
**APPLICATIONS OF THE MBPT IN THE LOCALIZED REPRESENTATION
THE BEHAVIOUR OF THE LOCALIZATION TERMS**

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

The behaviour of the localization corrections of the MBPT is investigated. It is shown that calculating the third and fourth order localization corrections we obtain sufficiently accurate results to the second order correlation energy both for cyclic polyenes and for saturated hydrocarbons. The evaluation of the localization diagrams does not require significant extra computer time. The extra computer time can be recovered if small non-local effects will be neglected.

One of the most important size extensive approaches that goes beyond the Hartree–Fock (HF) scheme is the diagrammatic many-body perturbation theory (MBPT).^{1–6} In the so-called algebraic approximation it has been used for atoms and small molecules through fourth order in the energy.^{7–10} As the evaluation of the energy through n -th order is an M^{2n-2} procedure (M is the number of basis functions) the application to larger systems is not feasible at present.¹¹ Formerly it was supposed that, for the correlation energy, local and nonlocal contribution could be distinguished with only the local contribution being important.^{12–14} Amos and Musher¹⁵ and Davidson¹⁶ have shown how the zero order Hamiltonian and the wavefunction can be chosen when the orbitals are unitary transforms of the canonical HF orbitals. Localized orbitals have also been applied in theories involving partial summations (CPMET^{17,18}, CEPA^{19,20} and other methods^{21,22}). One of the present authors (E.K.) has suggested a method which is based on the localized HF orbitals and has shown how the local and nonlocal contribution of the correlation energy can be separated and the computational work decreased²³. The method has been applied to cyclic polyenes (with PPP Hamiltonian)^{24–26} and to normal saturated hydrocarbons (on *ab initio* level).^{27,28} Taking the structure of the molecules into consideration, the localized orbitals and their contribution to the correlation energy

have been partitioned according to the "order of neighbourhood". It has been shown that contributions from distant neighbours can be neglected. Similar methods have been used by others,²⁰⁻³¹ Due to the off-diagonal Fock matrix element the perturbational series has extra terms not occurring with canonical HF orbitals. The aim of the present paper is to investigate the behaviour of these terms.

THEORETICAL

The Hamiltonian is partitioned in the following way:

$$\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{W}. \quad (1)$$

The occupied single-particle functions ψ_i , $i = 1, 2, \dots, N$, and the virtual single-particle functions ψ_a , $a = N + 1, N + 2, \dots, M$, are solutions of the canonical HF equations

$$\mathbf{F}\psi_k = \varepsilon_k\psi_k, \quad k = 1, 2, \dots, M, \quad (2)$$

where

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

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

$$\mathbf{H}^{(0)} = \sum_{i=1}^N \mathbf{F}(i). \quad (4)$$

The perturbation is the following

$$\mathbf{W} = 1/2 \sum_{i,j=1}^N r_{ij}^{-1} - \sum_{i,j=1}^N \langle j | r_{i2}^{-1} (1 - \mathbf{P}_{i2}) | j \rangle_i. \quad (5)$$

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

$$\varphi_i = \sum_{j=1}^N U_{ij}\psi_j, \quad (6)$$

$$\varphi_a = \sum_{b=N+1}^M V_{ab}\psi_b, \quad (7)$$

the localized orbitals satisfy the following non-diagonal HF equations:

$$\mathbf{F}\varphi_i = \sum_{j=1}^N \varepsilon_{ij}\varphi_j; \quad i, j = 1, 2, \dots, N, \quad (8)$$

$$\mathbf{F}\varphi_a = \sum_{b=N+1}^M \varepsilon_{ab}\varphi_b; \quad a, b = N + 1, N + 2, \dots, M. \quad (9)$$

The transformed single-particle functions φ_i , φ_a are eigenfunctions of the HF operator

$$\mathbf{F}^{\text{loc}} = \mathbf{F} - \sum_{\substack{i,j=1 \\ i \neq j}}^N |i\rangle \varepsilon_{ij} \langle j| - \sum_{\substack{a,b=N+1 \\ a \neq b}}^M |a\rangle \varepsilon_{ab} \langle b|. \quad (10)$$

The zero order Hamiltonian and the perturbation is chosen as follows:

$$\mathbf{H}^{\text{loc}}(0) = \sum_{i=1}^N \mathbf{F}^{\text{loc}}(i), \quad (11)$$

$$\mathbf{W}^{\text{loc}} = \mathbf{W} + \sum_{i=1}^N \left\{ \sum_{\substack{k,l=1 \\ k \neq l}}^N |k\rangle \varepsilon_{kl} \langle l| + \sum_{\substack{a,b=N+1 \\ a \neq b}}^M |a\rangle \varepsilon_{ab} \langle b| \right\}. \quad (12)$$

Due to the off-diagonal Fock matrix elements, the perturbation given by Eq. (12) has extra terms, compared with the one given by Eq. (5), entering the perturbational series from third order.

