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## General perturbation theory for the extended Hückel method

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The general perturbation theory for the LCAO-MO method is developed to include the change of the overlap integrals. The general formulae obtained are applied to an analysis of the extended Hückel theory developed by Hoffmann and some interesting characteristics of this method are discussed.

### 1. INTRODUCTION

The perturbation theory for the simple LCAO-MO method has been developed by many authors, notably Coulson and Longuet-Higgins [1], Dewar [2], Fukui *et al.* [3, 4]. The extended Hückel method [5] differs from the simple LCAO-MO theory primarily in the inclusion of overlap integrals, and no perturbation treatment for this method has yet been published. Recently Salem has developed a perturbation treatment including overlap for the special case of two interacting systems in which the interaction is treated as the perturbation [6, 7]. He applied his formalism to the interaction of two conjugated systems in the study of concerted reactions. In the present paper the author develops the general perturbation theory for the LCAO-MO method when all overlap integrals are retained. The general formulae developed are applied to an analysis of the extended Hückel theory developed by Hoffmann [5].

### 2. NON-DEGENERATE SYSTEMS

The following basic LCAO-MO equations are to be solved by a perturbation procedure:

$$\sum_s (H_{rs} - S_{rs}E_i)C_{si} = 0 \quad (r = 1, 2, \dots, n), \quad (1)$$

where the atomic orbitals are assumed to be real, so that the following relations apply:

$$\left. \begin{aligned} S_{rs} &= S_{sr} \\ H_{rs} &= H_{sr} \end{aligned} \right\} \quad (2)$$

In equation (1), the hamiltonian matrix elements and the overlap integrals are expanded as follows:

$$\left. \begin{aligned} S_{rs} &= S_{rs}^{(0)} + \lambda S_{rs}^{(1)} + \lambda^2 S_{rs}^{(2)} + \dots, \\ H_{rs} &= H_{rs}^{(0)} + \lambda H_{rs}^{(1)} + \lambda^2 H_{rs}^{(2)} + \dots \end{aligned} \right\} \quad (3)$$

The energy levels and atomic orbital coefficients are similarly expanded.

$$\left. \begin{aligned} E_i &= E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots, \\ C_{ri} &= C_{ri}^{(0)} + \lambda C_{ri}^{(1)} + \lambda^2 C_{ri}^{(2)} + \dots \end{aligned} \right\} \quad (4)$$

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By substituting equations (3) and (4) into equation (1), the following sets of equations are obtained for zero, first and second-order terms:

$$\sum_s (H_{rs}^{(0)} - S_{rs}^{(0)} E_i^{(0)}) C_{si}^{(0)} = 0 \quad (r=1, 2, \dots, n) \quad (S_{rr}^{(0)} = 1 \text{ for all } r) \quad (5)$$

$$\sum_s (H_{rs}^{(0)} - S_{rs}^{(0)} E_i^{(0)}) C_{si}^{(1)} + \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)} - S_{rs}^{(0)} E_i^{(1)}) C_{si}^{(0)} = 0$$

$$(r=1, 2, \dots, n) \quad (S_{rr}^{(1)} = 0 \text{ for all } r), \quad (6)$$

$$\sum_s \{H_{rs}^{(2)} - (S_{rs}^{(2)} E_i^{(0)} + S_{rs}^{(1)} E_i^{(1)} + S_{rs}^{(0)} E_i^{(2)})\} C_{si}^{(0)}$$

$$+ \sum_s \{H_{rs}^{(1)} - (S_{rs}^{(1)} E_i^{(0)} + S_{rs}^{(0)} E_i^{(1)})\} C_{si}^{(1)} + (H_{rs}^{(0)} - S_{rs}^{(0)} E_i^{(0)}) C_{si}^{(2)} = 0$$

$$(r=1, 2, \dots, n) \quad (S_{rr}^{(2)} = 0 \text{ for all } r). \quad (7)$$

Equation (5) represents the unperturbed problem, and their solutions are assumed to be available.

The first-order perturbation energies are obtained in the following manner. Equation (6) is multiplied by the coefficient  $C_{ri}^{(0)}$  for all  $r$  and the equations added. One obtains:

$$E_i^{(1)} = \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{si}^{(0)}. \quad (8)$$

To obtain this result the orthonormalization conditions of equation (9) as well as equations (2) and (5) were used:

$$\sum_r \sum_s C_{ri}^{(0)} C_{sj}^{(0)} S_{rs}^{(0)} = \delta_{ij}. \quad (9)$$

To obtain the first-order coefficients equation (6) are multiplied by  $C_{rj}^{(0)}$  for all  $r$ , and summed ( $j \neq i$ ). By applying the orthonormalization condition (9) the following equations are obtained:

$$\sum_s \sum_r (H_{rs}^{(0)} - S_{rs}^{(0)} E_i^{(0)}) C_{rj}^{(0)} C_{si}^{(1)} = - \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)}. \quad (10)$$

