Convergence Behavior of the Møller–Plesset Perturbation Series: Use of Feenberg Scaling for the Exclusion of Backdoor Intruder States

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ABSTRACT: The convergence behavior of the Møller–Plesset (MP) perturbation series is investigated utilizing MP correlation energies up to order 65 calculated at the full CI (FCI) level. Fast or slow convergence, initial oscillations, or divergence of the MPn series depend on the electronic system investigated and the basis set used for the FCI calculation. Initial oscillations in the MPn series are observed for systems with electron clustering due to the fact that MP theory exaggerates electron-correlation effects at even orders and corrects this at odd orders. In such cases, it is important that the s, p basis is first saturated before diffuse functions are added. With a VDZ + diff basis, too much weight is given to high-order correlation effects described by pentuple and higher excitations, which leads to the formation of artificial intruder states and to the divergence of the MPn series. This can be corrected by extending to VQZ or VPZ basis sets before one adds diffuse functions. Alternatively, one can use m-order Feenberg scaling to exclude backdoor intruder states from the convergence region of the MPn series. For all cases considered, divergence of the MPn series caused by unbalanced basis sets including diffuse functions can be suppressed by Feenberg scaling. Also, initial oscillations of the MPn series can be dampened and convergence acceleration of the MPn series achieved if the appropriate order of Feenberg scaling is determined for the problem in question. The relationship between electronic structure, basis set, and convergence of the MPn series is discussed. © 2000 John Wiley & Sons, Inc. Int J Quant Chem 76: 306–330, 2000

Introduction

The Møller–Plesset (MP) method for calculating correlation energies is based on Rayleigh–Schrödinger perturbation theory and the MP perturbation operator [1, 2]. MP correlation energies are easily calculated at second (MP2), third (MP3), and fourth order (MP4) [3–8]. The calculation of higher orders such as MP5 [9, 10] or MP6 [11, 12] is considerably more difficult since this implies M^8 and M^9 operations, where M is the number of basis functions. Only a few MP5 and MP6 calculations have been carried out [9–12], which is probably the reason why little is known about the convergence behavior of the MPn series. Generally, one assumes that for n approaching infinity the MPn energy approaches the full CI (FCI) energy of the electronic system investigated where the FCI energy is determined by the basis set and the geometry used in the calculation.

One normally assumes that MPn energies ($n = 2, \ldots, 6$) provide with increasing order reliable predictions of FCI energies [2]. Furthermore, it is assumed that relative MPn energies, which are needed for the description of chemical processes, closely parallel relative FCI energies because of extensive error cancellations. Of course, these assumptions do not consider the fact that the MPn series possesses rather different properties for different electronic systems: Fast or slow convergence behavior, strong initial oscillations, and even divergence have been observed for electronic systems, which one normally expects to represent typical closed-shell character without any multireference effects [13–18]. It has been claimed that MPn correlation energies for $n > 2$ may lack any physical meaning since divergent behavior of the MPn series may occur even for closed-shell systems such as Ne, FH, or H_2O [17, 18].

In this work, we analyzed the convergence behavior of the MPn series for electronic systems, for which MP6 calculations [11] or, alternatively, FCI calculations are possible. During the iterations of an FCI calculation, increasing orders of MPn energies are generated [19] so that FCI results are perfectly suited to describe the MPn series and its convergence behavior at higher orders. We will focus on the MPn series with erratic and/or divergent behavior and discuss the relationship among electronic structure, the influence of the basis set, and the role of intruder states. Schucan and Weidenmüller showed that the divergent behavior of the MPn series is caused by a radius of convergence $R_c < 1$ directly connected with the existence of an intruder state interacting with the ground state within the convergence range of the MPn series [20]. The intruder-state problem was discussed by various authors and recipes to avoid it were suggested [21–24]. We will show that intruder states can be avoided by using Feenberg scaling [25–31]. More than 40 years ago, first-order Feenberg scaling was suggested by Goldhammer and Feenberg to improve the results of low-order perturbation theory [26]. Dietz and coworkers [29] extended the original theory to be applicable in the case of multireference calculations. Schmidt et al. [30] showed that first-order Feenberg scaling can be applied with success to low-order MP theory. He and Cremer [31] developed second-order Feenberg scaling and used it in connection with MP6 to estimate FCI energies. Here, we will describe mth order Feenberg scaling as an effective tool to improve the convergence behavior of the MPn series and to cope with the problem of intruder states. Our investigation will be based on MP6 calculations and the analysis of FCI energies taken from the work of Olsen and coworkers [17, 18].

The present work is structured in the following way: In the second section, we will develop the theory of higher-order Feenberg scaling. The mathematical tools to describe the convergence behavior of an MPn series are given in the third section, followed by a short discussion of error analysis and implementation of Feenberg scaling within an MPn program (fourth section). The MPn series with convergent or divergent behavior are discussed in the fifth section. The results of Feenberg scaling are presented in the sixth section and analyzed on the basis of theoretical considerations in the seventh section.

Theory of Feenberg Scaling

The MPn energy at order n is given by expression (1) [2]:

$$E(MPn) = E_{HF} + \Delta E_{MP}^n = E_{HF} + \sum_{k=2}^{n} E_{MP}^{(k)}, \quad \text{(1a)}$$

where E_{HF} is the Hartree−Fock (HF) energy; ΔE_{MP}^n, the MP correlation energy at order n:

$$\Delta E_{MP}^n = E(MPn) - E_{HF} = \sum_{k=2}^{n} E_{MP}^{(k)}; \quad (1b)$$

and $E_{MP}^{(k)}$, the kth-order contribution to the MP correlation energy. Equation (1) is obtained by splitting the Hamiltonian $\hat{H}$ into the unperturbed Hamiltonian $\hat{H}_0$ and the perturbation operator $\hat{V}$:

$$\hat{H}(z) = \hat{H}_0 + z\hat{V}, \quad (2)$$

where

$$\hat{H}_0 \Phi^{(0)} = E^{(0)} \Phi^{(0)}. \quad (3)$$

In MP theory, $\hat{H}_0$ is given by the sum of Fock operators; $\Phi^{(0)}$, by the HF wave function; and $E^{(0)}$, by E_{HF}, that is, the unperturbed problem (3) is taken to be the HF problem. Then, the perturbation operator is defined by Eq. (4):

$$\hat{V} = \frac{1}{2} \sum_{p} \sum_{q} \frac{1}{r_{pq}} - \sum_{p} \hat{v}(p), \quad (4)$$

where $\hat{v}(p)$ is the HF potential. The perturbation can be switched on by a dimensionless strength parameter z leading to the perturbed problem (5):

$$\hat{H}(z)\Psi(z) = \mathscr{E}(z)\Psi(z), \quad (5)$$

which for $z = 1$ gives energy and wave function of the Schrödinger equation:

$$\left.\begin{array}{c} \mathscr{E}(z) \rightarrow \mathscr{E} \\ \Phi(z) \rightarrow \Psi \end{array}\right\} \quad z \rightarrow 1. \quad (6)$$

MP theory is based on the assumption that the energy $\mathscr{E}(z)$ and the wave function $\Psi(z)$ can be expressed as Taylor expansions at $z = 0$:

$$E(z) = \sum_{k=0}^{\infty} z^k E_{MP}^{(k)} \quad (7)$$

$$\Psi(z) = \sum_{k=0}^{\infty} z^k \Phi^{(k)}, \quad (8)$$

where different symbols E and $\mathscr{E}$ are used to clarify that the energy E does not necessarily converge to $\mathscr{E}$.

The nth-order contribution to the energy and wave function are given by

$$E^{(n)} = \langle \Phi^{(0)} | \hat{V} | \Phi^{(n-1)} \rangle \quad (9)$$

$$\Phi^{(n)} = \left(E^{(0)} - \hat{H}_0 \right)^{-1}$$

$$\times \left[(\hat{V} - E^{(1)})\Phi^{(n-1)} - \sum_{k=2}^{n} E^{(k)} \Phi^{(n-k)} \right]. \quad (10)$$

For a finite basis set, the MPn energy of an atom or molecule (at a given geometry) should approach the corresponding FCI energy for n approaching infinity:

$$E(MP\infty) = E(FCI) = E_{HF} + \sum_{k=2}^{\infty} E_{MP}^{(k)}, \quad (11)$$

provided that the MPn series $\mathscr{S}$ of correlation energies,

$$\mathscr{S}_1 = \{\Delta E_{MP}^n\}_{n=2}^{\infty}, \quad (12a)$$

converges to the FCI correlation energy, which implies that the series of MPn correlation energy contributions,

$$\mathscr{S}_2 = \{E_{MP}^{(k)}\}_{k=2}^{\infty}, \quad (12b)$$

converges against zero.

In general, there is no guarantee that series (12) converges fast or converges at all. Erratic or even divergent behavior of series (12) is possible, where this, of course, reflects whether the partitioning of $\hat{H}$ according to Eq. (2) is physically justified. On the other hand, it is possible to adjust the partitioning of $\hat{H}$ to the electronic problem considered so that convergence is improved. In this connection, various methods have been proposed to accelerate and enforce convergence, of which Feenberg scaling [25–31] as a simple and effective method is discussed in this work.

According to Feenberg [25] and Goldhammer and Feenberg [26], the convergence behavior of the MPn series (12) can be improved by introducing into Eq. (2) a scaling parameter λ ($|\lambda| < 1$):

$$\tilde{H}(z', \lambda) = \frac{1}{1-\lambda}\hat{H}_0 + z'\left(\hat{V} - \frac{\lambda}{1-\lambda}\tilde{H}_0\right) \quad (13a)$$

$$= \tilde{H}_0(\lambda) + z'\tilde{V}(\lambda). \quad (13b)$$

For positive λ, the $\hat{H}_0$ part of the Hamiltonian is increased, that is, the weight of the unperturbed problem, which can be viewed as scaling up HF electron−electron interactions with the purpose of

decreasing the perturbation. This may be necessary if the perturbation and, by this, the corrections for the true electron−electron interaction are too large to apply perturbation theory successfully. This could help to avoid erratic or divergent behavior of the MPn series (12).

For negative λ, the perturbation is increased while the weight of the unperturbed problem is decreased. In this way, lower orders of perturbation theory could cover a larger amount of electron correlation corrections. This could help to accelerate the convergence of a slowly converging MPn series (12). In both cases, the strength parameter z is scaled by λ to yield a new strength parameter z'. For any value of $|\lambda| < 1$, $z' = 1$ has to imply that $z = 1$ to guarantee the correct form of the physical Hamiltonian $\hat{H}$, which, of course, has to be independent of λ:

$$\left.\begin{array}{r} z' = 1 \\ z = 1 \end{array}\right\} \qquad \tilde{H}(z' = 1, \lambda) \rightarrow \hat{H}(z = 1). \quad (14)$$

The partitioning of the Hamiltonian according to (13) leads to a transformation of the MPn series $\{E_{MP}^{(n)}\}$ where each term is obtained now as a polynomial in λ [25−31]:

$$E_\lambda^{(n)} = E_{FE}^{(n)} = \sum_{k=1}^{n-1} \binom{n-2}{k-1} \lambda^{n-k-1}$$
$$\times (1 - \lambda)^k E_{MP}^{(k+1)} \qquad (n \geq 2). \quad (15)$$

Feenberg and Goldhammer [25, 26] suggested that the value of λ is obtained by minimizing the MP3 correlation energy $\sum_{n=2}^{3} E_\lambda^{(n)} = \Delta E_\lambda^{(3)} = E_\lambda^{(2)} + E_\lambda^{(3)}$, which leads to Eq. (16):

$$\lambda_3 = 1 - \frac{E_{MP}^{(2)}}{E_{MP}^{(2)} - E_{MP}^{(3)}}. \quad (16)$$

Replacing λ in Eq. (15) by λ_3, the Feenberg series $\{E_{\lambda_3}^{(n)}\}$ is obtained. Since the minimization of the MP3 correlation energy implies effective scaling of the first-order correction to the wave function

$$\Phi^{(1)}(z', \lambda_3) = \left(E^{(0)} - \tilde{H}_0(\lambda_3)\right)^{-1}$$
$$\times \left(\tilde{V}(\lambda_3) - E^{(1)}\right)\Phi^{(0)}, \quad (17)$$

the term first-order Feenberg scaling was coined for this approach. Second-order Feenberg scaling is obtained by minimizing the fifth-order MP correlation energy [31]:

$$\frac{\partial}{\partial \lambda} \sum_{k=2}^{5} E_\lambda^{(k)} = \frac{\partial \Delta E_\lambda^{(5)}}{\partial \lambda} = 0. \quad (18)$$

In this case, one obtains a cubic equation in λ,

$$\lambda^3 + P\lambda^2 + Q\lambda + R = 0, \quad (19)$$

with

$$P = \frac{3(E_{MP}^{(3)} - 2E_{MP}^{(4)} + E_{MP}^{(5)})}{E_{MP}^{(2)} - 3E_{MP}^{(3)} + 3E_{MP}^{(4)} - E_{MP}^{(5)}} \quad (20)$$

$$Q = \frac{3(E_{MP}^{(4)} - E_{MP}^{(5)})}{E_{MP}^{(2)} - 3E_{MP}^{(3)} + 3E_{MP}^{(4)} - E_{MP}^{(5)}} \quad (21)$$

and

$$R = \frac{E_{MP}^{(5)}}{E_{MP}^{(2)} - 3E_{MP}^{(3)} + 3E_{MP}^{(4)} - E_{MP}^{(5)}}. \quad (22)$$

Solving Eq. (19), one obtains for the electronic systems considered in this work just one real root, which defines the Feenberg scaling parameter λ_5:

$$\lambda_5 = +\sqrt[3]{\sqrt{C} - \frac{B}{2}} + \sqrt[3]{-\sqrt{C} - \frac{B}{2}} - \frac{P}{3}, \quad (23)$$

where C is given by

$$C = \frac{B^2}{4} + \frac{A^3}{27} > 0 \quad (24)$$

for all cases investigated. In Eqs. (23) and (24), A and B are given by

$$A = Q - \frac{P^2}{3} \quad (25)$$

$$B = 2\left(\frac{P}{3}\right)^3 - \frac{P \times Q}{3} + R. \quad (26)$$

One could also try to minimize the fourth-order correlation energy $\Delta E_\lambda^{(4)}$, which would lead to

$$\lambda^2 + Q'\lambda + R' = 0, \quad (27)$$

where

$$Q' = \frac{2(E_{MP}^{(3)} - E_{MP}^{(4)})}{E_{MP}^{(2)} - 2E_{MP}^{(3)} + E_{MP}^{(4)}} \quad (28)$$

$$R' = \frac{E_{MP}^{(4)}}{E_{MP}^{(2)} - 2E_{MP}^{(3)} + E_{MP}^{(4)}}. \quad (29)$$

It turns out that Eq. (27) does not contain a real root because for MPn series (12) it always holds

that

$$Q'^2 - 4R' = \frac{4\left[(E_{MP}^{(3)})^2 - E_{MP}^{(2)}E_{MP}^{(4)}\right]}{(E_{MP}^{(2)} - 2E_{MP}^{(3)} + E_{MP}^{(4)})^2} < 0 \quad (30a)$$

because

$$(E_{MP}^{(3)})^2 < E_{MP}^{(2)}E_{MP}^{(4)}. \quad (30b)$$

In the case of a true geometric series, the left side of Eq. (30a) would be equal to zero. However, because of the nature of the perturbation operator used in MP theory, absolute values of correlation contributions at even order are larger; those at odd orders lower than the values of an exact geometric series as will be discussed in more detail in the fifth section.

