# Bounding the Extrapolated Correlation Energy Using Padé Approximants

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**ABSTRACT:** We present a rigorous strategy, based on Stieltjes series and Padé approximants, to obtain suitable bounds for extrapolation of the quantum chemical correlation energy. Computational tests are performed for the second-order Møller–Plesset (MP2) correlation energy, and the bounds obtained are tight enough for practical calculational purposes: The associated error in most cases is much less than 1 kcal/mol. The bounds presented here are also shown to be rigorous for functional forms that represent a wide variety of methods in quantum chemistry and hence may be used in extrapolating a wide range of expressions, some of them yielding significant computational advantages compared to traditional techniques. © 2000 John Wiley & Sons, Inc. Int J Quantum Chem 79: 222–234, 2000

**Key words:** extrapolation; Padé approximants; Stieltjes series; MPZ; gap shift

## Introduction

**R**ecently, a number of efficient computational strategies have been developed to carry out calculations for the second-order Møller–Plesset (MP2) correlation energy [1–6]. One of these methods, Laplace–MP2 [1, 2, 5, 6] is based on the Laplace transform of the energy-dependent denominator in the MP2 correlation energy expression. The inte-

grand in this Laplace transform consists of two-electron integrals involving exponentially damped molecular orbitals [1, 5, 6], with the damping factor being proportional to the energy difference between the Fock eigenvalue of the respective (occupied or virtual) molecular orbital and the Fermi level. As a result of the exponential damping factor, when suitable quadrature schemes [7, 8] are adopted to approximate the Laplace transform by numerical integration, significant computational gains are obtained for large molecular systems [2, 5, 7, 9].

As an alternative to the quadrature scheme in Laplace–MP2 [1, 2], Ayala, Scuseria, and Savin [6] have recently proposed a rational polynomial ex-

trapolation method to calculate the MP2 correlation energy. They have shown that *any* "smooth function" that tends to the exact MP2 correlation energy in one of its limits may be used in a scheme to extrapolate the same. The values of the "smooth function" at various points away from the physical limit are used to obtain (by extrapolation) the function value in the said limit, which yields the correct MP2 correlation energy. In particular, they calculate the *uniform* and *nonuniform gap-shifted* [6] MP2 correlation energy for various (artificial) gap shifts and extrapolate to the correct MP2 correlation energy where the artificial gap shift is zero. The test calculations [6] have shown this method to be both robust and accurate.

In this work, further influenced by the close connection between quadrature and extrapolation [10], we take another step toward making extrapolation a robust computational tool. We note that there exist two different, but related, strategies to perform an extrapolation [11–13]. In the first case, the function is calculated at various values of the independent variable to produce a fit, which may be extrapolated. This is the procedure used in Ref. [6]. Alternatively, the knowledge of the function and its derivatives at any one point in space may be used in extrapolating the function elsewhere. In this study, we investigate the use of the second procedure.

Furthermore, as we will see later, a variety of expressions in quantum chemistry may be written as a series of Stieltjes [14–18]. This allows the use of extremely powerful mathematical theorems that state that Padé approximants* provide upper and lower bounds to an extrapolation of functions expressed as a series of Stieltjes. These concepts allow us to not only develop a method to extrapolate the MP2 correlation energy with proper error bounds but also suggest alternative computational schemes, based on extrapolation, to calculate various other expressions in quantum chemistry such as MP3 or MP4, various noniterative perturbational corrections [26, 27] to the coupled-cluster expressions, and energy expressions from Görling–Levy perturbation theory [28], among others.

Finally, we would like to point out that the extrapolation schemes discussed here bear no connections to other methods that extrapolate the correlation energy at the basis set limit using a series of calculations.[†]

*Padé approximants and continued fractions have been used in a variety of ways in quantum chemistry. See, for example, Refs. [10, 19–25].

[†]See, for example, Ref. [29].

This paper is organized as follows. In the following section, we first review the concept of a series of Stieltjes and then show how a variety of expressions in quantum chemistry have this form. Subsequently, upper and lower bounds to a series of Stieltjes are introduced and used to devise methods to extrapolate, with bounds, various expressions in quantum chemistry. In the third section, we evaluate the effectiveness of the upper and lower bounds introduced in the theory section, by performing gap-shifted MP2 correlation energy calculations [6]. Here, the highest occupied and lowest unoccupied molecular orbital (HOMO–LUMO) gap of the molecule is substantially increased, and the MP2 energy along with derivatives (with respect to the chosen gap) are calculated at this large gap value. These results are then used in the expressions provided in the theory section, to obtain rigorous bounds to the physically correct MP2 energy (i.e., without the artificial gap). This extrapolation procedure may yield a convenient practical tool for calculating the MP2 correlation energy since in large-gap systems, the correlation energy is more efficiently calculated than in small-gap systems. The computational advantage of the extrapolation technique is particularly clear when viewed from the Laplace transform formalism [7], as will be discussed here. The method presented in the following section is completely general and may be used, in a similar fashion, for extrapolating a variety of expressions in quantum chemistry. In the third section we present the results of our MP2 calculations and in the final section we present our conclusions.

## Theory

### BOUNDS TO SERIES OF STIELTJES

Following the ideas discussed in Refs. [15–18], we present here some definitions and discuss some concepts, which are used later to obtain suitable bounds to the correlation energy. In all our discussions below, we assume that the variable $z$ could lie anywhere on the complex plane, whereas variables $x$, $x_1$, $x_0$, and $u$ are always real.

A function $f(z)$, with a formal expansion $f(z) = \sum_{j=0}^{\infty} f_j(-z)^j$, may be considered a series of Stieltjes if and only if there exists a bounded, nondecreasing function, $\phi(u)$, taking on infinitely many values in $0 \leq u < \infty$, such that

$$f(z) = \int_0^\infty \frac{d\phi(u)}{1 + zu}, \qquad (1)$$

and $f(z)$ has real-valued moments given by

$$f_j = \int_0^\infty u^j \, d\phi(u), \qquad (2)$$

which are the coefficients of the formal expansion. From Eq. (1), it is clear that $f(z)$ may have poles on the negative real axis (i.e., for $\mathrm{Re}(z) < 0$) and is hence said to be defined on the cut-complex plane [15], with cut along the negative real axis.

