values were obtained from results of the elongation method.

[c] Energies are shown in eV unit.

TABLE 3.6. Total energies and energy increments for a cluster series of block copolymer which are including the interface between two blocks of polyacetylene and polydifluoroacetylene $H\text{-}(C_2H_2)_n\text{-}(C_2H_2\text{-}C_2F_2)\text{-}(C_2F_2)_n\text{-}H$ and the number of molecular orbitals included in the divided orbital space at each extension cycle by the elongation method. The starting cluster with n=0 was elongated from both ends of the cluster by thirteen units in two directions successively. These results were obtained by using the AM1 method.

					Orbital space			
	Total energy [a]		Energy increment [b]	Total	Active		Frozen	
n	Cluster	Elongation	$\Delta E_n = E_n - E_{n-1}$	AOs	Occ.	Vac.	Occ.	Vac.
0	-1536.454447 [c]							
1	-3045.309992	-3045.309992 [c]	-1508.855545 [c]	54	33	21	0	0
2	-4554.141914	-4554.141914	-1508.831922	80	49	31	0	0
3	-6062.964018	-6062.964011	-1508.822097	106	62	40	3	1
4	-7571.781362	-7571.781331	-1508.817320	132	65	45	16	5
5	-9080.596188	-9080.596136	-1508.814805	158	69	49	28	12
6	-10589.409610	-10589.409516	-1508.813380	184	66	47	47	24
7	-12098.222210	-12098.222074	-1508.812558	210	66	47	63	34
8	-13607.034288	-13607.034100	-1508.812026	236	66	48	79	43
9	-15115.846046	-15115.845798	-1508.811698	262	66	48	95	53
10	-16624.657616	-16624.657307	-1508.811509	288	66	48	111	63
11	-18133.469335	-18133.468960	-1508.811653	314	66	48	127	73
12	-19642.283202	-19642.282758	-1508.813798	340	66	48	143	83
13	-21151.122718	-21151.122189	-1508.839431	366	67	46	158	95

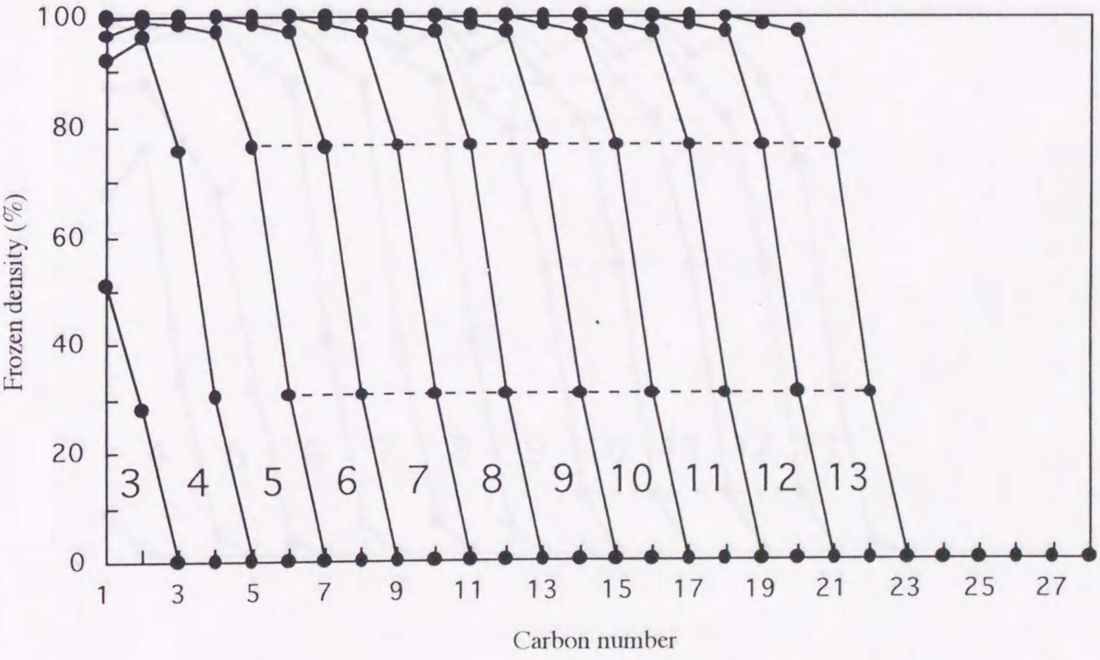
[a] Calculations were performed on IBM RISC System/6000 340.

[b] Values were obtained from results of the elongation method.

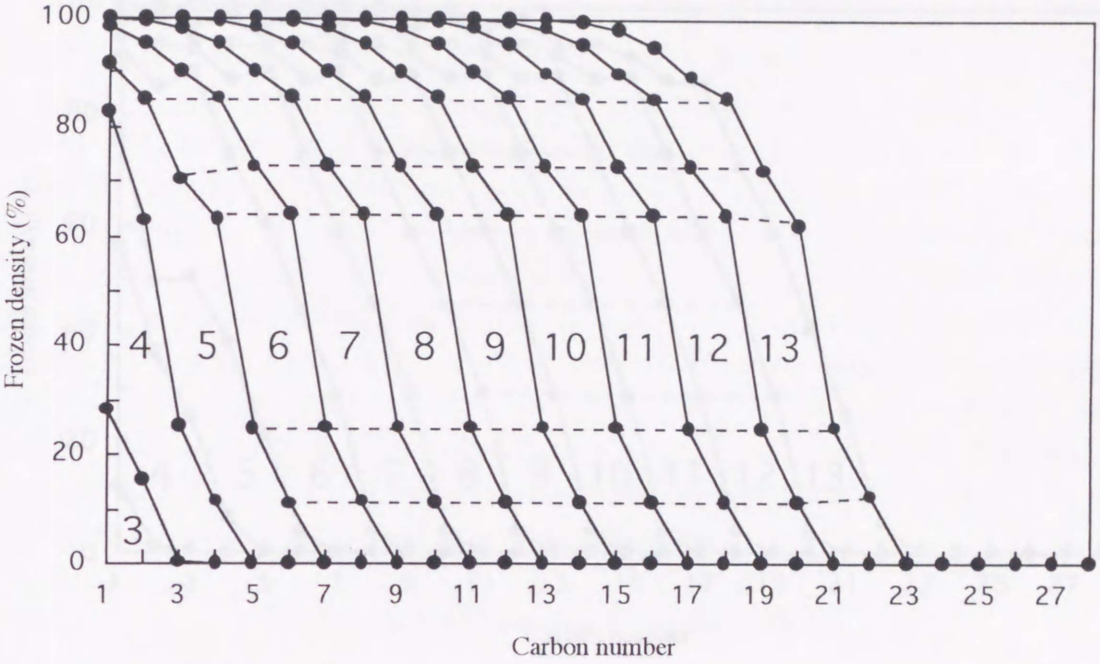
[c] Energies are shown in eV unit.

in PE-PFE and n=3 in PA-PFA. The dimension of the active space for PE-PFE interface becomes constant from n=5 to n=12 as 87 occupied and 52 vacant MOs, and 24 occupied and 12 vacant MOs are newly frozen against the 6-12th extension and the number of newly frozen MOs in those elongations is the same with the sum of that in the case of periodic PE (6 occupied and 6 vacant MOs) only and periodic PFE (18 occupied and 6 vacant MOs) only. Thus, the formation of electronic states with the periodicity in PE-PFE is suggested, that is, it seems that the effect of the interface is included in the extension process from n=1 to n=4. Against the addition of the last fragment at n=13, since the dimension of active orbitals is the same with n=5-12 except that the number of vacant orbitals decreases into 51 MOs, the periodicity of the electronic state in PE-PFE may not be destroyed by the unit at the cluster terminal with the end effect. On the other hand, in elongation cycles for the cluster series of PA-PFA interface, the constant active space with 66 occupied and 48 vacant MOs is limited within the extension cycles from n=8 to n=12 and the dimension of newly frozen space with 16 occupied and 10 vacant MOs against the 9-12th connection is consistent with the sum of that for periodic PA (5 occupied and 5 vacant MOs) and PFA (11 occupied and 5 vacant MOs) which form periodic electronic states as is shown in Sec. 3.3.1. At n=13, the space of active occupied MOs increases into 67 MOs and that of vacant MOs decreases into 46 MOs, thus, the periodic condition of the electronic structure may be perturbed by the influence of the interface until n=7 and by the end effect at n=13 in PA-PFA. As shown above, the range of the periodic state in PA-PFA is smaller than in PE-PFE. It may be caused by the long range interaction in the π electron system.

We have pointed out that the effect of a local defect in a periodic polymer chain can be detected as the disorder on the periodic freezing pattern of electron density.[20] Indeed, in the case of local interfaces like as PE-PFE and PA-PFA in this work, the disordering patterns are obtained and shown in Figs. 3.10(a)-3.10(d). A little change from the periodic condition in the pattern of PE-PFE appears and is well localized within the cluster center at the interface bonding. The aperiodic freezing is mainly limited within the central one unit in each ethylene and fluoroethylene block and the periodicity of electronic structure in the region around the interface is well preserved. The 24 occupied MOs which are newly frozen at each extension cycle contribute to the formation of the periodic freezing in extensions from n=6 to n=13. Moreover, it is found that the end effect included in the terminal unit does not affect on the electronic state at the terminal of ethylene and fluoroethylene chains judging from the nondisordered freezing pattern with n=13 at the region as is shown in Figs. 3.10(a) and 3.10(b). In contrast to the σ electron system of PE-PFE, in Figs. 3.10(c) and 3.10(d) of PA-PFA, the freezing pattern without the periodicity around PA-PFA interface is extracted in the wide range of the π electronic chain with conjugated acetylene backbone. The influence of the interface may be reached to C10-C11 in acetylene block and to C7-C8 in fluoroacetylene block at a viewpoint of the periodicity of the freezing pattern. This range with perturbed pattern suggests that the bulk state is more disturbed in PA chain than in PFA chain by the interface bonding. In the extensions which form the periodic

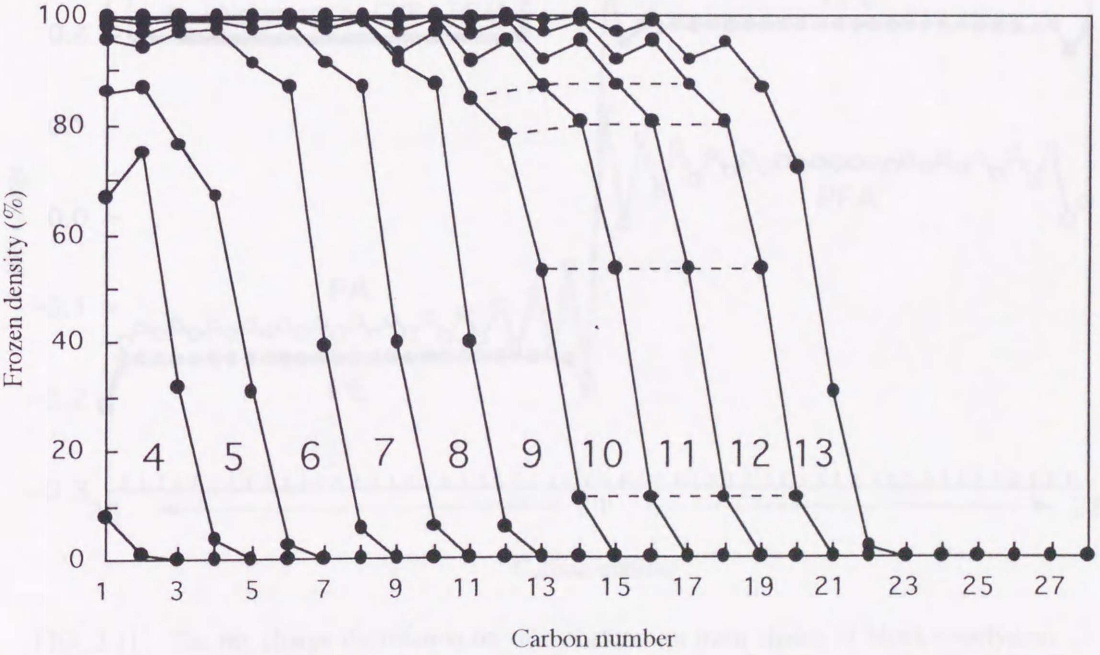


(a) PE

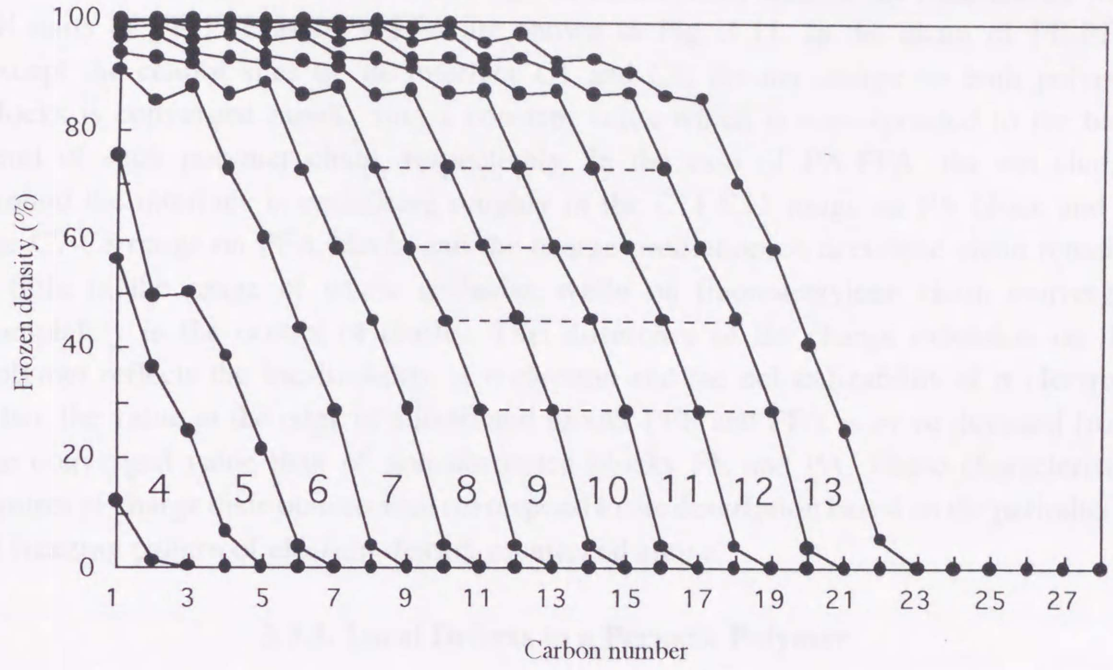


(b) PFE

pattern at n=9-12, the 16 occupied MOs are newly frozen at each elongation process. The last 13th pattern of PA-PFA chain is disturbed by the end effect in the terminal fragment at both ends of acetylene and fluoroacetylene blocks. By these analyses of the orbital space determined in elongation calculations, we can know the periodic and the aperiodic characters of electronic state in a nonperiodic polymer.



(c) PA



(d) PFA

FIG. 3.10. The freezing pattern of each block forming PE-PFE and PA-PFA interfaces, (a) PE, (b) PFE, (c) PA, and (d) PFA. The first carbon atom corresponds to the atom at the interface on the center of chain and the 28th carbon atom corresponds to the chain end in each block. The number of connected fragments with the starting cluster is included in the graph.