Equation (10) can be re-written by using equation (5):

$$(E_j^{(0)} - E_i^{(0)}) \left( \sum_r \sum_s C_{rj}^{(0)} C_{si}^{(1)} S_{rs}^{(0)} \right) = - \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)}. \quad (11)$$

For the coefficients of the atomic orbitals in the simple LCAO-MO method the following equations can be proved [1]:

$$\left. \begin{aligned} \sum_r C_{ri} C_{rj} &= \delta_{ij}, \\ \sum_i C_{ri} C_{si} &= \delta_{rs}. \end{aligned} \right\} \quad (12)$$

When overlap integrals are retained, the corresponding equations are (9) and (13):

$$\sum_r \sum_s C_{ri}^{(0)} C_{sj}^{(0)} S_{rs}^{(0)} = \delta_{ij}, \quad (9)$$

$$\sum_j \sum_t C_{rj}^{(0)} C_{ti}^{(0)} S_{st}^{(0)} = \delta_{rs}. \quad (13)$$

Equation (13) may be obtained from equation (9) in the following way. Equation (9) may be written in matrix form as:

$$CS^T C = I, \quad (14)$$

where  $C$  is the coefficient matrix,  ${}^T C$  its transpose,  $S$  the matrix of overlap integrals and  $I$  the unit matrix. Multiplying this equation on the left by  $C^{-1}$ , on the right by  $C$ , one obtains:

$$S {}^T C C = I \quad (15)$$

and each matrix element of (15) generates the formulae (13).

Equation (11) is then multiplied by  $C_{tj}^{(0)}$  and these equations are added for all  $j$  except  $i$ , obtaining:

$$\begin{aligned} \sum_j \{C_{tj}^{(0)} \sum_r \sum_s C_{rj}^{(0)} C_{si}^{(1)} S_{rs}^{(0)}\} - C_{ti}^{(0)} \sum_r \sum_s C_{ri}^{(0)} C_{si}^{(1)} S_{rs}^{(0)} \\ = - \sum_j' \sum_r \sum_s \frac{(H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)})}{E_j^{(0)} - E_i^{(0)}} C_{ri}^{(0)} C_{sj}^{(0)} C_{tj}^{(0)}, \end{aligned} \quad (16)$$

where  $\sum_j'$  means that the summation covers all levels except  $i$ . The orthonormalization condition for first order is given by equation (17):

$$\sum_r \sum_s 2C_{ri}^{(0)} C_{si}^{(1)} S_{rs}^{(0)} + \sum_r \sum_s C_{ri}^{(0)} C_{si}^{(0)} S_{rs}^{(1)} = 0. \quad (17)$$

By applying equations (17) and (13) the first-order coefficients are obtained:

$$\begin{aligned} C_{ti}^{(1)} = - \sum_j' \frac{C_{tj}^{(0)}}{E_j^{(0)} - E_i^{(0)}} \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \\ - (\frac{1}{2}) C_{ti}^{(0)} \sum_r \sum_s C_{ri}^{(0)} C_{si}^{(0)} S_{rs}^{(1)}. \end{aligned} \quad (18)$$

The second-order perturbation energies and coefficients may be calculated in the same way by using the first-order and zeroth-order coefficients and energies. Only the final results are given:

$$\begin{aligned} E_i^{(2)} = \sum_r \sum_s \{H_{rs}^{(2)} - (S_{rs}^{(2)} E_i^{(0)} + S_{rs}^{(1)} E_i^{(1)})\} C_{ri}^{(0)} C_{si}^{(0)} \\ + \sum_r \sum_s \{H_{rs}^{(1)} - (S_{rs}^{(0)} E_i^{(1)} + S_{rs}^{(1)} E_i^{(0)})\} C_{ri}^{(1)} C_{si}^{(0)}, \end{aligned} \quad (19)$$

$$\begin{aligned} C_{ti}^{(2)} = - \sum_j' \frac{C_{tj}^{(0)}}{E_j^{(0)} - E_i^{(0)}} \left[ \sum_r \sum_s \{H_{rs}^{(2)} - (S_{rs}^{(2)} E_i^{(0)} + S_{rs}^{(1)} E_i^{(1)})\} C_{ri}^{(0)} C_{sj}^{(0)} \right. \\ \left. + \sum_r \sum_s \{H_{rs}^{(1)} - (S_{rs}^{(0)} E_i^{(1)} + S_{rs}^{(1)} E_i^{(0)})\} C_{ri}^{(1)} C_{sj}^{(0)} \right] \\ - (\frac{1}{2}) C_{ti}^{(0)} \sum_r \sum_s \{C_{ri}^{(1)} C_{si}^{(1)} S_{rs}^{(0)} + (C_{ri}^{(1)} C_{si}^{(0)} + C_{ri}^{(0)} C_{si}^{(1)}) S_{rs}^{(1)} \\ + C_{ri}^{(0)} C_{si}^{(0)} S_{rs}^{(2)}\}. \end{aligned} \quad (20)$$

Third and higher-order terms can be derived in a similar manner.

