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An Extended PCILO Method

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The perturbative configuration interaction using localized orbitals (the PCILO method) was extended in the way that current limitations to the two-centre bond approach were overcome. The localized molecular orbitals contain an arbitrary number of the basis set components; this follows from the a priori stated localized bonding model of a molecule. The extended PCILO method was formulated for the CNDO, INDO and NDDO Hamiltonian approximations. The configuration interaction was performed using the Rayleigh–Schrödinger many-body perturbation theory with the Møller–Plesset type of Hamiltonian partitioning, similar to that used in the so-called modified PCILO method. Applications to molecules with semi-localized and/or semi-delocalized bonds, as benzene or diborane, are presented.

Key words: PCILO method – Localized orbitals.

1. Introduction

Several years ago a group of authors formulated the concept of the PCILO (Perturbative Configuration Interaction using Localized Orbitals) method [1–4]. Recently it was revised by other authors missing out the CNDO Hamiltonian approximation and considering the INDO type [5–8]. At the same time, a modified PCILO method including transition metal compounds was elaborated in our Laboratory where either the CNDO-UHF or the INDO-UHF approach was used for open shell systems [9–12]. This last version differs from the above in the sense that it is strictly derived from the diagrammatic Rayleigh–Schrödinger many-body perturbation theory; here the Møller–Plesset Hamiltonian partitioning is used [13] instead of the Epstein–Nesbet type [14, 15].

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The original and also the modified PCILO methods belong to the most popular quantum-chemical methods (see, for instance, the QCPE "Workshop" in 1980 and 1981 [16]), mainly for the following reasons:

(1) the zero-order wave function is obtained in a way being very near to classical chemical conceptions of atomic cores, valence lone pairs and the localized two-centre bonds;

(2) the corresponding computer programs are efficient in the sense that the delocalization and the correlation energy may be obtained saving of the computing time [17, 18].

Thus the PCILO method is based on the concept looking at the molecule as a cluster of "two-centre, two-electron fractions" (localized chemical bonds) being in a mutual interaction. This interaction is treated by the perturbation theory. The use of the perturbation theory is the very effective way to transform a rather poor basis set of localized orbitals to a useful molecular wave function including the electron delocalization and correlation.

The next stage in the development of the PCILO philosophy is the extension to such a localized MOs approach, where not only the strict localizations (two-centre bonds and lone lobes) are considered. This is the scope of the present paper. In the light of this conception the limitations of the original and also of the modified PCILO methods are overcome. No problems are there in applying the extended PCILO method to such compounds as benzene or diborane. However, the expected "working area" of the method covers large molecules (over 100 valence AOs) with "active" (e.g. transition metal) centres. These centres can be described using semi-delocalized MOs while their neighbourhood is approximated via strictly localized MOs. This model allows the application of the many-body perturbation theory up to the third order – in a reasonable computing time. Therefore, applications of the extended PCILO method to chemical reactivity and catalysis are expected in near future.

2. Localized Molecular Orbitals

The way of the construction of localized molecular orbitals (LMO) belongs to the category of external localization methods. Unlike the intrinsic methods, such as those by Edmiston and Ruedenberg [19–21], Boys [22–24], von Niessen [25] or Aufderheide [26, 27], the self-consistent-field level of the energy, E_0^{SCF} (in the given basis set and the Hamiltonian approximation), is not retained.

The basic idea used here lies in the limitation of the number of the basis set functions Ψ_i^A, usually the hybrid atomic orbitals (HAO), in the expansion of individual LMOs ϕ_μ:

$$\phi_\mu = \sum_A \sum_i^A c_{\mu i}^A \Psi_i^A \tag{1}$$

(i is an index of HAO on the atom A). In the other words, some of the LCHAO expanding coefficients $c_{\mu i}^{A}$ are fixed having the zero value. This condition is secured by two assumptions:

(1) a discrete topological function $f(A, i)$ has to be defined a priori; its value is equal to the ordering number, b, of a chemical bond: $f(A, i) = b$;

(2) each LMO is assigned to a certain bond; the relation $g(\mu) = b$ means that the μth LMO corresponds to the bth bond.

Then, for the non-zero expanding coefficients it holds:

$$c_{\mu i}^{A} = c_{\mu i}^{A} \delta_{g(\mu), f(A,i)} \tag{2}$$

(δ is a Kronecker factor). Thus, each LMO ϕ_μ has a limited number N_b of the basis set components being identical with the numerosity of $f(A, i) = g(\mu)$. On the other hand, a sub-set of the basis set functions with the same bond-number b forms a number N_b of LMOs via a linear combination. Such a description is explained in the following four examples in more detail.

