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Surprising cases of divergent behavior in Møller–Plesset perturbation theory

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High-order Møller–Plesset perturbation calculations have been carried out for several small molecules and compared to full configuration interaction (FCI) results. The convergence of the Møller–Plesset series is found to depend crucially on the one-electron basis sets. Addition of diffuse basis functions leads in some cases to divergent behavior of the Møller–Plesset series, even for highly single reference dominated systems as Ne and HF. The results thus questions the usefulness of higher-order perturbation calculations as a vehicle for obtaining arbitrary accuracy of quantum chemical calculations and raises the fundamental theoretical question: When does Møller–Plesset perturbation theory converge for many-electron systems in extended basis sets? © 1996 American Institute of Physics. [S0021-9606(96)00434-5]

I. INTRODUCTION

Møller–Plesset (MP) perturbation theory¹ is a standard tool to include dynamic electron correlation in electronic structure calculations. If the molecular system is single configuration dominated, it is generally assumed that increased accuracy can be obtained by going to higher order in the Møller–Plesset series. Second-order Møller–Plesset (MP2) theory gives remarkable good results and is the simplest and most widespread method for including electron correlation. During the last ten years, it has become popular to proceed to fourth order² (MP4). Recently, algorithms for explicit calculating all terms through fifth (MP5) and sixth (MP6) order^{3–5} have been implemented, in spite of the vast increasing number of terms that occur in higher-order perturbation theory and the rapidly increasing computational effort.

The convergence characteristics of the MP perturbation series are of fundamental importance for the understanding of the electron correlation problem in many-electron systems. The recent work^{3–5} in the calculations of perturbation contributions through still higher order makes the convergence characteristics of the MP perturbation series of immediate interest. Usually, it is assumed that the convergence only depends on the dominance of the single configuration reference in the exact solution and the related energy gaps in the spectrum. The ground states of molecules without near degeneracies or near lying excited states are thus considered to give convergent MP series. This were supported by calculations of Knowles *et al.*⁶ and Laidig *et al.*,⁷ who used full configuration interaction programs to determine high-order MP energies for small systems, e.g., H₂O in a valence double zeta basis. The relationship between the choice of one-electron functions and the convergence behavior was not examined in these papers, due to limitations of software and hardware.

The recent progress in FCI technology⁸ has made it possible to carry out MP calculations with extended basis sets containing polarization and diffuse functions. In this paper

MP calculations through high order will be presented for several small molecules using valence double zeta polarization (VDZP) and extended VDZP basis sets. In the VDZP basis calculations the convergence behavior of the MP series is found to reflect the dominance of the reference state in the exact solution. Extending the VDZP basis sets to valence triple zeta polarization (VTZP) quality leads typically to slower convergence. If the VDZP basis is augmented with diffuse functions the perturbation series often exhibit divergent behavior. This is found in several systems, including Ne, HF, and H₂O. For HF, which literally speaking is the most typical Hartree–Fock molecule, the contributions in sixth and twentieth order are equal and a clear divergent behavior is observed. Some molecules exhibiting significant near degeneracies as BH and CH₂ converge in all basis sets.

It is well known that many of the Rayleigh–Schrödinger perturbation series that frequently are used to describe a weld of physical situations are actually divergent.⁹ Examples of series that rigorously are proven to be divergent are the hydrogenic stark effect and the fourth power perturbation to the harmonic oscillator. In spite of this the lowest-order terms in an expansion of energies in terms of external electric fields has proven highly useful to describe many properties, including linear and nonlinear optics. In analogy we find here that the lowest-order terms in MP theory give physical reasonable results when the zeroth-order solution is a good approximation to the exact solution and recovers significant parts of the electron correlation. However, going to higher order we find an extreme dependence on the choice of one-electron basis sets, which indicate that the physical significance of higher-order MP perturbation theory is highly questionably.

In a perturbational expansion we expand the energy in terms of a perturbation parameter λ . The mathematical analysis of perturbation theory is given in detail by Kato.¹⁰ It is well known that the behavior in the complex λ -parameter plane is of crucial importance for the convergence of perturbation theory and will affect the behavior at the physical

point $\lambda = 1$. Recently,^{11–16} this has been demonstrated in several investigations on Multiconfigurational perturbation theory, both theoretically and numerically, and remedies for improving convergence in multireference theories have been given. In all these studies attention is paid to cases that are known to be difficult. In this study we investigate cases that for most parts are thought of as being easy, and where standard single reference perturbation theory can straightforwardly be applied. We demonstrate numerically that divergencies in many-body perturbation theories is not restricted to special and difficult cases, but rather that divergencies may occur in simple single reference dominated systems. The occurrence of these divergencies is surprising, in the sense that considering the physical systems under investigation there is no *a priori* reason to expect divergencies. Furthermore, our results demonstrate that the one-electron basis set plays a crucial role with respect to these divergencies. Thus this study brings important new information toward the understanding of the limitations of standard single reference perturbation theory.

In the next section, we give details about the perturbation calculations and in the last section we discuss some of the consequence these results may have for future applications of MP perturbation theory. To allow other workers to study in detail the numerical behavior of the convergent and divergent series, we include in the tables the energy corrections in full length.

