

Selfconsistentfield iterative transfer perturbation method and its application to the interaction between a polymer and a small molecule

Yuriko Aoki, Akira Imamura, and Keiji Morokuma

Citation: [The Journal of Chemical Physics](#) **89**, 1147 (1988); doi: 10.1063/1.455221

View online: <http://dx.doi.org/10.1063/1.455221>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/89/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Application of the local self-consistent-field method to core-ionized and core-excited molecules, polymers, and proteins: True orthogonality between ground and excited states](#)

J. Chem. Phys. **117**, 4119 (2002); 10.1063/1.1496462

[Calculation of barriers to proton transfer using variations of multiconfiguration selfconsistentfield methods. II. Configuration interaction](#)

J. Chem. Phys. **97**, 7519 (1992); 10.1063/1.463523

[Perturbational approach to the interaction between a polymer and a small molecule](#)

J. Chem. Phys. **83**, 5727 (1985); 10.1063/1.449648

[A numerical multiconfiguration selfconsistentfield method for diatomic molecules](#)

J. Chem. Phys. **75**, 2475 (1981); 10.1063/1.442277

[The partialwave selfconsistentfield method for diatomic molecules: Computational formalism and results for small molecules](#)

J. Chem. Phys. **62**, 3991 (1975); 10.1063/1.430322



Self-consistent-field iterative transfer perturbation method and its application to the interaction between a polymer and a small molecule

Yuriko Aoki and Akira Imamura

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

Keiji Morokuma

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

(Received 12 February 1988; accepted 1 April 1988)

An iterative transfer perturbation method is proposed to treat the interaction between a polymer and a small molecule at the level of the *ab initio* method. The validity of our method is examined by applying it to a simple model system and comparing the results with those from the conventional tight-binding SCF crystal orbital method. The interaction energies and charge distributions obtained are in excellent agreement between the two methods. The present perturbational approach is promising for application to the more complicated interaction between a polymer and impurities.

I. INTRODUCTION

In recent years, the interaction between a polymer and a small molecule has become more important in connection with the electron conduction mechanism of one-dimensional conducting polymers. The conductivity of intrinsically insulating organic polymers can be enhanced by about 10 to 15 orders of magnitude up to metallic or near metallic levels via doping with electron acceptors or donors. Calculations on the electronic structure of undoped and highly doped polymer chain are performed in the framework of the tight-binding crystal orbital method by treating these systems under the Bórn-Kármán periodic boundary condition. The method for periodical polymers has been established at the SCF level,^{1,2} and many studies have been reported. A few studies including electron correlation have been recently published as well.³⁻⁷

In the preceding paper we used an *ab initio* SCF perturbation theory proposed by O'Shea and Santry⁸ and applied to a few of aperiodical interactions of polymers.^{9,10} It has been shown that this method, the advantage of the perturbation method lies in the fact that one can avoid solving a very large secular equation for the aperiodic system, is applicable to a system having nearly degenerate occupied molecular orbitals as is the case with the energy bands of polymers, since their method employs the density matrix instead of individual molecular orbitals. The energy as well as the charge distribution thus obtained are in good agreement with those from the usual *ab initio* tight-binding crystal orbital method. However, the disadvantage of this method is that the expression for the second order density matrix in the perturbation expansion is extremely complicated and the third order term is very difficult to derive. Furthermore, for strongly interacting systems, the calculation often diverges, because the perturbation is too strong for this type of perturbation expansion.

Recently, we proposed an iterative transfer perturbation method¹¹ and applied it to the interaction between a polymer and a small molecule at the level of the extended Hückel method.^{12,13} This method iterates lower order (i.e., first or second order) perturbation calculations until the perturba-

tion terms converge. Consequently an infinite series of higher order terms of the perturbation expansion is introduced into the final results. For this method the difficulty in deriving higher order terms can be avoided, and the error caused by the truncation of these terms is removed completely. In the present study, we extend this iterative transfer perturbation method to the *ab initio* SCF level in order to obtain more exact results than those from the abovementioned SCF perturbation theory. It seems that this method may be widely applicable to the systems in which the interaction is so strong as not to be treated by the usual perturbation theory. In this paper, we describe the outline of this methodology and show the reliability of this treatment by applying it to a simple model system.

II. METHOD

Crystal orbitals of an isolated polymer without impurities can be obtained by using the tight-binding approximation in the following form:

$$\begin{aligned}\phi_{k,i}^{(0)}(\mathbf{r}) &= (1/N)^{-1/2} \sum_{l=0}^{N-1} \sum_{\mu=1}^n \exp(ikl) \\ &\quad \times C_{\mu i}^{(0)}(k) \chi_{\mu}(\mathbf{r} - \mathbf{r}_{\mu} - l\mathbf{a}), \\ k &= 2\pi p/N \quad (p = 1, 2, \dots, N).\end{aligned}\quad (1)$$

Here, l specifies a cell in the polymer consisting of N cells, k the wave number vector, \mathbf{a} the lattice vector, i an energy level, μ an atomic orbital, and \mathbf{r} the position vector of an electron.

