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Assessment of higher order correlation effects with the help of Møller–Plesset perturbation theory up to sixth order

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For 30 molecules and two atoms, MPn correlation energies up to $n = 6$ are computed and used to analyse higher order correlation effects and the initial convergence behaviour of the MPn series. Particularly useful is the analysis of correlation contributions $E_{XY\ldots}^{(n)}$ $(n = 4,5,6$; $X, Y, \ldots =$ S, D, T, Q denoting single, double, triple, and quadruple excitations) in the form of correlation energy spectra. Two classes of system are distinguished, namely class A systems possessing well separated electron pairs and class B systems which are characterized by electron clustering in certain regions of atomic and molecular space. For class A systems, electron pair correlation effects as described by D, Q, DD, DQ, QQ, DDD, etc., contributions are most important, which are stepwise included at MPn with $n = 2, \ldots, 6$. Class A systems are reasonably described by MPn theory, which is reflected by the fact that convergence of the MPn series is monotonic (but relatively slow) for class A systems. The description of class B systems is difficult since three- and four-electron correlation effects and couplings between two-, three-, and four-electron correlation effects missing for lower order perturbation theory are significant. MPn methods, which do not cover these effects, simulate higher order with lower order correlation effects thus exaggerating the latter, which has to be corrected with increasing n. Consequently, the MPn series oscillates for class B systems at low orders. A possible divergence of the MPn series is mostly a consequence of an unbalanced basis set. For example, diffuse functions added to an unsaturated sp basis lead to an exaggeration of higher order correlation effects, which can cause enhanced oscillations and divergence of the MPn series.

1. Introduction

Research in quantum chemistry has focused in the last decades on how to improve quantum chemical methods in such a way that calculated molecular properties are reliable and accurate. Since many quantum chemical methods start with the Hartree–Fock (HF) wavefunction, an improvement of an HF-based method primarily requires the addition of electron correlation effects. Many-body perturbation theory (MBPT) based on the Møller–Plesset (MP) perturbation operator [1] provides an excellent mechanism for adding stepwise from order to order higher and higher electron correlation effects [2]. For second-order MP perturbation theory (MP2) [3, 4] double (D) excitations are considered, which account for electron pair correlation effects. For third-order MP theory (MP3) [5, 6] couplings between the D excitations lead to a more realistic description of pair correlation effects. For fourth order MP theory (MP4) [7] D excitations are augmented by single (S), triple (T), and quadruple (Q) excitations describing orbital relaxations, three-electron correlation effects, and independent, but simultaneous correlations of two electron pairs (disconnected Q correlation effects). For fifth order MP theory (MP5) [8–10] couplings between S, D, T, and Q excitations lead to a more realistic description of these effects. Connected four-electron correlation effects, disconnected five- and six-electron correlation effects resulting from Q, pentuple (P), and hextuple (H) excitations, respectively, as well as various new coupling effects enter the MPn series for sixth-order MP theory (MP6) [11–13].

With increasing order n the number of individual electron correlation contributions $E_{XY\ldots}^{(n)}$ increases rapidly (table 1) from 4 (MP4) to 14 (MP5), 55 (MP6), etc. where, because of symmetry relationships, only 4 (MP4), 9 (MP5), 36 (MP6), etc. $E_{XY\ldots}^{(n)}$ values have to be calculated. The computational working load is determined by that energy term that arises from the highest excitation (cluster) operator $\hat{T}_i^{(p)}$ (p is the order of the wavefunction; i is the number of electrons excited) involved. So for MP4, the connected T term resulting from $\hat{T}_3^{(2)}$ determines the $O(M^7)$ dependence of MP4 (M

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Table 1. Comparison of MPn methods[a]

MP order n	Number of terms total/unique	Highest order of cluster operator	Highest connected contribution	Corresponding $E_{XY...}$ term	Cost	Highest disconnected contribution	Corresponding $E_{XY...}$ term	Cost
MP2	1/1	$\hat{T}_2^{(1)}$	$\hat{T}_2^{(1)}$		$O(M^5)$			
MP3	1/1	$\hat{T}_2^{(1)}$	$\hat{T}_2^{(1)}$		$O(M^6)$			
MP4	4/4	$\hat{T}_i^{(2)}\, i=1,\ldots,3$	$\hat{T}_3^{(2)}$	E_{T}	$O(M^7)$	$\hat{T}_2^2$	E_Q	$O(M^6)$
MP5	14/9	$T_i^{(2)} i=1,\ldots,3$	$\hat{T}_3^{(2)}$	E_{TT}	$O(M^8)$	$\hat{T}_2^2$	E_{QQ}	$O(M^6)$
MP6	55/36	$\hat{T}_i^{(3)} i=1,\ldots,4$	$\hat{T}_4^{(3)}$	E_{TQT}	$O(M^9)$	$\hat{T}_2^3$	E_{QHQ}	$O(M^6)$
MP7	221/141	$T_i^{(3)} i=1,\ldots,4$	$\hat{T}_4^{(3)}$	E_{TQQT}	$O(M^{10})$	$\hat{T}_2^3$	E_{QHHQ}	$O(M^6)$
MP8	915/583	$\hat{T}_i^{(4)} i=1,\ldots,5$	$\hat{T}_5^{(4)}$	E_{TQPQT}	$O(M^{11})$	$\hat{T}_2^4$	E_{QHOHQ}	$O(M^6)$
MP9	3865/2457	$\hat{T}_i^{(4)} i=1,\ldots,5$	$\hat{T}_5^{(4)}$	E_{TQPPQT}	$O(M^{12})$	$\hat{T}_2^4$	E_{QHOOHQ}	$O(M^6)$
MP10	16605/10553	$\hat{T}_i^{(5)} i=1,\ldots,6$	$\hat{T}_6^{(5)}$	E_{TQPHPQT}	$O(M^{13})$	$\hat{T}_2^5$	$E_{\mathrm{QHOD_{10}OHQ}}$	$O(M^6)$

[a] M is the number of basis functions; $\hat{T}_i^{(p)}$ denotes a pth order, i-particle excitation (cluster) operator. Note that p refers to the order in the wavefunction, while n refers to the order in the energy, and are related according to the Wigner theorem.

is the number of basis functions) while the Q-term $E_Q^{(4)}$ is a disconnected term resulting from the product $\hat{T}_2^{(2)}\hat{T}_2^{(2)}$ and, therefore its calculation scales with $O(M^6)$ rather than $O(M^8)$ as one might assume. Similar considerations apply to MP5 which, because of the TT term (resulting from $\hat{T}_3^{(2)}\hat{V}\hat{T}_3^{(2)}$ where $\hat{V}$ is the MP perturbation operator [1, 2]), scales with $O(M^8)$ while the QQ term as a disconnected term requires also $O(M^6)$ rather than $O(M^{10})$ operations. The connected Q appearing at MP6 in form of TQT, QQQ, and TQQ contributions raise the cost to $O(M^9)$ [10–12]. Table 1 shows how computational cost increases for even higher orders $(n \geqslant 6)$.

In view of the increasing cost of the MP*n* methods and computational limitations caused by the existing computer hardware, it is important to know which correlation effects are needed and which can be discarded for a reliable description of a particular atomic or molecular system. There is extensive literature on the importance of pair correlation effects for the correct description of energies, geometries, vibrational frequencies, and other properties of atoms and molecules [2, 10, 14–17]. There is also literature on the influence of three-electron correlation effects when describing systems with electron clustering [2, 7, 10, 14–17]. However, little information is available to assess the relevance of four- and even higher electron correlation effects involving five, six, etc. electrons. In continuation of previous work [12], we will make an assessment of these effects by analysing electron correlation contributions calculated in this work for 32 different electron systems at the MP2, MP3, MP4, MP5, and MP6 levels. The results of our analysis will be used in three ways. (i) We shall discuss the importance of electron correlation effects of increasing order for different classes of electron systems. (ii) Changes in magnitude and sign of individual correlation contributions will be the basis for a discussion of the convergence behaviour of the MP*n* series and, connected with this, the physical meaning of MP*n* perturbation theory. (iii) We shall make suggestions as to the proper use of MP*n* theory for a given chemical problem.

To address these aspects, we shall proceed by first describing the computational methods used and the details of the analysis of correlation energies applied (section 2). Then, we shall discuss the electron correlation effects covered at a given order n of MP perturbation theory in form of MP*n* spectra (section 3) [12]. The influence of basis set effects on the calculated correlation contributions can be understood readily with the help of the MP*n* spectra (section 4) so that general (not basis set dependent) conclusions (section 5) about the importance of higher order correlation effects can be drawn.

2. Computational methods

In this work, standard MP2, MP3, and MP4 theory [3–7] was used. In the case of MP5 and MP6, the approach by He and Cremer [10–12] was followed since it leads to the determination of 11 MP5 and 52 MP6 energy contributions, which can be contracted to the 9 unique $E_{XY}^{(5)}$ contributions and 28 MP6 correlation energy contributions (besides MP2, MP3, and MP4 correlation energies $\Delta E^{(n)}$) in one calculation where, because of computational convenience, 21 individual $E_{XYZ}^{(6)}$ terms and 7 sums of $E_{XYZ}^{(6)}$ terms are evaluated. If one considers in addition subsummations over all connected Q contributions, all SDQ or all T contributions, then a total of 55 energies were determined with one MP6 calculation.

