Sixth-Order Many-Body Perturbation Theory. IV. Improvement of the Møller–Plesset Correlation Energy Series by Using Padé, Feenberg, and Other Approximations up to Sixth Order

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ABSTRACT

Three different ways of getting reliable estimates of full configuration interaction (FCI) correlation energies are tested, namely (a) by Padé approximants $[k, k]$ and $[k, k-1]$, (b) by using extrapolation formulas, and (c) by Feenberg scaling of Møller–Plesset (MP) correlation energies. By using MPn energies up to sixth order, i.e., MP2, MP3, MP4, MP5, and MP6, it was possible to test the convergence behavior of the Padé series $[1, 0]$, $[1, 1]$, $[2, 1]$, $[2, 2]$ and the Feenberg series up to sixth order where in the latter case a scaling factor $\lambda^{(5)}$ (scaling of the second-order wave function, FE2) rather than the previously tested $\lambda^{(3)}$ (scaling of the first-order wave function, FE1) was considered. Investigation of 26 different correlation energies for systems with monotonic convergence in the MPn series (class A systems) or initially oscillatory convergence behavior (class B systems) indicates that Padé approximants lead in some cases to reasonable estimates of FCI correlation energies, but in other cases, in particular for class B systems, they give too negative correlation energies. Both monotonic and oscillatory behavior for the Padé series is observed where it is possible to predict its convergence behavior on the basis of calculated MPn energies. The best estimates of the FCI correlation energy are obtained by FE2 scaling. At sixth-order FE2, values for atoms and molecules with equilibrium geometry differ on the average by just 0.146 mhartree from FCI correlation energies. The FE2 correlation energies all converge monotonicly. Also, FE2 scaling reduces the exaggeration of MP6 correlation energies for class B systems. However, surprisingly good estimates of FCI energies are also obtained by simple extrapolation formulas based on MP4, MP5, and MP6 correlation energies.

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Introduction

One of the major goals in *ab initio* theory is to obtain correlation energies of full configuration interaction (FCI) accuracy. One comes close to this goal if one uses coupled cluster (CC) methods that involve single (S), double (D), and triple (T) excitations [1, 2]. Benchmark calculations for electronic systems for which FCI calculations are still possible have shown that exact correlation energies (calculated for a given basis set with a finite number M of basis functions at a given geometry) can be approached by *CCSDT* or the corresponding quadratic CI method, *QCISDT*, within 1 mhartree [2]. Reasonable correlation energies are also obtained with CC or QCI when the T excitations are included in a perturbative way such as for *CCSD*(T) [3] or *QCISD*(T) [4]. The success of CC methods in approximating FCI results is based on the fact that they include infinite-order effects and are size extensive where the latter property is more important for the calculation of relative energies.

Attempts to get reasonable estimates of FCI correlation energies from many-body perturbation theory (MBPT) with the Møller–Plesset (MP) perturbation operator [5] have been less successful. Methods for routine calculations of correlation energies at second-order MP (MP2) theory [6, 7], third-order MP (MP3) theory [8], and fourth-order MP (MP4) theory [9, 10] are available for the last 10 years. Recently, programs for determining fifth-order MP (MP5) theory have been developed independently by the Bartlett and the Pople group [11, 12]. Some years ago, we pointed out that it is possible to work out a method for calculating sixth-order MP (MP6) correlation energies [13]. In the three preceding articles to this work, we have described development, implementation, and first applications of a full MP6 method [14–16]. This work enables us now to reconsider the possibility of making reasonable estimates of FCI energies on the basis of calculated MP correlation energies. Such an investigation necessarily implies an analysis of the convergence behavior of the MPn series for $n = 2, 3, 4, 5, 6$ and a search for methods that may improve this convergence behavior.

At a time when routine calculations of MPn correlation energies where only possible for $n \leq 4$, Pople, Frisch, Luke, and Binkley (PFLB) [17] derived an extrapolation formula for estimating infinite-order MP correlation energies. Actually, this formula was based on the assumption of a geometrically progressing MPn series, which is not necessarily fulfilled. For example, Handy and coworkers [18, 19] could show with the help of MPn energies ($n \leq 48$) obtained in the nth iteration step of a FCI calculation that a MPn series does not necessarily converge monotonically. In many cases, there are initial oscillations in the correlation energy which make it difficult to extrapolate to infinite-order MP energies.

Oscillations in the correlation energy are a logical consequence of a stepwise improvement of MP theory with order n. At even orders n, new correlation effects described by new excitations are added to the perturbation series. For example, at MP2, D excitations are included to describe pair correlation effects. At MP4, S, T, and Q excitations are added to D excitations to cover orbital relaxations, three-electron correlation effects, and the simultaneous but independent correlations of two electron pairs. At the MP6 level, pentuple (P) and hextuple (H) excitations are included that cover higher order correlation effects [13–16]. In all these cases, the new correlation effects can be exaggerated because there is no coupling between D excitations at MP2, S, T, and Q excitations at MP4, or P and H excitations at MP6. This coupling, which leads to a more realistic description of electron correlation, is always included at the next higher odd order perturbation theory level. For example, at MP3 coupling between the D excitations leads to an improved description of pair correlation effects that avoids the typical overestimation of pair correlation by MP2. At MP5, couplings between S, T, and Q excitations are introduced which are important for a balanced description of correlation effects associated with these excitations. Hence, at the even orders new correlation effects normally lead to a significant increase of the absolute magnitude of the correlation energy while the latter increases only slowly or is even reduced at odd orders due to the couplings between excitations just introduced in the previous even order. This can lead to oscillations in the MPn correlation energy series as has been observed by various authors [18–20].

An improved understanding of the convergence behavior of the MPn series has been obtained from FCI calculations for electron systems of moderate size [18, 21]. Handy and co-workers have obtained MPn correlation energies up to order $n = 48$ from the iteration steps of a FCI calculation [18]. They found that the MPn series does not always converge uniformly. Four cases could be distinguished, namely (a) rapid convergence, (b) initial oscillations, (c) divergence, and (d) slow convergence of the MPn series. The latter case was found for unrestricted MPn calculations with considerable spin contamination in the unrestricted Hartree–Fock (UHF) reference function. The problem could be solved by using an appropriate restricted open-shell formalism.

Although the calculation of the MPn series up to $n = 6$ does not give much possibility of further detailing its convergence behavior, calculation of the MP2, MP3, MP4, MP5, and MP6 correlation contributions provides the basis of investigating those correlation effects that lead to monotonic or oscillatory convergence behavior of the MPn series at lower orders. In the third article of this series [16], we have already shown that initial oscillations of the MPn series result from oscillations in the T part of the correlation energy that cannot be compensated by the corresponding SDQ contributions. Any method for predicting FCI correlation energies has to consider these oscillations in some way and, therefore, we will investigate in this work how known procedures for estimating FCI correlation energies can handle slow convergence or initial oscillations of the MPn series. We will particularly focus on the following questions:

1. What are the predictive properties of sixth-order MP theory as compared to those of MP4 and MP5? Does MP6 suffice to obtain reliable estimates of FCI correlation energies?
2. What is the best way of using MP6 energies for the prediction of exact correlation energies?
3. Is it possible to dampen initial oscillations of the MPn series by an appropriate method?

These and some other questions will be discussed in this work which is structured in the following way. In the second section we will shortly describe three methods used in this work for predicting FCI correlation energies. Then, in the third section we will apply these methods to a set of test examples and discuss possibilities of getting improved estimates of FCI correlation energies.

Improvement of the MPn Series and Estimation of FCI Correlation Energies

The exact correlation energy ΔE for a given system is an eigenvalue of the Hamiltonian $\bar{H}$:

$$\bar{H}|\Phi\rangle = \Delta E|\Phi\rangle, \tag{1}$$

where $\bar{H}$ is defined by

$$\bar{H} = \hat{H} - \langle\Phi_0|\hat{H}|\Phi_0\rangle = \hat{H} - E(\mathrm{HF}). \tag{2}$$

The wave function $|\Phi_0\rangle$ is the Hartree–Fock (HF) reference wave function and E(HF) corresponds to the HF energy. The Schrödinger energy E and the Schrödinger wave function Φ are eigenvalue and eigenfunction of the energy operator $\hat{H}$.

The Hamiltonian $\bar{H}$ can be split into unperturbed Hamiltonian $\bar{H}_0$ and perturbation operator $\bar{V}$ [5]:

$$\bar{H} = \bar{H}_0 + \bar{V}. \tag{3}$$

Then, the correlation energy ΔE can be expanded in terms of contributions $E_{\mathrm{MP}}^{(n)} = E(\mathrm{MP}n)$ to the MPn correlation energy:

$$\Delta E = E - E(\mathrm{HF}) = \sum_{n=2}^{\infty} E_{\mathrm{MP}}^{(n)}. \tag{4}$$

In order to improve the convergence behavior of the MPn series (4), we will test three possibilities using calculated energies $E(\mathrm{MP}n)$ ($n = 2,3,4,5,6$), namely (1) Padé approximants $[k,l]$ [22–24], (2) the Pople–Frisch–Luke–Binkley extrapolation formula [17], and (3) the Feenberg perturbation series [25–28].

PADÉ APPROXIMANTS [K, L]

Calculation of the correlation energy expansion (4) must be terminated at some finite order n neglecting residuals of order $n + 1$. According to Padé [22], Eq. (4) can be considered as one of the $(n + 1)$ approximants that are given by the ratio of a polynomial of order k to a polynomial of order l where $k + l = n$. The coefficients of these polynomials are determined in the way that each approximant differs from the energy only by residuals of order $n + l$.

Bartlett and Shavitt have given general formulas for the $[k, k]$ and $[k, k-1]$ Padé approximants [24], which for $k = 1, 2$ lead to the following expressions:

$$[1,0] = E_{MP}^{(2)}(E_{MP}^{(2)} - E_{MP}^{(3)})^{-1} E_{MP}^{(2)}$$
$$= E_{MP}^{(2)} \frac{1}{1 - \frac{E_{MP}^{(3)}}{E_{MP}^{(2)}}} = E_{MP}^{(2)}\left(1 + \frac{E_{MP}^{(3)}}{E_{MP}^{(2)}} + \cdots\right)$$
$$= E_{MP}^{(2)} + E_{MP}^{(3)} + O(E_{MP}^{(4)}), \qquad (5)$$

$$[1,1] = E_{MP}^{(2)} + E_{MP}^{(3)}(E_{MP}^{(3)} - E_{MP}^{(4)})^{-1} E_{MP}^{(3)}$$
$$= E_{MP}^{(2)} + E_{MP}^{(3)} \frac{1}{1 - \frac{E_{MP}^{(4)}}{E_{MP}^{(3)}}}$$
$$= E_{MP}^{(2)} + E_{MP}^{(3)}\left(1 + \frac{E_{MP}^{(4)}}{E_{MP}^{(3)}} + \cdots\right)$$
$$= E_{MP}^{(2)} + E_{MP}^{(3)} + E_{MP}^{(4)} + O(E_{MP}^{(5)}), \qquad (6)$$

$$[2,1] = (E_{MP}^{(2)} \quad E_{MP}^{(3)}) \times \begin{pmatrix} E_{MP}^{(2)} - E_{MP}^{(3)} & E_{MP}^{(3)} - E_{MP}^{(4)} \\ E_{MP}^{(3)} - E_{MP}^{(4)} & E_{MP}^{(4)} - E_{MP}^{(5)} \end{pmatrix}^{-1} \begin{pmatrix} E_{MP}^{(2)} \\ E_{MP}^{(3)} \end{pmatrix}, \qquad (7)$$

and

$$[2,2] = E_{MP}^{(2)} + (E_{MP}^{(3)} \quad E_{MP}^{(4)}) \times \begin{pmatrix} E_{MP}^{(3)} - E_{MP}^{(4)} & E_{MP}^{(4)} - E_{MP}^{(5)} \\ E_{MP}^{(4)} - E_{MP}^{(5)} & E_{MP}^{(5)} - E_{MP}^{(6)} \end{pmatrix}^{-1} \begin{pmatrix} E_{MP}^{(3)} \\ E_{MP}^{(4)} \end{pmatrix}. \qquad (8)$$