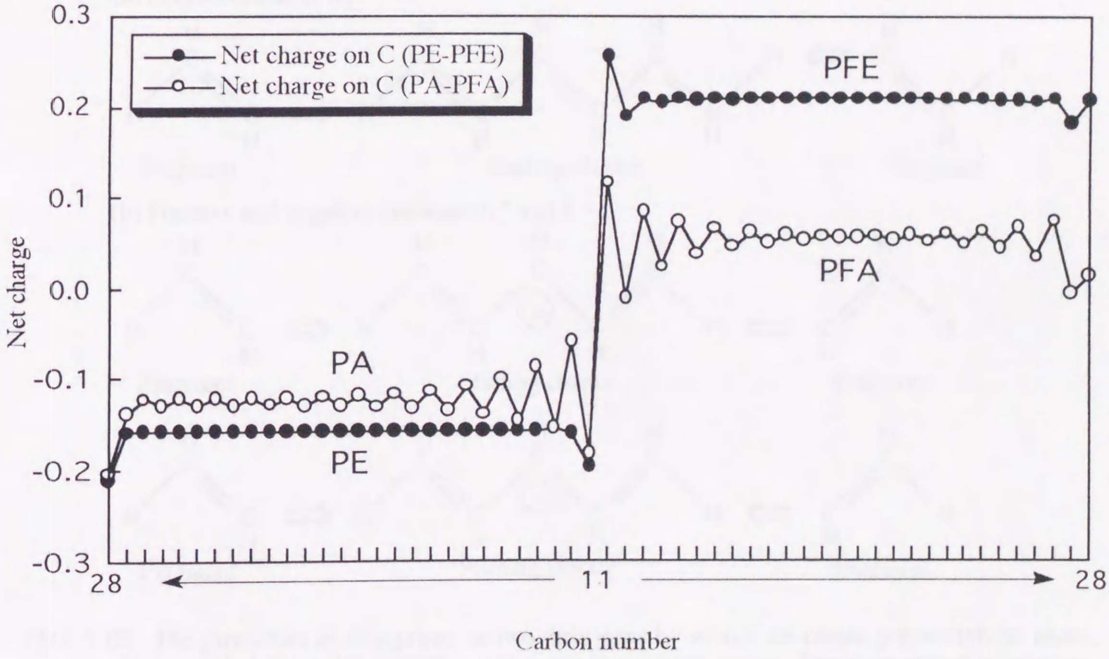


FIG. 3.11. The net charge distribution on carbon atoms in main chains of block copolymers including PE-PFE and PA-PFA interfaces. The sites numbered as 1 are the central carbon atoms forming the interface between each block and the sites numbered as 28 are the terminal carbon atoms in each block.

The distributions of the net charge on each carbon atom in the final cluster with 28 units of PE-PFE and PA-PFA are shown in Fig. 3.11. In the chain of PE-PFE, except the central sites of the interface C1 and C2, the net charge on both polymer blocks is converged rapidly into a constant value which is corresponded to the bulk limit of each polymer chain, respectively. In the case of PA-PFA, the net charge around the interface is oscillating roughly in the C11-C12 range on PA block and in the C7-C8 range on PFA block, and the charge oscillation on acetylene chain remains a little in the range of whole molecule while on fluoroacetylene chain converges completely in the central of cluster. This difference of the charge extension on the polymer reflects the localizability of σ electron and the delocalizability of π electron. Also, the value at the edge of substituted blocks PFE and PFA is more deviated from the converged value than of nonsubstituted blocks PE and PA. These characteristic natures of charge distributions well correspond to the description based on the periodicity of freezing pattern of electron density mentioned above.

3.3.3. Local Defects in a Periodic Polymer

Results for the periodic polyacetylene (PA) shown in Fig. 3.12(a) and the polyacetylene including a solitonic defect with plus or minus charge (S^+ or S^-) shown in Fig. 3.12(b) were obtained by using the AM1 method and are described in this section.

Here, before we show results by the elongation calculation, we mention a

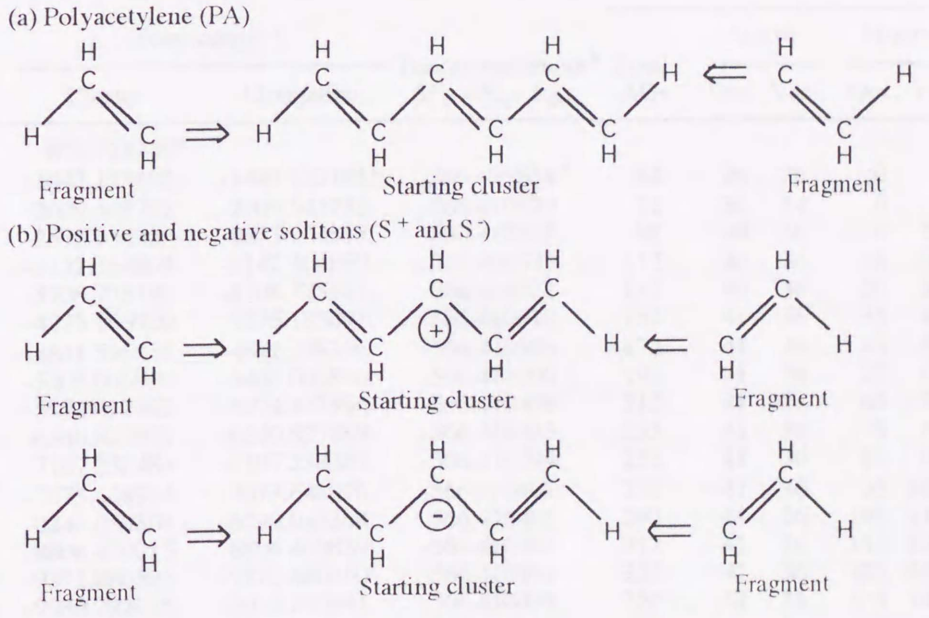


FIG. 3.12. The procedure of elongation in two directions by which we create polyacetylene chain, (a) periodic neutral chain and (b) positive and negative solitonic chains. The geometrical parameters of periodic polyacetylene used in the calculation are the same with those in Fig. 3.5. Also, polyacetylene with charged-soliton defects was optimized and the optimized structure was used in calculations as described in the text.

characteristic feature of charged-solitonic defect structures obtained by the optimization procedure briefly. A feature which characterizes the soliton defect may be considered as the change in the bond alternation on the main chain which consists of conjugated carbon atoms.[29] So, we checked the difference in the bond length between neighboring single and double bonds at each site in the optimized cluster. From the change in these differences, the bond alternation are almost recovered on the site C15 in half-side of the chain, and thus, the charged defects S^+ and S^- are almost localized within several units at the center in the chain. On the terminal, the alternating pattern is disturbed by the influence of the cluster end.

The total energies of PA, S^+, and S^- are listed in Tables 3.7-3.9 and the corresponding energy increments are also shown in these tables. The results obtained by using the cluster model and the elongation method agree excellently with each other. The energy per added two units of PA is almost constant in elongations and the value -566.4105 eV is determined at n=20. The energy increments for S^+ and S^- indicate that the energies of these defects are converged at the seventh elongation in which the elongated cluster has 33 carbon atoms in the chain in which main structural disorder is contained as mentioned above. The polymers with S^+ and S^- have the

TABLE 3.7. Total energies and energy increments for a cluster series of periodic polyacetylene H-$(C_2H_2)_n$-$(C_2H_2)_3$-$(C_2H_2)_n$-H. The dimension of each orbital space determined by the successive elongation calculations. Twenty units were connected successively with both ends of the starting cluster having n=0 by the two-directional elongation. Results were obtained by using the AM1 Hamiltonian.

					Orbital space			
	Total energy[a]				Active		Frozen	
n	Cluster	Elongation	Energy increment[b] $\Delta E_n = E_n - E_{n-1}$	Total AOs	Occ.	Vac.	Occ.	Vac.
0	-876.723249[c]							
1	-1443.133102	-1443.133103[c]	-566.409854[c]	52	26	26	0	0
2	-2009.543732	-2009.543732	-566.410629	72	36	34	0	2
3	-2575.954320	-2575.954317	-566.410585	92	40	36	6	10
4	-3142.364869	-3142.364859	-566.410542	112	40	36	16	20
5	-3708.775399	-3708.775381	-566.410522	132	40	36	26	30
6	-4275.185920	-4275.185891	-566.410510	152	41	36	35	40
7	-4841.596436	-4841.596396	-566.410505	172	41	36	45	50
8	-5408.006950	-5408.006896	-566.410500	192	41	36	55	60
9	-5974.417462	-5974.417394	-566.410498	212	41	36	65	70
10	-6540.827973	-6540.827889	-566.410495	232	41	36	75	80
11	-7107.238484	-7107.238383	-566.410494	252	41	36	85	90
12	-7673.648994	-7673.648876	-566.410493	272	41	36	95	100
13	-8240.059505	-8240.059368	-566.410492	292	41	36	105	110
14	-8806.470015	-8806.469859	-566.410491	312	41	36	115	120
15	-9372.880525	-9372.880350	-566.410491	332	41	36	125	130
16	-9939.291035	-9939.290841	-566.410491	352	41	36	135	140
17	-10505.701545	-10505.701331	-566.410490	372	41	36	145	150
18	-11072.112055	-11072.111821	-566.410490	392	41	36	155	160
19	-11638.522565	-11638.522311	-566.410490	412	41	36	165	170
20	-12204.933074	-12204.932801	-566.410490	432	41	36	175	180

[a] Calculations were performed on IBM RISC System/6000 340.

[b] Values were obtained from results of the elongation method.

[c] Energies are shown in eV unit.

TABLE 3.8. Total energies and energy increments for a solitonic polyacetylene cluster-series including one plus charge in the polymer chain H-$(C_2H_2)_n$-$(C_2H_2$-CH-$C_2H_2)$-$(C_2H_2)_n$-H. The dimension of each orbital space determined by the successive elongation calculations. Twenty units were connected successively with both ends of the starting cluster having n=0 by the two-directional elongation. Results were obtained by using the AM1 Hamiltonian.

	Total energy [a]		Energy increment [b] $\Delta E_n = E_n - E_{n-1}$	Total AOs	Orbital space			
					Active		Frozen	
n	Cluster	Elongation			Occ.	Vac.	Occ.	Vac.
0	-727.009323 [c]							
1	-1294.095528	-1294.095528 [c]	-567.086205 [c]	47	23	24	0	0
2	-1860.833218	-1860.833218	-566.737690	67	33	34	0	0
3	-2427.417913	-2427.417909	-566.584691	87	43	44	0	0
4	-2993.921775	-2993.921768	-566.503859	107	53	52	0	2
5	-3560.381511	-3560.381491	-566.459723	127	54	55	9	9
6	-4126.817576	-4126.817528	-566.436037	147	44	45	29	29
7	-4693.241204	-4693.241134	-566.423606	167	43	43	40	41
8	-5259.658418	-5259.658323	-566.417189	187	42	42	51	52
9	-5826.072323	-5826.072201	-566.413878	207	42	38	61	66
10	-6392.484539	-6392.484401	-566.412200	227	42	38	71	76
11	-6958.895865	-6958.895713	-566.411312	247	40	36	83	88
12	-7525.306742	-7525.306576	-566.410863	267	40	36	93	98
13	-8091.717387	-8091.717212	-566.410636	287	40	36	103	108
14	-8658.127921	-8658.127738	-566.410526	307	40	36	113	118
15	-9224.538403	-9224.538214	-566.410476	327	40	36	123	128
16	-9790.948891	-9790.948695	-566.410481	347	40	36	133	138
17	-10357.359477	-10357.359274	-566.410579	367	40	36	143	148
18	-10923.770457	-10923.770245	-566.410971	387	40	36	153	158
19	-11490.183497	-11490.183276	-566.413031	407	40	36	163	168
20	-12056.609594	-12056.609361	-566.426085	427	42	36	171	178

[a] Calculations were performed on IBM RISC System/6000 340.
[b] Values were obtained from results of the elongation method.
[c] Energies are shown in eV unit.

energy per combined two units at n=17 as -566.4106 eV and -566.4113 eV, respectively. In connecting of a few units at terminal, the stabilization in the energy occurs.

The orbital spaces of PA, S^+, and S^- determined by the elongation procedure are listed in Tables 3.7-3.9. As is expected from the constant increment in the energy per two units of PA listed in Table 3.7, the convergence into the constant active space is obtained quickly and 41 occupied and 36 vacant MOs are included in the space. In the case of the charged solitons, the number of MOs included in the active space is almost constant at the seventh extension. The active space is constant perfectly at n=11-19 in S^+ and n=12-18 in S^- and this results suggests that the electronic states become nearly periodic as the bulk limit of periodic PA. In comparison with PA, the delay of freezing of MOs in S^+ and S^- which may be caused by the influence of a given charge is detected, that is, the first frozen MOs appear against the second (vacant MOs) and the third (occupied MOs) connection of the fragment in neutral PA while against the fourth (vacant MOs) and the fifth (occupied MOs) in S^+ and S^-. The number of newly frozen 10 occupied and vacant MOs against the 12-19th (S^+) and the 13-18th (S^-) extensions agrees with that in PA.

TABLE 3.9. Total energies and energy increments for a solitonic polyacetylene cluster-series including one minus charge in the polymer chain $H-(C_2H_2)_n-(C_2H_2-CH-C_2H_2)-(C_2H_2)_n-H$. The dimension of each orbital space determined by the successive elongation calculations. Twenty units were connected successively with both ends of the starting cluster having $n=0$ by the two-directional elongation. Results were obtained by using the AM1 Hamiltonian.