All calculations were performed with the frozen core approximation. For open shell systems, unrestricted MP*n* rather than restricted open shell MP*n* theory was used. The following notation was applied to distinguish between total and partial correlation energies, for example at sixth order:

$$E(\mathrm{MP6}) = E(\mathrm{HF}) + \Delta E_{\mathrm{MP6}}(\mathrm{corr}), \tag{1}$$

$$\Delta E_{\mathrm{MP6}}(\mathrm{corr}) = \sum_{n=2}^{6} \Delta E^{(n)}, \tag{2}$$

$$\Delta E^{(6)} = \Delta E_{SDQ}^{(6)} + \Delta E_{\mathrm{T}}^{(6)} + \Delta E_{\mathrm{PH}}^{(6)} = \sum_{i=1}^{36} E_{XYZ(i)}^{(6)}, \tag{3}$$

where i runs over all allowed XYZ-combinations of S, D, T, Q, P, and H excitations. Accordingly, one has to distinguish between the total MP6 energy $E(\mathrm{MP6})$, the total correlation energy at MP6, $\Delta E_{\mathrm{MP6}}(\mathrm{corr})$, made up by the sum of the MP2,..., MP6 correlation energies $\Delta E^{(n)}$, the sum of all SDQ contributions at MP6, $\Delta E_{\mathrm{SDQ}}^{(6)}$, all T contributions, $\Delta E_{\mathrm{T}}^{(6)}$, all P or H contributions, $\Delta E_{\mathrm{PH}}^{(6)}$, and the individual (partial) correlation energy contributions of the type $E_{XYZ}^{(6)}$. Any term $E_{XYZ}^{(6)}$, which does not contain a T, P or H excitation, belongs to the SDQ correlation energy $\Delta E_{\mathrm{SDQ}}^{(6)}$ otherwise to the T correlation energy $\Delta E_{\mathrm{T}}^{(6)}$ or the PH correlation energy $\Delta E_{\mathrm{PH}}^{(6)}$ [11, 12].

For 32 different electron systems, 1760 correlation energies were analysed using the following strategy (1)–(4).

(1) Whereas in the investigation by Cremer and He [12] 15 different atoms and small molecules, for which full CI (FCI) energies were available, were calculated with different basis sets at different geometries since FCI results had to be taken from different investigations, in the present work the requirement of an avail-

able FCI energy was abandoned and examples were chosen to represent typical bonding situations of the atoms of the first row of the periodic table (first row sweep from Li to F) as they occur in well-known inorganic or organic molecules.

(2) For all atoms and molecules considered, Pople's (10s4p1d/4s1p) [3s2p1d/2s1p] basis set [18] was used, which is of VDZ+P quality as were the basis sets used by Cremer and He [12]. Clearly, a VDZ+P basis does not fulfil the requirements for high accuracy MP*n* calculations. However, the choice of the basis was a direct consequence of (a) the use of MP6 as an $O(M^9)$ method, which limits calculations to about 80 basis functions, (b) the need to carry out all MP*n* calculations under the same conditions (basis set, geometry, SCF convergence parameters), and (c) to have the possibility of extending the basis for basis set studies in selected cases. The influence of the basis on the accuracy of the MP*n* results, in particular MP2, MP3, and MP4, was tested by systematic calculations using Dunning's cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets, [19] which correspond to (9s4p1d/4s1p) [3s2p1d/2s1p], (10s5p2d1f/5s2p1d) [4s3p2d1f/3s2p1d], (12s6p3d2f1g/6s3p2d1f) [5s4p3d2f1g/4s3p2d1f], and (14s8p4d3f2g1h/8s4p3d2f1g) [6s5p4d3f2g1h/5s4p3d2f1g] decompositions, respectively. In some cases, these basis sets were augmented by a set of diffuse functions (aug-cc-pVDZ, aug-cc-pVTZ) [20].

(3) For all molecules investigated, accurate experimental geometries are available, which were used to obtain consistent MP*n* descriptions. In table 2, the electronic systems investigated and the geometries used [21–30] are summarized.

(4) Rather than discussing each electron system separately, the 1760 individual energy terms were analysed by first separating all electron systems into two classes (class A and class B) according to criteria which will be discussed in this paper. Second, within a class typical trends in calculated correlation energies were assessed by averaging over all members of the class. The energy contributions thus obtained are the basis for our analysis of electron correlation effects. They are presented in form of MP*n* spectra [12].

The MP*n* spectra for a given class of electronic systems were obtained by first scaling and then averaging calculated correlation energies $E^{(n)}_{X\ldots}$ over all members of the class. The scaling factor for the individual correlation contributions for a given MP*n* order was determined by

$$f = \{(E^{(n)}_{X\ldots})^2 + (E^{(n)}_{Y\ldots})^2 + \cdots\}^{1/2}. \qquad (4)$$

Using scale factor f, the scaled correlation energy contribution $\varepsilon^{(n)}_{X\ldots}$ is defined as

$$\varepsilon^{(n)}_{X\ldots} = \frac{E^{(n)}_{X\ldots}}{f}, \qquad (5)$$

where the $\varepsilon^{(n)}_{X\ldots}$ fulfil the normalization equation

$$(\varepsilon^{(n)}_{X\ldots})^2 + (\varepsilon^{(n)}_{Y\ldots})^2 + \cdots = 1. \qquad (6)$$

For each electron system, trends and relationships between individual correlation energy contributions can be described by scaled energy terms in a comparative way. Accordingly, one can present the scaled energy terms $\varepsilon^{(n)}_{X\ldots}$ in the form of bar diagrams, for which the term MP*n* spectrum was coined [12].

In order to obtain the MP*n* spectrum of a whole group of electronic systems, for example that of class A or B, the scaled energy terms are averaged over all electronic systems belonging to class A (or class B) according to

$$\bar{\varepsilon}^{(n)}_{X\ldots}(\text{class A}) = \frac{1}{N_A}\sum_{i}^{N_A} \varepsilon^{(n)}_{X\ldots}(i) \qquad \text{for } i \in \text{ class A} \quad (7)$$

where N_A is the total number of electronic systems of class A. The MP*n* spectra obtained in this work for the two classes A and B are shown in figures 1–3. The corresponding correlation energies are summarized in the appendix.

3. MP*n* spectra for classes A and B

For a subset of the electronic systems investigated, calculated MP*n* correlation energies $\Delta E^{(n)}$ are all negative and converge monotonically to zero. Each higher level of MP*n* theory leads to a better approximation to the correct correlation energy $\Delta E(\text{corr})$. However, for the remaining examples, MP*n* correlation energies $\Delta E^{(n)}$ can be negative or positive, thus leading to erratic convergence behaviour. These observations are in line with the results of previous investigations, which showed that the MP*n* series possesses different convergence behaviour depending on the electronic structure of the system investigated [12, 14, 31, 32]. (a) the MP*n* energies decrease monotonically approaching the FCI energy (equal to MP_∞) from above, where the MP6 energy presents the best approximation at the moment feasible when using standard MP*n* procedures. (b) There are initial oscillations in the MP*n* correlation energy, which result from an exaggeration of electron correlation effects for even orders of MP*n* theory and a reduction of correlation effects for odd orders. If oscillations are damped out with increasing n, the MP*n* series will converge to the FCI value. (c) If oscillations are not reduced with increasing order n, the MP*n* series will become divergent and, accordingly, MP*n* energies are no longer meaningful for describing the energy of an electron system.

Table 2. Geometries of molecules investigated[a]