From equations (8), (18), (19) and (20) the following general expressions may be derived, by assuming  $H_{rs}^{(2)}$  and  $S_{rs}^{(2)}$  to be zero:

$$\begin{aligned} E_i = E_i^{(0)} + E_i^{(1)} + E_i^{(2)} \\ = E_i^{(0)} + \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{si}^{(0)} - E_i^{(1)} \sum_r \sum_s C_{ri}^{(0)} C_{si}^{(0)} S_{rs}^{(1)} \\ + \sum_r \sum_s \{H_{rs}^{(1)} - (S_{rs}^{(0)} E_i^{(1)} + S_{rs}^{(1)} E_i^{(0)})\} C_{ri}^{(1)} C_{si}^{(0)}, \end{aligned} \quad (21)$$

$$\begin{aligned}
C_{ti} &= C_{ti}^{(0)} + C_{ti}^{(1)} + C_{ti}^{(2)} \\
&= C_{ti}^{(0)} - \sum_j' \frac{C_{tj}^{(0)}}{E_j^{(0)} - E_i^{(0)}} \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \\
&\quad - (\tfrac{1}{2}) C_{ti}^{(0)} \sum_r \sum_s C_{ri}^{(0)} C_{si}^{(0)} S_{rs}^{(1)} \\
&\quad - \sum_j' \frac{C_{tj}^{(0)}}{E_j^{(0)} - E_i^{(0)}} \left[ -E_i^{(1)} \sum_r \sum_s C_{ri}^{(0)} C_{sj}^{(0)} S_{rs}^{(1)} \right. \\
&\quad \quad \left. + \sum_r \sum_s \{H_{rs}^{(1)} - (S_{rs}^{(0)} E_i^{(1)} + S_{rs}^{(1)} E_i^{(0)})\} C_{ri}^{(1)} C_{sj}^{(0)} \right] \\
&\quad - (\tfrac{1}{2}) C_{ti}^{(0)} \sum_r \sum_s \{C_{ri}^{(1)} C_{si}^{(1)} S_{rs}^{(0)} + (C_{ri}^{(1)} C_{si}^{(0)} + C_{ri}^{(0)} C_{si}^{(1)}) S_{rs}^{(1)}\}, \quad (22)
\end{aligned}$$

where

$$\begin{aligned}
E_i^{(1)} &= \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{si}^{(0)}, \\
C_{ti}^{(1)} &= - \sum_j' \frac{C_{tj}^{(0)}}{E_j^{(0)} - E_i^{(0)}} \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \\
&\quad - (\tfrac{1}{2}) C_{ti}^{(0)} \sum_r \sum_s C_{ri}^{(0)} C_{si}^{(0)} S_{rs}^{(1)}.
\end{aligned}$$

### 3. DEGENERATE SYSTEMS

When degeneracies occur the appropriate zeroth-order wave functions must be determined in order to calculate first-order perturbation terms. Thus the perturbed energies and coefficients may be represented in the following form, where two solutions of the perturbation are distinguished by the second superscript, and the order of the perturbation is given by the first superscript:

$$E_{i1} = E_i^{(0)} + \lambda E_i^{(1,1)} + \lambda^2 E_i^{(2,1)} + \dots, \quad (23 a)$$

$$E_{i2} = E_i^{(0)} + \lambda E_i^{(1,2)} + \lambda^2 E_i^{(2,2)} + \dots, \quad (23 b)$$

$$C_{ri1} = (x_1^{(1)} C_{ri}^{(0,1)} + x_2^{(1)} C_{ri}^{(0,2)}) + \lambda C_{ri}^{(1,1)} + \lambda^2 C_{ri}^{(2,1)} + \dots, \quad (24 a)$$

$$C_{ri2} = (x_1^{(2)} C_{ri}^{(0,1)} + x_2^{(2)} C_{ri}^{(0,2)}) + \lambda C_{ri}^{(1,2)} + \lambda^2 C_{ri}^{(2,2)} + \dots \quad (24 b)$$

$x_1, x_2$  are coefficients which express the appropriate wave function of the zeroth and the two first-order perturbation energies as a linear combination of two degenerate wave functions. By substituting equations (23 a) and (24 a) etc., in equation (1), the following simultaneous equation is obtained for the first-order perturbation:

$$\begin{aligned}
&\sum_s (H_{rs}^{(0)} - S_{rs}^{(0)} E_i^{(0)}) C_{si}^{(1)} \\
&\quad + \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)} - S_{rs}^{(0)} E_i^{(1)}) (x_1 C_{si}^{(0,1)} + x_2 C_{si}^{(0,2)}) = 0 \quad (r = 1, 2, \dots, n).
\end{aligned} \quad (25)$$

Then equation (25) is multiplied by  $C_{ri}^{(0,1)}$  and added. Since  $C_{ri}^{(0,1)}$ 's are the solution of (5), that is, the solutions of the zeroth-order problem, and from equations (2) and (9), the following set is obtained.

$$\begin{aligned}
x_1 \left\{ \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{si}^{(0,1)} - E_i^{(1)} \right\} \\
+ x_2 \left\{ \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{si}^{(0,2)} \right\} = 0. \quad (26 a)
\end{aligned}$$

