

THIRD-ORDER ENERGY USING CNDO/2 AND INDO HAMILTONIAN APPROXIMATIONS IN THE MODIFIED PCILO METHOD

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The perturbative configuration interaction using strictly localized molecular orbitals, called the modified PCILO method, has been applied in this communication for the calculations of the energy terms of 15 small molecules up to the third order of the perturbation theory. For this method the use of the Rayleigh-Schrödinger many-body perturbation theory with the Moller-Plesset type of the Hamiltonian partitioning is characteristic. On the CNDO/2 and INDO level of approximations the strictly localized molecular orbitals have been constructed by solving the modified 2×2 Roothaan's equations. From the zeroth order ground-state wave function the charge distributions, dipole moments and carbon 13- proton nuclear spin-spin coupling constants have been calculated. Results show that the chemical formula, represented with the zeroth order of the perturbation theory, is a good order of the approximation for the study of the molecule. For diatomic molecules the equilibrium interatomic distances and harmonic force constants have been calculated up to the third order of the perturbation theory. The second order of the perturbation theory provides results which are very near to the MO-LCAO-SCF calculations. The main advantage of the PCILO method lies in much saving of the computing time.

The PCILO method (Perturbative Configuration Interaction using Localized Orbitals) is based on the concept that corresponds to the looking at the molecule as it would be built up from "two-centers, two-electron fragments" (localized chemical bonds) in the mutual interaction. This interaction is treated by the perturbation theory (PT). The use of PT is a very effective and powerful way to transform a rather poor basis of localized orbitals to the good molecular wave function including the electron delocalization and correlation.

The PCILO method was developed on two different approaches. The principal difference between them lies, of course, in the application of the perturbation theory. The original PCILO method was formulated by Malrieu and coworkers¹⁻⁴; they preferred the use of the Epstein-Nesbet (EN) type^{5,6} of the partition in the Hamiltonian partitioning scheme. The modified PCILO method⁷⁻⁹, in an accord with ref.¹⁰, exploits the Moller-Plesset (MP) type¹¹ of the Hamiltonian partitioning and it is strictly derived from the diagrammatic Rayleigh-Schrödinger many-body perturbation theory (MBPT) in contrast to the original PCILO, where the diagrammatic representation of individual energy terms has only the illustrative meaning.

The choice of the type of the Hamiltonian partitioning is a crucial point that has to be described in more details. It is well known that from the four most investigated many-body perturbation techniques: Rayleigh-Schrödinger with the Moller-Plesset (RS-MP) or Epstein-Nesbet (RS-EN)

partitioning and Brillouin-Wigner with the Moller-Plesset (BW-MP) or Epstein-Nesbet (BW-EN) partitioning, only the simplest RS-MP procedure is invariant with respect to the mixing of degenerate orbitals. The RS-MP procedure also provides the correct (linear) dependence of the correlation energy on the number of particles. Therefore, it is preferred as a general unambiguous perturbation technique¹². According to Claverie and coworkers^{13,14} the RS-EN procedure causes some lower energy with respect to the RS-MP procedure for the series of polyenes. These authors have preferred the RS-EN procedure. However, Bartlett and Shavitt¹⁵ on *ab initio* MBPT calculations have shown that the MP series converges faster than EN series in higher orders, unlike to the expectations of ref.^{13,14}. Further, Ostlund and Bowen¹² have shown that the RS-EN procedure offers also incorrect potential curves in 2nd order of PT. Finally, the RS-EN, BW-MP and BW-EN procedures all include the higher-order terms or diagrams in the given order of PT and they are not directly applicable in the framework of the second-quantization formalism. However, the modified partitioning procedures with a "denominator shift" approach were proposed¹⁵⁻¹⁹; they can be useful on the second-quantization formulations of the many-body perturbation theories but applications of these methods should be still studied.

The essential features of the PCILO method in its original and modified version are exactly the same: the construction of a likely fully localized zeroth order determinant, and of a basis of orthogonal excited determinants from an a priori set of fully localized bond MO's, perturbative obtention of the ground-state wave function and energy from the CI matrix or MBPT. To the significant improvements in the modified PCILO method belong⁷: (i) the introduction of the INDO Hamiltonian approximation into the PCILO method; (ii) the extension of the method on open shell systems (in UHF approach); (iii) the extension of the applicability of the method on compounds which consists from H to Br atoms including transition metals. The use of EMOA hybrid atomic orbitals instead of Del Re's ones and the solution of 2×2 Roothaan's equations instead of the bond-polarity parameter's optimization are minor modifications used here. It may be mentioned that also the original PCILO method was recently extended on the INDO Hamiltonian approximation²⁰. However, due to the different choice of the Hamiltonian partitioning in the perturbation technique the one-to-one correspondence between the original and modified PCILO methods does not exist.

In this paper the modified PCILO method is formulated up to the 3rd order of PT for the energy. Method is tested on the ground of two groups of criteria: (i) the zeroth order wave function is tested in terms of charge distribution, dipole moments, carbon 13- proton coupling constants and the "localization defect" (that represents, the deviation in the energy with respect to the SCF energy); (ii) the convergence of the used perturbation theory is examined in terms of the energy, equilibrium interatomic distances, harmonic force constants and curves of the adiabatic potential up to the 3rd order of PT. Results are compared, as possible, with those obtained by MO-LCAO-SCF and original PCILO methods.

Strictly Localized Molecular Orbitals

It is well known that in the Hartree-Fock equations for molecular orbitals (MO) the off-diagonal part of the Lagrangian multiplier's matrix must be fixed by additional conditions²¹. The most common canonical fixation in the MO-LCAO-SCF method corresponds to the choice of MOs which are rather delocalized throughout the mole-

cular skeleton. Another well-known fixations which well preserve the ground-state electronic energy, E_0^{SCF} , correspond to the choice of intrinsically localized MOs, according to Ruedenberg's²¹, Boys'²² or von Niessen's²³ localization criteria. However, these orbitals are not localized strictly; they have the non-zero components from more than two atoms, in general. Maintaining strictly localized (two-center) molecular orbitals corresponds to the introduction of some additional approximation into Hartree-Fock equations. These externally localized MOs produce the ground-state electronic energy, E_0 , which is to some extent higher than the energy E_0^{SCF} . As the strictly localized molecular orbitals (SLMO) are chosen with respect to the chemical formula of a molecule, the corresponding ground-state wave function, $|\Phi_0\rangle$, (the single Slater determinant) is a good order of approximation for the study of the molecule. Classical theoretical chemistry and the studies on the localization of the self-consistent-field orbitals provide a large justification for this approach²⁴.

A pair of SLMOs associated with i -th chemical bond: one bonding SLMO, $|i\rangle$, and one antibonding SLMO, $|i^*\rangle$, let be expressed in the form of a linear combination of a pair of hybrid atomic orbitals (HAO):

$$|i\rangle = b_{i\mu}|\mu\rangle + b_{i\nu}|\nu\rangle \quad (1)$$

$$|i^*\rangle = b_{i\mu}^*|\mu\rangle + b_{i\nu}^*|\nu\rangle. \quad (2)$$

The basis of HAOs, $\{\Psi_\mu^A\}$, is built up from atomic orbitals, $\{\chi_r^A\}$:

$$|\mu\rangle = \Psi_\mu^A = \sum_r^A a_{\mu,r}^A \chi_r^A, \quad (3)$$

where the hybridization coefficients, $a_{\mu,r}^A$, on all A-th centres in a polyatomic molecule by EMOA method^{25,26} can be obtained. To describe any bonding situation with respect to the chemical formula of the molecule, it is suitable to introduce a discrete topological function, $f(A, \mu)$ on the sets of atomic indices, A, and indices of HAOs on A-th centre, μ ; the value of the topological function is equal to the ordering number of i -th chemical bond: $f(A, \mu) = i$ (Fig. 1). This function enables

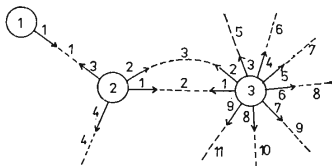


FIG. 1

The Numbering System for the Definition of the Topological Function $f(A, \mu)$ in a Molecule

○ Atom, → HAO, ----- bond.

the convenient selection of a pair of HAOs, $\Psi_\mu^A = |\mu\rangle$ and $\Psi_\nu^B = |\nu\rangle$, which are combined into a pair of SLMOs on i -th bond, on the condition: $f(A, \mu) = i = f(B, \nu)$. The lone lobes (non-bonding HAOs) are regarded as non-connected bonds for which the bonding partners do not exist.

In Appendix A, the modified 2×2 Roothaan's equations for expanding coefficients, $b_{i\mu}$, have been derived:

$$\begin{pmatrix} {}^\alpha F_{\mu\mu}^{AA} - \varepsilon_i^\alpha; & {}^\alpha F_{\mu\nu}^{AB} - \varepsilon_i^\alpha {}^\alpha S_{\mu\nu} \\ {}^\alpha F_{\nu\mu}^{BA} - \varepsilon_i^\alpha {}^\alpha S_{\mu\nu}; & {}^\alpha F_{\nu\nu}^{BB} - \varepsilon_i^\alpha \end{pmatrix} \begin{pmatrix} b_{i\mu}^\alpha \\ b_{i\nu}^\alpha \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \quad (4)$$

which are fulfilled for all i -th bonds: $i = (1 - \delta_{A,B}) \delta_{f(A,\mu),f(B,\nu)}$ and they have the simple explicit solutions. These equations fully correspond to a local Brillouin's theorem which states:

$$\langle i | \mathbf{F} | i^* \rangle = 0. * \quad (5)$$

In Eq. (4),

$$\begin{aligned} {}^\alpha F_{\mu\nu}^{AB} = & \langle \mu_A | \mathbf{h} | \nu_B \rangle + \sum_{C,D} \sum_{\lambda} \sum_{\sigma} [({}^\alpha P_{\lambda\sigma}^{CD} + {}^\beta P_{\lambda\sigma}^{CD}) (\mu_A \nu_B | \lambda_C \sigma_D) - \\ & - {}^\alpha P_{\lambda\sigma}^{CD} (\mu_A \sigma_D | \lambda_C \nu_B)] \delta_{f(C,\lambda),f(D,\sigma)} \delta_{f(A,\mu),f(B,\nu)} \end{aligned} \quad (6)$$

is the matrix element of the one-electron effective Fock operator, \mathbf{F} , in the basis of HAOs; the symbol α designates α - or β - set of SLMOs in the unrestricted open shell approach. The charge-density (bond-order) matrix elements ${}^\alpha P_{\mu\nu}^{AB}$ are defined as

$${}^\alpha P_{\mu\nu}^{AB} = (w_i^\alpha b_{i\mu}^\alpha b_{i\nu}^\alpha + w_i^{*\alpha} b_{i\mu}^{*\alpha} b_{i\nu}^{*\alpha}) \delta_{f(A,\mu),f(B,\nu)}, \quad (7)$$

where w_i is the occupation number of i -th bonding ($w_i^{*\alpha}$ for antibonding) strictly localized molecular spinorbital with α - or β -electron.

