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Application of the many-body perturbation theory to normal saturated hydrocarbons in the localized representation

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The second-order energy corrections are calculated for some normal saturated hydrocarbons by using the many body-perturbation theory (MBPT) based on localized orbitals. The correlation energies are expressed as the sum of contributions from virtual orbital pairs. We have found that these contributions are transferable and have interesting structural features: the trans-coplanar effects are relatively large. Partitioning the correlation energies according to the "order of neighbourhood" we have found that the zero order effects are the largest but the first and second neighbour contributions are also important.

Key words: Correlation energy — Many-body perturbation theory — Localized orbitals

1. Introduction

One of the more systematic approaches that goes beyond the independent particle scheme is based on the diagrammatic many-body perturbation theory (MBPT) [1–6]. In the so-called algebraic approximation this approach has been used to evaluate the energy for atoms and small molecules through the fourth order [7–13]. As the evaluation of the energy through the nth order is an M^{2n-2} procedure [14] (M: the number of basis functions), the extension to larger systems is not feasible at present. In the past decade considerable interest has been

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

devoted to the theoretical study of spatially extended electronic systems (e.g. large molecules, polymers, clusters and solids) where treatment with conventional methods on the *ab initio* level is out of the question, in the absence of translational symmetry. Previously, it was supposed that, for the correlation energy, local and non-local contributions could be distinguished with only the local contribution being important [15]. One of the present authors (EK) developed a perturbational approach where the zero order wavefunction is the APSG ground state [16]. The PCILO method [17] was also based on localized orbitals, which, however, are not solutions of the Hartree–Fock (HF) equations. Amos and Musher [18] and Davidson [19] have shown how the zero order Hamiltonian and the wavefunction can be chosen when the orbitals used are unitary transforms of the canonical HF orbitals. Localized orbitals have also been applied in theories involving partial summations (CPMET [20, 21], CEPA [22, 23] and other methods [24, 25]). One of the authors (EK) has proposed a method which is based on the localized HF orbitals and has shown how the local and non-local contribution of the correlation energy can be separated and the computational work decreased [26]. The method has been applied to cyclic polyenes (with PPP model Hamiltonian). The correlation energy through the fourth order (including some fifth-order terms) has been calculated and the results compared with those obtained by other methods (full CI, etc.) [27–29]. Taking the structure of the molecules into consideration, the localized orbitals and the correlation energy contributions 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 [30, 31]. The integrals over localized orbitals have been calculated (or estimated) and those not exceeding a certain threshold have been neglected. Our procedure needs less computational work because we determine the smallness of the contributions by considering the topological and geometrical structures of the molecule and not the values of the integrals. This means that integrals over localized orbitals which will be omitted will not be generated by integral transformation - the bottle-neck of the MBPT.

The aim of the present paper was to investigate the power of the method by applying it on the *ab initio* level to normal saturated hydrocarbons.

2. Theory

The exact (non-relativistic) Hamiltonian is partitioned as follows

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

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

$$\hat{F}\psi_k = \varepsilon_k\psi_k, \qquad k = 1, 2, \ldots, M, \tag{2}$$

where

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

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

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

the perturbation is as follows

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

Localizing the occupied and the virtual single-particle functions separately by unitary transformations,

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

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

the localized orbitals satisfy the following non-diagonal HF equations

$$\hat{F}\varphi_i = \sum_{j=1}^{N} \varepsilon_{ij}\varphi_j , \qquad i,j = 1,2,\ldots,N, \tag{8}$$

$$\hat{F}\varphi_a = \sum_{b=N+1}^{M} \varepsilon_{ab}\varphi_b , \qquad a,b = N+1, N+2,\ldots, M. \tag{9}$$

According to Amos and Musher [18] we can choose a new HF operator

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

the eigenfunctions of which are the transformed single-particle functions

$$\hat{F}^{\mathrm{loc}}\varphi_i = \varepsilon_i \varphi_i , \qquad i = 1,2,\ldots,N, \tag{11}$$

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

In this case the zero order Hamiltonian and the perturbation is chosen as follows:

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

$$\hat{W}^{\mathrm{loc}} = \hat{W} + \sum_{i=1}^{N} \left\{ \sum_{\substack{k,l=1 \\ k \neq l}}^{N} |k\rangle \varepsilon_{kl} \langle l| + \sum_{\substack{a,b=N+1 \\ a \neq b}}^{M} |a\rangle \varepsilon_{ab} \langle b| \right\}. \tag{14}$$

Due to the off-diagonal Fock matrix elements, the perturbation (14) has extra terms, compared with (5).

