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The Diagrammatic Perturbation Theory for the Interaction of Two Molecular Systems Treated by the Extended Hückel Theory

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The general diagrammatic perturbation theory for the interaction of two molecular systems treated by the extended Hückel method is elaborated.

Key words: Molecular interactions – Diagrammatic perturbation theory – Extended Hückel method

1. Introduction

The study of the interaction between the two molecular systems is important for the interpretation of the reactivity of the molecules and intermolecular interactions. One of the possible frameworks in which this study can be made is the extended Hückel method (EHM) [1]. In this method, the formulation of the above mentioned problem is somewhat complicated by the presence of the nonzero overlap between the molecular orbitals belonging to different molecular systems. As a consequence, a generalized version of the perturbation theory has to be adopted, which works with the non-orthogonal set of the unperturbed molecular orbitals [2, 3]. Salem [4] elaborated the appropriate perturbation procedure for the case of two interacting systems in the framework of π-electron Hückel method. This method has been generalized by Devaquet and Salem [5, 6] to include the electronic repulsion. The general perturbation theory for the EHM has been elaborated by Imamura [7]. In his approach the following two difficulties may be noted: (i) his formalism seems not to be quite suitable for calculations of the interaction energy to higher than the second order, and (ii) it is not quite clear from his derivation whether his formula for interaction energy can be applied to the interaction of the two identical molecular systems.

In the present paper the above problem is reformulated using the second-quantized formalism and the diagrammatic perturbation technique. This approach is shown to be free from the above mentioned shortcomings. The application of the diagrammatic method to the calculation of the interaction energy is complicated by the presence of the mentioned overlap. The unified system of the one-particle functions does not form an orthonormal set. Then the corresponding creation and annihilation operators do not obey the well-known anticommutation relations. Therefore the direct formulation of the diagrammatic perturbation theory leads to many formal difficulties [8, 9]. Basilevsky and Berenfeld [10] in their study of the general many-body theory of the intermolecular interactions have circumvented this formal difficulty by working with one-particle basis obtained by orthogonalizing the original one.

In this paper the similar approach is used to formulate the diagrammatic theory of the interaction energy calculated in the framework of the EHM. The present approach is general and may readily be either specified for simpler or more complex problems. Finally, the method used in this paper may be useful as a methodological basis for the study of the interaction of the molecules with explicit inclusion of the electronic repulsion by the diagrammatic perturbation technique.

2. Preliminary Considerations

Let us examine two molecular systems A and B. There exist two distinct orthonormal sets of molecular spinorbitals, localized on the molecular systems A and B

$$\{|\varphi_i\rangle ; i \in \mathrm{A}\} \qquad (\text{system A}), \tag{1a}$$

$$\{|\varphi_j\rangle ; j \in \mathrm{B}\} \qquad (\text{system B}), \tag{1b}$$

which form column vectors $\boldsymbol{\Phi}_{\mathrm{A}}$ and $\boldsymbol{\Phi}_{\mathrm{B}}$. Then we may define the new column vector

$$\boldsymbol{\Phi} = \begin{pmatrix} \boldsymbol{\Phi}_{\mathrm{A}} \\ \boldsymbol{\Phi}_{\mathrm{B}} \end{pmatrix}. \tag{2}$$

We assume that spinorbitals from (1a) and (1b) are non-orthogonal, i.e.

$$\boldsymbol{\Phi}\boldsymbol{\Phi}^{+} = \boldsymbol{T} = \mathbf{1} + \boldsymbol{S}, \tag{3a}$$

$$\boldsymbol{S} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\Phi}_{\mathrm{A}}\boldsymbol{\Phi}_{\mathrm{B}}^{+} \\ \boldsymbol{\Phi}_{\mathrm{B}}\boldsymbol{\Phi}_{\mathrm{A}}^{+} & \mathbf{0} \end{pmatrix}, \tag{3b}$$

where matrix $\boldsymbol{S}$ has elements $S_{ij} = \langle \varphi_i | \varphi_j \rangle$.

