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Self-consistent-field variational approach to the interaction between a polymer and a small molecule

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A variational SCF treatment based on a perturbational concept is developed and applied to the interaction between trans-polyacetylene and a small molecule. The validity of the present method is examined by comparing the results with those from the conventional tight-binding SCF crystal orbital method. The interaction energies and charge distributions obtained are in good agreement between the two methods. This result suggests that the present variational approach is promising for application to complicated interactions between a polymer and impurities.

Key words: Polymer — Impurity — *Ab initio* method

1. Introduction

Polyacetylene, a typical conducting polymer, has recently been the focus of enormous interest due to the discovery that the conductivity is increased by doping with appropriate electron donors and acceptors. Electronic states of trans-polyacetylene have been investigated by using the Hartree-Fock tight-binding approximation based on a periodic boundary condition both within the one-electron picture [1-10] and including electron correlation effects [11-14]. At the present stage of theoretical approach, on the other hand, little has been developed on the method of calculating electronic states of non-periodical polymers.

In a preceding paper we proposed an *ab initio* SCF perturbation method for aperiodic polymers which was developed based on the perturbation theory using the density matrix by O'Shea and Santry [15]. This method was applied to a few simple model systems, the interaction between two nearly incommensurable polymers [16] and between a polymer and a small molecule [17], obtaining good agreement in the calculated interaction energy as well as the charge distribution with those from the usual SCF procedure. For strongly interacting systems, however, perturbed matrix elements are often larger than energy differences and lead to unrealistically large mixing coefficients and time-consuming SCF iterations.

In order to remove this deficiency we will modify the above mentioned perturbation method so as to evaluate the perturbation terms and apply it at the *ab initio* level. This treatment requires a large amount of storage in the diagonalization procedure, but it is expected that the results thus obtained for the interaction between a one-dimensional simple chain and a small molecule are more reliable than the perturbational treatment. The polymer used in our approach consists of supercells each of which includes one small molecule. This supercell is to include so many cells that the interaction between supercells through the small molecule can be neglected. For the test calculations, trans-polyacetylene is selected as a polymer and hydrogen and lithium hydride molecules as small molecules. Finally, the limitations of applicability of this method are briefly discussed.

2. Method

Crystal orbitals of an isolated polymer consisting of N cells without impurities are expressed by using the tight-binding approximation in the following form:

$$\phi_{k,s}^{(0)}(\mathbf{r}) = (1/N)^{-1/2} \sum_{l=0}^{N-1} \sum_{\mu=1}^{n} \exp(\mathrm{i}kl) C_{\mu s}^{(0)}(k) \chi_\mu(\mathbf{r} - \mathbf{r}_\mu - l\mathbf{a}), \tag{1}$$

$$k = 2\pi p/N (p = 1, 2, \ldots, N).$$

Here, l specifies a cell in the polymer, **a** the lattice vector, i the imaginary number $\sqrt{-1}$, s an energy level, μ an atomic orbital, and **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 ($m = |\mathbf{b}|/|\mathbf{a}|$) unit cells of the unperturbed polymer as shown in Fig. 1. The molecular orbitals of this small molecule are written as

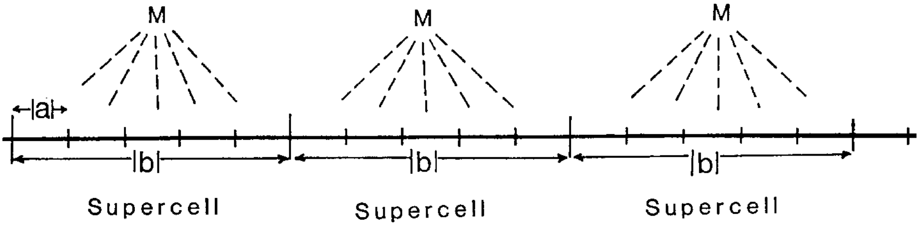

Fig. 1. Schematic model system of the interaction between a polymer and a small molecule

follows:

$$\phi_s^{(0)}(\mathbf{r}) = \sum_{\nu}^{n'} C_{\nu s}^{(0)} \chi_\nu(\mathbf{r}). \tag{2}$$

The interaction between the polymer and the small molecule is evaluated by a variational treatment based on a perturbational concept starting from these zero-order solutions for the isolated systems.

