Sixth-Order Møller−Plesset Perturbation Theory−On the Convergence of the MP*n* Series

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A new method of deriving higher order MP*n* correlation energies is presented. Application of this method to MP6 leads to the derivation of the total correlation energy $E^{(6)}$ and its dissection into 36 energy terms $E^{(6)}_{ABC}$. For 33 electron systems, for which full CI (FCI) correlation energies are known $E^{(6)}$ and $E^{(6)}_{ABC}$ values together with the corresponding MP5 and MP4 energies are computed and used to analyze the initial convergence behavior of the MP*n* series. Two classes of systems can be distinguished, namely systems with monotonic convergence of the MP*n* series (class A systems) and systems with initial oscillations in the MP*n* series (class B systems). Analysis of $E^{(4)}_A$, $E^{(5)}_{AB}$, and $E^{(6)}_{ABC}$ values reveals that oscillations in the MP*n* series are caused by similar oscillations in the T contributions. For class A systems, the T contributions are of minor importance and decrease monotonically with order n as do also the SDQ contributions. For class B systems, one observes a significantly increased importance of the T contributions and alternation in the sign of the T energy for $n = 4$, 5, 6. Results indicate that class A systems are electron systems with well-separated electron pairs. The most important correlation effects are pair correlations while three-electron correlations and couplings between pair correlations are relatively small. The latter become important when electrons cluster in certain regions of an atom or molecule. Clustering of electrons always means increased electron correlation and a more complicated correlation pattern including three-electron and pair-coupling effects. In this case, MP theory strongly exaggerates correlation effects at even orders *n*, which is corrected by positive correlation contributions, in particular three-electron contributions at odd orders thus leading to the oscillations observed for class B systems. Once the electron structure of an atom or molecule is understood, it is possible to identify the system as a class A or class B system and to predict the convergence behavior of the corresponding MP*n* series. If extrapolation formulas are used that do not distinguish between class A and class B systems, the mean deviation from FCI correlation energies is 12 mhartrees. If however, different extrapolation formulas are applied for class A and class B systems, the mean deviation obtained for the same set of molecules decreases to 0.3 mhartree, which corresponds to an improvement of FCI estimates by a factor of 36.

1. Introduction

Many body perturbation theory (MBPT) based on the Møller−Plesset (MP) perturbation operator[1] has led to the most popular correlation corrected ab initio methods in quantum chemistry.[2−9] This has to do with the relatively low computational cost of *n*th-order MP (MP*n*) methods and the size-extensivity property of all MP*n* methods.[10] Another advantage of MP*n* theory results from the fact that correlation effects are included stepwise via specific excitations (MP2, double (D) excitations describing pair correlations; MP3, couplings between D excitations; MP4, apart from D excitations also single (S), triple (T), and quadruple (Q) excitations describing orbital relaxations, three-electron correlations, and independent, but simultaneous correlations of two electron pairs; MP5, couplings between S, D, T, Q excitations; etc.), which provides a basis for the investigation of individual correlation effects.

Recently, we have developed sixth-order MP theory (MP6) starting from general Rayleigh−Schrödinger perturbation theory for $n = 6$.[11−14] (For alternative derivations of MP6 correlation energies, see refs 15 and 16.) At MP6, two new types of excitations are included, namely pentuple (P) and hextuple (H) excitations, which describe independent, but simultaneous pair, three-electron correlations and pair, pair, pair correlations, respectively. Classifying all contributions to the MP6 correlation energy according to the possible excitations involved, one can distinguish 55 energy terms $E^{(6)}_{ABC}$ where ABC represents

possible combinations of S, D, T, Q, P, and H excitations. Because of the equivalence of contributions ABC and CBA, the number of unique $E^{(6)}_{ABC}$ terms is 36, which is still a factor 4 larger than the number of unique $E^{(5)}_{AB}$ (nine out of 14) and a factor 9 larger than the number of $E^{(4)}_A$ terms (four). MP6 is an $O(M^9)$ method (M, number of basis functions), which means that the computational cost for the most expensive of the 36 MP6 terms scale with M^9. Therefore, MP6 can only be applied for relatively small molecules using presently available computational techniques and computational hardware. Nevertheless, there are a number of reasons to develop and use MP6 theory.

(1) MP6 is the last method that can be developed using traditional techniques. MP7 has already a total of 221 terms, 141 of which are unique.[17] Therefore, setting up MP7 or even higher MP*n* methods will require some form of automated method development strategy based on computer algebra languages. MP6 is the appropriate method to develop and test such strategies.

(2) MP6 is after MP2 and MP4 the next even-order method that should be of interest because of the introduction of new correlation effects described by P and H excitations.

(3) Although the cost of a MP6 calculation is proportional to $O(M^9)$, there is still the possibility of systematic studies on small molecules using MP6 theory.

(4) Apart from this, one can develop useful approximate MP6 methods, which are less costly than the full MP6 approach

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because they include just the more important energy contributions $E_{ABC}^{(6)}$ rather than the full set of all 36 terms.

(5) With MP6 one has three energies (MP2, MP4, MP6) in the class of even order methods and three in the class of odd order methods (MP1 = HF, MP3, MP5). In this way, one gets a somewhat more realistic basis to analyze the convergence behavior of the MP*n* series.

(6) Calculating the various $E_A^{(4)}$, $E_{AB}^{(5)}$, $E_{ABC}^{(6)}$ contributions to the MP4, MP5, and MP6 correlation energy, one can determine those terms that dominate the initial convergence behavior of the MP*n* series. It may be possible to relate monotonic or erratic convergence behavior to the electronic structure of the system investigated and to predict the former once the latter is known.

(7) Utilizing MP6 correlation energies it will be possible to test and improve existing extrapolation formulas, by which reliable estimates of the exact correlation energy can be obtained.

We have developed and programmed MP6 for routine calculations to investigate points 1−4. Results of these investigations are published elsewhere.[11−14] This work has revealed that MP6 energies provide reasonable approximations to full CI (FCI) correlation energies, which for a given basis set and geometry represent correct correlation energies corresponding to the MP*n* value $\Delta E^{(n)} = \sum_{m}^{n} E^{(m)}$ for $n = \infty$. However, in cases of an erratic convergence behavior of the MPn series, the (absolute) MP6 correlation energy is often larger than the corresponding FCI value.[13] We have found that better estimates of the FCI correlation energy are obtained by applying second-order Feenberg scaling, which is superior to first-order Feenberg scaling or Padé approximants.[14]

In this work, we investigate the convergence behavior of the MP*n* series along the lines described in points 5 and 6. For this purpose, we reprogrammed MP5 and MP6 to decompose each correlation energy $E^{(n)}$ for $n \leq 6$ into individual contributions representing specific correlation effects. In particular, we separated contributions that depend on T effects from contributions that depend on just S, D, Q or P, H excitations because the analysis of T terms provides evidence for the convergence behavior of the MP*n* series. We will show that in the case of strong pair and three-electron correlation effects, the MP*n* series will always tend to oscillate initially. Monotonic convergence behavior can be expected for those systems for which the electron pairs are well-separated and couplings between electron pairs are small. If for a given electronic systems convergence behavior of the MP*n* series can be predicted, it should be possible to derive appropriate extrapolation formulas, which lead to reliable estimates of FCI correlation energies (see point 7 above). The latter can be used to derive reliable energy differences for describing chemical processes.

2. Development of Sixth-Order MP (MP6) Perturbation Theory

There are two different ways of developing MP methods for use in quantum chemical calculations. The first way can be called the algebraic approach since it is based on an algebraic derivation of matrix elements from general perturbation theory formulas. It works well for low-order perturbation theory,[4,5,7] however, becomes problematic for higher orders. In the latter case, one can distinguish between a principal term and one or several renormalization terms in the general perturbation theory formula. According to the linked diagram theorem[18] it is superfluous to evaluate the renormalization terms since these are all canceled by appropriate parts of the principal term.

Because of the linked diagram theorem it is of advantage to derive MP*n* energy formulas by diagrammatic techniques which immediately identify those terms that really contribute to the correlation energy. Accordingly, diagrammatic derivations of the third-, fourth-, and even fifth-order MP energy have been made, which clearly demonstrated superiority over the algebraic approach.[6,8,19] However, the diagrammatic approach has also its disadvantages. This becomes obvious when considering the increase in linked diagrams contributing to the correlation energy. If one uses Brandow diagrams,[8] there are 1, 3, 39, 840, and 28 300 antisymmetrized diagrams at second-, third-, fourth-, fifth-, and sixth-order, respectively. This means that it is hardly possible to derive the sixth-order correlation energy in terms of linked diagrams.

Therefore, we used in previous work a third approach for developing higher order perturbation theory formulas. This third approach is based on a combination of algebraic and diagrammatic techniques and comprises the following steps:

(1) Principal term and renormalization terms are derived from the general perturbation theory formula.

(2) Since it is clear that all renormalization terms will be canceled by parts of the principal term, derivation of the MP*n* equations concentrates just on the principal term. This will be dissected into various parts according to the excitations involved at the corresponding order of perturbation theory. The various parts will be written in a cluster operator form.

(3) Each part of the principal term characterized by S, D, T, Q, P, H, etc. excitations can be described as representing connected or disconnected energy diagrams according to the nature of the cluster operators appearing in the energy formula.

(4) All connected (closed) energy terms correspond to linked diagram contributions and enter the formula for the correlation while the disconnected energy terms represent unlinked diagram contributions which according to the linked cluster theorem can be discarded.

(5) The final cluster operator form of the linked diagram contributions is transformed into two-electron integral formulas. This is facilitated by the fact that all those terms that originally involved disconnected cluster operator parts can be simplified by using intermediate arrays.[12]

The advantages of this approach are that (a) superfluous energy contributions are never determined within the algebraic derivation and (b) a tedious analysis of all linked diagram terms is not necessary.

The latter point will become clear if step 3 as the key step of the procedure 1−5 is described in more detail. Each cluster operator $\hat{T}$ can be described in terms of simplified Brandow diagrams.[8] Combination of the $\hat{T}$ diagrams with the diagrams of the perturbation operator $\hat{V}$ may lead to closed connected or closed disconnected diagrams, which means that the corresponding matrix elements represented linked or unlinked energy contributions. It is also possible that the combination of $\hat{T}$ and $\hat{V}$ diagrams leads to disconnected open diagrams. In this case, the diagrams correspond to the wave operator and cover both linked and unlinked contributions. One has to combine the wave operator part with further parts of the energy formula to get a separation into connected closed (= linked) and disconnected closed (= unlinked) energy diagrams. In any case, it is possible to identify for each part of the principal term whether it contains just linked or in addition unlinked diagram contributions. The diagrams one has to use for this purpose are rather simple because they correspond to some basic operators and need not to be specified with regard to hole and particle lines.[8]

According to Rayleigh−Schrödinger perturbation theory, the MP6 correlation energy is given by

$$E_{MP}^{(6)} = \langle \Phi_0 | \hat{V}(\hat{G}_0 \bar{V})^5 | \Phi_0 \rangle_L \tag{1}$$

(L, linked diagrams only) with the Møller−Plesset perturbation

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operator $\hat{V}$ being defined as the difference between exact Hamiltonian $\hat{H}$ and the zeroth-order Hamiltonian $\hat{H}_0$

$$\hat{H}_0 = \sum_p \hat{F}_p = \sum_p (\hat{h}_p + \hat{g}_p) \tag{2}$$

$$\hat{V} = \hat{H} - \hat{H}_0 = \sum_{p<q} \hat{r}_{pq}^{-1} - \sum_p \hat{g}_p \tag{3}$$

The reduced resolvent $\hat{G}_0$ is given by

$$\hat{G}_0 = \sum_{k=1}^{\infty} \frac{|\Phi_k\rangle\langle\Phi_k|}{E_0 - E_k} \tag{4}$$

and $\bar{V}$ by

$$\bar{V} = \hat{V} - \langle\Phi_0|\hat{V}|\Phi_0\rangle \tag{5}$$

where Φ_0 is the HF reference wave function. Using the definition of the resolvent and Slater rules, eq 1 can explicitly be written as

$$E_{\text{MP}}^{(6)} = \sum_{x_1,x_2}^{\text{SDTQ}} \sum_y^{\text{SDTQPH}} (\langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\bar{V}|\Phi_{x_1}\rangle(E_0 - E_{x_1})^{-1}\bar{V}_{x_1y}(E_0 - $$
$$E_y)^{-1}\bar{V}_{yx_2}(E_0 - E_{x_2})^{-1}\langle\Phi_{x_2}|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle)_L \tag{6a}$$

$$= \sum_{X_1,X_2}^{\text{SDTQ}} \sum_Y^{\text{SDTQPH}} \mathcal{A}(X_1, Y, X_2)_L \tag{6b}$$

with

$$\bar{V}_{xy} = \langle\Phi_x|\hat{V}|\Phi_y\rangle - \delta_{xy}\langle\Phi_0|\hat{V}|\Phi_0\rangle \tag{6c}$$