In the following, we orthogonalize the set of spinorbitals from column vector $\boldsymbol{\Phi}$ by Löwdin's orthogonalization procedure [11]

$$\boldsymbol{\Psi} = \boldsymbol{T}^{-1/2}\boldsymbol{\Phi}, \tag{4}$$

where the column vector $\boldsymbol{\Psi}$ is formed by the set of orthonormal spinorbitals $\{|\psi_i\rangle ; i \in \mathrm{A} + \mathrm{B}\}$. Under the assumption that eigenvalues λ of the overlap matrix $\boldsymbol{S}$ fulfill condition [12]: $|\lambda| < 1$, then the orthogonalization matrix $\boldsymbol{T}^{-1/2}$ may be expressed as expansion

$$\boldsymbol{T}^{-1/2} = \sum_{n=0}^{\infty} \binom{n}{-1/2} \boldsymbol{S}^{n} = \mathbf{1} - \tfrac{1}{2}\boldsymbol{S} + \tfrac{3}{8}\boldsymbol{S}^{2} - \cdots. \tag{5}$$

From this expansion for $T^{-1/2}$ directly follows that one has one-to-one mapping between the elements of the column vectors $\boldsymbol{\Phi}$ and $\boldsymbol{\Psi}$, realized by the limite process: $\boldsymbol{\Psi} \rightarrow \boldsymbol{\Phi}$ if $\boldsymbol{S} \rightarrow \boldsymbol{0}$. Introducing (5) to (4) and using the property that $S_{ij}=0$ for $i,j \in \mathrm{A}$ or $i,j \in \mathrm{B}$, we obtain the following expansion formula for the components of the column vector $\boldsymbol{\Psi}$

$$|\psi_i\rangle = |\varphi_i\rangle - \tfrac{1}{2}\sum_{j\in \mathrm{B}} S_{ij}|\varphi_j\rangle + \tfrac{3}{8}\sum_{k\in \mathrm{B}}\sum_{l\in \mathrm{A}} S_{ik}S_{kl}|\varphi_l\rangle + \cdots \tag{6}$$

for $i \in \mathrm{A}$; and similarly for $i \in \mathrm{B}$, only $\mathrm{A} \leftrightarrow \mathrm{B}$ must be exchanged. The effective Hamiltonian $\hat{H}$ of the supersystem A + B is represented in the basis of functions (1a–b) by the matrix

$$\boldsymbol{H} = \boldsymbol{\Phi}\hat{H}\boldsymbol{\Phi}^{+} \tag{7}$$

with the matrix elements $H_{ij} = \langle\varphi_i|\hat{H}|\varphi_j\rangle$. It is assumed that

$$H_{ij} = \varepsilon_i \delta_{ij} \tag{8}$$

for $i,j \in \mathrm{A}$ and/or $i,j \in \mathrm{B}$, where ε_i are eigenvalues of effective Hamiltonian of the isolated system A or B.

Similarly, Hamiltonian $\hat{H}$ can be also represented in the orthonormal basis (4) by matrix

$$\bar{\boldsymbol{H}} = \boldsymbol{\Psi}\hat{H}\boldsymbol{\Psi}^{+} = \boldsymbol{T}^{-1/2}\boldsymbol{H}\boldsymbol{T}^{-1/2} \tag{9}$$

with the matrix elements $\bar{H}_{ij} = \langle\psi_i|\hat{H}|\psi_j\rangle$. Substituting (5) into (9) the following expansion is obtained

$$\bar{\boldsymbol{H}} = \sum_{n=0}^{\infty} \boldsymbol{H}^{(n)}, \tag{10a}$$

$$\boldsymbol{H}^{(0)} = \boldsymbol{H}, \tag{10b}$$

$$\boldsymbol{H}^{(1)} = -\tfrac{1}{2}(\boldsymbol{HS}+\boldsymbol{SH}), \tag{10c}$$

$$\boldsymbol{H}^{(2)} = \tfrac{3}{8}(\boldsymbol{HS}^2+\boldsymbol{S}^2\boldsymbol{H}+\tfrac{2}{3}\boldsymbol{SHS}), \tag{10d}$$

etc.