Equations (7) and (8) can be rewritten in the form:

$$[2,1] = E_{MP}^{(2)} + E_{MP}^{(3)} + E_{MP}^{(4)}\left(1 + \frac{D}{\det A}\right) + E_{MP}^{(5)}\left(1 + \frac{D'}{\det A}\right), \qquad (9)$$

$$[2,2] = E_{MP}^{(2)} + E_{MP}^{(3)} + E_{MP}^{(4)} + E_{MP}^{(5)}\left(1 + \frac{\tilde{D}}{\det B}\right) + E_{MP}^{(6)}\left(1 + \frac{\tilde{D}'}{\det B}\right), \qquad (10)$$

where

$$D = (E_{MP}^{(4)})^2 - E_{MP}^{(3)} E_{MP}^{(5)}, \qquad (11)$$

$$D' = E_{MP}^{(5)}(E_{MP}^{(2)} - E_{MP}^{(3)}) - E_{MP}^{(4)}(E_{MP}^{(3)} - E_{MP}^{(4)}), \qquad (12)$$

$$\det A = \begin{vmatrix} E_{MP}^{(2)} - E_{MP}^{(3)} & E_{MP}^{(3)} - E_{MP}^{(4)} \\ E_{MP}^{(3)} - E_{MP}^{(4)} & E_{MP}^{(4)} - E_{MP}^{(5)} \end{vmatrix}, \qquad (13)$$

$$\tilde{D} = (E_{MP}^{(5)})^2 - E_{MP}^{(4)} E_{MP}^{(6)}, \qquad (14)$$

$$\tilde{D}' = E_{MP}^{(6)}(E_{MP}^{(3)} - E_{MP}^{(4)}) - E_{MP}^{(5)}(E_{MP}^{(4)} - E_{MP}^{(5)}), \qquad (15)$$

and

$$\det B = \begin{vmatrix} E_{MP}^{(3)} - E_{MP}^{(4)} & E_{MP}^{(4)} - E_{MP}^{(5)} \\ E_{MP}^{(4)} - E_{MP}^{(5)} & E_{MP}^{(5)} - E_{MP}^{(6)} \end{vmatrix}. \qquad (16)$$

Approximants [1,0], [1,1], [2,1], and [2,2] are correct up to third, fourth, fifth, and sixth order, respectively, and, therefore, it is justified to compare them with the corresponding MPn energies. To determine the $[k, k-1]$ and $[k, k]$ approximants, one has to calculate MPn correlation energies up to orders $2k + 1$ and $2k + 2$, respectively. Since we have evaluated $E_{MP}^{(n)}$ for $n = 2, 3, 4, 5, 6$, we are able to analyze improvements obtained by approximants (5)–(8) and study their convergence behavior. In addition, we can test whether the [2,2] approximant already provides a reasonable estimate of the FCI correlation energy.

Padé approximants have been used to improve the convergence behavior of the MPn series, and in some cases these attempts have been successful [24]. However, knowledge about the convergence properties of a sequence of Padé approximants is usually missing.

THE PFLB INFINITE-ORDER MPn FORMULA

Pople and co-workers have suggested an extrapolation formula to obtain from calculated $E_{MP}^{(n)}$ ($n = 2, 3, 4$) correlation contributions a reasonable approximation for the exact correlation energy ΔE [17]:

$$\Delta E(\text{PFLB, MP4}) = \frac{E_{MP}^{(2)} + E_{MP}^{(3)}}{1 - \frac{E_{MP}^{(4)}}{E_{MP}^{(2)}}}. \qquad (17)$$

Equation (17) is correct up to fourth order and is based on the assumption that $E_{MP}^{(5)}$ bears the same relationship to $E_{MP}^{(3)}$ as $E_{MP}^{(4)}$ does to $E_{MP}^{(2)}$. Even-and odd-order terms of the MPn series are supposed to form a geometrically progressive energy series where the ratio of successive even-order terms is similar to the ratio of successive odd-order terms. In so far, Eq. (17) is related to the Padé approximants [1,0] [Eq. (5)] and [1,1] [Eq. (6)], which also suggest approximations in the form of geometric series sums defined by the ratios $E_{MP}^{(3)}/E_{MP}^{(2)}$ and $E_{MP}^{(4)}/E_{MP}^{(3)}$, respectively.

The PFLB extrapolation equation is based just on fourth-order correlation energies because only these correlation energies were available at the time of development. Now, we can evaluate in addition E(MP5) and E(MP6) and, therefore, it is challenging to extend the PFLB equation to sixth-order MP perturbation theory and to examine its reliability:

$$\Delta E(\text{extrap}, \text{MP6}) = E_{MP}^{(2)} + E_{MP}^{(3)} + \frac{E_{MP}^{(4)} + E_{MP}^{(5)}}{1 - \dfrac{E_{MP}^{(6)}}{E_{MP}^{(4)}}}. \tag{18}$$

Formula (18) is correct up to sixth order. It assumes similar to the PFLB formula monotonic convergence of the MPn series, which, of course, is not fulfilled in all cases (see [16]). Therefore, it will be important to evaluate the reliability of (18) on the basis of FCI (exact) correlation energies.

FEENBERG SERIES

In a number of studies interest in the Feenberg series [25, 26] as a perturbation series with improved convergence characteristics has been reestablished [27, 28]. Since the relevant theory is amply documented in the literature, we summarize here just these equations relevant for an improvement of the convergence of the MPn series (4).

The contribution $E_{MP}^{(n)}$ to the total correlation energy ΔE of Eq. (4) is given by

$$E_{MP}^{(n)} = \langle \Phi_0 | \hat{V} \hat{\Omega}^{(n-1)} | \Phi_0 \rangle, \tag{19}$$

where the wave operator $\hat{\Omega}$ at nth order is defined by

$$\hat{\Omega}^{(n)} = \hat{G}_0 \left[\hat{V} \hat{\Omega}^{(n-1)} - \sum_{m=1}^{n-1} E_{MP}^{(m)} \hat{\Omega}^{(n-m)} \right]. \tag{20}$$

The reduced resolvent $\hat{G}_0$ takes the form of

$$\hat{G}_0 = \sum_{k=1}^{\infty} \frac{|\Phi_k\rangle\langle\Phi_k|}{E_0 - E_k}. \tag{21}$$

To improve the convergence of the series $E_{MP}^{(n)}(n = 2, 3, 4, \ldots)$ one introduces the Λ transformation [27]:

$$E_{\Lambda}^{(n)} = \langle \Phi_0 | \hat{V} \hat{\Omega}_{\Lambda}^{(n-1)} | \Phi_0 \rangle, \tag{22}$$

where

$$\hat{\Omega}_{\Lambda}^{(n)} = \Lambda \hat{\Omega}_{\Lambda}^{(n-1)} + (1 - \Lambda)\hat{G}_0 \left[\hat{V} \hat{\Omega}_{\Lambda}^{(n-1)} - \sum_{m=1}^{n-1} E_{\Lambda}^{(m)} \hat{\Omega}_{\Lambda}^{(n-m)} \right]. \tag{23}$$

The transformed series $E_{\Lambda}^{(n)}$ converges to the same limit as the original series $E_{MP}^{(n)}$ when $\det(1 - \Lambda) \neq 0$. In the most simple form, Λ can be written as a number operator

$$\Lambda = \lambda \hat{I}, \tag{24}$$

where $\hat{I}$ is the unit operator. Equation (24) leads to the Feenberg scaling of the Hamiltonian operator of Eq. (3):

$$\overline{H} = \frac{1}{1-\lambda}\overline{H}_0 + \left(\overline{V} - \frac{\lambda}{1-\lambda}\overline{H}_0 \right) \tag{25}$$

$$= \tilde{H}_0 + \tilde{V}. \tag{26}$$

The scaling of $\overline{H}_0$ leads to a transformation of the MPn series $\{E_{MP}^{(n)}\}$ where each term is obtained now as a polynomial in λ [27, 28]:

$$E_{\Lambda}^{(n)} = \sum_{k=1}^{n-1} C_{k-1}^{n-2} \lambda^{n-k-1} (1-\lambda)^k E_{MP}^{(k+1)} \quad (n \geq 2). \tag{27}$$

Feenberg [25] suggested that the value of λ is obtained by minimizing the third-order correlation energy $\sum_{n=2}^{3} E_{\Lambda}^{(n)} = \Delta E_{\Lambda}^{(3)} = E_{\Lambda}^{(2)} + E_{\Lambda}^{(3)}$, which leads to

$$\lambda^{(3)} = 1 - \frac{E_{MP}^{(2)}}{E_{MP}^{(2)} - E_{MP}^{(3)}}. \tag{28}$$

Substituting λ in Eq. (27) by $\lambda^{(3)}$, the Feenberg energy series $E_\lambda^{(n)}$ is obtained. Formulas for $n = 2$, 3, 4, 5, and 6 are given in Eqs. (29)–(33):

$$E_{\lambda^{(3)}}^{(2)} = (1 - \lambda^{(3)}) E_{MP}^{(2)}, \quad (29)$$

$$E_{\lambda^{(3)}}^{(3)} = 0, \quad (30)$$

$$E_{\lambda^{(3)}}^{(4)} = \lambda^{(3)}(1 - \lambda^{(3)})^2 E_{MP}^{(3)} + (1 - \lambda^{(3)})^3 E_{MP}^{(4)}, \quad (31)$$

$$E_{\lambda^{(3)}}^{(5)} = 2(\lambda^{(3)})^2 (1 - \lambda^{(3)})^2 E_{MP}^{(3)} + 3\lambda^{(3)}(1 - \lambda^{(3)})^3 E_{MP}^{(4)} + (1 - \lambda^{(3)})^4 E_{MP}^{(5)}, \quad (32)$$

$$E_{\lambda^{(3)}}^{(6)} = 3(\lambda^{(3)})^3 (1 - \lambda^{(3)})^2 E_{MP}^{(3)} + 6(\lambda^{(3)})^2 (1 - \lambda^{(3)})^3 E_{MP}^{(4)} + 4\lambda^{(3)}(1 - \lambda^{(3)})^4 E_{MP}^{(5)} + (1 - \lambda^{(3)})^5 E_{MP}^{(6)}. \quad (33)$$

An improved Feenberg parameter λ can be determined by minimizing the fifth-order correlation energy, $\Delta E_\lambda^{(5)}$:

$$\frac{\partial}{\partial \lambda} \sum_{n=2}^{5} E_\lambda^{(n)} = \frac{\partial \Delta E_\lambda^{(5)}}{\partial \lambda} = 0, \quad (34)$$

which leads to a cubic equation in λ:

$$\lambda^3 + P\lambda^2 + Q\lambda + R = 0 \quad (35)$$

with

$$P = \frac{3(E_{MP}^{(3)} - 2E_{MP}^{(4)} + E_{MP}^{(5)})}{E_{MP}^{(2)} - 3E_{MP}^{(3)} + 3E_{MP}^{(4)} - E_{MP}^{(5)}}, \quad (36)$$

$$Q = \frac{3(E_{MP}^{(4)} - E_{MP}^{(5)})}{E_{MP}^{(2)} - 3E_{MP}^{(3)} + 3E_{MP}^{(4)} - E_{MP}^{(5)}}, \quad (37)$$

$$R = \frac{E_{MP}^{(5)}}{E_{MP}^{(2)} - 3E_{MP}^{(3)} + 3E_{MP}^{(4)} - E_{MP}^{(5)}}. \quad (38)$$

For the electron systems investigated in this work, one finds that Eq. (35) possesses just one real root, which leads to the Feenberg parameter $\lambda^{(5)}$:

$$\lambda^{(5)} = \sqrt[3]{\sqrt{C} - \frac{B}{2}} + \sqrt[3]{-\sqrt{C} - \frac{B}{2}} - \frac{P}{3}, \quad (39)$$

where C is defined by

$$C = \frac{B^2}{4} + \frac{A^3}{27} > 0 \quad (40)$$

for all cases investigated. In Eqs. (39) and (40), A and B are given by

$$A = Q - \frac{P^2}{3}, \quad (41)$$

$$B = 2\left(\frac{P}{3}\right)^3 - \frac{P * Q}{3} + R. \quad (42)$$

Because of the minimum condition (34), Eq. (43) holds:

$$E_{\lambda^{(5)}}^{(5)} = 0, \quad (43)$$

which means that the Feenberg series $E_{\lambda^{(5)}}^{(n)}$ converges in second-order perturbation theory, i.e., the second-order perturbed wave function and the fifth-order energy, which is calculated from this function, are eigenfunction and eigenvalue of the Hamiltonian to be calculated.