Next, first- and second-order cluster operators $\hat{T}_2^{(1)}$ and $\hat{T}_i^{(2)}$ ($i = 1, 2, 3$) are defined:

$$\hat{T}_2^{(1)}|\Phi_0\rangle = \sum_d^D a_d|\Phi_d\rangle \tag{7}$$

$$\hat{T}_i^{(2)} = \sum_x^X b_x|\Phi_x\rangle \quad (i = 1, 2, 3) \tag{8}$$

where the first-order D excitation amplitudes a_d and the second-order amplitudes b_x are given by eqs 9 and 10:

$$a_d = (E_0 - E_d)^{-1}\langle\Phi_d|\hat{V}|\Phi_0\rangle \tag{9}$$

$$b_x = (E_0 - E_x)^{-1}\langle\Phi_x|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle \quad (x = s, d, t \text{ for } i = 1, 2, 3) \tag{10}$$

By using the cluster operators $\hat{T}_2^{(1)}$ and $\hat{T}_i^{(2)}$ ($i = 1, 2, 3$), one can partition the MP6 energy into three different $\mathcal{A}(X_1, Y, X_2)$ terms (compare with Figure 1):

$$E_{\text{MP}}^{(6)} = \mathcal{A}_1[(\bar{V}\hat{T}_i^{(2)})_C]_L + \mathcal{A}_2[(\hat{T}_2^{(1)})^2]_L + \mathcal{A}_3[(\bar{V}\hat{T}_i^{(2)})_D]_L$$
$$(i = 1, 2, 3) \tag{11}$$

The first part, $\mathcal{A}_1$, covers all connected cluster operator diagrams

resulting from $(\bar{V}\hat{T}_i^{(2)})_C$ and fully contributes to $E_{\text{MP}}^{(6)}$ in form of $E(\text{MP6})_1$:

$$\mathcal{A}_1[(\bar{V}\hat{T}_i^{(2)})_C]_L = E(\text{MP6})_1$$
$$= E_{\text{SSS}}^{(6)} + 2E_{\text{SSD}}^{(6)} + 2E_{\text{SST}}^{(6)} + E_{\text{SDS}}^{(6)} +$$
$$2E_{\text{SDD}}^{(6)} + 2E_{\text{SDT}}^{(6)} + E_{\text{DSD}}^{(6)} + 2E_{\text{DST}}^{(6)} +$$
$$E_{\text{DDD}}^{(6)} + 2E_{\text{DDT}}^{(6)} + E_{\text{TST}}^{(6)} + E_{\text{TDT}}^{(6)} +$$
$$E_{\text{DTD}}^{(6)} + 2E_{\text{DTT}}^{(6)} + E_{\text{TTT}}^{(6)} + E_{\text{TQT}}^{(6)} \tag{12}$$

The second and the third part, $\mathcal{A}_2$ and $\mathcal{A}_3$, cover all disconnected cluster operator diagram terms resulting from $(\hat{T}_2^{(1)})^2$ or various combinations of $\hat{T}_i^{(2)}$ with $\bar{V}$ as illustrated in Figure 1.

$$\mathcal{A}_2[(\hat{T}_2^{(1)})^2]_L = \sum_{X_1}^{\text{S,D,T,Q}} \sum_Y^{\text{D,T,Q,P,H}} (2 - \delta_{X_1,Q} - \delta_{X_1,S}\,\delta_{Y,T} -$$
$$\delta_{X_1,D}\,\delta_{Y,Q})\mathcal{A}(X_1, Y, Q)_L \tag{13}$$

where

$$\mathcal{A}(X_1, Y, Q) =$$
$$\sum_y^Y \langle\Phi_0|(\hat{T}_i^{(2)})^\dagger\bar{V}|\Phi_y\rangle(E_0 - E_y)^{-1}\langle\Phi_y|\bar{V}^1/_2(\hat{T}_2^{(1)})^2|\Phi_0\rangle$$
$$(i = 1, 2, 3 \text{ for } X_1 = \text{S, D, T}) \tag{14}$$

or

$$\mathcal{A}(Q, Y, Q) =$$
$$\sum_y^Y \langle\Phi_0|^1/_2((\hat{T}_2^{(1)})^\dagger)^2\bar{V}|\Phi_y\rangle(E_0 - E_y)^{-1}\langle\Phi_y|\bar{V}^1/_2(\hat{T}_2^{(1)})^2|\Phi_0\rangle$$
$$\tag{15}$$

As indicated in Figure 1, the disconnected Q cluster operator $(\hat{T}_2^{(1)})^2$ in $\mathcal{A}_2[(\hat{T}_2^{(1)})^2]_L$ couples with the perturbation operator $\bar{V}$. This leads to disconnected and connected cluster operator diagram parts, which in turn lead to the energy contributions $\mathcal{A}(X_1, Y, Q_D)_L$ and $\mathcal{A}(X_1, Y, Q_C)_L$ of eqs 16−19.

$$\mathcal{A}(X_1, Y, Q_D)_L =$$
$$\sum_y^Y (\langle\Phi_0|(\hat{T}_i^{(2)})^\dagger\bar{V}|\Phi_y\rangle(E_0 - E_y)^{-1}\langle\Phi_y|(\bar{V}^1/_2(\hat{T}_2^{(1)})^2)_D|\Phi_0\rangle)_L$$
$$(i = 1, 2, 3 \text{ for } X_1 = \text{S, D, T}; Y = \text{T, Q, P}) \tag{16}$$

$$\mathcal{A}(X_1, Y, Q_C)_L =$$
$$\sum_y^Y \langle\Phi_0|(\hat{T}_i^{(2)})^\dagger\bar{V}|\Phi_y\rangle(E_0 - E_y)^{-1}\langle\Phi_y|(\bar{V}^1/_2(\hat{T}_2^{(1)})^2)_C|\Phi_0\rangle$$
$$(i = 1, 2, 3 \text{ for } X_1 = \text{S, D, T}; Y = \text{D, T, Q}) \tag{17}$$

$$\mathcal{A}(Q, Y, Q_D)_L =$$
$$\sum_y^Y (\langle\Phi_0|^1/_2((\hat{T}_2^{(1)})^\dagger)^2\bar{V}|\Phi_y\rangle(E_0 - E_y)^{-1} \times$$
$$\langle\Phi_y|(\bar{V}^1/_2(\hat{T}_2^{(1)})^2)_D|\Phi_0\rangle)_L \quad (Y = \text{T, Q, P,H}) \tag{18}$$

$$\mathcal{A}(Q, Y, Q_C)_L = \sum_y^Y (\langle\Phi_0|^1/_2((\hat{T}_2^{(1)})^\dagger)^2\bar{V}|\Phi_y\rangle(E_0 - E_y)^{-1} \times$$
$$\langle\Phi_y|(\bar{V}^1/_2(\hat{T}_2^{(1)})^2)_C|\Phi_0\rangle)_L \quad (Y = \text{D, T, Q}) \tag{19}$$

The sum of $A(X_1, Y, Q_C)_L$ (eq 17), $A(Q, Y, Q_C)_L$ (eq 19), and $A(Q, H, Q_D)_L$ (eq 18 for $Y = H$) is denoted $E(MP6)_{2a}$,[11] which covers 12 different energy contributions:

$$E(MP6)_{2a} = \sum_{X_1}^{S,D,T} 2A(X_1, D, Q_C) + A(Q_C, D, Q_C) +$$
$$A(S, T, Q_C)$$
$$+ \sum_{X_1}^{D,T,Q} (2 - \delta_{X_1,Q})A(X_1, T, Q_C) + A(D, Q, Q_C)$$
$$+ \sum_{X_1}^{T,Q} (2 - \delta_{X_1,Q})A(X_1, Q, Q_C) + A(Q, H, Q_D)_L$$
$$(20a)$$

$$= 2\sum_X^{S,D,T} E_{XDQ}^{(6)} + E_{QDQ}^{(6)} + E_{STQ}^{(6)}(II) + E_{QTQ}^{(6)}(II)$$
$$+ 2\sum_X^{D,T} E_{XTQ}^{(6)}(II) + E_{DQQ}^{(6)}(II) + E_{QQQ}^{(6)}(II)$$

$$+ 2E_{TQQ}^{(6)}(II) + E_{QHQ}^{(6)} \qquad (20b)$$

In passing on, it is useful to note that some terms $E_{X_1YQ}^{(6)}$ are split into two parts I and II according to eq 21

$$E_{X_1YQ}^{(6)} = E_{X_1YQ}^{(6)}(I) + E_{X_1YQ}^{(6)}(II) \qquad (21)$$

where part II is covered in eqs 17 and 19 while part I is contained in eqs 16 and 18. Because of computational reasons, all terms contained in eqs 16 and 18 (excluding the term with $Y = H$, see above) are added to $A_3[(\bar{V}\hat{T}_i^{(2)})_D]_L$, which is defined by (compare with Figure 1)

$$A_3[(\bar{V}\hat{T}_i^{(2)})_D]_L = \sum_{X_1}^{D,T,Q} A(X_1, Q, D)_L +$$
$$\sum_{X_1}^{S,D,T,Q} A(X_1, T, S)_L + \sum_{X_1}^{T,Q} A(X_1, P, T)_L \quad (22)$$

Combining the terms of eq 22 with the terms $A(X_1, Y, Q_D)_L$ of eqs 16 and 18, one obtains simpler formulations in cluster operator form, namely eqs 23−25:

$$E(MP6)_{2b} = \sum_{X_1}^{D,T,Q} (A(X_1, Q, D)_L + A(X_1, Q, Q_D)_L)$$
$$= \langle\Phi_0|(\hat{T}_2^{(2)})^\dagger(\bar{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)})_C|\Phi_0\rangle +$$
$$2\langle\Phi_0|(\hat{T}_3^{(2)})^\dagger\bar{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)}|\Phi_0\rangle +$$
$$\langle\Phi_0|^1/_2((\hat{T}_2^{(1)})^\dagger)^2\bar{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)}|\Phi_0\rangle_C \quad (23a)$$

$$= [E_{DQD}^{(6)} + E_{DQQ}^{(6)}(I)] + 2[E_{TQD}^{(6)} + E_{TQQ}^{(6)}(I)]$$
$$+ [E_{QQD}^{(6)} + E_{QQQ}^{(6)}(I)] \qquad (23b)$$

$$E(MP6)_3 = \sum_{X_1}^{S,D,T} (A(X_1, T, S)_L + A(X_1, T, Q_D)_L) +$$
$$A(Q, T, S)_L + A(Q, T, Q_D)_L$$
$$= \sum_{i=1,2,3} (2 - \delta_{i,1})\langle\Phi_0|(\hat{T}_i^{(2)})^\dagger\bar{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}|\Phi_0\rangle_C +$$
$$\langle\Phi_0|^1/_2((\hat{T}_2^{(1)})^\dagger)^2\bar{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}|\Phi_0\rangle_C \quad (24a)$$

$$= E_{STS}^{(6)} + E_{STQ}^{(6)}(I) + 2[E_{DTS}^{(6)} + E_{DTQ}^{(6)}(I)] +$$
$$2[E_{TTS}^{(6)} + E_{TTQ}^{(6)}(I)] + E_{QTS}^{(6)} + E_{QTQ}^{(6)}(I) \quad (24b)$$

$$E(MP6)_4 = \sum_{X_1}^{T,Q} (A(X_1, P, T)_L + A(X_1, P, Q_D)_L)$$
$$= \langle\Phi_0|(\hat{T}_3^{(2)})^\dagger\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}|\Phi_0\rangle_C +$$
$$\langle\Phi_0|^1/_2((\hat{T}_2^{(1)})^\dagger)^2\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}|\Phi_0\rangle_C \quad (25a)$$

$$= [E_{TPT}^{(6)} + E_{TPQ}^{(6)}] + [E_{QPT}^{(6)} + E_{QPQ}^{(6)}] \qquad (25b)$$

