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Analysis of fourth-order Møller–Plesset limit energies: the importance of three-electron correlation effects

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Abstract. Fourth-order Møller–Plesset (MP4) correlation energies are computed for 28 atoms and simple molecules employing Dunning's correlation-consistent polarized-valence m-zeta basis sets for $m = 2$, 3, 4, and 5. Extrapolation formulas are used to predict MP4 energies for infinitely large basis sets. It is shown that both total and partial MP4 correlation energies can be extrapolated to limit values and that the sum of extrapolated partial MP4 energies equals the extrapolated total MP4 correlation energy within calculational accuracy. Therefore, partial MP4 correlation energies can be presented in the form of an MP4 spectrum reflecting the relative importance of different correlation effects. Typical trends in calculated correlation effects for a given class of electron systems are independent of the basis set used. As first found by Cremer and He [(1996) *J Phys Chem* 100:6173], one can use MP4 spectra to distinguish between electron systems with well-separated electron pairs and systems for which electrons cluster in a confined region of atomic or molecular space. MP4 spectra for increasing size of the basis set reveal that smaller basis set calculations underestimate the importance of three-electron correlation effects for both classes by overestimating the importance of pair correlation effects. The minimum size of a basis set required for reliable MP4 calculations is given by a valence triple-zeta polarized basis, which even in the case of anions performs better than a valence double-zeta basis augmented by diffuse functions.

Key words: Fourth-order Møller–Plesset spectrum – Complete-basis-set energies – Basis set dependence – Three-electron correlation effects – Electron correlation

1 Introduction

For almost 30 years, many-body perturbation theory (MBPT) with the Møller–Plesset (MP) perturbation operator [1] has been the most frequently used correlation-corrected ab initio method to calculate atomic and molecular energies with sufficient accuracy. The advantages of MBPT are well known and have been documented in the literature in various review articles [2, 3]. Even orders of MBPT introduce new correlation effects by increasing the number of correlating electrons, while odd orders of MBPT essentially introduce a coupling between the clusters of correlating electrons, thus correcting the correlation effects introduced at even orders. For example, second-order MP–MBPT (henceforth abbreviated as MP2) is the simplest Hartree–Fock (HF)-based ab initio method to introduce pair correlation effects (cluster of two electrons, which are separated in the left–right, angular, and in–out fashion) with the help of double (D) excitations [4, 5]. Pair correlation effects are corrected at third-order MBPT–MP (MP3) by a coupling between the D excitations [6, 7].

Fourth-order MP–MBPT (MP4), which covers electron correlation effects described by single (S), D, triple (T), and quadruple (Q) excitations, represents the simplest HF-based ab initio method to introduce three-electron correlation effects via the T excitations [8]. It covers beside pair (D) and three-electron correlation (T) also pair–pair correlation effects described by disconnected Q contributions (two electron pairs are correlated at the same time) and orbital relaxation effects described by the S excitations, which adjust orbitals to the correlated movement of the electrons. Since pair- and three-electron correlation can be considered to represent the most important mechanisms for electron correlation, while orbital relaxation and pair–pair correlation lead to significant corrections, MP4 is the first MBPT method that provides a realistic account of electron correlation. Higher-order correlation effects, which are introduced at fifth or sixth order MBPT–MP (MP5 [9, 10] and MP6 [11–13]) also play a role; however, routine calculations with these methods are costly and are limited to relatively small basis sets.

In quantum chemical investigations, MP calculations have been replaced more and more by coupled-cluster (CC) calculations [3, 14] when high accuracy is needed

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or by density functional theory (DFT) [15] calculations when an effective low-cost description of electron correlation is required. Nevertheless, MP methods are still attractive because they are the only size-extensive ab initio methods that make a systematic investigation of individual correlation effects possible [2]. In this respect, CC methods are difficult to analyze since they cover infinite-order correlation effects, which can only be split up by recording changes in the correlation energy from one iteration step to the next. It has been shown that these changes cover sums of MP correlation contributions for different orders, n [16–18]. DFT is even more difficult to analyze because electron correlation is incorporated in an unspecified way [15]. Correlation effects can only be described in an indirect way by comparing, for example, electron density distributions calculated with DFT and a suitable reference method such as MPn [19]. Therefore, MP theory is still the method best suited to compare different correlation contributions and to investigate the performance of other electron correlation methods on the background of how they perform relative to a given MPn method.

In a recent article, Cremer and He (CHE) [12] analyzed MP perturbation energies up to sixth order and introduced a new way of assessing the importance of correlation effects of a given type. Rather than discussing each electron system separately as is normally done in the literature, these authors grouped the electron systems investigated in two classes (A and B), where in class A, systems with well-separated electron pairs (core, bonding, and lone pairs) are collected while class B contains those electron systems with clustering of electrons in a confined region of atomic or molecular space. CHE could show that for class A systems the MPn series converges monotonically, while for class B systems convergence is erratic with typical initial oscillations. Hence, the convergence behavior of the MPn series for a given electron system calculated up to perturbation order $n = 6$ can be used to classify it as a class A or class B system.

It was argued that the oscillations in the MPn series are caused by strong changes in the magnitude of calculated T contributions when increasing the order n from 4 to 5 and 6 [12]. For class A systems, the three-electron correlation effects are less important because for reasonably separated electron pairs (as assumed in a Lewis pair structure) pair correlation represents the major part of the correlation energy. The description of the pair correlation effects as given by D, disconnected Q, and other pair–pair correlation effects is systematically improved in the MPn series and accordingly the total correlation energy decreases monotonically to the limit value for increasing order. For class B systems, three-electron correlation effects dominate the correlation energy, which oscillates between negative and positive contributions for increasing order, thus causing oscillations of the total correlation energy.

The behavior of pair and three-electron correlation effects with increasing order was made visible by introducing MPn spectra (for $n \geq 4$), which determine the relative contributions of individual correlation energies $E^{(n)}_{YZ\ldots}$, with $Y, Z, \ldots =$ S, D, T, Q averaged over a class of electron systems [12]. The MPn spectra facilitate the analysis and discussion of electron correlation effects by focusing on a whole class of electron systems rather than on individual examples. A number of useful conclusions could be drawn by CHE [12] by analyzing MP4, MP5, and MP6 spectra for classes A and B; however, these conclusions were only valid for the valence double-zeta (VDZ) basis sets used in the CHE study and could not be extended to larger basis sets or even to the limit of a complete basis set (CBS). The use of larger basis sets is, of course, difficult in the case of MP5 and MP6 because the computational cost of these methods rises with $O(M^8)$ and $O(M^9)$, respectively (M: number of basis functions) [2, 9–13]. The CHE study was also limited by the number of examples (15 in total) considered as these were chosen according to the availability of full configuration interaction (FCI) correlation energies. Finally, the CHE investigation suffered from the need of using different VDZ basis sets (employed in the FCI studies) and different geometries (both calculated and experimental) [12].

In this work, we will test the usefulness and the reliability of the information provided by correlation energy spectra in the case of MP4 since MP4 represents the most important MP method in terms of both applicability (cost scale with $O(M^7)$ [2, 8]) and reliability (the most important correlation effects are covered). We will proceed in the way that we

1. Select a set of examples (28 in total; ten from the CHE investigation and 18 new) that systematically represents bonding situations of molecules composed of first-row atoms (excluding Li because of the lack of suitable basis sets).
2. Employ for all examples systematically Dunning's correlation-consistent polarized basis sets [20–25] that provide excellent tools for extrapolating correlation energies to the basis set limit [26, 27].
3. Use consistently experimentally determined geometries [28–38].

Since an MP4 calculation automatically provides MP2 and MP3 correlation energies, we also investigated the behavior of HF, MP2, and MP3 energies and their contributions to the total MP4 energy for increasing size of the basis set. Our final analysis will focus on the ratio between pair and three-electron correlation effects, their importance for class A and class B systems, and the usefulness of MPn spectra for basis sets of given size. In particular, we want to clarify what suggestions can be made with regard to the application of MPn methods for a reliable description of atoms and molecules.

