

# A Complete Diagrammatic Construction of PCILO Method

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In the present short communication, the diagrammatic many-body perturbation theory for the rederivation of PCILO method (perturbation configuration interaction using localized orbitals, see Theoret. Chim. Acta (Berl.) 13, 1 (1969) and 15, 100 (1969)) is consequently used. Using the Goldstone-Hugenholtz linked-cluster theorem, the diagrammatic expression for the exact ground-state energy is obtained. An application of the present approach to the low-lying excited and/or ionized states is also discussed.

*Key words:* PCILO method – Diagrammatic perturbation theory – Localized orbitals

## 1. Introduction

The PCILO method [1–3] (perturbation configuration interaction using localized orbitals) can serve as a very effective approach for the calculation of the ground-state energy (and others ground-state characteristics) of the closed-shell molecular systems. Recently, this method has been generalized for the treating of the low-lying excited [4–5] as well as the ionized states [6]. Thus, the PCILO method covers a wide variety of theoretical problems of the ground state and excited states of molecular systems (namely small saturated organic molecules). The original derivation of the PCILO method is performed using the clumsy technique of the Slater determinants, where the Goldstone graphology [7, 8] has been merely used in an illustrative way. It seems that a correct establishment of any diagrammatic perturbation theory should be completely based on the second-quantization formalism, i.e. a Hamiltonian of a given molecular system is expressed in terms of the creation and annihilation operators. This assumption is not properly satisfied in the original construction of the PCILO method [1–5], where the Epstein-Nesbet [12] form of the perturbation theory is used. On the first sight, one may assume, that this approach of the construction of the diagrammatic perturbation theory is very effective and fruitful. But nevertheless, if it is used as a starting point for the construction of the diagrammatic perturbation theory, then it contains many unresolved theoretical pitfalls. For example, the linked-cluster theorem for the energy is not proved. The purpose of the present short communication is to use consequently the well-established “powerful machinery” of the diagrammatic perturbation theory for the correct rederivation of the PCILO method.

## 2. Theory

Let us study a closed-shell molecular system for which a set of the strictly localized molecular spinorbitals (SLMSO) is known

$$\{|\varphi_{i\alpha}\rangle\}, \quad (1)$$

where the index  $i$  runs over all bonds (and lone pairs), and  $\alpha$  describes whether the given SLMSO is bonding ( $\alpha=0$ ) or antibonding ( $\alpha=1$ ). In accordance with Ref. [3] we accept their form of ZDO approximation

$$\langle\varphi_{i\alpha}|\varphi_{j\beta}\rangle = \delta_{ij}\delta_{\alpha\beta}, \quad (2a)$$

$$\langle\varphi_{i\alpha}\varphi_{j\beta}|g|\varphi_{k\alpha'}\varphi_{l\beta'}\rangle = \delta_{ik}\delta_{jl}\langle\varphi_{i\alpha}\varphi_{j\beta}|g|\varphi_{i\alpha'}\varphi_{j\beta'}\rangle, \quad (2b)$$

i.e. the set (1) is an orthonormal one, and condition (2b) reduces the total number of explicitly treated two-particle matrix elements. In the second quantization formalism [8, 9], a Hamiltonian of the given molecular system than can be written as

$$H = \sum_{ij} \sum_{\alpha\beta} \langle\varphi_{i\alpha}|h|\varphi_{j\beta}\rangle X_{i\alpha}^+ X_{j\beta} \\ + (1/2) \sum_{ij} \sum_{\substack{\alpha\beta \\ \alpha'\beta'}} \langle\varphi_{i\alpha}\varphi_{j\beta}|g|\varphi_{i\alpha'}\varphi_{j\beta'}\rangle X_{i\alpha}^+ X_{j\beta}^+ X_{j\beta'} X_{i\alpha'}, \quad (3)$$

$X_{i\alpha}^+$  and  $X_{j\beta}$  being the creation and annihilation operators, respectively, defined on the orthonormal [cf. Eq. (2a)] set (1).

For the next considerations it is appropriate to introduce an unperturbed ground-state vector

$$|\Phi_0\rangle = \prod_i X_{i0}^+ |0\rangle, \quad (4)$$

where  $|0\rangle$  is the normalized state vector of vacuum, and product index  $i$  runs over all the "bonding" (occupied) SLMSO's.