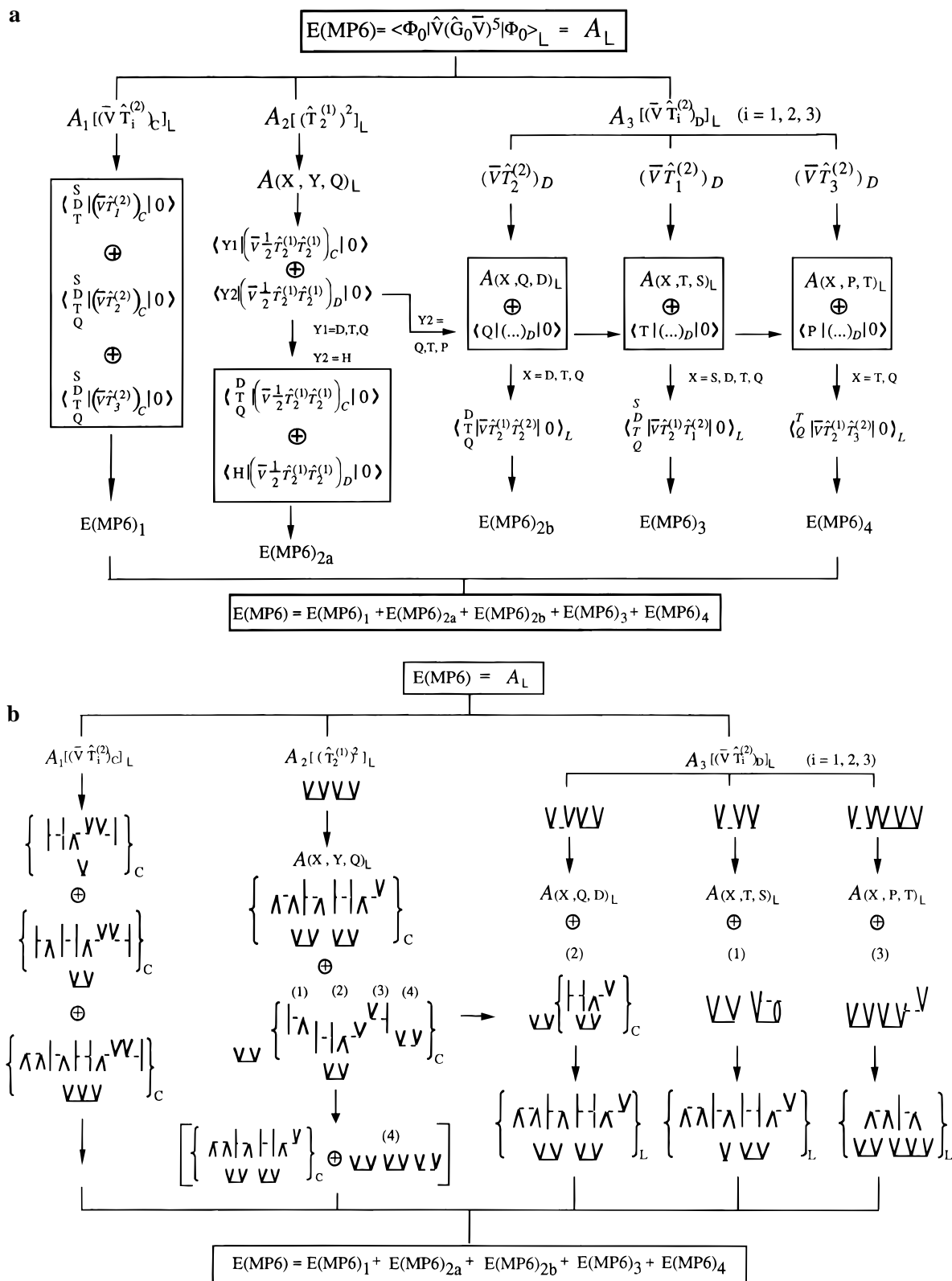The final MP6 energy expression covers the four energy parts $E(MP6)_1$, $E(MP6)_2$, $E(MP6)_3$, and $E(MP6)_4$:

$$E_{MP}^{(6)} = E(MP6)_1 + E(MP6)_{2a} + E(MP6)_{2b} +$$
$$E(MP6)_3 + E(MP6)_4 \quad (26)$$

which correspond to the connected cluster operator part $(E(MP6)_1)$, the disconnected Q cluster operator part $(E(MP6)_2)$, the disconnected T cluster operator part $(E(MP6)_3)$, and the disconnected P cluster operator part $(E(MP6)_4)$. Hence, the final form of the MP6 correlation energy is given by

$$E(MP6) = E_{SSS}^{(6)} + 2E_{SSD}^{(6)} + 2E_{SST}^{(6)} + E_{SDS}^{(6)} + 2E_{SDD}^{(6)} +$$
$$2E_{SDT}^{(6)} + E_{DSD}^{(6)} + 2E_{DST}^{(6)} + E_{DDD}^{(6)} + 2E_{DDT}^{(6)} + E_{TST}^{(6)} +$$
$$E_{TDT}^{(6)} + E_{DTD}^{(6)} + 2E_{DTT}^{(6)} + E_{TTT}^{(6)} + E_{TQT}^{(6)} + 2E_{SDQ}^{(6)} +$$
$$2E_{DDQ}^{(6)} + 2E_{TDQ}^{(6)} + E_{QDQ}^{(6)} + [E_{STS}^{(6)} + E_{STQ}^{(6)}(I)] +$$
$$[E_{STQ}^{(6)}(II) + E_{QTQ}^{(6)}(II)_a] + E_{QTQ}^{(6)}(II)_b + [E_{QTS}^{(6)} + E_{QTQ}^{(6)}(I)] +$$
$$2[E_{DTS}^{(6)} + E_{DTQ}^{(6)}(I)] + 2E_{DTQ}^{(6)}(II) + [E_{DQD}^{(6)} + E_{DQQ}^{(6)}(I)] +$$
$$[E_{DQQ}^{(6)}(II) + E_{QQQ}^{(6)}(II)_a] + [E_{QQD}^{(6)} + E_{QQQ}^{(6)}(I)] + E_{QQQ}^{(6)}(II)_b +$$
$$2[E_{TTS}^{(6)} + E_{TTQ}^{(6)}(I)] + 2E_{TTQ}^{(6)}(II) + 2[E_{TQD}^{(6)} + E_{TQQ}^{(6)}(I)] +$$
$$2E_{TQQ}^{(6)}(II) + E_{QHQ}^{(6)} + [E_{TPT}^{(6)} + E_{TPQ}^{(6)}] + [E_{QPT}^{(6)} + E_{QPQ}^{(6)}] \quad (27)$$

At this point, it is interesting to compare our development of MP6[11−13] with parallel work that was published by Kucharski and Bartlett (KB)[16] after this work was done. KB approach MP6 by exploiting a simplified CCSDTQ method corrected through sixth order with a noniterative inclusion of some connected Q contributions. They carry out two CC iterations to obtain the third-order cluster amplitudes for the calculations of S, D, T, and Q terms at MP6. While our approach starts from the general energy formula for MP6, which is expressed in terms of first- and second-order cluster operators, KB use third-order cluster operators to set up the third-order wave function. This has two important consequences, namely (a) it is no longer possible to partition the MP6 energy into individual contributions $E_{ABC}^{(6)}$ as done in eq 27 and b to guarantee efficient computing certain unlinked diagram contributions have to be calculated twice (eqs 18−21 of ref 16).

In short, the MP6 method by KB is based on CC theory and represents a two-step approach (step 1, two iterations with a simplified CCSDTQ method have to be carried out to get third-

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a

$$E(MP6) = \langle \Phi_0 | \hat{V}(\hat{G}_0 \bar{V})^5 | \Phi_0 \rangle_L = A_L$$

$A_1[(\bar{V}\hat{T}_i^{(2)})_C]_L$ 　　　 $A_2[(\hat{T}_2^{(1)})^2]_L$ 　　　 $A_3[(\bar{V}\hat{T}_i^{(2)})_D]_L$ 　(i = 1, 2, 3)

$E(MP6) = E(MP6)_1 + E(MP6)_{2a} + E(MP6)_{2b} + E(MP6)_3 + E(MP6)_4$

$$E(MP6) = A_L$$

b

$A_1[(\bar{V}\hat{T}_i^{(2)})_C]_L$ 　　　 $A_2[(\hat{T}_2^{(1)})^2]_L$ 　　　 $A_3[(\bar{V}\hat{T}_i^{(2)})_D]_L$ 　(i = 1, 2, 3)

$E(MP6) = E(MP6)_1 + E(MP6)_{2a} + E(MP6)_{2b} + E(MP6)_3 + E(MP6)_4$

Figure 1. Derivation of the MP6 energy formula described in form of a flow chart. (a) Connected (C) and disconnected (D) cluster operator terms lead to energy contributions $E(MP6)_1$, $E(MP6)_{2a}$, $E(MP6)_{2b}$, $E(MP6)_3$, and $E(MP6)_4$ corresponding to connected SDT contributions (1), disconnected Q contributions (2a + 2b), disconnected T contributions (3) and disconnected P contributions (4). Note that abbreviations such as $\langle \overset{S}{\underset{...}{D}}| ...\rangle$ indicate a sum of terms such as $\langle S|...\rangle + \langle D|...\rangle + ...$ (b) Matrix elements in form of simplified Brandow diagrams are shown (see text).

order amplitudes; step 2, evaluation of S, D, T, Q contributions from third-order amplitudes; addition of P, H contributions) while our approach represents the first single-step MP6 method developed in the spirit of the work carried out to get MP2, MP3, MP4, and MP5.[2-9] As a consequence, the analysis of MP6 presented in the following would not be possible with the KB approach. Furthermore, exploitation of approximated MP6 methods for which individual terms with high cost requirements are dropped as suggested by us in previous work[13] is rather difficult if not impossible.

	SDQ Space for MP5 (7/5)							T Space for MP5 (7/4)							pt	pq	hq
	SS	SD	DS	DD	DQ	QD	QQ	ST	TS	DT	TD	TT	TQ	QT			
MP4 — SDQ Space for MP6 (17/12)								T Space for MP6 (33/20)							PH Space for MP6 (5/4)		
S	SSS	SSD	SDS	SDD	SDQ			SST	STS	SDT	STD	STT	STQ				
D	DSS	DSD	DDS	DDD	DDQ	DQD	DQQ	DST	DTS	DDT	DTD	[DTT]	DTQ	DQT			
Q		QDS	QDD	QDQ	QQD	QQQ (shaded)		QTS	QDT	QTD	QTT	QTQ	QQT (shaded)		QPT	QPQ	QHQ
T	TSS	TSD	TDS	TDD	TDQ	TQD	TQQ	TST	TTS	TDT	TTD	[TTT]	[TTQ]	TQT (shaded)	TPT	TPQ	

☐ **M^8 Terms**   ▨ **M^9 Terms**

Figure 2. 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 SDQ, T, and PH space for MP6 are shown separated by dashed lines. In each case, the total number of $E^{(n)}_{A...}$ terms and the number of unique terms is given. Terms with a cost dependence of M^8 (white boxes) or M^9 (shaded boxes) are also indicated.

3. Analysis of MPn Correlation Energies

It is reasonable to group the various contributions to $E^{(6)}$ into T- and SDQ-dependent terms. Such a grouping of terms was first done for the MP4 correlation energy where one distinguishes between MP4(SDQ), MP4(T), and full MP4(SDTQ) according to eqs 28 and 29.[5]

$$E^{(4)}(SDQ) = E^{(4)}_S + E^{(4)}_D + E^{(4)}_Q \qquad (28)$$

$$E^{(4)}(T) = E^{(4)}_T \qquad (29)$$

Similarly, one can split the nine MP5 correlation energy contributions into SDQ and T part:

$$E^{(5)}(SDQ) = E^{(5)}_{SS} + 2E^{(5)}_{SD} + E^{(5)}_{DD} + 2E^{(5)}_{DQ} + E^{(5)}_{QQ} \quad (30)$$

$$E^{(5)}(T) = 2E^{(5)}_{ST} + 2E^{(5)}_{DT} + E^{(5)}_{TT} + 2E^{(5)}_{TQ} \qquad (31)$$

Figure 2 gives the 55 $E^{(6)}_{ABC}$ terms (36 unique terms are given in bold print) as a result of the combination of the four energy contributions $E^{(4)}_A$ of MP4 (given in the first column of Figure 2) with the 14 energy contributions $E^{(5)}_{AB}$ of MP5 (extended by the three additional combinations pt, pq, hq due to P and H excitations, see first row of Figure 2) according to Slater rules. Each of the terms shown in Figure 2 is size extensive and, therefore, it is possible to group terms characterized by a certain combination of excitations into subsets as indicated in Figure 2 by dashed lines. According to these dissections, we group the 55 (36) MP6 terms into 17 (12) SDQ terms that involve just S, D, and Q excitations; the T space covers those terms that describe the coupling between T and S, D, Q excitations (33 terms, 22 unique terms); the remaining five terms, namely QPQ, QHQ, TPT, TPQ, and QPT, define the PH part $E^{(6)}(PH)$.[13]

The cluster operator equations of MP6 were transformed into two-electron integral formulas and the 37 energy terms of eq 27 were programmed for the purpose of routine calculations of total MP6 correlation energies as well as the individual MP6 contributions $E^{(6)}_{ABC}$. Parallel to this work, MP5 was reprogrammed to determine the nine unique $E^{(5)}_{AB}$ terms shown in the

first row of the diagram in Figure 2. In this way, more than 53 (out of 60) correlation energy contributions $E^{(n)}$, $E^{(n)}(A...)$, and $E^{(n)}_{A...}$ for ($n \leq 6$) can be obtained with one single MP6 calculation.

