Correlation Energy Estimators based on
Møller-Plesset Perturbation Theory

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Abstract

Some methods for the convergence acceleration of the Møller-Plesset perturbation series for the correlation energy are discussed. The order-by-order summation is less effective than the Feenberg series. The latter is obtained by renormalizing the unperturbed Hamilton operator by a constant factor that is optimized for the third order energy. In the fifth order case, the Feenberg series can be improved by order-dependent optimization of the parameter. Alternatively, one may use Padé approximants or a further method based on effective characteristic polynomials to accelerate the convergence of the perturbation series. Numerical evidence is presented that, besides the Feenberg-type approaches, suitable Padé approximants, and also the effective second order characteristic polynomial, are excellent tools for correlation energy estimation.

Key words: Many-body perturbation theory, convergence acceleration, extrapolation, Møller-Plesset series, Feenberg series, Padé approximants, effective characteristic polynomials

1 Introduction

Quite often in theoretical work, approximation schemes for some quantities converge rather slowly. Thus, there is a need for means to accelerate convergence or, equivalently, to extrapolate from few members of a sequence to its limit. Fortunately, the development of such methods has become a rather active field at the borderline between mathematics and the sciences in recent years. Brezinski and Redivo Zaglia [1] have given an excellent mathematical introduction to such methods. There are many methods that can be used to

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accelerate slowly convergent (or to sum divergent) power series in terms of rational approximations, e.g., Padé approximants [2–4] that are related to the famous epsilon algorithm [5], Levin-type methods [6–9], and iterative methods [10] like the recently developed $J$ transformation [11–13]. There are also methods that can be used to accelerate the convergence of Fourier [14,15,8] and other orthogonal series [16,17]. One-dimensional iteration sequences can be accelerated very effectively as is demonstrated in [18] for the case of the inverse Dyson equation. There is also a growing literature on extrapolation of matrix and vector sequences (see [1] for an introduction) that have found applications to the computation of matrix functions [19] and the iterative solution of fixed-point equations [20]. The full potential for application of these methods in the sciences has still to be explored.

One of the fields where these methods may be applied is Many-Body Perturbation Theory (MBPT), that is one of the standard methods to obtain the correlation energy in molecular ab initio calculations. The convergence acceleration of many-body perturbation series has recently become a topic of increasing interest [21–27], also in the context of time-dependent phenomena [28]. Here, we restrict attention to approaches to correlation energy estimation that are based on the Møller-Plesset (MP) series since the latter is commonly and routinely used in quantum chemistry for closed-shell systems. For open-shell systems, the restricted MP (RMP) method has been developed [29] that is based on an restricted open-shell Hartree-Fock (ROHF) determination of the MP unperturbed Hamiltonian. In this way, the RMP approach largely avoids spin contaminations that are characteristic for unrestricted MP (UMP) based on an unrestricted HF (UHF) zero-order calculation. For smaller molecules, calculations up to fourth or even fifth order do not pose large problems, and MP$n$ ($n=2,4$) calculations are a popular approach to the correlation problem. However, the computational effort increases steeply with the order of the perturbation series, and with the size of the molecular system. Therefore, there is a need to make the best use of the lower-order terms since higher terms are difficult to obtain. Order-by-order summation of the perturbation expansion as given by

$$ E = E_0 + E_1 + E_2 + E_3 + E_4 + E_5 + \ldots, $$

(1)

i.e., using the $n$th order estimate

$$ E^{(n)} = \sum_{j=0}^{n} E_j, $$

(2)

is not the best way to exploit the information content of its terms. It has been shown by Schmidt, Warken and Handy [21] that a specific variant of a method originally proposed by Goldhammer and Feenberg [30,31] for the
Brillouin-Wigner perturbation expansion allows to obtain better estimates for the correlation energy than order-by-order summation of the usual MP series. This variant was called the Feenberg series in [21]. It is also a special case of the so-called Geometric Approximation [32–35]. Similar to the original approach of Goldhammer and Feenberg [30,31], the computation of the Feenberg series requires only the terms $E_j$ of the perturbation series.

Alternatively, one may use Padé approximants that provide rational approximations $[p, q]$ to power series, where $p$ denotes the order of the numerator polynomial, and $q$ that of the denominator polynomial. Padé approximants may be calculated for the original perturbation series, and also for the renormalized perturbation series. As shown by Wilson, Silver, and Farrell [35], the special Padé approximants $[n + 1, n]$ have the property that they are invariant under the scaling of the unperturbed Hamilton operator and, thus, are identical for the original and the renormalized case. This invariance is an important property of correlation energy estimators since the true correlation energy is independent of our choice of the unperturbed Hamiltonian.

Recently, a method based on effective characteristic polynomials has been applied to correlation energy computations of some model systems [36–42] and for the summation of perturbation expansions of anharmonic oscillators [43]. We will see that results based on low-order effective characteristic polynomials also have the desirable invariance property under rescaling of the unperturbed Hamiltonian.

All these methods require only the terms $E_i$ of the Møller-Plesset perturbation series. The additional effort to calculate them besides the usual perturbation series is very low. As will be shown, these methods allow to obtain much better estimates of the correlation energy in many cases, and allow the identification of cases where standard perturbation theory fails. In these cases, computationally more demanding correlation energy estimators have to be used [21–27,44–69].

