A Novel Iterative Transfer Perturbation Method and Its Application to the Extended Hückel Method

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An efficient iterative transfer perturbation method, which enabled us to take into account the contribution of the high order terms in the perturbation series without directly deriving the formulas for terms above third order, is proposed. Consequently we can calculate an infinite series of higher order terms in the perturbation expansion by applying this method iteratively until convergence in the expansion is obtained. By applying this method to methanol, the validity and applicability of our theory are shown at the level of the extended Hückel method.

Various types of perturbation methods have been developed in the field of quantum chemistry and have been applied to many interesting problems in physical chemistry. However, in many cases, the higher order terms in the perturbation expansion have been neglected past the second or the third order because of the intractability in the explicit expression of these terms. However, this truncation often leads to unreliable results.

In the present article, we propose a novel perturbation method in the Hartree-Fock-Roothaan formalism, in which the higher order terms are automatically transfered to the first and second order terms by iteration of this perturbation expansion, that is, by carrying over the perturbation terms into the next zero-order terms. This iterative procedure should be repeated until convergence in the density matrix and the total energy are achieved. For the simple test of this perturbation method, we applied this method to a simple system (methanol and its analogs) at the level of the extended Hückel method,[1] since the fundamental points in the perturbation method should be included even at the level of the extended Hückel method. In these test calculations, it is found that this novel perturbation method is able to remove completely the error caused by neglecting the terms of higher than second order.

Theoretical

The perturbation expansion is carried out with Roothaan's Hartree Fock SCF matrix equation,

$$FC = SCE \tag{1}$$

where F is the Fock matrix, C is the coefficient matrix, S is the overlap matrix and E the orbital energy matrix. These orbitals are normalized through the matrix equation

$$C^{\mathrm{T}}SC = 1. \tag{2}$$

Here, C^{T} is the transpose of the C matrix.

At the beginning, each matrix of Eq. 1 is expanded in a perturbation series as follows

$$F = F^{(0)} + F^{(1)} + F^{(2)} + \cdots, \tag{3}$$

$$S = S^{(0)} + S^{(1)}, \tag{4}$$

$$C = C^{(0)} + C^{(1)} + C^{(2)} + \cdots, \tag{5}$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots, \tag{6}$$

where in the overlap matrix, all the difference between the zero order term and the perturbed terms is included in the first-order perturbed term, $S^{(1)}$. On the other hand, in the Fock matrix, the integral for the perturbed terms includes the change in the density matrix, and this density matrix should be expanded in an infinite series because of Eq. 5. Consequently, the Fock matrix given by Eq. 3 should be expanded also in an infinite series. For the zero-order terms, the following equations are satisfied.

$$F^{(0)}C^{(0)} = S^{(0)}C^{(0)}E^{(0)} \tag{7}$$

$$C^{(0)\mathrm{T}}S^{(0)}C^{(0)} = 1 \tag{8}$$

By using formulas from general perturbation theory for the extended Hückel method, which had been reported previously,[2] the matrix elements of the perturbed matrices $C^{(1)}$, $C^{(2)}$, $E^{(1)}$, and $E^{(2)}$ are given as follows:

$$\begin{aligned} C_{ti}^{(1)} = &- \sum_{\substack{j \\ (j\neq i)}}{}' C_{tj}^{(0)}/(E_j^{(0)} - E_i^{(0)}) \\ &\sum_r\sum_s (F_{rs}^{(1)} - S_{rs}^{(1)}E_i^{(0)})C_{ri}^{(0)}C_{sj}^{(0)} \\ &- \frac{1}{2}C_{ti}^{(0)}\sum_r\sum_s C_{ri}^{(0)}C_{si}^{(0)}S_{rs}^{(1)}, \end{aligned} \tag{9}$$

$$E_i^{(1)} = \sum_r\sum_s (F_{rs}^{(1)} - S_{rs}^{(1)}E_i^{(0)})C_{ri}^{(0)}C_{si}^{(0)}, \tag{10}$$

