IS FIFTH-ORDER MBPT ENOUGH? [*]

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Fifth- and higher-order MBPT results are reported for a series of examples, BH, Be_2, HF and H_2O, for which higher-order perturbation theory might be important. MBPT(5) differs from MBPT(4) by as much as 4.3 mh, and by constructing the size-extensive [2,1] Padé approximant, which is possible with $E^{(5)}$, one can get exceptional agreement with the full CI results. Variational perturbation results are also reported.

1. Introduction

With the development of many-body perturbation theory (MBPT) [1–6] and coupled-cluster (CC) methods [2,6,7] for accurate ab initio quantum mechanical applications [2], great interest focused on the role of higher excitations in correlated wavefunctions. The proper treatment of such excitations in MBPT/CC is responsible for the absence of unlinked diagrams and the consequent size-extensive nature of MBPT/CC methods. Besides the size-extension property, MBPT/CC theory has other computational advantages that emerge due to the separation of the connected and disconnected parts of the problem and the evaluation of diagrams directly from molecular integrals [6].

The emphasis on higher-excitation contributions stimulated by MBPT/CC methods has spurred much improved procedures based upon the graphical unitary group approach [8] for direct configuration interaction (CI) calculations. These procedures are highly efficient at handling higher-excitation effects in CI via multi-reference expansions [9] compared to the previous generation of CI calculations, which, of necessity, were usually limited to single-reference single and double excitations (CISD) [10]. Now, a series of "model" full CI calculations (i.e. including all possible excitations for the problems) have been reported as benchmarks for various correlated methods [11–13].

The current state-of-the-art in MBPT is complete fourth-order calculations, which consist of all single, double, triple, and quadruple excitation contributions through that order [14]. This requires evaluating 39 diagrams in the SCF reference case, as counted in terms of the antisymmetrized form used by Bartlett [2], while fifth-order MBPT would require evaluating 840 such diagrams. The latter would appear to be impractical in a straight-forward way. However, CC theory is an infinite-order generalization of MBPT that sums categories of MBPT diagrams to all orders, but not necessarily *all* MBPT diagrams for a given order, and it may be used to evaluate classes of such higher-order diagrams.

In the coupled-cluster doubles (CCD) model, the excitation operator T is truncated to double excitation effects only, i.e. the wavefunction is $\exp(T_2)|\phi_0\rangle$, and introduces effects of doubles, disconnected quadruples, hextuples, octuples, etc. in all orders [6]. In the SCF case, the CCD result includes second- and third-order MBPT and fourth-order doubles and quadruples, as well as some higher-order MBPT contributions. CCSD [15] adds singles in fourth order and classes of triples (e.g. $T_1 T_2$ and $T_1^3/3!$) and higher-order contributions (e.g. $T_1 T_2^2/2$). The addition of T_3 into CC theory has been partially achieved in the CCSDT-1 model [16,17]. This model is correct through the complete fourth-order energy, MBPT(4), and the full second-order MBPT wavefunction, while augmenting CCSD with additional higher-order terms that arise from T_3. Most of the 840 diagrams in fifth-order MBPT are included

in this model, but not all. In particular, the diagrams that arise from T_4 (i.e. "true" rather than disconnected quadruples, $T_2^2/2$) are excluded.

To develop an idea of the value of higher-order MBPT energy contributions, while avoiding the evaluation of the diagrams via CC theory or directly with MBPT formulae, it is convenient to take advantage of configuration language and resort to straightforward Rayleigh–Schrödinger perturbation theory (RSPT) based on CI to obtain these terms. Although this appraoch is a much slower computational procedure than MBPT or CC, it is very easy to evaluate terms this way for relatively small examples.

It is well known that the CI energy can be obtained by a recursive perturbation theory solution of the CI problem [18–20]. It is also well known that there are no unlinked diagrams in each order of RSPT, due to their mutual cancellation, provided that *all* possible CI excitations that can contribute to that order are included [6]. Consequently, in the following we use configuration language to obtain high-order MBPT contributions for several examples for which the full CI result is available [12,13]. In addition, we report variational perturbation theory bounds and Padé approximant extrapolations based upon these higher-order perturbation energies [18,19].