The above definition may be generalized to functions having poles for $\mathrm{Re}(z) < (-R)$, i.e., when the poles of the function are further shifted away from the origin by a negative real quantity equal to $(-R)$ and the associated series expansion about the point $x_0$ has a radius of convergence [30] equal to $R$. This is done by simply replacing the upper limit in Eq. (1) from $\infty$ to $1/R$ [15]. It is clear that as $R$ tends to zero, the upper limit tends to infinity and we regain the definitions above. In Appendix A we further discuss a series of Stieltjes and present a computationally convenient, but equivalent [15], method to test if a function is a series of Stieltjes.

Padé approximants provide rigorous upper and lower bounds to values of functions that are series of Stieltjes [15–17]. For this reason, Padé approximants may be used to extrapolate, with suitable error bounds, functions that are known to be series of Stieltjes. A brief description of Padé approximants may be found in Appendix B.

If the value of the function and its first $2N$ derivatives are known at some point $x_0$ on the real axis, it is possible to construct Padé approximants, $[N, N]$ and $[N, N - 1]$ [11, 15] as outlined in Appendix B. In this case, it is known [15, 16] that the value of the function at any real $x_1 > x_0$, is bounded by the $[N, N]$ and $[N, N - 1]$ Padé approximants at $x_1 - x_0$, i.e.,

$$[N, N](x_1 - x_0) \geq f(x_1) \geq [N, N - 1](x_1 - x_0), \quad (3)$$

where $[N, N](x_1 - x_0)$ and $[N, N - 1](x_1 - x_0)$ signify that the Padé approximants are calculated at $(x_1 - x_0)$. If, however, bounds are desired on the left side of the origin ($x_0$), i.e., when $x_1 < x_0$, the sharp inequalities derived by Gilewicz and Magnus [17],

$$0 \geq f(x_1) - [N + 1, N + k](x_1 - x_0)$$
$$\geq \frac{x_0 - x_1}{R}\{f(x_1) - [N, N + k](x_1 - x_0)\}, \quad k \geq 0 \quad (4)$$

may be used where the function, $f(x)$, has *poles on the real axis* for $(x_1 - x_0) < -R$, as outlined in the paragraph following Eq. (2). Further, the left-hand inequality in Eq. (4) may be used to obtain a lower bound to the value of the function at $x_1$, satisfying

$0 > (x_1 - x_0) > -R$, as

$$f(x_1) \geq [N + 1, N + k](x_1 - x_0), \qquad (5)$$

while the right-hand inequality may be used to obtain an upper bound

$$f(x_1) \leq \frac{R}{R - (x_0 - x_1)}\left\{[N + 1, N + k](x_1 - x_0)\right.$$
$$\left. - \frac{x_0 - x_1}{R}[N, N + k](x_1 - x_0)\right\}. \quad (6)$$

Equations (5) and (6) represent a family of lower and upper bounds for $k \geq 0$. Further, given the value of the function at $x_0$ and an even number of derivatives, it is shown [18] that the best lower bound to $f(x_1)$, from the family of bounds represented by Eq. (5), is the Padé approximant with equal polynomial order in numerator and denominator [which is obtained by setting $k = 1$ in Eq. (5)]. Similarly, given an odd number of derivatives and $f(x_0)$, the best lower bound is obtained by setting $k = 0$ in Eq. (5) [18]. Furthermore, for fixed $k$ the lower bounds in Eq. (5) form a monotonically convergent sequence, converging to $f(x_1)$ [18]. The behavior of the expression for upper bound in Eq. (6) will be analyzed in a later section.

Another set of rigorous upper bounds to $f(x_1)$, for $x_1 < x_0$, may be obtained from Ref. [18]. The author defines

$$f(z) = \frac{f_0 R}{R + z} + z[zK'(z) + K(z)] \qquad (7)$$

where $K(z)$ is a new function, also a series of Stieltjes. The series expansion for $K(z)$ is defined as

$$K(z) = \sum_{i=0}^\infty k_i(-z)^i = \sum_{i=0}^\infty \frac{1}{i+1}\left[\frac{f_0}{R^{i+1}} - f_{i+1}\right](-z)^i. \quad (8)$$

Using this series expansion, the author [18] obtains $[N, M]$ Padé approximants to $K(z)$, which when used in Eq. (7), provide the new $(N, M)$ approximants to $f(z)$. In this case, $K'(z)$ in Eq. (7) represents the derivative of the $[N, M]$ Padé approximant to $K(z)$. It is rigorously shown [18] that the $(N, M)$ approximants form monotonically converging upper bounds to $f(x_1)$, for $x_1 < x_0$. It is also shown [18] that when an even number of derivatives of $f$ at $x_0$ are used, the best upper bound using Eq. (7) is obtained when $M = N - 1$, i.e.,

$$f(x_1) \leq (N, N - 1)(x_1 - x_0)$$
$$= \frac{f_0 R}{R + (x_1 - x_0)} + (x_1 - x_0)$$
$$\times [(x_1 - x_0)[N, N - 1]_{K'}(x_1 - x_0)$$
$$+ [N, N - 1]_K(x_1 - x_0)], \qquad (9)$$

where $[N, N-1]_K(x_1 - x_0)$ signifies that the Padé approximant corresponds to the function $K(x_1 - x_0)$. Similarly, it is also shown [18] that when an odd number of derivatives of $f$ at $x_0$ are used, the best upper bound using Eq. (7) is obtained by setting $M = N$, i.e.,

$$
\begin{aligned}
f(x_1) &\leq (N, N)(x_1 - x_0) \\
&= \frac{f_0 R}{R + (x_1 - x_0)} + (x_1 - x_0) \\
&\quad \times \left[ (x_1 - x_0)[N, N]_{K'}(x_1 - x_0) \right. \\
&\qquad \left. + [N, N]_K(x_1 - x_0) \right].
\end{aligned} \tag{10}
$$

## SERIES OF STIELTJES IN QUANTUM CHEMISTRY

Consider an expression of the form

$$
E_G = -\sum_{o,v} \frac{V_{o,v}}{\epsilon_{o,v} + G}, \tag{11}
$$

where $V_{o,v}$ and $\epsilon_{o,v}$ are both positive. It is clear that when $V_{o,v}$ represents the two-electron integrals between occupied ($o$) and virtual ($v$) orbitals, and $\epsilon_{o,v}$ represents the corresponding energy difference, this expression yields the gap-shifted MP2 correlation energy [6]. However, there are a variety of other expressions in quantum chemistry that are related to the functional form in Eq. (11). For example, from the expressions in Refs. [26, 27], the iterative perturbational triples energy correction to coupled cluster singles and doubles (CCSD) may also be presented in a gap-shifted form yielding an expression identical to Eq. (11). Alternately, second-order contributions from Görling–Levy perturbation theory in density functional theory [28] may also be expressed in a form similar to Eq. (11). Energy expressions from higher order perturbation theories may be expressed as products of functions similar to those in Eq. (11) [31].