For the application of this variational method, the crystal orbitals of the isolated polymer must be transformed so as to satisfy the symmetry of the supercell system. The relationship between k_p for the supercell system with the translational vector **b** and k for the unit cell system with the translational vector **a** is given as follows:

$$k_p = mk - 2j\pi \qquad (j\text{: integer}). \tag{3}$$

Details regarding this relationship have been explained in the previous paper [17]. By using Eq. (3), the coefficient for the supercell system, $C_{\mu s(l)}^{(0)}(k_p)$, is given in terms of that for the isolated system $C_{\mu s}^{(0)}(k)$ as follows:

$$C_{\mu s(l)}^{(0)}(k_p) = C_{\mu s}^{(0)}(k) \exp[\mathrm{i}(l-1)k], \tag{4}$$

where l in the subscript denotes the lth cell in the supercell of the interest, hereafter called the central supercell. With the aid of Eq. (4), the crystal orbitals of the isolated unit cell system are transformed into those for the supercell system. Similarly, orbital energies for the wave number vector k are also transformed into those for k_p. That is,

$$E_{s(l)}^{(0)}(k_p) = E_s^{(0)}(k). \tag{5}$$

Supercell Fock and overlap matrices can be expressed in terms of the unit cell matrices.

$$F_{\mu\nu}^{(0)}(k_p) = \sum_{j=0}^{\pm L} \exp(\mathrm{i}k_p j) F_{\mu\nu}^{[0,j]} \tag{6}$$

$$S_{\mu\nu}^{(0)}(k_p) = \sum_{j=0}^{\pm L} \exp(\mathrm{i}k_p j) S_{\mu\nu}^{[0,j]}, \tag{7}$$

where the index ${}_{\mu\nu}^{[0,j]}$ means that the atomic orbitals μ and ν belong to the central and the jth supercell, respectively, and the summation for j is to be done over a limited number of supercells $2L+1$ for which one- and two-electron integrals are taken into consideration. For the zero-order terms of the supercell system, the following equations are satisfied for each k_p:

$$\mathbf{F}^{(0)}(k_p)\mathbf{C}^{(0)}(k_p) = \mathbf{S}^{(0)}(k_p)\mathbf{C}^{(0)}(k_p)E^{(0)}(k_p) \tag{8}$$

$$\mathbf{C}^{(0)}(k_p)^{+}\mathbf{S}^{(0)}(k_p)\mathbf{C}^{(0)}(k_p) = 1. \tag{9}$$

Integrals which are related only to the polymer or the small molecule are considered to be the zero-order terms and all others the first-order terms. For the

Fock matrix, we introduce the following notations as was done in the previous paper [17].

$$T=-(1/2)\nabla^2, \tag{10}$$

$$V_{\mathrm{X}}=-\sum_{j_\alpha}\sum_{\alpha(X)} Z_\alpha/|\mathbf{r}-R_\alpha(j_\alpha)|(\mathrm{X}=\mathrm{M},\mathrm{P}), \tag{11}$$

$$\mathscr{H}_{\mathrm{RT}}(T+V_{\mathrm{X}})=\{\mathscr{H}_{\mathrm{RT};0\mu,j_\nu\nu}(T+V_{\mathrm{X}})\}, \tag{12}$$

$$\mathscr{H}_{\mathrm{RT};0\mu,j_\nu\nu}(T+X_{\mathrm{X}})=\{\chi^{\mathrm{R}}_\mu(0)|T+V_{\mathrm{X}}|\chi^{\mathrm{T}}_\nu(j_\nu)\}, \tag{13}$$

$$\mathscr{G}^{\mathrm{XY}(K)}_{\mathrm{RT}}=\{\mathscr{G}^{\mathrm{XY}(K)}_{\mathrm{RT};0\mu,j_\nu\nu}\}, \tag{14}$$

$$\begin{aligned}\mathscr{G}^{\mathrm{XY}(K)}_{\mathrm{RT};0\mu,j_\nu\nu}=\sum_{\rho(\mathrm{R})}\sum_{\sigma(\mathrm{T})}\sum_{j_\rho}\sum_{j_\sigma}\mathbf{P}^{(j_\rho,j_\sigma)(K)}\{&(\chi^{\mathrm{X}}_\mu(0)\chi^{\mathrm{Y}}_\nu(j_\nu)|\chi^{\mathrm{R}}_\rho(j_\rho)\chi^{\mathrm{T}}_\sigma(j_\sigma))\\ &-(1/2)(\chi^{\mathrm{X}}_\mu(0)\chi^{\mathrm{R}}_\rho(j_\rho)|\chi^{\mathrm{Y}}_\nu(j_\nu)\chi^{\mathrm{T}}_\sigma(j_\sigma))\},\end{aligned} \tag{15}$$

where X, Y, R and T stand either for P(polymer) or M(monomer), j indicates the supercell number to which the nucleus α belongs and α(X) denotes a nucleus on X. The AO ν, ρ and σ belong to the supercell j_ν, j_ρ and j_σ, respectively. The superscript(K) denotes the order of perturbation expansion in the density matrix **P**.