Results and Discussion

The electron systems investigated in this work are listed in Table I. They have been chosen from the pool of published FCI energies [29–33] for atoms and simple molecules and comprise charged and uncharged atoms (F and F^-), different states of molecules ($^3B_2$ and $^1A_1$ state of CH_2, $^2B_1$ and $^2A_1$ state of NH_2) as well as AH_n molecules both at their equilibrium geometry (R_e) and in geometries with (symmetrically) stretched AH bonds ($1.5R_e$, $2R_e$: "stretched geometries"). Calculation of molecules with stretched geometries represents a critical test on the performance of a correlation method because these electronic systems possess considerable multireference character.

In Table I, contributions $E_{MP}^{(n)}$ and correlation energies $\Delta E^{(n)} = \sum_{m=2}^{n} E_{MP}^{(m)}$ calculated for $n = 2, 3, 4, 5, 6$ are compared with FCI correlation energies. In addition, scaled Feenberg correlation energies for $\lambda^{(3)}$ (denoted by FE1) and $\lambda^{(5)}$ (denoted by FE2) are given where the former (apart from the sixth-order energies) have been taken from the work of Schmidt and co-workers [28] for reasons of comparison. Also given are correlation energies evaluated from Padé approximants and extrapolated values obtained with the PFLB equation (17). In Table II, Padé correlation energies are analyzed with the help of differences E(approximate) − E(FCI) and the ratios $E^{(n)}/E^{(n-1)}$ or the correction terms $D/\det A$, $D'/\det A$, $\tilde{D}/\det B$, $\tilde{D}'/\det B$ [Eqs. (9) and (10)]. The best estimates for the exact

TABLE I
Correlation energies [hartree] obtained at the MP*n* level, by first-order ($\lambda^{(3)}$) and second-order Feenberg scaling ($\lambda^{(5)}$), by Padé approximants or by extrapolation formulas.[a]

			Feenberg				
Systems	Order	MP*n*	FE1	FE2	[*k*, *l*]	Padé	*E*(extra, MP*n*)
Class A							
BH	$^1\Sigma$	$R_e = 2.329 a_0$	DZP	[29]			
R_e			$\lambda^{(3)} = -0.313$	$\lambda^{(5)} = -0.392$			
	E(HF)	−25.125260					
	$\Delta E^{(2)}$	−0.073728	−0.096810	−0.102641			
	$\Delta E^{(3)}$	−0.091306	−0.096810	−0.096458	[1, 0]	−0.096810	
	$\Delta E^{(4)}$	−0.097307	−0.100907	−0.101713	[1, 1]	−0.100417	−0.099396
	$\Delta E^{(5)}$	−0.099841	−0.101621	−0.101713	[2, 1]	−0.102042	
	$\Delta E^{(6)}$	−0.101062	−0.102152	−0.102313	[2, 2]	−0.102392	−0.102021
	FCI	−0.102355					
$1.5R_e$			$\lambda^{(3)} = -0.356$	$\lambda^{(5)} = -0.363$			
	E(HF)	−25.062213					
	$\Delta E^{(2)}$	−0.077656	−0.105287	−0.105870			
	$\Delta E^{(3)}$	−0.098036	−0.105287	−0.105284	[1, 0]	−0.105287	
	$\Delta E^{(4)}$	−0.106532	−0.113133	−0.113264	[1, 1]	−0.112607	−0.110080
	$\Delta E^{(5)}$	−0.110453	−0.113263	−0.113264	[2, 1]	−0.113919	
	$\Delta E^{(6)}$	−0.112315	−0.113964	−0.113984	[2, 2]	−0.114030	−0.113939
	FCI	−0.113763					
$2.0R_e$			$\lambda^{(3)} = -0.425$	$\lambda^{(5)} = -0.373$			
	E(HF)	−24.988201					
	$\Delta E^{(2)}$	−0.086302	−0.122938	−0.118525			
	$\Delta E^{(3)}$	−0.112020	−0.122938	−0.122780	[1, 0]	−0.122938	
	$\Delta E^{(4)}$	−0.125804	−0.140627	−0.138784	[1, 1]	−0.141723	−0.133312
	$\Delta E^{(5)}$	−0.133078	−0.138645	−0.138784	[2, 1]	−0.141209	
	$\Delta E^{(6)}$	−0.136946	−0.141585	−0.141110	[2, 2]	−0.141312	−0.141294
	FCI	−0.139132					
NH_2	$^2B_1$	$R_e = 1.024 a_0$	$\theta = 103.4°$	DZP	[30]		
R_e			$\lambda^{(3)} = -0.125$	$\lambda^{(5)} = -0.140$			
	E(HF)	−55.577182					
	$\Delta E^{(2)}$	−0.143266	−0.161223	−0.163370			
	$\Delta E^{(3)}$	−0.159223	−0.161223	−0.161194	[1, 0]	−0.161223	
	$\Delta E^{(4)}$	−0.163538	−0.164839	−0.164986	[1, 1]	−0.165137	−0.164107
	$\Delta E^{(5)}$	−0.164673	−0.164982	−0.164986	[2, 1]	−0.165078	
	$\Delta E^{(6)}$	−0.165102	−0.165305	−0.165327	[2, 2]	−0.165125	−0.165275
	FCI	−0.165438					
$1.5R_e$			$\lambda^{(3)} = -0.198$	$\lambda^{(5)} = -0.350$			
	E(HF)	−55.424272					
	$\Delta E^{(2)}$	−0.112964	−0.135348	−0.152450			
	$\Delta E^{(3)}$	−0.131646	−0.135348	−0.133187	[1, 0]	−0.135348	
	$\Delta E^{(4)}$	−0.141704	−0.147334	−0.152748	[1, 1]	−0.153435	−0.144480
	$\Delta E^{(5)}$	−0.147722	−0.151558	−0.152748	[2, 1]	−0.156790	
	$\Delta E^{(6)}$	−0.152673	−0.157401	−0.161584	[2, 2]	−0.151365	−0.163305
	FCI	−0.180937					
$2.0R_e$			$\lambda^{(3)} = -0.229$	$\lambda^{(5)} = -0.338$			
	E(HF)	−55.393626					
	$\Delta E^{(2)}$	−0.075370	−0.092648	−0.100831			
	$\Delta E^{(3)}$	−0.089426	−0.092648	−0.091925	[1, 0]	−0.092648	

(Continued)

TABLE I
(Continued)

Systems	Order	MPn	Feenberg FE1	FE2	$[k, l]$	Padé	E(extra, MPn)
	$\Delta E^{(4)}$	−0.093102	−0.094608	−0.095238	[1, 1]	−0.094407	−0.094012
	$\Delta E^{(5)}$	−0.094412	−0.095135	−0.095238	[2, 1]	−0.095408	
	$\Delta E^{(6)}$	−0.095210	−0.096016	−0.096447	[2, 2]	−0.086182	−0.095793
	FCI	−0.111898					
NH_2 R_e	$^2A_1$	$R_e = 1.000 a_0$	$\theta = 144.0°$ $\lambda^{(3)} = -0.116$	DZP $\lambda^{(5)} = -0.133$	[30]		
	E(HF)	−55.526382					
	$\Delta E^{(2)}$	−0.142090	−0.158666	−0.161024			
	$\Delta E^{(3)}$	−0.156935	−0.158666	−0.158631	[1, 0]	−0.158666	
	$\Delta E^{(4)}$	−0.160763	−0.161838	−0.161982	[1, 1]	−0.162094	−0.161281
	$\Delta E^{(5)}$	−0.161729	−0.161978	−0.161982	[2, 1]	−0.162055	
	$\Delta E^{(6)}$	−0.162105	−0.162276	−0.162299	[2, 2]	−0.162089	−0.162251
	FCI	−0.162380					
$1.5R_e$			$\lambda^{(3)} = -0.119$	$\lambda^{(5)} = -0.162$			
	E(HF)	−55.325078					
	$\Delta E^{(2)}$	−0.158512	−0.177337	−0.184129			
	$\Delta E^{(3)}$	−0.175339	−0.177337	−0.177077	[1, 0]	−0.177337	
	$\Delta E^{(4)}$	−0.184756	−0.188023	−0.189308	[1, 1]	−0.196725	−0.186415
	$\Delta E^{(5)}$	−0.188136	−0.189214	−0.189308	[2, 1]	−0.190239	
	$\Delta E^{(6)}$	−0.189950	−0.190887	−0.191221	[2, 2]	−0.191228	−0.191190
	FCI	−0.192535					
$2.0R_e$			$\lambda^{(3)} = -0.258$	$\lambda^{(5)} = -0.379$			
	E(HF)	−55.260731					
	$\Delta E^{(2)}$	−0.089090	−0.112038	−0.122828			
	$\Delta E^{(3)}$	−0.107338	−0.112038	−0.110999	[1, 0]	−0.112038	
	$\Delta E^{(4)}$	−0.114099	−0.118051	−0.120062	[1, 1]	−0.118078	−0.116153
	$\Delta E^{(5)}$	−0.117386	−0.119712	−0.120062	[2, 1]	−0.121011	
	$\Delta E^{(6)}$	−0.119592	−0.122053	−0.123296	[2, 2]	−0.168207	−0.122252
	FCI	−0.154402					
CH_3 R_e	$^2A''_2$	$R_e = 1.090 a_0$	$\theta = 120.0°$ $\lambda^{(3)} = -0.178$	DZP $\lambda^{(5)} = -0.205$	[33]		
	E(HF)	−39.570629					
	$\Delta E^{(2)}$	−0.125321	−0.147579	−0.151006			
	$\Delta E^{(3)}$	−0.144222	−0.147579	−0.147500	[1, 0]	−0.147579	
	$\Delta E^{(4)}$	−0.148602	−0.150076	−0.150256	[1, 1]	−0.149923	−0.149445
	$\Delta E^{(5)}$	−0.149813	−0.150248	−0.150256	[2, 1]	−0.150310	
	$\Delta E^{(6)}$	−0.150237	−0.150468	−0.150494	[2, 2]	−0.150608	−0.150413
	FCI	−0.150583					
$1.5R_e$			$\lambda^{(3)} = -0.213$	$\lambda^{(5)} = -0.277$			
	E(HF)	−39.298446					
	$\Delta E^{(2)}$	−0.128387	−0.155749	−0.164004			
	$\Delta E^{(3)}$	−0.150944	−0.155749	−0.155311	[1, 0]	−0.155749	
	$\Delta E^{(4)}$	−0.163548	−0.171180	−0.173790	[1, 1]	−0.179521	−0.167376
	$\Delta E^{(5)}$	−0.169885	−0.173530	−0.173790	[2, 1]	−0.176362	
	$\Delta E^{(6)}$	−0.174405	−0.178877	−0.180404	[2, 2]	−0.178311	−0.180476
	FCI	−0.184407					

(Continued)

TABLE I
(Continued)