3. Second-Quantization Representation

Let us define the creation $\hat{X}_i^{+}$ and annihilation $\hat{X}_j$ operators for the orthonormal set of spinorbitals $\{|\psi_i\rangle\}$ introduced by (4) satisfying the obvious anticommutation relations [13–14]. Then $|\psi_i\rangle = \hat{X}_i^{+}|0\rangle$, where $|0\rangle$ is the normalized vacuum state vector. The many-body effective Hamiltonian in the second-quantization representation has the form

$$\hat{\mathscr{H}} = \sum_{i,j} \bar{H}_{ij}\hat{X}_i^{+}\hat{X}_j, \tag{11}$$

where the matrix elements $\bar{H}_{ij}$ are defined by (9) and summation runs over all elements of the set of orthonormal spinorbitals $\{|\psi_i\rangle\}$. Substituing (10a) into (11) and using (8) after simple algebraic manipulations the following expression is obtained:

$$\begin{aligned}\hat{\mathscr{H}} = & \sum_{i\in \mathrm{A}} \varepsilon_i \hat{X}_i^+ \hat{X}_i + \sum_{j\in \mathrm{B}} \varepsilon_j \hat{X}_j^+ \hat{X}_j + \sum_{i\in \mathrm{A}} \sum_{j\in \mathrm{B}} H_{ij}^{(0)} (\hat{X}_i^+ \hat{X}_j + \hat{X}_j^+ \hat{X}_i) \\ & + \sum_{n=1}^{\infty} \left\{ \sum_{i,j\in \mathrm{A}} H_{ij}^{(n)} \hat{X}_i^+ \hat{X}_j + \sum_{i,j\in \mathrm{B}} H_{ij}^{(n)} \hat{X}_i^+ \hat{X}_j \right. \\ & \left. \sum_{i\in \mathrm{A}} \sum_{j\in \mathrm{B}} H_{ij}^{(n)} (\hat{X}_i^+ \hat{X}_j + \hat{X}_j^+ \hat{X}_i) \right\} .\end{aligned} \tag{12}$$

In the following the state vector is defined as

$$|\Phi_0\rangle = \prod_{i\in \mathrm{A}} \hat{X}_i^+ \prod_{j\in \mathrm{B}} \hat{X}_j^+ |0\rangle , \tag{13}$$

which is taken in the next as a new vacuum state [14]. The first product in (13) runs over all occupied spinorbitals of the system A collected in the set A; similarly second product runs over all occupied spinorbitals of the systems B collected in the set B. Then, we may define [13, 14] N-product and contraction of the creation and annihilation operators, which are related to the state vector $|\Phi_0\rangle$.

$$\hat{X}_i^+ \hat{X}_j = N[\hat{X}_i^+ \hat{X}_j] + \overline{\hat{X}_i^+ \hat{X}_j} , \tag{14}$$

where $N[\ldots]$ is N-product, and contraction is

$$\overline{\hat{X}_i^+ \hat{X}_j} = \begin{cases} \delta_{ij} & \text{for } \ i,j\in \mathrm{A} \ \text{ or } \ i,j\in \mathrm{B} \\ 0 & \text{other cases} . \end{cases} \tag{15}$$

Using these concepts it is possible to express the Hamiltonian defined by (11) in the form

$$\hat{\mathscr{H}} = E_0 + \hat{\mathscr{H}}_0 + \hat{\mathscr{H}}_1 , \tag{16}$$

where the scalar quantity E_0 is defined as follows

$$E_0 = \sum_{n=0}^{\infty} E_0^{(n)} , \tag{17a}$$

$$E_0^{(0)} = \sum_{i\in \mathrm{A}} \varepsilon_i + \sum_{j\in \mathrm{B}} \varepsilon_j , \tag{17b}$$

$$E_0^{(n)} = \sum_{i\in \mathrm{A}} H_{ii}^{(n)} + \sum_{j\in \mathrm{B}} H_{jj}^{(n)} , \tag{17c}$$

where $E_0^{(0)}$ is interpreted as the sum of ground-state energies of the systems A and B. The unperturbed effective Hamiltonian $\hat{\mathscr{H}}_0$ has diagonal form

$$\hat{\mathscr{H}}_0 = \sum_{i\in \mathrm{A}} \varepsilon_i N[\hat{X}_i^+ \hat{X}_i] + \sum_{j\in \mathrm{B}} \varepsilon_j N[\hat{X}_j^+ \hat{X}_j] \tag{18}$$

and perturbation $\hat{\mathscr{H}}_1$

$$\begin{aligned}\hat{\mathscr{H}}_1 = & \sum_{i\in \mathrm{A}} \sum_{j\in \mathrm{B}} H_{ij}^{(0)} (N[\hat{X}_i^+ \hat{X}_j] + N[\hat{X}_j^+ \hat{X}_i]) \\ & + \sum_{n=1}^{\infty} \left\{ \sum_{i,j\in \mathrm{A}} H_{ij}^{(n)} N[\hat{X}_i^+ \hat{X}_j] + \sum_{i,j\in \mathrm{B}} H_{ij}^{(n)} N[\hat{X}_i^+ \hat{X}_j] \right. \\ & \left. + \sum_{i\in \mathrm{A}} \sum_{j\in \mathrm{B}} H_{ij}^{(n)} (N[\hat{X}_i^+ \hat{X}_j] + N[\hat{X}_j^+ \hat{X}_i]) \right\} .\end{aligned} \tag{19}$$