Similarly:

$$x_1 \left\{ \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{si}^{(0,2)} \right\} + x_2 \left\{ \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,2)} C_{si}^{(0,2)} - E_i^{(1)} \right\} = 0. \quad (26 b)$$

These simultaneous equations give us the well-known eigenvalue problem:

$$\begin{vmatrix} A - E_i^{(1)} & B \\ B & C - E_i^{(1)} \end{vmatrix} = 0, \quad (27)$$

where

$$\left. \begin{aligned} A &= \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{si}^{(0,1)}, \\ B &= \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{si}^{(0,2)}, \\ C &= \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,2)} C_{si}^{(0,2)}. \end{aligned} \right\} \quad (28)$$

The first-order perturbation energies are:

$$E_i^{(1,1)} = \left(\frac{1}{2}\right) \{ (A + C) + \sqrt{(A - C)^2 + 4B^2} \} \quad (29 a)$$

$$E_i^{(1,2)} = \left(\frac{1}{2}\right) \{ (A + C) - \sqrt{(A - C)^2 + 4B^2} \} \quad (29 b)$$

The corresponding coefficients  $x_1^{(1)}$ ,  $x_2^{(1)}$ ,  $x_1^{(2)}$ ,  $x_2^{(2)}$  can also be derived.

In order to calculate the coefficients to the first order, new coefficients are defined as follows:

$$x_1^{(1)} C_{ri}^{(0,1)} + x_2^{(1)} C_{ri}^{(0,2)} \rightarrow C_{ri}^{(0,1)}$$

$$x_1^{(2)} C_{ri}^{(0,1)} + x_2^{(2)} C_{ri}^{(0,2)} \rightarrow C_{ri}^{(0,2)}$$

Then

$$C_{ri_1} = (x_1^{(1)} C_{ri}^{(0,1)} + x_2^{(1)} C_{ri}^{(0,2)}) + \lambda C_{ri}^{(1,1)} + \dots \rightarrow C_{ri}^{(0,1)} + \lambda C_{ri}^{(1,1)} + \dots,$$

$$C_{ri_2} = (x_1^{(2)} C_{ri}^{(0,1)} + x_2^{(2)} C_{ri}^{(0,2)}) + \lambda C_{ri}^{(1,2)} + \dots \rightarrow C_{ri}^{(0,2)} + \lambda C_{ri}^{(1,2)} + \dots$$

The following equation is obtained in a similar manner to that used in the non-degenerate system:

$$\sum_r \sum_s C_{rj}^{(0)} C_{si}^{(1,1)} S_{rs}^{(0)} = - \frac{1}{E_j^{(0)} - E_i^{(0)}} \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{sj}^{(0)} \quad (j \neq i_1, i_2). \quad (30)$$

Then equation (30) is summed over all  $j$  except  $i_1$  and  $i_2$  after multiplying by  $C_{tj}^{(0)}$  we have:

$$\begin{aligned} \sum_j C_{tj}^{(0)} \left\{ \sum_r \sum_s C_{rj}^{(0)} C_{si}^{(1,1)} S_{rs}^{(0)} \right\} - C_{ti}^{(0,1)} \left\{ \sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(1,1)} S_{rs}^{(0)} \right\} \\ - C_{ti}^{(0,2)} \left\{ \sum_r \sum_s C_{ri}^{(0,2)} C_{si}^{(1,1)} S_{rs}^{(0)} \right\} \\ = - \sum_{\substack{j \\ (j \neq i_1, i_2)}}'' \frac{C_{tj}^{(0)}}{E_j^{(0)} - E_i^{(0)}} \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{sj}^{(0)}. \quad (31) \end{aligned}$$

From the orthonormality condition:

$$\sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(1,1)} S_{rs}^{(0)} = -(\frac{1}{2}) \sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(0,1)} S_{rs}^{(1)}, \quad (32)$$

$$\sum_r \sum_s \{(C_{ri}^{(0,1)} C_{si}^{(1,2)} + C_{ri}^{(1,1)} C_{si}^{(0,2)}) S_{rs}^{(0)} + C_{ri}^{(0,1)} C_{si}^{(0,2)} S_{rs}^{(1)}\} = 0. \quad (33)$$

From equation (33), the following two expressions are tentatively assumed:

$$\sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(1,2)} S_{rs}^{(0)} = -(\frac{1}{2}) \sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(0,2)} S_{rs}^{(1)}, \quad (34)$$

$$\sum_r \sum_s C_{ri}^{(1,1)} C_{si}^{(0,2)} S_{rs}^{(0)} = -(\frac{1}{2}) \sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(0,2)} S_{rs}^{(1)}. \quad (35)$$

