

A Modified PCILO Method

I. Second-Order Energy Using CNDO/2 and INDO Hamiltonian Approximations

Roman Boča* and Peter Pelikán**

Slovak Technical University, Faculty of Chemical Technology, 880 37 Bratislava, Czechoslovakia

The perturbative configuration interaction using strictly localized molecular orbitals, called the modified PCILO method, for which the use of the Rayleigh–Schrödinger many-body perturbation theory with the Moller–Plesset Hamiltonian partitioning is characteristic, has been proposed in this communication. On the CNDO/2 and INDO levels of Hamiltonian approximations strictly localized molecular orbitals have been constructed by solving modified Roothaan equations. From the zero and second order energy interatomic distances and harmonic force constants for some diatomic molecules have been calculated. The linear dependence of the correlation energy on the number of valence electrons in the series of the molecules CH_4 , CH_3F , CH_2F_2 , CHF_3 and CF_4 is perfect.

Key words: PCILO method – Localized orbitals

1. Introduction

The original PCILO method (Perturbative Configuration Interaction using Localized Orbitals) formulated by Malrieu *et al.* [1–5] is based on the concept which corresponds to looking at the molecule as an assembly of “two-center, two-electron molecules” (chemical bonds) in interaction treated by perturbation theory. Classical theoretical chemistry and the studies on the localization of the self-consistent-field orbitals provide justification for this approach: the chemical formula is a very good approximation for the study of the molecule (see for instance [6]).

* Department of Inorganic Chemistry.

** Department of Physical Chemistry.

The present work actually uses the original PCILO method in a modified algorithm. The essential features of the PCILO method 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 calculation of the ground-state wave function and energy from a CI matrix or many-body perturbation theory (MBPT). The principal difference between the original and modified PCILO methods lies in the Hamiltonian partitioning scheme: the modified PCILO method (M-PCILO) exploits the Moller–Plesset (MP) Hamiltonian partitioning [7] in contrast to the original PCILO method (O-PCILO), where the Epstein–Nesbet (EN) partitioning [8] is used. The other significant improvements are [9]:

- 1) the introduction of the INDO Hamiltonian approximation in the PCILO method;
- 2) the extension of the applicability to compounds which consist of H to Br atoms, including transition metal atoms;
- 3) the applicability to open shell compounds (in the UHF approach). The use of EMOA hybrid atomic orbitals [10–12] instead of Del Re's ones and the solving of 2×2 Roothaan equations instead of bond-polarity parameter optimization are the minor technical modifications used here.

2. Method

A pair of strictly localized molecular orbitals (SLMO) associated with the i 'th covalent bond: one bonding SLMO, $|i\rangle$, and one antibonding SLMO, $|i^*\rangle$, is constructed in the form of a linear combination of a pair of hybrid atomic orbitals (HAO)

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

$$|i^*\rangle = b'_{i\mu}|\mu\rangle + b'_{iv}|v\rangle. \quad (2)$$

The basis of HAOs, $\{\psi_\mu\}$, is built up from atomic orbitals, $\{\chi_x\}$:

$$|\mu\rangle = \psi_\mu^A = \sum_x^A a_{\mu,x}^A \chi_x^A \quad (3)$$

where the hybridization coefficients, $a_{\mu,x}^A$, on all A'th centres in a polyatomic molecule can be obtained by the EMOA method [10–12].

To describe any bonding situation with respect to the chemical formula of the molecule it is suitable to introduce a discrete topological function $f(A, \mu)$; the value of the topological function is equal to the ordering number of the i 'th chemical bond: $f(A, \mu) = i$. This function enables the convenient selection of a pair of HAO's ψ_μ^A and ψ_ν^B , which are combined into a pair of SLMO's on i 'th bond, on the condition: $f(A, \mu) = i = f(B, \nu)$.

In the ZDO approximation the overlap integral matrices of AO's and HAO's are regarded as unit matrices. Thus the modified 2×2 Roothaan equations for the

LCHAO coefficients, $b_{i\mu}$, in the ZDO approximation take the form:

$$\begin{pmatrix} F_{\mu\mu}^{\kappa} - \varepsilon_i^{\kappa}; & F_{\mu\nu}^{\kappa} \\ F_{\mu\nu}^{\kappa}; & F_{\nu\nu}^{\kappa} - \varepsilon_i^{\kappa} \end{pmatrix} \begin{pmatrix} b_{i\mu}^{\kappa} & b_{i\mu}^{\prime\kappa} \\ b_{i\nu}^{\kappa} & b_{i\nu}^{\prime\kappa} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \quad (4)$$

