
Sixth-Order Many-Body Perturbation Theory. III. Correlation Energies of Size-Extensive MP6 Methods

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ABSTRACT

A comparison of sixth-order Møller–Plesset perturbation energies (MP6) with the corresponding full configuration interaction (FCI) energies shows that in the case of equilibrium geometries MP6 values differ by just 1.7 mhartree. MP6 correlation energies turn out to be important for systems with oscillatory convergence behavior as well as for systems with considerable multireference character. Contributions from pentuple (*P*) and hextuple (*H*) excitations are mostly positive and smaller than 1 mhartree in the cases investigated. Initial oscillations in the convergence behavior of a MP_n series result from positive fifth-order *T* energy contributions to the correlation energy. In these cases, MP6 correlation energies are relatively large (*T* contributions dominate the total correlation energy) and absolutely necessary when estimating the convergence limit of the MP_n series. MP6 is an $O(M^9)$ method and, therefore, can only be used for relatively small electron systems. More economic alternatives are given by the approximated MP6 methods MP6(M8) and MP6(M7), which involve $O(M^8)$ and $O(M^7)$ operations, respectively. According to calculated absolute and relative energies, MP6(M7) is an attractive alternative to full MP6 because it offers reasonable sixth-order results for cost comparable to those of MP4. © 1996 John Wiley & Sons, Inc.

Introduction

In the first two articles of this series, we developed sixth-order Møller–Plesset (MP6) perturbation theory in terms of cluster operators [1] and

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spin-orbital two-electron integral formulas [2]. First applications of the new perturbation theory method have revealed that MP6 correlation energies come close to full configuration interaction (FCI) correlation energies obtained with the same basis set at the same geometry. Comparison with FCI energies is a standard procedure to assess the accuracy of results obtained with a new correlation method. In

this work, we will extend the comparison with FCI energies started in [2] to a larger class of electron systems, for which FCI results are available. Since MP6 is nonvariational, we will check for which electron systems the MP6 correlation energy becomes more negative than the exact FCI correlation energy. In addition, we will compare relative MP6 energies with the corresponding FCI results.

Apart from analyzing sign and magnitude of MP6 correlation energies, we will also investigate the convergence behavior of the MP n series. This has been done by Handy and co-workers [3,4] who determined MP n energies up to as much as $n = 48$ within an FCI calculation. They found that most systems ultimately converge. However, there are electronic systems with rapid convergence beside those with slow convergence where initially oscillatory behavior or spin contamination of the unrestricted Hartree-Fock (UHF) reference function may be the cause for slow convergence [3,4]. Use of a routinely applicable MP6 method can only verify these observations with regard to monotonous or oscillatory convergence behavior at the start of the MP n series ($n \leq 6$). However, contrary to FCI, sixth-order MP theory provides the basis of analyzing individual energy contributions to $E(\text{MP6})$ and, thereby, it may offer some insight into the initial convergence behavior of the MP n series. In this connection, we will try to identify those energy contributions to the correlation energy which cause the MP n series either to converge monotonously or to oscillate. A better understanding of the convergence behavior will help to derive improved extrapolation formulas which could lead to reasonable approximations for correlation energies at infinite order MP theory.

From the derivation of MP6 presented in the first two articles in the series, it is obvious that MP6 is a $O(M^9)$ method and, therefore, can only be used for small electronic systems in connection with benchmark calculations and for testing purposes. However, previous work by Bartlett and co-workers in the case of fifth-order MP (MP5) perturbation theory, which is a $O(M^8)$ method, has shown that it is possible to derive a more economic approximated MP5 method with a $O(M^7)$ dependence by just dropping the expensive TT coupling term [5]. This means that T excitations will be somewhat exaggerated by this method, however, since all other fifth-order coupling terms are included, major fifth-order correlation effects are covered by this method. In view of the work of Bartlett and co-workers, we will inves-

tigate whether useful approximated MP6 methods can be defined.

Comparison of MP6 Energies with FCI Results

FCI energies have been calculated for the atoms and simple molecules listed in Table I [6-9], which accordingly provide an appropriate basis for a comparison with $E(\text{MP6})$ energies obtained with the same basis at the same geometry. The set of reference systems includes charged and uncharged atoms (F and F^-), different states of molecules (3B_2 and 1A_1 state of CH_2 , 2B_1 and 2A_1 state of NH_2) as well as AH_n molecules both at their equilibrium geometry (R_e) and in geometries with (symmetrically) stretched AH bonds ($1.5R_e$, $2R_e$: "stretched geometries"). Calculation of the latter represents a critical test on the performance of a correlation method because wave functions of molecules with stretched geometries possess considerable multireference character. Considering the variations in basis set and in geometry, altogether 26 energy calculations have been carried out.

Calculated MP6 energies and their deviation from FCI energies are given in Table I together with corresponding differences $E(\text{MP}n) - E(\text{FCI})$ obtained for MP4 [10] and MP5 [5]. Atoms and molecules in Table I have been grouped into classes A and B. For class A systems, the MP6 energy is always above (less negative) than the FCI energy, i.e., all differences are positive reaching from 0.275 (No. 7, NH_2 2A_1 , equilibrium) to 34.81 mhartree (No. 9, NH_2 2A_1 with bonds stretched to twice the equilibrium value) depending on the multireference character of the system in question. For class B, most MP6 energies are slightly more negative than FCI energies and, accordingly, differences $E(\text{MP6}) - E(\text{FCI})$ range from -0.004 (No. 16, F atom with $4s3p2d$ basis set) to -8 mhartree (No. 18, F^- , $4s3p1d$ basis set). This is not surprising since similar observations can be made at MP4 (see Table I) just reminding that perturbation theory is not variational.