In the present approach one small molecule is assumed to be included in a supercell consisting of many ($m = |b|/|a|$) unit cells of the unperturbed polymer as shown in Fig. 1. The molecular orbitals of this small molecule are written as follows:

$$\phi_j^{(0)}(\mathbf{r}) = \sum_{\nu} C_{\nu j}^{(0)} \chi_{\nu}(\mathbf{r}). \quad (2)$$

The interaction between the polymer and the small molecule is treated as a perturbation. In the present paper the iterative

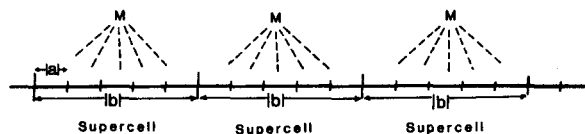


FIG. 1. Schematic model system of the interaction between a polymer and a small molecule.

transfer perturbation method is applied to this problem at the level of the *ab initio* method.

For the application of this perturbational method, the crystal orbitals of the isolated polymer must be transformed in order to suit the symmetry of the perturbed system. k_p is defined for the wave number vector for the supercell system with the translational vector of b ($=ma$). The relationship between k_p and k is given as follows:

$$k_p = mk - 2j\pi \quad (j; \text{integer}). \quad (3)$$

By using Eq. (3), the atomic orbital coefficients and orbital energies for the unit cell system are transformed to those for the supercell system. Details with regard to this relation are explained in the previous paper.¹⁰ The Fock matrix element as a function of the vector k_p for the supercell system is defined using the AO-based elements for each supercell as follows:

$$F_{\mu\nu}^{(0)}(k_p) = \exp(-ik_p) \mathcal{F}_{\mu\nu}^{[0,-1]} + \mathcal{F}_{\mu\nu}^{[0,0]} + \exp(ik_p) \mathcal{F}_{\mu\nu}^{[0,1]}. \quad (4)$$

Here we use the nearest neighbor approximation, where only the interaction between the nearest supercells is included. $[0, -1]$, $[0,0]$, or $[0,1]$ indicates that the AO μ belongs to the central supercell and the AO ν to the left-hand side, central, or right-hand side supercell, respectively. The overlap matrix for the supercell system is obtained in a similar manner. For the zero order terms for the supercell system, with the superscript (0), the following equations are satisfied for each k_p :

$$F^{(0)}(k_p)C^{(0)}(k_p) = S^{(0)}(k_p)C^{(0)}(k_p)E^{(0)}(k_p), \quad (5)$$

$$C^{(0)}(k_p)^\dagger S^{(0)}(k_p)C^{(0)}(k_p) = 1. \quad (6)$$

Integrals related only to the polymer or to the small molecule are classified into the zero order terms and the others into the first order terms. The first order terms of Fock matrix elements are given as

$$\begin{aligned} F_{\mu\nu}^{[0,j_\nu](1)} &= I_{\mu\nu}^{[0,j_\nu](1)} + \sum_{\rho=1}^n \sum_{\sigma=1}^n \sum_{j_\rho=0}^{\pm 1} \sum_{j_\sigma=0}^{\pm 1} P_{\rho\sigma}^{[j_\rho j_\sigma](0)} \\ &\times \left[\begin{pmatrix} 0 & j_\nu & j_\rho & j_\sigma \\ \mu & \nu & \rho & \sigma \end{pmatrix}^{(1)} - \frac{1}{2} \begin{pmatrix} 0 & j_\rho & j_\nu & j_\sigma \\ \mu & \rho & \nu & \sigma \end{pmatrix}^{(1)} \right] \\ &+ \sum_{\rho=1}^n \sum_{\sigma=1}^n \sum_{j_\rho=0}^{\pm 1} \sum_{j_\sigma=0}^{\pm 1} P_{\rho\sigma}^{[j_\rho j_\sigma](1)} \\ &\times \left[\begin{pmatrix} 0 & j_\nu & j_\rho & j_\sigma \\ \mu & \nu & \rho & \sigma \end{pmatrix}^{(0)} - \frac{1}{2} \begin{pmatrix} 0 & j_\rho & j_\nu & j_\sigma \\ \mu & \rho & \nu & \sigma \end{pmatrix}^{(0)} \right], \quad (7) \end{aligned}$$