Then, the one-particle states contained in  $|\Phi_0\rangle$  are called hole states, and antibonding SLMSO's as particle states. Using ZDO approximation (2a–b), the zero-order energy can be expressed in the form

$$\langle\Phi_0|H|\Phi_0\rangle = \sum_i \langle\varphi_{i0}|h|\varphi_{i0}\rangle + (1/2) \sum_{ij} \langle\varphi_{i0}\varphi_{j0}|g|\varphi_{i0}\varphi_{j0}\rangle \\ - (1/2) \sum_i \langle\varphi_{i0}\varphi_{i0}|g|\varphi_{i0}\varphi_{i0}\rangle. \quad (5)$$

Application of the Wick theorem [8–10] on the Hamiltonian (3) gives after simple algebraic manipulations

$$H = \langle\Phi_0|H|\Phi_0\rangle + \mathcal{H}_0 + \mathcal{H}_1. \quad (6)$$

The operator  $\mathcal{H}_0$  is determined by

$$\mathcal{H}_0 = \sum_i \sum_{\alpha\alpha'} \langle\varphi_{i\alpha}|f|\varphi_{i\alpha'}\rangle N[X_{i\alpha}^+ X_{i\alpha'}], \quad (7)$$

$N[\dots]$  being the normal product of the creation and annihilation operators [9, 10] defined with respect to  $|\Phi_0\rangle$ , and the matrix elements  $\langle\varphi_{i\alpha}|f|\varphi_{i\alpha'}\rangle$  are determined as follows

$$\begin{aligned} \langle\varphi_{i\alpha}|f|\varphi_{i\alpha'}\rangle &= \langle\varphi_{i\alpha}|h|\varphi_{i\alpha'}\rangle + \sum_j \langle\varphi_{i\alpha}\varphi_{j0}|g|\varphi_{i\alpha'}\varphi_{j0}\rangle \\ &\quad - \langle\varphi_{i\alpha}\varphi_{i0}|g|\varphi_{i0}\varphi_{i\alpha'}\rangle. \end{aligned} \tag{8}$$

We assume that the elements of (1) satisfy the condition

$$\langle\varphi_{i\alpha}|f|\varphi_{i\alpha'}\rangle = \varepsilon_{i\alpha}\delta_{\alpha\alpha'}. \tag{9}$$

Then, the operator  $\mathcal{H}_0$  (called unperturbed Hamiltonian) has a diagonal form

$$\mathcal{H}_0 = \sum_i \sum_\alpha \varepsilon_{i\alpha} N[X_{i\alpha}^+ X_{i\alpha}]. \tag{10}$$

Using the one-particle energies  $\varepsilon_{i\alpha}$ , the energy (5) can be rewritten (cf. similar expression in Hartree-Fock theory) in the form

$$\langle\Phi_0|H|\Phi_0\rangle = \sum_i (\varepsilon_{i0} + \langle\varphi_{i0}|h|\varphi_{i0}\rangle). \tag{11}$$

The operator  $\mathcal{H}_1$  (called perturbation) from the r.h.s. of Eq. (6) is defined by

$$\begin{aligned} \mathcal{H}_1 &= \sum_{ij} \sum_{\alpha\alpha'} (1 - \delta_{ij}) \langle\varphi_{i\alpha}|h|\varphi_{j\alpha'}\rangle N[X_{i\alpha}^+ X_{j\alpha'}] \\ &\quad + (1/2) \sum_{ij} \sum_{\alpha\beta} \sum_{\alpha'\beta'} \langle\varphi_{i\alpha}\varphi_{j\beta}|g|\varphi_{i\alpha'}\varphi_{j\beta'}\rangle N[X_{i\alpha}^+ X_{j\beta}^+ X_{j\beta'} X_{i\alpha'}]. \end{aligned} \tag{12}$$

The perturbation contains one-particle (first summation) as well as two-particle (second summation) terms, the diagrammatic interpretation of which is presented in Fig. 1. From the property of the normal product,  $\langle\Phi_0|N[\dots]|\Phi_0\rangle = 0$ , follows that matrix element of  $\mathcal{H}_1$  between two  $|\Phi_0\rangle$  is zero, i.e.  $\langle\Phi_0|\mathcal{H}_1|\Phi_0\rangle = 0$ .

In the following, let us turn our attention to the application of the diagrammatic perturbation theory [8] on the problem of calculation of the exact ground-state energy of molecular systems described by the Hamiltonian (6). Using the Goldstone-Hugenholtz linked-cluster theorem [7, 11], the diagrammatic expres-

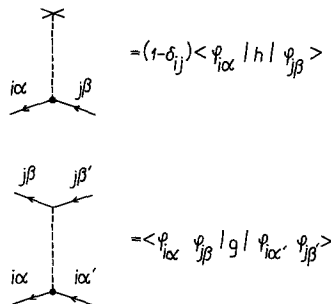


Fig. 1. The diagrammatic interpretation of the individual terms of the perturbation  $\mathcal{H}_1$  defined by (12)

