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Prediction of full CI energies with the help of sixth-order Møller–Plesset (MP6) perturbation theory[1]

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Abstract

The sixth-order Møller–Plesset (MP6) correlation energy is analysed by using first- and second-order cluster operators and distinguishing between connected and disconnected operator products. Each product is described by simplified Brandow diagrams that help to characterize the associated energy contributions in terms of orbital relaxation, pair correlation, three-electron correlation or four-electron correlation effects. The importance of the various correlation terms and their coverage at MP2, MP3, MP4, MP5, and MP6 are analysed to understand and to predict the convergence behaviour of the MP*n* series, which strongly depends on the electronic structure of the atoms and molecules investigated. Adjusting existing extrapolation procedures to the convergence behaviour of the MP*n* series leads to improved predictions of full CI (FCI) energies based on MP6 correlation energies. The best results are obtained by a combination of first-order and second-order Feenberg scaling, which produces the results of higher order Feenberg scaling. The mean absolute deviation of predicted FCI energies from exact values is found to be 0.07 mhartree for atoms and molecules in their equilibrium geometry and 1.03 mhartree for molecules with stretched geometries and, thereby, considerable multi-reference character. Reasonable FCI energies can also be obtained with approximate MP6 methods, the most economic method of which is MP6(M7) which scales with $O(M^7)$ (M is the number of basis functions). Mean absolute deviations of FCI energies based on MP6(M7) are 0.40 and 1.88 mhartree for equilibrium and stretched geometries, respectively. © 1997 Elsevier Science B.V. © 1997 Elsevier Science B.V.

Keywords: Møller–Plesset; Perturbation theory; Cluster operators; Correlation energy

1. Introduction

In previous work, we described the development and implementation of sixth-order Møller–Plesset (MP6) perturbation theory [1–6]. MP6 is the last MP*n* method that can be developed using traditional techniques, as can be seen from Table 1 which gives the number of partial energy terms covered at order *n*. In the case of MP6, there are 55 energy terms, of which 36 are unique. However, at MP7 and MP8, there are already 221 and 915 energy terms leading to 141 and 583 unique terms. Clearly, development of a method such as MP7 or MP8 requires some kind of automated method development strategy based on computer algebra. Although the most expensive energy term of MP6 scales with $O(M^{12})$ (M is the number of basis functions), it is possible to reduce computational cost to $O(M^9)$ [1,2]. However, this cost factor is still rather large and prevents routine calculations of larger molecules at the MP6 level of theory. On the other hand, it is possible to use MP6 for systematic investigations on small molecules. Based on these MP6 calculations and a partitioning of the

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Table 1
Number of energy contributions $E_{AB..}^{(n)}$ covered at MPn (n = 2,3,...,8)[a]

Order n	Total number terms	Number of unique terms	Cost
2	1	1	$O(M^5)$
3	1	1	$O(M^6)$
4	4	4	$O(M^7)$
5	14	9	$O(M^8)$
6	55	36	$O(M^9)$
7	221	141	$O(M^{10})$
8	915	583	$O(M^{11})$

[a] M denotes the number of basis functions.

MP6 correlation energy into individual energy contributions associated with specific excitations [1–5], we were able to show that the MPn convergence behaviour depends on the electronic structure of the system investigated [5]. The convergence characteristics of the MPn series are of fundamental importance for the understanding of the electron correlation problem in many-electron systems.

In this work, we continue our previous work [1–5] by setting up improved extrapolation procedures that adjust to the convergence characteristics of the MPn series and, in this way, lead to reliable predictions of MPn limit energies ($n = \infty$) that are identical with full CI (FCI) energies. For this purpose, it is important to clarify which electronic systems can reliably be described with MP6. MP6 covers connected quadruple (Q), disconnected pentuple (P), and disconnected hextuple (H) correlation effects not covered at lower orders of perturbation theory. Clearly, any correlation problem that involves strongly coupled correlated movements of more than four electrons, cannot be handled by MP6. Since our previous investigations included some of these systems it will be important to identify and exclude them from the present investigation. Our actual goal is to predict FCI correlation energies for single-reference systems with an accuracy of 0.1 mhartree or better, and for multi-reference systems which can still be handled at MP6, with an accuracy of 1 mhartree or better.

It is also important to investigate to what extent approximate MP6 methods can be used for the prediction of FCI energies. In recent work, we suggested the use of MP6(M8) and MP6(M7), which scale with $O(M^8)$ and $O(M^7)$, respectively, because all terms more expensive than $O(M^8)$ or $O(M^7)$ are deleted in the MP6 energy formula [3]. At MP6, all $O(M^9)$ terms are associated with connected Q correlation effects; however we will show that deleting these terms does not mean that connected Q terms are not covered by MP6(M8) or MP6(M7) at all. For this purpose, we will analyse in the following section the various energy contributions calculated at MP6 with the help of Brandow diagrams, thus showing which electron correlation effects are covered by a given term. This insight will lead to a better understanding of the performance of MP6 and the approximate MP6 methods, MP6(M8) and MP6(M7).

2. Partitioning and analysis of the MP6 correlation energy

MP6 requires the calculation of the third-order perturbed wave function, which can be expressed with the help of third-order cluster operators $\hat{T}_i^{(3)}$ (i = 1, 2, 3, 4), i.e. at MP6, for the first time, connected Q effects are included into the expansion of the correlation energy. A derivation of the MP6 energy formula in terms of third-order cluster operators has been described by Kucharski and Bartlett and it has been shown that the MP6 energy can easily be structured into just four terms associated with the four third-order cluster operators [7]. (For the derivation of MP6 energies from FCI calculations, see Refs. [8] and [9].)

We have refrained from using third-order cluster operators and, instead, have used a more elementary derivation of MP6 in terms of first- and second-order cluster operators, which makes it possible to partition the MP6 correlation energy into 28 (out of 36) partial contributions that provide a basis for the detailed analysis of correlation effects covered at this level of theory. Third-order cluster operators are related to second- and first-order cluster operators according to Eqs. (1)–(4)

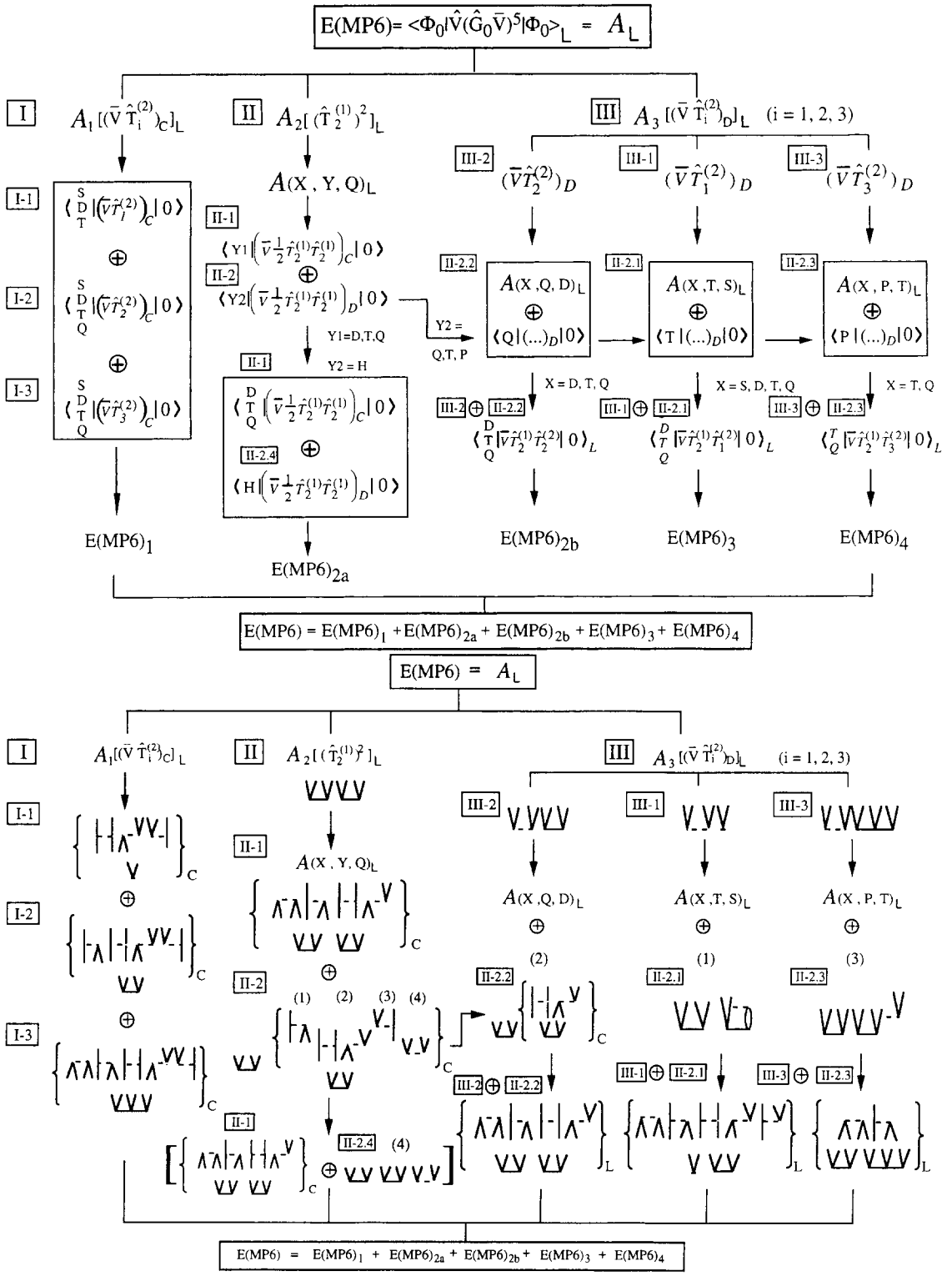
$$\hat{T}_1^{(3)} = \frac{1}{D_s}[\bar{V}(\hat{T}_1^{(2)} + \hat{T}_2^{(2)} + \hat{T}_3^{(2)})]_C \tag{1}$$

$$\hat{T}_2^{(3)} = \frac{1}{D_d}\left[\bar{V}\left(\hat{T}_1^{(2)} + \hat{T}_2^{(2)} + \hat{T}_3^{(2)} + \frac{1}{2}(\hat{T}_2^{(1)})^2\right)\right]_C \tag{2}$$

Table 2
Energy contributions covered by MP6, associated cluster operators, and computational cost[a]