where

$$P_{\rho\sigma}^{[j_\rho j_\sigma](0)} = 2 \sum_{k_p} \sum_i^{\text{occ}} \exp\{-ik_p(j_\rho - j_\sigma)\} \times C_{\rho i}^{(0)*}(k_p) C_{\sigma i}^{(0)}(k_p), \quad (8)$$

$$P_{\rho\sigma}^{[j_\rho j_\sigma](1)} = 2 \sum_{k_p} \sum_i^{\text{occ}} \exp\{-ik_p(j_\rho - j_\sigma)\} \times \{C_{\rho i}^{(0)*}(k_p) C_{\sigma i}^{(1)}(k_p) + C_{\rho i}^{(1)*}(k_p) C_{\sigma i}^{(0)}(k_p)\}. \quad (9)$$

The superscript (0) or (1) denotes the order of perturbation expansion. $I_{\mu\nu}^{[0,j_\nu](1)}$ is the matrix element of the core-resonance integrals (kinetic energy and core attraction) between the polymer and the small molecule. The j_ν , j_ρ , or j_σ indicates the supercell to which the atomic orbital ν , ρ , or σ belongs, respectively, if the atomic orbital μ lies on the polymer chain. The term $P_{\rho\sigma}^{[j_\rho j_\sigma](0)}$ given by Eq. (8) has already been determined by means of zero order coefficients for the supercell. The second term in Eq. (7) does not appear in the initial perturbation, since there is no perturbed density matrix given by Eq. (9) in the initial isolated systems. Therefore, only the first term in Eq. (7) is contained in the initial perturbation terms. Overlap integrals, related only to the polymer or to the small molecule, are in the zero order, and those between the polymer and the small molecule in the first order. Thus, there is no second order term in the Fock and overlap matrices.

The Hartree-Fock-Roothaan equation and the orthonormality condition are satisfied in the perturbed system as well as in the zero order isolated supercell system

$$F(k_p)C(k_p) = S(k_p)C(k_p)E(k_p), \quad (10)$$

$$C(k_p)^\dagger S(k_p)C(k_p) = 1. \quad (11)$$

At the beginning, each matrix of Eqs. (10) and (11) is expanded in a perturbation series as follows:

$$F(k_p) = F^{(0)}(k_p) + F^{(1)}(k_p) + \cdots, \quad (12)$$

$$S(k_p) = S^{(0)}(k_p) + S^{(1)}(k_p), \quad (13)$$

$$C(k_p) = C^{(0)}(k_p) + C^{(1)}(k_p) + C^{(2)}(k_p) + \cdots, \quad (14)$$

$$E(k_p) = E^{(0)}(k_p) + E^{(1)}(k_p) + E^{(2)}(k_p) + \cdots. \quad (15)$$

The Fock matrix should be expanded infinitely because the perturbed terms include the change in the density matrix defined by the coefficient matrix given by Eq. (14). By using formulas from the general perturbation theory for the extended Hückel method,¹⁴ the $C^{(1)}$ and $E^{(1)}$ included in Eqs. (14) and (15) are given as follows:

$$\begin{aligned} C_{\mu i}^{(1)}(k_p) &= - \sum_j' C_{\mu j}^{(0)}(k_p) / [E_j^{(0)}(k_p) - E_i^{(0)}(k_p)] \\ &\times \sum_{\rho} \sum_{\sigma} [F_{\rho\sigma}^{(1)}(k_p) - S_{\rho\sigma}^{(1)}(k_p)E_i^{(0)}(k_p)] \\ &\times C_{\rho j}^{(0)*}(k_p) C_{\sigma i}^{(0)}(k_p) - \frac{1}{2} C_{\mu i}^{(0)}(k_p) \\ &\times \sum_{\rho} \sum_{\sigma} C_{\rho i}^{(0)*}(k_p) C_{\sigma i}^{(0)}(k_p) S_{\rho\sigma}^{(1)}, \quad (16) \end{aligned}$$

$$\begin{aligned} E_i^{(1)}(k_p) &= \sum_{\rho} \sum_{\sigma} [F_{\rho\sigma}^{(1)}(k_p) - S_{\rho\sigma}^{(1)}(k_p)E_i^{(0)}(k_p)] \\ &\times C_{\rho i}^{(0)*}(k_p) C_{\sigma i}^{(0)}(k_p), \quad (17) \end{aligned}$$

where Σ'_j means that the summation covers all levels except i . At degenerate or nearly degenerate systems we avoid the divergence in the perturbation terms of molecular orbitals by solving the two-by-two secular equation between the degenerate orbitals.¹⁵ Equation (16) in principle has to be calculated iteratively since the evaluation of $C^{(1)}$ requires $F^{(1)}$ which itself requires $C^{(1)}$. However, if the SCF perturbation calculations are carried out until a consistent result is obtained, a large amount of computation time is required for making up the first order Fock matrix elements given by Eq. (7) and iterative transfer perturbation has to be repeated until the true convergence is obtained. To circumvent this true-consuming step, one may try to use the noniterative contribution to $C^{(1)}$ as a first guess to initiate the iterative transfer perturbation calculations.