2 Computational methods

Standard MP2, MP3, and MP4 theory [1–8] within the frozen-core approximation was employed throughout this work where radicals were described by unrestricted MPn theory. The following notation was used to distinguish between total and partial correlation energies at fourth order:

$$E(\mathrm{MP4}) = E(\mathrm{HF}) + \Delta E_{\mathrm{MP4}}(\mathrm{corr}) \ , \tag{1}$$

$$\Delta E_{\mathrm{MP4}}(\mathrm{corr}) = \sum_{n=2}^{4} \Delta E^{(n)} \ , \tag{2}$$

$$\Delta E^{(4)} = E_{\mathrm{S}}^{(4)} + E_{\mathrm{D}}^{(4)} + E_{\mathrm{T}}^{(4)} + E_{\mathrm{Q}}^{(4)} \ , \tag{3}$$

where the S, D, and Q part can be represented by $\Delta E_{\mathrm{SDQ}}^{(4)}$, while the T part ($\Delta E_{\mathrm{T}}^{(4)} = E_{\mathrm{T}}^{(4)}$) is taken separately [12]. One has to distinguish between the total MP4 energy, E(MP4), the total correlation energy at MP4, ΔE_{MP4}(corr), made up by the sum of the MP2, MP3, and MP4 correlation energies, $\Delta E^{(n)}$, with $n = 2, 3, 4$, and the individual (partial) correlation energy contributions of the type $E_Y^{(4)}$ ($Y = \mathrm{S}$, D, T, Q).

The MP4 spectra for the class A and class B systems were determined by first scaling the correlation energies for each electron system calculated with a given basis set and, then, averaging scaled correlation energies $\varepsilon_Y^{(4)}$ over all members of the class [12]. The scaling factor, f, for the individual correlation contributions at MP4 was determined using Eq. (4):

$$f = \left[\left(E_{\mathrm{S}}^{(4)} \right)^2 + \left(E_{\mathrm{D}}^{(4)} \right)^2 + \left(E_{\mathrm{T}}^{(4)} \right)^2 + \left(E_{\mathrm{Q}}^{(4)} \right)^2 \right]^{-1/2} \ . \tag{4}$$

The scaled correlation energy contribution, $\varepsilon_Y^{(n)}$, was defined as

$$\varepsilon_Y^{(4)} = \frac{E_Y^{(4)}}{f} \quad \text{with} \quad Y = \mathrm{S, D, T, Q} \ , \tag{5}$$

where the following normalization equation is satisfied:

$$\left(\varepsilon_{\mathrm{S}}^{(4)} \right)^2 + \left(\varepsilon_{\mathrm{D}}^{(4)} \right)^2 + \left(\varepsilon_{\mathrm{T}}^{(4)} \right)^2 + \left(\varepsilon_{\mathrm{Q}}^{(4)} \right)^2 = 1 \ . \tag{6}$$

Since the scaled energies, $\varepsilon_Y^{(4)}$, represent trends and relationships between individual correlation energy contributions in a comparative way, one can average the scaled energies over all examples of a given class according to Eq. (7):

$$\bar{\varepsilon}_Y^{(4)}(\text{class } X) = \frac{1}{N_X} \sum_i^{N_X} \varepsilon_Y^{(4)}(i) \quad \text{for} \quad i \ \varepsilon \ \text{class } X \ , \tag{7}$$

where N_{X} is the total number of electron systems in class $X = \mathrm{A}$, B and Y denotes excitations S, D, T, and Q.

Various extrapolation techniques have been used to predict energies for infinitely large basis sets [39–41]. Such approaches require the availability of basis sets of systematically increasing size so that energies calculated with these basis sets can be extrapolated in a meaningful way. Dunning and coworkers [20–25] solved this problem by developing the correlation-consistent polarized-valence m-zeta basis sets cc-pVmZ, where m is the cardinal number, which determines the size of the basis set ($m = 2$: cc-pVDZ; $m = 3$: cc-pVTZ; $m = 4$: cc-pVQZ; $m = 5$: cc-pV5Z; etc.). By stepwise increasing both the sp basis and the number of polarization functions added to the sp basis, polarized basis sets of monotonically increasing flexibility were obtained (Table 1). Woon and Dunning and Peterson et al. [26, 27] demonstrated that use of the cc-pVmZ basis sets leads to energies and other atomic or molecular properties which monotonically converge toward the CBS limit. Various exponential functions were suggested that model this convergence behavior [26, 27, 39–41], of which the three-parameter function of Eq. (8) turned out to be useful for the calculation of CBS limit energies [27, 39, 40]:

$$E(m) = E(\infty) + a\mathrm{e}^{-m} + b\mathrm{e}^{-m^2} \ , \tag{8}$$

where E stands for E(HF), E(MPn), $\Delta E^{(n)}$, etc., $E(\infty) = E$(CBS) denotes the CBS limit at a given level of theory, and a and b are fitting parameters, which have to be determined in a least-squares minimization procedure. We used Eq. (8) because it provides a simple basis for discussing the convergence behavior of the MPn series. The second and the third term of Eq. (8) describe a slowly ($a > b$) or a fast converging MPn series ($a < b$).

The reliability of $E(\infty)$ depends on the number of energies calculated with basis sets of increasing m, where Dunning used four or five energy points because of limitations resulting from the exponential increase in the size of the basis set with m that limit the cc-pV6Z basis [25], which requires two-electron integral calculations over i-type polarization functions (compare with Table 1).

In the present work, we follow a different strategy to constrain the computational work to a reasonable limit. First, we carried out MP4 calculations with the cc-pVDZ, the cc-VTZ, and the cc-VQZ basis sets to determine the coefficients a and b and the energy $E(\infty)$. Then, the cardinal number was set to $m = 5$ and $E(5)$ was predicted with the help of Eq. (8). For a limited number of electron systems, this energy was checked by MP4 calculations with the cc-pV5Z basis set (Table 1). If predicted and calculated energy differ by more than 1 mhartree, this can be considered as a failure of Eq. (8) because of multireference effects or alternatively a serious clustering of electrons in the system under investigation, which requires the use of larger basis sets for determining Eq. (8). For example, electron clustering occurs for electronegative atoms, such as O or F, for which one has to augment basis sets by diffuse functions. In such a situation, we repeated the fitting procedure using the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets of Kendall et al. [21] (Table 1). Peterson and Dunning [42] showed that augmentation with just one set of diffuse spdf... functions is both necessary and sufficient to describe diffuse charge distributions as found in anions or also electronegative atoms with lone pairs. The newly fitted Eq. (8) was tested in a third step using the aug-cc-pV5Z basis to see whether a satisfactory agreement between calculated and predicted MP4 energies could be obtained after refinement of Eq. (8).

The best MPn energies thus calculated were compared with results already available in the literature and then analyzed by considering partial MP4 contributions in the form of a spectrum.

Table 1. Specification of the basis sets used, from Refs. [20, 21]

Basis set	(primitive basis) [contracted basis]
cc-pVDZ	(9s4p1d/4s1p) [3s2p1d/2s1p]
cc-pVTZ	(10s5p2d1f/5s2p1d) [4s3p2d1f/3s2p1d]
cc-pVQZ	(12s6p3d2f1g/6s3p2d1f) [5s4p3d2f1g/4s3p2d1f]
cc-pV5Z	(14s8p4d3f2g1h/8s4p3d2f1g) [6s5p4d3f2g1h/ 5s4p3d2f1g]
aug-cc-pVDZ	(10s5p2d/5s2p) [4s3p2d/3s2p]
aug-cc-pVTZ	(11s6p3d2f/6s3p2d) [5s4p3d1f/4s3p2d]
aug-cc-pVQZ	(13s7p4d3f2g/7s4p3d2f) [6s5p4d3f2g/5s4p3d2f]
aug-cc-pV5Z	(15s9p5d4f3g2h/9s5p4d3f2g) [7s6p5d4f3g2h/ 6s5p4d3f2g]

3 Results and discussion

The electron systems investigated in this work can be grouped according to their convergence behavior as follows:

1. Class A systems (7): BH ($^1\Sigma^+$), BH$_3$ ($^1\mathrm{A}_1'$), CH$_2$ ($^1\mathrm{A}_1$), CH$_2$ ($^3\mathrm{B}_1$), CH_3^+ ($^1\mathrm{A}_1'$), CH$_3$ ($^2\mathrm{A}_2''$), CH$_4$ ($^1\mathrm{A}_1$).
2. Class B systems (21): CN ($^2\Sigma^+$), HCN ($^1\Sigma$), HNC ($^1\Sigma$), CO ($^1\Sigma^+$), CO$_2$ ($^1\Sigma_\mathrm{g}$), NH ($^1\Sigma^+$), NH$_2$ ($^2\mathrm{B}_1$), NH$_3$ ($^1\mathrm{A}_1$), N$_2$ ($^1\Sigma_g^+$), N$_2$H$_2$ ($^1\mathrm{A}_\mathrm{g}$), NO ($^2\Pi_\mathrm{r}$), HNO ($^1\mathrm{A}'$), H$_2$O ($^1\mathrm{A}_1$), O$_2$ ($^3\Sigma_g^-$), H$_2$O$_2$ (^{1}A), O$_3$ ($^1\mathrm{A}_1$), F$^-$ (^{1}S), FH ($^1\Sigma^+$), F$_2$ ($^1\Sigma_g^+$), HOF ($^1\mathrm{A}'$), Ne (^{1}S).