2. Theory

Assuming the separation $H = H_0 + V$, the recursive formulae of RSPT in intermediate normalization are

$$\phi^{(n)} = R_0(V - E^{(1)})\phi^{(n-1)} - \sum_{l=1}^{n-2} R_0 E^{(n-l)}\phi^{(l)} , \quad (1)$$

$$E^{(n+1)} = \langle\phi_0|V|\phi^{(n)}\rangle , \quad (2)$$

where the RS resolvent is

$$R_0 = Q(E_0 - H_0)^{-1}Q , \quad (3)$$

with Q the projector for the orthogonal complement to the reference function. In a finite space spanned by a set of orthonormal functions $|f\rangle$, characterized by the projector $O_f = |f\rangle\langle f|$, $Q = O_f - |\phi_0\rangle\langle\phi_0| = |h\rangle\langle h|$, we have the inner-projected form of R_0 [20],

$$R_0 = |h\rangle\langle h|E_0 - H_0|h\rangle^{-1}\langle h| = |h\rangle \mathbf{R}_0\langle h| , \quad (4)$$

which defines the RSPT quantities within the finite space,

$$\boldsymbol{\alpha}^{(n)} = \mathbf{R}_0\left(\langle h|V - E^{(1)}|h\rangle\boldsymbol{\alpha}^{(n-1)}\right.$$
$$\left. - \sum_{l=1}^{n-2} E^{(n-l)}\boldsymbol{\alpha}^{(l)}\right), \quad n \geqslant 2 , \quad (5)$$

$$\boldsymbol{\alpha}^{(1)} = \mathbf{R}_0\langle h|V|\phi_0\rangle = \mathbf{R}_0\boldsymbol{\alpha}^{(0)} , \quad (6)$$

$$E^{(2n+1)} = \boldsymbol{\alpha}^{(0)\dagger}\mathbf{V}\boldsymbol{\alpha}^{(2n)} = \boldsymbol{\alpha}^{(n)\dagger}\mathbf{V}\boldsymbol{\alpha}^{(n)}$$
$$- \sum_{k=1}^{n}\sum_{l=1}^{n} E^{(2n+1-k-l)}\boldsymbol{\alpha}^{(k)\dagger}\boldsymbol{\alpha}^{(l)} , \quad (7a)$$

$$E^{(2n)} = \boldsymbol{\alpha}^{(0)\dagger}\mathbf{V}\boldsymbol{\alpha}^{(2n-1)} = \boldsymbol{\alpha}^{(n)\dagger}\mathbf{V}\boldsymbol{\alpha}^{(n-1)}$$
$$- \sum_{k=1}^{n}\sum_{l=1}^{n-1} E^{(2n-k-l)}\boldsymbol{\alpha}^{(k)\dagger}\boldsymbol{\alpha}^{(l)} . \quad (7b)$$

In the CI case, the set of functions $|h\rangle$ are chosen to be the usual N-particle determinants or symmetry adapted configurations. If the functions $|h\rangle$ are eigenfunctions of H_0, then the $\mathbf{R}_0$ matrix is diagonal. The number of configuration functions $|h\rangle$ is approximately proportional to n^l, where n is the number of basis functions and l is the level of excitation. Consequently, the matrix $\langle h|V|h\rangle = \langle h|H - H_0|h\rangle$ has a number of elements approximately proportional to n^{2l}, and the limiting factor in a recursive calculation of RSPT to high order is the number of multiplications, which is proportional to n^{3l} per iteration. Obviously symmetry and intelligent evaluation schemes exploiting sparse matrix operations reduces this asymptotic dependence greatly, but this is still a much slower process than the direct evaluation of MBPT diagrams. For example, fourth-order perturbation theory requires consideration of quadruple excitations, $l = 4$, which could be close to an n^{12} process in a configuration based scheme, while the direct evaluation of MBPT(4) is only n^6 for quadruple excitations and n^7 for triple excitations. However, in higher order the proliferation of diagrams adds other formidable complications in MBPT, while higher orders may be easily, if more slowly, computed from eqs. (5)–(7) provided the large dimension of $\mathbf{V}$ is manageable.