Molecule	State	Symmetry	Geometrical parameters	Class A/B	Reference
Li_2	$^1\Sigma_g^+$	$D_{\infty h}$	$r(LiLi) = 2.670$	A	22
LiH	$^1\Sigma^+$	$C_{\infty h}$	$r(LiH) = 1.595$	A	22
BeH_2	$^1\Sigma_g$	$D_{\infty h}$	$r(BeH) = 1.326^*$	A	
BH	$^1\Sigma^+$	$C_{\infty h}$	$r(BH) = 1.233$	A	21
BH_3	$^1A_1'$	D_{3h}	$r(BH) = 1.186^*$	A	
CH_2	$^1A_1$	C_{2v}	$r(CH) = 1.113$	A	22
			$\theta(HCH) = 100.5$		
CH_2	$^3B_1$	C_{2v}	$r(CH) = 1.075$	A	23a
			$\theta(HCH) = 133.9$		
CH_3^+	$^1A_1'$	D_{3h}	$r(CH) = 1.087^*$	A	
CH_3	$^2A_2''$	D_{3h}	$r(CH) = 1.079$	A	22
CH_4	$^1A_1$	T_d	$r(CH) = 1.086$	A	23b
CN	$^2\Sigma^+$	$C_{\infty h}$	$r(CN) = 1.172$	B	22
HCN	$^1\Sigma$	$C_{\infty h}$	$r(CH) = 1.066$	B	26a
			$r(CN) = 1.153$		
HNC	$^1\Sigma$	$C_{\infty h}$	$r(NH) = 0.994$	B	26b
			$r(CN) = 1.169$		
CO	$^1\Sigma^+$	$C_{\infty h}$	$r(CO) = 1.128$	B	21
CO_2	$^1\Sigma_g$	$D_{\infty h}$	$r(CO) = 1.160$	B	27
NH	$^1\Sigma^+$	$C_{\infty h}$	$r(NH) = 1.045$	A	22
NH_2	$^2B_1$	C_{2v}	$r(HN) = 1.024$	A	22
			$\theta(HNH) = 103.4$		
NH_3	$^1A_1$	C_{3v}	$r(NH) = 1.012$	A	24a
			$\theta(HNH) = 106.7$		
N_2	$^1\Sigma_g^+$	$D_{\infty h}$	$r(NN) = 1.098$	B	21
N_2H_2	^1A_g	C_{2h}	$r(NH) = 1.028$	B	24b
			$r(NN) = 1.252$		
			$\theta(NNH) = 106.9$		
NO	$^3\Pi_r$	$C_{\infty h}$	$r(NO) = 1.151$	B	21
HNO	$^1A'$	C_s	$r(NH) = 1.063$	B	28
			$r(NO) = 1.212$		
			$\theta(HNO) = 108.6$		
H_2O	$^1A_1$	C_{2v}	$r(OH) = 0.957$	B	25a
			$\theta(HOH) = 104.5$		
O_2	$^3\Sigma_g^-$	$D_{\infty h}$	$r(OO) = 1.207$	B	21
H_2O_2	^1A	C_2	$r(OH) = 0.967$	B	25b
			$r(OO) = 1.456$		
			$\theta(OOH) = 102.3$		
			$\tau(HOOH) = 113.7$		
O_3	$^1A_1$	C_{2v}	$r(OO) = 1.272$	B	30
			$\theta(OOO) = 116.8$		
FH	$^1\Sigma^+$	$C_{\infty h}$	$r(FH) = 0.917$	B	21
LiF	$^1\Sigma^+$	$C_{\infty h}$	$r(LiF) = 1.564$	B	22
F_2	$^1\Sigma_g^+$	$D_{\infty h}$	$r(FF) = 1.412$	B	21
HOF	$^1A'$	C_s	$r(OH) = 0.966$	B	29
			$r(OF) = 1.435$		
			$\theta(HOF) = 97.6$		

[a] Bond distances are given in Å and angles in deg. Starred values denote parameters obtained by CCSD/[3s2p1d/2s1p] calculations.

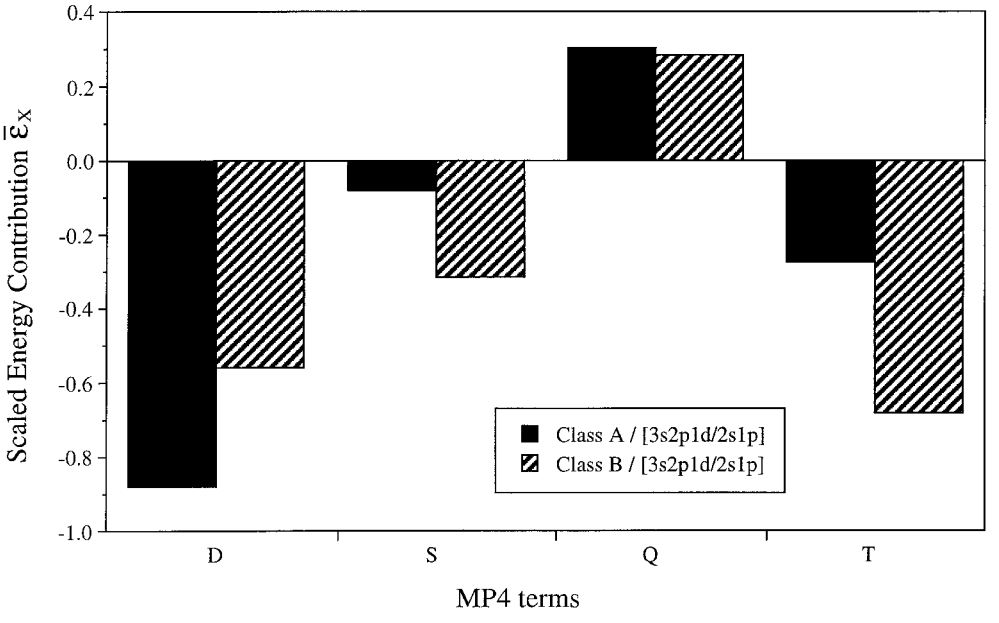

Figure 1. MP4 spectra for class A and class B systems. The averaged values for 13 class A systems and 19 class B systems are used (see table 2). All examples are calculated with a (10s4p1d/4s1p) [3s2p1d/2s1p] basis set.

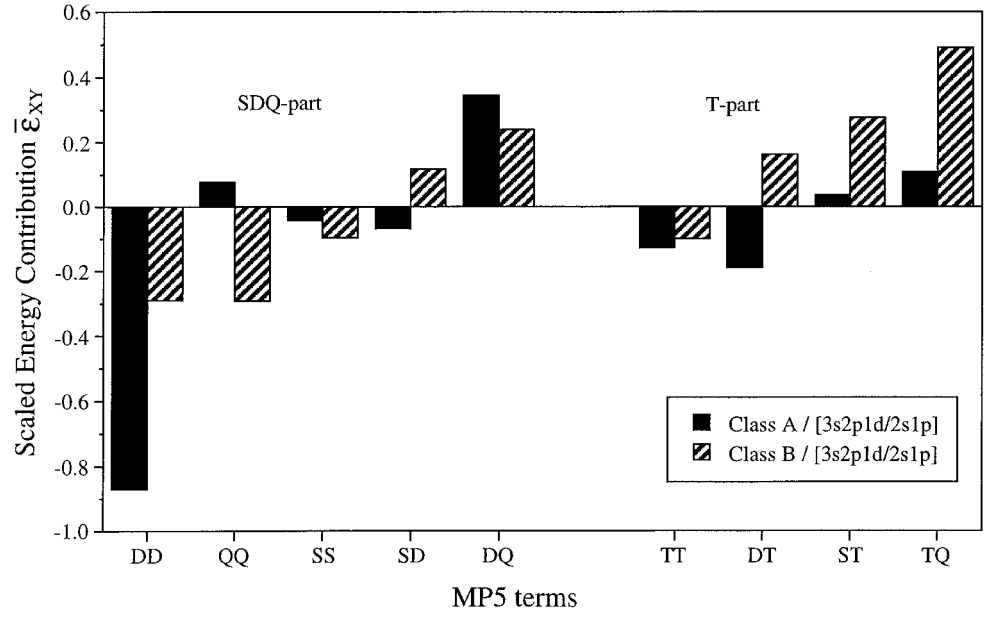

Figure 2. MP5 spectra for class A and class B systems. The averaged values for 13 class A systems and 19 class B systems are used (see table 2). All examples are calculated with a (10s4p1d/4s1p) [3s2p1d/2s1p] basis set.

Cremer and He [12] suggested grouping all electron systems according to the convergence behaviour of the MPn series into two classes A (case (a)) and B (cases (b) and (c)). It was shown that class A systems are those for which electron pairs (core, bond, lone pairs) are well separated and equally distributed over the whole space of the system in question. Examples are electropositive atoms and their hydrides, boranes, and saturated hydrocarbons. Class B systems are those which are characterized by electron clustering in a confined region of space (valence shell of an electronegative atom, multiple bond of a molecule, etc.). Applying this classification to the electronic systems investigated in this work, the grouping of atoms and molecules shown in table 2 is obtained.

In table 3, total correlation energies obtained at MP6 ordered according to classes and split up in contributions $\Delta E^{(2)},\ldots,\Delta E^{(6)}$ are compared. Pair correlation effects calculated at MP2 cover for class A systems 80% of the total MP6 correlation energy; however they cover 95% of the correlation energy for class B systems. Coupling of the pair correlation energies at MP3 increases the correlation energy (absolutely seen) by about 14% in the case of class A but decreases it by

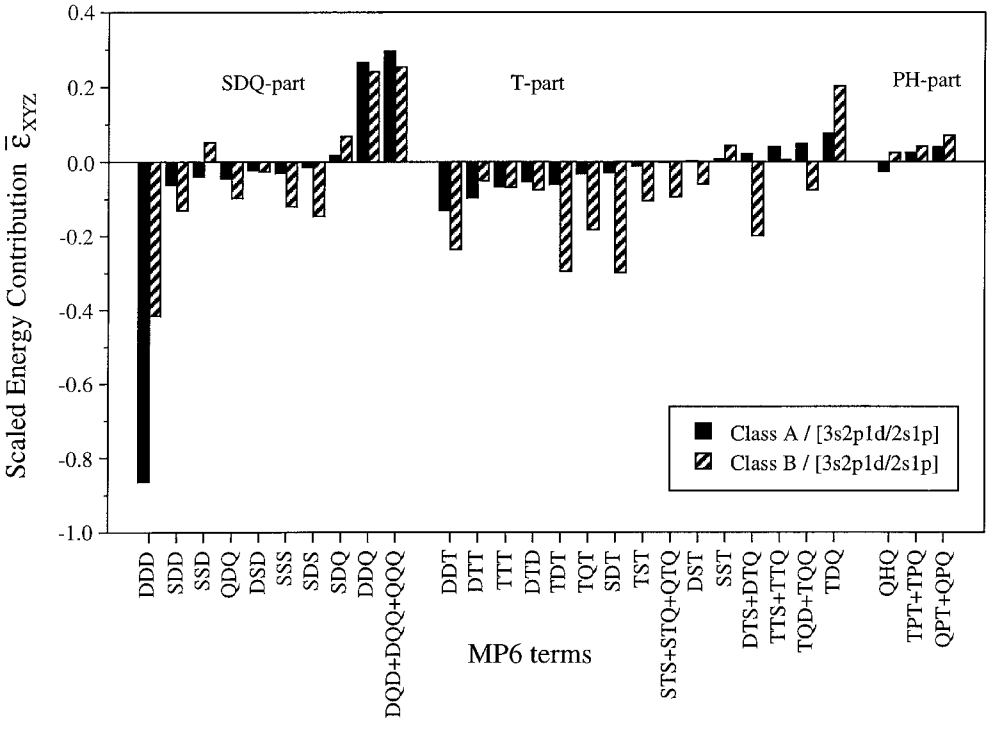

Figure 3. MP6 spectra for class A and class B systems. The averaged values for 13 class A systems and 19 class B systems are used (see table 2). All examples are calculated with a (10s4p1d/4s1p) [3s2p1d/2s1p] basis set.