For the next consideration we introduce the ZDO approximation on the basis of AOs. In effect of this approximation, the overlap integrals of HAOs, $S_{\mu\nu}$, in Eq. (4) are neglected. Further, the non-zero two-electron integrals in the HAO's basis are:

* The used convention for the integrals is:

$$\langle i | \mathbf{h} | j \rangle = \int \varphi_i^*(1) \mathbf{h}(1) \varphi_j(1) d\tau_1$$

$$\langle ij | kl \rangle = \langle ik | jl \rangle = \iint \varphi_i^*(1) \varphi_k^*(2) 1/r_{12} \varphi_j(1) \varphi_l(2) d\tau_1 d\tau_2$$

$$\langle ij || kl \rangle_A = \langle ij | kl \rangle - \langle ij | lk \rangle$$

$$\langle ij || kl \rangle_C = 2\langle ij | kl \rangle - \langle ij | lk \rangle$$

(i) the bicentric integrals

$$(\mu_A \lambda_A | v_B \sigma_B) = \sum_r^A a_{\mu,r}^A a_{\lambda,r}^A \sum_s^B a_{v,s}^B a_{\sigma,s}^B (r_A r_A | s_B s_B) \quad (8)$$

(ii) the monocentric integrals

$$(\mu_A \lambda_A | v_A \sigma_A) = \sum_{r,s,t,u}^A a_{\mu,r}^A a_{\lambda,t}^A a_{v,s}^A a_{\sigma,u}^A (rt | su) \quad (9)$$

(in CNDO approach $r = t$ and $s = u$). Thus, the matrix elements of the Fock operator in HAO's basis are simplified as:

$$\begin{aligned} {}^*F_{\mu\mu}^{AA} &= \langle \mu_A | \mathbf{h} | \mu_A \rangle - \sum_v^A {}^*F_{vv}^{AA} (\mu_A v_A | v_A \mu_A) + \\ &+ \sum_B^B \sum_v^B ({}^\alpha P_{vv}^{BB} + {}^\beta P_{vv}^{BB}) (\mu_A \mu_A | v_B v_B) \end{aligned} \quad (10)$$

$$\begin{aligned} {}^*F_{\mu\nu}^{AB} &= \{ \langle \mu_A | \mathbf{h} | \nu_B \rangle - \sum_{\lambda}^A \sum_{\sigma}^B {}^*P_{\lambda\sigma}^{AB} (\mu_A \lambda_A | v_B \sigma_B) \delta_{f(A,\lambda),f(B,\sigma)} \} \times \\ &\times (1 - \delta_{A,B}) \delta_{f(A,\mu),f(B,\nu)}. \end{aligned} \quad (11)$$

CNDO/2 Hamiltonian Approximation

The well-known CNDO/2 parametrization scheme on the basis of AOs can be applied. Two different cases: the $s-p$ or $s-p-d$ and the $d-s-p$ valence basis must be distinguished.

(i) $s-p$ or $s-p-d$ valence basis: The matrix elements $\langle r_A | \mathbf{h} | s_B \rangle$ using the standard Pople's approach²⁷ may be evaluated; for the elements Na—Cl the parametrization according to Santry and Segal²⁸ is convenient and for the elements Ge—Br the parameters derived by Hase and Schweig²⁹ can be used. As the two-electron integrals $(r_A r_A | s_B s_B)$ with the mean value γ_{AB} are approximated, due to the orthogonality condition for HAOs, the two-electron integrals do not depend on the hybridization:

$$(\mu_A \lambda_A | v_B \sigma_B) = \gamma_{AB} \delta_{\mu\lambda} \delta_{v\sigma}. \quad (12)$$

Thus, the large simplifications of the formulae (10) and (11) are allowed:

$${}^*F_{\mu\mu}^{AA} = \langle \mu_A | \mathbf{h} | \mu_A \rangle + \sum_B^B \gamma_{AB} \sum_v^B ({}^\alpha P_{vv}^{BB} + {}^\beta P_{vv}^{BB}) - \gamma_{AA} {}^*P_{\mu\mu}^{AA} \quad (13)$$

$${}^*F_{\mu\nu}^{AB} = \{ \langle \mu_A | \mathbf{h} | \nu_B \rangle - \gamma_{AB} {}^*P_{\mu\nu}^{AB} \} (1 - \delta_{A,B}) \delta_{f(A,\mu),f(B,\nu)}, \quad (14)$$

where

$$\langle \mu_A | \mathbf{h} | \nu_B \rangle = \sum_r \sum_s^A \sum_t^B a_{\mu,r}^A a_{\nu,s}^B \langle r_A | \mathbf{h} | s_B \rangle. \quad (15)$$

The large simplification also for two-electron integrals in SLMO's basis is obtained; the non-zero charge distributions are only $|ii\rangle$, $|ii^*\rangle$ and $|i^*i^*\rangle$, e.g. the non-zero integrals are of the type:

$$\left\langle \left\{ \begin{matrix} i \\ i^* \end{matrix} \right\} \left\{ \begin{matrix} j \\ j^* \end{matrix} \right\} \middle| \left\{ \begin{matrix} i \\ i^* \end{matrix} \right\} \left\{ \begin{matrix} j \\ j^* \end{matrix} \right\} \right\rangle.$$

Further, an integral in SLMO basis is composed of from 4 (or less than 4) terms expressed in the basis of AOs. For the orbital energies there are valid:

$$\begin{aligned} \varepsilon_i^x &= \langle i_x | \mathbf{F} | i_x \rangle = \langle i_x | \mathbf{h} | i_x \rangle - (i_x i_x | i_x i_x) - \\ &- (i_x i_x^* | i_x^* i_x)_{i_x^* \in \text{occ}} + \sum_{\eta}^{\alpha, \beta} \sum_{k_{\eta}}^{\text{occ}_{\eta}} (i_x i_x | k_{\eta} k_{\eta}) \end{aligned} \quad (16)$$

$$\begin{aligned} \varepsilon_i^{x*} &= \langle i_x^* | \mathbf{F} | i_x^* \rangle = \langle i_x^* | \mathbf{h} | i_x^* \rangle - (i_x^* i_x^* | i_x^* i_x^*) - \\ &- (i_x^* i_x^* | i_x^* i_x^*)_{i_x^* \in \text{occ}} + \sum_{\eta}^{\alpha, \beta} \sum_{k_{\eta}}^{\text{occ}_{\eta}} (i_x^* i_x^* | k_{\eta} k_{\eta}), \end{aligned} \quad (17)$$

where the symbol occ_{η} means the occupied molecular orbitals for electrons with η -spin.

(ii) *d-s-p valence basis*: The parametrization according to Clack, Hush and Yandle³⁰ is convenient in this case for transition metals Sc—Cu. As the two-electron integrals depend on the principal quantum number of the AOs considered, the integrals: $\gamma_{AB}(S, S)$, $\gamma_{AB}(S, D)$, $\gamma_{AB}(D, S)$ and $\gamma_{AB}(D, D)$ must be considered. Thus the transformations (8), (9) and the formulae (10), (11) must be used.

INDO Hamiltonian Approximation

The standard Pople's approach^{31,32} for *s-p* basis of AOs is convenient in this case. The formula (10) is simplified as

$$\begin{aligned} {}^x F_{\mu\mu}^{AA} &= \langle \mu_A | \mathbf{h} | \mu_A \rangle + \sum_{B \neq A} \gamma_{AB} \sum_{\nu}^B ({}^{\alpha} P_{\nu\nu}^{BB} + {}^{\beta} P_{\nu\nu}^{BB}) + \\ &+ \sum_{\nu}^A [({}^{\alpha} P_{\nu\nu}^{AA} + {}^{\beta} P_{\nu\nu}^{AA}) (\mu_A \mu_A | \nu_A \nu_A) - {}^x P_{\nu\nu}^{AA} (\mu_A \nu_A | \nu_A \mu_A)] \end{aligned} \quad (18)$$

and for the off-diagonal elements of the Fock operator the formula (14) is useful. In the *d-s-p* basis for elements Sc—Cu the parametrization according to Clack³³

can be used; the transformations (8), (9) and the formulae (10), (11) must be used in this case. Notice, that in the original Clack's approach only the number of 235 monocentric two-electron integrals of the type $(rr | ss)$ and $(rs | rs)$ is considered, since the total number of non-zero monocentric integrals on each atom is 735^{34} . For example, the integrals $(p_x d_{yz} | p_x d_{yz})$ and $(p_x d_{yz} | p_y d_{xz})$ are equal in their values, but in the original Clack's approach the second one is neglected. However, the consideration with all monocentric two-electron integrals in $d-s-p$ basis is not a large problem; the semiempirical parametrization scheme for all of these integrals is described in³⁵.