In addition to the linear sum of perturbed energies, we want to consider two other possibilities: variational upper bounds and Padé approximant non-linear summations [18,19]. The former are obtained by considering the trial wavefunction

$$\Psi = \phi_0 + \sum_k \lambda_k \phi^{(k)} . \tag{8}$$

Inserting this into a Rayleigh–Ritz upper bound formula, we have the secular equation [20],

$$(\mathbf{H} - E\mathbf{S}) = \mathbf{0} , \tag{9}$$

$$H_{mn} = \sum_{k=0}^{m} \sum_{l=0}^{n} (E^{(m+n+1-k-l)} - E^{(m+n-k-l)})$$
$$\times \langle \phi^{(k)} | \phi^{(l)} \rangle$$
$$+ \sum_{k=0}^{m} E^{(m-k)} \langle \phi^{(k)} | \phi^{(n)} \rangle$$
$$+ \sum_{k=0}^{n} E^{(n-k)} \langle \phi^{(k)} | \phi^{(m)} \rangle , \tag{10}$$

$$S_{mn} = \langle \phi^{(m)} | \phi^{(n)} \rangle = \boldsymbol{\alpha}^{(m)\dagger} \boldsymbol{\alpha}^{(n)} . \tag{11}$$

Diagonalization provides upper bounds, termed VPCI, which converge to the CI eigenvalue. Such perturbation–variation methods, some built upon Brillouin–Wigner instead of RS perturbation theory, form the basis for the large CI diagonalization scheme proposed by Bartlett and Brändas [15] and related methods suggested by others [21].

Another approach for extrapolating to the CI eigenvalue is to use some non-linear summation technique like Padé approximants [5,18,19]. Unlike VPCI, this does not require the various perturbation wavefunctions, $\boldsymbol{\alpha}^{(k)}$, but only the energies. The $[N,N-1]$ and $[N,N]$ Padé approximants are given by

$$[N,N-1] = \boldsymbol{a}^{\dagger} \mathbf{A}^{-1} \boldsymbol{a} , \tag{12}$$

$$[N,N] = E^{(2)} + \boldsymbol{b}^{\dagger} \mathbf{B}^{-1} \boldsymbol{b} , \tag{13}$$

$$\boldsymbol{a}^{\dagger} = (E^{(2)} E^{(3)} ... E^{(N+1)}), \tag{14}$$

$$\boldsymbol{b}^{\dagger} = (E^{(3)} E^{(4)} ... E^{(N+1)}) , \tag{15}$$

$$A_{pq} = E^{(p+q)} - E^{(p+q+1)} \quad (p, q = 1, 2, ...N) , \tag{16}$$

$$B_{pq} = E^{(p+q+1)} - E^{(p+q+2)} \quad (p, q = 1, 2, ...N) . \tag{17}$$

The calculation of the $[N,N-1]$ and $[N,N]$ Padé approximants requires perturbed energies of order $2N+1$ and $2N+2$, respectively. The N index in the Padé approximant notation is determined from the series for the correlation energy, where $E^{(2)}$ is considered the first term. The first approximant of each type $[1,0]$ and $[1,1]$ corresponds to the well-known "geometric" approximation based upon the $E^{(3)}/E^{(2)}$ and $E^{(4)}/E^{(3)}$ ratios, respectively. As shown by Bartlett and Brändas [15], the $[N,N-1]$ approximants are invariant to the reference energy, but more importantly, unlike the VPCI or any truncated CI results, the Padé extrapolation preserves the size-extensivity property. This property follows immediately from eqs. (12)–(17). Since the MBPT energies $E^{(n)}(M)$ for M separable identical units must be $ME^{(n)}$, we have $\boldsymbol{a}^{\dagger}(M) = M\boldsymbol{a}^{\dagger}(1)$, $\mathbf{A}(M) = M\mathbf{A}(1)$, and $\boldsymbol{a}^{\dagger}(M)\mathbf{A}(M)^{-1}\boldsymbol{a}(M) = M\boldsymbol{a}^{\dagger}(1)\mathbf{A}(1)^{-1}\boldsymbol{a}(1)$. Obviously, the $[N, N]$ approximant is also size-extensive by the same argument.