	Total energy [a]				Orbital space			
					Active		Frozen	
n	Cluster	Elongation	Energy increment[b] $\Delta E_n = E_n - E_{n-1}$	Total AOs	Occ.	Vac.	Occ.	Vac.
0	-735.695232 [c]							
1	-1302.876103	-1302.876103 [c]	-567.180871[c]	47	24	23	0	0
2	-1869.664373	-1869.664373	-566.788270	67	34	33	0	0
3	-2436.282934	-2436.282931	-566.618558	87	44	43	0	0
4	-3002.811890	-3002.811883	-566.528952	107	54	51	0	2
5	-3569.290699	-3569.290679	-566.478796	127	57	57	7	6
6	-4135.741169	-4135.741123	-566.450444	147	58	58	16	15
7	-4702.175601	-4702.175520	-566.434397	167	47	46	37	37
8	-5268.600847	-5268.600732	-566.425212	187	47	47	47	46
9	-5835.020738	-5835.020570	-566.419838	207	44	40	60	63
10	-6401.437443	-6401.437228	-566.416658	227	44	40	70	73
11	-6967.852153	-6967.851891	-566.414663	247	44	40	80	83
12	-7534.265629	-7534.265316	-566.413425	267	42	38	92	95
13	-8100.678276	-8100.677914	-566.412598	287	42	38	102	105
14	-8667.090377	-8667.089966	-566.412052	307	42	38	112	115
15	-9233.502097	-9233.501641	-566.411675	327	42	38	122	125
16	-9799.913574	-9799.913077	-566.411436	347	42	38	132	135
17	-10366.324958	-10366.324423	-566.411346	367	42	38	142	145
18	-10932.736599	-10932.736029	-566.411606	387	42	38	152	155
19	-11499.150152	-11499.149545	-566.413516	407	42	36	162	167
20	-12065.576629	-12065.575986	-566.426441	427	42	36	172	177

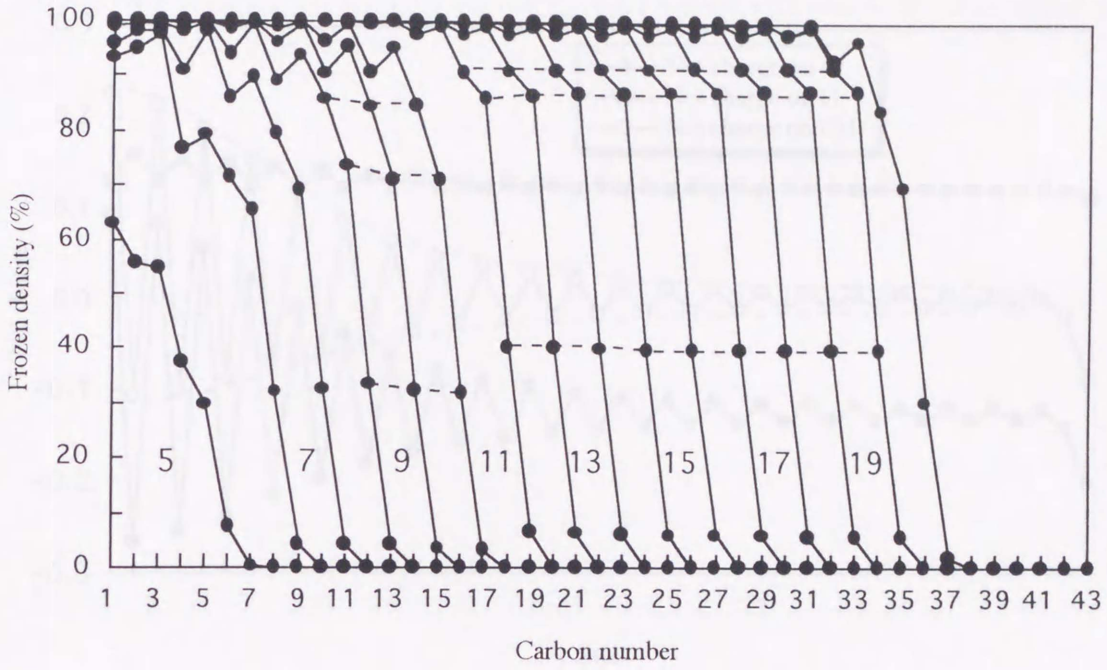
[a] Calculations were performed on IBM RISC System/6000 340.

[b] Values were obtained from results of the elongation method.

[c] Energies are shown in eV unit.

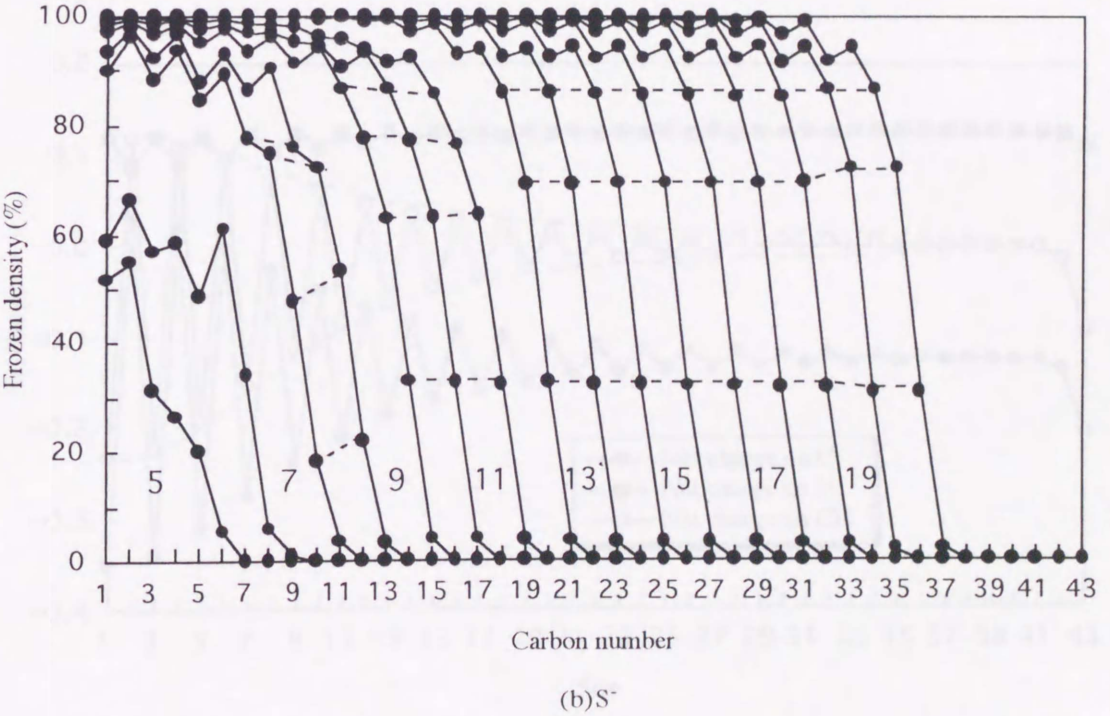
To investigate the periodic character of the electronic structure in a polymer at the MO level, diagrams of the frozen electron density at each cycle for S^+ and S^- are depicted and shown in Figs. 3.13(a) and 3.13(b). As for the freezing pattern of periodic PA, since the polymer is assumed to have the periodic geometry, the highly periodic states are formed in extending the polymer chain as is described in Sec. 3.3.1. On the other hand, the periodicity is destroyed in S^+ and S^- with charged defect in the chain. The range of disordering is extended to C17-C18 in the half-chain and the discontinuity between the aperiodic and the periodic patterns is observed in elongations of the polymer chains with the S^+ and S^- defects. This separation of the freezing patterns describes the interface of electronic states in the polymer. Also, in the periodic range, the number of newly frozen MOs is 10 occupied and vacant MOs and is consistent with that in periodic PA. The end effect appears in S^+ only at the last connection of the unit.

The distributions of net charge on each site in the chain of final S^+ and S^- clusters are plotted in Figs. 3.14(a) and 3.14(b). In both plots, the large and wide oscillation of charges on carbon atoms is shown but the charges on hydrogen atoms



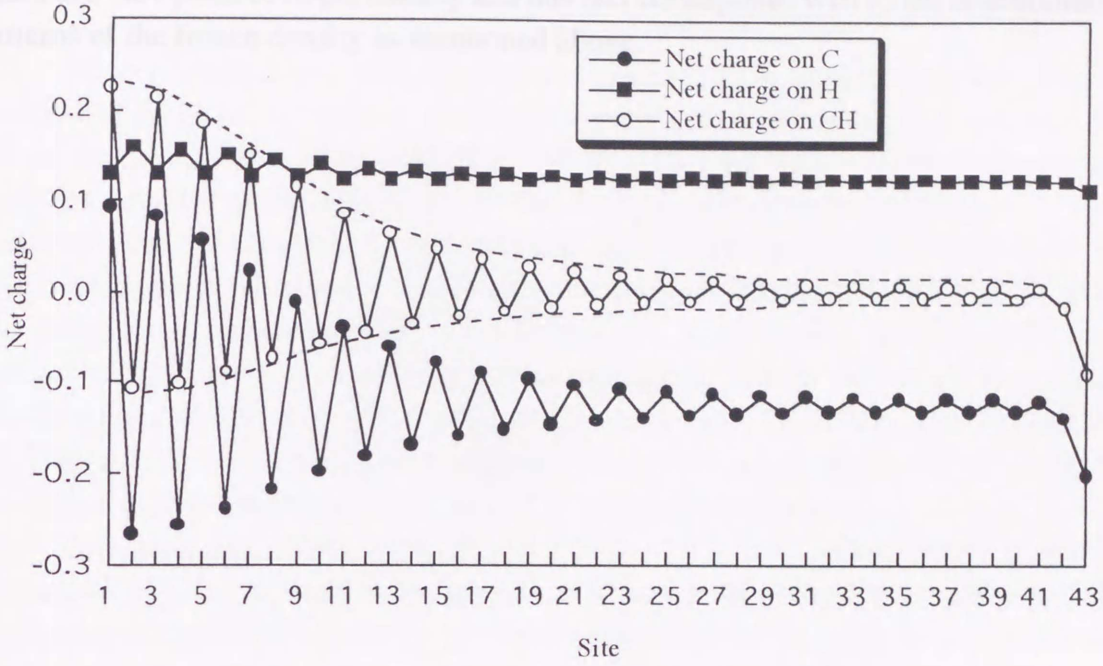
(a)S^+

remain as almost invariant as compared with oscillating charges on carbon atoms. That is, the given plus or minus charge in S^+ or S^- is extended in delocalized π electron



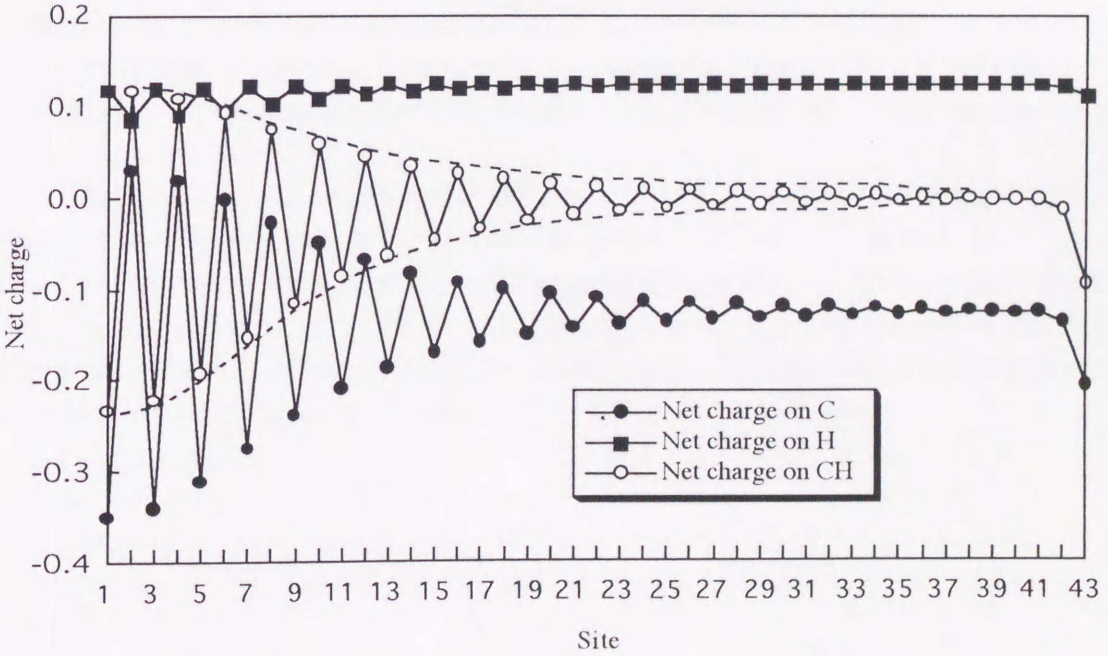
(b)S^-

FIG. 3.13. The freezing pattern of the electron density on each carbon atom in the polymer chain of (a) S^+ and (b) S^-. The carbon number 1 and 43 represent the atoms at the center and the end of the chain, respectively. The number of connected fragments with the starting cluster is included in the graph.



(a) S^+

system on conjugated carbon chain. The oscillation is converged more rapidly in S^- than in S^+. The end effect on charge distribution is almost limited in the terminal carbon. The amplitude of oscillation appears as changing around C17-C18 on the



(b) S^-

FIG. 3.14. The plot of charge distribution on each site of the polymer chain, (a) S^+ and (b) S^-. The site 1 is the central part and the site 43 is the end part of the chain.

chain at a viewpoint of its periodicity and this fact corresponds well to the discontinuous patterns of the frozen density as mentioned above.

3.4. SUMMARY

In this chapter, we tried to convert the elongation method into the program package of MOPAC in order to apply the approach to wide range of molecules. For the purpose that we confirm reliability and generality of the elongation method and show the samples of the analysis by using the approach, three polymer systems were dealt with by the cluster-series calculation. At first, we performed calculations for periodic clusters constructed with polyethylene, polytetrafluoroethylene, polyacetylene, and polydifluoroacetylene. Next, the interfaces of poly(ethylene-tetrafluoroethylene) and poly(acetylene-difluoroacetylene) were calculated. At last, the soliton defect with plus or minus charge in polyacetylene was created. By comparison with the original MOPAC results concerning total energies of these systems, it was confirmed that the elongation calculation has enough validity in practical calculations.

The calculated results were obtained at the AM1 level in this work. However, our approach does not include the special condition in theoretical treatment, thus, the application of the elongation method to the calculations at the *ab initio* level is accessible by selecting the orbitals which satisfy the orthonormality condition as mentioned in the text. Moreover, the elongation method based on the crystal orbital theory is now developed in order to study the electronic structure on a crystal surface.

The analysis by using the elongation calculation of polymers with or without periodicity enable us to determine and extract the periodic character of the electronic structure in a periodic chain and around a local interface or a defect at the molecular orbital level. The character of electronic states appears as the divided orbital spaces and the freezing pattern of electron density. The influence of the interface, the defect and the cluster end can be detected by the disordered diagram on the pattern of the frozen density. Thus, we can know the periodic and nonperiodic features of the electronic structure in a polymer.

The elongation method is based on the cluster-series calculation and its application is not restricted to periodic polymers and polymers with a local aperiodicity. That is, we can connect molecular fragments with each other one after another in any directions by any times and it is possible to elongate a random aperiodic polymer like as a biopolymer by using this approach. The calculation of several polypeptides is now in progress in our group and results will be reported in the near future.

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Chapter 4

Theoretical Approach for Locally Perturbed Periodic Systems: Development of Ab Initio Crystal Elongation Method

We have recently proposed the elongation method which is a novel molecular orbital method at the Hartree-Fock level to calculate the electronic structures of large periodic or aperiodic polymers efficiently. This method has an idea of the successive connection of any fragments to obtain the electronic properties of large molecules with any units by a cluster-series model. In this approach, the stationary conditions of the electronic states in a series of clusters against the size extension have been formulated. Studies for molecular systems have suggested that the elongation technique with the stationary conditions may be applicable to periodic systems described by the crystal orbital. In this study, we develop a new quantum chemical approach for the study of locally perturbed periodic systems by the *ab initio* crystal orbital calculation. A one-dimensional polymer, a two-dimensional surface, and a three-dimensional crystal with a local disordering part can be treated systematically by introducing the elongation technique based on the stationary conditions into a large extended supercell model. In the present chapter, we propose a general approach of the *ab initio* crystal elongation method to take into account the local perturbation destroying the perfect periodic arrangement directly in accordance with an effective variational treatment. The description for the methodology of this approach is given in detail. Results of test applications to a perturbed two-dimensional surface are shown. A local adsorption of carbon monoxide on (001) surface composed with magnesium oxide is examined as a sample model to confirm the accuracy of *ab initio* crystal elongation method. The utility of our method is clarified by an application to the perturbed surface.