Calculated MP2, MP3, and MP4 energies of some representative class A and class B electron systems are listed for the cc-pVDZ, cc-pVTZ, and the cc-pVQZ basis sets applied in this work in Tables 2 and 3.[1] Also given are the $E(\infty)$ values as well as the coefficients a and b of Eq. (8) obtained with three energy points.

The cases for which the differences between predicted and calculated MPn/cc-pV5Z energies were tested are summarized in Table 4. MPn energies obtained with the augmented basis sets aug-cc-pVDZ, aug-cc-pVTZ, and

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[1] The complete set of calculated energies can be found under http://www.theoc.gu.se.

Table 2. Hartree–Fock (*HF*), second-order, third-order, and fourth-order Møller–Plesset (*MP2*, *MP3*, and *MP4*) energies of some class A systems for different correlation-consistent polarized-valence *m*-zeta (cc-pV*m*Z) basis sets and the complete basis set (CBS) limit. All bond distances are given in Ångström, and bond angles as well as dihedral angles in degree. All energies are given in hartree. cc-pV∞Z denotes the CBS limit. The fitting coefficients *a* and *b* are defined in Eq. (8). The difference Δ is given by $\Delta = E_S^{(4)}(\mathrm{CBS}) + E_D^{(4)}(\mathrm{CBS}) + E_T^{(4)}(\mathrm{CBS}) + E_Q^{(4)}(\mathrm{CBS}) – \Delta E^{(4)}(\mathrm{CBS})$

System	Energy	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV∞Z	Fitting coefficients	
						a	*b*
BH ($^1\Sigma^+$)	E(HF)	−25.125333	−25.129928	−25.131290	−25.132079	0.043081	0.049991
	$\Delta E^{(2)}$	−0.060537	−0.073515	−0.078147	−0.080841	0.147096	0.021668
$C_{\infty h}$	$\Delta E^{(3)}$	−0.017751	−0.016554	−0.015112	−0.014262	−0.046417	0.152475
	$E_S^{(4)}$	−0.000200	−0.000272	−0.000315	−0.000340	0.001376	−0.002514
r(BH) = 1.233	$E_D^{(4)}$	−0.006718	−0.006312	−0.006172	−0.006091	−0.004443	−0.001425
	$E_T^{(4)}$	−0.000608	−0.001070	−0.001212	−0.001294	0.004495	0.004256
Ref. [28]	$E_Q^{(4)}$	0.001225	0.001679	0.001829	0.001916	−0.004756	−0.002590
	$\Delta E^{(4)}$	−0.006302	−0.005975	−0.005870	−0.005809	−0.003327	−0.002329
	Δ				$< 10^{-6}$		
	E(MP4)	−25.209923	−25.225972	−25.230419	−25.232991	0.140434	0.221806
$CH_2(^1A_1)$	E(HF)	−38.880950	−38.892045	−38.894799	−38.896387	0.086716	0.202097
	$\Delta E^{(2)}$	−0.110392	−0.138859	−0.148354	−0.153869	0.301119	0.148788
$C_{2\mu}$	$\Delta E^{(3)}$	−0.020904	−0.020005	−0.018177	−0.017097	0.058977	0.227922
	$E_S^{(4)}$	−0.000338	−0.000572	−0.000650	−0.000695	0.002474	0.001231
r(CH) = 1.113	$E_D^{(4)}$	−0.005904	−0.005770	−0.005703	−0.005664	−0.002139	0.002695
θ(HCH) = 100.5	$E_T^{(4)}$	−0.001619	−0.003285	−0.003805	−0.004107	0.016468	0.014140
	$E_Q^{(4)}$	0.001986	0.003009	0.003362	0.003567	−0.011203	−0.003553
Ref. [29]	$\Delta E^{(4)}$	−0.005876	−0.006618	−0.006795	−0.006897	0.005567	0.014608
	Δ				−0.000002		
	E(MP4)	−39.018122	−39.057526	−39.068125	−39.074251	0.334458	0.593206
$CH_2(^3B_1)$	E(HF)	−38.926715	−38.937745	−38.940226	−38.941653	0.077893	0.240014
	$\Delta E^{(2)}$	−0.092716	−0.117709	−0.125766	−0.130443	0.255332	0.173142
$C_{2\mu}$	$\Delta E^{(3)}$	−0.016432	−0.016081	−0.014731	−0.013932	−0.043624	0.185847
	$E_S^{(4)}$	−0.000315	−0.000583	−0.000687	−0.000748	0.003308	−0.000823
r(CH) = 1.075	$E_D^{(4)}$	−0.003804	−0.003714	−0.003675	−0.003652	−0.001243	0.000897
θ(HCH) = 133.9	$E_T^{(4)}$	−0.001172	−0.002563	−0.002989	−0.003236	0.013485	0.013049
	$E_Q^{(4)}$	0.001428	0.002167	0.002414	0.002557	−0.007834	−0.003785
Ref. [30]	$\Delta E^{(4)}$	−0.003863	−0.004694	−0.004938	−0.005079	0.007716	0.009393
	Δ				0.000001		
	E(MP4)	−39.039726	−39.076229	−39.085661	−39.091107	0.297317	0.608396

aug-cc-pVQZ are given in Table 5, while results of the aug-cc-pV5Z are shown in Table 6.

Calculated HF, MP2, MP3, and MP4 correlation energies depend exponentially on the size of the basis set defined by the cardinal number *m* [26, 27, 42–45]. The parameters *a* and *b* (Table 2), which according to Eq. (8) reflect the convergence behavior of calculated energies with increasing *m*, reveal that the HF energies and MP3 correlation energies converge much faster ($b > a$) than MP2 correlation energies ($a > b$). For class A systems, convergence of MP4 correlation energies as well as of total *E*(MP4) values is faster than for class B systems.

The usefulness of Eq. (8) and the three-point extrapolation procedure is reflected by the information given in Table 4. In most cases, predicted cc-pV5Z energies agree with the corresponding calculated energies within 1 mhartree or better (Table 4), where one has to consider that these differences will increase with the number of electrons, the electronegativity of the atoms involved, and the anisotropy of the electron density distribution of a given electron system. For the present investigation, we considered this accuracy as sufficient and focused on the obvious trends in the deviations as well as on the only case where the 1 mhartree limit was exceeded, namely the F^- anion (Table 4).

The comparison of calculated and predicted MP4/cc-pV5Z energies (Table 4) reveals that errors in total MP4 energies result from errors in the corresponding HF energies, *E*(HF), as well as in MP2 and MP3 correlation energies, $\Delta E^{(2)}$ and $\Delta E^{(3)}$ but only to a minor degree from MP4 correlation energies, $\Delta E^{(4)}$. The extrapolated HF energies are always too negative because the three-point extrapolation procedure exaggerates the basis set dependence of the HF energies, which after saturation with sp functions decrease much more slowly than predicted by the first three cc-pV*m*Z energy points. Clearly, this saturation is not reached by the cc-pVQZ basis, which was also observed by Dunning and coworkers [25–27, 42–45], who suggested an extrapolation based on four or even five cc-pV*m*Z points, i.e., use of a cc-pV6Z basis, which was not possible in this work. Hence, the three-point extrapolation procedure used in this work will not be sufficient to get a highly accurate HF–CBS energies for a given electron system.

Table 3. HF, MP2, MP3, and MP4 energies of some class B systems for different cc-pV*m*Z basis sets and the CBS limit. All bond distances are given in Ångström, and bond angles as well as dihedral angles in degree. All energies are given in hartree. cc-pV∞Z denotes the CBS limit. The fitting coefficients *a* and *b* are defined in Eq. (8). The difference, Δ, is given by $\Delta = E_{\mathrm{S}}^{(4)}$ (CBS) + $E_{\mathrm{D}}^{(4)}$ (CBS) + $E_{\mathrm{T}}^{(4)}$ (CBS) + $E_{\mathrm{Q}}^{(4)}$ (CBS)$-\Delta E^{(4)}$ (CBS)