(1) If in a molecule only one many-centre chemical bond is considered, then $g(\mu) = 1$ will be valid for all MOs ϕ_μ. Simultaneously it holds that $f(A, i) = 1$ for all A and i, so that all basis set functions contribute to each MO. This is the case of delocalized (e.g. canonical) MOs.

(2) A natural splitting of the basis set and the set of MOs into two groups is represented by the $\sigma - \pi$ separation: for the sub-set of the σ type basis set functions the $f(A, i) = 1$ and $g(\mu \in \sigma) = 1$ are valid while for the sub-group of the π type functions the relations of $f(A, i) = 2$ and $g(\mu \in \pi) = 2$ are fulfilled. If the basis set corresponds to the symmetry orbitals, another natural splitting will occur: each sub-group of the basis set functions and the corresponding MOs are represented by individual irreducible representations of the molecular point group of symmetry (in general this does not exhibit a localized picture).

(3) In the case of strictly localized (two-centre) MOs the bond-size is $N_b = 2$. There exists only one pair of HAOs, Ψ_i^A and Ψ_j^B, for which $f(A, i) = f(B, j) = b$ is valid. Such couple of HAOs is combined into two SLMOs: one bonding and one antibonding SLMO. For lone lobes it holds that $N_b = 1$ and they can be marked as "non-connected" bonds.

(4) A logical extension is the case of three-centre MOs. A trio of HAOs, Ψ_i^A, Ψ_j^B and Ψ_k^C, is used to form three LMOs: one bonding (without a nodal plane), one non-bonding (with one nodal plane) and one antibonding (with two nodal planes). Then $f(A, i) = f(B, j) = f(C, k) = b$ and $N_b = 3$ are valid. This procedure may be easily generalized for an arbitrary number of LCHAO components in individual LMOs. However, unlike the case 1 and 2 the condition (2) corresponds to an external, a priori limitation in the number of self-consistent-field variables (of varied LCHAO coefficients or the bond-order matrix elements), so that the best energy, E_0^{LMO}, obtained by using these LMOs is

$$E_0^{\mathrm{LMO}} > E_0^{\mathrm{SCF}}. \tag{3}$$

Taking into account the condition (2), the expression for the charge density (bond-order) matrix

$$ {}^{s}P_{ij}^{AB} = \sum_{\mu}^{\mathrm{occ}_s} c_{\mu i}^{A;s} c_{\mu j}^{B;s} \tag{4}$$

has to be modified (s means the spin index, α or β, in the unrestricted Hartree–Fock approach and μ runs over occupied MOs). For new density matrix the expression is obtained:

$$ {}^{s}R_{ij}^{AB} = {}^{s}P_{ij}^{AB} \delta_{f(A,i),f(B,j)} . \tag{5}$$

This is the modification which must be considered in the construction of the one-electron effective Fock operator matrix before solving the Roothaan equations. Moreover, in general, LMOs do not form an orthogonal set. However, if the ZDO approximation is used (e.g. in the CNDO, INDO or NDDO framework), this complication will vanish. The corresponding approximation of two-electron integrals has to be applied to the basis set of atomic orbitals χ_t^A. Considering the hybridization procedure on the given atom:

$$\psi_i^A = \sum_t^A a_{i,t}^A \chi_t^A \tag{6}$$

then the coulomb integrals are transformed as follows[1]

$$(i_A j_A | k_B l_B) = \sum_{t,u}^{A} \sum_{v,w}^{B} a_{i,t}^A a_{j,u}^A a_{k,v}^B a_{l,w}^B (t_A u_A | v_B w_B). \tag{7}$$

This general transformation may be somewhat simplified; it depends on additional assumptions accepted in the actual version of the CNDO, INDO or NDDO method. For example, the inclusion of the metal valence d orbitals (the $d-s-p$ type basis set) makes the CNDO algorithm more complex in comparison with the $s-p$ type basis set. In the latter case, due to the orthogonality conditions for HAOs, the two-electron integrals do not depend on the hybridization:

$$(i_A j_A | k_B l_B) = \gamma_{AB} \delta_{ij} \delta_{kl}. \tag{8}$$

On the contrary, there are four types of integrals γ_{AB} distinguished in the case of transition metals (i.e. the $S-S$, $S-D$, $D-S$ and $D-D$ type [28]) and no