2 Methods

The Goldhammer-Feenberg approach [30,31] renormalizes the unperturbed Hamiltonian $H_0$ by a constant factor according to

$$H_0(\alpha) = (1 - \alpha)H_0.$$  \hspace{1cm} (3)

This leads to a repartitioning of the total Hamiltonian $H = H_0 + H_1$ as

$$H = H_0(\alpha) + H_1(\alpha), \quad H_1(\alpha) = H_1 + \alpha H_0.$$  \hspace{1cm} (4)
It also leads to a renormalized perturbation series

\[ E(\alpha) = E_0(\alpha) + E_1(\alpha) + E_2(\alpha) + E_3(\alpha) + E_4(\alpha) + E_5(\alpha) + \ldots \] (5)

with partial sums — i.e., renormalized nth order energy estimates — given by

\[ E^{(n)}(\alpha) = \sum_{j=0}^{n} E_j(\alpha) \] (6)

depending on renormalized jth order contributions [31, Eq. (12)]

\[
E_0(\alpha) = (1 - \alpha) E_0, \quad E_1(\alpha) = E_1 + \alpha E_0, \\
E_n(\alpha) = \frac{1}{(1 - \alpha)^{n-1}} \sum_{j=2}^{n} \binom{n-2}{j-2} (-\alpha)^{n-j} E_j, \quad (n \geq 2). \] (7)

For the Feenberg series, the factor \( \alpha \) is determined by requiring that the third order energy \( E^{(3)}(\alpha) \) of the renormalized perturbation expansion is stationary with respect to variations of the factor \( \alpha \). This leads to an optimized value based on the third order result given by \( \alpha^{(3)} = E_3/E_2 \). In this way, the partitioning of the Hamiltonian is fixed, and the Feenberg series is obtained as the usual Rayleigh-Schrödinger series for the unperturbed Hamilton operator \( H_0(\alpha^{(3)}) \). The total energies are

\[ F_n = E^{(n)}(\alpha^{(3)}) = E^{(n)}(E_3/E_2). \] (8)

The stationarity of the eigenvalue is based on the observation that the exact value of the energy, i.e., the infinite order result should be independent of the value of \( \alpha \) that is used. When applying this to an approximation obtained in some finite order, that value of \( \alpha \) is best where the derivative of the approximation is as small as possible in absolute value, preferably zero. We remark that this is related to the concept of order-dependent mappings as discussed in [70, Sec. 18]. Since order-by-order summation of the \( \alpha \) dependent Rayleigh-Schrödinger expansion leads to the nth order estimate \( E^{(n)}(\alpha) \) defined in Eq. (6), the optimal value \( \alpha^{(n)} \) of \( \alpha \) in nth order is determined from the equation \((n > 1)\)

\[
0 = \frac{dE^{(n)}}{d\alpha}(\alpha^{(n)}), \quad \frac{dE^{(n)}}{d\alpha}(\alpha) = (n - 1) E_n(\alpha)/(1 - \alpha). \] (9)

The second equality here follows from an explicit calculation. A solution of this equation leads to an approximation

\[ GF_n = E^{(n)}(\alpha^{(n)}) \] (10)
for the total energy. Thus, in each order of the renormalized perturbation series, different values of \( \alpha \) are chosen. This approach has been proposed already by Feenberg. We will call its results the total \textit{Goldhammer-Feenberg energies} in order to distinguish it from the Feenberg total energies. Obviously, there can be several solutions of Eq. (9), and the Goldhammer-Feenberg energies are not guaranteed to be real.

In the case of fifth order, the condition (9) reduces in combination with Eq. (7) to requiring that \( \alpha^{(5)} \) is a root of the third order polynomial \( (1 - \alpha)^4 E_5(\alpha) \). The latter has real coefficients and, thus, is guaranteed to have a real solution \( \alpha_r^{(5)} \). The corresponding value \( E^{(5)}(\alpha_r^{(5)}) \) will be called GF5 later. Alternatively, one can use the average of the two (in the present case always) complex energies obtained from the other roots of the third order polynomial. This average will be called GF5b later.

As is well-known (see for instance [47,56]), Rayleigh-Schrödinger MBPT is size-extensive order by order, i.e., for a super-molecule build up from \( N \) non-interacting identical systems, the perturbation energies are linear in \( N \) in each order. Thus, if \( E_j \) is the \( j \)th term of the perturbation series of one of the \( N \) subsystems, the \( j \)th order term of the perturbation series for the super-molecule is \( N E_j \).

In the case of the Feenberg scaling, we note that Eq. (7) implies that for \( E_j \to N E_j \), we also have \( E_j(\alpha) \to N E_j(\alpha) \). Thus, for any \( \alpha \) that is independent of \( N \), also the renormalized perturbation series is size-extensive in each order. Since \( \alpha^{(3)} = E_3/E_2 \) is invariant under \( E_j \to N E_j \), all Feenberg energies \( F_n \) are size-extensive as a consequence of Eq. (8).