$$\begin{aligned} C_{ti}^{(2)} = &- \sum_{\substack{j \\ (j\neq i)}}{}' C_{tj}^{(0)}/(E_j^{(0)} - E_i^{(0)}) \\ &[\sum_r\sum_s \{F_{rs}^{(2)} - (S_{rs}^{(2)}E_i^{(0)} + S_{rs}^{(1)}E_i^{(1)})\}C_{ri}^{(0)}C_{sj}^{(0)} \\ &+ \sum_r\sum_s \{F_{rs}^{(1)} - (S_{rs}^{(0)}E_i^{(1)} + S_{rs}^{(1)}E_i^{(0)})\} \\ &\times C_{ri}^{(1)}C_{sj}^{(0)}] \\ &- \frac{1}{2}C_{ti}^{(0)}\sum_r\sum_s \{C_{ri}^{(1)}C_{si}^{(1)}S_{rs}^{(0)} \\ &+ (C_{ri}^{(1)}C_{si}^{(0)} + C_{ri}^{(0)}C_{si}^{(1)})S_{rs}^{(1)}\}, \end{aligned} \tag{11}$$

$$\begin{aligned} E_i^{(2)} = &\sum_r\sum_s (F_{rs}^{(2)} - S_{rs}^{(1)}E_i^{(1)})C_{ri}^{(0)}C_{si}^{(0)} \\ &+ \sum_r\sum_s \{F_{rs}^{(1)} - (S_{rs}^{(0)}E_i^{(1)} + S_{rs}^{(1)}E_i^{(0)})\} \\ &\times C_{ri}^{(1)}C_{si}^{(0)}, \end{aligned} \tag{12}$$

where *i,j* denote molecular orbitals and *r,s* atomic orbitals, and $\sum_j{}'$ means that the summation covers all levels except *i*. Strictly speaking, Eqs. 9—12 should be solved iteratively since the Fock matrices $F_{rs}^{(1)}$ and $F_{rs}^{(2)}$ include the perturbed density matrix that is calculated by using $C_{ti}^{(1)}$ and $C_{ti}^{(2)}$. By using Eqs. 9—12, we can obtain the first and the second order terms of *C* and *E*.

Next, we redefine the zero-order terms for *C* and *E* as follows:

$$C^{(0,1)} = C^{(0)} + C^{(1)} + C^{(2)}, \tag{13}$$

$$E^{(0,1)} = E^{(0)} + E^{(1)} + E^{(2)}, \tag{14}$$

where matrix elements of $C^{(1)}$ and $C^{(2)}$ are given by Eqs. 9 and 11 and that of $E^{(1)}$ and $E^{(2)}$ by Eqs. 10 and 12. The superscript (0,1) in $C^{(0,1)}$ and $E^{(0,1)}$ denotes the zero-order term defined by Eqs. 13 and 14 in the first iteration. In order that $C^{(0,1)}$ and $E^{(0,1)}$ are the zero-order terms, the corresponding zero-order Fock matrix $F^{(0,1)}$ and the overlap matrix $S^{(0,1)}$ must fulfill the following relations:

$$F^{(0,1)}C^{(0,1)} = S^{(0,1)}C^{(0,1)}E^{(0,1)}, \tag{15}$$

$$C^{(0,1)\mathrm{T}}S^{(0,1)}C^{(0,1)} = 1. \tag{16}$$

In other words, $F^{(0,1)}$ and $S^{(0,1)}$ are determined from the Eqs. 15 and 16. The explicit expressions for $S^{(0,1)}$ and $F^{(0,1)}$ are obtained by using $C^{(0,1)}$ and $E^{(0,1)}$ as follows. Multipling the Eq.16 on the left by $(C^{(0,1)\mathrm{T}})^{-1}$, on the right by $(C^{(0,1)})^{-1}$, the overlap matrix of the zero-order is

$$\begin{aligned} S^{(0,1)} &= (C^{(0,1)\mathrm{T}})^{-1}(C^{(0,1)})^{-1} = (C^{(0,1)}C^{(0,1)\mathrm{T}})^{-1} \\ &= (P^{(1)})^{-1} \end{aligned} \tag{17}$$

where the matrix $P^{(1)}$ has its element given by the Eq. 18.