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[1]

$$(ij|kl) = \langle ik|jl \rangle = \iint \phi_i^*(1)\phi_k^*(2)\frac{1}{r_{12}}\phi_j(1)\phi_l(2)\, d\tau_1\, d\tau_2$$

$$\langle ik||jl \rangle = \langle ik|jl \rangle - \langle ik|lj \rangle$$

$$\langle i|h|j \rangle = \int \phi_i^*(1)\hat{h}\phi_j(1)\, d\tau_1$$

significant simplifications are achieved, for example:

$$
\begin{aligned}
(i_A j_A|k_B l_B) = {} & \gamma_{AB}(S-S) \sum_{t}^{s,p}{}^{A}\, a^A_{it} a^A_{jt} \sum_{v}^{s,p}{}^{B}\, a^B_{kv} a^B_{lv} \\
& + \gamma_{AB}(S-D) \sum_{t}^{s,p}{}^{A}\, a^A_{it} a^A_{jt} \sum_{w}^{d}{}^{B}\, a^B_{kw} a^B_{lw} \\
& + \gamma_{AB}(D-S) \sum_{u}^{d}{}^{A}\, a^A_{iu} a^A_{ju} \sum_{v}^{s,p}{}^{B}\, a^B_{kv} a^B_{lv} \\
& + \gamma_{AB}(D-D) \sum_{u}^{d}{}^{A}\, a^A_{iu} a^A_{ju} \sum_{w}^{d}{}^{B}\, a^B_{kw} a^B_{lw}.
\end{aligned}
\tag{9}
$$

The types of non-zero two-electron integrals between HAOs for various methods and basis sets used are listed in Table 1. They are coming into the Fock-operator matrix elements (described often elsewhere). Their final expressions may be written as follows

$$
{}^sF^{AB}_{ij} = H^{AB}_{ij} + \sum_m X^s_m \tag{10}
$$

where the individual increments X^s_m over two-electron integrals are listed in Table 2 ($H^{AB}_{ij} = \langle i|h|j\rangle$ are the matrix elements of the one-electron part of the Fock operator).

Some remarks are required for the performance of the self-consistent-field procedure. An important feature of the LCHAO coefficient matrix $\boldsymbol{C}$ is that, after an appropriate re-ordering, it takes up a block diagonal form. The size of each block is equal to the number of components per bond N_b, so that there is a one-to-one correspondence between blocks and bonds. For example, in the benzene molecule the π ring is considered as one six-centre bond, thus having the bond-size $N_b = 6$. Six HAOs (in this case pure AOs) are used to form six LMOs but only three of them are doubly occupied.

Due to the block-diagonal form of the matrix $\boldsymbol{C}$, the matrices $\boldsymbol{R}$ and $\boldsymbol{F}$ also take up the block-diagonal form. Because in the ZDO approximation the overlap

Table 1. The non-zero two-electron integrals between HAOs using various basis sets of AOs for methods based on the ZDO approximation

Basis set type	Method	Non-zero integrals	
		One-center	Two-center
$s-p$	CNDO	$(i_A i_A \mid j_A j_A)$	$(i_A i_A \mid j_B j_B)$
	INDO	$(i_A j_A \mid k_A l_A)$	$(i_A i_A \mid j_B j_B)$
	NDDO	$(i_A j_A \mid k_A l_A)$	$(i_A j_A \mid k_B l_B)$
$d-s-p$	CNDO INDO NDDO	$(i_A j_A \mid k_A l_A)$	$(i_A j_A \mid k_B l_B)$

Table 2. The increments to the Fock-operator matrix elements over two-electron integrals

Indices[a]				Increments X^s_m for the method[b]		
A	i	A'	i'	NDDO	INDO	CNDO
$A \in T$	i	$A \in T$	i	$X_1+X_2+X^s_4$	$X_1+X_3+X^s_4$	$X_1+X_3+X^s_4$
$A \notin T$	i	$A \notin T$	i	$X_1+X_2+X^s_4$	$X_1+X_3+X^s_4$	$X_1+X_3+X^s_5$
$A \in T$	i	$A \in T$	j	$X_6+X_7+X^s_9$	$X_6+X_8+X^s_9$	$X_6+X_8+X^s_9$
$A \notin T$	i	$A \notin T$	j	$X_6+X_7+X^s_9$	X^s_9	X^s_{10}
$A \in T$	i	$B \in T$	j	X^s_{11}	X^s_{11}	X^s_{11}
$A \in T$	i	$B \notin T$	j	X^s_{11}	X^s_{12}	X^s_{12}
$A \notin T$	i	$B \in T$	j	X^s_{11}	X^s_{13}	X^s_{13}
$A \notin T$	i	$B \notin T$	j	X^s_{11}	X^s_{14}	X^s_{14}

[a] Atomic indices: A, B; orbital indices: i, j. $A \in T$ means that A is a transition metal ($d-s-p$ type element); $A \notin T - a$ non-transition metal ($s-p$ type element).