The Goldhammer-Feenberg energies \( GF_n \) for \( n > 1 \) are also size-extensive. To prove this, we note that under \( E_n \to N E_n \), we have \( dE_n/d\alpha \to N dE_n/d\alpha \). This follows from the last equality in Eq. (9), since \( E_n(\alpha) \to N E_n(\alpha) \) under \( E_n \to N E_n \). This implies that the positions of the zeros of \( dE_n/d\alpha \), and hence the positions \( \alpha^{(n)} \) of the extrema of \( E_n(\alpha) \) are invariant under \( E_n \to N E_n \). Since the \( \alpha^{(n)} \) are used to define the Goldhammer-Feenberg energies, the latter are size-extensive. In particular, this applies to GF5 and GF5b.

Now, we sketch the method of the effective characteristic polynomial that has recently been applied to the summation of divergent perturbation series [43]. In the linear variation method with \( n \) orthonormal basis functions \( \{ \phi_j \}_{j=1}^n \) applied to a Hamiltonian \( H \), the characteristic polynomial \( P_n(E) \) of degree \( n \) in the unknown energy \( E \) has the form

\[
P_n(E) = \det \left| \langle \phi_j | H | \phi_k \rangle - E \delta_{j,k} \right|.
\]  

(11)
If \( H = H_0 + \beta V \), the polynomial has the form ([43], Eq. (3.2))

\[
P_n(E) = \sum_{j=0}^{n} E^j \sum_{k=0}^{n-j} f_{n,j,k} \beta^k
\]

with \( f_{n,n,0} = 1 \). Thus, \( N = n(n+3)/2 \) coefficients \( f_{n,j,k} \) have to be determined. They could be obtained from the matrix elements of \( H_0 \) and \( V \). In the method of the characteristic polynomial, they are obtained from the coefficients of the perturbation series for \( E \)

\[
E = \sum_{j=0}^{\infty} E_j \beta^j.
\]

For this end, one uses (13) in (12) and does a Taylor expansion in \( \beta \) with the result

\[
P_n \left( \sum_{j=0}^{\infty} E_j \beta^j \right) = \sum_{k=0}^{N-1} A_k \beta^k + O \left( \beta^N \right).
\]

The \( A_k \) depend on the \( f_{n,j,k} \). Since \( P_n(E) = 0 \) for an eigenvalue \( E \), one demands

\[
A_k = 0, \quad 0 \leq k \leq N - 1.
\]

This yields a linear equation system for the unknown \( f_{n,j,k} \), and thus, these coefficients can be determined. After the determination, the effective characteristic equation \( P_n(E) = 0 \) is solved for \( E \). If only perturbation coefficients \( E_j \) up to \( j = 5 \) are available, only a second degree effective characteristic polynomial can be used. In our case, one finally puts \( \beta = 1 \). In this way, one obtains an explicit solution of \( P_2(E) = 0 \) as

\[
\Pi_2 = E_0 + E_1 + \frac{E_2}{2} - E_3 + \sqrt{(E_2 - E_3)^2 - 4 (E_2 E_4 - E_3^2)}
\]

\[
E_2 E_4 - E_3^2
\]

A further solution (with a minus sign of the square root) only yields the correct result for small \( \beta \) if \( E_2 > 0 \) holds which does not occur in perturbation theory calculations of ground states.

Direct calculation shows that the estimate \( \Pi_2 \) is independent under a scaling of \( H_0 \), i.e., we have

\[
\Pi_2(E_0, \ldots, E_4) = \Pi_2(E_0(\alpha), \ldots, E_4(\alpha)).
\]
Since the true characteristic polynomials — depending only on the total Hamiltonian — are invariant under Feenberg scaling, it may be conjectured that this invariance also holds for estimates obtained as roots of effective characteristic polynomials of higher degree. A proof of this conjecture is under investigation.

We denote \( \Pi_2 \) also as estimate \( \Pi2 \) for the total energy in the following.

It is easy to see from Eq. (16) that \( \Pi_2 \rightarrow N\Pi_2 \) if \( E_j \rightarrow NE_j \) for all \( j \) with \( 0 \leq j \leq 4 \). Thus, the \( \Pi_2 \) estimator is size-extensive.

Padé approximants [2–4] are defined with respect to a given power series as ratios of two polynomials. Given numerator and denominator polynomial degrees \( p \) and \( q \), the coefficients of these polynomials in the Padé approximant \([p,q]\) are determined by requiring that up to the order \( p+q \), the coefficients in the Taylor expansion of the ratio of polynomials are equal to the coefficients of the given power series. In the present contribution, we take as this power series the perturbation expansion (13) in the parameter \( \beta \) that is put equal to one in the final formulas. We note that a different power series that is not explicitly defined, seems to have been used for the Padé approximants in [71]. For the application of rational approximants to the Møller-Plesset series see also Ref. [72].

### 3 Numerical Results

Fortunately, excellent data for the test of the methods described in the previous section are available in [21]. This paper also includes results given in [71]. In these references, a large number of Møller-Plesset results up to fifth order, and FCI (Full Configuration Interaction) or CCSDT (Coupled Cluster Singles Doubles Triples) results are given for the ground states of benchmark molecules (BH, HF, CH\(_2\), H\(_2\)O, NH\(_2\), NH\(_3\), CO, C\(_2\)H\(_2\), O\(_3\), CN). The results of the reanalysis of these data is presented in Table 1. For completeness, the MP data are also plotted. If not stated otherwise, MPn means RMPn in open shell cases. Apart from case n (NH\(_3\)), the left half of the data in Table 1 is obtained from the data up to fourth order, while the right half also depends on the fifth order.