In equations (34) and (35), there is some arbitrariness, that is, only the sum of equations (34) and (35) is determined and one can divide equation (33) arbitrarily into two parts: equations (34) and (35). It is noteworthy that in any division the perturbed coefficient is the solution of the simultaneous equation (25) and also satisfies the orthonormality condition. Substituting equations (32), (34) and (13) into equation (31), the coefficient to the first order is obtained as follows:

$$\begin{aligned} C_{ti}^{(1,1)} = & - \sum_{\substack{j \\ (j \neq i_1, i_2)}}'' \frac{C_{tj}^{(0)}}{E_j^{(0)} - E_i^{(0)}} \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{sj}^{(0)} \\ & - (\frac{1}{2}) C_{ti}^{(0,1)} \sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(0,1)} S_{rs}^{(1)} - (\frac{1}{2}) C_{ti}^{(0,2)} \sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(0,2)} S_{rs}^{(1)}. \end{aligned} \quad (36a)$$

Similarly

$$\begin{aligned} C_{ti}^{(1,2)} = & - \sum_{\substack{j \\ (j \neq i_1, i_2)}}'' \frac{C_{tj}^{(0)}}{E_j^{(0)} - E_i^{(0)}} \sum_r \sum_s (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,2)} C_{sj}^{(0)} \\ & - (\frac{1}{2}) C_{ti}^{(0,2)} \sum_r \sum_s C_{ri}^{(0,2)} C_{si}^{(0,2)} S_{rs}^{(1)} - (\frac{1}{2}) C_{ti}^{(0,1)} \sum_r \sum_s C_{ri}^{(0,1)} C_{si}^{(0,2)} S_{rs}^{(1)}. \end{aligned} \quad (36b)$$

#### 4. APPLICATION TO SPECIAL CASES

##### 4.1. Intermolecular perturbation

(a) The perturbation of a Coulomb integral  $H_{rr}^{(1)}$

$$E_i = E_i^{(0)} + H_{rr}^{(1)} (C_{ri}^{(0)})^2 - \sum_j' \frac{(H_{rr}^{(1)})^2}{E_j^{(0)} - E_i^{(0)}} (C_{ri}^{(0)} C_{rj}^{(0)})^2 + \dots \quad (37)$$

This equation agrees with that of Coulson and Longuet-Higgins [1].

(b) The perturbation of a resonance integral  $H_{rs}^{(1)}$

$$\begin{aligned} E_i = & E_i^{(0)} + 2(H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{si}^{(0)} - 4(H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) (C_{ri}^{(0)} C_{si}^{(0)})^2 S_{rs}^{(1)} \\ & + \{H_{rs}^{(1)} - 2S_{rs}^{(0)} (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{si}^{(0)} - S_{rs}^{(1)} E_i^{(0)}\} \\ & \times \left\{ - \sum_j' \frac{H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}}{E_j^{(0)} - E_i^{(0)}} (C_{ri}^{(0)} C_{sj}^{(0)} + C_{rj}^{(0)} C_{si}^{(0)})^2 - 2(C_{ri}^{(0)} C_{si}^{(0)})^2 S_{rs}^{(1)} \right\}. \end{aligned} \quad (38)$$

From this equation, the effect of including the overlap integral is clearly shown in the first order, that is, the first-order perturbation energy depends sharply upon the

height of the energy level. In the extended Hückel calculation [5],  $H_{rs}$  is proportional to the overlap integral and has an opposite sign, so that the first-order perturbation term may be re-written as follows:

$$E_i^{(1)} = 2H_{rs}^{(1)}(1 - (1/K)E_i^{(0)})C_{ri}^{(0)}C_{si}^{(0)}, \quad (39)$$

where  $K$  is the coefficient of the overlap integral in the Wolfsberg–Helmholtz approximation [8] and has a negative value.

Therefore when  $E_i^{(0)}$  is positive the perturbation is very large, and correspondingly the perturbation is small in the case of negative  $E_i^{(0)}$ . This feature is made explicit in figure 1. Usually  $K$  is  $-10 \sim -20$  eV, so that the occupied and lowest vacant orbitals are little perturbed. Since many physical properties depend only on the occupied and lowest vacant orbitals, the perturbation method is of value.

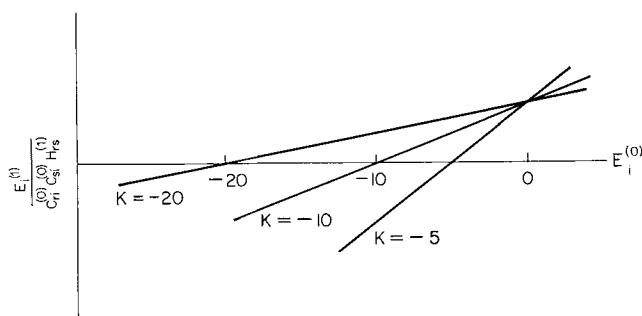


Figure 1. The first-order perturbation of a resonance integral.  $K = 0.875(w(r) + w(s))$ .

Figure 1 illustrates another characteristic feature of the extended Hückel method. In the simple Hückel method, in which all overlap integrals are completely neglected, the perturbation always stabilizes the perturbed molecule if  $C_{ri}^{(0)}C_{si}^{(0)}H_{rs}^{(1)}$  is negative for all occupied orbitals. This is not true for the extended Hückel method, where, as is clearly shown in figure 1, the stabilization or destabilization depends on the height of the occupied energy levels.