Using Eqs. (10)-(15), the first-order terms of the Fock matrix are represented as follows:

$$\mathscr{F}^{\mathrm{PP}(1)}=\mathscr{H}_{\mathrm{PP}}(V_{\mathrm{M}})+\mathscr{G}^{\mathrm{PP}(0)}_{\mathrm{MM}} \tag{16}$$

$$\mathscr{F}^{\mathrm{MM}(1)}=\mathscr{H}_{\mathrm{MM}}(V_{\mathrm{P}})+\mathscr{G}^{\mathrm{MM}(0)}_{\mathrm{PP}} \tag{17}$$

$$\mathscr{F}^{\mathrm{PM}(1)}=\mathscr{H}_{\mathrm{PM}}(T+V_{\mathrm{P}}+V_{\mathrm{M}})+\mathscr{G}^{\mathrm{PM}(0)}_{\mathrm{PP}}+\mathscr{G}^{\mathrm{PM}(0)}_{\mathrm{MM}}. \tag{18}$$

The perturbed terms in the density matrix of Eq. (15) do not appear in the initial perturbation, since there are no perturbed molecular orbitals in the initial isolated systems. 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 are in the first order. Therefore, there is no second-order terms in the Fock and overlap matrices. Thus, the total first-order terms for the Fock matrix and overlap integral are given by

$$\mathbf{F}^{(1)}=\mathscr{F}^{\mathrm{PP}(1)}+\mathscr{F}^{\mathrm{MM}(1)}+\mathscr{F}^{\mathrm{PM}(1)}+\mathscr{F}^{\mathrm{MP}(1)}, \tag{19}$$

$$\mathbf{S}^{(1)}=\mathscr{S}^{\mathrm{PM}(1)}+\mathscr{S}^{\mathrm{MP}(1)}. \tag{20}$$

In the present work, we apply a variational treatment to the sum of these zero- and first-order terms defined as above in Fock and overlap matrices

$$\mathbf{F}(k_{\mathrm{p}})=\mathbf{F}^{(0)}(k_{\mathrm{p}})+\mathbf{F}^{(1)} \tag{21}$$

$$\mathbf{S}(k_{\mathrm{p}})=\mathbf{S}^{(0)}(k_{\mathrm{p}})+\mathbf{S}^{(1)}. \tag{22}$$

These definitions of the matrices are applicable only at the first SCF iteration.

By using these matrices defined for the interacting system, the eigenvalue problem is solved for each k_{p}.

$$(\mathbf{F}(k_{\mathrm{p}})-\mathbf{S}(k_{\mathrm{p}})E(k_{\mathrm{p}}))\mathbf{C}'(k_{\mathrm{p}})=0. \tag{23}$$

From the obtained eigenvectors $C'_{\mu i}(k_{\mathrm{p}})$, new density matrix elements are calculated

$$P_{\rho\sigma}^{(j_\rho, j_\sigma)\prime} = 2 \sum_{k_p}^{\mathrm{BZ}} \sum_{i}^{\mathrm{occ}} \exp\{-\mathrm{i}k_{\mathrm{p}}(j_\rho - j_\sigma)\} C_{\rho i}^{*\prime}(k_{\mathrm{p}}) C'_{\sigma i}(k_{\mathrm{p}}). \tag{24}$$

By using the new density matrix elements given by Eq. (24) the new Fock matrix elements are constructed only for the central supercell including the small molecule,

$$F_{\mu\nu}^{[0,0]\prime} = H_{\mu\nu}^{[0,0]} + G_{\mu\nu}^{[0,0]\prime}, \tag{25}$$

where $'$ indicates that the density matrix changes its values at each SCF iteration process. In the contribution from the two-electron integrals $G_{\mu\nu}^{[0,0]\prime}$ the following terms are to be included