It is seen that in many cases, the correlation energy estimators provide excellent results. Problematic cases are s, t, and u. In case s corresponding to CN, the perturbation series is divergent, being based on doubly occupied ROHF orbitals where for alpha and beta spins the same orbitals are used, unlike the RMP orbitals where occupied alpha and beta set both are rotated. [21,66] In cases t and u corresponding to H\(_2\)O at stretched geometries, the approach
is based on an UMP series that is monotonously and very slowly convergent [21,72].

Table 1: Comparison of Correlation Energy Estimators

| Method | Energy  | %Corr | Method | Energy  | %Corr |
|--------|---------|-------|--------|---------|-------|
| Case a: BH ($^1\Sigma$, $r = 2.329 \, a_0$, DZP, [71,73,74]) |
| SCF    | -25.125260 | 0.00  | MP5    | -25.225101 | 97.53 |
| MP2    | -25.198988  | 72.02 | F5     | -25.226881  | 99.27 |
| MP3    | -25.216566  | 89.19 | GF5    | -25.226971  | 99.36 |
| MP4    | -25.222567  | 95.06 | GF5b   | -25.227088  | 99.47 |
| F4     | -25.226167  | 98.57 | [3,2]  | -25.227299  | 99.68 |
| [2,2]  | -25.225294  | 97.72 | [2,3]  | -25.227478  | 99.85 |
| Π2     | -25.226555  | 98.95 | FCI    | -25.227627  | 100.00 |
| Case b: BH ($^1\Sigma$, $r = 1.5 \times 2.329 \, a_0$, DZP, [71,75]) |
| SCF    | -25.062213  | 0.00  | MP5    | -25.172372  | 96.83 |
| MP2    | -25.139869  | 68.26 | F5     | -25.174484  | 98.69 |
| MP3    | -25.160249  | 86.18 | GF5    | -25.174544  | 98.74 |
| MP4    | -25.168745  | 93.64 | GF5b   | -25.177010  | 100.91 |
| F4     | -25.175345  | 99.45 | [3,2]  | -25.175078  | 99.21 |
| [2,2]  | -25.173623  | 97.93 | [2,3]  | -25.175106  | 99.24 |
| Π2     | -25.176791  | 100.72| FCI    | -25.175976  | 100.00 |
| Case c: BH ($^1\Sigma$, $r = 2 \times 2.329 \, a_0$, DZP, [71,75]) |
| SCF    | -24.988201  | 0.00  | MP5    | -25.121278  | 95.65 |
| MP2    | -25.074503  | 62.03 | F5     | -25.126844  | 99.65 |
| MP3    | -25.100221  | 80.51 | GF5    | -25.126983  | 99.75 |
| MP4    | -25.114005  | 90.42 | GF5b   | -25.130104  | 101.99 |
| F4     | -25.128829  | 101.08| [3,2]  | -25.129407  | 101.49 |
| [2,2]  | -25.124953  | 98.29 | [2,3]  | -25.129475  | 101.54 |
| Π2     | -25.137084  | 107.01| FCI    | -25.127333  | 100.00 |

Case d: HF ($r = 1.733 \, a_0$, DZP, [71,76])
| Method | Energy (a.u.) | ZPE (a.u.) | Energy (a.u.) | ZPE (a.u.) | Energy (a.u.) |
|--------|--------------|------------|---------------|------------|---------------|
| SCF    | -100.047087  | 0.00       | MP5           | -100.250158| 99.60         |
| MP2    | -100.243165  | 96.17      | F5            | -100.250099| 99.57         |
| MP3    | -100.245531  | 97.33      | GF5           | -100.250276| 99.66         |
| MP4    | -100.251232  | 100.13     | GF5b          | -100.251988| 100.50        |
| F4     | -100.251443  | 100.23     | [3,2]         | -100.250468| 99.75         |
| [2,2]  | -100.251547  | 100.28     | [2,3]         | -100.250481| 99.76         |
| Π2     | -100.251820  | 100.42     | FCI           | -100.250969| 100.00        |

Case e: HF (r = 1.5 × 1.733 a₀, DZP, [71,76])

| Method | Energy (a.u.) | ZPE (a.u.) | Energy (a.u.) | ZPE (a.u.) | Energy (a.u.) |
|--------|--------------|------------|---------------|------------|---------------|
| SCF    | -99.933230   | 0.00       | MP5           | -100.158121| 99.00         |
| MP2    | -100.149756  | 95.32      | F5            | -100.158152| 99.01         |
| MP3    | -100.148543  | 94.78      | GF5           | -100.158247| 99.05         |
| MP4    | -100.159627  | 99.66      | GF5b          | -100.161609| 100.53        |
| F4     | -100.159443  | 99.58      | [3,2]         | -100.158750| 99.28         |
| [2,2]  | -100.160091  | 99.87      | [2,3]         | -100.158757| 99.28         |
| Π2     | -100.160708  | 100.14     | FCI           | -100.160395| 100.00        |

