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# Many-Body Perturbation Theory Based on Localized Orbitals

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Diagrammatic formulation of the MBPT has been extended to the case when both the occupied orbitals and the virtual ones are separately localized, *i. e.*, they are unitary transforms of the canonical HF orbitals. All diagrams representing ground state correlation energy are generated through the fifth order. For cyclic polyenes $C_{4n+2}H_{4n+2}$ as model systems, in PPP approximation, all perturbation energy corrections through the fourth order have been calculated for a wide range of the coupling constant: $\beta^{-1}$. Some fifth order energy corrections have also been evaluated and the convergence of the localization corrections has been studied. For $C_6H_6$ the results of the canonical and the localized versions have been compared with those obtained by full CI. We have shown that in the localized representation the energy corrections can be partitioned into local and nonlocal contributions.

## 1. INTRODUCTION

One of the most systematic approaches that goes beyond the independent particle scheme is the diagrammatic manny-body perturbation theory[1–5]. In the algebraic approximation it is used for atoms and small molecules through fourth order in the energy.[6–10] The evaluation of all terms in fifth and higher orders is feasible only for model systems at present.[11] There exist methods where terms of certain types are summed over to infinite order (CPMET[12,13], CEPA[14,15] Green's functions[16,17], *etc.*). Formerly it was supposed that in calculating the correlation energies only the local contributions were important.[18] One of the authors (E. K.) elaborated a perturbational approach where the zeroth order wavefunction is the APSG ground state.[19] The PCILO method of Diner, Malrieu and Claverie is based also on localized orbitals, the latter are, however, not solutions of the Hartree-Fock (HF) equations.[20] Amos and Musher[21] and Davidson[22] have shown how the zeroth order Hamiltonian and wavefunctions can be chosen when the orbitals used are unitary transforms of the canonical HF orbitals.

To the knowledge of the authors the localized orbitals, up to the present, have been applied only in theories involving partial summations.[12–17,19,23]

The aim of the present paper is to show the applicability and the advantages of the many-body perturbation theory (MBPT) based on localized HF orbitals which are unitary tranforms of the canonical ones. As model systems we use cyclic polyenes in the Pariser — Parr — Pople (PPP) approximation for which other results including full CI are also available.[24] They are metallic-like one-dimensional, non well localized systems very suitable to study the importance of non-local effects.

## 2. THEORY

The exact (nonrelativistic) Hamiltonian is partitioned in the following way:

$$\hat{H} = \hat{H}^{(0)} + \hat{W}. \tag{1}$$

The occupied single-particle functions $\overline{\psi}_i$, $i = 1, 2, \ldots, N$, and the virtual ones $\overline{\psi}_a$, $a = N + 1, N + 2, \ldots, M$ are solutions of the canonical HF equations

$$\hat{F}\,\overline{\psi}_k = \overline{\varepsilon}_k\,\overline{\psi}_k, \quad k = 1, 2, \ldots, M, \tag{2}$$

where

$$\hat{F} = \hat{H}(1) + \sum_{j=1}^{N} \langle \overline{j} \,|\, r_{12}^{-1}\,(1 - \hat{P}_{12})\,|\, \overline{j}\rangle_1. \tag{3}$$

When $\hat{H}^{(0)}$ is chosen as

$$\hat{H}^{(0)} = \sum_{i=1}^{N} \hat{F}\,(i), \tag{4}$$

the perturbation is the following

$$\hat{W} = \tfrac{1}{2} \sum_{i,j=1}^{N} r_{ij}^{-1} - \sum_{i,j=1}^{N} \langle \overline{j} \,|\, r_{i2}^{-1}\,(1 - \hat{P}_{i2})\,|\, \overline{j}\rangle_i. \tag{5}$$