With this simplification, we sum the zero order and the first order solutions which are obtained without iteration between Eqs. (7) and (16):

$$C^{(0,1)}(k_p) = C^{(0)}(k_p) + C^{(1)}(k_p), \quad (18)$$

$$E^{(0,1)}(k_p) = E^{(0)}(k_p) + E^{(1)}(k_p). \quad (19)$$

The superscript (0,1) in $C^{(0,1)}$ and $E^{(0,1)}$ denotes the newly defined zero order term in the first iteration. As the numerator in mixing coefficient of Eq. (16) becomes large enough compared with the corresponding energy difference, these new zero order solutions should give the more exact values approximating to the converged ones. In order that $C^{(0,1)}$ and $E^{(0,1)}$ are the zero order solutions at this step, the corresponding zero order Fock matrix $F^{(0,1)}$ and the overlap matrix $S^{(0,1)}$ must fulfill the following relationship:

$$F^{(0,1)}(k_p)C^{(0,1)}(k_p) = S^{(0,1)}(k_p)C^{(0,1)}(k_p)E^{(0,1)}(k_p), \quad (20)$$

$$C^{(0,1)}(k_p)^\dagger S^{(0,1)}(k_p)C^{(0,1)}(k_p) = 1. \quad (21)$$

From Eqs. (20) and (21), the explicit expressions for $S^{(0,1)}$ and $F^{(0,1)}$ are obtained by using $C^{(0,1)}$ and $E^{(0,1)}$ as follows¹¹:

$$S^{(0,1)}(k_p) = [C^{(0,1)}(k_p)C^{(0,1)}(k_p)^\dagger]^{-1}, \quad (22)$$

$$F^{(0,1)}(k_p) = [C^{(0,1)}(k_p)C^{(0,1)}(k_p)^\dagger/E^{(0,1)}(k_p)]^{-1}. \quad (23)$$

The residual perturbed terms in $F^{(1)}$ and $S^{(1)}$ are defined as the differences between the matrices for the perturbed system and those from Eqs. (22) and (23):

$$F^{(1,1)}(k_p) = [F^{(0)}(k_p) + F^{(1)}] - F^{(0,1)}(k_p), \quad (24)$$

$$S^{(1,1)}(k_p) = [S^{(0)}(k_p) + S^{(1)}] - S^{(0,1)}(k_p). \quad (25)$$

By using these new first order terms the next perturbation calculations are continued returning to Eqs. (16) and (17). In the present perturbation method, the perturbed terms change their values at each perturbation iteration, and the higher order terms in the perturbation expansion are incorporated automatically by iterations mentioned as above.

Throughout this process the zero order coefficient matrix and orbital energy matrix at the t th iteration step are defined as follows:

$$C^{(0,t)}(k_p) = C^{(0,t-1)}(k_p) + C^{(1,t-1)}(k_p), \quad (26)$$

$$E^{(0,t)}(k_p) = E^{(0,t-1)}(k_p) + E^{(1,t-1)}(k_p). \quad (27)$$

The next perturbed terms in the Fock and overlap matrices at the t th iteration are defined as follows:

$$F^{(1,t)}(k_p) = [F^{(0)}(k_p) + F^{(1)}] - F^{(0,t)}(k_p), \quad (28)$$

$$S^{(1,t)}(k_p) = [S^{(0)}(k_p) + S^{(1)}] - S^{(0,t)}(k_p). \quad (29)$$

By means of these equations the perturbation calculations are iterated until convergence on $C^{(0,t)}$ and $E^{(0,t)}$ are attained and the values of $F^{(1,t)}$ and $S^{(1,t)}$ become zero. We define the zero order solutions converged with f th iteration as the $C^{(0,f)}$, $E^{(0,f)}$, $S^{(0,f)}$, and $F^{(0,f)}$, which satisfy the Hartree-Fock-Roothaan equation and the orthonormality condition.