Table 3. Comparison of the convergence behaviour of class A and class B systems[a]

MP*n*	Class A system	Class B system
MP2	79.7%	94.7%
MP3	14.0%	−0.4%
MP4	4.3%	5.6%
MP5	1.4%	−1.2%
MP6	0.7%	1.5%

[a] Correlation energies are given in % of the total MP6 correlation energy $\Delta E^{(6)}(\text{corr}) = \sum_{n=2}^{6} \Delta E^{(n)}$ averaged over all class A and Class B systems investigated. All calculations with a (10s4p1d/4s1p) [3s2p1d/2s1p] basis set.

the tiny amount of 0.1% for class B systems. These contributions clearly reflect the fact that for class B systems the pair effects are largely exaggerated. It is well known that MP2 exaggerates correlation effects; however this seems to preferentially apply to electron systems with a clustering of electrons. MP perturbation theory attempts to separate electrons in a cluster of three or more electrons by the inappropriate tool of pair correlation, which leads to an exaggeration of electron correlation since the pairwise treatment of electrons does not consider that, after separation, electrons can cluster in new regions (e.g. the six electrons of a triple bond form two clusters of three electrons each after left–right pair correlation).

This pattern of correlation contributions repeats itself for class B systems at the MP4-MP5 level of theory and probably also at the MP6-MP7 level, where oscillations in the non-divergent cases should be slowly damped out. The data in table 3 suggest that for class A systems the MP*n* series converges slowly but steadily. At MP5 and MP6, 2% of the total correlation energy is added; however, using appropriate extrapolation techniques such as Feenberg scaling [11, 31, 32], MP4 calculations are sufficient to obtain reliable MP_∞ energies. For class B systems, oscillations between even and odd orders of MP theory require calculations up to MP6 to obtain a reliable estimate of the correlation energy at infinite order [31, 32]. In the following sections, we will investigate which correlation effects are responsible for monotonic or erratic convergence behaviour at MP4, MP5, and MP6.

3.1. *MP4 spectrum*

In figure 1, the MP4 spectra for class A and class B systems are shown. For class A systems, the MP4 contribution is on average 4.3% and for class B systems 5.6% of the total MP6 correlation energy, which again suggests that correlation effects are more important for class B systems (in line with their electronic structure), although the MP4 contribution may also be exaggerated in this case. Both for class A and class B systems correlation contributions $E_X^{(4)}$ with X = S, D or T are always

negative (stabilizing) while Q correlation effects are always positive (destabilizing). For class A systems, the term $E_D^{(4)}$ is absolutely the largest since it represents pair correlation effects (left–right, angular, in–out). Since class A systems are characterized by an electron pair structure with well separated electron pairs, it is reasonable that pair correlation effects are the most important correlation effects and that other correlation effects such as orbital relaxation (S excitations) or three-electron correlation effects (T excitations) are of lower importance. The term $E_Q^{(4)}$ associated with the disconnected cluster operator $\hat{T}_2^{(2)}\hat{T}_2^{(2)}$ (table 1) covers correlation effects resulting from the independent but simultaneous correlation of two electron pairs. Obviously, the Q term at MP4 corrects for an exaggeration of pair correlation effects typical of MP2 and, therefore, it is positive (for a detailed discussion of the Q term at MP4, see [33]).

For class B systems, $E_D^{(4)}$ and $E_T^{(4)}$ become similarly important where the T term is often larger (absolutely seen) than the D term. Clearly, three-electron correlation effects play a more important role for class B than class A systems. This is a direct result of electron clustering typical of class B systems, since three-electron correlation provides the simplest mechanism for effectively separating electrons in a cluster. While D excitations at MP2 separate electrons pairwise without considering that this might lead to new electron clusters, three-electron correlation corrects pair correlations with regard to a third electron and, by taking all possible combinations of three-electron clusters, gets to a first effective separation of the electrons in the cluster. This will lead to a stronger change in the electronic structure and, accordingly, requires a larger adjustment of the orbitals, as is reflected by an increase in orbital relaxation (S contribution, figure 1).

3.2. *MP5 spectrum*

The MP5 contributions to the total electron correlation energy at MP6 are 1.4% and −1.2% on average for class A and class B systems, respectively (table 3). The MP5 spectra (shown in figure 2) are related to the MP4 spectra in several ways. First, there is a similar difference between class A and class B systems concerning the importance of pair and three-electron correlation effects. The MP5 correlation energy for a class A system is clearly dominated by pair–pair correlation effects covered by $E_{DD}^{(5)}$. The second largest term is the DQ term, which is positive similarly to the Q term at MP4, and obviously corrects for an overestimation of pair correlation effects. All other terms are relatively small with a dominance of the negative terms, so that the total MP5 correlation contribution is negative but absolutely seen three times smaller than the total MP4 contribution (table 3, figure 2).

For class B systems, the DD contribution is much smaller than for class A systems and similar in magnitude to the QQ contribution, which is now also negative. The spectrum is dominated by three-electron correlation contributions, which are all positive (DT, ST, TQ) with the exception of the negative TT contribution. The largest contribution in the spectrum results from the TQ part, which means that the coupling of independent pair correlations (all Q terms at MP5 are disconnected) with three-electron correlations leads to an important correction at MP5 for case B systems, probably because of an exaggeration of these terms at lower orders. Orbital relaxation effects are more important for class B systems since the reorganization of electrons at MP5 is larger for class B than class A systems. The total T part (figure 2) is positive and has to be added to a total SDQ part at MP5, which is much less negative for class B systems than for class A systems, thus yielding a total MP5 contribution that is positive rather than negative. Alternatively, one can say that the positive correction terms DQ and TQ for pair and three-electron correlation dominate the MP5 spectrum and are responsible for the positive MP5 correlation energies in the case of class B systems.

Electronic systems with a clustering of electrons, as for example in the valence space of electronegative atoms, in the region of multiple bonds or at the central atom of hypervalent molecules, are easy to identify as class B systems. Of course, there is a continuous transition from class A to class B systems and, therefore, it will be difficult to describe electronic systems with moderate electron clustering as class A or class B systems if just qualitative information on the electronic structure is available. As summarized in table 4, it is easy to identify a class A or class B system by comparing MP2/MP3 or MP3/MP4 correlation energies (criteria (1)–(4) in table 4). Alternatively, one can use MP5 correlation contributions to distinguish between a class A and a class B system. The total T contribution $\Delta E_T^{(5)}$ as well as the DT, SD, and the QQ terms are less suitable for this purpose since there are always electronic systems which do not follow the general trends listed in table 4. However, the scaled correlation energy contributions $\varepsilon_{DD}^{(5)}$ and $\varepsilon_{TQ}^{(5)}$ provide a clear separation of A and B systems since the first term reflects the dominance of pair correlation effects in class A while the second term is at MP5 the most important correction for an exaggeration of pair and three-electron correlation effects in class B.

Table 4. Comparison of various criteria used for the classification into class A and class B systems[a]

Number	Criterion	Class A	Class B	Exceptions	Comments
(1)	convergence of MP*n*	monotonic	oscillations	no	
(2)	$1/C_1$	small	large	no	reflecting convergence behaviour
(3)	C_2	> 2.0	< 2.0	no	reflecting convergence behaviour
(4)	$C_1 \cdot C_2$	~1.0	~0.01	no	reflecting convergence behaviour
(5)	$\Delta E_{\mathrm{T}}^{(5)}$	> 0	< 0	NH_3	characterization of MP5
(6)	$E_{\mathrm{DT}}^{(5)}$	< 0	> 0	F^-, H_2O	characterization of MP5
(7)	$E_{\mathrm{SD}}^{(5)}$	< 0	> 0	F^-	characterization of MP5
(8)	$E_{\mathrm{QQ}}^{(5)}$	> 0	< 0	NH_3	characterization of MP5
(9)	$\lvert\varepsilon_{\mathrm{DD}}^{(5)}\rvert$	> 0.7	< 0.7	no	characterization of MP5
(10)	$\lvert\varepsilon_{\mathrm{TQ}}^{(5)}\rvert$	< 0.4	> 0.4	no	characterization of MP5

[a] C_1 and C_2 denote the following absolute ratios: $C_1 = |\Delta E^{(2)}/\Delta E^{(3)}|$, $C_2 = |\Delta E^{(3)}/\Delta E^{(4)}|$.

