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# Local density of states of aperiodic polymers using the localized orbitals from an *ab initio* elongation method

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An elongation method, which was already proposed to calculate efficiently the electronic states of aperiodic polymers, is developed to provide the local density of states. Elongation method is carried out by repeating the *uniform localization of wave functions* with inclusion of the interaction between the cluster and an attacking molecule. At first, we develop this method to the *ab initio* level. Next, we show that the local density of states (LDOS) is obtained efficiently following the elongation step without treating the whole system directly. The validity of our method is examined via application to a hydrogen molecule cluster by comparing the results with those by the conventional *ab initio* method for the whole system. This approach makes it possible to investigate the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and their density of states on each site of a polymer chain, which will provide a novel approach to examine intra- and intermolecular reactivities within and between aperiodic polymers.

## I. INTRODUCTION

The Hartree-Fock method for periodic polymers<sup>1,2</sup> has already been established by the tight-binding approximation under the Bórn-von Kármán periodic boundary condition. Many studies have been reported within the one-electron picture and, also, including electron correlation.<sup>3-8</sup> Calculations on the electronic structure of an undoped and highly doped polymer chain can be calculated by this treatment.

On the other hand, at the present stage of theoretical approach, little has been developed on the method of calculating electronic states of nonperiodical polymers. Properties of aperiodic one-dimensional polymers have been a subject of interest in the field of physics, e.g., soliton, polaron, lattice defects, conducting polymers, etc. The theoretical approach for such problems has rarely been developed, although there are a few reports using the self-consistent field Green's function approach<sup>9</sup> to a local perturbation in a periodic system.<sup>10-13</sup> This treatment was applied to chemisorption and localized defects. Aperiodicity in biopolymers also plays an essential role in hopping conduction in proteins, charge transport in polypeptide chain, catalytic activity of enzymes, etc. Some strategies and methods for aperiodic DNA and proteins are presented and band structures and conduction properties are discussed.<sup>14-17</sup> In these works, the localization properties of one-electron wave functions and the density of states (DOS) distributions are used as main parameters in describing characteristic properties of biomolecules. However, the DOS of completely periodic polymers provides identical values on every site because the electron density is independent of the unit cell under the periodic boundary condition. Therefore, aperiodic properties of random poly-

mers cannot be provided in the viewpoint of DOS, as far as the conventional tight-binding approximation is employed.

A general numerical technique<sup>18</sup> for calculating the local physical quantities, especially the LDOS, is proposed by using the recursion method.<sup>19</sup> This treatment is applied to the end effects on the bond length alternation in polyacetylene. It is expected that the LDOS can be adopted as a useful indication for describing local electronic structures for such large aperiodic polymers as previously mentioned biopolymers.

On the other hand, we are developing a new approach,<sup>20</sup> the elongation method, for calculating electronic structures of aperiodic polymers with random arrangements without treating the whole system directly. This treatment is based on the localization of the wave functions of an oligomer on a specified part of the polymer. By using this method, we can increase the length of the polymer chain to any extent desired, i.e., the theoretical synthesis of polymers. Under this procedure, the localized molecular orbitals (LMOs) on each site are obtained for any type of random arrangements and also periodic and block copolymers. No general method is perhaps proposed for obtaining LMOs on each site of random arrangement, except for our elongation method within our knowledge.

In the present work, the LMOs from the elongation method are used to describe the LDOS based on Ref. 18 after the elongation method is developed at the level of the *ab initio* method. As the first step to make sure that the LDOS can be efficiently accessible from the elongation method with good accuracy, the calculations are carried out for a regularly arranged hydrogen molecule cluster. It should be noticed that this treatment is substantially applicable for any type of aperiodic polymers.

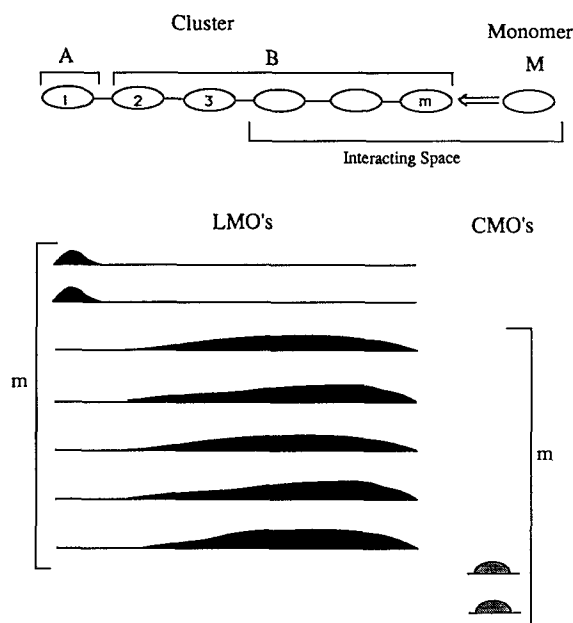


FIG. 1. A schematic illustration of the region  $A$  and the region  $B$  defined in the cluster and the LMOs obtained by the localization of the CMOs. The  $A$  part is represented by one unit.

## II. METHOD

First, we developed the elongation method to the *ab initio* level. Details of the elongation method are described in our previous paper.<sup>20</sup> We outline briefly the importance items among this procedure, since the formulas of the *ab initio* method are very similar to those of the extended Hückel method.

As a starting point, we choose a cluster that is an oligomer consisting of an appropriate number of  $n$  monomer units. The CMOs (canonical molecular orbitals) of this cluster  $\{\psi_i\}$  are obtained by the conventional *ab initio* method

$$\psi_i = \sum_{\mu}^{\text{all}} C_{\mu i} \chi_{\mu}. \quad (1)$$

In Eq. (1),  $\chi_{\mu}$  indicates the  $\mu$ th atomic orbital (AO) of the cluster. The cluster is then divided into two parts  $A$  and  $B$  with the assumption that a new monomer is added to the end of  $B$  as shown in Fig. 1. Part  $A$  is the furthest removed in space from the attacking monomer and, in this study, usually consists of one unit. For the defined regions  $A$  and  $B$ , particular CMOs are localized in the region  $A$  and the others are in the region  $B$  among CMOs  $\{\psi_i\}$ . This localization method is efficient for such a model hydrogen molecule polymer ( $\text{H}_2 \cdots \text{H}_2 \cdots \text{H}_2 \cdots \text{H}_2 \cdots$ ) as weakly bounded by van der Waal's interaction, but difficult for such polyethylene and polypropylene as strongly bounded by chemical bonds. In the previous work applying polyethylene-like polymers, it was found to be efficient to use the hybridized AOs instead of the usual AOs as a basis function of MOs before the localization of wave functions. We did not apply here the hybridized transformation for the original CMOs, since the purpose of the present work

is to develop the elongation method to the *ab initio* level and demonstrate the validity and the applicability of the LDOS treatment for a simple model polymer system.