After the convergent results are obtained, the new density matrix elements for each supercell j_p and j_σ are calculated from the finally obtained coefficient matrix $C^{(0,f)}(k_p)$:

$$P_{\rho\sigma}^{[j_p j_\sigma]'} = 2 \sum_{k_p}^{\text{BZ}} \sum_i^{\text{occ}} \exp\{-ik_p(j_p - j_\sigma)\} \times C_{\rho i}^{(0,f)*}(k_p) C_{\sigma i}^{(0,f)}(k_p). \quad (30)$$

By using this density matrix the new Fock matrix is made up only for the central supercell including the small molecule

$$\mathcal{F}_{\mu\nu}^{[0,0]'} = I_{\mu\nu}^{[0,0]} + \sum_{\rho=1}^n \sum_{\sigma=1}^n \sum_{j_p=0}^{\pm 1} \sum_{j_\sigma=0}^{\pm 1} P_{\rho\sigma}^{[j_p j_\sigma]'} \times \left[\begin{pmatrix} 0 & 0 & j_p & j_\sigma \\ \mu & \nu & \rho & \sigma \end{pmatrix} - \frac{1}{2} \begin{pmatrix} 0 & j_p & 0 & j_\sigma \\ \mu & \rho & \nu & \sigma \end{pmatrix} \right], \quad (31)$$

where the prime means that the included density matrix elements change their values at each SCF iteration. The superscript [0,0] in Eq. (31) means that both of the μ and ν run over all the atomic orbitals in the central supercell including the small molecule. The present model is based on the assumption that the supercell includes enough area so that the individual small molecule has no influence on the neighboring supercell. Thus, we assume that only the central Fock matrix $\mathcal{F}^{[0,0]}'$ among the new Fock matrices $\mathcal{F}^{[0,j]}'$ ($j=0, \pm 1$ at this work) is changed at each SCF iteration and the others $\mathcal{F}^{[0,j]}'$ ($j=\pm 1$) are the same as those in the initial step.

The next perturbation term, therefore, can be defined as

$$F^{(1,1)'} = [\exp(-ik_p)\mathcal{F}^{[0,-1]'} + \mathcal{F}^{[0,0]}' + \exp(ik_p)\mathcal{F}^{[0,1]'}] - F^{(0,f)}(k_p). \quad (32)$$

The values $F^{(1,1)'}$ can be obtained so as to be independent on k_p , because the terms depending on k_p in Eq. (32) was cancelled with those included in $F^{(0,f)}(k_p)$. The computation time required for calculating Eq. (32) is reduced compared with those from the conventional *ab initio* tight-binding crystal orbital method, because it is assumed here that the Fock matrix elements only for the central supercell suffice for the SCF corrections. There is no perturbation term in the overlap matrix which does not include atomic orbital coefficients. The next iterative transfer perturbation calculations are repeated returning to Eqs. (16) and (17) in which the $F^{(1,1)'}$ given by Eq. (32) is used as the $F^{(1)}$. At the first SCF step the perturbation term at the t th iterative transfer perturbation step is defined as

$$F^{(1,t)'}(k_p) = [F^{(0,f)}(k_p) + F^{(1,1)'}] - F^{(0,t)'}(k_p) \quad (33)$$

instead of Eq. (24) at the initial step. After the $F^{(1,t)'}$ (k_p) has converged to be zero with f th iteration, the obtained

zero order solutions are denoted by $C^{(0,f)'}$, $E^{(0,f)'}$, $S^{(0,f)'}$, and $F^{(0,f)'}$. Using the newly obtained coefficient matrix $C^{(0,f)'}$, the new Fock matrix is made up by returning to Eq. (31).

Defining the calculated new Fock matrix as $\mathcal{F}^{[0,0]''}$, the next SCF correction is given by

$$F^{(1,1)''} = \mathcal{F}^{[0,0]''} - \mathcal{F}^{[0,0]'}. \quad (34)$$

The perturbation term at t th iterative transfer perturbation step at the second SCF is defined as

$$F^{(1,t)''}(k_p) = [F^{(0,f)'}(k_p) + F^{(1,1)''}] - F^{(0,t)''}(k_p). \quad (35)$$

This procedure is repeated until the perturbation terms from the SCF correction given by Eq. (34) become zero. Finally, we can calculate the total density matrices and hence the total electron energy as well as the orbital energies in the usual manner. The outline of the entire calculation process is shown in Fig. 2.