System	Energy	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV∞Z	Fitting coefficients	
						a	*b*
NH ($^1\Sigma^+$)	E(HF)	−54.857510	−54.874020	−54.878465	−54.881034	0.140268	0.247926
	$\Delta E^{(2)}$	−0.120090	−0.157602	−0.170636	−0.178213	0.413697	0.116588
$C_{\infty h}$	$\Delta E^{(3)}$	−0.019743	−0.019682	−0.018104	−0.017169	−0.051068	0.236794
	$E_{\mathrm{S}}^{(4)}$	−0.000385	−0.000672	−0.000735	−0.000771	0.001976	0.006482
r(NH) = 1.045	$E_{\mathrm{D}}^{(4)}$	−0.005666	−0.005797	−0.005732	−0.005693	−0.002133	0.017231
	$E_{\mathrm{T}}^{(4)}$	−0.001400	−0.003640	−0.004425	−0.004881	0.024920	0.005944
Ref. [29]	$E_{\mathrm{Q}}^{(4)}$	0.001847	0.003111	0.003605	0.003893	−0.015714	0.004415
	$\Delta E^{(4)}$	−0.005604	−0.006999	−0.007286	−0.007451	0.008984	0.034432
	Δ				−0.000002		
	E(MP4)	−55.002946	−55.058303	−55.074491	−55.083866	0.511880	0.635796
F$^-$ (^{1}S)	E(HF)	−99.365984	−99.424299	−99.444620	−99.456434	0.645022	0.172301
	$\Delta E^{(2)}$	−0.188609	−0.269089	−0.302043	−0.321258	1.049105	−0.509505
	$\Delta E^{(3)}$	−0.001504	0.002783	0.006254	0.008295	−0.111420	0.288298
	$E_{\mathrm{S}}^{(4)}$	−0.000017	−0.001218	−0.001875	−0.002260	0.021004	−0.032755
	$E_{\mathrm{D}}^{(4)}$	−0.001884	−0.003510	−0.004538	−0.005141	0.032921	−0.065430
	$E_{\mathrm{T}}^{(4)}$	−0.000632	−0.006274	−0.009686	−0.011686	0.109213	−0.203436
	$E_{\mathrm{Q}}^{(4)}$	0.000303	0.001996	0.003107	0.003759	−0.035593	0.074313
	$\Delta E^{(4)}$	−0.002230	−0.009006	−0.012992	−0.015328	0.127545	−0.227309
	Δ				$< 10^{-6}$		
	E(MP4)	−99.558327	−99.699611	−99.753401	−99.784725	1.710251	−0.276214
FH ($^1\Sigma^+$)	E(HF)	−100.019415	−100.058016	−100.067690	−100.073271	0.304690	0.689046
	$\Delta E^{(2)}$	−0.201623	−0.271769	−0.297511	−0.312492	0.817910	0.009631
$C_{\infty h}$	$\Delta E^{(3)}$	−0.002909	−0.000192	0.001514	0.002515	−0.054629	0.107542
	$E_{\mathrm{S}}^{(4)}$	−0.000645	−0.001557	−0.001743	−0.001850	0.005821	0.022758
r(FH) = 0.917	$E_{\mathrm{D}}^{(4)}$	−0.002512	−0.003597	−0.003979	−0.004201	0.012128	0.002611
	$E_{\mathrm{T}}^{(4)}$	−0.002028	−0.007037	−0.008859	−0.009919	0.057881	0.003152
Ref. [28]	$E_{\mathrm{Q}}^{(4)}$	0.000985	0.002686	0.003500	0.003976	−0.025977	0.028654
	$\Delta E^{(4)}$	−0.004200	−0.009505	−0.011081	−0.011994	0.049853	0.057176
	Δ				$< 10^{-6}$		
	E(MP4)	−100.228148	−100.339482	−100.374768	−100.395242	1.117825	0.863339
Ne (^{1}S)	E(HF)	−128.488776	−128.531862	−128.543470	−128.550179	0.366312	0.645805
	$\Delta E^{(2)}$	−0.185523	−0.264323	−0.293573	−0.310599	0.929570	−0.039746
	$\Delta E^{(3)}$	−0.002359	−0.000904	−0.000275	0.000092	−0.020042	0.014269
	$E_{\mathrm{S}}^{(4)}$	−0.000272	−0.000999	−0.001124	−0.001195	0.003887	0.021684
	$E_{\mathrm{D}}^{(4)}$	−0.001327	−0.002113	−0.002446	−0.002640	0.010607	−0.006675
	$E_{\mathrm{T}}^{(4)}$	−0.001182	−0.004631	−0.006136	−0.007014	0.047962	−0.035953
	$E_{\mathrm{Q}}^{(4)}$	0.000388	0.001666	0.002354	0.002757	−0.021991	0.033162
	$\Delta E^{(4)}$	−0.002393	−0.006078	−0.007353	−0.008094	0.040465	0.012275
	Δ				0.000001		
	E(MP4)	−128.679051	−128.803166	−128.844670	−128.868779	1.316305	0.632547

The HF error is partially compensated by predicting MP2 correlation energies, which are too positive (Table 4) where absolute errors are normally larger than at the HF level of theory. This confirms that a flexible basis set is much more important for the calculation of correlation energies rather than the HF energy and that even for a V5Z or V6Z basis set electron-pair correlation energies are significantly lowered. Table 4 reveals that the more the MP2 correlation energy is underestimated (large positive errors in Table 3), the more are pair correlation corrections obtained at MP3 are exaggerated (large negative errors), where absolute errors can become even larger than at MP2. This trend can be understood when considering that a rigid basis set does not provide sufficient flexibility for pair correlation and so the mechanism of separating pairs at MP2 leads to new electron clusters so corrections at MP3 become more important the more rigid the basis set is. These trends are, in general, small for class A systems (see BH in Table 4) and increase with increasing clustering of electrons as given by the electronegativity of the heavy atoms of the systems listed in Table 4.

Since new correlation effects enter at MP4, it is not surprising that errors in $\Delta E^{(4)}$ show similar trends to

Table 4. Comparison of energies calculated with the cc-pV5Z basis with those predicted with Eq. (8) for $m = 5$. Differences Δ are given by $\Delta = E_{\mathrm{S}}^{(4)}(5) + E_{\mathrm{D}}^{(4)}(5) + E_{\mathrm{T}}^{(4)}(5) + E_{\mathrm{S}}^{(4)}(5) - \Delta E^{(4)}(5)$, where the 5 in *parentheses* indicates that Eq. (8) was applied with parameters *a* and *b* of Tables 2 and 3 for $m = 5$

System	Energy	Calculated E (hartree)	Extrapolated E (hartree)	Error	
				($\times 10^{-6}$ hartree)	(%)
BH ($^1\Sigma^+$)	E(HF)	−25.131551	−25.131789	−238	
	$\Delta E^{(2)}$	−0.079924	−0.079850	74	−0.09
	$\Delta E^{(3)}$	−0.014154	−0.014575	−421	2.97
	$E_{\mathrm{S}}^{(4)}$	−0.000329	−0.000331	−2	−0.51
	$E_{\mathrm{D}}^{(4)}$	−0.006199	−0.006121	79	1.27
	$E_{\mathrm{T}}^{(4)}$	−0.001265	−0.001264	1	0.07
	$E_{\mathrm{S}}^{(4)}$	0.001884	0.001884	0	0.00
	$\Delta E^{(4)}$	−0.005909	−0.005831	78	1.32
	Δ		$< 10^{-6}$		
	E(MP4)	−25.231539	−25.232045	−506	
NH ($^1\Sigma^+$)	E(HF)	−54.879786	−54.880089	−303	
	$\Delta E^{(2)}$	−0.176056	−0.175426	630	−0.36
	$\Delta E^{(3)}$	−0.016590	−0.017513	−923	5.56
	$E_{\mathrm{S}}^{(4)}$	−0.000769	−0.000758	11	1.46
	$E_{\mathrm{D}}^{(4)}$	−0.005712	−0.005707	5	0.09
	$E_{\mathrm{T}}^{(4)}$	−0.004767	−0.004714	53	1.12
	$E_{\mathrm{S}}^{(4)}$	0.003811	0.003787	−24	−0.63
	$\Delta E^{(4)}$	−0.007437	−0.007390	47	0.64
	Δ		0.000002		
	E(MP4)	−55.079868	−55.080417	−549	
F^- (^{1}S)	E(HF)	−99.455426	−99.452088	3338	
	$\Delta E^{(2)}$	−0.319107	−0.314189	4918	−1.54
	$\Delta E^{(3)}$	0.011234	0.007544	−3690	−32.85
	$E_{\mathrm{S}}^{(4)}$	−0.002912	−0.002118	794	27.25
	$E_{\mathrm{D}}^{(4)}$	−0.005547	−0.004919	628	11.33
	$E_{\mathrm{T}}^{(4)}$	−0.012645	−0.010950	1695	13.40
	$E_{\mathrm{S}}^{(4)}$	0.003747	0.003519	−227	−6.07
	$\Delta E^{(4)}$	−0.017358	−0.014469	2889	16.64
	Δ		$< 10^{-6}$		
	E(MP4)	−99.780657	−99.773202	7445	
FH ($^1\Sigma^+$)	E(HF)	−100.070435	−100.071218	−783	
	$\Delta E^{(2)}$	−0.308300	−0.306981	1319	−0.43
	$\Delta E^{(3)}$	0.003551	0.002146	−1404	−39.57
	$E_{\mathrm{S}}^{(4)}$	−0.001871	−0.001810	61	3.25
	$E_{\mathrm{D}}^{(4)}$	−0.004114	−0.004119	−6	−0.14
	$E_{\mathrm{T}}^{(4)}$	−0.009670	−0.009529	141	1.46
	$E_{\mathrm{S}}^{(4)}$	0.003832	0.003801	−32	−0.82
	$\Delta E^{(4)}$	−0.011823	−0.011658	164	1.39
	Δ		$< 10^{-6}$		
	E(MP4)	−100.387007	−100.387710	−703	
Ne (^{1}S)	E(HF)	−128.546770	−128.547711	−941	
	$\Delta E^{(2)}$	−0.306166	−0.304335	1831	−0.60
	$\Delta E^{(3)}$	0.001344	−0.000043	−1387	−103.20
	$E_{\mathrm{S}}^{(4)}$	−0.001205	−0.001169	36	2.96
	$E_{\mathrm{D}}^{(4)}$	−0.002503	−0.002569	−66	−2.64
	$E_{\mathrm{T}}^{(4)}$	−0.006818	−0.006691	127	1.86
	$E_{\mathrm{S}}^{(4)}$	0.002641	0.002609	−33	−1.24
	$\Delta E^{(4)}$	−0.007884	−0.007821	63	0.79
	Δ		0.000001		
	E(MP4)	−128.859476	−128.859910	−434	