The LMOs  $\phi_i$  and  $\phi_j$  are obtained by a unitary transformation between occupied CMOs  $\psi_i$  and  $\psi_j$

$$\phi_i = \sin \theta \psi_i + \cos \theta \psi_j, \quad (2)$$

$$\phi_j = -\cos \theta \psi_i + \sin \theta \psi_j. \quad (3)$$

Using  $\theta_{\max}$  to give the maximum value of the following  $L_{ij}$ :

$$L_{ij} = \langle \phi_i(A) | \phi_i(A) \rangle + \langle \phi_j(B) | \phi_j(B) \rangle, \quad (4)$$

where  $\phi_i(A)$  or  $\phi_j(B)$  means that the  $i$ th LMO includes the summation only on the AOs in the region  $A$  or in the region  $B$ , respectively. These are written by dividing the summations on AOs in Eq. (1) into those on the two regions  $A$  and  $B$ , and substituting it into Eqs. (2) and (3) as

$$\begin{aligned} \phi_i &= \left( \sum_{\mu}^{\text{on } A} + \sum_{\mu}^{\text{on } B} \right) (\sin \theta C_{\mu i} + \cos \theta C_{\mu j}) \chi_{\mu} \\ &= \phi_i(A) + \phi_i(B), \end{aligned} \quad (5)$$

$$\begin{aligned} \phi_j &= \left( \sum_{\nu}^{\text{on } A} + \sum_{\nu}^{\text{on } B} \right) (-\cos \theta C_{\nu i} + \sin \theta C_{\nu j}) \chi_{\nu} \\ &= \phi_j(A) + \phi_j(B). \end{aligned} \quad (6)$$

For details of the formula, our paper<sup>20</sup> should be referred to. After this transformation,  $\psi_i(A)$  is localized into the  $A$  part and  $\psi_j(B)$  into the  $B$  part as much as possible. This procedure is repeated in order to obtain the more localized molecular orbitals  $[\phi_i^{\text{occ}}(A)]$  and  $[\phi_j^{\text{occ}}(B)]$  until any pair of MOs gives no further localization. The same procedure is applied to the vacant CMOs of the cluster, giving the more localized orbitals  $[\phi_i^{\text{vac}}(A)]$  and  $[\phi_j^{\text{vac}}(B)]$ . After the localization, the LMOs as shown schematically in Fig. 1 are given.

Next, molecular orbital calculations are carried out for the attacking monomer and then the matrix elements are also calculated for the system in which the cluster interacts with a monomer approaching one end of the  $B$  part (interacting space in Fig. 1). The eigenvalue problem for the whole system is represented with the occupied and the vacant LMOs as

$$\begin{vmatrix}
 \mathbf{F}^{\text{occ}}(A,A) - \epsilon \mathbf{I} & 0 & \mathbf{F}^{\text{occ}}(A,B) & 0 & \sim 0 \\
 0 & \mathbf{F}^{\text{vac}}(A,A) - \epsilon \mathbf{I} & 0 & \mathbf{F}^{\text{vac}}(A,B) & \sim 0 \\
 \mathbf{F}^{\text{occ}}(B,A) & 0 & \mathbf{F}^{\text{occ}}(B,B) - \epsilon \mathbf{I} & 0 & \mathbf{F}^{\text{occ}}(B,M) - \epsilon \mathbf{S}^{\text{occ}}(B,M) \\
 0 & \mathbf{F}^{\text{vac}}(B,A) & 0 & \mathbf{F}^{\text{vac}}(B,B) - \epsilon \mathbf{I} & \mathbf{F}^{\text{vac}}(B,M) - \epsilon \mathbf{S}^{\text{vac}}(B,M) \\
 \sim 0 & \sim 0 & \mathbf{F}^{\text{occ}}(M,B) - \epsilon \mathbf{S}^{\text{occ}}(M,B) & \mathbf{F}^{\text{vac}}(M,B) - \epsilon \mathbf{S}^{\text{vac}}(M,B) & \mathbf{F}(M) - \epsilon \mathbf{I}
 \end{vmatrix} = 0, \quad (7)$$

where  $\mathbf{F}^{\text{occ}}(X,Y)$  indicates the matrix of Hamiltonian between the  $X$  part and the  $Y$  part of the cluster in the occupied space. The matrix element for  $\mathbf{F}^{\text{occ}}(X,Y)$  is given as follows:

$$\mathbf{F}_{ij}^{\text{occ}}(X,Y) = \int \phi_i^{\text{occ}}(X) H \phi_j^{\text{occ}}(Y) d\tau, \quad (8)$$

where  $\phi_i^{\text{occ}}(X)$  is the  $i$ th occupied orbital localized on the  $X$  part. The same notation is used for the vacant space.  $M$  is used to denote the CMOs of the attacking monomer.  $\mathbf{I}$  is a unit matrix and  $\epsilon$  indicates eigenvalues. The matrices between the occupied space and the vacant space of the cluster vanish completely since all the matrix elements between the canonical occupied and the vacant orbitals are zero. This feature is retained throughout the unitary transformation among the occupied or the vacant orbitals. The expression of Eq. (7) shows that the dimension of  $n \times n$  based on the LMOs can be reduced to the dimension of  $m \times m$  surrounded by the broken line for the eigenvalue problem. The  $m$  is the same as the dimension of the starting cluster because the dimension of the  $A$  part to be dropped out from the eigenvalue problem and that of the attacking molecule to be added to the eigenvalue problem are the same. This means that, as shown schematically in Fig. 2, the diagonalization based on the LMOs should be carried out with a constant number of  $m \times m$  dimension corresponding to the  $I$  part. By the procedure described above, we can diminish the dimension of the matrix and the electronic structure for the cluster elongated by one unit is obtained. By repeating this procedure, it is possible to lengthen the cluster without increasing the dimension to be treated and obtain the electronic structures for random

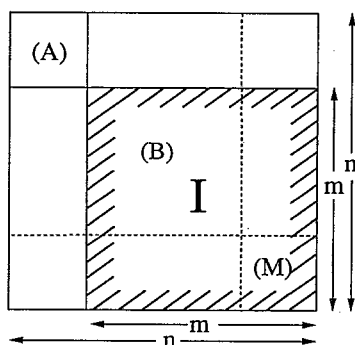


FIG. 2. A schematic illustration of Eq. (7). The shaded area corresponds to that surrounded by the broken line in Eq. (7), which is denoted by  $I$ .

polymers. A schematic representation of the elongation method is shown in Fig. 3.