APPLICATION OF THE MANY-BODY PERTURBATION THEORY

In the Rayleigh-Schrödinger many-body perturbation theory^{36,37} the electronic Hamiltonian H is splitted into unperturbed Hamiltonian H_0 and the perturbation H_1 . If the Moller-Plesset type of the Hamiltonian partitioning is applied¹¹, they take the form:

$$H_0 = \langle \Phi_0 | H | \Phi_0 \rangle + \sum_i \varepsilon_i N[\mathbf{X}_i^+ \mathbf{X}_i] \quad (19)$$

$$H_1 = \sum_{i,j} (1 - \delta_{ij}) \langle i | F | j \rangle N[\mathbf{X}_i^+ \mathbf{X}_j] + \\ + \frac{1}{4} \sum_{i,j,k,l} \langle ij || kl \rangle_A N[\mathbf{X}_i^+ \mathbf{X}_j^+ \mathbf{X}_l \mathbf{X}_k] \quad (20)$$

Here,

$$\langle i | F | j \rangle = \langle i | h | j \rangle + \sum_k^{occ} \langle ik || jk \rangle_A \quad (21)$$

is the matrix element of the one-electron effective Fock operator in the basis of molecular spinorbitals;

$$\varepsilon_i = \langle i | F | i \rangle \quad (22)$$

is the one-electron orbital energy; the symbol *occ* means the occupied spinorbitals included in the unperturbed ground-state eigenvector $|\Phi_0\rangle$, (*vir* means the unoccupied, virtual spinorbitals); $N[\dots]$ is the normal product of the creation, \mathbf{X}_i^+ , and annihilation, \mathbf{X}_j , operators. With these definitions, the ground-state electronic energy, E_0^{e1} , is given by Goldstone's linked cluster expansion³⁸:

$$E_0^{e1} = \sum_{n=0} E_0^{(n)} = E_0^{(0)} + \langle \Phi_0 | H_1 \left\{ \sum_{m=0} \frac{1}{E_0^{(0)} - H_0} H_1 \right\}^m | \Phi_0 \rangle_{Link}, \quad (23)$$

where the subscript *Link* indicates that only linked diagrams are to be included, in the framework of the diagrammatic MBPT. The first terms of the expansion (23) are:

(i) the zeroth order energy

$$E_0^{(0)} = \langle \Phi_0 | \mathbf{H}_0 | \Phi_0 \rangle = \frac{1}{2} \sum_i^{\text{occ}} (\langle i | \mathbf{h} | i \rangle + \varepsilon_i) \quad (24)$$

(ii) the first-order correction

$$E_0^{(1)} = \langle \Phi_0 | \mathbf{H}_1 | \Phi_0 \rangle = 0 \quad (25)$$

(iii) the second-order correction

$$E_0^{(2)} = \langle \Phi_0 | \mathbf{H}_1 \frac{1}{E_0^{(0)} - \mathbf{H}_0} \mathbf{H}_1 | \Phi_0 \rangle = E_{m-m}^{(2)} + E_{b-b}^{(2)}, \quad (26)$$

where

$$E_{m-m}^{(2)} = L_1 = \sum_i^{\text{occ}} \sum_a^{\text{vir}} (F_{ia})^2 / D_{ia} \quad (27)$$

$$E_{b-b}^{(2)} = L_2 = \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} \langle ij || ab \rangle_A^2 / D_{iajb} \quad (28)$$

(iv) the third-order correction

$$E_0^{(3)} = \langle \Phi_0 | \mathbf{H}_1 \frac{1}{E_0^{(0)} - \mathbf{H}_0} \mathbf{H}_1 \frac{1}{E_0^{(0)} - \mathbf{H}_0} \mathbf{H}_1 | \Phi_0 \rangle = E_{m-m}^{(3)} + E_{m-b}^{(3)} + E_{b-b}^{(3)}, \quad (29)$$

where

$$E_{m-m}^{(3)} = L_3 + L_4 = \sum_i^{\text{occ}} \sum_a^{\text{vir}} F_{ia} / D_{ia} \left\{ \sum_c^{\text{vir}} F_{ac} F_{ci} / D_{ic} - \sum_k^{\text{occ}} F_{ak} F_{ki} / D_{ka} \right\} \quad (30)$$

$$\begin{aligned} E_{m-b}^{(3)} &= L_5 + L_6 + L_7 + L_8 + L_9 + L_{10} + L_{11} + L_{12} + L_{13} = \\ &= \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} \langle ij || ab \rangle_A / D_{iajb} \{ F_{ia} F_{jb} (3/D_{jb} + 1/D_{ia}) - \\ &- [\sum_k^{\text{occ}} (\langle ij || kb \rangle_A F_{ka} / D_{ka} + \frac{1}{2} \langle kj || ab \rangle_A F_{ik} / D_{kajb})] + \\ &+ [\sum_c^{\text{vir}} (\langle cj || ab \rangle_A F_{ic} / D_{ic} + \frac{1}{2} \langle ij || cb \rangle_A F_{ac} / D_{icjb})] \} \end{aligned} \quad (31)$$

$$\begin{aligned}
 E_b^{(3)} - b = L_{14} + L_{15} + L_{16} = & \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} \langle ij \| ab \rangle_A / D_{iajb} \times \\
 & \times \left\{ \sum_k^{\text{occ}} \sum_c^{\text{vir}} \langle cb \| kj \rangle_A \langle ka \| ci \rangle_A / D_{kcb} + \right. \\
 & + \frac{1}{8} \sum_{c,d}^{\text{vir}} \langle ab \| cd \rangle_A \langle cd \| ij \rangle_A / D_{icjd} + \\
 & \left. + \frac{1}{8} \sum_{k,l}^{\text{occ}} \langle ab \| kl \rangle_A \langle kl \| ij \rangle_A / D_{kalb} \right\}. \quad (32)
 \end{aligned}$$

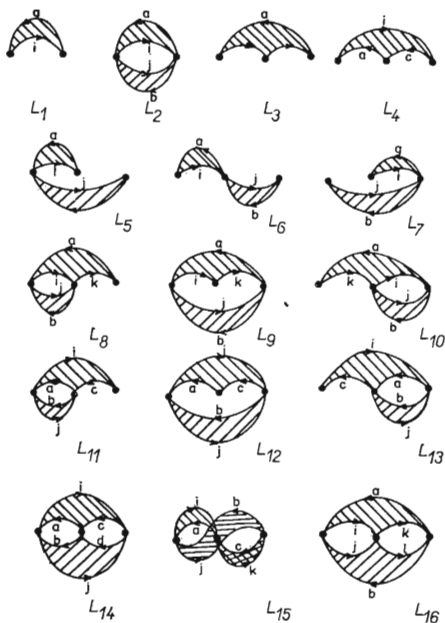


FIG. 2

Linked Antisymmetrized Diagrams up to the Third Order of MBPT

In Eqs (27)–(32), the symbols L_1, \dots, L_{16} designe the linked antisymmetrized diagrams (Fig. 2), where the rules for evaluating of these diagrams are collected in Table I. Integrating over the spin-coordinates in Eqs (24)–(32), the separate formulae for the closed shell and the unrestricted open shell systems can be easily derived (Appendix B).

RESULTS

Calculations presented in this paper are based on three fundamental steps:

- (i) the construction of the basis of HAOs by the EMOA method; calculations of particular binding energies and the molecular binding energy in this approximation;
- (ii) the construction of SLMOs using CNDO/2 and INDO Hamiltonian approximations in the modified 2×2 Roothaan's equations; calculations of the zeroth-order ground-state energy, charge distributions and the molecular dipole moment;
- (iii) the calculation of the energy terms up to the 3rd order of MBPT.

Calculations were performed for 15 small molecules using the valence $s-p$ basis of Slater AOs (with the exponent for the hydrogen orbital $\xi_H = 1.2$). In the individual

TABLE I
Rules for Evaluating of Linked Antisymmetrized Diagrams

1. Label each diagram with general "hole" (i, j, k, l) and "particle" (a, b, c, d) indices.
2. The numerator of the diagram is obtained by the product of one-electron integrals $F_{ij} = (1 - \delta_{ij}) \langle i | F | j \rangle$ (if any) and of antisymmetrized two-electron integrals $\langle ij | kl \rangle_A$ (Fig.3).
3. The denominator of the diagram is given by a product of terms $\sum_p D_{ia} = \sum_p \varepsilon_i - \varepsilon_a$ where p is a number of pairs of "hole" (i) and "particle" (a) lines between each two vertices ($D_{iajb} = D_{ia} + D_{jb}$).
4. Sum the ratio (numerator/denominator) over all "hole" and "particle" indices.
5. The sign of the diagram is given by $(-1)^{h+1}$ where h is the number of "hole" lines and l is the number of continuous lines forming the closed loops (the fermion loops are designed on Fig. 2).
6. Multiply the diagram by a factor $1/2$ for each pair of "equivalent" lines. An equivalent pair of lines is defined to be two lines beginning at one vertex and ending at another and going in the same direction (e.g. diagrams $L_8, L_9, L_{10}, L_{11}, L_{12}, L_{13}$ have one pair, L_2 two pairs and L_{14}, L_{16} three pairs).

molecules following bonding models were considered: (i) the bonding model with σ - and π -bonds: $\text{Li}\equiv\text{F}$, $\text{F}=\text{Be}=\text{F}$, $|\text{C}\equiv\text{O}|$, $\text{CH}_2=\text{O}$ and $|\text{O}\equiv\text{O}|$ (unpaired electrons occupy the antibonding SLMOs); (ii) the bonding model with σ -bonds only: $\text{Li}-\text{H}$, $\text{H}-\text{F}$, $\text{Li}-\text{F}$, $|\text{F}-\text{Be}-\text{F}|$, H_2O , NH_3 , CH_4 , CH_3F , CH_2F_2 , CHF_3 , CF_4 and CH_3CH_3 .

Hybrid Atomic Orbitals and Binding Energies by EMOA Method

In the EMOA (Extended Maximum Overlap Approximation) method^{25,26} the particular binding energy, $E_{\mu,\nu}^{\text{A,B}}$, that corresponds to a chemical bond, is defined as

$$E_{\mu,\nu}^{\text{A,B}} = K_{\mu,\nu}^{\text{A,B}} \langle \psi_{\mu}^{\text{A}} | \psi_{\nu}^{\text{B}} \rangle \quad (33)$$

and for the molecular binding energy, ε , it is valid:

$$\varepsilon = \frac{1}{2} \sum_{\text{A,B}} \sum_{\mu} \sum_{\nu} E_{\mu,\nu}^{\text{A,B}} (1 - \delta_{\text{A,B}}) \delta_{r(\text{A},\mu), r(\text{B},\nu)}, \quad (34)$$

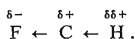
where $K_{\mu,\nu}^{\text{A,B}}$ are the semiempirical weighting parameters transferable from one molecule to another.

