

# MB-RSPT calculations of reaction energies for the series of reactions including C<sub>1</sub> to C<sub>4</sub> molecules

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Received 6 July 1984

*Paper published on the occasion of the 20th anniversary of the foundation of the Department of Physical Chemistry, Faculty of Natural Sciences, Komenský University, Bratislava*

The many-body Rayleigh—Schrödinger perturbation theory (MB-RSPT) up to the fourth-order was applied to calculations of reaction energies of 59 gas-phase reactions (including C<sub>1</sub> to C<sub>4</sub> hydrocarbons and some small organic oxygen-containing molecules) using the Gaussian double zeta plus polarization (DZ + P) basis set. We have shown types of reactions, for which MB-RSPT gives reaction energies within the chemical accuracy and types of reactions where even the complete fourth-order does not give the demanding accuracy.

Многочастичная теория возмущений Рэля—Шредингера (МЧТВРШ) до четвертого порядка была применена для расчета энергий 59 газофазовых реакций (включая C<sub>1</sub> до C<sub>4</sub> углеводороды и некоторые небольшие органические кислородсодержащие молекулы), используя гауссовский расширенный базисный набор с двумя экспонентами и набором поляризационных функций. Мы указали на типы реакций, для которых МЧТВРШ дает значения реакционных энергий в границах химической точности и типы реакций, где даже при полном четвертом порядке не достигается требуемая точность.

Almost twenty years have elapsed since the first *ab initio* SCF calculations of gas-phase reaction energies appeared [1]. Since that time a large number of papers concerning predictions of thermochemical data have arisen, e.g. [2—14]. During this time, used basis sets have been augmented, calculated molecules have been larger, and manners of including the correlation energy have been improved as well. With that, there was a gradual increase of pretensions to the quality of obtained values of the reaction energies as well. While Snyder and Basch in 1969

wrote “theoretical estimates of  $\Delta E$  must be accurate to  $\pm 40 \text{ kJ mol}^{-1}$  to begin to be of value to chemists” [2], in 1983, according to *Pople et al.*, an accuracy about  $\pm 5 \text{ kJ mol}^{-1}$  “would have some value” [13], since experimental techniques cannot often achieve this accuracy, either [15]. In spite of a strong scepticism of some experimentalists about perspectives of *ab initio* methods to reach the mentioned accuracy  $\pm 5 \text{ kJ mol}^{-1}$  [16], the problem of predictions of thermochemical data remains highly topical for present-day quantum chemistry.

In this paper we would like to show the possibility of such calculations when the correlation effects are included by MB-RSPT. The size-extensivity of this method (in contrast to the incomplete configuration interaction) is very important in the chemical reactivity, as discussed by *Bartlett et al.* [8, 10, 11]. In our previous paper [17] the correlation energies in the series of molecules, including  $C_1$  to  $C_4$  hydrocarbons and some small oxygen-containing organic molecules have been calculated by means of MB-RSPT up to the fourth order. These results formed the suitable basis for calculations of thermochemical data for the row of reactions which are presented and confronted with experiment.

### Calculations

In the quoted paper [17] the Gaussian basis set of the DZ+P quality and experimental geometries have been used. The valence shell correlation energies for given molecules have been calculated up to the full fourth-order MB-RSPT and contributions of individual types of excitations were analyzed in detail.

The  $H_2$  molecule was not given in [17]. For purposes of this paper we have calculated it in the same basis set and experimental geometry [18]. The SCF energy for  $H_2$  is  $-1.131181 E_H$  and the contributions of individual orders of the perturbation expansion to the correlation energy are presented in Table 1.

Let us define the reaction energy  $\Delta E$  as

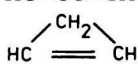
$$\Delta E = \sum_{\text{products}} E - \sum_{\text{reactants}} E \quad (1)$$

where  $E$  are total energies of molecules without zero-point energy (ZPE). The difference between SCF energies is denoted by the symbol  $\Delta E_{\text{SCF}}$ , similarly by  $\Delta E^{(2)}$ ,  $\Delta E^{(3)}$ ,  $\Delta E^{(4)}$  are denoted differences between contributions to the correlation energy from the second-, third-, and fourth-order MB-RSPT. So if we are speaking about the SCF level, for the calculated reaction energy  $\Delta E_{\text{calc}} = \Delta E_{\text{SCF}}$  and at the fourth-order level  $\Delta E_{\text{calc}} = \Delta E_{\text{SCF}} + \Delta E^{(2)} + \Delta E^{(3)} + \Delta E^{(4)}$ . For the experimental value  $\Delta E_{\text{exp}}$  it holds

$$\Delta E_{\text{exp}} = \sum_{\text{products}} (\Delta H^\circ(0 \text{ K}) - \text{ZPE}) - \sum_{\text{reactants}} (\Delta H^\circ(0 \text{ K}) - \text{ZPE}) \quad (2)$$