3. Boron hydride

As a first example of higher-order MBPT results we consider the BH molecule in a DZP basis, for which the full CI result has been reported [12]. This molecule is known since the first MBPT calculations [4] to be a poorly convergent case, and the fourth-order energy is still 3 kcal/mol away from the full CI value (table 1). Hence, fifth order is expected to be significant, and $E^{(5)}$ amounts to 2.5 mh, which is almost half of $E^{(4)}$, while $E^{(6)}$ is again about half of $E^{(5)}$. In fact, assuming a geometric series after $E^{(4)}$, with $r = 0.5$, would give $E_{corr} = -0.0886$ hartree, which is quite close to the full CI result. The perturbation sum through sixth order is within 1 kcal/mol of the full CI energy, while a variational upper bound (VPCI-2), which can be evaluated with energies through $E^{(5)}$ and the first- and second-order MBPT wavefunction, is also within 1 kcal/mol of the full CI. Since VPCI-2 is an upper bound to CISDTQ for any problem, it would be a very interesting result to have available for chemically interesting examples. However, the best convergence is provided by Padé approximants, for which the [2,1] approximant is also available once $E^{(5)}$ is known. Padé approximants also have the considerable advantage over the VPCI results in that the former are size-extensive [2]. The infinite-order

Table 1
MBPT, Padé approximants and VPCI results for boron hydride, R = 2.329 au, with DZP basis [12]

Order	MBPT			Padé approximants			VPCI	
	$E(N)$ [a]	E_{corr}	delta [b]		E_{corr}	delta	E_{corr}	delta
1	−25.125260	0.0	55.07					
2	−0.060297	0.060297	17.24					
3	−0.016482	−0.076779	6.89	[1,0]	−0.082980	22.10	−0.078677	5.70
4	−0.005924	−0.082703	3.18	[1,1]	−0.086027	1.10		
5	−0.002540	−0.085242	1.58	[2,1]	−0.087518	0.15	−0.086608	0.73
6	−0.001226	−0.086469	0.81	[2,2]	−0.087817	−0.03		
7	−0.000629	−0.087098	0.42	[3,2]	−0.087817	−0.03	−0.087651	0.07
8	−0.000330	−0.087429	0.21	[3,3]	−0.087817	−0.03		
9	−0.000173	−0.087601	0.10	[4,3]	−0.087734	0.02	−0.087748	0.01
10	−0.000088	−0.087690	0.05	[4,4]	−0.087768	0.00		
11	−0.000043	−0.087733	0.02	[5,4]	−0.087763	0.00	0.087762	0.00
12	−0.000020	−0.087753	0.01	[5,5]	−0.087764	0.00		
13	−0.000009	−0.087762	0.00	[6,5]	−0.087764	0.00	−0.087764	0.00
14	−0.000003	−0.087765	0.00	[6,6]	−0.087764	0.00		
15	−0.000001	−0.087766	0.00	[7,6]	−0.087764	0.00	−0.087764	0.00
16	0.000000	−0.087766	0.00	[7,7]	−0.087764	0.00		
17	0.000000	−0.087765	0.00	[8,7]	−0.087764	0.00	−0.087764	0.00
18	0.000000	−0.087765	0.00	[8,8]	−0.087764	0.00		
19	0.000000	−0.087764	0.00	[9,8]	−0.087764	0.00	−0.087764	0.00
20	0.000000	−0.087764	0.00	[9,9]	−0.087764	0.00		
CCSDT-1 [c]		−0.087322	0.28					
full CI		−0.087764	0.00					

[a] All results in au except for those under "delta" which are in kcal/mole.

[b] Delta is the correlation energy at this level minus the full CI value in kcal/mol.

[c] From ref. [17].

CCSDT-1 result is considerably better than MBPT(5), and much closer to the [2,1] approximant result.