In this work, individual energy contributions to MP correlation energies $E^{(n)}$ for $n \leq 6$ are determined for 33 electronic systems to analyze the convergence behavior of the MPn series:

BH, $^1\Sigma^+$, R_e, 1.5R_e, 2R_e;

basis set (9s5p1d/4s1p)[4s2p1d/2s1p][20]

NH$_2$, ^{2}B$_1$, R_e, 1.5R_e, 2R_e;

basis set (9s5p1d/4s1p)[4s2p1d/2s1p][21]

NH$_2$, ^{2}A$_1$, R_e, 1.5R_e, 2R_e;

basis set (9s5p1d/4s1p)[4s2p1d/2s1p][22]

CH$_3$, ^{2}A$''_2$, R_e, 1.5R_e, 2R_e;

basis set (9s5p1d/4s1p)[4s2p1d/2s1p][23]

CH$_2$, ^{2}B$_1$, CH$_2$, ^{1}A$_1$; basis set (9s5p1d/4s1p)[4s2p1d/2s1p][24]

Ne, ^{1}S, basis sets 4s2p1d, 5s3p2d, 6s4p1d[25]

F, ^{2}P, basis sets 4s3p1d, 4s3p2d, 5s3p2d[25]

F$^-$, ^{1}S, basis sets 4s3p1d, 4s3p2d, 5s3p2d[25]

FH, $^1\Sigma^+$, R_e, 1.5R_2, 2R_e;

basis set (9s5p1d/4s1p)[4s2p1d/2s1p][26]

H$_2$O, ^{1}A$_1$, R_e, 1.5R_e, 2R_e;

basis set (9s5p1d/4s1p)[4s2p1d/2s1p][26]

HCCH, $^1\Sigma^+_g$, R_e; basis set (9s5p1d/4s1p)[4s2p1d/2s1p][27]

CO, $^1\Sigma^+$, R_e, basis set (9s5p1d)[4s2p1d][27]

O$_3$, ^{1}A$_1$, R_e; c-O$_3$, ^{1}A$_1$, R_e; basis set (9s5p1d)[4s2p1d][28]

The set of reference systems includes charged and uncharged atoms (F and F$^-$), radicals and biradicals (CH$_3$, ^{2}A$_2''$ and CH$_2$,

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$^3B_2$), different states of molecules ($^3B_2$ and $^1A_1$ state of CH_2, $^2B_1$ and $^2A_1$ state of NH_2), two-heavy atom systems (HCCH, CO), three-heavy atom systems (O_3, c-O_3) as well as AH_n molecules both at their equilibrium geometry (R_e) and in geometries with (symmetrically) stretched AH bonds ($1.5R_e$, $2R_e$: "stretched geometries"). Calculation of the latter represents a critical test on the performance of a correlation method because wave functions of molecules with stretched geometries possess considerable multireference character. For 29 of these electronic systems, FCI correlation energies are known[23,24,29-31] while for the remaining four systems (HCCH, CO, O_3, c-O_3), we have used CCSDT correlation energies obtained in this work as approximations to the unknown FCI values. In previous work, in which we analyzed infinite order contributions to CCSDT with the help of perturbation theory,[17] we showed that among all correlation corrected methods that scale with $O(M^8)$ or better, CCSDT comes closest to FCI. For example, CCSDT covers 91% of all MP6 (QTD, DQT, QQT, QTT, TQT are missing), 87% of all MP7, and 85% of all MP8 terms, some of which are covered only partially (at MP6: DQQ, QQD, QQQ, QTQ, TQQ, QPQ, QHQ, TPQ, QPT). In view of this, CCSDT energies should provide a reasonable estimate of FCI values, although their accuracy (mean deviation from FCI values: 0.53 mhartree for 20 CCSDT calculations[32]) is lower than that achieved in this work.

Rather than listing and discussing the large set of correlation energies obtained in this work (more than 1700 energy values, $E^{(n)}$ values are published in refs 13 and 14), we concentrate on describing trends and relationships between individual values. For this purpose, the various contributions to the correlation energy of a given system are scaled by an appropriate energy quantity to make them comparable and to take averages over classes of systems. As scale factors FCI correlation energies[23,24,29-31] or the quantities EN defined by eq 32 are used.

$$EN = \{[E^{(n)}(SDQ)]^2 + [E^{(n)}(T)]^2 + ...\}^{-1/2} \quad (32a)$$

$$EN = \{[E^{(n)}_{A...}]^2 + [E^{(n)}_{B...}]^2 + ...\}^{-1/2} \quad (32b)$$

Averages over scaled energy contributions within a given class are denoted by $\epsilon^{(n)}(A...)$, etc. and presented in form of bar diagrams, which we call "spectra" of the MP correlation energy. In this way, we have derived $E^{(n)}(SDQ)$, $E^{(n)}(T)$, and $E^{(n)}_{A...}$ spectra for MP4, MP5, and MP6 using the more than 1700 energy values generated in this work. We will analyze in the following the convergence behavior of the MPn series by comparing FCI with MP6 correlation energies, SDQ,T-partitioning of the total correlation space, and discussing MPn spectra for different classes of electron systems.

4. Convergence Behavior of the MPn Series

It is well-known that the MPn series can show different convergence behavior at lower orders.[13,14,33-36] This is shown in Figure 3 for some typical examples. One can distinguish between two different situations: (a) The MPn energies decrease monotonically approaching the FCI energy from above (Figure 3a,b). (b) There are initial oscillations in the MPn correlation energy which can lead to an exaggeration of electron correlation effects at sixth-order or even at fourth-order MP theory (Figure 3c,d). However, in each case investigated so far, the MPn series converges to the FCI value as has been demonstrated by Handy and co-workers[15] who investigated convergence behavior up to $n = 48$ by generating MPn energies during the iterations of a FCI calculation. We have grouped electron systems, which

possess monotonic convergence in the MPn series, in class A. Those systems, which possess erratic convergence with initial oscillations, we have grouped in class B.

The 29 FCI systems investigated in this work can be grouped into 14 class A systems and 15 class B systems.

Class A: BH, $^1\Sigma^+$, R_e, $1.5R_e$, $2R_e$; NH_2, $^2B_1$, R_e, $1.5R_e$, $2R_e$;
NH_2, $^2A_1$, R_e, $1.5R_e$, $2R_e$; CH_3, $^2A''_2$, R_e, $1.5R_e$, $2R_e$;
CH_2, $^2B_1$, CH_2, $^1A_1$

Class B: Ne, ^1S, basis sets 4s2p1d, 5s3p2d, 6s4p1d;
F, ^2P, basis sets 4s3p1d, 4s3p2d, 5s3p2d;
F^-, ^1S, basis sets 4s3p1d, 4s3p2d, 5s3p2d,
FH, $^1\Sigma^+$, R_e, $1.5R_e$, $2R_e$; H_2O, $^1A_1$, R_e, $1.5R_e$, $2R_e$

In Figure 4, MPn energies ϵ are given in % with regard to the corresponding FCI values. For class A systems, the correlation energy increases monotonically from 73 (MP2) to 87 (MP3), 91 (MP4), 93 (MP5), and finally 95% (MP6) obviously approaching the FCI limit rather slowly but asymptotically. For class B systems, the spectrum of MPn energies based on the pool of examples investigated in this work is totally different: The MP2 energy already covers 95% of the FCI correlation energy, which could mean that pair correlation is much more important for class B systems than class A systems or that MP2 exaggerates pair correlation by a considerable amount. Most likely both factors are responsible for the large MP2 correlation energy in the case of class B systems. At MP3 the correlation energy is 0.1% smaller (for class A, 14% larger) than the MP2 correlation energy which suggests that the MP3 contribution covers beside stabilizing (negative) also large destabilizing (positive) pair correlation contributions thus correcting partially the exaggeration of pair correlation effects at MP2. MP4 correlation effects lead to another 5% increase of the total correlation energy, which is larger than the corresponding increase calculated for class A systems (4%, Figure 4). Again, one can speculate that S, T, and Q correlation corrections newly added at MP4 are more important for class B systems than for class A systems. Alternatively, these effects (as well as pair correlation effects) may be overestimated at MP4. The latter effect seems to be corrected by a relatively large positive MP5 correlation contribution decreasing the correlation energy by almost 2% at the MP5 level. MP6 correlation contributions increase the absolute value of the correlation energy to 100.6% thus slightly overshooting the FCI correlation energy. This suggests that at MP6 certain correlation effects are still exaggerated which is confirmed by the fact that for class B MP6 correlation energies are on the average 6% larger than for class A (4.7% at MP5, Figure 4).

We conclude that for class A systems the MPn series possesses normal convergence behavior. Each higher level of MPn theory represents a better approximation to the correct correlation energy with the MP6 energy presenting the best approximation at the moment feasible when using standard MPn procedures. For class B systems, the MPn series initially oscillates which leads to an exaggeration of calculated correlation energies at even orders. It is much more difficult to predict the FCI correlation energy for class B than for class A systems. However, it could be that if the initial oscillations in class B are dampened out the MPn series converges faster than for class A systems. In any case, reasonable predictions of FCI correlation energies should be based for both classes on MP6 energies.[14]
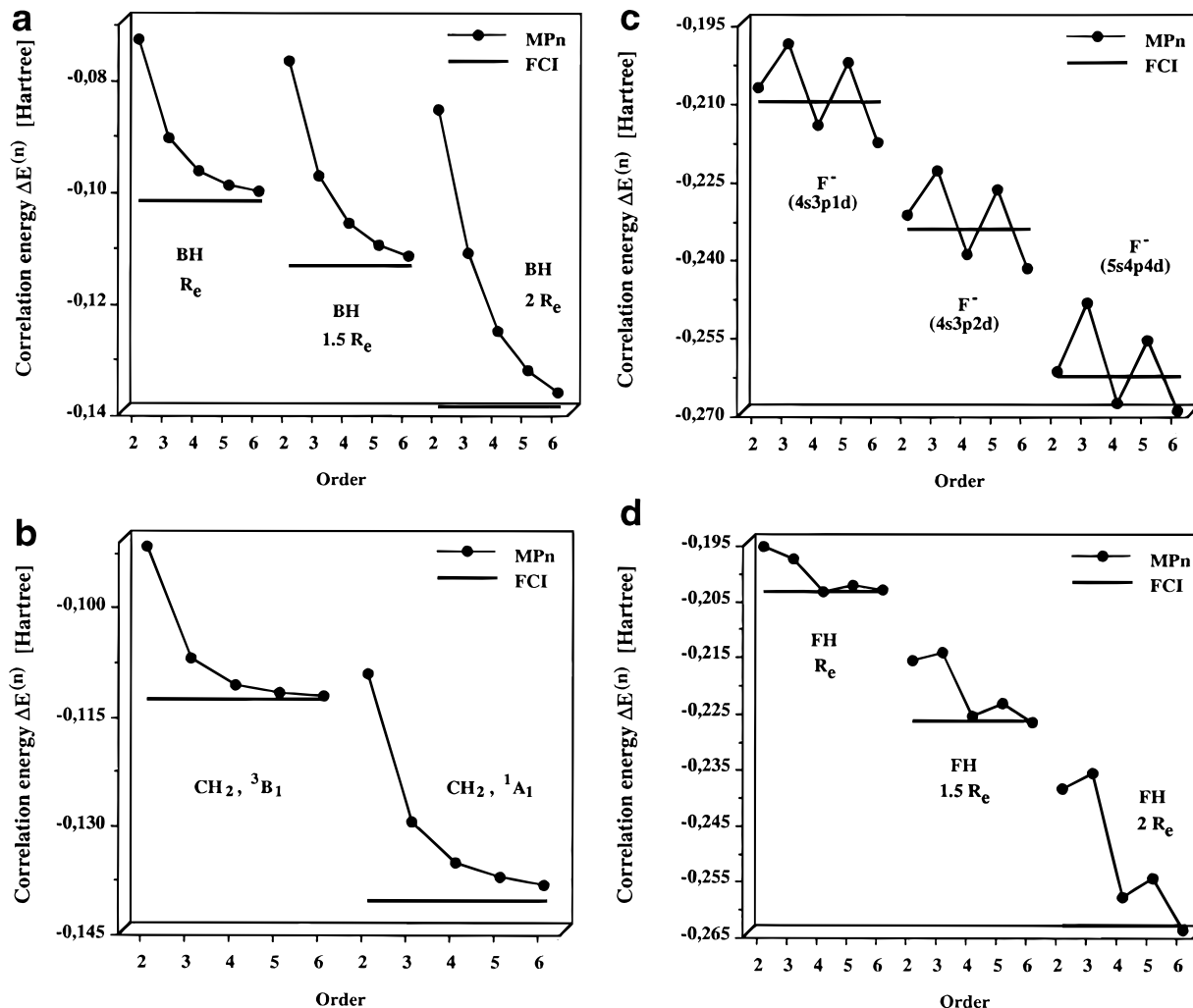
Figure 3. Graphical representation of the MPn correlation energy $\Delta E^{(n)}$ (in hartree) of (a) BH, $^1\Sigma^+$ at the equilibrium geometry R_e and the two stretched geometries $1.5R_e$ and $2.0R_e$; (b) CH$_2$, $^3B_1$, and CH$_2$, $^1A_1$; (c) F$^-$, ^{1}S obtained with three different basis sets of increasing size; (d) FH, $^1\Sigma^+$ at the equilibrium geometry R_e and the two stretched geometries $1.5R_e$ and $2.0R_e$ as a function of the order n of perturbation theory applied. In each case, MPn values are compared with the full CI (FCI) energy obtained with the same basis set at the same geometry (compare with refs 20−24).
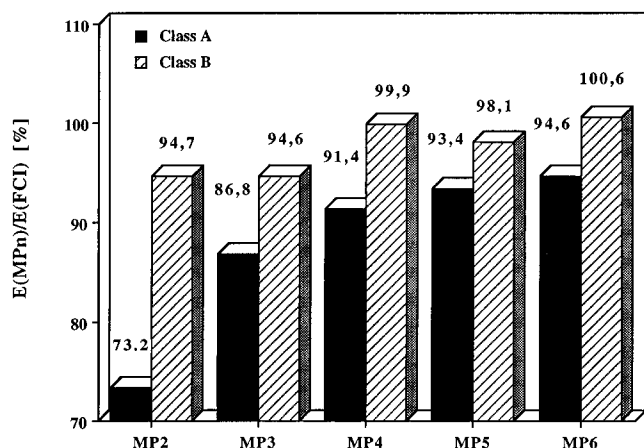