Table 1

Contributions of the correlation energy from individual orders of MB-RSPT

Molecule	$E^{(2)}/10^{-3} E_H$	$E^{(3)}/10^{-3} E_H$	$E^{(4)}/10^{-3} E_H$
H <sub>2</sub>	- 26.802	- 5.673	- 1.443
CH <sub>4</sub>	-160.764	-19.387	- 5.366
CH <sub>3</sub> CH <sub>3</sub>	-300.889	-31.449	-10.553
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	-442.859	-42.810	-16.007
CH <sub>2</sub> =CH <sub>2</sub>	-273.929	-24.440	-11.830
CH <sub>3</sub> CH=CH <sub>2</sub>	-415.829	-35.400	-17.368
H <sub>2</sub> C=C=CH <sub>2</sub>	-390.009	-28.194	-19.052
CH <sub>2</sub> =CHCH=CH <sub>2</sub>	-531.328	-38.567	-24.583
CH≡CH	-253.488	-11.925	-14.500
CH <sub>3</sub> C≡CH	-394.243	-22.418	-20.893
HC≡CC≡CH	-493.009	-10.945	-33.058
	-399.104	-24.845	-18.383
H <sub>2</sub> O	-200.873	- 5.971	- 5.798
CH <sub>3</sub> OH	-336.517	-18.475	-12.374
CO	-285.731	+ 1.165	-23.089
CO <sub>2</sub>	-478.267	+13.884	-37.114
H <sub>2</sub> CO	-315.385	- 7.520	-18.252
HCOOH	-494.238	- 2.771	-27.518
H <sub>2</sub> C=CO	-434.203	- 6.826	-28.875

where  $\Delta H^\circ(0\text{ K})$  is the heat of formation at 0 K. It can be calculated from the heat of formation at a certain temperature  $\Delta H^\circ(T)$  [9],

$$\Delta H^\circ(0\text{ K}) = \Delta H^\circ(T) - RT(3 + \Delta N) - N_A h \sum_i \nu_i / [\exp(h\nu_i/kT) - 1] \quad (3)$$

$\nu_i$  are vibration frequencies,  $N_A$  — the Avogadro constant, and  $\Delta N$  is the difference of numbers of molecules. ZPE is given by

$$\text{ZPE} = \frac{1}{2} h \sum_i \nu_i \quad (4)$$

For a linear molecule the factor by the  $RT$  term must be changed appropriately.

## Results

The main body of this paper lies in Table 2, where deviations of calculated  $\Delta E_{\text{calc}}$  from the  $\Delta E_{\text{exp}}$  values are presented. The investigated reactions can be divided into four classes:

Table 2. Differences between calculated and experimental reaction energies and  $\Delta E_{\text{exp}}$ 