Case f: HF (r = 2 × 1.733 a₀, DZP, [71,76])

| Method | Energy (a.u.) | ZPE (a.u.) | Energy (a.u.) | ZPE (a.u.) | Energy (a.u.) |
|--------|--------------|------------|---------------|------------|---------------|
| SCF    | -99.817571   | 0.00       | MP5           | -100.073004| 96.93         |
| MP2    | -100.057062  | 90.88      | F5            | -100.073139| 96.98         |
| MP3    | -100.054148  | 89.77      | GF5           | -100.073301| 97.04         |
| MP4    | -100.076267  | 98.16      | GF5b          | -100.079678| 99.46         |
| F4     | -100.075480  | 97.86      | [3,2]         | -100.075064| 97.71         |
| [2,2]  | -100.077899  | 98.78      | [2,3]         | -100.075072| 97.71         |
| Π2     | -100.080476  | 99.76      | FCI           | -100.081107| 100.00        |

Case g: CH₂ (¹A₁, r = 2.11 a₀, θ = 102.4°, DZP, [71,77])

| Method | Energy (a.u.) | ZPE (a.u.) | Energy (a.u.) |
|--------|--------------|------------|---------------|
| SCF    | -38.886297   | 0.00       | MP5           |
| MP2    | -38.996127   | 77.96      | F5            |
| MP3    | -39.016593   | 92.48      | GF5           |
| MP4    | -39.022203   | 96.47      | GF5b          |
(Table 1 – continued)

| Case | Method | SCF | Energy (a.u.) | Case | Method | SCF | Energy (a.u.) |
|------|--------|-----|--------------|------|--------|-----|--------------|
| h: H₂O (¹A₁, r = 1.88973 a₀, θ = 104.5°, DZP, [71,78]) | SCF | -76.040542 | 0.00 | MP5 | -76.255924 | 99.68 |
|      | MP2   | -76.243660 | 94.00 | F5  | -76.255918 | 99.67 |
|      | MP3   | -76.249403 | 96.66 | GF5 | -76.255929 | 99.68 |
|      | MP4   | -76.255706 | 99.58 | GF5b| -76.257338 | 100.33 |
|      | F4    | -76.256262 | 99.83 | [3,2]| -76.256134 | 99.77 |
|      | [2,2] | -76.256282 | 99.84 | [2,3]| -76.256135 | 99.77 |
|      | Π₂    | -76.256729 | 100.05 | FCI | -76.256624 | 100.00 |
| i: H₂O (¹A₁, r = 1.5 × 1.88973 a₀, θ = 104.5°, DZP, [71,78]) | SCF | -75.800494 | 0.00 | MP5 | -76.066422 | 98.16 |
|      | MP2   | -75.848095 | 91.40 | F5  | -76.066368 | 98.14 |
|      | MP3   | -75.845081 | 90.28 | GF5 | -76.066442 | 98.17 |
|      | MP4   | -75.865641 | 97.87 | GF5b| -76.068395 | 98.89 |
|      | F4    | -75.864909 | 97.60 | [3,2]| -76.068528 | 98.94 |
|      | [2,2] | -75.866937 | 98.35 | [2,3]| -76.068533 | 98.94 |
|      | Π₂    | -75.868954 | 99.10 | FCI | -76.071405 | 100.00 |
| j: H₂O (¹A₁, r = 2 × 1.88973 a₀, θ = 104.5°, DZP, [71,78]) | SCF | -75.582286 | 0.00 | MP5 | -75.935304 | 95.41 |
|      | MP2   | -75.898603 | 85.50 | F5  | -75.934525 | 95.20 |
|      | MP3   | -75.877664 | 79.84 | GF5 | -75.935353 | 95.43 |
|      | MP4   | -75.937410 | 95.98 | GF5b| -75.923566 | 92.24 |
|      | F4    | -75.927115 | 93.20 | [3,2]| -75.949379 | 99.22 |
|      | [2,2] | -75.941045 | 96.97 | [2,3]| -75.949401 | 99.22 |
|      | Π₂    | -75.954930 | 100.72 | FCI | -75.952269 | 100.00 |
| k: NH₂ (²B₁, r = 1.013 Å, θ = 103.2°, 6-31G, [72,29]) | SCF | -75.582286 | 0.00 | MP5 | -75.935304 | 95.41 |
|      | MP2   | -75.898603 | 85.50 | F5  | -75.934525 | 95.20 |
|      | MP3   | -75.877664 | 79.84 | GF5 | -75.935353 | 95.43 |
|      | MP4   | -75.937410 | 95.98 | GF5b| -75.923566 | 92.24 |
|      | F4    | -75.927115 | 93.20 | [3,2]| -75.949379 | 99.22 |
|      | [2,2] | -75.941045 | 96.97 | [2,3]| -75.949401 | 99.22 |
|      | Π₂    | -75.954930 | 100.72 | FCI | -75.952269 | 100.00 |
| Method | Energy (a.u.) | Basis Set |
|--------|--------------|-----------|
| SCF    | -55.530177   | 6-31G, [72,29] |
| MP2    | -55.617272   | 6-31G, [72,29] |
| MP3    | -55.627501   | 6-31G, [72,29] |
| MP4    | -55.631220   | 6-31G, [72,29] |
| F4     | -55.632525   | 6-31G, [72,29] |
| [2,2]  | -55.632204   | 6-31G, [72,29] |
| Π2     | -55.632825   | 6-31G, [72,29] |