$$\begin{aligned} G_{\mu\nu}^{[0,0]\prime} = {} & \sum_{\rho}\sum_{\sigma} P_{\rho\sigma}^{(0,0)\prime}\Bigl[\Bigl({}^{00}_{\mu\nu}\Bigm|{}^{00}_{\rho\sigma}\Bigr) - \tfrac{1}{2}\Bigl({}^{00}_{\mu\rho}\Bigm|{}^{00}_{\nu\sigma}\Bigr)\Bigr] \\ & + \sum_{\rho}\sum_{\sigma} P_{\rho\sigma}^{(1,1)\prime}\Bigl[\Bigl({}^{00}_{\mu\nu}\Bigm|{}^{11}_{\rho\sigma}\Bigr) - \tfrac{1}{2}\Bigl({}^{01}_{\mu\rho}\Bigm|{}^{01}_{\nu\sigma}\Bigr)\Bigr] \\ & + \sum_{\rho}\sum_{\sigma} P_{\rho\sigma}^{(-1,-1)\prime}\Bigl[\Bigl({}^{00}_{\mu\nu}\Bigm|{}^{-1-1}_{\rho\sigma}\Bigr) - \tfrac{1}{2}\Bigl({}^{0-1}_{\mu\rho}\Bigm|{}^{0-1}_{\nu\sigma}\Bigr)\Bigr] \\ & + \sum_{\rho}\sum_{\sigma} P_{\rho\sigma}^{(0,1)\prime}\Bigl[\Bigl({}^{00}_{\mu\nu}\Bigm|{}^{01}_{\rho\sigma}\Bigr) - \tfrac{1}{2}\Bigl({}^{00}_{\mu\rho}\Bigm|{}^{01}_{\nu\sigma}\Bigr)\Bigr] \\ & + \sum_{\rho}\sum_{\sigma} P_{\rho\sigma}^{(1,0)\prime}\Bigl[\Bigl({}^{00}_{\mu\nu}\Bigm|{}^{10}_{\rho\sigma}\Bigr) - \tfrac{1}{2}\Bigl({}^{01}_{\mu\rho}\Bigm|{}^{00}_{\nu\sigma}\Bigr)\Bigr] \\ & + \sum_{\rho}\sum_{\sigma} P_{\rho\sigma}^{(0,-1)\prime}\Bigl[\Bigl({}^{00}_{\mu\nu}\Bigm|{}^{0-1}_{\rho\sigma}\Bigr) - \tfrac{1}{2}\Bigl({}^{00}_{\mu\rho}\Bigm|{}^{0-1}_{\nu\sigma}\Bigr)\Bigr] \\ & + \sum_{\rho}\sum_{\sigma} P_{\rho\sigma}^{(-1,0)\prime}\Bigl[\Bigl({}^{00}_{\mu\nu}\Bigm|{}^{-1,0}_{\rho\sigma}\Bigr) - \tfrac{1}{2}\Bigl({}^{0-1}_{\mu\rho}\Bigm|{}^{00}_{\nu\sigma}\Bigr)\Bigr], \end{aligned} \tag{26}$$

where superscripts indicate the supercells to which the AO's μ, ν, ρ or σ belongs. In Eq. (26) the first three terms including $P_{\rho\sigma}^{(0,0)\prime}$, $P_{\rho\sigma}^{(1,1)\prime}$ and $P_{\rho\sigma}^{(-1,-1)\prime}$ are the density matrix elements between AO's ρ and σ within the same supercell, that is, within central $(0, 0)$, right side $(1, 1)$ and left side $(-1, -1)$ supercells, respectively. In our model in which the polymer interacts only with one small molecule, the density $P_{\rho\sigma}^{(0,0)\prime}$ must be explicitly calculated from the newly obtained eigenvectors $C'_{\mu i}(k_{\mathrm{p}})$, whereas $P^{(1,1)\prime}$ and $P^{(-1,-1)\prime}$ may be assumed to be equal to the initially defined isolated zero-order terms, and therefore the Fock matrix derived from $P^{(1,1)\prime}$, $P^{(-1,-1)\prime}$ need not to be recalculated at each SCF iteration. This would result in considerable time consuming in computation. However, in the present work these three terms are exactly calculated in order to compare our results with the *ab initio* tight-binding crystal orbital method for periodic polymers. The final four terms in Eq. (26) correspond to the contributions between the central and neighboring supercells under the nearest neighbor approximation.

The matrix elements of $\mathbf{F}(k_{\mathrm{p}})$ included in the eigenvalue problem Eq. (23) are usually given by the transformation of $F^{[0,j]\prime}$ as follows

$$F_{\mu\nu}(k_{\mathrm{p}}) = \sum_{j=0}^{\pm L} \exp(\mathrm{i}k_{\mathrm{p}}j) F_{\mu\nu}^{[0,j]\prime}. \tag{27}$$

However, our model is based on the assumption that the supercell includes a large enough area so that the individual small molecule has no influence on the neighboring supercell. Then, only $F^{[0,0]\prime}$ given by Eq. (25) in the new Fock matrix must be changed in each SCF iteration and the terms for $j \neq 0$ can be replaced by the initially defined zero-order Fock matrix Eq. (6). Therefore, the new Fock matrix element is represented by

$$F_{\mu\nu}(k_p) = \exp(-ik_p)F^{[0,-1]} + F^{[0,0]\prime}_{\mu\nu} + \exp(ik_p)F^{[0,1]}_{\mu\nu}, \qquad (28)$$

under the nearest neighbor approximation. The computational time required for calculating Eq. (28) is substantially less than that for Eq. (27) which corresponds to the usual *ab initio* tight-binding method.