For the first molecule of class A, BH, the MP6 results differ from FCI by 1.293, 1.448, and 2.186 mhartree at $R = R_e$, $1.5R_e$ and $2.0R_e$. This is about half of the fifth-order differences $E(\text{MP5}) - E(\text{FCI})$ (2.514, 3.310, and 6.054 mhartree, Table I). Clearly the improvement of the MP5 result by MP6 is modest in these cases, which means that the MP n

TABLE I
Comparison of MPn (n = 4, 5, 6) energies with full CI (FCI) energies.^a

Number	Molecule state	Basis	Geom	RHF UHF	$E(\text{MPn}) - E(\text{FCI})$ [mhartree]			Absolute energy		Ref.
					MP4	MP5	MP6	$E_T(\text{MP6})$	$E_T(\text{FCI})$	
Class A										
	BH, $^1\Sigma^+$									
1		(9s5p1d/4s1p)	1.0R _e	R	+5.048	+2.514	+1.293	-25.226322	-25.227615	[6]
2		[4s2p1d/2s1p]	1.5R _e	R	+7.231	+3.310	+1.448	-25.174528	-25.175976	[6]
3			2.0R _e	R	+13.328	+6.054	+2.186	-25.125147	-25.127333	[6]
	NH ₂ , 2B_1									
4		(9s5p1d/4s1p)	1.0R _e	U	+1.900	+0.765	+0.336	-55.742284	-55.742620	[7]
5		[4s2p1d/2s1p]	1.5R _e	U	+39.230	+33.215	+28.264	-55.576945	-55.605209	[7]
6			2.0R _e	U	+18.790	+17.486	+16.688	-55.488836	-55.505524	[7]
	NH ₂ , 2A_1									
7		(9s5p1d/4s1p)	1.0R _e	U	+1.615	+0.651	+0.275	-55.688487	-55.688762	[7]
8		[4s2p1d/2s1p]	1.5R _e	U	+7.779	+4.399	+2.585	-55.515029	-55.517614	[7]
9			2.0R _e	U	+41.297	+37.016	+34.810	-55.380323	-55.415133	[7]
	CH ₂									
10	3B_1	(9s5p1d/4s1p)	R _e	U	+1.880	+0.784	+0.364	-39.045896	-39.046260	[9]
		[4s2p1d/2s1p]								
11	1A_1	(9s5p1d/4s1p)	R _e	R	+4.980	+2.949	+1.977	-39.025206	-39.027183	[9]
		[4s2p1d/2s1p]								
Class B										
	Ne, 1S									
12		4s2p1d		R	-0.873	+0.643	-0.227	-128.702689	-128.702462	[6]
13		5s3p2d		R	-0.563	+0.448	-0.127	-128.769004	-128.768877	[6]
14		6s4p1d		R	-0.651	+0.827	-0.368	-128.768257	-128.767889	[6]
	F, 2P									
15		4s3p1d		U	+0.279	+0.540	+0.021	-99.546599	-99.546620	[8]
16		4s3p2d		U	+0.268	+0.516	-0.004	-99.566487	-99.566483	[8]
17		5s4p2d		U	+0.529	+0.461	+0.020	-99.594857	-99.594877	[8]
	F ⁻ , 1S									
18		4s3p1d		R	-4.748	+7.462	-7.979	-99.661320	-99.653341	[6]
19		4s3p2d		R	-5.044	+7.242	-7.841	-99.685517	-99.677676	[6]
20		5s4p2d		R	-5.398	+6.671	-6.928	-99.713618	-99.706690	[6]
	FH, $^1\Sigma^+$									
21		(9s5p1d/4s1p)	1.0R _e	R	-0.263	+0.811	-0.230	-100.251199	-100.250969	[6]
22		[4s2p1d/2s1p]	1.5R _e	R	+0.769	+2.794	-0.406	-100.160801	-100.160393	[6]
23			2.0R _e	R	+4.841	+8.103	-1.132	-100.082240	-100.081108	[6]
	H ₂ O, 1A_1									
24		(4s1p/9s5p1d)	1.0R _e	R	+0.917	+0.704	+0.078	-76.256546	-76.256624	[6]
25		[2s1p/4s2p1d]	1.5R _e	R	+5.764	+4.984	+1.816	-76.069589	-76.071405	[6]
26			2.0R _e	R	+14.860	+16.965	+4.058	-75.948211	-75.952269	[6]
Mean abs. deviation (all systems)					7.263	6.474	4.672			
Mean abs. deviation (R _e geometries and atoms)					2.185	2.124	1.754			

^aTotal energies $E_T(\text{MP6})$ and $E_T(\text{FCI})$ in hartree, all other energies in mhartree.

series is slowly convergent. This can also be observed for other systems of class A. Nevertheless, the MP6 correlation energy leads to a 98–99% coverage of the exact correlation energy at equilibrium geometries as is indicated by the data of Table II. At stretched geometries (1.5 and 2.0R_e),

this coverage can drop to 80–85% (Table II) because of difficulties in describing a problem with relatively high multireference character by a single determinant approach.