(for all i 'th bonds) and they have simple explicit solutions. These equations fully correspond to a local Brillouin theorem which states: $\langle i|F|i^*\rangle = 0$. In Eq. (4),¹

$$\begin{aligned} F_{\mu\nu}^{\kappa} &= \langle \psi_{\mu} | F | \psi_{\nu} \rangle \\ &= \langle \mu | h | \nu \rangle + \sum_{\lambda, \delta} [(P_{\lambda\delta}^{\alpha} + P_{\lambda\delta}^{\beta})(\mu\nu | \lambda\delta) - P_{\lambda\delta}^{\kappa}(\mu\delta | \lambda\nu)] \end{aligned} \quad (5)$$

is the matrix element of the one-electron effective Fock operator in the basis of HAO's; the symbol κ designs the α or β set of SLMO's in the unrestricted open shell approach. The charge-density (bond-order) matrix elements $P_{\mu\nu}^{\kappa}$ are defined as

$$P_{\mu\nu}^{\kappa} = (w_i^{\kappa} b_{i\mu}^{\kappa} b_{i\nu}^{\kappa} + w_i^{\prime\kappa} b_{i\mu}^{\prime\kappa} b_{i\nu}^{\prime\kappa}) \delta_{f(A, \mu), f(B, \nu)} \quad (6)$$

where w_i^{κ} is the occupation number of the i 'th bonding ($w_i^{\prime\kappa}$ for antibonding) strictly localized molecular spin-orbital.

Using the standard diagrammatic Rayleigh–Schrödinger MBPT [13] with the Moller–Plesset partitioning of the electronic Hamiltonian, H , into the unperturbed part, H_0 , and the perturbation, H_1 , the well-known ground-state electronic energy terms are obtained:

a) the zero-order energy

$$E^{(0)} = \langle \Phi_0 | H_0 | \Phi_0 \rangle = \frac{1}{2} \sum_i^{\text{occ}} (\langle i | h | i \rangle + \langle i | F | i \rangle) \quad (7)$$

b) the second-order correction to the energy

$$\begin{aligned} E^{(2)} &= \langle \Phi_0 | \left\{ H_1 \frac{1}{E^{(0)} - H_0} H_1 \right\}_C | \Phi_0 \rangle \\ &= \sum_i^{\text{occ}} \sum_j^{\text{vir}} \frac{|\langle i | F | j \rangle|^2}{\varepsilon_i - \varepsilon_j} + \frac{1}{2} \sum_{i,k}^{\text{occ}} \sum_{j,l}^{\text{vir}} \frac{(ij | kl) [(ij | kl) - (il | kj)]}{\varepsilon_i + \varepsilon_k - \varepsilon_j - \varepsilon_l} \end{aligned} \quad (8)$$

where the subscript C means that only the connected diagrams contribute. In Eq. (8),

$$\langle i | F | j \rangle = \langle i | h | j \rangle + \sum_k^{\text{occ}} [(ij | kk) - (ik | kj)] \quad (9)$$

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

$(ij | kl) = \int \int \varphi_i^*(1) \varphi_k^*(2) \frac{1}{r_{12}} \varphi_j(1) \varphi_l(2) d\tau_1 d\tau_2$

is the matrix element of the one-electron effective Fock operator; $\varepsilon_i = \langle i|F|i\rangle$ is the one-electron orbital energy; symbol occ means the occupied spinorbitals included in the unperturbed ground-state eigenvector, $|\Phi_0\rangle$, and vir means unoccupied (virtual) spinorbitals. As the polarization term by the use of SLMO's vanishes, the monoelectronic part of the second-order correction to the energy

$$E_{\text{mono}}^{(2)} = \sum_i^{\text{occ}} \sum_{j \neq i^*}^{\text{vir}} \frac{|\langle i|F|j\rangle|^2}{\varepsilon_i - \varepsilon_j} \quad (10)$$

is directly equal to the delocalization energy. Integrating over the spin-coordinates in Eqs. (7–9), the separate formulae for the closed shell and unrestricted open-shell system can be easily obtained. Introducing the CNDO/2 and INDO Hamiltonian approximations [14] into Eqs. (7–9) the resulting formulae are rapidly simplified. The higher-order contributions to the energy can be obtained by applying standard diagrammatic technique, taking into account the diagrams with more than two vertices.

3. Results

Our calculations are based on three fundamental steps:

- 1) the construction of the basis of HAO's by the EMOA method;
- 2) the construction of SLMO's using CNDO/2 and INDO Hamiltonian approximations [14] in the modified 2×2 Roothaan equations (4); the calculation of the zero-order ground-state electronic energy;
- 3) the calculation of the second-order correction to the energy by M-PCILO method.