In equation (39), if  $S_{rs}^{(0)}$  and  $S_{rs}^{(1)}$  are set to zero, the following expression is obtained in accordance with the results of Coulson and Longuet-Higgins [1]:

$$E_i = E_i^{(0)} + 2H_{rs}^{(1)}C_{ri}^{(0)}C_{si}^{(0)} - \sum_j' \frac{(H_{rs}^{(1)})^2}{E_j^{(0)} - E_i^{(0)}} (C_{ri}^{(0)}C_{sj}^{(0)} + C_{rj}^{(0)}C_{si}^{(0)})^2. \quad (40)$$

#### 4.2. Intermolecular perturbation

##### (a) Perturbation between different molecules

In this case, the coefficients of one molecule are  $C_{1i}, C_{2i}, \dots, C_{mi}$  and those of the other molecule  $C_{m+1i}, C_{m+2i}, \dots, C_{ni}$ . Then if  $E_i$  belongs to the energy level of one molecule which has coefficient are  $C_{1i}, C_{2i}, \dots, C_{mi}$ , the following relation should be retained, since the non-perturbed wave function should be localized in one molecule:

$$C_{m+1i}^{(0)} = C_{m+2i}^{(0)} = \dots = C_{ni}^{(0)} = 0. \quad (41)$$

Applying this relation to equation (8), the first-order perturbation energy is found to be zero:

$$E_i^{(1)} = 0. \quad (42)$$



The second-order perturbation energy of the  $i$ th level is represented as follows, using equations (19) and (41):

$$E_i^{(2)} = - \sum_j \frac{2}{E_j^{(0)} - E_i^{(0)}} \left\{ \sum_{r=1}^m \sum_{s=m+1}^n (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \right\}^2, \quad (43)$$

where the summation goes over all energy levels of other molecule. This equation agrees with that given by Salem [6, 7].

The energy change of the system as a result of the intermolecular perturbation between two closed shell systems is the following:

$$\begin{aligned} \Delta E &= 2 \sum_i^{\text{occ}} E_i^{(2)} + 2 \sum_j^{\text{occ}} E_j^{(2)} \\ &= - \sum_i^{\text{occ}} \sum_j^{\text{all}} \frac{2}{E_j^{(0)} - E_i^{(0)}} \left\{ \sum_{r=1}^m \sum_{s=m+1}^n (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \right\}^2 \\ &\quad - \sum_j^{\text{occ}} \sum_i^{\text{all}} \frac{2}{E_i^{(0)} - E_j^{(0)}} \left\{ \sum_{r=1}^m \sum_{s=m+1}^n (H_{rs}^{(1)} - S_{rs}^{(1)} E_j^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \right\}^2, \end{aligned} \quad (44)$$

where  $i$  indicates the energy level belonging to one molecule and  $j$  to another molecule.

$$\begin{aligned} \Delta E &= - \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \frac{2}{E_j^{(0)} - E_i^{(0)}} \left\{ \sum_{r=1}^m \sum_{s=m+1}^n (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \right\}^2 \\ &\quad - \sum_j^{\text{occ}} \sum_i^{\text{unocc}} \frac{2}{E_i^{(0)} - E_j^{(0)}} \left\{ \sum_{r=1}^m \sum_{s=m+1}^n (H_{rs}^{(1)} - S_{rs}^{(1)} E_j^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \right\}^2 \\ &\quad - 2 \sum_i^{\text{occ}} \sum_j^{\text{occ}} \left( \sum_{r=1}^m \sum_{s=m+1}^n S_{rs}^{(1)} C_{ri}^{(0)} C_{sj}^{(0)} \right) \\ &\quad \times \left[ \sum_{r=1}^m \sum_{s=m+1}^n C_{ri}^{(0)} C_{sj}^{(0)} \{ 2H_{rs}^{(1)} - S_{rs}^{(1)} (E_i^{(0)} + E_j^{(0)}) \} \right]. \end{aligned} \quad (45)$$

In equation (45), the first and second terms are always negative, and give a stabilization energy. However the sign of the third term depends upon the sign of the coefficients of the interacting atomic orbitals, the corresponding overlap integral, as well as on the height of the energy levels.

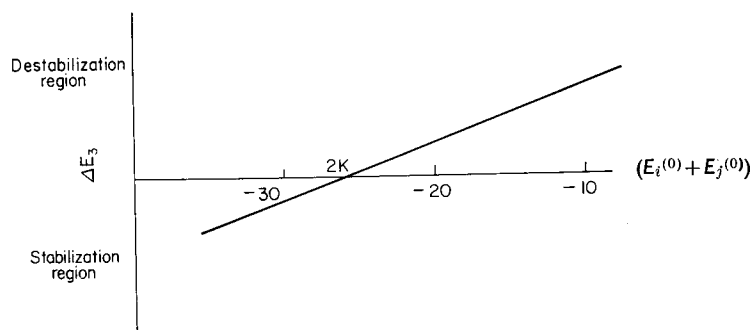


Figure 2. The schematic illustration of the intermolecular perturbation.  $\Delta E_3$  is the third term in equation (46).