3.3. *MP6 spectrum*

The MP6 correlation contribution for class A (0.7%, table 3) is relatively small; however, for class B it is larger (absolutely seen) than the MP5 contribution (1.5 versus −1.2%, table 3). In the MP6 spectrum (figure 3) there are always more negative electron correlation contributions than positive ones so that the total MP6 correlation contribution is (similar to MP2 or MP4) always negative. For class A systems, the DDD contribution is dominant and determines the magnitude of the MP6 correlation energy $\Delta E^{(6)}$. However, it is corrected by positive DQ (QQ) couplings covered by the DDQ, DQD, DQQ, and QQQ terms (figure 3), which again correct the exaggeration of pair correlation effects at lower orders. Correlation terms involving S, T, P, H contributions are small and largely cancel each other out, so they may be neglected.

For class B systems, the DDD terms still represents the largest (negative) contribution to the MP6 correlation energy. However, there are five T terms (DDT, TDT, TQT, DTS + DTQ, and SDT), which are also relatively large and show the increased importance of three- electron correlation for class B systems. The positive correlation corrections arise mainly from the three terms DDQ, DQD + DQQ + QQQ, and TDQ. The latter terms are as large as found for class A; however, the ratio of negative and positive MP6 contributions is still larger for class B than for class A systems. The PH part represents a relatively small positive correction, as is found also in the case of class A systems since it predominantly adds to the pair and three-electron correlation corrections. In general, there is much less possibility of neglecting one of the 28 calculated terms for B than for A systems.

4. Influence of the basis

Because of the computational cost of an MP5 or MP6 calculation, expansion of the basis set to triple-, quadruple-, or pentuple-zeta quality, for example within the Dunning hierarchy of correlation-consistent basis sets (cc-pVTZ, cc-pVQZ, cc-pV5Z), could only be done in the following way. First, extended basis sets were employed at the MP4 level of theory and the results used to extrapolate to the basis set limit [33]. Then, MP5 and MP6 energies were obtained selectively with cc-pVTZ basis sets for some class A and class B systems to predict the dependence of calculated correlation energies on the basis set used.

Since the results of the basis set dependence of MP4 correlation energies are published elsewhere [33] we summarize here the most important conclusions drawn from this work in the form of the MP4 spectra for the complete basis set (CBS) limit (figure 4).

Comparison of the MP4 spectra in figures 1 and 4 reveals that the overall pattern of the spectra does not change when the basis set is extended from VDZ quality to the CBS limit. There are only gradual changes, which concern the ratio of pair and three-electron correlation contributions. For both class A and class B systems, the former are reduced while the magnitude of the latter is increased, i.e. the importance of three-electron correlation effects at MP4 is larger in the CBS limit than suggested with VDZP calculations. Coupled with these changes are typical changes in orbital relaxation effects (S excitations) and disconnected pair correlations (Q excitations), which both increase in magnitude. This simply reflects the necessity of adjusting orbitals to the stronger three-electron correlation effects and of using the larger flexibility of the basis set for stronger pair

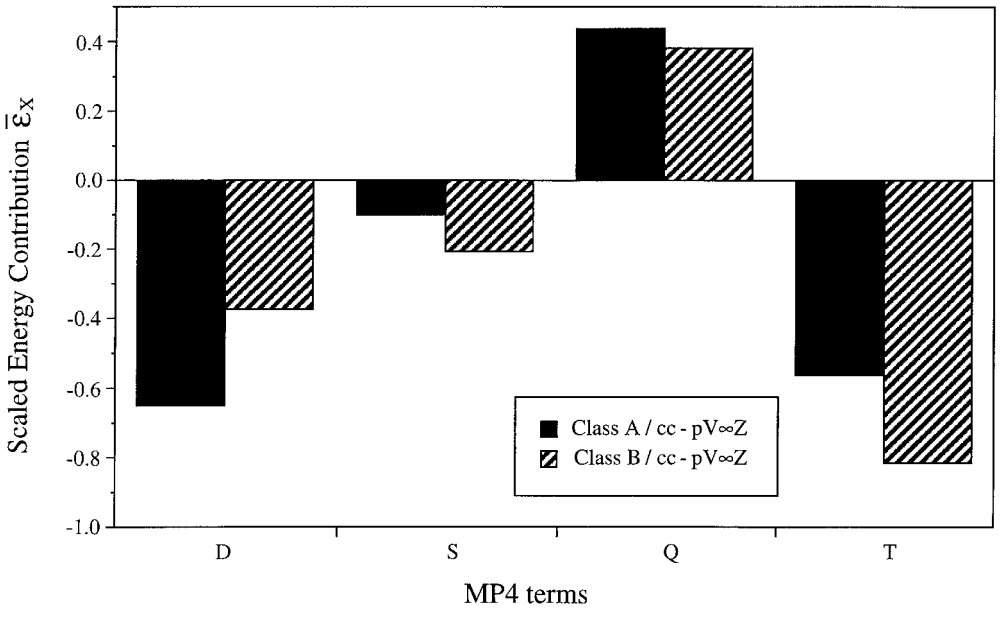

Figure 4. The MP4/CBS limit spectra for class A and class B systems obtained from 9 class A and 18 class B systems.

correlation corrections. Nevertheless, the basic pattern of class A and class B spectra and the typical differences between these spectra are retained so that one can conclude that the VDZP spectra presented in this work for MP5 and MP6 are equally as valid and meaningful as the MP4 spectra.

Central to all correlation corrected *ab initio* calculations is the choice of the appropriate basis set. In recent work, various authors tested the use of a VDZ basis augmented with diffuse basis functions (aug-VDZP basis sets [20]) to describe electron lone pairs or the diffuse charge distributions in anions. It has been argued that the choice of an unbalanced basis set can lead to artificial convergence problems in the MP*n* series such as divergent behaviour [32]. In figures 5 and 6 the MP*n* spectra of a typical class A molecule, namely $CH_2(^3B_1)$, and a typical class B system with a diffuse charge distribution, namely $F^-(^1S)$, are compared for Dunning's cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets.

For $CH_2(^3B_1)$, changes in the MP*n* spectra with increasing basis set size are monotonic with a few, non-significant exceptions (figures $5(a,b,c)$). The aug-cc-pVDZ results nicely fit between cc-pVDZ and cc-pVTZ results, which is reasonable in view of the fact that the aug-cc-pVDZ set has the same number of spd functions as the cc-pVTZ set but lacks the f-type polarization functions of the latter. Inspection of the calculated energies indicates that despite the somewhat larger cost for the cc-pVTZ calculation it is much more effective to use a VTZP basis rather than to augment a VDZP basis by diffuse functions.

For the $F^-(^1S)$ anion, changes in the spectra with increasing size of the basis set are erratic, as for the S, Q, and D contributions at MP4 (figure $6(a)$). Actually, a major reorganization of electron correlation is enforced by the aug-cc-pVDZ basis by pushing up the three-electron correlation effects at the cost of the pair correlation effects, which implies a large relaxation of the orbitals of the $F^-(^1S)$ anion at MP4/aug-cc-pVDZ. At MP5, under- and overestimation of correlation effects caused by the use of an aug-cc-pVDZ basis set is even more pronounced (figure $6(b)$). The important DD contributions become negligible (similarly the QQ and DQ effects decrease) while orbital relaxation effects (SD and ST) and three-electron correlation effects (DT and TQ) are exaggerated. The important TT contribution becomes positive even though it describes a new correlation effect, and should be negative as correctly described with the cc-pVTZ basis set. Because of the underestimation of pair correlation effects and the exaggeration of correcting coupling effects, the MP5 correlation energy $\Delta E^{(5)}$ of the $F^-(^1S)$ anion becomes too positive.

These trends continue at the MP6 level of theory (figure $6(c)$), but now in the way that the negative (stabilizing) electron correlation contributions are exaggerated by the use of the aug-cc-pVDZ basis set. Positive corrections (DDQ, DQD + DQQ + QQQ, QHQ, etc.) are strongly underestimated, as are the negative pair correlation effect DDD; however, the decrease in the latter is more than compensated for by relatively large negative orbital relaxation effects (SDS, SDD) and three-electron correlation effects (SDT, DTS + DTQ, TTS + TTQ, TQD + TQQ), so that the MP6 electron correlation energy $\Delta E^{(6)}$ becomes more negative than expected from cc-pVDZ or cc-pVTZ calculations (figure 6).

From these observations important conclusions as to the use of basis sets with diffuse functions can be drawn.