No.	Reaction	$(\Delta E_{\text{calc}} - \Delta E_{\text{exp}})/(\text{kJ mol}^{-1})$				$\Delta E_{\text{exp}}/(\text{kJ mol}^{-1})^c$
		SCF <sup>a</sup>	2nd <sup>b</sup>	3rd <sup>c</sup>	4th <sup>d</sup>	
<i>A class</i>						
1	$\text{CH}_3\text{CH}_3 + \text{H}_2 \rightarrow 2\text{CH}_4$	-14.8	1.4	-2.9	0.4	-76.3
2	$\text{CH}_3\text{CH}_2\text{CH}_3 + 2\text{H}_2 \rightarrow 3\text{CH}_4$	-33.5	3.7	-6.8	0.6	-144.2
3	$\text{CH}_3\text{CH}_2\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{CH}_3\text{CH}_3$	-18.7	2.3	-3.8	0.2	-67.9
4	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4 + \text{CH}_2=\text{CH}_2$	-19.1	1.8	-5.5	-1.2	-55.9
5	$\text{CH}_3\text{C}\equiv\text{CH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{CH}\equiv\text{CH}$	-12.4	5.5	-3.0	3.5	-45.7
6	$\text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_4 \rightarrow 2\text{CH}_3\text{CH}_3$	-3.9	0.9	-0.9	-0.2	8.4
7	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{CH}_3 + \text{CH}_2=\text{CH}_2$	-4.3	0.4	-2.5	-1.6	20.4
8	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{CH}_3 \rightarrow$ $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_2=\text{CH}_2$	-0.4	-0.6	-1.6	-1.4	12.0
9	$\text{H}_2\text{C}=\text{C}=\text{CH}_2 + \text{CH}_4 \rightarrow 2\text{CH}_2=\text{CH}_2$	-10.1	-2.5	-5.9	-3.9	-15.0
10	$\text{H}_2\text{C}=\text{C}=\text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow$ $2\text{CH}_3\text{CH}=\text{CH}_2$	-5.4	-2.3	-1.7	-0.9	-47.4
11	$\text{CH}_3\text{C}\equiv\text{CH} + \text{CH}_4 \rightarrow \text{CH}_3\text{CH}_3 + \text{CH}\equiv\text{CH}$	2.4	4.1	-0.1	3.1	30.6
12	$\text{CH}_3\text{C}\equiv\text{CH} + \text{CH}_3\text{CH}_3 \rightarrow$ $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}\equiv\text{CH}$	6.3	3.1	0.8	3.3	22.2
13	$\text{CH}_3\text{C}\equiv\text{CH} + \text{CH}_2=\text{CH}_2 \rightarrow$ $\text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}\equiv\text{CH}$	6.7	3.7	2.5	4.7	10.2
14	$\text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_4$	-1.2	3.2	0.0	7.0	-127.1
15	$\text{CH}_3\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{CH}_3 + \text{H}_2\text{O}$	13.5	1.8	2.9	6.6	-50.8
<i>B class</i>						
16	$\text{CH}_2=\text{CHCH}=\text{CH}_2 + \text{H}_2 \rightarrow 2\text{CH}_2=\text{CH}_2$	-26.3	0.7	-11.5	-5.3	-19.0
17	$\text{CH}_2=\text{CHCH}=\text{CH}_2 + \text{CH}_4 \rightarrow$ $\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}=\text{CH}_2$	-7.2	-1.1	-6.0	-4.1	36.8
18	$\text{CH}_2=\text{CHCH}=\text{CH}_2 + \text{CH}_3\text{CH}_3 \rightarrow$ $2\text{CH}_3\text{CH}=\text{CH}_2$	-2.9	-1.5	-3.5	-2.5	16.4
19	$\text{HC}\equiv\text{CC}\equiv\text{CH} + \text{H}_2 \rightarrow 2\text{CH}\equiv\text{CH}$	-8.6	25.1	6.1	20.5	-32.3

Table 2 (Continued)