If we transform the occupied and the virtual single-particle functions separately by unitary transformations

$$\psi_i = \sum_{j=1}^{N} U_{ij}\,\overline{\psi}_j, \tag{6}$$

$$\psi_a = \sum_{b=N+1}^{M} V_{ab}\,\overline{\psi}_b, \tag{7}$$

the localized single-particle functions obtained satisfy the following non-diagonal HF equations

$$\hat{F}\,\psi_i = \sum_{j=1}^{N} \varepsilon_{ij}\,\psi_j, \quad i, j = 1, 2, \ldots, N, \tag{8}$$

$$\hat{F}\,\psi_a = \sum_{b=N+1}^{M} \varepsilon_{ab}\,\psi_b, \quad a, b = N + 1, N + 2 \ldots, M. \tag{9}$$

According to Amos and Musher[21] we can choose a new HF operator

$$\hat{F}^{\text{loc}} = \hat{F} - \sum_{\substack{i,j \\ i \neq j}} |\, i > \varepsilon_{ij} < j \,| - \sum_{\substack{a,b \\ a \neq b}} |\, a > \varepsilon_{ab} < b \,|, \tag{10}$$

the eigenfunctions of which are the transformed single-particle functions

$$\hat{F}^{\text{loc}}\,\psi_i = \varepsilon_i\,\psi_i, \quad i = 1, 2, \ldots, N, \tag{11}$$

$$\hat{F}^{\mathrm{loc}}\,\psi_a = \varepsilon_a\,\psi_a,\quad a = N+1,\ N+2,\ldots,M. \tag{12}$$

In this case the zeroth order Hamiltonian and the perturbation can be chosen in the following way

$$\hat{H}^{\mathrm{loc}(0)} = \sum_{i=1}^{N} \hat{F}^{\mathrm{loc}}(i), \tag{13}$$

$$\hat{W}^{\mathrm{loc}} = \tfrac{1}{2} \sum_{\substack{i,j=1\\ i\neq j}}^{N} r_{ij}^{-1} -$$

$$-\sum_{i=1}^{N} \Big\{ \sum_{j=1}^{N} < j \,|\, r_{i2}^{-1}\,(1-\hat{P}_{i2})\,|\, j >_i - \sum_{\substack{k,l=1\\ k\neq l}}^{N} |\,k > \varepsilon_{kl} < l\,| - \sum_{\substack{a,b=N+1\\ a\neq b}}^{M} |\,a > \varepsilon_{ab} < b\,| \Big\} \tag{14}$$

As a consequence of the nonzero off-diagonal Lagrangian multipliers $\varepsilon_{kl}$, $\varepsilon_{ab}$, perturbation (14) has extra terms as compared to (5).

In the diagrammatic formulation the terms of the perturbation series are represented by graphs. We apply the »mixed« Hugenholtz — Feynman representation proposed by Brandow[2] (details can be found also in Refs. 25 and 26). One of us (Z. Cs.) elaborated and programmed an algorithm that constructs the Hugenholtz and Feynman diagrams and automatically picks out conjugate pairs and equivalent diagrams.[27] Through fourth order, all diagrams necessary when using canonical orbitals can be found in the literature.[8,25] The rules of how to translate graphs into formulae can also be found in many places.[2,8,25,26]

In the following each Hugenholtz diagram is represetned by a Feynman graph with antisymmetrized vertices

$$\langle kl \,|\, r_{12}^{-1}\,(1-\hat{P}_{12})\,|\, mn\rangle \equiv \langle kl \,\|\, mn\rangle = \langle kl \,|\, mn\rangle - \langle kl \,|\, nm\rangle.$$

The diagrams which represent the second and third order energy corrections using canonical HF orbitals are shown in Figure 1. (In the following we call them canonical diagrams).