By using $S(k_p)$ given by Eq. (22) and $F(k_p)$ by Eq. (28) the eigenvalue problem Eq. (23) is solved. From the obtained density matrix Eq. (24), the new Fock matrix given by Eq. (25)-(26) and Eq. (28) is calculated. In the succeeding SCF iteration process, the diagonalization of Eq. (28) is carried out directly without defining perturbation terms in the Fock and overlap matrices such as Eqs. (16)-(20). This procedure is repeated until the density matrix given by Eq. (24) becomes consistent with that used in forming the Fock matrix of Eq. (25). After one has obtained the converged density matrix, one can calculate in the usual manner the total density matrix and hence the total electronic energy as well as the orbital energies.

For a test calculation, we select all-trans polyacetylene as a polymer, and a hydrogen molecule or lithium hydride as a small molecule. Polyacetylene consists of an infinite number of periodic supercells, each consisting of seven unit cells with a small molecule, as shown in Fig. 2. A small molecule is placed on the polyacetylene chain above the central unit cell of each supercell at a distance *d*.

Programming of the variational method was carried out by combining the crystal orbital program package, which our research group has developed, with essential

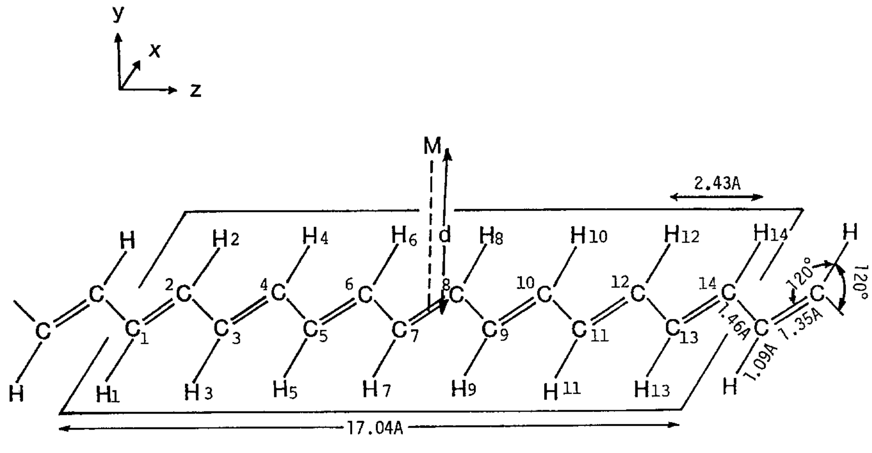

Fig. 2. Model system for the calculations and the numbering of the atoms in Tables 2 and 4

parts of the Polymer GAUSSIAN 74 program based on the *ab initio* tight-binding SCF crystal orbital method. For the calculation of the Fock matrix for Eqs. (16)-(18) and Eq. (25) the one- and two-electron integrals obtained by the Polymer GAUSSIAN 74 program were employed. In the present test calculation, we adopt the nearest neighbor approximation for the supercell system, which means that the kinetic energy, the nuclear-electron attraction, the overlap, and the two-electron repulsion integrals are cutoff at an appropriate interatomic distance. This approximation could cause a serious problem in obtaining the correctly converged energy values, since the total energy depends strongly upon the number of neighbors included [8, 10]. However, this is the test calculation for the applicability of our variational method to be compared with the usual *ab initio* tight-binding crystal method, and the nearest neighbor assumption does not obscure the present purpose.

Prior to the supercell calculations the following three files are obtained from the Polymer GAUSSIAN 74 program. The first file contains the intra-chain zero order wave functions and integrals in the isolated polymer system corresponding to Eq. (1). In this calculation all the interactions beyond the cutoff distance of 6.0 Å was neglected; this was done since the third neighbor unit cells in a polymer with the cell-cell distance of 2.4315 Å are at least 6.1887 Å away from the central cell and we wanted the third neighbor interaction to be truncated. The second file has the zero order wave functions and the integrals within the small molecule. The calculations for isolated small molecules are also performed using this program, in which the interactions between the neighboring molecules are truncated. The third file has 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 interacting space only within which all integrals over AO's between the polymer and small molecules are explicitly evaluated. For comparison with this variational calculation, 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 package. All the calculations in this paper were performed with an STO-3G basis set with the standard exponents. The convergence criterion of 10^{-6} for the difference of 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.