Terms	Associated cluster operators $\hat{T}_i^{(n)}$	Cost
$E(\mathrm{MP6})_1$		
$E_{SSS}^{(6)}$	$(\hat{T}_1^{(2)})^+$, $\hat{T}_1^{(3)}[\hat{T}_1^{(2)}]$	M^6
$E_{SSD}^{(6)}$ (× 2)	$(\hat{T}_1^{(2)})^+$, $\hat{T}_1^{(3)}[\hat{T}_2^{(2)}]$	M^6
$E_{SST}^{(6)}$ (× 2)	$(\hat{T}_1^{(2)})^+$, $\hat{T}_1^{(3)}[\hat{T}_3^{(2)}]$	M^7
$E_{SDS}^{(6)}$	$(\hat{T}_1^{(2)})^+$, $\hat{T}_2^{(3)}[\hat{T}_1^{(2)}]$	M^6
$E_{SDD}^{(6)}$ (× 2)	$(\hat{T}_1^{(2)})^+$, $\hat{T}_2^{(3)}[\hat{T}_2^{(2)}]$	M^6
$E_{SDT}^{(6)}$ (× 2)	$(\hat{T}_1^{(2)})^+$, $\hat{T}_2^{(3)}[\hat{T}_3^{(2)}]$	M^7
$E_{DST}^{(6)}$	$(\hat{T}_2^{(2)})^+$, $\hat{T}_1^{(3)}[\hat{T}_2^{(2)}]$	M^6
$E_{DST}^{(6)}$ (× 2)	$(\hat{T}_2^{(2)})^+$, $\hat{T}_1^{(3)}[\hat{T}_3^{(2)}]$	M^7
$E_{DDD}^{(6)}$	$(\hat{T}_2^{(2)})^+$, $\hat{T}_2^{(3)}[\hat{T}_2^{(2)}]$	M^6
$E_{DDT}^{(6)}$ (× 2)	$(\hat{T}_2^{(2)})^+$, $\hat{T}_2^{(3)}[\hat{T}_3^{(2)}]$	M^7
$E_{TST}^{(6)}$	$(\hat{T}_3^{(2)})^+$, $\hat{T}_1^{(3)}[\hat{T}_3^{(2)}]$	M^7
$E_{TDT}^{(6)}$	$(\hat{T}_3^{(2)})^+$, $\hat{T}_2^{(3)}[\hat{T}_3^{(2)}]$	M^7
$E_{DTD}^{(6)}$	$(\hat{T}_2^{(2)})^+$, $\hat{T}_3^{(3)}[\hat{T}_2^{(2)}]$	M^7
$E_{DTT}^{(6)}$ (× 2)	$(\hat{T}_2^{(2)})^+$, $\hat{T}_3^{(3)}[\hat{T}_3^{(2)}]$	M^8
$E_{TTT}^{(6)}$	$(\hat{T}_3^{(2)})^+$, $\hat{T}_3^{(3)}[\hat{T}_3^{(2)}]$	M^8
$E_{TQT}^{(6)}$	$(\hat{T}_3^{(2)})^+$, $\hat{T}_4^{(3)}[\hat{T}_3^{(2)}]$	M^9
$E(\mathrm{MP6})_{2a_1}$		
$E_{SDQ}^{(6)}$ (× 2)	$(\hat{T}_1^{(2)})^+$, $\hat{T}_2^{(3)}[(1/2)(\hat{T}_2^{(1)})^2]$	M^6
$E_{DDQ}^{(6)}$ (× 2)	$(\hat{T}_2^{(2)})^+$, $\hat{T}_2^{(3)}[(1/2)(\hat{T}_2^{(1)})^2]$	M^6
$E_{TDQ}^{(6)}$ (× 2)	$(\hat{T}_3^{(2)})^+$, $\hat{T}_2^{(3)}[(1/2)(\hat{T}_2^{(1)})^2]$	M^7
$E_{QDQ}^{(6)}$	$(1)/(2)(\hat{T}_2^{(1)})^+)^2$, $\hat{T}_2^{(3)}[(1)/(2)(\hat{T}_2^{(1)})^2]$	M^6
$E(\mathrm{MP6})_{2a_2}$		
$E_{STQ}^{(6)}(\mathrm{II}) + E_{QTQ}^{(6)}(\mathrm{II})_a$	$(\hat{T}_1^{(2)})^+(\hat{T}_2^{(1)})^+$, $D_f\hat{T}_3^{(3)}[(1)/(2)(\hat{T}_2^{(1)})^2]$	M^6
$E_{QTQ}^{(6)}(\mathrm{II})_b$	$(1)/(2)((\hat{T}_2^{(1)})^+)^2$, $\hat{T}_3^{(3)}[(1)/(2)(\hat{T}_2^{(1)})^2]$	M^7
$E_{DTQ}^{(6)}(\mathrm{II})$ (× 2)	$(\hat{T}_2^{(2)})^+$, $\hat{T}_3^{(3)}[(1)/(2)(\hat{T}_2^{(1)})^2]$	M^7
$E_{TTQ}^{(6)}(\mathrm{II})$ (× 2)	$(\hat{T}_3^{(2)})^+$, $\hat{T}_3^{(3)}[(1)/(2)(\hat{T}_2^{(1)})^2]$	M^8
$E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(II)_a$	$(\hat{T}_2^{(1)})^+(\hat{T}_2^{(2)})^+$, $D_q\hat{T}_4^{(3)}[(1)/(2)(\hat{T}_2^{(1)})^2]$	M^6
$E_{QQQ}^{(6)}(\mathrm{II})_b$	$(1)/(2)((\hat{T}_2^{(1)})^+)^2$, $\hat{T}_4^{(3)}[(1)/(2)(\hat{T}_2^{(1)})^2]$	M^9
$E_{TQQ}^{(6)}(\mathrm{II})$ (× 2)	$(\hat{T}_3^{(2)})^+$, $\hat{T}_4^{(3)}[(1)/(2)(\hat{T}_2^{(1)})^2]$	M^9
$E(\mathrm{MP6})_{2a_1}$		
$E_{QHQ}^{(6)}$	$(1)/(2)((\hat{T}_2^{(1)})^+)^2$, $(1)/(3!)(\hat{T}_2^{(1)})^3$	M^6
$E(\mathrm{MP6})_{2b}$		
$E_{DQD}^{(6)} + E_{DQQ}^{(6)}(\mathrm{I})$	$(\hat{T}_2^{(2)})^+$, $\hat{T}_2^{(1)}\hat{T}_2^{(2)}$	M^6
$E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I})$ (× 2)	$(\hat{T}_3^{(2)})^+$, $\hat{T}_2^{(1)}\hat{T}_2^{(2)}$	M^7
$E_{QQD}^{(6)} + E_{QQQ}^{(6)}(\mathrm{I})$	$D_q\hat{T}_4^{(3)}[(1)/(2)((\hat{T}_2^{(1)})^+)^2]$ and $D_d(\hat{T}_2^{(2)})^+(\hat{T}_2^{(1)})^+$, $\hat{T}_2^{(1)}\hat{T}_2^{(2)}$	M^6
$E(\mathrm{MP6})_3$		
$E_{STS}^{(6)} + E_{STQ}^{(6)}(\mathrm{I})$	$(\hat{T}_1^{(2)})^+$, $\hat{T}_1^{(2)}\hat{T}_2^{(1)}$	M^6
$E_{DTS}^{(6)} + E_{DTQ}^{(6)}(\mathrm{I})$ (× 2)	$(\hat{T}_2^{(2)})^+$, $\hat{T}_1^{(2)}\hat{T}_2^{(1)}$	M^6
$E_{TTS}^{(6)} + E_{TTQ}^{(6)}(\mathrm{I})$ (× 2)	$(\hat{T}_3^{(2)})^+$, $\hat{T}_1^{(2)}\hat{T}_2^{(1)}$	M^7
$E_{QTS}^{(6)} + E_{QTQ}^{(6)}(\mathrm{I})$	$(1)/(2)((\hat{T}_2^{(1)})^+)^2$, $\hat{T}_1^{(2)}\hat{T}_2^{(1)}$	M^6
$E(\mathrm{MP6})_4$		
$E_{TPT}^{(6)}(\mathrm{I}) + E_{TPQ}^{(6)}(\mathrm{I})$	$(\hat{T}_3^{(2)})^+$, $\hat{T}_2^{(1)}D_3\hat{T}_1^{(3)}[\hat{T}_3^{(2)}]$	M^7
$E_{TPT}^{(6)}(\mathrm{II}) + E_{TPQ}^{(6)}(\mathrm{II})$	$(\hat{T}_3^{(2)})^+$, $(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_C$	M^8
$E_{QPT}^{(6)}(\mathrm{I}) + E_{QPQ}^{(6)}(\mathrm{I})$	$(1)/(2)((\hat{T}_2^{(1)})^+)^2$, $\hat{T}_2^{(1)}D_q\hat{T}_2^{(3)}[\hat{T}_3^{(2)}]$	M^7
$E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})$	$(1)/(2)((\hat{T}_2^{(1)})^+)^2$, $(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_C$	M^8

[a] M denotes the number of basis functions and D the denominator in Eqs. (1)–(4).


E(MP6)= <Φ0|V̂(Ĝ0V̄)5|Φ0>L = AL
I
II
III
III-2
III-1
III-3
I-1
I-2
I-3
II-1
II-2
II-2.2
II-2.1
II-2.3
II-2.4
Y2 =
Q,T, P
Y1=D,T,Q
Y2 = H
X = D, T, Q
X = S, D, T, Q
X = T, Q
E(MP6)1
E(MP6)2a
E(MP6)2b
E(MP6)3
E(MP6)4
E(MP6) = E(MP6)1 +E(MP6)2a+ E(MP6)2b +E(MP6)3+ E(MP6)4
E(MP6) = AL
E(MP6) = E(MP6)1 + E(MP6)2a + E(MP6)2b + E(MP6)3 + E(MP6)4

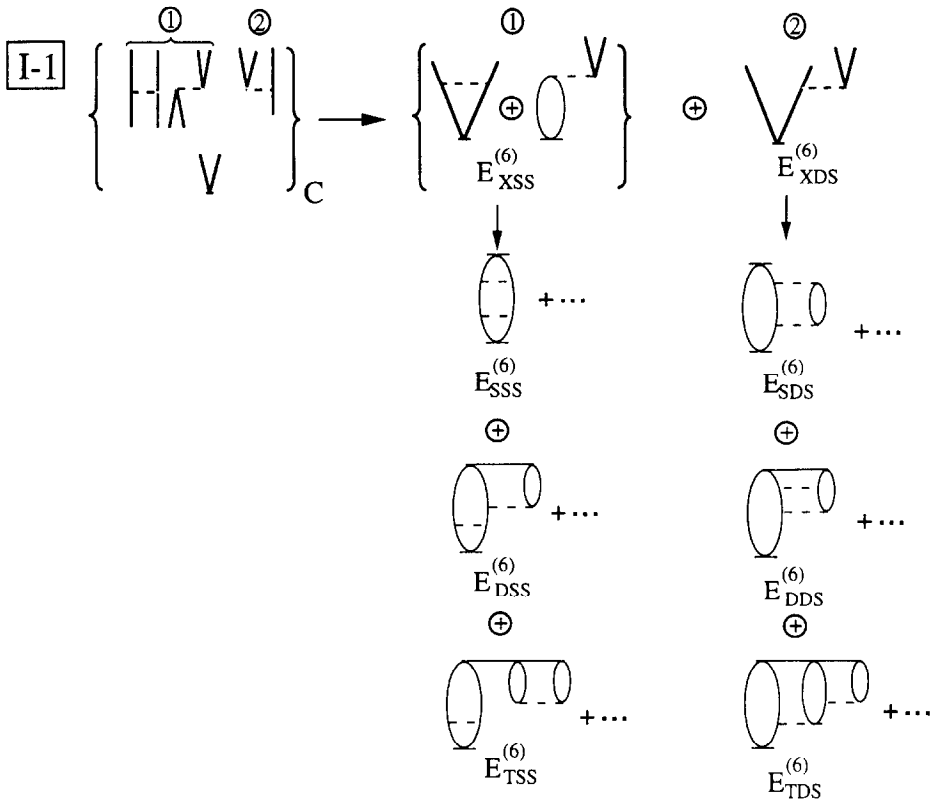


Fig. 2. Simplified Brandow diagrams for the term I-1.

$$\hat{T}_3^{(3)} = \frac{1}{D_t}\left[\bar{V}\left(\hat{T}_2^{(2)} + \hat{T}_3^{(2)} + \frac{1}{2}(\hat{T}_2^{(1)})^2\right)\right]_C \tag{3}$$

$$\hat{T}_4^{(3)} = \frac{1}{D_q}\left[\bar{V}\left(\hat{T}_3^{(2)} + \frac{1}{2}(\hat{T}_2^{(1)})^2\right)\right]_C \tag{4}$$

where $D_x(=E_0-E_x)$ (x = s, d, t, q) is the energy denominator and the second-order cluster operators $\hat{T}_j^{(2)}$ (j = 1, 2, 3) are given by

$$\hat{T}_j^{(2)} = \frac{1}{D_y}\bar{V}\hat{T}_2^{(1)} \quad (y = s,d,t \text{ for } j = 1,2,3) \tag{5}$$

with $\hat{T}_2^{(1)}$ being defined by

$$\hat{T}_2^{(1)}|\Phi_0\rangle = \sum_d^D |\Phi_d\rangle(E_0 - E_d)^{-1}V_{d0} \tag{6}$$