In the diagrammatic formulation the terms of the perturbation series are represented by graphs. We apply the "mixed" Hugenholtz–Feynman representation proposed by Brandow.^{3,2} Through fourth order all diagrams of the canonical representation have been reported.^{3,4,6} The extra terms due to the off-diagonal Fock matrix element are given in Figs 1–3 (see also refs^{24–26}).



FIG. 1

Third order localization diagrams

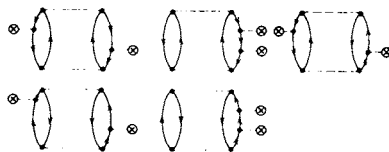


FIG. 2

Fourth order localization diagrams derivable from the second order canonical diagram

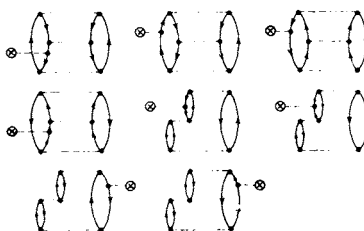


FIG. 3

Fourth order localization diagrams derivable from the third order canonical diagrams

We use in this paper the following denotations. The total energy correction of a given order n in the canonical representation is denoted by $\mathcal{E}_{\text{can}}^{(n)}$. In the localized representation for $n > 2$ $\mathcal{E}_{\text{loc}}^{(n)}$ consists of two terms

$$\mathcal{E}_{\text{loc}}^{(n)} = \mathcal{E}_{\text{lc}}^{(n)} + \mathcal{E}_{\text{ll}}^{(n)}, \quad (13)$$

the first one is the contribution of the canonical diagrams evaluated by localized orbitals whereas the second one is the contribution of the extra (localization) terms.

The total energy corrections through n -th order are denoted as

$$E_{\text{can}}^{(n)} = \sum_{i=2}^n \mathcal{E}_{\text{can}}^{(i)} \quad (14)$$

and

$$E_{\text{loc}}^{(n)} = \sum_{i=2}^n \mathcal{E}_{\text{loc}}^{(i)}, \quad (15)$$

respectively.

The localization diagrams can be derived from the canonical ones by inserting "crosses in circle" (i.e., single particle potentials) in the hole and/or in the particle lines. Thus the localization diagrams in Figs 1 and 2 can be generated by inserting into the second order canonical diagram one or two crosses, respectively. Inserting three crosses we obtain 14 distinct fifth order localization diagrams at the Hugenholtz level (they represent 45 Feynman diagrams).

RESULTS

Cyclic Polyenes in PPP Approximation

The calculations for the cyclic polyenes: $C_N H_N$, $N = 4n + 2$, $n = 1, 2, 3, 4, 5, 6, 7$, were carried out in PPP approximation with Mataga–Nishimoto parametrization.^{24–26,33}

The Hamiltonian is the following

$$\mathbf{H} = \beta \sum_{\substack{\mu, \nu, \sigma \\ \mu \neq \nu}} \mathbf{a}_{\mu\sigma}^+ \mathbf{a}_{\nu\sigma} + \frac{1}{2} \sum_{\substack{\mu, \nu \\ \sigma, \tau}} \gamma_{\mu\nu} \mathbf{a}_{\mu\sigma}^+ \mathbf{a}_{\nu\tau}^+ \mathbf{a}_{\nu\tau} \mathbf{a}_{\mu\sigma}, \quad (16)$$

where μ, ν and σ, τ are atomic orbital and spin indices, respectively. β^{-1} can be regarded as coupling constant, whose "physical" value is about -2.5 eV.

The canonical HF orbitals are completely fixed by symmetry. We applied those sets of localized orbitals which formally corresponds to a Kekulé structure. The

(equivalent) localized orbitals of this set are the following:

$$\varphi_i = \sum_{\mu=1}^N C_{i\mu} \chi_{\mu}, \quad (17)$$

where χ_{μ} are the atomic $2p_z$ basis functions. The coefficients for the occupied orbitals equal

$$C_{i\mu} = 2^{1/2} N^{-1} \left\{ 1 + 2 \sum_{p=1}^{N/4-1/2} \cos \pi p (2\mu - 4i + 1) / N \right\}, \quad (18)$$

and for the virtual orbitals equal

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

where $i = 1, 2, 3, \dots, N/2$.

In Fig. 4 we show the dependence of the third order localization correction $\mathcal{E}_{11}^{(3)}$ (Fig. 1) and the total fourth order localization correction $\mathcal{E}_{11}^{(4)}$ (Figs 2 and 3) per particle on the size of the systems. As can be seen, for smaller systems these corrections rapidly increase with the size but for larger systems they apparently go to saturation. Except for C_6H_6 the third order term is larger than the fourth order one, their order of magnitude is, however, comparable everywhere. It means that the third and fourth order terms are of equal importance.