3. Results and discussion

This variational method using the zero order solutions of the isolated systems and the first order interaction terms is applied to a trans-polyacetylene interacting with a hydrogen molecule (Model I) or a lithium hydride molecule (Model II), shown as the small molecule (M) in Fig. 2. The hydrogen or lithium hydride molecule (with H down) is placed perpendicular to the polyacetylene chain at various chain-H distances *d*.

The calculated total energies for Model I using our method (method A) are

Table 1. Total energies and interaction energies per supercell obtained by Method A and Method B[a] for the interacting trans-polyacetylene and hydrogen molecule impurity system[b]

Method	d(Å)	Nuc.rep.	$I^{(1)}$	$F^{(1)}$	Electronic energy	Total energy	Interaction energy	SCF iterations
A	1.0	616.498	264.025	27.365	−1148.972	−532.474	0.314	10
B					−1148.974	−532.476	0.312	14
A	2.0	609.275	109.838	6.074	−1142.082	−532.806	−0.018	9
B					−1142.082	−532.806	−0.018	11
A	3.0	604.413	60.238	0.865	−1137.201	−532.788	0.0	3
B					−1137.201	−532.788	0.0	9
A	4.0	600.645	39.795	1.273	−1133.411	−532.766	0.022	7
B					−1133.410	−532.765	0.023	11
A	5.0	595.705	18.574	2.780	−1128.500	−532.794	−0.006	9
B					−1128.503	−532.798	−0.010	11
Isolated		590.326	0.0	0.0	−1123.114	−532.788	0.0	

[a] Method B is carried out by Polymer Gaussian 74 program package

[b] All energies are in a.u

compared in Table 1 at five distances with those by the direct tight-binding crystal orbital method (method B).

The total electronic energies obtained by method A are in good agreement with those by method B. Since method A neglects the change of Fock matrix due to the neighboring supercell density matrix, the present results suggest that the supercell composed of seven (C_2H_2) unit cells is large enough to allow exact evaluation of the interaction under the present cutoff distance. $I^{(1)}$ is the sum of the absolute values of all the perturbed core-Hamiltonian matrix elements defined at the initial SCF step, and $F^{(1)}$ the sum of the absolute values of the perturbed Fock matrix elements defined by Eq. (19). The values of $I^{(1)}$ decreases with increasing distances, while $F^{(1)}$ has a minimum value at the distance of 3.0 Å. This may be due to the incidental cancellation of the core-electron attraction with the electron-electron repulsion at the short cutoff distance with 6.0 Å. As the distance increases, the total electronic energies increase and the nuclear repulsion energies decrease smoothly, approaching those of the isolated polymer system. However, the total energy given as the sum of those two terms behaves irregularly for the distance change in both methods. Suhai has mentioned [8] that the most difficult problem in obtaining reliable results in *ab initio* polymer calculations is how to truncate two "electrostatic" interactions, namely, core attraction and Coulomb repulsion terms. It seems that the short cutoff distance of 6.0 Å is too short and has led to this erratic behavior. This difficulty should be removable by using larger cutoff distances including a large enough number of neighbors so that the balance between core electron attraction and electron-electron repulsion is maintained.

The numbers of SCF iterations required are shown in the right-most column in the Table 1. The number of SCF iterations by method A is less than that by method B. This is more remarkable at smaller values of $F^{(1)}$, because the solutions already converged independently for the isolated polymer (Eq. (1)) and the small molecule (Eq. (2)) are used in method A as the initial guess for the interacting system. In addition, in method A, the simplified Eq. (28) is used to construct the Fock matrix for substantial computer time saving; the computational time per SCF iteration in method A is reduced to about one half of that in method B.

The total electron density obtained by the Mulliken population analysis is shown in Table 2. As the distances increase, the effects of charge transfer interaction from polyacetylene to the hydrogen molecule disappear. The HOMO of trans-polyacetylene is symmetric between the π orbitals on C_7 and C_8 and the LUMO is antisymmetric. Both the occupied and unoccupied orbitals of the hydrogen molecule perpendicular to this polyacetylene chain are symmetric with respect to C_7-C_8. Consequently, the charge transfer from the HOMO of polyacetylene to the unoccupied antibonding orbital of the hydrogen molecule is allowed, but the charge transfer to the polyacetylene LUMO is forbidden. The behavior of electron distribution at various distances seems to be intimately related to the magnitude of the initially defined perturbation terms $F^{(1)}$. At the 3.0 Å where the perturbation term is the smallest, the change in electron density is the smallest. Rather diverse values obtained at the distance of 5.0 Å are probably artifacts of

Table 2. Total electron density by Mulliken's population analysis for the interacting trans-polyacetylene and hydrogen molecule impurity system[a]