On the other hand, before the diagonalization after localization, the contribution from some AOs situated on part  $A$  is examined by the following quantity:

$$S_{ii}(A) = \sum_{\mu}^{\text{on } j_{\mu}} \sum_{\nu}^{\text{on } j_{\nu}} \sum_{j_{\mu}}^{\text{on } A} \sum_{j_{\nu}}^{\text{on } A} L_{\mu i}^{(j_{\mu})}(B) L_{\nu i}^{(j_{\nu})}(B) S_{\mu\nu}^{(j_{\mu}j_{\nu})}, \quad (9)$$

where  $L_{\mu i}^{(j_{\mu})}(X)$  represents the coefficient of the  $\mu$ th AO in the  $j_{\mu}$ th cell on the  $i$ th LMO that is localized on the  $X$  part. If the value of Eq. (9) is negligibly small, it is suggested that the AOs  $\mu(\in A)$  are free from the bases of the LMO  $L_{\mu i}^{(j_{\mu})}(B)$ . The notations used here are indicated in Fig. 4.  $j_{\mu}$  and  $j_{\nu}$  indicate the cell in the cluster chain to which the atomic orbitals  $\mu$  and  $\nu$  belong, respectively.  $S_{\mu\nu}^{(j_{\mu}j_{\nu})}$  is the overlap matrix element between the  $\mu$ th atomic orbital in the  $j_{\mu}$ th cell and the  $\nu$ th atomic orbital in the  $j_{\nu}$ th cell. After several cycles, the contribution from some AOs situated on the terminal region

$$S_{ii}(\text{terminal}) = \sum_{\mu}^{\text{on } j_{\mu}} \sum_{\nu}^{\text{on } j_{\nu}} \sum_{j_{\mu}}^{\text{terminal}} \sum_{j_{\nu}}^{\text{terminal}} L_{\mu i}^{(j_{\mu})}(B) L_{\nu i}^{(j_{\nu})}(B) \times S_{\mu\nu}^{(j_{\mu}j_{\nu})} \quad (10)$$

becomes smaller than the assumed threshold ( $10^{-5}$  was used in this work) and then the AOs are dropped out. Thereafter, a constant number of AOs can be cut off in each cycle, and we define the  $J$ th cell, which satisfies the normalization condition

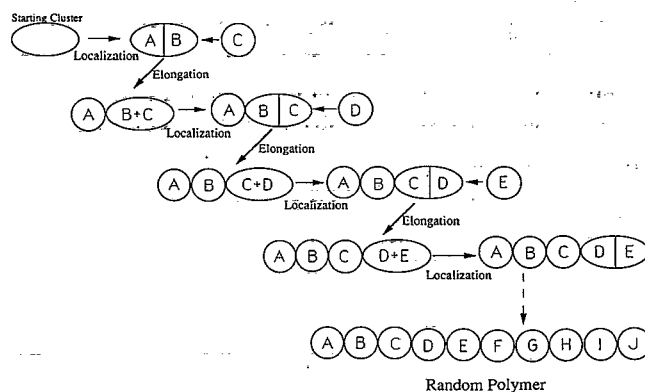


FIG. 3. A schematic illustration for the procedure of the theoretical synthesis of a random polymer by the elongation method.

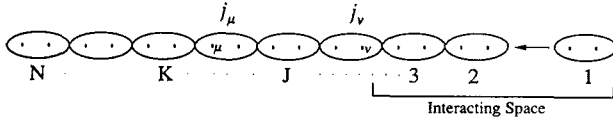


FIG. 4. Numbering and index of sites used in the text.

$$S_{ii}(N \text{ terminal}) = \sum_{\mu=1}^{\text{on } j_{\mu}} \sum_{\nu=1}^{\text{on } j_{\nu}} \sum_{j_{\mu}=1}^J \sum_{j_{\nu}=1}^J L_{\mu i}^{(j_{\mu})}(B) L_{\nu i}^{(j_{\nu})}(B) \times S_{\mu\nu}^{(j_{\mu}j_{\nu})} = 1, \quad (11)$$

indicated in Fig. 4.

This manipulation is of great importance in making Fock matrix elements, because keeping the useless AOs that give little contribution leads to enormously futile efforts. The Fock matrix elements at the *ab initio* level are written by

$$\begin{aligned} F_{\mu\nu}^{(j_{\mu}j_{\nu})} &= I_{\mu\nu}^{(j_{\mu}j_{\nu})} + \sum_{\rho=1}^{\text{on } j_{\rho}} \sum_{\sigma=1}^{\text{on } j_{\sigma}} \left( \sum_{j_{\rho}=1}^J \sum_{j_{\sigma}=1}^J + \sum_{j_{\rho}=1}^J \sum_{j_{\sigma}=J+1}^K + \sum_{j_{\rho}=J+1}^K \sum_{j_{\sigma}=1}^J + \sum_{j_{\rho}=J+1}^K \sum_{j_{\sigma}=J+1}^K \right) P_{\rho\sigma}^{(j_{\rho}j_{\sigma})} \\ &\times \left[ \begin{pmatrix} j_{\mu} & j_{\nu} \\ \mu & \nu \end{pmatrix} \begin{pmatrix} j_{\rho} & j_{\sigma} \\ \rho & \sigma \end{pmatrix} - \frac{1}{2} \begin{pmatrix} j_{\mu} & j_{\rho} \\ \mu & \rho \end{pmatrix} \begin{pmatrix} j_{\nu} & j_{\sigma} \\ \nu & \sigma \end{pmatrix} \right], \end{aligned} \quad (12)$$

where

$$P_{\rho\sigma}^{(j_{\rho}j_{\sigma})} = 2 \sum_i^{\text{occ}} L_{\rho i}^{(j_{\rho})} L_{\sigma i}^{(j_{\sigma})}. \quad (13)$$

$I_{\mu\nu}^{(j_{\mu}j_{\nu})}$  is the matrix element of the core-resonance integrals (kinetic energy and core attraction) between the  $\mu$ th atomic orbital in the  $j_{\mu}$ th cell and the  $\nu$ th atomic orbital in the  $j_{\nu}$ th cell. The term  $P_{\rho\sigma}^{(j_{\rho}j_{\sigma})}$  given by Eq. (13) has been determined by means of the LMOs  $L_{\rho i}^{(j_{\rho})}$ , which should be invariant under the unitary transformation. In Eq. (12), summations on  $j_{\rho}$  and  $j_{\sigma}$  are classified into four groups. The first one covers over atomic orbitals whose coefficients have nonnegligible absolute value in LMOs, and the procedure for the calculations is the same as one in the usual *ab initio* SCF method. In the second and the third summations in Eq. (12), two-electron integrals are calculated by means of Mulliken's approximation. For the fourth summation, two-electron integrals are calculated with the point charge approximation and Mulliken's approximation. In correspondence with these summations, nuclear attraction integrals  $I_{\mu\nu}^{(j_{\mu}j_{\nu})}$  are included in the range from first cell to the  $K$ th cell that is shown in Fig. 4. The range from 1 to  $K$  is determined so that the range over  $K$  gives negligible contribution to the Fock matrix. By using the approximation, we can save much computation time of the two-electron integrals for very huge polymeric systems without loss of the accuracy of computational results.