**Case l: NH$_2$ ($^2B_1$, $r = 1.5 \times 1.013$ Å, $\theta = 103.2^\circ$, 6-31G, [72,29])**

| Method | Energy (a.u.) | Basis Set |
|--------|--------------|-----------|
| SCF    | -55.367729   | 6-31G, [72,29] |
| MP2    | -55.489967   | 6-31G, [72,29] |
| MP3    | -55.504270   | 6-31G, [72,29] |
| MP4    | -55.516470   | 6-31G, [72,29] |
| F4     | -55.521456   | 6-31G, [72,29] |
| [2,2]  | -55.521125   | 6-31G, [72,29] |
| Π2     | -55.526202   | 6-31G, [72,29] |

**Case m: NH$_2$ ($^2B_1$, $r = 2 \times 1.013$ Å, $\theta = 103.2^\circ$, 6-31G, [72,29])**

| Method | Energy (a.u.) | Basis Set |
|--------|--------------|-----------|
| SCF    | -55.181593   | DZ, [73,74] |
| MP2    | -55.357617   | DZ, [73,74] |
| MP3    | -55.375463   | DZ, [73,74] |
| MP4    | -55.409165   | DZ, [73,74] |
| F4     | -55.421427   | DZ, [73,74] |
| [2,2]  | -55.426946   | DZ, [73,74] |
| Π2     | -55.478348   | DZ, [73,74] |

**Case n: NH$_3$ ($r = 1.91165 a_0$, $\theta = 106.7^\circ$, DZ, [73,74])**

| Method | Energy (a.u.) | Basis Set |
|--------|--------------|-----------|
| SCF    | -56.165931   | DZ, [73,74] |
| MP2    | -56.277352   | DZ, [73,74] |
| MP3    | -56.285281   | DZ, [73,74] |
| MP4    | -56.290692   | DZ, [73,74] |
| F4     | -56.291937   | DZ, [73,74] |
| [2,2]  | -56.291782   | DZ, [73,74] |
| Π2     | -56.292636   | DZ, [73,74] |
| Π2     | -56.292871   | DZ, [73,74] |
| FCI    | -56.292612   | DZ, [73,74] |
Table 1 – continued

| Case | Molecule | State | Method | Energy (a.u.) | Error (a.u.) |
|------|----------|-------|--------|---------------|--------------|
| Case o: CO ($^1\Sigma$, DZ, [71]) | SCF | -112.760093 | 0.00 | MP5 | -113.059117 | 98.36 |
| | MP2 | -113.045824 | 93.99 | F5 | -113.059254 | 98.41 |
| | MP3 | -113.044659 | 93.61 | GF5 | -113.060859 | 98.93 |
| | MP4 | -113.067749 | 101.20 | GF5b | -113.073579 | 103.12 |
| | F4 | -113.067469 | 101.11 | [3,2] | -113.062479 | 99.47 |
| | [2,2] | -113.069566 | 101.80 | [2,3] | -113.062539 | 99.49 |
| | Π2 | -113.072074 | 102.62 | CSDT | -113.064100 | 100.00 |
| Case p: C$_2$H$_2$ ($^1\Sigma_g$, DZP, [71]) | SCF | -76.831819 | 0.00 | MP5 | -77.118892 | 102.18 |
| | MP2 | -77.085307 | 90.23 | F5 | -77.120192 | 102.65 |
| | MP3 | -77.097232 | 94.47 | GF5 | -77.122141 | 103.34 |
| | MP4 | -77.111732 | 99.63 | GF5b | -77.117205 | 101.58 |
| | F4 | -77.113928 | 100.42 | [3,2] | -77.127079 | 105.10 |
| | [2,2] | -77.114110 | 100.48 | [2,3] | -77.127731 | 105.33 |
| | Π2 | -77.116235 | 101.24 | CSDT | -77.112760 | 100.00 |
| Case q: O$_3$ ($^1A_1$, DZP, [71]) | SCF | -224.295920 | 0.00 | MP5 | -224.929902 | 97.54 |
| | MP2 | -224.931924 | 97.86 | F5 | -224.933812 | 98.15 |
| | MP3 | -224.888104 | 91.11 | GF5 | -224.934513 | 98.25 |
| | MP4 | -224.952784 | 101.07 | GF5b | -224.952167 | 100.97 |
| | F4 | -224.941418 | 99.32 | [3,2] | -224.938301 | 98.84 |
| | [2,2] | -224.950280 | 100.68 | [2,3] | -224.938367 | 98.85 |
| | Π2 | -224.952387 | 101.00 | CSDT | -224.945859 | 100.00 |
| Case r: CN ($^2\Sigma$, $r = 1.1619$ Å, STO-3G, RMP [29]) | SCF | -90.99752 | 0.00 | MP5 | -91.16157 | 95.07 |
| | MP2 | -91.15437 | 90.90 | F5 | -91.16165 | 95.12 |
| | MP3 | -91.14799 | 87.20 | GF5 | -91.16166 | 95.12 |
(Table 1 – continued)

|       |        |        |       |        |        |
|-------|--------|--------|-------|--------|--------|
| MP4   | -91.16300 | 95.90  | GF5b  | -91.16360 | 96.24  |
| F4    | -91.16133 | 94.93  | [3,2] | -91.16297 | 95.88  |
| [2, 2]| -91.16321 | 96.02  | [2,3] | -91.16297 | 95.88  |
| Π2   | -91.16426 | 96.63  | FCI   | -91.17008 | 100.00 |