In this section, we study the properties of such functions and show that the quantity $\{-E_G\}$ is a series of Stieltjes.

We, first, note that

$$
\begin{aligned}
E_G &= -\sum_{o,v} \frac{V_{o,v}}{\epsilon_{o,v}} \frac{1}{1 + G/\epsilon_{o,v}} \\
&= -\sum_{j=0}^{\infty} \left\{ \sum_{o,v} \frac{V_{o,v}}{\epsilon_{o,v}} \epsilon_{o,v}^{-j} \right\} (-G)^j \\
&= -\sum_{j=0}^{\infty} f_j (-G)^j, \tag{12}
\end{aligned}
$$

where we have expanded $1/(1 + G/\epsilon_{o,v})$ in a Taylor series and defined the quantity in curly brackets (in the second equality) as $f_j$. The convergence of this formal Taylor expansion, however, depends on the magnitude of $G/\epsilon_{o,v}$ and the Taylor expansion may diverge for

$$
\left| \frac{G}{\min_{o,v} \epsilon_{o,v}} \right| \geq 1.
$$

Regardless of its convergence properties, though, we may write $f_j$ as the $j$th moment of a bounded, nondecreasing function since

$$
\begin{aligned}
f_j &= \sum_{o,v} \frac{V_{o,v}}{\epsilon_{o,v}} \epsilon_{o,v}^{-j} \\
&= \int_0^\infty u^j \left[ \sum_{o,v} \frac{V_{o,v}}{\epsilon_{o,v}} \delta \left( u - \frac{1}{\epsilon_{o,v}} \right) du \right] \\
&= \int_0^\infty u^j \, d\phi(u), \tag{13}
\end{aligned}
$$

where

$$
\phi(u) = \int_0^u \sum_{o,v} \frac{V_{o,v}}{\epsilon_{o,v}} \delta \left( u' - \frac{1}{\epsilon_{o,v}} \right) du', \tag{14}
$$

which is clearly bounded and nondecreasing. Furthermore,

$$
\begin{aligned}
f(G) &\equiv \int_0^\infty \frac{d\phi(u)}{1 + Gu} \\
&= \int_0^\infty \frac{\sum_{o,v} (V_{o,v}/\epsilon_{o,v}) \delta(u - 1/\epsilon_{o,v}) \, du}{1 + Gu} \\
&= \sum_{o,v} \frac{V_{o,v}}{\epsilon_{o,v}} \frac{1}{1 + G/\epsilon_{o,v}} = -E_G. \tag{15}
\end{aligned}
$$

Therefore, $\{-E_G\}$ (as a function of $G$) satisfies all the requirements placed by Eqs. (1) and (2). Hence, $\{-E_G\}$, as a function of $G$, is a series of Stieltjes and the bounds introduced above may be used for $E_G$. As noted earlier in this section, a variety of expressions in quantum chemistry may be written as in Eq. (11); consequently the bounds introduced in the previous section may be used for all these expressions. Moreover, two-electron integrals in quantum chemistry may be written using a short-range, exponentially damped kernel, $\exp(-\alpha r_{12}/r_{12})/r_{12}$, and we have recently shown [32] that such short-range two-electron integrals have the same form as in Eq. (1), with respect to the damping parameter $\alpha$.

## RIGOROUS BOUNDS TO THE EXTRAPOLATION OF $E_G$

In this section, we show how the information given above can be used to obtain rigorous upper and lower bounds to an extrapolation of $E_G$.

Suppose we are given the values of the function $\{-E_G\}$ and its derivatives at some large, positive value of $G = G_0$ and are required to extrapolate the value of the function at $G = 0$, i.e., $E_{G=0}$. Clearly upper and lower bounds to the extrapolation could be obtained using the expressions presented above. Further, for $G_0 > 0$, the upper bound to $\{-E_{G=0}\}$ may be obtained either by using Eq. (6) or by using Eq. (9) or (10) depending on whether an even or odd number of derivatives of $\{-E_G\}$ are known at $G = G_0$. Similarly, a rigorous lower bound to $\{-E_{G=0}\}$ may be obtained from Eq. (5). Therefore (since $-E_G$ is a series of Stieltjes) by substituting $G_0$ for $x_0$ and 0 for $x_1$ in Eqs. (5) and (6) we obtain bounds to $E_{G=0}$ as

$$\frac{R}{R - G_0}\left\{[N+1, N+k](-G_0) - \frac{G_0}{R}[N, N+k](-G_0)\right\}$$

$$\geq \{-E_{G=0}\} \geq [N+1, N+k](-G_0), \quad (16)$$

where

$$0 < (R - G_0) \leq \min_{o,v} \epsilon_{o,v}. \quad (17)$$

From the discussion following Eq. (4), we note that the poles of $E_G$ should occur for $(G - G_0) < -R$. Further, from Eq. (11), it follows that the first pole on the negative real axis is at $G = -\min_{o,v} \epsilon_{o,v}$; hence, we have chosen $R$ according to Eq. (17) for use in Eq. (16). (Note that for the MP2 energy, $\min_{o,v} \epsilon_{o,v}$ is twice the difference between the HOMO and the LUMO.) Further, since $[N+1, N+k](-G_0) \geq [N, N+k](-G_0)$ [18], the upper bound in Eq. (16), i.e.,

$$g_N(R) = \frac{R}{R - G_0}\left\{[N+1, N+k](-G_0)\right.$$

$$\left. - \frac{G_0}{R}[N, N+k](-G_0)\right\}, \quad (18)$$

always has a negative derivative with respect to $R$ (for positive values of $G_0$); hence $g_N(R)$ is a monotonic decreasing function of $R$. Therefore, the least upper bound to $\{-E_{G=0}\}$, consistent with Eq. (17), may be found at

$$R = R_{UB} \equiv G_0 + \min_{o,v} \epsilon_{o,v} \quad (19)$$

(i.e., $R = R_{UB} \equiv 2[E_{HOMO} - E_{LUMO}]$ for the MP2 energy). The upper bound thus obtained is signified by $g_N(R_{UB})$.