For class A examples, MPn (n = 2, 3, 4, 5, 6) energies are all more positive than the corresponding

TABLE II
Percentage of the correlation energy covered by MP n methods up to the order n ($n = 2, 3, 4, 5, 6$).^a

#	System	MP2	MP3	MP4	MP5	MP6
Class A						
	BH, $^1\Sigma^+$					
1	R_e	72.0	89.2	95.1	97.5	98.7
2	$1.5R_e$	68.0	86.2	93.6	96.8	98.7
3	$2.0R_e$	62.0	80.5	90.4	95.6	98.4
	NH ₂ , 2B_1					
4	R_e	86.6	96.2	98.9	99.5	99.8
5	$1.5R_e$	62.4	72.7	78.3	81.6	84.4
6	$2.0R_e$	67.7	79.9	83.2	84.4	85.1
	NH ₂ , 2A_1					
7	R_e	87.5	96.6	99.0	99.6	99.8
8	$1.5R_e$	82.3	91.1	96.0	97.7	98.7
9	$2.0R_e$	57.7	69.5	73.9	76.0	77.5
	CH ₂					
10	$^3B_1 R_e$	81.5	95.1	98.3	99.3	99.7
11	$^1A_1 R_e$	78.0	92.5	96.5	97.9	98.6
Class B						
	Ne, 1S					
12	$4s2p1d$	96.9	98.1	100.5	99.6	100.1
13	$5s3p2d$	98.8	98.3	100.6	100.2	100.0
14	$6s4p1d$	97.9	97.2	99.8	99.2	100.2
	F, 2P					
15	$4s3p1d$	91.2	97.5	99.8	99.6	100.0
16	$4s3p2d$	91.5	97.5	99.8	99.7	100.0
17	$5s4p2d$	93.3	97.5	99.7	99.7	100.0
	F ⁻ , 1S					
18	$4s3p1d$	98.8	94.7	102.3	96.5	103.8
19	$4s3p2d$	99.0	95.4	102.1	96.9	103.3
20	$5s4p2d$	99.8	94.7	102.1	97.5	102.6
	FH, $^1\Sigma^+$					
21	R_e	96.2	97.3	100.1	99.6	100.1
22	$1.5R_e$	95.3	94.8	99.7	99.0	100.1
23	$2.0R_e$	90.9	89.8	98.2	96.9	100.4
	H ₂ O, 1A_1					
24	R_e	94.0	96.7	99.6	99.7	100.0
25	$1.5R_e$	91.4	90.3	97.9	98.2	99.3
26	$2.0R_e$	85.5	79.8	96.0	95.4	98.9

^aCalculated using FCI energies of Table II.

FCI results, and the contribution $E_{MP}^{(n)} = E(MPn)$ is negative at all orders (see Tables I and II). The differences $E(MPn) - E(FCI)$ monotonously decrease in magnitude with increasing order n of perturbation theory. Excluding the cases with stretched geometries one can observe that at MP4 more than 90% of the FCI correlation energy is covered. At MP5, about half of the remaining correlation energy is recovered. The sixth-order correlation corrections add another quarter of the

difference $E(MP4) - E(FCI)$, which means that for class A the MP n series has more or less the character of a geometrically progressive series.

Class B comprises examples such as Ne, F, F⁻, FH, and H₂O (Table I), for which the convergence behavior of the MP n series is no longer monotonous. In these cases, the sixth-order corrections increase the absolute magnitude of total correlation energies to FCI or even beyond FCI values. This occurs also at the MP4 level in some

cases and in most cases absolute MP4 correlation energies are larger than the corresponding MP5 correlation energies (Table II): $|E(\text{MP6})| > |E(\text{MP4})| > (\text{or } \sim) |E(\text{MP5})|$, and $E(\text{MP6}) \geq 100\%$ with the exception of H_2O ($R = 1.5R_e, 2.0R_e$, see Table II). This means that the correlation energies of class B systems often oscillate in the first five or six orders of the MP_n series. Because of this, sixth-order correlation corrections are relatively important for class B systems.

In Table I, mean absolute deviations for MP4, MP5, and MP6 correlation energies with regard to FCI correlation energies are given. If just equilibrium geometries are considered, then there is a slight improvement from MP4 \sim MP5 energies (mean absolute deviation 2.12 mhartree) to MP6 energies (mean absolute deviation 1.75 mhartree, Table I). If stretched geometries are included in the comparison, then mean absolute deviations become larger by a factor of 3 and decrease more clearly with increasing order n of MP_n perturbation theory (MP4: 7.26, MP5: 6.47, MP6: 4.67 mhartree, Table I). This suggests that fifth- and sixth-order corrections become more important with increasing multireference character of a system and that the relative improvement of energies is larger at the MP6 than the MP5 level of theory.

Size-Extensive MP6(*SDQ*), MP6(*SDTQ*), and MP6(*SDTQPH*)

Table III gives a dissection of the MP6 correlation energy into the 55 partial energy terms that result from the coupling between specific excitations [1]. The terms have been derived by combining, according to Slater rules, the four energy contributions $E_A^{(4)}$ of MP4 due to single (*S*), double (*D*), triple (*T*), and quadruple (*Q*) excitations (given in the first column of Table III) with the 14 energy contributions $E_{AB}^{(5)}$ of MP5 (given in the first row of Table III) and extended by the three additional combinations *pt*, *pq*, *hq* due to pentuple (*P*) and hextuple (*H*) excitations. The 55 MP6 terms $E_{ABC}^{(6)}$ are reduced to 36 unique (given in bold print in Table III) by using symmetry. Each of these terms is size-extensive and, therefore, it is possible to group terms characterized by a certain combination of excitations into subsets, which is indicated in Table III by dashed lines. Such a grouping of terms was first done for the MP4 correlation energy where one distinguishes be-

tween MP4(*SDQ*), MP4(*T*), and full MP4(*SDTQ*) according to Eqs. (1) and (2) [11].