The indices s,d,t,q denote single (S), double (D), triple (T), and Q excitations. Each part of the operators $\hat{T}_j^{(3)}$ in Eqs. (1)–(4), indicated in the following as $\hat{T}_i^{(3)}[\hat{T}_j^{(2)}]$ (or $\hat{T}_i^{(3)}[\frac{1}{2}(\hat{T}_2^{(1)})^2]$), can lead to the construction of different MP6 energy terms. For example, the first term in Eq. (1), $\hat{T}_1^{(3)}[\hat{T}_1^{(2)}]$ (= (1)/(D_s) $\bar{V}\hat{T}_1^{(2)}$), generates the energy term *SSS* when combined with the cluster operator $(\hat{T}_1^{(2)})^\dagger$. In Table 2, for each energy term calculated at MP6 the associated cluster operators are given, where individual energy terms are grouped

Fig. 1. Partitioning of the MP6 energy formula. (a) Connected (C) and disconnected (D) cluster operator terms lead to energy contributions I, II, III that are converted in calculational steps 1, 2, 3, 4 to energy sums $E(MP6)_1$, $E(MP6)_{2a}$, $E(MP6)_{2b}$, $E(MP6)_3$, and $E(MP6)_4$. Note that abbreviations such as $\left\langle \begin{matrix} S \\ D \\ \vdots \end{matrix} \middle| \ldots \right\rangle$ indicate a sum of terms such as $\langle S|\ldots\rangle + \langle D|\ldots\rangle + \ldots$. (b) Wave operator products of (a) are given in the form of simplified Brandow diagrams (L: linked energy diagrams) (see text).

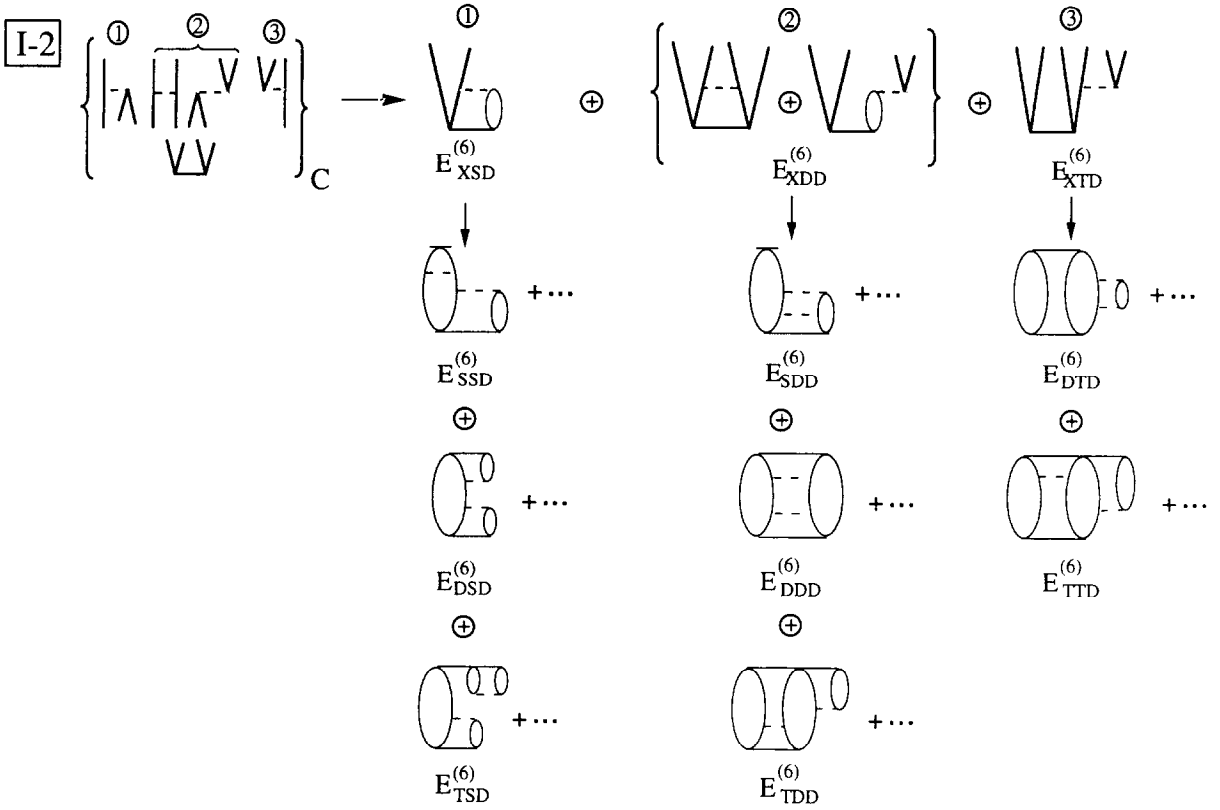


Fig. 3. Simplified Brandow diagrams for the term I-2.

according to the calculational steps Eq. (1), Eq. (2), Eq. (3), Eq. (4) leading to the partial sums $E(\mathrm{MP6})_1$, $E(\mathrm{MP6})_2$, $E(\mathrm{MP6})_3$, and $E(\mathrm{MP6})_4$ [1]. Also given are the computational cost for each energy contribution $E_{ABC}{}^{(6)}$.

Using first- and second-order cluster operators, the MP6 energy can be partitioned as shown in Fig. 1. First, $E(MP6)$ is separated into three parts A_1, A_2, and A_3, where A_1 is associated with the connected operator product $(\bar{V}\hat{T}_i^{(2)})_C$, while A_2 and A_3 are associated with disconnected operator products $(\hat{T}_2^{(1)})^2$ (A_2) and $(\bar{V}\hat{T}_i^{(2)})_D$ (A_3). We assign to A_1, A_2, and A_3 the symbols I, II, III (see Fig. 1) and discuss each of the three parts separately.

Part I: A_1 covers all connected $(\bar{V}\hat{T}_i^{(2)})_C$ terms and, therefore, automatically leads to linked diagram contributions. It can be split into terms I – 1 ($i = 1$), I – 2 ($i = 2$), and I – 3 ($i = 3$) which arise from second-order cluster operators $\hat{T}_1^{(2)}$, $\hat{T}_2^{(2)}$, and $\hat{T}_3^{(2)}$, respectively. In Fig. 1b, simplified Brandow diagrams are given to represent the operator products $\bar{V}\hat{T}_i^{(2)}$ which are converted to linked energy diagrams in Fig. 2 (I – 1), Fig. 3 (I – 2), and Fig. 4 (I – 3).

The energy diagrams belong to one of the 36 energy terms of MP6. Since it is not possible to give all 28 300 antisymmetrized Brandow diagrams associated with the MP6 energy, for each term just one typical Brandow diagram is shown in Figs. 2, 3, and 4. They indicate that term I-1 covers contributions of the type *XSS* and *XDS* with *X* = S, D, T. Term I-2 (Fig. 3) covers contributions *XSD*, *XDD* (*X* = S, D, T) and *XTD* (*X* = D, T) where in the latter case the T excitation results from the $\hat{T}_3^{(3)}$ cluster operator as is revealed by the cluster operator diagram 3 of Fig. 3 (see also Table 2). In the case of part I-3, contributions *XST*, *XDT* (*X* = S, D, T), *XTT* (*X* = D, T) and, *TQT* result. The cluster operator diagram 4 of Fig. 4 shows that the *Q* excitations in term *TQT* represent the first connected *Q* correlation effect associated with $\hat{T}_4^{(3)}$.

All terms of A_1 are calculated and collected in the

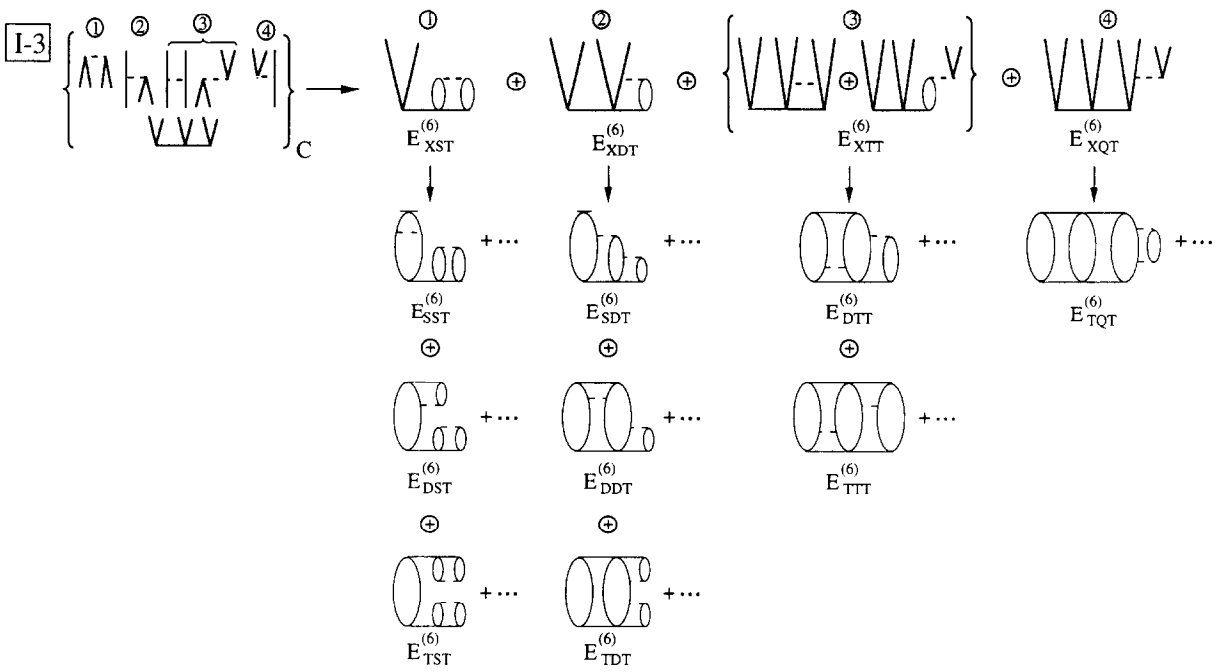


Fig. 4. Simplified Brandow diagrams for the term I-3.

sum $E(\mathrm{MP6})_{\mathrm{I}}$ (see Fig. 1)

$$E(\mathrm{MP6})_{\mathrm{I}} = E^{(6)}_{SSS} + 2E^{(6)}_{SSD} + 2E^{(6)}_{SST} + E^{(6)}_{SDS} + 2E^{(6)}_{SDD} + 2E^{(6)}_{SDT} + E^{(6)}_{DSD} + 2E^{(6)}_{DST} + E^{(6)}_{DDD} + 2E^{(6)}_{DDT} + E^{(6)}_{TST} + E^{(6)}_{TDT} + E^{(6)}_{DTD} + 2E^{(6)}_{DTT} + E^{(6)}_{TTT} + E^{(6)}_{TQT} \quad (7)$$

Part II: Energy part A_2 is characterized by the disconnected first-order cluster operator $(\hat{T}_2^{(1)})^2$, which leads to disconnected Q contributions collected in the term $A(X, Y, Q)_L$. Combination of the perturbation operator $\bar{V}$ with $(\hat{T}_2^{(1)})^2$ leads to the connected and disconnected wave operator terms II-1 and II-2, respectively (Fig. 1a), the diagrams of which are given in Fig. 1b.