For the test calculations of our method, we select a simple model polymer system composed of hydrogen atoms as a polymer system and a hydrogen molecule as a small molecule. The polyhydrogen chain consists of infinite periodic supercells within each of which has five unit cells interacting with a small molecule as shown in Fig. 3. Geometries of the atoms in a unit cell are selected in such a way that the symmetry is as low as possible, since this application is a check of

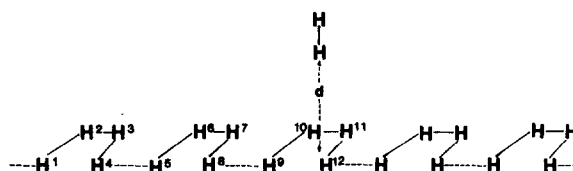


FIG. 3. Model system for the calculations and the numbering of the atoms in Table III. $r(\text{H1-H2}) = 0.74 \text{ \AA}$, $r(\text{H2-H3}) = 1.0 \text{ \AA}$, $r(\text{H3-H4}) = 0.89 \text{ \AA}$, $r(\text{H1-H4}) = 1.5 \text{ \AA}$, $r(\text{H4-H5}) = 2.0 \text{ \AA}$.

our method for extending to more complicated polymer systems. Small molecules are placed on the polyhydrogen chain above the central unit cell of each supercell at a distance d .

The programming of the SCF perturbation method was performed by combining the crystal orbital program package, which our research group has developed, with essential parts of the Polymer GAUSSIAN 74 program based on the *ab initio* tight-binding SCF crystal orbital method. For the calculations of the Fock matrices given by Eqs. (7) and (31), the one- and two-electron integrals of the Polymer GAUSSIAN 74 program were employed. In the calculations, the nearest neighbor approximation for the supercell system is employed, which means that the kinetic energy, nuclear-electron attraction, overlap, and two-electron repulsion integrals are cut off at an appropriate distance between atomic orbitals, or an atomic orbital and a nucleus. This approximation could cause a serious problem in obtaining the correctly converged energy values.^{16,17} However, the present test calculation is intended to study the applicability of our perturbational method in comparison with the usual *ab initio* tight-binding crystal orbital method.

Prior to the supercell calculations the following three files are obtained from the Polymer GAUSSIAN 74 program. The first includes the intrachain zero order wave functions integrals within the isolated polymer system corresponding to Eq. (1). In this calculation all the interactions beyond the cutoff distance of 8.9 \AA were neglected; This is to say that the interaction between a unit cell and the third neighbor unit cells was dropped at the AO integral level. The second file has the zero order wave functions and the integrals within a small molecule. The third is the first order terms for the interacting space between the supercell in the polymer chain and the small molecule. In order to obtain these terms, the nearest neighbor approximation was used on the periodically interacting system composed of a small molecule and the interacting space only for which all integrals over AOs between the polymer and small molecules are explicitly evaluated as the perturbation terms in the core Hamiltonian and two-electron integrals. For comparison with the perturbation calculations, the direct SCF calculation was also performed independently on the periodic interacting system composed of the supercell with a small molecule by using the Polymer GAUSSIAN 74 program. All the calculations in this paper were performed with an STO-3G basis set with standard exponents. The convergence criterion of 10^{-6} for the

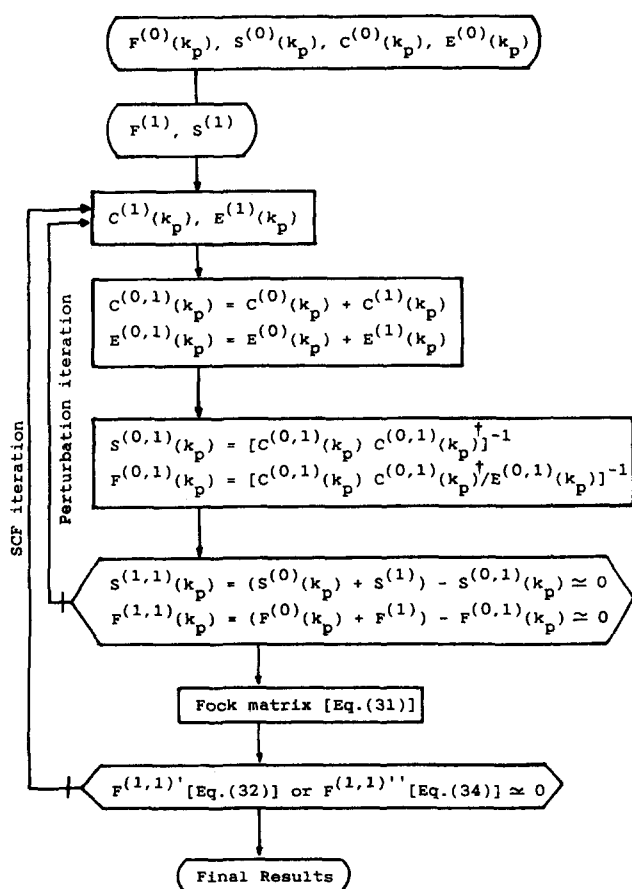


FIG. 2. Outline of this SCF perturbational approach.