In the diagrammatic formulation the terms of the perturbation series are represented by graphs. Through fourth order all diagrams of the canonical representation have been reported [32]. The extra terms due to the off-diagonal Fock matrix elements are given in [27-29]. These terms enter the perturbation correction in third and higher orders.

Introducing orbitals instead of the single-particle functions (spin-orbitals) we obtain the second-order correction

$$E^{(2)}=\sum_{ij}\sum_{ab}\frac{\langle ij\,|\,ab\rangle(2\langle ij\,|\,ab\rangle-\langle ij\,|\,ba\rangle)}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}. \tag{15}$$

The individual pair corrections can be partitioned as the sum of contributions of given virtual orbital pairs *ab*

$$\begin{aligned} E_{ij}&=\sum_{ab} e_{ij}(ab),\\ e_{ij}(ab)&=\frac{\langle ij\,|\,ab\rangle(2\langle ij\,|\,ab\rangle-\langle ij\,|\,ba\rangle)}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}. \end{aligned} \tag{16}$$

Since the normal alkanes in the ground state are linear chain molecules, the partitioning of the localized orbitals in the valence shell according to the "order of neighbourhood" is relatively simple. At the end of the chain a C_1H localized orbital has three first neighbours (2 C_1H and C_1C_2), three second neighbours (2 C_2H and C_2C_3). In the middle of the chain a CH localized orbital has three first neighbours but six second and up to six third neighbours. All CC bonds have six first neighbours. The partitioning of the virtual orbitals depends upon the basis [33]. By using bases with equal numbers of *s* and *p* sets, each virtual orbital can be assigned to one of the occupied orbitals. Adding polarization functions to *sp* bases we obtain virtual orbitals which can be assigned to more than one of the occupied orbitals.

In this paper we are using a standard STO-3G basis. Each occupied orbital in the valence shell has one virtual orbital which is localized in the same spatial region. For the partitioning of the integrals $\langle ij\,|\,ab\rangle$ we used the simplest procedure: if a is the μth neighbour of i and b is the νth neighbour of j and $\mu\geq\nu$ then we consider the contribution of the integral as the μth neighbour effect. In this case we have for every ij pair only one zero neighbour contribution when a is the zero neighbour of i and, simultaneously, when b is the zero neighbour of j. Other partitions are also possible. The contributions of the same order are added for the individual pair correlations and for the total correlation energy. The partition of higher order corrections can be carried out in a similar fashion. Systematically omitting "higher neighbourhood" effects, the MBPT using the localized representation becomes an M^n procedure (instead of M^{2n-2}).

3. Calculations

The canonical HF equations have been solved for $C_{2n+1}H_{4n+4}$ ($n=0,1,2,3,4$) applying the program system SYCETY, thus efficiently utilizing the C_{2v} symmetry of the systems [34–36]. A standard STO-3G basis set has been used with a model geometry $R_{CH}=1.094$ Å, $R_{CC}=1.526$ Å and tetrahedral valence angles. The occupied and virtual orbitals have been localized in a separate manner by using the procedure of Boys [37]. Both the occupied and the virtual orbitals are well

Table 1. The second-order correlation energy calculated in the canonical and in the localized representation (in a.u.) with the STO-3G basis

	$E^{(2)}_{\text{can}}$	$E^{(2)}_{\text{loc}}$
CH_4	−0.05710777	−0.05601692
C_3H_8	−0.15907730	−0.15454196
C_5H_{12}	−0.26211500	−0.25378924

localized and the localized contributions of certain properties (Fock matrix elements, charge distributions etc.) are transferable to a very good approximation [38]. After suitable integral transformations the second-order corrections have been calculated in the localized representation and in the canonical representation and displayed in Table 1. The results of the two representations are very similar, which can be attributed to the localizability of the systems and of the basis sets. This suggests that the higher-order localization corrections are small.