Systems	Order	MP*n*	Feenberg FE1	Feenberg FE2	[*k*, *l*]	Padé	*E*(extra, MP*n*)
$2.0R_e$			$\lambda^{(3)} = -0.332$	$\lambda^{(5)} = -0.632$			
	E(HF)	−39.123546					
	$\Delta E^{(2)}$	−0.036568	−0.048709	−0.059697			
	$\Delta E^{(3)}$	−0.045683	−0.048709	−0.046230	[1, 0]	−0.048709	
	$\Delta E^{(4)}$	−0.051745	−0.057668	−0.065761	[1, 1]	−0.063789	−0.054762
	$\Delta E^{(5)}$	−0.056814	−0.062919	−0.065761	[2, 1]	−0.087664	
	$\Delta E^{(6)}$	−0.061754	−0.070139	−0.080227	[2, 2]	−0.014410	−0.105754
	FCI	−0.179586					
CH_2	$^3B_1$	$R_e = 1.912a_0$	$\theta = 106.7°$ $\lambda^{(3)} = -0.200$	DZP $\lambda^{(5)} = -0.251$	[32]		
	E(HF)	−38.933045					
	$\Delta E^{(2)}$	−0.092290	−0.110742	−0.115476			
	$\Delta E^{(3)}$	−0.107668	−0.110742	−0.110540	[1, 0]	−0.110742	
	$\Delta E^{(4)}$	−0.111335	−0.112651	−0.112915	[1, 1]	−0.112483	−0.112123
	$\Delta E^{(5)}$	−0.112431	−0.112893	−0.112915	[2, 1]	−0.112973	
	$\Delta E^{(6)}$	−0.112851	−0.113110	−0.113157	[2, 2]	−0.113243	−0.113047
	FCI	−0.113215					
CH_2	$^1A_1$	$R_e = 2.110a_0$	$\theta = 102.4°$ $\lambda^{(3)} = -0.229$	DZP $\lambda^{(5)} = -0.318$	[32]		
	E(HF)	−38.886297					
	$\Delta E^{(2)}$	−0.109830	−0.134983	−0.144790			
	$\Delta E^{(3)}$	−0.130296	−0.134983	−0.134270	[1, 0]	−0.134983	
	$\Delta E^{(4)}$	−0.135907	−0.138319	−0.139152	[1, 1]	−0.138025	−0.137310
	$\Delta E^{(5)}$	−0.137937	−0.139039	−0.139152	[2, 1]	−0.139375	
	$\Delta E^{(6)}$	−0.138909	−0.139682	−0.139923	[2, 2]	−0.140369	−0.139537
	FCI	−0.140886					
Class B							
Ne	^1S						
4*s*2*p*1*d*			$\lambda^{(3)} = 0.013$	$\lambda^{(5)} = 0.090$	[29]		
	E(HF)	−128.522354					
	$\Delta E^{(2)}$	−0.174449	−0.176704	−0.158717			
	$\Delta E^{(3)}$	−0.176676	−0.176704	−0.174873	[1, 0]	−0.176704	
	$\Delta E^{(4)}$	−0.180981	−0.181149	−0.179739	[1, 1]	−0.172065	−0.181146
	$\Delta E^{(5)}$	−0.179465	−0.179381	−0.179739	[2, 1]	−0.179942	
	$\Delta E^{(6)}$	−0.180335	−0.180396	−0.180081	[2, 2]	−0.180048	−0.180172
	FCI	−0.180108					
5*s*3*p*2*d*			$\lambda^{(3)} = 0.004$	$\lambda^{(5)} = 0.055$			
	E(HF)	−128.524013					
	$\Delta E^{(2)}$	−0.240859	−0.239834	−0.227647			
	$\Delta E^{(3)}$	−0.239829	−0.239834	−0.239215	[1, 0]	−0.239834	
	$\Delta E^{(4)}$	−0.245427	−0.245356	−0.244525	[1, 1]	−0.240699	−0.245536
	$\Delta E^{(5)}$	−0.244416	−0.244433	−0.244525	[2, 1]	−0.244660	
	$\Delta E^{(6)}$	−0.244991	−0.244979	−0.244868	[2, 2]	−0.244874	−0.244941
	FCI	−0.244864					
6*s*4*p*1*d*			$\lambda^{(3)} = 0.007$	$\lambda^{(5)} = 0.072$			
	E(HF)	−128.543823					
	$\Delta E^{(2)}$	−0.220236	−0.218700	−0.204381			
	$\Delta E^{(3)}$	−0.218689	−0.218700	−0.217762	[1, 0]	−0.218700	
	$\Delta E^{(4)}$	−0.224716	−0.224591	−0.223447	[1, 1]	−0.219920	−0.224843

(Continued)

TABLE I
(Continued)

Systems	Order	MP*n*	Feenberg FE1	Feenberg FE2	[*k*, *l*]	Padé	*E*(extra, MP*n*)
	$\Delta E^{(5)}$	−0.223239	−0.223278	−0.223447	[2, 1]	−0.223626	
	$\Delta E^{(6)}$	−0.224434	−0.224393	−0.224107	[2, 2]	−0.224161	−0.224364
	FCI	−0.224066					
F	^2P	[31]					
4*s*3*p*1*d*			$\lambda^{(3)} = -0.073$	$\lambda^{(5)} = 0.023$			
	E(HF)	−99.398964					
	$\Delta E^{(2)}$	−0.134714	−0.144604	−0.131617			
	$\Delta E^{(3)}$	−0.143928	−0.144604	−0.143438	[1, 0]	−0.144604	
	$\Delta E^{(4)}$	−0.147377	−0.148091	−0.147129	[1, 1]	−0.149440	−0.147710
	$\Delta E^{(5)}$	−0.147116	−0.146920	−0.147129	[2, 1]	−0.147262	
	$\Delta E^{(6)}$	−0.147635	−0.147886	−0.147579	[2, 2]	−0.147498	−0.147681
	FCI	−0.147656					
4*s*3*p*2*d*			$\lambda^{(3)} = -0.070$	$\lambda^{(5)} = 0.020$			
	E(HF)	−99.399543					
	$\Delta E^{(2)}$	−0.152758	−0.163450	−0.149771			
	$\Delta E^{(3)}$	−0.162751	−0.163450	−0.162306	[1, 0]	−0.163450	
	$\Delta E^{(4)}$	−0.166672	−0.167453	−0.166434	[1, 1]	−0.169203	−0.167039
	$\Delta E^{(5)}$	−0.166424	−0.166232	−0.166434	[2, 1]	−0.166576	
	$\Delta E^{(6)}$	−0.166944	−0.167181	−0.166896	[2, 2]	−0.166823	−0.166986
	FCI	−0.166940					
5*s*3*p*2*d*			$\lambda^{(3)} = -0.047$	$\lambda^{(5)} = -0.005$			
	E(HF)	−99.399983					
	$\Delta E^{(2)}$	−0.181771	−0.190338	−0.182719			
	$\Delta E^{(3)}$	−0.189953	−0.190338	−0.190033	[1, 0]	−0.190338	
	$\Delta E^{(4)}$	−0.194365	−0.194982	−0.194434	[1, 1]	−0.199530	−0.194678
	$\Delta E^{(5)}$	−0.194433	−0.194387	−0.194434	[2, 1]	−0.194546	
	$\Delta E^{(6)}$	−0.194874	−0.194991	−0.194886	[2, 2]	−0.194851	−0.194931
	FCI	−0.194894					
F^-	^1S	[29]					
4*s*3*p*1*d*			$\lambda^{(3)} = 0.040$	$\lambda^{(5)} = 0.188$			
	E(HF)	−99.442848					
	$\Delta E^{(2)}$	−0.208035	−0.199729	−0.168915			
	$\Delta E^{(3)}$	−0.199384	−0.199729	−0.194975	[1, 0]	−0.199729	
	$\Delta E^{(4)}$	−0.215241	−0.213444	−0.207292	[1, 1]	−0.204981	−0.215836
	$\Delta E^{(5)}$	−0.203031	−0.204726	−0.207292	[2, 1]	−0.208481	
	$\Delta E^{(6)}$	−0.218472	−0.215796	−0.210609	[2, 2]	−0.212862	−0.337984
	FCI	−0.210493					
4*s*3*p*2*d*			$\lambda^{(3)} = 0.035$	$\lambda^{(5)} = 0.186$			
	E(HF)	−99.442848					
	$\Delta E^{(2)}$	−0.232450	−0.224354	−0.189239			
	$\Delta E^{(3)}$	−0.224062	−0.224354	−0.218858	[1, 0]	−0.224354	
	$\Delta E^{(4)}$	−0.239872	−0.238297	−0.231861	[1, 1]	−0.229542	−0.240414
	$\Delta E^{(5)}$	−0.227586	−0.229103	−0.231861	[2, 1]	−0.233083	
	$\Delta E^{(6)}$	−0.242669	−0.240352	−0.235094	[2, 2]	−0.236558	−0.300600
	FCI	−0.234828					
5*s*3*p*2*d*			$\lambda^{(3)} = 0.035$	$\lambda^{(5)} = 0.186$			
	E(HF)	−99.443696					
	$\Delta E^{(2)}$	−0.262406	−0.249781	−0.218641			

(Continued)

TABLE I
(Continued)

Systems	Order	MPn	Feenberg		$[k,l]$	Padé	E(extra, MPn)
			FE1	FE2			
	$\Delta E^{(3)}$	−0.249143	−0.249781	−0.245899	[1, 0]	−0.249781	
	$\Delta E^{(4)}$	−0.268392	−0.265805	−0.260044	[1, 1]	−0.256995	−0.268866
	$\Delta E^{(5)}$	−0.256323	−0.258236	−0.260044	[2, 1]	−0.261161	
	$\Delta E^{(6)}$	−0.269922	−0.267184	−0.263481	[2, 2]	−0.266306	−0.273605
	FCI	−0.262994					
FH	$^1\Sigma$	$R_e = 1.733a_0$	DZP	[29]			
R_e			$\lambda^{(3)} = -0.012$	$\lambda^{(5)} = 0.058$			
	E(HF)	−100.047087					
	$\Delta E^{(2)}$	−0.196078	−0.198473	−0.183952			
	$\Delta E^{(3)}$	−0.198444	−0.198473	−0.197522	[1, 0]	−0.198473	
	$\Delta E^{(4)}$	−0.204146	−0.204356	−0.203152	[1, 1]	−0.194398	−0.204387
	$\Delta E^{(5)}$	−0.203023	−0.202962	−0.203152	[2, 1]	−0.203346	
	$\Delta E^{(6)}$	−0.204112	−0.204181	−0.203854	[2, 2]	−0.203858	−0.204103
	FCI	−0.203882					
$1.5R_e$			$\lambda^{(3)} = 0.006$	$\lambda^{(5)} = 0.057$			
	E(HF)	−99.933229					
	$\Delta E^{(2)}$	−0.216526	−0.215319	−0.204268			
	$\Delta E^{(3)}$	−0.215312	−0.215319	−0.214752	[1, 0]	−0.215319	
	$\Delta E^{(4)}$	−0.226397	−0.226213	−0.224591	[1, 1]	−0.216406	−0.226929
	$\Delta E^{(5)}$	−0.224368	−0.224410	−0.224591	[2, 1]	−0.225090	
	$\Delta E^{(6)}$	−0.227572	−0.227484	−0.226081	[2, 2]	−0.227360	−0.228049
	FCI	−0.227166					
$2.0R_e$			$\lambda^{(3)} = 0.012$	$\lambda^{(5)} = 0.047$			
	E(HF)	−99.817572					
	$\Delta E^{(2)}$	−0.239491	−0.236612	−0.228291			
	$\Delta E^{(3)}$	−0.236577	−0.236612	−0.236320	[1, 0]	−0.236612	
	$\Delta E^{(4)}$	−0.258696	−0.257908	−0.255729	[1, 1]	−0.239152	−0.260650
	$\Delta E^{(5)}$	−0.255433	−0.255568	−0.255729	[2, 1]	−0.257493	
	$\Delta E^{(6)}$	−0.264667	−0.264130	−0.262744	[2, 2]	−0.266895	−0.268948
	FCI	−0.263536					
H_2O	$^1A_1$	$R_e = 1.8897a_0$	$\theta = 104.5°$	DZP	[29]		
R_e			$\lambda^{(3)} = -0.029$	$\lambda^{(5)} = -0.012$			
	E(HF)	−76.040541					
	$\Delta E^{(2)}$	−0.203117	−0.209027	−0.205486			
	$\Delta E^{(3)}$	−0.208860	−0.209027	−0.208967	[1, 0]	−0.209027	
	$\Delta E^{(4)}$	−0.215263	−0.215720	−0.215384	[1, 1]	−0.144215	−0.215549
	$\Delta E^{(5)}$	−0.215379	−0.215373	−0.215384	[2, 1]	−0.215589	
	$\Delta E^{(6)}$	−0.216005	−0.216101	−0.216042	[2, 2]	−0.216056	−0.216098
	FCI	−0.216083					
$1.5R_e$			$\lambda^{(3)} = 0.012$	$\lambda^{(5)} = -0.013$			
	E(HF)	−75.800494					
	$\Delta E^{(2)}$	−0.247600	−0.244587	−0.250758			
	$\Delta E^{(3)}$	−0.244550	−0.244587	−0.244431	[1, 0]	−0.244587	
	$\Delta E^{(4)}$	−0.265147	−0.264405	−0.265947	[1, 1]	−0.247207	−0.266739
	$\Delta E^{(5)}$	−0.265927	−0.265872	−0.265947	[2, 1]	−0.268041	
	$\Delta E^{(6)}$	−0.269095	−0.268905	−0.269301	[2, 2]	−0.270096	−0.269813
	FCI	−0.270911					

(Continued)

TABLE I
(Continued)

Systems	Order	MPn	Feenberg FE1	Feenberg FE2	$[k, l]$	Padé	E(extra, MPn)
$2.0R_e$			$\lambda^{(3)} = 0.062$	$\lambda^{(5)} = 0.012$			
	E(HF)	−99.817572					
	$\Delta E^{(2)}$	−0.316317	−0.296679	−0.312608			
	$\Delta E^{(3)}$	−0.295379	−0.296679	−0.295823	[1, 0]	−0.296679	
	$\Delta E^{(4)}$	−0.355124	−0.344829	−0.353055	[1, 1]	−0.310883	−0.364160
	$\Delta E^{(5)}$	−0.353006	−0.352229	−0.353055	[2, 1]	−0.367072	
	$\Delta E^{(6)}$	−0.365926	−0.362327	−0.365188	[2, 2]	−0.369810	−0.368907
	FCI	−0.369984					

[a]Extrapolated correlation energies E(extrap, MPn) have been obtained with Eq. (17) for $n = 4$ (PFBL formula) and Eq. (18) for $n = 6$.

correlation energies (= FCI values) are based on calculated MP6 energies. They are listed and compared in Table III.