The calculated hybridization on given atoms in sp^x form is listed in Table II. The deviation angles of the direction of HAOs from the bond directions have been also calculated and they are included in Table II, too. Notice, that in the series of the molecules CH_3F , CH_2F_2 , CHF_3 and CF_4 the particular binding energies of C—H and C—F bonds increase. It is in a good harmony with the observable thermal stability of trihalogen methanes in contrast to monohalogen methanes. Calculated values of the particular binding energies: $E_{\sigma}^{\text{C,H}} \approx 420$, $E_{\sigma}^{\text{C,F}} \approx 460$, $E_{\sigma}^{\text{C,C}} \approx 320$, $E_{\sigma}^{\text{C,O}} \approx 570$ and $E_{\pi}^{\text{C,O}} \approx 220$ (kJ/mol) are in an agreement with expected stabilities of these bonds³⁹⁻⁴¹. Calculated molecular binding energies are in remarkable agreement with the experimental ones (Table II.).

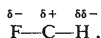
Charge Distributions

The elements of the total charge-density (bond-order) matrix, $P_{\mu\nu} = {}^{\text{a}}P_{\mu\nu} + {}^{\text{b}}P_{\mu\nu}$, and the atomic charges have been calculated from SLMOs and for a set of selected molecules they are collected in Table III. The trinity of the elements: $P_{\mu\mu}^{\text{AA}}$, $P_{\mu\nu}^{\text{AB}}$, $P_{\nu\nu}^{\text{BB}}$ gives the information about the polarity of corresponding bond.

In the series of the molecules CH_4 , CH_3F , CH_2F_2 , CHF_3 and CF_4 the positive atomic charge on the carbon atom increases and the positive atomic charge on hydrogen atom also increases. It is in good agreement with the classical chemical assumptions, according to which the negative electron-withdrawing effect of the fluorine extends throughout the molecular skeleton with a decreasing intensity:



In the given series, the negative atomic charge on fluorine decreases and the polarity of the C—F bond also decreases. It is in an agreement with the ideas about the competing effect of electronegative substituents in manifold substituted molecules. Notice, that our calculated charge distributions are in a rough disagreement with the original Pople's CNDO/2 and INDO calculations²⁷, which are based on canonical MO-LCAO-SCF approach. Pople's calculations show that a "charge alternation" may be characteristic of the inductive effect:



or in larger molecules

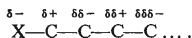


TABLE II

The Calculated Hybridization in sp^x Form, Deviation Angles of HAOs from Bonds ($^\circ$), Particular Binding Energies $E_{\mu,v}^{A,B}$ (kJ/mol) and Molecular Binding Energy ϵ (kJ/mol) by EMOA Method^a

Molecule	Bond A—B	sp^x on atom		Deviation		$E_{\mu,v}^{A,B}$	ϵ	
		A	B	A	B		calc.	exptl. ^b
CH ₃ F	C—H	2.699		1.81		416.9	1 697.4	1 682.0
	C—F	4.293	0.593			446.6		
CH ₂ F ₂	C—H	2.440		2.45		420.6	1 768.2	1 762.0
	C—F	3.777	0.577	1.47	0.50	463.5		
CHF ₃	C—H	2.184		1.48	0.52	421.7	1 868.3	1 867.8
	C—F	3.374	0.559			481.8		
CF ₄	C—F	3.000	0.554					
	C—O	1.172	0.457			595.6		
CO	π : C—O					239.9		
	C—H	1.946		2.21		417.5	1 593.5	1 516.3
CH ₂ O	C—O	2.113	0.512			553.3		
	π : C—O					205.3		
CH ₃ CH ₃	C—H	0.510		0.86		417.0		
	C—C	0.469	0.469			320.6		

^a Parameters used in the EMOA method (kJ/mol): $K_{\sigma}^{C,H} = 610.3507$, $K_{\sigma}^{C,F} = 852.9078$, $K_{\sigma}^{C,C} = 503.7407$, $K_{\sigma}^{C,O} = 753.1441$, $K_{\pi}^{C,O} = 933.5052$. ^b Experimental binding energies have been evaluated from standard molar enthalpies of formation $\Delta H_{f,298}^0$ by ref.⁴⁶.

TABLE III
Charge Distributions Calculated from SLMOs

Molecule	Bond A—B	CNDO/2 Hamiltonian						INDO Hamiltonian					
		elements of matrix $P \cdot 10^3$			atomic charges			elements of matrix $P \cdot 10^3$			atomic charges		
		$P_{\mu\mu}^{AA}$	$P_{\mu\nu}^{AB}$	$P_{\nu\nu}^{BB}$	A	B		$P_{\mu\mu}^{AA}$	$P_{\mu\nu}^{AB}$	$P_{\nu\nu}^{BB}$	A	B	
CH ₄	C—H	1 018	1 000	982	-0.073	+0.018	1 002	1 000	998	-0.006	+0.002		
CH ₃ F	C—H	1 042	999	958	+0.261	+0.042	1 011	1 000	989	+0.397	+0.011		
	C—F	613	922	1 387		-0.387	570	903	1 430		-0.430		
CH ₂ F ₂	C—H	1 060	998	940	+0.607	+0.060	1 013	1 000	987	+0.800	+0.013		
	C—F	636	932	1 364		-0.364	587	911	1 413		-0.413		
CHF ₃	C—H	1 077	997	923	+0.957	+0.077	1 013	1 000	987	+1.192	+0.013		
	C—F	655	939	1 345		-0.345	598	916	1 402		-0.402		
CF ₄	C—F	671	944	1 329	+1.317	-0.329	605	919	1 395	+1.578	-0.395		
	C—H	1 049	999	951	+0.130	+0.049	1 021	1 000	979	+0.254	+0.021		
CH ₂ O	C—O	747	967	1 253		-0.227	723	961	1 277		-0.296		
	C—O	1 026	1 000	974			980	1 000	1 019				

The "charge alternation" hypothesis on *ab initio* calculations has been criticized⁴², and also the de-orthogonalization approach⁴³ applied on the CNDO/2 MO-coefficient matrix gives the correct charge distribution trends, in an agreement with the classical chemical assumptions⁴⁴.

Dipole Moments

The calculated molecular dipole moments are listed in Table IV. The experimental dipole moments and the values obtained by canonical MO-LCAO-SCF calculations are also included in this table. Our calculated values deviate from the experimental data with deviations less than 1.5 Debyes. Higher deviations are observed in the molecules with polar π -bonds: LiF and CO. However, in the valence $s-p$ basis of AOs, after ZDO approximation, π -bonds do not contribute to the molecular dipole moment. The wrong sign of the calculated dipole moment of HF molecule connects with the neglect of the bicentric first-moment integrals which give the high negative contribution. From this point of view it is assumed, that the dipole moment is not a suitable property to test the molecular wave function in the ZDO approximation. As bicentric first-moment and also higher-moment integrals possess in general with significant values, the neglect of them by the ZDO approximation provides rather poor molecular electric moments, especially quadrupole moments⁴⁵.

TABLE IV
Dipole Moments, D

Molecule	Exptl. ^a	from SLMOs		from CMOs	
		CNDO/2	INDO	CNDO/2	INDO
LiH	-5.88	-6.09	-6.16	-6.19	-6.23
HF	-1.82	+2.73	+2.86	+1.85	+1.96
LiF	-6.60	-4.54	-4.61	-4.82	-4.73
CO	+0.11	+1.51	+1.61	-0.96	-0.94
NH ₃	1.47	1.60	1.62	2.10	2.02
H ₂ O	1.85	2.28	2.40	2.15	2.18
CH ₃ F	1.85	2.87	2.91	1.73	1.77
CH ₂ F ₂	1.96	3.21	3.21	1.94	1.94
CHF ₃	1.65	2.70	2.67	1.68	1.64
CH ₂ O	2.31	2.10	2.31	1.89	1.88

^a Ref.^{47,48}.

J_{C-H} Coupling Constants

In the paper²⁵ a simple formula for the correlation of experimental carbon 13-proton nuclear spin-spin coupling constants, J_{C-H} , with *s*-electron densities on C—H bonds was proposed:

$$J_{C-H} = A + B\varepsilon_i C_i(2s)^2 H_i(1s)^2. \quad (35)$$

In this approximate formula, ε_i is the orbital energy of the bonding SLMO on *i*-th C—H bond; $C_i(2s) = b_{i\mu} a_{\mu,s}^C$ and $H_i(1s) = b_{i\nu}$ are the *s*-characters of *i*-th bonding SLMO. Using calculated quantities $X_{C-H} = \varepsilon_{C-H} C(2s)^2 H(1s)^2$ and the experimental values of J_{C-H} , least square regression has been performed and has a high correlation coefficient (=0.99). Results of the correlation are listed in Table V.

Electronic and Total Energy Terms

In this part the following important aspects of the modified PCILO method (M-PCILO) were studied in more details: (i) the dependence of the electronic energy terms on the basis of HAOs in various orders of PT; (ii) the deviation of the zeroth-order energy with respect to self-consistent-field electronic energy — localization defect $E_0^{SCF} - E^{(0)}$; (iii) the compensation of the localization defect with the 2nd-order delocalization energy; (iv) the sensitivity of the electronic energy on the use of localized bonding model in various orders of PT; and (v) the dependence of the correlation energy on the number of valence electrons.

The calculated electronic energy terms are listed in Table VI (for INDO Hamiltonian approximation). Two different bases of HAOs were chosen: (i) HAOs cal-

TABLE V
 J_{C-H} Coupling Constants, Hz

Molecule	Exptl. ^a J_{C-H}	CNDO/2 method		INDO method	
		X_{C-H} ^b	J_{C-H}	X_{C-H} ^b	J_{C-H}
CH ₃ CH ₃	126.0	1.5203	127.0	1.5176	126.8
CH ₄	125.0	1.4570	118.2	1.4555	118.2
CH ₃ F	149.1	1.7148	153.8	1.7159	154.1
CH ₂ F ₂	184.5	1.9889	191.7	1.9906	192.0
CHF ₃	239.1	2.2878	233.0	2.2846	232.6

^a Ref. 49. ^b $X_{C-H} = \varepsilon_i C(2s)^2 H(1s)^2$ (eV).

culated by the EMOA method, and (ii) the canonical (sp , sp^2 , sp^3) HAOs. It can be concluded that in general the zeroth-order energy is better in the case of canonical HAOs (and the MBPT converges faster) than in the case of EMOA HAOs. The zeroth-order energy deterioration using the EMOA HAOs probably is connected with the fact that the overlap integrals on bonds are maximized in the first step and neglected in the second step, *e.g.* if the ZDO approximation is used in the 2×2 Roothaan equations.