The Fock matrix elements and the overlap integrals on the basis of LMOs are, given respectively, as

$$S_{ij}(X, Y) = \sum_{\mu=1}^{\text{on } j_{\mu}} \sum_{\nu=1}^{\text{on } j_{\nu}} \sum_{j_{\mu}=1}^J \sum_{j_{\nu}=1}^J L_{\mu i}^{(j_{\mu})}(X) S_{\mu\nu}^{(j_{\mu}j_{\nu})} L_{\nu j}^{(j_{\nu})}(Y), \quad (14)$$

$$F_{ij}(X, Y) = \sum_{\mu=1}^{\text{on } j_{\mu}} \sum_{\nu=1}^{\text{on } j_{\nu}} \sum_{j_{\mu}=1}^J \sum_{j_{\nu}=1}^J L_{\mu i}^{(j_{\mu})}(X) F_{\mu\nu}^{(j_{\mu}j_{\nu})} L_{\nu j}^{(j_{\nu})}(Y), \quad (15)$$

where  $S_{ij}(X, Y)$  and  $F_{ij}(X, Y)$  indicate the  $m \times m$  matrix elements in the  $I$  part of Fig. 2 between the  $i$ th LMO localized on the  $X$  part and the  $j$ th LMO on the  $Y$  part. As the results, the number of AOs and MOs included in the problem remain nearly constant throughout the calculations for all the propagation steps, which is the most characteristic feature of the elongation method.

The total energy for the whole system is given by

$$E = \frac{1}{2} \sum_{\mu=1}^{\text{on } j_{\mu}} \sum_{\nu=1}^{\text{on } j_{\nu}} \sum_{j_{\mu}=1}^J \sum_{j_{\nu}=1}^J (I_{\mu\nu}^{(j_{\mu}j_{\nu})} + F_{\mu\nu}^{(j_{\mu}j_{\nu})}) P_{\mu\nu}^{(j_{\mu}j_{\nu})}. \quad (16)$$

Next we define the local density of states from the LMOs obtained by this procedure. It seems important for investigating the band structure of aperiodic polymers. For the extended Hückel method in which explicit electron-electron repulsion integrals are neglected, total energy can be represented by

$$E = 2 \int_{-\infty}^{E_f} E N(E) dE, \quad (17)$$

where the density of states  $N(E)dE$  gives the number of states in the interval  $[E, E+\Delta E]$  and  $E_f$  is the Fermi level.  $N(E)$  is the density of states (DOS) at  $E$  and defined by the quantity  $\sum_i \delta(E-E_i)$ . Using the normalization condition of a complete set of eigenfunctions  $\{\varphi_i(\mathbf{r})\}$ ,

$$N(E) = \sum_i^{\text{all}} \delta(E-E_i) = \sum_i^{\text{all}} \int \delta(E-E_i) |\varphi_i(\mathbf{r})|^2 d\mathbf{r}. \quad (18)$$

Defining  $\rho(\mathbf{r}; E)$  as the DOS per unit volume,  $N(E)$  is represented by

$$N(E) = \int \rho(\mathbf{r}; E) d\mathbf{r}. \quad (19)$$

Comparing Eqs. (18) and (19), the expression for  $\rho(\mathbf{r}; E)$  becomes

$$\rho(\mathbf{r}; E) = \sum_i^{\text{all}} \delta(E-E_i) |\varphi_i(\mathbf{r})|^2. \quad (20)$$

The completeness of the set  $\{\varphi_i(\mathbf{r})\}$  means that

$$\int_{-\infty}^{\infty} \rho(\mathbf{r}; E) dE = 1. \quad (21)$$

The normalization condition of wave functions can be written in our treatment based on the molecular orbital theory as

$$\int |\varphi_i(\mathbf{r})|^2 d\mathbf{r} = \sum_{\mu} \sum_{j_{\mu}}^{\text{on } j_{\mu}} \sum_{\nu}^{\text{all}} \sum_{j_{\nu}}^{\text{on } j_{\nu}} C_{\mu i}^{(j_{\mu})} C_{\nu i}^{(j_{\nu})} S_{\mu\nu} = 1. \quad (22)$$

$C_{\mu i}^{(j_{\mu})}$  represents a  $\mu$ th AO coefficient in the  $j_{\mu}$ th cell of the  $i$ th molecular orbital that gives the eigenstate  $E_i$ . The DOS of Eq. (19) is represented to be partitioned into individual LDOS terms on a basis of AOs in the molecular orbital method as follows:

$$N(E) = \sum_{\mu} \sum_{j_{\mu}}^{\text{all}} \rho_{\mu}^{j_{\mu}}(E). \quad (23)$$

By substituting Eqs. (22) and (23) into Eq. (18), the following DLOS can be defined:

$$\rho_{\mu}^{j_{\mu}}(E) = \sum_i^{\text{all}} \delta(E - E_i) \sum_{\nu}^{\text{on } j_{\nu}} \sum_{j_{\nu}}^{\text{all}} C_{\mu i}^{(j_{\mu})} C_{\nu i}^{(j_{\nu})} S_{\mu\nu}^{(j_{\mu}j_{\nu})}. \quad (24)$$

This quantity can be calculated for each cell  $j$  from the eigenvalue problem in the molecular orbital method.

On the other hand, a crystal orbital of periodic polymer systems is represented by

$$\varphi_{ki}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \sum_{\mu=1}^n \exp(ikj) C_{\mu i}(k) \chi_{\mu}(\mathbf{r} - \mathbf{r}_{\mu} - j\mathbf{a}), \quad (25)$$

where  $j$  specifies a cell in the polymer consisting of  $N$  cells,  $k$  specifies the wave number vector, and  $a$  specifies the

lattice vector. The LDOS based on the crystal orbital is given, corresponding to Eq. (24), by

$$\rho_{\mu k}(E) = \sum_i^{\text{all}} \delta[E - E_i(k)] \sum_{\nu}^{\text{on unit cell}} C_{\mu i}(k) C_{\nu i}(k) S_{\mu\nu}(k). \quad (26)$$

It is noticed that the LDOS is no longer specified on the cell number  $j$  because the phase factor vanishes in the electron density expression (22) by

$$|\exp(ikj)|^2 = 1, \quad \text{for any } j.$$

As a result, the LDOS on a polymer chain becomes constant for all the unit cells which suit the symmetry to the translational vector. Therefore, characteristic properties localized on a particular segment cannot be provided within the framework of the tight-binding approximation.