The connected part II-1 is shown in Fig. 5. There are three different ways, 1, 2, and 3, to connect $\bar{V}$ with $(\hat{T}_2^{(1)})^2$. One obtains wave operator diagrams that are associated with D (1), connected T (2) and connected Q (3) excitations. When properly closed to energy diagrams, they lead to the MP6 energy terms XDQ, XTQ(II) (X = S, D, T, Q) and XQQ(II) (X = D, T, Q). The four-electron nature of the XQQ terms can be verified by realizing that they result from the second part of the operator $\hat{T}_4^{(3)}$ given in Eq. (4) (compare with Table 2). DQQ(II) does not contain the denominator $(E_0 - E_q)$, which makes its calculation rather simple (Table 2) while the terms TQQ(II) and $QQQ(\mathrm{II})_b$ are difficult to calculate since they scale with $O(M^9)$ (Table 2).

The terms of II-1 are collected in the sums $E(\mathrm{MP6})_{2a_1}$ and $E(\mathrm{MP6})_{2a_2}$ defined in the original derivation of the MP6 energy [1]

$$E(\mathrm{MP6})_{2a_1} = 2E^{(6)}_{SDQ} + 2E^{(6)}_{DDQ} + 2E^{(6)}_{TDQ} + E^{(6)}_{QDQ} \quad (8)$$

$$E(\mathrm{MP6})_{2a_2} = [E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a] + E^{(6)}_{QTQ}(\mathrm{II})_b + [E^{(6)}_{DQQ}(\mathrm{II}) + E^{(6)}_{QQQ}(\mathrm{II})_a] + E^{(6)}_{QQQ}(\mathrm{II})_b + 2E^{(6)}_{DTQ}(\mathrm{II}) + 2E^{(6)}_{TTQ}(\mathrm{II}) + 2E^{(6)}_{TQQ}(\mathrm{II}) \quad (9)$$

It is useful to add to $E(\mathrm{MP6})_{2a_1}$ and $E(\mathrm{MP6})_{2a_2}$, the term $E(\mathrm{MP6})_{2a_3}$, which is identical to II-2.4 of Fig. 1. It results from the disconnected part II-2. There are four possibilities to arrange the $\bar{V}$ operator with one of the two first-order $\hat{T}_2^{(1)}$ operators (Fig. 1b), three of which lead by using the factorization theorem [10] to products of $\hat{T}_2^{(1)}$ and $\hat{T}_i^{(2)}$ (i = 1,2,3), i.e. these

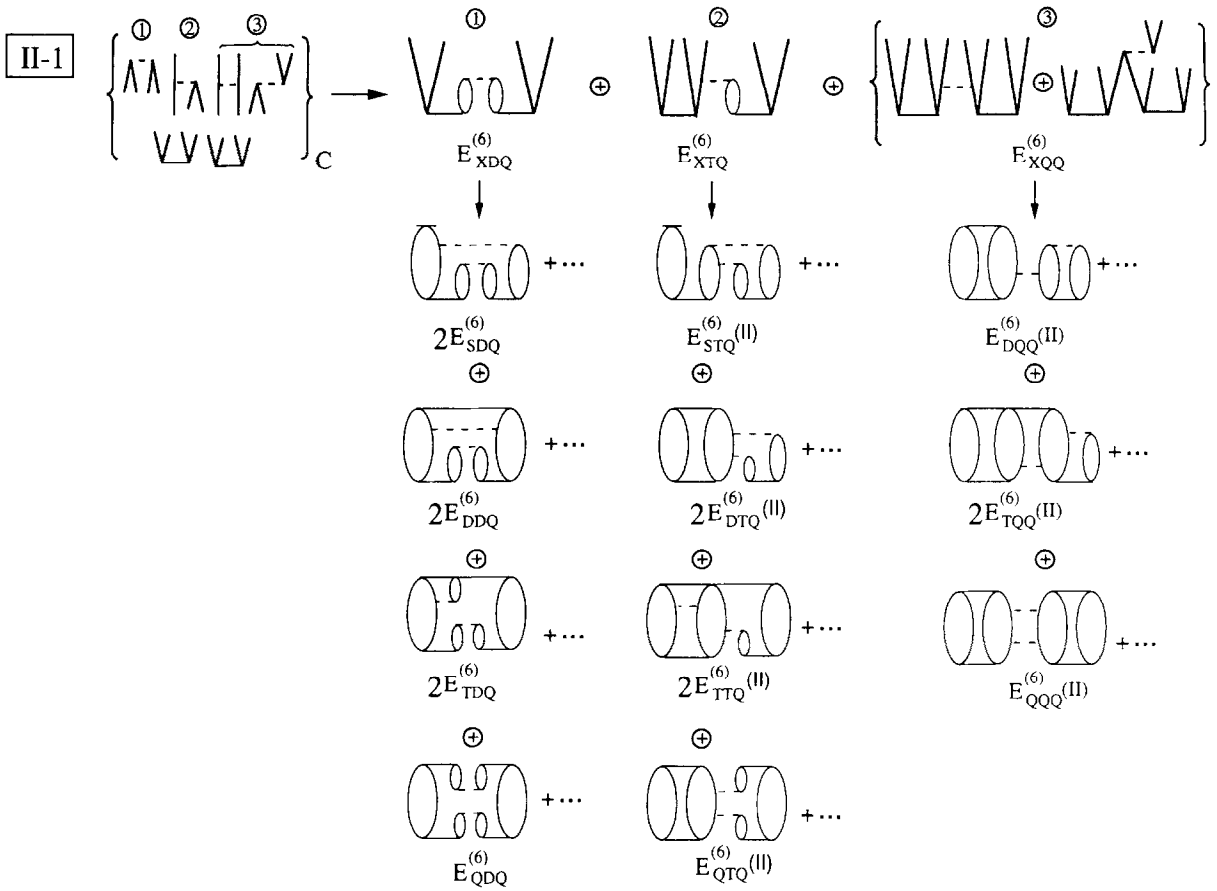


Fig. 5. Simplified Brandow diagrams for the term II-1.

terms will cover disconnected T, disconnected Q, and disconnected P correlation effects. For combination possibility 4, one gets the disconnected wave operator part $\bar{V}\hat{T}_2^{(1)}\hat{T}_2^{(1)}$, which is shown in II-2.4 of Fig. 6. As discussed in Ref. [1], the wave operator part can be rearranged to lead to $(1)/(3!)(\hat{T}_2^{(1)})^3$ (Fig. 6) which indicates a disconnected H contribution. Closing of the wave operator diagram in all possible ways gives the *QHQ* contribution, which is added as $E(\mathrm{MP6})_{2a_3}$

$$E(\mathrm{MP6})_{2a_3} = E^{(6)}_{QHQ} \tag{10}$$

to $E(\mathrm{MP6})_{2a_1}$ and $E(\mathrm{MP6})_{2a_2}$ to give $E(\mathrm{MP6})_{2a}$.

Part III: The term A_3 splits into three contributions III-1, III-2, and III-3, which are associated with disconnected T, Q, and P excitations (Fig. 1) and which can be combined with similar terms from II-2. Hence, disconnected Q correlation effects are given by III-2 and II-2.2, disconnected T effects by III-1 and II-2.1, and disconnected P effects by III-3 and II-2.3. Details of the derivation of these terms can be found in Ref. [1]. Fig. 1 and Fig. 6 show that III-2 + II-2.2 define the energy terms of $E(\mathrm{MP6})_{2b}$

$$E(\mathrm{MP6})_{2b} = [E^{(6)}_{DQD} + E^{(6)}_{DQQ}(\mathrm{I})] + 2[E^{(6)}_{TQD} + E^{(6)}_{TQQ}(\mathrm{I})] + [E^{(6)}_{QQD} + E^{(6)}_{QQQ}(\mathrm{I})] \tag{11}$$

As can be seen from Fig. 6, *QQD* + *QQQ*(I) cover connected Q excitations coupled with disconnected Q excitations, where again their calculation is facilitated as indicated in Table 2. It is useful to collect all terms that result from products $\hat{T}_2^{(1)}\hat{T}_2^{(j)}$ (j = 1,2) in the sum $E(\mathrm{MP6})_2$ [1]

$$E(\mathrm{MP6})_2 = E(\mathrm{MP6})_{2a} + E(\mathrm{MP6})_{2b} \tag{12}$$

The terms associated with the cluster operator

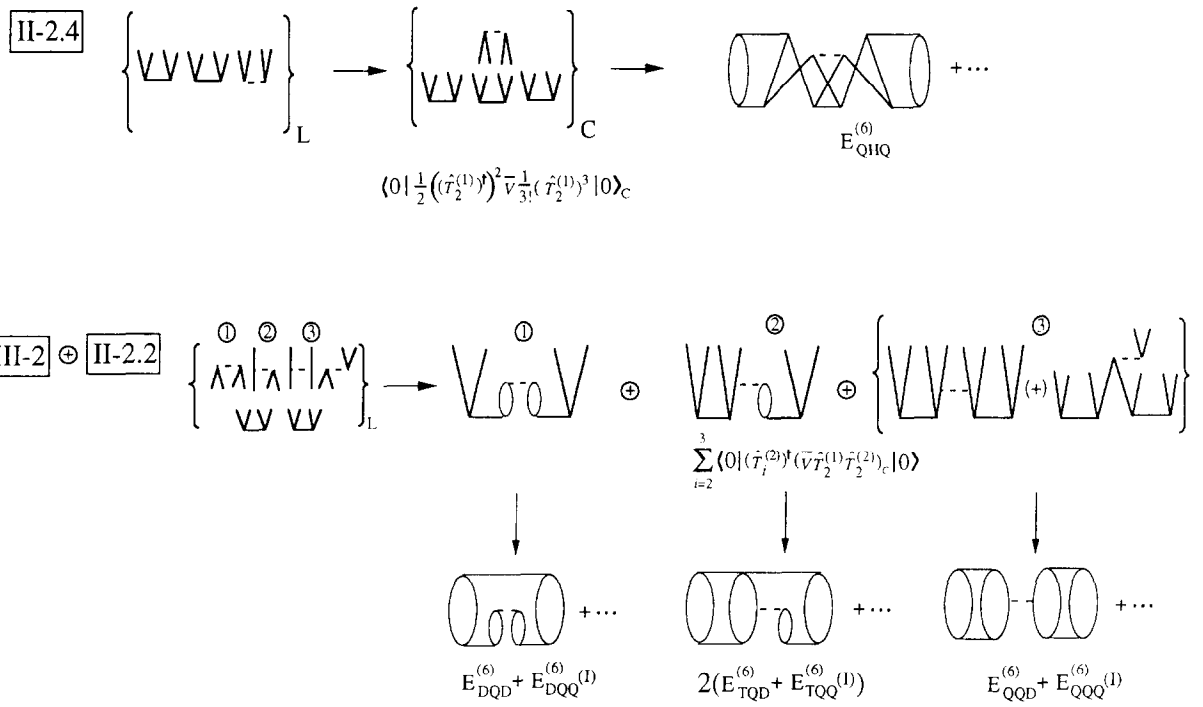


Fig. 6. Simplified Brandow diagrams for terms II-2.4, III-2 and II-2.2.

product $\hat{T}_1^{(2)}\hat{T}_2^{(1)}$ are collected in diagrams III-1 + II-2.1 given in Fig. 7. They represent combinations of disconnected T with S excitations (diagram 1), D excitations (2), connected T excitations (3) and disconnected Q excitations (4), where the Q can represent couplings between three-electron correlation and orbital relaxation effects or pair–pair coupling effects. These terms are collected in $E(\mathrm{MP6})_3$

$$E(\mathrm{MP6})_3 = E^{(6)}_{STS} + E^{(6)}_{STQ}(\mathrm{I}) + 2[E^{(6)}_{DTS} + E^{(6)}_{DTQ}(\mathrm{I})] + 2[E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I})] + E^{(6)}_{QTS} + E^{(6)}_{QTQ}(\mathrm{I}) \quad (13)$$