Testing the localization defect the polar molecules were chosen because of the large localization of the electronic density at lone pairs on O and F atoms. The magnitude of this defect is less than 1% of the electronic energy in the studied molecules, so that the used localized bonding models can be regarded as suitable for description of the collective molecular properties in the zeroth order of PT. On the other hand, the localization defect represents a part of the energy which is to be compensated with the sum of all diagrams with one-particle vertices, in the framework of the diagrammatic MBPT. The greater part of this quantity may be compensated with the delocalization energy $E_{m-m}^{(2)}$ in the 2nd order of PT. Really, this compensation $E_{m-m}^{(2)}/(E_0^{SCF} - E_0^{(0)})$ is quite satisfactory: about 50–80%.

In paper⁵¹, using the Padé approximants, the alternative expressions of the Rayleigh-Schrödinger perturbation series for the energy were proposed. The most common 3rd-order series

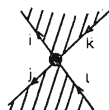
$$E_{\text{Padé}}^{[3/0]} = E_0^{(0)} + E_0^{(2)} + E_0^{(3)} \quad (36)$$

is only the special case of the general form of the Padé approximant $E^{[m/n]}$ for $m = 3$ and $n = 0$ ($m + n = p$ is the order of PT). The alternative expression for the energy in the 3rd order of PT, is for example, the approximant $E_{\text{Padé}}^{[2/1]}$. That is defined as

$$E_{\text{Padé}}^{[2/1]} = E_0^{(0)} + E_0^{(2)} / (1 - E_0^{(3)} / E_0^{(2)}) \quad (37)$$



$$= F_{ij} = (1 - \delta_{ij}) \langle i | F | j \rangle$$



$$= \langle ij | k l \rangle_A = -\langle ij | lk \rangle_A$$

FIG. 3
The Definition of Antisymmetrized Vertices
in MBPT

Comparing the series (37) and (36) the former is better because of its smaller complement to the exact series for the electronic energy E_0^e . Secondly, the approximant of the type $E_{\text{Padé}}^{[n+1/n]}$ is to be invariant with respect to shifted or scaled denominators^{15,51}. Thus, both of this alternative corrections after the 3rd order of PT: $E_0^{(2)} + E_0^{(3)}$ and $E_0^{(2)}/(1 - E_0^{(3)}/E_0^{(2)})$ were calculated and they are included in Table VI too.

TABLE VI
Electronic Energy Terms (eV) by Modified PCILO Method (INDO Hamiltonian)

Molecule	$-E_0^{(0)}$	Local defect ^a	2nd-order corrections			3rd-order corrections	
			$-E_{m-m}^{(2)}$	$-E_{b-b}^{(2)}$	$-E_0^{(2)}$	[3/0] ^b	[2/1] ^c
A) HAOs by EMOA method							
LiH	38.20	0.16	0.08	0.26	0.33	0.42	0.46
NH ₃	602.28	1.21	0.64	0.86	1.50	1.70	1.73
H ₂ O	704.67	2.71	1.46	0.64	2.10	2.11	2.11
HF	844.19	3.32	2.00	0.23	2.23	1.94	1.97
CO	953.93	3.65	2.39	2.32	4.71	4.70	4.70
O ₂	1 378.00	7.19	4.88	2.53	7.41	7.45	7.45
CH ₄	527.26	0.15	0.13	0.96	1.09	1.38	1.48
CH ₃ F	1 584.33	4.36	3.14	1.15	4.28	4.20	4.20
CH ₂ F ₂	2 883.36	9.26	6.78	1.31	8.09	7.69	7.71
CH ₂ O	1 177.96	4.38	2.59	1.97	4.55	4.98	5.03
B) Canonical HAOs							
LiH	37.87	0.49	0.23	0.25	0.47	0.58	0.61
NH ₃	603.20	0.30	0.21	0.85	1.06	1.28	1.33
H ₂ O	706.99	0.39	0.26	0.66	0.93	1.03	1.05
HF	847.30	0.21	0.15	0.32	0.47	0.49	0.49
CO	954.92	2.55	1.58	2.32	3.90	3.92	3.92
O ₂	1 377.11	8.07	5.50	2.53	8.03	8.07	8.07
CH ₃ F	1 587.26	1.42	0.94	1.29	2.23	2.54	2.59
CH ₂ O	1 180.34	2.01	1.02	2.07	3.09	3.64	3.76

^a $E_0^{(0)} - E_0^{\text{SCF}}$, ^b $-E_0^{(2)} - E_0^{(3)} = E_0^{(0)} - E_{\text{Padé}}^{[3/0]}$, ^c $E_0^{(0)} - E_{\text{Padé}}^{[2/1]}$.

The energy terms calculated by the modified PCILO method have been compared with original PCILO calculations⁴ and also with MO-LCAO-SCF + PCI calculations⁵² (Perturbative Configuration Interaction using the Moller-Plesset type of the Hamiltonian partitioning). The zeroth-, 2nd-, and 3rd-order total molecular energies are listed in Table VII (for CNDO/2 Hamiltonian approximation), where the total SCF energy is chosen as the referential level. It can be concluded that the Epstein-Nesbet denominator (by the original PCILO method) provides a larger contribution in the energy terms than does the Moller-Plesset denominator (by the modified PCILO method).

The dependence of the electronic energy terms on the use of a molecular bonding model has been also tested. Two quite different bonding models have been considered for the LiF molecule: $\text{Li} \equiv \text{F}|$ and $\text{Li} - \overline{\text{F}}|$. Since the zeroth-order ground-state energies for this models differ from each other by 4 eV, the corrected 2nd-order energies differ only by 2 eV. A similar situation has been observed in M-PCILO calculations of the BeF_2 molecule using two different bonding models: $\overline{\text{F}} = \text{Be} = \overline{\text{F}}$ and $|\overline{\text{F}} - \text{Be} - \overline{\text{F}}|$. The difference in the zeroth-order energies is approximately 7 eV and the one in the corrected 2nd-order energies is approximately 2 eV. It shows that the corrected 2nd-order ground-state energy is little sensitive on the basis of SLMOs by the M-PCILO method.

On Fig. 4, the correlation energy, $E_{b-b}^{(2)}$, versus the number of valence electrons, n_e , is plotted for the series of the molecules CH_4 , CH_3F , CH_2F_2 , CHF_3 and CF_4 . The

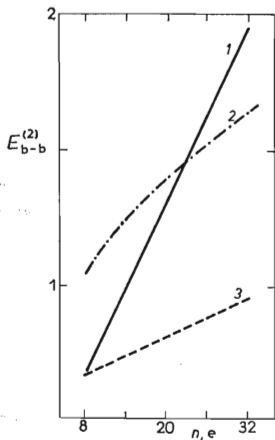


FIG. 4

The Second-Order Correlation Energy $E_{b-b}^{(2)}$, vs the Number of Valence Electrons in the Series of Fluoromethanes (CNDO/2 Hamiltonian approximation)

1 MO-LCAO-SCF+PCI method; 2 original PCILO method; 3 modified PCILO method.

TABLE VII
Total Molecular Energy (eV) in Various Orders of the Perturbation Theory with Respect to the SCF Energy (CNDO/2 Hamiltonian)

Molecule	SCF + PCI ^a		Modified PCILO ^b			Original PCILO ^c				
	$-E_{\text{SCF}}^{\text{a}}$	2.	0. ^d	2.	3.	[2/1] ^e	0. ^d	2.	3.	[2/1] ^e
LiH	29.596	-0.239	0.351	-0.051	-0.139	-0.164	0.680	-0.290	-0.376	-0.384
NH ₃	377.487	-0.613	0.225	-0.474	-0.657	-0.723	0.144	-0.959	-0.869	-0.876
H ₂ O	540.605	-0.491	0.274	-0.340	-0.454	-0.479	0.172	-0.777	-0.628	-0.648
HF	773.275	-0.232	0.144	-0.164	-0.205	-0.211	0.053	-0.352	-0.302	-0.308
CO	681.367	-2.393	1.797	-1.596	-1.434	-1.442	1.287	-3.634	-1.452	-2.122
O ₂	1 000.589	-2.889	6.567	-0.260	-0.337	-0.338				
CH ₄	275.183	-0.664	0.038	-0.641	-0.871	-0.988	0.032	-1.039	-1.019	-1.019
CH ₃ F	1 009.303	-0.989	1.076	-0.447	-0.720	-0.780	0.879	-1.063	-1.163	-1.169
CH ₂ F ₂	1 743.851	-1.311	2.478	-0.027	-0.400	-0.464	2.241	-0.899	-1.205	-1.239
CHF ₃	2 478.661	-1.617	4.318	+0.619	+0.077	-0.016	4.096	-0.627	-1.199	-1.278
CF ₄	3 213.643	-1.936	6.366	+1.318	+0.544	+0.404	6.205	-0.346	-1.228	-1.365
CH ₂ O	730.088	-2.147	1.583	-0.958	-1.390	-1.478	1.715	-2.309	-1.781	-1.842
LiF ^f	752.840	-0.663	5.300	+2.366	+2.350	+2.349	5.670	+0.114	+1.660	+1.323
LiF ^g			0.583	-0.574	-0.318	-0.364	0.201	-0.654	-0.481	-0.510
BeF ₂ ^f	1 534.075	-1.469	12.871	+4.916	+4.326	+4.279	16.981	-2.086	+0.017	-0.192
BeF ₂ ^g			5.865	+1.489	+1.287	+1.277	11.134	-1.374	-2.737	-2.904

^a MO-LCAO-SCF method with MP type of PCI. ^b MP type of PCI, canonical HAOs are used. ^c EN type of PCI. ^d Localization defect. ^e Padé approximant $E_{\text{SCF}}^{[2/1]}$. ^f Bonding model with σ bonds only. ^g Bonding model with σ and π bonds.

linear dependence is perfect in the case of the MP type of the Hamiltonian partitioning, so that the correct dependence of the correlation energy on the number of particles is demonstrated in M-PCILO as well as in MO-LCAO-SCF + PCI calculations. The EN denominator in the original PCILO method (O-PCILO) provides the incorrect dependence of the correlation energy on the number of particles.