Method	d(Å)	H_2	C1	C2	C3	C4	C5	C6	C7
A	1.0	2.2298	6.0522	6.1275	5.9376	6.1203	6.0410	6.0584	6.0372
B		2.2298	6.0515	6.1278	5.9376	6.1196	6.0429	6.0572	6.0372
A	2.0	2.0226	6.0790	5.9605	6.2549	5.9537	6.0575	6.0644	6.0641
B		2.0223	6.0793	5.9602	6.2551	5.9537	6.0568	6.0648	6.0641
A	3.0	2.0015	6.0622	6.0619	6.0622	6.0617	6.0615	6.0623	6.0626
B		2.0015	6.0622	6.0618	6.0621	6.0617	6.0615	6.0623	6.0627
A	4.0	2.0000	6.0489	6.0777	6.0078	6.1944	6.0105	6.0845	6.0477
B		2.0000	6.0490	6.0776	6.0075	6.1952	6.0101	6.0848	6.0476
A	5.0	2.0000	6.0725	6.0442	6.0518	6.0336	6.1157	6.1138	6.0054
B		2.0000	6.0717	6.0443	6.0522	6.0321	6.1193	6.1114	6.0057
Isolated		2.0000	6.0620	6.0620	6.0620	6.0620	6.0620	6.0620	6.0620
Method	d(Å)		H1	H2	H3	H4	H5	H6	H7
A	1.0		0.9384	0.9411	0.9204	0.9374	0.9349	0.9328	0.9059
B			0.9385	0.9412	0.9204	0.9374	0.9351	0.9327	0.9059
A	2.0		0.9359	0.9312	0.9620	0.9294	0.9291	0.9351	0.9320
B			0.9359	0.9311	0.9621	0.9293	0.9290	0.9352	0.9320
A	3.0		0.9380	0.9380	0.9380	0.9378	0.9378	0.9378	0.9376
B			0.9380	0.9380	0.9380	0.9378	0.9378	0.9378	0.9376
A	4.0		0.9351	0.9377	0.9353	0.9067	0.9375	0.9400	0.9361
B			0.9348	0.9377	0.9353	0.9068	0.9375	0.9401	0.9361
A	5.0		0.9379	0.9335	0.9320	0.9346	0.9492	0.9478	0.9280
B			0.9381	0.9336	0.9320	0.9346	0.9496	0.9476	0.9279
Isolated			0.9380	0.9380	0.9380	0.9380	0.9380	0.9380	0.9380

[a] The numbering of the atoms is shown in Fig. 2

the short cutoff distance as was seen in the interaction energy. At all the other distances, the density values obtained by method A differ somewhat from those by method B.

Total energies for Model II, in which lithium hydride with the hydrogen end down is used as the small molecule, are shown in Table 3 for five distances. The cutoff distance is 6.0 Å and the bond distance of Li–H (1.5949 Å) is long, and then relatively shorter chain-H distances ($d = 1.0$–3.5 Å) are selected so that many of the interacting terms between polyacetylene and LiH can be included. The interaction energy here again behaves erratically for both methods, as was in Model I, due to the cutt-off distance that is too short. The difference in the total energies between the two methods is in the range of 1–2.5 kcal for the distances of 2.0–3.5 Å. This implies that the size of the supercell composed of seven (C_2H_2) units is not large enough for the use of unperturbed density matrix elements on the edge of the supercell.

The number of SCF iterations required by method A is again smaller than that by method B, particularly at the distances of 3.0 and 3.5 Å. The computational time per SCF iteration is about a half of that in method B, as SCF in the case of model I. In the case of strong perturbation at 1.0 Å, the SCF converged in 10 iterations in method A, but never in method B. These results suggest that method A show a potential of providing SCF results for systems in which the interaction is so strong that the conventional method fails to converge.

The total electron density by the Mulliken population analysis is listed in Table 4. The charge transfer from the symmetric occupied π orbitals of polyacetylene to the LUMO (empty Li $2p_y$ orbital) of lithium hydride is allowed. The maximum in the magnitude of charge transfer and that of the stabilization energy occur at the same distance, 2.5 Å. The noticeable difference in density between two methods indicates that the end of the supercell is not free from the influence of interaction between lithium hydride and the supercell. This suggests that a larger supercell has to be adopted in order to describe the interacting system correctly. As discussed above, a larger supercell is also essential to avoid artifacts of integral truncation.

An extension of a supercell can be achieved combining the Fock matrix of a smaller supercell system converged already by SCF calculation and the zero-order Fock matrix of an adjacent unit cell to which the supercell should be expanded. The newly linked area interacts indirectly in the first iteration, because the density matrix, therefore, the Fock matrix has no value between the old and new areas. The wave function and the energy of the newly expanded supercell can be obtained by the diagonalization procedure given by Eq. (23). The supercell can be extended sequentially until the end effect of a supercell become negligible, where the interaction with a simple impurity molecule is described exactly.