The discussion following Eq. (7) provides us an alternative approach to obtain upper bounds to $\{-E_{G=0}\}$. Using Eqs. (9) and (10), it is clear that when an even number of derivatives of $E_G$ are

known at $G = G_0$, we have

$$\{-E_{G=0}\} \leq (N, N-1)(-G_0)$$

$$= \frac{f_0 R}{R - G_0} - G_0\big[(-G_0)[N, N-1]_{K'}(-G_0)$$

$$+ [N, N-1]_K(-G_0)\big], \quad (20)$$

where the zeroth-order coefficient for the series expansion of $E_G$ (i.e., $f_0$ in the above expression) is defined by Eq. (13). Similarly, for a given odd number of derivatives of $E_G$ at $G = G_0$

$$\{-E_{G=0}\} \leq (N, N)(-G_0)$$

$$= \frac{f_0 R}{R - G_0} - G_0\big[(-G_0)[N, N]_{K'}(-G_0)$$

$$+ [N, N]_K(-G_0)\big]. \quad (21)$$

Since the right-hand sides of Eqs. (20) and (21) form a monotonic decreasing sequence with increasing $N$ (converging to $\{-E_{G=0}\}$), the best upper bound for both bounds above may be obtained for the value of $R$ given in Eq. (19), i.e., $R = R_{UB}$.

Equations (16), (19), (20), and (21) provide a set of rigorous bounds to $E_{G=0}$. These bounds may be directly used in an extrapolation calculation. The effectiveness of these bounds will be discussed later.

In some cases, as will be seen in the Results section, the bounds obtained by using Eqs. (16), (19), (20), and (21) may not be "tight," thus reducing their computational effectiveness. In the next section, we introduce a new set of tight estimates that become bounds in the asymptotic limit of large $N$ (i.e., when large number of Padé approximants are used).

## "TIGHTER" NONRIGOROUS ESTIMATES TO BOUNDS

It is interesting to note the behavior of $g_N(R)$, in Eq. (18), when the restriction on the range of $R$ in Eq. (17) is lifted. As shown in the discussion before Eq. (18), the derivative of $g_N(R)$ with respect to $R$ is always negative (for positive $G_0$) and hence $g_N(R)$ is monotonically decreasing for increasing $R \in [G_0, \infty)$. A typical case of the behavior of $g_N(R)$ with respect to $R$ is shown in Figure 1. Further, as $R \to \infty$, $g_N(R) \to [N+1, N+k](-G_0)$, the lower bound in Eq. (16). Hence, while $g_N(R)$ is an upper bound for smaller values of $R$ satisfying Eq. (17), it is a lower bound to $\{-E_{G=0}\}$ as $R \to \infty$.

Now consider the behavior of $g_N(R)$, for fixed $R$, as $N \to \infty$. Clearly as $N \to \infty$, $[N, N+k](-G_0) \to [N+1, N+k](-G_0)$ and hence $g_N(R = G_0) \to [N+1, N+k](-G_0)$, the lower bound in Eq. (16). Therefore, as $N \to \infty$, both the upper and lower bounds
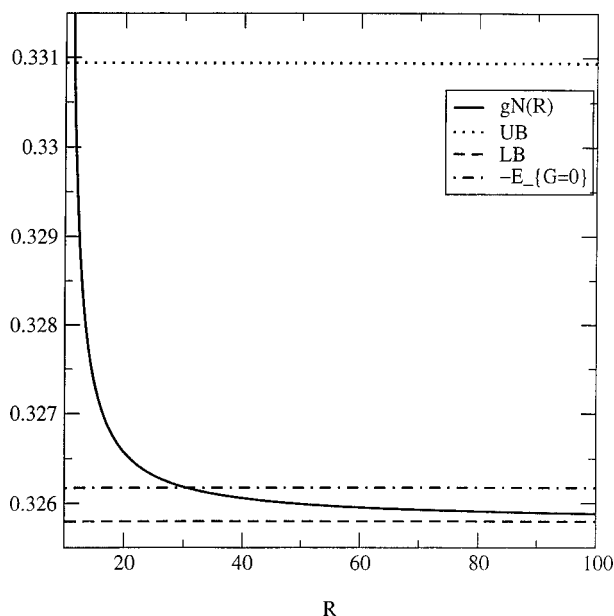
**FIGURE 1.** Behavior of $g_N(R)$ as a function of $R$. Case shown is for $N_2$, artificial gap shift = 10.0 a.u., and number of Padé approximants, $N = 3$. The quantity $\{-E_{G=0}\}$ represents the negative correlation energy as in the text. UB is the upper bound to $\{-E_{G=0}\}$ from Eqs. (16) and (19) and LB is the lower bound to $\{-E_{G=0}\}$ from Eq. (16).

given by Eq. (16) converge to the same value, which should be $\{-E_{G=0}\}$, since we know from the discussion following Eq. (6) that the lower bound in Eq. (16) converges monotonically to $\{-E_{G=0}\}$ with increasing $N$. Therefore, we conclude that $g_N(R)$ (for all $R \in [G_0, \infty)$) converges to $\{-E_{G=0}\}$ as $N \to \infty$. While this convergence is monotonic for values of $R \to \infty$, the convergence may or may not be monotonic for small [given by Eq. (17)] and intermediate values of $R$. In the rest of this section we evaluate the possibility of using intermediate values of $R \in [G_0, \infty)$ to obtain "tighter" estimates to bounds.

From the above discussion, it follows that if there exists an $R_{\min} \geq R_{UB}$ [see Eq. (19) for definition of $R_{UB}$] such that $g_N(R_{\min})$ is monotonically decreasing with increasing $N$, then $g_N(R_{\min})$ is an upper bound to $\{-E_{G=0}\}$ [since as $N \to \infty$, $g_N(R) \to \{-E_{G=0}\}$, for all $R$]. Further, $g_N(R_{\min})$ is at least as tight an upper bound as the one obtained from Eqs. (16) and (19) [i.e., $g_N(R_{UB})$], since $g_N(R)$ is a monotonically decreasing function of $R$. Similarly, it is clear that if there exists an $R_{\max} \geq R_{\min} \geq R_{UB}$, such that $g_N(R_{\max})$ is monotonically increasing with increasing $N$, then $g_N(R_{\max})$ is a lower bound to $\{-E_{G=0}\}$.