Disconnected P excitations generated by the cluster operator product $\hat{T}_3^{(2)}\hat{T}_2^{(1)}$ lead to the diagrams III-3 + II-2.3 also shown in Fig. 7. There are two combination possibilities, the first of which (diagram 1) leads to terms *TPT* and *TPQ*, while the second couples disconnected Q to P effects in the terms *QPT* and *QPQ*. These energy contributions are collected in $E(\mathrm{MP6})_4$

$$E(\mathrm{MP6})_4 = [E^{(6)}_{TPT} + E^{(6)}_{TPQ}] + [E^{(6)}_{QPT} + E^{(6)}_{QPQ}] \quad (14)$$

Hence, the total MP6 correlation energy is derived in Figs. 1–7 and can be calculated according to Eq. (15)

$$\begin{aligned}
E(\mathrm{MP6}) &= E(\mathrm{MP6})_1 + E(\mathrm{MP6})_2 + E(\mathrm{MP6})_3 + E(\mathrm{MP6})_4 \\
&= E^{(6)}_{SSS} + 2E^{(6)}_{SSD} + 2E^{(6)}_{SST} + E^{(6)}_{SDS} + 2E^{(6)}_{SDD} + 2E^{(6)}_{SDT} \\
&\quad + E^{(6)}_{DSD} + 2E^{(6)}_{DST} + E^{(6)}_{DDD} + 2E^{(6)}_{DDT} + E^{(6)}_{TST} \\
&\quad + E^{(6)}_{TDT} + E^{(6)}_{DTD} + 2E^{(6)}_{DTT} + E^{(6)}_{TTT} + E^{(6)}_{TQT} \\
&\quad + 2E^{(6)}_{SDQ} + 2E^{(6)}_{DDQ} + 2E^{(6)}_{TDQ} + E^{(6)}_{QDQ} \\
&\quad + [E^{(6)}_{STS} + E^{(6)}_{STQ}(\mathrm{I})] + [E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a] \\
&\quad + E^{(6)}_{QTQ}(\mathrm{II})_b + [E^{(6)}_{QTS} + E^{(6)}_{QTQ}(\mathrm{I})] \\
&\quad + 2[E^{(6)}_{DTS} + E^{(6)}_{DTQ}(\mathrm{I})] + 2E^{(6)}_{DTQ}(\mathrm{II}) \\
&\quad + [E^{(6)}_{DQD} + E^{(6)}_{DQQ}(\mathrm{I})] + [E^{(6)}_{DQQ}(\mathrm{II}) + E^{(6)}_{QQQ}(\mathrm{II})_a] \\
&\quad + [E^{(6)}_{QQD} + E^{(6)}_{QQQ}(\mathrm{I})] + E^{(6)}_{QQQ}(\mathrm{II})_b \\
&\quad + 2[E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I})] + 2E^{(6)}_{TTQ}(\mathrm{II}) \\
&\quad + 2[E^{(6)}_{TQD} + E^{(6)}_{TQQ}(\mathrm{I})] + 2E^{(6)}_{TQQ}(\mathrm{II}) \\
&\quad + E^{(6)}_{QHQ} + [E^{(6)}_{TPT} + E^{(6)}_{TPQ}] + [E^{(6)}_{QPT} + E^{(6)}_{QPQ}]
\end{aligned} \quad (15)$$

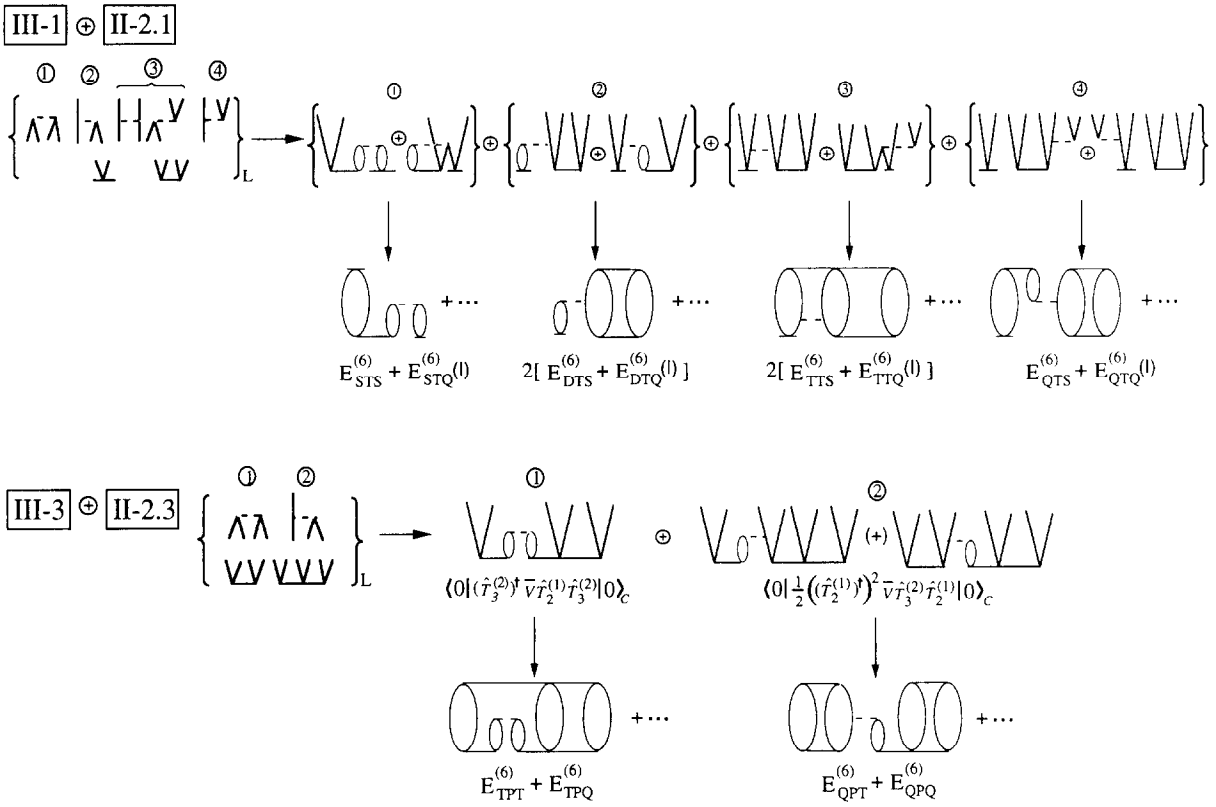


Fig. 7. Simplified Brandow diagrams for terms III-1, II-2.1, III-3 and II-2.3.

3. Derivation of approximate MP6 methods

Fig. 8 gives an overview over all energy terms calculated at MP6 [1–3]. For each term, computational cost are indicated ($O(M^9)$ terms in shaded boxes, $O(M^8)$ terms in white boxes, $O(M^7)$ terms in ellipses, all other terms lower than $O(M^7)$) and the computational step (1, 2*a*, 2*b*, 3, 4, see Section 2), in which the term in question is calculated, is also given. Two of the 17 MP6 terms in *SDQ* space, namely *DQQ* and *QQQ*, are split in part I and part II since they are evaluated and collected in different steps (2*b* and $2a_2$) of the MP6 calculation. The four partial terms are generated by different parts of $\hat{T}_4^{(3)}$ (see Table 2) and, therefore, they all cover connected Q excitations; however, only *QQQ*(II) scales with $O(M^9)$. Apart from *QQQ*(II), the *SDQ* part of MP6 can be calculated with an $O(M^6)$ cost dependence, i.e. cost requirements are comparable to MP3 or MP4(SDQ). We denote such a method MP6(SDQ,M6) indicating that only those terms with an $O(M^6)$ cost dependence are included. However, in view of the 33 T terms (Fig. 8), calculation of MP6(SDQ,M6) is of academic rather than of any practical use.

In the T part, there are three terms with an $O(M^9)$ cost dependence (*QQT*(II) = *TQQ*(II), *TQT*) and five terms with an $O(M^8)$ cost dependence (*DTT*, *QTT*(II) = *TTQ*(II), *TTD* and *TTT*, Fig. 8) while 23 of the remaining terms scale with $O(M^7)$ and the rest requires just $O(M^6)$ operations. The PH part covers the two M^6-dependent terms *QHQ*(I) and *QHQ*(II), the M^7-dependent terms *QPT*(I) = *TPQ*(I), *QPQ*(I), and *TPT*(I), while *QPT*(II) = *TPQ*(II), *QPQ*(II), and *TPT*(II) scale with $O(M^8)$.

The derivation of an MP6(SDTQ) method is as useless as the derivation of an MP6(SDQ) method since both cover expensive terms that lead to an overall $O(M^9)$-dependence. More promising is the

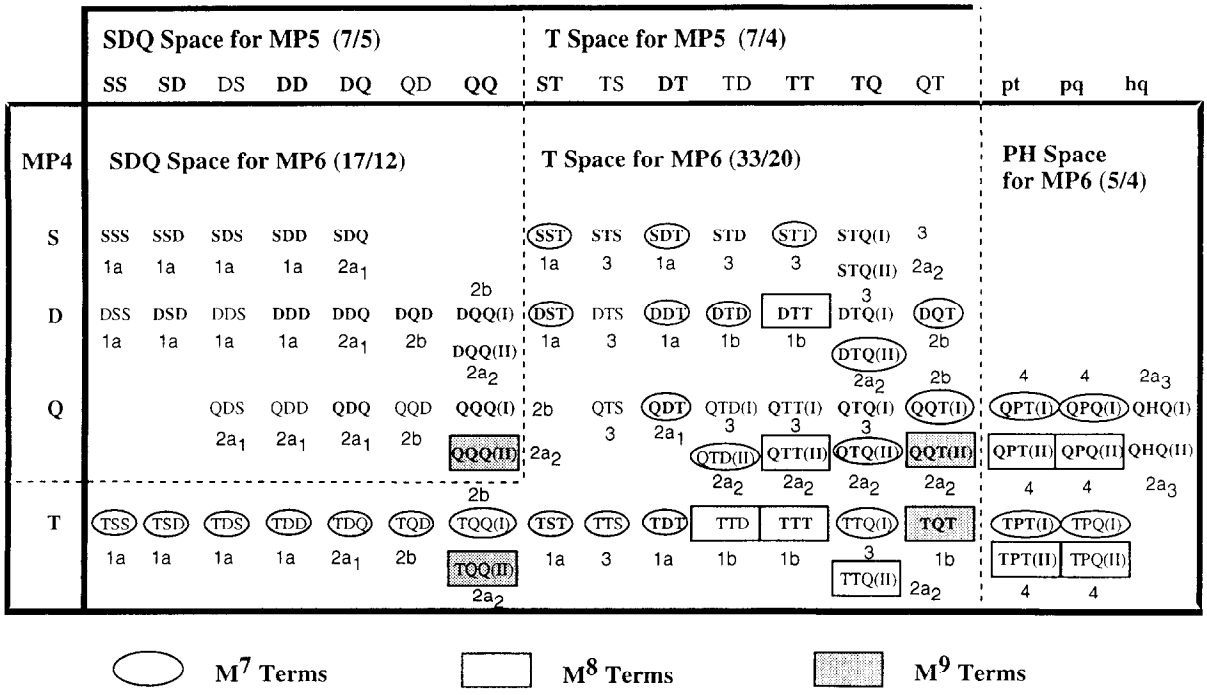


Fig. 8. Partitioning of the MP6 space. In the top row and in the left column, SDQ space and T space are given for MP5 and MP4, respectively, while in the central box the SDQ, T, and PH space for MP6 is shown separated by dashed lines. In each case, the total number of *ABC* terms and the number of unique terms is given, where the latter are indicated by bold print. Terms with a cost dependence of M^7 (ellipses), M^8 (white boxes) or M^9 (shaded boxes) are also indicated. For each term, it is shown in which step (1,2,3,4) of the calculation the term in question is determined (Eqs. (7)–(15), see text).