Similar relationships such as (30) hold at higher even orders. Therefore, it is reasonable to scale just the mth-order correction to the HF wave function, $\Phi^{(m)}$ (mth-order Feenberg scaling) which by the Wigner theorem corresponds to the minimization of the MP correlation energy $\Delta E_\lambda^{(n=2m+1)}$:

$$\frac{\partial}{\partial \lambda} \sum_{k=2}^{n} E_\lambda^{(k)} = \frac{\partial \Delta E_\lambda^{(n)}}{\partial \lambda} = \frac{1-n}{1-\lambda}E_\lambda^{(n)} = 0, \quad (31)$$

where Eq. (15) has been used.

Equation (31) involves a set of nonlinear equations in λ when $n = 7, 9, \ldots$:

$$\lambda_7^5 E_{MP}^{(2)} + 5\lambda_7^4(1-\lambda_7)E_{MP}^{(3)} + 10\lambda_7^3(1-\lambda_7)^2 E_{MP}^{(4)}$$
$$+ 10\lambda_7^2(1-\lambda_7)^3 E_{MP}^{(5)} + 5\lambda_7(1-\lambda_7)^4 E_{MP}^{(6)}$$
$$+ (1-\lambda_7)^5 E_{MP}^{(7)} = 0 \quad (32)$$

$$\lambda_9^7 E_{MP}^{(2)} + 7\lambda_9^6(1-\lambda_9)E_{MP}^{(3)} + 21\lambda_9^5(1-\lambda_9)^2 E_{MP}^{(4)}$$
$$+ 35\lambda_g^4(1-\lambda_9)^3 E_{MP}^{(5)} + 35\lambda_9^3(1-\lambda_9)^4 E_{MP}^{(6)}$$
$$+ 21\lambda_9^2(1-\lambda_9)^5 E_{MP}^{(7)} + 7\lambda_9(1-\lambda_9)^6 E_{MP}^{(8)}$$
$$+ (1-\lambda_9)^7 E_{MP}^{(9)} = 0, \quad (33)$$

or, in general,

$$\sum_{k=1}^{2m} \binom{2m-1}{k-1} \lambda_{2m+1}^{2m-k}(1-\lambda_{2m+1})^{k-1} E_{MP}^{(k+1)} = 0, \quad (34)$$

which can be solved numerically.

From Eq. (31), one can see that because of the minimum condition, Eq. (35), holds:

$$E_\lambda^{(2m+1)}\big|_{\lambda=\lambda_{2m+1}} = 0, \quad (35)$$

so that the Feenberg series $\{E_{\lambda_{2m+1}}^{(n)}\}$ converges in $(2m+1)$th-order perturbation theory. In other words, the mth-order perturbed wave function and the $(2m+1)$th-order energy are the eigenfunction and eigenvalue of the Hamiltonian $\tilde{H}(z', \lambda)$. This suggests an improvement of the Feenberg series and more reliable estimates of FCI correlation energies. We note that the Feenberg energies are all size-extensive, which can be seen by inspection of Eqs. (15) and (16).

Description of the Convergence Behavior of the MPn Series

The convergence behavior of the MPn series can be investigated by applying d'Alembert's ratio test and considering the series of ratios R between successive MP correlation contributions $E_{MP}^{(n)}$:

$$R = \{r_k\}_{k=2}^{n} = \left\{\frac{E_{MP}^{(k+1)}}{E_{MP}^{(k)}}\right\}_{k=2}^{n}, \quad (36)$$

where n is the largest perturbation order, for which the ratio is defined. If $E_{MP}^{(n)} < 0$ is fulfilled for all n, the ratio $r_n \to \tau$ for $n \to \infty$. The series $\mathscr{S}_1$ and $\mathscr{S}_2$ [see Eq. (12)] will converge if $0 < \tau < 1$ and diverge if $\tau > 1$. In the case $\tau = 1$, a finite MP correlation energy ΔE_{MP}^∞ does not exist and, therefore, this (unlikely) case also excludes convergent behavior of the MPn series. If successive $E_{MP}^{(n)}$ have alternating signs, then the ratios of $|E_{MP}^{(n)}|$ must generate a convergent series to ensure the convergence of the original series $\mathscr{S}$.

In practice, the correlation energy contribution at the highest-order n calculated will always have a finite value. In this case, convergence will be reached at some order n provided $|E_{MP}^{(n+1)}| \le \varepsilon$, where ε is the convergence criterion.

As for the convergence behavior of the Feenberg series, Eq. (35) suggests one to apply the Cauchy root test defined by Eq. (37):

$$R' = \{r_k'\}_{k=2}^{n} = \left\{\sqrt[k]{\left|\frac{E_{FE}^{(k)}}{E_{FE}^{(2)}}\right|}\right\}_{k=2}^{n}. \quad (37)$$

Ratios R' will be less sensitive to the error progression in energies $E_{FE}^{(n)}$ (see next section) and, in addition, denominators equal to zero will be avoided. In the same way as for the d'Alembert's

ratio test, the set

$$\mathcal{S}' = \{\Delta E_{FE}^{(n)}\}_{n=2}^{\infty} \qquad (38)$$

will converge if $r_n' \to \tau' < 1$ for $n \to \infty$.

The limit values τ and τ' for d'Alembert and Cauchy ratios, respectively, were obtained by fitting ratio values for $n > 10$ to the trial function $f(n) = a - e^{-bn} - e^{-cn}$, which defines the constant a for $n \to \infty$ as an upper limit to the correct τ or τ'.

As indicated in Scheme 1, one can distinguish five different types (A, B, C, D, E) of the MPn series classified according to their convergence behavior. For positive ratios r_n, $E_{MP}^{(n)}$ will have negative signs for all orders n, while for negative r_n, successive $E_{MP}^{(n)}$ values will have different signs.

The MPn series A represents a divergent series because $r_n > 1$ for increasing n, which means that

$\tau > 1$. For series B, ΔE_{MP}^n converges to the FCI correlation energy for increasing n because $r_n < 1$ and $0 < \tau < 1$. Hence, B represents a converging MPn series. Series C is also converging because $|r_n| < 1$ for increasing n. Series D represents a divergent series because $|r_n| > 1$ for increasing n while $E_{MP}^{(n)}$ values switch signs regularly. Case E represents an oscillating MPn series caused by a regular switch in sign of the correlation energy contribution. Nevertheless, E is converging as long as the ratio $|r_n| < 1$. Initial oscillations of the MPn series (including or not including a switch in sign) are frequently observed; however, most of these oscillations just slow down convergence and do not lead to divergent behavior.

The rate of the convergence can be determined by the value of $|r_n|$. The smaller $|r_n|$ becomes, the faster does the MPn series converge. This becomes obvious when expressing the correlation contribu-
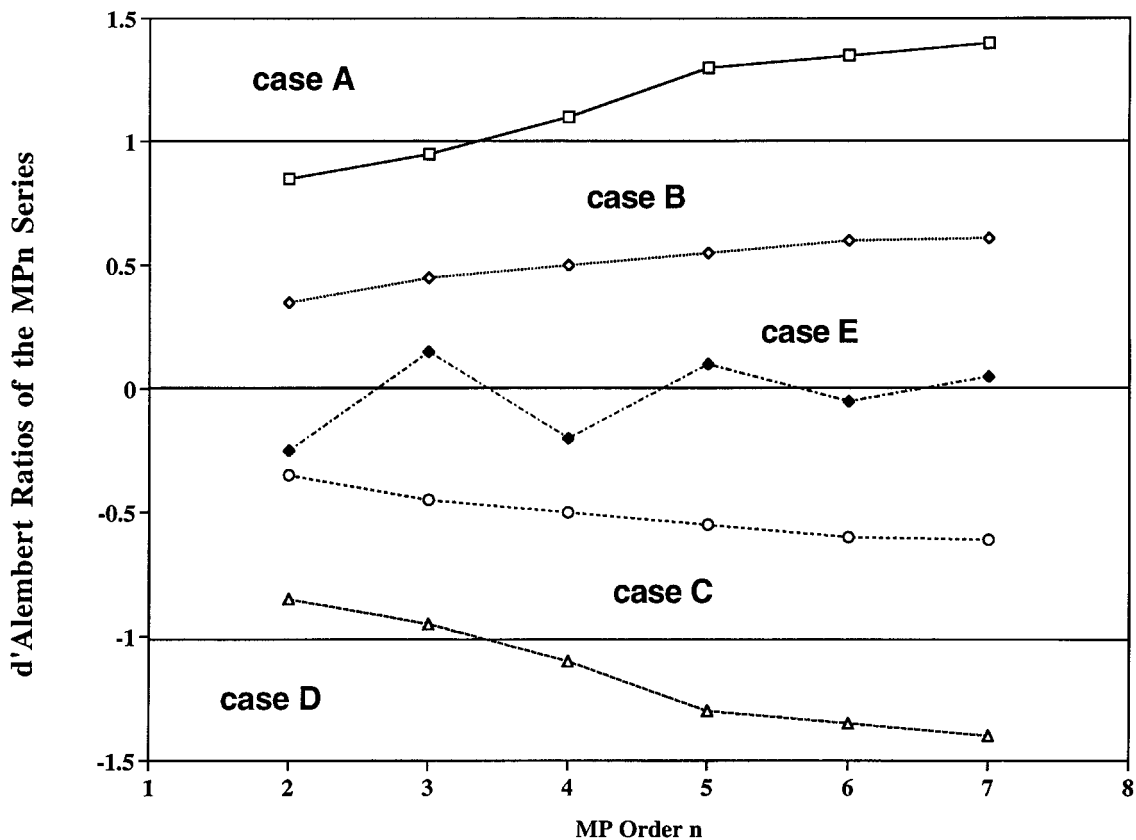
SCHEME 1

TABLE I
Basis-set specification.

Basic set	Specification	Molecules
cc-pVDZ	$(9s4p1d)[3s2p1d] / (4s2p)[2s1p]$	F^-, Ne, BH, CH_2, H_2O, FH
cc-pVDZ(+)	cc-pVDZ + diff(s, p)	H_2O
aug-cc-pVDZ	cc-pVDZ + diff(s, p, d)	BH, CH_2, FH, F^-, Ne
daug-cc-pVDZ	cc-pVDZ + 2 diff(s, p, d)	BH
cc-pVTZ	$(10s5p2d1f)[4s3p2d1f] / (6s2p1d)[3s2p1d]$	BH, CH_2, FH
cc-pVTZ	$(10s5p2d)[4s3p2d]$	F^-, Ne
aug-cc-pVTZ	cc-pVTZ + diff(s, p, d)	BH

tion at order n in terms of ratios r_j:

$$E_{MP}^{(n)} = E_{MP}^{(2)} \cdot \prod_{j=2}^{n-1} |r_j|. \tag{39}$$

Implementation of Higher-order Feenberg Scaling and Error Analysis

A simple program based on the equations derived in the previous section was added to an existing program code for calculating MP correlation energies up to sixth order (MP6) [11] so that with each MP calculation Feenberg perturbation energies were automatically generated. In addition, available higher-order MP energies (n up to 65) were taken from the literature [17, 18] to study the convergence behavior of the MPn series and to test the usefulness of higher-order Feenberg scaling. The basis sets used and the electronic systems investigated in this way are listed in Tables I and II.

TABLE II
Description of the convergence behavior of various MPn series.

System	Basis set	FCI energy	Correlation energy	n(max) / n(conv)	Description of convergence behavior	Class
BH ($^1\Sigma_g$)	cc-pVDZ	−25.215126	−0.089794	24 / 22	Fast conv., nonoscill.	B
	aug-cc-pVDZ	−25.218227	−0.091850	24 / 22	Fast conv., nonoscill.	B
	daug-cc-pVDZ	−25.218430	−0.091954	24 / —	Fast conv., nonoscill.	B
	cc-pVTZ	−25.231132	−0.101199	24 / 17	Fast conv., nonoscill.	B
	aug-cc-pVTZ	−25.232008	−0.101807	24 / 17	Fast conv., nonoscill.	B
CH_2 ($^3B_1$)	cc-pVDZ	−39.023280	−0.142287	33 / —	Slow conv., nonoscill.	B
	aug-cc-pVDZ	−39.032446	−0.148192	33 / —	Slow conv., nonoscill.	B
	cc-pVTZ	−39.049940	−0.158327	24 / —	Slow conv., nonoscill.	B
Ne (^1S)	cc-pVDZ	−128.679025	−0.190250	33 / 11	Fast conv., initially oscill.	C
	aug-cc-pVDZ	−128.709476	−0.213126	65 / —	Diverging, oscill.	D
	cc-pVTZ	−128.777048	−0.245186	33 / 16	Fast conv., initially oscill.	C
F^- (^1S)	cc-pVDZ	−99.558917	−0.192934	33 / 11	Fast conv., nonoscill.	B
	aug-cc-pVDZ	−99.669369	−0.241086	33 / —	Diverging, oscill.	D
	cc-pVTZ	−99.675158	−0.250859	21 / 14	Fast conv., initially oscill.	C
FH ($^1\Sigma_g$)	cc-pVDZ	−100.228640	−0.209227	21 / 15	Fast conv., initially oscill.	C
	aug-cc-pVDZ	−100.264113	−0.230645	21 / —	Diverging, oscill.	D
	cc-pVTZ	−100.312756	−0.255923	15 / —	Fast conv., oscill.	C
H_2O ($^1A_1$)	cc-pVDZ	−76.241650	−0.214842	21 / 10	Fast conv., nonoscill.	B
	cc-pVDZ(+)	−76.258208	−0.220651	31 / —	Diverging, oscill.	D

Energies in Hartrees from [18]. conv.: converging; oscill.: oscillating. n(max): largest MPn order calculated; n(conv): MPn order, at which MP and FCI correlation energy differ by not more than 10^{-6} Hartrees.