In the fourth order we have 39 Hugenholtz diagrams (among them 8 conjugate pairs).[8]

Due to the nonzero off-diagonal Fock matrix elements in (14), new terms enter the perturbation corrections in third and higher orders. We call these terms localization corrections. In the diagrams representing the localization terms the off-diagonal Fock matrix elements are denoted by crosses in circle. The latter are called localization diagrams.[28]

As the occupied and the virtual orbitals are localized separately, no off-diagonal Fock matrix element connects particle and hole states. Thus the localization diagrams can be derived from the canonical ones by inserting crosses in the hole and/or in the particle lines. By putting just one cross in the second order canonical diagram (Figure 1) we obtain the two third order localization diagrams (Figure 2). By inserting two crosses in the second order diagram or one cross in the third order diagrams (Figure 1) we get the fourth order localization diagrams. We obtain 22 antisymmetrized Feynman diagrams but among them 18 form 9 conjugate pairs so only 13 are different (see Figure 3).

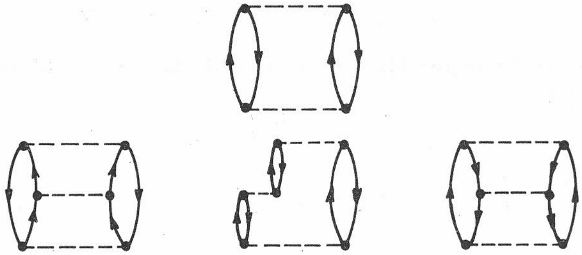

Figure 1. Second and third order antisymmetrized Feynman diagrams.

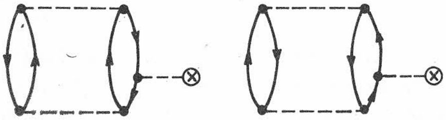

Figure 2. Third order localization diagrams.

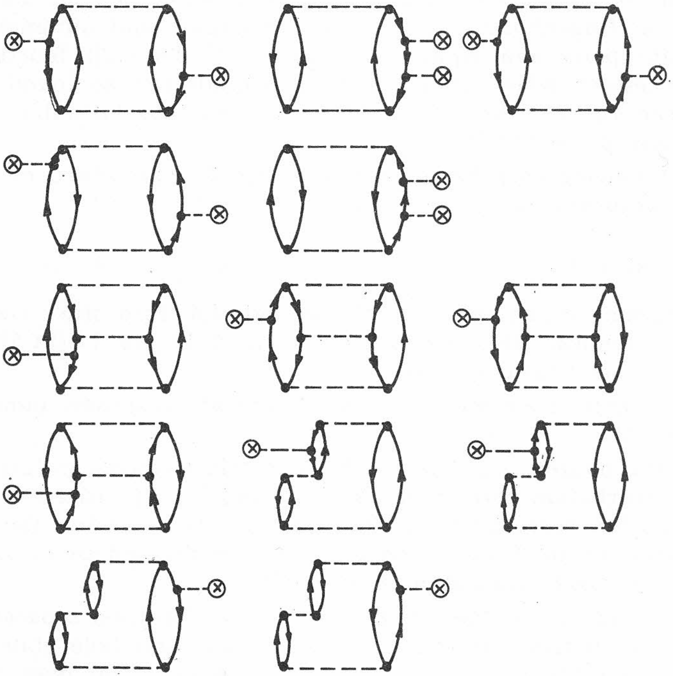

Figure 3. Fourth order localization diagrams.

In the fifth order we have 462 different canonical diagrams and 300 different localization diagrams. Among them there are 14 different diagrams which can be derived from the second order canonical diagram by inserting three crosses.

Due to the localization terms, in the localized representation extra computational work is necessary. In a given order, however, it is only a fraction of the computing time because the number of indices to be summed over are always less in the localization terms then in the canonical ones.

The possible advantage of the localized representation is that the computational work can be decreased, namely, if the orbitals are well localized into different spatial regions, for the matrix elements $\langle ij \mid kl \rangle$ the zero differential overlap approximation is applicable. It means that all terms containing at least one factor $\langle ij \mid kl \rangle$ in which $\psi_i \psi_k$ and/or $\psi_j \psi_l$ are localized into different spatial regions can be neglected. In evaluating a perturbation correction the summation in a closed loop should only be extended over indices of orbitals which are localized into the same spatial region. This advantage is partly cancelled by the occurrence of the localization terms the importance of which depends on the magnitude of the off-diagonal Fock matrix elements. Whether the smallness of these terms or the localization of the orbitals are more important can be decided only by actual calculations. For weakly localizable systems these two requirements might not be satisfied simultaneously.