those observed for $\Delta E^{(2)}$ although the former are much smaller. In general, the MP4 correlation energy error is due to underestimating (in absolute terms) the three-electron correlation while overestimating at the same time pair electron correlation, which may lead to cancellation of errors as in the case of the Ne atom. The more class A character an electron system possesses the more these trends may be reverted (see BH, Table 4).

In the case of the F^- anion, the extrapolated MP4 total energy is 7 mhartree above the calculated value (errors in HF energy, MP2, MP3, and MP4 correlation energies are 3, 5, −4, and 3 mhartree, respectively,

Table 5. HF, MP2, MP3, and MP4 energies for different augmented cc-pVmZ (*aug-cc-pVmZ*) basis sets and the CBS limit. All energies are given in hartree. cc-pV∞Z denotes the CBS limit. The fitting coefficients a and b are defined in Eq. (8). The difference Δ is given by $\Delta = E_{\mathrm{S}}^{(4)}(\mathrm{CBS}) + E_{\mathrm{D}}^{(4)}(\mathrm{CBS}) + E_{\mathrm{T}}^{(4)}(\mathrm{CBS}) + E_{\mathrm{S}}^{(4)}(\mathrm{CBS}) - \Delta E^{(4)}(\mathrm{CBS})$

System	Energy	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVSZ	aug-cc-pV∞Z	Fitting coefficients	
						a	*b*
BH ($^1\Sigma^+$)	E(HF)	−25.126427	−25.130200	−25.131370	−25.132049	0.037047	0.033186
	$\Delta E^{(2)}$	−0.062373	−0.074390	−0.078634	−0.081102	0.134747	0.026914
	$\Delta E^{(3)}$	−0.017886	−0.016323	−0.014819	−0.013934	−0.048343	0.141417
	$E_{\mathrm{S}}^{(4)}$	−0.000184	−0.000255	−0.000303	−0.000331	0.001538	−0.003331
	$E_{\mathrm{D}}^{(4)}$	−0.006796	−0.006277	−0.006172	−0.006112	−0.003285	−0.013081
	$E_{\mathrm{T}}^{(4)}$	−0.000716	−0.001122	−0.001235	−0.001300	0.003569	0.005535
	$E_{\mathrm{S}}^{(4)}$	0.001332	0.001726	0.001852	0.001925	−0.003992	−0.002884
	$\Delta E^{(4)}$	−0.006365	−0.005927	−0.005858	−0.005819	−0.002138	−0.014025
	Δ				0.000001		
	E(MP4)	−25.213052	−25.226840	−25.230681	−25.232903	0.121313	0.187437
NH ($^1\Sigma^+$)	E(HF)	−54.865488	−54.876329	−54.879286	−54.880996	0.093343	0.156971
	$\Delta E^{(2)}$	−0.128731	−0.161510	−0.172528	−0.178929	0.349475	0.158423
	$\Delta E^{(3)}$	−0.020031	−0.019347	−0.017601	−0.016569	−0.056370	0.227480
	$E_{\mathrm{S}}^{(4)}$	−0.000706	−0.000759	−0.000764	−0.000767	0.000150	0.002207
	$E_{\mathrm{D}}^{(4)}$	−0.005832	−0.005849	−0.005739	−0.005674	−0.003565	0.017697
	$E_{\mathrm{T}}^{(4)}$	−0.002400	−0.004196	−0.004677	−0.004955	0.015177	0.027356
	$E_{\mathrm{S}}^{(4)}$	0.002326	0.003380	0.003733	0.003938	−0.011196	−0.005289
	$\Delta E^{(4)}$	−0.006612	−0.007425	−0.007447	−0.007457	0.000534	0.042179
	Δ				$< 10^{-6}$		
	E(MP4)	−55.020861	−55.064609	−55.076862	−55.083951	0.387047	0.584692
F^- (^{1}S)	E(HF)	−99.428282	−99.450807	−99.457462	−99.461317	0.210489	0.248352
	$\Delta E^{(2)}$	−0.237666	−0.295072	−0.316945	−0.329683	0.695461	−0.114855
	$\Delta E^{(3)}$	0.009274	0.011862	0.013188	0.013964	−0.042356	0.056921
	$E_{\mathrm{S}}^{(4)}$	−0.005525	−0.005206	−0.004860	−0.004656	−0.011130	0.034806
	$E_{\mathrm{D}}^{(4)}$	−0.005179	−0.006418	−0.006691	−0.006848	0.008566	0.027827
	$E_{\mathrm{T}}^{(4)}$	−0.008815	−0.013663	−0.015003	−0.015778	0.042314	0.067508
	$E_{\mathrm{S}}^{(4)}$	0.001322	0.003077	0.003898	0.004378	−0.026192	0.026696
	$\Delta E^{(4)}$	−0.018196	−0.022211	−0.022657	−0.022905	0.013557	0.156949
	Δ				0.000001		
	E(MP4)	−99.674871	−99.756227	−99.783875	−99.799941	0.877151	0.347254
FH ($^1\Sigma^+$)	E(HF)	−100.033470	−100.061070	−100.068560	−100.072900	0.236437	0.405461
	$\Delta E^{(2)}$	−0.222266	−0.279790	−0.301194	−0.313653	0.680253	−0.036854
	$\Delta E^{(3)}$	−0.000704	0.001147	0.002439	0.003198	−0.041418	0.093017
	$E_{\mathrm{S}}^{(4)}$	−0.002132	−0.002159	−0.001992	−0.001893	−0.005412	0.026933
	$E_{\mathrm{D}}^{(4)}$	−0.003179	−0.003980	−0.004147	−0.004243	0.005230	0.019435
	$E_{\mathrm{T}}^{(4)}$	−0.004864	−0.008563	−0.009509	−0.010055	0.029812	0.063141
	$E_{\mathrm{S}}^{(4)}$	0.001635	0.003053	0.003676	0.004040	−0.019856	0.015427
	$\Delta E^{(4)}$	−0.008540	−0.011650	−0.011972	−0.012150	0.009741	0.125144
	Δ				−0.000001		
	E(MP4)	−100.264980	−100.351370	−100.379290	−100.395500	0.884981	0.586977
Ne (^{1}S)	E(HF)	−128.496350	−128.533270	−128.543760	−128.549820	0.331247	0.471928
	$\Delta E^{(2)}$	−0.206874	−0.272519	−0.297243	−0.311638	0.785944	−0.087461
	$\Delta E^{(3)}$	−0.001547	−0.000207	0.000405	0.000762	−0.019517	0.018121
	$E_{\mathrm{S}}^{(4)}$	−0.001586	−0.001511	−0.001339	−0.001237	−0.005551	0.021983
	$E_{\mathrm{D}}^{(4)}$	−0.001728	−0.002379	−0.002555	−0.002657	0.005555	0.009665
	$E_{\mathrm{T}}^{(4)}$	−0.003340	−0.005896	−0.006674	−0.007125	0.024624	0.024706
	$E_{\mathrm{S}}^{(4)}$	0.000968	0.001995	0.002509	0.002810	−0.016413	0.020731
	$\Delta E^{(4)}$	−0.005686	−0.007791	−0.008059	−0.008209	0.008214	0.077084
	Δ				$< 10^{-6}$		
	E(MP4)	−128.710460	−128.813790	−128.848650	−128.868910	1.105887	0.479672