Again, from the above discussion, we may conclude that $g_N(R_{\min})$ and $g_N(R_{\max})$ converge to $\{-E_{G=0}\}$ as $N \to \infty$. It may also be noted that if $R_{\min}$ and $R_{\max}$ exist, then an intermediate value may be used to provide an approximation for $\{-E_{G=0}\}$ with very clear error estimates. Further, the convergence of a sequence of such approximations to $\{-E_{G=0}\}$ may be accelerated by use of a method similar to Aitkin's $\Delta^2$ method [15] or the Shanks' extrapolation method [33].

Our aim here is to devise an algorithm to obtain approximations to the largest $R_{\min}$ and smallest $R_{\max}$ (that satisfy the above monotonicity criteria). Given $2N$ derivatives of the function, we may obtain the set $\{g_1(R), g_2(R), \ldots, g_{N-1}(R)\}$ for any $R$. To obtain an approximation to the largest $R_{\min}$, one may start with $R = R_{UB}$ and check the monotonicity of the sequence $g_i(R)$ for $i = 1, \ldots, N-1$. If the sequence is not monotonic decreasing, $R_{\min}$ does not exist in the region $R \geq R_{UB}$ and $g_N(R_{UB})$ provides the best upper bound to $\{-E_{G=0}\}$. But, if the sequence is monotonic decreasing, the value of $R$ is raised till the maximum value of $R$ is found for which the set of $g_i(R)$ are still monotonic decreasing for $i = 1, \ldots, N-1$. (The precise algorithm may be similar in form to the ones used to find the maximum/minimum values of a function [11].) This yields an *approximation* to $R_{\min}$ (within the $2N$ derivatives used). To obtain a corresponding estimate for the upper bound, one may use any $g_i(R_{\min})$ for $i = 1, \ldots, N-1$. In the results provided, we have chosen to use $g_{N-2}(R_{\min})$ for this purpose.

From our discussion earlier in this section, it is clear that any $g_i(R_{\min})$ is a rigorous upper bound to $\{-E_{G=0}\}$ if and only if, $g_i(R_{\min})$ is monotonic decreasing with increasing $i$, *for all i*. But, in the present algorithm we consider only a finite $N$, and hence the $g_i(R_{\min})$ obtained from here is *not a rigorous upper bound* to $\{-E_{G=0}\}$. It is only the best approximation within the number of derivatives provided ($2N$ in this case). However, this approximation may be expected to provide accurate bounds when a larger number of derivatives are included. This aspect is considered in the results section. An approximation to $R_{\max}$ and $g_N(R_{\max})$ may be obtained in a similar fashion.

As is evident from the above discussion, there are two conditions that may affect the results when the above algorithm is used. The first condition is the existence of $R_{\min}$ and $R_{\max}$. It is easily shown that $R_{\max}$ exists since, as seen above, the lower bound in Eq. (16) is monotonic increasing with respect to $N$. The existence of $R_{\min}$ can also be proved if the

upper bound, $g_N(R_{UB})$, converges monotonically to $\{-E_{G=0}\}$. But if this condition is not satisfied, $R_{min}$ may still exist, but $R_{min} < R_{UB}$, and is not practically relevant since it will not provide a better upper bound than $g_N(R_{UB})$. In any case, if $R_{min}$ exists, it will be found when the algorithm presented in the previous paragraph is implemented.

Secondly, as discussed above, the choice of a finite $N$ affects the rigorousness of the estimates obtained from the algorithm, for use as bounds. But, including additional higher order derivatives may result in these estimates providing good approximations to bounds.

To briefly summarize, we look for approximations to $R_{min}$ and $R_{max}$ such that $g_i(R_{min})$ is monotonically decreasing with increasing $i$ and $g_i(R_{max})$ is monotonically increasing with increasing $i$, for all $i$. Since, $g_i(R)$ for all $R$ converges to $\{-E_{G=0}\}$ as $i \to \infty$, $g_i(R_{min})$ and $g_i(R_{max})$ form upper and lower bounds to $\{-E_{G=0}\}$. In order to implement this concept, we construct approximations to $R_{min}$ and $R_{max}$ based on a finite number of derivatives. Clearly, for a small number of derivatives the approximation to $R_{min}$ and $R_{max}$ may be poor, and this would lead only to estimates and not rigorous bounds. However, as the number of derivatives included increases, these estimates may be expected to become rigorous bounds.

Another set of (empirical) bounds may be obtained by considering the arithmetic, geometric, and harmonic means of the upper and lower bounds in Eqs. (16), (19), (20), and (21). These bounds will be discussed in greater detail in the results section.

## Results

To test the effectiveness of the rigorous bounds [i.e., bounds given by Eqs. (16), (19), (20), and (21)] and estimates (i.e., as introduced in the discussion of tighter nonrigorous estimates), we perform gap-shifted MP2 correlation energy calculations [6] for a subset of molecules in the G2 set [34].

The canonical MP2 correlation energy for closed-shell systems has the form

$$E_{MP2} = -\sum_{ij}^{O}\sum_{ab}^{V} \frac{(ia|jb)[2(ia|jb) - (ib|ja)]}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (22)$$

where, as usual, $i$ and $j$ denote occupied ($O$) molecular orbitals, $a$ and $b$ denote virtual ($V$) molecular orbitals and $\epsilon$ denotes the corresponding Fock eigenvalue. If, now, the virtual orbitals are shifted by the amount $G$ (i.e., if we introduce an artificial gap shift), then the gap shifted MP2 correlation energy for closed-shell systems may be written as

$$E_{MP2}^{G} = -\sum_{ij}^{O}\sum_{ab}^{V} \frac{(ia|jb)[2(ia|jb) - (ib|ja)]}{\Delta_{ijab} + G}, \quad (23)$$

where $\Delta_{ijab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$. We note that Eq. (23) has the exact same form as chosen in Ref. [6] for *uniform shift of the virtual orbital energies*. Clearly Eq. (23), as a function of $G$, is a series of Stieltjes since it has a form similar to Eq. (11). (It may also be noted here that the *nonuniform shift of virtual energy levels* introduced in Ref. [6] is also a series of Stieltjes.) Hence, we may use the value of $E_{MP2}^{G}$ at arbitrary (large and positive) gap, $G$, along with derivatives of $E_{MP2}^{G}$ with respect to $G$ (obtained analytically) to produce bounds to the correct MP2 correlation energy [i.e., $E_{MP2}^{G}$ at $G = 0$, as in Eq. (22)] using the expressions introduced in the previous section. (A brief account of how the Padé approximants may be determined is presented in Appendix B.) The effectiveness of these bounds may then be evaluated by comparison with the actual MP2 correlation energy, which is easily calculated. Our implementation of the upper and lower bounds and the estimates to MP2 correlation energy is based on a development version of the Gaussian [35] suite of programs.