II. DETAILS OF CALCULATIONS

Calculations are carried out for Ne, F^- , HF, H_2O , CH_2 , BH, C_2 , and N_2 . For the diatomic molecules we used the following internuclear distances: 0.91694 Å (HF), 2.32898 a.u. (BH), 2.068 a.u. (N_2), and 2.348 a.u. (C_2). For H_2O we used C_{2v} symmetry with the Cartesian coordinates in atomic units O(0,0,0) and H(0, ±1.429 937 284, −1.107 175 113). For CH_2 we used C_{2v} symmetry with the coordinates in atomic units C(0,0,0) and H(±1.644 403, 0, 1.322 13). For all systems we have used the correlation consistent polarized valence double zeta (cc-pVDZ) basis set of Dunning.¹⁷ For C_2 and H_2O , diffuse functions were added with the exponents taken from the aug-cc-pVDZ basis sets.¹⁸ No diffuse polarization functions were included, so the added basis functions are C: $s(0.0469)$, $p(0.040 41)$; O: $s(0.07896)$, $p(0.06856)$; and H: $s(0.02974)$, where the number in parenthesis is the exponent of the augmented orbital. We denote these basis sets as pVDZ(+). For Ne, F^- , CH_2 , BH, and HF we carried out calculations with cc-pVDZ and the aug-cc-pVDZ basis. For Ne, F^- , CH_2 , and HF we performed, in addition, calculations with the cc-pVTZ basis set, where we have left out the f functions on F and Ne and the d functions on H. This basis, denoted pVTZ-(f/d), contains the same number of functions as the aug-pVDZ basis, but the latter contains more diffuse functions. These choices of basis sets thus allow us to compare results obtained with basis set completely equivalent in size, but very different in construction with respect to diffuseness. For BH we performed calculations with double augmented cc-pVDZ, denoted daug-cc-

pVDZ, where the exponents were taken from a geometric succession. Further, we present results for BH using the cc-pVTZ basis and aug-cc-pVTZ. The FCI energies for N_2 , and C_2 , and H_2O in the augmented basis sets have previously been presented in benchmark calculations of excitation energies.²⁰ The above choices of diffuse functions are appropriate for the description of the lowest excited states. The pVDZ(+) basis has been successfully used to calculate the FCI excitation energy spectrum.²⁰

The $1s$ orbitals on the first row atoms were frozen to be the canonical Hartree–Fock orbital in most calculations (indicated by f.c. in the tables). The effect of freezing the core was investigated by performing all electron calculations on BH and H_2O . All MP and FCI calculations obtained have been carried out using the LUCIA program.¹⁹ The energy corrections were evaluated using $2n+1$ formulas. The lower-energy corrections were in addition obtained using the $n+1$ form. The two different ways of obtaining the lowest-order perturbational corrections gave contributions that agreed to 10^{-13} a.u. The MP2 results for all calculations and selected MP3 and MP4 results have been checked against results from standard programs. The calculations cover a wide range of size with the largest (N_2) comprising more than 500 million determinants.

III. RESULTS

In the following sections we describe the results obtained for each molecule separately. We discuss the Ne and F^- cases thoroughly, while we only give brief comments for the rest of the considered molecules.

A. Ne

Table I contains results for Ne obtained in the MP perturbation and FCI calculations using different basis sets. The large weight of the HF reference in the FCI state confirm that Ne is very much single configuration dominated. The weight of the Hartree–Fock reference is approximately the same for all basis sets. The HOMO–LUMO gap differ somewhat in the three basis sets with the smallest gap in the aug-cc-pVDZ basis set, as expected. However, the gap is still rather large in this basis, 1.140 a.u.

The MP series for the cc-pVDZ basis set converges fast. The small error in MP4 may be fortuitous, since the fifth-order contribution is large relative to this error. We find a significant decrease in the errors at even orders MP4, MP6, and MP8. At the MP8 level the error is a few μ hartree. Going from the cc-pVDZ basis to the cc-pVTZ-(f/d) basis the correlation contributions have increased in size and the series is more slowly convergent. The MP4 error is significantly larger than in the cc-pVDZ basis, but the MP4 result is still within one mhartree of the FCI result. To obtain an error of the size of the MP8 error in the cc-pVDZ calculation it is necessary to go to order 12–16 in the cc-pVTZ-(f/d) basis set calculation. For the aug-cc-pVDZ basis set we have carried out MP calculations up to order 65. Unlike for the other two basis sets, we cannot establish convergence in this series. The errors in MP1–MP4 is roughly of the same mag-

TABLE I. MPn and FCI results for Ne in various basis sets. W_{HF} is the weight of the Hartree–Fock reference in the FCI wave function. The FCI energy is given in hartree and the MPn energies is given as the deviation from FCI in mhartree (MPn-FCI). The abbreviation f.c. designate that the 1s(Ne) orbital is frozen.