A direct impression of the convergence behavior of MP, Feenberg, and Padé series is provided by Figures 1–10, which give absolute energies as a function of the order of perturbation theory. In these figures as well as in Table I, II, and III, Padé approximants $[k, l]$ with $l = k, k - 1$, namely [1, 0], [1, 1], [2, 1], [2, 2], etc., are considered to form a series, each member of which can be related to order $n = k + l + 2$ of perturbation theory as has been described in the previous section.

The systems considered in this work are dissected into two classes A and B depending on whether they show monotonic or erratic (initial oscillations) convergence behavior as has been discussed in [16]. Beside the systems discussed in [16], we have also included equilibrium and two stretched geometries of CH_3 into the set of test systems because in this way our data become more comparable with results obtained by Schmidt and co-workers in a similar study on the Feenberg series [28].

PADÉ APPROXIMANTS

Inspection of Tables I and II as well as Figures 1–10 reveals that Padé approximants improve MP energies in some cases; however, they fail in many cases to lead to acceptable predictions. These failures can be found for class A as well as class B systems, for equilibrium geometries as well as stretched geometries, for ground states as well as excited states.

If one considers class A systems, then one realizes that with the exception of NH_2, $^2A_1$ the [2, 2] approximant leads to an improvement of MP6 energies in the direction of FCI energies in the case of equilibrium geometries. For stretched geometries, however, both improved and deteriorated energies are obtained. It can happen as in the case of BH that the FCI value is considerably overshot. The latter applies also to several class B examples simply reflecting in these cases that MP6 energies are too negative. Compared to MP6 correlation energies, the [2, 2] energies are actually somewhat better.

Figures 1–10 show that the convergence behavior of the Padé series [1, 0], [1, 1], [2, 1], and [2, 2] does not always follow that of the MPn series. There are examples (class A: stretched geometries of CH_3 and NH_2, $^2B_1$, equilibrium geometry of NH_2, $^2A_1$), for which the Padé series oscillates despite the monotonic behavior of the MPn series, and there are examples (class B: Ne [$5s3p2d$], Ne [$6s4p1d$], F^-, and stretched geometries of FH and H_2O, for which the Padé series is dampened (more monotonic) in contrast to the MPn series.

Comparison of the data in Table II reveals that the ratios $E^{(n)}/E^{(n-1)}$ or the correction terms $D/\det A$, $\tilde{D}/\det B$, etc. [Eqs. (9) and (10)] provide a basis to predict the convergence behavior of the Padé series. They reflect the descent of the function $E[k, l] = f(n)$, partially scaled by using curvature and geometric means. If $E^{(n)}/E^{(n-1)}$ and $D/\det A$, $\tilde{D}/\det B$, etc. increase successively from the [1, 0] or [1, 1] approximant to the [2, 2] approximant, then the Padé energies decrease more or less monotonicly. However, if there are oscillations in

TABLE II
Differences E(approx) − E(FCI) [mhartree] between FCI, MPn, and Padé correlation energies.

System	Order n	MPn − FCI	$[k, l]$	Padé − FCI	$\frac{E^{(n)}}{E^{(n-1)}}, \frac{D'}{\det A}, \frac{\tilde{D}'}{\det B}$
Class A					
BH	$^1\Sigma^+$	$R_e = 2.329\,a_0$	DZP	[29]	
R_e					
	3	11.049	[1, 0]	5.545	0.238
	4	5.048	[1, 1]	1.938	0.341
	5	2.514	[2, 1]	0.313	1.202
	6	1.293	[2, 2]	−0.037	1.677
$1.5R_e$					
	3	15.727	[1, 0]	8.476	0.262
	4	7.231	[1, 1]	1.156	0.417
	5	3.310	[2, 1]	−0.156	1.023
	6	1.448	[2, 2]	−0.267	1.191
$2.0R_e$					
	3	27.112	[1, 0]	16.194	0.298
	4	13.328	[1, 1]	−2.591	0.536
	5	6.054	[2, 1]	−2.077	1.096
	6	2.186	[2, 2]	−2.180	0.675
NH_2	$^2B_1$	$R_e = 1.024\,a_0$	$\theta = 103.4°$	DZP	[30]
R_e					
	3	6.215	[1, 0]	4.215	0.111
	4	1.900	[1, 1]	0.301	0.270
	5	0.765	[2, 1]	0.360	0.350
	6	0.336	[2, 2]	0.313	−0.733
$1.5R_e$					
	3	46.026	[1, 0]	45.589	0.165
	4	39.233	[1, 1]	27.502	0.538
	5	33.215	[2, 1]	24.147	1.568
	6	28.264	[2, 2]	29.572	−2.584
$2.0R_e$					
	3	22.472	[1, 0]	19.250	0.186
	4	18.796	[1, 1]	17.491	0.262
	5	17.486	[2, 1]	16.490	1.128
	6	16.688	[2, 2]	25.716	−18.429
NH_2	$^2A_1$	$R_e = 1.000\,a_0$	$\theta = 144.0°$	DZP	[30]
R_e					
	3	5.445	[1, 0]	3.714	0.104
	4	1.617	[1, 1]	0.286	0.258
	5	0.651	[2, 1]	0.325	0.332
	6	0.275	[2, 2]	0.291	−0.810
$1.5R_e$					
	3	17.196	[1, 0]	15.198	0.106
	4	7.779	[1, 1]	−4.190	0.560
	5	4.399	[2, 1]	2.296	0.511
	6	2.585	[2, 2]	1.307	0.281

(Continued)

TABLE II
(Continued)

System	Order n	MPn − FCI	$[k, l]$	Padé − FCI	$\frac{E^{(n)}}{E^{(n-1)}}, \frac{D'}{\det A}, \frac{\tilde{D}'}{\det B}$
$2.0R_e$					
	3	47.064	[1, 0]	42.364	0.205
	4	40.303	[1, 1]	36.324	0.371
	5	37.016	[2, 1]	33.391	1.360
	6	34.810	[2, 2]	−13.805	39.363
CH_3	$^2A''_2$	$R_e = 1.090a_0$	$\theta = 120.0°$	DZP	[33]
R_e					
	3	6.361	[1, 0]	3.004	0.151
	4	1.981	[1, 1]	0.660	0.232
	5	0.770	[2, 1]	0.273	0.517
	6	0.346	[2, 2]	−0.025	1.682
$1.5R_e$					
	3	33.463	[1, 0]	28.658	0.176
	4	20.859	[1, 1]	4.886	0.559
	5	14.522	[2, 1]	8.045	0.966
	6	10.002	[2, 2]	6.096	−0.247
$2.0R_e$					
	3	133.903	[1, 0]	130.877	0.249
	4	127.841	[1, 1]	115.797	0.665
	5	122.772	[2, 1]	91.922	6.712
	6	117.832	[2, 2]	165.176	−16.926
CH_2	$^3B_1$	$R_e = 1.912a_0$	$\theta = 106.7°$	DZP	[32]
	3	5.547	[1, 0]	2.473	0.167
	4	1.880	[1, 1]	0.732	0.238
	5	0.784	[2, 1]	0.242	0.682
	6	0.364	[2, 2]	−0.028	1.611
CH_2	$^1A_1$	$R_e = 2.110a_0$	$\theta = 102.4°$	DZP	[32]
	3	10.590	[1, 0]	5.930	0.186
	4	4.979	[1, 1]	2.861	0.274
	5	2.949	[2, 1]	1.511	0.989
	6	1.977	[2, 2]	0.517	2.453

System	Order n	MPn − FCI	$[k, l]$	Padé − FCI	$\frac{E^{(n)}}{E^{(n-1)}}, \frac{D'}{\det A}, \frac{\tilde{D}'}{\det B}$
Class B					
Ne	^1S	[29]			
4*s*2*p*1*d*					
	3	+3.432	[1, 0]	+3.404	+0.013
	4	−0.873	[1, 1]	+8.043	+1.934
	5	+0.643	[2, 1]	+0.166	+0.022
	6	−0.227	[2, 2]	+0.060	+0.050
5*s*3*p*2*d*					
	3	+5.035	[1, 0]	+5.030	−0.004
	4	−0.563	[1, 1]	+4.165	−5.439
	5	+0.448	[2, 1]	+0.204	+0.019
	6	−0.127	[2, 2]	−0.010	+0.066

(Continued)

TABLE II
(Continued)

System	Order n	MPn − FCI	$[k, l]$	Padé − FCI	$\frac{E^{(n)}}{E^{(n-1)}}, \frac{D'}{\det A}, \frac{\tilde{D}'}{\det B}$
$6s4p1d$					
	3	+5.377	[1, 0]	+5.366	−0.007
	4	−0.650	[1, 1]	+4.146	−3.895
	5	+0.827	[2, 1]	+0.440	+0.021
	6	−0.368	[2, 2]	−0.095	+0.139
F	^2P	[31]			
$4s3p1d$					
	3	+3.728	[1, 0]	+3.052	+0.068
	4	+0.279	[1, 1]	−1.784	+0.374
	5	+0.540	[2, 1]	+0.394	+0.033
	6	+0.021	[2, 2]	+0.158	+0.094
$4s3p2d$					
	3	+4.189	[1, 0]	+3.490	+0.065
	4	+0.268	[1, 1]	−2.263	+0.392
	5	+0.516	[2, 1]	+0.364	+0.032
	6	−0.004	[2, 2]	+0.117	+0.090
$5s3p2d$					
	3	+4.941	[1, 0]	+4.556	−0.045
	4	+0.529	[1, 1]	−4.636	−0.539
	5	+0.461	[2, 1]	+0.348	+0.030
	6	+0.020	[2, 2]	+0.043	+0.137
F^-	^1S	[29]			
$4s3p1d$					
	3	+11.109	[1, 0]	+10.764	−0.042
	4	−4.748	[1, 1]	+5.512	−1.833
	5	+7.462	[2, 1]	+2.012	+0.027
	6	−7.979	[2, 2]	−2.369	+0.870
$4s3p2d$	3	+10.766	[1, 0]	+10.474	−0.036
	4	−5.044	[1, 1]	+5.286	−1.885
	5	+7.242	[2, 1]	+1.745	+0.024
	6	−7.841	[2, 2]	−1.730	+0.688
$5s3p2d$					
	3	+13.851	[1, 0]	+13.213	−0.051
	4	−5.398	[1, 1]	+5.999	−1.451
	5	+6.671	[2, 1]	+1.833	+0.028
	6	−6.928	[2, 2]	−3.312	+0.794
FH	$^1\Sigma^+$	$R_e = 1.733 a_0$	DZP	[29]	
R_e					
	3	+5.438	[1, 0]	+5.409	+0.012
	4	−0.264	[1, 1]	+9.484	+2.409
	5	+0.859	[2, 1]	+0.536	+0.027
	6	−0.230	[2, 2]	+0.024	+0.126
$1.5R_e$					
	3	+11.854	[1, 0]	+11.847	−0.006
	4	+0.769	[1, 1]	+10.760	−9.133
	5	+2.798	[2, 1]	+2.076	+0.045
	6	−0.406	[2, 2]	−0.194	+0.292

(Continued)

TABLE II
(Continued)

System	Order n	MPn − FCI	$[k,l]$	Padé − FCI	$\frac{E^{(n)}}{E^{(n-1)}}, \frac{D'}{\det A}, \frac{\tilde{D}'}{\det B}$
$2.0R_e$					
	3	+26.958	[1,0]	+26.923	−0.012
	4	+4.841	[1,1]	+24.384	−7.591
	5	+8.103	[2,1]	+6.043	+0.087
	6	−1.132	[2,2]	−3.360	+0.584
H_2O	$^1A_1$	$R_e = 1.8897a_0$	$\theta = 104.5°$	DZP	[29]
R_e					
	3	+7.223	[1,0]	+7.056	+0.028
	4	+0.920	[1,1]	+71.868	+1.098
	5	+0.704	[2,1]	+0.494	+0.032
	6	+0.078	[2,2]	+0.027	+0.106
$1.5R_e$					
	3	+26.316	[1,0]	+26.324	−0.012
	4	+5.764	[1,1]	+23.704	−6.752
	5	+4.984	[2,1]	+2.870	+0.098
	6	+1.816	[2,2]	+0.815	+0.192
$2.0R_e$					
	3	+74.605	[1,0]	+73.305	−0.066
	4	+14.860	[1,1]	+59.101	−2.853
	5	+16.978	[2,1]	+2.912	+0.246
	6	+4.058	[2,2]	+0.174	+0.294

these values (see Table II), then the Padé series also will oscillate.