As noted above, we could have used expressions from a number of quantum chemical methods to test the bounds obtained here. We, however, chose to study the MP2 energy due to its appealing simplicity and the fact that many reliable models in chemistry are based on MP2. Moreover, as noted in the introductory section, the MP2 correlation energy has been the subject of a number of recent studies [1–6].

It is interesting to consider the practicality of calculating the gap-shifted MP2 correlation energy from Eq. (23). The direct calculation of Eq. (23) for any value of $G$ requires the same amount of CPU time. However, if we invoke the idea of Laplace transforms, we may write

$$\frac{(ia|jb)[2(ia|jb) - (ib|ja)]}{\Delta_{ijab} + G}$$
$$= \int_{0}^{\infty} \{(ia|jb)[2(ia|jb) - (ib|ja)]\}$$
$$\times \exp[-t(\Delta_{ijab} + G)] dt, \quad (24)$$

and when the exponential damping factor (which is now a function of the artificial gap, $G$) is absorbed into the occupied and virtual molecular orbitals, we

obtain damped molecular orbitals (MOs) that decay exponentially just as seen in Refs. [7] and [5]. However, in this case each MO is damped to an even greater extent due to the artificial gap, $G$. Following the arguments of Ref. [5], it may then be proved that the CPU time required to evaluate the expression in Eq. (24) reduces as the value of $G$ increases. The same set of arguments hold for the derivatives of $E_{MP2}^G$, with respect to $G$. In this study, however, we obtain the value of $E_{MP2}^G$ and its derivatives directly by using Eq. (23). This is done so we could exactly evaluate the effectiveness of the bounds obtained in the theory section.

Although a number of molecules and a great variety of different values of $G$ [the artificial gap in Eq. (23)] were considered in our study, for the sake of brevity, we present results here only for four molecules, $N_2$, $F_2$, $O_3$, and ClO, and two different values of $G$, namely, 10.0 and 2.0 a.u. The results for the rigorous bounds may be found in Tables I and II, whereas the results for the nonrigorous bounds estimates may be found in Tables III and IV. In each

case the basis set chosen is 6-31G*. It may be noted here that while the bounds provided in Eqs. (16), (19), (20), and (21) are for $\{-E_{G=0}\}$ (i.e., the negative of the correlation energy), the bounds provided in the tables are for $E_{G=0}$, i.e., the actual MP2 correlation energy itself.

It was found that both upper and lower rigorous bounds to $E_{G=0}$ [obtained using Eqs. (16), (19), (20), and (21)] became increasingly tight with the inclusion of higher order Padé approximants (as seen in Tables I and II). But in all cases, the upper bound to $E_{G=0}$ was always tighter than the lower bound to $E_{G=0}$. Hence, arithmetic, geometric, and harmonic means of the upper and lower bounds were found to be lower bounds. In Tables III and IV, however, we present only the harmonic means. Since the magnitudes of the geometric and arithmetic means of any two numbers is always greater than (or equal to) the magnitude of the harmonic mean, the quality of the geometric and arithmetic mean as lower bounds is never better than the lower bounds produced by the harmonic mean. Further, it was also

**TABLE I**

**Relative errors for the rigorous upper bound (UB) and the rigorous lower bound (LB) with respect to the exact MP2 correlation energy (Exact) at gap shift = 10.0 a.u. and a 6-31G* basis set.[a]**

| | $N_2$ | | $F_2$ | | $O_3$ | | ClO | |
|---|---|---|---|---|---|---|---|---|
| Exact ($E_h$) | −0.326173 | | −0.365996 | | −0.638686 | | −0.286574 | |
| $N$[b] | UB | LB | UB | LB | UB | LB | UB | LB |
| 3 | +1.680 | −21.756 | +1.163 | −10.799 | +6.775 | −73.937 | +0.986 | −16.034 |
| | | −8.128 | | −12.470 | | −120.773 | | −25.582 |
| 4 | +0.375 | −4.766 | +0.201 | −3.550 | +2.186 | −32.220 | +0.276 | −2.815 |
| | | −1.917 | | −3.286 | | −45.757 | | −8.288 |
| 5 | +0.054 | −1.003 | +0.042 | −0.373 | +0.796 | −7.148 | +0.068 | −0.721 |
| | | −0.409 | | −0.736 | | −14.972 | | −2.561 |
| 6 | +0.006 | −0.191 | +0.003 | −0.130 | +0.190 | −4.313 | +0.018 | −0.165 |
| | | −0.086 | | −0.167 | | −4.997 | | −0.765 |
| 7 | +0.001 | −0.017 | +0.000 | −0.011 | +0.045 | −1.089 | +0.004 | −0.040 |
| | | −0.018 | | −0.035 | | −1.574 | | −0.224 |
| 8 | +0.000 | −0.003 | +0.000 | −0.000 | +0.014 | −0.171 | +0.000 | −0.012 |
| | | −0.003 | | −0.008 | | −0.505 | | −0.063 |
| 9 | +0.000 | −0.000 | +0.000 | −0.000 | +0.003 | −0.069 | +0.000 | −0.002 |
| | | −0.000 | | −0.002 | | −0.160 | | −0.018 |

[a] The relative error (in millihartrees) for the upper bound (UB) is obtained by subtracting the upper bound to $E_{G=0}$ in Eq. (16) and the exact MP2 correlation energy. The relative error (in millihartrees) for the lower bounds are obtained by subtracting the exact MP2 correlation energy from the lower bound to $E_{G=0}$ in Eqs. (16) and (19) (upper entry) and Eq. (20) (lower entry).

[b] Reflects maximum order of Padé used, as outlined in text.