$$P_{rs}^{(1)} = \sum_i^{\text{all}} C_{ri}^{(0,1)}C_{si}^{(0,1)} \tag{18}$$

Eq. 15 is multiplied by $(C^{(0,1)})^{-1}$ on the right followed by a substitution of Eq. 17.

$$\begin{aligned} F^{(0,1)} &= S^{(0,1)}C^{(0,1)}E^{(0,1)}(C^{(0,1)})^{-1} \\ &= (C^{(0,1)\mathrm{T}})^{-1}(C^{(0,1)})^{-1}(C^{(0,1)}E^{(0,1)}(C^{(0,1)})^{-1} \\ &= (C^{(0,1)\mathrm{T}})^{-1}E^{(0,1)}(C^{(0,1)})^{-1} \\ &= (P_E^{(1)})^{-1}, \end{aligned} \tag{19}$$

where, $P_E^{(1)}$ is defined as follows:

$$P_E^{(1)} = \sum_i^{\text{all}} C_{ri}^{(0,1)}C_{si}^{(0,1)}/E_i^{(0,1)}. \tag{20}$$

The perturbed terms in the first iteration are defined by using the Eqs. 3 and 4 as follows:

$$F^{(1,1)} = F - F^{(0,1)} = (F^{(0)} + F^{(1)} + F^{(2)}) - F^{(0,1)}, \tag{21}$$

$$S^{(1,1)} = S - S^{(0,1)} = (S^{(0)} + S^{(1)}) - S^{(0,1)}. \tag{22}$$

In the Eq. 21, the expansion is truncated at the second order term. $F^{(2,1)}$ should be calculated by including $C^{(1,1)}$ and $C^{(2,1)}$. In the present perturbation method, the perturbed terms change their value each iteration and the higher order terms in the perturbation expansion are incorporated automatically by iterations of the above-mentioned procedure. Therefore, for the *t*-th iteration, the following general expressions are obtained.

Each matrix of Eq. 1 is expanded in the perturbation series as follows:

$$F = F^{(0,t)} + F^{(1,t)} + F^{(2,t)}, \tag{23}$$

$$C = C^{(0,t)} + C^{(1,t)} + C^{(2,t)} + \cdots, \tag{24}$$

$$S = S^{(0,t)} + S^{(1,t)}, \tag{25}$$

$$E = E^{(0,t)} + E^{(1,t)} + E^{(2,t)} + \cdots, \tag{26}$$

where the subscript t denotes the iterative step. Throughout this process the zero order coefficient matrix and orbital energy matrix are obtained as follows, respectively:

$$C^{(0,t)} = C^{(0)} + C^{(1)} + C^{(2)}, \tag{27}$$

$$E^{(0,t)} = E^{(0)} + E^{(1)} + E^{(2)}. \tag{28}$$

By means of these equations perturbation calculations are iterated until convergence on $C^{(0,t)}$ and $E^{(0,t)}$ is obtained. The matrices $C^{(1)}$, $E^{(1)}$, $C^{(2)}$, and $E^{(2)}$ can be obtained for each iteration from Eps. 9—12 derived by the usual perturbation expansion up to second order.