Case s: CN ($^2\Sigma$, $r = 1.1619$ Å, STO-3G, Hubac-Carsky, [66,79])

|       |        |        |       |        |        |
|-------|--------|--------|-------|--------|--------|
| SCF   | -90.99752 | 0.00  | MP5   | -91.12039 | 71.20  |
| MP2   | -91.17762 | 104.37 | F5    | -91.15212 | 89.59  |
| MP3   | -91.14160 | 83.50  | GF5   | -91.15998 | 94.15  |
| MP4   | -91.19422 | 113.99 | GF5b  | -91.18190 | 106.85 |
| F4    | -91.17389 | 102.21 | [3,2] | -91.16350 | 96.19  |
| [2, 2]| -91.18753 | 110.11 | [2,3] | -91.16359 | 96.24  |
| Π2   | -91.19152 | 112.42 | FCI   | -91.17008 | 100.00 |

Case t: H$_2$O ($r = 1.5 \times 0.967$ Å, $\theta = 107.6^\circ$, 6-21G,[72])

|       |        |        |       |        |        |
|-------|--------|--------|-------|--------|--------|
| RHF   | -75.707206 | 0.00  | UMP5  | -75.853895 | 76.41  |
| UHF   | -75.735012 | 14.48 | F5    | -75.855560 | 77.28  |
| UMP2  | -75.829388 | 63.65 | GF5   | -75.856608 | 77.82  |
| UMP3  | -75.836823 | 67.52 | GF5b  | -75.850870 | 74.84  |
| UMP4  | -75.848211 | 73.45 | [3,2] | -75.862349 | 80.81  |
| F4    | -75.851276 | 75.05 | [2,3] | -75.862421 | 80.85  |
| [2, 2]| -75.851994 | 75.42 | FCI   | -75.899180 | 100.00 |
| Π2   | -75.857074 | 78.07 |        |        |        |

Case u: H$_2$O ($r = 2 \times 0.967$ Å, $\theta = 107.6^\circ$, 6-21G,[72])

|       |        |        |       |        |        |
|-------|--------|--------|-------|--------|--------|
| RHF   | -75.491406 | 0.00  | UMP5  | -75.763370 | 90.72  |
| UHF   | -75.699298 | 69.35 | F5    | -75.763704 | 90.83  |
| UMP2  | -75.754669 | 87.82 | GF5   | -75.763826 | 90.88  |
| UMP3  | -75.760219 | 89.67 | GF5b  | -75.763657 | 90.82  |
| UMP4  | -75.762422 | 90.41 | [3,2] | -75.764089 | 90.96  |
| F4    | -75.763098 | 90.63 | [2,3] | -75.764104 | 90.97  |
Apart from these problematic cases, it is seen that in case m corresponding to NH$_2$ at twice the equilibrium distances, the errors are rather high. Excluding this case also, one may study the performance of the correlation energy estimators statistically as shown in Table 2. Plotted are the maximal error, the mean absolute error, the root mean square (rms) absolute error, and the mean percentage of the correlation energy as obtained with the various methods. In cases o, p, and q corresponding to the molecules CO, C$_2$H$_2$, O$_3$, respectively, no FCI result is available. The statistical comparison is done once excluding these cases, and once including these cases where as reference for the error calculation the CCSDT result is taken. For these cases, the given correlation energies should thus be taken with care. Carefully designed fourth order methods like $\Pi_2$ yield correlation energy estimates that can compete with fifth order results. As regards the fifth order methods, it seems that the Goldhammer-Feenberg estimator GF5 is slightly superior to the Feenberg energy F5, and the somewhat ad hoc estimator GF5b performs surprisingly well. Among the Padé approximants, the [3, 2] approximant (that is invariant under the Feenberg scaling) is a rather successful correlation estimator while the [2, 3] approximant performs very similarly. Other Padé approximants (not displayed in Table 1) do not perform as well as the ones given in this table when applied to the same data.

A careful analysis of the data in Table 1 reveals that the correlation energy estimation based on MP perturbation theory is the better the closer one is to the optimal geometries of the molecule under consideration. This is not very much surprising since it is well-known that the quality of the MP series deteriorates with increasing separations from the equilibrium geometries. Compare for instance the triples of cases (a,b,c) for BH, (d,e,f) for HF, (h,i,j) for H$_2$O, and (k,l,m) for NH$_2$, with ratios 1:1.5:2 of the relevant distances. The values away from the equilibrium geometries may or may not be reliable. The data, however, suggest that then the correlation energy estimates are reliable if — as in cases f for HF at $2 \times r_e$ and i for H$_2$O at $1.5 \times r_e$— the values of $\Pi_2$, F4 and [2, 2] do not differ too much from each other. In this situation, the $\Pi_2$ estimator seems to provide the best results. On the other hand, large differences between the estimates $\Pi_2$, F4 and [2, 2] — as in the cases j for H$_2$O at $2 \times r_e$ and m for NH$_2$ at $2 \times r_e$ — clearly indicate that in these cases more sophisticated methods (for instance the \Lambda transformation [21–27] or multi-reference methods [51,56,69,80–83]) are needed to calculate the correlation energies reliably. As regards the fifth order estimates, it is similarly

| [2, 2] | -75.762941 | 90.58 | FCI | -75.791180 | 100.00 |
|-------|------------|-------|-----|------------|-------|
| $\Pi_2$ | -75.763281 | 90.69 |     |            |       |