4.1. INTRODUCTION

Recently, the molecular orbital method becomes a powerful tool which enable us to study the electronic structures of small molecules. By this method, various properties of molecules, for example, their geometrical structures, electron density distributions, energetic, and so on, can be obtained theoretically.[1] Furthermore, the methodology of molecular orbital theory is much sophisticated at present and many advanced program packages are developed and used. On the other hand, the bulk electronic characters of the systems as one-dimensional polymers, two-dimensional surfaces, and three-dimensional crystals with perfect periodic arrangements can be determined by the crystal orbital method under the periodic boundary condition. Also, from the crystal orbital calculation, we can obtain the band structure and the density of states which characterize the perfect periodic systems.[2,3] However, the improvement of packaging for the crystal calculation is delayed in comparison with the molecule calculation.

But, there are some problems in applying these quantum chemical methods to the systems with both periodic and aperiodic parts in their geometry. In other words, it is difficult to study locally perturbed periodic systems by the molecular orbital or the crystal orbital calculation. In these systems, because the periodicity of systems is broken in a local region, it is not easy to apply the crystal orbital theory to the perturbed systems. This theory assumes the perfect periodicity of whole systems, and, it is so restricted by the periodic boundary condition itself. In contrast with the crystal orbital method, the molecular orbital method has no limitation concerning the periodic sequence of constituent in the systems. However, this method can not reproduce the bulk electronic distributions since neighboring molecules are absent by its free boundary condition, thus, the electronic states at the center and at the edge are different.

In applying these calculation methods to the periodic systems perturbed in a local region, we must take the systems larger to satisfy the local or the bulk nature of the electronic states. In the crystal approach, a supercell which is an extended unit for the periodicity of the system must be large enough so that the interactions among perturbed parts in neighboring cells are negligible small and do not affect on the local electronic states with each other (local nature). In the molecule approach, the size of a cluster molecule has to be sufficiently large.in which the influences of molecular edges do not reach to the region around a local perturbed part and do not disturb the bulk electronic condition in its surrounding (bulk nature).

These situations suggest the serious problem that the larger the perturbed systems become, the more enormous the computational efforts like as the calculations of one- and two-electron integrals or the diagonalization of matrices in the iterations of the self-consistent-field (SCF) procedure become. Moreover, as another side of the problem, it is pointed out that we can not know *a priori* the effective size of a supercell or a cluster in which the electronic structures of the perturbed systems can be described correctly without the effects of boundary conditions. Therefore, we need to repeat the calculations against the systems with different sizes to find the optimal size by monitoring the convergence of the local perturbed electronic property.

The cluster model which approximates an extended perturbed system by a finite molecule and the supercell model which uses a large cell including a locally perturbed part as a unit cell have conventionally been applied to the studies of locally perturbed periodic systems by using the molecular orbital and the crystal orbital methods, respectively. However, in these models, a similar neck point exists in their applications to practical calculations as mentioned above. That is, a most important problem is the size selection of the system which can give the exact electronic states for both of a local-perturbing aperiodic and an extent-surrounding periodic regions in the system. But, we can not determine the effective size of a cluster or a supercell for the system before practical calculations with various sizes are carried out.

Attempts to treat the locally perturbed periodic systems by the quantum chemical methods are now in progress. The embedded cluster model is adapted in these calculations based on the Green function technique as an approach. This method may surely be useful, but it may appear as to be more complicated in the practical works for the calculations of its formulation. Moreover, in these approaches, the partition for the perturbed and the unperturbed regions in the system must be assumed before the calculation of the system is performed in practice, and also, the former region is calculated exactly while the latter region is treated approximately in evaluating the total electronic structure. Therefore, the determination of the interacting region is arbitrary and the calculated results may largely depend on its selection.[4-10]

Also, trials for the molecular orbital calculations of the large extended molecular systems have been proposed. Results for many molecules are reported. But, because the fragmentation of the system is pre-assumed, further calculations against the different selection of fragments must be required in order to find an suitable size of the fragment.[11-19]

To overcome the problem of the size effects in the cluster model or the supercell model, we should determine uniquely the general interaction space among the partitioned fragments in an extended molecule or between the periodic and aperiodic parts in a perturbed periodic system in the calculation procedure with no assumption for its range. It may be available by the following calculation of two-step procedure. Firstly, we obtain the electronic structure of an appropriate cluster or a periodic system exactly. Secondly, an interaction space is extracted from.the starting system under a perturbation such as a connection with other fragments or aperiodic parts, and then, the eigenvalue problem is solved within the interaction space only to evaluate the electronic state of whole system successively. The most important point is that this approach should not have any assumptions with regard to the range of given perturbation in the system when we estimate the electronic property of the perturbed system.

In order to realize this idea in practical calculations, we must divide the total orbital space of a system into the interaction space and the noninteraction space under a given perturbation by a general formulation theoretically. As an approach for that purpose, we have developed the elongation technique by the uniform localization at the levels of extended Hückel,[20,21] *ab initio*,[22] and local density functional[23,24] calculations for many molecular systems. Also, the stationary conditions of electronic state have been introduced into the elongation method as the cluster-series models for various polymer systems.[25-28] The utility of this approach by the crystal orbital calculation has already been suggested in a one-dimensional case.[29,30]

In the original formulation for the stationary conditions by the molecular orbital method, we consider the extension process that a cluster molecule with an appropriate size is extended by connecting a molecular fragment with the cluster end. The molecular orbital calculation of the original and the extended clusters is performed successively. Then, the molecular orbitals in the original cluster which satisfy both the orthonormality and the variational conditions of the extended system are extracted as the stationary orbitals against the molecular extension. That is, the stationary orbitals are defined as the orbitals included in the original cluster which can be regarded as good molecular orbitals also in the extended cluster without changing by an adding fragment. In other words, the stationary orbitals are well-defined original orbitals also in the extended system, thus, those are unaltered under the connection with a fragment and stationary against the size extension of a starting cluster.

We can repeatedly extend the system by freezing the stationary orbitals in interacting with a next fragment by any times until the polymer constructed with any units with desired length can be obtained finally. Because the adding fragments which are continuously connected with an extended cluster one by one must not be limited to be the same species with each other, this elongation method can be applied to any periodic and aperiodic polymers.

These stationary conditions of the electronic structure enable us to determine the stationary orbitals uniquely by a simple manner, and this method can give us an information concerning the periodic and the aperiodic characteristics of electronic states in a periodic or an aperiodic polymer as a freezing pattern of electron density by an analysis of the stationary space.[25-28] We employ the conditions in this work to find the interaction and the noninteraction orbitals in a locally perturbed periodic system.

A local perturbation in an extended periodic system has mainly been dealt with by using the cluster model. Several reasons for using the cluster model instead of the supercell model may exists. Important one of them may be that the molecular orbital theory is very advanced and the calculations at the Hartree-Fock and the beyond-Hartree-Fock levels can be carry out by the general program packages with easy use. In other words, there is few packaged tools with popularity which can be used handily in the field of crystal orbital calculation. However, as for the evaluation of the bulk electronic structures in the pure and perfect periodic systems, it should be expected that the crystal orbital is more advantageous than the molecular orbital, because the former satisfies the translational symmetry of the perfect periodic system without the boundary effect while the latter includes the edge effect by the free boundary condition. Furthermore, the program package which enable us to calculate the bulk electronic properties for one-, two-, and three-dimensional crystalline systems at the *ab initio* level is developed and released recently. That is, we have now arrived at the starting stage toward the development of a new method to examine the effects of local disordering in periodic systems effectively.

On the other hand, the steps of integration and diagonalization require much computations in the *ab initio* calculation. However, it is considered that the latter may become more serious in an extended system in comparison with the former, because the many-centered integral can be neglected or approximated with long distance between basis functions while the number of basis orbitals of the eigenvalue problem can not be reduced by a large size of the system.

Therefore, as the first step in this direction to develop a useful approach with generality by the quantum chemical calculation for the efficient study of locally perturbed periodic systems, we try to introduce the elongation method into the periodic Hartree-Fock calculation in order to carry out a more effective variational treatment for large extended supercell systems.

In the present study, we formulate a general approach by using the elongation procedure at the level of the *ab initio* crystal orbital calculation in order to obtain the electronic natures of locally perturbed periodic systems, for example, a polymer interacting with a small molecule and an abnormal bonding in a polymer (one-dimensional), a surface having a defect structure and a local adsorption on a surface (two-dimensional), a crystal including an impurity atom and a lattice defect within a crystal (three-dimensional). The procedure of this approach is essentially similar to that for the corresponding orbital or the interaction frontier orbital.[31-33] It includes the determination of the interaction and the noninteraction regions in the orbital space of the perturbed system, in which the periodic orbitals are perturbed or not, by applying the stationary conditions of the elongation method.

For the purpose that we make it possible to perform the calculations of various systems, the elongation method is introduced into the general program package of CRYSTAL88.[3,34] By CRYSTAL88 and 92 programs, we can calculate the electronic states at the *ab initio* level both for molecules by the molecular orbital method and for one-, two-, and three-dimensional periodic systems such as polymers, surfaces, and crystals by the crystal orbital method.[35-43]

In order to check and confirm the generality of our *ab initio* crystal elongation approach, several test calculations are performed on the two-dimensional locally perturbed system with a molecular adsorption on a crystal surface. As a sample system, we treat the system in which a carbon monoxide adsorbs on (001) face of magnesium oxide. This system has been studied by the cluster approach and by the suprecell approach.[44-46] The perturbed cluster calculation of this system has also been reported.[8]

In Section 4.2, we give the formulation of the *ab initio* crystal elongation method in detail, and in Section 4.3, we demonstrate the utility of this method by comparing obtained results from this approach with those from the conventional supercell calculation. Section 4.4 gives the summary of this study.

4.2. METHOD

Previously, in our works by the molecular orbital calculation, the stationary conditions of the electronic structure against the extension of cluster series have been defined as follows. As is explained below briefly, the stationary orbitals must satisfy both the orthonormality and the variational conditions.[25-27]

Now, consider that a starting cluster A is extended by bonding with an adding fragment B to produce an extended cluster $A+B$. In order to be well-defined molecular orbitals (MOs) in the extended cluster $A+B$, $\{\psi_i^o(A)\}$ and $\{\psi_j^v(A)\}$, which are MOs of the original cluster A, must satisfy the following two conditions as is shown in Fig. 4.1:

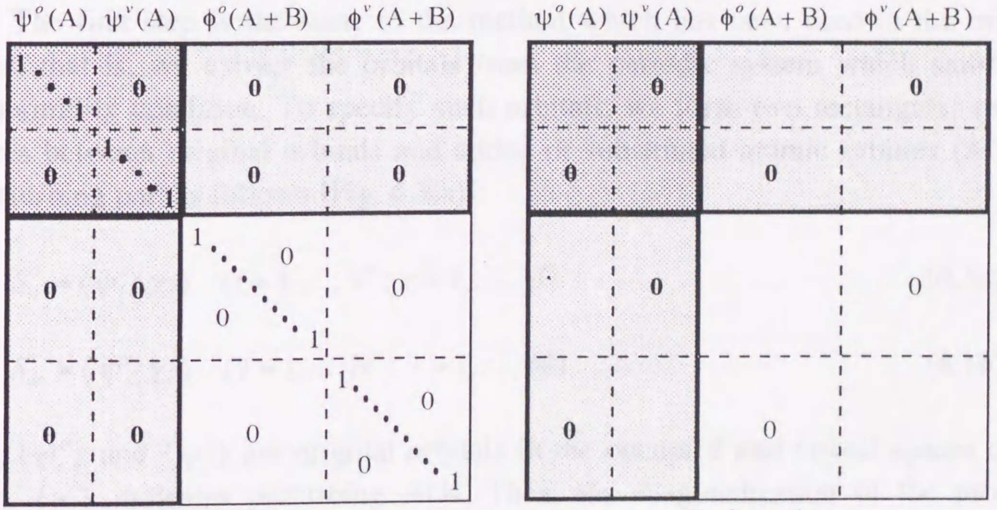
(i) The orthonormality condition,

$$\langle \psi_i^a(A)|\psi_j^b(A)\rangle = \delta_{ij}\delta_{ab},$$
$$\langle \psi_i^a(A)|\phi_r^b(A+B)\rangle = 0,$$

(ii) The variational condition,

$$\langle \psi_i^o(A)|\hat{F}(A+B)|\psi_j^v(A)\rangle = 0,$$
$$\langle \psi_i^o(A)|\hat{F}(A+B)|\phi_s^v(A+B)\rangle = \langle \psi_j^v(A)|\hat{F}(A+B)|\phi_t^o(A+B)\rangle = 0,$$

where, the symbols $a,b = o$ or v, the superscripts o and v indicate occupied and virtual MOs, respectively, and $\hat{F}(A+B)$ is the Fock operator of the extended cluster $A+B$. $\{\phi_t^o(A+B)\}$ and $\{\phi_s^v(A+B)\}$ represent the remaining MOs of the cluster $A+B$. Then, $\{\psi_i^o(A)\}$ and $\{\psi_j^v(A)\}$ can be called stationary orbitals against the extension from A to $A+B$. Thus, if the electronic structures of both clusters A and $A+B$ are



Overlap matrix

Fock matrix

FIG. 4.1. Matrix representations of the orthonormality condition and the variational condition by displaying the MO-based overlap and Fock matrices. The shaded parts in these matrices must be satisfied by the stationary orbitals. In other words, the orbitals satisfying these conditions can be regarded as to be stationary.

determined and $\hat{F}(A+B)$ is known, it is possible to define the stationary space uniquely based on these orthonormality and variational conditions.

The procedure to extract the stationary orbitals has already been proposed and applied to elongation calculations for hydrogen fluoride and three isomers of periodic polyacetylene.[25] Stationary space analysis of the electronic structure of a polymer system by the cluster-series model has also been reported.[26] Then, applications of an analysis by the cluster-series model to electronic states around the local defects in all-*trans* polyacetylene has been published.[27]

As is shown above, the original procedure assumes that $\hat{F}(A+B)$ is known. In this work, we use an approach which does not need the assumption as is explained in the following.

Of course, this method to extract the stationary orbitals is not limited to the calculation for the extension of a molecular system, for example, a cluster A is extended to a cluster $A+B$ by connecting with a fragment B as mentioned above. That is, we apply the stationary conditions of the electronic state to the locally perturbed periodic system in which a crystal surface with two-dimensional periodicity C is perturbed by adsorbing a molecule D in this study.

Three-step procedure is developed to extract the stationary orbitals in our present study. Here, we note that the crystal orbital and the Fock operator in a periodic Hartree-Fock scheme depend on the wave number vectors, thus, the steps for elongation procedure described below in details must be carried out at each representation point in the wave number vector space. Also, the general procedure of this approach can be applied directly to the molecular systems by regarding the crystal orbitals as the molecular orbitals such as in the case of the extension of molecular clusters as well as in the case that the periodic crystalline systems are perturbed. This three-step procedure is summarized in Fig. 4.2 schematically.