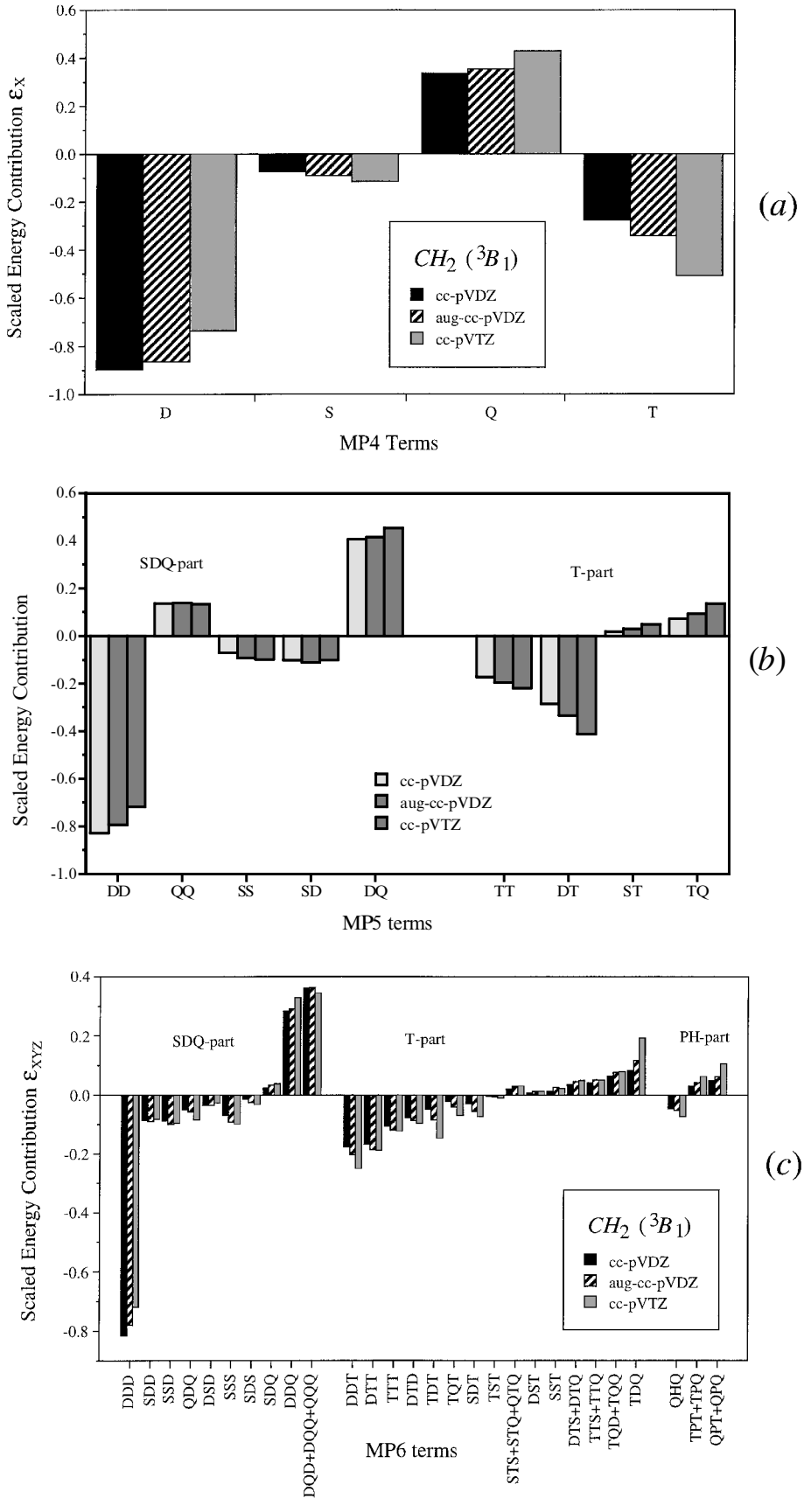

Figure 5. (*a*) MP4, (*b*) MP5, and (*c*) MP6 spectra calculated for CH_2 ($^3B_1$) with the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis set.

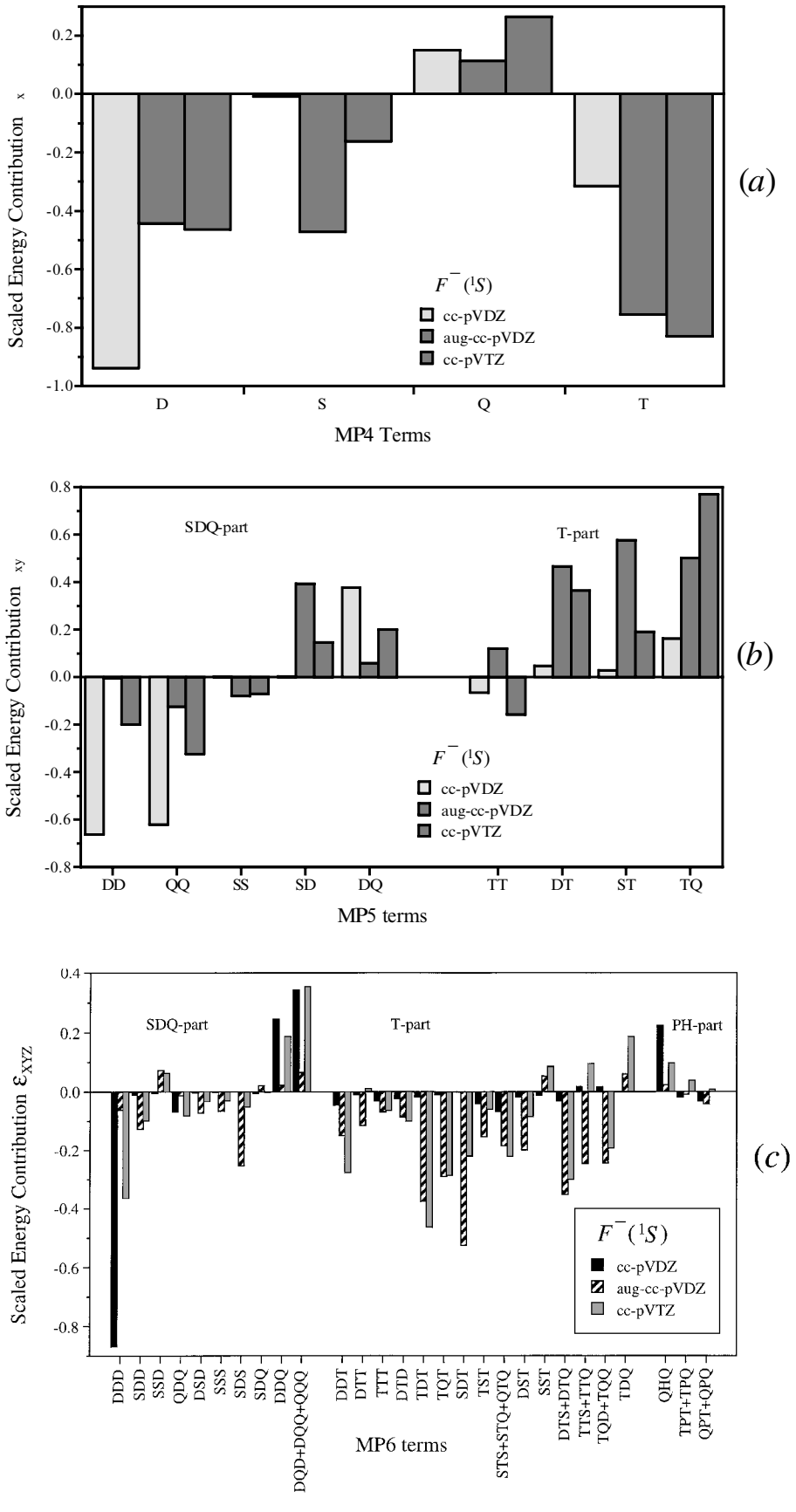

Figure 6. (*a*) MP4, (*b*) MP5, and (*c*) MP6 spectra calculated for the $F^-(^1S)$ anion with the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis set.

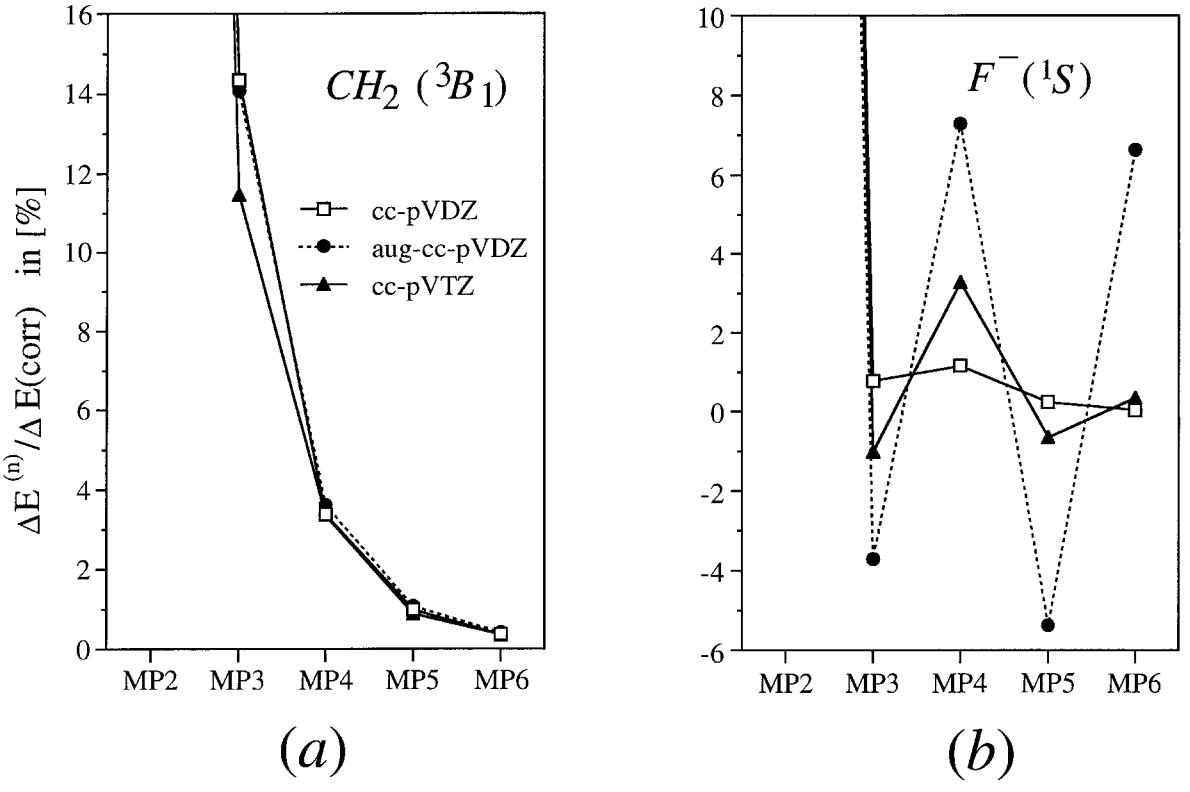

Figure 7. Relative MPn correlation energy contributions $\Delta E^{(n)}$ given in % and plotted for $n = 2,\ldots,6$ and for the three basis sets cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ in the case of (a) $CH_2(^3B_1)$ and (b) the $F^-(^1S)$ anion.