4. Transferability and structural features of the correlation energy contributions

The virtual orbital pair contributions (16) for certain correlating pairs are shown in Tables 2 and 3. The contributions of the electron pair on the localized orbital CH lying in the mirror plain of the molecules are displayed in Table 2. Since there is one occupied and one virtual localized orbital for each bond, they can be uniquely characterized by the symbols of the corresponding bond. The carbon atoms are denoted consecutively, beginning at one end of the chain: C_1, C_2, C_3, C_4, C_5. The H atoms lying in the mirror plane of the molecule are denoted as H and H′ and those lying below and above the mirror plane are denoted as H_L and H_R, respectively. For the sake of simplicity, only the contributions of the doubly-occupied virtual orbitals ($a = b$) are displayed. Comparing the results obtained for the molecules investigated, we can see that the orbital pair contributions are transferable to a very good approximation. It is also remarkable that the contributions of the virtual orbitals of the CC bonds are larger than those of the CH bonds lying outside the mirror plane of the molecules. The difference is particularly large in the "second neighbourhood" where the C_2C_3 bond is trans-coplanar to C_1H.

In Table 3 we show the contributions to the correlations of the orbital pair: $i = C_1H$, $j = C_1H_L$. One virtual orbital (a) is fixed at the position C_1H while the position of the other (b) is altered. The contributions are again transferable to a very good approximation. It should be noted that the contribution of the virtual orbital at the position C_2H_R which is trans-coplanar to C_1H_2 is very important. It was found in the independent particle approximation, on semi-empirical [39] and *ab initio* [40] levels, that the vicinal coplanar tails of the localized orbitals are appreciable. The large contribution to the correlation energy can be explained in a similar way.

Table 2. The pair correlation contributions $e_{ii}(aa)$ in a.u. when $i = C_1H$ and a varies from C_1H to C_5H'

"Neighbourhood order"	Zero	1st		2nd		3rd		4th	5th
a	C_1H	C_1C_2 (C_1H')	C_1H_L C_1H_R	C_2C_3	C_2H_L C_2H_R	C_3C_4 (C_3H')	C_3H_L C_3H_R	C_4C_5	C_5H'
CH_4	−0.10222−1	−0.1579−3	−0.1579−3	—	—	—	—	—	—
C_3H_8	−0.10201−1	−0.1543−3	−0.1588−3	−0.1466−5	−0.9029−7	−0.3750−7	−0.1148−8	—	—
C_5H_{12}	−0.10199−1	−0.1532−3	−0.1543−3	−0.1420−5	−0.8948−7	−0.3691−7	−0.1112−8	−0.3820−9	−0.2799−10

Table 3. The pair correlation contributions $e_{ij}(ab)$ in a.u. when $i = C_1H$, $j = C_1H_L$, $a = C_1H$ and b goes from C_1H_L to C_3H_L

"Neighbourhood order"	Zero	1st		2nd			3rd		
b	C_1H_L	C_1C_2 (C_1H')	C_1H_R	C_2C_3	C_2H_R	C_2H_L	C_3C_4 (C_3H')	C_3H_R	C_3H_L
CH_4	−0.1856−2	−0.7086−5	−0.7086−5	—	—	—	—	—	—
C_3H_8	−0.1806−2	−0.5187−5	−0.7598−5	−0.1033−4	−0.1117−4	−0.2725−5	−0.1830−5	−0.1270−6	−0.6889−6
C_5H_{12}	−0.1805−2	−0.5396−5	−0.7574−5	−0.1022−4	−0.1113−4	−0.2729−5	−0.1820−5	−0.1135−6	−0.6414−6

Table 4. The total pair correlation energy, E_{ij}, for $i=j=\mathrm{C_1H}$ (in a.u.) and the partitioning according to the "neighbourhood order" (in %)