	cc-pVDZ (f.c.)	aug-cc-pVDZ (f.c.)	cc-pVTZ-(f) (f.c.)
E_{FCI}	-128.679 025	-128.709 476	-128.777 048
gap	2.527	1.140	1.944
W_{HF}	0.972	0.964	0.966
MP1	190.250	213.126	245.186
MP2	4.726	6.252	4.307
MP3	2.368	4.705	5.314
MP4	-0.025	-0.981	-0.643
MP5	0.230	1.032	0.521
MP6	-0.027	-0.550	-0.176
MP7	0.018	0.409	0.103
MP8	-0.002	-0.298	-0.048
MP9	0.001	0.240	0.026
MP10	-0.000	-0.200	-0.013
MP11	0.000	0.175	0.007
MP12	0.000	-0.159	-0.004
MP13	0.000	0.149	0.002
MP14	0.000	-0.144	-0.001
MP15	0.000	0.142	0.005
MP16	0.000	-0.144	0.000
MP17	0.000	0.148	0.000
MP18	0.000	-0.156	0.000
MP19	0.000	0.166	0.000
MP20	0.000	-0.180	0.000
MP21	0.000	0.197	0.000
MP22	0.000	-0.218	0.000
MP23	0.000	0.244	0.000
MP24	0.000	-0.275	0.000
MP25	0.000	0.313	0.000
MP26	0.000	-0.359	0.000
MP27	0.000	0.414	0.000
MP28	0.000	-0.480	0.000
MP29	0.000	0.559	0.000
MP30	0.000	-0.655	0.000
MP31	0.000	0.769	0.000
MP32	0.000	-0.907	0.000
MP33	0.000	1.072	0.000
MP34		-1.270	
MP35		1.509	
MP36		-1.797	
MP37		2.143	
MP38		-2.559	
MP39		3.061	
MP40		-3.665	
MP41		4.393	
MP42		-5.272	
MP43		6.330	
MP44		-7.608	
MP45		9.148	
MP46		-11.007	
MP47		13.251	
MP48		-15.959	
MP49		19.229	
MP50		-23.176	
MP51		27.942	
MP52		-33.700	
MP53		40.653	
MP54		-49.052	
MP55		59.199	
MP56		-71.458	
MP57		86.270	
MP58		-104.167	

TABLE I. (Continued.)

	cc-pVDZ (f.c.)	aug-cc-pVDZ (f.c.)	cc-pVTZ-(f) (f.c.)
MP59		125.795	
MP60		-151.931	
MP61		183.518	
MP62		-221.694	
MP63		267.836	
MP64		-323.609	
MP65		391.024	
% E_{corr} in MP2	97.516	97.066	98.243
% E_{corr} in MP4	100.013	100.460	100.262
% E_{corr} in MP6	100.014	100.258	100.072
% E_{corr} in MP8	100.001	100.140	100.020

nitude in the various basis sets. Beyond MP4 the relative size of the correlation contributions in the aug-cc-pVDZ basis set is much larger than in the cc-pVTZ-(f/d) basis sets. The MP series in the aug-cc-pVDZ basis set shows contributions decreasing in numerical size up to order 15. In MP16, where both the cc-pVDZ and the cc-pVTZ-(f/d) MP series are converged to within one μ -hartree, we find errors of order 0.2 mhartree in the aug-cc-pVDZ basis calculation. The convergence behavior of the MP series for the aug-cc-pVDZ and the cc-pVTZ-(f/d) basis sets is clearly seen from Fig. 1, where the contributions in each order are plotted. We note that from MP4 to MP15, the contributions in consecutive orders approach each other in magnitude. Beyond MP15 the difference between contributions in subsequent orders increase again. We find that the MP series is alternating in all basis sets.

To summarize on neon: addition of diffuse functions turns a fast convergent series into a divergent series.

B. F^-

In Table II results are given for F^- obtained in the MP perturbation and FCI calculations using various basis sets.

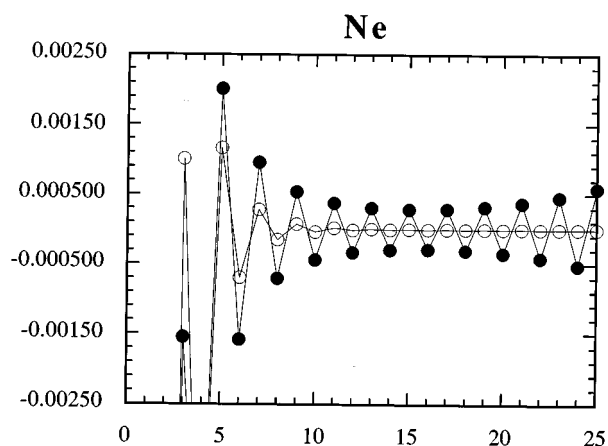


FIG. 1. Correlation contributions for Ne in the cc-pVTZ-(f/d) (○) and aug-cc-pVDZ (●) basis sets.