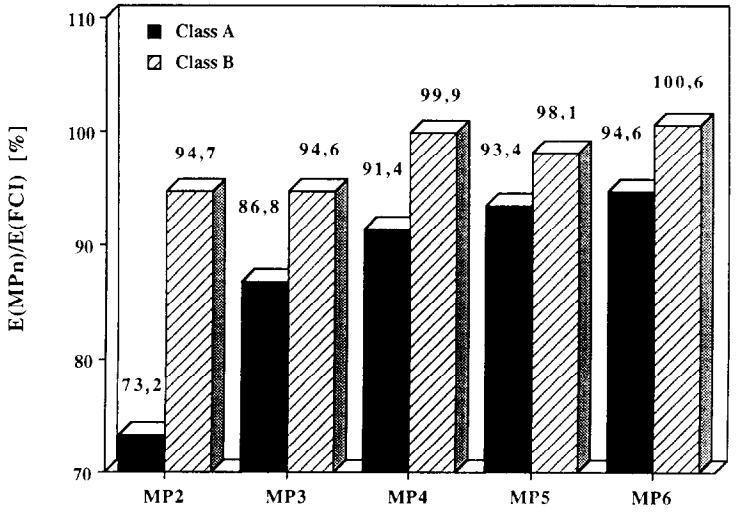


Fig. 9. Fractions of FCI correlation energies covered at the MP*n* level of theory given in % and averaged over all members of class A (black bars) or class B (hatched bars).

development of an MP6(M8) and an MP6(M7) method with computational requirements $\leq O(M^8)$ and $\leq O(M^7)$, respectively, since more expensive terms are deleted [3]

$$E(\text{MP6, M8}) = E(\text{MP6, SDTQPH}) - E^{(6)}_{TQT} - E^{(6)}_{QQQ}(\text{II})_b - 2E^{(6)}_{TQQ}(\text{II}) \quad (16)$$

$$E(\text{MP6, M7}) = E(\text{MP6, M8}) - 2E^{(6)}_{DTT} - E^{(6)}_{TTT} - 2E^{(6)}_{TTQ}(\text{II}) - E^{(6)}_{TPT}(\text{II}) - 2E^{(6)}_{QPT}(\text{II}) - E^{(6)}_{QPQ}(\text{II}) \quad (17)$$

The four terms excluded at the M8 level cover connected Q effects; however, this does not mean that all connected Q terms are excluded. As can be seen from Table 2 and Figs. 1–7, there still remain connected Q terms covered by *QQD*, *DQQ*, and $QQQ(\text{II})_a$, so that neither MP6(M8) nor MP6(M7) are methods without $\hat{T}_4$ contributions.

In MP6(M7), *QPT*(II), *TPQ*(II), *QPQ*(II), and *TPT*(II) are deleted since they represent $O(M^8)$ terms. Again, the remaining terms *QPT*(I), *TPQ*(I), *QPQ*(I), and *TPT*(I) guarantee that MP6(M7) covers half of the disconnected P correlation effects. The other terms deleted at MP6(M7) represent TT coupling effects. Table 2 as well as Figs. 1–7 reveal that *TTT*, *DTT*, *TTD*, and *TTQ*(II) all involve connected T correlation effects and, therefore, are important to avoid an exaggeration of three-electron correlation. Other terms such as *TST* or *TDT* represent just an indirect TT coupling and are not so effective, while *TTS* or *TTQ* describe just the coupling between connected and disconnected T correlation effects.

A priori, it is not possible to predict whether MP6(M8) or MP6(M7) will lead to reasonable approximations of full MP6 correlation energies because this will depend on the electronic structure of a given atom or molecule. For example, if the electron system in question is characterized by electron clustering, three-electron correlation and even four-electron correlation will be important [5]. A possible exaggeration of three-electron correlation at MP4 will be partially corrected at MP5 by the TT term; however, additional corrections at MP6 might also become necessary. We will investigate these situations in the following sections.

4. Prediction of full CI (FCI) correlation energies

In recent work, we have shown that the convergence behaviour of the MP*n* series can be predicted for a given electron system by considering its electronic structure and bonding pattern [5]. We could distinguish between two classes of electron systems, namely class A and class B systems, which differ basically with regard to their electronic structure. Class A molecules have core, bond, and lone electron pairs well separated and distributed over the whole space of an atom or molecule. For example, in the molecule BH($^1\Sigma^+$), the three electron pairs are localized in different parts of the molecule, namely in the core, the bonding and the non-bonding region. The same is true in the case of Li or Be compounds, boranes, alkanes and many other molecules. Since the electron pairs of class A systems are well-separated, the correlation energy is dominated by pair correlation effects and the importance of three-electron correlations and pair–pair couplings is moderate [5]. Pair correlation effects determine at each order of the MP*n* series the magnitude of the MP*n* correlation energy, which increases slowly but steadily to the FCI value, i.e. convergence in the MP*n* series is monotonic. This is shown in Fig. 9 where the correlation energy for class A systems (black bars) is given as a fraction of the FCI correlation energy. The MP*n* correlation energy steadily increases from 73% (MP2) to 87% (MP3), 91% (MP4), 93% (MP5) and 95% (MP6), dominated at each level of theory by pair correlation effects.

For class B systems, clustering of electron pairs in certain regions of an atom or molecule is typical [5]. For example, for electronegative atoms such as F or Ne, three or even four electron pairs share the available space in the valence sphere, which is rather limited due to the orbital contracting and charge attracting force of the nucleus. Clustering of electron pairs is also found for molecules with multiple bonds (ethylene, acetylene) in the bond region, for hypervalent molecules at the central atom or for molecules

with two and more electron lone pairs (e.g. H_2O or FH) in the nonbonding region. If electrons cluster in confined regions of atomic or molecular space, three-electron correlation or even four-electron correlation effects will become important since these effects provide simple mechanisms to protect the region of an electron pair against occupation by other electrons. Accordingly, T correlation effects can become as large or even larger than pair correlation effects and connected Q effects cannot be neglected [5].

Clearly, dynamic electron correlation is more important for class B than class A systems. If the correlation problem has to be handled just by pair correlations at MP2, their effects are exaggerated, in particular since the electrons of a pair are separated without considering that there are other pairs in the same region of space. Of course, this leads to relatively large positive corrections at MP3 due to the inclusion of pair–pair coupling effects. A more effective correction of pair correlation effects is included at MP4 by three-electron correlations, which provide the simplest mechanism for complicated correlated movements between an electron pair and a single electron in a confined region of space. The larger the clustering of electrons in a class B system, the larger the possibility that T correlation effects are exaggered so that they have to be corrected by TQ, TD, and TS coupling effects at MP5. Even connected Q correlation effects introduced at MP6 might be exaggerated so that a correction by appropriate coupling terms at MP7 becomes necessary.

Electron clustering observed for class B systems will lead to an exaggeration of simple correlation effects (pair correlations, three-electron correlations, etc.) if one tries to solve the electron correlation problem with MP2, MP4, etc. As a consequence, these exaggerations have to be corrected at odd orders by including coupling effects. The MPn series oscillates at low orders of MPn until a more realistic description of correlation is possible by the inclusion of sophisticated correlation effects.

In principle, it is possible to predict the convergence behaviour of a given molecule just by investigating its electronic structure. With this knowledge it is possible to set up suitable extrapolation procedures that adjust to the different convergence behaviour of class A and class B systems. In this connection, we have suggested the two extrapolation formulas Eq. (18) and Eq. (19) [4,5]

$$\Delta E^{(A)}(\text{extrapII, MP6}) = \sum_{n=2}^{4} E_{MP}^{(n)} + \frac{E_{MP}^{(5)}}{1 - \frac{E_{MP}^{(6)}}{E_{MP}^{(5)}}} = \sum_{n=2}^{6} E_{MP}^{(n)} + E_{MP}^{(5)} \left(\frac{E_{MP}^{(6)}}{E_{MP}^{(5)}} \right)^2 + \ldots \tag{18}$$

and

$$\Delta E^{(B)}(\text{extrapII, MP6}) = E_{MP}^{(2)} + E_{MP}^{(3)} + (E_{MP}^{(4)} + E_{MP}^{(5)}) e^{\frac{E_{MP}^{(6)}}{E_{MP}^{(4)}}}$$

$$= \sum_{n=2}^{6} E_{MP}^{(n)} + E_{MP}^{(5)} \frac{E_{MP}^{(6)}}{E_{MP}^{(4)}} + \frac{1}{2!}(E_{MP}^{(4)} + E_{MP}^{(5)}) \left(\frac{E_{MP}^{(6)}}{E_{MP}^{(4)}} \right)^2 + \frac{1}{3!}(E_{MP}^{(4)} + E_{MP}^{(5)}) \left(\frac{E_{MP}^{(6)}}{E_{MP}^{(4)}} \right)^3 + \ldots \tag{19}$$

As shown in Fig. 9, E(MP6) correlation energies already overshoot FCI energies, which indicates that certain correlation effects are still exaggerated. Therefore, their contributions to $E^{(n)}$ have to be scaled down, which is done in Eq. (19) by using an exponential formula. Both $(1)/(1 - x)$ (Eq. (18)) and e^x (Eq. (19)) lead to similar series; however in the exponential series higher powers k of x are scaled down by prefactors $(1)/(k!)$ that effectively reduce higher order correlation effects.

Applying extrapolation formulas Eq. (18) and Eq. (19), one can reproduce FCI correlation energies with an average deviation of 0.3 mhartree in the case of atoms and molecules in their equilibrium geometry [5]. However, even better predictions can be made with the help of second-order Feenberg scaling based on MP6 energies [4,5]. The theory of second-order Feenberg scaling has been described elsewhere [4] and, therefore, we summarize here just the most important results achieved with this method:

1. Second-order Feenberg scaling effectively dampens out initial oscillations observed for class B systems by minimizing the fifth-order Feenberg correlation energy.
2. Contrary to Padé approximants, which can lead to artificial oscillations [4], second-order Feenberg

scaling retains the monotonic convergence behaviour of class A systems.

3. In total, second-order Feenberg scaling is more effective than using either Padé approximants or extrapolation formulas Eq. (18) and Eq. (19) [5].

Applying second-order Feenberg scaling, we obtained correlation energies that differ from FCI correlation energies by just 0.15 mhartree on average [5]. However, in the case of multi-reference systems with stretched geometries, deviations are as large as 10 mhartree.

Although the use of Feenberg scaling or other extrapolation procedures led to considerably improved correlation energies at negligible additional cost, it did not fulfil the actual goal of our investigation, namely to reproduce FCI correlation energies with the help of MP6 energies with an accuracy of 0.1 mhartree or even better. To achieve such an accuracy one has to clarify

1. whether for all electron systems considered the MP6 correlation energy is a reasonable starting energy for the extrapolation procedures applied, and
2. whether a given extrapolation procedure adjusts to the convergence behaviour of class A or class B systems in the optimal way.