We conclude that Padé approximants may not generally be suited to be used for the extrapolation to infinite-order correlation energies. In selected cases, improvements are possible, however, it seems that each case has to be investigated separately using correlation contributions up to sixth-order MP theory.

PFLB AND OTHER INFINITE-ORDER MPn FORMULAS

On first sight, it seems that the infinite-order correlation energies ΔE(extrap, MP6) based on calculated MP6 energies [see Eq. (18)] do not lead to any improvement with regard to extrapolated correlation energies obtained with the PFLB formula [Eq. (17)], which is based on calculated MP4 correlation energies. The mean absolute deviation from exact FCI correlation energies is for ΔE(extrap, MP6) 12.529 mhartree (12.207 for equilibrium geometries, Table III) while it is 10.236 mhartree (1.599 for equilibrium geometries, Table I) for ΔE(PFLB, MP4). However, these deviations are misleading since they are dominated by an unusually large failure in the prediction of the infinite-order correlation energy by Eq. (18) in the case of F^- (Table I). At the MP level, there are strong initial oscillations for this ion. For smaller basis sets, the value of $E_{MP}^{(6)}$ is comparable in magnitude with that of $E_{MP}^{(4)}$. As a consequence, the correction factor $[1 - (E_{MP}^{(6)}/E_{MP}^{(4)})]^{-1}$ in Eq. (18) becomes very large and leads to an unreasonable value for ΔE(extrap, MP6). If one excludes the predictions for F^-, the mean absolute deviation of ΔE(extrap, MP6) values from FCI correlation energies will become 6.132 (all systems) and 0.260 mhartree (atoms an equilibrium geometries), which is clearly smaller than the corresponding values for ΔE(PFLP, MP4) (10.767 and 1.071 mhartree).

Further improvements of predictions based on Eq. (18) can be achieved if one splits Eq. (18) into two formulas, which reflect the different convergence properties of class A and class B systems. For the latter, E(MP6) values are mostly more negative than FCI energies, which indicates that higher order correlation effects are exaggerated.

TABLE III
Energy differences $E^{(6)}$(approx) − E(FCI) in mhartree.

	Systems	MP6	FE1	FE2	Padé [2, 2]	ΔE(extrap, MP6)	$\Delta E^{(A,B)}$(extrap, MP6)
Class A							
BH							
	R_e	1.293	0.203	0.042	−0.037	0.334	0.158
	$1.5R_e$	1.448	−0.201	−0.221	−0.267	−0.171	−0.233
	$2.0R_e$	2.186	−2.453	−1.978	−2.180	−2.162	−2.210
NH_2	$^2B_1$						
	R_e	0.336	0.133	0.111	0.313	0.163	0.075
	$1.5R_e$	28.264	23.536	19.353	29.572	17.632	5.308
	$2.0R_e$	16.688	15.882	15.451	25.716	16.105	15.448
NH_2	$^2A_1$						
	R_e	0.275	0.104	0.081	0.291	0.129	0.004
	$1.5R_e$	2.585	1.648	1.314	1.307	1.346	0.485
	$2.0R_e$	34.810	32.349	31.107	13.080	32.150	30.310
CH_2							
	$^3B_1$	0.364	0.105	0.058	−0.028	−0.722	0.103
	$^1A_1$	1.977	1.204	0.963	0.517	1.349	1.086
CH_3							
	R_e	0.346	0.115	0.089	−0.025	0.170	0.117
	$1.5R_e$	10.002	5.530	4.003	6.096	3.931	−1.251
	$2.0R_e$	117.832	109.447	99.359	165.176	73.832	−70.327
Class B							
Ne							
	$4s2p1d$	−0.227	−0.288	0.027	0.060	0.064	0.018
	$5s3p2d$	−0.127	−0.115	−0.004	−0.010	−0.077	−0.048
	$6s4p1d$	−0.368	−0.327	−0.041	−0.095	−0.298	−0.170
F							
	$4s3p1d$	0.021	−0.230	0.077	0.158	−0.024	0.022
	$4s3p2d$	−0.004	−0.241	0.044	0.117	−0.046	−0.005
	$5s3p2d$	0.020	−0.097	0.008	0.043	−0.037	−0.010
F^-							
	$4s3p1d$	−7.979	−5.303	−0.116	−2.369	−127.491	1.452
	$4s3p2d$	−7.841	−5.524	−0.266	−1.730	−65.772	1.616
	$5s3p2d$	−6.928	−4.190	−0.487	−3.312	−10.611	0.701
FH							
	R_e	−0.230	−0.299	0.028	0.024	−0.221	−0.104
	$1.5R_e$	−0.406	−0.318	0.365	−0.194	−0.883	−0.237
	$2.0R_e$	−1.132	−0.594	0.791	−3.360	−5.412	−1.668
H_2O							
	R_e	0.078	−0.018	0.041	0.027	−0.015	0.023
	$1.5R_e$	1.816	2.006	1.610	0.815	1.098	1.430
	$2.0R_e$	4.058	7.657	4.796	0.174	1.077	3.065
Mean abs. dev.		8.608	7.590	6.304	8.865	12.529; 6.132[a]	4.748; 5.149[a]
Mean abs. dev.	(R_e)	1.671	1.088	0.146	0.539	12.207; 0.260[a]	0.336; 0.139[a]

[a] The second entry gives the mean absolute deviation excluding extrapolated energies for F^-

Therefore, one has to scale down their contribution to the infinite-order correlation energy. However, for class A systems, for which the MPn series has initially monotonic convergence behavior, the original assumption of a geometric series is largely fulfilled and, accordingly, extrapolation formulas of type (17) or (18) are appropriate. We retain these equations and only describe the ratio of subsequent correlation contributions by the best MPn values available at the moment, namely $E_{MP}^{(5)}$ and

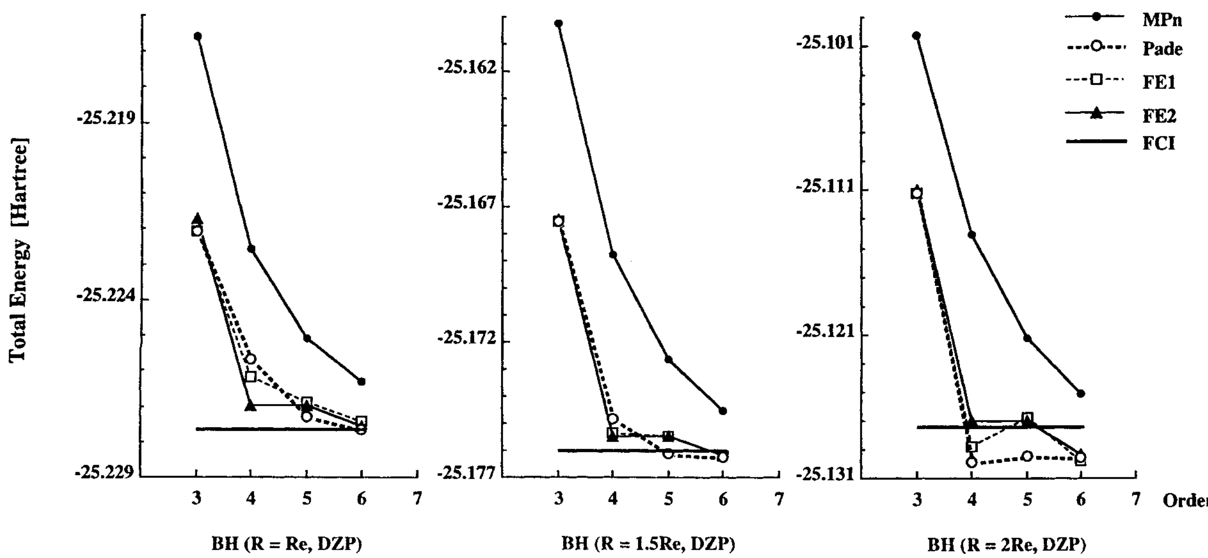

FIGURE 1. Graphical representation of the total MP*n* energy of BH, $^1\Sigma^+$, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

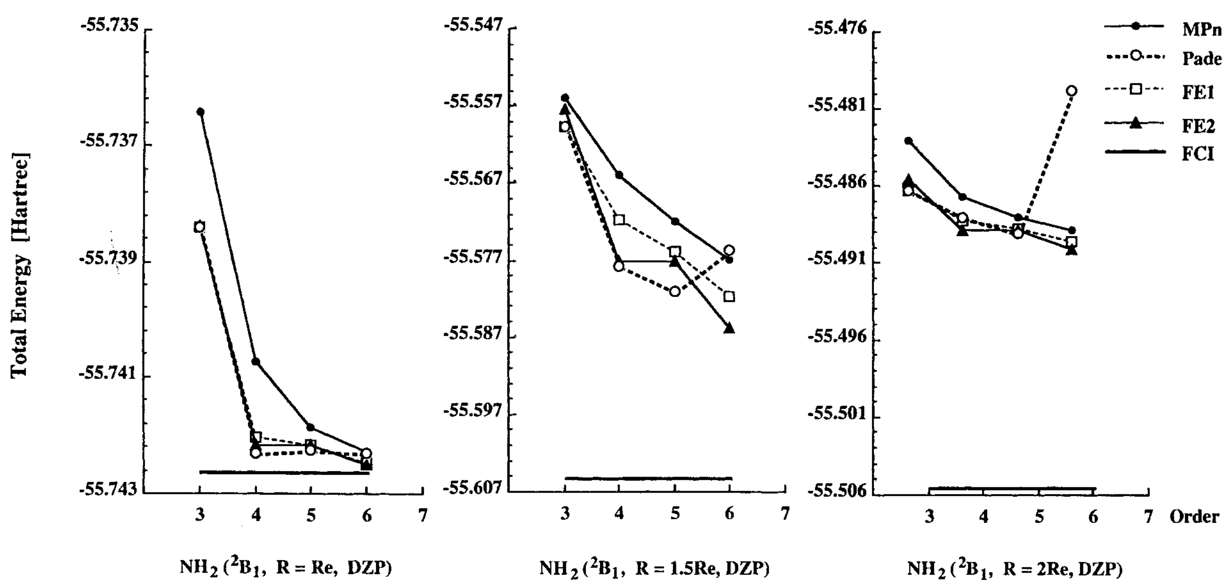

FIGURE 2. Graphical representation of the total MP*n* energy of NH_2, $^2B_1$, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

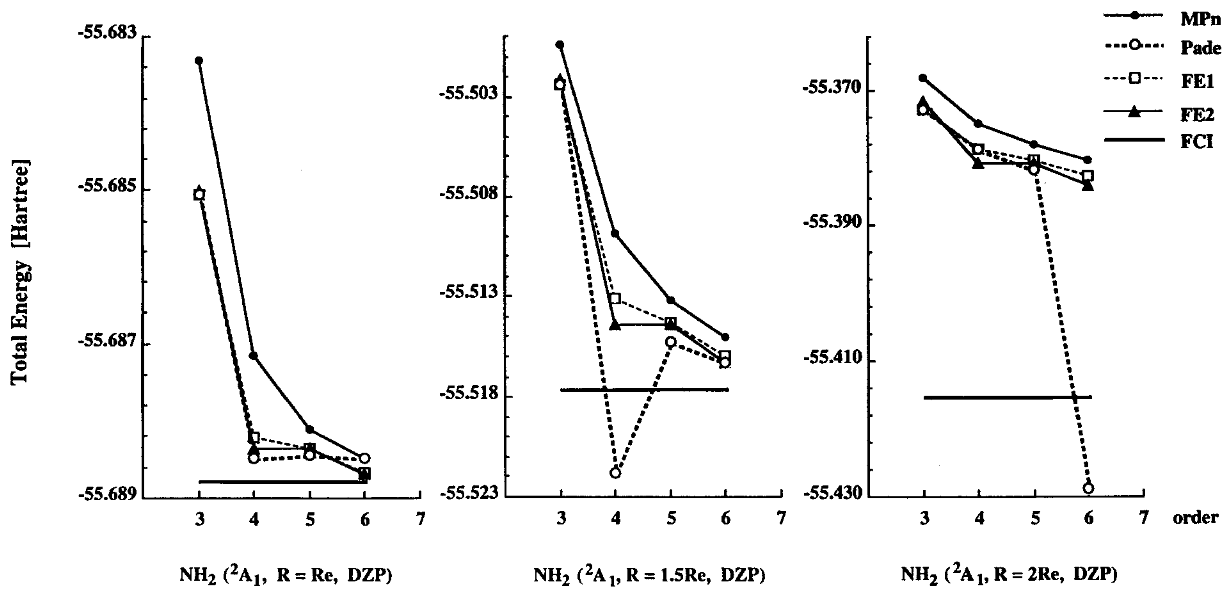

FIGURE 3. Graphical representation of the total MP*n* energy of NH_2, $^2A_1$, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