$$E^{(4)}(\text{SDQ}) = E_S^{(4)} + E_D^{(4)} + E_Q^{(4)}, \quad (1)$$

$$E^{(4)}(\text{T}) = E_T^{(4)}. \quad (2)$$

Similarly, one can split MP5 into *SDQ* and *T* part:

$$E^{(5)}(\text{SDQ}) = E_{SS}^{(5)} + 2E_{SD}^{(5)} + E_{DD}^{(5)} + 2E_{DQ}^{(5)} + E_{QQ}^{(5)}, \quad (3)$$

$$E^{(5)}(\text{T}) = 2E_{ST}^{(5)} + 2E_{DT}^{(5)} + E_{TT}^{(5)} + 2E_{TQ}^{(5)}. \quad (4)$$

According to these dissections, we group the 55 (36) MP6 terms into a *SDQ* space, a *T* space, and a *PH* space [12]. $E^{(6)}(\text{SDQ})$ covers 17 (12 unique) terms that involve just *S*, *D*, and *Q* excitations. The *T* excitations can couple with all other but the *H* excitations. If one considers just the coupling between *T* and *S*, *D*, *Q* excitations, 33 (20 unique) *T* terms will be obtained that form the *T* part $E^{(6)}(\text{T})$. There remain the 5 terms *QPQ*, *QHQ*, *TPT*, *TPQ*, and *QPT* that define the *PH* part $E^{(6)}(\text{PH})$ [12].

The dissection given in Table III suggests that one can distinguish between three different MP6 methods, namely the full method MP6(*SDTQPH*), the *SDTQ* method MP6(*SDTQ*), and the *SDQ* method MP6(*SDQ*). Contrary to MP4(*SDQ*) and full MP4(*SDTQ*), where the former method represents a cheaper alternative [$O(M^6)$] to the latter method [$O(M^7)$], all three MP6 methods require $O(M^9)$ operations. This cost factor is due to the $\text{QQQ}(\text{II})_b$ term in the *SDQ* part and the *TQT* and $\text{TQQ}(\text{II})$ terms in the *T* part (see [2]). Hence, the motivation for considering partial MP6 methods is different from that which has led to partial MP4 methods [11]. While in the latter case a partial MP4 method depending on $O(M^6)$ computational steps can be run at about the same cost level as MP2 and MP3, in the case of MP6 the development of approximated methods is motivated by the chance of getting a better knowledge about the convergence behavior of the MP_n series. For example, by analyzing groups of MP6 terms, it is possible to find out which of these groups disturb a monotonous convergence in the case of class B systems (Table I).

The MP6 program described [2] provides the possibility of calculating the three sixth-order energies MP6(*SDQ*), MP6(*SDTQ*), and MP6(*SDTQPH*). The differences of the latter two energies give the

TABLE IV
Energy contributions from SDQ, T, and PH space to $E(MPn)$ ($n = 4, 5, 6$).^a

Systems	n th order	$E^{(n)}(SDQ)$	$E^{(n)}(T)$	$E^{(n)}(P, H)$	$E(MPn)$
Class A					
BH					
R_e	4th	-5.374	-0.627		-6.001
	5th	-2.077	-0.457		-2.534
	6th	-0.960	-0.264	+0.003	-1.221
$1.5R_e$	4th	-7.530	-0.966		-8.496
	5th	-3.276	-0.644		-3.920
	6th	-1.527	-0.346	+0.011	-1.862
$2.0R_e$	4th	-12.127	-1.657		-13.784
	5th	-6.256	-1.018		-7.274
	6th	-3.369	-0.516	+0.016	-3.869
$NH_2, {}^2B_1$					
R_e	4th	-2.129	-2.186		-4.315
	5th	-0.780	-0.345		-1.135
	6th	-0.311	-0.168	+0.049	-0.430
$1.5R_e$	4th	-8.038	-2.020		-10.058
	5th	-5.696	-0.322		-6.018
	6th	-4.778	-0.216	+0.044	-4.950
$2.0R_e$	4th	-2.937	-0.740		-3.677
	5th	-1.024	-0.286		-1.310
	6th	-0.681	-0.119	+0.003	-0.797
$NH_2, {}^2A_1$					
R_e	4th	-1.777	-2.052		-3.829
	5th	-0.685	-0.281		-0.966
	6th	-0.260	-0.158	+0.043	-0.375
$1.5R_e$	4th	-5.584	-3.834		-9.418
	5th	-2.944	-0.436		-3.380
	6th	-1.281	-0.691	+0.158	-1.814
$2.0R_e$	4th	-5.624	-1.137		-6.761
	5th	-2.774	-0.513		-3.287
	6th	-1.901	-0.322	+0.017	-2.206
CH_2					
${}^3B_1, R_e$	4th	-2.462	-1.205		-3.667
	5th	-0.611	-0.485		-1.096
	6th	-0.262	-0.176	+0.018	-0.420
${}^1A_1, R_e$	4th	-4.138	-1.472		-5.610
	5th	-1.363	-0.668		-2.031
	6th	-0.678	-0.318	+0.025	-0.971
Class B					
Ne					
$4s2p1d$	4th	-1.743	-2.562		-4.305
	5th	-0.076	+1.591		+1.515
	6th	-0.074	-0.704	-0.092	-0.870
$5s3p2d$	4th	-1.741	-3.857		-5.598
	5th	-0.290	+1.301		+1.011
	6th	-0.055	-0.534	+0.014	-0.575
$6s4p1d$	4th	-2.815	-3.212		-6.027
	5th	-0.250	+1.728		+1.478
	6th	-0.159	-1.029	-0.007	-1.195

TABLE IV
Energy contributions from SDQ, T, and PH space to $E(MP_n)$ ($n = 4, 5, 6$).^a