[b] Individual increments X^s_m are listed below:

$$X_1 = \sum_{\substack{B \neq A \\ B \in T}} \sum_k^B \sum_l^B R_{kl}^{BB}(i_A i_A | k_B l_B)$$

$$X_2 = \sum_{\substack{B \neq A \\ B \notin T}} \sum_k^B \sum_l^B R_{kl}^{BB}(i_A i_A | k_B l_B)$$

$$X_3 = \sum_{\substack{B \neq A \\ B \notin T}} \sum_k^B R_{kk}^{BB}(i_A i_A | k_B k_B)$$

$$X^s_4 = \sum_k^A \sum_l^A [R_{kl}^{AA}(i_A i_A | k_A l_A) - {}^sR_{kl}^{AA}(i_A l_A | k_A i_A)]$$

$$X^s_5 = \sum_k^A R_{kk}^{AA}(i_A i_A | k_A k_A) - {}^sR_{ii}^{AA}(i_A i_A | i_A i_A)$$

$$X_6 = \sum_{\substack{B \neq A \\ B \in T}} \sum_k^B \sum_l^B R_{kl}^{BB}(i_A j_A | k_B l_B)$$

$$X_7 = \sum_{\substack{B \neq A \\ B \notin T}} \sum_k^B \sum_l^B R_{kl}^{BB}(i_A j_A | k_B l_B)$$

$$X_8 = \sum_{\substack{B \neq A \\ B \notin T}} \sum_k^B R_{kk}^{BB}(i_A j_A | k_B k_B)$$

$$X^s_9 = \sum_k^A \sum_l^A [R_{kl}^{AA}(i_A j_A | k_A l_A) - {}^sR_{kl}^{AA}(i_A l_A | k_A j_A)]$$

$$X^s_{10} = -{}^sR_{ij}^{AA}(i_A i_A | j_A j_A)$$

$$X^s_{11} = -\sum_k^B \sum_l^A {}^sR_{kl}^{BA}(i_A l_A | k_B j_B)$$

$$X^s_{12} = -\sum_l^A {}^sR_{lj}^{AB}(i_A l_A | j_B j_B)$$

$$X^s_{13} - \sum_k^B {}^sR_{kj}^{BA}(i_A i_A | k_B j_B)$$

$$X^s_{14} = -{}^sR_{ji}^{BA}(i_A i_A | j_B j_B)$$

where $R_{ij}^{AB} = {}^{\alpha}R_{ij}^{AB} + {}^{\beta}R_{ij}^{AB}$.

integral matrix between LMOs is considered to be a unit matrix, the net result is a full factorization of Roothaan equations into a set of matrix equations:

$$ {}^{s}\boldsymbol{F}_b({}^{s}\boldsymbol{C}_b)^T = ({}^{s}\boldsymbol{C}_b)^T\, {}^{s}\boldsymbol{\Lambda}_b \tag{11}$$

for spin index $s = \alpha$ or β ($\boldsymbol{\Lambda}_b$ is a diagonal matrix of eigenvalues – the orbital energies). Since individual N_bs are many times less than the total basis set size, saving much of the computing time is achieved in the step of the eigenvalue-eigenvector problem (each block can be diagonalized independently).

The following algorithm is recommended for the self-consistent-field procedure. First, the necessary one- and two-electron integrals are calculated in the basis set of AOs. They are successively transformed into the basis set of HAOs; the matrix $\boldsymbol{H}$ and the list of two-electron integrals are kept either in the core memory or on the external data set device. Secondly, the initial approximation of the matrix $\boldsymbol{C}^{(0)}$ is chosen. Then the density matrix $\boldsymbol{R}^{(0)}$ is obtained using Eqs. (4) and (5). Next, the Fock-operator matrix $\boldsymbol{F}^{(1)}$ is constructed via Eq. (10) and Table 2. This matrix is re-ordered so that its block-diagonal form is obtained. Each block is diagonalized independently and thus the sets of eigenvector sub-matrices $\{\boldsymbol{C}_b^{(1)}\}$ and the eigenvalues sub-vectors $\{\boldsymbol{\Lambda}_b^{(1)}\}$ are obtained. They are used to form the next approximation of matrix $\boldsymbol{C}^{(1)}$ and the vector $\boldsymbol{\Lambda}^{(1)}$. Then the vector $\boldsymbol{\Lambda}^{(1)}$ undergoes re-ordering in ascending order of the eigenvalues. The occupation numbers are attributed to the lowest eigenvalues and the corresponding eigenvectors are used in constructing the next approximation of $\boldsymbol{R}^{(1)}$. The procedure is repeated until a self-consistency is achieved.