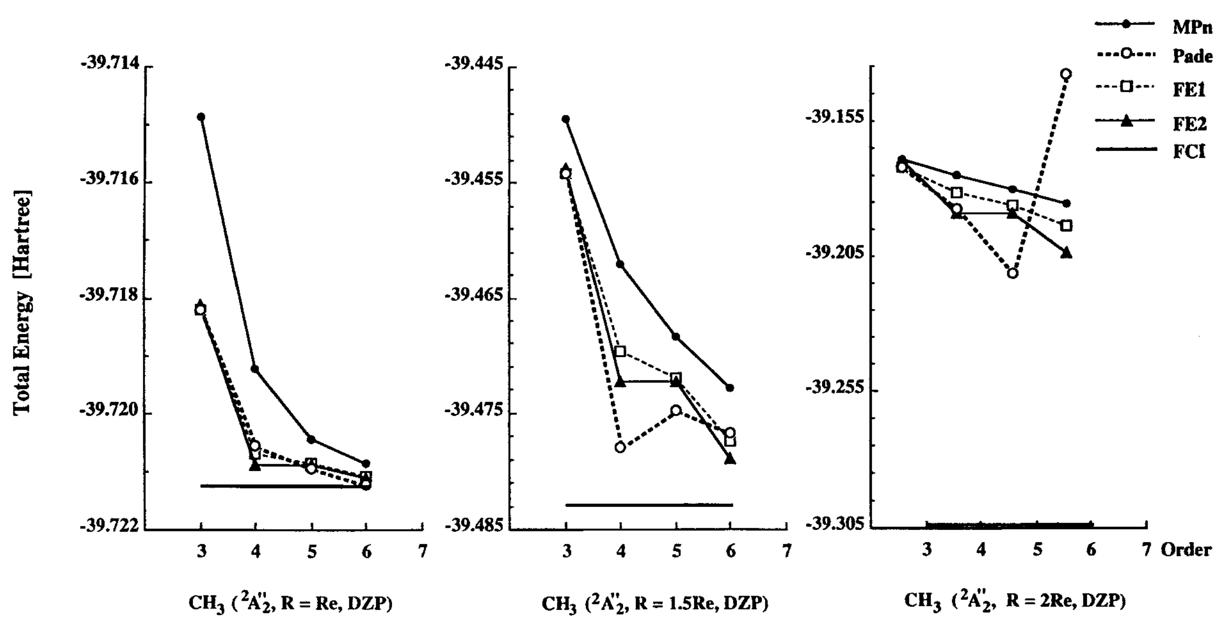

FIGURE 4. Graphical representation of the total MP*n* energy of CH_3, $^2A_2''$, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

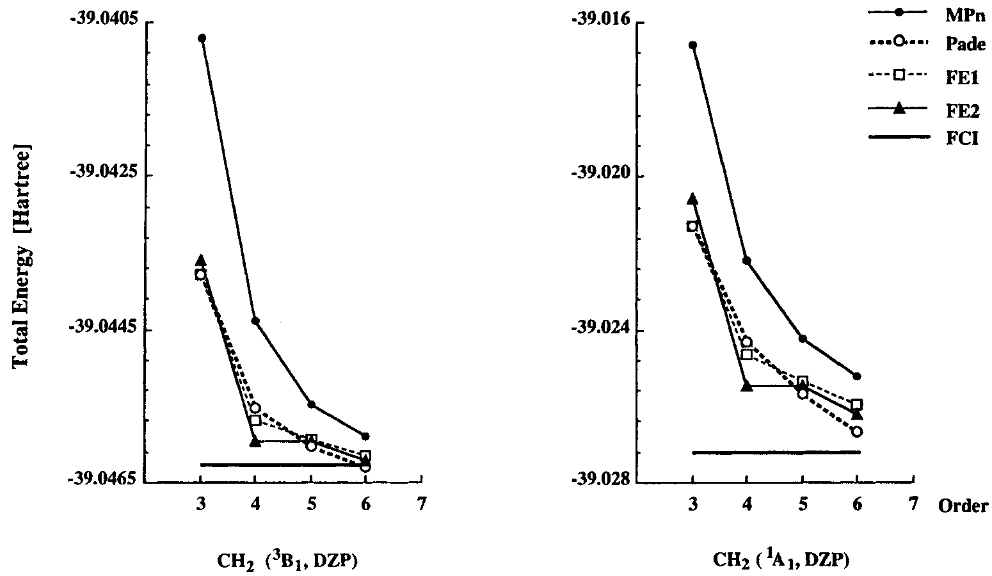

FIGURE 5. Graphical representation of the total MP*n* energy of CH_2, $^3B_1$, and CH_2, $^1A_1$, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

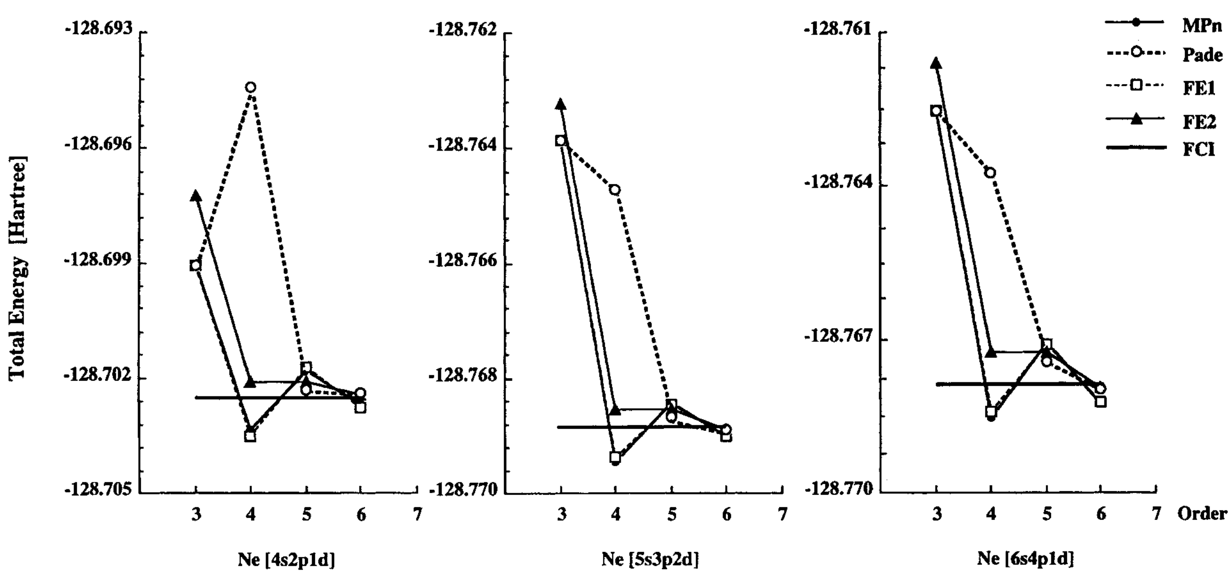

FIGURE 6. Graphical representation of the total MP*n* energy of Ne, ^1S, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

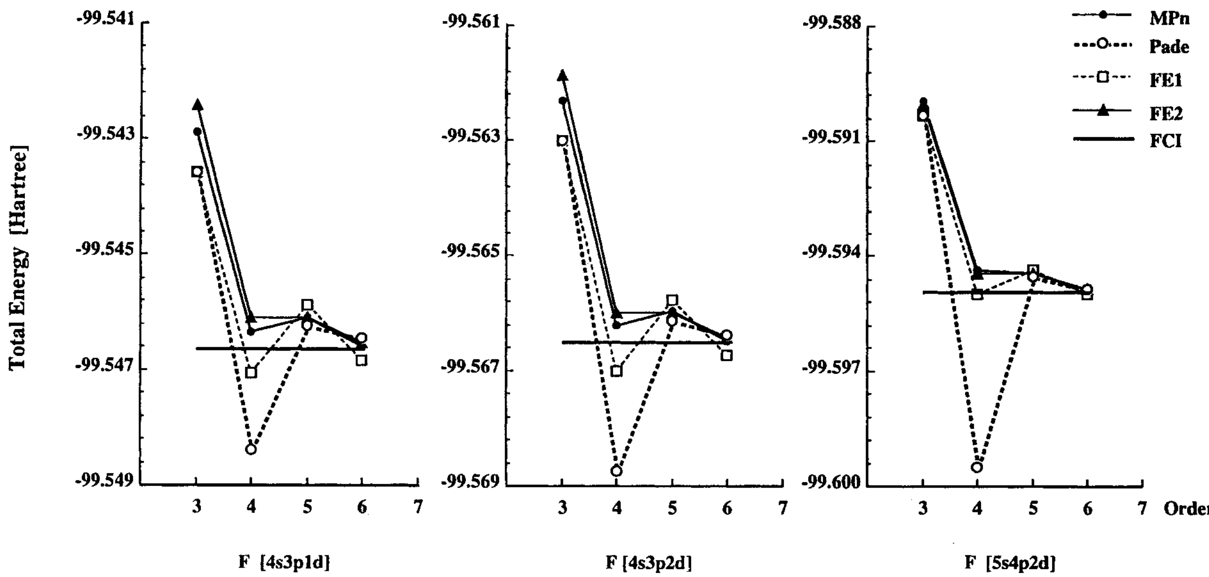

FIGURE 7. Graphical representation of the total MP*n* energy of F, ^2P, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

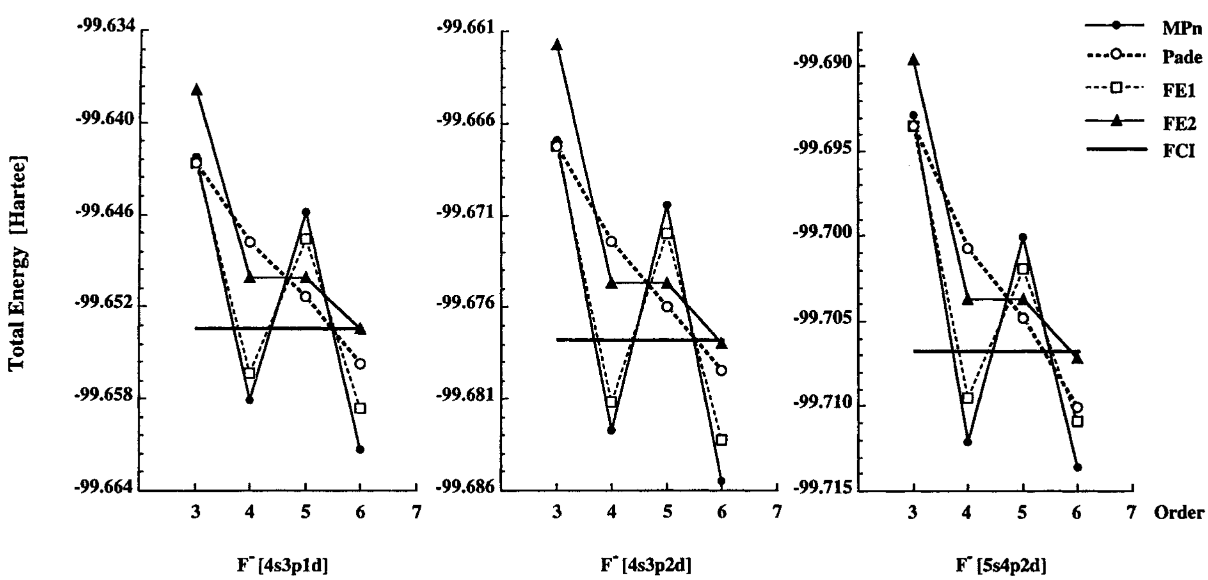

FIGURE 8. Graphical representation of the total MP*n* energy of F^-, ^1S, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