MPn energies taken from the literature are accurate up to $0.5 \cdot 10^{-6}$ Hartrees, which has to be considered when calculating Feenberg energies. Apart from this, the convergence of the calculated Feenberg series can be affected by errors in calculated scaling factors λ and Feenberg energies [see Eqs. (15) and (34)]. The maximal error in a calculated Feenberg correlation energy contribution, $\delta E_\lambda^{(n)}$, can be formulated according to the maximal error propagation method as

$$|\delta E_\lambda^{(n)}| \Leftrightarrow |\delta E_\lambda^{(n)}(\lambda, E_{MP}^{(2)}, E_{MP}^{(3)} \ldots, E_{MP}^{(n)})|$$

$$\leq \left| \frac{\partial E_\lambda^{(n)}}{\partial \lambda} \cdot \delta\lambda \right| + \sum_{k=2}^{n} \left| \frac{\partial E_\lambda^{(n)}}{\partial E_{MP}^{(k)}} \cdot \delta E_{MP}^{(k)} \right|, \quad (40)$$

where $\delta\lambda$ is the error in the scaling factor and $\delta E_{MP}^{(n)}$ is the error in the MP energies. The magnitude of $\delta\lambda$ depends on the error of the MPn correlation energy contributions and can be calculated with the help of Eqs. (41) and (42), where the former is a consequence of Eq. (31):

$$\sum_{k=2}^{m} \frac{\partial E_\lambda^{(m)}}{\partial E_{MP}^{(k)}} \cdot \delta E_{MP}^{(k)} + \frac{\partial E_\lambda^{(m)}}{\partial \lambda} \cdot \delta\lambda_m = 0 \quad (41)$$

$$\delta\lambda_m = - \sum_{k=2}^{m} \frac{\partial E_\lambda^{(m)}}{\partial E_{MP}^{(k)}} \cdot \delta E_{MP}^{(k)} \cdot \left(\frac{\partial E_\lambda^{(m)}}{\partial \lambda} \right)^{-1}. \quad (42)$$

By this, the inaccuracy of the mth-order Feenberg correlation energy at perturbation order n is determined by

$$|\delta E_\lambda^{(n)}| \leq \left| \frac{\partial E_\lambda^{(n)}}{\partial \lambda} \cdot \sum_{k=2}^{m} \frac{\partial E_\lambda^{(m)}}{\partial E_{MP}^{(k)}} \cdot \delta E_{MP}^{(k)} \cdot \left(\frac{\partial E_\lambda^{(m)}}{\partial \lambda} \right)^{-1} \right|$$

$$+ \sum_{k=2}^{n} \left| \frac{\partial E_\lambda^{(n)}}{\partial E_{MP}^{(k)}} \cdot \delta E_{MP}^{(k)} \right|, \quad (43)$$

where $\lambda = \lambda_m$. If $\delta E_{MP}^{(k)} = 0.5 \cdot 10^{-6}$ for all k, then Eq. (43) will adopt form (44):

$$|\delta E_\lambda^{(n)}| \leq 0.5 \cdot 10^{-6} \cdot \left(\left| \frac{\partial E_\lambda^{(n)}}{\partial \lambda} \left(\frac{\partial E_\lambda^{(m)}}{\partial \lambda} \right)^{-1} \right| \right.$$

$$\left. \times \sum_{k=2}^{m} \frac{\partial E_\lambda^{(m)}}{\partial E_{MP}^{(k)}} + \sum_{k=2}^{n} \left| \frac{\partial E_\lambda^{(n)}}{\partial E_{MP}^{(k)}} \right| \right). \quad (44)$$

Errors in calculated Feenberg correlation energy contributions were estimated with the help of Eq. (44). The error in $\Delta E_{FE}^{(n)}$ values was estimated

using Eq. (45):

$$|\delta\Delta E_{FE}^{(n)}| = \sum_{k=2}^{n} |\delta E_{FE}^{(k)}|. \quad (45)$$

The value of $\Delta E_{FE}^{(n)}$ was considered to be reliable if the maximal error is smaller than 10 μHartrees.

Similarly, calculated ratios r_n of successive MPn energies were considered to be reliable provided the relative error

$$\left| \frac{\delta r_n}{r_n} \right| = \left| \frac{\delta E_{MP}^{(n+1)}}{E_{MP}^{(n+1)}} \right| + \left| \frac{\delta E_{MP}^{(n)}}{E_{MP}^{(n)}} \right|$$

$$= 0.5 \cdot 10^{-6} \left(\left| \frac{1}{E_{MP}^{(n+1)}} \right| + \left| \frac{1}{E_{MP}^{(n)}} \right| \right) \quad (46)$$

is less than 0.5%. If $E_{MP}^{(n+1)} \leq 10^{-6}$, ratio r_{n+1} will not be defined and r_n will be the last ratio in R.

Finally, the relative error in the Cauchy root of the correlation energy contribution $E_{FE}^{(n)}$ was estimated by

$$\left| \frac{\delta r_n'}{r_n'} \right| = \left(\frac{1}{n} \right) \left(\left| \frac{\delta E_{FE}^{(2)}}{E_{FE}^{(2)}} \right| + \left| \frac{\delta E_{FE}^{(n)}}{E_{FE}^{(n)}} \right| \right). \quad (47)$$

The value of r_n' was considered to be acceptable when the relative error was less than 5%. For the examples investigated, convergence is achieved when $|E_{MP}^{(n+1)}| < 0.5 \cdot 10^{-6}$ Hartrees and by this $E(MPn) = E(FCI)$.

Convergent and Divergent MPn Series

In Table II, the electronic systems investigated, basis sets used, FCI total energies, and FCI correlation energies are listed together with some information about the convergence behavior of the corresponding MPn series [17, 18]. Calculated d'Alembert ratios of the MPn series of BH($^1\Sigma_g$), CH$_2$($^3B_1$), Ne(^1S), F$^-$(^1S), FH($^1\Sigma_g$), and H$_2$O($^1A_1$) for different basis sets (in total 19 examples) as a function of perturbation order n are shown in Figures 1–6.

As shown in Figure 1, the MPn series of BH($^1\Sigma_g$) exhibits a typical case B behavior with $0.2 < r_j < 0.65$ (for $j = 2, \ldots 10$ or 11), where, because of error progression, higher orders are not given. Convergence is relatively fast for all basis sets considered. In the beginning, it is slightly better for the VDZ than for the VTZ descriptions,
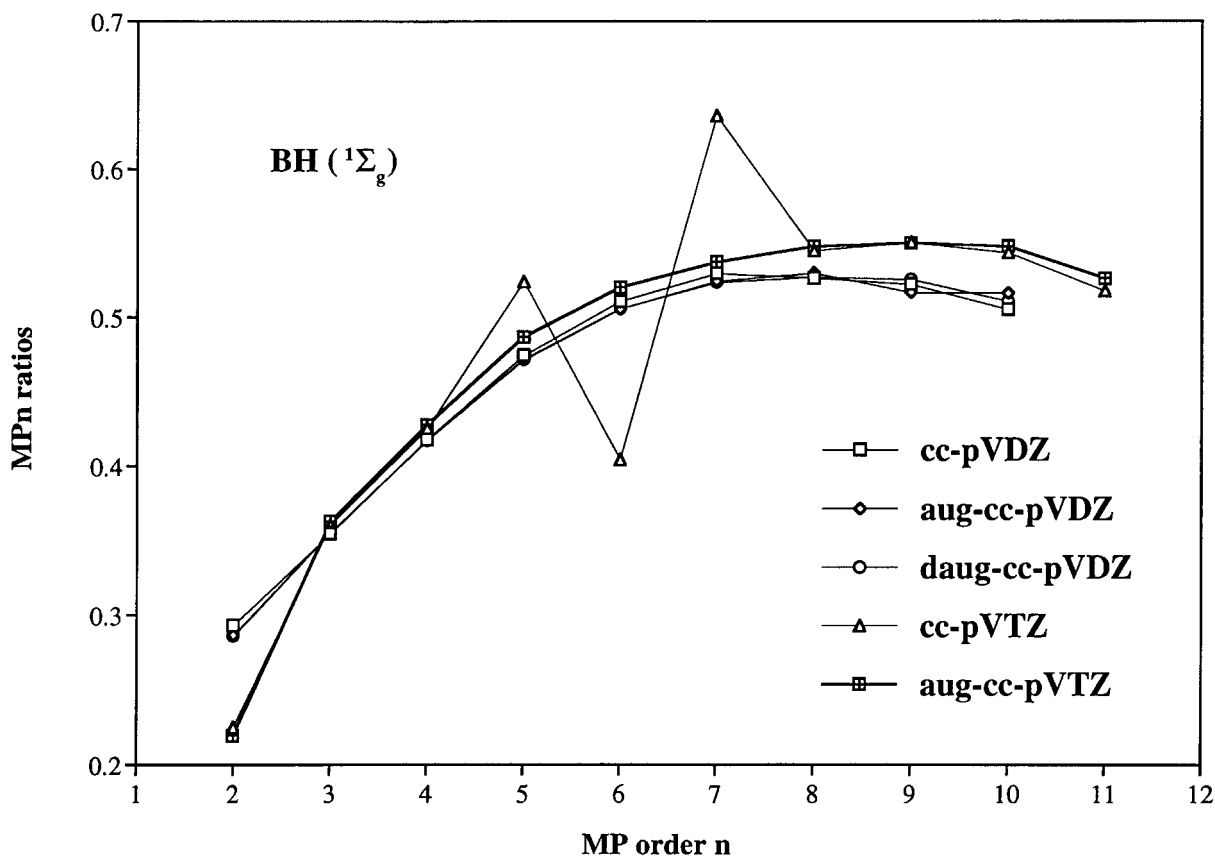
FIGURE 1. MPn ratios calculated for BH($^1\Sigma_g$) with various basis sets.

but for higher orders, this trend is reversed. Also, there are some oscillations for the latter between orders 5 and 8 which may affect convergence. The investigated MPn series for CH$_2$($^3B_1$) all converge (Fig. 2, case B), possessing $0.15 < r_j < 0.85$ ($j = 2, \ldots$ 20 or 21). Obviously, convergence is much slower than for BH($^1\Sigma_g$). The increase of r_j values for $j = 2$ to $j = 10$ suggests that higher-order correlation effects play for CH$_2$($^3B_1$) a larger role than for BH($^1\Sigma_g$), thus causing a slowing down of convergence. Again, there are some oscillations for the cc-pVTZ basis set.

For the MPn series of the Ne atom, both case C and case D behavior is observed (Fig. 3). The correlation energy contributions for Ne(^1S) calculated either with the cc-VDZ or the cc-pVTZ basis set oscillate regularly in sign, but converge at order 11 and 16, respectively (Table II). Convergence is somewhat faster for the smaller basis despite the fact that initial oscillations are larger in this case. As soon as diffuse s, p and d functions are added to the cc-pVDZ basis, thus leading to an aug-cc-pVDZ basis, the MPn series of Ne(^1S) di-

verges (case D) as indicated by r_j ratios smaller than -1. They seem to approach a value $\tau = -1.3$ for larger n. Similar observations can be made for the three MPn series investigated for F$^-$(^1S) (Fig. 4). Employing either the cc-pVDZ or the cc-pVTZ basis convergence is obtained within 11 and 14 steps, however, after strong initial oscillations. Calculations with the aug-cc-pVDZ basis set led to d'Alembert ratios between -0.8 and -2 that approach for large j the value $\tau = -1.55$ (case D). Hence, divergence is more pronounced than for Ne calculated with the same basis set.