The present study is a starting point of investigation of the reliability and applicability of our method at the *ab initio* SCF level. We believe that the excellent agreement with the conventional and more time-consuming tight-binding SCF method can be obtained by using a sufficiently large supercell and a long cutoff

Table 3. Total energies and interaction energies per supercell obtained by Method A and Method B for the interacting trans-polyacetylene and lithium hydride molecule impurity system[a]

Method	d(Å)	Nuc.rep.	$I^{(1)}$	$F^{(1)}$	Electronic energy	Total energy	Interaction energy	SCF iterations
A	1.0	642.440	866.255	100.093	−1181.424	−538.984	0.549	10
B[b]								
A	2.0	630.061	515.155	46.041	−1169.652	−539.591	−0.058	9
B					−1169.655	−539.594	−0.061	11
A	2.5	622.014	349.305	30.198	−1161.617	−539.602	−0.069	11
B					−1161.620	−539.606	−0.073	12
A	3.0	617.744	250.834	20.398	−1157.295	−539.551	−0.018	12
B					−1157.297	−539.553	−0.020	19
A	3.5	614.943	185.571	14.060	−1154.507	−539.564	−0.031	10
B					−1154.510	−539.567	−0.034	19
Isolated		590.606	0.0	0.0	−1130.139	−539.533	0.0	

[a] All energies are in a.u.

[b] Convergent results could not be obtained by Polymer Gaussian 74 program package

Table 4. Total electron density by Mulliken's population analysis for the interacting trans-polyacetylene and lithium hydride molecule impurity system[a]

Method	d(Å)	LiH	C1	C2	C3	C4	C5	C6	C7
A	1.0	3.9508	6.0701	6.0069	6.1837	5.9714	6.0065	6.0644	6.2816
B[b]									
A	2.0	4.1833	6.0751	5.9844	6.2065	5.9689	6.0210	6.0794	6.0805
B		4.1831	6.0746	5.9842	6.2071	5.9678	6.0229	6.0781	6.0807
A	2.5	4.2777	6.0600	6.0413	6.1019	5.9721	6.0277	6.0706	6.0367
B		4.2776	6.0591	6.0415	6.1020	5.9710	6.0308	6.0685	6.0369
A	3.0	4.1577	6.0444	6.0702	6.0071	6.1690	5.9788	6.1016	6.0322
B		4.1576	6.0433	6.0707	6.0071	6.1686	5.9808	6.1004	6.0322
A	3.5	4.0741	6.0332	6.0887	5.9554	6.2298	5.9179	6.1040	6.0339
B		4.0740	6.0318	6.0891	5.9551	6.2298	5.9205	6.1024	6.0338
Isolated		4.0000	6.0620	6.0620	6.0620	6.0620	6.0620	0.0620	6.0620
Method	**d(Å)**		**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**
A	1.0		0.9339	0.9321	0.9486	0.9202	0.9112	0.9206	0.8733
B									
A	2.0		0.9341	0.9300	0.9522	0.9228	0.9169	0.9259	0.9104
B			0.9342	0.9301	0.9524	0.9228	0.9172	0.9258	0.9104
A	2.5		0.9332	0.9312	0.9373	0.9988	0.9211	0.9224	0.9068
B			0.9333	0.9314	0.9373	0.9989	0.9215	0.9222	0.9068
A	3.0		0.9308	0.9324	0.9316	0.9467	0.9274	0.9317	0.9171
B			0.9307	0.9325	0.9317	0.9468	0.9277	0.9316	0.9170
A	3.5		0.9284	0.9322	0.9246	0.9545	1.0063	0.9323	0.9218
B			0.9282	0.9324	0.9246	0.9547	1.0068	0.9321	0.9217
Isolated			0.9380	0.9380	0.9380	0.9380	0.9380	0.9380	0.9380

[a] The numbering of the atoms is shown in Fig. 2

[b] Convergent results could not be obtained by Polymer Gaussian 74 program package

distance. We intend to develop this method with hope of making it computationally feasible with good accuracy for interaction of various larger polymers with small molecules.

4. Conclusions

In the present paper the variational method is proposed and applied to the interaction between trans-polyacetylene and a small molecule such as H_2 and LiH. It is found that the agreement in the total energy and the total electron density is fairly good between this method and the usual, more time-consuming tight-binding *ab initio* crystal orbital method. Consequently, the variational method developed in this work can be an economical alternative for calculating with good accuracy the interaction between real polymers and impurity molecules.

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