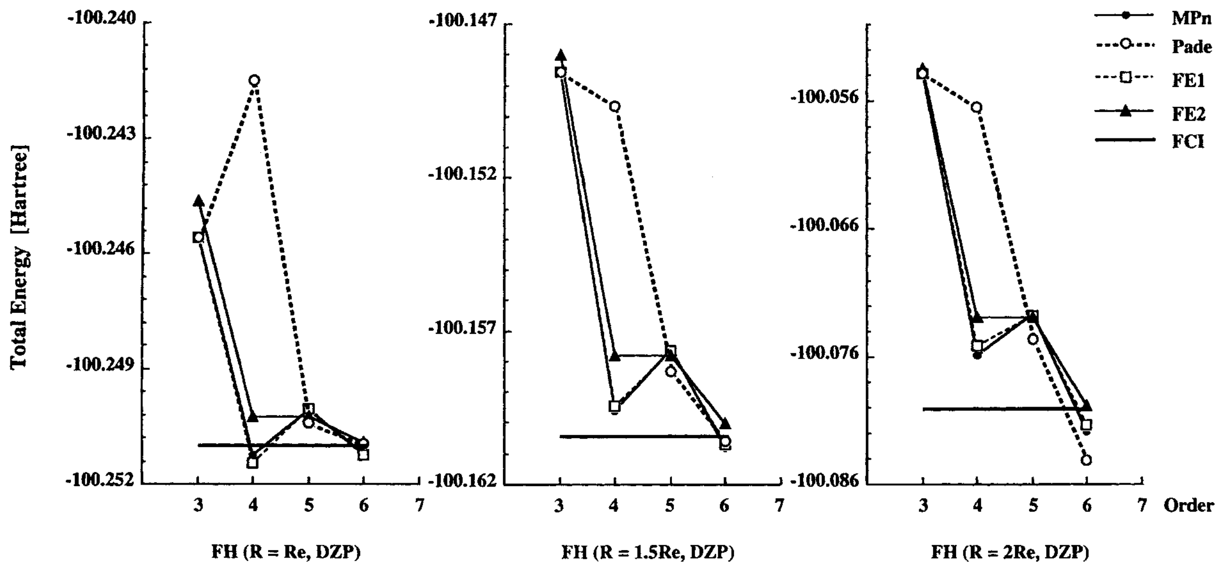

FIGURE 9. Graphical representation of the total MP*n* energy of FH, $^1\Sigma^+$, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

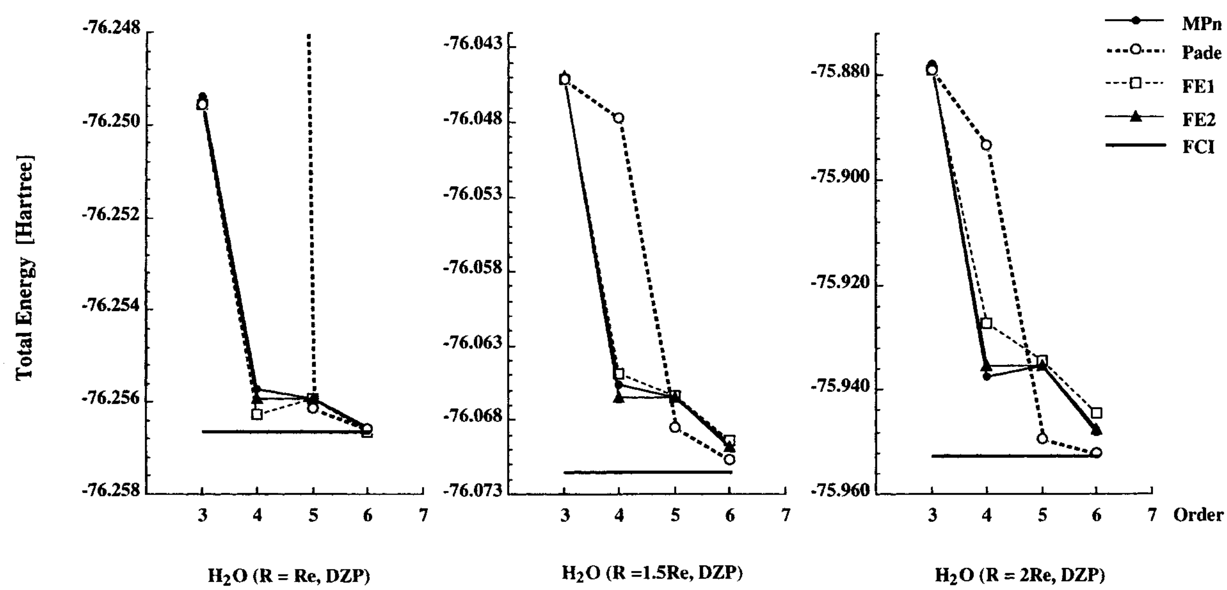

FIGURE 10. Graphical representation of the total MP*n* energy of H_2O, $^1A_1$, as a function of the order of perturbation theory applied. MP*n* values are compared with the corresponding energies obtained by Padé approximants, by first-order (FE1) and second-order (FE2) Feenberg scaling and the FCI energy obtained with the same basis set at the same geometry (see text).

$E_{MP}^{(6)}$. In this way, the extrapolation equation for class A systems becomes

$$\Delta E^{(A)}(\text{extrap, MP6}) = \sum_{n=2}^{4} E_{MP}^{(n)} + \frac{E_{MP}^{(5)}}{1 - \frac{E_{MP}^{(6)}}{E_{MP}^{(5)}}}. \tag{44}$$

For class B systems, we use

$$\Delta E^{(B)}(\text{extrap, MP6}) = E_{MP}^{(2)} + E_{MP}^{(3)} + (E_{MP}^{(4)} + E_{MP}^{(5)})e^{E_{MP}^{(6)}/E_{MP}^{(4)}}, \tag{45}$$

where the exponent is chosen in view of the oscillations in the MPn series. Actually, both $1/(1 - x)$ and e^x lead to similar series, however, in the exponential series higher powers k of x are scaled down by prefactors $1/k!$. In this way, higher excitation effects are reduced in Eq. (45).

Application of Eqs. (44) and (45) leads to infinite-order correlation energies superior to energies predicted by either the PFLB Eq. (17) or the MP6 extrapolation equation (18). This is reflected by mean absolute deviations of 4.748 and 0.336 mhartree for the complete set of correlation energies given in Table III and the problems with equilibrium geometries, respectively. Particularly noteworthy is the significant improvement for the correlation energies of F^- (deviations from FCI values are just 1.452, 1.616, and 0.701 mhartree, Table III). The only failures of extrapolation formulas (44) and (45) occur for the strongly stretched geometries of CH_3 and NH_2. However, in these cases MP6 correlation energies differ from FCI values so strongly because of the inherent multireference character of the systems considered that it is unrealistic to expect clearly better values from any extrapolation formula.

We conclude that by the use of MP6 correlation energies and an improvement of the original PFLB extrapolation formula, errors in predicted infinite-order correlation energies can be reduced to 0.3 mhartree for equilibrium geometries and to 4.7 mhartree for systems including both equilibrium and stretched geometries.

FEENBERG SERIES

The calculated Feenberg correlation energies listed in Table I confirm the expected improvement in line with the observations made by Schmidt and co-workers [28]. It is particularly interesting to compare correlation energies obtained by these authors [$\lambda^{(3)}$, Feenberg 1 (FE1), first-order perturbation theory] and the Feenberg energies obtained in this work [$\lambda^{(5)}$, Feenberg 2 (FE2), second-order perturbation theory]. The scaling factors $\lambda^{(3)}$ and $\lambda^{(5)}$ possess in most cases similar values. However, $\lambda^{(5)}$ values calculated in this work are somewhat more negative for class A systems, which means that FE2 correlation energies are more negative than the corresponding MPn or FE1 values for class A systems. Since MPn energies approach in these cases the FCI energy monotonically from above, the FE2 values are closer to the latter than either MPn or FE1 values.

In the case of class B systems, the MP6 correlation energy is often more negative than the corresponding FCI value (Table I). To reduce the magnitude of the correlation energy, both $\lambda^{(3)}$ and $\lambda^{(5)}$ values are positive where the latter are slightly larger than the former thus leading to a better agreement between FE2 and FCI correlation energies for class B systems. Hence, for both class A and class B systems a significant improvement of correlation energies is obtained by using the FE2 scaling of MPn energies. At sixth-order, the mean absolute deviation from FCI values is for FE2 0.146 mhartree provided just atoms and molecules in their equilibrium geometry are considered while it is 6.304 mhartree if stretched geometries are included into the comparison. Hence, compared to FE1 results an improvement of the mean absolute deviation by almost 1 mhartree can be considered. Compared to ΔE(extrap, MP6), FE2 offers also an improvement if equilibrium geometries are compared. For stretched geometries, sixth-order FE2 values are not as close to FCI correlation energies as ΔE(extrap, MP6) values. However, in these cases correlation errors because of multireference effects are rather large and, therefore, none of the approximation methods considered here may be useful as long as it is based on a single determinant approach.

The convergence behavior of FE2 correlation energies seems to be also considerably improved as compared to the MPn or FE1 series. Oscillations typical of MPn and even FE1 correlation energies for class B systems are dampened out. This is quite obvious for Ne, F, FH and in particular F^- where FE2 scaling leads to a leveling of the MP4/MP5 oscillation. In the particular case of F^-, the Padé approximants [1, 0], [1, 1], [2, 1], and [2, 2] also provide a smoothly converging series (see discussion above), however, FE2 scaling is clearly superior to the Padé series because it leads to the more accurate prediction of FCI values.

The dampening of the MP4/MP5 oscillation by FE2 scaling, of course, is a consequence of the minimization of $E^{(5)}$ and the resulting equality of $\Delta E_{\lambda}^{(4)} = \Delta E_{\lambda}^{(5)}$. In this way, the improvement obtained for fifth-order energies is fully transferred to fourth-order energies leading there to a substantially large improvement (see Table I and Figs. 1–10). The second largest improvement is obtained for sixth-order energies, which provide a useful basis for a prediction of the corresponding FCI values.

If one calculates MP5 or even MP6 energies, it is an advantage to apply FE2 scaling, which is as simple as the calculation of FE1 values, which, however, leads to significantly improved convergence behavior (no initial oscillations) and the most accurate predictions for infinite-order MP energies (FCI energies) presently possible.

Conclusions

The following conclusions can be drawn from this work.

1. Using the Padé approximants [1, 0], [1, 1], [2, 1], and [2, 2], one can expect improved correlation energies in some but not all cases. At the moment, it seems to be impossible to predict under which conditions Padé approximants lead to reliable estimates of the FCI correlation energy. The Padé series [1, 0], [1, 1], [2, 1], [2, 2] is monotonicly convergent if the ratios $E^{(4)}/E^{(3)}$, $D/\det A$, $\tilde{D}/\det B$, etc. become successively more positive; otherwise it oscillates.
2. The Pople–Frisch–Luke–Binkley (PFLB) infinite-order MPn formula [17] can be considerably improved by using MP6 correlation energies. The best estimates are obtained by using for class A and class B systems separate formulas, where in the former case the series $1/(1 - x)$ with $x = E^{(6)}/E^{(5)}$ is used while in the latter case the series e^x with $x = E^{(6)}/E^{(4)}$ is more appropriate to avoid an exaggeration of the magnitude of the correlation energy. In this way, the mean absolute deviation of predicted infinite-order correlation energies from FCI values is decreased to 0.3 mhartree for atoms and molecules in their equilibrium geometry investigated in this work.
3. Feenberg scaling can be significantly improved if second-order perturbation theory (FE2) is applied and $\lambda^{(5)}$ is evaluated from MP5 energies. FE2 correlation energies up to sixth-order are significantly better than either MPn or FE1 correlation energies. At sixth order, the mean absolute deviation of FE2 correlation energies from FCI values is just 0.1 mhartree for equilibrium geometries. Initial oscillations in the correlation energies of case B systems are suppressed at the FE2 level. FE2 scaling is clearly superior to predictions being based either on Padé approximants or extensions of the PFLB extrapolation formula.

Future work has to prove whether FE2 scaling is also useful when only approximated rather than full MP5 and MP6 energies, for example from MP6(M7) or MP6(M8) calculations, are available.

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