The calculated internal barriers of rotation for the ethane molecule are presented in Table VIII. The results for the conformational analysis are as reasonable as in MO-LCAO-SCF resp. O-PCILO calculations.

Interatomic Distances and Harmonic Force Constants

In the series of diatomic molecules $\text{Li}-\text{H}$, $\text{H}-\overset{\ominus}{\text{F}}$, $\text{Li}\equiv\overset{\ominus}{\text{F}}$ and $|\text{C}\equiv\text{O}|$ the different bonding situations were considered. The potential curve around the energetic minimum (in steps of order pm) was fitted as a quadratic function; from its derivations

TABLE VIII
The Internal Barrier of Rotation in Ethane Molecule

Method	Order of PT	Total energy, eV		Barrier eV ^a
		staggered	eclipsed	
<i>A) CNDO/2 Hamiltonian</i>				
MO-LCAO-SCF+PCI	0.	511·794	511·694	0·100
	2.	513·171	513·068	0·103
M-PCILO	0.	510·154	510·143	0·011
	2.	512·549	512·472	0·077
	3.	513·025	512·949	0·076
O-PCILO	[2/1]	513·143	513·071	0·072
	0.	510·306	510·295	0·011
	2.	513·582	513·500	0·082
	3.	513·626	513·533	0·093
<i>B) INDO Hamiltonian</i>				
MO-LCAO-SCF	0.	497·980	497·879	0·101
M-PCILO	0.	496·200	496·189	0·011
	2.	499·243	499·165	0·078

^a Experimental value is 0·124 eV.

the equilibrium interatomic distance, R_0 , and the harmonic force constant, k_0 , were calculated (Table IX). Interatomic distances calculated by M-PCILO method possess the values in the region of MO-LCAO-SCF + PCI calculations as well as in O-PCILO calculations. It is expected in effect of the use of the same Hamiltonian approximation. The zeroth-order force constants are somewhat worse with respect to MO-LCAO-SCF calculations. The zeroth- and 2nd-order force constants calculated by various methods give the following relations:

$k_e^{(0)}(\text{M-PCILO}) > k_e^{(0)}(\text{O-PCILO}) > k_e^{(0)}(\text{SCF}) > k_e^{(2)}(\text{M-PCILO}) > k_e^{(2)}(\text{SCF} + \text{PCI}) > k_e^{(2)}(\text{O-PCILO})$, what is in an accord with expectations. However, the improvement of the force constants by PT is rather neglectible with respect to experiments. It seems to be a consequence of the simple ZDO Hamiltonian approximation rather than makes a failure of the perturbation technique.

The shape of the potential curve (the curve of the adiabatic potential) in the larger atomic separations has been also tested for the HF molecule (Fig. 5 and Fig. 6).

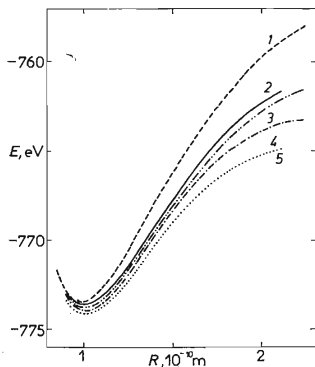


FIG. 5

Curves of the Adiabatic Potential for HF Molecule by Modified PCILO Method in Comparison with the MO-LCAO-SCF+PCI Method

1 Zero-order energy $E^{(0)}$; 2 SCF energy; 3 third-order energy $E^{(3)}$; 4 second-order energy $E^{(2)}$; 5 second-order energy $E_{\text{SCF+PCI}}^{(2)}$.

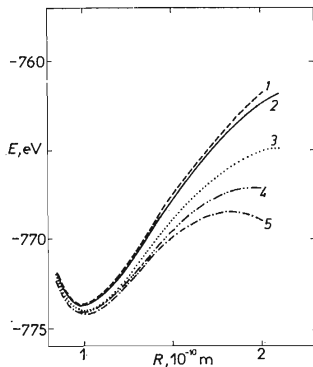


FIG. 6

Curves of the Adiabatic Potential for HF Molecule by Original PCILO Method in Comparison with the MO-LCAO-SCF+PCI Method

1 Zero-order energy $E^{(0)}$; 2 SCF energy; 3 second-order energy $E_{\text{SCF+PCI}}^{(2)}$; 4 third-order energy $E^{(3)}$; 5 second-order energy $E^{(2)}$.

The 2nd-order potential curve has a correct form in the case of MO-LCAO-SCF + + PCI method as well as by M-PCILO method. On the contrary, the vanishing EN denominator in the 2nd-order energy causes the incorrect form of the potential curve by O-PCILO method; there is a local maximum approaching the dissociation limit from above.

DISCUSSION AND CONCLUSION

To open the discussion notice that the principal difference between the original and the modified PCILO methods lies in the Hamiltonian partitioning scheme. The differences between O-PCILO and M-PCILO methods are collected in Table X.

Due to the Moller-Plesset type of the Hamiltonian partitioning, the effect of the overcounting of some diagrams does not exist in the M-PCILO method. That is in contrast with the O-PCILO method where the Epstein-Nesbet type of the Hamiltonian partitioning is used. The 2nd-order corrections to the ground-state energy are to be smaller by M-PCILO than by O-PCILO. However, the single fact that the quantity $E_{m-m}^{(2)}/(E_0^{SCF} - E_0^{(0)})$ is equal to 1 ± 0.1 by O-PCILO instead of 0.7 by M-PCILO did not give a favourisation of O-PCILO (or the Epstein-Nesbet partitioning).

TABLE IX

Equilibrium Interatomic Distances R_e and Harmonic Force Constants k_e in Various Orders of the Perturbation Theory (CNDO/2 Hamiltonian)

Method	Order of PT	$R_e, 10^{-10}$ m				$k_e, \text{N/cm}$			
		LiH	HF	LiF	CO	LiH	HF	LiF	CO
M-PCILO ^a	0.	1.572	0.982	2.109	1.180	1.95	20.65	2.25	43.08
	2.	1.587	1.000	2.115	1.212	1.88	18.25	2.24	35.54
	3.	1.592	0.993	2.108	1.201	1.83	19.68	2.25	39.74
M-PCILO ^b	0.	1.604	0.984	2.148	1.163	1.95	21.74	2.32	48.29
	2.	1.603	1.002	2.131	1.204	1.86	18.50	2.26	38.10
	3.	1.607	1.000	2.134	1.193	1.85	19.89	2.27	41.88
O-PCILO	0.	1.588	1.000	2.151	1.180	1.98	18.62	2.22	42.93
	2.	1.953	1.015	2.137	1.237	1.83	16.71	2.19	31.68
	3.	1.593	1.015	2.144	1.185	1.82	16.78	2.12	47.10
SCF + PCI	0.	1.573	1.000	2.161	1.191	1.94	18.56	1.98	40.51
	2.	1.588	1.009	2.157	1.218	1.88	18.18	1.96	34.70
Exptl.		1.595	0.917	1.51	1.128	1.02	9.59	2.50	19.02

^a HAOs by EMOA method. ^b Canonical HAOs.

On the calculations it can be concluded that the PCILO method is sensitive on the use of a basis set of hybrid atomic orbitals. When the basis set of canonical HAOs is used the quite good zeroth-order energy is obtained: the localization defect is small and the fast convergence of the perturbation series is secured. The use of EMOA hybrids gives an inconsistency with the other steps in the PCILO method: the EMOA method maximize overlaps of HAOs at bonds but in the next step the ZDO approximation is applied which neglect them. However, in some cases, the EMOA-basis set of HAOs can be more suitable for construction of SLMOs.

The progress of the PCILO method with respect to MO-LCAO-SCF + PCI calculations lies in the rapid reductions of two time consuming steps. As the diagonalization procedure is unnecessary for the construction of SLMOs, they are calculated by much saving of the computing time. Secondly, the tedious step in calculating the two-electron integrals over MOs is rapidly reduced by the use of SLMOs to the simple sum of 16 (by INDO) or 4 (by CNDO) terms. Using the convenient basis of HAOs, PCILO method can give a better energy than the MO-LCAO-SCF procedure in a much shorter time. For example, by the CNDO/2 Hamiltonian approximation 20 seconds is consumed at SIEMENS 4004 computer in 3rd-order energy calculations of CF₄ molecule by M-PCILO method⁵³, as opposed to the 1 000 seconds required to calculate a second-order correlation energy by MO-LCAO-SCF + PCI method⁵². However, the consideration of the INDO Hamiltonian approximation makes the PCILO algorithm more complex. Similarly, if the *d*-orbitals are included into the basis set the requirement on the computing time considerably increases.

TABLE X

The Mutual Comparison of the Original and Modified PCILO Methods

Approach	Original PCILO	Modified PCILO
1. Perturbation theory	ordinary	diagramatic MBPT
2. Hamiltonian partitioning	Epstein-Nesbet	Moller-Plesset
3. Hamiltonian approximation	CNDO/2	CNDO/2 and INDO
4. Basis set of HAOs	Del Re method	EMOA method
5. Basis set of SLMOs	optimization of bond-polarities	solution of modified Roothaan equations
6. Applications	a) only closed shell systems	also open shell systems (UHF approach)
	b) only elements H—Cl	elements H—Br (including transition metals)

Appendix A:

Modified Roothaan Equations for Strictly Localized Molecular Orbitals

In the general matrix notation, the column vector of hybrid atomic orbitals, Ψ , is transformed into a column vector of strictly localized molecular orbitals, Φ^x , as:

$$\Phi^x = \mathbf{B}^x \Psi \quad (38)$$

(index x designates α - or β -SLMOs' set in the unrestricted open shell approach). In all rows and columns of the LCHAO coefficient matrix \mathbf{B}^x only two elements are non-zero. Thus, the elements of column vectors Φ^x and Ψ can be arranged in such a way, that the matrix \mathbf{B}^x is a block-diagonal

$$\mathbf{B}^x = \begin{pmatrix} \mathbf{B}_1^x & 0 & \dots & 0 & \dots \\ 0 & \mathbf{B}_2^x & \dots & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \mathbf{B}_i^x & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (39)$$

A 2×2 block \mathbf{B}_i^x combines a pair of HAOs into a pair of SLMOs: one bonding SLMO, $|i\rangle$, and one antibonding SLMO, $|i^*\rangle$, associated with i -th covalent bond. For a lone lobe (usually occupied with an electron pair) the block \mathbf{B}_i^x contains from the single element with the unity value.