TABLE II. MPn and FCI results for F^- in various basis sets. W_{HF} is the weight of the Hartree–Fock reference in the FCI wave function. The FCI energy is given in hartree and the MPn energies is given as the deviation from FCI in mhartree (MPn-FCI). Core orbital is frozen.

	cc-pVDZ (f.c.)	aug-cc-pVDZ (f.c.)	cc-pVTZ-(<i>f</i>) (f.c.)
E_{FCI}	-99.558 917	-99.669 369	-99.675 158
gap	2.021	0.690	1.493
W_{HF}	0.964	0.931	0.951
MP1	192.934	241.086	250.859
MP2	4.324	3.421	3.259
MP3	2.820	12.694	7.904
MP4	0.590	-5.502	-1.016
MP5	0.127	7.901	0.864
MP6	0.044	-8.663	-0.194
MP7	0.017	10.870	0.125
MP8	0.004	-13.971	-0.036
MP9	0.002	18.682	0.020
MP10	0.001	-25.686	-0.007
MP11	0.000	36.129	0.003
MP12	0.000	-51.767	-0.001
MP13	0.000	75.291	0.001
MP14	0.000	-110.856	0.000
MP15	0.000	164.861	0.000
MP16	0.000	-247.190	0.000
MP17	0.000	373.123	0.000
MP18	0.000	-566.302	0.000
MP19	0.000	863.347	0.000
MP20	0.000	-1320.006	0.000
MP21	0.000	2027.281	0.000
MP22	0.000	-3118.694	
MP23	0.000	4807.118	
MP24	0.000	-7421.461	
MP25	0.000	11472.422	
MP26	0.000	-17753.108	
MP27	0.000	27495.361	
MP28	0.000	-42 612.629	
MP29	0.000	66 077.304	
MP30	0.000	-102 506.932	
MP31	0.000	159 074.892	
MP32	0.000	-246 925.056	
MP33	0.000	383 369.208	
% E_{corr} in MP2	97.759	98.581	98.701
% E_{corr} in MP4	99.694	102.282	100.405
% E_{corr} in MP6	99.997	103.593	100.077
% E_{corr} in MP8	99.998	105.795	100.014

F^- is isoelectronic with Ne, but as an anion is considerably more diffuse. The effect on the FCI energy of adding a diffuse function is therefore three to four times larger in F^- than in Ne, emphasizing the importance of diffuse functions for obtaining a reasonably description of anions. The Hartree–Fock weight in F^- and Ne is of the same size and approximately the same for all basis sets. The HOMO–LUMO gap differs in the three basis sets with a significantly smaller gap in the aug-cc-pVDZ basis. In the cc-pVDZ the MP series is monotonically converging from above to the FCI energy, similar to that observed for Ne. In the aug-cc-pVDZ basis set the correlation contribution in MP3 and MP4 is considerably larger than in the cc-pVDZ basis. The aug-cc-pVDZ MP4 error is also considerably larger than the corresponding MP4

TABLE III. MPn and FCI results for HF in various basis sets. W_{HF} is the weight of the Hartree–Fock reference in the FCI wave function. The FCI energy is given in hartree and the MPn energies is given as the deviation from FCI in mhartree (MPn-FCI). $1s(F)$ is frozen.

	cc-pVDZ (f.c.)	aug-cc-pVDZ (f.c.)	cc-pVTZ-(<i>f/d</i>) (f.c.)
E_{FCI}	-100.228 640	-100.264 113	-100.312 756
gap	0.813	0.687	0.786
W_{HF}	0.957	0.946	0.949
MP1	209.227	230.645	255.923
MP2	7.602	8.377	6.977
MP3	4.693	7.673	8.467
MP4	0.492	-0.868	-0.851
MP5	0.431	1.684	1.027
MP6	-0.008	-0.972	-0.305
MP7	0.071	0.880	0.235
MP8	-0.013	-0.712	-0.119
MP9	0.014	0.637	0.085
MP10	-0.005	-0.582	-0.054
MP11	0.004	0.553	0.040
MP12	-0.002	-0.538	-0.028
MP13	0.001	0.537	0.021
MP14	-0.001	-0.548	-0.015
MP15	0.000	0.570	0.013
MP16	0.000	-0.602	
MP17	0.000	0.645	
MP18	0.000	-0.702	
MP19	0.000	0.771	
MP20	0.000	-0.858	
MP21	0.000	0.963	
% E_{corr} in MP2	96.367	96.368	97.274
% E_{corr} in MP4	99.765	100.376	100.333
% E_{corr} in MP6	100.004	100.421	100.119
% E_{corr} in MP8	100.006	100.308	100.046

errors in the other calculations in this study. Beyond MP4 the correlation contributions increase in size and the divergent behavior is thus seen very clearly already at the MP5 level. The cc-pVDZ MP series converge monotonically from above, the aug-cc-pVDZ series is oscillating beyond MP3 and divergent. The cc-pVTZ-(*f/d*) series is oscillating and convergent. In the aug-cc-pVDZ basis we find that the smallest error is obtained at the MP2 level. Beyond second-order MP perturbation theory is definitely not a practical approach for obtaining the total energy for F^- . The divergency affects crucially the reliability of the results already in fourth order in the smallest basis set that is reasonably to use for the F^- anion.