Adding the contributions of all localization diagrams together, which can be generated from the second order canonical diagram if the perturbation series converges, the result should be equal to $E_{\text{can}}^{(2)} - E_{\text{loc}}^{(2)}$. Taking this difference as 100% we display for $C_{10}H_{10}$ in Fig. 5 the contributions with increasing order as the function of the coupling constant (β). The third order term $\mathcal{E}_{11}^{(2,1)} = \mathcal{E}_{11}^{(3)}$ can only reproduce 45% of the difference at the „physical value” of the coupling constant ($\beta = -2.5$ eV). The fourth order contribution $\mathcal{E}_{11}^{(2,1)} + \mathcal{E}_{11}^{(2,2)}$ gives 85% and the fifth order contribution $\mathcal{E}_{11}^{(2,1)} + \mathcal{E}_{11}^{(2,2)} + \mathcal{E}_{11}^{(2,3)}$ reproduces 93%. It means that the error is 15% and 7%, respectively. The third order ($\mathcal{E}_{11}^{(2,1)}$) and the fourth order ($\mathcal{E}_{11}^{(2,2)}$) terms are again of comparable magnitude. If we take the canonical second order correction $E_{\text{can}}^{(2)}$ as 100%, we obtain for the errors only 1.72% and 0.84%, respectively. It means that the contribution through fourth order is sufficient in most cases.

Normal Saturated Hydrocarbons

The canonical HF equations have been solved for normal saturated hydrocarbons $C_{2n+1}H_{4n+4}$, $n = 0, 1, 2$, with standard STO-3G basis set, and model geometry: $R_{\text{CH}} = 1.094 \text{ \AA}$,* $R_{\text{CC}} = 1.526 \text{ \AA}$ and tetrahedral valence angles. Program system

* $1 \text{ \AA} = 10^{-10} \text{ m}$.

SYCETY has been applied efficiently utilizing the C_{2v} symmetry of the systems.³⁴⁻³⁶ The canonical occupied and virtual orbitals have been localized by Boys' method,³⁷ separately. After appropriate integral transformation the second order energy

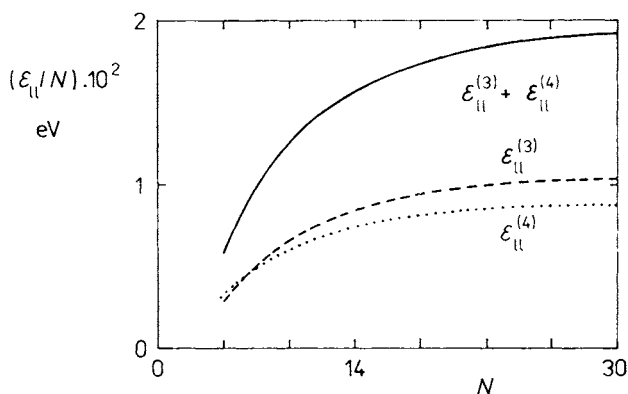


FIG. 4

Third and fourth order localization corrections per particle for cyclic polyenes $C_N H_N$ as function of N

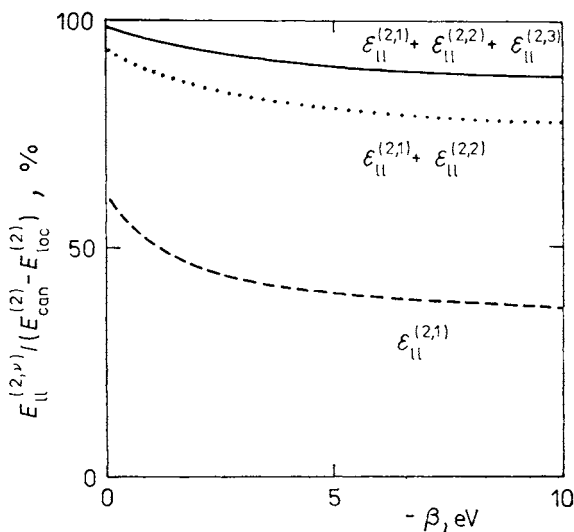


FIG. 5

Proportions of the localization correction for $C_{10} H_{10}$ recovered by the contributions of localization diagrams derivable from the second order canonical diagram as function of the coupling constant. $E_{can}^{(2)} - E_{loc}^{(2)}$ is taken as 100%

corrections have been evaluated in the localized and in the canonical representation and shown in Table I. Due to the localizability of the systems the results in the two representations are very close together. In Table II we display the third order localization corrections $\mathcal{E}_{11}^{(2,1)} = \mathcal{E}_{11}^{(3)}$, and those fourth order localization corrections $\mathcal{E}_{11}^{(2,2)}$ the graphs of which can be generated from the second order canonical diagram.