In order to obtain SCF equations for matrices \mathbf{B}_i^x , it is necessary to introduce some approximations into well-known Roothaan equations

$$\mathbf{F}^x(\mathbf{B}^x)^{-1} = \mathbf{S}(\mathbf{B}^x)^{-1} \mathbf{E}^x, \quad (40)$$

which are fulfilled for orthonormal canonical MOs expanded into fixed basis of one-centric functions Ψ . In Eq. (40),

$${}^x F_{\mu\nu} = \langle \psi_\mu | \mathbf{F} | \psi_\nu \rangle = \langle \mu | \mathbf{h} | \nu \rangle + \sum_{\lambda, \sigma} \{ ({}^\alpha P_{\lambda\sigma} + {}^\beta P_{\lambda\sigma}) \langle \mu\lambda | \nu\sigma \rangle - {}^x P_{\lambda\sigma} \langle \mu\lambda | \sigma\nu \rangle \} \quad (41)$$

is the matrix element of one-electron effective Fock operator in HAOs' basis;

$$S_{\mu\nu} = \langle \mu | \nu \rangle \quad (42)$$

is an element of the overlap integral matrix \mathbf{S} and \mathbf{E}^x is the diagonal matrix of one-electron orbital energies ϵ_i^x . The charge-density (bond-order) matrix P^x is defined as

$$P^x = (\mathbf{B}^x)^T \mathbf{W}^x \mathbf{B}^x \quad (43)$$

where \mathbf{W}^x is the diagonal matrix of MOs' occupation numbers with diagonal elements equal to 1 or 0. Multiplying Eq. (40) from the left side by matrix \mathbf{B}^x , a form of Hartree-Fock equations is obtained

$$\mathcal{F}^x = \mathcal{S}^x \mathbf{E}^x, \quad (44)$$

where \mathcal{F}^x is the matrix of elements of Fock operator in the basis of MOs. The MOs' overlap integral matrix can be written in the form

$$\mathcal{S} = \begin{pmatrix} \mathcal{S}_1^x & 0 & \dots & 0 & \dots \\ 0 & \mathcal{S}_2^x & \dots & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \mathcal{S}_i^x & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} + \begin{pmatrix} 0 & \Delta_{12}^x & \dots & \Delta_{11}^x & \dots \\ \Delta_{21}^x & 0 & \dots & \Delta_{2i}^x & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \Delta_{i1}^x & \Delta_{i2}^x & \dots & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}. \quad (45)$$

In the case of SLMOs, \mathcal{S}_i^x is the 2×2 block of overlap integrals between bonding and antibonding SLMO, which are associated with the same i -th bond. They, both can be chosen to be orthonormal: $\mathcal{S}_i^x = \mathbf{I}$. The symbol Δ_{ij}^x denotes a 2×2 block of overlap integrals of SLMOs, which are associated with different i -th and j -th bond and which have small values (of order ~ 0.1), in the general case. As a consequence of the complete neglect of elements Δ_{ij}^x , Eq. (44) is factorized:

$$\mathcal{F}_i^x = \mathcal{S}_i^x \mathbf{E}_i^x, \quad (46)$$

or

$$\begin{pmatrix} \langle i | \mathbf{F} | i \rangle & \langle i | \mathbf{F} | i^* \rangle \\ \langle i^* | \mathbf{F} | i \rangle & \langle i^* | \mathbf{F} | i^* \rangle \end{pmatrix} = \begin{pmatrix} \varepsilon_i & 0 \\ 0 & \varepsilon_i^* \end{pmatrix}. \quad (47)$$

Eq. (47) represent the Hartree-Fock equations for SLMOs, where the non-orthogonality of SLMOs is neglected. Similarly, a form of modified Roothaan equations for the coefficient matrices \mathbf{B}_i^x easily is obtained:

$$\mathbf{F}_i^x (\mathbf{B}_i^x)^T = S_i (\mathbf{B}_i^x)^T \mathbf{E}_i^x \quad (48)$$

with the following simple solutions:

$$\begin{aligned} \varepsilon_i^x &= \frac{1}{2} [1 - (S_{\mu\nu})^2]^{-1} \{ (F_{\mu\mu}^x + F_{\nu\nu}^x - 2F_{\mu\nu}^x S_{\mu\nu}) \pm \\ &\pm [(F_{\mu\mu}^x - F_{\nu\nu}^x)^2 + 4(F_{\mu\nu}^x - F_{\mu\mu}^x S_{\mu\nu})(F_{\mu\nu}^x - F_{\nu\nu}^x S_{\mu\nu})]^{1/2} \} \end{aligned} \quad (49)$$

$$b_v^x = (G^2 + 2GS_{\mu\nu} + 1)^{-1/2} \quad (50)$$

$$b_\mu^x = Gb_\nu^x, \quad (51)$$

where

$$G = \frac{\varepsilon_1^x S_{\mu\nu} - F_{\mu\nu}^x}{F_{\mu\mu}^x - \varepsilon_1^x}. \quad (52)$$

In Eqs (49)–(52), the lower eigenvalue ε_1^x (with the negative sign of the discriminant) corresponds to the bonding SLMO and the second one to the antibonding SLMO. As \mathbf{B}^x is a block-diagonal matrix in the case of SLMOs, the matrix \mathbf{P}^x defined by Eq. (42) also must take the block-diagonal form. Thus, the matrix elements of the Fock operator defined by Eq. (40) can be still simplified.

Appendix B:

The Electronic Energy Terms up to the Third Order of MBPT

(i) Closed shell system

$$E_0^{(0)} = \sum_i^{\text{occ}_\alpha} (\langle i | \mathbf{h} | i \rangle + \varepsilon_i) \quad (53)$$

$$E_{m-m}^{(2)} = 2 \sum_i^{\text{occ}_\alpha} \sum_a^{\text{vir}_\alpha} (F_{ia})^2 / D_{ia} \quad (54)$$

$$E_{b-b}^{(2)} = \sum_{i,j}^{\text{occ}_\alpha} \sum_{a,b}^{\text{vir}_\alpha} \langle ij || ab \rangle_c \langle ij | ab \rangle / D_{iajb} \quad (55)$$

$$E_{m-m}^{(3)} = 2 \sum_i^{\text{occ}_\alpha} \sum_a^{\text{vir}_\alpha} F_{ia} / D_{ia} (\sum_c^{\text{vir}_\alpha} F_{ac} F_{ci} / D_{ic} - \sum_k^{\text{occ}_\alpha} F_{ak} F_{ki} / D_{ka}) \quad (56)$$

$$\begin{aligned} E_{m-b}^{(3)} = & 2 \sum_{i,j}^{\text{occ}_\alpha} \sum_{a,b}^{\text{vir}_\alpha} \langle ij || ab \rangle_c / D_{iajb} [F_{ia} F_{jb} (3/D_{jb} + 1/D_{ia}) - \\ & - \sum_k^{\text{occ}_\alpha} (2 \langle ij | kb \rangle F_{ka} / D_{ka} + \langle kj | ab \rangle F_{ik} / D_{kajb}) + \\ & + \sum_c^{\text{vir}_\alpha} (2 \langle cj | ab \rangle F_{ic} / D_{ic} + \langle ij | cb \rangle F_{ac} / D_{icjb})] \end{aligned} \quad (57)$$

$$\begin{aligned}
E_{b-b}^{(3)} = & \sum_{i,j}^{\text{occ}_\alpha} \sum_{a,b}^{\text{vir}_\alpha} \langle ij \| ab \rangle_C / D_{iajb} \times \\
& \times \left[\sum_{c,d}^{\text{vir}_\alpha} \langle ab | cd \rangle \langle cd | ij \rangle / D_{icjd} + \sum_{k,l}^{\text{occ}_\alpha} \langle ab | kl \rangle \langle kl | ij \rangle / D_{kalb} + \right. \\
& + 2 \sum_k^{\text{occ}_\alpha} \sum_c^{\text{vir}_\alpha} (\langle ka \| ci \rangle_C \langle cb | kj \rangle / D_{kcjb} - \\
& \left. - \langle kb | ic \rangle \langle ac | kj \rangle / D_{kajc} - \langle ka | ci \rangle \langle bc | kj \rangle / D_{kbjc} \right]. \quad (58)
\end{aligned}$$