Systems	n th order	$E^{(n)}(SDQ)$	$E^{(n)}(T)$	$E^{(n)}(P, H)$	$E(MP_n)$
Class B					
F					
4s3p1d	4th	-1.699	-1.750		-3.449
	5th	-0.405	+0.666		+0.261
	6th	-0.189	-0.316	-0.014	-0.519
4s3p2d	4th	-1.417	-2.504		-3.921
	5th	-0.394	+0.642		+0.248
	6th	-0.183	-0.335	-0.001	-0.519
5s4p2d	4th	-1.337	-3.075		-4.412
	5th	-0.512	+0.444		-0.068
	6th	-0.181	-0.301	+0.041	-0.441
F ⁻					
4s3p1d	4th	-9.336	-6.522		-15.858
	5th	+1.711	+10.499		+12.210
	6th	-2.200	-12.986	-0.254	-15.440
4s3p2d	4th	-7.975	-7.835		-15.810
	5th	+1.585	+10.700		+12.285
	6th	-1.937	-12.949	-0.196	-15.082
5s4p2d	4th	-8.967	-10.283		-19.249
	5th	+1.325	+10.744		+12.069
	6th	-1.552	-12.061	+0.013	-13.600
FH					
R_e	4th	-2.686	-3.015		-5.701
	5th	-0.496	+1.618		+1.122
	6th	-0.164	-0.901	-0.023	-1.088
1.5 R_e	4th	-6.461	-4.623		-11.084
	5th	-1.308	+3.337		+2.029
	6th	-0.774	-2.433	+0.003	-3.204
2.0 R_e	4th	-14.444	-7.674		-22.118
	5th	-3.311	+6.574		+3.263
	6th	-3.657	-5.573	-0.004	-9.234
H ₂ O					
R_e	4th	-2.821	-3.482		-6.303
	5th	-1.011	+0.795		-0.216
	6th	-0.207	-0.516	+0.097	-0.626
1.5 R_e	4th	-13.008	-7.589		-20.597
	5th	-4.301	+3.521		-0.780
	6th	-1.248	-2.505	+0.585	-3.168
2.0 R_e	4th	-40.433	-19.312		-59.745
	5th	-14.894	+17.012		+2.118
	6th	-2.044	-13.782	+2.905	-12.921

^aAll energies in mhartree.

cases of stretched geometries investigated in this work as many as six electrons are involved in such a reorganization process, which means that the observation made in this work, namely that $E^{(6)}(PH)$ values are mostly small, cannot be generalized because their importance will increase with

the number of electrons involved in correlation phenomena.

In Table IV, $E^{(n)}(SDQ)$ and $E^{(n)}(T)$ correlation energies, classified according to a class A or B association of the system in question, are given for $n = 4, 5$, and 6. Analysis of these values reveals

some interesting trends which can be best discussed on the basis of Figures 1 and 2. These Figures give in form of bar diagrams the SDQ (black bars) and T parts (hatched bars) for BH (class A) and FH (class B), respectively.

In the case of BH or any other class A examples $E^{(n)}(SDQ)$ and $E^{(n)}(T)$ correlation energies ($n = 4, 5, 6$) represent negative contributions to $E(MPn)$. Both $E^{(n)}(SDQ)$ and $E^{(n)}(T)$ monotonically decrease with increasing order n thus guaranteeing a monotonic decrease of total energies $E^{(n)}$ and, by this, normal convergence of the MPn series. For BH (and most other class A Systems), the absolute value of $E^{(n)}(SDQ)$ is always larger than the corresponding $E^{(n)}(T)$ value. However, as can be seen from Figure 1, the SDQ contributions decrease almost exponentially with order n while the T contributions decrease only linearly where changes with order n become stronger for the stretched geometries of BH. It appears that the relative importance of the T contributions increases with order n , e.g., in the case of BH from 10 to 18 and 22% for n increasing from 4 to 5 and 6. Of course, this reflects the increase in the number of T terms when going from MP4 (25% T terms) to MP5 (50%) and MP6 (60%).

Class B systems possess a basically different convergence behavior of their T contributions. In Figure 2, the calculated bar diagram for FH (No. 21 – No. 23, $R = R_e, 1.5R_e, 2.0R_e$) is shown. Contrary to BH, the absolute T contributions at MP5 and MP6 are significantly larger than the corresponding SDQ contributions and, in addition, they are positive at fifth-order. Hence, the T contributions dominate the convergence of the MPn series and lead to an initial oscillatory behavior, in par-

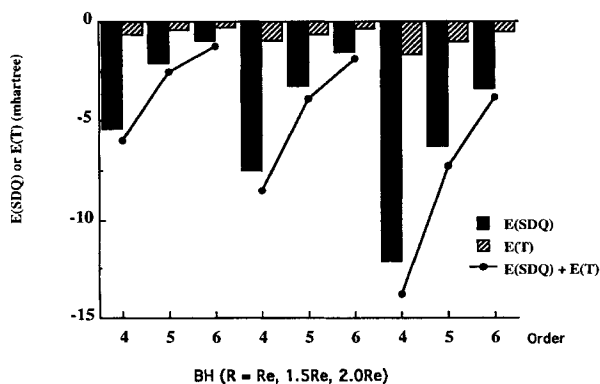


FIGURE 1. SDQ and T contributions to MPn energies for BH for $R = R_e$ (left), $1.5 R_e$ (middle), and $2.0 R_e$ (right).