Calculations in experimental geometries [15, 16] of 10 small molecules using the valence s - p basis of Slater AO's have been performed. In the individual molecules the following bonding models have been considered:

- a) the bonding model with σ bonds only: CH_4 , CH_3F , CH_2F_2 , CHF_3 , CF_4 , LiH , HF , LiF , BeF_2 ;
- b) the bonding model with σ and π bonds: CO , LiF , BeF_2 .

The calculated zero-order ground-state electronic energy, $E^{(0)}$, and the terms of the second-order correction to the energy: the monoelectronic term, $E_{\text{mono}}^{(2)}$, and the bielectronic term, $E_{\text{bi}}^{(2)}$, by the M-PCILO method are listed in Table 1. The monoelectronic term (equal to the delocalization energy) gives information about the extent of the suitability of the localized bonding model of a molecule: if the term $E_{\text{mono}}^{(2)}$ is small, the localized bonding model is suitable for the description of the collective molecular properties in zeroth order of the perturbation theory (PT). For example, the bonding model with σ bonds only of the BeF_2 molecule badly describes the collective molecular properties in zeroth order of PT, as the delocalization energy is too large. A very interesting aspect of our calculations is the dependence of the electronic energy terms on the use of a molecular bonding model. For the LiF molecule two quite different bonding models have been considered. Since the zeroth order ground-state electronic energies for these models

Table 1. Electronic energy (in eV)

Mole- cule	CNDO/2 Hamiltonian					INDO Hamiltonian				
	Zero-order energy		Second-order correction			Zero-order energy		Second-order correction		
	$E^{(0)} - E^{\text{SCF}}$	$-E^{(0)}$	$-E_{\text{mono}}^{(2)}$	$-E_{\text{bi}}^{(2)}$	$-E^{(2)}$	$E^{(0)} - E^{\text{SCF}}$	$-E^{(0)}$	$-E_{\text{mono}}^{(2)}$	$-E_{\text{bi}}^{(2)}$	$-E^{(2)}$
LiH	0.078	38.545	0.039	0.234	0.273	0.236	38.199	0.077	0.256	0.332
HF	3.404	879.787	2.010	0.138	2.148	3.323	844.190	2.005	0.228	2.233
CO ^b	2.988	984.737	1.853	2.333	4.187	3.696	953.827	2.393	2.320	4.713
LiF ^a	4.410	815.180	3.032	0.059	3.091	4.560	779.917	3.092	0.091	3.183
LiF ^b	0.290	819.300	0.156	0.622	0.778	0.467	784.010	0.154	0.547	0.701
BeF ₂ ^a	13.758	2076.163	9.693	0.176	9.870	13.723	2005.005	9.642	0.308	9.950
BeF ₂ ^b	6.844	2083.077	4.139	0.875	5.014	6.857	2011.871	4.099	0.877	4.976
CH ₄	0.045	534.235	0.031	0.649	0.679	0.154	527.256	0.127	0.962	1.089
CH ₃ F	4.164	1626.951	2.887	0.735	3.623	4.357	1584.328	3.136	1.148	4.284
CH ₂ F ₂	8.968	2961.564	6.375	0.805	7.180	9.262	2883.356	6.780	1.315	8.092
CHF ₃	14.345	4553.462	10.437	0.862	11.299	14.706	4439.781	10.971	1.462	12.434
CF ₄	20.234	6371.828	15.036	0.938	15.974	20.541	6222.840	15.628	1.625	17.253

^aBonding model with σ -bonds only.

^bBonding model with σ - and π -bonds.

differ from each other by 4 eV, the corrected second-order energies differ only by 2 eV. A similar situation by M-PCILO calculations of the BeF₂ molecule in two different bonding models have been observed: the difference in the zeroth order energies is approximately 7 eV and the difference in the corrected second-order energies is about 2 eV. It is found that the corrected second-order ground-state electronic energy by the M-PCILO method is little sensitive to the basis of the SLMO's.

The zero-order ground-state electronic energy based on (canonical) MO LCAO SCF calculations, E^{SCF} , using Pople's original approach [14] has been obtained and the quantity $E^{(0)} - E^{\text{SCF}}$ is also included in Table 1. This quantity represents a part of the energy which corresponds to the sum of all diagrams with one-particle vertices in the framework of MBPT. Here we see that in the M-PCILO method the higher-order mono-electronic contributions to the energy, in general, must be considered, if the SCF level of approximation for the energy with the perturbation expression $E_0 = E^{(0)} + E_{\text{mono}}^{(2)} + E_{\text{bi}}^{(2)} + E_{\text{mono}}^{(3)} + \dots$ has to be overcome. However, in the original PCILO method the second order of PT is already sufficient, as the EN denominator in the second order of perturbation provides a larger contribution to the energy.