(ii) Open shell system (UHF approach)

$$E_0^{(0)} = \frac{1}{2} \sum_x^{\alpha,\beta} \sum_{i_N}^{\text{occ}_N} (\langle i | h | i \rangle + e_i^x) \quad (59)$$

$$E_{m-m}^{(2)} = \sum_x^{\alpha,\beta} \sum_{i_N}^{\text{occ}_N} \sum_{a_N}^{\text{vir}_N} (F_{ia}^x)^2 / D_{ia}^x \quad (60)$$

$$\begin{aligned}
E_{b-b}^{(2)} = & \frac{1}{4} \sum_x^{\alpha,\beta} \sum_{i_N}^{\text{occ}_N} \sum_{a_N}^{\text{vir}_N} \left\{ \sum_{j_N}^{\text{occ}_N} \sum_{b_N}^{\text{vir}_N} \langle ij \| ab \rangle_A^2 / D_{iajb}^x + \right. \\
& \left. + 2 \sum_{j_\eta}^{\text{occ}_\eta} \sum_{b_\eta}^{\text{vir}_\eta} \langle ij | ab \rangle^2 / (D_{ia}^x + D_{jb}^\eta) \right\} \quad (61)
\end{aligned}$$

$$E_{m-m}^{(3)} = \sum_x^{\alpha,\beta} \sum_{i_N}^{\text{occ}_N} \sum_{a_N}^{\text{vir}_N} F_{ia}^x / D_{ia}^x \left(\sum_{c_N}^{\text{vir}_N} F_{ac}^x F_{ci}^x / D_{ic}^x - \sum_{k_N}^{\text{occ}_N} F_{ak}^x F_{ki}^x / D_{ka}^x \right) \quad (62)$$

$$\begin{aligned}
E_{m-b}^{(3)} = & \sum_x^{\alpha,\beta} \sum_{i_N}^{\text{occ}_N} \sum_{a_N}^{\text{vir}_N} \left\{ \sum_{j_N}^{\text{occ}_N} \sum_{b_N}^{\text{vir}_N} \langle ij \| ab \rangle_A / D_{iajb}^x [F_{ia}^x F_{jb}^x (3/D_{jb}^x + 1/D_{ia}^x) - \right. \\
& - \sum_{k_N}^{\text{occ}_N} (\langle ij \| kb \rangle_A F_{ka}^x / D_{ka}^x + \frac{1}{2} \langle kj \| ab \rangle_A F_{ik}^x / D_{kajb}^x) + \\
& + \sum_{c_N}^{\text{vir}_N} (\langle cj \| ab \rangle_A F_{ic}^x / D_{ic}^x + \frac{1}{2} \langle ij \| cb \rangle_A F_{ac}^x / D_{icjb}^x) \left. \right\} + \\
& + \sum_{j_\eta}^{\text{occ}_\eta} \sum_{b_\eta}^{\text{vir}_\eta} \langle ij | ab \rangle / (D_{ia}^x + D_{jb}^\eta) \{ F_{ia}^x F_{jb}^\eta (3/D_{jb}^\eta + 1/D_{ia}^x) - \\
& - 2 \sum_{k_N}^{\text{occ}_N} [\langle ij | kb \rangle F_{ka}^x / D_{ka}^x + \frac{1}{2} \langle kj | ab \rangle F_{ik}^x / (D_{ka}^x + D_{jb}^\eta)] + \\
& \left. + 2 \sum_{c_N}^{\text{vir}_N} [\langle cj | ab \rangle F_{ic}^x / D_{ic}^x + \frac{1}{2} \langle ij | cb \rangle F_{ac}^x / (D_{ic}^x + D_{jb}^\eta)] \right\} \quad (63)
\end{aligned}$$

$$\begin{aligned}
E_{b-b}^{(3)} = & \sum_{\kappa} \sum_{i_{\kappa}}^{\alpha, \beta} \sum_{j_{\kappa}}^{\text{occ}_{\kappa}} \sum_{b_{\kappa}}^{\text{vir}_{\kappa}} \{ \sum_{j_{\eta}}^{\text{occ}_{\eta}} \sum_{b_{\eta}}^{\text{vir}_{\eta}} \langle ij \| ab \rangle_{\Lambda} / D_{iajb}^{\kappa} [\frac{1}{8} \sum_{c_{\kappa}, d_{\kappa}}^{\text{vir}_{\kappa}} \langle ab \| cd \rangle_{\Lambda} \langle cd \| ij \rangle_{\Lambda} / D_{icjd}^{\kappa} + \\
& + \frac{1}{8} \sum_{k_{\kappa}, l_{\kappa}}^{\text{occ}_{\kappa}} \langle ab \| kl \rangle_{\Lambda} \langle kl \| ij \rangle_{\Lambda} / D_{kalb}^{\kappa} + \\
& + \sum_{k_{\kappa}}^{\text{occ}_{\kappa}} \sum_{c_{\kappa}}^{\text{vir}_{\kappa}} \langle ic \| ak \rangle_{\Lambda} \langle kj \| cb \rangle_{\Lambda} / D_{kcjb}^{\kappa} + \\
& + \sum_{k_{\eta}}^{\text{occ}_{\eta}} \sum_{c_{\eta}}^{\text{vir}_{\eta}} \langle ic | ak \rangle \langle kj | cb \rangle / (D_{kc}^{\eta} + D_{jb}^{\kappa}) + \\
& + \sum_{j_{\eta}}^{\text{occ}_{\eta}} \sum_{b_{\eta}}^{\text{vir}_{\eta}} \langle ij | ab \rangle / (D_{ia}^{\kappa} + D_{jb}^{\eta}) \times \\
& \times [\frac{1}{2} \sum_{c_{\kappa}}^{\text{vir}_{\kappa}} \sum_{d_{\eta}}^{\text{vir}_{\eta}} \langle ab | cd \rangle \langle cd | ij \rangle / (D_{ic}^{\kappa 1} + D_{jd}^{\eta}) + \\
& + \frac{1}{2} \sum_{k_{\kappa}}^{\text{occ}_{\kappa}} \sum_{l_{\eta}}^{\text{occ}_{\eta}} \langle ab | kl \rangle \langle kl | ij \rangle / (D_{ka}^{\kappa} + D_{lb}^{\eta}) + \\
& + \sum_{k_{\eta}}^{\text{occ}_{\eta}} \sum_{c_{\eta}}^{\text{vir}_{\eta}} \langle ic | ak \rangle \langle kj \| cb \rangle_{\Lambda} / D_{kcjb}^{\eta} + \\
& + \sum_{k_{\kappa}}^{\text{occ}_{\kappa}} \sum_{c_{\kappa}}^{\text{vir}_{\kappa}} \langle ic \| ak \rangle_{\Lambda} \langle kj | cb \rangle / (D_{kc}^{\kappa} + D_{jb}^{\eta}) - \\
& - \sum_{k_{\kappa}}^{\text{occ}_{\kappa}} \sum_{c_{\eta}}^{\text{vir}_{\eta}} \langle ic | kb \rangle \langle kj | ac \rangle / (D_{ka}^{\kappa} + D_{jc}^{\eta}) \} . \quad (64)
\end{aligned}$$

In Eqs (53)–(64), κ is the spin-index (α or β); η designates the complementary spin-index with respect of κ , which is defined as: $\eta(\alpha) = \beta$ and $\eta(\beta) = \alpha$; occ_{κ} and occ_{η} are the occupied orbitals; vir_{κ} and vir_{η} are the unoccupied (virtual) orbitals. The other symbols are defined in the main text.

If the CNDO/2 Hamiltonian approximation on the $s-p$ valence basis of AOs is applied, the large simplification of the electronic energy terms is obtained; only charge densities $|ii\rangle$, $|ii^*\rangle$ and $|i^*i^*\rangle$ contribute. For example, for closed shell systems following formulae have been derived:

$$E_0^{(0)} = \sum_i^{\text{occ}_{\kappa}} (H_{ii} + \varepsilon_i) + \sum_{i^*}^{\text{occ}_{\kappa}} (H_{i^*i^*} + \varepsilon_{i^*}) \quad (65)$$

$$E_{m-m}^{(2)} = 2 \sum_i^{\text{occ}_{\kappa}} \sum_{a^* \neq i^*}^{\text{vir}_{\kappa}} (H_{ia^*})^2 / D_{ia^*} \quad (66)$$

$$E_{b-b}^{(2)} = \sum_i^{\text{occ}_\alpha} [\langle ii | i^*i^* \rangle^2 / (2D_{ii}) + 4 \sum_{j>i}^{\text{occ}_\alpha} \langle ij | i^*j^* \rangle^2 / D_{ii^*jj^*}]$$

for $i^*, j^* \in \text{vir}_\alpha$;

(67)

$$E_{m-m}^{(3)} = 4 \sum_i^{\text{occ}_\alpha} \sum_{n^* \neq i^*}^{\text{vir}_\alpha} H_{in^*} / D_{in^*} \left(\sum_{b^* > a^*}^{\text{vir}_\alpha} H_{n^*b^*} H_{ib^*} / D_{ib^*} - \sum_{j>i}^{\text{occ}_\alpha} H_{ja^*} H_{ij} / D_{ja^*} \right)$$
(68)

$$E_{m-b}^{(3)} = -2 \sum_i^{\text{occ}_\alpha} \sum_{j \neq i}^{\text{occ}_\alpha} H_{ij} H_{j1^*} \langle ij | i^*j^* \rangle (2/D_{ii^*jj^*} + 1/D_{j1^*}) / D_{ij}$$

for $i^*, j^* \in \text{vir}_\alpha$;

(69)

$$E_{b-b}^{(3)} = 2 \sum_{i,j}^{\text{occ}} \langle ij | i^*j^* \rangle / D_{ii^*jj^*} \left[8 \sum_{k>i}^{\text{occ}_\alpha} \langle jk | j^*k^* \rangle \langle ik | i^*k^* \rangle / D_{jj^*kk^*} + \right.$$

$$\left. + \langle ij | i^*j^* \rangle / D_{ii^*jj^*} (\langle ij | ij \rangle + \langle i^*j^* | i^*j^* \rangle - 2 \langle ii^* | ii^* \rangle + \right.$$

$$\left. + 4 \langle ii | i^*i^* \rangle) - 4 \langle ij | i^*j^* \rangle \langle ii | i^*i^* \rangle / (2D_{ii}) \right] +$$

$$+ \sum_i^{\text{occ}_\alpha} [\langle ii | i^*i^* \rangle / (2D_{ii})]^2 (-\langle ii | ii \rangle + 2 \langle ii | i^*i^* \rangle +$$

$$+ 4 \langle ii^* | ii^* \rangle - \langle i^*i^* | i^*i^* \rangle) \text{ for } i^*, j^*, k^* \in \text{vir}_\alpha ;$$
(70)

where

$$H_{ij} = (1 - \delta_{ij}) \langle i | h | j \rangle .$$
(71)

In Eqs (65)–(70) only the restriction that bonding SLMOs are occupied is used; some antibonding SLMOs can be occupied, too. If the restriction, that antibonding SLMOs are unoccupied is considered, the formulae firstly derived by Kvasnička³⁹ for the second-order correction to the energy can be obtained. Finally, notice, that the formula (70) for the third-order correlation energy differs from analogous term published in² by simple replacing the Epstein–Nesbet denominator with the Moller–Plesset one. Therefore, a simple one-to-one correspondence between the original formulation of the PCILO method and the present modified PCILO approach does not exist.

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