The virtual orbitals, in general, cannot be localized uniquely into the spatial regions of the occupied orbitals.[29] There are exceptions: when some small bases (single zeta, double zeta, *etc.*) are used, or for model systems where the localized orbitals are completely determined by symmetry. A considerable amount of exploratory calculations is necessary in order to decide which localization procedure (Edmiston — Ruedenberg[30], Boys[31]) is the most suitable.

## 3. CALCULATIONS

We carried out actual calculations for the cyclic polyenes $C_{4n+2} H_{4n+2}$, $n = 1, 2, 3, 4, 5, 6, 7$, in the PPP approximation. These systems being only weakly localizable are well suited to study the importance of the localization terms because the contribution of the latter is a sizable fraction of the total correction. In addition, for $C_6 H_6$ and $C_{10} H_{10}$ full CI is also available.[24]

The PPP Hamiltonian is the following

$$\hat{H}^{\mathrm{PPP}} = \beta \sum_{\substack{\mu,\nu,\sigma \\ \mu \neq \nu}} \hat{a}_{\mu\sigma}^{+} \hat{a}_{\nu\sigma} + \tfrac{1}{2} \sum_{\substack{\mu,\nu \\ \sigma,\tau}} \gamma_{\mu\nu} \hat{a}_{\mu\sigma}^{+} \hat{a}_{\nu\tau}^{+} \hat{a}_{\nu\tau} \hat{a}_{\mu\sigma}, \tag{16}$$

where $\mu, \nu$ and $\sigma, \tau$ are atomic orbital and spin indices, respectively. For the matrix elements $\gamma_{\mu\nu}$ we used the Mataga — Nishimoto parametrization.[32] The CC bond length was taken to be 0.14 nm. An advantage of the PPP approximation is that $\beta^{-1}$ can be regarded as the coupling constant of the electron-electron interaction.

The canonical HF orbitals are completely fixed by symmetry

$$\bar{\varphi}_j = N^{-1/2} \sum_{\mu=1}^{N} \exp\left(\frac{2\pi i \mu j}{N}\right) X_\mu,$$

$$j = 0, \pm 1, \pm 2, \ldots \pm \left(\frac{N}{2} - 1\right), + \frac{N}{2}, \left(\frac{N}{2}: \text{odd}\right), \tag{17}$$

where $X_\mu$ is an atomic orbital centered on atom $\mu$.

It is well known that for $N \geq 3$ ($N \neq 4$), there exists a continuum of sets of localized orbitals.[33] We applied the set which formally corresponds to a

Kekule structure. The (equivalent) localized orbitals of this set are the following:

$$\varphi_i = \sum_{\mu=1}^{N} C_{i\mu} X_\mu, \tag{18}$$

where for the occupied orbitals

$$C_{i\mu} = 2^{1/2} N^{-1} \{1 + 2 \sum_{p=1}^{\left(\frac{N}{4} - \frac{1}{2}\right)} \cos \frac{p\pi}{N} (2\mu - 4i + 1)\}, \quad i = 1, 2, \ldots, N/2; \tag{19}$$

and for the virtual ones

$$C_{i\mu}^* = 2^{1/2} N^{-1} (-1)^{\mu-1} \{1 + 2 \sum_{p=1}^{\left(\frac{N}{4} - \frac{1}{2}\right)} \cos \frac{p\pi}{N} (2\mu - 4i + 1)\}, \quad i = 1, 2, \ldots, N/2. \tag{20}$$

Having evaluated the matrix elements of the HF orbitals (17)—(20) within the framework of the PPP scheme no further approximation was made, the calculation of the energy corrections was carried out on *ab initio* level.

The energy corrections were calculated through fourth order in both the canonical and the localized representation for the interval $0 \geq \beta \geq -10.0$.