The MPn series for FH($^1\Sigma_g$) could be investigated up to order $n = 14$ (Fig. 5). All series start with strong oscillations which are effectively damped out in the case of the cc-pVTZ calculations—however, less when employing the cc-pVDZ basis. In both cases, convergence is achieved according to type C in Scheme 1. Again, use of diffuse functions as in the aug-cc-pVDZ basis leads to d'Alembert ratios $r_j < -1$ and a divergent MPn series (case D). The MPn series of H$_2$O($^1A_1$) was investigated just with two basis sets (Fig. 6). De-
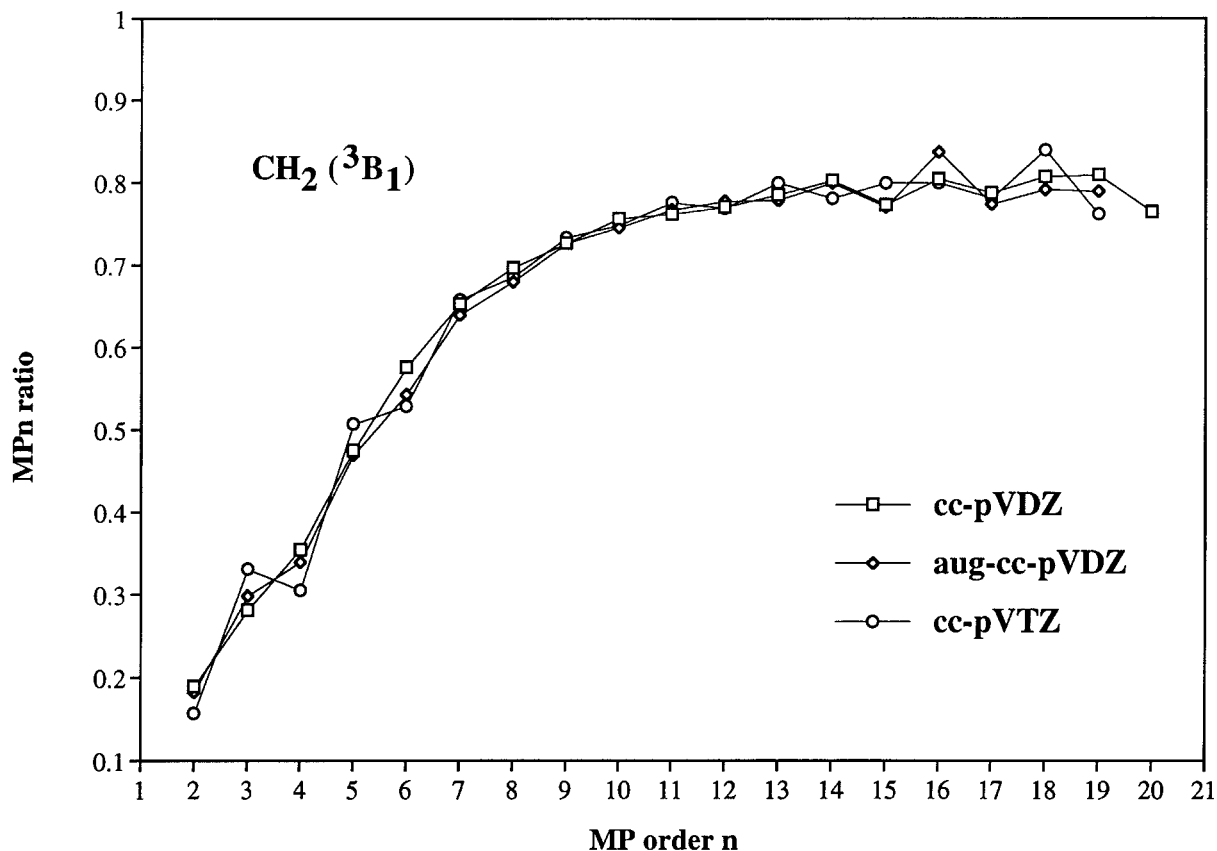
FIGURE 2. MP*n* ratios calculated for $CH_2(^3B_1)$ with various basis sets.

spite the initial oscillations, convergence according to case B was found for the cc-pVDZ basis while the addition of diffuse functions leads to divergence.

ELECTRONIC SYSTEMS OF TYPE I AND TYPE II

The electronic systems investigated can be grouped in two different classes, namely, class I and class II systems [15]. In the first class, there are electronic systems, for which electrons are well distributed in pairs over the whole space of an atom or molecule. There are no locations of electron clustering in atomic or molecular space. Typical examples for class I systems are $BH(^1\Sigma^+)$ or $CH_2(^1A_1)$, because in these molecules the core electron pair, bonding electron pair, and lone pair are localized in different parts of the molecule. Because of the separation of electron pairs, the correlation energy is dominated by pair-correlation effects. A large part of the pair-correlation energy is covered at MP2 while more complicated electron-correlation effects come in slowly at higher orders of perturbation theory. Typically, the convergence of the MP*n* series for a case I system is steady without larger oscillations, but convergence is relatively slow where it is a general observation that convergence can be slowed down the more electron–electron interactions have to be described.

Class II systems are characterized by a clustering of electron pairs in a constrained region of an atom or molecule. For example, for $Ne(^1S)$ and $F^-(^1S)$, four electron pairs share the available space in the valence sphere, which is rather limited due to orbital contraction caused by the nucleus. For $H_2O(^1A_1)$ and $FH(^1\Sigma_g)$, there are two or even three electron pairs that cluster in the lone-pair region of the center atom. Similarly, molecules with multiple bonds belong to class II since more than one electron pair can be found in the bonding region. For electronic systems with electron clustering, three-electron correlations are important since they provide a simple mechanism to protect the region
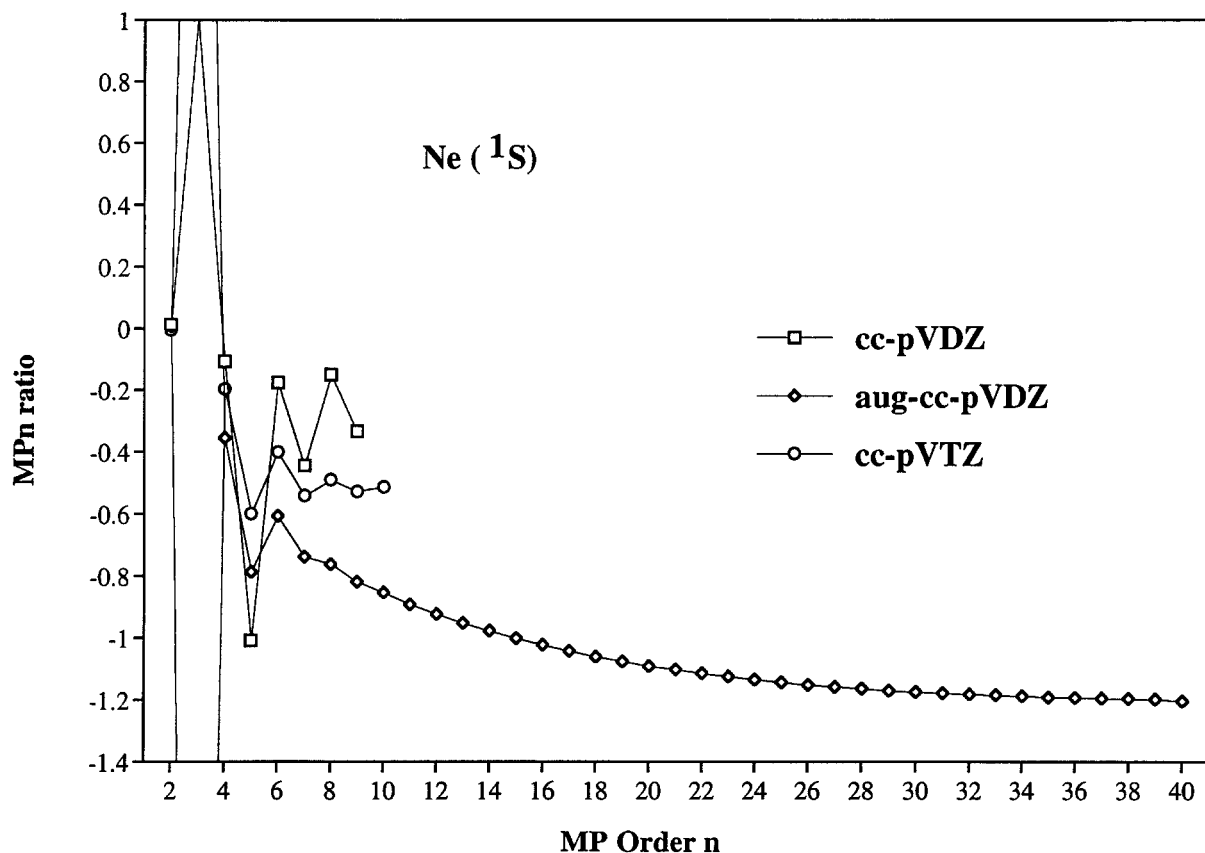
FIGURE 3. MPn ratios calculated for Ne(^1S) with various basis sets.

of an electron pair against occupation by other electrons. Accordingly, three-electron correlation effects can become as large or even larger than pair-correlation effects.

MP theory includes three-electron correlation effects at fourth order. At lower orders, the separation of electrons is accomplished by pair-correlation effects, which is not efficient since pair correlation just separates the two electrons within a pair using the available space (as described by the basis function) irrespective of the fact of how many electron pairs are clustered in that region. At MP2, the two electrons of a pair do not "see" the other electrons and, therefore, pair correlation is largely exaggerated, thus leading to an MP2 correlation energy, which seems to cover more correlation effects as for case I systems. At MP3, coupling effects between the electron pairs come in (the electron pairs start to "see" each other) and the exaggeration of pair-correlation effects is partially corrected. As a consequence, MP3 contributions $|E_{MP}^{(3)}|$ are smaller and their value can even be positive in the extreme case. A similar situation is

found at MP4 and MP5, where at the even order new correlation effects (orbital relaxation, three-electron correlation, and disconnected pair correlations) come in, which are urgently needed to improve electron correlation of clustered electrons in a type II system. Again, these correlation effects are somewhat exaggerated, but because of the couplings between these correlation effects at the next higher odd order (MP5), exaggerations are (partially) corrected. Hence, it can happen that the MP5 contribution becomes positive or at least it is smaller (absolutely seen) than one could expect by extrapolation of even-order MP correlation contributions.

Because of the exaggeration of correlation effects at even orders and their correction by appropriate couplings at odd orders, initial oscillations will be typical of the MPn series if electron clustering requires distinct electron correlation. The more important correlation becomes because of electron clustering, the more pronounced are the initial oscillations of the MPn series, which is clearly reflected by Figures 1–6. Class I (no or moderate
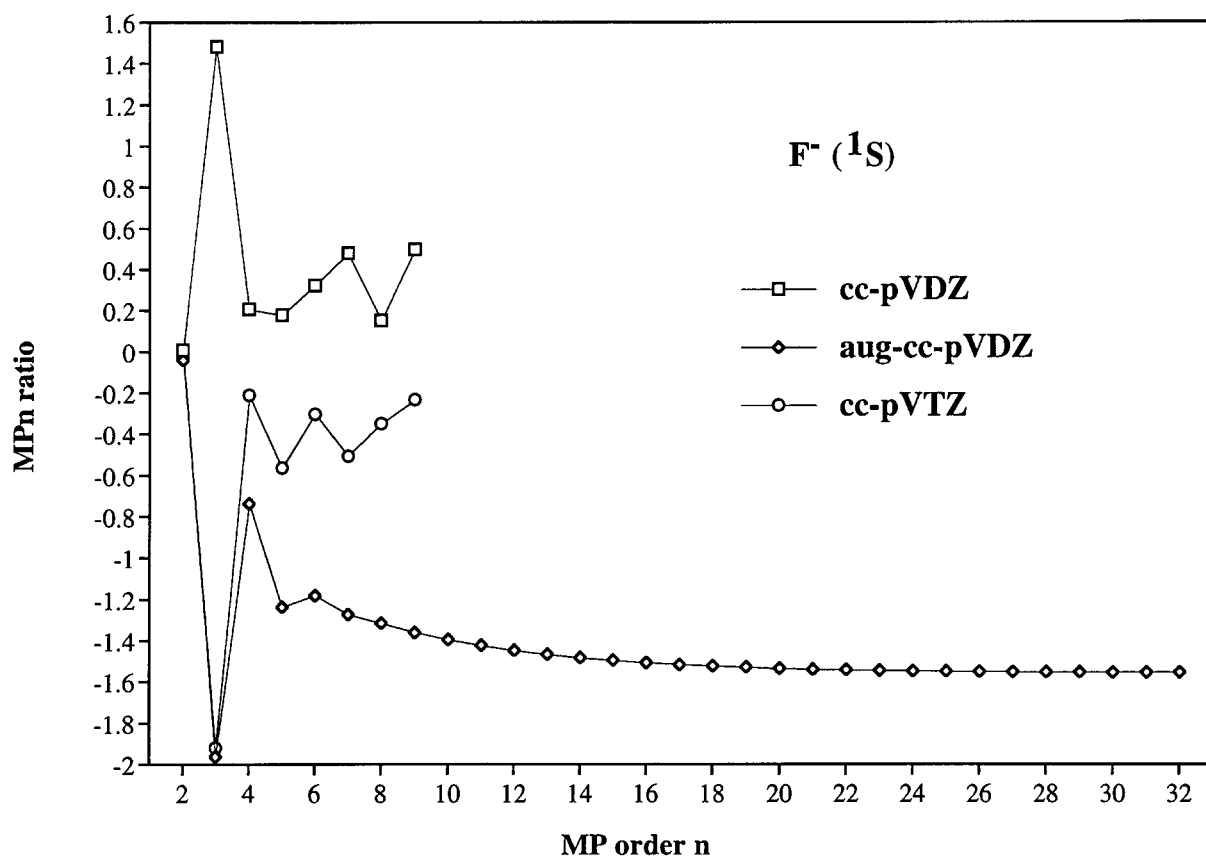
FIGURE 4. MPn ratios calculated for F$^-$ (^1S) with various basis sets.

electron clustering) have a slowly converging MPn series with only small or negligible oscillations while class II have MPn series with initial oscillations and/or erratic behavior.

BASIS-SET DEPENDENCE

Apart from the electronic structure (distribution of electron pairs) of the system investigated, one has to consider the basis set used for the description, which defines the space available for the electrons. The basis set must be flexible to cover all regions of atomic or molecular space occupied by electrons adequately. In particular, the valence shell has to be accurately described, which requires correlation-consistent basis sets of QZ and PZ quality [32]. A TZ description of the valence shell will include more pair correlation effects than will a DZ description and, therefore, the exaggeration of pair correlation at MP2, its correction at MP3, and the repetition of this interplay at even and odd orders is more pronounced. Consequently, initial oscillation can be larger for type II

systems. On the other hand, the larger basis also includes more coupling effects with increasing order n and therefore it can happen that the oscillations are faster damped out than for the VDZ basis set (see Figs. 3–5).