We note that in the PCILO method both the zero-order and corrected energies depend on the basis of the HAO's. In O-PCILO the lone pair lobes are fixed in directions to the fictitious atoms and their arrangement in space, especially their "distances", have a significant influence on the energy; so that in O-PCILO the criteria for the choice of HAO's are not uniquely defined. In M-PCILO the zero-order energy is invariant with respect of the fixation of occupied lone-pair lobes;

these are fixed to be orthogonal between themselves and with bonding HAOs and equivalent in their *s*-characters.

For diatomic molecules the potential curve around the energetic minimum has been fitted by a quadratic function and the equilibrium interatomic distance, r_e , and the harmonic force constant, k_e , have been calculated (Table 2). Interatomic

Table 2. Equilibrium interatomic distances and harmonic force constants

Mole- cule	CNDO/2 Hamiltonian									INDO Hamiltonian		
	Exptl. ^b	M-PCILO ^c order:		SCF + PCI ^c order:		Original PCILO ^d order:			M-PCILO ^c order:		SCF	
		0.	2.	0.	2.	0.	2.	3.	0.	2.	0.	
A) Equilibrium interatomic distances (in 10^{-10} m)												
LiH	1.595	1.574	1.588	1.574	1.590	1.589	1.594	1.594	1.570	1.584	1.570	
HF	0.917	0.986	1.003	1.003	1.014	1.004	1.021	1.020	0.990	1.011	1.010	
LiF ^a	1.51	2.111	2.117	2.163	2.159	2.152	2.139	2.145	2.124	2.128	2.172	
CO ^a	1.128	1.183	1.216	1.194	1.222	1.184	1.241	1.189	1.185	1.222	1.198	
B) Harmonic force constants (in N/cm)												
LiH	1.02	1.95	1.92	1.95	1.92	2.03	1.91	1.89	1.93	1.89	1.91	
HF	9.59	22.20	16.36	16.58	16.29	16.74	15.89	15.98	22.09	16.29	16.74	
LiF ^a	2.50	2.13	2.18	1.91	1.87	2.03	2.22	2.23	2.12	2.17	1.87	
CO ^a	19.02	45.59	35.33	45.18	34.62	33.46	28.98	48.98	45.51	33.78	35.22	

^a Bonding model with σ - and π -bonds.

^b Krasnov, K. S., Timoschinin, V. S., Danilova, T. G., Khandozhko, S. V.: *Molekulyarnye postoyannye neorganicheskikh soedinenii*. Khimiya, Leningrad, 1968.

^c Moller–Plesset partitioning.

^d Epstein–Nesbet partitioning.

distances calculated by the M-PCILO method possess values similar to those obtained by the MO LCAO SCF calculations and also by O-PCILO calculations. Force constants calculated from the zero-order ground-state energy are somewhat worse than the MO LCAO SCF values. Since the SCF level of approximation for the energy with the second-order corrected energy in the M-PCILO calculations, in general, is not overcome, the force constants calculated in the second order of PT are somewhat better than the values obtained from MO LCAO SCF energy. As the INDO approach includes a larger part of the correlation energy than the CNDO/2 approach, a little improvement of the force constants in the second order of PT is registered with respect to the CNDO/2 calculations. Comparing interatomic distances and harmonic force constants calculated by the M-PCILO method with those obtained from MO LCAO SCF + PCI (perturbative configuration interaction with Moller–Plesset Hamiltonian partitioning) calculations we conclude that the negligible improvement of the force constants in the second order of

PT with respect to experiment is rather a consequence of the use of the simple CNDO/2 Hamiltonian approximation than an effect of a failure of the perturbation technique.

In Fig. 1, the correlation energy, $E_{bi}^{(2)}$, versus number of valence electrons, n_e , for the series of molecules CH_4 , CH_3F , CH_2F_2 , CHF_3 and CF_4 is plotted. The

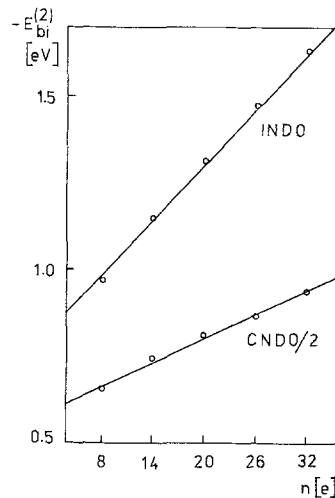


Fig. 1. Correlation energy by modified PCILO method versus number of valence electrons for CH_4 , CH_3F , CH_2F_2 , CHF_3 and CF_4 molecules

linear dependence is perfect, so that the correct dependence of the correlation energy on the number of particles in M-PCILO calculations is demonstrated.