The total energy correction of a given order, $n$, in the canonical representation is denoted by $\zeta_{\text{can}}^{(n)}$. In the localized representation for $n > 2$, $\zeta_{\text{loc}}^{(n)}$ consists of two terms: $\zeta_{\text{cl}}^{(n)}$, $\zeta_{\text{ll}}^{(n)}$. The former is the total contribution of the canonical diagrams with localized orbitals whereas the latter is the total contribution of the localization terms.

The total energy corrections through a given order, $n$, are denoted as follows

$$E_{\text{can}}^{(n)} = \sum_{i=2}^{n} \zeta_{\text{can}}^{(i)},$$

$$E_{\text{loc}}^{(n)} = \sum_{i=2}^{n} \zeta_{\text{loc}}^{(i)},$$

where

$$\zeta_{\text{loc}}^{(i)} = \begin{cases} \zeta_{\text{cl}}^{(i)}, & \text{if } i = 2, \\ \zeta_{\text{cl}}^{(i)} + \zeta_{\text{ll}}^{(i)}, & \text{if } i > 2. \end{cases}$$

For $C_6H_6$ in the interval $0.0 \geq \beta \geq -10.0$ $E_{\text{can}}^{(4)}$ and $E_{\text{loc}}^{(4)}$ are compared to the result obtained by full CI[24] and displayed in Figure 4. For $\beta > -2$ both versions fail to give a sizable fraction of the exact result. It has been shown[34] that the interval $0.0 \geq \beta \geq -2$ is outside the convergence radius of the perturbation expansion in terms of $\beta^{-1}$.

It is apparent that as $|\beta| \rightarrow \infty$, the relative contribution of the localization terms increases but never becomes larger than 5.5% of the total contribution $E_{\text{loc}}^{(4)}$. The localization diagrams represent a small but non negligible fraction of the total correlation energy.

In order to illustrate the convergence of the MBPT for $C_6H_6$ we display perturbation corrections $\zeta_{\text{cl}}^{(2)}$, $\zeta_{\text{cl}}^{(3)}$, $\zeta_{\text{cl}}^{(4)}$ in Figure 5. It can be seen that for

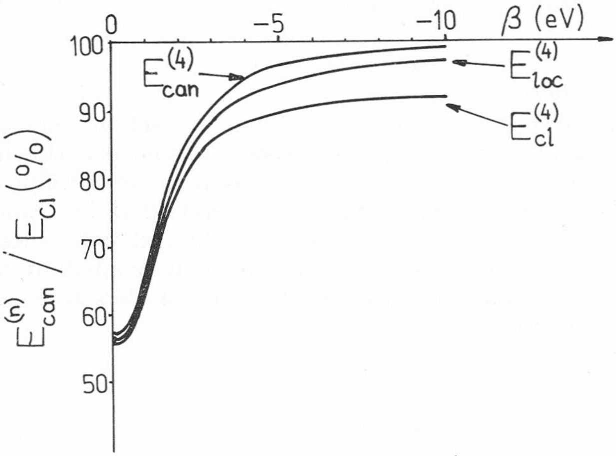

Figure 4. Portions of the total correlation energy for $C_6H_6$ (in %) recovered by the corresponding perturbation correction. The results obtained by full CI are taken as 100%.

$\beta \rightarrow 0$ $\zeta_{cl}^{(4)}$ goes below $\zeta_{cl}^{(2)}$ and $\zeta_{cl}^{(3)}$, *i. e.*, the perturbation series fails to converge, but for the interval $-2.0 > \beta \geq -10.0$ the convergence is satisfactory.