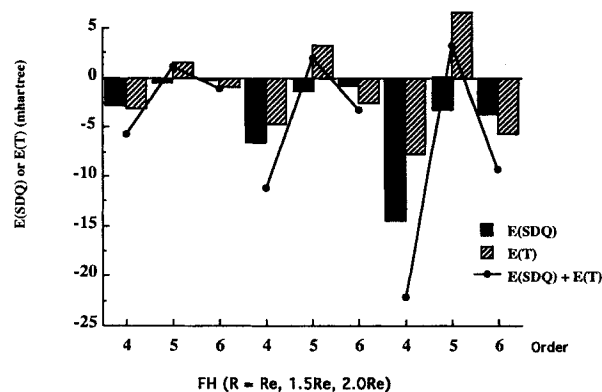


FIGURE 2. SDQ and T contributions to MPn energies for FH for $R = R_e$ (left), $1.5 R_e$ (middle), and $2.0 R_e$ (right).

ticular due to the positive $E^{(5)}(T)$ contributions. This trend is enhanced when considering stretched geometries rather than equilibrium geometries thus indicating that the T excitations cover some of the multireference character typical of geometries with stretched bonds. Although most $E^{(n)}(SDQ)$ energies of class B systems are negative, there are also some small oscillations in these contributions thus adding to the erratic convergence behavior of the MPn series.

Sixth-order correlation energies, in particular the $E^{(6)}(T)$ contributions, are important for class B systems. This is shown by the fact that their absolute values are larger than the corresponding fifth-order values. Apart from this, the convergence behavior of class B molecules can only be determined with the help of MP6 correlation energies.

The data in Table IV and Figures 1 and 2 suggest a regular pattern of $E^{(n)}(SDQ)$ and $E^{(n)}(T)$ correlation contributions in the case of class A systems:

A relatively large value of $|E^{(n)}(SDQ)|$ is complemented by a relatively small value of $|E^{(n)}(T)|$ where both values are negative and decrease with an increase of n . This guarantees a monotonic convergence of the MPn series provided higher terms resulting from P , H , etc. excitations are small and do not play any role.

The difference between class A and B molecules is due to the increased importance of the T contributions and the positive sign of $E^{(5)}(T)$ values in the latter case. This indicates that class A and B systems basically differ with regard to their electronic structure thus leading to differences in their T correlation energies. We are presently investigat-

ing these differences in order to predict convergence behavior of the MP_n series for a given molecule.

MP6(M8) and MP6(M7)

SIZE-EXTENSIVE MP6 METHODS WITH $O(M^8)$ AND $O(M^7)$ DEPENDENCIES

Because of the $O(M^9)$ dependence of all size-extensive MP6 methods discussed above, the ap-

plication of these methods is limited to relatively small atoms and molecules. Therefore, it is interesting to test whether deletion of costly MP6 energy terms leads to useful approximate MP6 methods that are more economic and can be applied to larger molecules. Kucharski and co-workers [13] have investigated because of a similar reason approximate MP5, in which the TT coupling term was neglected and which, therefore, required just $O(M^7)$ rather than $O(M^8)$ operations. Following the spirit of the MP5 investigation, we have

TABLE V
Comparison between full MP6 and the approximate MP6 methods MP6(M8) and MP6(M7).^a

System	$E^{(6)}(M7)$	$\Delta E^{(6)}(M7)$	$\frac{E^{(6)}(M7)}{E^{(6)}} (\%)$	$E^{(6)}(M8)$	$\Delta E^{(6)}(M8)$	$\frac{E^{(6)}(M8)}{E^{(6)}} (\%)$
Class A						
BH						
R_e	-1.104	-0.117	90.38	-1.213	-0.008	99.34
$1.5R_e$	-1.674	-0.189	89.85	-1.842	-0.020	98.90
$2.0R_e$	-3.509	-0.360	90.70	-3.822	-0.047	98.80
$NH_2 \ ^2B_1$						
R_e	-0.328	-0.102	76.33	-0.380	-0.050	88.39
$1.5R_e$	-4.760	-0.190	96.16	-4.911	-0.039	99.21
$2.0R_e$	-0.719	-0.078	90.17	-0.791	-0.007	99.17
$NH_2 \ ^2A_1$						
R_e	-0.279	-0.096	74.31	-0.327	-0.048	87.17
$1.5R_e$	-1.504	-0.309	82.95	-1.674	-0.140	92.28
$2.0R_e$	-2.046	-0.160	92.77	-2.190	-0.016	99.29
CH_2						
$^3B_1 R_e$	-0.317	-0.103	75.47	-0.405	-0.015	96.46
$^1A_1 R_e$	-0.818	-0.154	84.20	-0.947	-0.024	97.48
Class B						
Ne						
$4s2p1d$	-0.793	-0.077	91.11	-0.836	-0.034	96.09
$5s3p2d$	-0.504	-0.071	87.66	-0.492	-0.083	85.64
$6s4p1d$	-1.002	-0.194	83.81	-1.044	-0.151	87.33
F						
$4s3p1d$	-0.469	-0.049	90.48	-0.479	-0.040	92.39
$4s3p2d$	-0.466	-0.054	89.70	-0.471	-0.049	90.61
$5s4p2d$	-0.375	-0.066	85.12	-0.369	-0.072	83.70
F^-						
$4s3p1d$	-13.216	-2.224	85.60	-14.355	-1.085	92.97
$4s3p2d$	-12.890	-2.191	85.47	-13.966	-1.116	92.60
$5s4p2d$	-11.146	-2.183	83.95	-12.365	-1.235	90.92
FH						
R_e	-0.962	-0.126	88.41	-0.992	-0.095	91.19
$1.5R_e$	-2.910	-0.294	90.83	-2.992	-0.212	99.34
$2.0R_e$	-8.670	-0.564	93.89	-8.840	-0.394	95.73
H_2O						
R_e	-0.504	-0.122	80.47	-0.483	-0.143	77.13
$1.5R_e$	-2.760	-0.408	87.13	-2.538	-0.630	80.12
$2.0R_e$	-11.096	-1.825	85.88	-9.450	-3.470	73.14