The basis set must provide the possibility that the electrons separate from each other and that orbitals (the size of the electronic system) can extend. As indicated in Scheme 2, expansion of the system becomes the more important the more electrons are involved in the correlation, that is, five-electron correlation requires more space than does pair or three-electron correlation. Actually, this could be best accomplished by reoptimization of the orbitals under the impact of dynamic electron correlation. However, in MP theory, orbital relaxations can only be introduced by mixing in single (S) excitations. Hence, the separation of electrons in an extended space must be provided by the basis set. An increase in the basis set leads to additional virtual orbitals, from which additional excited configurations for the calculation of correlation energy contributions can be constructed. If
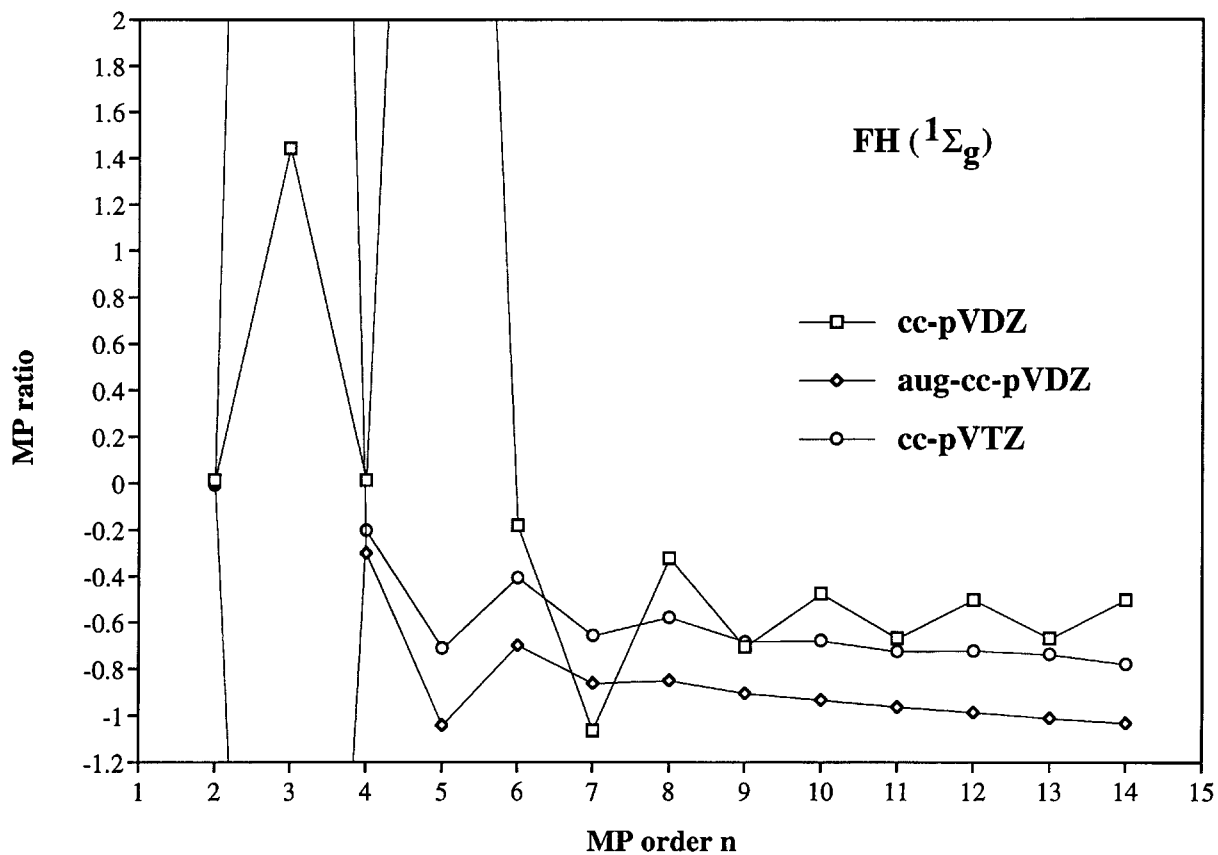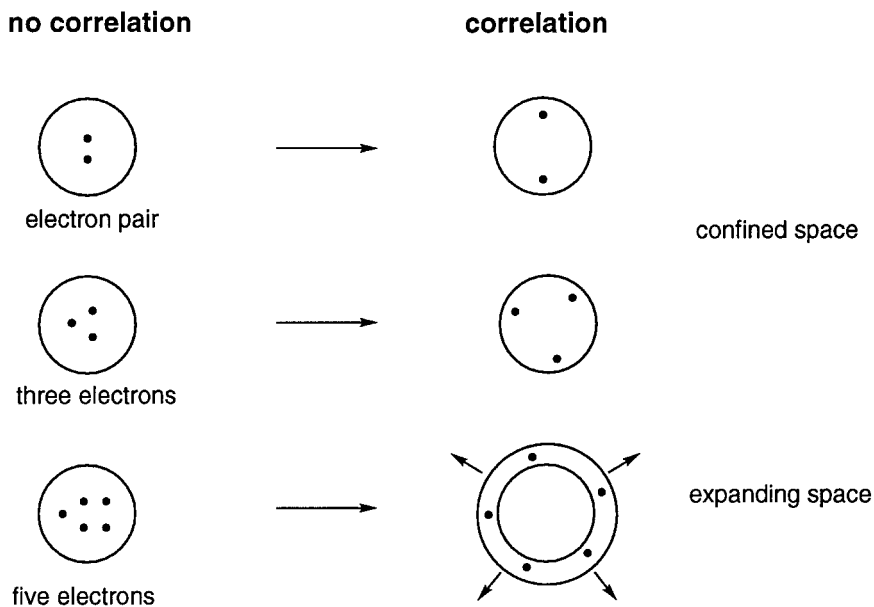
FIGURE 5. MP*n* ratios calculated for FH($^1\Sigma_g$) with various basis sets.

no correlation

correlation

electron pair

confined space

three electrons

five electrons
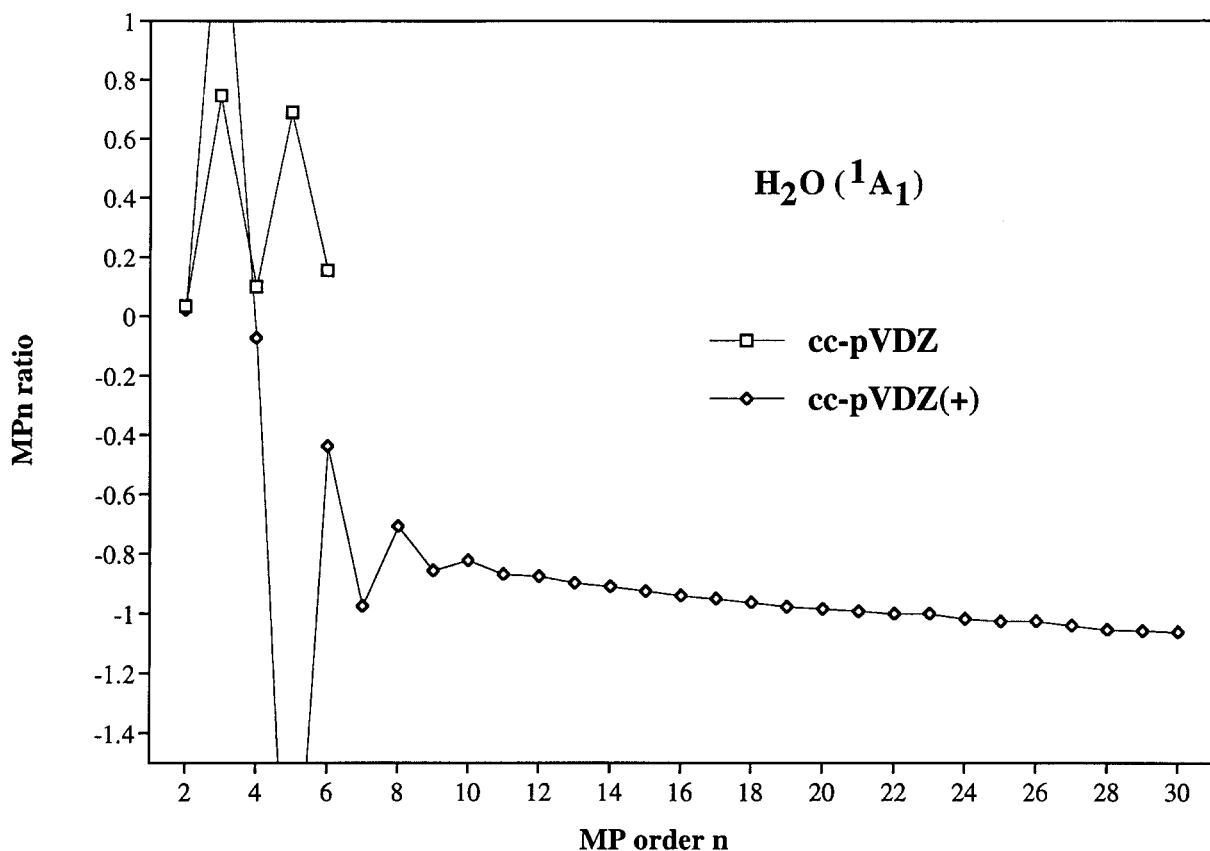
expanding space

SCHEME 2

FIGURE 6. MPn ratios calculated for $H_2O(^1A_1)$ with various basis sets.

the basis functions added are highly diffuse, the new virtual orbitals will also be diffuse and will badly be suited as correlation orbitals since their overlap with the occupied orbitals is small. This is particularly problematic if the inner regions of the valence shell, in which the electrons are predominantly located, are not accurately described by the inner (more contracted) functions in the basis set so that diffuse functions are also used to improve these regions.

Higher electron correlation effects are included into MP theory at a specific order n, for example, five-electron correlation effects at MP7 since at this order connected pentuple excitations are included. The importance of five-electron correlation is given by the number and magnitude of matrix elements involving pentuple excitations that can be constructed from the more diffuse virtual orbitals, that is, those orbitals that are spanned by diffuse basis functions. On the other hand, if a basis set provides diffuse functions for effectively describing five-electron correlation without providing at the same time somewhat less diffuse functions for

four- or three-electron correlation, then an unphysical exaggeration of higher-order correlation effects as compared to lower-order correlation effects leads to an unbalanced MPn description, which will become divergent. At even orders, higher correlation effects are switched on, which will be more exaggerated because of the basis set the higher the order is. At odd orders, couplings between the new high-order effects will reduce the later the more they have been exaggerated at even orders. Consequently, d'Alembert ratios $|r_j|$ will become larger than 1 and will continue to increase typical of a divergent MPn series.

This is demonstrated in Figure 7, which summarizes the results of MPn ($n = 2, \ldots, 6$) calculations on Ne carried out with different basis sets always augmented by diffuse s, p functions. For a minimal basis set, which is definitely not s, p-saturated, the MP2 correlation energy contribution covers just 72% of the total correlation energy calculated at MP6, while with better basis sets, this value increases to 90% and more. At the same time, the MP4, MP5, and MP6 contributions ob-
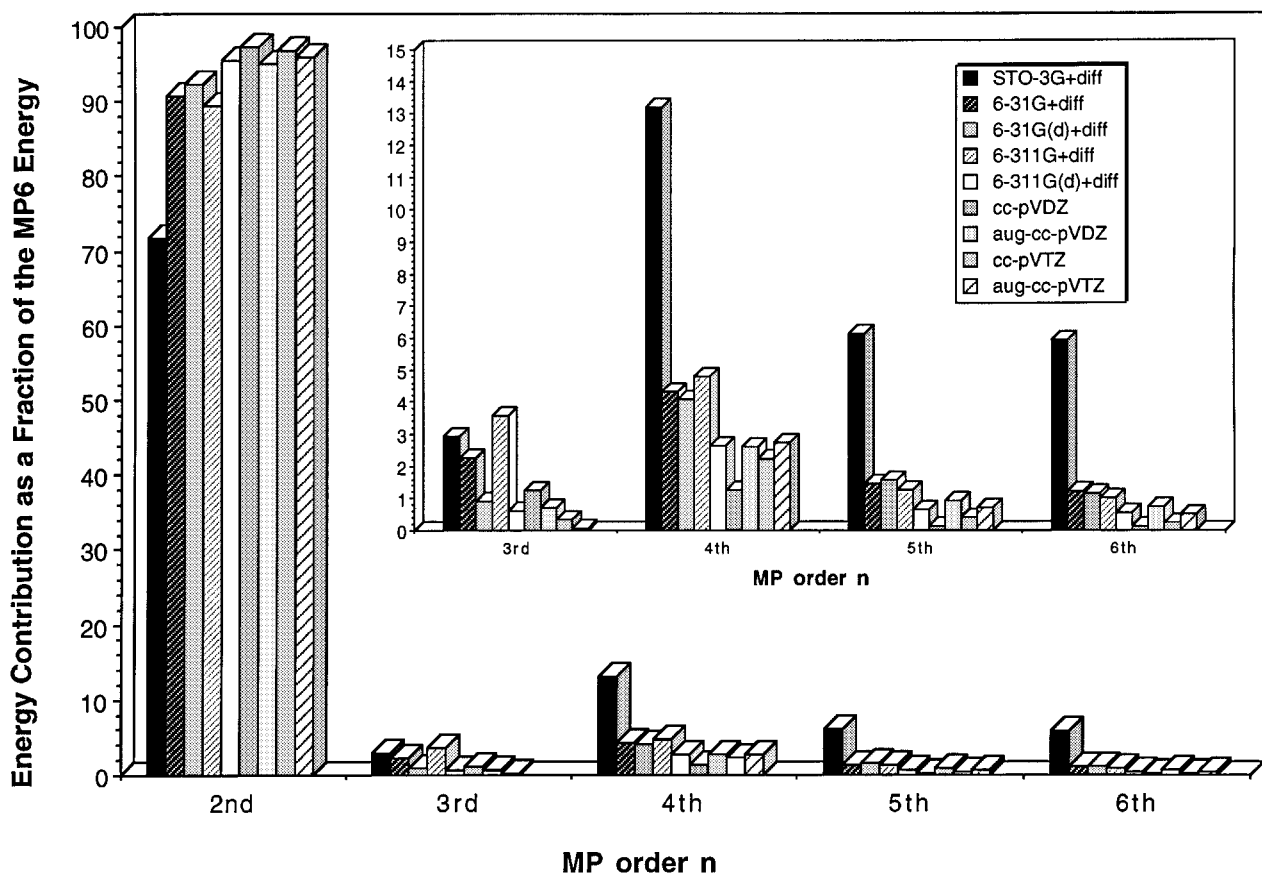
FIGURE 7. Relative correlation contributions at MP2, MP3, MP4, MP5, and MP6 as fractions of the MP6 correlation energy calculated for Ne with various basis sets containing or not containing diffuse functions.

tained with the minimal basis set are three times as large (13, 6, and 6%) than the corresponding contributions calculated with larger basis sets. Hence, diffuse basis functions added to a nonsaturated s, p basis set lead to an unrealistic exaggeration of higher-order correlation effects, to strong initial oscillations, and, most probably, to a nonconvergent MPn series.