No.	Reaction	$(\Delta E_{\text{calc}} - \Delta E_{\text{exp}})/(\text{kJ mol}^{-1})$				$\Delta E_{\text{exp}}/(\text{kJ mol}^{-1})^{\text{r}}$
		SCF <sup>a</sup>	2nd <sup>b</sup>	3rd <sup>c</sup>	4th <sup>d</sup>	
20	$\text{HC}\equiv\text{CC}\equiv\text{CH} + \text{CH}_4 \rightarrow \text{CH}\equiv\text{CH} + \text{CH}_3\text{C}\equiv\text{CH}$	3.8	19.6	9.1	17.0	13.3
21	$\text{HC}\equiv\text{CC}\equiv\text{CH} + \text{CH}_3\text{CH}_3 \rightarrow 2\text{CH}_3\text{C}\equiv\text{CH}$	1.4	15.6	9.2	13.9	-17.3
<i>C class</i>						
22	$\text{H}_2\text{C}=\text{C}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4 + \text{CH}\equiv\text{CH}$	-11.9	-5.2	1.5	3.2	-53.6
23	$\text{CH}_3\text{C}\equiv\text{CH} \rightarrow \text{H}_2\text{C}=\text{C}=\text{CH}_2$	-0.5	10.6	-4.5	0.3	7.9
24	$\text{H}_2\text{C}=\text{C}=\text{CH}_2 \rightarrow$ $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \end{array}$	19.2	-4.6	4.2	5.9	83.9
25	$\text{CH}_3\text{C}\equiv\text{CH} \rightarrow$ $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \end{array}$	18.8	6.0	-0.4	6.2	91.8
26	$\text{CH}\equiv\text{CH} + \text{CH}_3\text{CH}_3 \rightarrow 2\text{CH}_2=\text{CH}_2$	-13.0	4.1	-10.3	-6.7	-37.7
27	$\text{CH}_2=\text{CHCH}=\text{CH}_2 + \text{CH}\equiv\text{CH} \rightarrow$ $2\text{H}_2\text{C}=\text{C}=\text{CH}_2$	-4.3	8.3	-7.2	-4.6	49.5
28	$\text{CH}_3\text{C}\equiv\text{CH} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow$ $2\text{CH}_3\text{CH}=\text{CH}_2$	-5.9	8.4	-6.2	-0.5	-39.5
29	$\text{CH}_3\text{OH} + \text{HC}\equiv\text{CC}\equiv\text{CH} \rightarrow$ $\text{CH}_3\text{C}\equiv\text{CH} + \text{H}_2\text{C}=\text{CO}$	2.9	5.7	6.2	-5.2	-143.3
30	$\text{H}_2\text{O} + \text{HC}\equiv\text{CC}\equiv\text{CH} \rightarrow \text{CH}\equiv\text{CH} + \text{H}_2\text{C}=\text{CO}$	-8.3	8.0	3.2	-8.7	-61.9
<i>D class</i>						
31	$\text{CH}\equiv\text{CH} + \text{H}_2 \rightarrow \text{CH}_2=\text{CH}_2$	-26.4	-9.7	-27.7	-16.9	-201.8
32	$\text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3$	-13.4	-13.8	-17.3	-10.2	-164.2
33	$\text{CH}_3\text{C}\equiv\text{CH} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2$	-19.7	-6.0	-25.2	-12.1	-191.7
34	$\text{H}_2\text{C}=\text{C}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2$	-19.2	-16.7	-20.7	-12.5	-199.6
35	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \end{array} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2$	-38.5	-12.0	-24.8	-18.4	-283.4
36	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$	-13.8	-14.4	-19.0	-11.6	-152.1

Table 2 (Continued)

No.	Reaction	$(\Delta E_{\text{calc}} - \Delta E_{\text{exp}})/(\text{kJ mol}^{-1})$				$\Delta E_{\text{exp}}/(\text{kJ mol}^{-1})^e$
		SCF <sup>a</sup>	2nd <sup>b</sup>	3rd <sup>c</sup>	4th <sup>d</sup>	
37	$\text{HC}\equiv\text{CC}\equiv\text{CH} + 2\text{H}_2 \rightarrow \text{CH}_2=\text{CHCH}=\text{CH}_2$	-35.1	5.0	-37.7	-7.9	-417.0
38	$\text{CH}\equiv\text{CH} + \text{CH}_4 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2$	-7.3	-11.5	-22.2	-15.6	-146.0
39	$\text{CH}_2=\text{CH}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$	5.3	-16.2	-13.5	-10.4	-96.3
40	$\text{CH}\equiv\text{CH} + 2\text{CH}_4 \rightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}_3$	-11.6	-11.1	-24.7	-17.2	-125.5
41	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HC} \quad \quad \text{CH} \\ \parallel \\ \text{C} \end{array} + 2\text{CH}_4 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{CH}_3$	-23.7	-13.4	-21.9	-18.8	-207.1
42	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HC} \quad \quad \text{CH} \\ \parallel \\ \text{C} \end{array} + 3\text{CH}_4 \rightarrow 2\text{CH}_3\text{CH}_3 + \text{CH}_2=\text{CH}_2$	-28.0	-13.1	-24.4	-20.4	-186.7
43	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HC} \quad \quad \text{CH} \\ \parallel \\ \text{C} \end{array} + \text{CH}_2=\text{CH}_2 + 2\text{CH}_3\text{CH}_3 \rightarrow$	-15.5	-14.7	-18.5	-16.9	-235.9
44	$2\text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_3$ $\text{HC}\equiv\text{CC}\equiv\text{CH} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow$ $\text{CH}_2=\text{CHCH}=\text{CH}_2 + \text{CH}_3\text{C}\equiv\text{CH}$	-1.6	25.4	6.4	15.9	-73.2
45	$\text{CO} + \text{H}_2 \rightarrow \text{H}_2\text{CO}$	17.6	10.1	2.2	18.7	-26.8
46	$\text{CO} + 3\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_4$	6.4	18.2	-6.7	36.0	-268.4
47	$\text{CO}_2 + 4\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{CH}_4$	-18.2	42.1	-17.0	51.0	238.8
48	$\text{H}_2\text{CO} + 2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_4$	-11.1	8.2	-8.9	17.3	-241.6
49	$\text{HCOOH} + 3\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{CH}_4$	-11.3	20.5	-9.8	29.3	-230.8
50	$\text{H}_2\text{C}=\text{CO} + 4\text{H}_2 \rightarrow \text{H}_2\text{O} + 2\text{CH}_4$	-55.0	-5.1	-45.0	2.5	-412.8
51	$\text{CO} + \text{CH}_4 \rightarrow \text{CH}\equiv\text{CH} + \text{H}_2\text{O}$	61.0	40.4	41.2	62.6	173.9
52	$\text{CO} + 2\text{CH}_4 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{O}$	53.7	28.9	19.0	47.0	27.9
53	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{HCOOH}$	17.8	-2.3	3.1	6.6	-37.6
54	$\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{H}_2\text{CO}$	4.1	25.8	0.7	16.4	244.5
55	$\text{CO}_2 + \text{CH}_4 \rightarrow \text{H}_2\text{C}=\text{CO} + \text{H}_2\text{O}$	36.8	47.2	28.0	48.5	174.0
56	$\text{CO}_2 + 2\text{CH}_4 \rightarrow \text{H}_2\text{C}=\text{C}=\text{CH}_2 + \text{H}_2\text{O}$	48.3	69.4	29.4	74.6	257.2
57	$\text{HCOOH} + \text{CH}_4 \rightarrow \text{CH}\equiv\text{CH} + 2\text{H}_2\text{O}$	43.3	42.7	38.2	56.0	211.5
58	$\text{HCOOH} + 2\text{CH}_4 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + 2\text{H}_2\text{O}$	35.9	31.2	16.0	40.4	65.5
59	$\text{H}_2\text{C}=\text{CO} + \text{CH}_4 \rightarrow \text{H}_2\text{C}=\text{C}=\text{CH}_2 + \text{H}_2\text{O}$	11.5	22.3	1.4	26.1	83.1