	E_{ij}	Zero	1st	2nd	3rd	4th	5th
CH_4	−0.10838 − 1	94.32%	5.68%	0.00%	0.00%	0.00%	0.00%
C_3H_8	−0.10836 − 1	94.13%	5.74%	0.12%	0.01%	0.00%	0.00%
C_5H_{12}	−0.10834 − 1	94.14%	5.73%	0.12%	0.01%	—	—

Table 5. The total pair correlation energy, E_{ij}, for $i=\mathrm{C_1H}$, $j=\mathrm{C_1H_L}$ (in a.u.) and the partitioning according to the "neighbourhood order" (in %)

		Zero	1st	2nd	3rd	4th	5th
CH_4	−0.20326 − 2	114.42%	−14.42%	0.00%	0.00%	0.00%	0.00%
C_3H_8	−0.21412 − 2	110.82%	−14.23%	3.05%	0.34%	0.00%	0.00%
C_5H_{12}	−0.21397 − 2	110.88%	−14.27%	3.01%	0.37%	0.01%	—

Table 6. The total second-order correlation energy for the localized representation (in a.u.) and the partitioning according to the "neighbourhood order" (in %)

		Zero	1st	2nd	3rd	4th	5th
CH_4	−0.56017 − 1	97.89%	2.21%	0.00%	0.00%	0.00%	0.00%
C_3H_8	−1.54542 − 1	94.17%	3.46%	2.29%	0.08%	0.00%	0.00%
C_5H_{12}	−2.53789 − 1	93.03%	3.84%	2.95%	0.17%	—	—

5. Partitioning of the pair correlations according to the "order of neighbourhood"

Our procedure used was described in Sect. 2. In Tables 4 and 5 we show the partitioning for the pairs $i=j=\mathrm{C_1H}$ and $i=\mathrm{C_1H}$, $j=\mathrm{C_1H_L}$, respectively. In the first case (intrapair correlation) more than 94% is contributed by the "zero order neighbourhood" and the effects of third and higher "order" can be neglected. In the second case (interpair correlation) the deviation is larger: the zero "order" terms overestimate the correlation energy by more than 10% but the first "order" contributions correct the error almost completely. Finally in Table 6 we display the partitioning of the total correlation energies. As can be seen, the "zero order" terms give more than 93% of the correlation energy and including the first and second neighbour effects we obtain more than 99%. The importance of the "second neighbour" contributions should be emphasized. They can be explained by the relatively large trans-coplanar effects mentioned in Sect. 4.

6. Conclusions

The method proposed by us to partition the correlation energy corrections according to the topological and geometrical structures of the molecules is

Table 7. The second-order correlation energy of CH_4 (in a.u.) for the canonical and for the localized representations with different basis sets

Basis set	$E^{(2)}_{\mathrm{can}}$	$E^{(2)}_{\mathrm{loc}}$
STO-3G	−0.05710777	−0.05601692
6-31G	−0.09931265	−0.09209949
6-31G*	−0.14120751	−0.11332266

apparently a useful one. It should be noted, however, that due to the STO-3G basis, the localizability of the wavefunction is exaggerated and the correlation energies calculated are less than a third of the "experimental". Nevertheless the terms occurring in this approximation represent the leading terms, in the sense that they give the largest contributions when using systematically extended basis sets. This can be demonstrated on the CH intrapair correlation of CH_4: for STO-3G we obtain −0.010838 a.u., with 6-31G we obtain −0.013921 a.u., and adding six *d* functions to the former basis we obtain −0.015283 a.u. By using larger basis sets the importance of localization corrections increases. This can be illustrated by the results obtained for CH_4 with different basis sets (Table 7). Applying the 6-31G basis we obtain three virtual orbitals for each occupied orbital in the valence shell. Adding six *d* orbitals to the 6-31G basis we obtain six new virtual orbitals, four of which can be uniquely assigned to the four occupied orbitals of the valence shell. The remaining two virtual orbitals cannot be assigned to any one bond but belong to all occupied orbitals of the same centre, forming a separate group. The partitioning of the correlation energy corrections can be carried out in this way for all standard basis sets. Calculations on larger systems are in progress.

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