3. Perturbative Configuration Interaction

In accordance with the arguments suggested for the modified PCILO method [10–12], the Rayleigh–Schrödinger many-body perturbation theory is preferred for performing the configuration interaction. The formulae for the electrostatic correlation energy (using the diagrammatic technique and the Møller–Plesset type of Hamiltonian partitioning) were derived elsewhere [11]. Therefore, only the final result is here briefly presented.

The matrix elements of the one-electron effective Fock operator in the basis set of molecular spin-orbitals are defined as follows:

$$F_{ij} = \langle i|\hat{F}|j\rangle = \langle i|\hat{h}|j\rangle + \sum_{k}^{\text{occ}} \langle ik\|jk\rangle. \tag{12}$$

Only the diagonal elements

$$\varepsilon_i = \langle i|\hat{F}|i\rangle \tag{13}$$

are considered in the unperturbed Hamiltonian $\hat{H}_0$ while the off-diagonal elements are included in the perturbation $\hat{H}_1$. The ground-state electronic energy is expressed by a series:

$$E_0^{el} = \sum_{n=0}^{\infty} E_0^{(n)} \tag{14}$$

where the individual energy terms are:

(1) the zero-order (SCF) energy

$$E_0^{(0)} = \tfrac{1}{2}\sum_{i}^{\mathrm{occ}} (\langle i|\hat{h}|i\rangle + \varepsilon_i) \tag{15}$$

(2) the first-order correction

$$E_0^{(1)} = 0 \tag{16}$$

(3) the second-order correction

$$E_0^{(2)} = E_{m-m}^{(2)} + E_{b-b}^{(2)} \tag{17}$$

where

$$E_{m-m}^{(2)} = \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{vir}} (F_{ia})^2 / D_{ia} \tag{18}$$

is a part of the delocalization energy, and

$$E_{b-b}^{(2)} = \sum_{i,j}^{\mathrm{occ}} \sum_{a,b}^{\mathrm{vir}} (\langle ij\|ab\rangle)^2 / D_{iajb} \tag{19}$$

being a part of the correlation energy;

(4) the third-order correction

$$E_0^{(3)} = E_{m-m}^{(3)} + E_{b-b}^{(3)} + E_{m-b}^{(3)} \tag{20}$$

where

$$E_{m-m}^{(3)} = \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{vir}} F_{ia}/D_{ia} \left(\sum_{c}^{\mathrm{vir}} F_{ac}F_{ci}/D_{ic} - \sum_{k}^{\mathrm{occ}} F_{ak}F_{ki}/D_{ka} \right) \tag{21}$$

is the third-order delocalization energy term over two Hugenholtz diagrams,

$$\begin{aligned} E_{b-b}^{(3)} = \sum_{i,j}^{\mathrm{occ}} \sum_{a,b}^{\mathrm{vir}} \langle ij\|ab\rangle / D_{iajb} \Bigg(& \sum_{k}^{\mathrm{occ}} \sum_{c}^{\mathrm{vir}} \langle cb\|kj\rangle \langle ka\|ci\rangle / D_{kcjb} \\ & + \tfrac{1}{8} \sum_{c,d}^{\mathrm{vir}} \langle ab\|cd\rangle \langle cd\|ij\rangle / D_{icjd} + \tfrac{1}{8} \sum_{k,l}^{\mathrm{occ}} \langle ab\|kl\rangle \langle kl\|ij\rangle / D_{kalb} \Bigg) \end{aligned} \tag{22}$$

being the third-order correlation energy term over three Hugenholtz diagrams, and

$$\begin{aligned} E_{m-b}^{(3)} = \sum_{i,j}^{\mathrm{occ}} \sum_{a,b}^{\mathrm{vir}} \langle ij\|ab\rangle / D_{iajb} \Bigg\{ & F_{ia}F_{jb}(3/D_{jb} + 1/D_{ia}) \\ & - \left[\sum_{k}^{\mathrm{occ}} (\langle ij\|kb\rangle F_{ka}/D_{ka} + \tfrac{1}{2}\langle kj\|ab\rangle F_{ik}/D_{kajb}) \right] \\ & + \left[\sum_{c}^{\mathrm{vir}} (\langle cj\|ab\rangle F_{ic}/D_{ic} + \tfrac{1}{2}\langle ij\|cb\rangle F_{ac}/D_{icjb}) \right] \Bigg\} \end{aligned} \tag{23}$$

represents the energy term over remaining nine Hugenholtz diagrams.