The first step is the same to the method which has been used in the original version, that is, we extract the orbitals from the periodic system which satisfy the orthonormality condition. To specify such orbitals, we form two rectangular overlap matrices between original orbitals and added or substituted atomic orbitals (AOs) in the perturbing part as follows [Fig. 4.3(a)]:

$$S_{ir}^{o} = \langle \psi_{i}^{o} | \chi_{r} \rangle \quad (i = 1, \ldots, N^{o};\ r = 1, \ldots, M) \tag{4.1a}$$

$$S_{jr}^{v} = \langle \psi_{j}^{v} | \chi_{r} \rangle \quad (j = 1, \ldots, N^{v};\ r = 1, \ldots, M) \tag{4.1b}$$

where, $\{\psi_{i}^{o}\}$ and $\{\psi_{j}^{v}\}$ are original orbitals in the occupied and virtual spaces of the system, $\{\chi_{r}\}$ indicates perturbing AOs. Then, the diagonalization of the products $\mathbf{S}^{o}\mathbf{S}^{o+}$ and $\mathbf{S}^{v}\mathbf{S}^{v+}$ are carried out to evaluate the eigenvalues of these matrices, respectively. From estimation of the eigenvalues obtained here, we classify the original occupied and virtual orbital spaces into $\{\psi(0)\}$ with the zero eigenvalues and $\{\psi'(0)\}$ with the

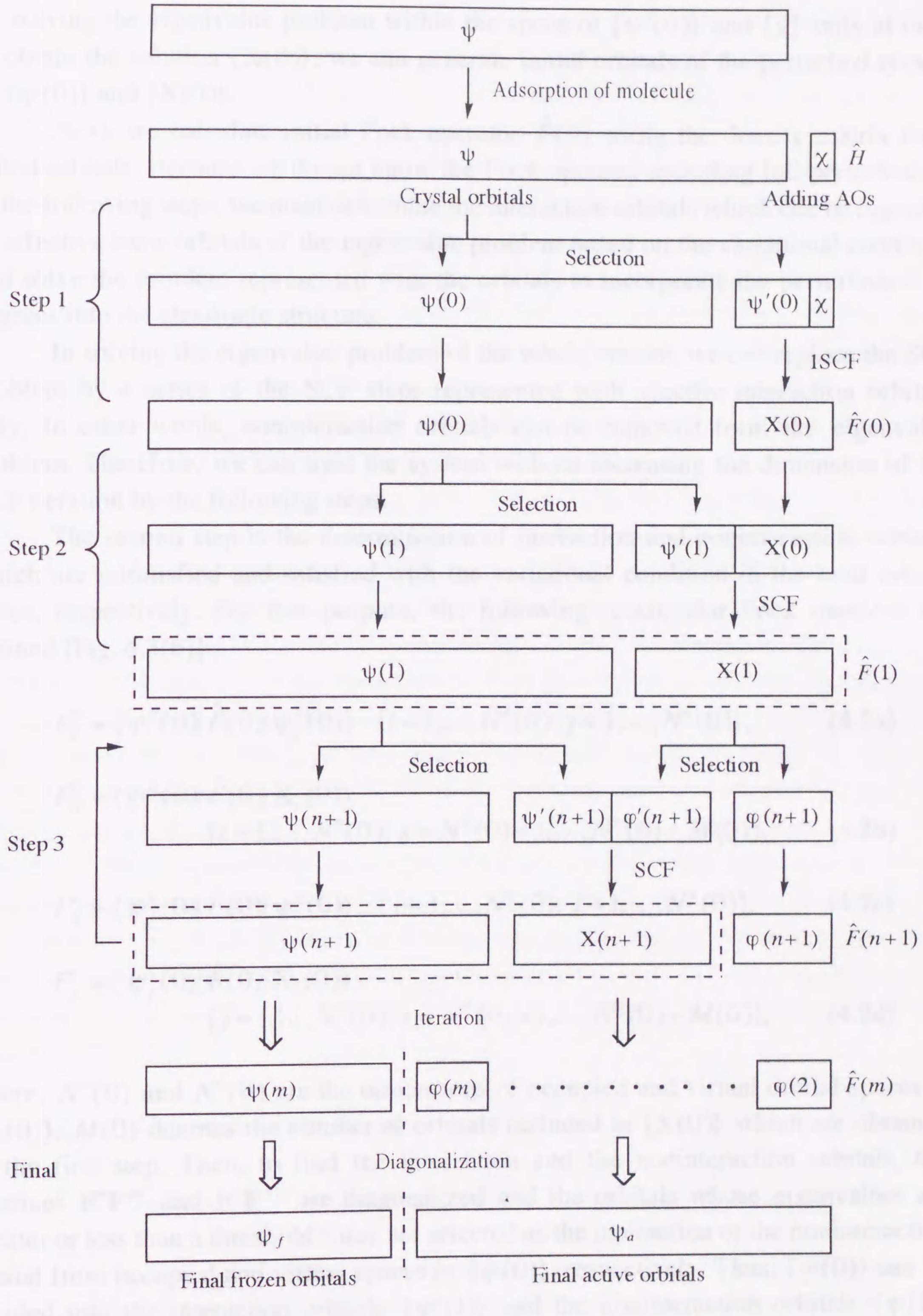


FIG. 4.2. Schematic illustration for the calculation procedure of the crystal elongation method. The explanations of steps 1-3 are given in the text in detail and these steps are carried out for each wave number vector.

nonzero eigenvalues. In other word, the former space satisfies and the latter space breaks the orthonormality condition of system, respectively. After this orbital selection, by solving the eigenvalue problem within the space of $\{\psi'(0)\}$ and $\{\chi\}$ only at once to obtain the solution $\{\mathrm{X}(0)\}$, we can generate initial orbitals of the perturbed system as $\{\psi(0)\}$ and $\{\mathrm{X}(0)\}$.

Next, we calculate initial Fock operator $\hat{F}(0)$ using the density matrix from initial orbitals. Because we do not know the Fock operator including full perturbation, in the following steps, we must determine the interaction orbitals which can be regarded as effective basis orbitals of the eigenvalue problem based on the variational condition and solve the problem represented with the orbitals to incorporate the perturbation by degrees into the electronic structure.

In solving the eigenvalue problem of the whole system, we can replace the SCF problem by a series of the SCF steps represented with specific interaction orbitals only. In other words, noninteraction orbitals can be removed form the eigenvalue problem. Therefore, we can treat the system without increasing the dimension of the SCF iteration by the following steps.

The second step is the determination of interaction and noninteraction orbitals which are unsatisfied and satisfied with the variational condition in the total orbital space, respectively. For that purpose, the following rectangular Fock matrices are defined [Fig. 4.3(b)]:

$$F^{o}_{ij} = \langle \psi^{o}_{i}(0)|\, \hat{F}(0)|\, \psi^{v}_{j}(0)\rangle \quad [i=1,\ldots,N^{o}(0);\, j=1,\ldots,N^{v}(0)], \tag{4.2a}$$

$$F^{o}_{is} = \langle \psi^{o}_{i}(0)|\, \hat{F}(0)|\, \mathrm{X}_{r}(0)\rangle \quad [i=1,\ldots,N^{o}(0);\, s=N^{v}(0)+1,\ldots,N^{v}(0)+M(0)], \tag{4.2b}$$

$$F^{v}_{ji} = \langle \psi^{v}_{j}(0)|\, \hat{F}(0)|\, \psi^{o}_{i}(0)\rangle \quad [j=1,\ldots,N^{v}(0);\, i=1,\ldots,N^{o}(0)], \tag{4.2c}$$

$$F^{v}_{jt} = \langle \psi^{v}_{j}(0)|\, \hat{F}(0)|\, \mathrm{X}_{r}(0)\rangle \quad [j=1,\ldots,N^{v}(0);\, t=N^{o}(0)+1,\ldots,N^{o}(0)+M(0)], \tag{4.2d}$$

where, $N^{o}(0)$ and $N^{v}(0)$ are the dimensions of occupied and virtual orbital spaces in $\{\psi(0)\}$, $M(0)$ denotes the number of orbitals included in $\{\mathrm{X}(0)\}$ which are obtained in the first step. Then, to find the interaction and the noninteraction orbitals, the matrices $\mathbf{F}^{o}\mathbf{F}^{o+}$ and $\mathbf{F}^{v}\mathbf{F}^{v+}$ are diagonalized and the orbitals whose eigenvalues are greater or less than a threshold value are selected as the interaction or the noninteraction orbital from occupied and virtual spaces in $\{\psi(0)\}$, respectively. Thus, $\{\psi(0)\}$ can be divided into the interaction orbitals $\{\psi'(1)\}$ and the noninteraction orbitals $\{\psi(1)\}$ which satisfy and do not satisfy the variational condition. After solving the eigenvalue problem within $\{\psi'(1)\}\oplus\{\mathrm{X}(0)\}$ according to the SCF technique, we obtain resulting orbitals $\{\mathrm{X}(1)\}$ which include partial perturbation within $\{\psi'(1)\}\oplus\{\mathrm{X}(0)\}$ while remained orbitals $\{\psi(1)\}$ are unchanged without any perturbations in the SCF iterations because this space is removed from basis orbitals of the eigenvalue problem as an invariant. Next, new Fock operator $\hat{F}(1)$ is calculated by using $\{\psi(1)\}$ and $\{\mathrm{X}(1)\}$.

As is shown in the second step, the noninteraction orbitals are fixed in the SCF procedure, but the other orbitals are relaxed by mixing with each other, thus, the variational condition of $\{\psi(1)\}$ may be broken against $\hat{F}(1)$. So, we must repeat the steps for the orbital selection and the eigenvalue problem until the perturbation is included fully to obtain the electronic state which satisfy the variational condition self-consistently. This convergence can be checked by the number of interaction orbitals, that is, when all of the interaction orbitals vanish, we can recognize that the perturbation is taken into completely. Then, the all orbitals which satisfy the variational condition in the total orbital space can approximately be obtained, and thus, the electronic structure of the perturbed system can be correctly evaluated. In the next step, we describe the procedure of this repeating process.

The third step is iterations of the eigenvalue problem within the interaction orbital space. In this step, the SCF process of the whole system can be replaced by a series of SCF steps in the interaction space only as follows. To make this step more effectively, the basis orbitals of the eigenvalue problem are selected from both spaces of $\{\psi\}$ and $\{\mathrm{X}\}$ by checking whether the variational condition is satisfied or not in each space. That is, the orbitals which do not satisfy the variational condition in these spaces are regarded as the interaction orbitals and used as basis orbitals. The remaining orbitals in these spaces are the noninteraction orbitals which satisfy the condition and are not perturbed in the eigenvalue problem by fixing those. In other words, we take into account only the orbital mixing among the interaction orbitals, therefore, what we have to do is to solve the eigenvalue problem within the interaction space. By applying the selection of interaction and noninteraction orbitals in the total orbital space, it is possible to reduce reasonably the number of basis orbitals for the eigenvalue problem. That is, we can carry out the SCF problem of large system without increasing its dimension. Two-step procedure is applied in order to perform the orbital selection as is described below. Here, we explain the $(n+1)$th cycle of this step. At first, we test the variational condition of $\{\mathrm{X}(n)\}$ by taking the rectangular Fock matrices as follows [Fig. 4.3(c)]:

$$F_{rj}^{o} = \langle \mathrm{X}_r^{o}(n)|\hat{F}(n)|\psi_j^{v}(n)\rangle \quad [r=1,\ldots,M^{o}(n);\ j=1,\ldots,N^{v}(n)], \tag{4.3a}$$

$$F_{si}^{v} = \langle \mathrm{X}_s^{v}(n)|\hat{F}(n)|\psi_i^{o}(n)\rangle \quad [s=1,\ldots,M^{v}(n);\ i=1,\ldots,N^{o}(n)], \tag{4.3b}$$

where, $M^{o}(n)$ and $M^{v}(n)$ denote the numbers of occupied and virtual spaces in $\{\mathrm{X}(n)\}$ which corresponds to the orbitals obtained by the eigenvalue problem at the (n)th cycle of this step, $\{\psi(n)\}$ is the orbital space with $N^{o}(n)$ occupied and $N^{v}(n)$ virtual orbitals which remain with no perturbation after the (n)th repetition, and $\hat{F}(n)$ specifies the Fock operator evaluated by the (n)th iteration. The interaction orbitals in $\{\mathrm{X}(n)\}$ can be selected by diagonalizing $\mathbf{F}^{\mathbf{o}}\mathbf{F}^{\mathbf{o}+}$ and $\mathbf{F}^{\mathbf{v}}\mathbf{F}^{\mathbf{v}+}$ matrices and evaluating their eigenvalues, respectively. At second, we can find the interaction orbitals in $\{\psi(n)\}$ by the following rectangular Fock matrices [Fig. 4.3(d)]:

$$F_{ij}^{o} = \langle \psi_i^{o}(n)|\,\hat{F}(n)\,|\psi_j^{v}(n)\rangle \quad [i=1,\ldots,N^{o}(n);\ j=1,\ldots,N^{v}(n)], \tag{4.4a}$$

$$F_{is}^{o} = \langle \psi_i^{o}(n)|\,\hat{F}(n)\,|\varphi_r'^{v}(n+1)\rangle$$
$$[i=1,\ldots,N^{o}(n);\ s=N^{v}(n)+1,\ldots,N^{v}(n)+M'(n+1)], \tag{4.4b}$$

$$F_{ji}^{v} = \langle \psi_j^{v}(n)|\,\hat{F}(n)\,|\psi_i^{o}(n)\rangle \quad [j=1,\ldots,N^{v}(n);\ i=1,\ldots,N^{o}(n)], \tag{4.4c}$$

$$F_{ju}^{v} = \langle \psi_j^{v}(n)|\,\hat{F}(n)\,|\varphi_t'^{o}(n+1)\rangle$$
$$[j=1,\ldots,N^{v}(n);\ u=N^{o}(n)+1,\ldots,N^{o}(n)+M'(n+1)], \tag{4.4d}$$

where, $\{\varphi'(n+1)\}$ represents the interaction orbitals in $\{\mathrm{X}(n)\}$ selected by the first

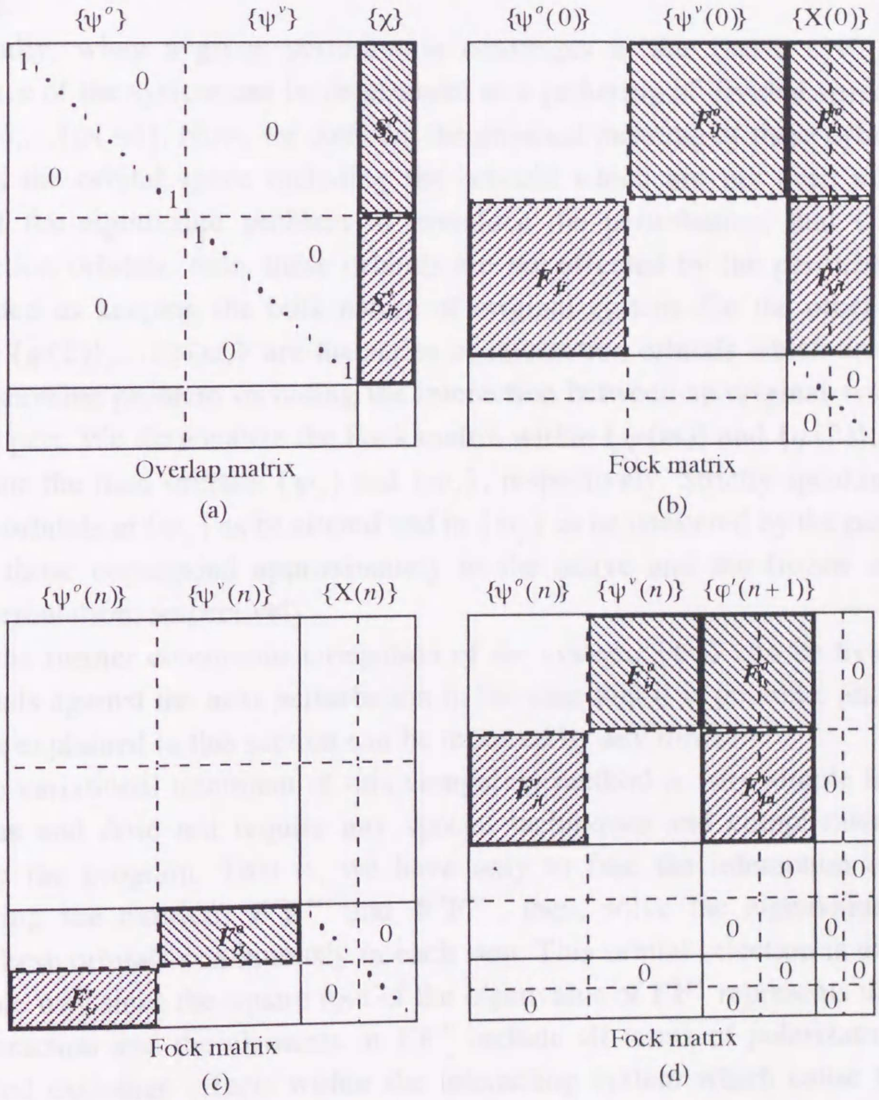


FIG. 4.3. Structures of $\mathbf{SS}^{+}$ and $\mathbf{FF}^{+}$ matrices employed in (a) step 1, (b) step 2, (c) step 3, and (d) step 3 of the *ab initio* elongation method. The marked blocks correspond to $\mathbf{S}$ or $\mathbf{F}$ matrix. $\langle \psi|\hat{F}|\psi\rangle$ includes the polarization interaction within $\{\psi\}$ and also, $\langle \psi|\hat{F}|\mathrm{X}\rangle$ or $\langle \psi|\hat{F}|\varphi'\rangle$ represents the charge transfer and exchange effects between $\{\psi\}$ and $\{\mathrm{X}\}$ or $\{\varphi'\}$.