Calculations

In the present work, the test calculations for the iterative transfer perturbation method are carried out using the extended Hückel method. The concrete procedures for this test calculation are as follows:

1. The Hamiltonian $F^{(0,0)}$, overlap integral $S^{(0,0)}$, eigenvector $C^{(0,0)}$ and energy $E^{(0,0)}$ matrices obtained by the extended Hückel method in the non-perturbed system are stored as the zero order matrix.
2. In a similar manner, the Hamiltonian matrix and overlap integrals in the perturbed system are also obtained.
3. The difference between the non-perturbed system 1 and the perturbed system 2 for the Hamiltonian matrix and the overlap integrals are taken to be the first order terms, $F^{(1,0)}$ in the Eq. 23 and $S^{(1,0)}$ in the Eq. 25, respectively.
4. From these matrix elements the first and second order terms in the eigenvector and energy, that is $C^{(1)}$, $E^{(1)}$, $C^{(2)}$, and $E^{(2)}$ in the Eqs. 9—12, are obtained by using general perturbation theory for the extended Hückel method. Theoretical details of this perturbation method have been extensively described in the previous paper.[2]
5. By using the Eqs. 13 and 14, we can obtain the next zero order terms in the eigenvector $C^{(0,1)}$ and energy $E^{(0,1)}$ equal

to the sum up to second order terms in this iterative step; then the next iteration is started.

6. Using the matrices $C^{(0,1)}$ and $E^{(0,1)}$ obtained at 5, zero-order terms in the Hamiltonian $F^{(0,1)}$ and the overlap $S^{(0,1)}$ matrices in the next iterative step are determined again from the Eqs. 17—20.
7. The first order terms of the Hamiltonian and the overlap integrals in the iterative step are defined as the difference between the zero-order terms obtained in 6 and the sum up to the initial second order term obtained in 1 and 2, that is, $F^{(1,1)}$ in an Eq. 21 and $S^{(1,1)}$ in an Eq. 22, respectively.
8. If these first order terms obtained in 7 are larger than some fixed threshold value, the succeeding iteration is restarted by returning to 4. This means that if there are relatively large contributions of the terms higher than second order, the third and fourth order terms are introduced in succession. These perturbation calculations are iterated until the first order terms converge to a negligibly small value.

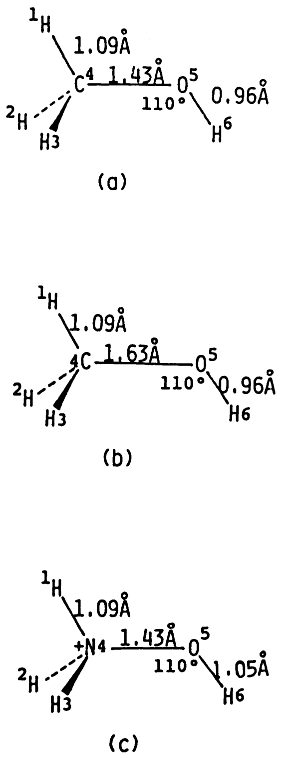
Results

This iterative transfer perturbation theory was tested on methanol with bond distances of C–O=1.43 Å (Fig. 1(a)) for the zero-order terms and C–O=1.63 Å (Fig. 1(b)) for the perturbed terms. Furthermore, this procedure was also applied to the perturbed system shown in Fig. 1(c), in which N is substituted for C. The results of these perturbation calculations are

TABLE 1. THE ORBITAL ENERGIES AND THE HIGHEST OCCUPIED MOLECULAR ORBITALS FOR THE NON-PERTURBED AND THE PERTURBED SYSTEMS BY USING THE EXTENDED Hückel AND PERTURBATION CALCULATIONS