Here, indices i, j, k, l run over occupied spin-orbitals and a, b, c, d over virtual ones. The denominator parts are defined as $D_{ia} = \varepsilon_i - \varepsilon_a$ and $D_{iajb} = D_{ia} + D_{jb}$. Integrating over the spin-coordinates in Eqs. (12)–(23), the separate formulae for the closed shell and the unrestricted open shell systems can easily be derived. In certain special cases some simplifications may be obtained. For example, the CNDO Hamiltonian approximation on the valence $s-p$ basis set of AOs leads for strictly localized MOs to the significant reduction: the six-fold summation in term $E^{(3)}_{b-b}$ simplifies only to three-fold one [11].

4. Computer Program PCILO3

The extended PCILO method was realized by the computer program PCILO3 [29] which exceeds 13 000 cards. Its basic features are briefly mentioned below.

(1) All functions running in the previous level (the modified PCILO method and the computer program PCILO2 [19]) are included as a part of PCILO3.

(2) The case of delocalized (canonical) MOs is realized with the possibility of a variable damping procedure (necessary often for transition metal compounds).

(3) There are no principal restrictions for the number of components per LMOs. Therefore, the last case represents a middle way between above limit cases.

(4) An automatic geometry optimization acts over cartesian or selected bonding coordinates (bond lengths, bond and dihedral angles). They can be optimized on the zero-order (SCF) energy, on the second-order delocalization energy, on the full second-order energy or on the full third-order energy. However, considering the complicated energy expression in the perturbative configuration interaction, the geometry optimization cannot be based on gradient methods.

(5) The program covers the CNDO/2 parametrization for elements from H to Br and the INDO parametrization from H to Cu including the first transition metal row elements. All parameters can be read from cards in a non-standard run for elements from H to Xe.

(6) The hybrid atomic orbitals may be read or produced by the EMOA method [30–32].

(7) The case of open shell systems is realized in the unrestricted Hartree–Foch approach.

(8) The usual software (e.g. IBM) and a current language (FORTRAN IV) were used as well as the overlay structure.

5. Applications and Discussion

First, two practical questions require an answer:

(1) how to select an appropriate localized bonding model of a molecule;

(2) how to measure its quality.

Canonical (in principle delocalized) MOs are the most frequently used approach, because they are the most simple orbitals to calculate the SCF energy. They also represent a good starting point for the study of excited and ionized states owing to their proper symmery. However, the net result of the self-consistent-field procedure is the symmetric bond-order matrix ${}^{s}P$, which is invariant with respect to a unitary transformation of molecular orbitals. Thus, the LMOs obtained by intrinsic methods of localization produce the same bond-order matrix. This is a non-scalar (tensor) criterion to measure the quality of external localization methods. A scalar criterion is, of course, the energy. The localization defect

$$\Delta_{\mathrm{loc}} = E_0^{\mathrm{SCF}} - E_0^{\mathrm{LMO}} \tag{24}$$

and the relative localization defect

$$X_{\mathrm{loc}} = \Delta_{\mathrm{loc}} / E_T^{\mathrm{SCF}} \tag{25}$$

may be used to measure the quality of the localization procedure (the subscript T designates the total molecular energy).

The bond-order matrix can be used in definition of the Wiberg (bond strength) index W_{AB} [33] which gives a direct information about the multiplicity of a bond between atoms A and B. The value of $W_{AB} \approx 1$ corresponds to a single bond, $W_{AB} \approx 2$ to a double bond, etc. A non-integer value of $W_{AB} \approx 1.5$ indicates that the concept of localized two-centre bonds fails, so that a semi-delocalized, many-centre description is required.