Table 4), which clearly indicates that the lack of diffuse functions leads to erroneous energies at both the HF and MP levels of theory. Therefore, we repeated the three-point extrapolation approach for the aug-cc-pVmZ basis sets (Table 5). Figure 1 summarizes the decrease in absolute HF and correlation energies for the problem case F^- (top) and some typical class B (middle) or class A systems (bottom). Comparison of predicted and calculated MP4/aug-cc-pV5Z energies (Table 6) reveals that discrepancies are still as large as 1 mhartree at the MP2 and MP3 levels, while the MP4 correlation energy becomes reasonable. In general, the aug-cc-pVmZ basis

Table 6. Comparison of energies calculated with the aug-cc-pV5Z basis with those predicted with Eq. (8) for $m = 5$. The differences Δ are given by $\Delta = E_S^{(4)}(5) + E_D^{(4)}(5) + E_T^{(4)}(5) + E_S^{(4)}(5) - \Delta E^{(4)}(5)$, where the 5 in *parentheses* indicates that Eq. (8) was applied with the parameters *a* and *b* of Tables 2 and 3 for $m = 5$

System	Energy	Calculated E (hartree)	Extrapolated E (hartree)	Error ($\times 10^{-6}$ hartree)	Error (%)
BH ($^1\Sigma^+$)	E(HF)	−25.131596	−25.131799	−203	
	$E^{(2)}$	−0.080212	−0.080194	18	−0.02
	$\Delta E^{(3)}$	−0.013923	−0.014259	−336	2.41
	$E_S^{(4)}$	−0.000321	−0.000321	0	0.09
	$E_D^{(4)}$	−0.006227	−0.006134	93	−1.50
	$E_T^{(4)}$	−0.001275	−0.001276	−1	0.08
	$E_S^{(4)}$	0.001896	0.001898	2	0.12
	$\Delta E^{(4)}$	−0.005927	−0.005833	94	−1.58
	Δ		$< 10^{-6}$		
	E(MP4)	−25.231658	−25.232086	−427	
NH ($^1\Sigma^+$)	E(HF)	−54.879974	−54.880367	−393	
	$\Delta E^{(2)}$	−0.177018	−0.176574	444	−0.25
	$\Delta E^{(3)}$	−0.016186	−0.016948	−763	4.71
	$E_S^{(4)}$	−0.000775	−0.000766	9	−1.19
	$E_D^{(4)}$	−0.005740	−0.005698	42	−0.73
	$E_T^{(4)}$	−0.004870	−0.004853	18	−0.36
	$E_S^{(4)}$	0.003867	0.003865	−4	−0.11
	$\Delta E^{(4)}$	−0.007518	−0.007453	65	−0.86
	Δ		$< 10^{-6}$		
	E(MP4)	−55.080696	−55.081343	−393	
F^- (^{1}S)	E(HF)	−99.459261	−99.459899	−638	
	$\Delta E^{(2)}$	−0.326296	−0.324997	1299	−0.40
	$\Delta E^{(3)}$	0.015043	0.013678	−1365	−9.07
	$E_S^{(4)}$	−0.004729	−0.004731	−2	0.04
	$E_D^{(4)}$	−0.006780	−0.006790	−10	0.15
	$E_T^{(4)}$	−0.015590	−0.015493	97	−0.62
	$E_S^{(4)}$	0.004223	0.004201	−22	−0.52
	$\Delta E^{(4)}$	−0.022876	−0.022814	62	−0.27
	Δ		0.000001		
	E(MP4)	−99.793390	−99.794030	−640	
FH ($^1\Sigma^+$)	E(HF)	−100.070578	−100.071301	−724	
	$\Delta E^{(2)}$	−0.309979	−0.309070	909	−0.29
	$\Delta E^{(3)}$	0.004115	0.002919	−1197	−29.08
	$E_S^{(4)}$	−0.001947	−0.001929	17	−0.89
	$E_D^{(4)}$	−0.004183	−0.004208	−25	0.59
	$E_T^{(4)}$	−0.009905	−0.009854	51	−0.51
	$E_S^{(4)}$	0.003911	0.003906	−5	−0.14
	$\Delta E^{(4)}$	−0.012123	−0.012085	38	−0.31
	Δ		$< 10^{-6}$		
	E(MP4)	−100.388564	−100.389537	−973	
Ne (^{1}S)	E(HF)	−128.546786	−128.547591	−806	
	$\Delta E^{(2)}$	−0.307970	−0.306342	1627	−0.53
	$\Delta E^{(3)}$	0.001871	0.000631	−1241	−66.29
	$E_S^{(4)}$	−0.001278	−0.001275	3	−0.27
	$E_D^{(4)}$	−0.002554	−0.002619	−65	2.54
	$E_T^{(4)}$	−0.007033	−0.006959	74	−1.05
	$E_S^{(4)}$	0.002714	0.002699	−15	−0.54
	$\Delta E^{(4)}$	−0.008152	−0.008154	−2	0.03
	Δ		$< 10^{-6}$		
	E(MP4)	−128.861036	−128.861457	−421	

sets lead to a 20–30% improvement in correlation energies where these values clearly depend for a given electron system on the clustering of electrons and the anisotropy of the charge distribution (e.g., given by the existence of electron lone pairs).

We conclude that the three-point extrapolation procedure applied in this work leads to reasonable CBS limit values for MP4 correlation energies and thereby fulfills the purpose of this investigation, while on the other hand HF, MP2, and MP3 CBS limit values are questionable, which is also confirmed by a direct comparison with CBS limit values published by Dunning and coworkers [42–45] (Table 7). For those electron systems which were studied previously, the differences in

$\Delta E^{(4)}$(CBS) are all smaller than 1 mhartree, mostly in the range from 0 to −0.3 mhartree, although Dunning and coworkers used partially different methods (restricted open-shell rather than unrestricted open-shell theory for radicals as in the present work), partially different basis set combinations for heavy atoms and hydrogen atoms (not done in this work), and always optimized geometries rather than experimental geometries. Clearly, these differences can matter for smaller cardinal numbers, *m*, (less flexible basis sets) and lower orders of MP*n* so the CBS values of Dunning and coworkers are sometimes more negative (Table 7). The three-point extrapolation procedure implies errors of the opposite sign by predicting too negative CBS values for a given geometry. At MP4, calculated CBS values deviate only slightly from those obtained by Dunning and coworkers [42–45] with the help of four- or five-point extrapolations. Since these authors showed that in the case of MP2 their CBS values are close to exact values, [44, 46], we conclude that the MP2/CBS correlation energies given in the present work deviate from the true values on the average by 1.7 mhartree; however, in the case of MP4/CBS correlation energies the deviations are smaller than 0.2 mhartree.

As shown in Table 2, the difference between the sum of extrapolated individual contributions $E_Y^{(4)}$ and the extrapolated total MP4 correlation energy is mostly below 10^{-6} hartree with a few exceptions where the