A chosen basis set must be flexible to cover adequately all regions of atomic or molecular space occupied by electrons. If the basis functions added are highly diffuse, the new virtual orbitals will also be diffuse. Accordingly, they will not be suitable as correlation orbitals since their overlap with the occupied orbitals is relatively small. This will be particularly problematic if the inner regions of the valence shell, in which the electrons are predominantly located, are not accurately described by sp basis functions. Diffuse functions force the electrons out of these regions, as would be the case for higher order correlation effects involving clusters of three, four, five etc., electrons. Hence, higher order electron correlation effects and the orbital relaxation effects accompanying these electron correlation effects are exaggerated, thus leading to unbalanced MPn energies. This is illustrated in figure 7, which gives the relative values of correlation energies $\Delta E^{(n)}$ for $n = 2,\ldots,6$ in % for the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets in the case of the typical class A molecule $CH_2(^3B_1)$ (figure 7(a)) and in the case of the typical class B system $F^-(^1S)$ (figure 7(b)).

Although for $CH_2(^3B_1)$, the monotonic convergence behaviour of the MPn series is not changed by adding diffuse functions, the typical initial oscillations of the class B system are exaggerated so that the MPn series becomes divergent as full CI (FCI) calculations show [32, 34]. Hence, the divergence of the MPn series does not indicate a basic failure of perturbation theory to describe electron correlation correctly, as some authors speculated [34]: it indicates the use of an unbalanced basis set. The addition of diffuse functions to an unsaturated sp basis as in the case of any VDZ basis enforces higher order correlation effects while lower order correlation effects are not properly described. This is similar to giving highly excited configurations artificially more weight in a CI calculation, which can lead to unexpected back-door intruder states and divergence of the MPn series [32].

The present study underlines the necessity of using cc-pVTZ basis sets for reasonably accurate electron correlation studies at the MPn level. This is particularly important when systems with diffuse charge distributions are investigated, most of which represent a class B system. However, class A systems also are sensitive to the basis set in connection with the correct description of the ratio of pair and three-electron correlation effects.

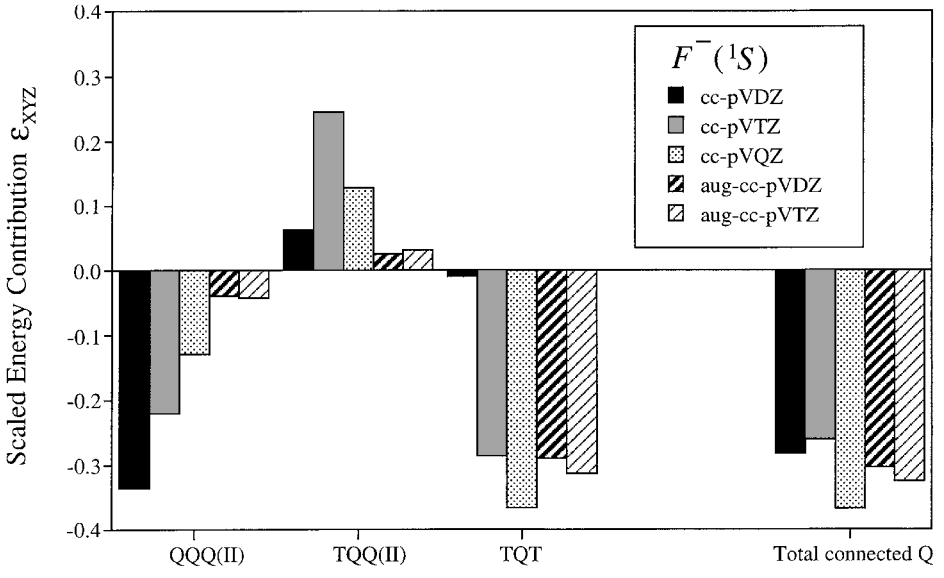

Figure 8. MP6 spectra for the connected four-electron correlation contributions calculated with the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets for the $F^-(^1S)$ anion.

5. Appropriate description of four-electron correlation effects

At MP6, four-electron correlation effects as described by connected Q excitations enter for the first time (see table 1). He and Cremer showed that connected Q effects are represented by the terms QQQ(II), TQQ(II), and TQT, where the number in parentheses indicates that only the second parts of the QQQ and TQQ terms contain connected Q while the first parts are completely made up from disconnected Q excitations [11, 12]. The QQQ(II) contributions describe the coupling between pair–pair correlations (disconnected Q excitations) with four-electron correlations (connected Q excitations), the TQQ(II) contributions describe a similar coupling between pair–pair, three-electron, and four-electron correlation effects, and the TQT contributions describe the coupling between two three-electron and one four-electron cluster, i.e. the TQT term represents the electron correlation effect of highest order.

In the MP6 spectra of figure 3, the QQQ(II) and TQQ(II) parts are hidden in the sum terms DQD + DQQ + QQQ and TQD + TQQ, respectively, which collect correlation effects of similar nature. Because of this, we analysed the four-electron correlation effects separately for different basis sets up to the cc-pVQZ basis, and found a regular pattern that is reflected by the connected Q spectra of the $F^-(^1S)$ anion (figure 8).

There are large changes in the four-electron correlation effects, depending on the basis set. The cc-pVDZ and aug-ccpVDZ basis sets are unable to describe the QQQ(II) and TQQ(II) effects correctly although in all cases the sign (negative for the former, positive for the latter) is given in the right way. The cc-pVDZ basis set exaggerates the coupling between pair–pair and four-electron correlations while underestimating the TQT effects, as also found at lower levels of MP*n* theory. The cc-pVTZ basis exaggerates the three-electron–four-electron corrections (figure 8), otherwise it gives a reasonable description. For the $F^-(^1S)$ anion as well as all other examples investigated, a fortuitous cancellation of errors with the small basis set results can be observed, which seems to be the consequence of the fact that two negative connected Q contributions are corrected by the positive TQQ(II) contribution. The total contribution of the connected Q at MP6 is only weakly dependent on the size of the basis set (figure 8).

Another observation concerning the Q diagram in figure 8 is that the total contribution of connected Q correlations is well represented by the TQT part, since the two other contributions cancel each other out provided that the basis set is at least of cc-pVTZ quality. We can conclude that the representation of four-electron correlation effects by the TQT energy part as in figures 5 and 6 is sufficient, but the MP6 diagram in figure 3, which is based on VDZ calculations, is misleading in the way that it underestimates the importance of four-electron correlation effects.

5. Conclusion

The separation of electronic systems into those (class A) which can be characterized by a structure of well separated electron pairs and those (class B) which are characterized by electron clustering in some regions of atomic and molecular space simplifies the discussion of electron correlation effects, in particular when one uses

MP*n* theory and discusses calculated correlation energies in form of MP*n* correlation energy spectra.

(1) We find in a systematic study of 32 electronic systems (13 class A systems, 19 class B systems, table 2) carried out with just one basis set at experimental geometries that previous results of Cremer and He [12] are confirmed. For class A systems, convergence of the MP*n* series is slow but monotonic, while for class B systems convergence is erratic with typical initial oscillations.

(2) The MP*n* spectra obtained with a given basis set possess the same pattern of correlation contributions as those obtained with another basis set for a different selection of electronic systems. We have shown that indeed the MP4 spectra at the CBS limit are comparable with those obtained with a small basis set, and we predict that this should also hold for MP5 and MP6 spectra.

(3) MP*n* spectra calculated for a class of electronic systems or just for a single atom or molecule provide an excellent basis for the analysis of electron correlation effects in a consistent manner and for describing the dependence of results on the size of the basis set.

(4) The oscillations observed for class B systems are a consequence of MP*n* theory, namely to introduce higher order correlation effects needed for the correct description of electron correlation in these systems stepwise. If, for example, three-electron correlation is required for a proper account of electron correlation in a cluster of electrons, MP2 theory describes these effects by an exaggeration of pair correlation, which has to be corrected at higher orders. Hence, one can say that a given level of MP*n* theory is inappropriate for a given electronic system with strong electron clustering but this does not mean that MP*n* theory for a sufficiently larger order *n* is unable to describe electron correlation in this system.