The aug-cc-pVDZ basis is a typical example of a basis, which is not saturated in the sp space (to effectively describe low-order correlation effects), but includes diffuse functions important for high-order correlation effects. One could argue that this is not problematic because all the high-order correlation effects are tiny as is the probability that n electrons interact at the same time with the result of carrying out a correlated movement in space. However, the number of these high-order correlation effects increases exponentially (compare with Table III) and, therefore, even tiny contributions, if slightly exaggerated, can lead to a breakdown of

the MP description. Our experience shows that for an MP6 calculation (including up to disconnected pentuple and hextuple excitations) one needs a cc-pVTZ or cc-pVQZ basis to describe three- and four-electron correlation correctly. There is no indication (in form of exaggerated initial oscillations) that the addition of diffuse functions leads to a divergent basis set.

The MPn series for Ne calculated with the aug-cc-pVDZ basis starts to diverge at $n = 15$ although divergent behavior becomes already obvious at lower orders (increasing $|r_j|$ for $j \geq 6$, Fig. 4). Olsen and coworkers [17, 18] investigated the divergent behavior of the MPn series and found that an avoided crossing of the ground state and an excited state dominated by pentuple an higher excitations (see below) is responsible for the divergent behavior of the MPn series. As is shown in Table III, more than 80% of the terms adding to the correlation contribution $E_{MP}^{(15)}$ involve pentuple or higher excitations, namely, 24,140,727 as compared

TABLE III _____

Number of energy terms $E(ABC \cdots)(A, B, C \cdots = S, D, T, \ldots)$ appearing in the final energy expression of the MPn correlation energy.

MP order n	Total no. Terms $N(Total)$	Terms with $Q, P, \ldots$ excitations $N(Q, P, \ldots)$	$N(Q, P, \ldots)$ expressed in %	Terms with $P, H, \ldots$ excitations $N(P, H, \ldots)$	$N(P, H, \ldots)$ expressed in %
4	4	1	25	0	0
5	14	5	36	0	0
6	55	28	51	5	9
7	221	140	63	43	19
8	915	672	73	281	31
9	3865	3136	81	1607	42
10	16,605	14,418	87	8563	52
11	72,325	65,764	91	43,683	60
12	318,670	298,987	94	216,660	68
13	1,417,846	1,358,797	96	1,054,532	74
14	6,361,389	6,184,242	97	5,067,427	80
15	28,749,241	28,217,800	98	24,140,727	84

to a total of 28,749,241 terms. Hence, a tiny exaggeration of the pentuple excitations relative to D, T, or Q excitations caused by augmentation of a non-sp-saturated basis by diffuse functions leads to divergence of the MPn series.

Several conclusions can be drawn from these observations:

(1) The choice of the basis set is more important for a type II system than for a type I system. In the latter case, pair correlation dominates and higher-order correlation effects play a smaller role. Hence, requirements for the basis are not so distinct. One can use non-sp-saturated basis sets with diffuse functions although this may lead to some small oscillations (see Fig. 3). For type II systems with pronounced electron clustering, three- and four-electron correlation effects become more important and, therefore, the choice of the basis set is essential for adequately describing and for not exaggerating higher-order effects. Clearly, cc-pVTZ, cc-pVQZ, and cc-pVPZ basis sets [32] are needed, depending on the degree of electron clustering.

(2) If MPn theory is applied, which today is possible up to MP6 [11], one has to use increasingly improved basis sets for increasing n. This reflects the contents of a simple rule, namely, that the more advanced electron correlation calculation requires the more extended basis set. A trivial consequence of this rule is that minimal basis sets are not suited for MP2 or any other pair correlation calculation. For an MP2 calculation, an aug-cc-pVDZ basis set may be used without problems. However, calculated properties can become unreasonable if the same basis set is used at MP6 or even higher orders (as generated in an FCI calculation).

(3) In an FCI calculation, higher and higher orders of MP theory are generated with increasing number of iterations. Subsummation of MPn energies leads to an approximate FCI energy at a given iteration step. A divergent MPn series slows down the convergence of the FCI calculation, which does not mean that the FCI calculation does not converge. However, deficiencies of the basis turn up in an unusually long iteration to achieve convergence for a given convergence criterion. Similarly, many convergence problems of a CCSD or CCSDT calculation, which also adds up higher and higher MP terms (depending on the excitations included in the CC calculation [33]), can be caused by an unbalanced basis set. We note that VDZ basis sets with diffuse functions such as the 6-31 + + G(d, p) basis frequently causes convergence problems in CCSD calculations.

Results of Feenberg Scaling

In Table IV, the λ values at different Feenberg orders (first order: λ_3; second order: λ_5; third order: λ_7; fourth order: λ_9; etc.) are listed for the systems investigated. In addition, the fraction of the FCI correlation energy covered either by MP or Feenberg energies at that order n, at which λ_n is determined, is given since it provides a reasonable

TABLE IV
Convergence behavior of the Feenberg series.[a]

System	Basis set	n	λ_n	z range	Intruder state	Class	MP % FCI	FE % FCI	Improved[b]
BH ($^1\Sigma_g$)	cc-pVDZ	3	−0.414	{−2.42, 1}	No	B	87.18	95.38	Yes
		5	−0.504	{−3.04, 1}		B	97.13	99.56	Yes
		11	−0.196	{−1.49, 1}		Conv	99.96	100.00	Yes
	aug-cc-pVDZ	3	−0.402	{−2.34, 1}	No	B	87.38	95.21	Yes
		5	−0.469	{−2.76, 1}		B	97.20	99.48	Yes
		9	−0.347	{−2.06, 1}		Conv	99.81	100.00	Yes
	daug-cc-pVDZ	3	−0.400	{−2.34, 1}	No	B	87.39	95.19	Yes
		5	−0.467	{−2.75, 1}		B	97.20	99.48	Yes
		9	−0.342	{−2.04, 1}		Conv	99.81	100.00	Yes
	cc-pVTZ	3	−0.291	{−1.82, 1}	No	B	89.00	93.75	Yes
		5	−0.338	{−2.02, 1}		B	97.41	99.07	Yes
		13	−0.226	{−1.58, 1}		Conv	99.99	100.00	Yes
	aug-cc-pVTZ	3	−0.281	{−1.78, 1}	No	B	89.10	93.61	Yes
		5	−0.330	{−1.99, 1}		B	97.41	99.04	Yes
		11	−0.465	{−2.74, 1}		B	99.94	100.00	Yes
CH$_2$ ($^3B_1$)	cc-pVDZ	3	−0.234	{−1.61, 1}	No	B	92.27	95.70	Yes
		5	−0.300	{−1.86, 1}		B	97.86	98.68	Yes
		13	−0.779	{−8.05, 1}		—[c]	99.78	102.10	No
	aug-cc-pVDZ	3	−0.224	{−1.58, 1}	No	B	92.33	95.52	Yes
		5	−0.243	{−1.64, 1}		B	98.03	98.69	Yes
		15	−0.349	{−2.07, 1}		—	99.87	99.92	(Y)
	cc-pVTZ	3	−0.187	{−1.46, 1}	No	B	92.68	95.03	Yes
		5	−0.172	{−1.41, 1}		B	98.12	98.55	Yes
		7	−0.202	{−1.51, 1}		B	99.11	99.34	Yes
		15	−0.178	{−1.43, 1}		—	99.87	99.92	(Y)
Ne (^1S)	cc-pVDZ	3	−0.013	{−1.02, 1}	No	C	98.76	98.77	Yes
		5	0.032	{−0.94, 1}		B	99.88	99.89	Yes
		7	0.035	{−0.93, 1}		B	99.99	99.99	Yes
		9	0.024	{−0.95, 1}		Conv	100.00	100.00	Yes
	aug-cc-pVDZ	3	−0.008	{−1.02, 1}	Yes	D	97.79	97.80	No
		5	0.093	{−0.83, 1}	−0.83	C	99.52	99.69	Yes
		7	0.132	{−0.77, 1}		C	99.81	99.95	Yes
		9	0.161	{−0.72, 1}		C	99.89	99.99	Yes
		11	−0.183	{−0.69, 1}		Conv	99.92	100.00	Yes
	cc-pVTZ	3	0.004	{−0.99, 1}	No	C	97.83	97.83	Yes
		5	0.059	{−0.89, 1}		C	99.79	99.84	Yes
		7	0.087	{−0.84, 1}		C	99.96	99.98	Yes
		9	0.099	{−0.82, 1}		Conv	99.99	100.00	Yes

(Continued)

TABLE IV
(Continued)

System	Basis set	n	λ_n	z range	Intruder state	Class	MP % FCI	FE % FCI	Improved[b]
F$^-$ (^1S)	cc-pVDZ	3	-0.008	$\{-1.02, 1\}$	No	B	98.54	98.54	Yes
		5	-0.069	$\{-1.15, 1\}$		B	99.93	99.97	Yes
		7	-0.143	$\{-1.33, 1\}$		Conv	99.99	100.00	Yes
	aug-cc-pVDZ	3	0.038	$\{-0.96, 1\}$	Yes	D	94.73	94.88	No
		5	0.182	$\{-0.69, 1\}$	-0.69	C	96.72	98.60	Yes
		7	0.247	$\{-0.60, 1\}$		C	95.49	99.60	Yes
		9	0.282	$\{-0.56, 1\}$		C	92.25	99.80	Yes
		15	0.330	$\{-0.50, 1\}$		Conv	31.62	100.00	Yes
	cc-pVTZ	3	0.018	$\{-0.96, 1\}$	No	C	96.85	96.88	Yes
		5	0.065	$\{-0.88, 1\}$		B	99.66	99.75	Yes
		7	0.068	$\{-0.87, 1\}$		B	99.95	99.97	Yes
		9	0.063	$\{-0.88, 1\}$		Conv	99.99	100.00	Yes
FH ($^1\Sigma_g$)	cc-pVDZ	3	-0.015	$\{-1.03, 1\}$	No	C	97.76	97.78	No
		5	-0.005	$\{-1.01, 1\}$		C	99.79	99.79	Yes
		7	0.034	$\{-0.93, 1\}$		C	99.79	99.89	Yes
		9	0.047	$\{-0.91, 1\}$		Conv	99.99	100.00	Yes
	aug-cc-pVDZ	3	-0.003	$\{-1.01, 1\}$	Yes	D	96.67	96.67	No
		5	0.084	$\{-0.85, 1\}$	-0.85	C	99.27	99.45	Yes
		7	0.138	$\{-0.76, 1\}$		C	99.62	99.89	Yes
		9	0.168	$\{-0.71, 1\}$		C	99.72	99.98	Yes
		13	0.206	$\{-0.66, 1\}$		Conv	99.77	100.00	Yes
	cc-pVTZ	3	0.006	$\{-0.99, 1\}$	No	C	96.69	96.70	Yes
		5	0.061	$\{-0.86, 1\}$		C	99.60	99.69	Yes
		7	0.086	$\{-0.84, 1\}$		C	99.91	99.96	Yes
		9	0.106	$\{-0.81, 1\}$		B	99.97	99.99	Yes
		11	0.121	$\{-0.78, 1\}$		Conv	99.98	100.00	Yes
H$_2$O ($^1A_1$)	cc-pVDZ	3	-0.036	$\{-1.07, 1\}$	No	C	97.10	97.22	No
		5	-0.036	$\{-1.07, 1\}$		C	99.78	99.80	No
		7	-0.034	$\{-1.07, 1\}$		C	99.97	99.97	No
		9	-0.006	$\{-1.01, 1\}$		Conv	100.00	100.00	Yes
	cc-pVDZ(+)	3	-0.024	$\{-1.05, 1\}$	Yes	D	96.47	96.52	No
		5	0.023	$\{-0.96, 1\}$	-0.96	C	99.54	99.55	Yes
		7	0.079	$\{-0.85, 1\}$		C	99.85	99.90	Yes
		9	0.112	$\{-0.80, 1\}$		C	99.92	99.98	Yes
		13	0.150	$\{-0.74, 1\}$		Conv	99.96	100.00	Yes

[a] Some low orders and that order of Feenberg scaling are given, at which minimization of ΔE_{MP}^n with regard to λ leads to the FCI correlation energy. For the intruder state, an approximate location is determined by the z value for $z' = -1$ obtained for that Feenberg scaling order, which leads for the first time to convergence although the corresponding MPn series is diverging. MP % FCI and FE % FCI give the fraction of the FCI correlation energy covered by the MP or Feenberg correlation energy at the order defined by n. For the classification of Feenberg series, see text. Conv: converged.
[b] Improvement of the convergence behavior will be given (Yes) if the Feenberg energy for the last order n considered is closer to the FCI energy than is the corresponding MPn energy and, at the same time, the Feenberg energy is converging (see text). (Y): improvement not clear because of error progression.
[c] Oscillations because of error progression.

estimate for the improvement of the convergence behavior of the MPn series. The speed of convergence can be estimated by giving that order m for which Feenberg scaling leads to a 100% coverage of the FCI correlation energy within the accuracy possible in this work, that is, 0.5×10^{-6}. In general, Feenberg scaling up to order seven (λ_{15}) was performed; however, only in the case of a divergent MPn series is high-order scaling interesting. In other cases, error progression makes results of higher-order Feenberg scaling dubious.