4. Hydrogen fluoride

Unlike BH and Be_2, for which the perturbation series are slowly convergent, HF is usually thought to represent a rapidly convergent case. This is seen to be somewhat accidental once $E^{(5)}$ is obtained, since $E^{(4)}$ overshoots the full CI and $E^{(5)}$, which is positive, corrects in the opposite direction, and MBPT(5) is actually farther from the full CI than MBPT(4) (table 2). However, the [2,1] Padé approximant is once again quite close, while the VPCI-2 result is worse than the linear MBPT. Like BH, the MBPT(5) result is poorer than the [2,1] approximant value, which is not quite as accurate as the infinite-order CCSDT-1 energy. As

illustrated by the HF example, odd orders in MBPT should each be smaller than the preceding even-ordered term (except in divergent cases), because two new excitation levels are introduced in each even order. Also, if such higher excitations are comparatively important (which we would expect to be true for HF), $E^{(4)}$ will be greater in magnitude than $E^{(3)}$, and $E^{(6)}$ greater than $E^{(5)}$. $E^{(2n)}$ is usually negative, while $E^{(2n+1)}$ can be negative or positive.

5. Beryllium dimer

The potential energy curve for Be_2 is a very interesting case for assessing the importance of higher-order perturbation theory, since the molecule's ≈2 kcal/mol inner well at ≈2.5 Å is very sensitive to the delicate balance between the separated atom and dimer energies

Table 2

MBPT, Padé approximants and VPCI results for hydrogen fluoride at R = 1.732 au, with DZP basis [12]

Order	MBPT				Padé approximants		VPCI	
	$E(N)$ [a]	E_{corr}	delta [b]		E_{corr}	delta	E_{corr}	delta
1	−100.048009	0.0	125.3					
2	−0.192124	0.0192124	4.7					
3	−0.002032	−0.194157	3.5	[1,0]	−0.194178	3.4	−0.186352	8.4
4	0.005964	−0.200120	−0.3	[1,1]	−0.191074	5.4		
5	0.001385	−0.198736	0.6	[2,1]	−0.199142	0.3	−0.198314	0.9
CCSDT-1 [c]		0.199519	0.1					
full CI		−0.199675	0.0					

[a] All results in au except for those under "delta" which are in kcal/mole.

[b] Delta is the correlation energy at this level minus the full CI value in kcal/mole.

[c] From ref. [17].

Table 3

MBPT, Padé approximants and VPCI results in au for beryllium dimer at R = 5.25 au, with 7s3p1d basis [13]

Order	MBPT				Padé approximants E_{corr}	VPCI E_{corr}
	$E(N)$	E_{corr}	D_e [a]			
1	−29.138980	0.0				
2	−0.061081	−0.061081	0.29			
3	−0.020769	−0.081850	0.75	[1,0]	−0.092551	−0.081780
4	0.009118	−0.090968	0.86	[1,1]	0.098104	
5	−0.004283	−0.095252	0.79	[2,1]	−0.099165	−0.096024
6	−0.002107	−0.097359	0.72	[2,2]	−0.099574	
7	−0.000984	−0.098343	0.68	[3,2]	−0.099314	−0.098297
8	−0.000429	−0.098772	0.66	[3,3]	0.099139	
9	0.000156	−0.098927	0.66	[4,3]	−0.098814	−0.098773
10	−0.000034	−0.098962	0.66	[4,4]	−0.098844	
11	0.000013	−0.098949	0.66	[5,4]	−0.098842	−0.098844
12	0.000026	−0.098923	0.66	[5,5]	0.098844	
13	0.000025	−0.098898	0.66	[6,5]	−0.098888	−0.098853
14	0.000019	−0.098879	0.66	[6,6]	−0.098858	
15	0.000012	−0.098867	0.66	[7,6]	−0.098853	−0.098854
16	0.000007	−0.098859	0.65	[7,7]	−0.098854	
17	0.000004	−0;098855	0.65	[8,7]	−0.098854	−0.098854
18	0.000002	−0.098854	0.65	[8,8]	−0.098854	
19	0.000001	−0.098853	0.65	[9,8]	−0.098854	−0.098854
20	0.000000	−0.098853	0.65	[9,9]	−0.098854	
CCSDT-1 [b]		−0.09778	−0.02			
full CI [c]		0.098854	0.65			

[a] Dissociation energies are in kcal/mole and are computed as $E(R = 5.25$ au$) - 2E$(Be atom). Full CI energy of the Be atom is −14.618397 au.