**TABLE II**

**Relative errors for the rigorous upper bound (UB) and the rigorous lower bound (LB) with respect to the exact MP2 correlation energy (Exact) at gap shift = 2.0 a.u. and a 6-31G\* basis set.[a]**

| | $N_2$ | | $F_2$ | | $O_3$ | | ClO | |
|---|---|---|---|---|---|---|---|---|
| Exact ($E_h$) | −0.326173 | | −0.365996 | | −0.638686 | | −0.286574 | |
| $N$[b] | UB | LB | UB | LB | UB | LB | UB | LB |
| 3 | +0.0082 | −0.0624 | +0.0036 | −0.0362 | +0.1159 | −0.9213 | +0.0077 | −0.0525 |
| | | −0.0359 | | −0.0508 | | −1.4578 | | −0.1634 |
| 4 | +0.0002 | −0.0018 | +0.0001 | −0.0006 | +0.0104 | −0.0641 | +0.0003 | −0.0029 |
| | | −0.0016 | | −0.0024 | | −0.1514 | | −0.0114 |
| 5 | +0.0000 | −0.0000 | +0.0000 | −0.0000 | +0.0006 | −0.0048 | +0.0000 | −0.0001 |
| | | −0.0000 | | −0.0001 | | −0.0139 | | −0.0007 |

[a] The relative error (in millihartrees) for the upper bound (UB) is obtained by subtracting the upper bound to $E_{G=0}$ in Eq. (16) and the exact MP2 correlation energy. The relative error (in millihartrees) for the lower bounds are obtained by subtracting the exact MP2 correlation energy from the lower bound to $E_{G=0}$ in Eqs. (16) and (19) (upper entry) and Eq. (20) (lower entry).
[b] Reflects maximum order of Padé used, as outlined in text.

**TABLE III**

**Relative errors for the bound estimates to the MP2 correlation energy at gap shift = 10.0 a.u. and a 6-31G\* basis set.**

| | $N_2$ | | $F_2$ | | $O_3$ | | ClO | |
|---|---|---|---|---|---|---|---|---|
| Exact ($E_h$) | −0.326173 | | −0.365996 | | −0.638686 | | −0.286574 | |
| $N$[a] | UB[b] | LB[c] | UB[b] | LB[c] | UB[b] | LB[c] | UB[b] | LB[c] |
| 3 | | −1.064 | | −0.073 | | −1.309 | | −0.153 |
| | | −9.629 | | −4.721 | | −31.158 | | −7.278 |
| 4 | +0.009 | −1.064 | −0.072 | −0.238 | +1.309 | −1.223 | +0.119 | −0.153 |
| | | −2.174 | | −1.665 | | −14.564 | | −1.261 |
| 5 | +0.009 | −0.226 | +0.022 | −0.238 | +0.378 | −1.224 | +0.119 | −0.002 |
| | | −0.473 | | −0.165 | | −3.152 | | −0.325 |
| 6 | −0.004 | −0.069 | +0.022 | −0.014 | +0.378 | −0.603 | +0.028 | −0.002 |
| | | −0.092 | | −0.063 | | −2.054 | | −0.073 |
| 7 | +0.000 | −0.016 | +0.000 | −0.014 | −0.004 | −0.603 | +0.008 | −0.000 |
| | | −0.008 | | −0.005 | | −0.522 | | −0.018 |
| 8 | +0.000 | −0.001 | +0.000 | −0.001 | +0.008 | −0.155 | +0.002 | −0.000 |
| | | −0.001 | | −0.000 | | −0.078 | | −0.005 |
| 9 | +0.000 | −0.000 | +0.000 | −0.000 | +0.008 | −0.019 | +0.000 | −0.000 |
| | | −0.000 | | −0.000 | | −0.033 | | −0.001 |

[a] Reflects maximum order of Padé used, as outlined in text.
[b] $g_N(R_{max})$ minus exact in millihartrees (see text for details).
[c] $g_N(R_{min})$ minus exact in millihartrees (upper entry). Harmonic mean of the upper and lower bounds from Eqs. (16) and (19) (lower entry).

**TABLE IV**

Relative errors for the bound estimates to the MP2 correlation energy at gap shift = 2.0 a.u. and a 6-31G* basis set.

| | N$_2$ | | F$_2$ | | O$_3$ | | ClO | |
|---|---|---|---|---|---|---|---|---|
| Exact ($E_h$) | −0.326173 | | −0.365996 | | −0.638686 | | −0.286574 | |
| $N$[a] | UB[b] | LB[c] | UB[b] | LB[c] | UB[b] | LB[c] | UB[b] | LB[c] |
| 3 | | +0.0021 −0.0271 | | −0.0006 −0.0163 | | +0.0167 −0.4022 | | +0.0018 −0.0024 |
| 4 | +0.0021 | −0.0000 −0.0007 | +0.0006 | −0.0000 −0.0002 | +0.0168 | −0.0023 −0.0268 | +0.0019 | −0.0000 −0.0012 |
| 5 | +0.0000 | −0.0000 −0.0000 | +0.0000 | −0.0000 −0.0000 | +0.0033 | −0.0001 −0.0021 | +0.0000 | −0.0000 −0.0000 |

[a] Reflects maximum order of Padé used, as outlined in text.
[b] $g_N(R_{max})$ minus exact in millihartrees (see text for details).
[c] $g_N(R_{min})$ minus exact in millihartrees (upper entry). Harmonic mean of the upper and lower bounds from Eqs. (16) and (19).

seen that in most cases Eqs. (16) and (19) provided better lower bounds to $E_{G=0}$ (and hence better upper bounds to $\{-E_{G=0}\}$) than Eqs. (20) and (21). But, in all cases both bounds were close to each other, and hence we have maintained results for both in our tables. The results for the harmonic mean of the lower bound to $E_{G=0}$ in Eqs. (20) and (21) with the upper bound to $E_{G=0}$ in Eq. (16) are not provided here since the quality of these as lower bounds were similar to those obtained from the harmonic mean of the upper and lower bounds in Eqs. (16) and (19) (which are provided in Tables III and IV as stated above).

The nonrigorous bounds estimates introduced above provided tight estimates in most cases. The bounds estimates obtained by this method could be thought of as a weighted average of the rigorous upper and lower bound, the weights based on the criteria provided in the previous section. (This may be contrasted with the "fixed-weight" averages provided by the arithmetic, geometric, and harmonic means discussed above.) In a few cases, however, the estimates did not bracket the correct MP2 correlation energy (i.e., the estimates were not bounds to the correct MP2 correlation energy in these cases). This occurred only for the lower order Padé approximants, as indicated above. For higher order approximants, the estimates got tighter and became bounds. In fact, for the molecules studied it was possible to obtain estimates within a microhartree (∼0.0006 kcal/mol) from the correct MP2 correla-

tion energy, with less than 10 Padé approximants, even when the gap was 10 a.u. (Of course, as stated in the theory section, it may be possible to further improve this accuracy by employing convergence accelerators such as the Aitkin's $\Delta^2$ method [15] or the Shanks' extrapolation method [33]. We, however, have not considered this in our current study.)