The data of Table IV suggest that first-order Feenberg scaling is not sufficient to significantly improve the convergence behavior of the MPn series. Second-order Feenberg scaling leads to satisfactory improvements. In general, adjustment of electron-correlation contributions can be made better, the higher the order of Feenberg scaling is, that is, the higher the order of the MP correlation energy that is used in the Feenberg minimization. For a steadily converging a MPn series of a type I system, scaling factors should be negative and approach a zero value for increasing scaling order. Absolute values of λ_m at a given order m decrease when improving the basis set, which reflects the fact that for type I systems the larger basis covers more electron correlation and, therefore, the upscaling of the perturbation operator is needed less. It also seems that with increasing complexity of the electronic structure (i.e., more electrons, lower symmetry, higher anisotropy of electron distribution) the $|\lambda|$ values become smaller, corresponding in the case of type I systems to a more moderate enlargement of the perturbation.

In general, there is a close relationship between the convergence behavior of the MPn series as reflected by the d'Alembert ratios r_j (Figs. 2–7) and the calculated scaling factors λ_n (Table IV). Positive ratios r_j (oscillating or nonoscillating) lead to negative scaling factors, which means that the perturbation is enlarged to cover more correlation effects at lower orders. For the converging MPn series of type I systems, λ_n values become more negative with increasing scaling order. At some order, this trend is reverted, that is, absolute scaling factors become smaller again and may finally approach a zero value, which means that the original MPn series was close to the FCI energy at this order. We found this trend for the MPn series of BH (turning point at order 5 or 7), while for the MPn series of CH_2, the calculated λ values decrease steadily up to order 15 (cc-pVDZ basis, Table IV) typical of a slowly converging series.

Oscillations in the r_j ratios are also reflected by the scaling factors but in a damped form.

Negative ratios of d'Alembert ratios (caused by oscillations between negative and positive MP correlation energy contributions) lead to a positive value of λ. In this way, the perturbation is decreased and the contribution of the unperturbed system scaled up. In all cases of initial oscillations in the MPn series, these are reduced by Feenberg scaling and convergence is accelerated (indicated in Table IV as improved convergence). For a divergent series, the scaling factor is positive and steadily increases through all orders of Feenberg scaling investigated (for an example, see Table V). In these cases, first-order Feenberg scaling (λ_3) can increase oscillations and does not lead to convergence. However, second-order Feenberg scaling (λ_5) leads a convergent series in all cases considered and, in this way, will cure the divergent behavior of the MPn series if a VDZ basis with diffuse functions is used. Larger-order Feenberg scaling leads to more rapid convergence. This is illustrated in Figures 8–11, in which Cauchy ratios of Feenberg correlation contributions are compared with the corresponding MPn ratios. Estimates of limit values τ' are also given, which clearly show that improved convergence is obtained for increasing order of λ.

We note that second-order Feenberg scaling is already sufficient to enforce convergence of the Feenberg series even if the associated MPn series is divergent. It also dampens initial oscillations of the MPn series and, by this, improves convergence. For second-order Feenberg scaling, MP5 energies are required, which are accessible for a large number of small molecules. Higher-order

TABLE V

Radius of convergence for the MPn series of Ne calculated with the aug-cc-pVDZ basis after Feenberg scaling.

Feenberg order m	n of λ_n	Value of λ_n	$z \in \left[-\dfrac{1-\lambda}{1+\lambda}, 1 \right]$
1	3	-0.008	$[-1.016, 1]$
2	5	0.093	$[-0.830, 1]$
3	7	0.132	$[-0.767, 1]$
4	9	0.161	$[-0.723, 1]$
5	11	0.182	$[-0.692, 1]$
6	13	0.198	$[-0.669, 1]$
7	15	0.200	$[-0.667, 1]$
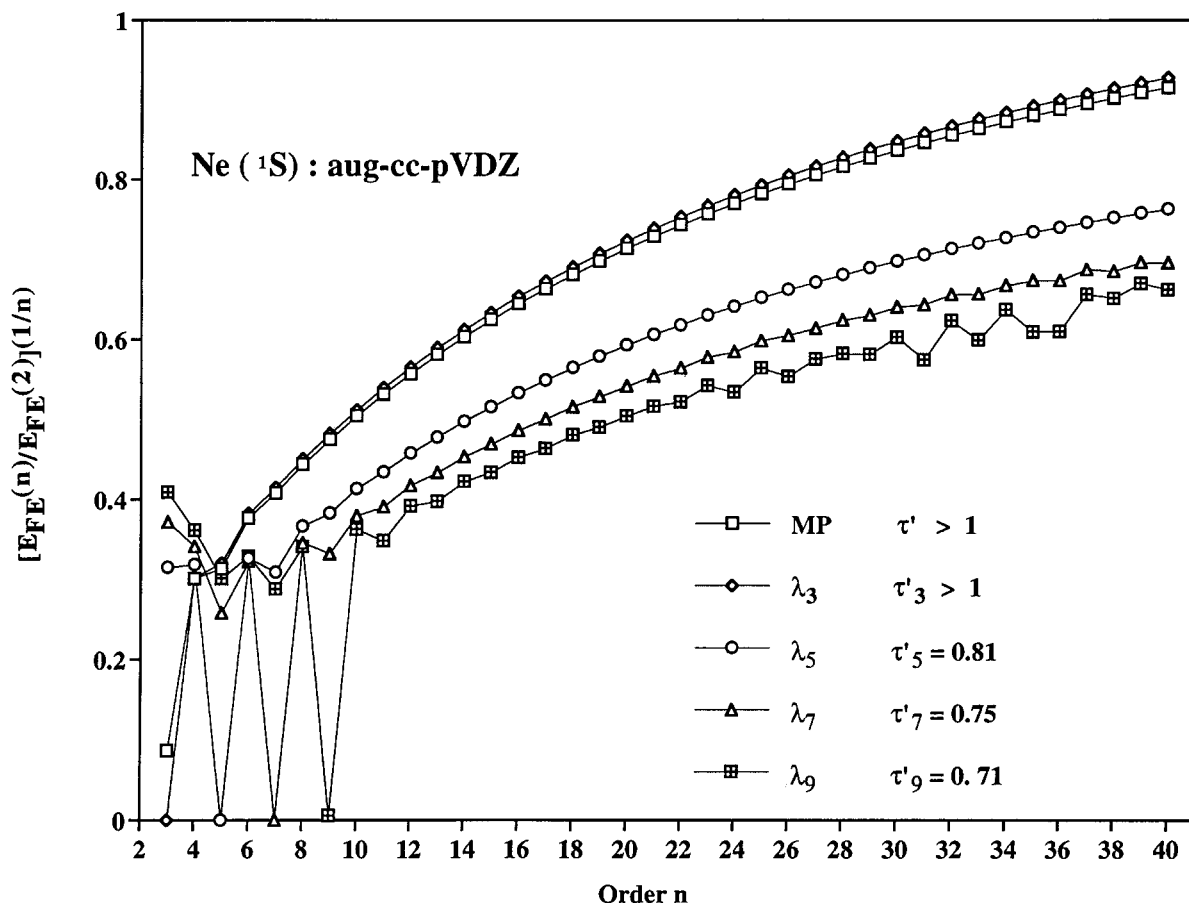
FIGURE 8. Cauchy ratios of Feenberg correlation energy contributions calculated for Ne(^1S) with the aug-cc-pVDZ basis set for a given order of Feenberg scaling. Estimated limit values τ' indicate whether the series is divergent ($\tau' > 1$) or convergent ($\tau' < 1$) (see text).

Feenberg scaling cannot play a role in MP calculations since, presently, MP6 is the highest order of MP theory that can be carried out with available programs [11]. On the other hand, higher orders of Feenberg scaling are useful in connection with FCI calculations to investigate the convergence behavior of the MPn series. Calculated scaling factors directly reflect convergence/divergence properties and can be used to analyze the latter.

Convergence Radius of the MPn Series and the Exclusion of Intruder States

In MP theory, the effective electron interaction described with operator $\hat{V}$ of Eq. (4) is defined in the model space ($\mathscr{P}$ space) to reproduce the lowest energy of the electronic system under consideration. Since the action of $\hat{V}$ is switched on with the strength parameter z [see Eq. (2)], the correct en-

ergy $\mathscr{E}$ of the perturbed system is also obtained as a function of z. A necessary condition for the applicability of MPn theory is that the energy spectra for the model space $\mathscr{P}$ (unperturbed problem) and for the orthogonal complement space ($\mathscr{Q}$-space) do not overlap, but are well separated for $-1 < z < 1$. However, if two of the eigenvalues $\mathscr{E}_l$ of $\hat{H}(z)$, described as functions of z, that is, $\mathscr{E}_l(z)$, one from $\mathscr{P}$ and one from $\mathscr{Q}$ space, cross at a point inside the unit circle drawn in the complex plane at $z = 0$, then the MPn series will diverge [20, 21]. Because of the hermiticity of the operators of Eq. (2), each crossing point $x_b = z_b + iy_b$ of functions $\mathscr{E}_l(z)$ will lead to an equivalent crossing point $x_b^* = z_b - iy_b$ placed symmetrically with regard to the real axis. For z_b, an avoided crossing is observed as a result of an eigenstate $\mathscr{E}_l(z)$ from $\mathscr{Q}$-space intruding into $\mathscr{P}$-space (*intruder state*).

The MPn series is converging for a convergence radius $R_c > 0$. However, in case of an intruder
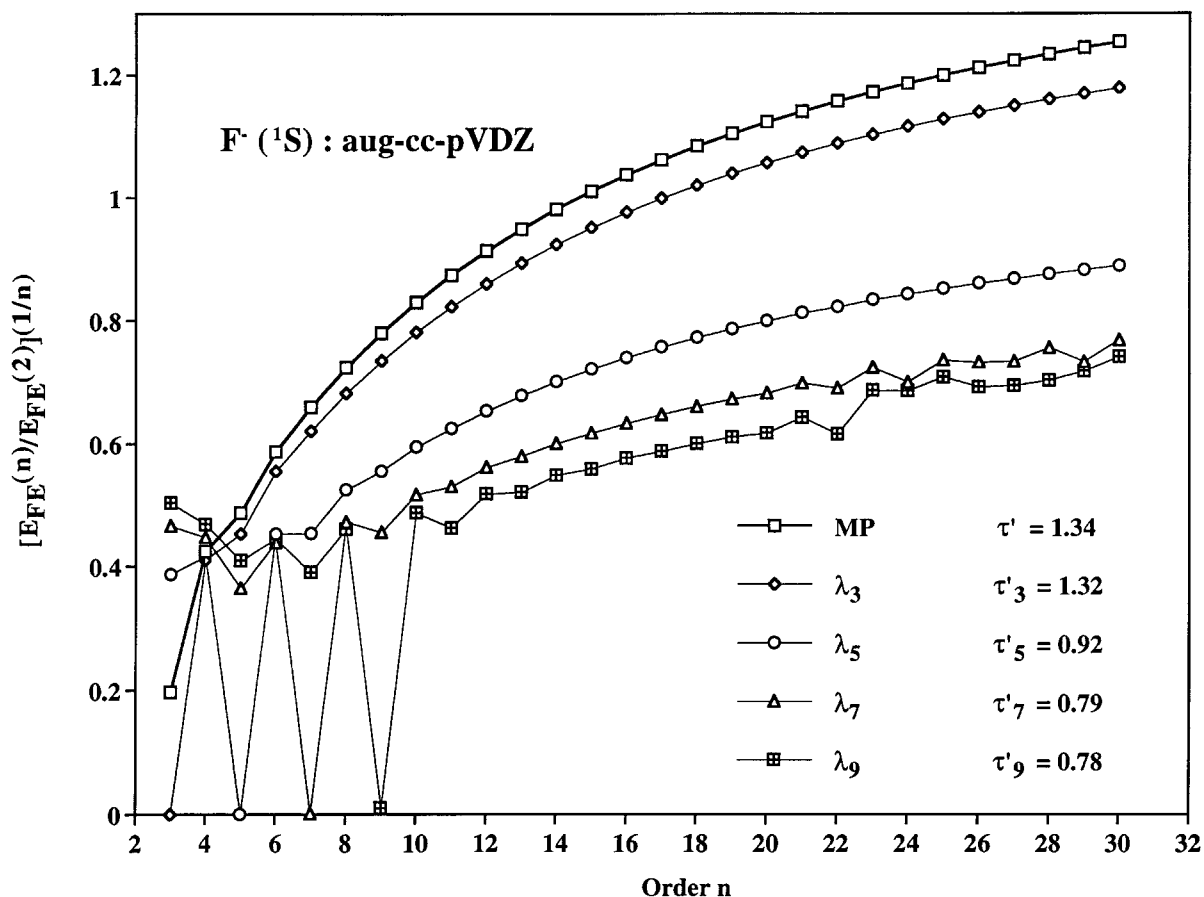
FIGURE 9. Cauchy ratios of Feenberg correlation energy contributions calculated for $F^-(^1S)$ with the aug-cc-pVDZ basis set for a given order of Feenberg scaling. Estimated limit values τ' indicate whether the series is divergent ($\tau' > 1$) or convergent ($\tau' < 1$) (see text).

state, R_c is given by the distance from $z = 0$ to the avoided crossing point z_b and, therefore, R_c is smaller than 1. Consequently, the MPn series diverges [20, 21]. On the other hand, it is possible to *push* crossing points $\{z_b, z_b^*\}$ out of the unit circle by modifying $\hat{H}_0$ as, for example, by appropriate scaling. The Hamiltonian $\tilde{H}(z', \lambda)$ described in Eq. (13), can be rewritten in the form

$$\tilde{H}(z', \lambda) = \frac{1 - z'\lambda}{1 - \lambda} \hat{H}_0 + z'\hat{V} \qquad (48a)$$

$$= \frac{1 - z'\lambda}{1 - \lambda} \left(\hat{H}_0 + \frac{z'(1 - \lambda)}{1 - z'\lambda} \hat{V} \right) \quad (48b)$$

$$= \frac{1 - z'\lambda}{1 - \lambda} \hat{H} \left(z = \frac{z'(1 - \lambda)}{1 - z'\lambda} \right). \quad (48c)$$