(Table 1 – continued)
Table 2
Statistical comparison of various correlation energy estimators

| Method | max $|error|$ | mean $|error|$ | rms $|error|$ | mean %Corr |
|--------|------------|-------------|-------------|-------------|
|        | Sampling 14 cases (a-l,n,r) | | | |
| F4     | 0.02515    | 0.00433     | 0.00767     | 98.3        |
| $[2,2]$| 0.01122    | 0.00319     | 0.00433     | 98.3        |
| II2    | 0.00975    | 0.00199     | 0.00329     | 100.1       |
|        | Sampling 17 cases (a-l,n-r) | | | |
| F4     | 0.02515    | 0.00409     | 0.00710     | 98.6        |
| $[2,2]$| 0.01122    | 0.00329     | 0.00430     | 98.8        |
| II2    | 0.00975    | 0.00269     | 0.00398     | 100.3       |
|        | Sampling 13 cases (a-l,r) | | | |
| F5     | 0.01774    | 0.00407     | 0.00628     | 98.2        |
| GF5    | 0.01692    | 0.00394     | 0.00607     | 98.2        |
| GF5b   | 0.02870    | 0.00400     | 0.00834     | 99.0        |
| $[3,2]$| 0.00711    | 0.00228     | 0.00308     | 99.1        |
| $[2,3]$| 0.00711    | 0.00224     | 0.00307     | 99.1        |
|        | Sampling 16 cases (a-l,o-r) | | | |
| F5     | 0.01774    | 0.00483     | 0.00678     | 98.5        |
| GF5    | 0.01692    | 0.00470     | 0.00664     | 98.6        |
| GF5b   | 0.02870    | 0.00452     | 0.00811     | 99.6        |
| $[3,2]$| 0.01432    | 0.00332     | 0.00492     | 99.4        |
| $[2,3]$| 0.01497    | 0.00332     | 0.00503     | 99.5        |

seen that a large spread of the values of the various estimates reveals that the MP based methods do not provide sufficiently accurate results. Reversely, a small spread of the various estimates indicates that with a high probability, the (R)MP based correlation energy estimates are reliable.

Comparing fourth and fifth order based estimators, it is seen that the latter do not always provide better estimates of the correlation energy. In many cases, the II2 estimate that is based on fourth order, provides results of comparable quality.

In Tables 3 and 4 the correlation energy estimators are used to calculate the dissociation barrier for $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$, and the barrier height and the heat of reaction for $\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_7$. 

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Table 3  
Dissociation barrier (kJ/mol) of H₂CO→H₂ + CO using a TZ2P basis at MP2 geometries  
| Method | Minimum       | Transition state | Barrier | Ref.  |
|--------|---------------|------------------|---------|-------|
| SCF    | −113.912879   | −113.748693      | 431.1   | [21]  |
| MP2    | −114.329202   | −114.182435      | 385.3   | [21]  |
| MP3    | −114.334186   | −114.185375      | 390.7   | [21]  |
| MP4    | −114.359894   | −114.219892      | 367.6   | [21]  |
| F4     | −114.360838   | −114.220603      | 368.2   | [21]  |
| [2, 2] | −114.362267   | −114.223409      | 364.6   | This work |
| Π2    | −114.364840   | −114.227767      | 359.9   | This work |
| BEb    |                |                  | 360     | [84]  |

a [21]  
b Best estimate [84]  

Table 4  
Barrier height and heat of reaction (kJ/mol) for CH₃ + C₂H₄ → C₃H₇ with a 6-31G* basis
| Method | Reactants       | TSb           | Product        | Barrier | HRc  |
|--------|-----------------|---------------|----------------|---------|------|
| RHF    | −117.585674     | −117.553736   | −117.626572    | 83.8    | −107.4|
| RMP2   | −117.967150     | −117.952092   | −118.014126    | 39.5    | −123.3|
| RMP3   | −118.004259     | −117.986543   | −118.049999    | 46.5    | −120.1|
| RMP4   | −118.022888     | −118.008072   | −118.066816    | 38.9    | −115.3|
| F4     | −118.028674     | −118.014137   | −118.071720    | 38.2    | −113.0|
| [2, 2] | −118.027529     | −118.013226   | −118.070703    | 37.6    | −113.3|
| Π2    | −118.030923     | −118.017302   | −118.073432    | 35.8    | −111.6|
| expd   |                |               |                | 33.1    | −107 |

a [21]  
b Transition state  
c Heat of reaction  
d [85–87,21]  

In both examples, the calculation is based on known Møller-Plesset energies up to fourth order [21, Tab. 2-4]. The results show that reliable correlation energy estimates as provided by the Feenberg energy F4 [21], the Padé approximant [2, 2], and the effective characteristic polynomial estimate Π2 lead to good agreement with experimental data. The Π2 estimator yields in both cases the best results.

In summary, it has been shown that the availability of various estimators
based on (R)MP results allows in many cases the accurate calculation of the correlation energy at negligible additional computational costs. Also, larger deviations between the values indicate clearly cases where further work is necessary.

Finally, we note that the above estimators are expected to be useful to improve convergence of perturbation series for the energies also for the multi-reference case. This conjecture is a promising topic for further investigations.

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