C. HF

Table III contains results for HF obtained in MP perturbation and FCI calculations using various basis sets. The results are similar to the Ne results. The cc-pVDZ series converges within a few μ hartree in MP12, while the cc-pVTZ-(*f/d*) series is more slowly convergent. Addition of diffuse functions leads to a divergent behavior with correlation contributions increasing in size beyond MP13. The HF aug-cc-pVDZ and cc-pVTZ-(*f/d*) results are displayed in Fig. 2. Using the cc-pVDZ basis the energy corrections are

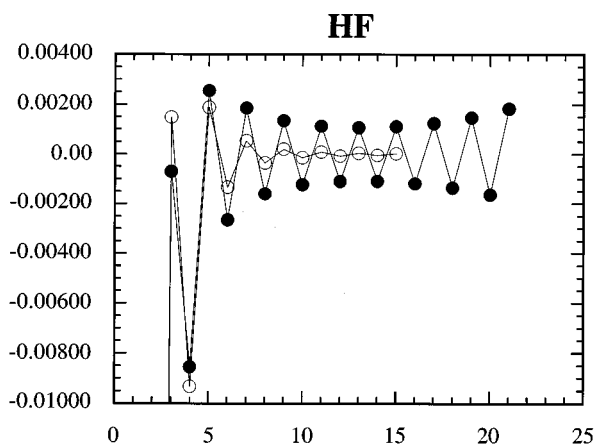


FIG. 2. Correlation contributions for HF in the cc-pVTZ-(*f/d*) (○) and aug-cc-pVDZ (●) basis set.

negative through sixth order, and oscillates through higher order. In the cc-pVTZ-(*f/d*) and aug-cc-pVDZ basis sets the energy corrections oscillate from fourth order.

D. H₂O

In Table IV results are given for H₂O in MP and FCI calculations using various basis sets. In the cc-pVDZ basis the MP series is monotonic and clearly convergent. For the augmented basis set [cc-pVDZ(+)] the MP series becomes alternating after fourth order. The contributions in subsequent orders seem to approach each other in absolute value beyond fourth order and up to order 23, where the perturbation contributions again start to increase in size. Numerical experiments were performed where the core electrons were included. As observed in another recent benchmark calculation, the MP series converges in an all electron cc-pVDZ calculation.²¹

E. CH₂

In Table V are given results for CH₂ in FCI and Møller–Plesset theory. The Hartree–Fock reference has a weight of about 90% in the FCI wave function. This is smaller than for the systems considered up to this point. The cc-pVDZ series is also found to be more slowly convergent than in the previously discussed cc-pVDZ calculations. Inspection of the %E_{corr} in the MP models as given in the tables shows that the MP contributions generally are larger for this molecule than for the previously considered. The MP4 error is five to ten times larger. However, the basis set dependency of the MP series is much smaller than for the previously considered systems. Thus the inclusion of diffuse functions in the basis set does not effect the convergence significantly, and the MP series appears convergent in all basis sets. The convergence is monotonically from above in all basis sets.

TABLE IV. MPn and FCI results for H₂O in various basis sets. W_{HF} is the weight of the Hartree–Fock reference in the FCI wave function. The FCI energy is given in a.u. and the MPn energies is given as the deviation from FCI in mhartree (MPn-FCI) f.c. designate that the 1*s*(O) orbital is frozen.

	cc-pVDZ (f.c.)	cc-pVDZ(+) (f.c.)
E_{FCI}	-76.241 650	-76.258 208
gap	0.679	0.545
W_{HF}	0.942	0.937
MP1	214.842	220.651
MP2	13.233	12.628
MP3	6.228	7.789
MP4	1.000	0.487
MP5	0.477	1.010
MP6	0.116	-0.204
MP7	0.060	0.327
MP8	0.011	-0.190
MP9	0.009	0.176
MP10	0.001	-0.137
MP11	0.000	0.120
MP12	0.000	-0.103
MP13	0.000	0.092
MP14	0.000	-0.083
MP15	0.000	0.076
MP16	0.000	-0.071
MP17	0.000	0.067
MP18	0.000	-0.064
MP19	0.000	0.062
MP20	0.000	-0.061
MP21	0.000	0.060
MP22		-0.060
MP23		0.060
MP24		-0.060
MP25		0.062
MP26		-0.063
MP27		0.065
MP28		-0.068
MP29		0.072
MP30		-0.076
MP31		0.081
% E_{corr} in MP2	93.841	94.277
% E_{corr} in MP4	99.534	99.779
% E_{corr} in MP6	99.946	100.092
% E_{corr} in MP8	99.995	100.086

F. BH

Table VI contains results for BH in FCI and Møller–Plesset theory for a range of basis sets. The Hartree–Fock weight in the FCI wave function is similar to the one in CH₂. In BH we find only minor effects of increasing the basis set size beyond valence double zeta polarization quality. The convergence is unaffected by the addition of diffuse functions. Going from double zeta to triple zeta basis sets gives larger effects, but the general behavior of the perturbation series is unchanged. We note that the BH series converge slowly and monotonically, in accordance with previous investigations on BH.^{5–7} Table VI also give results from all electron calculations in the aug-cc-pVDZ basis sets. Freezing the core electrons does not have significant effect on the convergence of the MP series.