This suggests that  $m$  eigenvalues and eigenstates obtained from the  $m \times m$  secular determinant in Fig. 2 provide efficiently the LDOS of the end part of the cluster in the process of the elongation. The Hartree-Fock equation for the MO-based Fock and the overlap matrix is written for the  $B$  part and an attacking monomer (the  $I$  part in Fig. 2) by

$$\mathbf{F}(I)\mathbf{U}(I) = \mathbf{S}(I)\mathbf{U}(I)\mathbf{E}(I). \quad (27)$$

Multiplying  $\mathbf{U}^\dagger$  from the left-hand side and substituting Eqs. (14) and (15), the orthonormalization condition and the orbital energies for this interacting space are represented by Eqs. (28) and (29), respectively,

$$\sum_{i=1}^m \sum_{j=1}^m U_{ik}(I) S_{ij}(I) U_{jl}(I) = \sum_{i=1}^m \sum_{j=1}^m \sum_{\mu=1}^{\text{on } j_{\mu}} \sum_{\nu=1}^{\text{on } j_{\nu}} \sum_{j_{\mu}=1}^J \sum_{j_{\nu}=1}^J [U_{ik}(I) L_{\mu i}^{(j_{\mu})}(I)] S_{\mu\nu}^{(j_{\mu}j_{\nu})} [L_{\nu j}^{(j_{\nu})}(I) U_{jl}(I)] = \delta_{kl}(I), \quad (28)$$

$$\sum_{i=1}^m \sum_{j=1}^m U_{ik}(I) F_{ij}(I) U_{jl}(I) = \sum_{i=1}^m \sum_{j=1}^m \sum_{\mu=1}^{\text{on } j_{\mu}} \sum_{\nu=1}^{\text{on } j_{\nu}} \sum_{j_{\mu}=1}^J \sum_{j_{\nu}=1}^J [U_{ik}(I) L_{\mu i}^{(j_{\mu})}(I)] F_{\mu\nu}^{(j_{\mu}j_{\nu})} [L_{\nu j}^{(j_{\nu})}(I) U_{jl}(I)] = \epsilon_k \delta_{kl}(I). \quad (29)$$

The newly obtained molecular orbital coefficients are written on the basis of AOs as

$$C_{\mu k}^{(j_{\mu})}(I) = \sum_{i=1}^m U_{ik}(I) L_{\mu i}^{(j_{\mu})}(I), \quad (30)$$

where the LMOs  $L_{\mu i}^{(j_{\mu})}(I)$ , which already localized on the  $B$  part, have a nonzero value up to the  $J$ th cell. The AO coefficients at the remote region beyond the  $J$ th cell are cut off because of those negligibly small values of Eq. (10) and, therefore, the coefficients given by Eq. (30) become also negligibly small values beyond the  $J$ th cell. In the process of the diagonalization for elongating with an approaching monomer, the LDOS at the interval of  $E \sim E + \Delta E$  is obtained numerically by

$$\rho_{\mu}^{(j_{\mu})}(E, E + \Delta E) = \sum_{k(=E)}^{(E+\Delta E)} \delta(E - E_k) \sum_{\nu}^{\text{on } j_{\nu}} \sum_{j_{\nu}=1}^J C_{\mu k}^{(j_{\mu})}(I) \times C_{\nu k}^{(j_{\nu})}(I) S_{\mu\nu}^{(j_{\mu}j_{\nu})}, \quad (31)$$

where  $\sum_{k(=E)}^{(E+\Delta E)}$  means that  $k$  is summed over only the eigenstates that are lied between  $E$  and  $E + \Delta E$ , and  $\sum_{j_{\nu}=1}^J$  means for the summation on the AOs,  $\mu$  is adequate up to the ones in the  $J$ th cell in Fig. 4. It is noticed that this quantity can be assigned a significance only in the  $I$  part. The LDOS at the  $A$  part can be obtained in a similar manner, after the rediagonalization for the LMOs that are localized on the  $A$  part. However, Eq. (31) that represents the LDOS at the end part of the polymer can be obtained automatically in the process of the elongation calculations and any more efforts for obtaining this quantity are

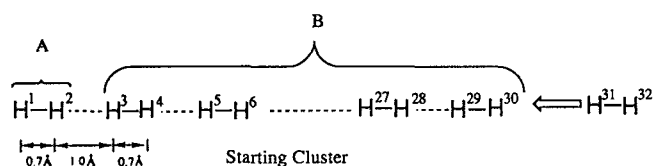


FIG. 5. The hypothetical polymer system consisting of regularly arranged hydrogen molecules.

scarcely needed. Furthermore, according to Eq. (17), the total energy can be divided approximately into the local site energies

$$E = \sum_{\mu}^{\text{all}} \sum_{j_{\mu}}^{\text{all}} \epsilon_{\mu}^{j_{\mu}} = 2 \sum_{\mu}^{\text{all}} \sum_{j_{\mu}}^{\text{all}} \int_{-\infty}^{E_f} E \rho_{\mu}^{j_{\mu}}(E) dE, \quad (32)$$

where  $E_f$  is Fermi level and  $\rho_{\mu}^{j_{\mu}}(E)$  is the LDOS on the AO  $\mu$  in the  $j_{\mu}$ th cell. The local site energies are given approximately by

$$\epsilon_{\mu}^{j_{\mu}} \approx 2 \sum_{i=1}^{\text{occ}} E \phi_{\mu}^{j_{\mu}}(E_i) \quad (33)$$

within the Hückel approximation. This expression does not hold for the treatment with the self-consistent density matrix, but these values will be expected to provide an insight on the local stability on an aperiodic polymer chain. As a result, the LDOS approach will provide significant information regarding local band structures of aperiodic polymers including end effects of polymers.