If we assume that distance between molecular systems increases to infinity, then the overlap matrix S and the matrix elements H_{ij} for $i \in \mathrm{A}$ and $j \in \mathrm{B}$ tend to zero, i.e. perturbation $\hat{\mathscr{H}}_1$ tends to zero for non-interacting molecular systems A and B. This means, that we divided the effective Hamiltonian $\hat{\mathscr{H}}$ into two parts. The first part $E_0^{(0)} + \hat{\mathscr{H}}_0$ describes the noninteracting molecular systems A and B. The second part $E_0 - E_0^{(0)} + \hat{\mathscr{H}}_1$ describes the interaction between systems.

4. Diagrammatic Perturbation Method

For the application of the diagrammatic technique in order to calculate the perturbed eigenvalues of the effective Hamiltonian $\hat{\mathscr{H}}$ it is necessary to introduce diagrammatic interpretation of the single terms in the expression (19) for the perturbation $\hat{\mathscr{H}}_1$. Collection of diagrammatic vertices for all terms in (19) is shown on Fig. 1. As usual in Hugenholtz's graphology [15] the particles (holes) are represented by directed lines which go from right (left) to left (right). The vertices are represented as a heavy dot or integer encircled with one outgoing and one incoming line. In order to distinguish between hole and/or particle lines from

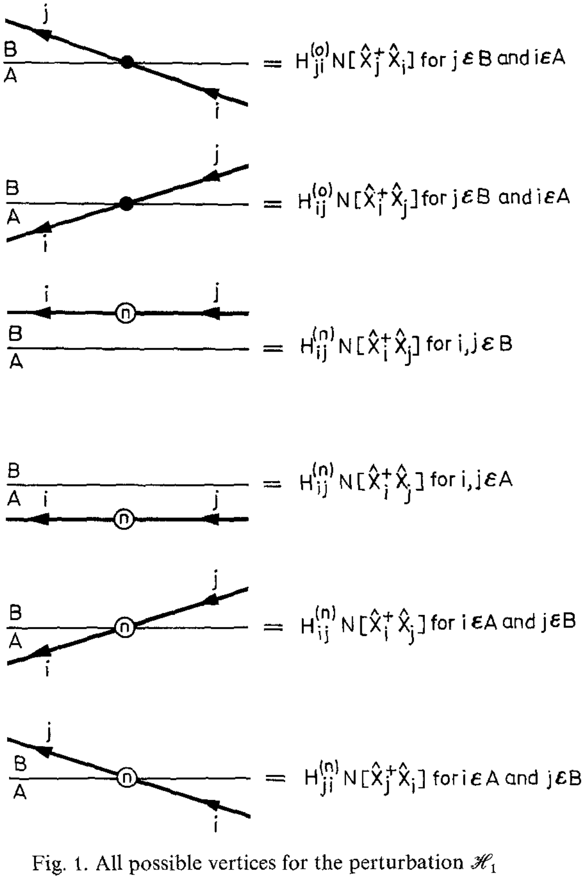

Fig. 1. All possible vertices for the perturbation $\mathscr{H}_1$

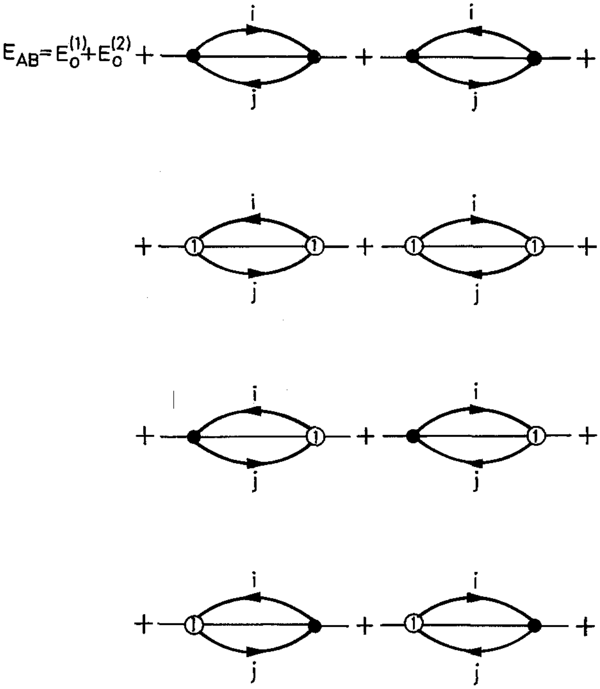

Fig. 2. Diagrammatic expression for the interaction energy up to the second order