For brevity, the perturbation energy arising from only one interaction term between  $r$  and  $s$  is obtained as follows:

$$\begin{aligned}\Delta E = & - \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \frac{2}{E_j^{(0)} - E_i^{(0)}} \{ (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \}^2 \\ & - \sum_j^{\text{occ}} \sum_i^{\text{unocc}} \frac{2}{E_i^{(0)} - E_j^{(0)}} \{ (H_{rs}^{(1)} - S_{rs}^{(1)} E_j^{(0)}) C_{ri}^{(0)} C_{sj}^{(0)} \}^2 \\ & - 2 \sum_i^{\text{occ}} \sum_j^{\text{occ}} (C_{ri}^{(0)} C_{sj}^{(0)})^2 \{ 2 S_{rs}^{(1)} H_{rs}^{(1)} - (S_{rs}^{(1)})^2 (E_i^{(0)} + E_j^{(0)}) \}. \quad (46)\end{aligned}$$

From the third term, the following interesting conclusion is derived†, namely that since  $S_{rs}^{(1)} H_{rs}^{(1)}$  is negative the highest occupied, or the levels in the vicinity of the highest occupied level, contribute to the destabilization of the molecule. On the other hand the lowest occupied level, or the levels in the vicinity of the lowest occupied level, give the stabilization energy. This situation can be depicted in figure 2 in a similar manner as in figure 1. In figure 2,  $K$  is given in the following form:

$$K = 0.875(W(r) + W(s))$$

where  $W(r)$  is the valence-state ionization potential of the atomic orbital  $r$ . From this figure, it is clear that the interaction between the lower occupied levels contributes to the stabilization of the system, and the higher occupied levels to the destabilization.

On the other hand, in the simple Hückel method in which all overlap integrals are neglected, the third term in equation (46) vanishes so that the system is always stabilized. The perturbation energy in this case is obtained from equation (45) by setting all overlap integrals to zero:

$$\Delta E = - \left( \sum_i^{\text{occ}} \sum_j^{\text{unocc}} - \sum_i^{\text{unocc}} \sum_j^{\text{occ}} \right) \frac{2}{E_j^{(0)} - E_i^{(0)}} \left( \sum_{r=1}^m \sum_{s=m+1}^n H_{rs}^{(1)} C_{ri}^{(0)} C_{sj}^{(0)} \right)^2.$$

This equation agrees with the equation given by Dewar [2], and by Fukui *et al.* [3, 4]. Thus, this perturbation formula reveals the essential characteristic of the extended Hückel method; namely that this method often gives destabilization as a result of interaction of two systems.

### (b) Perturbation between identical molecules

In this case the treatment of the degenerate system is necessary. By using equation (27), the first-order perturbation energies are given as follows:

$$E_i^{(1,1)} = \sum_{r=1}^m \sum_{s=m+1}^n (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{si}^{(0,2)}, \quad (47)$$

$$E_i^{(1,2)} = - \sum_{r=1}^m \sum_{s=m+1}^n (H_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}) C_{ri}^{(0,1)} C_{si}^{(0,2)}. \quad (48)$$

† The similar but somewhat different discussions were given in [7] by Salem, that is, in his paper  $H_{jj'}$  is approximated as follows in equation (3) of [7]:

$$H_{jj'}^{(1)} = \frac{1}{2}(E_j^{(0)} + E_{j'}^{(0)}) S_{jj'}^{(1)} + I_{jj'}^{(1)}.$$

In the present paper,  $H_{jj'}$  is given by means of the approximation of the Hückel method in the following form:

$$H_{jj'}^{(1)} = \sum_r \sum_s C_{jr}^{(0)} C_{js}^{(0)} H_{rs}^{(1)}.$$

This equation is quite similar to the perturbation of the NBMO method introduced by Dewar [2], since  $(H_{rs}^{(1)} - S_{rs}^{(1)}E_i^{(0)})$  is substituted in equation (47) instead of  $H_{rs}^{(1)}$ . Therefore, if two systems have a closed-shell electronic structure, there is no contribution from the first-order perturbation. If, on the other hand, the two systems possess an open shell, there is a large contribution, as in the NBMO method and for the same reason.

## 5. EXAMPLE

As an example, the numerical perturbation of a methane-like molecule in which all hydrogens are assumed to have different valence state ionization potential is treated. The non-perturbed hamiltonian matrix and the overlap matrix are given as follows.