TABLE I. Total energies and interaction energies per supercell obtained by method A and method B* for the interacting hydrogen model polymer and hydrogen molecule impurity system.^{b,c}

	$d(\text{\AA})$	Nuc. Rep.	$I^{(1)}$	$F^{(1)}$	Electronic energy	Total energy	Interaction energy	SCF ^d	Perturbation ^e
Isolated Method		34.376	0.0	0.0	- 45.638	- 11.262	0.0		
A	2.0	39.285	24.652	1.329	- 50.542	- 11.257	0.005	3	4,3,1
B					- 50.542	- 11.257	0.005	7	
A	3.0	38.458	17.313	0.207	- 49.719	- 11.261	0.001	3	2,1,1
B					- 49.719	- 11.261	0.001	7	
A	4.0	37.764	13.809	0.085	- 49.025	- 11.261	0.001	2	2,1
B					- 49.025	- 11.261	0.001	7	

* Method B is carried out by Polymer GAUSSIAN 74 program package.

^b All energies are in a.u.

^c Cutoff distance is fixed at 8.9 Å (including up to second neighbor interaction).

^d Number of SCF cycles.

^e Number of iterative transfer perturbations for each SCF cycle.

difference in the density matrix elements was used. The numerical calculations were carried out on the HITAC M-680H and S-810 systems of the Institute for Molecular Science.

III. RESULTS AND DISCUSSION

The calculated energies for the interacting system with the supercell shown in Fig. 3 are listed in Table I for three distances, $d = 2.0, 3.0$, and 4.0 Å. The agreement between the SCF perturbation method (method A) and the usual *ab initio* tight-binding crystal orbital method (method B) is very good, in spite of the fact that the present perturbation procedure did not take into account the change of the Fock matrix through the density matrix from the neighboring supercell. This means that the supercell composed of five H_4 unit cells is large enough for exact evaluation of the interaction under the given cutoff distance. $I^{(1)}$ is the sum of the absolute values of all the matrix elements for the perturbed core Hamiltonian, and those of $F^{(1)}$ the perturbed Fock matrix corresponding to Eq. (7) including the two-electron parts. The values of $I^{(1)}$ and $F^{(1)}$ decrease reasonably as the distances increase. The electronic energies are smoothly stabilized with decreasing distances because of the strong core-electron attraction term. The same values of the total energies at the distance of 3.0 and 4.0 Å are due to the incidental cancellation between the nuclear repulsion energy and the electronic energy under the artificial cutoff.

The number of SCF iteration steps by method A is less than that by method B at all the distances. This is because in method A we used as the starting MOs those converged for isolated polymer [Eq. (1)] and a small molecule [Eq. (2)], whereas in method B we used the solutions obtained by using the extended Hückel method. The number of iteration steps for each perturbation iteration are listed in the last column of Table I for each SCF step. It is seen that only two to four perturbation iterations are required for even the first SCF step, and less are required for subsequent SCF steps. The convergence behavior of $F^{(1)}$ in the first SCF cycle is shown in Table II. For larger distances d , the initial perturbation term is smaller and the convergence is smoother and more rapid. The poor convergence in the strongly interacting sys-

tems comes from the large numerator of the mixing coefficients in Eq. (16) relative to the energy denominator and could cause serious trouble. There is still a great deal of room for improvement in the definition of perturbation terms.

The total electron density is shown in Table III for the atoms in the furthestmost cell within a supercell in Fig. 2. The values of the total electron density obtained by method A are virtually identical with those by method B. The very small change in electron density of atoms $H^{(1)}$ to $H^{(4)}$ indicates that the edge of the supercell is almost free from the influence of the interaction between the hydrogen molecule, and the supercell is large enough for this kind of interaction.

The feature of this perturbation method is that all of the higher order terms in the perturbation expansion can be incorporated iteratively and automatically only by considering first order term, without even solving the large secular equation for the supercell. The results thus obtained are found to be in good agreement with those by the direct variational method. Furthermore, the SCF correction only for the central supercell gives sufficiently accurate results in accord with those from the usual *ab initio* tight-binding crystal orbital method. This leads to a considerable reduction in computational time required for making the Fock matrix. This technique becomes efficient for the more complicated large supercell systems in which an impurity molecule interacts strongly with a wide range of polymer chains.

Finally, in this model system, we would like to mention that the computation time using this iterative transfer per-

TABLE II. Convergence in $F^{(1)}$ at $K = 0^\circ$ for each perturbation iteration at first SCF (in a.u.).