It should be noted that in the interval $-1.5 \geq \beta \geq -10.0$ $\zeta_{ll}^{(4)}$ goes below $\zeta_{ll}^{(3)}$ and in addition $\zeta_{loc}^{(3)}$ and $\zeta_{loc}^{(4)}$ go below the corresponding canonical

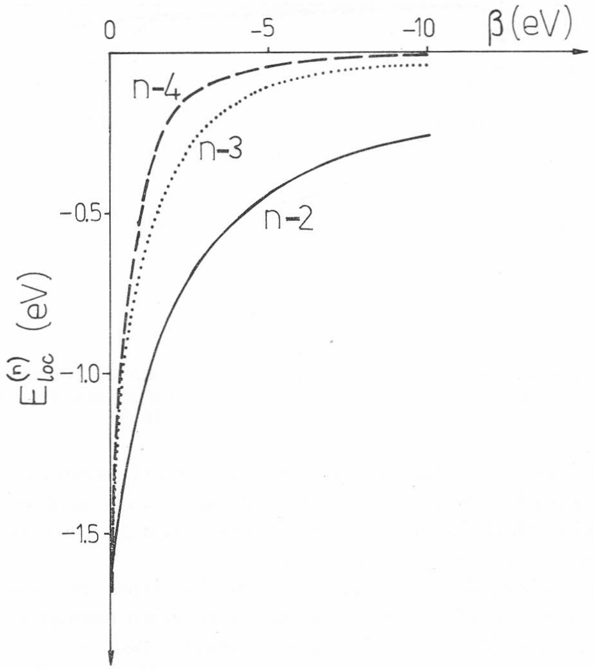

Figure 5. Perturbation energy corrections $E_{loc}^{(n)}$ for $C_6H_6$ as functions of $\beta$ : ——— second order; ....... third order; — — — — fourth order.

quantities $\zeta_{can}^{(3)}$ and $\zeta_{can}^{(4)}$, respectively. For the total contributions, however, inequalities

$$E_{can}^{(n)} \leqslant E_{loc}^{(n)}, \quad \mu = 2, 3, 4,$$

are valid everywhere.

It is easy to show that the localization corrections converge even with increasing $|\beta|$, while the rate of convergence is, however, slowing down.

If, in the localized representation, we sum up to infinite order the contributions of diagrams derivable from the second order canonical diagram (Figure 1) by inserting crosses on the particle and hole lines, provided the series converges, the result should be equal to the contribution of the second order canonical diagram in the canonical representation. In Figure 6. we show for $C_6H_6$ the corrections

$$E_{cl}^{(2)}, \; E_{cl}^{(2)} + E_{ll}^{(n)}[2], \quad n = 3, 4, 5,$$

where

$$E_{ll}^{(n)}[2] = \sum_{i=3}^{n} \zeta_{ll}^{(i)}[2],$$

and 2 in the square bracket means that only those contributions are included whose diagram is derivable from the second order canonical diagram. The difference between the fourth and fifth order terms is already small, and the latter is very close to the second order result in the canonical representation, demonstrating the convergence of the series.

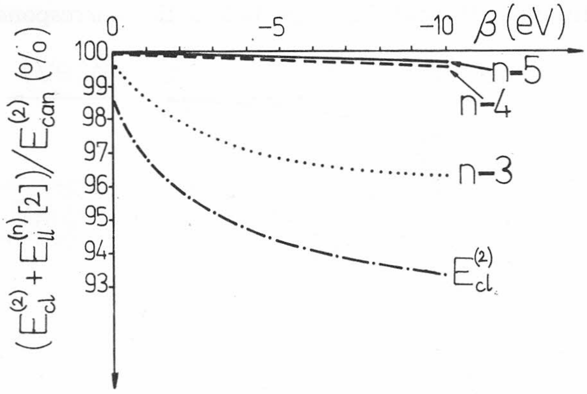

Figure 6. The convergence of the localization corrections derivable from the second order canonical diagrams for $C_6H_6$. The second order results of the canonical representation are taken as 100%.

We obtained very similar results for other $C_NH_N$ systems with an axception: the minimum of $\zeta_{ll}^{(3)}$ and $\zeta_{ll}^{(4)}$ as functions of $\beta$ are shifted towards larger $|\beta|$ values showing that the relative importance at a given $\beta$ of the localization correction depends on the particle number.