selection. Diagonalization of products $\mathbf{F}^{o}\mathbf{F}^{o+}$ and $\mathbf{F}^{v}\mathbf{F}^{v+}$ enable us to specify the interaction orbitals according to the magnitude of eigenvalues. At last, the eigenvalue problem is solved within $\{\psi'(n+1)\} \oplus \{\varphi'(n+1)\}$ determined as the interaction space in this step by the SCF method to obtain resulting orbitals $\{\mathrm{X}(n+1)\}$ and new Fock operator $\hat{F}(n+1)$.

In repeating the next cycle, we assume $\{\psi(n+1)\}$ and $\{\mathrm{X}(n+1)\}$ as the interactive space for the $(n+2)$th cycle. In other words, at each cycle of this step, if there is, $\{\varphi\}$ is removed from the interactive space and each $\{\varphi\}$ is kept as invariant through all cycles. This treatment is reasonable based on the fact that the interaction between $\{\varphi(n+1)\}$ and $\{\psi(n)\}$ is sufficiently weak because it is confirmed that the eigenvalues of rectangular Fock matrices between them are less than a threshold value, thus, the variational condition of $\{\varphi(n+1)\}$ will not be broken by the interaction with $\{\psi(n+1)\}$.

Finally, when a given perturbation converges at the (m)th cycle, the total orbital space of the system can be determined as a gathering of divided spaces $\{\psi(m)\}$ and $\{\varphi(2)\},\ldots,\{\varphi(m)\}$. Now, we consider the physical meaning of these orbital spaces. $\{\psi(m)\}$ is the orbital space including the orbitals which are not used as the basis orbitals of the eigenvalue problem to introduce the perturbation, that is, the final noninteraction orbitals, thus, these orbitals are not affected by the perturbation at all and regarded as keeping the bulk nature of original system. On the other hand, the orbitals in $\{\varphi(2)\},\ldots,\{\varphi(m)\}$ are the series of interaction orbitals which are perturbed by the eigenvalue problem including the interaction between an original system and a perturbing part. We diagonalize the Fock matrix within $\{\psi(m)\}$ and $\{\varphi(2)\},\ldots,\{\varphi(m)\}$ to determine the final orbitals $\{\psi_a\}$ and $\{\psi_f\}$, respectively. Strictly speaking, we can regard the orbitals in $\{\psi_a\}$ as be altered and in $\{\psi_f\}$ as be unaltered by the perturbation, and thus, those correspond approximately to the active and the frozen orbitals by original formulation, respectively.

In the further continuous elongation of the system, $\{\psi_f\}$ can be treated as the fixed orbitals against the next perturbation in the case that it is possible, and then, the procedures explained in this section can be repeated by any times.

The variational treatment of this elongation method is very simple in practical calculations and dose not require any special techniques and complicated skills in developing the program. That is, we have only to find the interaction orbitals by diagonalizing the matrices $\mathbf{F}^{o}\mathbf{F}^{o+}$ and $\mathbf{F}^{v}\mathbf{F}^{v+}$, then, solve the eigenvalue problem based on these orbitals continuously in each step. This orbital selection is expected as a reasonable way since the square root of the eigenvalue of $\mathbf{F}\mathbf{F}^{+}$ represents the strength of the interaction and the elements in $\mathbf{F}\mathbf{F}^{+}$ include all terms of polarization, charge transfer, and exchange effects within the interacting system which cause the orbital mixing. In other words, it can be considered that by creating the orbital pairs with zero values of Fock matrix elements, they do not mix with each other. Thus, in the calculation of our elongation method, only the orbital mixing among the interaction orbitals is introduced by the stepwise procedure as a more effective treatment for the SCF step.

Moreover, because this approach includes the specification of the orbitals in which the perturbation is dominant by divided orbital spaces, we need not to assume the interaction space before the calculation. In other words, we do not have to monitor the calculated results for various systems with different ranges of interaction and the size dependence of results by changing the cluster size variously in the cases for the conventional cluster model and the embedded cluster approach. Therefore, our method can be expected as a starting point toward a general quantum chemical approach in order to study the electronic structures of the locally perturbed periodic systems by the periodic Hartree-Fock scheme.

4.3. RESULTS AND DISCUSSION

To confirm the utility of our *ab initio* crystal elongation method in practical calculations, we perform calculations for the locally perturbed two-dimensional periodic surface systems. The perturbed systems in which a carbon monoxide is adsorbed vertically on (001) surface for magnesium oxide crystal with various coverages are treated as is shown in Fig. 4.4.

The following conditions of crystal Hartree-Fock calculations for truncation parameters are adopted in this study; monoelectronic integral overlap threshold: 10^{-4}, Coulomb overlap threshold: 10^{-4}, Coulomb penetration threshold: 10^{-4}, exchange overlap threshold: 10^{-4}, and exchange pseudo-penetration threshold: 10^{-6}. The meanings of these thresholds are explained in more detail in Refs. 3 and 9. These values have been suggested as a standard conditions in this system by the authors of CRYSTAL88.[8] The specific points with fifteen number in the two-dimensional space of wave number vectors are extracted as the representation points in the eigenvalue problem. The convergence of SCF iterations in the calculation is considered to be reached when the absolute value for the deviation of the total energy of the system from that at the preceding SCF cycle is below 10^{-8} a.u. The Pisani's basis sets constructed with nine independent functions (three s and six p) are applied for Mg^{2+} (8-61G) and O^{2-} (8-51G) which have been optimized for the bulk MgO crystal.[36] Since it has already been shown that the electronic structure is almost unaltered by using a minimal STO-3G instead an extended 3-21G as the basis set,[46] the Pople's STO-3G basis set is employed for CO molecule.[47,48]

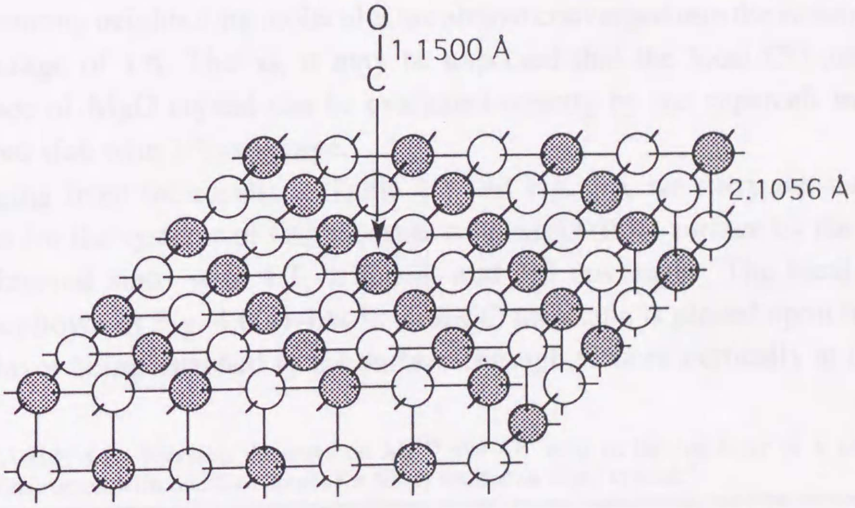


FIG. 4.4. A local CO adsorption on (001) surface of MgO crystal. The adsorption is simulated by approaching CO molecule vertically to MgO surface through C atom. The distance between lattice points of a square lattice for MgO (001) surface is 2.1056 Å and the bonding distance in CO molecule is 1.1500 Å. The shaded and the white balls correspond to Mg^{2+} and O^{2-} ions in MgO (001) surface, respectively.

An important point in the calculation of molecular adsorption is the size of system which can describe exactly the electronic states of both the adsorption site perturbed by a molecule and the periodic unperturbed surrounding sites in a bulk crystal surface. As the periodicity is assumed in the supercell model, we must take the size of supercell so as to be large enough in which adsorbates do not affect on the electronic structures with each other and each of them can be regarded as an isolated molecule. On the other hand, the bulk condition of adsorbent within a given layer may probably be satisfied by the crystal orbital without the end effect. However, it must be examined that how many layers should be required in order to be able to represent correctly the electron density distribution in the most outer layer of crystal on which a molecule adsorbs as the bulk limit of surface for a real crystal. For that reason, we should evaluate these effects before the adsorption calculations.

Therefore, we calculate the perfect MgO crystal surfaces which consist of up to five layers and the CO molecules arranged periodically corresponding to the various surface coverages. The (001) surface of MgO crystal forms a square lattice and the value of 2.1056 Å for the bulk MgO crystal is applied to the distances between nearest-neighboring Mg^{2+} ion and O^{2-} ion in the surfaces. The intramolecular bonding distance of CO molecule is fixed as 1.1500 Å and the coverages correspond to 1/1, 1/2, 1/4, 1/8, 1/9, 1/16, and 1/18 (a coverage 1/x means that one CO molecule adsorbs on per x Mg^{2+} ions). The electron densities of Mg^{2+} and O^{2-} ions in the top layer are listed in Table 4.1. From these results, it is clarified that a three-layered slab should be required at least to give the correct electron density distributions on (001) surface. On the other hand, we give the plot of total energies for periodic CO molecules together with that for isolated molecule in Fig. 4.5. This energy profile indicates that the influences among neighboring molecules are almost converged into the isolated molecule at the coverage of 1/8. That is, it may be expected that the local CO adsorption on (001) surface of MgO crystal can be evaluated exactly by the supercell model as the three-layered slab with 1/8 coverage.

Judging from the results in Table 4.1 and Fig. 4.5, we carry out the perturbed calculations for the systems of CO adsorption on MgO (001) surface by the one-, two-, and three-layered slabs with 1/1, 1/2, 1/4, and 1/8 coverages. The local adsorption systems are shown in Fig. 4.6(a)-4.6(d). The CO molecule is placed upon the Mg^{2+} ion in the top layer being attached to the surface through C atom vertically at the distance

TABLE 4.1. Electron densities on Mg^{2+} and O^{2-} ions in the top layer of a slab constructed with one-five planes for (001) surface of MgO crystal.[a]

Number of layers	1	2	3	4	5
Mg^{2+} ion	10.0550	10.0406	10.0370	10.0371	10.0371
O^{2-} ion	9.9450	9.9594	9.9575	9.9575	9.9575

[a] The electron densities on Mg^{2+} and O^{2-} using 8-61G (Mg^{2+}) and 8-51G (O^{2-}) basis sets obtained from the periodic Hartee-Fock calculation by CRYSTAL88 are listed.

d between C atom in CO molecule and Mg^{2+} ion in MgO surface. The point for energy minimum is searched by changing the distance *d* by 0.1 Å. In CO adsorption calculations on (001) surface of MgO crystal, the value of 10^{-6} is applied as the threshold to the orbital selection of interaction and noninteraction orbitals in the *ab initio* crystal elongation method.