Figure 4. Fractions of total correlation energies ΔE(FCI) covered by a given MPn correlation energy $\Delta E^{(n)}$ given in % and averaged over all examples investigated within a class.

A reason for the different convergence behavior of class A and class B systems can be found when analyzing the different contributions to the MPn correlation energy. Therefore, we evaluated correlation energy contributions $E^{(n)}$(SDQ) and $E^{(n)}$-(T) at MP4, MP5, and MP6 for the pool of the 29 test systems with available FCI energies. In Figure 5, calculated energies are shown in form of bar diagrams (SDQ, black bars; T, hatched

bars) for two typical class A systems (BH, R_e, $1.5R_e$, $2R_e$, CH$_2$, $^3B_1$, $^1A_1$) and two typical class B systems (F$^-$ for three different basis sets; FH, R_e, $1.5R_e$, $2R_e$), respectively. The corresponding SDQ,T diagrams obtained by appropriate scaling according to eq 32 and averaging over all members of a given class are shown in Figure 6.

Inspection of the diagrams in Figures 5 and 6 reveals a number of interesting trends: For class A systems, $E^{(n)}$(SDQ) and $E^{(n)}$(T) correlation energies ($n = 4-6$) are always negative. Their absolute magnitude decreases exponentially with increasing order n thus guaranteeing a monotonic decrease of correlation energies $E^{(n)}$ and, by this, normal convergence of the MPn series. The absolute value of $E^{(n)}$(SDQ) is always significantly larger than the corresponding $E^{(n)}$(T) value where the ratio $|E^{(n)}$-(SDQ)$|$:$|E^{(n)}$(T)$|$ becomes even larger for stretched geometries, i.e. with increasing multireference character of the system in question. Figure 6 reveals that for class A systems the ratio between $E^{(n)}$(SDQ) and $E^{(n)}$(T) correlation contributions is approximately 3 to 1 (MP4, 2.5; MP5, 3.5; MP6, 3.0) at all orders investigated. Since the number of T contributions to the total correlation energy increases with n (MP4, 25%; MP5, 50%; MP6, 60%) while their coupling pattern to other correlation effects becomes more and more complicated, individual three-electron correlation effects seem to become less important. It seems that the large number of T correlation effects keeps the

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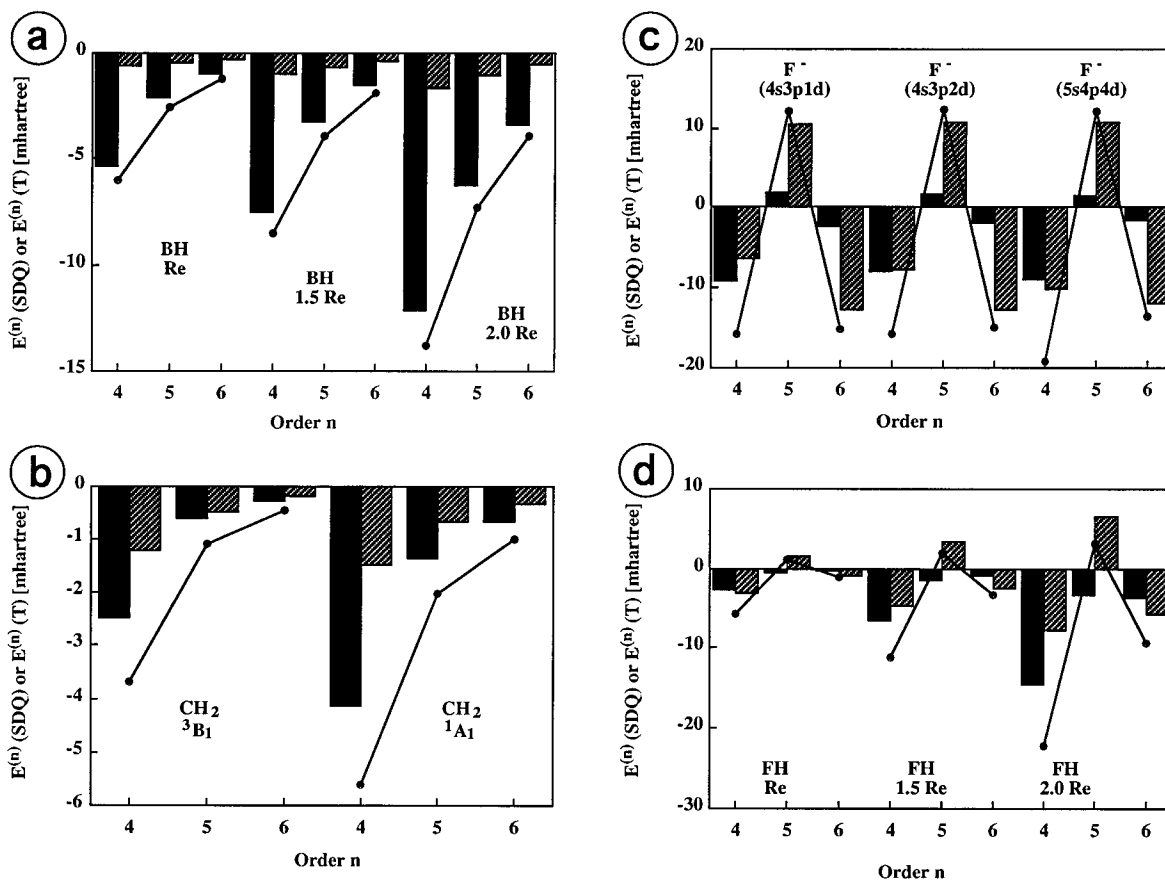
Figure 5. Energy contributions from SDQ and T space for (a) BH, $^1\Sigma^+$ at the equilibrium geometry R_e and the two stretched geometries $1.5R_e$ and $2.0R_e$; (b) CH$_2$, $^3B_1$, and CH$_2$, $^1A_1$; (c) F$^-$, ^{1}S obtained with three different basis sets of increasing size; (d) FH, $^1\Sigma^+$ at the equilibrium geometry R_e and the two stretched geometries $1.5R_e$ and $2.0R_e$ as a function of the order n of perturbation theory applied. Solid bars: $E^{(n)}$(SDQ). Hatched bars: $E^{(n)}$(T). Lines: $E^{(n)}$(SDQ) + $E^{(n)}$(T).

ratio between $E^{(n)}$(SDQ) and $E^{(n)}$(T) correlation contributions at about the same value. This ratio and the exponential decrease of the SDQ part of the correlation energy with order n guarantee the monotonic convergence of the MPn series for class A systems.

Class B systems differ considerably from class A systems with regard to both sign and magnitude of the T contributions to the correlation energy $E^{(n)}$. Contrary to class A systems, the absolute value of the T contribution at MP4 (not always), MP5, and MP6 is larger than the corresponding SDQ contribution and, in addition, the T part is positive at fifth-order. Some of the $E^{(5)}$(SDQ) energies can also be positive (see, e.g. F$^-$, Figure 5b), however on the average the SDQ contributions are negative and decrease in magnitude with increasing order (see Figure 6). As a consequence, the ratio between $E^{(n)}$(T) and $E^{(n)}$(SDQ) correlation contributions increases from 1.2 (MP4) to 2.4 (MP5) and 3.7 (MP6), which is much stronger than the increase in the number of T correlation terms (1:2:2.4). Hence, oscillations in the T correlation energies dominate the convergence behavior of the MPn series and lead to the initial oscillations of the MPn correlation energies typical of class B systems.

One could speculate that the initial oscillations found for class B systems have to do with multireference effects that cannot be covered by the lower MPn methods. To test this we investigated various stretched geometries of simple AH$_n$ molecules such as BH, NH$_2$, FH, or H$_2$O, where the first two examples belong to class A and the last two class B. Results of the analysis of their correlation energy contributions are summarized in Figure 7. They reveal that despite of increasing multireference character when going from the equilibrium to a stretched geometry, convergence behavior of the MPn series

does not change. The SDQ,T diagrams possess the same pattern as observed for the equilibrium geometries. However, there is a significant increase in the importance of pair correlation effects with increasing multireference character. For class A, this leads to increasing dominance of the SDQ part over the T part and for class B systems it reduces somewhat the dominance of the T part. For example, for class B the SDQ part at MP4 becomes larger in magnitude than the T part with increasing multireference character. This is in line with the observation that multireference systems are well described by MRD-CI calculations. We conclude that initial oscillations observed for class B systems are not caused by multireference character of the system in question. Multireference character may lead to an enhancement of these oscillations provided these oscillations are already triggered by peculiarities in the electronic structure of the system in question.

The data presented in Figures 5−7 suggest that the convergence behavior of the MPn series depends on magnitude and sign of the T contributions.

(1) A relatively large ratio $|E^{(n)}$(SDQ)$|$:$|E^{(n)}$(T)$|$, i.e. a relatively small importance of T contributions typical of class A systems seems to guarantee monotonic convergence of the MPn series provided higher terms resulting from P, H, etc., excitations are also small and do not play a significant role.