TABLE V. MPn and FCI results for CH₂ in various basis sets. W_{HF} is the weight of the Hartree–Fock reference in the FCI wave function. The FCI energy is given in a.u. and the MPn energies is given as the deviation from FCI in mhartree (MPn-FCI). f.c. designates that the $1s(\text{C})$ orbital is frozen.

	cc-pVDZ (f.c.)	aug-cc-pVDZ (f.c.)	cc-pVTZ-(<i>f/d</i>) (f.c.)
E_{FCI}	−39.023 280	−39.032 446	−39.049 940
gap	0.453	0.421	0.443
W_{HF}	0.906	0.902	0.902
MP1	142.287	148.192	158.327
MP2	31.914	32.510	31.535
MP3	11.005	11.372	11.593
MP4	5.126	5.059	4.990
MP5	3.040	2.914	2.973
MP6	2.049	1.907	1.950
MP7	1.478	1.360	1.409
MP8	1.105	1.010	1.053
MP9	0.845	0.772	0.809
MP10	0.656	0.599	0.630
MP11	0.513	0.470	0.496
MP12	0.404	0.371	0.392
MP13	0.320	0.294	0.312
MP14	0.254	0.234	0.248
MP15	0.201	0.186	0.198
MP16	0.160	0.149	0.158
MP17	0.127	0.118	0.126
MP18	0.101	0.094	0.101
MP19	0.080	0.075	0.080
MP20	0.063	0.060	0.064
MP21	0.050	0.047	0.051
MP22	0.039	0.038	0.040
MP23	0.031	0.030	0.032
MP24	0.024	0.024	0.025
MP25	0.019	0.019	0.020
MP26	0.015	0.015	0.016
MP27	0.012	0.011	0.012
MP28	0.009	0.009	0.010
MP29	0.007	0.007	0.008
MP30	0.005	0.005	0.006
MP31	0.004	0.004	0.005
MP32	0.003	0.003	0.004
MP33	0.002	0.003	0.003
% E_{corr} in MP2	77.571	78.062	80.082
% E_{corr} in MP4	96.397	96.586	96.848
% E_{corr} in MP6	98.560	98.713	98.768
% E_{corr} in MP8	99.223	99.319	99.335

G. C₂

In Table VII results are given for C₂ in MP perturbation calculations and FCI calculations using cc-pVDZ and cc-pVDZ(+) basis sets. As seen from the low weight of the HF reference, this molecule has large nondynamical correlation contributions. In both basis sets we find a very poor convergence of the perturbation series, in fact, we cannot establish convergence numerically. The convergence behavior of the two series is rather similar, exhibiting a highly irregular and unpredictable behavior. While C₂ from the outset is the most difficult case, it appears that the behavior of the MP series is not affected significantly by augmenting the double zeta quality basis set with diffuse functions.

H. N₂

In Table VIII results are given for N₂ in Møller–Plesset and FCI calculations using cc-pVDZ basis sets. We have not been able to carry out calculations for N₂ augmenting this basis set. The convergence is slower for N₂ than for H₂O and HF in similar basis sets but the convergence is significantly faster than for example, for BH.

IV. DISCUSSION

We have presented FCI and MP results for several small molecules close to their equilibrium geometry. Calculations were carried out using valence double zeta basis sets with polarization functions (VDZP), basis sets of valence triple zeta with polarization quality (VTZP), and basis sets where the VDZP basis sets were augmented with diffuse functions. Excluding C₂, all systems are single configuration dominated with a weight of the HF reference in the FCI wave function of 88%–97%. In Table IX, we have summarized the most important features of the MP series.

The convergence up to fourth order reflect to some degree the weight of the Hartree–Fock reference in the FCI solution. MP2 has been very widely used and recovers a large fraction of the correlation energy. Generally MP3 gives no significant improvement compared to MP2, while MP4 improves the energy considerably. The MP4 error may change both sign and magnitude when increasing the basis set, as exemplified by the HF and F[−] calculations, respectively. Thus MP4 does not necessarily give consistent improvements when improving the basis set. The rather large error in the F[−] calculations in fourth order indicates that even fourth-order perturbation theory can be dangerous to use.

Beyond fourth order the convergence behavior is very much dependent on the choice of the one-electron basis set. Going to larger basis sets, the characteristics of the MP series may change dramatically both quantitatively and qualitatively. The qualitative characteristics of the MP series in VTZP quality basis sets appear to be the same as in the VDZP basis, but with somewhat larger contributions in each order and a generally slower convergence. However, augmenting the VDZP basis set with diffuse functions leads in many cases to drastic changes in the behavior of the high-order MP series. In many cases (Ne, F[−], HF, and H₂O) a relatively stable convergent series is turned into a divergent series, while for BH and CH₂ the MP series maintained approximately the same convergent behavior. With the exception of C₂ the systems exhibiting divergent behavior are single configuration dominated, with a large HOMO–LUMO gap between the highest occupied and lowest unoccupied molecular orbitals. All the monotonic series exhibited convergent behavior, whereas in the series exhibiting divergent behavior the MP series were oscillatory beyond fourth order. Oscillatory but convergent behavior was observed in VDZP and VTZP calculations on Ne and HF. For F[−] the VDZP calculation converged monotonically, the augmented VDZP calculation was oscillatory and diverging, and the VTZP cal-