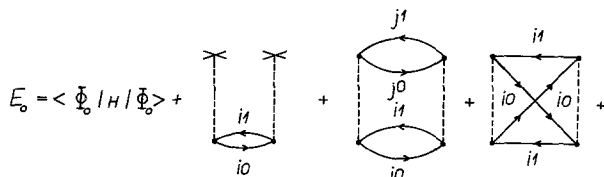


Fig. 2. The diagrammatic expression up to the second order for the exact ground-state energy  $E_0$

sion for the exact ground-state energy is obtained (principal result of this communication)

$$E_0 = \langle \Phi_0 | H | \Phi_0 \rangle + \sum_{n=1}^{\infty} \langle \Phi_0 | \left\{ \mathcal{H}_1 \left( \frac{1}{-\mathcal{H}_0} \mathcal{H}_1 \right)^n \right\}_C | \Phi_0 \rangle, \quad (13)$$

where the subscript  $C$  means that only connected diagrams contribute. The diagrammatic expression up to the second order for the exact energy calculated by the use of Goldstone's graphology [7, 8] is presented in Fig. 2. Using the simple diagrammatic rules [7, 8, 10] we obtain from Fig. 2 the following expression

$$\begin{aligned} E_0 = & \langle \Phi_0 | H | \Phi_0 \rangle + \sum_{i \neq j} \frac{|\langle \varphi_{j0} | h | \varphi_{i1} \rangle|^2}{\epsilon_{j0} - \epsilon_{i1}} \\ & + (1/2) \sum_{ij} \frac{|\langle \varphi_{i0} \varphi_{j0} | g | \varphi_{i1} \varphi_{j1} \rangle|^2}{\epsilon_{i0} + \epsilon_{j0} - \epsilon_{i1} - \epsilon_{j1}} \\ & - (1/2) \sum_i \frac{|\langle \varphi_{i0} \varphi_{i0} | g | \varphi_{i1} \varphi_{i1} \rangle|^2}{2\epsilon_{i0} - 2\epsilon_{i1}}, \end{aligned} \quad (14)$$

where the summation indices run over all bonds. The higher order contributions can be obtained by straightforward procedure by the inclusion of the diagrams with more than two vertices.

### 3. Discussion

To open this discussion we stress that the present final expression for the exact ground-state energy [13, 14] is different from the one obtained in the original formulation of the PCILO method [1–3]. Namely, 1) the basis of the one-particle functions (1) is defined through the two-dimensional self-consistent conditions (9), and 2) our denominators are built from the “effective” one-particle energies  $\epsilon_{i\alpha}$  in contrast to Ref. [3], where the diagonal matrix elements  $E_I = \langle \Phi_I | H | \Phi_I \rangle$  appear. This second discrepancy is originating from the fact that we have consequently used the diagrammatic perturbation theory fully based on the second-quantization formalism. Then, the lower-order original contributions to the exact ground-state energy may be obtained in our approach by the infinite summation of some pertinent diagrams. For the higher-order contributions this summation procedure is applicable only for carefully selected types of the diagrams due to the effect of the overcounting of some diagrams. Therefore, a simple one-to-one correspondence between the original formulation of the PCILO method and the present correct approach does not exist.

The first order reduced density matrix can be calculated in the framework of the present diagrammatic method using the Thouless linked-cluster theorem [8] for the calculation of the exact ground-state mean value of the one-particle observable.

The present approach might be of value also for the calculation of the low-lying excited [4, 5] as well as the single ionized [6] states in the framework of PCILO method. These states may be calculated using the diagrammatic degenerate Rayleigh-Schrödinger perturbation theory [13, 14]. For example, the excitation energy  $\Delta E_{i \rightarrow j}$ , corresponding to the single excitation of an electron from the occupied orbital  $|\varphi_{i0}\rangle$  into virtual  $|\varphi_{j1}\rangle$  is equal to

$$\Delta E_{i \rightarrow j} = \varepsilon_{j1} - \varepsilon_{i0} + \langle \Phi_{i \rightarrow j} | G | \Phi_{i \rightarrow j} \rangle, \quad (15)$$

where  $|\Phi_{i \rightarrow j}\rangle = X_{j1}^+ X_{i0} |\Phi_0\rangle$  is the particle-hole unperturbed state vector, and  $G$  is an effective interaction operator [13] with the diagrammatic interpretation. Furthermore, it is also possible to calculate the first-order density matrices of the corresponding excited states by the generalized Thouless theorem [14]. Thus, we have obtained all necessary informations characterizing the excited state of the given closed-shell molecular system. The same approach may be also applied for treating the ionized states.

To conclude, we point out our belief that present systematic diagrammatic theory of PCILO method may serve as an useful background for better understanding and more detailed study of this method, and moreover, it also gives us the possibility to extend it to the study of more complex problems.

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