(2) A relatively small ratio $|E^{(n)}$(SDQ)$|$:$|E^{(n)}$(T)$|$, i.e. a relatively large importance of T contributions, combined with an alternation of the sign of $E^{(n)}$(T) with n typical of class B systems, seems to lead to initial oscillation in the MPn series.
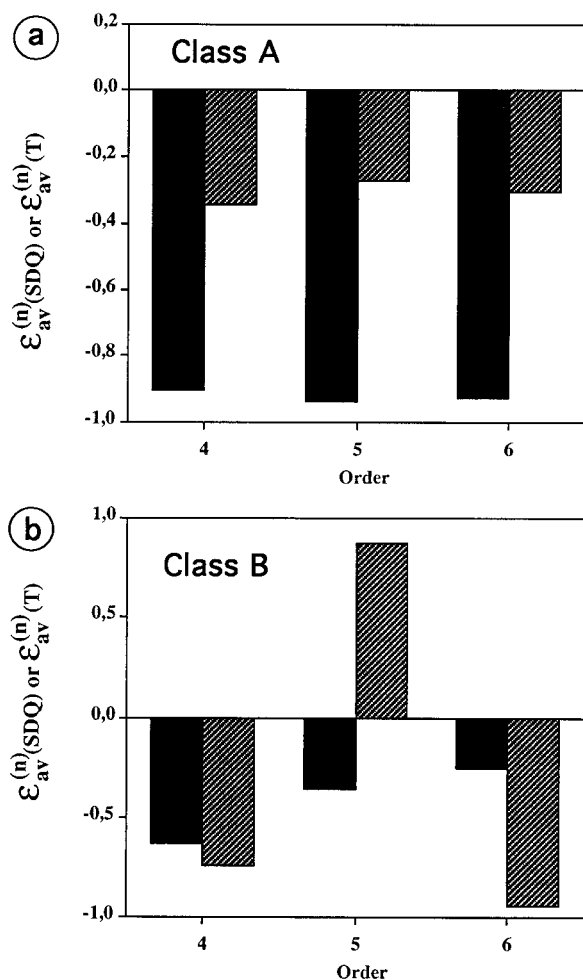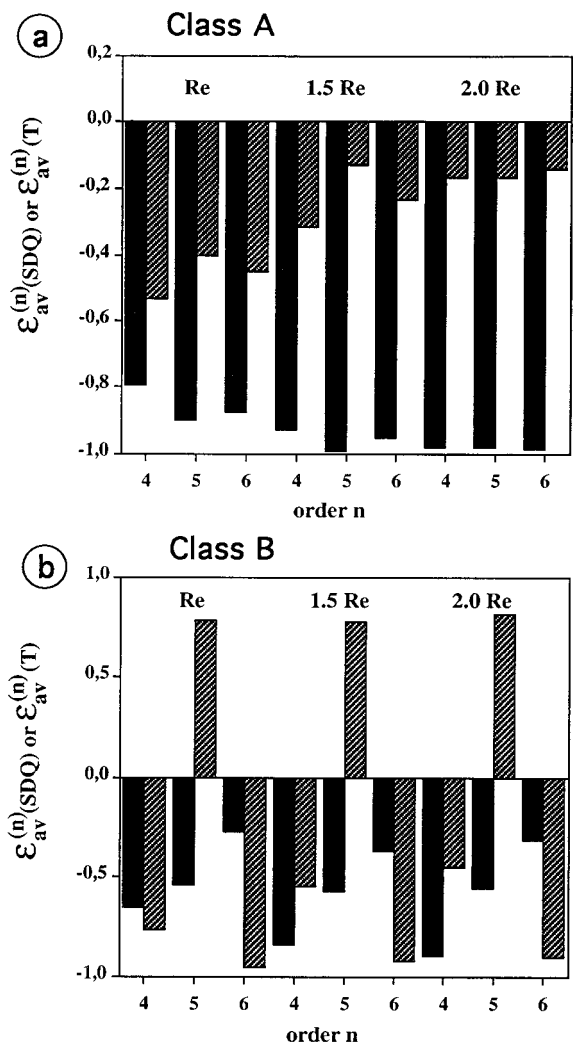
Figure 6. Energy contributions $\epsilon^{(n)}$(SDQ) and $\epsilon^{(n)}$(T) for (a) class A and (b) class B. Solid bars: $\epsilon_{av}^{(n)}$(SDQ). Hatched bars: $\epsilon_{av}^{(n)}$(T).

5. Analysis of the MP*n* Spectra

For further analysis of the SDQ and T contributions to the correlation energy $E^{(n)}$, we discuss in the following $E_{A...}^{(n)}$ spectra for $n = 4$, 5, and 6, which are shown in Figures 8 and 9.

MP4 Spectrum. Both for class A and class B systems, S, D, and T correlation corrections are always negative (stabilizing) while Q correlation effects are always positive (destabilizing). The two classes differ with regard to the importance of pair correlation versus three-electron correlation effects. For class A, the former are significantly more important than either T, Q, or S correlation effects while for class B systems pair correlations are of reduced importance. In the latter case, three-electron correlation effects as well as orbital relaxation effects are significantly larger than for class A systems. Actually, T effects represent the largest contribution to the MP4 correlation energy. Absolutely seen they are even larger than the sum of S, D, and Q contributions, which is a result of the fact that the Q part at MP4 is always positive and in this way cancels a part of the negative D contribution. Obviously, the Q correlation effects correct for an exaggeration of pair correlation effects typical of MP2.

MP5 Spectrum. For all systems investigated, the DD, SS, and TT terms are negative while ST, TQ, and DQ are positive. The three remaining MP5 terms (DT, ST, QQ) have different signs for class A and B. There are some significant differences between class A and B systems as far as individual contributions

Figure 7. Energy contributions $\epsilon^{(n)}$(SDQ) and $\epsilon^{(n)}$(T) for stretched geometries of (a) class A and (b) class B systems. Solid bars: $\epsilon_{av}^{(n)}$(SDQ). Hatched bars: $\epsilon_{av}^{(n)}$(T).

are concerned. The MP5 correlation energy for a class A system is clearly dominanted by DD (pair−pair) correlation effects. The second largest term is the (positive) DQ term, which obviously corrects for an overestimation of pair correlation effects. All other terms are relatively small with a slight dominance of the negative terms. Considering both negative and positive MP5 terms, the former dominate for class A and lead to a negative MP5 correlation contribution.

For class B systems, five of the nine MP5 terms are positive (TQ, ST, DT, SD, DQ) and, by this, lead to a positive MP5 correlation energy. None of the terms (absolutely seen) is as large as the DD term in class A. The largest term is the TQ term, but ST, DD, SD, QQ, and DQ contributions also possess considerable magnitude. Hence, both three-electron correlation, pair correlation as well as orbital relaxation influence the magnitude of the MP5 correlation energy in the case of a class B system while for class A only pair correlations seem to be important. The T part gets its positive sign from positive TQ and ST contributions while the negative SDQ part is dominated by negative DD and QQ contributions significantly reduced by a positive DQ contribution. There are three terms, which change sign when going from a class A to a class B example, namely DT (− to +), SD (− to +), and QQ term (+ to −). It seems that at the MP5 level the correlation energy of class B systems is predominantly corrected with regard to an exaggeration of correlation effects that occurred at a lower MP*n* level.

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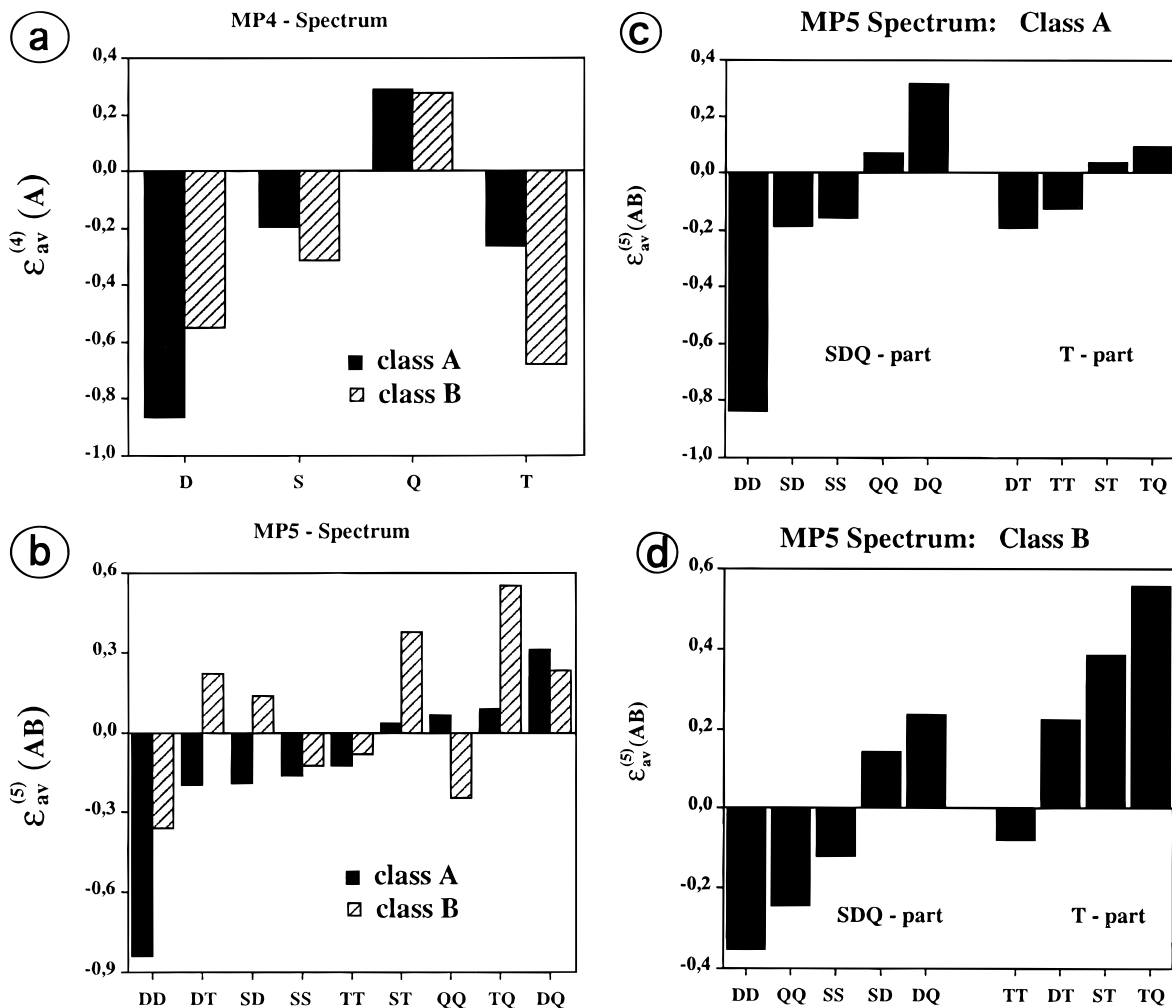
Figure 8. (a) MP4 spectrum, (b) MP5 spectrum for classes A and B, (c) MP5 spectrum for class A, and (d) MP5 spectrum for class B. For c and d, the MP5 spectrum has been separated into SDQ and T contributions and energy terms $\epsilon_{AB}^{(5)}$ are ordered according to their magnitude.

MP6 Spectrum. The spectra of the MP6 correlation energy contributions shown in Figure 9 for class A (Figure 9a) and class B systems (Figure 9b) possesses a similar pattern as those obtained for the MP5 correlation energy contributions (Figure 8b,c,d). For example, in class A the pair correlation term DDD clearly dominates the MP6 correlation energy, only reduced by the positive DDQ and (DQD + DQQ + QQQ) terms. All other terms are relatively small, which holds in particular for the T and the PH terms. Since about half of the 15 T terms that were explicitly evaluated in this work are positive, the T contribution to MP6 becomes small being about one-third of the SDQ contribution similarly as found in the case of MP4 and MP5.

For class B systems, the DDD term still represents the largest (negative) contribution to the MP6 correlation energy. However, there are two T terms (SDT and TDT) of similar magnitude. Six out of 10 SDQ terms are negative while 13 out of 15 T terms are negative. Just SST and TDQ represent positive contributions. This is the reason why the T part for class B systems is negative and about 4 times as large as the SDQ part. The PH part represents a relatively small positive correction as is also found in the case of class A.

Approximate MP*n* Methods. Before we discuss the question how convergence behavior depends on electronic structure, it is useful to consider some of the approximate MP*n* methods presently in use. For example, MP4(SDQ) used at fourth order to reduce calculational cost from $O(M^7)$ to $O(M^6)$ is certainly a useful method when calculating relative energies of class A systems since in this case the importance of the T contributions

is relatively small. For class B systems, the inclusion of the T part seems to be advisable in view of its magnitude. One could speculate that it keeps its relative magnitude for all samples of class B and cancellation of errors leads to reasonable MP4-(SDQ) energy differences. However, the spectrum given in Figure 8 is just an average over a limited number of examples which does not exclude that the ratio $|E^{(4)}(T)|:|E^{(4)}(SDQ)|$ changes considerably within class B (see, e.g., Figure 5b).

The inclusion of the T part at MP4 will definitely be important if one wants to compare the energies of class A and class B systems. As is obvious from Figure 8a, the MP4(SDQ) approximation underestimates the stability of class B systems relative to that of class A systems due to the neglect of T contributions. In summary, one can expect that the reliability of MP4(SDQ) energy differences is more or less limited to cases in which class A systems are compared.

For MP5, Kucharski, Noga, and Bartlett[37] suggested an approximate method that by neglecting the TT term requires an $O(M^7)$ rather than an $O(M^8)$ computational cost dependence. From Figure 8b–d, it can be seen that this should be an useful approximation for both class A and class B systems since the TT term represents in both cases a relatively small fraction of the MP5 correlation energy. On the other hand, the usefulness of a MP5(SDQ) approximation covering the DD, SD, DQ, and QQ terms is limited in the same way as the corresponding MP4 approximation to class A systems.