^aAll energies in mhartree. $\Delta E^{(6)}(M7)$ and $\Delta E^{(6)}(M8)$ are the energy differences $E^{(6)} - E^{(6)}(M7)$ and $E^{(6)} - E^{(6)}(M8)$, respectively.

checked two alternatives. First, we have deleted the three terms $E_{TQT}^{(6)}$, $E_{QQQ}^{(6)}(\text{II})_b$, and $E_{TQQ}^{(6)}(\text{II})$ that require $O(M^9)$ computational steps. In this way, we have obtained an approximate MP6 method [MP6(M8)] with computational requirements $\leq O(M^8)$:

$$E^{(6)}(M8) = E^{(6)}(SDTQPH) - E_{TQT}^{(6)} - E_{QQQ}^{(6)}(\text{II})_b - 2E_{TQQ}^{(6)}(\text{II}). \quad (5)$$

In a second step, we have eliminated all terms that require $O(M^8)$ computational steps. Thus, an approximate $O(M^7)$ method has been obtained [MP6(M7)]:

$$E^{(6)}(M7) = E^{(6)}(M8) - 2E_{DTT}^{(6)} - E_{TTT}^{(6)} - 2E_{TTQ}^{(6)}(\text{II}) - E_{TPT}^{(6)}(\text{II}) - E_{TPQ}^{(6)}(\text{II}) - E_{QPT}^{(6)}(\text{II}) - E_{QPQ}^{(6)}(\text{II}). \quad (6)$$

The performance of MP6(M8) and MP6(M7) is documented in Table V where approximate MP6 correlation energies and their errors are listed. The average errors of MP6(M8) and MP6(M7) are 8 and 13%, respectively, of the total MP6 correlation energy. The difference $\Delta E^{(6)}(M8)$ is with the exception of F^- and the stretched geometry of H_2O considerably smaller than 1 mhartree. This is also true in the case of $\Delta E^{(6)}(M7)$.

The relatively small errors of $E^{(6)}(M8)$ and $E^{(6)}(M7)$ suggest that these methods may be used as economic alternatives to full MP6. There is, however, the necessity of considering two warnings in connection with the use of $E^{(6)}(M8)$ and $E^{(6)}(M7)$. First, it is not sufficient that absolute MP6(M8) and MP6(M7) correlation energies do not differ very much from exact MP6 energies. More important is that relative MP6(M8) and MP6(M7) correlation energies reflect relative MP6 correlation energies in a consistent way. Second, one has to consider that all the observations made in this

TABLE VI
Relative energies (kcal/mol) calculated at the MP n ($n = 2, 3, 4, 5$, and 6) and the full CI (FCI) level of theory.

Problem	$\Delta E(\text{MP}2)$	$\Delta E(\text{MP}3)$	$\Delta E(\text{MP}4)$	$\Delta E(\text{MP}5)$	$\Delta E(\text{MP}6)(M7)$	$\Delta E(\text{MP}6)(M8)$	$\Delta E(\text{MP}6)$	ΔFCI
BH								
$1.5R_e - R_e$	37.10	35.34	33.77	32.90	32.59	32.51	32.50	32.40
$2.0R_e - R_e$	78.11	73.01	68.12	65.15	63.78	63.51	63.49	62.93
$\text{NH}_2, {}^2B_1$								
$1.5R_e - R_e$	114.97	113.26	109.65	106.69	103.85	103.74	103.75	86.23
$2.0R_e - R_e$	157.79	158.98	159.38	159.27	158.92	159.01	159.04	148.78
$\text{NH}_2, {}^2A_1$								
$1.5R_e - R_e$	116.01	114.77	111.26	109.75	109.20	108.90	108.84	107.40
$2.0R_e - R_e$	199.95	197.82	195.98	194.52	193.38	193.35	193.37	171.70
$\text{NH}_2, {}^2A_1 - {}^2B_1$								
R_e	32.62	33.31	33.62	33.72	33.74	33.76	33.76	33.80
$1.5R_e$	33.66	34.83	35.23	36.88	39.09	38.92	38.85	54.97
$2.0R_e$	74.78	72.15	70.22	68.98	68.20	68.10	68.10	56.72
CH_2								
${}^1A_1 - {}^3B_1$	18.33	15.14	13.92	13.33	13.06	12.99	12.98	11.97
$F - F^-$								
$4s3p1d$	73.55	62.34	70.12	62.62	71.22	71.33	71.99	66.97
$4s3p2d$	77.18	65.65	73.11	65.55	73.94	74.02	74.69	69.77
$5s3p2d$	78.03	74.84	84.15	76.53	73.70	73.79	74.52	70.16
FH								
$1.5R_e - R_e$	58.61	60.86	57.48	58.05	56.83	56.80	56.72	56.84
$2.0R_e - R_e$	116.96	120.31	110.01	111.36	106.32	106.21	106.02	106.59
H_2O								
$1.5R_e - R_e$	122.72	128.23	119.26	118.91	117.75	117.62	117.32	116.22
$2.0R_e - R_e$	216.52	233.27	199.73	201.09	195.36	195.57	193.48	190.98
Mean abs. dev. ^a	12.20	12.26	8.26	7.31	5.82	5.80	5.80	

^aThe mean absolute deviation is given with regard to the FCI results of the last column.

work apply to relatively small electron systems. For larger systems, T , Q , P , and H excitations and by this TT , TQ , QQ , etc. coupling effects become more important so that the errors in MP6(M8) and MP6(M7) automatically become larger.