TABLE VI. MPn and FCI results for BH in various basis sets. W_{HF} is the weight of the Hartree–Fock reference in the FCI wave function. The FCI energy is given in hartree and the MPn energies is given as the deviation from FCI in mhartree (MPn-FCI). f.c. designates the core orbital is frozen.

	cc-pVDZ (f.c.)	aug-cc- pVDZ (f.c.)	daug-cc- pVDZ (f.c.)	cc-pVTZ (f.c.)	aug-cc-pVTZ (f.c.)	aug-cc- pVDZ
E_{FCI}	-25.215 126	-25.218 277	-25.218 430	-25.231 132	-25.232 008	-25.219 573
gap	0.404	0.374	0.355	0.397	0.374	0.374
W_{HF}	0.908	0.905	0.905	0.905	0.905	0.905
MP1	89.794	91.850	91.954	101.199	101.807	93.145
MP2	29.262	29.477	29.469	27.686	27.418	29.325
MP3	11.513	11.591	11.591	11.134	11.095	11.514
MP4	5.213	5.227	5.229	5.161	5.168	5.200
MP5	2.580	2.571	2.573	2.620	2.633	2.568
MP6	1.331	1.319	1.320	1.288	1.399	1.324
MP7	0.693	0.686	0.686	0.749	0.757	0.692
MP8	0.355	0.354	0.354	0.406	0.412	0.359
MP9	0.177	0.178	0.179	0.219	0.223	0.183
MP10	0.084	0.087	0.087	0.116	0.119	0.090
MP11	0.037	0.040	0.040	0.060	0.062	0.042
MP12	0.014	0.017	0.017	0.031	0.032	0.018
MP13	0.004	0.006	0.006	0.015	0.016	0.007
MP14	-0.001	0.001	0.001	0.007	0.007	0.002
MP15	-0.002	-0.001	-0.001	0.003	0.003	0.000
MP16	-0.002	-0.001	-0.001	0.001	0.001	0.000
MP17	-0.002	-0.001	-0.001	0.000	0.000	0.000
MP18	-0.001	-0.001	-0.001	0.000	0.000	0.000
MP19	-0.001	-0.001	-0.001	0.000	0.000	0.000
MP20	-0.001	-0.001	-0.001	0.000	0.000	0.000
MP21	-0.001	-0.001	-0.001	0.000	0.000	0.000
MP22	0.000	0.000	-0.001	0.000	0.000	0.000
MP23	0.000	0.000	-0.001	0.000	0.000	0.000
MP24	0.000	0.000	-0.001	0.000	0.000	0.000
% E_{corr} in MP2	67.412	67.907	67.952	72.642	73.069	68.517
% E_{corr} in MP4	94.194	94.309	94.313	94.900	94.923	94.417
% E_{corr} in MP6	98.517	98.563	98.564	98.628	98.626	98.579
% E_{corr} in MP8	99.605	99.615	99.615	99.599	99.595	99.614

ulation was oscillatory and converging. Using augmented VDZP we found that the MP contributions began to increase in numerical value beyond, respectively, order 15, 14, and 24 for Ne, HF, and H₂O. In these systems it was observed that the even- and odd-order contributions are of opposite sign and approach each other in magnitude up to the point where the contributions starts to increase in size. After this the difference between contributions in subsequent order increase.

In a recent investigation³ Cremer and He have divided molecules into classes according to different characteristics of the MP series up to sixth order. Indeed we have observed that the calculated MP series in most cases agree with these classifications. However, we have also found that the size of the MP contributions depends crucially on the basis sets employed, and the convergence of the MP series may completely change nature upon extension of the basis set. While the investigation in Ref. 3 is restricted to low order and convergence is assumed, we have carried out high-order calculations using various basis sets and demonstrated that diver-

gent series are obtained in a number of cases. Cremer and He's division of molecules into classes with different convergence behavior is, in fact, even more interesting in light of the present work.

By augmenting a basis set with diffuse functions we expand the region in ordinary configuration space that we are able to describe without improving the valence space description considerably. It is, of course, possible that the augmented basis sets in some sense induce divergence in an artificial way, since the valence basis sets are rather small. However, the basis sets we have used are standard type basis sets. The use of augmented functions is mandatory in some situation, for example, in calculations on anions, excited states, and polarizabilities. Even if one could argue that the divergent behavior only occurs for specific choices of basis sets, there are severe problems in MP theory if one cannot expect standard basis set to give convergent MP series. And going to larger and more complete basis sets, one will eventually enter into the region described by the augmented dif-

TABLE VII. MPn and FCI results for C_2 in various basis sets. W_{HF} is the weight of the Hartree–Fock reference in the FCI wave function. The FCI energy is given in hartree and the MPn energies is given as the deviation from FCI mhartree (MPn-FCI). $1s(C)$ is frozen.