There were 33 electron systems included in our previous investigation [4,5]: BH, $^1\Sigma^+$, R_e, $1.5R_e$, $2R_e$; R; basis set: (9s5p1d/4s1p)[4s2p1d/2s1p]; [11] NH_2, $^2B_1$, R_e, $1.5R_e$, $2R_e$; U; basis set: (9s/5p1d/4s1p)[4s2p1d/2s1p]; [12] NH_2, $^2A_1$, R_e, $1.5R_e$, $2R_e$; U; basis set: (9s5p1d/4s1p)[4s2p1d/2s1p]; [13] CH_3, $^2A_2''$, $1.5R_e$, $2R_e$; U; basis set: (9s5p1d/4s1p)[4s2p1d/2s1p]; [14] CH_2, $^2B_1$; U; CH_2, $^1A_1$; R; basis set: (9s5p1d/4s1p)[4s2p1d/2s1p]; [15] Ne, ^1S; R; basis sets: $4s2p1d$, $5s3p2d$, $6s4p1d$; [16] F, ^2P; U; basis sets: $4s3p1d$, $4s3p2d$, $5s4p2d$; [16] F^-, ^1S; R; basis sets: $4s3p1d$, $4s3p2d$, $5s4p2d$; [16] FH, $^1\Sigma^+$, R_e, $1.5R_e$, $2R_e$; R; basis set: (9s5p1d/4s1p)[4s2p1d/2s1p]; [17] H_2O, $^1A_1$, R_e, $1.5R_e$, $2R_e$; R; basis set: (9s5p1d/4s1p)[4s2p1d/2s1p]; [17] HCCH, $^1\Sigma_g^+$, R_e; R; basis set: (9s5p1d/4s1p)[4s2p1d/2s1p]; [18] CO, $^1\Sigma^+$, R_e; R; basis set: (9s5p1d)[4s2p1d]; [18] O_3, $^1A_1$, R_e; R; c-O_3, $^1A_1$, R_e; R; basis set: (9s5p1d)[4s2p1d]; [19].

Open shell systems were calculated employing an unrestricted (U) reference wave function and closed shell systems employing a restricted (R) reference wave function. In this connection, it is appropriate to note that the UMPn series converges much slower than the RMPn series because of spin contamination of UMPn energies [8,20]. Particular slow convergence is found for O_2, O_2^+ or F_2; however in all cases investigated convergence was achieved for high orders n of MPn.

It has to be clarified which of the electron systems listed above can reasonably be described at MP6. Olsen and co-workers have recently determined higher order MPn correlation energies by FCI calculations [9]. Their calculations show that divergent behaviour of the MPn series can be generated artificially by using unbalanced based sets. For example, addition of diffuse basis functions to a VDZ basis leads to divergent convergence behaviour for several class B systems such as Ne or FH. There is just one system in our previous study which may suffer in a similar way from the chosen basis set. This is the F^- anion for which in the original FCI investigations the three basis sets 4s3p1d, 4s3p2d, and 5s4p2d were used [16]. Our calculations indicate that these basis sets may be too small to lead to reasonable MP6 energies and, therefore, we excluded F^- from the present investigation.

Some of the multi-reference systems with stretched geometries were also excluded because for these systems it is unlikely that any reasonable description can be obtained at MP6. For example, stretching the three CH bonds of the methyl radical to twice their equilibrium value affects the three CH bonding electron pairs. Three of these electrons arrange together with the single electron in the valence sphere of the C atom, while the other three electrons localize at the three hydrogens. It is clear that there are strong couplings between the three bonding electron pairs which require higher order correlation effects that cannot be described by connected Q or disconnected H correlations. An accurate description of electron correlation in the $2R_e$ geometry can probably be obtained if not just disconnected but also connected H correlation effects are covered by the calculation. However, the latter are included at MP10 and, therefore, one cannot expect that at CH distances of more than 2 Å the CH_3 radical has any chance of being correctly described at MP6. This is confirmed by a

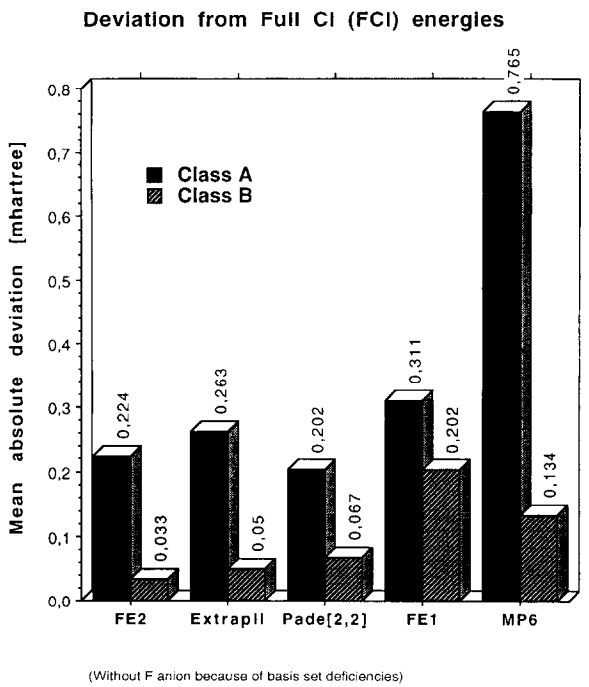


Fig. 10. Mean absolute deviations (in mhartree) of estimated FCI correlation energies from exact FCI energies for class A (black bars) and class B systems (hatched bars) in the case of atoms and molecules in their equilibrium geometry. FCI energies are estimated by first-order Feenberg scaling (FE1), second-order Feenberg scaling (FE2), [2,2] Padé approximants, MP6 correlation energies or MP6 based extrapolation formulas. ExtrapII: Two extrapolation formulas (Eq. (18) and Eq. (19)) are used which reflect the different convergence behaviour of class A and class B systems.

quasi-linear decrease of MPn correlation energies for $n = 4,5,6$ [4].

Similar considerations also apply to the $2R_e$ geometries of NH_2 (stretching and reorganization of the valence electrons at N involves two bonding electron pairs and an electron lone pair) and H_2O (two bonding pairs and two electron lone pairs are involved), however not necessarily to the single-bonded molecules FH and BH. One could also expect that the $1.5R_e$ geometries of CH_3, NH_2 and H_2O may cause problems since reorganization at the heavy atom may already lead to a coupling of the electron correlation of six electrons. On the other hand, typical transition state geometries of bond-forming or bond-breaking processes are closer to the $2R_e$ rather than the $1.5R_e$ geometries and, therefore, one has to decide from case to case whether the $1.5R_e$ geometry can still be described by MP6. Hence, the set of atoms and molecules covered in our analysis comprises the following systems:

Equilibrium geometries : BH, $^1\Sigma^+, R_e$; l NH_2, $^2B_1, R_e$; NH_2, $^2A_1, R_e$; CH_3, $^2A_2'', R_e$; CH_2, $^2B_1$, CH_2, $^1A_1$; Ne, ^1S, basis sets : $4s2p1d, 5s3p2d, 6s4p1d$; F, ^2P, basis sets : $4s3p1d, 4s3p2d, 5s3p2d$; FH, $^1\Sigma^+, R_e$; H_2O, $^1A_1, R_e$; HCCH, $^1\Sigma_g^+, R_e$; CO, $^1\Sigma^+, R_e$; O_3, $^1A_1, R_e$; $c-O_3$, $^1A_1, R_e$; (20)

Stretched geometries : BH, $^1\Sigma^+, 1.5R_e, 2R_e$; NH_2, $^2B_1, 1.5R_e$; NH_2, $^2A_1, 1.5R_e$; CH_3, $^2A_2'', 1.5R_e$; FH, $^1\Sigma^+, 1.5R_e, 2R_e$, H_2O, $^1A_1, 1.5R_e$; (21)

For the electron systems listed in Eq. (20) and Eq. (21), we have determined MP6, MP6(M8), and MP6(M7) energies [4], which we have used for predicting FCI energies either by first-order and second-order Feenberg scaling, the extrapolation formulas Eq. (18) and Eq. (19) or by the [2,2] Padé approximant [4,5]. As can be seen from Fig. 10, where the mean absolute deviations of predicted FCI energies from exact FCI values are given for atoms and molecules in their equilibrium geometry, there is a considerable difference whether FCI energies are predicted for class A or class B systems. Reasonable estimates of FCI energies are obtained for class B systems by second-order Feenberg scaling, extrapolation formula Eq. (19) or the [2,2] Padé approximant. However, for class A systems, the mean absolute deviations of estimated FCI energies are larger by a factor of 3 to 7 depending on what extrapolation procedure has been used. In view of the fact that class A systems possess monotonic convergence behaviour in the MPn series, while class B systems show initial oscillations, one should expect that it is easier to predict FCI energies for class A systems.

An explanation for the different performance of extrapolation methods in the case of class A and class B systems can be found by inspection of Fig. 9, in which the convergence behaviour of class A and class B systems is shown. For class A systems, the fraction of the correlation energy covered by MP2 is just 73%, but increases steadily to 94.6% at MP6. One can predict that if coverage of the correlation energy increases at the same rate, MP10 will cover more than 99% of the correlation energy. However, for class B systems, coverage of the total correlation energy is already close to 100% for MP6 and even for MP4.

Hence, with an extrapolation method that handles oscillations of the MPn series as effectively as second-order Feenberg scaling, it is much easier to predict FCI energies for class B systems than for class A systems. Clearly, one has to accelerate convergence for class A systems to obtain improved estimates of FCI energies.

We have tested various acceleration procedures and have found that the best results are obtained by a simple combination of first-order and second-order Feenberg scaling. The scale factors λ are always negative for class A systems and they are even more negative for second-order Feenberg scaling ($\lambda^{(5)}$) than for first-order Feenberg scaling ($\lambda^{(3)}$) [4]. This suggests that an optimal scale factor will only be found at third-order or fourth-order Feenberg scaling (corresponding to minimizing the MP7 or MP9 energy). Since this is not possible, we estimate an improved scaling factor by combining $\lambda^{(3)}$ and $\lambda^{(5)}$ according to Eq. (22)

$$\lambda_{\text{opt}} = \lambda^{(5)} + c(\lambda^{(5)} - \lambda^{(3)}) \tag{22}$$

where the factor c has been determined to be 2.1 for a number of test systems. In a similar way, one can improve the extrapolation formula (Eq. (18)) according to

$$\begin{aligned}\Delta E^{(\text{A})}(\text{extrapII, MP6}) &= \sum_{n=2}^{5} E_{\text{MP}}^{(n)} + \frac{E_{\text{MP}}^{(6)}}{1-\left(\frac{E_{\text{MP}}^{(6)}}{E_{\text{MP}}^{(5)}}\right)^{a}} \\ &= \sum_{n=2}^{6} E_{\text{MP}}^{(n)} + E_{\text{MP}}^{(6)}\left(\frac{E_{\text{MP}}^{(6)}}{E_{\text{MP}}^{(5)}}\right)^{a} \\ &\quad + E_{\text{MP}}^{(6)}\left(\frac{E_{\text{MP}}^{(6)}}{E_{\text{MP}}^{(5)}}\right)^{2a} + \cdots\end{aligned} \tag{23}$$

with $0 < a < 1$ to accelerate convergence. In the present case, $a = 0.85$ was found to lead to reasonable results.

FCI energies obtained by Feenberg scaling with λ_{opt} are compared with MP6 energies and exact FCI energies in Fig. 11. Improvements are significant in the case of multi-reference systems (indicated in Fig. 11 by a star). The mean absolute deviation from exact FCI energies is just 0.073 mhartree in the case of

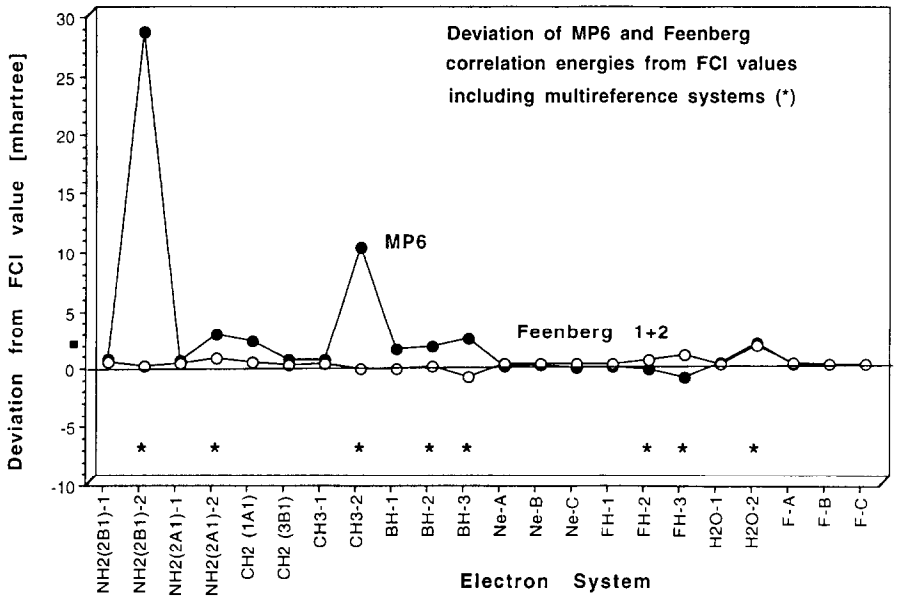


Fig. 11. Differences between Feenberg energies calculated with Eq. (22) (circles), MP6 energies (dots), and exact FCI energies in mhartree for 22 electron systems. Multi-reference systems are indicated by stars.