In Table VI, relative energies (in kcal/mol) are compared for various MP_n methods where the corresponding FCI results obtained for the same basis set and geometry are used as the appropriate reference. In this way, we can test the convergence of MP_n relative energies and at the same time also compare approximate MP6 methods with MP6 itself. The mean absolute deviation of MP2 relative energies from the corresponding FCI values is rather large (12.2 kcal/mol), which has to do with the fact that the majority of the problems listed in Table VI involves systems with multireference character. At MP4, the mean absolute deviation decreases to 8.3 kcal/mol, then to 7.3 at MP5 and, finally, to 5.8 at MP6, i.e., the largest reduction in the mean absolute deviation is obtained at MP4 and MP6, which underlines that MP6 leads to the largest improvements after MP4.

The approximate MP6 methods give about the same mean absolute deviations (5.8 kcal/mol, Table VI) than MP6, i.e., the three methods MP6, MP6(M8), and MP6(M7) give very similar relative energies. For example, the singlet-triplet splitting in the case of CH_2 is calculated to be 12.98, 12.99, and 13.06 kcal/mol at MP6, MP6(M8), and MP6(M7), respectively (FCI value 11.97 kcal/mol, Table VI). A similarly good agreement is obtained for the differences between the 2A_1 and the 2B_1 state of NH_2 taken at R_e , $1.5R_e$ and $2R_e$ of the NH bond distance. On the other hand, there is a clear improvement of relative energies when going from MP5 to MP6(M8) or MP6(M7). Since the latter method has similar time requirements as MP4, MP6(M7) is an attractive new method for getting higher order correlation corrections for small and medium-sized molecules.

Conclusions

In the present study, we have reported MP6 correlation energies for small systems, for which FCI values are available. Analysis of these results leads to the following conclusions:

1. The systems investigated in this work can be grouped into classes A and B where $E^{(n)}(MP)$ energies of the first class decrease

monotonically and those of the second class oscillate in the first orders ($n = 2, \dots, 6$) of the MP_n series. This is in line with observations made by Handy and co-workers on the basis of FCI calculations [3, 4].

2. For group A systems, calculated MP6 energies are somewhat more positive than the corresponding FCI energies suggesting that the MP_n correlation energies approach the exact correlation energy value from above. The mean absolute deviation from FCI correlation energies is slightly better at MP6 (1.75 mhartree, Table I) than at MP5. MP6 energies of group B systems are mostly more negative than FCI energies. Mean absolute deviations from FCI energies are clearly better than the corresponding values obtained at MP5 or MP4.
3. MP6 correlation corrections become more important for systems with multireference character.
4. The pentuples-hexuples (PH) part of the MP6 correlation energies normally possesses a positive value clearly smaller than 1 mhartree. Negative values seem to be an artifact of the basis set used.
5. The convergence behavior of the $E^{(n)}(MP)$ series has been analyzed by dissecting calculated correlation energies for $n = 4, 5, 6$ into SDQ , T , and PH part. The analysis shows that differences in the convergence behavior of the MP_n series result from differences in the $E^{(n)}(T)$ values.
 - 5a. For group A systems SDQ and T part are always negative. Because absolute SDQ and T contributions decrease (exponentially or linearly) with increasing n , total correlation energies converge monotonically.
 - 5b. For group B systems, the $|E^{(n)}(T)|$ part of the correlation energy is relatively large (at MP5 and MP6 larger than $|E^{(n)}(SDQ)|$) and oscillates between negative ($n = 4, 6$) and positive values ($n = 5$) while $E^{(n)}(SDQ)$ ($n = 4, 5, 6$) is in most cases negative. Hence, the initial oscillations and nonmonotonic convergence behavior of MP_n correlation energies result from similar oscillations in the $E^{(n)}(T)$ correlation energies.
6. It becomes clear from these observations that an effective way of damping out oscillations in the T part is given by the inclusion of infinite-order contributions from T excita-

tions. For example, in the series *CCSD* [14], *CCSD(T)* [15], and *CCSDT* [6], successively more *TT* terms are included and, in this way, an attractive way of avoiding oscillations in the MP_n series is provided.

7. MP_6 is an $O(M^9)$ method and, therefore, can only be used for relatively small electron systems. More economic alternatives are given by the approximated MP_6 methods $MP_6(M_8)$ and $MP_6(M_7)$, which involve no steps more expensive than $O(M^8)$ and $O(M^7)$, respectively. According to calculated absolute and relative energies, $MP_6(M_7)$ is an attractive alternative to full MP_6 because it offers reasonable MP_6 results for cost comparable to those of a MP_4 calculation.

After this work was submitted, a communication by Kucharski and Bartlett [18] appeared, in which the authors describe how MP_6 can be projected out from the *CCSDTQ* iterations [19,20] with only few terms calculated in addition. *CCSDTQ* is correct in sixth-order and, therefore, presents a starting point for a MP_6 calculation. It is pleasing to see that for the three systems (BH, FH, H_2O) discussed in Ref. 18 the same MP_6 energies are obtained as calculated in the present work thus indicating that both developments lead to reliable results. Apart from this we note that the approach by Kucharski and Bartlett requires the existence of a functioning *CCSDTQ* program, which only few groups [19,20] have managed to set up. It also makes it difficult to determine all MP_6 terms individually, to analyze MP_6 in terms of *SDQ*, *T*, *P*, and *H* excitations and to construct approximate MP_6 methods as done in the present work. The present work develops MP_6 along the lines used for lower order MP_n theory and, therefore, does not require any extra programming in *CC* theory.

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