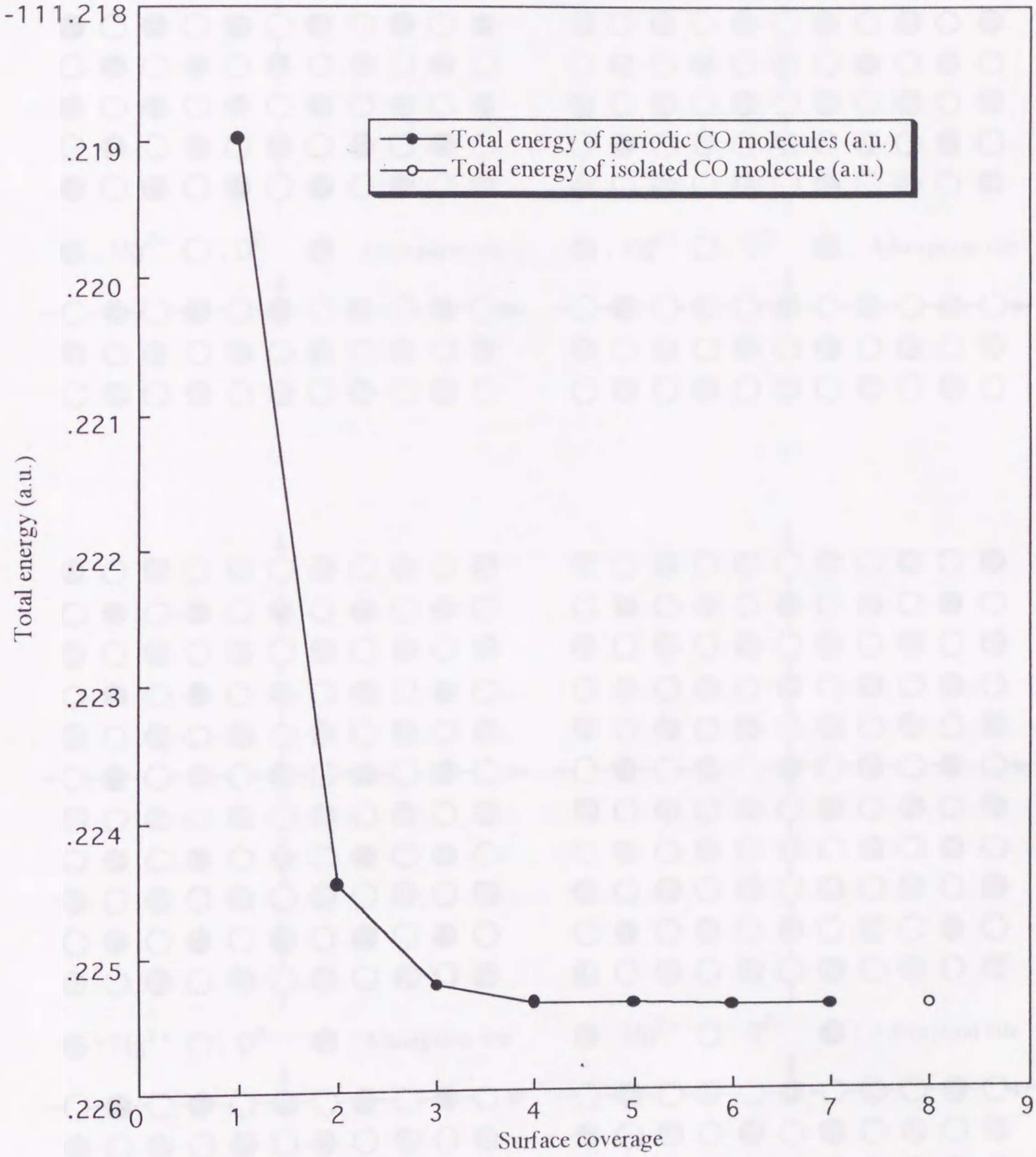
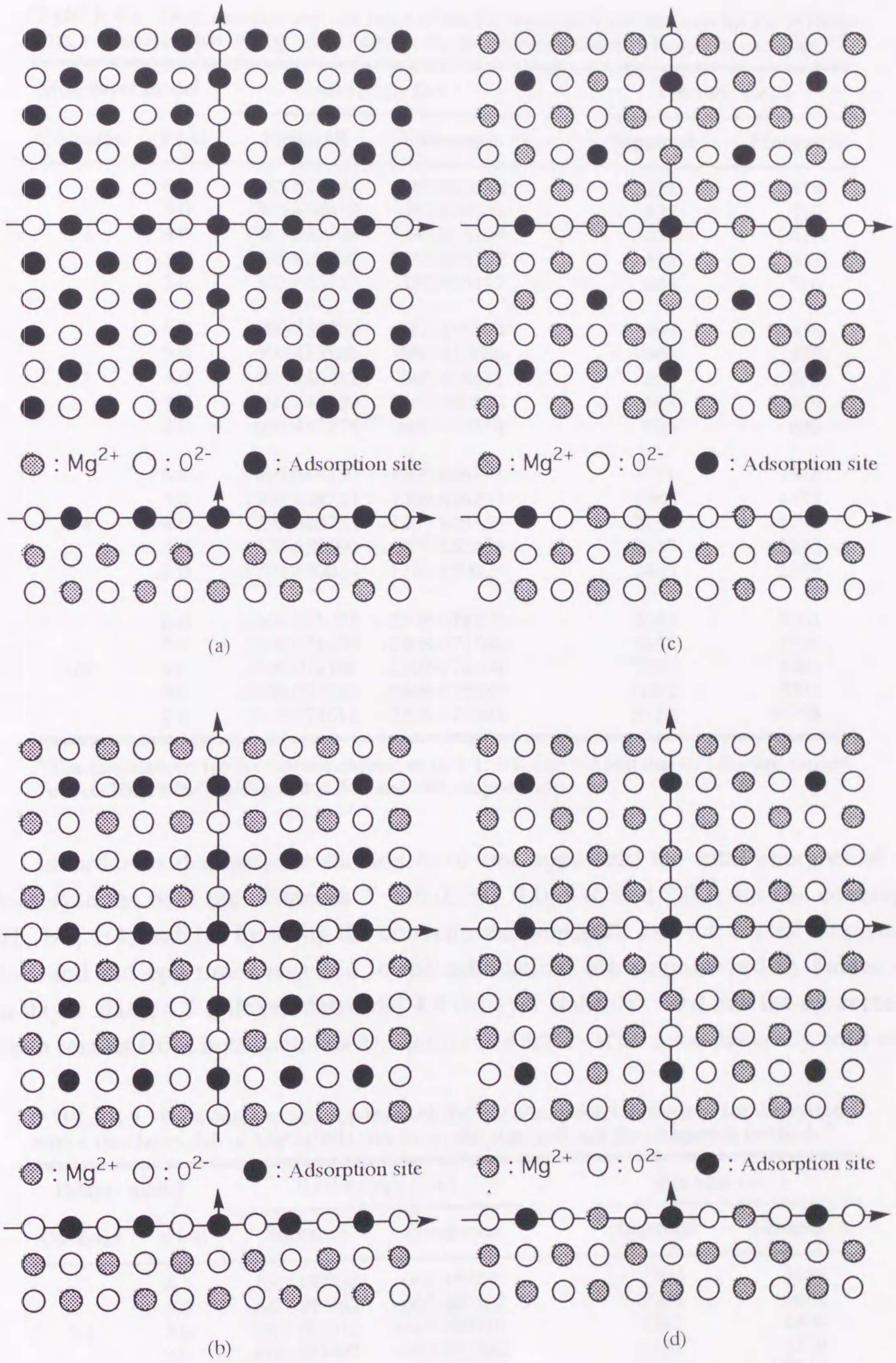


FIG. 4.5. Total energies of periodically arranged CO molecules corresponding to the following surface coverages of 1/1, 1/2, 1/4, 1/8, 1/9, 1/16, 1/18, and isolated CO molecule. The energies per one molecule using STO-3G basis set obtained by CRYSTAL88 are plotted. In order to estimate the molecule-molecule interactions on MgO surface with various surface coverages, the periodic Hartree-Fock calculations were performed on seven periodic arrangements of CO molecules in the absence of the underlying MgO surface. We should select the coverage by which the interaction between molecules can be regarded as be negligible small in order to simulate the local CO adsorption on MgO surface.



(a)

(c)

(b)

(d)

FIG. 4.6. The systems of CO adsorption on MgO (001) surface used in this study by slabs for one-three layers with the surface coverage of (a) 1/1, (b) 1/2, (c) 1/4, and (d) 1/8. The coverages indicate the following concentrations of CO molecule adsorbed on MgO surface, 1/1 = 100%, 1/2 = 50%, 1/4 = 25%, and 1/8 = 12.5%. The black circles are the adsorption sites and Mg^{2+} and O^{2-} ions in surroundings are indicated by the shaded and the white circles, respectively.

TABLE 4.2. Total energies and cpu times of the CO adsorption calculations for the systems with a one-layer slab of MgO (001) surface by the supercell and the elongation methods.[a]

Monolayer model		Total energy (a.u.)		cpu time (sec.)	
Coverage	d (Å)	Supercell	Elongation	Supercell	Elongation
1/1	6.0	-385.824544	-385.824544	321	318
	5.0	-385.824632	-385.824632	322	319
	4.0	-385.825144	-385.825144	407	416
	3.0	-385.828597	-385.828597	512	523
	2.0	-385.825117	-385.825117	686	716
1/2	6.0	-660.435794	-660.435794	499	478
	5.0	-660.435886	-660.435886	503	479
	4.0	-660.436412	-660.436411	608	595
	3.0	-660.440089	-660.440086	683	759
	2.0	-660.437274	-660.437274	795	840
1/4	6.0	-1209.648130	-1209.648131	1771	1428
	5.0	-1209.648223	-1209.648223	1786	1432
	4.0	-1209.648753	-1209.648753	2157	1771
	3.0	-1209.652500	-1209.652498	2657	2220
	2.0	-1209.650024	-1209.650023	2463	2533
1/8	6.0	-2308.071475	-2308.071474	5549	3761
	5.0	-2308.071570	-2308.071568	5657	3726
	4.0	-2308.072108	-2308.072104	7280	4486
	3.0	-2308.075898	-2308.075889	6032	5581
	2.0	-2308.073612	-2308.073604	8122	6793

[a] The calculations for the surface coverages of 1/1, 1/2, and 1/4 and that of 1/8 were carried out on IBM RISC System/6000 340 and 580, respectively.

In order to demonstrate the utility of our approach, the total energies of the various systems with the distances d = 6.0, 5.0, 4.0, 3.0, and 2.0 Å for the coverages of 1/1, 1/2, 1/4, and 1/8 by using the conventional supercell and the crystal elongation models and the cpu times required in the calculations are summarized in Tables 4.2 (monolayer slab), 4.3 (bilayer slab), and 4.4 (trilayer slab). We find that the agreements between results from both methods are quite satisfactory with good accuracy with each

TABLE 4.3. Total energies and cpu times of the CO adsorption calculations for the systems with a two-layer slab of MgO (001) surface by the supercell and the elongation methods.[a]

Bilayer model		Total energy (a.u.)		cpu time (sec.)	
Coverage	d (Å)	Supercell	Elongation	Supercell	Elongation
1/1	6.0	-660.489238	-660.489238	1704	1659
	5.0	-660.489362	-660.489362	1708	1664
	4.0	-660.489910	-660.489910	1542	1496
	3.0	-660.493492	-660.493492	2161	2279
	2.0	-660.489955	-660.489955	2513	2614
1/2	6.0	-1209.765449	-1209.765449	3292	3037
	5.0	-1209.765582	-1209.765582	3319	3048
	4.0	-1209.766149	-1209.766148	3648	3368
	3.0	-1209.769975	-1209.769973	3189	3955
	2.0	-1209.767203	-1209.767202	3791	4482

TABLE 4.3. (*Continued.*)

Bilayer model		Total energy (a.u.)		cpu time (sec.)	
Coverage	d (Å)	Supercell	Elongation	Supercell	Elongation
1/4	6.0	-2308.307783	-2308.307783	14123	10564
	5.0	-2308.307916	-2308.307916	14221	10585
	4.0	-2308.308487	-2308.308488	15542	11366
	3.0	-2308.312388	-2308.312386	16835	13328
	2.0	-2308.310001	-2308.309999	16664	15646
1/8	6.0	-4505.391123	-4505.391123	55110	30184
	5.0	-4505.391259	-4505.391258	53950	30560
	4.0	-4505.391839	-4505.391836	57084	30990
	3.0	-4505.395786	-4505.395774	65263	35555
	2.0	-4505.393611	-4505.393603	64803	50494

[a] The calculations for the surface coverages of 1/1, 1/2, and 1/4 and that of 1/8 were carried out on IBM RISC System/6000 340 and 580, respectively.

other at the various distance and it is confirmed that the crystal elongation approach is sufficiently reliable and applicable. The cpu times by two methods indicate that our calculation becomes as to be increasingly advantageous when the system becomes much larger. Especially, as for the system of a three-layered slab model with the low coverage of 1/8 which can be expected to describe the most realistic situation of local

TABLE 4.4. Total energies and cpu times of the CO adsorption calculations for the systems with a three-layer slab of MgO (001) surface by the supercell and the elongation methods.[a]

Trilayer model		Total energy (a.u.)		cpu time (sec.)	
Coverage	d (Å)	Supercell	Elongation	Supercell	Elongation
1/1	6.0	-935.153876	-935.153876	4068	3859
	5.0	-935.154035	-935.154035	4077	3857
	4.0	-935.154618	-935.154618	4512	4241
	3.0	-935.158238	-935.158238	4985	5036
	2.0	-935.154759	-935.154759	4712	5244
1/2	6.0	-1759.095062	-1759.095062	8322	7554
	5.0	-1759.095234	-1759.095234	8379	7580
	4.0	-1759.095839	-1759.095839	9092	8285
	3.0	-1759.099709	-1759.099706	7863	9959
	2.0	-1759.097009	-1759.097008	9563	10802
1/4	6.0	-3406.967434	-3406.967434	52025	30987
	5.0	-3406.967606	-3406.967606	52098	30964
	4.0	-3406.968216	-3406.968216	53598	34564
	3.0	-3406.972160	-3406.972157	55696	40156
	2.0	-3406.969850	-3406.969847	59769	45123
1/8	6.0	-6702.710855	-6702.710855	191961	96178
	5.0	-6702.711030	-6702.711028	195294	96209
	4.0	-6702.711648	-6702.711645	205696	108359
	3.0	-6702.715639	-6702.715627	227956	129320
	2.0	-6702.713544	-6702.713532	235161	153267

[a] The calculations for the surface coverages of 1/1, 1/2, and 1/4 and that of 1/8 were carried out on IBM RISC System/6000 340 and 580, respectively.

TABLE 4.5. cpu times required in the integral and the SCF steps for CO adsorption calculations on a three-layered slab of MgO (001) surface with 1/8 surface coverage by the supercell and the elongation approaches.[a]

d (Å)	Integral	SCF by supercell	SCF by elongation
6.0	8494	183467	87684
5.0	8497	186797	87712
4.0	8537	197159	99822
3.0	8618	219338	120702
2.0	8778	226383	144489

[a] The cpu times on IBM RISC System/6000 580 are shown in seconds.

CO adsorption on MgO (001) surface, our approach show obviously the great advantage in computation times. The cpu times consumed in the integral and the SCF steps are listed in Table 4.5 for the model system of three planes with 1/8 coverage. It is shown in this table that the latter step is much time-consuming than the former step and our approach can succeed in reducing the computation time in this step by the treatment of the elongation technique.

Results of our crystal elongation calculations for the one-, two-, and three-plane surfaces at the energy minimum are shown in Table 4.6. The surface-molecule distance which gives the minimum energy appears to exist around the value of 2.3 Å. The binding energy defined as the energy difference between the isolated and perturbed systems increases with decreasing the surface coverage as from 1/1 to 1/8 (particularly

TABLE 4.6. Summaries of calculated results for CO adsorption on MgO (001) surface obtained at the configuration for the energy minimum.

Coverage	1/1	1/2	1/4	1/8
(a) One-plane slab				
ΔE (kcal/mol)[a]	2.1214	6.1022	6.8058	7.0102
Q(CO)[b]	13.9850	13.9807	13.9787	13.9781
ΔQ(CO)[c]	0.0150	0.0193	0.0213	0.0219
Q(Mg^{2+})[d]	10.0667	10.0668	10.0653	10.0653
Q(O^{2-})[d]	9.9482	9.9479	9.9467	9.9462
(b) Two-plane slab				
ΔE (kcal/mol)[a]	2.1177	6.1311	6.8516	7.0667
Q(CO)[b]	13.9829	13.9784	13.9766	13.9760
ΔQ(CO)[c]	0.0171	0.0216	0.0234	0.0240
Q(Mg^{2+})[d]	10.0532	10.0532	10.0519	10.0518
Q(O^{2-})[d]	9.9649	9.9634	9.9617	9.9609
(c) Three-plane slab				
ΔE (kcal/mol)[a]	2.0048	5.9711	6.6917	6.9061
Q(CO)[b]	13.9858	13.9784	13.9764	13.9759
ΔQ(CO)[c]	0.0142	0.0216	0.0236	0.0241
Q(Mg^{2+})[d]	10.0462	10.0497	10.0484	10.0484
Q(O^{2-})[d]	9.9632	9.9615	9.9598	9.9590

[a] ΔE = E(perfect MgO) + E(isolated CO) - E(MgO with adsorbed CO) is the binding energy.

[b] Total electron density of adsorbed CO molecule.

[c] ΔQ = Q(isolated CO) - Q(adsorbed CO) indicates transferred electrons from CO molecule.

[d] Electron densities on Mg2+ and O2- ions at the adsorption and the nearest neighboring sites on the top layer of adsorbed surface.