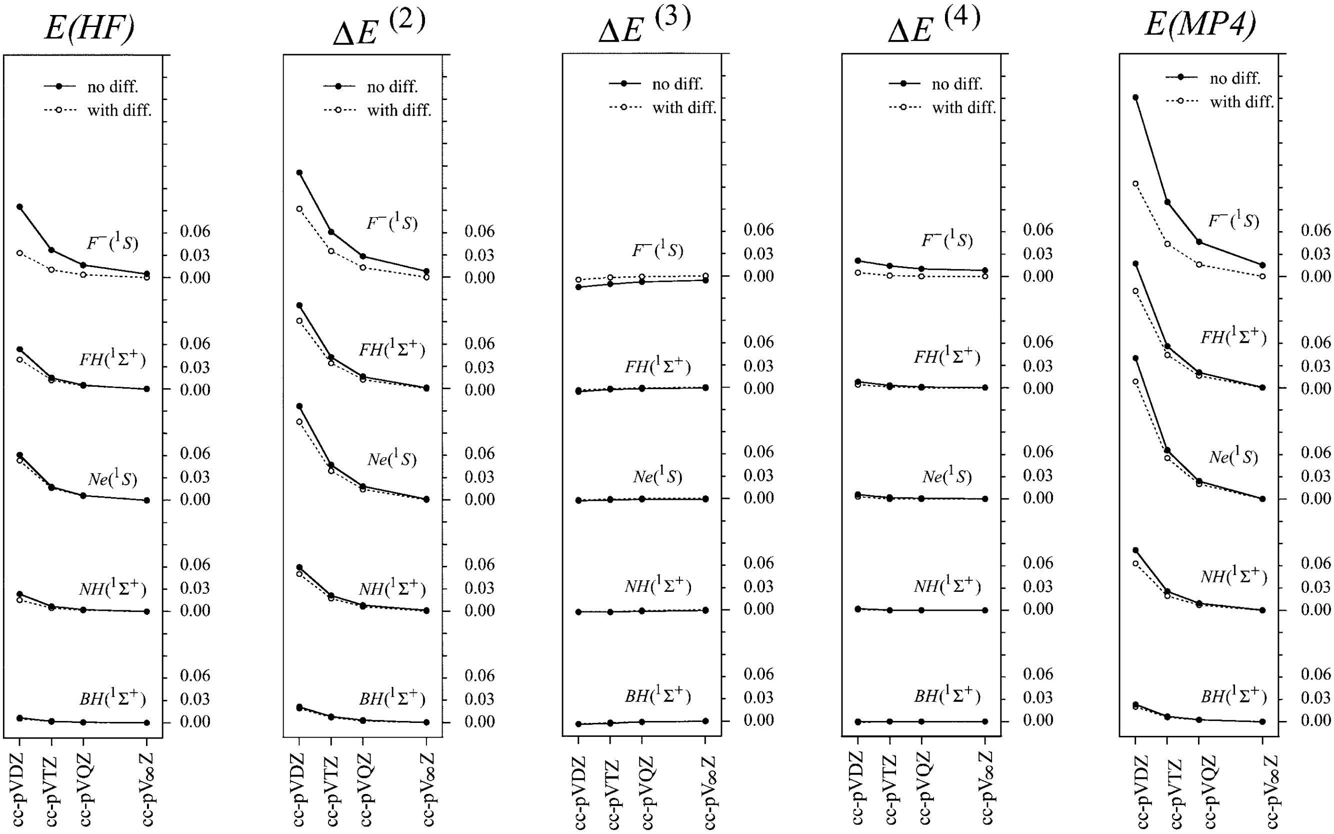

Fig. 1. Dependence of absolute Hartree–Fock energies, *E*(HF), second-order, third-order, and fourth-order Møller–Plesset (*MP2*, *MP3*, and *MP4*) correlation energies, $\Delta E^{(n)}$, on the use of correlation-consistent polarized-valence *m*-zeta (*cc-pVmZ*) (●) and augmented cc-pV*m*Z (*aug-cc-pVmZ*) basis sets (○). Energies are represented in units of 30 mhartree

Table 7. Comparison of CBS limit energies with values published previously. The differences *E* (this work)–*E* (literature) are given in millihartree. See text

Molecule	Basis set	HF	$\Delta E^{(2)}$	$\Delta E^{(3)}$	$\Delta E^{(4)}$	Total	Reference
BH ($^1\Sigma^+$)	cc-pV6Z	−0.4	−0.1	−0.7	0.2	−1.0	43
	CBS	−0.2	0.1	−0.6	0.1	−0.6	
CH_2 ($^3B_1$)	cc-pV5Z/QZ	−6.1	2.8	0.4	−0.1	−3.0	45
CH_3 ($^2A''_2$)	cc-pV5Z/QZ	−5.5	1.6	0.2	−0.2	−3.9	45
CH_4 ($^1A_1$)	cc-pV5Z/QZ	−1.1	−4.4	0.5	−0.1	−5.1	45
CO ($^1\Sigma^+$)	CBS	−0.7	0.3	−2.7	0.0	−3.1	42
N_2 ($^1\Sigma_g^+$)	cc-pV6Z	1.0	−2.6	−2.5	0.0	−4.1	25
	CBS	2.1	−1.9	−2.9	−0.3	−3.0	
FH ($^1\Sigma^+$)	cc-pV6Z	−2.0	0.0	−2.2	0.0	−4.2	25
	CBS	−0.7	0.3	−2.4	0.1	−2.7	
F_2 ($^1\Sigma_g^+$)	cc-pV6Z	2.0	−4.6	−3.5	−0.8	−6.9	43
	CBS	4.2	−2.4	−2.5	−0.6	−1.3	

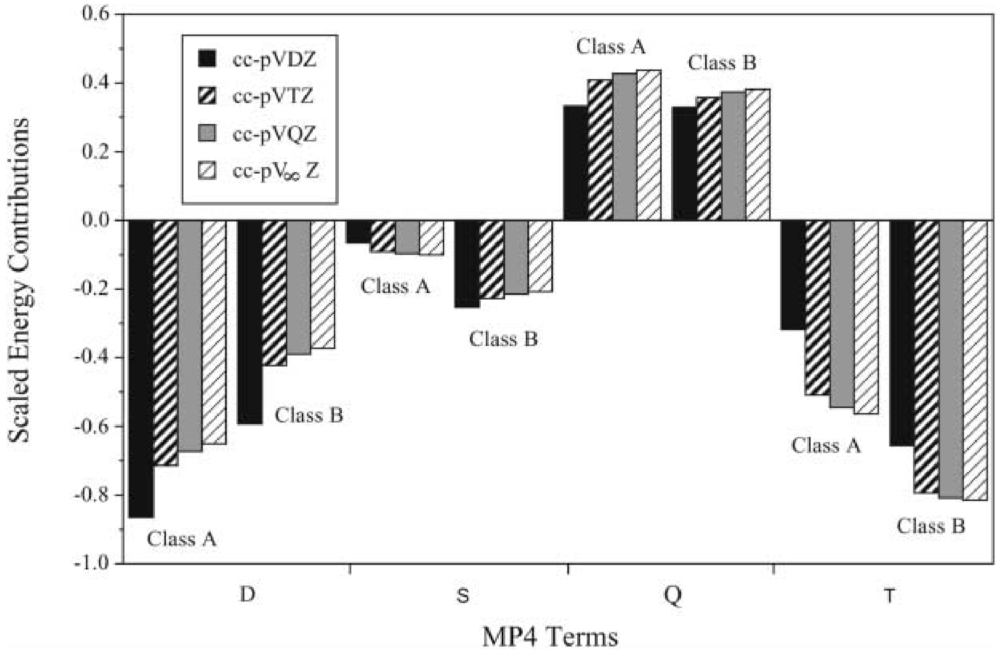

Fig. 2. MP4 spectra shown in the form of a bar diagram for class A and class B systems and for different basis sets of the cc-pVmZ type. The complete basis set (CBS) limit, cc-pV∞Z, is also given

largest difference is just 2×10^{-6} hartree. We can conclude that the monotonic convergence behavior of the $E_Y^{(4)}$ contributions as a function of m is responsible for the monotonic decrease in the MP4 correlation energies. There is no erratic increase (decrease) in two-electron or three-electron correlation effects at MP4 for increasing basis set size, which is a nontrivial observation since the erratic convergence behavior of the three-electron effects, $\Delta E_T^{(n)}$, with increasing n (observed for $m = 2$ [12], but probably valid for any m) is the reason why extrapolation equations such as Eq. (8) cannot be applied to determine MP∞ limit energies [12, 47, 48, 49]. In any case, the data in Table 2 confirm that it is reasonable to investigate MP4 spectra for increasing size of the basis set.

Calculated MP4/cc-pVmZ spectra including the corresponding MP4/CBS spectra are shown in Fig. 2 for class A and class B systems. A number of observations can be made as for the dependence of MP4 partial correlation energies on the basis set size.

1. Although S, D, T, and Q correlation energy contributions change smoothly when the basis set is extended from cc-pVDZ to cc-pV∞Z, the overall pattern of class A and class B spectra is retained, which confirms that conclusions as to the importance of S, D, T, and Q contributions at MP4 made on the basis of VDZ calculations [12] are basically right.
2. Comparison of the MP4/cc-pVDZ spectra with those obtained by CHE [12] reveals that they are largely independent of the type and number of electron systems investigated.
3. The largest changes in the MP4 spectra occur when extending the basis set from cc-pVDZ to cc-pVTZ quality, while the changes accompanying the replacement of the cc-pVTZ basis set by a cc-pVmZ ($m > 3$) basis set are relatively small. This underlines the necessity of using TZP basis sets for standard MP4 calculations.
4. The most interesting changes in the relative magnitude of individual contributions is found for the D excitation effects, which steadily decrease in absolute magnitude while the T contributions steadily increase in absolute magnitude where these effects can be found for both class A and class B systems. (These trends should not be confused with trends in absolute energies, $E_A^{(4)}$.
5. There are small increases in the magnitudes of the Q contributions for the class A and the class B systems.
6. The class A and the class B systems differ slightly with regard to the S contributions since in the former case S contributions become larger in absolute terms, while the absolute values decrease in the latter case with increasing size of the basis set.