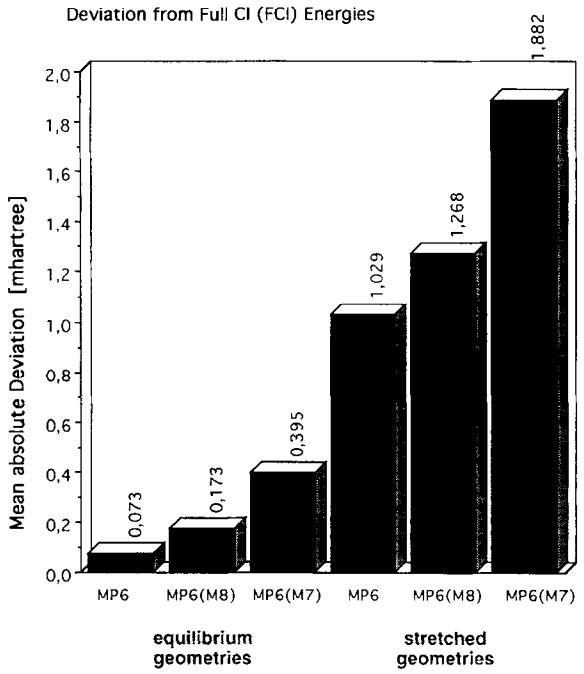


Fig. 12. Comparison of mean absolute deviations of estimated from true FCI correlation energies when using first- and second-order Feenberg scaling according to Eq. (22). FCI energies are based on MP6, MP6(M8), and MP6(M7) energies. Both class A and class B cases are considered; however electron systems are grouped into those with equilibrium geometries and those with stretched geometries.

equilibrium geometries (Fig. 12) and 1.03 mhartree when all systems are considered. Hence, our goal to get reliable predictions of FCI energies is fulfilled.

5. Prediction of FCI correlation energies using approximate MP6 methods

Using the MP6(M8) and MP6(M7) methods described in Section 3, we have calculated approximate MP6 correlation energies. For 22 electron systems considered, MP6(M8) energies differ from exact MP6 energies on average by 0.2 mhartree, while MP6(M7) energies lead to an average deviation of 0.5 mhartree. Inspection of Fig. 13, in which differences between approximate MP6 energies and exact MP6 energies are given in mhartree, reveals that the largest deviations (about 1 mhartree) are obtained at MP6(M7) for systems with multi-reference effects. If one would include systems with strong multi-reference character such as the $2R_e$ geometry of H_2O, then deviations of 3.5 mhartree (Fig. 13) and more are obtained. Since in the latter case the deviation is about the same for MP6(M8) and MP6(M7), clearly the connected Q correlation effects covered by the $O(M^9)$ terms QQQ(II), QQT(II) or TQT are responsible for the difference in calculated correlation energies. This is in line with the understanding that at $2R_e$ there is considerable coupling between the two bonding electron pairs and the two electron lone pairs, in particular in connection with a reorganization of electrons in the valence sphere of oxygen which increases the importance of connected Q correlation effects.

Apart from those cases in which multi-reference effects play an important role, both MP6(M8) and MP6(M7) lead to reasonable sixth-order correlation energies, which in turn can be used to extrapolate to FCI correlation energies using improved second-order Feenberg scaling according to Eq. (22). Mean absolute deviations of FCI correlation energies obtained in this way from exact values are compared with those of MP6-based FCI correlation energies in Fig. 12. Clearly, there will be a loss in accuracy if one uses approximate MP6 methods for the prediction of FCI correlation energies. However, this loss is moderate considering that the mean absolute deviation of predicted from exact FCI energies increases from just 0.073 (MP6) to 0.173 (MP6(M8)) and 0.395 mhartree (MP6(M7)) in the case of atoms and molecules in their equilibrium geometries, and from 1.029 (MP6) to 1.268 (MP6(M8)) and 1.882 mhartree (MP6(M7)) in the case of stretched geometries. Hence, for the cost of essentially an MP4 calculation, one can obtain reasonable estimates of FCI correlation energies.

6. Summary and conclusions

Our work on MP6 has led to an understanding of the convergence behaviour of the MPn series. Thereby, it is possible to adjust existing extrapolation procedures to the different convergence behaviour of class A and class B systems and to predict reliable FCI correlation energies. The understanding of the convergence behaviour of the MPn series also has direct consequences for the daily use of low-order MPn methods as is indicated in Fig. 14.

We can correct some of the common beliefs on the

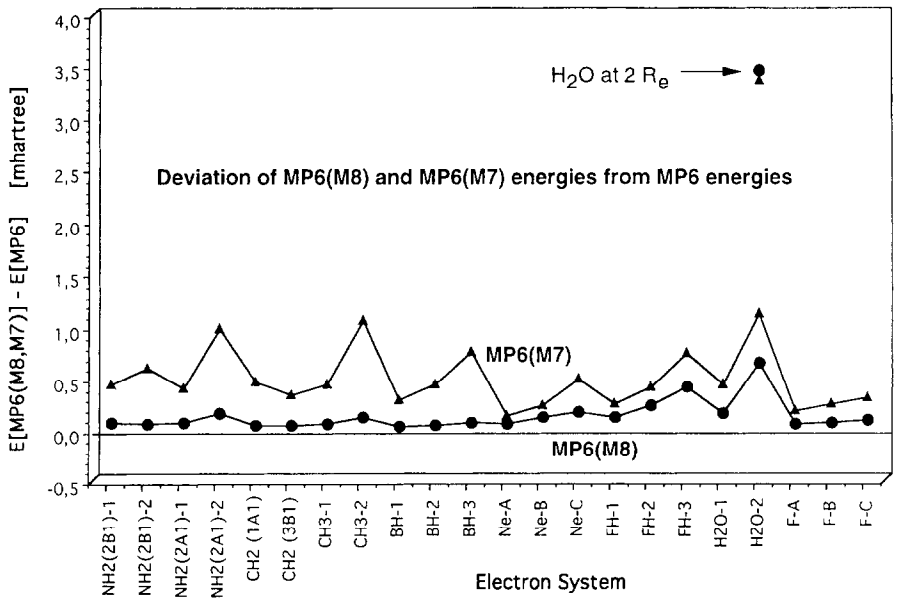


Fig. 13. Differences between MP6 energies (references) and MP6(M8) (dots) or MP6(M7) energies (triangles) in mhartree.

performance of MP2, MP3, and MP4. For example, it is not true that MP2 always largely exaggerates pair correlation effects. For class A systems, such an exaggeration does not play a significant role since only 73% of the total correlation energy is covered at this level of theory. In this situation, MP3 is a rather useful and economic method to significantly improve correlation energies. Of course, for almost the same costs one can also carry out an MP4(SDQ) calculation, which leads to an even better improvement of MP2 results by including more pair–pair correction terms. However, the additional cost factor for including the T excitations at MP4 does not pay off for class A systems.

Use of MPn Methods within

	Class A	Class B	Class A + B
MP2	73%	95%	errors
MP3	significant improvement	superfluous	errors
MP4(SDQ)	improvement	superfluous	errors
MP4(SDTQ)	small improvement	ok	reduced errors

Fig. 14. Recommended use of low-order MPn methods (n = 2,3,4) in the case of class A, class B, and class A + B systems.

For class B systems, MP2 covers more than 90% of the total correlation energy due to an exaggeration of pair correlation. Although MP3 and MP4(SDQ) partially correct for an exaggeration of pair correlation, these corrections are in a way superfluous since it is much more important to include three-electron correlation effects and to proceed right away from MP2 to MP4(SDTQ). Depending on the degree of electron clustering in class B systems, MP4 might exaggerate T effects and, then, it is also advisable to calculate MP5 and MP6 correlation energies.

Of course, it occurs more often that class A and class B systems are mixed in a chemical reaction. For example, the hydrogenation reaction of ethylene or acetylene leading to ethane is such a reaction. In this case, one will have relatively large errors at MP2, which are stepwise reduced from MP3 to MP4; however even at MP4 one will encounter considerable errors. These can be reduced by carrying out MP6(M7) calculations and extrapolating to FCI energies with the help of Feenberg scaling.

MP6(M7) is a suitable method for routine calculations since it possesses the same cost dependence as MP4. One can obtain FCI energies at no additional cost by an improved version of second-order Feenberg scaling (FE1 + FE2). Although any of these calculations will clearly show whether a class A or class

Class A Systems: systems with well-separated electron pairs

Li-, Be-compounds	LiH, Lithioalkanes, BeH_2, et
Boranes	BH_3, B_2H_6, etc.
Carboranes	$B_nC_2H_{n+2}$
Carbenes	CH_2, CR_2, etc.
Linear alkanes	CH_4, C_2H_6, etc.
Cassical carbocations	CH_3^+,
Alkyl radicals	$CH_3^{\cdot}$, $CH_5^{\cdot}$, etc.
Amines	R-NH_2, R_2NH, R_3N, etc.
etc.	

Class B Systems: systems with electron clustering

Electron-rich atoms	Ne, F, O, etc.
Halogen compounds	R-CH_nF_m
Peroxides, Ketones, Acids	R-OO-R, RC(=O)OR, etc.
Molecules with multiple bonds	N_2, CO, HCCH, $H_2C{=}CH_2$, e
Conjugated systems	benzene, butadiene, O_3, etc.
Hypervalent molecules	SF_6, PF_5, etc.
Nonclassical carbocations	vinyl cation, etc.
Transition metal compounds	
etc.	

Fig. 15. Examples for class A and class B systems.

B system is investigated, it might be useful to predict whether a given molecule belongs to class A or class B. By inspection of the electron pair structure of an atom or molecule, it is easy to clarify whether a given electron system belongs to class A or class B and, accordingly, whether the MP*n* series for this system possesses monotonic or erratic convergence behaviour (see Fig. 15). Of course, there are border cases between the two classes for which predictions may be difficult. Examples are water and alcohols in their equilibrium geometry, for which correlation contributions seem not to oscillate although convergence is not monotonic. However, investigation of the MP4, MP5, and MP6 spectrum will clearly reveal whether the system in question belongs to class A or B.

Comparing class A and class B systems and the convergence behaviour of the MP*n* series for these systems, it is appropriate to consider a class B system as the normal case which reveals the typical deficiencies of MP perturbation theory. MP theory is characterized by an inclusion of new correlation effects at even orders and a coupling between these effects at odd orders, thus reducing part of the correlation effects obtained at the previous order. In the case of strong electron correlation, this must lead to oscillations in the MP*n* correlation energy. With increasing number of electrons, there will be more systems with clustering of electron pairs in certain regions of atomic or molecular space and a strongly correlated movement of the electrons.

One can compare MP perturbation theory with a bad driving style. The perturbation engine is accelerated at even orders *n* by 'fuelling' it with new correlation effects. However, it is slowed down at odd orders by pushing the 'coupling brake'. This must lead to initial oscillations in the MP*n* series as observed in many cases. The exceptions to this are the class A systems, for which, as a result of weak couplings between different correlation effects, the typical MP*n* oscillations do not occur and monotonic convergence of the MP*n* series is obtained.

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