### III. RESULTS AND DISCUSSION

The elongation method outlined in the previous section was tested on a hypothetical polymer system consisting of regularly arranged hydrogen molecules. The first system to test the present method was the hypothetical polymer system consisting of many hydrogen molecules shown in Fig. 5. The distance between hydrogen molecules was tentatively assumed to be 1.0 Å and the distance between two hydrogen atoms in the molecule 0.7 Å. A cluster with 15  $\text{H}_2$  molecules was calculated initially and the attacking hydrogen molecule was added to the cluster one by one. The region *A* was the furthest removed hydrogen molecule moiety from the attacking molecule. Accordingly, we omitted two orbitals that were localized on the region *A* (one is the occupied orbital and the other is the vacant one). In other words, we diminished the dimension of the matrix in Eq. (7) by two. At the same time, however, we added two orbitals, the occupied and the vacant CMOs of the attacking hydrogen molecule. As a whole, the dimension of the matrix in Eq. (7) remained constant after the cluster was elongated by one hydrogen molecule. The repetition of this procedure has made it possible to calculate the electronic structure of polymers with nearly infinite length with a matrix of constant dimension. After elongation with nine  $\text{H}_2$  molecules, it was found that the coefficients of AOs in the remotest hydrogen molecule moiety became negligibly small in all MOs [the contribution of this part [Eq. (10)]

is less than  $10^{-5}$ ], and hence the AOs in the remotest hydrogen molecule was dropped thereafter. Accordingly, the number of AOs in all localized orbitals was 46 and the dimension of the eigenvalue problem was 30, which was equal to that of the starting cluster. The LMOs obtained at the final step are not symmetric on each end part because the region *B* (14  $\text{H}_2$ ) that we defined here is larger than the region *A* (1  $\text{H}_2$ ). The finally obtained LMOs on the reaction part are broadly localized on the region *B* composed of 14  $\text{H}_2$ . We can obtain properly symmetric orbitals by localizing the LMOs on the region *B* furthermore into each unit cell by the same localization procedure. However, this treatment need not be employed because the LMOs localized broadly on the region *B* are substantially required for the LDOS calculations. These asymmetric LMOs give no problem on the electronic state, since they do not affect the total energy as well as the electron density which is of course symmetric.

To prove the validity of the present method, the usual *ab initio* calculations were performed on the elongated cluster for comparison. The total energies for various lengths of clusters were calculated by both the present elongation method and the usual *ab initio* method, and good agreement is obtained. The atomic and bond populations determined by the two methods are in excellent agreement. The populations in one end part are also in excellent agreement with those in another end part, i.e., the symmetry in the electron distribution is naturally conserved by the elongation method. Besides, the elongation method saves much computational time in comparison with the usual *ab initio* method and this advantage increases efficiently with the length of clusters. Here we do not list the numerical results because the purpose of the present work is not to demonstrate the validity of the *ab initio* elongation method developed here. Concerning the applicability and the reliability of the *ab initio* elongation method, we will report next time the results applied to more realistic systems.

The most significant interest of our method lies in the reliability of the LDOS calculations of aperiodic polymers by means of the elongation method. The LDOS calculations are performed on the model hydrogen polymer  $(\text{H}_2)_{16}$ , i.e., starting from the  $(\text{H}_2)_{15}$  cluster, elongated by one unit  $\text{H}_2$ . In Fig. 6, the LDOS is represented graphically for each hydrogen atom  $\text{H}_1\text{--H}_2, \text{H}_3\text{--H}_4, \dots, \text{H}_{31}\text{--H}_{32}$ . The results for the whole system by the conventional *ab initio* method are also listed in the upper line. The LDOS curves obtained by the elongation method are in excellent agreement with the usual *ab initio* method in the sites close to the end part of the cluster (about  $\text{H}_{19}\text{--H}_{20} \sim \text{H}_{31}\text{--H}_{32}$  atoms). The LMOs used in the LDOS calculations are those localized on the *B* part (from  $\text{H}_3\text{--H}_{30}$  atoms in the starting cluster) and, therefore, the AO coefficients on  $\text{H}_1\text{--H}_2$  become negligibly small values. As a result, the LDOS on  $\text{H}_1\text{--H}_2$  is meaningless and can be assigned a significance only at  $\text{H}_3\text{--H}_{30}$ . The LDOS at  $\text{H}_1\text{--H}_2$  should be obtained from the LMOs on  $\text{H}_1\text{--H}_2$ , which are localized on the *A* part in the starting cluster in the localization process and removed from the eigenvalue problem in the elongation