Hamiltonian matrix  $H_{rs}^{(0)}$ :

-21.4	0.0	0.0	0.0	-17.30	-16.62	-15.72	-15.24
	-11.4	0.0	0.0	0.0	-5.74	3.08	3.16
		-11.4	0.0	0.0	0.0	-5.34	5.47
			-11.4	-10.15	9.93	10.69	10.94
				-13.6	-3.71	-3.11	-2.86
					-15.6	-14.39	-14.10
						-17.6	-13.69
							-18.6

Overlap matrix  $S_{rs}^{(0)}$ :

1.0	0.0	0.0	0.0	0.565	0.513	0.461	0.436
	1.0	0.0	0.0	0.0	0.243	-0.122	-0.120
		1.0	0.0	0.0	0.0	0.211	-0.208
			1.0	0.464	-0.420	-0.421	-0.417
				1.0	0.145	0.114	0.102
					1.0	0.495	0.471
						1.0	0.432
							1.0

The first-order perturbed hamiltonian matrix and the overlap matrix corresponding to a change of the distance between carbon and hydrogen atoms (0.2 Å) are given as follows.

The first-order perturbed hamiltonian matrix  $H_{rs}^{(1)}$ :

0.0	0.0	0.0	0.0	3.16	3.43	3.56	3.59
	0.0	0.0	0.0	0.0	0.82	-0.52	-0.57
		0.0	0.0	0.0	0.0	0.90	-0.98
			0.0	1.14	-1.41	-1.80	-1.98
				0.0	1.56	1.39	1.31
					0.0	2.87	2.94
						0.0	3.18
							0.0

The first-order perturbed overlap matrix  $S_{rs}^{(1)}$ :

0.0	0.0	0.0	0.0	-0.103	-0.106	-0.104	-0.103
	0.0	0.0	0.0	0.0	-0.035	0.021	0.022
		0.0	0.0	0.0	0.0	-0.036	0.038
			0.0	-0.052	0.060	0.071	0.075
				0.0	-0.061	-0.051	-0.046
					0.0	-0.099	-0.098
						0.0	-0.100
							0.0

The second-order perturbed hamiltonian matrix and the overlap matrix corresponding to the change of the distance between carbon and hydrogen atom ( $-0.05 \text{ \AA}$ ) are given as follows.

The second-order perturbed hamiltonian matrix  $H_{rs}^{(2)}$ :

0.0	0.0	0.0	0.0	-0.765	-0.819	-0.842	-0.845
	0.0	0.0	0.0	0.0	-0.216	0.134	0.145
		0.0	0.0	0.0	0.0	-0.232	0.252
			0.0	-0.314	0.375	0.465	0.504
				0.0	-0.321	-0.280	-0.261
					0.0	-0.681	-0.693
						0.0	-0.739
							0.0

The second-order perturbed overlap matrix  $S_{rs}^{(2)}$ :

0.0	0.0	0.0	0.0	0.025	0.025	0.025	0.024
	0.0	0.0	0.0	0.0	0.009	-0.005	-0.006
		0.0	0.0	0.0	0.0	0.009	-0.010
			0.0	0.014	-0.016	-0.018	-0.019
				0.0	0.013	0.010	0.009
					0.0	0.023	0.023
						0.0	0.023
							0.0

By using general first-order and second-order equations (equations (8), (18) and (19)), the perturbed energies are calculated and collected in the table. From this example it is clear that the perturbation energies are large for vacant orbitals and small for the occupied levels, in agreement with the discussion in the previous section. The perturbation treatment is thus accurate for the ground state. In the excited states the trends in energies and electronic distributions are correctly reproduced, but these features are exaggerated. For the ground state the inclusion of second-order perturbations gives remarkable agreement with the exact solution. Since we are mostly concerned with ground and lower excited state properties, we find the results very encouraging and intend to explore the perturbation treatment in the study of large molecules.

I am grateful to Dr. Roald Hoffmann for the opportunity to carry out this study and for his stimulating discussion. I would also like to express my gratitude to Dr. Chikayoshi Nagata for his continued interest and encouragement in this work.

The first order only								
Energy level	1	2	3	4	5	6	7	8
Non-perturbed energy	17.42	15.60	5.33	1.02	-13.49	-14.43	-18.51	-26.88
First-order perturbation energy	-22.11	-18.01	-10.55	-8.45	-0.01	-0.17	0.03	0.71
Non-perturbed + perturbation	-4.69	-2.41	-5.22	-7.43	-13.50	-14.60	-18.48	-26.17
Exact energy	3.99	1.83	-2.63	-5.33	-13.54	-14.71	-18.53	-26.07
Total energy by perturbation = -145.49. Total energy by exact solution = -145.72. Difference = -0.23.								
The first order and second order								
Energy level	1	2	3	4	5	6	7	8
Non-perturbed energy	17.42	15.60	5.33	1.02	-13.49	-14.43	-18.51	-26.88
First-order perturbation energy	-22.11	-18.01	-10.55	-8.45	-0.01	-0.17	0.03	0.71
Second-order perturbation energy	17.83	11.06	6.01	4.67	-0.04	-0.07	-0.06	-0.09
Non-perturbed + perturbation	13.14	8.65	0.79	-2.76	-13.54	-14.67	-18.54	-26.26
Exact energy	6.30	4.53	-1.06	-4.12	-13.53	-14.63	-18.53	-26.29
Total energy by perturbation = -146.00. Total energy by exact solution = -145.97. Difference = -0.03.								

The calculated results of the perturbation energy.

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