[b] From ref. [16].

[c] All results including full CI include 6 Cartesian d functions. The 5 d-function full CI correlation energy from ref. [13] is −0.098817 h.

[13,16,22,23]. Treating Be_2 as a four-electron problem, MBPT(4) has recently been shown to be qualitatively correct in a large 7s3p1d basis set, but to exceed the full CI dissociation energy in the same basis [13], by ≈0.2 kcal/mol [16]. This preserves a trend, since even in MBPT(3) the well is ≈0.1 kcal/mol too deep. Hence the question arose whether MBPT(5) would correct this overestimate or increase the discrepancy. Fortunately, MBPT(5) does reverse the trend and reduces the MBPT(4) dissociation energy (table 3). However, even MBPT(6) still overshoots slightly, although the trend is toward the correct value for the dissociation energy. (Note that the current calculations use all six d-function compounts, while those of ref. [13] were limited to five.) Again the VPCI-2 result is a bit better than the fifth-order linear sum and the [2,1] Padé approximant would appear to be in excellent agreement with the full CI for the slightly larger basis. Like BH, also a four-electron problem, the perturbation series is almost exactly geometric between fourth order and ninth order. Assuming the sum beyond fourth order is geometric, with a term ratio of 0.5, the

correlation energy obtained would be −0.100 hartree, which is ≈1 mh from the exact result. As discussed elsewhere [16], this is an example for which CC methods fail to obtain the inner minimum, even though they are only 1.1 mh in error at that geometry, because CCSD (or CCSDT-1) is exact for the separated atoms, and and the well depth amounts to just 1.1 mh.

6. Water

A third example for which higher-order perturbation corrections would be expected to be important is provided by symmetrically stretched H_2O. Full CI results are available in a DZ basis [11,12] for bond stretches of 1.5 and 2.0 times the computed equilibrium value R of the OH bond length. In each case the reference function is the RHF solution. From table 4, the $E^{(5)}$ contribution at equilibrium is only 0.18 mh, while at $1.5R$ it is an order of magnitude la ·er. Surprisingly, at $2.0R$ $E^{(5)}$ is only 0.33 mh, despite being 10.1 kcal/mol from the full CI energy for this extreme case. The

Table 4
MBPT, Padé approximants, VPCI and selected CI and CC results [a] for DZ water at three symmetrically stretched geometries

Calculation type	1.0R		1.5R		2.0R	
	total energy	delta	total energy	delta	total energy	delta
SCF	−76.009838	92.9	−75.803529	132.4	−75.595180	194.6
MBPT(2)	−76.149315	5.4	−75.994577	12.5	−75.852460	33.1
MBPT(3)	−76.150707	4.5	−75.989391	15.8	−75.834803	44.2
[1,0]	−76.150721	4.5	−75.989528	15.7	−75.835937	43.5
VPCI-1	−76.145220	7.9	−75.984190	19.0	−75.805139	62.8
MBPT(4)	−76.156876	0.6	−76.008395	3.8	−75.888867	10.3
[1,1]	−76.148910	5.6	−75.993465	13.2	−75.848113	35.9
MBPT(5)	−76.157056	0.5	−76.009771	3.0	−75.889199	10.1
[2,1]	−76.157358	0.3	−76.012555	1.2	−75.905780	−0.3
VPCI-2	−76.156617	0.8	−76.006723	4.9	−75.871078	21.4
CCSD	−76.156076	1.1	−76.008931	3.5	−75.895913	5.9
CCSDT-1	−76.157414	0.3	−76.013067	0.9	−75.910821	−3.5
CISD	−76.150015	4.9	−75.992140	14.0	−75.844817	37.9
CISDTQ	−76.157626	0.2	−76.013418	0.7	−75.900896	2.7
MR CISD	−76.155808	1.3	−76.012274	1.4	−75.903250	1.3
MR LCCM	−76.157898	0.0	−76.013729	0.5	−75.904152	0.7
full CI	−76.157866	0.0	−76.014521	0.0	−75.905247	0.0