TABLE 4.7. Change of electron densities on independent ions in MgO surface before and after CO adsorption.[a]

Site	Adsorption	Nearest 1	Nearest 2	Nearest 3	Nearest 4	Nearest 5
(a) One-plane slab						
Layer 1	0.0103	0.0012	0.0005	0.0012	0.0005	0.0003
(b) Two-plane slab						
Layer 1	0.0112	0.0015	0.0005	0.0011	0.0008	0.0004
Layer 2	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001
(c) Three-plane slab						
Layer 1	0.0114	0.0015	0.0005	0.0011	0.0008	0.0004
Layer 2	-0.0003	-0.0001	-0.0001	-0.0001	-0.0001	0.0000
Layer 3	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000

[a] The six sites in the table is given in Fig. 4.7 and the layers 1-3 are the top, the second, and the third layers of MgO surface.

as from 1/1 to 1/2). This stabilization of adsorbed system may arise essentially due to reduced repulsive interaction between adsorbates as is shown in Fig. 4.5. It is indicated that the electron density of adsorbed molecule decreases in comparison with that of the isolated molecule and a small amount of electrons transfer from CO molecule to MgO surface. Also, this tendency of electron transfer increases a little by reducing the surface coverage from high coverage (1/1) to low coverage (1/8).

We list the change of electron densities on 1/8 covered surface before and after adsorption obtained by subtracting the values of ions in the perfect MgO from that in the adsorbed MgO for one-three slabs in Table 4.7. This system have six independent

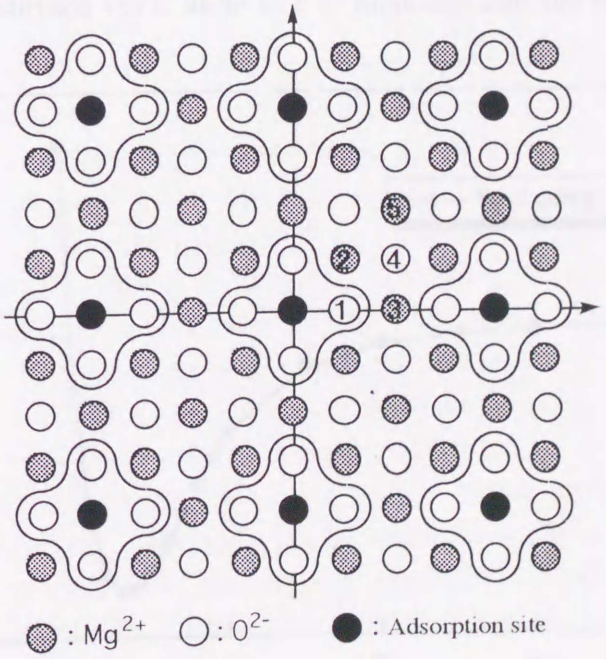
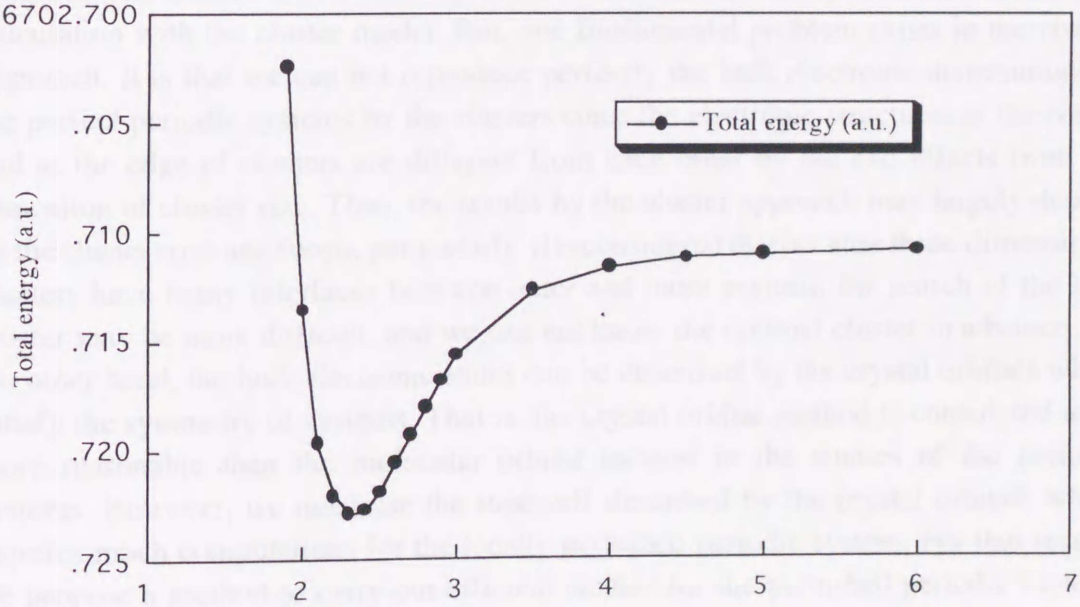


FIG. 4.7. The six independent sites in the top layer of CO-adsorbed MgO (001) surface with 1/8 coverage. The six independent sites correspond to the adsorption site and the first-fifth nearest neighboring sites. The adsorption sites are specified by the blacked positions. The five nearest sites are represented by numbers on the shaded Mg^{2+} and the whitened O^{2-} positions.

sites of the adsorption and the first-fifth nearest sites by the symmetry of CO-adsorbed MgO surface as is given in Fig. 4.7. At the energy minimum, the electrons from CO molecule distribute almost on Mg^{2+} ion at the adsorption site in the top layer. The electron density on the first nearest O^{2-} site increases a little. The third nearest Mg^{2+} site may be affected by two neighboring CO molecules since this site is located halfway between the nearest adsorption sites. There may be little influence on the second Mg^{2+}, the fourth O^{2-}, and the fifth Mg^{2+} sites. From these results of local CO adsorption on MgO (001) surface, the interaction may almost localized on the adsorption site and the first nearest site, and also, it may give no effects on the electron density distributions of Mg^{2+} and O^{2-} ions in the second and the third layers by the screening of the top layer.

The potential energy curve and the change of electron density for the three-layered model with 1/8 coverage are shown in Figs. 4.8(a) and 4.8(b). The stabilization of CO-adsorbed MgO system is mainly observed at the points within the surface-molecule distance of 3.5 Å, and also, the energy minimum may exist at the distance of 2.3 Å with the stabilization energy of 6.9 kcal/mol. The electron densities of MgO surface and CO molecule are hardly affected by their interactions at the surface-molecule distances of 6.0-3.5 Å. In the range with 3.5-3.0 Å separations between Mg^{2+} ion in surface and C atom of molecule, CO molecule appears to be polarized weakly in the crystal field of surface by transferring small amount of electrons from O atom to C atom within CO molecule and there is little transfer of electrons between surface and molecule. By approaching CO molecule into the region within the distance of 3.0 Å from adsorption site, a few electrons on O atom in CO molecule mainly transfer to Mg^{2+} ion in MgO surface via C atom in CO molecule and the electron density of the



(a)

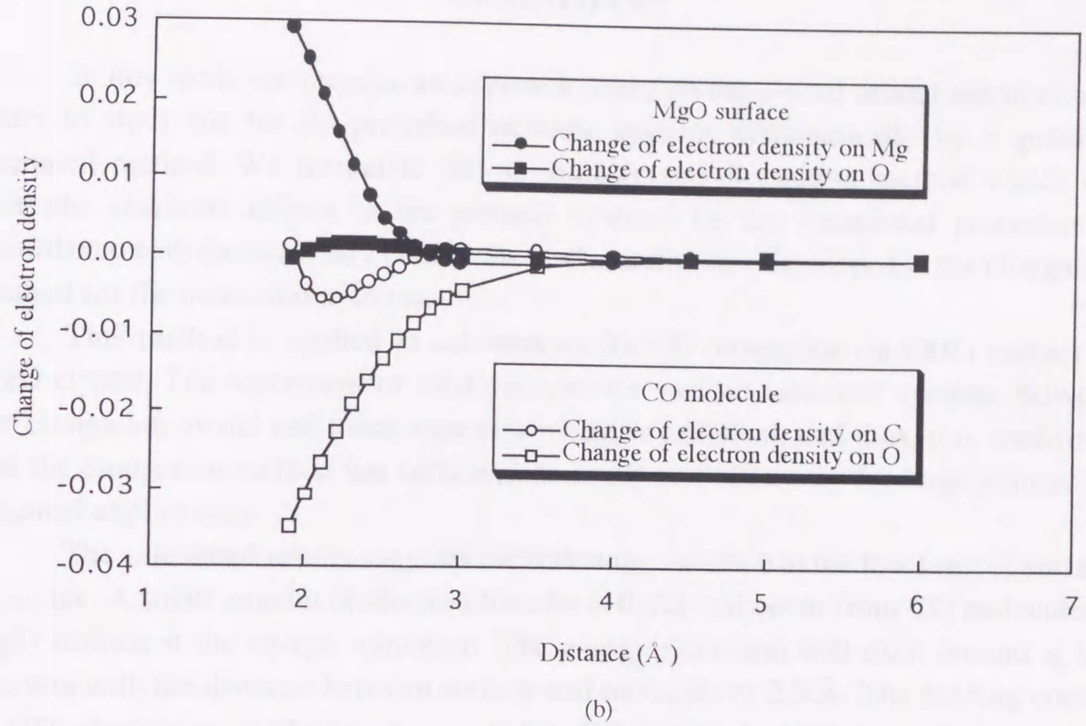


FIG. 4.8. Dependence of (a) total energy and (b) electron density for the three-layered model with 1/8 coverage versus the surface-molecule distance in the vertical adsorption process.

nearest neighboring O^{2-} ion is kept to be almost invariant without the influence of adsorbing CO molecule.

At last of this section, we should give a brief discussion for the utility of molecular orbital and crystal orbital calculations for the locally perturbed periodic systems. The studies about this subject have been carried out by the molecular orbital calculation with the cluster model. But, one fundamental problem exists in the cluster approach. It is that we can not reproduce perfectly the bulk electronic distributions of the perfect periodic systems by the clusters since the electronic structures at the center and at the edge of clusters are different from each other by the end effects from the truncation of cluster size. Thus, the results by the cluster approach may largely depend on the cluster sizes and forms, particularly, it is considered that because three-dimensional clusters have many interfaces between inner and outer regions, the search of the best cluster may be more difficult, and we can not know the optimal cluster in advance. On the other hand, the bulk electronic states can be described by the crystal orbitals which satisfy the symmetry of systems. That is, the crystal orbital method is considered to be more reasonable than the molecular orbital method in the studies of the periodic systems. However, we must use the supercell described by the crystal orbitals which requires much computations for the locally perturbed periodic system. For that reason, we propose a method to carry out efficient studies for the perturbed periodic systems from a standpoint of the crystal orbital approach and expect that this approach can contribute to the development of surface science.

4.4. SUMMARY

In this work, we propose an approach based on the crystal orbital calculation in order to study the locally perturbed periodic systems systematically by a quantum chemical method. We formulate the *ab initio* crystal elongation method which can treat the aperiodic effects in the periodic systems by the variational procedure in accordance with the stationary conditions of electronic state developed in the elongation method for the molecular systems.

This method is applied to calculations for CO adsorption on (001) surface of MgO crystal. The agreement of total energies for various adsorbed systems between our elongation model and usual supercell model is excellent, and thus, it is confirmed that the elongation method has sufficient accuracy and efficiency for large systems in practical applications.

The calculated results suggests the following situation at the low limit of surface coverage. A small amount of electron transfer (~0.02) will occur from CO molecule to MgO surface at the energy minimum. The energy minimum will exist around at the position with the distance between surface and molecule of 2.3 Å. The binding energy of CO adsorption on MgO surface will be ~7.0 kcal/mol. Also, from the change of electron density distributions before and after CO adsorption for a slab with one-three planes, it finds that the effects of CO molecule on MgO surface will be almost localized on the adsorption Mg^{2+} site and a little influence will be given on the first nearest neighboring O^{2-} sites in the top layer. In other words, the second and the third layers are not affected by the adsorbed CO molecule.

The crystal elongation calculation can be performed at the various levels of approximation within the periodic Hartree-Fock scheme by a simple procedure of the orbital selection under the influence of the aperiodic part. The main technique of this approach is the diagonalization of $\mathbf{SS}^{+}$ and $\mathbf{FF}^{+}$ matrices based on the orthonormality and the variational conditions in order to find the interaction and the noninteraction orbitals. Furthermore, this approach requires no assumption of the interaction range by the aperiodic effects in the perturbed system. We can determine the region self-consistently in the elongation calculation.

We propose the crystal elongation method to study the locally perturbed periodic systems based on a view point of the crystal orbital calculation and we expect that this approach will be able to contribute the new development of surface science as well as the advanced cluster approach.

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General Conclusion

Progresses on the Theoretical Treatment of Electronic Structures for Extended Aperiodic Systems by Quantum Chemical Calculations

In the previous four chapters, a new quantum chemical approach on theoretical studies for electronic structures of extended aperiodic systems by molecular orbital and crystal orbital methods has been formulated, and the generalities and usefulness of its treatment have been demonstrated on the various examples by applying the method to extended nonperiodic systems. In this chapter, some progresses in this work are summarized and some perspectives are discussed as a conclusion of this thesis.

On the theoretical approach of extended systems with no periodicity, for instance, polymers, surfaces, and crystals including localized defects or interacting with molecules, some problems exist in the conventional treatment of those systems using the molecular orbital (MO) and crystal orbital (CO) methods. The most important point is summarized as follows. Since the usual cluster or supercell approach represents an extended system as a finite model, the definition of model system affects largely on calculated results. That is, the size of cluster or supercell must be sufficiently large so that the electronic structure can be described correctly only within the finite region. But, the optimal size of model can not be determined in advance, and also, the computer has the upper limit in practical calculations of the systems with various sizes as the maximum size depends on the power and capacity of machine. Thus, a new theoretical treatment for extended aperiodic systems must be developed.

As mentioned in Chaps. 1-4, it is clarified that the large reduction in computer time as compared to the conventional treatment can be achieved without loss of accuracy by the method formulated in those works. The key point of this approach is that it is possible to separate the total orbital space in the large system into the interactive and noninteractive spaces. By this orbital division, the SCF calculation of the system can be replaced by a series of the SCF steps with small number of effective basis orbitals and the eigenvalue problem can be solved without increasing the dimension. And also, the regions in which the electronic structure is altered and unaltered by a perturbation can be specified as active and frozen orbitals. The unperturbed range within the perturbed system can be represented by the freezing pattern of electron densities which enables us to analyze the periodicity of the electronic state in a nonperiodic system.

The utility of its application is demonstrated at the semiempirical and *ab initio* levels and the generality of its formulation is confirmed by the MO and CO calculations for various systems. The most characteristic feature of this method in comparison with the conventional treatment is that no assumption for the size of fragments is required in partitioning the whole system into subsystems of perturbed and unperturbed regions. That is, it is concluded that this approach can be regarded as a new theoretical method to study extended aperiodic systems by a more general procedure with great advantage in computational time which is applicable to both the cluster model based on the MO theory and the supercell model based on the CO theory.

To carry out the more quantitative calculation and analysis of electronic structure, the post-Hartree-Fock treatment including the effect of electron correlation must be introduced into the MO and CO studies of large systems. The progress in this direction will be realized by developing the method to estimate the local electron correlation such as the CI technique within a local region described by the localized orbitals.

Finally, it is noted that although only the starting stage on this field has been established in this thesis, as mentioned above, this new quantum chemical approach on theoretical studies for electronic structures of extended aperiodic systems by the MO and CO methods has enough potential to contribute the further advance of polymer and surface science.

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***The contents of these papers are included in the thesis.**