Recently, we have suggested two approximated MP6 methods [MP6(M8) and MP6(M7)], the computational cost of which
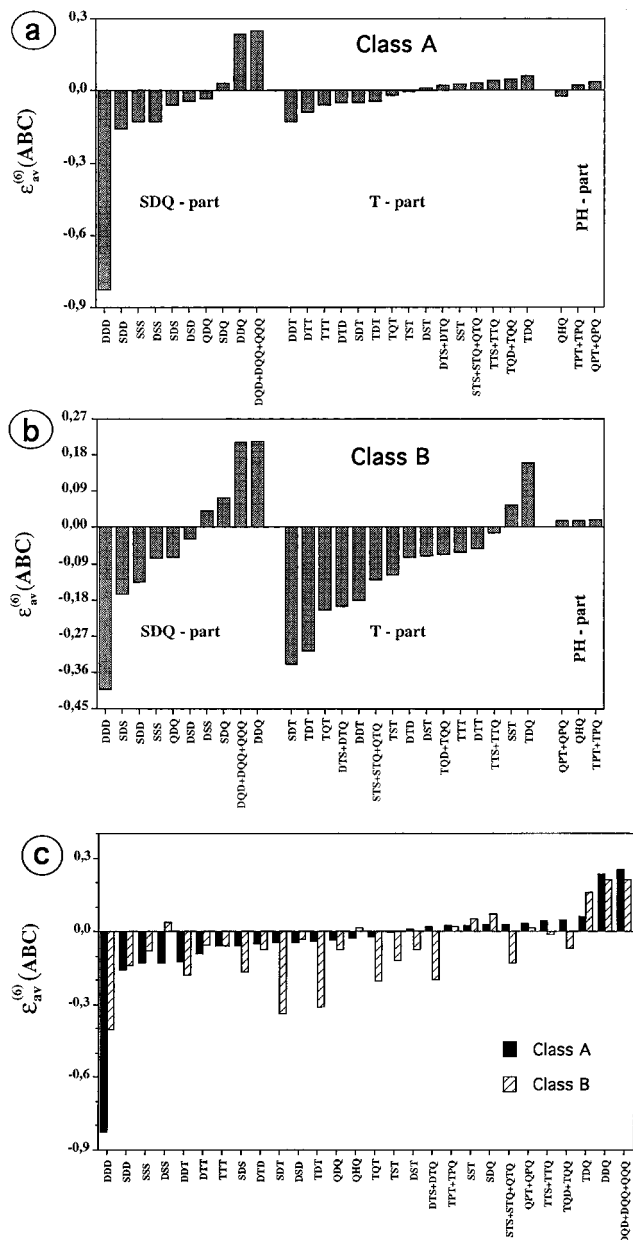
Figure 9. MP6 spectrum for (a) class A, (b) class B, and (c) classes A and B. For a and b, the MP6 spectrum has been separated into SDQ, T, and PH contributions and energy terms $\epsilon_{\mathrm{ABC}}^{(6)}$ are ordered according to their magnitude.

scale with $O(M^8)$ and $O(M^7)$.[13] MP6(M8) and MP6(M7) are obtained by dropping all M^9 terms in the first case and, additionally, all M^8 terms in the second case (compare with Figure 2). The corresponding terms are indicated in Figure 10a,b by hatched (M^9 terms) or white bars (M^8 terms). In Figure10c,d, sums of all M^9 and M^8 contributions are compared with the total MP6 correlation energy and its SDQ, T and PH parts. Inspection of Figure 10a,b suggests that only for class A systems MP6(M8) and MP6(M7) are reasonable approximations because in this case all M^9 and M^8 contributions are rather small. For class B systems, the TQT term is rather large and, therefore, should not be neglected in the T part of MP6. However, Figure 10c,d reveal that for both class A and class B systems M^9 and M^8 terms represent a relative small fraction (~12%) of the total MP6 correlation energy since positive and negative terms (see Figure 10) cancel largely. Hence, MP6-(M8) and MP6(M7) present reasonable and economically attractive alternatives to the costly MP6 method.

One could also consider MP6(SDQ) or MP6(SDTQ) as interesting approximations to MP6; however, these methods do not lead to any cost reduction since they possess an $O(M^9)$ cost dependence as has been pointed out previously.[13]

6. Convergence Behavior and Electronic Structure

If we consider all results and observations summarized in Figures 3−10 as well as the electronic structures and bonding patterns of class A and class B systems, then we come to the conclusion that systems of the two classes basically differ with regard to their electron distribution. Class A covers those molecules, the bond and lone electron pairs of which are well separated and distributed over the whole space of the molecule. For example, in BH, $^1\Sigma^+$, core electron pair, bonding electron pair, and lone pair are localized in different parts of the molecule. The same is true in the case of NH_2, CH_3, or CH_2 as indicated in Figure 11. Because the electron pairs of class A systems are well-separated, the importance of three-electron correlations and couplings between the correlation modes of the various electron pairs is moderate and the molecular correlation energy is dominated by pair correlation effects.

For class B systems, a clustering of electron pairs in certain regions of an atom or molecule is observed (Figure 11). For example, for F, F^- and 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. For H_2O and FH, there are two or even three electron pairs that cluster in the lone pair region. Similarly, molecules with multiple bonds should belong to class B since more than one electron pair can be found in the bonding region. We tested this for CO, HCCH, and O_3 and found our prediction to be confirmed in all three cases.

If electrons cluster in regions of atomic or molecular space, three-electron correlations become important since they provide a simple mechanism 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. In view of the basically different electron structures of class A and class B systems, one can predict that coupling effects are much more important for the latter than the former systems. Couplings will lead at the MP3 and the MP5 level to significant corrections. We have found that all SDQ couplings taken together at the MP5 level can actually lead to positive contributions for class B systems. Since positive contributions in the T part comprising ST, DT, TT, and TQ terms make this always positive, positive MP5 correlation contributions and accordingly oscillatory convergence behavior for class B systems result.

In view of the fact that MP6 covers both connected and disconnected T contributions, one could ask whether three-electron correlation effects (connected T contributions associated with $\hat{T}_3$) or orbital relaxation plus pair correlation effects (disconnected T contributions associated with $\hat{T}_1\hat{T}_2$) are more important for class B molecules. Such a question can easily be answered by inspection of the MP6 spectra shown in Figure 9. On the average, disconnected T contributions represented by the energy terms DTS + DTQ, STS + STQ + QTQ, TTS + TTQ in Figure 9 cover about 17% of the total T energy in case of class B systems while the corresponding value for class A systems is 13%. Obviously, orbital relaxation plus pair correlation effects are of limited but similar importance for both class A and class B systems. The dominant role of T correlation contributions in the case of class B systems clearly results from three-electron correlation effects (more than 80% of the T contributions are connected T contributions) in the way described above.

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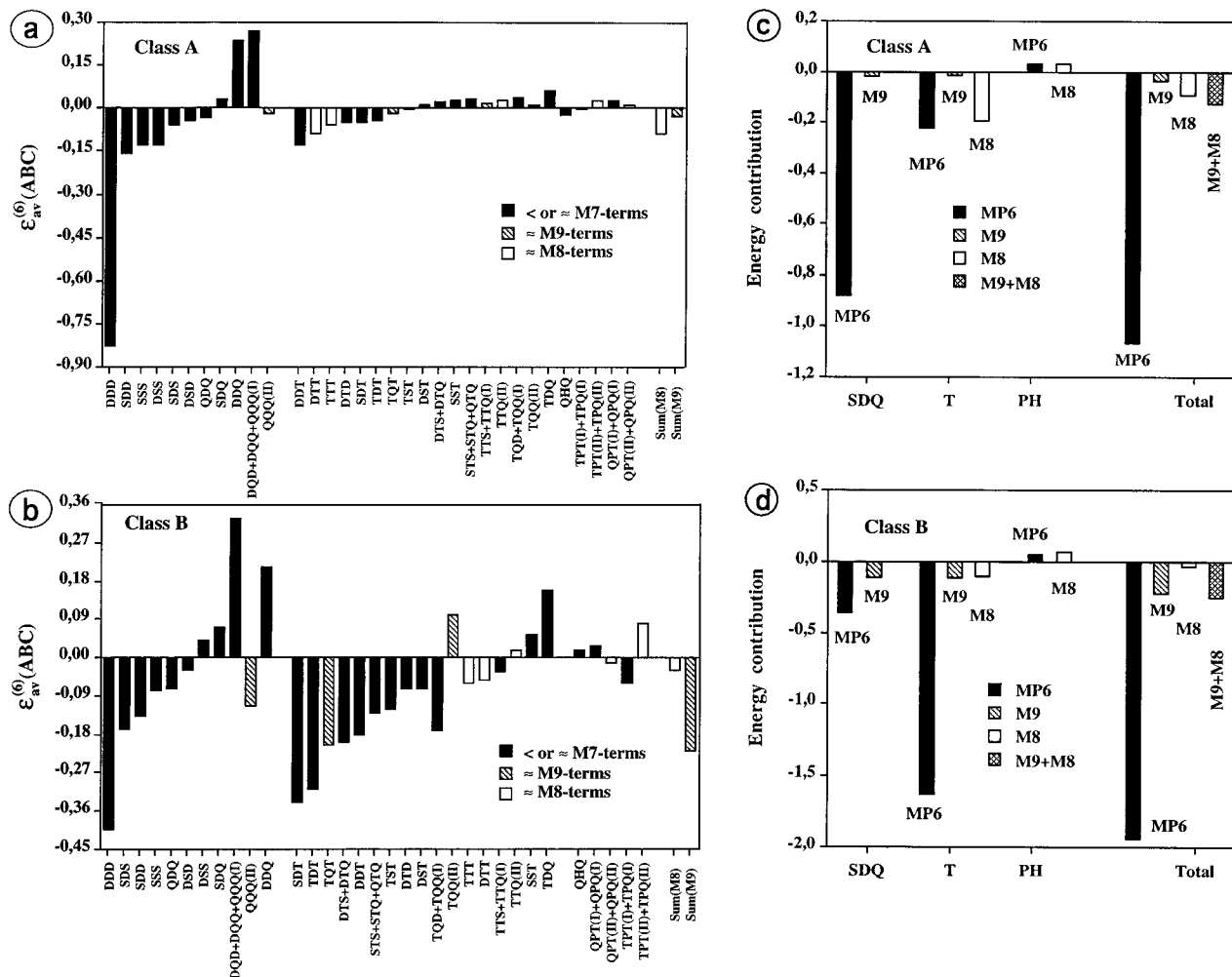
Figure 10. MP6 spectrum for (a) class A and (b) class B indicating all terms with $O(M^9)$ and $O(M^8)$ dependence. In c and d the sums of $O(M^8)$ and $O(M^9)$ terms are compared with SDQ, T, PH and total MP6 correlation energies.

It is interesting to note that the connected Q contribution associated with $\hat{T}_4$ and represented by the term TQT plays almost no role for class A systems (Figure 9a) in line with the general understanding that four-electron correlation effects are normally rather small. For class B systems, the energy contribution TQT is on the average the third most important T contribution comparable in magnitude with the DDQ or DQD + DQQ + QQQ contributions (Figure 9b). However, while the latter terms are positive, TQT is negative indicating that a new correlation effect is added to the MP6 energy. Obviously, four-electron correlation effects become important for systems with a clustering of electrons in a confined space such as class B systems. Four-electron and three-electron correlation make it possible that, e.g., the electrons of multiple bonds can predominantly be located in the bond region despite unfavorable Coulombic interactions.

By inspection of the pair structure of an atom or molecule it is easy to predict whether the system in question belongs to class A or class B and whether it possesses monotonic or erratic convergence behavior. Of course, there are border cases between the two classes for which predictions may be difficult. An example is H_2O in its equilibrium geometry, for which $E^{(n)}$ seems not to oscillate although convergence is not monotonic.[14] However, investigation of its SDQ,T spectrum or the MPn values for stretched geometries of H_2O clearly indicates strong initial oscillations typical of a class B system.

Comparing class A and class B systems and the convergence behavior of the MPn series for these systems, it is appropriate

to consider class B system as the normal case which reveals the typical deficiencies of the MP perturbation theory description. MPn 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 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. This means that there will also be more systems with initial oscillations in the MPn series. Accordingly, class A systems should be considered as the exceptions, for which as a result of a fortuitous cancellation or dampening of the typical MPn oscillations a monotonic convergence is obtained.