a)  $\Delta E_{\text{SCF}} - \Delta E_{\text{exp}}$ . b)  $\Delta E_{\text{SCF}} + \Delta E^{(2)} - \Delta E_{\text{exp}}$ . c)  $\Delta E_{\text{SCF}} + \Delta E^{(2)} + \Delta E^{(3)} - \Delta E_{\text{exp}}$ . d)  $\Delta E_{\text{SCF}} + \Delta E^{(2)} + \Delta E^{(3)} + \Delta E^{(4)} - \Delta E_{\text{exp}}$ .

e) Experimental heat of reaction adjusted to 0 K and corrected for zero-point energy,  $\Delta H^\circ(0\text{ K}) - \Delta\text{ZPE}$ . Vibrational frequencies from [18–21],

*A class* — reactions 1—15. These are reactions with the conserved numbers of single, double, and triple bonds, besides the reactions belonging to the *B* class. For all of them, a perfect agreement with experiment was reached if the correlation energy was included. The standard deviations from experiment were 13.3, 2.8, 3.4, and 3.4 kJ mol<sup>-1</sup> at the SCF, second-, third-, and fourth-order level, respectively. The maximum deviation at the SCF level was 33.5 kJ mol<sup>-1</sup>, at the second-order it was no more than 5.5 kJ mol<sup>-1</sup> and for calculations up to the fourth-order 7.0 kJ mol<sup>-1</sup>. Generally, an inclusion of the correlation energy by the very simple second-order significantly improved SCF reaction energies. The  $\Delta(E_{\text{SCF}} + E^{(2)})$  values are very close to fourth-order ones. In those cases, where remains a conserved number of single C—C and also C—H bonds excellent agreements with experiment were achieved already at the SCF level (according to the assumption of the correlation energy conservation [26]).

*B class* — reactions 16—21. For these reactions remain conserved numbers of single, double, and triple bonds. However the conjugation between the multiple bonds is broken in the course of a reaction. The influence of the conjugation upon the correlation energy in the case of butadiene was not exhibited significantly [17], and we have achieved similar agreement with experiment as for reactions of the *A* class. On the other hand, in butadiyne the significance of the double conjugation was larger [17] and results are significantly worsened.