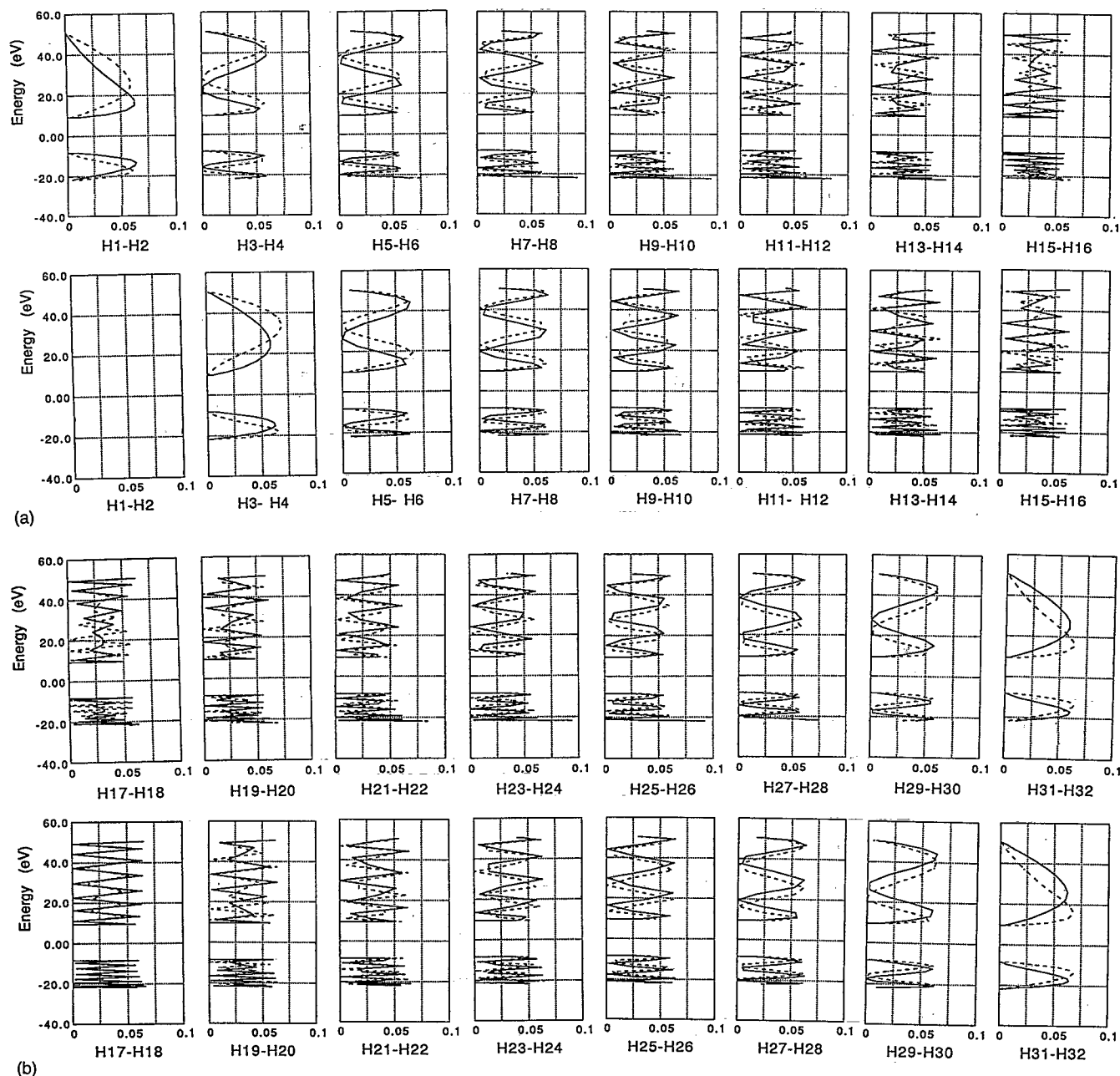


FIG. 6. The local density of states for each hydrogen atom of the model hydrogen polymer  $(\text{H}_2)_{16}$ , i.e., starting from the  $(\text{H}_2)_{15}$  cluster, elongated by one unit  $\text{H}_2$ . The solid lines—show the local density of states on the odd-numbered hydrogen atoms and the broken lines --- show that of the even-numbered hydrogen atoms. Upper graphs are the results for the whole system by the usual *ab initio* method (with the basis set of STO-3G by the Gaussian 70 program package) and lower ones are those by our *ab initio* elongation method with the basis set of STO-3G.

process. Therefore, the number of states that are used to plot a LDOS diagram remains to be 30, i.e., the number of MOs of the starting cluster. The shape of the LDOS curve becomes smooth when increasing the number of states included in the interval of  $E \sim E + \Delta E$  in Eq. (31). When we need greater accuracy in the LDOS curve, the length of the starting cluster should be fairly long. The LDOS curves from the elongation method for the system to be added by two more units  $(\text{H}_2)_{17}$  are shown in Fig. 7 to compare with those of the  $(\text{H}_2)_{16}$  system. It can be seen that the LDOS gives no more contribution on the first two  $\text{H}_2$  units. The results for the system elongated up to  $(\text{H}_2)_{30}$  are shown in

Fig. 8 for the sites near the end. It can be confirmed that the excellent agreement in the diagram between the usual *ab initio* method and the elongation method is retained even after being elongated up to 30  $\text{H}_2$ . These results mean that the end effect of the large polymer chain is efficiently obtained successively with good accuracy in the process of the elongation calculations. Furthermore, the LDOS diagrams on the sites  $\text{H}_{29}\text{--}\text{H}_{30}$ ,  $\text{H}_{39}\text{--}\text{H}_{40}$ ,  $\text{H}_{49}\text{--}\text{H}_{50}$ , and  $\text{H}_{59}\text{--}\text{H}_{60}$  of the 30  $\text{H}_2$  system are depicted in Fig. 9. If we need to obtain the LDOS on the inner sites of the elongated polymer chain, the LDOS of a few inner sites from the end of the cluster, which is free from the end effect, should be



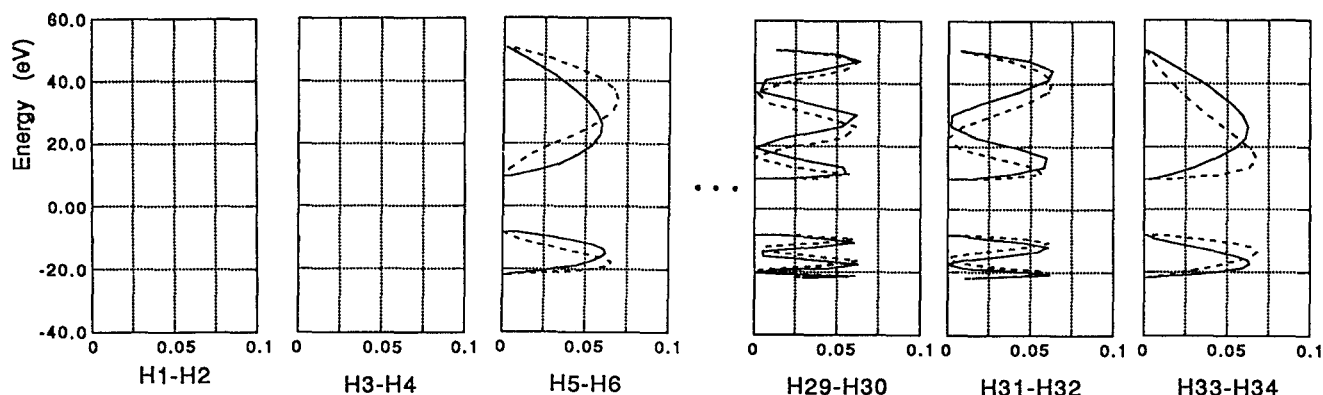


FIG. 7. The local density of states by the elongation method for the both end parts of the hydrogen polymer  $(\text{H}_2)_{17}$  which is, starting from the  $(\text{H}_2)_{15}$  cluster, elongated by two more unit  $2 \text{ H}_2$ . The solid lines—indicate the local density of states on the odd-numbered hydrogen atoms and the broken lines — that of the even-numbered hydrogen atoms.

stored in the process of the elongation calculations because the LDOS of the sites near the end is changed each time when a monomer added.

Finally, we calculated the approximate local site energy (33) to ensure the reliability of the present LDOS approach by the elongation method, especially, on the end part of the polymer. In Fig. 10, the local site energies on the site  $\text{H}_{25}\text{--H}_{60}$  of the  $30 \text{ H}_2$  system were plotted for the elongation method and the conventional *ab initio* method.

Concerning the characteristic properties on the end part, we do not discuss that here, but it can be remarked that the elongation method provides reliable results in comparison with the direct *ab initio* calculations for the whole system.

#### IV. CONCLUDING REMARKS

The elongation method, which is developed in our laboratory, is extended to provide the local density of states of