0-th order	Perturbed system			
CH_3OH	CH_3OH		$+NH_3OH$	
C-O (1.43 Å) O-H (0.96 Å)	C-O (1.63 Å) O-H (0.96 Å)	C-O (1.63 Å) O-H (0.96 Å)	N-O (1.43 Å) O-H (1.05 Å)	N-O (1.43 Å) O-H (1.05 Å)
E. H.	E. H.	I. P.	E. H.	I. P.
		Orbital energy (in eV)		
34.423	32.052	32.054	14.040	14.041
9.745	9.454	9.454	3.225	3.231
9.587	9.411	9.411	2.301	2.301
7.917	6.764	6.764	1.577	1.572
−0.671	−5.433	−5.433	−4.953	−4.953
−13.761	−14.167	−14.167	−14.281	−14.281
−14.037	−14.421	−14.422	−14.719	−14.719
−15.571	−15.433	−15.433	−16.924	−16.924
−15.788	−15.507	−15.508	−17.123	−17.124
−16.573	−16.302	−16.303	−17.479	−17.479
−23.072	−23.674	−23.675	−26.819	−26.820
−33.850	−33.472	−33.472	−34.808	−34.808
		HOMO		
H1				
0.3202 (1s)	−0.2968	0.2968	0.1675	0.1675
H2				
−0.0000 (1s)	0.0000	0.0000	0.0000	−0.0000
H3				
−0.3202 (1s)	0.2968	−0.2968	−0.1675	−0.1675
C4				
−0.0000 (2s)	−0.0000	0.0000	0.0000	0.0000
0.0000 ($2p_x$)	0.0000	0.0000	0.0000	0.0000
0.4176 ($2p_y$)	−0.4082	0.4082	0.2927	0.2927
0.0000 ($2p_z$)	0.0001	0.0000	0.0000	0.0000
O5				
0.0000 (2s)	−0.0000	0.0000	0.0000	0.0000
0.0000 ($2p_x$)	−0.0000	0.0000	−0.0000	0.0000
0.7768 ($2p_y$)	0.7773	−0.7773	−0.9465	−0.9465
0.0001 ($2p_z$)	−0.0001	0.0000	−0.0000	0.0000
H6				
0.0000 (1s)	0.0000	0.0000	−0.0000	0.0000

E. H.: Extended Hückel method. I. P.: Iterative transfer perturbation method.



(a)

(b)

(c)

Fig. 1. (a) Structure of methanol in the non-perturbed system. (b), (c) Structures of model molecules in the perturbed systems.

listed in Table 1 compared to the direct extended Hückel calculations. The first column of Table 1 contains the orbital energies and coefficients of the highest occupied molecular orbitals for the non-perturbed system in Fig. 1(a) from the usual extended Hückel method. The second and third columns are for the perturbed system shown in Fig. 1(b) and the fourth and fifth are for the one in Fig. 1(c), showing the extended Hückel and iterative transfer perturbation methods for comparison. In Table 2 the energy of the highest occupied molecular orbitals are listed each iteration for the perturbed systems shown in Fig. 1(b) and (c). After the orbital energies have quickly converged within four iterations (Table 2), they are in good agreement with the direct method (Table 1). This shows that the approximations made within this iterative transfer perturbation method are comparable to those made in the general extended Hückel method.

Table 2. Energies of the highest occupied molecular orbitals for the perturbed systems shown in Fig. 1(b) and Fig. 1(c) each iteration

Iteration	CH_3OH	$+NH_3OH$
0	−13.761486	−13.761486
1	−14.174451	−14.312610
2	−14.167489	−14.280391
3	−14.167489	−14.280800
4	−14.167489	−14.280800

Conclusions

We could concisely show the validity and the applicability of this method that incorporates the higher order terms in the perturbation expansion in a fairly simple way. There is little advantage of this method compared to direct extended Hückel calculations in the present case using these simple molecules. But it should be mentioned further that this perturbation method can be applied also in the case that a polymer interacts with an impurity molecule at short range and the change of the charge is localized within only a part of the polymer. This approach is rather straightforward if the perturbation method for the interaction between polymers[3] is applied to the above-mentioned problem. This method may be of use to us in the interpretation of various phenomena in the electronic states of biopolymers. However, for the general use of this method it is indispensable to formulate equations, in which the divergence due to the nearly degenerate molecular orbitals is avoided, as has already been done by O'Shea and Santry.[4] Based on this, work is in progress applying this iterative transfer perturbation method to *ab initio* calculations on polymer systems.

Numerical calculations were performed on the HITAC M-200H computer system at the Information Center of Hiroshima University. The authors are grateful to Dr. D. Munch for his stimulating suggestions.

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