*C class* — reactions 22—30. To this class belong reactions for which the total unsaturation of the system is conserved. It means that there is a mutual substitution of one C≡C bond, two C=C bonds, and one three-member ring with the double bond. Belonging to this class are also two reactions of molecules involving the CO bond. Concerning the accuracy similar conclusions as for the *A* class also for these reactions are valid. The standard deviations of  $\Delta E$  from experiment were 11.4, 7.1, 5.6, and 5.3 kJ mol<sup>-1</sup> at the SCF, second-, third-, and fourth-order level, respectively.

*D class* — reactions 31—59. In course of these reactions the multiple bonds are partly or completely saturated, the rings are broken. The reactions of the CO molecule or molecules with the C=O bond (the character of bonds in these molecules is significantly changed during a reaction) belong also to this class. Considerable disagreements with experimental values of  $\Delta E$  were found for most of these reactions.

## Discussion

There are at least two obvious reasons for errors in calculated reaction energies: The basis set deficiency and the unbalanced convergence of the perturbation expansion for reactants and products. The problem is, however that it is difficult to separate the errors produced by these two reasons. Undoubtedly, the basis set

effect may be important even in the SCF part of  $\Delta E$ . According to the accumulated experience [27] the difference between DZ + P results and the Hartree—Fock limit is usually within 5—10 kJ mol<sup>-1</sup>, but for some reactions it may be larger [28]. At the fourth-order MB-RSPT level we have at our disposal results of *Pople et al.* [13] and *Binkley and Frisch* [29] for dissociation energies of small hydrides and some diatomic molecules. These studies revealed that even *f*-functions are important to achieve accuracy of  $\pm 8$  kJ mol<sup>-1</sup>. Including *f*-functions is clearly not possible within the fourth-order MB-RSPT calculations for our large molecules, but one hopes that some compensation of errors may occur with closed-shell reactants and products, which is a basic presumption of the present work. This seems to be true for reactions in the *A* class, where molecules with similar bonding properties participate on the left and the right hand sides of reaction schemes. This guarantees the compensation of the basis set error and also similar convergence of the perturbation series for products and reactants. The similar convergence for molecules with conserved numbers of single, double, and triple bonds and the additivity of bond correlation energies has been demonstrated in our previous paper [17]. Quite similar conclusions as for the *A* class are also valid for reactions in the *C* class, though the explanation of these findings is not so much transparent. Obviously, the conservation of the total unsaturation is sufficient for the compensation of the basis set effects. Moreover, the total convergence for molecules at the right and left hand sides of the reaction scheme also seems to be approximately the same. This point of view is supported by the fact that standard deviation from experiment is improved smoothly from SCF up to the fourth order. As well, the difference of the third-order and the fourth-order MB-RSPT is relatively small for most *C* class reactions (as well as for reactions of the *A* class).

Very disappointing results were obtained for reactions of the *D* class. The large discrepancies between the second-, third-, and fourth-order indicate that the unbalanced convergence of MB-RSPT is the main reason of the deviation of  $\Delta E$  from experiment (see *e.g.* reactions 46—50). On the other hand some calculations by the CI-SD method [28] corrected for the unlinked cluster contributions demonstrated quite considerable defect of the DZ + P basis. It should be mentioned that the contraction of the DZ + P basis of Ref. [28] has later been criticized by *Ahlrichs and Taylor* [30].

Clearly, the solution of the problem calls for calculations with sufficiently large basis sets, using the coupled cluster methods including at least single and double excitation clusters (CCSD method, developed by *Purvis and Bartlett* [31]) or even triple excitation clusters (approximate CCSDT methods, developed in *Bartlett's* [32, 33] and our laboratories). Since such calculations are beyond our computer capacities, we plan to perform the DZ + P CCSDT calculations and the fourth-order MB-RSPT calculations with the large basis set, at least for some typical reactions with small molecules. This should clarify the relative influence of higher



orders and some types of higher excitations and the basis set effects. Finally we can conclude: MB-RSPT provides satisfactory predictions of  $\Delta E$  (even at the very simple second-order) for those reactions where the perturbation expansion for reactants and products converged at the fourth order, or where the mutual compensation of higher order contributions has occurred, and where the basis set effects are also compensated. The fourth-order MB-RSPT is not an appropriate method for predictions of  $\Delta E$  within the chemical accuracy for those reactions where the mentioned compensations cannot be expected. This concerns preferably reactions of the *D* class.

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Translated by V. Kellő