TABLE I

The second order correlation energy calculated in the localized and in the canonical representation (in a.u.)^a with STO-3G basis set

Molecule	$E_{loc}^{(2)}$	$E_{can}^{(2)}$
CH ₄	-0.0560169	-0.0571078
C ₃ H ₈	-0.1545420	-0.1590773
C ₅ H ₁₂	-0.2537892	-0.2621150

^a 1 a.u. = 4.3598 · 10⁻¹⁸ J.

TABLE II

The contributions of the third and fourth order localization diagrams derivable from second order canonical diagram with STO-3G basis set (in %, $E_{can}^{(2)} - E_{loc}^{(2)}$ is taken as 100%)

Molecule	$\mathcal{E}_{11}^{(2,1)}$	$\mathcal{E}_{11}^{(2,2)}$	$\mathcal{E}_{11}^{(2,1)} + \mathcal{E}_{11}^{(2,2)}$
CH ₄	26.98	81.86	108.83
C ₃ H ₈	37.53	66.74	104.26
C ₅ H ₁₂	40.63	62.57	103.20

TABLE III

Contributions of the third and fourth order localization diagrams derivable from the second order canonical diagram for CH₄ with 6-31G and 6-31G* basis sets and two different sets of localized virtual orbitals (in %, the corresponding $E_{can}^{(2)} - E_{loc}^{(2)}$ is taken as 100%)

Basis set		$(E_{can}^{(2)} - E_{loc}^{(2)}) \cdot 10^2$	$\mathcal{E}_{11}^{(2,1)}$	$\mathcal{E}_{11}^{(2,2)}$	$\mathcal{E}_{11}^{(2,1)} + \mathcal{E}_{11}^{(2,2)}$
6-31G	(i)	-0.72132	4.77	84.47	89.14
6-31G	(ii)	-0.31276	47.41	37.47	84.88
6-31G*	(i)	-2.78849	53.41	32.14	85.54
6-31G*	(ii)	-1.15346	68.50	37.19	105.69

If the perturbation series converges their sum $\mathcal{E}_{11}^{(2,1)} + \mathcal{E}_{11}^{(2,2)}$ should be close to the difference $E_{\text{can}}^{(2)} - E_{\text{loc}}^{(2)}$ which we take as 100%. It can be seen, that the third order contributions are smaller than the fourth order ones, their sum slightly overshoots the difference, but the error is smaller than 9%, in every case. (If we would take $E_{\text{can}}^{(2)}$ as 100% the error would be less than 0.2%.)

The results depend strongly upon the basis set. Applying larger basis sets there will be more diffuse orbitals among the virtual ones and different sets of localized virtual orbitals are obtained if the localization procedure is used for all orbitals at once (i) or step by step(ii). In Table III we show for CH_4 with 6-31G and 6-31G* basis sets the second order correction in the canonical ($E_{\text{can}}^{(2)}$) and in the localized ($E_{\text{loc}}^{(2)}(\text{i})$ and $E_{\text{loc}}^{(2)}(\text{ii})$) representations. We can see that the results in the two localized representations are significantly different from each other. In Table III we display $\mathcal{E}_{11}^{(2,1)}$ and $\mathcal{E}_{11}^{(2,1)} + \mathcal{E}_{11}^{(2,2)}$ taking the corresponding $E_{\text{can}}^{(2)} - E_{\text{loc}}^{(2)}$ difference as 100%. Here again the third and fourth order terms are of the same magnitude. The actual values depend on the basis and on the localization. If we apply the step by step procedure (ii) the difference $E_{\text{can}}^{(2)} - E_{\text{loc}}^{(2)}$ is smaller but $\mathcal{E}_{11}^{(2,1)} + \mathcal{E}_{11}^{(2,2)}$ differs from it slightly the error is 16%, and 6%, respectively. If we compare the error to $E_{\text{can}}^{(2)}$ we obtain only 0.5% in both cases. By using the other localization procedure the difference $E_{\text{can}}^{(2)} - E_{\text{loc}}^{(2)}$ is larger and the errors are 11% and 15%, or 3% in both cases.

CONCLUSION

In the localized representation of the MBPT we have to evaluate extra terms, which requires extra computer time. It is, however, a small fraction of the total computer time. Evaluating $\mathcal{E}_{11}^{(2,1)}$ and $\mathcal{E}_{11}^{(2,2)}$ we have to sum over 5 and 6 indices (and not over 6 and 8 indices as in conventional third and fourth order terms). The advantage of the localized representation is that the local and non-local effects can be separated by partitioning the "localized orbitals according to the order of neighbourhood" and neglecting terms which are of higher order^{27,28}. It would drastically decrease the computer time because the integrals over localized orbitals which will be omitted will not be generated by integral transformation.

The results of this paper clearly show that calculation of the third and fourth order localization corrections give sufficiently accurate energies.

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