The classical example of a compound where the concept of two-centre bonds fails is the benzene molecule ($W_{\mathrm{C-C}} \approx 1.5$). An individual Kekule structure exhibits the incorrect spatial symmetry of the electronic wave function. The geometry optimization performed for such a structure leads to the prediction of the D_{3h} instead of right D_{6h} symmetry. At least two resonance structures must be considered in order to obtain an acceptable picture. Additional Dewar-type structures can be included in a more sophisticated approach via the valence-bond method. Thus, neither the original, nor the modified PCILO methods can be successfully applied to aromatic compounds. There are, however, no serious reasons to restrict ourselves only to the two-centre bond approach.

The systems under study are listed in Table 3; the simplest approach (the CNDO/2 Hamiltonian approximation and the second-order perturbation theory) is presented here. In order to describe a bonding model used in a more condensed form, the following notation was proposed: $N_1(n_1)/N_2(n_2)/\cdots/N_x(n_x)$. The first number N_x means the bond-size of equivalent or similar bonds while the second number n_x denotes their numerosity. The results show that the localized bonding model used is a good starting point to study the molecule: the relative localization defect is less than 1%. The localization defect is partially compensated in the second step of the PCILO method; this compensation seems to be satisfactory since the compensation index:

$$X_{\mathrm{com}} = E_{m-m}^{(2)} / \Delta_{\mathrm{loc}} \tag{26}$$

Table 3. Calculated energy terms using CNDO/2 Hamiltonian

System[a]	HAOs	Bonding model	Total energy terms (eV)				X_{loc} (%)	X_{com} (%)
			$-E_T^{(0)}$	$-E_{m-m}^{(2)}$	$-E_{b-b}^{(2)}$	$-E_T^{(2)}$		
H_2O	[b]	2(2)/1(2)	538.23	1.54	0.55	540.31	0.56	51.2
	[b]	4(1)/1(2)	538.68	1.13	0.57	540.38	0.47	44.4
	[c]	6(1)	541.23	0.0	0.65	541.88		
B_2H_6	[d]	3(2)/2(2)/2(2)	340.41	1.49	1.09	343.00	0.56	78.3
	[c]	14(1)	342.31	0.0	1.16	343.47		
C_6H_6	[b]	6(1)/2(6)/2(6)	1275.47	4.60	5.49	1285.56	0.48	74.9
	[c]	30(1)	1281.61	0.0	24.61	1306.21		
$CuBr_4^{2-}$	[d]	2(4)/1(5)/1(12)	2641.30[e]	6.56	0.15	2648.01	0.34	73.4
	[d]	8(1)/1(5)/1(12)	2641.44	6.62	0.15	2648.21	0.33	75.2
	[d]	13(1)/1(12)	2641.88	[f]			0.32	
	[c]	25(1)	2650.24[e]	[f]				

[a] Geometries used: H_2O in C_{2v} symmetry, $R_{O-H} = 1.03$, $\measuredangle HOH = 104.0^0$; B_2H_6 in D_{2h} symmetry, $R_{B-H} = 1.187$, $R_{B-H'} = 1.334$ (H' as a bridge), $\measuredangle HBH = 121.5^0$, $R_{B-B} = 1.770$; C_6H_6 in D_{6h} symmetry, $R_{C-C} = 1.387$, $R_{C-H} = 1.084$; $CuBr_4^{2-}$ in T_d symmetry, $R_{Cu-Br} = 2.34$. Distances in units of 10^{-10} m.

[b] HAOs fixed by the EMOA method.

[c] Canonical MOs.

[d] Canonical HAOs: sp^3 on B, Cu and Br.

[e] The energy slightly differs from that previously reported [12] as a consequence of modification in the one-center integrals for transition metals. This, however, does not effect conclusions.

[f] A degenerate state – PCI not performed.

exceeds 70%. Moreover, the correlation energy secures that in some compounds the SCF level of the energy can be overcome. Thus, regarding these results the applicability of the extended PCILO method seems to be well documented.

The case of $CuBr_4^{2-}$ requires some more detailed discussion. This is a system where canonical MOs yield a triply degenerate electronic ground state $^2T_2$. A single determinant type wave function leads to the prediction of unequivalent ligands: different atomic charges on bromines are obtained in tetrahedral geometry. On the other hand, this is an example of the Jahn–Teller active system. As a consequence of the vibronic coupling between the electronic wave function and e-, t_2'- and t_2''- modes of normal vibrations, the adiabatic potential surface does not exhibit any minimum in the tetrahedral geometry. One of the active modes which removes the degeneracy and yields the minimum on the adiabatic potential surface is represented by geometry distortion to the D_{2d} symmetry (a slightly flattened or elongated bisphenoid along the e-mode). The localized bonding models 2(4)/1(5)/1(12) and 8(1)/1(5)/1(12) with an unpaired electron on a copper $3d$ orbital do not exhibit the electronic state of the T_2 symmetry. Therefore, the distortion to the D_{2d} symmetry does not give here an energy lowering compared with the optimum tetrahedron, because the vibronic coupling vanishes. On the contrary, the extended localized bonding model 13(1)/1(12) with a five-centre thirteen-component "bond" is of the same quality as the case