A trend commonly observed for both the rigorous bounds and the estimates was that as the size of the artificial gap was increased the accuracy at a given order of Padé approximants decreased. Our study at gap equal to 20 a.u. (not shown here) showed that a greater number of Padé approximants (greater than 10) were required for accuracy beyond the millihartree (∼0.6 kcal/mol) level while using both the rigorous bounds and the estimates. (The estimates were always closer to the correct answer.) As expected, this illustrates the fact that it is more difficult to extrapolate from farther out.

## Conclusions

In this study we have introduced upper and lower bounds to the extrapolated correlation energy using the concepts of a series of Stieltjes and Padé approximants. The bounds introduced here are general and apply to all expressions that can be written as a series of Stieltjes. Such expressions include energy expressions arising from the Møller–Plesset perturbation theory up to various levels of approxi-

mations, perturbative corrections to coupled-cluster approximations, energy expressions obtained from the Görling–Levy perturbation theory in density functional theory, and other expressions of relevance in quantum chemistry.

The bounds were tested by performing calculations for the gap-shifted MP2 correlation energy for a subset of molecules from the G2 set. Various values for the gap shift were studied and the results analyzed. It was found that at all gap shifts, rigorous bounds to the correct MP2 correlation energy were obtained using the methods described here. In the case of smaller gap shifts, the bounds were found to be extremely tight. In fact, bounds "tighter" than 1 kcal/mol were regularly obtained even when a relatively small number of Padé approximants and large gap shifts were employed. This is particularly interesting because calculations for larger HOMO–LUMO gaps may be performed with greater computational ease than those for smaller gap systems. Hence, the extrapolation technique, with suitable error bounds, may be useful in developing a powerful method for the evaluation of MP2 correlation energy.

A novel, interesting algorithm was developed to produce accurate estimates. These estimates become rigorous bounds as the number of Padé approximants employed increases. For relatively small number of Padé approximants, this method provided tight estimates, accurate to beyond a fraction of 1 kcal/mol, even when large gap shifts were employed.

We believe that the methods introduced in this study will be very useful in performing extrapolation on all functions that may be written as a series of Stieltjes. In density functional theory we expect this extrapolation method to be useful in the derivation of new functionals based on gap-shifted uniform electron gas [36, 37]. Another interesting area where fruitful applications may be expected is the recently developed adiabatic connection [38–41] in density functional theory.

## Appendix A: Computational Determination of a Series of Stieltjes

A computationally convenient, but equivalent [15], method to test if a function is a series of Stieltjes is by the calculation of the determinants obtained by using the coefficients of the series ex-

pansion, i.e.,

$$D(m,n) = \begin{vmatrix} f_m & f_{m+1} & \cdots & f_{m+n} \\ f_{m+1} & f_{m+2} & \cdots & f_{m+n+1} \\ \vdots & \vdots & & \vdots \\ f_{m+n} & f_{m+n+1} & \cdots & f_{m+2n} \end{vmatrix}. \quad (A1)$$

It has been shown [15, 16] that $f(z)$ is a series of Stieltjes if and only if $D(m,n) > 0$, for all $m, n \geq 0$, provided the series expansion, $f(z) = \sum_{j=0}^{\infty} f_j(-z)^j$, is unique.

During the MP2 calculations performed in this study, the determinant in Eq. (A1) was evaluated from the coefficients of the Taylor expansion, i.e., those given by Eq. (13). It was found that all determinants were positive except the $D(0,1)$ determinant, which was always a very small negative number (with magnitude less that $10^{-6}$). This could be due to round-off errors caused by the solution to the stiff set of equations described in Appendix B. The magnitude of $D(0,1)$ (or any other such determinant that does not satisfy the above requirements) could limit the accuracy and effectiveness of the bounds introduced here. However, since the magnitude of such determinants are generally very small [as found here for $D(0,1)$], the effect on the bounds may be expected to be minimal.

## Appendix B: Brief Description of the Padé Approximants

Consider the function $h(x)$ represented by the truncated series expansion

$$h(x) \approx \sum_{i=0}^{L} c_i(x - x_0)^i, \quad (B1)$$

where the coefficients $\{c_i\}$ may be obtained from the derivatives of $h(x)$ at the point $x_0$.

The $[N, M]$ Padé approximant to this function is defined as a rational polynomial, with numerator of order $M$ and denominator of order $N$, i.e.,

$$h(x) \approx \sum_{i=0}^{L} c_i(x - x_0)^i = \frac{\sum_{k=0}^{M} a_k(x - x_0)^k}{1 + \sum_{k=1}^{N} b_k(x - x_0)^k}$$

$$\equiv [N, M], \quad (B2)$$

where the zeroth-order coefficient in denominator of the approximant is assumed to be 1, for uniqueness [15]. Equation (B2) contains $M + N + 1$ unknowns $(a_0, \ldots, a_M, b_1, \ldots, b_N)$ and to solve for these we need $M+N+1$ equations, which may be obtained by choosing $L = M + N$ [i.e., $M + N + 1$ coefficients,

$\{c_i\}$, which may be found using the value of the function and its first $(M + N)$ derivatives at the point $x_0$]. This leads to the set of equations

$$a_i = c_i + \sum_{k=1}^{\min(N,i)} c_{i-k} b_k, \qquad i \leq M, \qquad \text{(B3)}$$

$$-c_{M+i} = \sum_{k=1}^{\min(N,M+i)} b_k c_{M+i-k}. \qquad \text{(B4)}$$

We may first obtain the set $\{b_i\}$ from Eq. (B4), which constitutes an $Ax = B$ type linear system of equations, but it is found [11] that the matrix $A$ in this case is almost singular. Hence, we follow Ref. [11] to first perform a full LU decomposition [11, 42] of $A$ followed by iterative improvement of the solution obtained [11, 42]. Once the $\{b_i\}$ are obtained, $\{a_i\}$ may be found by using Eq. (B3).

Once the coefficients of the Padé approximants, $\{a_i\}$ and $\{b_i\}$, are obtained as outlined above, it may noted that

$$h(x) = \frac{\sum_{k=0}^{M} a_k (x - x_0)^k}{1 + \sum_{k=1}^{N} b_k (x - x_0)^k} + O\big((x - x_0)^{M+N+1}\big). \qquad \text{(B5)}$$

Hence, the Padé approximant of order $[N, M]$ agrees with the corresponding series expansion of the function up to order $(N + M)$.

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