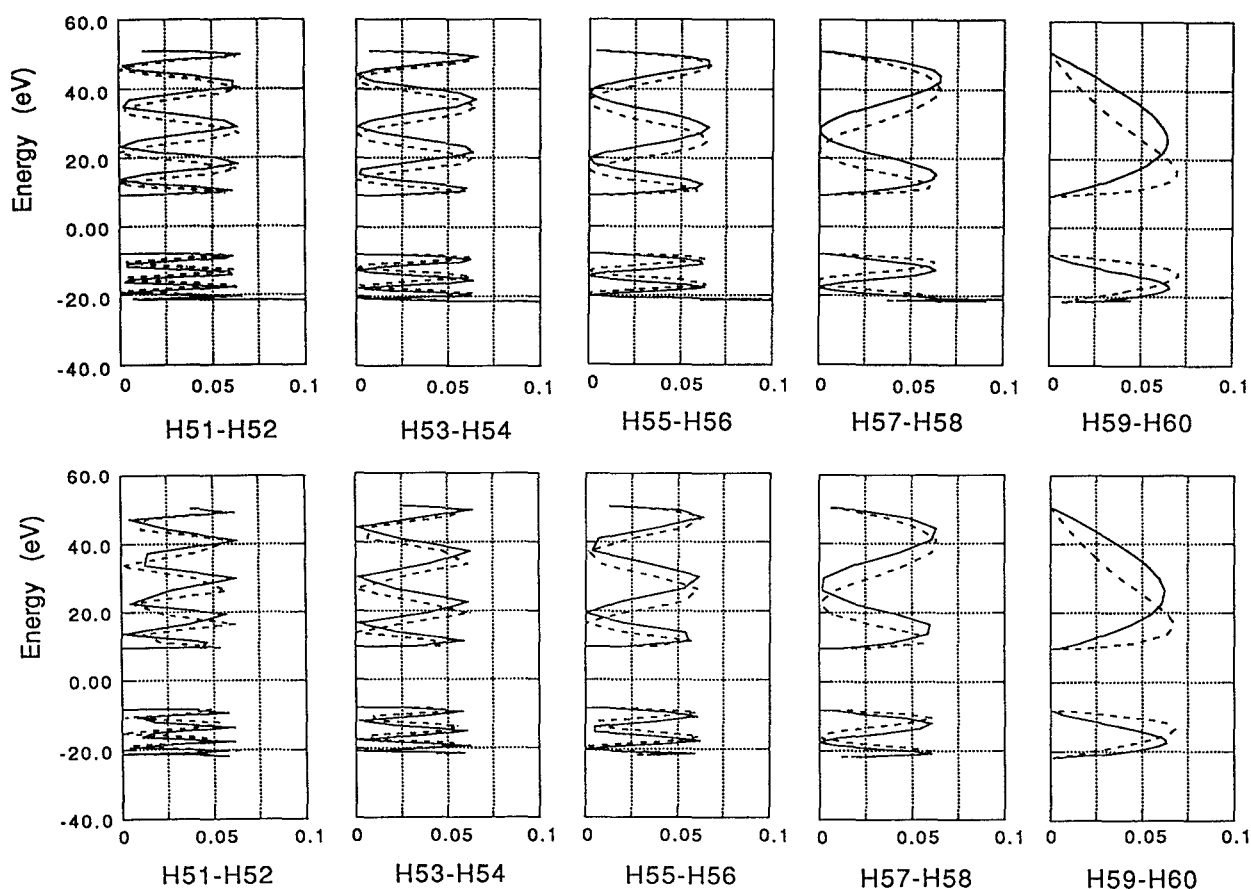


FIG. 8. The local density of states for the end part of the hydrogen polymer  $(\text{H}_2)_{30}$ , i.e., starting from the  $(\text{H}_2)_{15}$  cluster, elongated by  $15 \text{ H}_2$ . The meaning of these figures is referred to in Fig. 6.

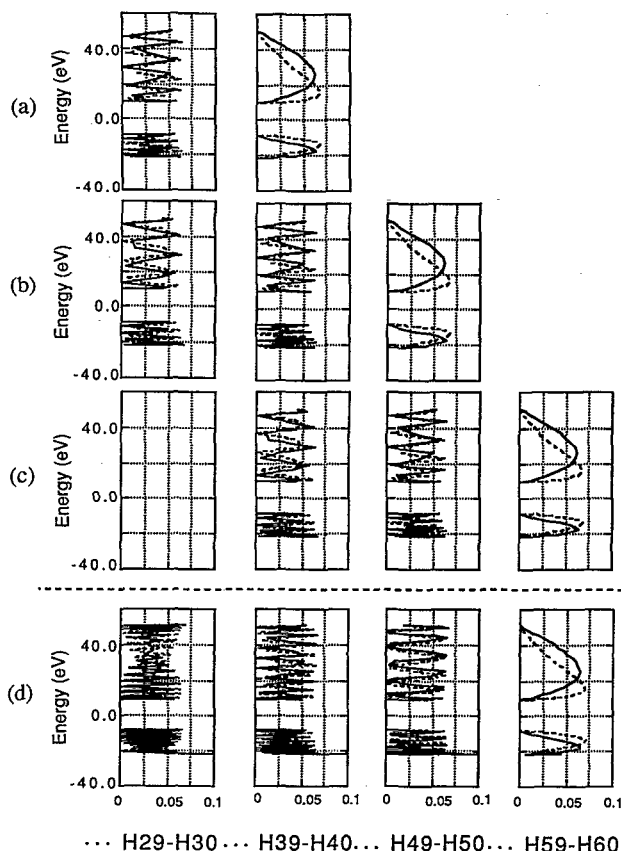


FIG. 9. The local density of states on the selected hydrogen atoms. The first, the second, and the third lines are the results for 20  $H_2$ , 30  $H_2$ , and 40  $H_2$ , respectively, by the elongation method. For comparison, the LDOS diagrams by the conventional *ab initio* method are shown in the fourth line.

a polymer chain. This method has proved to be reliable for a simple model  $H_2$  polymer system by comparing the results from the conventional *ab initio* method. This treatment is also applicable for aperiodic systems, since no condition of periodicity is assumed here. Advantages in computational time and storage will become significant for such larger systems as DNA and proteins. Furthermore, this approach makes it possible to examine HOMO, LUMO, and their density of states on a local site of the polymer chain. This will provide some insight into the intra- and intermolecular reactivities of large aperiodic polymers.

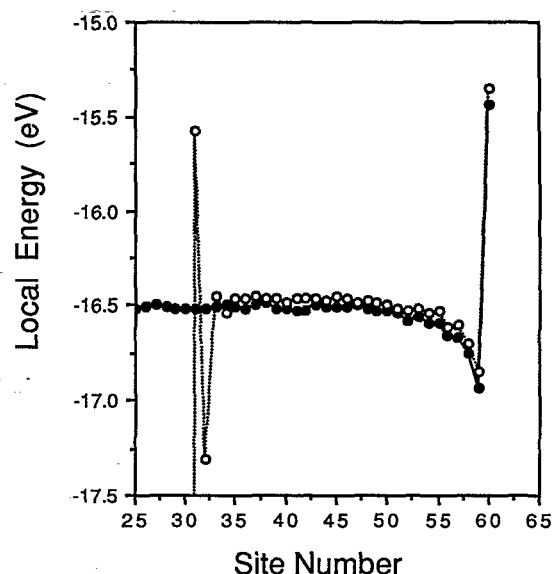


FIG. 10. Local site energies on the sites  $H^{25}$ – $H^{60}$ . The points—●—show the local site energies obtained by the conventional *ab initio* method and ...○... show those obtained by the elongation method.

#### ACKNOWLEDGMENTS

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