Table 4. Calculated energy terms using INDO Hamiltonian

System[a]	HAOs	Bonding model	Total energy terms (eV)				X_{loc}	X_{com}
			$-E_T^{(0)}$	$-E_{m-m}^{(2)}$	$-E_{b-b}^{(2)}$	$-E_T^{(2)}$	%	%
H_2O	[b]	2(2)/1(2)	514.94	1.71	0.78	517.42	0.60	54.8
	[b]	4(1)/1(2)	515.61	1.13	0.79	517.53	0.47	46.2
	[c]	6(1)	518.06	0.0	0.83	518.88		
B_2H_6	[d]	3(2)/2(2)/2(2)	333.63	1.79	1.44	336.86	0.67	79.2
	[c]	14(1)	335.89	0.0	1.50	337.40		
C_6H_6	[b]	6(1)/2(6)/2(6)	1233.64	4.58	6.33	1244.55	0.52	71.3
	[c]	30(1)	1240.06	0.0				
$CuBr_4^{2-}$	[b]	2(4)/1(5)/1(12)	2582.17	9.02	0.27	2591.47	0.43	80.5
	[b]	8(1)/1(5)/1(12)	2582.37	9.03	0.27	2591.67	0.42	82.1
	[b]	13(1)/1(12)	2582.78	[f]			0.41	
	[c]	25(1)	2593.38	[f]				

Footnotes a–f see Table 3.

of canonical MOs: the electronic ground state is again $^2T_2$ and it exhibits an activity by means of the Jahn–Teller effect. Thus, the choice of an appropriate bonding model can affect the results obtained not only quantitatively but also qualitatively. Because of the degeneracy, the use of the degenerate Rayleigh–Schrödinger many-body perturbation theory is recommended for $CuBr_4^{2-}$ in the $^2T_2$ state; this approach, however, exceeds the scope of the present paper.

Table 5. Calculated energy (eV) relative to SCF level in various orders of the perturbative CI

System[a]	HAOs	Bonding model	Order of PCI			CPU time[e] (s)	
			zero	second	third	SCF	PCI
(A) CNDO/2 Hamiltonian							
H_2O	[b]	2(2)/1(2)	3.007	0.920	0.911	2	7
	[b]	4(1)/1(2)	2.553	0.850	0.740	2	40
	[c]	6(1)	0.0	−0.647	−0.870	3	650
B_2H_6	[d]	3(2)/2(2)/2(2)	1.903	−0.682	−0.879	7	1600
	[c]	14(1)	0.0	−1.157		16	200
(B) INDO Hamiltonian							
H_2O	[b]	2(2)/1(2)	3.119	0.630	0.621	3	7
	[b]	4(1)/1(2)	2.448	0.524	0.378	4	42
	[c]	6(1)	0.0	−0.827	−1.121	5	660
B_2H_6	[d]	3(2)/2(2)/2(2)	2.265	−0.969	−1.208	8	1600
	[c]	14(1)	0.0	−1.505		16	3300

Footnotes a–d see Table 3.

[e] CPU time on IBM 370/148 computer.

Nearly the same conclusions can be drawn from Table 4 using the INDO Hamiltonian in the PCILO framework. The localization defect and its compensation by the second-order delocalization energy are of the same order as for the CNDO Hamiltonian. On the other hand, the calculated second-order correlation energy exhibits a systematic trend: it is significantly higher in the absolute value for the INDO Hamiltonian in comparison with the CNDO Hamiltonian. Thus, the advantage of a more sophisticated Hamiltonian is expected for molecular properties derived from the adiabatic potential surfaces, like the equilibrium geometries or the force constants. Such results will be presented in forthcoming papers.

Finally, Table 5 illustrates the time consumption of the extended PCILO method up to the third order of the perturbation theory. It can be concluded: the more localized bonds, the less the computing time required and vice versa. Thus, the extended PCILO method allows to find a compromise between computing facilities and the level of obtaining the electronic wave function or molecular properties.

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