the system A or B, the horizontal line is drawn, which is considered as a border [10]. Then, the upper (down) half-plane is reserved for the holes and/or particles from the system B(A).

We are now ready to use the well-known Goldstone-Hugenholtz [15, 17] linked-cluster theorem for the calculation of the perturbed (exact) ground-state energy E of interacting systems A and B.

$$E = E_0 + \langle \Phi_0 | \left\{ \hat{\mathscr{H}}_1 + \hat{\mathscr{H}}_1 \frac{1}{E_0^{(0)} - \hat{\mathscr{H}}_0} \hat{\mathscr{H}}_1 + \cdots \right\}_C | \Phi_0 \rangle , \tag{20}$$

where index C means that in the above expansion contribute only the terms which in the diagrammatic interpretation are denoted as the ground-state connected diagrams (in Hugenholtz's notation [15]). Substracting from the energy E defined by (20) the ground-state unperturbed energy $E_0^{(0)}$ the interaction energy between systems A and B treated in the framework of EHM is obtained, i.e.

$$E_{\mathrm{AB}} = E - E_0^{(0)} . \tag{21}$$

If we assume that the matrix elements H_{ij} and S_{ij} (for $i \in \mathrm{A}$ and $j \in \mathrm{B}$) are the first order quantities, then the interaction energy E_{AB} up to the second order is expressed on Fig. 2. After using standard rules of Hugenholtz's graphology [15] the following explicite expression for interaction energy up to the second order is obtained

$$
\begin{aligned}
E_{\mathrm{AB}} = {} & \sum_{j\in \mathrm{A}} (H_{jj}^{(1)} + H_{jj}^{(2)}, + \sum_{i\in \mathrm{B}} (H_{ii}^{(1)} + H_{ii}^{(2)}) \\
& + \sum_{i\in \overline{\mathrm{B}}} \sum_{j\in \mathrm{A}} \frac{(H_{ij}^{(0)} + H_{ij}^{(1)})^2}{\varepsilon_j - \varepsilon_i} \\
& + \sum_{i\in \mathrm{B}} \sum_{j\in \overline{\mathrm{A}}} \frac{(H_{ij}^{(0)} + H_{ij}^{(1)})^2}{\varepsilon_i - \varepsilon_j},
\end{aligned}
\tag{22}
$$

where in the third (fourth) term the summation with $i \in \overline{\mathrm{B}}$ ($j \in \overline{\mathrm{A}}$) runs over all unoccupied molecular spinorbitals from B (A). Introducing (10b–c) into (22) and after simple algebraic manipulations the final expression for the interaction energy is obtained

$$
\begin{aligned}
E_{\mathrm{AB}} = {} & -\sum_{j\in \mathrm{A}} \sum_{i\in \mathrm{B}} S_{ij}[2H_{ij} - S_{ij}(\varepsilon_i + \varepsilon_j)] \\
& - \sum_{i\in \mathrm{B}} \sum_{j\in \overline{\mathrm{A}}} \frac{(H_{ij} - \varepsilon_i S_{ij})^2}{\varepsilon_j - \varepsilon_i} \\
& - \sum_{i\in \overline{\mathrm{B}}} \sum_{j\in \mathrm{A}} \frac{(H_{ij} - \varepsilon_j S_{ij})^2}{\varepsilon_i - \varepsilon_j}.
\end{aligned}
\tag{23}
$$

This result is identical with the Imamura expression [7]. As follows from our derivation, the interaction energy (23) is applicable not only to the different molecular systems but also for the identical ones. Further contribution to the interaction energy can easily be obtained by inclusion the next terms in and corresponding diagrams of the particular type. It seems that using this procedure the diagrammatic technique can be useful for the interpretation of the individual contributions to the interaction energy calculated in the framework of EHM.

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