4. Discussion

It is well-known that to the most time-consuming operations in MO LCAO SCF + PCI calculations belong:

- 1) the diagonalization procedure in the SCF step;
- 2) the transformation of integrals into the basis of MO's and handling them.

The success of the PCILO method lies in the rapid reduction of these steps. In the PCILO method the zero-order ground-state electronic wave function $|\Phi_0\rangle$ is constructed from SLMO's and two alternative methods for obtaining SLMO's have been proposed:

- 1) the optimization of bond-polarity parameters (used in O-PCILO);
- 2) the solution of a set of modified 2×2 Roothaan equations (used in M-PCILO).

Both these methods give the zero-order ground-state electronic energy which is higher to some extent than the SCF energy, calculated using the canonical MO's or intrinsically localized MO's (according to Ruedenberg's [18], Boys' [19] and von Niessen's [20] localization criteria). As the SLMO's are chosen to correspond to the chemical formula of a molecule, the corresponding ground-state wave

function is a good approximation for the study of the molecule. This conclusion is also confirmed by our results of atomic charges, dipole moments and NMR coupling constants between “bonded” atoms, which will be published later. As a diagonalization procedure is unnecessary for the construction of SLMO’s, the SLMO’s may be chosen so that much computing time is saved. Secondly, the time-consuming N^5 step in calculating the two-electron integrals over MO’s ($ij | kl$) is rapidly reduced by the use of SLMO’s to the simple sum of 16 (or less than 16) terms. It is the main advantage of the PCILO method.

To compare the modified PCILO method with the original version, we note that the principal difference between O-PCILO and M-PCILO lies in the Hamiltonian partitioning scheme. It is well known that from the four most investigated many-body perturbation techniques: Rayleigh–Schrödinger (RS) with MP or EN partitioning and Brillouin–Wigner (BW) with MP or EN partitioning, only the simplest RS–MP procedure is invariant with respect to mixing of degenerate orbitals. The RS–MP procedure also provides the correct dependence of the correlation energy on the number of particles. Therefore, it is preferred as a general unambiguous perturbation technique [17]. According to Claverie *et al.* [21, 22], the RS–EN procedure converges faster than the RS–MP procedure for the series of polyenes. These authors have preferred the RS–EN procedure. However, Bartlett and Shavitt [23] have shown by *ab initio* MBPT calculations that the MP series converges faster than the EN series in higher orders, in contrast to previous expectations [21, 22]. The single fact that the quantity $E_{\text{mono}}^{(2)}/(E^{\text{SCF}} - E^{(0)})$ in the O-PCILO is equal to 1 ± 0.1 instead of 0.7 in M-PCILO (at the equilibrium geometry of some molecules) did not favor the O-PCILO method (EN denominator, respectively). Ostlund and Bowen [17] have shown that the RS–EN procedure also offers incorrect potential curves with a local maximum and approaching the dissociation limit from above. Finally, the RS–EN, BW–MP and BW–EN procedures all include the higher-order terms or diagrams, and they are not directly applicable in the framework of the second-quantization formalism. However, the modified partitioning procedures with “denominator shift” have been proposed [24–27]; they can be useful in the second-quantization formulation of MBPT, but applications of these methods should still be studied.

In the M-PCILO method with the MP partitioning the effect of overcounting of some diagrams in higher orders of PT does not exist in contrast to the O-PCILO method with EN partitioning. The estimated second-order corrections to the ground-state energy in the M-PCILO method are smaller with respect to O-PCILO, but the dependence of the correlation energy on the number of electrons is correct. The small improvement of the harmonic force constants is rather a consequence of the use of the simple ZDO Hamiltonian approximations than an effect of the failure of the perturbation technique.

Finally the program written in FORTRAN IV enables the study of closed- or open-shell compounds consisting of H to Br atoms, including transition metal atoms, by much saving of computing time. The CNDO/2, INDO and IEHT Hamiltonian approximations can be used by this program. The characteristics of

transition metal compounds and the weak molecular interactions have also been studied, and the results obtained will be published in forthcoming papers. The third-order correction to the energy and the density matrix, dipole moments and coupling constants calculated from the first- and second-order wave function may be included in our program in the near future.

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