	cc-pVDZ (f.c.)	cc-pVDZ(+) (f.c.)
E_{FCI}	-75.721 843	-75.730 209
gap	0.349	0.341
W_{HF}	0.687	0.687
MP1	334.940	342.245
MP2	24.167	30.735
MP3	56.545	63.222
MP4	-12.927	-6.468
MP5	22.899	29.733
MP6	-14.763	-8.429
MP7	8.421	15.383
MP8	-12.150	-5.817
MP9	-0.430	6.530
MP10	-8.735	-2.300
MP11	-5.745	1.113
MP12	-6.082	0.513
MP13	-8.387	-1.666
MP14	-4.777	1.969
MP15	-9.083	-2.473
MP16	-4.716	2.122
MP17	-8.586	-2.021
MP18	-5.426	1.428
MP19	-7.600	-1.011
MP20	-6.359	0.449
MP21	-6.667	-0.011
MP22	-7.093	-0.361
MP23	-6.098	0.632
MP24	-7.427	-0.763
MP25	-5.967	0.815
MP26	-7.373	
MP27	-6.170	
MP28	-7.077	
MP29	-6.520	
MP30	-6.729	
MP31	-6.837	
% E_{corr} in MP2	92.785	91.020
% E_{corr} in MP4	103.859	101.890
% E_{corr} in MP6	104.408	102.463
% E_{corr} in MP8	103.627	101.700

fuse functions. Furthermore, judged from the relative stability of the Hartree–Fock weight of the reference function in the FCI function as well as the HOMO–LUMO gap, the physics in our description is essentially unchanged.

The combined consideration of the physical relevant situation (perturbation parameter $\lambda=1$) and the zeroth-order spectrum (perturbation parameter $\lambda=0$) is not sufficient to predict the behavior of MP perturbation theory. Although this is obvious from a mathematical point of view, it has only been demonstrated in difficult cases like excited states and typical multireference problems with near lying physical states. However, in this study, the systems exhibiting divergent behavior are commonly thought of as standard examples of cases where single reference perturbation theory is an appropriate tool, since the lowest energies are well separated for $\lambda=0, 1$. No physical states occur as intruder states.

TABLE VIII. MPn and FCI results for N_2 in a cc-pVDZ basis set. W_{HF} is the weight of the Hartree–Fock reference in the FCI wave function. The FCI energy is given in hartree and the MPn energies is given as the deviation from FCI in mhartree (MPn-FCI). $1s(N)$ is frozen.

	cc-pVDZ (f.c.)
E_{FCI}	-109.276 527
gap	0.787
W_{HF}	0.879
MP1	321.974
MP2	16.686
MP3	20.726
MP4	-1.450
MP5	3.244
MP6	-0.321
MP7	0.532
MP8	0.021
MP9	0.063
MP10	0.034
MP11	0.001
MP12	0.012
MP13	-0.002
MP14	0.002
MP15	-0.001
% E_{corr} in MP2	94.817
% E_{corr} in MP4	100.450
% E_{corr} in MP6	100.100
% E_{corr} in MP8	99.994

TABLE IX. Summary of the most important characteristics of the numerical MP series.

Molecule	Basis	Convergence	Oscillating/monotonic beyond MP4
Ne	VDZP	conv.	osc.
	aug-VDZP	div.	osc.
	VTZP	conv.	osc.
F^-	VDZP	conv.	mon.
	aug-VDZP	div.	osc.
	VTZP	conv.	osc.
HF	VDZP	conv.	osc.
	aug-VDZP	div.	osc.
	VTZP	conv.	osc.
H_2O	VDZP	conv.	mon.
	aug-VDZP	div.	osc.
CH_2	VDZP	conv.	mon.
	aug-VDZP	conv.	mon.
	VTZP	conv.	mon.
BH	VDZP	conv.	mon.
	aug-VDZP	conv.	mon.
	VTZP	conv.	mon.
	aug-VTZP	conv.	mon.
C_2	VDZP	?	irregular
	aug-VDZP	?	irregular
N_2	VDZP	conv.	irregular

Thus, even for cases where we for physical reasons should expect perturbation theory to be a reliable and accurate approach, artificial degeneracies in the complex plane may deteriorate the physically relevant series at $\lambda=1$. In this numerical study of high-order MP theory, we have demonstrated that the presence of these problems depends crucially on the used basis sets.

The present study questions the use of higher-order MP in quantum chemistry. There is little consistency, neither quantitatively nor qualitatively, in the results obtained in different basis sets. The result therefore clearly shows the difficulty in using MP perturbation theory as a scheme for obtaining increasingly accurate approximations to the solution of the Schrödinger equation. This has practical significance, as seen from our F^- calculation. For the systems exhibiting divergent behavior the reference state is clearly nondegenerate and constitutes a large fraction of the exact state, so the absence of near degeneracies is no guarantee for a convergent MP series, and it is difficult to predict *a priori* whether in a given basis set the MP series will converge. Since the size of the correlation contributions and the overall convergence in the MP series is crucially affected by the choice of one-electron basis sets, it raises the fundamental theoretical question if one can expect higher-order MP contributions to have physical significance at all in extended basis sets?

In this paper we have abstained from any form of resummation techniques such as Padé approximants or Feenberg scaling.^{22,23} It is possible to extract a convergent behavior for the Ne, HF, and H_2O cases using very simple resummation techniques. This will be addressed in a subsequent paper, where we also analyze the nature of the singularities in more detail. We are, however, skeptical to the idea of calculating high-order corrections at great expense if these corrections only have importance in connection with resummation techniques.

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