According to Eq. (48), the relationship between the Feenberg energy $E_\lambda(z')$ associated with the Hamil-

tonian $\tilde{H}(z', \lambda)$ and the energy $E(z)$ associated with $\hat{H}(z)$ of Eq. (5) is given by Eq. (49):

$$E_\lambda(z') = \frac{1 - z'\lambda}{1 - \lambda} E \left(z = \frac{z'(1 - \lambda)}{1 - z'\lambda} \right). \quad (49)$$

Obviously, the Feenberg energy E_λ in Eq. (49) is independent of λ when $z' = 1$, which means that the Feenberg series $\{E_\lambda^{(n)}\}$ and the MP series $\{E_{MP}^{(n)}\}$ will converge to the same limit. However, the Hamiltonian $\tilde{H}(z', \lambda)$ depends on λ for z' different from 1 as revealed by Eq. (48). For the series $\{E_\lambda^{(n)}\}$ to converge, the zeroth-order Hamiltonian $\tilde{H}_0(\lambda) [= 1/(1 - \lambda)\hat{H}_0]$ and the total Hamiltonian $\tilde{H}(z' = 1, \lambda)$ must possess well-separated energy spectra, which means that the convergence behavior of $\{E_\lambda^{(n)}\}$ is determined by the scalar parameter λ.
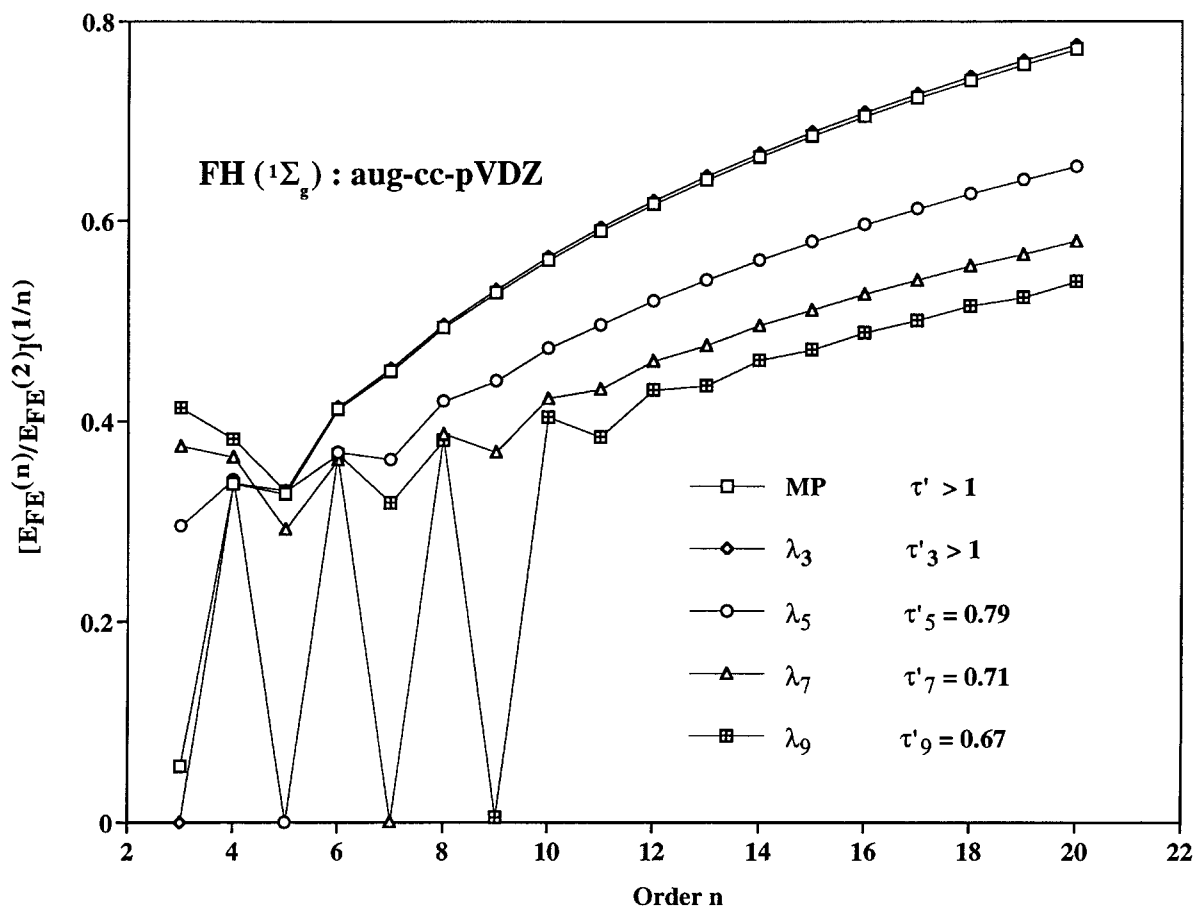
FIGURE 10. Cauchy ratios of Feenberg correlation energy contributions calculated for $FH(^1\Sigma_g)$ with the aug-cc-pVDZ basis set for a given order of Feenberg scaling. Estimated limit values τ' indicate whether the series is divergent ($\tau' > 1$) or convergent ($\tau' < 1$) (see text).

To show the dependence of the convergence radius of the Feenberg series on λ, z' is set equal to 1, 0, and -1 in Eq. (49), which leads to Eqs. (50), (51), and (52):

$$E_\lambda(z' = 1) = E(z = 1) \qquad (50)$$

$$E_\lambda(z' = 0) = \frac{1}{1 - \lambda} E(z = 0) \qquad (51)$$

$$E_\lambda(z' = -1) = \frac{1 + \lambda}{1 - \lambda} E\left(z = -\frac{1 - \lambda}{1 + \lambda}\right). \quad (52)$$

Now, the convergence radius $R_c(z')$ of the Feenberg series depends on the behavior of $E(z)$ in the range $-(1 - \lambda)/(1 + \lambda) \leq z \leq 1$. Hence, the scaling of $\bar{H}_0$ makes the convergence range $z \in [-1, 1]$ of the MPn series flexible, that is, $[-1, 1] \overset{\lambda}{\Rightarrow} [-(1 - \lambda)/(1 + \lambda), 1]$. If $0 < \lambda < 1$, then $[-(1 - \lambda)/(1 + \lambda), 1] \subset [-1, 1]$, so that an intruder state with

$z_b < 0$, that is, a *back-door intruder state* is pushed out the convergence range of the Feenberg series. The convergence radius $R_c(z')$ becomes larger than 1 and the Feenberg series converges.

The position z_b of an intruder state can approximately determined by the λ value of that order of Feenberg scaling for which the transformed MPn series becomes convergent for the first time. For the cases considered, this is always λ_5 and, accordingly, it is used in Table IV to estimate the value of z_b. In the case of the MPn series of the Ne atom calculated with the aug-cc-pVDZ basis, Olsen and coworkers [17, 18] calculated z_b to be 0.82, in good agreement with our estimate of 0.83 (see Table IV). As shown in Table V, higher-order Feenberg scaling reduces the z' convergence range from $[-0.83, 1]$ to $[-0.67, 1]$, thereby accelerating convergence of the MPn series. This is contrary to what was found by Olsen and coworkers [17, 18]
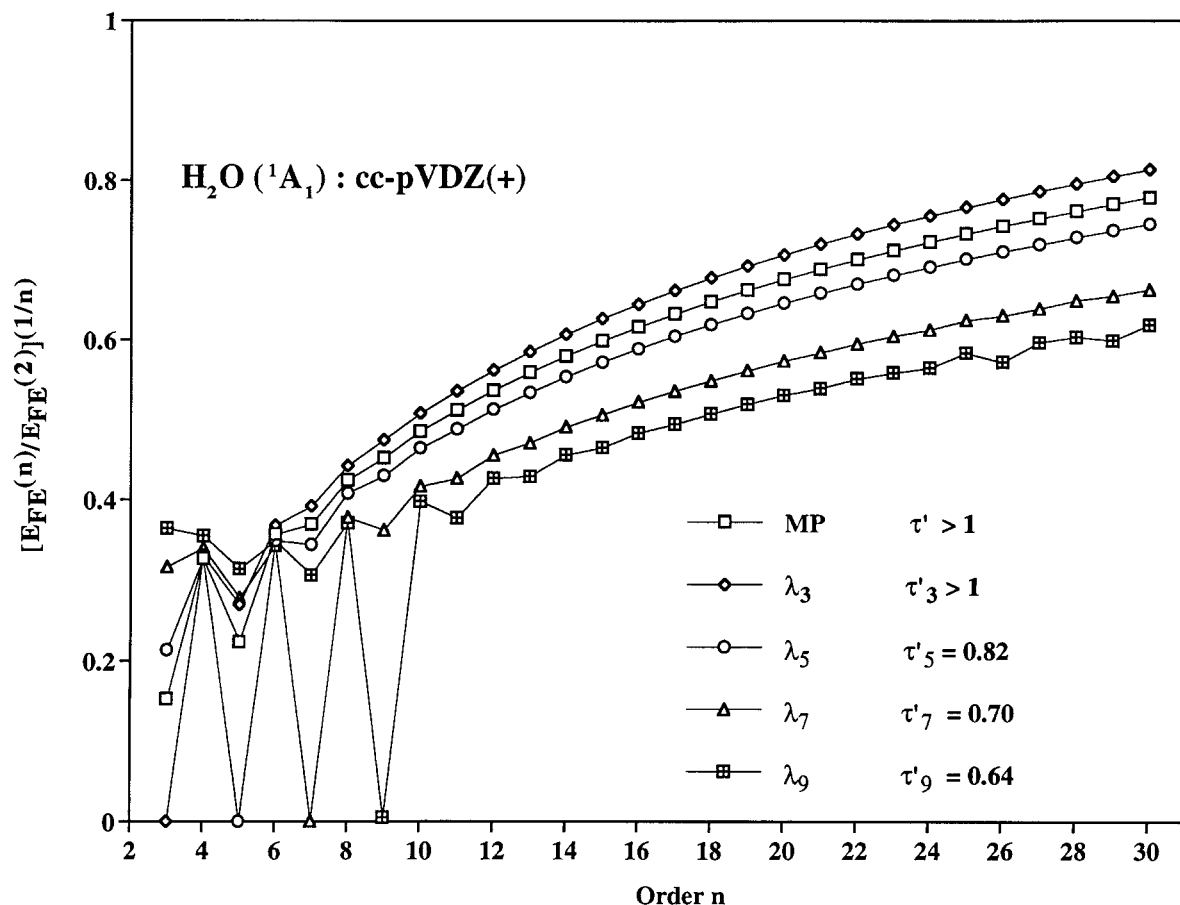
FIGURE 11. Cauchy ratios of Feenberg correlation energy contributions calculated for $H_2O(^1A_1)$ with the aug-cc-pVDZ basis set for a given order of Feenberg scaling. Estimated limit values τ' indicate whether the series is divergent ($\tau' > 1$) or convergent ($\tau' < 1$) (see text).

who used an arbitrary scaling factor. These authors described the intruder state to be dominated by pentuple and higher excitations. This is typical of an unbalanced basis set, for which diffuse functions have been added to a basis unsaturated in the s, p space (see the sixth section).

Back-door intruder states will occur at $z_b = -0.69$ for F^-, -0.85 for FH, and -0.96 for H_2O if the VDZ is augmented by diffuse functions. Hence, the MPn series of F^- represents the most and that of H_2O the least problematic case. This is parallel to the observation that electron clustering decreases from F^- to H_2O for the type II systems investigated. For the electronic systems considered, a *front-dor intruder state* with $z_b > 0$ was not found. We note that simple Feenberg scaling cannot help to push out *front-door intruder states* from the convergence range. In this case, other techniques have to be applied.

Conclusions

For type I systems with well-separated electron pairs, the MPn series is slowly converging. Feenberg scaling leads to λ values smaller than zero, which means that the perturbation is increased and lower orders of perturbation theory cover more correlation effects (scaling up of pair correlations). In all type I cases considered, Feenberg scaling accelerates convergence significantly. For larger basis sets, the importance of Feenberg scaling is reduced.

Type II systems are characterized by electron clustering in a confined region of space. Three- and four-electron correlation effects are needed to distribute electrons in the best way possible. Since a description of these effects with pair correlation

leads to an exaggeration of pair correlation energies, which is corrected at higher orders, strong initial oscillations are typical of the MPn series. By reducing the perturbation (positive λ, reduction of pair correlation), Feenberg scaling dampens oscillations and improves the convergence behavior of the perturbation series.

For type II systems, divergent behavior of the MPn series is induced by the choice of an unbalanced basis set, which is not saturated in s, p-space, but contains already diffuse functions that artificially increase the importance of higher correlation effects. For the Ne atom, divergence is observed at $n = 15$ when calculations are done with an aug-cc-pVDZ. At this order, more than 80% of all MP terms contain P and higher excitation effects, which is in line with the observation that the intruder state causing the divergence is P, H, etc., dominated. We have demonstrated the problems caused by diffuse functions by carrying out a series of MP6 calculations. They suggest that a physically useful description can only be obtained if QZ or PZ basis sets (including diffuse functions) are used.

All divergent cases investigated can be transformed in such a way by Feenberg scaling that relative fast convergence is enforced. In this case as well as in general, second-order Feenberg scaling is the method of choice since it can be carried out with available MP5 energies and it improves the convergence behavior of the MPn series significantly.

Care has to be taken with regard to low-order Feenberg energies, which are smaller than the order at which the energy minimization step has been performed. Scaling may introduce strong oscillations. Therefore, one should use only Feenberg energies with $n \geq 2m + 1$ if m is the order of Feenberg scaling.

In conclusion, it is not justified to interpret a divergent or erratic behavior of the MPn series as an indication that MP theory is physically not sound. We find that the convergence/divergence behavior can be used as an indicator for deficiencies of the basis set used that are not so obvious. Also, this work shows that there is reason to calculate MP5 energies because in this way reasonable estimates of FCI energies can be obtained.

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