(5) The choice of an inappropriate basis set can lead to exaggeration of the initial oscillations of the MP*n* series to the point that the MP*n* series becomes divergent. The use of an aug-cc-pVDZ basis set in the case of the $F^-(^1S)$ anion is a typical example of an artificial increase of oscillations in the MP*n* correlation energies and a divergent MP*n* series caused by adding diffuse basis functions to an unsaturated sp basis set. The importance of higher order correlation effects that in reality play only a minor role in the mechanism of electron correlation is artificially enhanced for even orders *n*, but overcorrected for odd order MP*n*.

(6) For class B systems the use of a cc-pVTZ basis is absolutely necessary to describe three-electron correlation effects. However, even for class A systems, a cc-pVTZ basis is desirable to avoid an exaggeration of pair correlation effects and to achieve a balanced description of pair and three-electron correlation effects.

(7) MP4 is the first MP*n* method which is able to describe a class B system reasonably, since it is the first method to introduce the three-electron correlation effects absolutely necessary for systems with electron clustering. Similarly, MP6 is needed more for a class B than a class A system to add to the three-electron connected four-electron correlation effects needed.

(8) Four-electron correlation effects as described by connected Q excitations are best represented at MP6 by the TQT term, which covers the coupling with three-electron correlation effects since other connected four-electron effects cancel each other out at the MP6. The TQT term is not negligible and is needed to give a proper account of correlation effects.

(9) One can expect relatively large errors in relative MP*n* energies if a class A and a class B system are compared at MP2, MP3 or MP4(SDQ). The first proper account of the energy difference is given by MP4(SDTQ). On the other hand, reasonable descriptions should be obtained at MP2 or MP4(SDQ) if just class A systems are compared, while a comparison of class B systems does not necessarily lead to a cancellation of errors.

Despite the fact that the convergence of the MP*n* series is a direct consequence of the stepwise introduction of correlation effects, which must lead to initial oscillations in the MP*n* series for class B systems, we predict that the MP*n* series will always be convergent, i.e. $E(\mathrm{FCI}) = E(\mathrm{MP}_\infty)$ for a sufficiently large basis set. By this, we underline the physical usefulness of MP*n* perturbation theory as a description of electron correlation in molecules, contrary to other claims [34].

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Appendix

Table A1. MPn($\leqslant 6$) energies obtained with a (10s4p1d/4s1p) [3s2p1d/2s1p] basis set.[a]

System	HF	MP2	MP3	MP4	MP5	MP6
$Li_2(^1\Sigma_g^+)$[b]	−14.866 363	−14.886 539	−14.892 868	−14.895 632	−14.896 898	−14.897 480
		−20.176	−6.329	−2.765	−1.266	−0.581
$LiH(^1\Sigma^+)$[b]	−7.981 187	−8.002 101	−8.006 680	−8.008 047	−8.008 512	−8.008 694
		−20.913	−4.579	−1.368	−0.465	−0.182
$BeH_2(^1\Sigma_g)$	−15.766 877	−15.815 742	−15.826 341	−15.829 112	−15.829 897	−15.830 143
		−48.866	−10.598	−2.771	−0.785	−0.246
$BH(^1\Sigma^+)$	−25.119 227	−25.179 674	−25.195 695	−25.201 704	−25.204 384	−25.205 724
		−60.447	−16.021	−6.009	−2.679	−1.341
$BH_3(^1A_1')$	−26.392 865	−26.486 158	−26.503 337	−26.507 547	−26.508 564	−26.508 856
		−93.293	−17.179	−4.210	−1.017	−0.292
$CH_2(^1A_1)$	−38.875 979	−38.987 138	−30.006 302	−39.012 018	−39.014 025	−39.015 034
		−111.159	−19.164	−5.716	−2.007	−1.010
$CH_2(^3B_1)$	−38.925 338	−39.019 196	−39.034 170	−39.037 787	−39.038 821	−39.039 226
		−93.859	−14.973	−3.617	−1.034	−0.405
$CH_3^+(^1A_1')$	−39.236 195	−39.346 620	−39.364 620	−39.368 917	−39.369 993	−39.370 321
		−110.425	−18.000	−4.298	−1.076	−0.328
$CH_3(^2A_2'')$	−39.564 375	−39.694 601	−39.710 151	−39.714 747	−39.715 826	−39.716 265
		−128.285	−17.490	−4.596	−1.079	−0.439
$CH_4(^1A_1)$	−40.201 692	−40.364 626	−40.382 849	−40.388 644	−40.389 370	−40.389 843
		−162.934	−18.224	−5.794	−0.727	−0.472
$CN(^2\Sigma^+)$	−92.024 659	−92.429 916	−92.438 217	−92.460 021	−92.461 985	−92.469 997
		−225.258	−8.301	−21.804	−1.964	−8.012
$HCN(^1\Sigma)$	−92.875 994	−93.164 898	−93.166 072	−93.187 083	−93.183 182	−93.186 886
		−288.905	−1.174	−21.011	3.900	−3.704
$HNC(^1\Sigma)$	−92.859 026	−93.133 477	−93.140 715	−93.159 697	−93.155 479	−93.160 972
		−274.452	−7.238	−18.982	4.219	−5.493
$CO(^1\Sigma^+)$	−112.737 337	−133.020 036	−113.018 344	−113.041 577	−113.032 531	−113.042 698
		−282.700	1.693	−23.233	9.046	−10.167
$CO_2(^1\Sigma_g)$	−187.632 847	−188.106169	−188.091660	−188.128 967	−188.111 609	−188.129 976
		−473.322	14.509	−37.307	17.358	−18.367
$NH(^1\Sigma^+)$	−54.853 407	−54.957 190	−54.994 553	−55.000 086	−55.002 427	−55.003 736
		−121.783	−19.364	−5.533	−2.342	−1.308
$NH_2(^2B_1)$	−55.564 593	−55.709 950	−55.725 681	−55.729 867	−55.730 967	−55.731 382
		−145.357	−15.731	−4.186	−1.100	−0.415
$NH_3(^1A_1)$	−56.195 200	−56.383 195	−56.295 963	−56.401 375	−56.402 044	−56.402 474
		−187.995	−12.768	−5.412	−0.668	−0.430
$N_2(^1\Sigma_g^+)$	−108.942 662	−109.252 604	−109.247 553	−109.270 688	−109.265 375	−109.269 337
		−309.942	5.051	−23.135	5.313	−3.962
$N_2H_2(^1A_g)$	−109.998 780	−110.333 255	−110.344 139	−110.361 968	−110.361 020	−110.363 579
		−334.475	−10.884	−17.829	0.948	−2.559
$NO(^2\Pi_r)$	−129.246 581	−129.558 317	−129.556 742	−129.580 729	−129.574 661	−129.582 277
		−311.736	1.575	−23.987	6.068	−7.616
$HNO(^1A')$	−129.785 844	−130.132 774	−130.134 719	−130.156 618	−130.152 866	−130.157 862
		−346.930	−1.944	−21.899	3.752	−4.995
$H_2O(^1A_1)$	−76.023 163	−76.219 744	−76.226 097	−76.231 201	−76.231 669	−76.232 052
		−196.581	−6.353	−5.104	−0.467	−0.383
$O_2(^3\Sigma_g^-)$	−149.614 861	−149.947 831	−149.943 164	−149.963 413	−149.960 443	−149.963 284
		−332.970	4.668	−20.249	2.969	−2.840
$H_2O_2(^1A)$	−150.773 501	−151.151 247	−151.157 902	−151.182 927	−151.173 023	−151.174 639
		−377.746	−6.655	−15.025	−0.096	−1.616
$O_3(^1A_1)$	−224.248 888	−224.867 954	−224.826 762	−224.887 000	−224.865 813	−224.889 221
		−619.066	41.192	−60.238	21.187	−23.408

continued

Table A1. *Continued*

System	HF	MP2	MP3	MP4	MP5	MP6
$FH(^1\Sigma^+)$	−100.011 355	−100.194 616	−100.196 399	−100.201 410	−100.201 053	−100.201 621
		−183.262	−1.783	−5.011	0.357	−0.567
$LiF(^1\Sigma^+)$	−106.934 197	−107.126 317	−107.121 279	−107.131 644	−107.125 954	−107.132 474
		−192.120	5.038	−10.365	5.690	−6.520
$F_2(^1\Sigma_g^+)$	−198.673 832	−199.034 838	−199.033 989	−199.050 926	−199.050 441	−199.052 330
		−361.006	0.849	−16.937	0.485	−1.889
$HOF(^1A')$	−174.733 081	−175.099 410	−175.102 226	−175.118 977	−175.117 570	−175.120 260
		−366.329	−2.816	−16.750	1.406	−2.689
$F^-(^1S)$	−99.350 482	−99.526 607	−99.527 506	−99.530 748	−99.530 793	−99.531 036
		−176.125	−0.900	−3.241	−0.046	−0.243
$Ne(^1S)$	−128.474 407	−128.624 722	−128.624 761	−126.629 214	−128.628 220	−128.628 755
		−150.316	−0.038	−4.454	0.995	−0.536

[a] For each example, the first line gives absolute total energies in E_h and the second line absolute energies $\Delta E^{(n)}$ defined by equation (2) in mE_h.
[b] All electrons are included in the MP*n* calculations.

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