One of the expected advantages of the localized representation is that the local and nonlocal contributions of the correlation energy can be separated. In the case of the cyclic polyenes to every orbital pair $\psi_j \psi_k$ we can uniquely assign a number characterizing the distance of their centers. The integral $\langle ij | kl \rangle$ can also be partitioned according to the distances of orbital pairs $\psi_i \psi_k$ and $\psi_j \psi_l : d = |i-k|$, or $d = |j-l|$.

Evaluating the perturbation corrections the summations in a closed loop of the diagrams should only be extended over indices of orbitals whose distance: $|i - k|$ and/or $|j - l|$ does not exceed a certain number. In the case of $C_{14}H_{14}$ the possible values of $d$ are 0, 1, 2, 3. If only $d = 0$ was allowed, we would get an approximation which is closely related to the conventional separated pair theory (see Ref. 19). When $d = 1$ or 2 the first or the first and second neighbour indices are also included. If $d = 3$, no terms are omitted from the summations.

TABLE

*Portions of the Total Correlation Energy of $C_{14}H_{14}$ when Nonlocal Contributions are Gradually Separated out. $E_{loc}^{(4)}$ is Taken as 100%. $E_{loc}^{(4)}$ (2): Third Neighbor Indices Omitted; $E_{loc}^{(4)}$ (1): Second and Third Neighbour Indices Omitted; $E_{loc}^{(4)}$ (0): only the Strictly Local Contributions are Retained (: First, Second and Third Neighbour Indices Omitted)*

| $\beta$/eV | 0 | —1.0 | —2.5 | —5.0 | —10.0 |
|---|---|---|---|---|---|
| $E_{loc}^{(4)}$ (2) (%) | 87.0 | 85.0 | 84.9 | 84.0 | 83.3 |
| $E_{loc}^{(4)}$ (1) (%) | 75.8 | 73.0 | 71.0 | 69.5 | 68.2 |
| $E_{loc}^{(4)}$ (0) (%) | 56.5 | 55.0 | 53.9 | 51.5 | 50.2 |

In the Table we show the effect of the gradual separation of nonlocal contributions to the correlation energy of $C_{14}H_{14}$ as function of $\beta$. The results are compared to the case when no omissions are made ($d = 3$). It is rather surprising that even for this weakly localizable system more than 50% of the correlation energy consists of strictly local contributions ($d = 0$).

Investigating the pair correlation energies we obtained similar results.[28]

## 4. CONCLUSIONS

We have shown that the diagrammatic MBPT can be used without any difficulty also in the localized representation. The practical calculation of the extra terms (missing in the canonical representation) does not require significant amount of computer time.

The convergence properties of the two representations are very similar for the model systems investigated.

The main advantage of the localized representation is that nonlocal effects can be gradually separated from the local ones by partitioning the localized orbitals according to the »order of neighbourhood« (in our case: d) and truncating the summations in the perturbation corrections to a given »order«. This would decrease the required computer time drastically at least for extended systems.

If there exist local symmetries in the system considered further simplifications can be expected.

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## SAŽETAK

### Perturbacijska teorija više tijela na temelju lokaliziranih orbitala

*Ede Kapuy, Zoltán Csépes i Cornelia Kozmutza*

Dijagramska formulacija perturbacijske teorije više tijela (MBPT) proširena je na slučaj u kojemu su posebno lokalizirane zaposjednute orbitale, a posebno nezaposjednute ili virtualne orbitale. Svi dijagrami koji opisuju korelacijsku energiju osnovnog stanja dani su do aproksimacije petog reda. Za modelne sustave-prstenaste poliene $C_{4n+2}H_{4n+2}$ — sve perturbacijske korekcije izračunane su do četvrtog reda za vrlo širok raspon konstante sprezanja međuelektronskog djelovanja $\beta^{-1}$. Procijenjene su također neke korekcije petog reda i razmatrana je konvergencija postupka s lokaliziranim orbitalama (LO). Pokazano je da se u LO slici korelacijske energije mogu raščlaniti na lokalne i nelokalne doprinose.