$d(\text{\AA})$	2.0	3.0	4.0
Iteration			
0	1.329	0.207	0.085
1	1.970	0.109	0.014
2	0.491	0.083	0.007
3	0.021	0.002	0.000
4	0.000	0.000	

TABLE III. Total electron density by Mulliken's population analysis for the interacting hydrogen model polymer and hydrogen molecule.*

	$d(\text{\AA})$	H ₂	H1	H2	H3	H4
Isolated		2.0000	0.9195	1.0146	0.9480	1.1179
A	2.0	2.0017	0.9195	1.0145	0.9480	1.1180
B		2.0017	0.9195	1.0145	0.9480	1.1180
A	3.0	2.0001	0.9195	1.0145	0.9480	1.1179
B		2.0001	0.9195	1.0145	0.9480	1.1179
A	4.0	2.0000	0.9195	1.0145	0.9480	1.1180
B		2.0000	0.9195	1.0145	0.9480	1.1180
			H5	H6	H7	H8
Isolated			0.9195	1.0146	0.9480	1.1179
A	2.0		0.9193	1.0146	0.9477	1.1183
B			0.9193	1.0146	0.9477	1.1183
A	3.0		0.9194	1.0146	0.9479	1.1181
B			0.9194	1.0146	0.9479	1.1181
A	4.0		0.9194	1.0146	0.9480	1.1180
B			0.9194	1.0146	0.9480	1.1180
			H9	H10	H11	H12
Isolated			0.9195	1.0146	0.9480	1.1179
A	2.0		0.9193	1.0139	0.9491	1.1161
B			0.9193	1.0139	0.9491	1.1161
A	3.0		0.9195	1.0145	0.9483	1.1177
B			0.9195	1.0145	0.9483	1.1177
A	4.0		0.9195	1.0145	0.9481	1.1179
B			0.9195	1.0145	0.9481	1.1179

* The numbering of the atoms is shown in Fig. 2.

turbation method is comparable or somewhat longer than that using the usual direct variational method. The computational time in both cases is proportional to N^3 (where N is the number of basis functions per supercell) but for larger values of N the standard variational method is more efficient. However, the direct variational calculation for a local perturbation on the large systems such as biopolymers would become impossible because of required diagonalization of a very large HF matrix. Perturbation calculations, on the other hand, can be performed by resolving the matrix into the individual basis orbitals with small dimension. The present model calculations provide a first estimate of the perturbational approach to large interacting systems. The

application for the interaction between conducting polymers and dopants is in progress in our laboratory.

IV. CONCLUDING REMARKS

In the present paper the proposed perturbation method is applied to the interaction between a model hydrogen polymer and a hydrogen molecule. It is found that the agreement in the total energy and the total electron density is excellent between this method, which avoids the direct diagonalization of a very large supercell secular equation, and the usual tight-binding *ab initio* crystal orbital method, which requires the diagonalization. Consequently, the perturbation method developed in this work can be applied with good accuracy to interaction between real polymers and impurity molecules.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan, for which we express our gratitude. The computations were carried out on HITAC M680H and S810 computers at the Institute for Molecular Science. The authors are grateful to Dr. S. Yabushita, Dr. K. Yamashita, and Dr. N. Koga for their hearty guidance and instructive discussions.

- ¹J. M. Andre, J. Chem. Phys. **50**, 1536 (1969).
- ²G. Del Re, J. Ladik, and G. Biczko, Phys. Rev. **155**, 997 (1967).
- ³S. Suhai, Int. J. Quantum Chem. **23**, 1239 (1980).
- ⁴S. Suhai, Chem. Phys. Lett. **96**, 619 (1983).
- ⁵S. Suhai, J. Polym. Sci. **21**, 1341 (1983).
- ⁶S. Suhai, Int. J. Quantum Chem. Symp. **18**, 161 (1984).
- ⁷S. Suhai, J. Chem. Phys. **84**, 5071 (1985).
- ⁸S. F. O'Shea and D. P. Santry, Theor. Chim. Acta **37**, 1 (1975).
- ⁹A. Imamura, S. Suhai, and J. Ladik, J. Chem. Phys. **76**, 6067 (1982).
- ¹⁰A. Imamura, Y. Aoki, S. Suhai, and J. Ladik, J. Chem. Phys. **83**, 5727 (1985).
- ¹¹A. Imamura and Y. Aoki, Bull. Chem. Soc. Jpn. **58**, 1376 (1985).
- ¹²A. Imamura and Y. Aoki, Chem. Phys. Lett. **130**, 390 (1986).
- ¹³A. Imamura and Y. Aoki, Synth. Met. **17**, 135 (1987).
- ¹⁴A. Imamura, Mol. Phys. **15**, 225 (1968).
- ¹⁵A. Imamura and Y. Aoki, Int. J. Quantum Chem. Symp. **21**, 137 (1987).
- ¹⁶S. Suhai, J. Chem. Phys. **73**, 3843 (1980).
- ¹⁷H. Teramae, J. Chem. Phys. **85**, 990 (1986).