[a] Total energies are in au and delta, the remaining correlation energy, is in kcal/mole.

implication is that higher-order MBPT terms will only slowly accumulate corrections to approach the full CI energy in the difficult $2.0R$ example, while at equilibrium there is little to gain, and at $1.5R$ there is a more intermediate rate of convergence showing substantive improvement at $E^{(5)}$. Again, the [2,1] Padé approximants show exceptional convergence, while the VPCI-2 is even worse than the linear MBPT(5) and much worse at $2.0R$. CCSDT-1 is about the same as the [2,1] Padé approximant although it tends to overshoot at $2.0R$.

No higher than quadruple excitations contribute through $E^{(5)}$, so the difference between MBPT(5) and CISDTQ accounts for infinite-order summations of these categories of CI excitations. In $E^{(6)}$ pentuple and hextuple excitations are first introduced, and these plus higher excitations amount to 2.7 kcal/mol at $2.0R$. The multi-reference linearized CC method (MR LCCM) is exceptionally accurate for this example, as discussed elsewhere [24].

In table 5 we also report MBPT(5) results for H_2O in the same DZ basis but using a crude set of localized, minimum basis bond orbitals to construct the reference function [25]. The reference function's energy is higher than the corresponding SCF result by 152 kcal/mol, posing a difficult case for MBPT to recover the energy

corrections to the full CI. Fourth order reduces the error to only 4.1 kcal/mol, while MBPT(5) improves this by another 2 kcal/mol. Once again, the size-extensive [2,1] Padé approximant shows nearly perfect agreement between results obtained with SCF orbitals and those from the crude localized orbitals. The VPCI-2 is much poorer.

7. Conclusion

In the examples studied, $E^{(5)}$ was as large as 4.3 mh and as small as 0.2 mh, the former in Be_2 with a comparatively large basis and the latter in H_2O at equilibrium in a small DZ basis. Clearly, the larger the basis the greater effect $E^{(5)}$ should have. However, the linear sum MBPT(5) was not found to be much better than MBPT(4) unless the [2,1] Padé approximant was constructed. The latter value was typically as accurate as CCSDT-1 for these examples. Because even-order contributions must be negative (and introduce two more excitation levels if these are available for the problem), $E^{(6)}$ will typically have a larger magnitude than $E^{(5)}$, and thereby would probably offer better results when stopping at that level. However, in the BH

Table 5
MBPT, Padé approximants and VPCI results [a] for DZ water employing canonical SCF and localized orbitals

Calculation type	Canonical SCF orbital		Localized orbital	
	total energy	delta	total energy	delta
reference	−76.009838	92.9	−75.768438	244.4
MBPT(2)	−76.149315	5.4	−76.125978	20.0
MBPT(3)	−76.150707	4.5	−76.126578	19.6
[1,0]	−76.150721	4.5	−76.126579	19.6
VPCI-1	−76.145220	7.9	−76.074547	52.3
MBPT(4)	−76.156876	0.6	−76.151260	4.1
[1,1]	−76.148910	5.6	−76.125963	20.0
MBPT(5)	−76.157056	0.5	−76.154465	2.1
[2,1]	−76.157358	0.3	−76.157366	0.3
VPCI-2	−76.156617	0.8	−76.140498	10.9
CISD	−76.150015	4.9	−76.126161	19.9
CCSD	−76.156076	1.1	−76.155627	1.4
full CI	−76.157866	0.0	−76.157866	0.0

[a] Total energies are in au and delta, the remaining correlation energy, is in kcal/mole.

and Be_2 cases, for which at most only quadruple excitations are possible, $E^{(6)}$ is typically about one-half of $E^{(5)}$, and the series generated is nearly geometric in both cases. The variation—perturbation CI approximations suffer from all the problems of truncated CI, such as the lack of size-extensivity, and do not show particularly good convergence to the full CI result. Their main asset is guaranteeing a variational bound and, hence, convergence from above to the CI result. However, the Padé extrapolation, although occasionally passing slightly below the full CI, provides fast, size-extensive convergence.

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