The changes in the MP4 spectra can easily be explained by considering the flexibility of the various basis sets employed. The cc-pVDZ basis is relatively rigid and describes only confined regions of atomic and molecular space. Because of this, pair correlation is the major mechanism for electron correlation, while higher-order correlation effects are suppressed. This leads to an artificial exaggeration of pair correlation effects in relation to the three-electron correlation effects. If the flexibility of the basis set increases, i.e., a larger atomic and molecular region is covered by the basis functions, three-electron correlation effects are better described at MP4 and will substantially add to the correlated movements of the electrons. The exaggeration of pair correlation effects is corrected (D contributions are reduced) as can be seen from Fig. 2 both for class A and for class B systems. Consequently, D and T contributions become similar for class A systems, still with a dominance of the latter in the CBS limit (Fig. 2). However, for class B systems T contributions become twice as large as D contributions. The VDZ characterization of class A systems as electron systems, for which pair correlation effects dominate, is still valid

[12]; however, it must be noted from the observation that three-electron correlation effects are almost equally important. This shows that the description of a class A systems as one for which electron pairs are nicely separated is only valid in the model sense of the Lewis electron pair description, while in reality the various electron pairs clearly interact.

The most important correction for an exaggeration of pair correlation at MP4 is provided by the Q contribution, which represents the simultaneous (but disconnected) correlation of two electron pairs. This effect increases with increasing basis set, however it increases less than the three-electron correlation because in its nature it is still a pair correlation effect. For class A systems, this correction is more important since D contributions are more important than for class B systems. In this way, three- and (disconnected) four-electron correlations effects become important and orbital relaxation effects as represented by the S contributions increase; hence, they are larger for class B systems than for class A systems, but increase for the latter in absolute magnitude because of the increased importance of the three electron correlation effects. For class B systems, the balanced adjustment of all MP4 correlation effects with increasing basis set size leads to a slight reduction, which is difficult to explain in terms of a qualitative description.

It is interesting to discuss the MP4 spectra of the F^- anion for the basis sets used (Fig. 3) because the MP4 spectrum uncovers the typical errors, which an inappropriate basis set can cause in a correlation-corrected ab initio calculation. It is well known that the description of electron systems with diffuse charge distributions (such as found in anions or molecules containing atoms with electron lone pairs) requires the use of diffuse basis functions. Figure 3 reveals that a VDZ basis without diffuse functions leads to a large exaggeration of pair correlation effects relative to all other MP4 effects, but in particular with regard to S and T contributions.

The normal suggestion to improve the basis set for an anion is to use a VDZ set augmented by diffuse functions. MP4 calculations with the aug-cc-pVDZ basis are similar in cost to MP4/cc-pVTZ calculations and, therefore, one might ask whether it would not be better to use the cc-pVTZ rather than the aug-cc-pVDZ basis although most quantum chemists would prefer the augmented VDZ basis. Figure 3 clarifies that there are three reasons why a cc-pVTZ basis actually performs better than an aug-cc-pVDZ in such a case.

1. The aug-cc-pVDZ basis leads to an artificial exaggeration of orbital relaxation effects at MP4, which become twice as large as in the CBS limit. For the cc-pVTZ basis, S effects are reasonable although somewhat too small in absolute terms.
2. As a further consequence of the use of the aug-cc-pVDZ basis, both T and Q effects are significantly underestimated compared to the CBS limit, while for the cc-pVTZ basis a better account of these MP4 correlation effects is provided.
3. Calculated $E_Y^{(4)}$ energies based on cc-pVDZ, aug-cc-pVDZ, and aug-cc-pVmZ basis sets behave erratically, while $E_Y^{(4)}$ energies based on cc-V*m*Z basis sets converge monotonically to CBS values largely identical to the CBS values obtained from a series of aug-cc-pV*m*Z calculations.

The comparison given in Fig. 3 underlines recent observations by Cremer et al. [49], namely that the extension of nonsaturated sp basis sets by diffuse functions leads to an unbalanced description of correlation effects at a given order *n*. Clearly, it is much better for a balanced description to increase the basis to VTZ size before adding diffuse functions. Improvements of

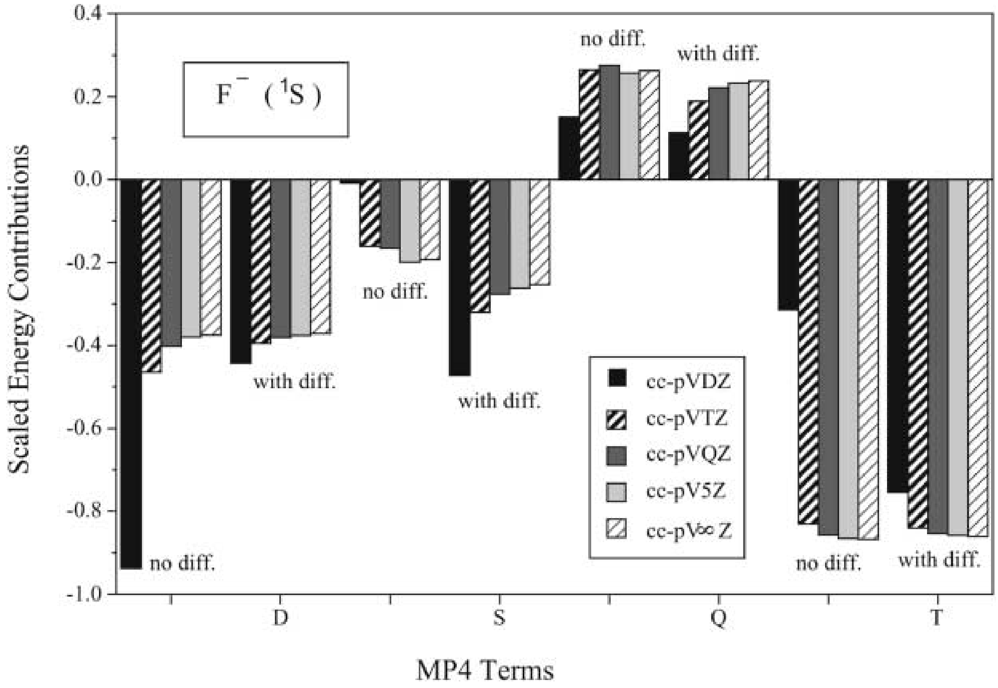

Fig. 3. MP4 spectra of the F^- anion shown in the form of a bar diagram for cc-pV*m*Z (*no diff.*: no diffuse functions) and aug-cc-pV*m*Z (*with diff.*: with diffuse functions). The CBS limits cc-pV∞Z and aug-cc-pV∞Z are also given

both absolute and relative magnitude of calculated $E_Y^{(4)}$ values are not so large when augmenting the cc-pVTZ basis to aug-cc-pVTZ quality (Fig. 3) and, therefore, one might compromise and do all MP4 calculations indiscriminately with the cc-pVTZ basis at the cost of using an extra set of f-type polarization functions. This conclusion is in line with results by Peterson and Dunning [42] for the CO molecule. It also sheds some light on reports about diverging MP*n* series for simple closed-shell systems [50]. These investigations were carried out with aug-cc-pVDZ basis sets, which artificially exaggerate higher-order correlation effects while reducing lower-order effects, thus causing divergence of the MP*n* series [49].

4 Conclusions

A number of conclusions can be drawn from the present investigation.

1. Dunning's extrapolation formulas turn out to be valid for both total MP*n* correlation energies as well as for partial correlation energies $E_Y^{(4)}$. For the 28 electron systems investigated, the sum of extrapolated partial correlation energies is equal to the extrapolated MP4 total correlation energy. This provides the basis for determining MP4/CBS limit spectra.
2. MP4 spectra do not change their general pattern when extending the number and type of electron systems considered in a balanced manner.
3. The MP4 spectra change only gradually with increasing basis set size where the overall pattern of the spectrum is retained. This indicates that even with moderate basis sets, such as VDZ, the basic features of an MP4 spectrum can be assessed and, by this, conclusions with regard to the importance of the various electron correlation effects can be drawn.
4. The most significant basis-set-dependent feature in the MP4 spectra is the ratio of pair and three-electron correlation effects. For class A and class B systems, pair correlation contributions (as covered by the D excitations) decrease, while the three-electron correlation contributions increase with increasing size of the basis set. Class A systems are characterized by D contributions being somewhat larger than the T contribution, while for class B systems three-electron correlation effects are twice as large as pair correlation contributions (in absolute terms).
5. Observation 4 can be generalized by pointing out that with increasing size of the basis set higher-order correlation effects become more important relative to lower-order correlation effects. In the case of MP4, it turns out that three-electron correlation effects are much more important than generally believed.
6. In view of the significant changes in the MP4 spectrum when replacing a cc-pVDZ basis by a cc-pVTZ basis and the moderate changes for any further increase in the basis set, we emphasize the necessity of using TZP basis sets for routine MP4 investigations no matter whether a class A or a class B system is investigated.
7. In general, it is better to use a VTZP basis when describing diffuse charge distributions rather than augmenting a VDZP basis by diffuse functions.

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