## 7. Improvement of the Convergence Behavior of the MPn Series

In recent work, we investigated various approaches to improve the convergence behavior of the MPn series.[14] We found that with the help of MP6 correlation energies useful estimates of FCI correlation energies are obtained by applying either Feenberg scaling or Padé approximants.[14] We could demonstrate that second-order Feenberg scaling (FE2) leads to the best estimates that differ from FCI correlation energies on the average by just 0.15 mhartree for atoms and molecules in their equilibrium geometry. First-order Feenberg scaling (FE1) or
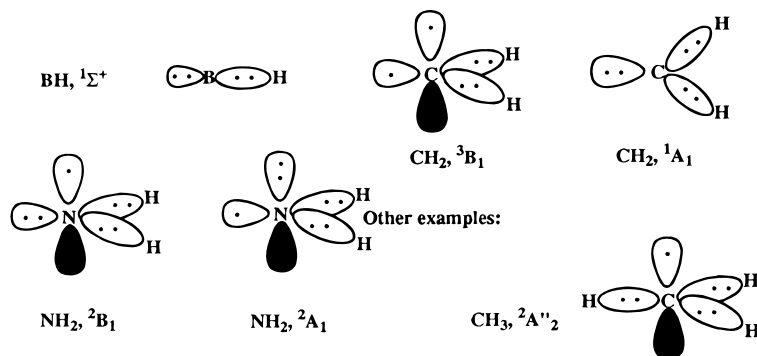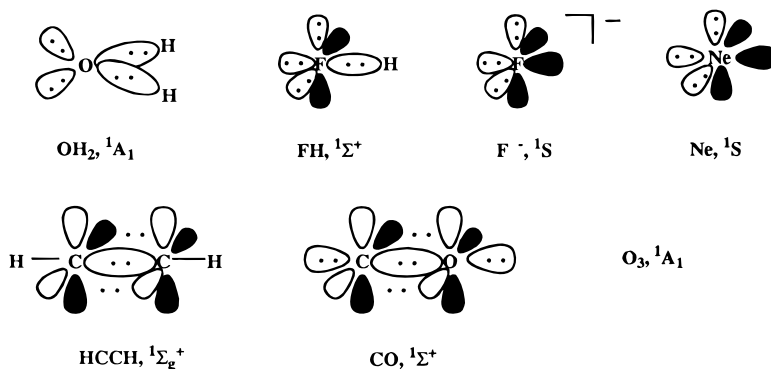
Figure 11. Electronic structures of class A and class B systems.
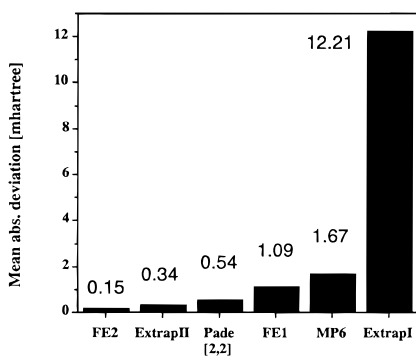
Figure 12. Comparison of the mean absolute deviation of estimated from true FCI correlation energies when approximating FCI values by first-order Feenberg scaling (FE1), second-order Feenberg scaling (FE2), [2,2] Padé approximants, MP6 correlation energies or MP6 based extrapolation formulas. ExtrapI: One extrapolation formula (eq 34) is used that does not distinguish between class A and class B systems. ExtrapII: Two extrapolation formulas (eqs 35 and 36) are used that reflect the different convergence behavior of class A and class B systems. Atoms and molecules in their equilibrium geometry are used.

[2,2] Padé approximants are also useful but lead to deviations of 1.09 and 0.54 mhartree (see Figure 12).

Although the calculational work to get FE or Padé estimates of the FCI correlation energy is negligible, it is even simpler to

apply extrapolation formulas. At a time when routine calculations of MPn correlation energies were only possible for $n \leq 4$, Pople, Frisch, Luke, and Binkley (PFLB)[38] derived an extrapolation formula for estimating the exact correlation energy ΔE:[38]

$$\Delta E(\text{PFLB,MP4}) = \frac{E_{\text{MP}}^{(2)} + E_{\text{MP}}^{(3)}}{1 - (E_{\text{MP}}^{(4)}/E_{\text{MP}}^{(2)})} \tag{33}$$

Equation 33 is correct up to fourth order and is based on the assumption that even- and odd-order terms of the MPn series form a geometrically progressive energy series where the ratio of successive even-order terms is similar to the ratio of successive odd-order terms.

Extension of the PFLB extrapolation equation to sixth-order MP perturbation theory leads to

$$\Delta E(\text{extrapI,MP6}) = E_{\text{MP}}^{(2)} + E_{\text{MP}}^{(3)} + \frac{E_{\text{MP}}^{(4)} + E_{\text{MP}}^{(5)}}{1 - (E_{\text{MP}}^{(6)}/E_{\text{MP}}^{(4)})} \tag{34}$$

where formula 34 is correct up to sixth order and also based on the assumption of monotonic convergence of the MPn series, which of course is not fulfilled for case B systems. This is

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reflected by an unreasonably large mean absolute deviation of 12.21 mhartrees from exact FCI correlation energies, which is seven times larger than that obtained for MP6 correlation energies (see Figure 12). Analysis of the failure of eq 34 reveals that this is due to the problem of covering with one formula the basically different convergence behavior of class A and class B systems.

As we have shown above it is possible to clarify whether a given electronic system belongs to class A or class B. Accordingly, it is also possible to apply for the two classes two different extrapolation formulas which reflect the different convergence properties of the two classes. For class A, we suggest eq 35:

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

$$= \sum_{n=2}^{6} E_{MP}^{(n)} + E_{MP}^{(5)}(E_{MP}^{(6)}/E_{MP}^{(5)})^2 + ... \quad (35)$$

where the original PFLB formula is retained in view of the monotonic convergence found for class A systems; however, the ratio of subsequent correlation contributions is given by the best MPn values available at the moment, namely $E_{MP}^{(5)}$ and $E_{MP}^{(6)}$.

As was discussed above, for class B systems E(MP6) values are mostly more negative than FCI energies, which indicates that higher order correlation effects are exaggerated. Therefore, their contributions to $E^{(n)}$ have to be scaled down, which is done in eq 36 in three different ways:

$$\Delta E^{(B)}(\text{extrapII,MP6}) = E_{MP}^{(2)} + E_{MP}^{(3)} + (E_{MP}^{(4)} + E_{MP}^{(5)}) \exp(E_{MP}^{(6)}/E_{MP}^{(4)}) \quad (36)$$

$$= \sum_{n=2}^{6} E_{MP}^{(n)} + E_{MP}^{(5)}(E_{MP}^{(6)}/E_{MP}^{(4)}) +$$
$$1/2! (E_{MP}^{(4)} + E_{MP}^{(5)})(E_{MP}^{(6)}/E_{MP}^{(4)})^2 +$$
$$1/3! (E_{MP}^{(4)} + E_{MP}^{(5)})(E_{MP}^{(6)}/E_{MP}^{(4)})^3 + ...$$

Both $1/(1 - x)$ (eq 35) and $\exp x$ (eq 36) lead to similar series, however, in the exponential series higher powers k of x are scaled down by prefactors $1/k!$ thus effectively reducing higher correction terms. Secondly, all correction terms in eq 35 are negative ($E_{MP}^{(5)} < 0$ and $E_{MP}^{(6)}/E_{MP}^{(5)} > 0$) while this is no longer true for the first correction term of eq 36. Since both $E_{MP}^{(5)}$ and $E_{MP}^{(6)}/E_{MP}^{(4)} > 0$, the first correction is positive thus leading to a substantial reduction in the magnitude of the correlation energy. All other correction terms are negative because ($E_{MP}^{(4)} + E_{MP}^{(5)}) < 0$; however, corrections are smaller than in the case of A because $E_{MP}^{(6)}/E_{MP}^{(4)} < E_{MP}^{(6)}/E_{MP}^{(5)}$). In summary, correction terms are significantly reduced for class B energies because MP6 overshoots the FCI value for these systems.

Application of eqs 35 and 36 leads to infinite-order correlation energies superior to energies predicted by either the PFLB eq 33 or the MP6 extrapolation eq 34. This is reflected by a mean absolute deviation of 0.34 mhartree for atoms and molecules at their equilibrium geometries.

We conclude that by the use of MP6 correlation energies and an improvement of the original PFLB extrapolation formula based on a clear distinction of class A and class B systems, errors in predicted infinite order correlation energies can be reduced by a factor of 5 with regard to predictions based on MP6 energies alone and by a factor of about 36 with regard to

predictions based on just one extrapolation formula (eq 34) for both class A and class B systems. FCI values derived from eqs 35 and 36 are comparable with those obtained by second-order Feenberg scaling (see Figure 12) and, therefore, guarantee energy differences of FCI quality.

8. Conclusions

This work explains for the first time the convergence behavior of the MPn series. This explanation is based on a detailed analysis of MP4, MP5, and MP6 correlation energies of 33 examples for which FCI or at least CCSDT correlation energies are available. We have appropriately scaled correlation energies and correlation energy contributions to better compare them for different electronic systems and to derive averaged values which facilitate the discussion of individual correlation energies. In this way, we have obtained "MPn spectra", which provide a detailed insight into the decomposition of MPn correlation energies into S, D, T, Q, P, and H contributions for $n \le 6$. The analysis of MPn correlation energies and correlation energy spectra leads to the following conclusions.

(1) For a group of atoms and molecules (class A), the MPn series converges monotonically while for another group (class B) convergence is erratic with typical initial oscillations.

(2) Oscillations are caused by strong changes in the magnitude of calculated T contributions when increasing n from 4 to 5 and 6. For class A systems, the T part is not important. The correlation energy $E^{(n)}$ is dominated by the SDQ part, which decreases monotonically with increasing n. For class B systems, the T part dominates the correlation energy. It oscillates between negative and positive values with increasing order n thus causing similar oscillations of the total correlation energy.

(3) The analysis reveals that monotonic convergence is parallel to a dominance of pair correlation effects (D at MP4, DD at MP5, DDD at MP6) and a relatively slow convergence rate (at MP6 only 96% of the FCI correlation energy is covered). For class B systems, both pair correlation effects and three-electron correlation effects are of large importance to describe electron correlation in those regions where electrons cluster. This leads to a significant exaggeration of correlation effects in particular at even orders, which can only be compensated by positive correlation energy corrections at odd orders. Both facts taken together cause the initial oscillations in the MPn series of class B systems.

(4) Class A systems are characterized by electronic structures with well-separated electron pairs while class B systems are characterized by electronic structures with electron clustering in one or more regions. As indicated in Figure 11, one can expect that Li and Be compounds, boranes and carboranes, carbenes, classical carbocations, alkyl radicals, linear alkanes, etc. are typical class A systems, which show monotonic convergence in the MPn series. Typical examples of class B systems with initial oscillations in the MPn series should be atoms with almost or totally filled valence shells such as, e.g., F, F$^-$, Ne, etc., molecules with multiple bonds such as CO, HCCH, etc.; conjugated systems (annulenes, polyenes, etc.); nonclassical carbocations; and hypervalent compounds.

We predict that class B systems represent the majority while class A systems represent a minority, i.e. there exist more systems which possess initial oscillations in the MPn series.

(5) By recognizing that convergence behavior in the MPn series is a direct consequence of the electronic structure of class A and class B systems, it is possible to predict the convergence behavior of a given system and to apply an appropriate extrapolation formula for estimating FCI correlation energies. In this work, we suggest two new extrapolation formulas for

class A and class B systems, which lead to significant better predictions of FCI correlation energies than any previous extrapolation formula (Figure 12).

(6) The analysis of the various MPn spectra reveals the applicability of MPn approximations presently in use. For example, the error in relative energies obtained with MP4(SDQ) should be considerable if class A systems are compared with class B systems. Neglect of the TT term at MP5[37] or all M^9 and M^8 terms at MP6[13] to obtain M^7 methods should lead to reasonable approximations to full MP5 and full MP6, respectively.

The discussion presented above makes it rather clear that the convergence of the MPn series is a direct consequence of the perturbation theory formalism, which may be compared with a bad driving style: The "perturbation engine" is accelerated at even orders n by "fueling" it with new correlation effects (D at MP2, STQ at MP4, PH at MP6, etc.); however, it is slowed down at odd orders by pushing the "coupling brake" (DD coupling at MP3, SDTQ,SDTQ coupling at MP5, etc.). This must lead to initial oscillations in the MPn series which becomes obvious in the way electron correlation is important. Since the latter depends on the number of electrons and a clustering of electrons in certain regions of space, the deficiencies of the perturbation engine become obvious for class B systems (i.e. the majority of electronic systems) while they are reflected for class A systems just by the relatively slow convergence of the MPn series.

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